DEVELOPING STRUCTURE-PROPERTY RELATIONSHIPS IN BRANCHED 
WORMLIKE MICELLES VIA ADVANCED RHEOLOGICAL AND NEUTRON 
SCATTERING TECHNIQUES

by

Michelle A. Calabrese

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical and Biomolecular Engineering

2017

© 2017 Michelle A. Calabrese 
All Rights Reserved
DEVELOPING STRUCTURE-PROPERTY RELATIONSHIPS IN BRANCHED WORMLIKE MICELLES VIA ADVANCED RHEOLOGICAL AND NEUTRON SCATTERING TECHNIQUES

by

Michelle A. Calabrese

Approved: ____________________________________________
Abraham M. Lenhoff, Ph.D.
Chair of the Department of Chemical and Biomolecular Engineering

Approved: ____________________________________________
Babatunde A. Ogunnaike, Ph.D.
Dean of the College of Engineering

Approved: ____________________________________________
Ann L. Ardis, Ph.D.
Senior Vice Provost for Graduate and Professional Education
I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ________________________________
Norman J. Wagner, Ph.D.
Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ________________________________
Antony N. Beris, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ________________________________
Eric M. Furst, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ________________________________
Kathleen M. Weigandt, Ph.D.
Member of dissertation committee
I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: Paul D. Butler, Ph.D.
Member of dissertation committee
ACKNOWLEDGEMENTS

Many people have assisted with the work presented in this dissertation. I would like to thank Ryan Murphy from the Wagner group for performing cryo-TEM imaging, and Peng Cheng in the Helgeson group at the University of California, Santa Barbara for performing the particle tracking velocimetry. Much of the flow-small angle neutron scattering data was collected with Simon Rogers, now at the University of Illinois at Urbana-Champaign, and Lionel Porcar at the Institut Laue-Langevin (ILL) in Grenoble, France. Miguel Gonzalez at ILL was instrumental in implementing the list mode data collection, which enabled many of the time-resolved SANS studies performed in this work. The CaBER measurements were performed with Simon Rogers, and Florian Nettesheim at DuPont, who also provided the instrument. For help setting up the numerous experiments at the NIST Center for Neutron Research (NCNR) in Gaithersburg, MD, I would like to thank Cedric Gagnon and Jeff Krzywon. My brother, Daniel Calabrese, helped improve the NCNR Igor codes used for time-resolved SANS. Finally, I would like to thank Paul Butler and Katie Weigandt at the NCNR and Lionel Porcar at ILL for their generosity in scheduling SANS discretionary time. This work could not be completed without this beam time outside of the proposal process.

I spent the first two years of my graduate work at Delaware, and the remaining three years at the NCNR, which was an invaluable research experience. My time as a graduate student and the resulting work has been influenced by many friends and colleagues at UD, the NCNR, and ILL. I would first like to thank Norm Wagner for all of the wonderful and unique research opportunities I have had over the past five years, and for the academic freedom I was given throughout my PhD. While I had no background in rheology, Norm always pushed me to pursue new and interesting ideas, and gave me the opportunity to spend half of my graduate career at the NCNR. I have learned so much by having this intellectual freedom and the opportunity to work daily at a national research facility like NIST. Additionally, I
was allowed to pursue experiments and visiting scientists rotations at the ILL in France, which have been equally valuable in my growth as a scientist and collaborator. Norm’s enthusiasm for research is contagious and his interest in his students is unparalleled. I am a better scientist because of his influence, and I hope that I can provide my future students the same support and freedom that I was given. At Delaware, I would also like to thank my friends in the Wagner group, especially Ru and (formerly) Simon, and my friends in the department. At the NCNR, Paul Butler and Katie Weigandt were great resources and looked out for me, which I greatly appreciate. At the ILL, I want thank Lionel Porcar and Anne Martel for their generosity and hospitality. I always felt welcome in France (despite not speaking French), and appreciate everything they did for me. Thank you to Lionel for having me as a visiting scientist twice, which was an incredible and productive opportunity.

When I first joined the Wagner group, I had no background rheology. Luckily, as a first year I was paired to work with a former postdoc, Simon Rogers. Simon taught me nearly everything I know about rheology, but also much more about myself both professionally and personally. Simon is endlessly enthusiastic and energetic, and his influence definitely altered the course of my graduate studies which resulted in my decision to go into academia. Through countless drives to the NCNR, a trip to the ILL, nights and weekends of scattering with no sleep, and a never-ending supply of snacks and music, I learned so much and had a blast. Recently, Simon was invaluable giving me advice for faculty interviews. I know I have a life-long friend and collaborator, and I’m excited to work together again soon.

Lastly, I would like to thank all of my friends outside of Delaware and my family. I would not have enjoyed my time in Delaware as much, especially my first year, without Cristina close by in Philadelphia, and Catherine and Christina in New York. Moving to D.C. to work at NIST would have been much harder without Irene and Ryan, Erika, and Brenna. Kelsey, Marisa, and Caroline have also been wonderful and supportive friends. I would not have survived (or enjoyed) the busiest times in graduate school and thesis writing without Jon. Finally, I would like to thank my family, especially my parents. My mom and dad constantly encouraged and supported me throughout the entire process (and even read my papers!). I would not be where I am today without them.
# TABLE OF CONTENTS

**LIST OF TABLES**  ................................................................. xvii  
**LIST OF FIGURES**  ............................................................... xix  
**ABSTRACT**  ................................................................................ lixii  

Chapter

1 INTRODUCTION  ............................................................................. 1  

1.1 Motivation  ............................................................................... 1  
1.2 Self-assembly in surfactant solutions  ....................................... 2  
1.3 Wormlike micelles: theory and scaling  ................................. 9  

1.3.1 Micellar growth  ................................................................. 9  
1.3.2 Stress relaxation and scaling rules in wormlike micelles  ....... 13  

1.4 Branching in wormlike micelles  ........................................... 19  
1.5 Theory of WLM branching  ................................................... 21  
1.6 Objectives and approach  ....................................................... 24  

2 MATERIALS AND METHODS  ..................................................... 37  

2.1 Introduction  ............................................................................ 37  
2.2 Materials  ............................................................................... 37  
2.3 Rheological characterization  ................................................. 39  

2.3.1 Linear viscoelastic (LVE) rheology  .................................. 40  
2.3.2 Steady shear rheology and shear startup  ......................... 41  
2.3.3 Particle tracking velocimetry (PTV)  .................................. 42  
2.3.4 Large amplitude oscillatory shear (LAOS) ....................... 43  
2.3.5 Orthogonal superposition rheology (OSP) ....................... 45  

2.3.5.1 Background  .................................................................. 45
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.3.5.2</td>
<td>Experimental details</td>
<td>46</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Cryo-transmission electron microscopy (cryo-TEM)</td>
<td>47</td>
</tr>
<tr>
<td>2.4</td>
<td>Small angle neutron scattering (SANS)</td>
<td>49</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Background</td>
<td>49</td>
</tr>
<tr>
<td>2.4.2</td>
<td>SANS data analysis</td>
<td>54</td>
</tr>
<tr>
<td>2.4.2.1</td>
<td>Guinier approximation</td>
<td>54</td>
</tr>
<tr>
<td>2.4.2.2</td>
<td>Porod limit</td>
<td>55</td>
</tr>
<tr>
<td>2.4.2.3</td>
<td>Form factor</td>
<td>56</td>
</tr>
<tr>
<td>2.4.2.4</td>
<td>Structure factor</td>
<td>59</td>
</tr>
<tr>
<td>2.4.3</td>
<td>SANS data reduction</td>
<td>60</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Static SANS Experimental details</td>
<td>62</td>
</tr>
<tr>
<td>2.5</td>
<td>Small angle neutron scattering (SANS) under flow</td>
<td>64</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Motivation</td>
<td>64</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Sample environments for SANS under flow</td>
<td>64</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Rheo-SANS in the 1-3 (flow-vorticity) plane</td>
<td>65</td>
</tr>
<tr>
<td>2.5.3.1</td>
<td>Background on rheo-SANS</td>
<td>65</td>
</tr>
<tr>
<td>2.5.3.2</td>
<td>Experimental details</td>
<td>68</td>
</tr>
<tr>
<td>2.5.4</td>
<td>Flow-SANS in the 1-2 (flow-gradient) plane</td>
<td>69</td>
</tr>
<tr>
<td>2.5.4.1</td>
<td>Background</td>
<td>69</td>
</tr>
<tr>
<td>2.5.4.2</td>
<td>Experimental details</td>
<td>70</td>
</tr>
<tr>
<td>2.5.5</td>
<td>Summary of all SANS experiments</td>
<td>73</td>
</tr>
<tr>
<td>2.6</td>
<td>Analysis of anisotropic scattering data</td>
<td>74</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Shear-induced microstructural rearrangements</td>
<td>74</td>
</tr>
<tr>
<td>2.6.2</td>
<td>SANS reproducibility and determining ( q^* ) for alignment factor calculation</td>
<td>77</td>
</tr>
<tr>
<td>2.6.3</td>
<td>Alignment factor calculations</td>
<td>79</td>
</tr>
</tbody>
</table>
### 2.6.4 Repeatability of LAOS structural response in time

#### 2.7 Solution dynamics

##### 2.7.1 Neutron spin echo (NSE)

- **2.7.1.1 Background**
- **2.7.1.2 Experimental details**

##### 2.7.2 Dynamic light scattering (DLS)

- **2.7.2.1 Background**
- **2.7.2.2 Experimental details**

### 3 DEVELOPMENT OF INSTRUMENTATION AND DATA ANALYSIS METHODS

#### 3.1 Introduction

#### 3.2 Time-resolved neutron scattering analysis

- **3.2.1 Motivation**
- **3.2.2 Processing time-dependent scattering**
- **3.2.3 Convolution and deconvolution**
- **3.2.4 Discretization**
- **3.2.5 Noise effects**
- **3.2.6 Time-step and bin-width effects**
- **3.2.7 Experimental results and accessibility**

#### 3.3 Implementation of time-resolved analysis at ILL and the NCNR

- **3.3.1 Motivation**
- **3.3.2 ILL time-resolved analysis**
  - **3.3.2.1 List mode versus kinetic mode**
  - **3.3.2.2 Large array manipulation program (LAMP) list mode processing**
- **3.3.3 NCNR time-resolved analysis: improved Igor codes and capabilities**
  - **3.3.3.1 New Igor reduction codes for SANS**
  - **3.3.3.2 Event Mode Processing**
  - **3.3.3.3 Multiple Reduce**
### 3.3.3.4 Annular and Sector Averaging

126

### 3.4 Analysis of SANS configuration parameters

- **3.4.1 Motivation**
  - 128
- **3.4.2 Reproducibility between repeated trials and effect on $A_f$**
  - 130
- **3.4.3 Effect of detector distance**
  - 132
- **3.4.4 Effect of the number of guides**
  - 137
- **3.4.5 Effect of the aperture and rheometer slit width**
  - 140
- **3.4.6 Effect of slit dimensions for 1-2 shear cell**
  - 145
- **3.4.7 Discussion on configuration effects**
  - 151

152

### 3.5 Conclusions

152

### 4 EQUILIBRIUM STATIC AND DYNAMIC PROPERTIES

158

#### 4.1 Introduction

158

#### 4.2 Structure confirmation

- **4.2.1 Cryo-transmission electron microscopy (cryo-TEM)**
  - 159
- **4.2.2 Static small angle neutron scattering (SANS)**
  - 161

165

#### 4.3 Micellar properties as a function of added salt

- **4.3.1 Relaxation time and zero-shear viscosity**
  - 165
- **4.3.2 Linear viscoelastic regime (LVE) rheology**
  - 168
- **4.3.3 Discussion: salt effect on WLM topology and LVE rheology**
  - 170

174

#### 4.4 Solution dynamics

- **4.4.1 Motivation**
  - 174
- **4.4.2 Theory**
  - 175
- **4.4.3 Sample characterization: LVE and SANS**
  - 178
- **4.4.4 Segmental dynamics via neutron spin echo (NSE)**
  - 180
- **4.4.5 Validation of NSE parameters**
  - 186
  - **4.4.5.1 Comparison between NSE configurations**
    - 186
  - **4.4.5.2 Long Fourier time and long $\lambda$ measurements**
    - 187
  - **4.4.5.3 Spatial bin size resolution and accuracy**
    - 188
- **4.4.6 Diffusive dynamics via dynamic light scattering (DLS)**
  - 190
- **4.4.7 DLS data fitting**
  - 193
- **4.4.8 Quantitative DLS results and link to NSE**
  - 198
4.4.9 Interpretation of DLS results ............................................. 201
4.4.10 Discussion: Solution dynamics ........................................... 203

4.5 Conclusions ........................................................................... 206

5 STRUCTURE AND RHEOLOGY: STEADY SHEAR ....................... 215

5.1 Introduction ........................................................................... 215
5.2 Shear thinning in wormlike micelles ....................................... 216
5.3 Shear banding in wormlike micelles ....................................... 218
5.4 Theory: shear banding ............................................................ 220
5.5 Low vs. highly branched solutions: rheology and microstructure ...... 225
  5.5.1 Steady shear rheology ........................................................ 225
  5.5.2 1-3 plane small angle neutron scattering (SANS) ....................... 227
  5.5.3 1-2 plane SANS ............................................................... 231
5.6 Discussion: low vs. highly branched solutions ......................... 235
  5.6.1 Salt effect on SANS .......................................................... 235
  5.6.2 Interpretation of 1-2 plane SANS results ............................... 239
  5.6.3 High salt solution - shear thickening structural transition ............. 241
    5.6.3.1 Rheology ................................................................ 241
    5.6.3.2 1-3 plane SANS ......................................................... 244
  5.6.4 The Cox-Merz rule and Laun’s rule ...................................... 245
  5.6.5 Summary: low vs. high branching ...................................... 247
5.7 Mildly branched solution: rheology and microstructure .............. 248
  5.7.1 Steady shear rheology ........................................................ 248
  5.7.2 1-3 plane SANS ............................................................... 250
  5.7.3 1-2 plane SANS ............................................................... 252
5.8 Discussion: mildly branched solution .................................... 257
  5.8.1 1-3 plane SANS ............................................................... 257
  5.8.2 Mechanism of flow-alignment and shear banding: low vs. mild branching .... 258
  5.8.3 Shear banding and interface fluctuations ............................. 261
5.8.4 Summary: mild branching ........................................ 263

5.9 High branching levels: rheology and microstructure ............... 264

5.9.1 Steady shear rheology ........................................... 264
5.9.2 1-3 plane SANS .................................................... 266
5.9.3 1-2 plane SANS .................................................... 271

5.10 Discussion: all branching levels .................................... 276

5.10.1 Steady shear rheology ........................................... 276
5.10.2 Empirical relationship for the power law index .................. 278
5.10.3 1-3 plane comparison: all branching levels ...................... 278

5.11 Conclusions .......................................................... 281

6 STRUCTURE AND RHEOLOGY: SHEAR STARTUP ................. 291

6.1 Introduction .................................................................. 291
6.2 Rheological signatures of shear banding .............................. 292
6.3 Mechanisms of shear banding ........................................ 295
6.4 Mechanism of shear banding: low vs. mild branching ............ 297
6.5 Shear startup: low branching solution .............................. 298

6.5.1 Startup rheology ....................................................... 298
6.5.2 Startup 1-3 plane SANS ............................................ 307
6.5.3 Startup 1-2 plane SANS ............................................ 310

6.6 Discussion: low branching solution .................................. 317

6.6.1 Structural mechanism of shear banding .......................... 317
6.6.2 Particle tracking velocimetry (PTV) measurements ........... 321

6.7 Shear startup: mildly branched solution ............................ 324

6.7.1 Startup rheology ....................................................... 324
6.7.2 Startup 1-3 plane SANS ............................................ 330
6.7.3 Startup 1-2 plane SANS ............................................ 333

6.8 Discussion: mildly branched solution ............................... 337

6.8.1 Structural mechanism of shear banding .......................... 337
123

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8.2 Shear banding mechanism: low vs. mild branching</td>
<td>340</td>
</tr>
<tr>
<td>6.9 Shear startup: higher branching levels</td>
<td>342</td>
</tr>
<tr>
<td>6.9.1 Startup rheology</td>
<td>342</td>
</tr>
<tr>
<td>6.9.2 Startup 1-3 plane SANS</td>
<td>345</td>
</tr>
<tr>
<td>6.9.3 Startup 1-2 plane SANS</td>
<td>347</td>
</tr>
<tr>
<td>6.9.4 Summary: high branching</td>
<td>348</td>
</tr>
<tr>
<td>6.10 Discussion: all branching levels</td>
<td>350</td>
</tr>
<tr>
<td>6.10.1 Signatures of shear banding vs. shear thinning</td>
<td>350</td>
</tr>
<tr>
<td>6.10.2 Particle tracking velocimetry: low vs. high branching</td>
<td>352</td>
</tr>
<tr>
<td>6.10.3 Shear startup to determine micellar morphology</td>
<td>353</td>
</tr>
<tr>
<td>6.11 Conclusions</td>
<td>355</td>
</tr>
<tr>
<td>7 STRUCTURE AND RHEOLOGY: LARGE AMPLITUDE OSCILLATORY SHEAR (LAOS)</td>
<td>363</td>
</tr>
<tr>
<td>7.1 Introduction</td>
<td>363</td>
</tr>
<tr>
<td>7.2 Background</td>
<td>364</td>
</tr>
<tr>
<td>7.3 Shear banding under LAOS</td>
<td>367</td>
</tr>
<tr>
<td>7.4 Model predictions of shear banding under LAOS</td>
<td>369</td>
</tr>
<tr>
<td>7.5 Large amplitude oscillatory shear: mildly branched solution</td>
<td>370</td>
</tr>
<tr>
<td>7.5.1 Vasquez-Cook-McKinley (VCM) model and mildly branched solution</td>
<td>370</td>
</tr>
<tr>
<td>7.5.2 Revisiting linear viscoelastic regime (LVE) rheology</td>
<td>371</td>
</tr>
<tr>
<td>7.5.3 LAOS rheology</td>
<td>372</td>
</tr>
<tr>
<td>7.5.4 LAOS 1-2 plane flow-SANS</td>
<td>376</td>
</tr>
<tr>
<td>7.5.4.1 Design of experiments</td>
<td>376</td>
</tr>
<tr>
<td>7.5.4.2 Primary experiments: $De = 0.17, Wi = 75$ and $De = 0.58, Wi = 75$</td>
<td>377</td>
</tr>
<tr>
<td>7.5.4.3 LAOS Condition 1, $De = 0.17, Wi = 75$</td>
<td>378</td>
</tr>
<tr>
<td>7.5.4.4 LAOS Condition 2, $De = 0.58, Wi = 75$</td>
<td>380</td>
</tr>
<tr>
<td>7.5.4.5 Comparison of LAOS results between conditions 1 and 2</td>
<td>382</td>
</tr>
<tr>
<td>7.5.4.6 Comparison of LAOS results with steady shear</td>
<td>384</td>
</tr>
<tr>
<td>7.5.5 Additional conditions to validate VCM model predictions</td>
<td>388</td>
</tr>
<tr>
<td>7.6 Discussion: mildly branched solution</td>
<td>391</td>
</tr>
</tbody>
</table>
### 7.7 LAOS shear banding: low branching solution

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7.1</td>
<td>Design of experiments</td>
<td>395</td>
</tr>
<tr>
<td>7.7.2</td>
<td>LAOS rheology</td>
<td>396</td>
</tr>
<tr>
<td>7.7.3</td>
<td>LAOS 1-3 plane SANS</td>
<td>405</td>
</tr>
<tr>
<td>7.7.4</td>
<td>LAOS 1-2 plane flow-SANS</td>
<td>409</td>
</tr>
</tbody>
</table>

#### 7.7.4.1 Condition one: \( De \approx 1, Wi = 295 \)

#### 7.7.4.2 Condition two: \( De = 1, Wi = 450 \)

#### 7.7.4.3 Condition three: \( De = 1.4, Wi = 450 \)

#### 7.7.4.4 Condition four: \( De = 2, Wi = 300 \)

#### 7.7.4.5 Condition five: \( De = 2, Wi = 450 \)

#### 7.7.4.6 Condition six: \( De = 3, Wi = 450 \)

#### 7.7.4.7 Condition seven: \( De = 4.2, Wi = 450 \)

#### 7.7.4.8 Condition eight: \( De = 9, Wi = 450 \)

#### 7.7.4.9 Condition nine: \( De = 1.4, Wi = 300 \)

#### 7.7.4.10 Condition ten: \( De = 1.4, Wi = 400 \)

### 7.8 Discussion: low branching solution

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.8.1</td>
<td>Phase of the alignment factor response</td>
<td>451</td>
</tr>
<tr>
<td>7.8.2</td>
<td>Conditions where ( De = 1.4 )</td>
<td>453</td>
</tr>
<tr>
<td>7.8.3</td>
<td>Alignment factor at equivalent ( Wi )</td>
<td>454</td>
</tr>
<tr>
<td>7.8.4</td>
<td>LAOS results in the context of steady shear</td>
<td>459</td>
</tr>
<tr>
<td>7.8.5</td>
<td>Summary: low branching</td>
<td>461</td>
</tr>
</tbody>
</table>

### 7.9 LAOS shear thinning: highly branched solution

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.9.1</td>
<td>Sample characterization: 0.10% wt NaTos</td>
<td>462</td>
</tr>
<tr>
<td>7.9.2</td>
<td>LAOS rheology</td>
<td>467</td>
</tr>
<tr>
<td>7.9.3</td>
<td>1-3 plane LAOS SANS</td>
<td>469</td>
</tr>
<tr>
<td>7.9.4</td>
<td>1-2 plane LAOS SANS</td>
<td>474</td>
</tr>
<tr>
<td>7.9.5</td>
<td>Discussion: high branching</td>
<td>477</td>
</tr>
</tbody>
</table>

### 7.10 Discussion: all branching levels

### 7.11 Conclusions

### 8 CONCLUSIONS AND OUTLOOK

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1</td>
<td>Introduction</td>
<td>489</td>
</tr>
<tr>
<td>8.2</td>
<td>Equilibrium structure and rheology</td>
<td>490</td>
</tr>
<tr>
<td>8.3</td>
<td>Dynamic equilibrium properties</td>
<td>492</td>
</tr>
<tr>
<td>8.4</td>
<td>Steady shear: shear banding vs. shear thinning</td>
<td>494</td>
</tr>
</tbody>
</table>

xiv
8.5  Shear startup and the mechanism of shear band formation .......................... 497
8.6  Mild branching: shear banding under LAOS and VCM model predictions ........ 499
8.7  LAOS responses based on branching ......................................................... 501
8.8  Advances in SANS data collection and analysis ......................................... 503
8.9  Recommendations for future work ............................................................. 507
      8.9.1  Separating the impact of electrostatic interactions and branching .......... 507
            8.9.1.1  Inducing branching via alternative methods ............................... 508
            8.9.1.2  The effect of charge on shear band formation ............................ 509
8.9.2  Beyond shear: extensional rheology ...................................................... 511
8.9.3  Improving SANS experiments ............................................................... 512
            8.9.3.1  Time-resolved data collection .................................................. 513
            8.9.3.2  Use of encoder for 1-2 plane LAOS experiments ......................... 513
8.10  Outlook ....................................................................................................... 514

Appendix
A  NOMENCLATURE AND ACRONYMS ............................................................... 522
B  ALIGNMENT FACTOR Q-RANGE FOR EACH SAMPLE .................................... 525
C  AMPLITUDE SWEEPS TO DETERMINE THE LINEAR VISCOELASTIC REGIME OF THE WLM SOLUTIONS ................................................................. 527
D  CALCULATIONS OF THE BEAM DIVERGENCE FOR RHEO- AND FLOW-SANS EXPERIMENTS ................................................................. 529
E  ADDITIONAL CRYO-TEM MICROGRAPHS .................................................. 534
F  COMPARISON OF WLM RHEOLOGY IN WATER VS. D2O ................................ 536
G  RHEOLOGICAL RESPONSE OF WLMS BETWEEN REPEATED SAMPLE PREPARATIONS ................................................................. 545
H  NEUTRON SPIN ECHO DETECTOR DIVISION AND UNCERTAINTY ................. 549
I  FULL ANGULAR DLS SPECTRA FOR WLM SOLUTIONS .................................. 552
J  CONSIDERATIONS SURROUNDING ELASTIC FLOW INSTABILITIES AND ELASTIC TURBULENCE ................................................................. 556
            J.0.1  Calculations from rheometrical geometries ....................................... 556
            J.0.2  Shear thickening of the highly branched solution .............................. 558
K  ORTHOGONAL SUPERPOSITION RHEOLOGY (OSP) ....................................... 561
L  COMPARISON OF FLOW CURVES FROM 1-3 PLANE SANS AND RHEOLOGY ........ 565
M ADDITIONAL STARTUP TRIALS .................................................. 571
  M.1 0.01% wt NaTos ......................................................... 571
    M.1.1 Startup rheology ................................................... 571
    M.1.2 1-3 plane SANS: additional shear rates ..................... 574
    M.1.3 1-3 plane SANS: effect of the curvature, ε .................. 575
    M.1.4 1-3 plane SANS: individual trials .......................... 581
    M.1.5 1-3 plane SANS: additional trials .......................... 582
    M.1.6 1-2 plane SANS: additional shear rates ..................... 585
    M.1.7 1-2 plane SANS: individual trials .......................... 592
  M.2 0.05% wt NaTos ......................................................... 592
    M.2.1 1-3 plane startup: additional shear rates ................... 592
    M.2.2 1-3 plane startup: individual trials ......................... 593
  M.3 Highly branched: 0.10% wt NaTos .................................. 596
    M.3.1 Startup rheology .................................................. 596
  M.4 Network-like: 0.25% wt NaTos ...................................... 599
    M.4.1 Startup rheology .................................................. 599
N NORMALIZED LISSAJOUS-BOWDITCH PROJECTIONS OF LAOS
CONDITIONS FOR MILDLY BRANCHED SOLUTION ............................ 602
O TIME DIVISIONS OF LAOS SCATTERING DATA ............................... 604
  O.1 Low branching solution: 0.01% wt NaTos .......................... 604
    O.1.1 Condition one: De ≈ 1, Wi = 295 ............................. 604
    O.1.2 Condition four: De = 2, Wi = 300 ............................ 605
    O.1.3 Condition five: De = 2, Wi = 450 ............................ 606
    O.1.4 Condition six: De = 3, Wi = 450 ............................ 607
    O.1.5 Condition eight: De = 9, Wi = 450 ............................ 608
    O.1.6 Condition nine: De = 1.4, Wi = 300 ........................... 610
    O.1.7 Condition ten: De = 1.4, Wi = 400 ........................... 611
  O.2 High branching solution: 0.10% wt NaTos .......................... 612
P PERMISSIONS FOR FIGURE AND ARTICLE REPRINTING ....................... 614
LIST OF TABLES

1.1

Methods of inducing branching in WLMs and references for each method.

24

2.1

Configuration parameters for rheo- and flow-SANS, where ε is the
gap-to-radius ratio, ε = H/R1 , and Γ is the aspect ratio, where Γ = L/H.

68

2.2

Summary of all performed SANS experiments . . . . . . . . . . . . . .

73

2.3

Summary of NSE configurations. ∗ symbol indicates follow-up
experiments using different sample preparations and configurations. . . .

88

Characteristic length and time scales of low and high salt (0.01%, 0.10%
wt NaTos) WLMs . . . . . . . . . . . . . . . . . . . . . . . . . . . .

171

4.2

Average characteristic properties of the 0.05% wt NaTos WLM solution

172

4.3

Calculated diffusion coefficients from NSE and DLS for the 0.01%,
0.25%, and 0.50% wt NaTos WLMs. DG is the segmental diffusion
coefficient from the high-q NSE data where Γ ∝ q8/3 ; D1 and D2 are the
diffusion coefficients calculated from DLS corresponding to the fast and
slow relaxation mode, respectively. The associated uncertainty gives the
95% confidence interval. . . . . . . . . . . . . . . . . . . . . . . . . .

200

7.1

LAOS conditions and parameters for the 0.05% wt NaTos solution. . . .

377

7.2

0.05% wt NaTos LAOS time scales and properties across conditions.
Alignment factors for calculation of the maximum cycle over-orientation
(O-O) were interpolated when necessary. . . . . . . . . . . . . . . . .

392

LAOS parameters for the 0.01% wt NaTos solution. The nomenclature
from the first and second columns is used to refer to each condition. . . .

396

LAOS local modulus, G0local , yield strain, γyield , and magnitude of the
stress overshoot, σmax for the 0.01% wt NaTos solution, when applicable.

404

4.1

7.3

7.4

xvii


7.5 LAOS average and root-mean-square average stress, $\sigma^*$, for the 0.01% wt NaTos solution. Averages are calculated using the absolute value of the cycle stress. .............................................. 461

7.6 LAOS conditions and parameters for the 0.10% wt NaTos solution. The nomenclature from the first and second columns (new solution) will be used to refer to each condition throughout the text. .............................................. 467

7.7 LAOS average and root-mean-square average stress for the 0.10% wt NaTos solution. Averages are calculated using the absolute value of the cycle stress. .............................................. 479

A.1 Nomenclature ......................................................... 522

A.2 Acronyms ............................................................. 524

D.1 Beam divergence for different slit configurations on the 1-2 shear cell. The * indicates the standard configuration for the 1-2 shear cell used in this work. ......................................................... 531

D.2 Beam divergence for different slit configurations on the rheometer. The * indicates the typical 1-3 plane configuration. ......................................................... 532

F.1 Comparison of rheological properties for WLMs in H$_2$O vs. D$_2$O, labelled by the % wt NaTos in each solution followed by the solvent. Note that the power lax index, $N$, could not be calculated from the steady state flow curves for the solutions in water, so these values should be interpreted with caution. ......................................................... 542

J.1 Stress fluctuations in the shear thickening regime for the branched 0.10% wt NaTos solution ................................................................. 559
1.1 Schematic of wormlike micelle assembly. Assembly is dictated by the surfactant geometry and resulting packing parameter, \( p \) (a), which, paired with the electrostatic interactions around the micellar head groups, governs the local ordering or persistence length, \( l_p \) (b). (c) Long-range order is also achieved, where long, entangled wormlike structures are observed. Image in (c) reprinted with permission from reference [13]. Copyright 2003 American Chemical Society, see Appendix P. 3

1.2 Phase diagram for wormlike micelles proposed by Lequeux and Candau [18], where the x-axis, \( C_s/C \), is the salt-to-surfactant ratio, and the y-axis, \( \phi \), is the surfactant volume fraction. Branching is possible in the semi-dilute regime, above the overlap concentration (\( C^* \) or \( \phi^* \)). Network-like structures form as the salt-to-surfactant ratio is increased for the same volume fraction. The entrance into the concentrated regime, which is still isotropic at rest, is denoted by \( C^{**} \) or \( \phi^{**} \). Reprinted with permission from reference [18]. Copyright 1994 American Chemical Society; see Appendix P. 8

1.3 Schematic of wormlike growth and branching with added hydrotropic salt. The micelles transition from spherical to rod-like with small changes in \( \eta_0 \). A transition to linear, entangled WLMs is marked by a drastic increase in \( \eta_0 \). Branched, entangled micelles are observed after the viscosity maximum. Branched WLMs are also observed near the second viscosity maximum, but the overall contour length shortens in this region. 18

1.4 WLM assembly altered by branching. (a) Adding hydrotropic salt, like NaTos, alters the local order (\( l_p \)) when the salt penetrates the structure of the micelle. This salt addition decreases \( l_p \) by screening the electrostatic interactions around the micellar head groups. (b) The long-range order is also altered, as salt addition makes the formation of branch points (bottom) more energetically favorable, reducing the number of endcaps (top). 23
2.8 Methods of reducing and analyzing SANS data. (a) The standard circular average method averages the 1-D curve from all 2-D data. In the case of isotropic scattering, the circular average gives the same result as the sector averages in (b) and (c). (b) Sector average in the vertical direction. When the anisotropy is in the direction of the sector average, \( I(q) \) increases. (c) Horizontal sector average, where \( I(q) \) decreases. (d) Annular average over a fixed \( q \)-range, used to calculate the order parameter. Data shown from the 0.01% wt NaTos solution.

2.9 An illustration of the three shear planes accessible by SANS. In order to access the 2-3 flow-vorticity (a) and 1-3 flow-vorticity (b) planes, a rheometer is aligned in the neutron beam. To access the 1-2 flow-gradient plane (c), a sample environment has been developed through a collaboration between the Institut Laue-Langevin (ILL, France), the National Institute of Standards and Technology Center for Neutron Research (NCNR, USA), and the University of Delaware (UD, USA). The micelles align along the direction of shear flow in each plane, and sample WLM scattering patterns are provided for each plane.

2.10 Current rheo-SANS instruments. The beam direction is represented by the blue arrows, the shear plane directions by the red arrows, and the rotation direction by the green arrows. (a) Anton-Paar MCR rheometer used at the NCNR aligned in the beam line for the 1-3 plane measurements, which also may be aligned for 2-3 plane measurements. (b) The 1-2 plane shear cell aligned in the beam for spatially-resolved measurements.

2.11 Determination of the 1-2 shear cell gap edges. The gap width, \( r/H = 1 \) mm, and is identified by a large change in the intensity with gap position. Arrows signify the edges of the gap.

2.12 Defining parameters for alignment factor calculation. (L) 2-D SANS pattern from 1-2 plane measurements, where the region \( q^* \) of rod-like scattering is shown between concentric circles. The angle \( \phi = 0^\circ \) along the gradient direction, and \( \phi = 90^\circ \) along the flow direction. Near perfect flow-alignment corresponds to \( \phi_0 \approx 0^\circ \), as the direction of increased intensity due to micellar alignment is oriented at 90° from the flow direction.
2.13 Static scattering from four sample cells/configurations used in this work: static quartz cells with 2mm path length, two rheometer configurations with a 1mm and 2mm path length, and the 1-2 shear cell with a 5 mm path length. The static scattering shows excellent agreement across cells for both samples, verifying that effects from multiple scattering or geometry are insignificant.

2.14 Determination of $q^*$ for the 0.05% wt NaTos solution. (a) 1-D intensity with $q^{-1}$ shown between dotted lines. A sample 2-D pattern highlighting $q^*$ (shaded in blue) is shown in the top inset ($Wi = 75$, $r/H = 0.15$). The bottom inset shows the resulting $I(q^*, \phi)$. (b) 1-2 plane $A_f$ at $Wi = 75$ for $q^*$ (□), the full $q^{-1}$ range (○), and the second half of the $q$-range (△). At all but $r/H = 0.15$, the $A_f$ is independent of $q$-range. Inset: $A_f$ calculated across the relevant $q$-range in small $q$-increments (x-error); the chosen $q$-range is highlighted in blue. Most points are within the uncertainty of one other.

2.15 Individual LAOS SANS trials at $r/H = 0.15$ for condition 2. Despite hours of time between individual measurements, the alignment factor response is not significantly different between trials. The individual trials are then added together to calculate the alignment factors shown in Figures 7.6 and 7.8.

2.16 Schematic of a neutron spin echo (NSE) spectroscopy experiment. Reprinted from the NIST Center for Neutron Research, reference [61]. This sequence enables detecting small changes in neutron velocities, as amplified using the echo condition.

3.1 Example time-resolved neutron scattering experiment of period $T$, where the detector records the spatial X and Y positions, and time of detection, for each scattered neutron. Each red dot represents an individual scattering event. The standard binning method for an oscillatory shear experiment groups neutrons registered within an interval of time, $t_w$, together (indicated by colored and black lines), forming a single scattering pattern with temporal resolution $t_w$. Here, $t_w = T/10$. Note the two temporal ends of the figure are joined, such that $t/T = 0 = 1$.

3.2 Visual representation of the convolution in terms of scattering data. On the left is the boxcar function in terms of the time bin, $t_w$, which is convolved with the scattering data (middle) to produce the observed scattering data, shown here for the 1-2 plane (right).
3.3 Sinc function and data inversion issues. (a) Standard sinc function. The negative lobes of the function can lead to issues in data inversion, where an example is shown in (b). (b) Sample data, ‘M,’ which when binned at a bin width of $t_w$, leads to inversion.

3.4 The results of binning only (a) and binning and deconvolving (b) time-resolved sample data set from bins of width $T/N$, where $T$ is the period of oscillation and $N$ is an even integer. Only the first half of the oscillation is shown for clarity. The solid black line indicates the underlying material function, and the colored lines indicate the results of the two procedures. Only by deconvolution can the true material response be determined without artifacts from the analysis.

3.5 Flow chart illustrating the data processing and deconvolution procedure, with a Matlab example for reference. Steps 2. to 4. correspond to equations discussed in the text, whereas step 1. is performed in the scattering reduction software. Step 3a. allows the user to determine the optimal truncation frequency for the inverse transform.

3.6 Binning and deconvolution of noisy data at different bin (time) widths. Noise levels of 0.1, 0.25 and 0.5% were added to the time-average of the original signal from bin widths of $T/2$, $T/10$ and $T/32$. The full frequency spectrum transform always returns noisy data. However, truncating the Fourier transforms (denoted as a fraction of the full spectrum) removes noise from the signal so that the true signal is more closely approximated. The original signal (black) has frequencies corresponding to 1/32 of the full Fourier transform. The true signal at 1/32 of the full transform is best approximated using bins of $T/32$, and deviates significantly with increasing bin size. Data is shifted vertically for visual aid.

3.7 LAOS experimental results from a mildly branched WLM solution at $\omega = 0.2 \text{ rad} \cdot s^{-1}$ and $\gamma_0 = 225$. The time-periodic 1-3 plane alignment factor $(A_f)$, $c(t)$, is binned into 150 bins of width $t_w = T/30$ ($t_s = t_w/5$). The standard binning method (red) is compared to the sliding binning method (gray) and the full deconvolution (black). Small oscillations in the $A_f$ signal from $0.45 \leq t/T \leq 0.65$ are not resolved via the standard method. Residuals show the impact of deconvolution, where the deconvolved signal exhibits sharper, more pronounced oscillations that represent the true response. Error bars span $t_w$. 
3.8 Direct comparison of the sliding bin method with (a) the deconvolved data, which shows sharper features than the sliding bin method; and (b) the deconvolved data re-smeread with the time bin, $t_w = T/30$. As expected, re-smearing the data leads to a recovery of the sliding bin data.

3.9 Comparison of the deconvolved signal (black) and the shear stress (blue). The oscillations detected in the deconvolved signal directly reflect the features in the stress response. The enhanced temporal resolution and sharpness of the features gained by deconvolution enables quantitative relationships to be developed between the alignment and stress.

3.10 New LAMP program module for processing time-resolved data. (a) The main LAMP interface, where the working path and data path can be specified. Upon starting LAMP, ‘event_file’ is entered in the manipulations section (bottom left) to open the ‘Event file analysis’ module. (b) To perform the event file analysis, a list mode file is selected from the working path specified in (a), as the input file. Before loading the file, the ‘Use trigger?’ and time delay box must be specified. For LAOS files, the ‘Use trigger?’ is set to sample; for stream files, it is set to no. For LAOS files, the time delay (min delay in ms) should be set to a time slightly shorter than the cycle time to account for cycle variation; no delay time is needed for stream files. The bin width is entered in the time/slice box (here 598.66 ms = 0.59866 s per slice) and the temporal resolution is set by the number of slices. Here, the time/slice corresponds to $T/30$, but the number of slices = 60, such that the temporal resolution is 2-fold greater than the temporal precision, $n = 2$.

3.11 New event mode processing panel for implementing the sliding bin method. The original panel included the ‘max time’ and ‘number of slices’ inputs only. The ‘slice width of period’ corresponds to the bin width, and the ‘number of slices’ can now be chosen as a multiple of the slice width. Here, $n = 8 = \text{number of slices/slice width of period}$.

3.12 New multiple reduce panel for improved processing of time-resolved data. The ‘Flow $A_f$’ and ‘Rheo $A_f$’ boxes were added to allow the alignment factor (and $\phi_0$ for flow-SANS) to be calculated during data reduction. The ‘Set Q’ button allows the $q^*$ range to be specified. The file number and label, as well as calculated values, are all printed after reduction in the ‘Files and Factors’ table.
3.13 New averaging panel for determination of $q^*$ region and associated error in alignment factor calculation. a) Printed values of the angle, $\phi$, $I(q, \phi)$ (labeled aveint), and uncertainty associated with the intensity at each angle (sigave); values are used to calculate the uncertainty in $A_f$. b) Average panel, where the q-center is specified in $\AA^{-1}$ and $\Delta q$ in pixels. c) Visual representation of the specified q-annulus (between the blue concentric circles) on the 2-D scattering pattern; q-center is shown by the green middle circle. d) $I(q, \phi)$ output as specified by the q-center and $\Delta q$ inputs. e) Printout of the calculated $A_f$ and upper and lower integral values.  

3.14 Sample data for the 0.01% wt NaTos solution illustrating the effect of the background on the absolute intensity, intensity distribution, $I(q^*, \phi)$, and resulting $A_f(q^*)$ calculation. Data is shown for a configuration of 1 guide and a detector distance of 12 m, at a shear rate of $\dot{\gamma} = 45$ s$^{-1}$ for a trial of 300 s. (a) 1-D absolute scattering intensity for the sample at rest and under shear with different backgrounds. While the intensities of the shear data (□) and simulated data (● = +1, △ = −1) are close to, if not within, uncertainty of one another in the $q^*$ region, the absolute intensity for data at rest is significantly higher. (b) $I(q^*, \phi)$ for the shear and simulated data. Despite the three distributions appearing nearly identical, the calculated $A_f$ values are not within uncertainty.  

3.15 Reproducibility of the microstructural response to shear between steady shear trials, as represented by $I(q^*, \phi)$. The trials were taken 11 hours apart from one another, for 300 s each. The calculated alignment factor, $A_f$, between trials is identical between two significant digits, confirming that the WLM response is not affected by shear, evaporation, aging, or other effects during the duration of the SANS experiments.  

3.16 Effect of the detector distance and associated resolution on the 1-D absolute intensity of the 0.01% wt NaTos solution at rest. (a) 1-D absolute intensity for distances 1.65 to 8 m. The absolute intensity of the scattering from the 8 m configuration is clearly higher than the other configurations. (b) The absolute intensity of the scattering from the 8 m to 13 m configurations is identical within uncertainty. The absolute intensities for the shorter detector distances (< 4m) are evidently lower than in the longer distances.
3.17 Effect of the detector distance on the resolution of the microstructural response to shear, as represented by $I(q^*, \phi)$ for two shear rates: $\dot{\gamma} = 4.2$ s$^{-1}$ (a, b) and $\dot{\gamma} = 45$ s$^{-1}$ (c, d). Distances 1.65 to 6 m are shown in (a, c), and 6 to 13 m are shown in (b, d). For both shear rates, longer detector distances lead to sharper intensity distributions and higher calculated values of $A_f$. Higher $A_f$ values are obtained at longer distances despite the lower background values at shorter detector distances, which serves to artificially increase the value of $A_f$ (see Figure 3.14b). The low background is most drastic in $I(q^*, \phi)$ from at 1.65 m, where the 1-D absolute intensity is the lowest due to poor q-resolution.

3.18 Effect of the number of guides, width of slits, and associated resolution on the 1-D absolute intensity of the 0.01% wt NaTos solution at rest. (a) 1-D absolute intensity for distances 1.65 to 8 m at one and four guides. The absolute intensity of the scattering does not appear to be altered by the use of one vs. four guides. (b) The 8 m configuration is examined with different sized apertures (at nozzle) and slits (front of rheometer). The absolute scattering intensity at rest does not appear to be altered by the aperture or slit size.

3.19 Effect of the number of guides on the resolution of $I(q^*, \phi)$ for the 0.01% wt NaTos solution at $\dot{\gamma} = 26.4$ s$^{-1}$. (a) Steady state intensity distributions for configurations with 1, 4 or 5 guides at 8 m. The background is unchanged by the number of guides, but increasing the number of guides decreases the peak intensity of $I(q^*, \phi)$, thereby decreasing $A_f$. (b) As there is little difference between the 4 and 5 guide configurations in (a), the 1 and 5 guide configurations are compared for a longer duration of time ($\Delta t = 360$ s). Similar to the result seen in (a), the 5 guide configuration leads to a lower value of $A_f$ because of peak-smearing, leading to a lower peak intensity than in the 1 guide configuration.

3.20 Placement of the source aperture and sample slit for a standard rheo-SANS configuration. The black boxes detail the full cadmium slit piece, whereas the smaller rectangles inside specify the slit location and dimensions. In (a), the source aperture and nozzle are highlighted, where the actual aperture height, $h$, and width, $w$, are specified by the yellow rectangle. The back side of the sample slit is shown in blue. Photos adapted from reference [21].

3.21 Triangular wavelength distribution for the neutron beam, where $\lambda$ is the wavelength and $\Delta\lambda$ is the wavelength spread. Reprinted from reference [20].
3.22 Effect of the width of the source aperture (at nozzle) and sample slit (in front of rheometer) on the resolution of $I(q^*, \phi)$. (a) When the source aperture is decreased from 8 mm to 5 mm, and the slit size is reduced from 5 mm to 2 mm, the effect of the number of guides seen above in Figure 3.19 is minimized. The background is higher in the wide slit configuration ($w_{aperture}$=8 mm, $w_{slit}$=5 mm) than in the two narrow slit configurations, leading to a lower value of $A_f$. (b) The source aperture is changed from 5 mm to 3 mm with no noticeable change in $I(q^*, \phi)$. $A_f$ is slightly larger for the 3 mm configuration, however, this is likely due to poor statistics and not a true structural change, as the intensity distributions are nearly identical.

3.23 Effect of the width of the sample slit (in front of the rheometer) on $I(q^*, \phi)$ (a) While the distributions are similar, the narrow slit (2 mm) provides a lower background and lower orientational smearing as compared to the wide slit (5 mm) configuration for 1 guide. This results in an alignment factor that is 10% higher in the narrow slit case. (b) The same effect is observed in the configurations with 4 guides. The alignment factor is only 5% higher in the narrow slit case with 4 guides.

3.24 Shear cell configuration with the stationary and translating slits. The stationary slit region is encompassed by the black square, where the actual slit dimensions are within the smaller blue rectangle, where $h$ is the slit height and $w$ is the width. The translating slit is highlighted by the red rectangle and arrow, where the width is significantly smaller than the width of the stationary slit to further confine the scattering volume.

3.25 Effect of the width of the translating slit on $I(q^*, \phi)$ and $A_f$ for the 0.01% wt NaTos solution at $\dot{\gamma} = 45$ s$^{-1}$. The dimensions of the stationary slit were 2x5 mm for all experiments. (a) $A_f$ as a function of gap position, $r/H$ for different slit widths and different facilities. The slit width appears to have little effect on $A_f$, even when the width increases five-fold from 0.05 to 0.25 mm. (b) $I(q^*, \phi)$ is nearly identical between trials at the NCNR and ILL with slit widths of 0.1 and 0.3 mm, respectively. $A_f$ is within the uncertainty, as shown for the gap position $r/H = 0$ from the curve in (a). $A_f$ appears to be independent of the translating slit width for this configuration, indicating that spatial smearing is not significant.
3.26 Effect of the width of the stationary slit and translating slit on $I(q^*, \phi)$ and $A_f$ for the 0.05% wt NaTos solution. The dimensions are specified as translating slit width x shear cell slit height (the two smallest dimensions). (a) $I(q^*, \phi)$ and $A_f$ are nearly identical between facility and choice of slit at the inner wall for $\dot{\gamma} = 45 \text{ s}^{-1}$. (b) $A_f$ was calculated across the gap for the two NIST configurations, where the translating slit was identical (0.1mm) between the two. The $A_f$ calculation is independent of the height of the shear cell slit, indicating that spatial smearing is not significant.

4.1 Comparison between CTAT/SDBS worm-like micellar solutions with a fixed surfactant concentration ($C^* \approx C_D = 1.5\%$ wt) with low salt (a, 0.01% wt NaTos, red) and high salt (b, 0.10% wt NaTos, blue). (a) Chains are highly linear. The inset provides a larger scale view of the long, linear structures apparent throughout the sample. (b) Micelles have identifiable branch points, as indicated by the arrows, and form a variety of junctions, loops, and other structures. The inset shows the larger scale morphology that contrasts the linear micelles observed in the (a) inset.

4.2 Top: 1-D azimuthally-averaged static SANS for CTAT/SDBS WLM solutions with a range of salt (0.01% wt NaTos) to (0.25% wt NaTos). 2-D scattering patterns are highlighted for the low salt (0.01% wt NaTos, red) and high salt system (0.10% wt NaTos, blue). The strong interaction peak at low salt concentration manifests itself as a ring in the 2-D scattering pattern (red), whereas the electrostatic interactions are screened at high salt concentrations (blue), leading to the disappearance of the interaction peak. The 0.15% wt NaTos 1-D scattering is also shown (purple) to highlight the structural similarities between the 0.15% wt and 0.10% wt sample, in qualitative agreement with the cryo-TEM results. Bottom: Static SANS of the 0.05% wt NaTos solution, where the static 2-D pattern from the 1-2 shear cell is shown and the faint ring leads to the mild interaction peak in the 1-D scattering. The color scheme difference in the SANS patterns reflects data taken at ILL vs. NIST above.

4.3 Static SANS measurements for very highly branched solutions. The 0.25% (black) and 0.50% (blue) wt NaTos solutions are highlighted, as they are discussed further in the section on solution dynamics.
4.4 Zero-shear viscosity, $\eta_0$, and rheological relaxation time, $\tau_R$, as a function of salt concentration (a) and ion concentration ratio (b). Both parameters are decreasing functions of salt and ion ratio, indicating that the system has surpassed the commonly-observed first viscosity maximum in WLM systems. The range of salt concentration is limited such that a second viscosity maximum is not observed. The associated error in both metrics determined in samples with multiple preparations is smaller than the symbol size.

4.5 Dynamic moduli, $G'$ and $G''$, as a function of salt (0.01% - 0.25% wt NaTos). (a) The low salt system is a nearly perfect Oldroyd-B fluid, with the exception of a slight upturn in $G'$ in the plateau region. With increasing NaTos, the upturn in $G'$ at $\omega > \omega_c$ becomes significant; the 0.25% wt NaTos sample has no plateau over the measured $\omega$. (b) Deviations from the Oldroyd-B model with NaTos are more apparent when the moduli are normalized by the crossover modulus, $G_c$.

4.6 Cole-Cole representation of LVE data, $G''/G_c$ vs. $G'/G_c$, normalized by the crossover modulus. Deviations from Maxwell behavior (semi-circular response) are observed at high salt contents, which may result from branching.

4.7 Crossover modulus, $G_c$, as a function of salt concentration (branching level). Error bars are calculated for samples with multiple preparations. $G_c$ is more sensitive to sample preparation than $\eta_0$ or $\tau_R$. The crossover modulus significantly increases when network-like structures become prevalent.

4.8 LVE rheology (a) and SANS (b) characterization of the low branched (0.01%, red $\bigtriangleup$), highly branched (0.25%, black $\Box$) and branched network (0.50%, blue $\bigcirc$) solutions. (a) LVE results confirm a decrease in $\tau_R$, increase in $G_c$ ($\bigstar$), and deviations from Maxwell behavior with branching. (b) While differences in structure result at low q-values due to electrostatic interactions (see insets), at high-q values, the cylindrical structure between samples is identical.

4.9 Normalized intermediate scattering functions (NISFs) for the low branching (0.01% wt, solid symbol, dotted line) and branched network (0.50% wt, open symbol, solid line) solutions. At high $q$-values (short Fourier times), the NISFs are identical within uncertainty. As the $q$-values decrease, subtle but significant changes are seen in the NISFs.
4.10 WLM relaxation rate, $\Gamma(q)$, as a function of $q$. (a) $\Gamma(q)$ across the full $q$-range. $\Gamma(q)$ and $\beta$ are statistically identical at high $q$, where the scaling $\Gamma(q) \propto q^{8/3}$ holds. (b) As $q$ decreases, significant differences in $\Gamma(q)$ and $\beta$ are observed (solid points, $q < 0.02 \text{Å}^{-1}$). Trends continue to lower $q$ (open symbols, second experiment), but uncertainty is higher from using fewer Fourier times.

4.11 Comparison of the low-$q$ ($q = 0.018 \text{Å}^{-1}$), long Fourier time ($\tau = 290 \text{ ns}$) NISFs for the low branched (red) and branched network (blue) solutions. Fits to the data show significant differences in $\beta$, where the low branched $\beta = 0.771 \pm 0.053$ is within error of the theoretical $\beta = 3/4$ for a wormlike chain, and the branched network solution $\beta = 0.628 \pm 0.047$ is within error of the expected value for membranes, $\beta = 2/3$.

4.12 NISFs for low-$q$ configurations ($q < 0.03 \text{Å}^{-1}$) for the 0.01% wt NaTos solution. (a) NISFs from 17 Å (red, blue) and 15 Å (pink, green). Additional Fourier times at 17 Å result in a smaller uncertainty in $\beta$ than at 15 Å. All fits agree with the expected $\beta = 3/4$, within uncertainty. (b) NISFs at $q \approx 0.02 \text{Å}^{-1}$ at: 17 Å centered at $q = 0.018 \text{Å}^{-1}$ and 15 Å at $q = 0.025 \text{Å}^{-1}$. The additional Fourier times at 17 Å lead to a smaller uncertainty in $\beta$, which is closer to $\beta = 3/4$.

4.13 Comparison of the NISFs and fit when the detector is sliced into multiple bins of different widths. (a) NISFs for the same $q$-position ($q \approx 0.018 \text{Å}^{-1}$) when the detector is sliced into 5, 7, or 9 bins produce the same decay constant, $C$ (Equation 4.10) and $\beta$ within the uncertainty. The uncertainty is highest at the smallest bin width (9 bins) (b) Fits to $C$ and $\beta$ are reasonable and follow expected trends regard of bin size for the $q$-range $0.015 < q < 0.021 \text{Å}^{-1}$.

4.14 DLS angular spectra of the normalized, first-order correlation function, $g_1(t)$, vs. the delay time, $t$, as a function of scattering angle, $\theta$, for the network-like, 0.50% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all $\theta$.

4.15 DLS spectra $g_1(t)$ vs. $t$ for the highly branched, 0.25% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all $\theta$; the slow mode is more pronounced (smaller $\beta_2$) than at 0.50% wt NaTos.

4.16 DLS spectra $g_1(t)$ vs. $t$ for the low branching, 0.01% wt NaTos solution in linear-log (a) and log-log scaling (b). Both modes are visible at all $\theta$; the slow mode is the most pronounced (smallest $\beta_2$) in this solution.
4.17 Scaling of $\beta_1$ for the 0.50% wt NaTos solution on a linear-log (a) and log-log (b) scale. To determine $\beta_1$, $g_1(t)$ vs. $q^2t^{\beta_1}$ should collapse wrt the fast mode. Here, $\beta_1 = 1$ and the curves collapse well. As $\theta$ decreases, $\beta_2$ and the fast mode amplitude, $A_1$, increase, as seen by the sharper decay in the slow mode.

4.18 Scaling of $\beta_1$ for the 0.25% wt NaTos solution on a linear-log (a) and log-log (b) scale. As in Figure 4.17, a value of $\beta_1 = 1$ leads to the collapse of $g_1(t)$ vs. $q^2t^{\beta_1}$ for the fast mode. With decreasing $\theta$, $\beta_2$ and $A_1$ increase.

4.19 Scaling of $\beta_1$ for the 0.01% wt NaTos solution on a linear-log (a) and log-log (b) scale. Using $\beta_1 = 1$ leads to a near, but not perfect, collapse of $g_1(t)$ vs. $q^2t^{\beta_1}$ wrt the fast mode. With decreasing $\theta$, $\beta_2$ increases but $A_2$ increases as the slow mode becomes more pronounced.

4.20 Comparison of NSE and DLS. (a) Differences in the low-$q$ NSE data are more distinguishable via DLS, and are likely a result of the solution electrostatics. (b) While the low branching solution exhibits the fastest ‘fast mode’ ($\Gamma_1(q)$), it also exhibits the slowest ‘slow mode’ ($\Gamma_1(q)$). Error bars in the DLS data are the standard deviation calculated from multiple trials.

4.21 $\Gamma(q)$ versus $q^2$ for the fast relaxation mode (a) and the slow relaxation mode (b). The $y$-intercept is negligible in all cases, indicating purely translational diffusion. Error bars are the standard deviation from multiple trials.

4.22 Comparison of the NSE low-$q$ results for the two highly branched solutions, 0.25% wt NaTos and 0.50% wt NaTos. Nearly identical NISFs are obtained between the two samples, confirming the similarity between the two solutions and the presence of highly branched, network-like features.

5.1 Illustration of the velocity profiles corresponding to shear banding (a) and shear thinning (b) across a Couette geometry gap. The shear banding profile is discontinuous with regard to velocity, whereas the shear thinning velocity profile is continuous.

5.2 Concentric cylinder Couette flow resulting in shear banding. Bands of distinct velocity, viscosity and structure (via SANS, inset) are observed.
5.3 Schematic flow curves for shear banding WLMs, with homogeneous constitutive curve ACEG. BF shows the stress selection and steady shear banded flow curve from stress or rate diffusion models. B’F’ shows the steady shear banded flow curve for systems with concentration coupling, or those in measured in a concentric cylinder Couette geometry. The three regions of the flow curve are indicated below the plot. Reprinted with minor revisions with permission from reference [14] from Springer-Verlag (see Appendix P).

5.4 Steady-shear flow curve of the low (0.01% wt NaTos) and high salt (0.10% wt NaTos) solutions on an absolute scale (a) and Weissenberg number scale (b).

5.5 Alignment factor and 1-3 plane 2-D scattering patterns of the low (0.01% wt NaTos, red) and high salt (0.10% wt NaTos, blue) solutions at multiple shear rates across the steady shear flow curve. The mechanism of anisotropy clearly differs between the two series of scattering patterns due to the presence of the interaction peak in the low salt sample and its absence in the high salt sample. The resulting 1-3 $A_f$ is lower in the high salt case until the viscosity upturn. Two points of equal $A_f$ between solutions are highlighted for further discussion: one before and one after the viscosity upturn in the high salt solution.

5.6 Normalized intensity distribution (a,c) and sector-averaged 1-D SANS in the anisotropy direction (b,d) for the low and high salt samples before (a,b) and after shear thickening (c,d), corresponding to the bolded points from Figure 5.5. (a) For equal $A_f$, the intensity distribution of the low salt sample is much sharper than the high salt sample, reflecting the micellar orientation and topology. (B) The SANS structure for the high salt sample under shear is nearly identical to the static high salt structure (blue line). (c) Both samples have equal $A_f$ and nearly identical intensity distributions. This structural change is detected in the 1-D SANS (d), where the sector average scattering from the high salt system under strong flow is nearly identical to that of the low salt system (red line). In contrast, the structure for the low salt system under shear shows increased flow alignment but the correlation peak maintains its position with increasing rate.
5.7 Alignment factor and 1-2 plane SANS 2-D patterns at $\dot{\gamma} = \{45, 26.4, 15\}$ s$^{-1}$ in the 0.01% wt (a) and 0.10% wt NaTos (b) solutions. Symbols denote different experiments: NCNR with 0.1 mm straight slit (□), NCNR with 0.1 mm curved slit (▽), and ILL with 0.3 mm curved slit (○). Inset: relative location of shear rates along flow curve. Shear banding is supported in the low salt system, where $A_f$ is constant at $r/H \geq 0.5$ at all rates. Conversely, the 1-2 plane $A_f$ provides evidence of shear thinning only in the high salt system, as $A_f$ continually decreases across the gap at all rates. The equivalent 1-3 plane $A_f$ is shown by ×. Dotted lines for visual aid only.

5.8 1-3 alignment factor and stress of the low salt (0.01% wt NaTos) and high salt (0.10% wt NaTos) solutions on a Weissenberg number scale. Both samples show nearly linear increases in alignment with increasing $Wi$ or shear rate.

5.9 1-3 $A_f$ vs. viscosity for the low and high salt samples using different sample preparations, geometries, and beamlines. Dotted lines are for visual aid. (a) Results reported in Figure 5.5, on NG-3. (b) Additional trials on NGB-10. The different $A_f$ measured for samples of the same viscosity strongly suggests that topological differences lead to the observed $A_f$ trends. At a critical shear rate, $A_f$ becomes independent of solution viscosity.

5.10 Repeatability of shear thickening in the 0.10% wt NaTos solution over different geometries and sample preparations. (a) Flow curves from two samples are nearly identical, including the shear thickening response. The first curve (solid, 1) was determined by a flow sweep up test, whereas the second curve (open, 2) was determined by startup measurements. (b) Flow curves from the ARES G2 ($\varepsilon = 0.084$) and MCR 502 ($\varepsilon = 0.074$) used for SANS. Shear thickening is preserved despite differences in geometry, instrument, and sample.

5.11 Prediction of $N_1$, $\sigma$ and $\eta$ using Laun’s rule and the Cox-Merz rule from $\sigma^*$ and $\eta^*$ for the 0.01% wt (a) and 0.10% wt NaTos (b) solutions. Quantitatively accurate predictions are shown in the dark, solid lines. The rules provide reasonable values for a larger range of shear rates in the linear case, exceeding the inverse of the material relaxation time. The estimates deviate from the measured values before the inverse of the relaxation time in the branched case.
5.12 Steady shear flow curve for the 0.05% wt NaTos solution. Regions I, II and III are estimated using Equation 5.3 and the Bingham model past region II. The * indicates the maximum Wi for the majority of the LAOS measurements discussed in Chapter 7. Similar features are observed between the experimental data and the VCM model flow curve (digitized from Zhou et al. [65]).

5.13 1-3 plane $A_f$ as a function of applied $Wi$. Excellent agreement is obtained between two rheometer configurations and sample preparations. $A_f$ increases with $Wi$ until $Wi = 250$, at which $A_f$ becomes shear rate independent. Scattering patterns are shown for $Wi = 25$ (region II, a), $Wi = 75$ (end of region II, b) and $Wi = 250$ (region III, c). Evidence of shear banding is seen in (a) and (b), as the anisotropy is superimposed with an isotropic ring in the flow direction; however this ring disappears at $Wi = 250$.

5.14 Steady shear results: 1-2 plane alignment factor and scattering patterns as a function of gap position, $r/H$, and applied shear rate, $Wi$. 2-D patterns are shown for $Wi = 25$ (region II), $Wi = 75$ (end of region II) and $Wi = 247$ (region III). Significant decreases in $A_f$ from the inner to outer wall are most prevalent for $Wi$ well within region II. In and near region III, the alignment factor decreases more linearly with gap position. The estimated width of the high shear band, $\alpha$, is shown in the legend. Dotted lines are for visual aid only.

5.15 1-2 plane orientation angle, $\phi_0$, vs. $r/H$. The dotted line corresponds to the maximum $\phi_0$ observed in the high shear rate band ($\phi_{0,high} \leq 5^\circ$), and the dash-dot line to the minimum $\phi_0$ in the low shear rate band ($\phi_{0,low} > 10^\circ$). A discontinuity in $\phi_0$ is observed between the bands, indicative of the discontinuous structure, orientation, and velocity profile in shear banding solutions.

5.16 1-3 $A_f$ of the 0.01% wt, 0.05% wt, and 0.10% wt NaTos solutions on a shear rate (a) and Weissenberg number (b) scale. As $A_f(\dot{\gamma})$ and $A_f(Wi)$ show opposite trends between the low and high salt solutions, it is unsurprising that the alignment of the mild salt solution falls between the two in both cases.

5.17 1-2 $A_f$ comparison between the 0.01% wt and 0.05% wt NaTos solutions at an equivalent Weissenberg number. The magnitude of $A_f$ and location of the band interface differs between the two solutions.
5.18 1-2 plane $A_f$ fluctuations based on $r/H$ after shear startup at $Wi = 75$. The dotted vertical line at $r/H = 0.15$ indicates the time after startup until steady state is reached. The alignment in time is fairly constant at $r/H \leq 0.5$; fluctuations occur at $r/H = 0.65, 0.85$, indicating proximity to the shear band interface.

5.19 Steady shear flow curves for the 0.125% wt NaTos (a) and 0.15% wt NaTos (b) WLM solutions. $N$ increases from $N = 0.15$ in the 0.10% wt NaTos solution to $N = 0.18$ and $N = 0.2$ for the 0.125% wt and 0.15% wt NaTos solutions, respectively. In (b), shear startup measurements are used to corroborate the flow curve and verify the reproducibility of the observed high rate shear thickening.

5.20 Steady shear flow curves for the 0.185% wt NaTos (a) and 0.25% wt NaTos (b) WLM solutions. $N$ increases with branching to $N = 0.24$ and $N = 0.30$ for the 0.185% wt and 0.25% wt NaTos solutions, respectively. Shear startup measurements are used to corroborate the flow curve in both cases.

5.21 Shear stress (a,b) and 1-3 $A_f$ (c,d) for the 0.15% wt and 0.25% wt NaTos high salt solutions on a shear rate scale (a,c) and Weissenberg number scale (b,d). (a,c) On a shear rate scale, the shear stress and 1-3 $A_f$ are generally higher in the 0.15% wt NaTos solution until the critical shear rate. 2-D SANS patterns are shown for the shear rates indicated by dotted lines, with the 0.15% wt NaTos solution in the first row (purple box). (b,d) Using $Wi$, the shear stress and 1-3 $A_f$ are consistently larger for the 0.25% wt NaTos solution. (c,d) For the 0.15% wt NaTos solution, two sample preparations were examined using different geometries; good agreement was observed between the trials.

5.22 1-3 $A_f$ as a function of shear stress and 2-D scattering patterns for the 0.15% wt and 0.25% wt NaTos solutions. Both 1-3 plane experiments for the 0.15% wt NaTos solution are included. The 1-3 $A_f$ is always greater for equivalent shear stresses in the 0.15% wt NaTos before $\gamma_c$ (patterns a, b). After $\gamma_c$, the 1-3 $A_f$ and associated shear stress are similar between solutions (pattern c).

5.23 1-2 alignment factor, $A_f$, and orientation angle, $\phi_0$, for the 0.15% wt NaTos high salt solution. The continuous change in $A_f$ and $\phi_0$ across the gap indicate shear thinning, similar to the 0.10% wt NaTos solution.
5.24 1-2 alignment factor, $A_f$, and orientation angle, $\phi_0$, for the 0.25% wt NaTos high salt solution. The continuous change in $A_f$ and $\phi_0$ across the gap indicate shear thinning, similar to the 0.10% wt NaTos solution. 274

5.25 1-2 $A_f$ (a) and orientation angle, $\phi_0$, (b) at the inner wall ($r/H = 0.167$) for the 0.25% wt NaTos solution as a function of shear rate. 275

5.26 Steady shear flow curves as a function of added salt, $C_s$ (% wt NaTos) on a shear rate (a) and Weissenberg number (b) basis. (a) The shear stress, $\sigma$, is higher in region I for low $C_s$; in regions II and II, $\sigma$ is similar in magnitude when $C_s > 0.01$% wt NaTos. (b) $\sigma, N$ increase with NaTos based on Wi. 277

5.27 Power law index, $N$, as a function of added salt in terms of $C_s$ (% wt NaTos) (a) and in $R$, the ratio of the molarity of anionic species to cationic species. Empirical relationships are developed in each case that describe the data well. 279

5.28 1-3 $A_f$ as a function of added NaTos for WLM solutions of all branching levels on an absolute shear rate (a) and Weissenberg number (b) scale. 280

5.29 1-3 $A_f$ as a function of shear stress for WLM solutions of all branching levels. $A_f$ for equal stress is highest at low branching levels, indicating that the stress-SANS coefficient (Equation 2.37) increases with branching. 281

6.1 Features of the startup stress response indicative of shear banding at shear rates well within (a) and at the onset of (b) region II. Note that region II refers to the shear banding regime in the three-region, steady shear flow curve. (a) Five stages of the startup response determined by Hu et al. [2]. Linear velocity profiles are observed in I, that become highly nonlinear in II when elastic recoil is observed. In III, a shoulder-like region and stress undershoot are followed by a secondary overshoot (inset). The secondary overshoot marks the onset of IV, where the shear band interface becomes discernible. In V, steady state shear banding occurs. (b) Near the onset of region II, a metastable plateau region is observed (i), which is followed by a sharp decrease in stress (ii), and the steady state stress (iii). 294

6.3 Startup flow curve for the 0.01% wt NaTos solution. The overshoot at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ indicates that steady state has not been reached. Inset shown on a linear-log scale to show the uncertainty in stress at high $\dot{\gamma}$. Dotted lines are for visual aid only; the thick dashed line corresponds to the anticipated steady state behavior at the onset of region II.

6.4 Stress response as a function of time after shear startup for the 0.01% wt NaTos solution for shear rates near the onset of region II. A close-up of the responses in (a) is shown in (b), such that the nonlinear features of the response can be seen more easily. Error bars are the standard deviation of three measurements. Nonlinear features, including stress overshoots, shoulders, undershoots, and secondary overshoots are observed.

6.5 Startup stress response for shear rates near the onset of region II on a log-log (a) and log-linear (b) scaling. Extremely long transients are observed at the lowest rate ($\dot{\gamma} = 0.5 \text{ s}^{-1}$); oscillating stress responses are observed when $\dot{\gamma} = 2.5 \text{ s}^{-1}$.

6.6 Startup stress response at shear rates within the shear banding regime corresponding to the 1-2 plane flow-SANS measurements. Error bars represent the standard deviation of three startup measurements. A close-up of the responses in (a) is shown in (b), such that the nonlinear features of the response can be seen more easily. The shape of the stress response at $\dot{\gamma} = 45 \text{ s}^{-1}$ is distinct from the response at all lower shear rates.

6.7 Startup stress response at shear rates near the onset of region III. A close-up of the responses in (a) is shown in (b), such that the chaotic responses can be seen more easily. Error bars represent the standard deviation of three startup measurements.

6.8 Startup stress responses for the three trials at each shear rate within the shear banding regime. (a,b) Fairly stable, reproducible stress responses are observed between trials. (c) The fluctuations of the stress response are larger and become chaotic; the response varies further between trials.

6.9 1-3 plane $A_f$ as a function of time after shear startup at shear rates near the onset of region II, on a log-log (a) and log-linear (b) scale. A long transient in $A_f$ is observed at all rates, and is consistent with the long transient in the stress response that indicates shear banding. The maximum startup $A_f$ is several-fold larger than the steady state values.
1-3 plane $A_f$ as a function of time after shear startup, on a log-log (a) and log-linear (b) scale. A long transient in the $A_f$ response is consistent with shear banding when $\dot{\gamma} \leq 90 \text{ s}^{-1}$. At $\dot{\gamma} = 150 \text{ s}^{-1}$, the fast structural transient indicates little to no shear banding.

Steady state 1-2 plane alignment factor for the 0.01% wt NaTos solution as a function of gap position, $r/H$. (a) Measurements taken at the end of shear startup. An upturn in alignment at the outer wall is most apparent at $\dot{\gamma} = 90$ and $150 \text{ s}^{-1}$, suggesting the presence of a third shear band. (b) The presence of a third band is further suggested by separate measurements at $\dot{\gamma} = 45 \text{ s}^{-1}$, where the upturn is also observed.

1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 15 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.

1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.

1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 45 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.

1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ and time after shear startup. (a) Highly shear thinning behavior is observed at early times. (b) The shear bands begin to form. (c) The material at the outer wall re-entangles and settles; the shear band interface is pronounced. An alignment band is formed at the outer wall. $A_f$ at $r/H = 0.9$ is lower than at the other positions. (d) $A_f$ in the alignment band increases in magnitude. (e) $A_f$ in the alignment band begins to settle. (f) An approximate steady state is reached.

Gap-dependent 1-2 plane $A_f$ at different time points (in seconds) after shear startup at (a) $\dot{\gamma} = 15 \text{ s}^{-1}$, and (b) $\dot{\gamma} = 45 \text{ s}^{-1}$. ‘Re-alignment’ is observed at both rates.

1-2 plane $A_f$ at the outer wall as a function of time after shear startup at (a) $\dot{\gamma} = 15 \text{ s}^{-1}$, (b) $\dot{\gamma} = 26.4 \text{ s}^{-1}$, and (c) $\dot{\gamma} = 45 \text{ s}^{-1}$. At all shear rates, $A_f$ ‘re-aligns’ and increases in time after reaching its minimum value.
6.18 Velocity profile for the 0.01% wt NaTos solution at $\dot{\gamma} = 45 \text{ s}^{-1}$. Three distinct shear bands can be identified, where the lowest shear rate is in the second band. Profile measurements were taken twenty minutes after shear startup. Dotted lines are approximate and for visual aid only. 

6.19 Velocity profile for the 0.01% wt NaTos solution at $\dot{\gamma} = 8.5, 26.4, \text{ and } 45 \text{ s}^{-1}$. Three distinct shear bands can be identified in all three cases, and the same degree of wall slip is observed for each shear rate. Profile measurements were taken twenty minutes after shear startup, which may not be sufficient for the profile to reach steady state.

6.20 Startup flow curve for the 0.05% wt NaTos solution, which is similar to the steady shear curve shown in Chapter 5. Inset shown on a linear-log scale to show the fluctuations in the stress response at high $\dot{\gamma}$.

6.21 Stress response as a function of time after shear startup for the 0.05% wt NaTos solution for shear rates near the onset of region II. Error bars are the standard deviation of three trials. Nonlinear features including stress overshoots, undershoots, secondary overshoots, and a metastable plateau region are observed.

6.22 Stress response as a function of time after shear startup for shear rates within region II, which are used in the 1-2 plane measurements. Error bars are the standard deviation of three trials. The stress overshoot becomes sharper and more pronounced with increasing shear rate; the stress undershoot and secondary overshoot become less pronounced with rate.

6.23 Stress response as a function of time after shear startup for shear rates at and above the onset of region III. Error bars are the standard deviation of three trials. The shape of the stress overshoot does not change significantly with rate; fluctuations in the stress response increase with increasing shear rate.

6.24 1-3 plane alignment factor as a function of time after startup for the 0.05% wt NaTos solution at shear rates near the onset of region II on a (a) log-log and (b) log-linear scale for clarity. A long, gradual transient is observed at each of the three shear rates, similar to the stress response shown in Figure 6.22.

6.25 1-3 plane $A_f$ as a function of time after startup at shear rates well within region II and into region III on a (a) log-log and (b) log-linear scale for clarity. A long, gradual transient is observed that is distinct in shape from the pronounced transient observed in the low branching solution.
6.26 Steady shear 1-2 plane $A_f$ for the 0.05% wt NaTos solution as a function of gap position, $r/H$, taken at the end of shear startup measurements. Results are consistent with the steady shear results presented in Chapter 5, Section 5.7.3. An increase in the width of the high shear rate band is observed with increasing shear rate (Equation 5.4).

6.27 1-2 plane $A_f$ for the 0.05% wt NaTos solution as a function of time after shear startup at $\dot{\gamma} = 15$ s$^{-1}$ (a) and corresponding steady state $A_f$ as a function of gap position (b). The location of the shear band interface is depicted for visual aid using the critical values set forth by Helgeson et al. [23].

6.28 1-2 plane $A_f$ as a function of time after shear startup at $\dot{\gamma} = 26.4$ s$^{-1}$ (a) and corresponding steady state $A_f$ as a function of gap position (b). The location of the shear band interface is estimated for visual aid.

6.29 1-2 plane $A_f$ as a function of time after shear startup at $\dot{\gamma} = 45$ s$^{-1}$ (a) and corresponding steady state $A_f$ as a function of gap position (b). The location of the shear band interface is estimated for visual aid.

6.30 1-2 plane $A_f$ for $\dot{\gamma} = 26.4$ s$^{-1}$ as a function of $r/H$ and time after shear startup. (a) The low shear band has started to form, including three positions where $r/H \geq 0.65$. (b) The alignment in the low shear rate band decreases, while the high shear rate band alignment increases. (c) The material at the outer wall re-entangles and settles, further decreasing in $A_f$. The location of the shear band interface moves to lower $r/H$. (d) The location of the band interface continues shifting to lower $r/H$, consistent with the disentangle, re-entangle mechanism. (e) $A_f$ in both bands begins to settle. (f) An approximate steady state is reached, where the interface is located between $0.3 < r/H < 0.5$.

6.31 Time-dependent 1-2 plane $A_f$ for (a) $\dot{\gamma} = 15$ s$^{-1}$ and (b) $\dot{\gamma} = 45$ s$^{-1}$. (a) The location of the shear band interface continues moving to the left, indicating a growth of the low shear rate band. (b) A faster transient is observed at higher rates. Results at both shear rates are consistent with the disentangle, re-entangle mechanism.

6.32 Steady shear 1-2 plane $A_f$ for the 0.01% wt and 0.05% wt NaTos solutions at equivalent Weissenberg numbers, $Wi \approx 80$, taken at the end of shear startup measurements.
6.33 Stress response as a function of time after startup for the 0.10% wt NaTos solution. (a,b) The stress response near the onset of region II exhibits a rounded stress overshoot and at higher rates, a minor stress undershoot. No secondary overshoot is observed. (c,d) At the three shear rates well within region II, the rounded stress overshoots and undershoots are still observed. Secondary overshoots are also observed, but no shoulder-like features are present. (e,f) At the highest rates in region III, shoulder-like features are finally observed but are distinct from those in the shear banding solutions. At all shear rates, the stress response reaches its steady state value in $t \leq 5 \; \text{s}$ ($t \leq 12 \tau_R$).  

6.34 1-3 plane $A_f$ for the 0.10% wt NaTos solution as a function of time after startup for shear rates well within region II and region III on a (a) log-log and (b) linear-linear scaling. $A_f$ exhibits some fluctuations due to poor statistics. No time dependence is observed at startup, indicating shear thinning.  

6.35 Steady shear 1-2 plane $A_f$ for the 0.10% wt NaTos solution as a function of gap position, $r/H$, taken at the end of shear startup measurements. Results are consistent with the steady shear results presented in Chapter 5, Section 5.5.3. No shear banding is observed.  

6.36 1-2 plane $A_f$ as a function of time after startup at (a,b) $\dot{\gamma} = 15 \; \text{s}^{-1}$, (c,d) $\dot{\gamma} = 45 \; \text{s}^{-1}$, and (e,f) $\dot{\gamma} = 60 \; \text{s}^{-1}$ on a (a,c,e) log-log and (b,d,f) linear-linear scale. No transience or shear banding is observed at any shear rate. The fluctuations in $A_f$ when $\dot{\gamma} = 60 \; \text{s}^{-1}$ may be due to the proximity to region III.  

6.37 Comparison of velocity profiles for the 0.01% wt and 0.10% wt NaTos solutions at $\dot{\gamma} = 45 \; \text{s}^{-1}$. A nearly linear velocity profile with no slip is observed for the highly branched solution, indicating shear thinning. The velocities are nearly identical at the outer wall.  

6.38 Ratio of the overshoot (maximum) to steady state viscosity as a function of $Wi$ and branching level. As is observed in entangled polymers, the ratio of the overshoot to steady state viscosity or stress is a signature of solution morphology. The ratio decreases with branching, suggesting branching mitigates breakage upon startup.
7.1 Oscillatory shear applied deformations and analysis. a) The applied strain and strain rate are sinusoidal and co-sinusoidal in time (top), and the resulting linear regime stress responses in time (bottom). A response in phase with the strain is a classical elastic response, and with the rate is a viscous response; phase shifted responses are viscoelastic. b) Elastic (top) and viscous (bottom) Lissajous-Bowditch curves of the linear stress responses, where the stress is analyzed in terms of the strain and the strain rate. The linear responses represent classical elastic (top) and viscous (bottom) behaviors. c) Microstructure or alignment factor responses that display elastic (top) and viscous (bottom) behavior through the oscillation. In each case, the alignment factor closely follows the phase and shape of the magnitude of the applied deformation, as $A_f$ is a positive scalar quantity. In this WLM solution, the $A_f$ response is elastic at high $De$ and viscous at low $De$ for the same maximum shear rate, as is expected.

7.2 Dynamic moduli $G'$ (□) and $G''$ (△) of the 0.05% wt NaTos WLM solution. The Oldroyd-B model fit is shown by solid line. The two Deborah numbers that will be examined by LAOS section are highlighted in red ($De = 0.17$, $\omega = 0.1$ rad · s$^{-1}$) and blue ($De = 0.58$, $\omega = 0.35$ rad · s$^{-1}$).

7.3 Pipkin diagrams of the Lissajous-Bowditch projections: (top) Elastic ($\sigma(t)$ vs $\gamma(t)$) and (bottom) viscous ($\sigma(t)$ vs $\dot{\gamma}(t)$). The bolded red and blue spectra correspond to the conditions explored using flow-SANS.

7.4 Lissajous-Bowditch projections of the LAOS stress response for (a) condition one ($De = 0.17$, $Wi = 75$), and (b) condition two ($De = 0.58$, $Wi = 75$). Red outlined portions of the curves denote elastic-like behavior, where a linear relationship in $\sigma$ vs. $\gamma$ is observed. The micelles break and yield after this stress overshoot. Blue outlined curves denote fluid-like behavior, where a linear relationship in $\sigma$ vs. $\dot{\gamma}$ is observed, indicating viscous flow after micelle breakage. While the classic elastic and viscous behaviors are observed in both conditions, the behaviors are more pronounced in condition one.

7.5 Comparison of experimental LAOS conditions with VCM model predictions (open circles). Equal strain amplitudes are shown by color, $Wi$ by symbol, and $De$ by open/closed symbols. All but two conditions are predicted to shear band under LAOS. Alignment banding is observed for conditions marked by □. VCM predictions are digitized from [10].
7.6 (a) 1-2 plane $A_f$ as a function of cycle time, $t/T$, and gap position, $r/H$, at $De = 0.17, Wi = 75$. The shape and time-dependence of $A_f$ closely tracks that of $|\dot{\gamma}|$. (b) 1-2 $A_f$ as a function of gap position at select $t/T$ as indicated in (a). The alignment factor as a function of gap position decreases significantly when $A_f > 0$, leading to a similar mechanism of shear banding as is observed under steady shear.

7.7 Orientation angle, $\phi_0$, as a function of cycle time, $t/T$, and gap position, $r/H$, at $De = 0.17, Wi = 75$. Based on $\phi_0$, the three inner positions ($r/H = 0.15, 0.35, 0.5$) appear to cluster together to form the high shear rate band, whereas $r/H = 0.65, 0.85$ form the low shear rate band.

7.8 (a) 1-2 plane $A_f$ at $De = 0.58, Wi = 75$. At all $r/H$, $A_f$ is in phase with the stress response and roughly in phase with $|\dot{\gamma}|$. As the shape of $A_f$ contains local extrema, $A_f$ is a function of both $|\gamma|$ and $|\dot{\gamma}|$. (b) 1-2 plane $A_f$ at select $t/T$ indicated in (a). $A_f$ is more discontinuous across the gap than in condition one, indicating shear banding that is also fairly independent of $t/T$.

7.9 Orientation angle, $\phi_0$, as a function of $t/T$ and $r/H$ at $De = 0.58, Wi = 75$. As in condition one, the three inner positions appear to form the high shear rate band, whereas the outer two form the low shear rate band.

7.10 1-2 plane $A_f(t/T)$ at $r/H = 0.15$ and LAOS stress for condition one (L) and two (R); steady shear stress at $Wi = 75$ given by $. The maximum $A_f$ and stress are greater in condition two. The alignment follows the shape of $|\dot{\gamma}|$ in condition one; whereas the 1-2 $A_f$ in condition two is influenced by the stress response.

7.11 1-2 plane $A_f$ at three conditions: $Wi = 75$ steady shear ($\Box$); condition one at $Wi = 75$ ($\bigcirc$); and condition two at $Wi = 75$ ($\triangle$). The condition one $A_f$ is similar, but less than, the steady shear $A_f$. Condition two exhibits ‘over-orientation,’ where the 1-2 $A_f$ is always greater than that of steady shear. Over-orientation is more pronounced near the outer wall, in the low shear band.

7.12 1-2 plane $A_f$ as a function of $t/T$ and $r/H$ for both conditions. Condition one ($De = 0.17, Wi = 75$) is shown with solid lines whereas condition two ($De = 0.58, Wi = 75$) is shown with data points. With decreasing $|\dot{\gamma}| (0 \leq t/T \leq 0.25, 0.5 \leq t/T \leq 0.75), A_f$ is similar between conditions at $r/H = 0.15$ and 0.35. When $r/H \geq 0.5$, the alignment factor deviates, suggesting a different mechanism of shear banding.
7.13 1-2 plane $A_f$ and shear stress for $De = 0.33$, $Wi = 75$. The alignment during the oscillation contains features of conditions one and two, including an overshoot and maximum alignment when $t/T = 0.5$. 

7.14 1-2 plane $A_f$ and shear stress for $De = 0.50$, (L) $Wi = 64$ (region II), and (R) $Wi = 113$ (region III). (L) The material appears to shear band due to the outer wall over-orientation and large decrease in $A_f$ across the gap. (R) Aligned material has filled the gap, leading to a metastable, non-shear banded state in region III. 

7.15 1-2 plane $A_f$ and shear stress for conditions where $\gamma_0 = 128.5$. (L) $De = 0.67$, $Wi = 84$. (R) $De = 0.75$, $Wi = 95$. While the magnitude of the alignment differs, the qualitative trends indicate a metastable structural state in region III. 

7.16 LAOS stress response of the 0.01% wt NaTos solution based on equivalent Weissenberg number (shear rate) amplitude, $Wi_0$, in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) $Wi_0 \approx 300$. The stress overshoot becomes less pronounced and lower in magnitude as $De$ is increased, which leads to a decreasing enclosed area in the secondary loops of the viscous projections. (c,d) $Wi_0 = 450$. The same behaviors are observed as in (a,b); however, the stress overshoot has nearly disappeared when $De = 4.2$ and has fully disappeared when $De = 9$. The disappearance of the overshoot indicates that micellar breakage is limited, which may mitigate shear banding or lead to a different shear banding mechanism. 

7.17 LAOS stress response based on equivalent Deborah number, $De$, in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) $De = 1.4$. While all curves are similar in shape, the magnitude of the stress overshoot is not a simple function of $Wi_0$. Nearly equivalent local moduli are seen in all conditions; equal LAOS stresses are observed at the maximum shear rate ($\gamma = 0$). (c,d) $De = 2$. Similar behaviors are observed as in (a,b). The LAOS stresses are nearly equal when $\gamma = 0$, but are actually equal at strains closer to the stress overshoot than in (a,b).
7.18 LAOS stress response based on equivalent strain amplitude, $\gamma_0$, in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) $\gamma_0 = 321$. The two curves are similar in shape, but the prominence and magnitude of the stress overshoot is greater at lower frequency. A steeper slope in (a) in the region of the stress overshoot when $De \approx 1$ indicates a larger local modulus. The LAOS stresses are equal at the maximum strain. (c,d) $\gamma_0 = 150$. Similar behaviors are observed as in (a,b), where the stress overshoot is more pronounced at lower $De$, and a larger local modulus is observed. The LAOS stresses are equal at the maximum strain.

7.19 LAOS stress response for all conditions. The dotted vertical lines indicate the phase of a viscous fluid response. As $De$ increases, the phase of the response shifts more toward elastic-like behavior.

7.20 LAOS 1-3 plane $A_f$ for three conditions where $Wi = 321$ and $De = 1, 3, 9$. Nearly fluid behavior is observed when $De = 1$ and nearly elastic behavior is observed when $De = 9$; the phase of the response when $De = 3$ falls in between. The magnitude of the $A_f$ response is not affected between $De = 1$ and $De = 3$ but decreases when $De = 9$.

7.21 LAOS 1-3 plane $A_f$ for $De = 0.48, Wi = 321$ and $De = 9, Wi = 3210$, with the conditions from Figure 7.20. The phase when $De = 0.48$ is closer to fluid behavior than when $De = 1$. When $Wi$ is increased 10-fold when $De = 9$, the magnitude of $A_f$ doubles. The phase of the $A_f$ response also shifts to the left, and is similar to when $De = 3$. This response illustrates that the relative magnitude of $De : Wi$ contributes to the phase of $A_f$.

7.22 1-2 plane $A_f$ for the 0.01% wt NaTos solution for $De \approx 1, Wi = 295$. (a) An alignment band is observed when $r/H > 0.5$, where $A_f$ is similar between positions. $A_f(r/H = 0.525)$ is higher in magnitude than $A_f(r/H = 0.675)$, suggesting it is near the band interface. $A_f(r/H = 0.825)$ is larger than when $r/H = 0.675$, suggesting the presence of a third shear band. (b) $A_f$ profiles at select $t/T$ indicated by vertical lines in (a), along with the steady shear profiles for $Wi = 264$ and 450. The LAOS alignment band is similar to steady shear.
7.23 1-2 plane \( A_f \) during the LAOS cycle for the 0.01% wt NaTos solution for \( De = 1, Wi = 450 \) (a) the cycle average response, (b) hour-long trials during the experiment. Similar results are obtained between trials, indicating the response is stable over the course of the experiment. An alignment band occurs when \( r/H \geq 0.675 \), where \( A_f \) is indistinguishable between positions. \( A_f(r/H = 0.525) \) is similar in magnitude to the alignment band, suggesting that \( r/H = 0.525 \) is near the shear band interface.

7.24 1-2 plane \( A_f \) for \( De = 1, Wi = 450 \) where select \( t/T \) are shown by the dotted lines in (a), for which the \( A_f \) profiles are shown as a function of \( r/H \) in (b), along with the steady shear profile for \( Wi = 450 \). Clear alignment banding is observed throughout the cycle, which is similar to the steady shear banding at \( Wi = 450 \).

7.25 1-2 plane \( A_f \) for \( De = 1.4, Wi = 450 \) for different times in the experiment at two gap positions: \( r/H = 0.825 \) (a) and \( r/H = 0.725 \) (b). (a) The phase of the \( A_f \) response clearly shifts in time to the left. (b) The \( A_f \) response starts with the same phase as in (a) and then the phase shifts to the left, before reversing and shifting to the right.

7.26 1-2 plane \( A_f \) for \( De = 1.4, Wi = 450 \) for different experiment times at three gap positions: \( r/H = 0.725 \) (a,b), \( r/H = 0.825 \) (b), \( r/H = 0.875 \) (b). (a) The phase of the \( A_f \) response shifts in time regardless of experiment time. The response moves to the right before reversing and moving to the left. (b) \( A_f \) at all \( r/H \) appears to shift in unison. The phase moves continuously in time to the left regardless of \( r/H \). Despite the poor statistics associated with 0.5 hour trials, \( A_f \) at \( r/H = 0.875 \) is clearly larger than at \( r/H = 0.725 \).

7.27 1-2 plane \( A_f \) for \( De = 1.4, Wi = 450 \) at different experiment times at the inner wall (a) and near the outer wall (b). (a) In the high shear rate band \( (r/H = 0.125, 0.325) \), the phase of the \( A_f \) response does not appear to shift in time. (b) When \( r/H = 0.475 \), the phase of the \( A_f \) response shifts to the left in time. At \( r/H = 0.625 \), the \( A_f \) response shifts to the right; experiments were taken immediately prior to the \( r/H = 0.475 \) data. Dotted lines which indicate the response phases are for visual aid.
7.28 1-2 plane $A_f$ for $De = 1.4$, $Wi = 450$ for experiment times where the $A_f$ phases are roughly equivalent at all $r/H$. (a) An alignment band is formed between $r/H = 0.625$ and 0.825, indicative of shear banding. $A_f(r/H = 0.475)$ is similar in magnitude to the alignment band, suggesting it is near the shear band interface. $A_f(r/H = 0.875)$ is greater than in the alignment band, giving evidence of a third shear band. (b) $A_f(r/H)$ for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 450$ are shown for comparison. Shear banding and the presence of a third band are suggested throughout the cycle.

7.29 1-2 plane $A_f$ for $De = 2$, $Wi = 300$. (a) An alignment band is formed between $r/H = 0.675$ and 0.825, where $A_f$ is nearly identical throughout the cycle. $A_f(r/H = 0.525)$ is similar in magnitude to the alignment band, suggesting that $r/H = 0.525$ is near the shear band interface. (b) $A_f$ as a function of $r/H$ for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 264$ and $Wi = 450$ are shown for comparison.

7.30 1-2 plane $A_f$ during $t/T$ for $De = 2$, $Wi = 450$. A clear alignment band indicative of shear banding occurs for positions $r/H = 0.675$ and 0.825, where $A_f$ is identical within the uncertainty throughout $t/T$.

7.31 1-2 plane $A_f$ during $t/T$ for $De = 3$, $Wi = 450$ for two gap positions. $A_f$ does not appear fully two-fold symmetric for $r/H = 0.675$.

7.32 1-2 plane $A_f$ during the LAOS cycle for $De = 4.2$, $Wi = 450$. (a) The first two measurements at the inner and outer wall, where the outer wall phase appears shifted from the inner wall phase. (b) The phase of the $A_f$ response at the outer wall, which gradually shifts in time. The minima in the $A_f$ response for each time point are indicated by the dotted vertical lines.

7.33 1-2 plane $A_f$ as a function of time at the inner wall when $De = 4.2$, $Wi = 450$. (a) The $A_f$ response at $r/H = 0.325$ shifts significantly from startup to $t = 2.5$ hours. $A_f$ at $r/H = 0.125$ is further shifted and nearly perfectly in phase with the applied strain. (b) Both positions exhibit nearly perfect elastic-like responses. The minima in the $A_f$ response for each time point are indicated by the dotted vertical lines.

xlvi
7.34 1-2 plane $A_f$ when $De = 4.2$, $Wi = 450$. (a) $A_f$ at $r/H$ is recorded consecutively to probe similar time points in the experiment; the response phases are similar. Dotted lines indicate times examined in (b). (b) $A_f$ profiles at select $t/T$, and the corresponding steady shear $A_f$. The alignment band in the outer two gap positions and the magnitude of the alignment during the cycle is similar to that observed in steady shear.

7.35 1-2 plane $A_f$ during the LAOS cycle for $De = 9$, $Wi = 450$. The first measurements at each $r/H$ are shown in (a), whereas the second round of measurements at each $r/H$ are shown for comparison in (b). The phase of the $A_f$ response at each position gradually shifts in time toward more elastic behavior.

7.36 1-2 plane $A_f$ for $De = 9$, $Wi = 450$ with cycle times indicated by dotted lines (a) that are used to show the alignment profiles during the cycle in (b). A comparison to the steady shear alignment is also shown in (b). A clear banded structure is apparent throughout the oscillation, that differs in the type of banding from steady shear.

7.37 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$. (a) The $A_f$ responses are shifted so the phases are aligned at all $r/H$. (a) An alignment band is formed between $r/H = 0.625$ and $0.825$, indicative of shear banding. $A_f(r/H = 0.475)$ is similar in magnitude to the alignment band, suggesting it is near the shear band interface. (b) $A_f$ as a function of gap position for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 264$ and $Wi = 450$ are shown for comparison. Banded structures similar to the steady shear profiles are observed throughout the cycle.
7.40 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times when $r/H = 0.675$. (a) The phase shifts to the right between $t = 0$ and $t = 2$ hours. (b) After $t = 2$ hours, the phase of the $A_f$ response reverses and shifts to the left. Dotted vertical lines estimate the phases of the $A_f$ response.

7.41 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times for: (a) $r/H = 0.125$ through $r/H = 0.325$ and (b) $r/H = 0.225$ and $r/H = 0.525$ through $r/H = 0.825$. (a) No phase shifts occur within individual half-hour trials at the inner wall; however, a significant phase shift is observed between $r/H = 0.225$ (which was taken at later times) and the other positions. (b) With increasing time, the phase of the $A_f$ response shifts to the right, regardless of gap position. Dotted vertical lines estimate the phases of the $A_f$ response.

7.42 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times for trial two when: (a) $r/H = 0.325$, and (b) $r/H = 0.675$. (a) At the inner wall, no phase shift is observed in $A_f$ from $t = 0 - 1.5$ h. A small, left shift is observed between $t = 1.5 - 2$ h. (b) At the outer wall, the phase of the response shifts continuously to the left. At $t = 2$ h, the phase at the outer wall and inner wall are nearly equal. Dotted vertical lines estimate the phases of the $A_f$ response.

7.43 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ for all gap positions for three continuous trials of three hours each. (a) The phase shifts to the left in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.2$ and $t/T = 0.7$. (b) The phase reverses and shifts to the right in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.27$ and $t/T = 0.77$. (c) The phase one again reverses and shifts to the left in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.22$ and $t/T = 0.72$.

7.44 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times when (a) $r/H = 0.125$, and (b) $r/H = 0.675$. (a) The phase of the alignment factor response at the inner wall does not change over a 1.5h time frame, similar to results seen in conditions three and nine. (b) At the outer wall, the phase shifts to the left before reversing and shifting to the right. Dotted vertical lines estimate the phases of the $A_f$ response.

7.45 1-2 plane $A_f$ during $t/T$ at $r/H = 0.125$ for three conditions: $De \approx 1$, $Wi = 295$, $De = 1$, $Wi = 450$, and $De = 2$, $Wi = 300$. Dotted vertical lines correspond to the phases of the responses. As $De$ is increased, the phase of the $A_f$ response shifts further from fluid-like behavior.
7.46 1-2 plane $A_f$ during $t/T$ at $r/H = 0.125$ for three conditions when
$De = 1.4$: $Wi = 300$, $Wi = 400$ and $Wi = 450$, corresponding to strain
amplitudes of $\gamma_0 = 215, 286, 321$, respectively.

7.47 1-2 plane $A_f$ when $t/T = 0.5$ ($Wi = 300$) for the three conditions where
$Wi_0 \approx 300$: $De = 1, 1.4, 2$. At all gap positions, $A_f$ is approximately
identical between conditions. Dotted lines are for visual aid only.

7.48 1-2 plane $A_f$ when $t/T = 0.5$ for the conditions where $Wi_0 = 450$:
$De = 1, 1.4, 2, 4.2$, and $9$. $A_f(t/T = 0.25)$ is also shown for conditions 7
and 8, which exhibited strain-dependent alignment. In conditions 2, 3, and
5, $A_f$ is approximately identical between conditions. Dotted lines are for
visual aid.

7.49 Steady shear stress and (a) stress at the equivalent, maximum shear rate
during LAOS, and (b) the root-mean-square average LAOS stress, $\sigma^*$, for
the low branching solution. The larger LAOS stresses in both cases help
explain the observed over-orientation. In (a), when $De = 9$, the steady
shear and LAOS stresses are approximately equal.

7.50 Comparison of 0.10% wt NaTos ‘original’ sample used for previously
reported experiments (blue) vs. the solution for the LAOS experiments.
The LAOS sample has a longer relaxation time and a similar structure to
the 0.075% wt NaTos solution, suggesting it has an effective salt content
less than the original 0.10% wt NaTos solution.

7.51 Comparison of the 1-3 plane $A_f$ for the 0.10% wt NaTos ‘original’ sample
and the ‘new’ LAOS sample. The higher 1-3 $A_f$ in the new LAOS sample
suggests it has a lower effective salt concentration, which is consistent
with our estimates based on the rheology and static SANS.

7.52 Comparison of the 1-2 plane $A_f$ for the 0.10% wt NaTos ‘original’ sample
and the ‘new’ LAOS sample. The higher 1-2 $A_f$ in the new LAOS sample
further supports that it has a lower effective salt concentration. Dotted
lines are for visual aid only.

7.53 Lissajous-Bowditch representation of the stress response for $De \approx 1,$
$Wi = 25$. Reported values of $De$ and $Wi$ are based on the new 0.10% wt
NaTos solution. (a) Elastic representation, $\sigma$ vs. $\gamma$, and (b) viscous
representation, $\sigma$ vs. $\dot{\gamma}$.
Lissajous-Bowditch representation of the stress response for two conditions: $De = 2.5$, $Wi = 8.3$, and $De = 7.5$, $Wi = 25$. Reported values of $De$ and $Wi$ are based on the new 0.10% wt NaTos solution. (a) Elastic representation, $\sigma$ vs. $\gamma$, and (b) viscous representation, $\sigma$ vs. $\dot{\gamma}$. 

1-3 plane $A_f$ and LAOS stress during $t/T$ for the 0.10% wt NaTos solution at $De \approx 1$, $Wi = 25$. The $A_f$ response is in phase with the stress and is nearly in phase with the applied shear rate, indicating primarily fluid-like behavior.

1-3 plane $A_f$ and LAOS stress during $t/T$ at $De = 2.5$, $Wi = 8.3$. The $A_f$ response is in phase with the stress and is nearly in phase with the applied strain, indicating elastic-like behavior.

1-3 plane $A_f$ and LAOS stress during $t/T$ at $De = 0.08$, $Wi = 25$. The $A_f$ response is in phase with the applied shear rate, indicating fluid behavior.

1-2 plane $A_f$ during the LAOS cycle for the 0.10% wt NaTos solution for (a) $De \approx 1$, $Wi = 25$ and (b) $De = 7.5$, $Wi = 25$. 

Steady shear stress (from rheo-SANS) and the stress at the equivalent, maximum shear rate during LAOS for the highly branched solution. The larger LAOS stress at $De \approx 1$, $Wi = 25$ explains the observed over-orientation.

Illustration of branch formation in WLMs by adding NaTos. The WLMs transition from long and entangled species (a) to branched and entangled species (b), and finally, an interconnected network (c).

1-2 plane $A_f$ at two gap positions during LAOS, where list mode is not used and phase shifts are observed between the two positions. In both cases, the inner wall was measured first. (a) Initial experiments on the 0.01% wt NaTos solution. (b) Initial experiments on the 0.05% wt NaTos solution.

Possible surface charge profiles in ionic WLM solutions. (a) Uniform (b) Uniform distribution of hydrotropic counterion salt (c) Uniform counterion at higher ratio (d) Non-uniform counterion.

CaBER results from multiple trials for the: (a) 0.01% wt and (b) 0.10% wt NaTos solutions. Dotted vertical lines indicate the elastocapillary regime used to calculate the extensional relaxation time and viscosity.
8.5 1-2 plane $A_f$ under LAOS ($De = 1, Wi = 321$) for the 0.01% wt NaTos solution for thirty minute trials using the NCNR 1-2 shear cell. A flat, instead of rounded, response is seen, which reflects the non-sinusoidal waveform applied by the motor.

B.1 Static scattering of the 0.01% wt (a) and 0.05% wt (b) NaTos solutions across multiple configurations. The interaction peak region is shown in blue; $q^*$ is shown in pink. In (b), the lower peaks for NGB10 configurations are a result of the instrument resolution and closer detector distance.

B.2 Static scattering of the 0.10% wt (a) and 0.15% wt (b) NaTos solutions across multiple configurations. The $q^{-1}$ region is highlighted in blue; $q^*$ is highlighted in pink.

B.3 Static scattering of the 0.25% wt NaTos solution across multiple configurations. The $q^{-1}$ region is highlighted in blue; $q^*$ is highlighted in pink.

C.1 Amplitude sweep for the 0.25% wt NaTos solution (in water) to determine the linear viscoelastic regime across the relevant frequency range, where $\omega_c \approx 4.5 \text{ rad} \cdot \text{s}^{-1}$. (a) $\omega = 0.45 \text{ rad} \cdot \text{s}^{-1}$, well below the crossover frequency $\omega_c$ where $De = 0.1$ (b) $\omega = 10 \text{ rad} \cdot \text{s}^{-1}$, near $\omega_c$ where $De = 2.2$ (c) $\omega = 45 \text{ rad} \cdot \text{s}^{-1}$, well above $\omega_c$ where $De = 10$.

C.2 Amplitude sweep at high frequencies for the 0.10% wt NaTos solution (D$_2$O). (a) $\omega = 20$ to 32 rad·s$^{-1}$. At $\omega = 30$ and 32 rad·s$^{-1}$, the LVE window is small due to changes in $G''$. Responses at these frequencies are likely inaccurate, as the transducer torque range changes and produces unreliable data. (b) $\omega = 34$ to 40 rad·s$^{-1}$; the LVE window appears wider than in (a) despite higher $\omega$.

D.1 Relevant length scales for SANS instrumental smearing. Note that $L_1$ extends before the source aperture at the nozzle, such that collimation effects are accounted for. Reprinted from reference [2].
E.1 Cryo-TEM images of the low branching (0.01% wt NaTos, top red), high branching (0.10% wt NaTos, middle blue) and very high branching (0.15% wt NaTos, bottom purple) solutions. Images were taken at different magnifications and grid locations. The 1D static scattering of the 0.15% wt NaTos solution is also highlighted in purple in the static SANS plot Chapter 4. Similar to the 0.10% wt NaTos solution, a variety of irregular structures, junctions and loops are observed in the 0.15% wt NaTos solution; however, the 0.01% wt NaTos solution shows primarily linear structures in all images.

F.1 Frequency sweep (a) and flow curve (b) for the 0.25% wt NaTos solution in water. The crossover frequency, \( \omega_c \), is \( \omega_c = 4.6 \text{ rad}\cdot\text{s}^{-1} \), such that \( \tau_R = 0.22 \text{ s} \). The crossover modulus is \( G_c = 2.6 \text{ Pa} \), which is about half that of the solution in D\(_2\)O; the zero-shear viscosity is \( \eta_0 = 1.2 \text{ Pa}\cdot\text{s} \), which is about 10-fold higher than for the D\(_2\)O solution.

F.2 Frequency sweep (a) and flow curve (b) for the 0.01% wt NaTos solution in water. (a) Here, \( \omega_c = 0.019 \text{ rad}\cdot\text{s}^{-1} \), such that \( \tau_R = 54 \text{ s} \). The crossover modulus is \( G_c = 2.0 \text{ Pa} \), compared to 3.0 Pa for the solution in D\(_2\)O; the zero-shear viscosity is \( \eta_0 = 230 \text{ Pa}\cdot\text{s} \), which is about 7-fold higher than for the D\(_2\)O solution. (b) An artificial power law index of \( N \approx 0.06 \) can be determined from the end of the flow curve beyond the metastable regime; points along the flow curve were collected after 300 s. However, the true \( N \) should be determined from the steady state flow curve which requires much longer wait times.

F.3 Frequency sweep (a) and flow curve (b) for the 0.05% wt NaTos solution in water. (a) Here, \( \omega_c = 0.07 \text{ rad}\cdot\text{s}^{-1} \), such that \( \tau_R = 14 \text{ s} \). The crossover modulus is \( G_c = 2.2 \text{ Pa} \), compared to 3.0 Pa for the solution in D\(_2\)O; the zero-shear viscosity is \( \eta_0 = 65 \text{ Pa}\cdot\text{s} \), which is about 6-fold higher than for the D\(_2\)O solution. (b) \( N \approx 0.10 \) is determined from the higher shear rates; points along the flow curve were collected after 60 s. The true \( N \) should be determined from the steady state flow curve which requires much longer wait times.
F.4 Flow curve time dependence and hysteresis for different acquisition times for the 0.05% wt NaTos solution in water. (a) Three trials - 1. 10 s equilibration time, 5 s averaging time, 5 points per decade; 2. 10 s/5 s/10 ppd; 3. 45 s/15 s/10 ppd. The behavior at low shear rates (start of region II) approaches that of the steady state as longer equilibration times are used. (b) Two trials - 45 s/15 s/10 ppd versus 60 s/15 s/10 ppd. The two trials are nearly identical, indicating that significantly longer equilibration times are required near the start of region II. The high rate behavior and calculated power law index $N$ is similar between all trials.

G.1 LVE spectra of the 0.01% wt (a) and 0.05% wt (b) NaTos solutions between multiple sample preparations and instruments. Good agreement is seen in all sample preparations.

G.2 LVE spectra of the 0.10% wt (a) and 0.15% wt (b) NaTos solutions between multiple sample preparations and instruments. Good agreement is seen in all sample preparations.

G.3 LVE spectra (a) and steady shear flow curves (b) of the 0.25% wt NaTos solution between multiple sample preparations and instruments. The spectrum taken at the ILL on an Anton-Paar MCR rheo-SANS rheometer is boxed and varies the most from the other sample preparations. Despite the larger variation in the LVE spectra than in other solutions, the steady shear flow curves in (b) are not significantly different between trials.

G.4 LVE spectra of the two 0.10% wt NaTos solutions: the original sample used for Chapters 4 through 6, and the new sample used for LAOS measurements (Chapter 7). The new sample has a slightly lower crossover frequency ($\omega_c = 1.8$ vs. 2.6 rad·s$^{-1}$), resulting in a longer relaxation time ($\tau_R = 0.5$ vs. 0.4 s).

H.1 Division of the detector in a typical NSE experiment, shown for the $q$-position $q = 0.08$ Å$^{-1}$. Here, the detector is divided into 5 slices; however only 3 slices produce normalized intermediate scattering functions $I(q,t)/I(q,0)$, because the detector is masked for the entirety of the two end bins. The highlighted box in the center of the detector corresponds to $q = 0.0770$ Å$^{-1}$.

H.2 Example fit to an echo from the detector bin highlighted in Figure H.1, where $q = 0.0770$ Å$^{-1}$. 
I.1 Full DLS angular spectrum of the normalized, first-order correlation function, $g_1(t)$, vs. the delay time, $t$, for the branched network, 0.50% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all angles.

I.2 Full DLS spectra $g_1(t)$ vs. $t$ for the high branching, 0.25% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all $\theta$; however, the slow mode appears to have a more stretched response (lower stretch exponent, $\beta_2$) vs. the branched network solution shown in Figure I.1.

I.3 Full DLS spectra $g_1(t)$ vs. $t$ for the low branching, 0.01% wt NaTos solution in a linear-log scaling (a) and log-log scaling (b). Two relaxation modes are visible at all angles; however, the slow relaxation mechanism here appears to have the most pronounced and stretched response (lower stretch exponent, $\beta_2$) vs. the two branched solutions.

I.4 Comparison of DLS spectra across WLM solutions on a linear-log (a) and log-log (b) scale at $\theta = 27.5^\circ$, 50$^\circ$, and 125$^\circ$. While the 0.01% wt NaTos solution exhibits the fasted primary relaxation mode ($\Gamma_1(q)$), it also exhibits the slowest secondary relaxation mode, $\Gamma_2(q)$. The branched network solution (0.50% wt NaTos) has the fastest of the second, slow relaxation mode.

K.1 Dynamic moduli, $G'$ and $G''$, under shear measured by OSP for the (a) 0.10% wt, and (b) 0.125% wt NaTos solutions. The crossover frequency increases with shear rate, indicating a decrease in $\tau_R$. The plateau modulus, $G_0^N$, also decreases with shear.

K.2 Normalized crossover frequency, $\omega_c$, and crossover modulus, $G_c$, during shear, measured via OSP. A faster breakdown of network-like structures, indicated by $G_c$, occurs with branching. Branching also appears to mitigate breakage, causing a slower decrease in $\tau_R$ with shear.

L.1 Flow curves for the 0.15% wt NaTos WLM solution for two sample preparations and instruments. Flow sweep and startup measurements were taken on the ARES G2; 1-3 SANS flow curves were taken on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparation and instrument, including the shear thickening. $N$ is identical within two significant digits for the ARES G2 and 1-3 plane (purple, $\diamond$) measurements.
L.2 Comparison of flow curves for the 0.10% wt NaTos WLM solution for two sample preparations for SANS, and two additional sample preparations for rheometry on the ARES G2. The two 1-3 SANS flow curves were taken during experiments on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparation and instrument, including in the shear thickening region. All four trials exhibit the shear thickening behavior.

L.3 Flow curves for the 0.01% wt NaTos WLM solution for multiple sample preparations for SANS; the ARES G2 curve reported in Chapter 5, Section 5.5.1 is shown for reference. All 1-3 SANS flow curves were taken on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparations, instruments, and curvatures. The trials where $\varepsilon = 0.074$ and $\varepsilon = 0.111$ were performed on a sample from the same batch in the same experiment to examine the effect of $\varepsilon$. The power law index, $N$, increases with increasing $\varepsilon$.

M.1 Startup stress response for the 0.01% wt NaTos solution at low shear rates before or at the onset of region II. In this solution, $\omega_c = 0.18$ rad·s$^{-1}$. (a) Despite $Wi < 1$, long transience in the stress response is observed. The transient is more pronounced with increasing shear rate. (b) Long transients still occur at each rate, where $Wi$ ranges from 0.69 to 1.11. Interestingly, the magnitude of the maximum stress decreases between $\dot{\gamma} = 0.1$ and 0.125 s$^{-1}$ in (a), and between $\dot{\gamma} = 0.125$ and 0.158 s$^{-1}$ in (b).

M.2 Startup stress response at low shear rates at and beyond the onset of region II. (a) $1.11 \leq Wi \leq 2.22$. The metastable plateau region evolves to a shoulder-like feature with increasing rate. (b) $2.22 \leq Wi \leq 4.44$. Long transients still occur at each rate. In both (a) and (b), the stress transient appears to be longer than the measurement time, which is one hour for most shear rates.

M.3 Startup stress response at low shear beyond the onset of region II. (a) $4.44 \leq Wi \leq 8.77$. The shoulder-like feature evolves more quickly with increasing rate. When $\dot{\gamma} = 1.58$ s$^{-1}$, a sharp drop in $\sigma$ is seen after long times, indicating steady state. (b) $8.77 \leq Wi \leq 17.56$. Shoulder-like features still occur at each rate. At $\dot{\gamma} = 3.16$ s$^{-1}$, oscillations in the steady state response are observed, similar to those reported in Chapter 6.

M.4 1-3 plane $A_f$ as a function of time after shear startup on a log-log (a) and log-linear (b) scale. At $\dot{\gamma} = 60$ s$^{-1}$, a long transient in the $A_f$ response is consistent with shear banding and is similar to when $\dot{\gamma} = 45$ s$^{-1}$. When $\dot{\gamma} \geq 225$ s$^{-1}$, the fast structural transient indicates little to no shear banding.
M.5 1-3 plane $A_f$ for the 0.01% wt NaTos solution in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup near the onset of region II, on a log-log (a) and linear-linear (b) scale. Long, pronounced transients in $A_f$ are observed at all shear rates.

M.6 1-3 plane $A_f$ in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup, at shear rates well within region II, on a log-log (a) and linear-linear (b) scale. Long transients in $A_f$ are observed at all shear rates. Pronounced steady state oscillations in $A_f$ are observed when $\dot{\gamma} \geq 26.4 \text{ s}^{-1}$.

M.7 Comparison of the startup 1-3 plane $A_f$ between geometries at shear rates near the onset of region II, on a linear-linear (a-d) and log-log (e-h) scale. The shear rate is equivalent in the vertical direction and increases from left to right. The small gap geometry ($\varepsilon = 0.071$) is always shown in front. Results are similar between geometries at all rates.

M.8 Comparison of the startup 1-3 plane $A_f$ between geometries at shear rates well within region II, on a linear-linear (a-d) and log-log (e-h) scale. The responses in the small gap geometry ($\varepsilon = 0.071$) show a longer transient than the large gap geometry ($\varepsilon = 0.111$). The shape of the responses also differs; pronounced oscillations in the steady state $A_f$ response are observed when $\varepsilon = 0.111$.

M.9 Comparison of the steady state 1-3 plane $A_f$ between geometries. Error bars are the standard deviation of the steady state $A_f$, which are larger when $\varepsilon = 0.111$ due to fluctuations at steady state. When $\dot{\gamma} \geq 26.4 \text{ s}^{-1}$, the steady state $A_f$ is larger for $\varepsilon = 0.071$.

M.10 1-3 plane $A_f$ over repeated trials from the results shown in Chapter 6, Section 6.5.2 ($\varepsilon = 0.071$) as a function of time after shear startup. The $A_f$ response is reproducible between trials.

M.11 1-3 plane $A_f$ for three trials in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup for (a) $\dot{\gamma} = 45 \text{ s}^{-1}$, and (b) $\dot{\gamma} = 26.4 \text{ s}^{-1}$. The pronounced steady state oscillations in $A_f$ when $\dot{\gamma} \geq 26.4 \text{ s}^{-1}$ are reproducible.

M.12 Startup 1-3 plane $A_f$ for the 0.01% wt NaTos solution, in a geometry where $\varepsilon = 0.042$. Results are shown on a log-log (a,c,e) and linear-linear (b,d,f) scale for clarity. The shear rates examined are: $\dot{\gamma} = 4.2$ (a,b), 15 (c,d), and 45 s$^{-1}$. Two trials were recorded for each shear rate; excellent agreement in obtained between trials. The $A_f$ transient lasts hundreds of seconds in each case.
M.13 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 10.5 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interfaces is depicted. Three clear shear bands are observed.

M.14 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 10.5 \text{ s}^{-1}$ as a function of time after shear startup on a (a) log-log and (b) linear-linear scale for clarity.

M.15 Gap-dependent 1-2 plane $A_f$ at different time points after shear startup, indicated in seconds, at $\dot{\gamma} = 10.5 \text{ s}^{-1}$. ‘Re-alignment’ is observed in time. Distinct behavior near the outer wall and the development of the third shear band is apparent even from early times.

M.16 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 2.5 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted. Despite the low shear rate, a clear alignment band is observed.

M.17 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 2.5 \text{ s}^{-1}$ as a function of time after shear startup on a (a) log-log and (b) linear-linear scale for clarity.

M.18 Gap-dependent 1-2 plane $A_f$ at different time points after shear startup, indicated in seconds, at $\dot{\gamma} = 2.5 \text{ s}^{-1}$. A long transient and ‘re-alignment’ is observed in time.

M.19 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 150 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state. Shear banding does not appear to occur.

M.20 1-2 plane $A_f$ over repeated trials from the results shown in Section M.1.6 above for $\dot{\gamma} = 10.5 \text{ s}^{-1}$ at $r/H = 0.1$. The $A_f$ response is reproducible between trials.

M.21 1-3 plane $A_f$ as a function of time after startup at shear rates in region III on a (a) log-log and (b) log-linear scale for clarity. No transient is observed when $\dot{\gamma} \geq 225 \text{ s}^{-1}$.

M.22 1-3 plane $A_f$ as a function of time after startup for three trials where $\dot{\gamma} = 45 \text{ s}^{-1}$. While the magnitude of the $A_f$ response slightly differs between trials, the features of the response are all preserved.
M.23 1-3 plane $A_f$ as a function of time after startup for three trials at $\dot{\gamma} = 26.4$ s$^{-1}$. The magnitude and fluctuations of the $A_f$ response are reproducible between the three trials. ................................. 595

M.24 Startup stress response in regions II and III for the 0.10% wt NaTos solution for 1800 s, on a log-log (a) and linear-linear (b) scale. At all shear rates, a fast transient is observed ($t \leq 5$ s). The features of the stress response are similar to those shown in Chapter 6, Section 6.9.1, verifying that these stress response features are independent of sample preparation. 596

M.25 Long-time startup stress response in region III on a log-log (a) and linear-linear (b) scale for the highly branched solution. A fast transient is observed at all shear rates ($t \leq 10$ s). The fluctuations in the steady state response increase with increasing shear rate until $\dot{\gamma} = 185$ s$^{-1}$, as is expected in region III [9]. ................................. 597

M.26 Startup stress response at long times for shear rates well within region III for the highly branched solution, in a log-log (a) and linear-linear (b) scale. At all shear rates, a fast transient is observed ($t \leq 10$ s). The fluctuations in the steady state response are $\approx 2\%$ of the average value for all shear rates. 598

M.27 Startup stress response for the network-like, 0.25% wt NaTos solution. Fast transients, along with rounded overshoots and undershoots, are observed, similar to the 0.10% wt NaTos solution. ................................. 599

N.1 Elastic (L) and viscous (R) Lissajous-Bowditch projections for the LAOS conditions featured, on a normalized strain, shear rate and stress scale. Similar qualitative features are seen in the projections in all conditions, despite significant differences in the shear banding behavior. ................................. 602

O.1 1-2 plane $A_f$ at the outer wall during the LAOS cycle for $De \approx 1$, $Wi = 295$. The phase of the $A_f$ response does not appear to shift in time, and the response remains the same through multiple measurements. (a) $r/H = 0.825$, (b) $r/H = 0.675$, with a comparison to $r/H = 0.825$. $A_f$ at $r/H = 0.825$ is larger at many $t/T$, suggesting the presence of a third band. ................................. 604

O.2 1-2 plane $A_f$ for $De = 2$, $Wi = 300$ across the duration of the experiment. (a) At the two outer wall positions ($r/H = 0.675, 0.825$), the phase of the $A_f$ response does not appear to shift in time. (b) Near the inner wall ($r/H = 0.325$), the phase of the response is also stable. ................................. 606

lix
O.3 1-2 plane $A_f$ at two outer wall positions for $De = 2$, $Wi = 450$. The phase of the $A_f$ response does not appear to shift in time over the two-hour experiment.

O.4 1-2 plane $A_f$ at $r/H = 0.675$ for $De = 3$, $Wi = 450$. The phase of the $A_f$ response does not appear to shift in time over the two hour experiment.

O.5 1-2 plane $A_f$ at the inner wall for $De = 9$, $Wi = 450$ as a function of experiment time. (a) $r/H = 0.125$. The phase of the $A_f$ response shifts in time before becoming nearly in phase with the applied strain. (b) $r/H = 0.325$. $A_f$ shifts continuously in time before reaching steady state.

O.6 1-2 plane $A_f$ at the outer wall for $De = 9$, $Wi = 450$. (a) The phase of the $A_f$ response appears to shift in time between the measurement at 1.5 to 2h and 4 to 4.5h at $r/H = 0.675$. (b) The phase and response of $A_f$ appears steady between the two measurements, indicating steady state has been reached after 2h.

O.7 1-2 plane $A_f$ at the outer wall ($r/H = 0.675$) during the LAOS cycle for $De = 1.4$, $Wi = 300$ for a repeated experiment. The phase of the $A_f$ response shifts significantly in time over the two hour experiment. Dotted lines correspond to the symmetric minima in the $A_f$ response.

O.8 1-2 plane $A_f$ at the outer wall ($r/H = 0.675$) during the LAOS cycle for $De = 1.4$, $Wi = 400$ for a repeated experiment. The phase of the $A_f$ response shifts significantly in time over the 2.5 hour experiment. Dotted lines correspond to the symmetric minima in the $A_f$ response.

O.9 1-3 plane $A_f$ during $t/T$ at $De = 2.5$, $Wi = 8.3$. The $A_f$ response for the whole experiment is shown in black, for the first 900 s in pink, and for the final 900 s in blue. Fairly good agreement is observed between the trials.

P.1 Permissions for reprinting Figure 1.1. Figure reprinted (adapted) with permission from reference [7]. Copyright 2003 American Chemical Society.

P.2 Permissions for reprinting Figure 1.2. Figure reprinted (adapted) with permission from reference [8]. Copyright 1994 American Chemical Society.
<table>
<thead>
<tr>
<th>Page</th>
<th>Permissions for reprinting Figure 5.3 from reference [10]. From: the European physical journal. E, Soft matter by European Physical Society; Societa italiana di fisica. Reproduced with permission of SPRINGER-VERLAG in the format Thesis/Dissertation via Copyright Clearance Center.</th>
<th>616</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permissions for reprinting Figure 6.2. Reprinted figure with permission from reference [9]. Copyright 2014 by the American Physical Society.</td>
<td>617</td>
</tr>
</tbody>
</table>
ABSTRACT

The molecular design of soft materials with optimal flow properties is highly desired in applications ranging from polymer processing to drug delivery, where materials undergo both steady and dynamic nonlinear deformations during processing, transport, and use. To design such materials, a thorough understanding of the coupling between the molecular topology and the flow properties is required. Flow-small angle neutron scattering (flow-SANS) presents a unique opportunity to understand this non-trivial coupling between the macroscopic flow behavior, molecular topology, and material performance by combining rheometry with time- and spatially-resolved SANS. Such methods enable simultaneous measurements of the material microstructure during an applied rheometrical deformation, which quantifies the flow properties. Therefore, the development of ‘structure-property relationships’ that link the material microstructure to its macroscopic flow behavior is the first step toward the ultimate goal of designing soft materials \textit{a priori}.

Wormlike micelles (WLMs) are surfactant solutions that self-assemble to form long and wormlike chains. WLMs are of particular scientific and technological interest due to their ability to branch, break, and reform under shear. These unique properties can lead to nonlinear flow phenomena and instabilities such as shear banding. WLMs are also often used as a model system for studying polymers and polyelectrolytes. As the self-assembly of these ‘living polymers’ is tunable, WLMs are ubiquitous in a broad range of applications ranging from consumer products to oil and energy recovery fluids. Altering the topology of WLM solutions provides a microstructural pathway to rationally design and optimize the flow properties for targeted applications. Specifically, inducing branching in WLM solutions is an attractive route to achieve this goal, as branching has the potential to alter or eliminate undesirable flow instabilities such as shear banding.
The goal of this thesis is to understand the role of micellar branching on the resulting equilibrium and non-equilibrium properties, while advancing instrumentation and analysis methods in rheology and neutron scattering. Multiple rheological and neutron techniques are employed to explore the relationship between branching, microstructure, dynamics and nonlinear flow properties using a model series of WLMs. The degree of branching in the mixed cationic/anionic surfactant (CTAT/SDBS) solutions is controlled via the addition of the hydrotropic salt sodium tosylate. A combination of techniques, including static small angle neutron scattering (SANS), cryo-TEM, and linear viscoelastic rheology (LVE), are used to quantify the equilibrium microstructures, including the relevant micellar length and time scales. Dynamic scattering methods including neutron spin echo (NSE) and dynamic light scattering (DLS) identify characteristic differences in the solution dynamics.

Combining nonlinear rheological measurements with spatiotemporally-resolved SANS enables unambiguous identification of non-equilibrium rheological and scattering signatures of branching and shear banding. The shear-induced ordering of the micelles is spatially and temporally characterized via flow-SANS under various nonlinear deformations, including steady shear, shear startup, and large amplitude oscillatory shear (LAOS). New methods of time-resolved data analysis are developed, which improve the resolution of the experiments by several-fold. Local segmental orientation and the presence of flow instabilities is found to be a complex function of the branching level, radial position, and deformation type. Using time- and spatially-resolved flow-SANS, the complex structural mechanisms behind shear band formation are elucidated for steady and dynamic flows, which differ based on branching level. These microstructural responses to deformation are then used to experimentally validate constitutive modeling predictions of shear banding under dynamic deformation for the first time. Quantitative metrics to predict dynamic shear banding from rheology or flow-induced orientation alone are also developed. Branching is associated with a disappearance of the shear banding flow instability under both steady and dynamic deformations.

Together, advanced rheological and neutron techniques provide a platform for creating structure-property relationships that predict flow and structural phenomena in WLMs and other soft materials. These methods have enabled characteristic differences in linear versus
branched WLMs to be determined. This research is part of a broader effort to characterize branching in chemical polymers and self-assembled systems, and may aid in the formulation of WLMs for specific applications. Finally, this work provides a basis for critically testing and developing microstructure-based constitutive equations that incorporate micellar breakage and branching.
Chapter 1
INTRODUCTION

1.1 Motivation

The formulation of soft materials with optimal structure and flow properties is a critical design criteria in applications ranging from polymer processing to drug delivery, where materials undergo nonlinear deformations during processing, transport and use. Understanding how the flow behavior and molecular topology are coupled requires advanced techniques that can link the flow properties to the microstructure under deformation. Static small angle neutron scattering (SANS) measurements are not sufficient for achieving this goal, as the microstructure not only changes under deformation, but also responds differently to steady versus dynamic deformations. Flow-small angle neutron scattering (flow-SANS), however, integrates rheology measurements of the flow behavior with time- and spatially-resolved microstructure measurements. Recent advances in time-resolved data analysis allow microstructure changes to be measured continuously, during complex deformations ranging from shear to extension and microchannel flows. Unlike x-rays, neutrons are non-destructive, making flow-SANS of unique and growing interest for applications ranging from biological materials, to consumer products and oil field fluids.

Wormlike micelles (WLMs) are self-assembled surfactant solutions which are commonly used as a model system for studying polymers and polyelectrolytes [1, 2]. WLMs are of particular scientific interest due to their ability to self-assemble, break, and reform under shear [3–5]. WLMs are ubiquitous in applications ranging from consumer products, cosmetics, and pharmaceuticals to industrial materials such as oil field fluids and drag reduction agents [6–9]. The tunable self-assembly of these “living” surfactant solutions enables a wide variety of solution morphologies and rheological characteristics that can be tailored
for targeted applications. Wormlike micelles are also a commonly used model system for studying non-linear flow phenomena and flow instabilities such as shear banding [3,10,11]. These nonlinear flow phenomena imply that the microstructure of WLMs may be significantly different under flow than that at rest. Such flow-induced changes in microstructure may be beneficial, such as reducing the viscosity during the pouring of liquid detergents or transporting fluids while drilling oil and gas wells, or detrimental, such as the degradation of product stability during shipping. Understanding the response of WLM solutions to flow is important for these applications, where materials undergo both steady and dynamic nonlinear deformations. Static SANS is therefore insufficient for fully characterizing these materials, as the microstructure changes under such flows, and responds differently based on the deformation type. Flow-SANS methods present a unique solution, as the WLM microstructure and macroscopic flow properties can be linked by making simultaneous rheometry and SANS measurements while imposing various types of nonlinear deformations.

1.2 Self-assembly in surfactant solutions

Surfactants self-assemble to form wormlike micelles. Surfactants are amphiphilic molecules that consist of a hydrophilic head group covalently bound to a hydrophobic tail group. Throughout this chapter, the surfactant head group will be depicted as a sphere, which is attached to the surfactant tail, as seen in Figure 1.1a for a cationic surfactant. All surfactants discussed in this work are ionic in nature. The structures that can be formed when surfactants self-assemble in aqueous solution are dictated by the geometry of the particular surfactant, the surfactant concentration, and other factors such as temperature. Surfactants are mildly soluble as monomers in solution below a threshold known as the critical micelle concentration (c.m.c.). Above the c.m.c., the surfactants rearrange to form aggregate-like structures which shield the hydrophobic surfactant tail from the solvent, such as water or D2O. Common shapes of these aggregate structures include spheres, cylinders, worms, lamellar sheets and bilayers, and vesicles. At very high surfactant concentrations, crystal-like structures can be formed in solution. The structure that is formed when a particular surfactant self-assembles is primarily dictated by the packing parameter, $p$, of the particular
surfactant, which gives rise to a rich and complex phase behavior based on surfactant geometry. The packing parameter is the ratio of the surfactant volume to the area of the head group, which is estimated based on the surfactant geometry and is given by Equation 1.1 below:

\[
p = \frac{v}{a_0 l}
\]  

(1.1)

where \( v \) is the volume occupied by the surfactant molecule, \( a_0 \) is the area of the head group, and \( l \) is the length of the surfactant tail, which is usually a hydrocarbon chain (see Figure 1.1a). Typically, the tail consists of \( n_c \) carbon atoms, where \( n_c > 8 \), such that its length and the surfactant volume can be approximated by [12]:

\[
l \approx 1.54 + 1.265 n_c
\]

\[
v \approx 27.4 + 26.9 n_c
\]  

(1.2)

where \( l \) is measured in Å and \( v \) is measured in Å\(^3\). The head group area, \( a_0 \), is more difficult to estimate. As the surfactant head groups can be ionic or nonionic, the head group area depends on the interactions between the head groups.

Figure 1.1: Schematic of wormlike micelle assembly. Assembly is dictated by the surfactant geometry and resulting packing parameter, \( p \) (a), which, paired with the electrostatic interactions around the micellar head groups, governs the local ordering or persistence length, \( l_p \) (b). (c) Long-range order is also achieved, where long, entangled wormlike structures are observed. Image in (c) reprinted with permission from reference [13]. Copyright 2003 American Chemical Society, see Appendix P.

The packing parameter ultimately dictates what structures can self assemble from
surfactants in solution. At low $p$-values ($p < 1/3$), spherical micelles tend to form. With increasing values of $p$ ($1/3 < p < 1/2$), short rod-like micelles will form. When $p \approx 1/2$, wormlike micelles (WLMs) will form, which are long and flexible thread-like structures. A cartoon representation of the long, entangled wormlike structure can be seen in Figure 1.1c. As $p$ is further increased ($1/2 < p < 1$), vesicles and flexible bilayers will form. Finally, when the packing parameter is close to unity ($p \approx 1$), planar bilayers form in solution.

A schematic of wormlike micelle assembly can be seen in Figure 1.1 on three relevant length scales. The initial assembly is dictated by the surfactant geometry and packing parameter. In this work, mixed cationic and anionic surfactants are used in a 97/3 weight ratio (see Chapter 2), such that the head groups are primarily cationic as shown in Figure 1.1a. The packing parameter and the charges around the head groups ultimately dictate the local ordering in the micelles, known as the persistence length, $l_p$ (Figure 1.1b, also shown in c). While WLMs are long, flexible structures, the worms behave as stiff rods on the length scale of the persistence length, such that $l_p$ is a measure of the overall chain flexibility [13]. The persistence length is related to the overall contour length of the micelles, $L_c$, by:

$$L_c = l_p \langle N \rangle$$

(1.3)

where $\langle N \rangle$ is the average number of chain segments. The persistence length is not to be confused with the Kuhn length, $b$, which is another measure of the micelle flexibility. In WLM solutions, the Kuhn length is typically approximated as twice the persistence length, such that $b \approx 2l_p$ [14]. In polymer solutions, the Kuhn length is the length scale over a portion of the contour length past which fluctuations in the orientation of the chain are no longer correlated [15]. The interactions between the surfactant head groups are primarily electrostatic in nature. When the micelle consists of head groups of all or primarily the same charge, strong electrostatic repulsions are present around the head groups. The range of these electrostatic interactions is governed by the Debye length, which is the inverse of the Debye
constant, $\kappa$, given by [16]:

$$\kappa^{-1} = \left( \frac{\varepsilon k_B T}{e \sum z_i^2 n_{i,\infty}} \right)^{1/2} \quad (1.4)$$

where $\varepsilon$ is the dielectric permittivity of the solvent, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $e$ is the elementary charge. The charge number, $z_i$, is the valence of ions of type $i$, which, along with the number concentration, $n_{i,\infty}$, is summed over all ionic species, $i$, in solution. In this work, monovalent surfactants and a monovalent, hydrotropic salt compose the WLMs. Accordingly, assuming full dissociation of the added monovalent salt, the summation in Equation 1.4 reduces to:

$$\sum_i z_i^2 n_{i,\infty} = N_A (\alpha C_D + C_s) \quad (1.5)$$

where $N_A$ is Avogadro’s number, $\alpha$ is the fractional dissociation of the surfactant head groups, $C_D$ is the molar surfactant concentration, and $C_s$ is the molar salt concentration. Determining $\alpha$ is difficult, but typically $\alpha < 1$.

While the value of $p$ is based on the geometry of the surfactant, its value can be altered by changing the solution conditions, including the temperature, salinity, and counterions. The electrostatic interactions around the head groups lead to a slightly smaller packing parameter than if the head group was uncharged, as the effective head group area, $a_0$, increases. The projected head group area when strong electrostatic interactions are present can be related to the Debye length [17]. These repulsions around the head groups thus result in stiff micelles with long persistence lengths. When the head groups are of mixed charges, or if a counterion salt is added to the solution, the electrostatic interactions are slowly screened, effectively increasing the value of $p$ by decreasing $a_0$. With added counterion, the persistence length is effectively reduced for the same surfactant concentration due to the screening of the electrostatic repulsions. Added counterions serve to increase the micelle flexibility and can dramatically alter $p$, which enables a variety of new structures, like branch points, to be formed. Accordingly, wormlike micelles exhibit a rich phase behavior that is enhanced
when counterions are added to solution. This phase behavior is described extensively in the phase diagram proposed by Lequeux and Candau [18], shown in Figure 1.2 below. Finally, at length scales longer than the persistence length, wormlike micelles form long and entangled structures in solution, as seen in Figure 1.1c. As seen in Figure 1.1c, a variety features become important in describing the WLM properties, including the overall contour length, $L_c$, the distance between entanglements, $l_e$, and the mesh size, $\xi_M$, among others. The length scales shown in Figure 1.1c may span several orders of magnitude and are reminiscent of the features of entangled polymer solutions. For example, in a typical WLM solution, the cross-sectional radius shown in Figure 1.1c, $r_{cs}$, spans approximately 20 to 30 Å. However, typical persistence lengths are on the order of $10^2$ Å, and overall contour lengths may be on the order of microns, $L_c \approx 10^4$ Å. The theory governing these length scales and the properties that correspond to these lengths will be discussed further in Section 1.3 below.

Concentration and salt addition also play a role in surfactant self-assembly and affect micellar growth and scaling, which will be discussed in Section 1.3. These concentration and additive effects are also detailed in Figure 1.2 for WLM solutions. In dilute solutions, spherical micelles are more energetically favorable. Here, the concentration, $C$, is less than that of the overlap concentration, $C^*$ (in terms of volume fraction), which indicates the start of the semi-dilute regime. The overlap concentration is the concentration at which overlap occurs between the volume occupied by individual micelle chains. The threshold for $\phi^*$ is illustrated in Figure 1.2, which is dependent on the ratio of the surfactant concentration, $C$ or $C_D$, to the salt concentration, $C_s$. When $C \geq C^*$, rod-like micelles become more energetically favorable. Further concentration increase leads to micellar growth, which enables the long and wormlike structures to form. This growth process leads to a dramatic increase in the solution viscosity and elasticity. In this concentration regime, linear, branched, and network-like structures are possible (Figure 1.2). The transition from the dilute ($C < C^*$) to semi-dilute ($C \geq C^*$) regime is marked by a change in the scaling rules for the micellar length and time scales [13]. At very high concentrations ($C \geq C^{**}$ or $\phi \geq \phi^{**}$), the WLMs enter the concentrated regime, where $C^{**}$ indicates the entrance to the concentrated regime. In this concentration regime, the micellar growth and scaling rules again change [13, 19]. As seen
in Figure 1.2, in the concentrated regime, WLMs can form nematic structures at rest, which can transition into hexagonal or biphasic structures as the concentration is further increased.

As entangled wormlike micelles are similar in structure to entangled polymers, the two systems share many of the same rheological characteristics. In polymer solutions, the stress relaxation is controlled by reptation. However, WLMs are self-assembled and not chemically bound like their polymeric counterparts, so reptation only accounts for part of the stress relaxation process. As WLMs can reversibly break and recombine, the rate of breakage also accounts for the stress relaxation, which will be discussed below in Section 1.3.2. This reversible breakage in WLMs leads to a near perfect, single relaxation time in the linear viscoelastic rheology (LVE) that can be described by the Maxwell model. Despite the ideal behavior in the LVE rheology, WLMs exhibit surprisingly rich nonlinear behavior, depending on the concentration regime. Shear thickening in WLM solutions has been commonly observed at high shear rates when the surfactant concentration is approximately equal to or less than that of the overlap concentration to the semi-dilute regime, $C^*$. Dilute WLM solutions are known to exhibit Newtonian behavior; however, above a critical shear rate, these solutions can display a Newtonian-to-shear thickening transition [20–23]. In semi-dilute solutions near $C^*$, WLMs are known to exhibit shear thinning behavior. At high shear rates, these semi-dilute WLMs may exhibit a shear thinning-to-shear thickening transition [23,24]. The mechanism for this shear thickening has been attributed to SIS formation and micellar growth, which may also include elastic turbulence [25]. In the semi-dilute regime where the concentration is close to $C^{**}$, WLMs may undergo a different shear-induced transition, known as the isotropic-to-nematic transition. This I-N transition is induced by shear, as opposed to concentration, which typically induces the transition, as shown in Figure 1.2.

Additionally, wormlike micelle solutions may exhibit a variety of flow instabilities, the most common of which is shear banding. During shear banding, the flow exhibits spatial heterogeneities and organizes into macroscopic bands of high shear rate (low viscosity) and low shear rate (high viscosity). Shear banding may occur along the gradient direction of the flow, referred to as gradient shear banding, such that the high shear rate band exists near the inner Couette wall and the low shear rate band forms near the outer Couette wall. Shear
Figure 1.2: Phase diagram for wormlike micelles proposed by Lequeux and Candau [18], where the x-axis, $C_s/C$, is the salt-to-surfactant ratio, and the y-axis, $\phi$, is the surfactant volume fraction. Branching is possible in the semi-dilute regime, above the overlap concentration ($C^*$ or $\phi^*$). Network-like structures form as the salt-to-surfactant ratio is increased for the same volume fraction. The entrance into the concentrated regime, which is still isotropic at rest, is denoted by $C^{**}$ or $\phi^{**}$. Reprinted with permission from reference [18]. Copyright 1994 American Chemical Society; see Appendix P.
bANDING MAY OCCUR AT SURFACTANT CONCENTRATIONS NEAR THE I-N TRANSITION (NEAR C***) [10, 26–28], OR AT CONCENTRATIONS MUCH CLOSER TO THE OVERLAP CONCENTRATION, C* [29–33]. SHEAR BANDING MAY ALSO OCCUR IN THE VORTICITY DIRECTION, KNOWN AS VORTICITY BANDING, WHERE THE MACROSCOPIC BANDS ORGANIZE ALONG THE VORTICITY DIRECTION AS OPPOSED TO AS ALONG THE GRADIENT DIRECTION [34, 35]. SHEAR MAY ALSO INDUCE PHASE SEPARATION (SIPS) IN WLMs, WHERE THE SHEAR-INDUCED BANDED STRUCTURE IS DISTINCTLY DIFFERENT THAN THAT OF SHEAR BANDING NEMATIC-LIKE MICELLES [36].

1.3 WORMLIKE MICELLES: THEORY AND SCALING

1.3.1 MICELLAR GROWTH

Cates and Candau [37] developed a mean field theory to describe micellar growth in solution. This micellar growth can be divided into three concentration regimes: the dilute, semi-dilute, and concentrated regimes. Long and entangled wormlike micelles can often grow to micrometers in length. This overall contour length, \( L_c \), for non-ionic or electrostatically screened micelles in the semi-dilute regime \( (C > C^*) \) is given by:

\[
L_c \sim \phi^{1/2} \exp \left[ -\frac{E_c}{2k_BT} \right]
\]

where \( \phi \) is the volume fraction, \( T \) is the temperature, \( k_B \) is the Boltzmann constant, and \( E_c \) is the energy required to form an two end caps. There is a broad distribution of micelle lengths, where the number density, \( N(L) \), of micelles of length \( L \) is given by:

\[
N(L) \sim \exp \left[ -\frac{L}{L_c} \right]
\]

In this theory, the micelles can reversibly break and reform with equal probability at any point along the micelle chain. In the case of non-ionic or screened micelles, \( E_c \) equals the scission energy, \( E_{sciss} \), which dictates the overall micelle contour length. Based on Equation
The average number of surfactant molecules per chain can be estimated by [4]:

\[ n = \frac{\langle N \rangle l_p \pi r_{cs}^2}{v} \]  

(1.8)

such that the volume fraction, \( \phi \), of surfactant in solution can be determined based on the individual surfactant molecule volume by \( \phi = \bar{n}v \).

Many wormlike micelles, however, are composed of cationic or anionic surfactants with little to no added salt. In the case of ionic micelles where the electrostatic interactions are not screened, an additional electrostatic component must be added to the scission energy [12]. Now, the scission energy is the difference between the endcap formation energy and the electrostatic energy of the micelle,

\[ E_{\text{sciss}} = E_c - E_e \]  

(1.9)

and the average contour length is given by:

\[ \bar{L}_c \sim \phi^{1/2} \exp \left[ \frac{E_c - E_e}{2k_B T} \right] \]  

(1.10)

The electrostatic contribution to the scission energy, \( E_e \), is given as:

\[ E_e \equiv k_B T \frac{l_B r_{cs} v^*}{2} \phi^{-1/2} \]  

(1.11)

where \( l_B \) is the Bjerrum length, \( r_{cs} \) is the micelle radius, \( v^* \) is the effective charge per unit length, and \( \phi \) is the volume fraction of the cylindrical wormlike micelles. The effective charge per unit length is related to the fractional dissociation of the micellar head groups, \( \alpha \). In the semi-dilute regime, the range of the electrostatic interactions is smaller than the mean micelle size. A low scission energy favors the formation of short, cylindrical micelles, whereas high scission energies lead to the formation of longer, worm-like micelles. In solutions with little to no added salt, the micellar head groups are primarily of the same charge,
leading to stiff cylinders with a high electrostatic energy that repel each other. Here, Bjerrum length is the length scale or separation distance at which the electrostatic interactions are equal to the thermal energy scale, $k_B T$. The magnitude of the Bjerrum length used to determine $E_e$ is defined as [38]:

$$l_B = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r k_B T},$$

(1.12)

where $e$ is the elementary charge, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_r$ is the dielectric constant of the medium. In wormlike micelles, $\varepsilon_r$ is usually the dielectric constant of either water or D$_2$O. For the WLMs used in this work, where $T = 35^\circ$ C and $\varepsilon_{r,D2O}(35^\circ$ C) = 74.427 [39], $l_B = 7.3$ Å. As water and D$_2$O are isotopes, $l_B$ is relatively insensitive to temperature and water versus D$_2$O; for WLMs in water at room temperature, $l_B = 7.1$ Å. The Debye length given in Equation 1.4 above can also be written in terms of the Bjerrum length as:

$$\kappa^{-1} = [4\pi l_B C_D (\alpha + 2C_s/C_D)]^{1/2}$$

(1.13)

While Equations 1.10 and 1.11 are derived for charged micelles in the absence of salt, this model can be extended to micelles with intermediate added salt concentrations. Here, an effective volume fraction, $\phi$, can be substituted for $\phi$ in Equations 1.10 and 1.11, where $\phi$ is given by:

$$\bar{\phi} = \phi + 8\pi l_B r_{cs}^2 C_s$$

(1.14)

As $E_e$ is inversely related to the volume fraction, in the limit of high salt concentrations, $C_s$, the equations for nonionic or screened micelles are recovered.

In the concentrated regime ($C \geq C^{**}$), the effect of the electrostatic contribution, $E_e$, to the scission energy decreases. In this region, the micellar growth is dominated by the increased entropy of counterions near the endcaps, such that the growth is instead characterized
by a power law scaling [12]. Here,

$$L_c \sim \phi^{1/2(1+\Delta)}$$ (1.15)

where $\Delta$ is logarithmically related to the volume fraction, $\phi$, and is a function of the ambient charge density and endcap charge. Conversely, in the dilute regime ($C < C^*$), micellar growth is only weakly related to the volume fraction. In the dilute regime, the micelles are nearly monodisperse and are fairly short, where the average contour length is given by:

$$L_c \sim \left( \frac{1}{l_B r_{cs} v^2} \right) \left( \frac{E_c}{k_B T} + \log \left( \frac{\phi}{L_c} \right) \right)$$ (1.16)

The volume occupied by micelles in this dilute limit is characterized by an average radius of gyration, $R_g$. The occupied volume scales as $R_g^3$, which for ideal chains is given by [40]:

$$R_g = \langle N \rangle^{1/2} l_p$$ (1.17)

In the dilute regime, for charged, unscreened micelles, the range of the electrostatic interactions is larger than the mean size of the micelles, as depicted in Figure 1.2. The surfactant concentration regime used in this work is near the overlap concentration to the semi-dilute regime, $C^*$. At the overlap volume fraction, MacKintosh et al. [12] postulated that the micelle endcap and electrostatic energies (Equation 1.11) are approximately equal. The resulting expression for the the overlap volume fraction, $\phi^*$, is given by:

$$\phi^* \approx \left( \frac{k_B T l_B r_{cs} v^2}{E_c} \right)^2$$ (1.18)

Combining Equations 1.8 and 1.17 yields another expression for the overlap concentration, using a spherical approximation for the volume, given by:

$$\phi^* \approx \frac{3 \bar{n} v}{4 \pi R_g^3}$$ (1.19)
where $v$ is the volume occupied by the surfactant molecule given in Equation 1.1, which is not to be confused with the effective charge per unit length, $v^*$. 

1.3.2 Stress relaxation and scaling rules in wormlike micelles

Granek and Cates [41] and Cates and Candau [37] describe the stress relaxation of linear wormlike micelles by a combination of reptation, breakage, and reformation dynamics. While strictly applicable to the nonionic systems described by Equations 1.6-1.8 above, the theory and scaling laws agree reasonably with experimentally-measured values when applied to ionic, linear systems near the overlap concentration [13,19,32]. In the slow-breaking limit, a micelle has sufficient time to reptate out of its tube before breaking ($\tau_{\text{break}} \gg \tau_{\text{rep}}$), which leads to a spectrum of relaxation times due to the broad distribution of chain lengths. In the fast-breaking limit, the time required for a micelle to reptate out of its tube is much greater than the breakage time ($\tau_{\text{break}} \ll \tau_{\text{rep}}$), so that any linear chain undergoes many breakage and recombination events before reptation processes alone could relax the entirety of the material stress. In this work, all WLMs are in the fast-breaking limit. Linear wormlike micelles in the fast-breaking limit are therefore well described by a simple Maxwell model with a single relaxation time, $\tau_R$ [37,41]. The relaxation time for a Maxwell fluid is related to the geometric average breakage and reptation times ($\tau_{\text{break}}, \tau_{\text{rep}}$) via:

$$\tau_R = (\tau_{\text{break}} \tau_{\text{rep}})^{1/2} \quad (1.20)$$

as given by Cates and Candau [37]. Combining the mean-field theory of Cates and co-workers [37] with the Doi-Edwards tube model [42] gives a reptation time in the semi-dilute regime that depends on the curvilinear diffusion of a chain within its tube. The reptation time scales as:

$$\tau_{\text{rep}} \sim \frac{L_c^2}{D_c} \quad (1.21)$$

where $D_c$ is the curvilinear diffusion coefficient. Doi and Edwards [42] showed that $D_c$
depends on the volume fraction and overall contour length as:

\[ D_c \sim \frac{1}{L_c \phi^{3/2}} \]  

(1.22)

which leads to a scaling of the reptation time in terms of the contour length and volume fraction as:

\[ \tau_{\text{rep}} \sim L_c^3 \phi^{3/2} \]  

(1.23)

Small amplitude oscillatory shear measurements are often used to determine \( \tau_R \), which in a Maxwell framework is defined as the timescale (inverse of the angular frequency) at which the dynamic moduli are equal. The elastic or storage modulus, \( G' \), and viscous or loss modulus, \( G'' \), are given for a Maxwell fluid by:

\[
G'(\omega) = \frac{G_0^N \omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2}
\]

\[
G''(\omega) = \frac{G_0^N \omega \tau_R}{1 + \omega^2 \tau_R^2}
\]  

(1.24)

where \( G_0^N \) is the plateau modulus. At the crossover frequency, the viscous and loss moduli are equal \( (G'(\omega_c) = G''(\omega_c)) \), known as the crossover modulus, \( G_c \). The relaxation time for a Maxwell fluid is then defined as:

\[ \tau_R = 1/\omega_c \]  

(1.25)

where \( \omega_c \) is in units of rad \cdot s\(^{-1}\). The plateau modulus for a Maxwell fluid can be estimated from the crossover modulus as:

\[ G_0^N = 2G_c \]  

(1.26)

A parametric representation of the linear viscoelastic (LVE) data, often referred to as a Cole-Cole plot, where \( G'' \) is plotted against \( G' \), is perfectly semicircular for a Maxwell
fluid. In linear WLMs, the experimental data shows excellent agreement with the Maxwell model at low frequencies. However, as the angular frequency increases, deviations from the model, including a local minimum in $G''$, are observed due to Rouse modes [41]. The high frequency plateau modulus $G_N^0$ is determined by the value of $G'$ at the frequency at which the $G''$ minimum is observed, when $\omega > \omega_c$. For entangled WLM or polymer solutions where Rouse modes play a role, the ‘extended Maxwell’ or Oldroyd-B model may be more appropriate than the Maxwell model. In the Oldroyd-B model, $G''$ is augmented with a high frequency viscosity (or solvent viscosity in polymer solutions), as:

$$G'(\omega) = \frac{G_N^0 \omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2}$$

$$G''(\omega) = \frac{G_N^0 \tau_R}{1 + \omega^2 \tau_R^2} + \eta_\infty \omega$$

(1.27)

Simplifying gives:

$$G'' = G_{\text{Maxwell}}'' + \eta_\infty \omega$$

(1.28)

The frequency at which $G''$ exhibits a local minimum, $\omega_{min}$, is often used to give an estimate of the breakage time [9]:

$$\omega_{min} \approx \frac{1}{\tau_{\text{break}}}.$$

(1.29)

Although this estimate is commonly used, it is not strictly correct; there is no physical basis for determining the breakage time in this manner.

Micellar breakage can either occur through unimolecular scission or end-interchange [43–46]. The breakage is often assumed to be entirely through unimolecular scission, which is governed by the rate constant, $k_1$. From this, the breakage time is specifically related to the overall contour length, $L_c$, by [43–46]:

$$\tau_{\text{break}} = \frac{1}{k_1 L_c}$$

(1.30)
where $k_1$ is in units of per unit arc length per unit time [13]. When unimolecular scission is assumed, the relaxation time and zero-shear viscosity, $\eta_0$, of the WLM solution scale as:

\[
\tau_R \sim L_c \phi^{3/4} \sim \phi^{5/4} \quad (1.31)
\]
\[
\eta_0 \sim L_c \phi^3 \sim \phi^{7/2} \quad (1.32)
\]

However, breakage can also occur through end-to-end exchange, or end-interchange, which occurs when the free end of one chain collides with another chain. When end-interchange occurs, the breakage is governed by rate constant $k_3$, given by [43–46]:

\[
\tau_{\text{break}} = \frac{1}{k_3 \phi} \quad (1.33)
\]

which leads to a scaling in the relaxation time and zero-shear viscosity given by:

\[
\tau_R \sim L_c^{3/2} \phi^{1/4} \sim \phi \quad (1.34)
\]
\[
\eta_0 \sim \phi^{3.25} \quad (1.35)
\]

The micellar growth and rheological parameters can then be used with scaling rules to determine estimates for other important length scales, such as the entanglement and persistence lengths, $l_e$ and $l_p$, respectively. In addition to giving estimates of the plateau modulus and the breakage time, the minimum in $G''$ is related to $l_e$ and $l_p$ by [41,47]:

\[
\frac{G''_{\text{min}}}{G_N^0} \approx \frac{l_e}{L_c} \quad (1.36)
\]

From the theory of rubber elasticity, the entanglement length is related to the mesh size, $\xi_M$, by [42,48]:

\[
l_e \approx \frac{\xi_M^{5/3}}{l_p^{2/3}} \quad (1.37)
\]
Another estimate of the mesh size relates $\xi_M$ to the plateau modulus, $G_N^0$, by [42,48]:

$$\xi_M \approx \left( \frac{k_B T}{G_N^0} \right)^{1/3},$$

where the tube theory of Doi and Edwards [42] predicts that the plateau modulus scales with concentration in the semi-dilute regime as:

$$G_N^0 \sim \phi^{9/4}$$

Finally, the plateau modulus can be related to the zero-shear viscosity, $\eta_0$, of the wormlike micelles or any Maxwell fluid by:

$$\eta_0 = G_N^0 \tau_R$$

The zero-shear viscosity corresponds to the viscosity measured in the low shear rate, Newtonian branch of the WLM flow curve. This scaling for $\eta_0$ can be compared to the measured $\eta_0$ in this region of the flow curve to test the validity of the scaling relationships. The zero-shear viscosity can also be compared to $\eta^*(\omega)$, the complex viscosity from a linear viscoelastic test, where $\eta^*(\omega \to 0) \approx \eta_0$.

While these scalings are constructed for linear, nonionic micelles, they have been verified in solutions with high amounts of added salt, where the electrostatic interactions are screened [49,50]. Significant deviations have been observed when the interactions are not fully screened, including a steeper power law scaling in the zero-shear viscosity [21,24,51,52]. However, the most commonly observed deviation from these scalings is the presence of one or two maxima in the viscosity as a function of concentration or salt, which can be seen in the schematic in Figure 1.3. The double viscosity maxima has been observed in WLM solutions as a function of added hydrotropic salt [53,54]. A single viscosity maximum has been observed in solutions based on the concentration of surfactant [24,51,55] or added salt [13,55–58], or the ratio of surfactants in mixed systems [13,24,55]. These viscosity maxima have often been interpreted in the context of micellar branching, a shortening of the micelle.
contour length, or both, which will be discussed in Section 1.4 [2, 13, 53, 54, 59, 60]. In solutions with high salt concentrations that exhibit this behavior, the power law dependence of the zero-shear viscosity has been observed to be weaker than the scaling proposed in Equations 1.32 and 1.35 [56, 57, 61, 62]. In charged solutions, the stronger dependence of $\eta_0$ on $\phi$ can be explained by electrostatic interactions and the corrections set forth by MacKintosh et al. [12] (Equations 1.10, 1.11). However, the weaker dependence of $\eta_0$ on $\phi$ cannot be explained with solely linear structures; therefore, branching is hypothesized at high salt concentrations.

Figure 1.3: Schematic of wormlike growth and branching with added hydrotropic salt. The micelles transition from spherical to rod-like with small changes in $\eta_0$. A transition to linear, entangled WLMs is marked by a drastic increase in $\eta_0$. Branched, entangled micelles are observed after the viscosity maximum. Branched WLMs are also observed near the second viscosity maximum, but the overall contour length shortens in this region.
1.4 Branching in wormlike micelles

The linear rheology of WLMs is often well-described by an extended Maxwell (Oldroyd-B) model, where the structure breakage and reformation is significantly faster than reptation [37, 41] such that there is a single, average relaxation time. By altering the solution composition or temperature, a maximum in the zero-shear viscosity, $\eta_0$, is often observed which violates the scaling rules presented in Section 1.3.2 above. As mentioned previously, this viscosity maximum has been shown to correspond to changes in the micellar topology [2, 13, 53, 54, 59, 60]. As discussed above, the increase in viscosity with added surfactant or salt results from micellar growth and entanglement (see Figure 1.2, Figure 1.3). In contrast, micellar branching has been shown to lower $\eta_0$ regardless of whether the contour length is increasing (first maximum, Figure 1.3) or decreasing (second maximum, Figure 1.3) [2, 13, 53, 54, 59, 60]. Branching has been proposed to provide another mechanism for stress relaxation. Unlike in polymers, micellar branch points are fluid and branches slide along a contour, thereby relieving stress. The presence of branches reduces the stress-carrying portion of the micelle to the sections between branch points. The effective micellar length is thus decreased by inducing branching, which leads to decreased viscosities [2, 13, 63]. As branching increases, large deviations from Maxwellian behavior are observed [64–66]. Further increases in salt concentration lead to network condensation [67, 68].

In addition to serving as a model system that can aid future studies of branched polymers, branched WLMs are of particular scientific and industrial interest due to their tunable, highly non-Newtonian flow properties. Linear WLMs tend to exhibit shear banding, a phenomenon where the flow exhibits spatial heterogeneities such that the material separates into regions of high velocity (low viscosity) and low velocity (high viscosity). Branched WLMs have shown the potential to eliminate the shear banding flow instability, which is suggested by the mitigation of the stress plateau along the flow curve [9, 50, 57, 69]. However, shear banding has been shown to be possible in models of entangled polymers that exhibit monotonic flow curves [70], such that the mechanism by which branching may or may not suppress shear banding is still under investigation. While shear thinning is optimal for injectable fracking and carrier fluids [71], shear banding is seemingly detrimental as fluid components
may stratify or phase separate [72,73].

While branching is widely accepted as an explanation of nonmonotonic zero-shear viscosity trends, there has been limited experimental evidence to corroborate this theory. Cryo-TEM is the most commonly used method, which provides visual evidence of branching [59,74–76]. However, this method is limited to dilute solutions and is difficult to use in studies of WLMs due to the elastic nature and high viscosities of the solutions. The blotting procedure performed while preparing cryo-TEM grids may also enforce aligned structures, and the organic nature of the materials leads to poor image quality, making quantifying information from the images difficult. PGSE-NMR diffusion measurements have been successfully used to confirm the presence of branching in reverse micellar solutions of lecithin and oil [64,65], with deviations from Maxwellian behavior observed at high frequencies. Koshy et al. [66] noted differences in the scaling laws for Maxwell fluids [37,41] past the viscosity maximum in solutions of catanionic CTAB-NaOL. As the observed scaling of the plateau modulus, \( G^0_N \), was stronger at lower surfactant concentrations than at higher values where branching was proposed, it was concluded that \( G^0_N \) of branched systems has a weaker dependence on surfactant concentration than linear worm-like solutions. Oelschlaeger et al. [53] used DWS optical microrheology and macroscopic mechanical rheology to investigate the underlying cause of two local maxima in the zero-shear viscosity and relaxation time in solutions of CPyCl with added NaSal. They determined that the peak at low salt concentration was a transition between linear micellar growth and micellar branching. Recently, Sachsenheimer et al. [60] investigated six different WLM systems covering a broad range of surfactant concentrations and salt/surfactant ratios using capillary breakup elongational rheometry (CaBER). The filament lifetime, \( t_{fil} \), measured from the CaBER experiments was shown to depend on the plateau modulus, \( G^0_N \), and the breakage time, \( \tau_{break} \), obtained from small-amplitude oscillatory shear rheology parameters by the scaling law [60]:

\[
\frac{t_{fil}}{G^0_N} \propto \tau_{break}^{2/3}
\]  

(1.41)
Furthermore, it was shown that the filament lifetime depends more strongly on the zero-
shear viscosity in the case of linear micelles than in the branched regime, suggesting that
CaBER can be used to distinguish micellar topology. Scattering techniques have also been
developed for the determination of branching [77]; however, it is generally accepted that
static scattering can detect micellar growth but is insufficient to determine branching [66,75,
76,78]. These, and related methods, are reviewed by Rogers et al. [9].

1.5 Theory of WLM branching

The formation of ‘branched cylinder’ micelles was first proposed by Porte et al. [79]
to describe the phase behavior and phase separation in solutions of CPyCl micelles in brine.
Cartoon depictions of branched micelles and interconnected networks can be seen in the
phase diagram proposed by Lequeux and Candau [18] in Figure 1.2. Drye and Cates [72]
considered the role of branching in forming living networks that can saturate and lead to
eventual phase separation [72], which had been experimentally observed by Porte et al. [79].
Lequeux [63] then extended the results of Cates for linear micelles given in Equations 1.20,
1.30, and 1.36 to account for micellar branching and interconnections. In this model, branch
points move fluidly along a contour and act as another mechanism for stress relaxation,
unlike in chemically-bound polymers. When branch points and interconnections are present,
the average contour length, $L_c$, is replaced by the average distance between branch points,
$L_m$, given by [63]:

$$L_m = \frac{n_2}{n_1 + 2n_3} l_p$$

(1.42)

where $n_1$ is the concentration of end caps, $n_2$ is the number density of segments of length $l_p$,
and $n_3$ is the concentration of three-fold junctions. In the limit of linear micelles ($n_3 \to 0$),
the average contour length is recovered from Equation 1.42. Conversely, in a fully saturated
network (shown in Figure 1.2), $n_1 \to 0$, and $L_m$ scales with volume fraction as $L_m \sim \phi^{-1/2}$.
As $L_m$ represents an effective decrease in the contour length, the reptation time of the micelles
in solution decreases (Equation 1.23), which leads to a faster relaxation time (Equation 1.20)
and lower viscosity (Equation 1.40).

Notably, the more charged or branched the system, the higher the expected deviation from such scaling laws presented in Section 1.3. As branch points form, the length scales defined for linear micelles, such as the entanglement length, become ill-defined. The effective micelle length becomes the distance between branch points, as given in Equation 1.42. In linear WLMs in the fast breaking limit, breakage and reformation dynamics lead to a single relaxation time, which is manifested as a semi-circle in the Cole-Cole representation. However, LVE data from polymeric systems, where breakage and reformation are not available mechanisms for stress relaxation, are almost never semicircular in the Cole-Cole representation. While both polymers and WLMs have inherent polydispersities in the average chain length, the chemically-bonded nature of the polymer requires reptation of the full chain for complete stress relaxation, whereas the living nature of the micelles leads to a single effective chain length. Polymeric branching also leads to significant deviations from Maxwellian behavior [80] and increases in viscosity because the branch points are not mobile as they are for WLMs. Similar trends in the LVE rheology have been observed in micellar solutions with high salt concentrations and branching [32,50,57,69], with anomalous behavior at high frequencies. Therefore, as branching increases and more mechanisms of relaxation become available, the LVE rheology increasingly deviates from Maxwellian behavior.

In this dissertation, the hydrotropic salt sodium tosylate (NaTos) is added to the WLMs to induce branching. As the overall micelle contour length is governed by the micelle scission energy (Equations 1.9, 1.10), the addition of NaTos increases structural flexibility by screening headgroup repulsions and inter-micelle electrostatic interactions. This salt addition thus reduces the net micelle surface charge, which can be seen in Figure 1.4a. The reduction of the electrostatic energy of the system thereby increases the scission energy and decreases the micellar persistance length, \( l_p \). The increasing scission energy makes the formation of branch points more energetically favorable [12,13]. The penetration of the small molecule NaTos into the micelle also increases flexibility and serves to increase the packing parameter (Equation 1.1), enabling the surfactants to more easily rearrange into junctions needed to form branches as opposed to conventional convex endcaps (Figure 1.4b).
Figure 1.4: WLM assembly altered by branching. (a) Adding hydrotropic salt, like NaTos, alters the local order ($l_p$) when the salt penetrates the structure of the micelle. This salt addition decreases $l_p$ by screening the electrostatic interactions around the micellar head groups. (b) The long-range order is also altered, as salt addition makes the formation of branch points (bottom) more energetically favorable, reducing the number of endcaps (top).

Many recent experimental studies of micellar solutions have invoked branching to describe their results. The method of inducing branching in each system falls into three categories that are summarized in Table 1.1: surfactants with simple inorganic salts, surfactants with penetrating salts, and mixed surfactants or emulsions. Simple salts, such as NaCl, alter the ionic strength of solution but do not penetrate the structure of the micelles as shown in Figure 1.4a, thereby having less of an effect on the micelle topology as compared to the effect of hydrotropic salts such as NaSal or NaTos [13]. In contrast, the branching effects are more pronounced upon the addition of a hydrotropic salt, as illustrated in Figure 1.4a. In this dissertation, the WLMs used consist of a total surfactant concentration $C_D$ that is held constant at 1.5% wt, with an added hydrotropic salt, sodium tosylate (NaTos). In these solutions, $C_D$ is approximately that of the overlap concentration, $C^*$, between the dilute and semi-dilute regimes (see Equations 1.18, 1.19). The location of $C^*$ was determined by a change in the scaling rules at $C_D = 1.5\%$ wt [13]. In this system, the use of oppositely charged surfactants is sufficient to induce branching at low levels with no added salt; thus the “micellar growth”
Table 1.1: Methods of inducing branching in WLMs and references for each method.

<table>
<thead>
<tr>
<th>Method of Inducing Branching</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single surfactant with simple inorganic salt</td>
<td>[54,69,75,81,82]</td>
</tr>
<tr>
<td>Single surfactant with penetrating salt</td>
<td>[53,67,83–89]</td>
</tr>
<tr>
<td>Mixed surfactants or mixed emulsions</td>
<td>[13,19,32,33,59,64–66,76,90–96]</td>
</tr>
</tbody>
</table>

region of increasing zero-shear viscosity is already surpassed. As the first viscosity maximum is not observed and the range of salt concentrations is sufficiently small so as to avoid phase separation, the zero-shear viscosity decreases monotonically with added salt.

1.6 Objectives and approach

The aims of this dissertation are two-fold, and pertain to both instrumentation-related and system-specific research. One major aim is to advance analysis methods and experimental techniques in neutron scattering specifically, but also in rheology. The second aim is to apply these new techniques and analysis methods to a particular soft matter system, in this case, surfactant wormlike micelles. The overarching goal is to use a combination of neutron scattering and rheological methods to help better understand the flow-structural properties of WLMs. While the majority of the chapters in this dissertation focus on the properties of WLM solutions, which are aided by the development of scattering and rheological tools, Chapter 3 specifically focuses on new techniques, data collection procedures, and data analysis methods that have been developed in this work.

A broad objective of this dissertation is to develop quantitative ‘structure-property’ relationships in a model series of wormlike micelles with different topologies. The mixed cationic and anionic wormlike micelles are composed of cetyltrimethylammonium tosylate (CTAT) and sodium dodecylbenzenesulfonate (SDBS), with different concentrations of added hydrophilic salt, sodium tosylate (NaTos). This salt addition is known to induce morphological changes in these particular WLM solutions [13]. These mixed surfactant systems have been previously well characterized [13,19,24] in terms of the phase behavior and linear
rheology. To build on this work, major objectives of this thesis include exploring the nonlinear rheological behavior, the flow-induced microstructure, and solution dynamics of the WLMs. This dissertation will specifically investigate the effect of added salt on the underlying micellar topology, and how these changes in topology affect the nonlinear rheology, shear-induced structures, and solution dynamics. From these investigations, the overall goal is to develop quantitative relationships that link the underlying microstructure and topology to these nonlinear and dynamic properties. By developing structure-property relationships in a model system like WLMs, these techniques and findings can be extended to characterize a wide array of soft matter systems.

The structure-property relationships discussed in this thesis specifically focus on linking the solution microstructure with the macroscopic flow behavior, as measured by the solution rheology. Specifically, controlling the level of branching in WLMs should allow the rheological properties to be tuned for specific applications. However, in order to do this, a complete and thorough understanding of the effect of branching on the flow properties is required. In this dissertation, the macroscopic flow behavior that will be discussed pertains to both the linear and nonlinear shear rheological properties. In terms of the dynamic rheology, both linear viscoelastic (LVE) regime rheology and large amplitude oscillatory shear (LAOS) rheology will be discussed. These regimes are distinct, as WLMs often exhibit model LVE behavior, but highly unpredictable nonlinear behavior. WLMs often exhibit flow instabilities, such as shear banding, which will be discussed in-depth on the basis of added salt and branching level. Steady shear rheology and shear startup rheology cover the remaining shear rheological methods that will be investigated on a basis of branching level. Investigations of the extensional rheology and the orthogonal superposition rheology (OSP) will also be discussed and linked to the micellar topology. By understanding how the underlying microstructure and topology affect the macroscopic properties, materials with desirable flow properties can ultimately be designed.

Understanding how the flow behavior and molecular topology are coupled requires techniques outside of rheology, as rheological measurements only provide information about the bulk flow properties. Small angle neutron scattering (SANS) measurements can be used
to measure the microstructure of a material, which can complement rheological measurements. Static SANS measurements alone are not sufficient to understand how the structure and flow properties are linked, as the microstructure under flow greatly differs from the microstructure at rest. However, recent advancements in experimental methods combine time- and spatially-resolved small angle neutron scattering (flow-SANS) measurements of structure with rheometry for various types of nonlinear deformations [36, 97, 98]. Flow-SANS enables the measurement of the flow-induced microstructure in different shear planes while a material is being deformed, allowing quantitative structure-property relationships to be developed. Here, these newly developed flow-SANS methods are used to explore the microstructure of the wormlike micelles undergoing steady shear, shear startup, and LAOS deformations. In Chapter 3 of this dissertation, improvements to the flow-SANS method are proposed based on newly developed methods in time-resolved analysis, as well as analysis of the optimal configurations for flow-SANS experiments.

The research presented in this dissertation quantitatively links micellar microstructure and topology to the measured nonlinear shear rheology and dynamics of WLM solutions using a combination of advanced techniques in rheology and neutron scattering. To develop these structure-property relationships, advances in time-resolved neutron scattering techniques and analysis methods have been developed, which can now benefit the greater scientific and engineering community. In addition, when appropriate, the results have used to validate constitutive modeling efforts that specifically incorporate micellar breakage into predictions of the flow behavior; this work also provides a necessary data set for critically testing and improving additional microstructure-based constitutive equations. The findings from this dissertation can be used to aid in the formulation of WLMs for specific applications, and are part of a broader effort to characterize branching in chemical polymers and self-assembled systems.

**A note on the organization of the dissertation:** For clarity, a reference for nomenclature and acronyms used in this dissertation can be seen in the first appendix, Appendix A. The permissions for any reprinted or adapted text and figures can be seen in the final appendix, Appendix P.
References


Chapter 2
MATERIALS AND METHODS

2.1 Introduction

This chapter presents detailed information on all of the materials and experimental procedures described in this work. New analysis methods developed to treat time-resolved neutron scattering data will be discussed in Chapter 3. Furthermore, the calculation of the alignment factor to quantify microstructural rearrangements from small angle neutron scattering (SANS) data will be introduced. All experiments follow the procedures described in this chapter unless specifically noted. The procedures in this chapter have been published in references [1–3].

2.2 Materials

The wormlike micelles (WLMs) examined in this work are composed of a mixed cationic and anionic surfactant with an added hydrotrropic salt to induce branching, previously characterized over a range of added salt concentrations by Schubert [4] using rheology, small angle neutron scattering (SANS), and flow birefringence methods [4, 5]. The primary WLM solutions studied consist of the cationic surfactant cetyltrimethylammonium tosylate (CTAT) and the anionic surfactant sodium dodecylbenzenesulfonate (SDBS) with a total surfactant concentration held constant at 1.5% wt (97/3 weight ratio of CTAT/SDBS; 35.8 mM CTAT/1.45 mM SDBS). The majority of the work in this dissertation focuses on the 1.5% wt surfactant solutions. Sodium tosylate (NaTos) was added as a hydrotrropic salt to induce structural changes, ranging from 0.0% wt NaTos to 0.25% wt NaTos. The chemical structure of the surfactants and salt can be seen in Figure 2.1. Sodium tosylate and CTAT were obtained from Sigma-Aldrich. CTAT was recrystallized twice from a 50/50 mixture of ethanol and acetone, which has been previously described by Schubert [4]. Sodium tosylate
was used as received. Soft-type (linear chain) SDBS was obtained from TCI and used as received. All surfactant solutions were prepared at room temperature in D$_2$O (Cambridge Isotopes, 99.8%) that was filtered before use. All samples were incubated in a 35 °C water bath for 3 days before performing SANS or rheological measurements to ensure chemical, kinetic, and thermal stability.

Figure 2.1: Structure of the surfactants and salts used in this work. (a) cetyltrimethylaminomium tosylate (CTAT), the cationic surfactant, (b) sodium dodecylbenzenesulfonate (SDBS), the anionic surfactant, and (c) sodium tosylate (NaTos), the hydrotropic salt.

Throughout this work, we will use the results of Schubert et al. [5] as a basis for comparing our results [4,5]. One major difference between this work and the work of Schubert et al. [5] is that the solutions here are prepared in D$_2$O as opposed to in water. This isotopic substitution has a relatively minor effect on the micellar length scales; the greater polarity of D$_2$O leads to an increase in the micellar persistence length of about 10% [6]. This result helps to justify using the work of Schubert et al. [5] as a baseline. However, from our own experiments, the isotopic substitution from water to D$_2$O had the effect of decreasing the relaxation time by approximately one order of magnitude (see in Appendix F); this effect is
likely due to the increased polarity and strength of the deuterium bonding versus hydrogen bonding, which leads to vastly different nonlinear rheological properties when the solutions in water versus D$_2$O are compared.

For the orthogonal superposition (OSP) studies (see Section 2.3.5), the WLM solutions were composed of the same surfactants and salt, but a higher weight fraction was used. The OSP measurements require larger volumes than standard experiments, and also require higher modulus materials to obtain a reasonable signal due to the OSP geometry and issues with measurement sensitivity associated with the experiment. Here, we use higher surfactant concentrations due to the low modulus values that resulted in the 1.5% wt surfactant solutions. In these OSP experiments, the ratio of CTAT to SDBS was held constant at a 97/3 weight ratio, but the total surfactant concentration was increased to 4.0% wt. The sodium tosylate concentration ranged from 0.01% wt to 0.10% wt. Due to the large volume requirements for OSP experiments, these solutions were prepared using filtered Millipore water as the solvent instead of D$_2$O.

2.3 Rheological characterization

The majority of rheometry measurements reported in this dissertation were performed on an ARES G2 strain-controlled rheometer (TA Instruments, New Castle, DE) using the TA Instruments TRIOS software. Temperature control was maintained using a ThermoCube circulating chiller (AMS Technologies) and the Advanced Peltier System (APS) environment. All rheological measurements were performed at 35 °C ± 0.1 °C, unless otherwise noted. A concentric-cylinder Couette geometry was used with a stationary inner cylinder, stainless steel DIN bob (R$_1$ = 13.84 mm) and a rotating outer cylindrical cup made of hard anodized aluminum (R$_2$ = 15.00 mm), such that the gap width, H, was 1.16 mm. Using the length of the Couette bob, L, the resulting aspect ratio, $\Gamma = L/H$, was 35 and the gap to radius ratio, $\varepsilon = H/R_1$, was 0.084. Rheological measurements were often repeated during SANS on an Anton-Paar MCR-502 stress-controlled rheometer operating in strain-controlled mode, with a solvent trap filled with D$_2$O to provide a saturated atmosphere. Data was recorded in the Anton-Paar RheoPlus or RheoCompass software. A concentric-cylinder Couette geometry
with a moving inner cylinder and stationary outer cup was used, with a gap size of 1 mm unless otherwise noted. The three most common SANS geometries used in this work are given by, a) \( R_1 = 13.5 \) mm, \( R_2 = 14.5 \) mm, \( \varepsilon = 0.074, \Gamma = 36 \); b) \( R_1 = 14 \) mm, \( R_2 = 15 \) mm, \( \varepsilon = 0.071, \Gamma = 36 \); and c) \( R_1 = 24.0 \) mm, \( R_2 = 25.0 \) mm, \( \varepsilon = 0.042, \Gamma = 36 \). A summary of all SANS rheometer configurations can be seen in Table 2.1 below. Samples were conditioned in the rheometer for 10 minutes at 35 \( ^\circ \)C to achieve thermal equilibrium; repeated frequency sweeps were performed after the equilibration time to ensure reproducibility. Rheology was verified to be independent of instrument and geometry.

2.3.1 Linear viscoelastic (LVE) rheology

To determine the linear viscoelastic (LVE) response and relaxation time of the WLM solutions (\( \tau_R = 1/\omega_c \), Equations 1.20 and 1.25), frequency sweeps were performed on all samples. The crossover frequency was calculated using the TA Instruments TRIOS software. In LVE rheology, also known as small amplitude oscillatory shear (SAOS), the applied strain, \( \gamma \), is sinusoidal and the applied strain rate, \( \dot{\gamma} \), is co-sinusoidal and are given by:

\[
\gamma(t) = \gamma_0 \sin(\omega t) \quad \text{(2.1)}
\]

\[
\dot{\gamma}(t) = \gamma_0 \omega \cos(\omega t) = \dot{\gamma}_0 \cos(\omega t) \quad \text{(2.2)}
\]

where \( \gamma_0 \) is the strain amplitude, \( \omega \) is the frequency in \( \text{rad} \cdot \text{s}^{-1} \) and \( \dot{\gamma}_0 \) is the shear rate amplitude, or maximum shear rate during the cycle, where \( \dot{\gamma}_0 = \gamma_0 \omega \). Here, \( \gamma_0 \) is sufficiently ‘small’ such that the resulting stress response is sinusoidal in time and independent of the applied \( \gamma_0 \), indicating linear regime behavior. The LVE stress response is given by:

\[
\sigma(t) = G' \gamma_0 \sin(\omega t) + G'' \gamma_0 \cos(\omega t) = G' \gamma + G'' \dot{\gamma} / \omega \quad \text{(2.3)}
\]

where \( G' \) is the elastic or storage modulus, and \( G'' \) is the viscous or loss modulus. Additional background on oscillatory shear experiments can be seen in Chapters 1 and 7. The crossover
frequency, $\omega_c$, that defines the relaxation time above, is defined as the frequency at which $G' = G''$ in an LVE experiment.

Frequency sweeps were performed using strain amplitudes ranging from $\gamma_0 = 5\%$ to $20\%$ to measure the linear viscoelastic response of each sample. The ‘frequency based correlation’ option in the TRIOS software was used to detect the steady state response, and at minimum, one half cycle of data was discarded before measuring the dynamic moduli. Amplitude sweeps were performed on each sample to determine the strain amplitudes constraining the linear viscoelastic window, as determined by the region in which the response of the dynamic moduli was independent of $\gamma_0$. In these experiments, the waveform was not analyzed; instead, the dynamic modulus values ($G', G''$) were calculated by the TRIOS software. Note that beyond the LVE window, TRIOS reports the value of the first harmonic of $G'$ and $G''$, $G'_1$ and $G''_1$, respectively. The linear viscoelastic window was found to be relatively constant between WLM samples ($\gamma_0 = 5 - 20\%$). Generally, strain amplitudes lower than $\gamma_0 = 5\%$ did not provide sufficient signal for the measurement, although these amplitudes are also within the linear viscoelastic window. Select amplitude sweeps can be seen in Appendix C. The delay time between consecutive frequency sweeps was at least ten relaxation times, $10\tau_R$, where the relaxation time is defined as the inverse of the crossover frequency (Equation 1.25). Frequency sweeps were performed in triplicate over the course of one hour to ensure structural and thermal equilibrium after loading, in both the increasing and decreasing directions with no observable hysteresis. Frequency sweeps were also performed at the start of and throughout all rheological measurements to confirm the absence of foaming, evaporation, or irreversible changes from shear.

2.3.2 Steady shear rheology and shear startup

Steady shear flow sweeps were performed to measure the steady-state material viscosity and stress over a range of shear rates ($\dot{\gamma} = 0.1 - 1000 \text{ s}^{-1}$, depending on the sample). In a standard steady shear flow sweep, the shear rate is changed in small steps, with no rest time in between shear rates. Flow sweeps were performed to determine the steady state flow curve using the TA Instruments TRIOS software steady state sensing feature, with a tolerance level
set to 5%. Additional flow sweeps were recorded in the increasing and decreasing directions with at least $10\tau_R$ of rest time between each datum without observable hysteresis. In all cases, shear startup measurements were used to corroborate the flow sweep data. In shear banding solutions (0.01% wt, 0.05% wt NaTos), the steady state flow curves were further verified with long-time ($t = 600 - 5400$ s) startup measurements of the stress. To examine the transient features of the stress response in more detail, select startup measurements were repeated in triplicate; this was also done for startup rheo-SANS measurements to corroborate the startup results. Repeating the measurements in triplicate allows us to identify significant features of the stress response that may indicate shear banding, such as stress overshoots, undershoots, and even secondary overshoots. For all solutions, even in cases of shear banding, the startup results did not vary significantly between trials.

2.3.3 Particle tracking velocimetry (PTV)

Velocity profiles were measured for select WLM solutions using particle tracking velocimetry (PTV) to verify results from the rheology and SANS measurements. All velocity profiles were measured by Peng Cheng (M. Helgeson group) at the University of California, Santa Barbara. The PTV system is adapted from an Anton-Paar Physica MCR strain-controlled rheometer. A concentric-cylinder Couette geometry was used with a rotating inner cylinder of anodized aluminum ($R_1 = 17.0$ mm) and a stationary outer cylindrical cup made of quartz ($R_2 = 17.5$ mm), such that the gap width, $H$, was 0.5 mm. The 0.5 mm gap width was chosen to most closely approximate the gap-to-radius ratio, $\varepsilon$, of the 1-2 plane shear cell from the SANS experiments. Here, $\varepsilon = 0.029$, whereas in the 1-2 shear cell, $\varepsilon = 0.039$.

Samples for particle tracking were prepared using tracer particles in a concentration of approximately 200 ppm. The particles were silica spheres, with dimensions ranging from $d = 3 - 10 \mu$m. Particle addition did not affect the measured sample rheology. A horizontal sheet laser is incident upon the middle of the quartz outer cylinder, which illuminates the particles. The particles were imaged using a CCD camera. The location of the particles within the gap and their velocities were analyzed using standard particle tracking algorithms [7,8].
For the 0.01% wt NaTos solution, a delay time of 20 minutes was used before calculating the steady state velocity profile; for the 0.10% wt NaTos solution, this delay time was 5 minutes.

2.3.4 Large amplitude oscillatory shear (LAOS)

Large amplitude oscillatory shear (LAOS) deformations are of the same waveform as those applied in the LVE regime, however significantly larger strain amplitudes are used in the applied deformation. As a result, the material stress response is periodic, but no longer sinusoidal, and depends on the value of $\gamma_0$ and the applied frequency $\omega$. Additional background information on LAOS will be covered in Chapter 7. In all solutions, LAOS measurements were performed from startup to the steady alternance state, with no delay time, to watch the evolution of the rheological response to the steady alternance state. Several LAOS cycles were recorded once the steady alternance state was achieved to determine the significant features of the LAOS stress response. Unlike in Section 2.3.1, the waveform of the LAOS stress response was always recorded and analyzed for these measurements.

LAOS measurements can be performed in two ways: as part of an amplitude sweep or as a standalone experiment. When amplitude sweeps were performed to record the LAOS data (constant $\omega$, variable $\gamma_0$), the measurements were performed consecutively without rest time between changing $\gamma_0$. When the frequency was changed between LAOS experiments, greater than $10\tau_R$ of delay time was used between experiments. No significant differences were observed when the LAOS response was measured as one step of an amplitude sweep versus measured as an individual experiment, confirming that rest time is not required between LAOS measurements at the same frequency. All experiments were performed using a suitable number of points for Fourier transform analysis, i.e., 128, 256, or 512 points per cycle.

To demonstrate the significance of the features of the LAOS stress response, the LAOS experiments were performed for several cycles at the steady alternance state. Additionally, select conditions were repeated after a significant wait time (30 minutes or more) to ensure the reproducibility of the stress response. An example of these reproducibility experiments can be seen in Figure 2.2 below for the mildly branched, 0.05% wt NaTos solution. The absolute value of the stress response at steady alternance state can be seen in Figure 2.2
for two conditions discussed in Chapter 7 for this solution, where the error bars represent the standard deviation of the average stress over several cycles at the steady alternance state. We show the absolute value of the stress response in Figure 2.2 so that the stress response is averaged over cycles in both directions. This method ensures that that the stress response is symmetric and does not depend on the flow direction.

We show the absolute value of the stress response in Figure 2.2 so that the stress response is averaged over cycles in both directions. This method ensures that that the stress response is symmetric and does not depend on the flow direction.

Figure 2.2: Two sample LAOS conditions for the mildly branched solution (0.05% wt NaTos), discussed in Chapter 7. LAOS condition 1 (a) and condition two (b) average stress response and standard deviation over several cycles at steady alternance state for two trials. The stress overshoots, undershoots, and inflection points are significant features of the stress response, when compared to the size of the error bars. Repeated trials show excellent reproducibility. The uncertainty in the stress response is similar in the remaining conditions.

In Figure 2.2a, the overshoots and undershoots observed in ‘condition one’ are significant aspects of the stress response, as they are not only much larger than the uncertainty, but also persistent in both trials. This analysis shows that the stress response has clear rheological signatures, similar to those observed in shear startup measurements, which allows us to link the steady and dynamic flow properties. The same is true of the inflection points in the stress response in ‘condition 2,’ seen in Figure 2.2b. Both stress responses were within error between trials one and two, showing the reproducibility of the LAOS stress response. The repeated trials and multiple cycles also allow us to quantify the uncertainty in features of the LAOS response. In Chapter 7, the uncertainty reported in Table 7.2 for the maximum
stressed is the standard deviation (shown by the error bars in Figure 2.2) around the maximum stress. The uncertainty in the yield strain results from the strain step size between data points in the vicinity of the maximum stress; each test reported in Table 7.2 was performed at 256 points per cycle.

2.3.5 Orthogonal superposition rheology (OSP)

2.3.5.1 Background

Orthogonal superposition rheology (OSP) is a tool that can be used to probe a material’s nonlinear viscoelasticity or linear viscoelasticity with directional control, as detailed by Vermant et al. [9]. In OSP rheology, the dynamic moduli $G'$ and $G''$ are measured in the direction orthogonal to the standard shear (or oscillation) direction. In the standard configuration, a small amplitude oscillation is applied in the vertical direction, while the material is either sheared or oscillated in the horizontal direction, as shown in Figure Ka and b [10]. Here, the strain in the orthogonal direction, $\gamma_\perp(t)$, is of the same form as in Equation 2.1, given by:

$$\gamma_\perp(t) = \gamma_{0,\perp} \sin(\omega_\perp t) \quad (2.4)$$

where $\gamma_{0,\perp}$ and $\omega_\perp$ are the strain amplitude and frequency in the orthogonal direction, respectively. When the dynamic moduli are probed under shear, OSP rheology is able to detect changes in the viscoelasticity of the material with a structural rearrangement such as flow alignment or yielding. When applied to the WLM solutions examined in this work, steady shear OSP rheology has the potential to detect differences in the dynamic moduli that result from the alignment of the wormlike chains or micellar breakage under shear. When a 2-D oscillation is applied, the amplitudes of the individual components are orthogonal to one another in space, as illustrated in Figure Kb. The dynamic moduli can be probed at different angles by changing the amplitude or phase shift of the individual components composing the
total wave, which are:

\[ \gamma(t) = \gamma_0 \sin(\omega t) \]
\[ \gamma_\perp(t) = \gamma_{0,\perp} \sin(\omega t + \delta) \] (2.5)

Here, \( \delta \) is the phase shift between the two waves, which can be selected by the user, and the frequency must be identical between deformations. The total deformation wave is simply the addition of the two component vectors. The 2-D oscillation mode is useful for anisotropic materials, as a direction-dependent LVE spectrum can be determined. The OSP tooling is now commercially available for use on the TA Instruments ARES G2 rheometer, which was used for all experiments. The tooling consists of a double-wall concentric cylinder Couette geometry, which can be seen in Figure Kc.

![Image of OSP tooling](image)

Figure 2.3: Orthogonal superposition rheology schematic. (a) Configuration for measuring the dynamic moduli under shear. (b) 2-D oscillation configuration, for anisotropic LVE spectra. (c) Double-wall Couette geometry commercialized for OSP, reprinted from [10].

### 2.3.5.2 Experimental details

All OSP experiments were performed using the TA Instruments ARES G2 rheometer with the slotted, double-wall concentric cylinder Couette geometry. The operating temperature and temperature control are described at the start of Section 2.3. The WLM solutions were prepared in water as opposed to D\(_2\)O, at a surfactant concentration of \( C_D = 4.0\% \) wt.
The OSP geometry consists of a slotted, double-gap cup made of hard anodized aluminum \((R_1 = 13.85 \text{ mm}, R_2 = 17.0 \text{ mm})\). The slotted, double-gap bob is made of titanium, with smaller dimensions \((R_3 = 14.7 \text{ mm}, R_4 = 16.0 \text{ mm})\), for a minimum sample volume of approximately 37 mL. The length of the Couette cup was \(L = 51.6 \text{ mm}\). The double-gap cup rotates in the horizontal direction, while the bob oscillates in the vertical direction.

OSP measurements were performed to determine the WLM dynamic moduli under shear (configuration 1, Figure Ka) using the TRIOS ‘rotation mode’ option. A standard frequency sweep was performed at the start of each test; the result was then compared to the frequency sweep in ‘rotation mode’ at \(\dot{\gamma} = 0 \text{ s}^{-1}\) before performing the OSP tests. The modulus values were always slightly higher (\(\approx 20\%\)) in the ‘rotation mode’ at zero-shear versus the standard frequency sweep mode, which is an effect of the instrument sensitivity in the OSP rotation mode. This sensitivity effect is shown in Figure 2.4 for the 4% CTAT/SDBS solution with 0.10% wt NaTos and is similar for all WLM solutions; the measurement sensitivity does not appear to affect the qualitative results as the shape of the two curves is similar. As seen in Figure 2.4, the accessible frequency window is also smaller in OSP rotation mode than in the standard oscillation mode. Startup measurements were performed on the WLM solutions before performing OSP measurements. From the startup measurements, the time for each WLM solution to reach its steady state stress was determined for each shear rate. This time determined via startup, plus an additional delay time, was used as the ‘delay before oscillation’ time. This delay time indicates the amount of time the WLM solution is sheared before OSP measurements were started. For all measurements, the strain amplitude in the normal direction, \(\gamma_0_{\perp} = 5\%\) (the maximum allowable by the instrument) to achieve the best signal. To measure the LVE spectrum under shear, the ‘frequency based correlation’ option in the TRIOS software was used to detect the steady state response. At least one half cycle of data was discarded before measuring the dynamic moduli.

\subsection*{2.3.6 Cryo-transmission electron microscopy (cryo-TEM)}

Cryo-transmission electron microscopy (cryo-TEM) imaging was performed on the wormlike micelle (WLM) solutions with a fixed surfactant concentration \((C_D = 1.5\% \text{ wt})\)
Figure 2.4: Standard frequency sweep vs. frequency sweep at zero shear rate in OSP rotation mode, shown for the 4% wt CTAT/SDBS, 0.10% wt NaTos WLM solution. The frequency sweep in OSP rotation mode gives larger modulus values due to poorer measurement sensitivity; however, the overall shape of the spectrum does not appear to be affected. OSP rotation mode also has a shorter window of accessible frequencies due to sensitivity issues.

and various salt concentrations to visualize the effect of salt concentration on the structure: low (0.01% wt NaTos), high (0.10% wt NaTos), and very high salt (0.15% wt NaTos). These images can be seen in Chapter 4 for the low and high branched solutions, and Appendix E for additional images of the low, high and very high branching solutions. Cryo-TEM micrographs were taken by Ryan Murphy [1].

Cryo-TEM was performed on a Technai G2 12 Twin TEM operating at 120 kV. Samples were prepared using an FEI Vitrobot at 35 °C and 100% relative humidity. Prior to sample preparation, the TEM grids (Quantifoil R 2/1 or lacey carbon) were plasma cleaned for 60 s. A 3 µl volume of each sample solution was pipetted onto the grid inside the sample chamber. Using an automated system, each sample was blotted twice to remove excess sample prior to vitrification in liquid ethane. The blotting conditions were consistent for each sample: 3 s blot time, 5 s wait time, 10 s drain time, and 0 blot force. The grids were transferred into liquid nitrogen for storage before imaging. Images were recorded using a Gatan CCD camera and were imaged at a nominal underfocus to enhance phase contrast. The temperature of the probe was maintained between -178 and -180 °C during imaging.
2.4 Small angle neutron scattering (SANS)

2.4.1 Background

The relevant length scales of the wormlike micelles used in this work range from angstroms (1 Å = 10^{-10} m) to microns. Micron-scale lengths, such as the contour length (L_c), can be detected using cryo-TEM or light scattering techniques. However, neutron scattering is optimal for examining smaller length scales of the WLMs, like the cross-sectional radius and persistence length (r_{cs} and l_p, respectively). These smaller distances are particularly relevant to the flow properties and flow-induced microstructure of the WLMs because the micelles tend to orient under flow on a segmental length scale. An illustration of the standard static SANS experiment can be seen in Figure 2.5a below.

In a typical static SANS experiments, the cold neutron beam is produced from a reactor source after the neutrons are cooled to lower energies. A velocity selector is used to filter the neutrons based on wavelength, where a typical wavelength spread (FWHM) \( \Delta \lambda / \lambda \) is on the order of 10 to 15\%. All experiments in this work were performed using a continuous reactor source with a velocity selector, as opposed to a spallation neutron source, which uses neutrons of all wavelengths. The incident beam from the reactor (denoted by the vector \( \vec{k}_i \) in Figure 2.5) then interacts with a stationary sample. The neutrons are scattered at an angle, \( \theta \), to the detector, and this scattered beam is denoted by the vector \( \vec{k}_s \). The scattering wave vector \( \vec{q} \) (also denoted as \( q \)) is defined as \( \vec{q} = \vec{k}_s - \vec{k}_i \). The magnitude of \( q \) is given by:

\[
q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)
\]

(2.6)

where \( \lambda \) is the neutron wavelength (typically reported in Å) and \( \theta \) is the scattering angle. As scattering measurements are taken in reciprocal space, \( q \) is typically reported in Å^{-1}. Because SANS is considered an elastic scattering method, the energy transfer is not recorded and is assumed to be negligible. Quasi-elastic scattering methods such as neutron spin echo do involve energy transfer and will be discussed further in Section 2.7.1 below.

The magnitude of \( q \) is then used to determine the accessible length scales in real
Figure 2.5: An illustration of the typical static SANS measurement (a) versus the typical flow-SANS measurement, shown for the 1-3 flow-vorticity plane (b). (a) In a static SANS experiment, the observed scattering pattern is isotropic for semi-dilute WLMs, as the WLMs have no net orientation at rest. (b) A rheometer is aligned in the neutron beam to take SANS measurements under flow. Unlike in (a), the scattering pattern becomes anisotropic due to shear-induced micellar alignment. As the micelles align along the flow direction (horizontal), the scattering shows increased intensity in the vorticity direction (vertical).
space, where \( q \) is related to the real-space dimension, \( d \), by the Bragg relation:

\[
q \approx \frac{2\pi}{d}
\]  \hspace{1cm} (2.7)

The typical wavelength of a SANS experiment is \( \lambda = 5 \) to 6 Å, giving real-space dimensions on the order of 1 to 1000 Å. In the WLM solutions relevant to this dissertation, the static SANS patterns are isotropic with regard to angle, as seen in Figure 2.5a. However, these solutions do exhibit anisotropic scattering when subjected to flow, which can be seen in Figure 2.5b. Here, the scattering orientation angle becomes more important, which is denoted by \( \phi \) in Figure 2.5b. The absolute scattering intensity and amplitude as a function of \( \vec{q} \) determined via SANS depends on the size and shape of the particles (or macromolecules) in solution, as well as the interactions between species and whether or not the particles are oriented.

Neutrons incident upon a sample have a total neutron cross-section, \( \Sigma_t \), which is broken down into contributions from scattered neutrons, \( \Sigma_s \), and absorbed neutrons, \( \Sigma_a \). Neutron absorption is small for most materials [11]. The scattered cross-section \( \Sigma_s \) can be divided into contributions from the coherent scattering, \( \Sigma_c \), which is \( q \)-dependent, and incoherent scattering, \( \Sigma_i \), which is \( q \)-independent. While a SANS detector is 2-dimensional, neutrons are scattered in 3-dimensions. A 3-D representation of this scattering is seen in Figure 2.6, where \( d\Omega \) is the solid angle the neutrons are scattered into. From Figure 2.6, we can define the microscopic scattering cross-section, \( d\sigma/d\Omega \), which is the fraction of neutrons scattered into solid angle \( d\Omega \) at angle \( \theta \) [11]. This microscopic cross-section is the elastic cross-section (as we do not consider inelastic scattering), and is related to the macroscopic scattering cross-section, \( d\Sigma/d\Omega \), by [11,12]:

\[
\frac{d\Sigma(q)}{d\Omega} = \frac{N}{V} \frac{d\sigma(q)}{d\Omega} = n_p \frac{d\sigma(q)}{d\Omega}
\]  \hspace{1cm} (2.8)

where \( n_p \) is the number density of particles or scatterers.

The scattering intensity from a collection of discrete particles, \( N \) can be defined by
Figure 2.6: Schematic of neutrons scattered with scattering angle $\theta$ (depicted in Figure 2.5) into a solid angle $d\Omega$. Reprinted from reference [11].

This macroscopic coherent scattering cross-section by [11–13]:

$$
\frac{d\Sigma_c(q)}{d\Omega} = \frac{1}{V} \sum_{j=1}^{N} |F_j(q)|^2 + \frac{1}{V} \left\{ \sum_{j=1}^{N} \sum_{k=1}^{N} F_j(q) F_k^*(q) e^{iq(r_j-r_k)} \right\} 
$$

(2.9)

where $r_j$ and $r_k$ are the centers of mass of particles $j$ and $k$. The single particle scattering amplitude $F_j(q)$ is given by:

$$
F_j(q) = \int_V [\rho_j(r) - \rho_0] e^{iq \cdot r} \, dr 
$$

(2.10)

where $\rho_0$ and $\rho_j(r)$ are the scattering length density of the surrounding medium (or solvent) and particle, respectively. When the particles are monodisperse and spherically symmetric, $F_j(q) = F_k^*(q) = F(q)$ [13]. While the WLM solutions are not monodisperse or spherically symmetric, it is reasonable to calculate the contribution to the scattering intensity based on the orientational average of the average particle size and shape [14]. In this case, the equation can be factored to give:

$$
\frac{d\Sigma_c(q)}{d\Omega} = n_p \langle |F_j(q)|^2 \rangle \left\{ 1 + \sum_{j=1}^{N} \sum_{k=1}^{N} e^{iq(r_j-r_k)} \right\} 
$$

(2.11)

where the term in $\langle$ braces $\rangle$ is referred to as the form factor, $P(q)$, and the term in $\{$ brackets $\}$ is referred to as the structure factor, $S(q)$. With this, the coherent scattering cross-section
then simplifies to [11]:

\[ \frac{d\Sigma_c(q)}{d\Omega} = n_p P(q) S(q) \] (2.12)

The form factor describes the size and shape of the particles (see Section 2.4.2.3), whereas the structure factor accounts for interparticle interactions (see Section 2.4.2.4). In the case of anisotropic particles, or the WLMs in this case, the structure factor is orientationally averaged to account for directional interactions between scatterers. Adding in the incoherent contribution gives the total, absolute scattering intensity:

\[ I(q) = n_p P(q) S(q) + I_{\text{incoh}} \] (2.13)

where \( I_{\text{incoh}} \) is the intensity of the incoherent scattering, known as the incoherent background. Here, the scattering is assumed to be isotropic. In the case of anisotropic scattering, which results when the WLMs are aligned under shear, the absolute intensity is dependent on the angle, \( \phi \), depicted in Figure 2.5b,

\[ I(q, \phi) = n_p P(q, \phi) S(q, \phi) + I_{\text{incoh}} \] (2.14)

Changes in a material structure or orientation will clearly change \( I(q) \) as shown by Equation 2.14. However, by the principle of the scattering invariant, \( I(q) \) may vary while the total scattering must remain constant for the same amount of material in solution, given by:

\[ C = \int_V \frac{d\Sigma(q)}{d\Omega} dq = \int_I I(q) dq \]

\[ = 2\pi \int_0^\pi \int_0^\infty \int_0^\infty d\phi d\theta q^2 I(q) dq \]

\[ = 4\pi \int_0^\infty q^2 I(q) dq \] (2.15)

where \( C \) is a constant, or the scattering invariant. As was the case for Equation 2.9 above,
however, \( I(q) \) must be calculated over all configurations. Equation 2.15 will hold when the sample scattering is isotropic, because the measured \( I(q) \) from SANS in one plane is representative of the scattering from the entire sample. However, when significant orientation is present in the system, SANS cannot measure all particle configurations, as it can only measure one scattering plane at a time. This can lead to a decrease in the total measured \( I(q) \) when the micelles are oriented, but this does not violate Equation 2.15 since Equation 2.15 is only valid for isotropic scattering.

### 2.4.2 SANS data analysis

#### 2.4.2.1 Guinier approximation

The Guinier approximation is used in the limit as \( q \to 0 \) to obtain structural information without having to make assumptions or fit a model to the data. Guinier realized that at low \( q \)-values, the scattered signal is insensitive to the particle shape, and only their overall size was important [15, 16]. The approximation is used in the dilute limit where interactions are not significant, where the structure factor \( S(q) \approx 1 \). In this limit, Equation 2.13 becomes a function of the form factor and scattering number density only. In this regime, the intensity \( I(0) \) cannot be measured from the nature of the SANS set-up. Instead, the scattering intensity at low-\( q \) is related to \( I(0) \) by [15, 16]:

\[
I(q) \approx I(0)e^{-\frac{R_g^2q^2}{3}}
\]  

(2.16)

where \( R_g \) is the radius of gyration or the ‘Guinier radius,’ which is the root mean square (RMS) distance from the center of the scattering density. Equation 2.16 is derived from the first two terms of a McLaurin expansion, which results from a Taylor series expansion around the form factor that is simplified using the zero-angle approximation. From Equation 2.16, a Guinier plot can be constructed by plotting the natural log of \( I(Q) \) vs. \( q^2 \):

\[
\ln[I(q)] = \ln[I(0)] - \frac{R_g^2q^2}{3}
\]

(2.17)
where the slope of the plot gives $-R_g^2/3$. Here, the maximum $q$-value over which the slope of the Guinier plot should be analyzed (to calculate the radius of gyration) is given by $q_{\text{max}} R_g \ll 1$. For a cylinder, the radius of gyration is related to the cylinder dimensions via:

$$R_g^2 = \frac{L^2}{12} + \frac{d^2}{8} = \frac{L^2}{12} + \frac{r_{cs}^2}{2}$$  \hspace{1cm} (2.18)

where $L$ is the length, $d$ is the diameter, and $r_{cs}$ is the cross-sectional radius. For wormlike micelles, the cross-sectional radius of gyration is then simplified from Equation 2.27 as:

$$R_{g,cs} = \frac{r_{cs}}{\sqrt{2}}$$  \hspace{1cm} (2.19)

### 2.4.2.2 Porod limit

In solutions like WLMs, the scattering intensity at high $q$-values reaches asymptotic values known as the Porod limit [16]. Valuable structural information about the system can be obtained in this high $q$ regime without making assumptions or using a model to fit the data. Here, high-$q$ is defined as $q \gg 1/d$, where $d$ is the size of the scattering object. In this limit, there must exist a sharp, defined surface or interface with a sharp transition in the scattering length density between the two species [12]. In this case, the intensity scales as $q^{-4}$, given by Porod’s law [16]:

$$\lim_{q \to \infty} I(q) = \frac{C_p}{q^4} + I_{\text{incoh}} = \frac{2\pi \Delta \rho^2 S_v}{q^4}$$  \hspace{1cm} (2.20)

where $C_p$ is the Porod constant, $\Delta \rho$ is the scattering length density difference between the two species, and $S_v$ is the specific surface area of the sample. The Porod constant is related to the ratio of the surface area to volume of the sample. For the WLMs discussed in this dissertation, the sharp interface between the micelles and the D$_2$O solvent results from the micellar cross-section. For objects with diffuse or rough interfaces, $I(q) \propto q^{-n}$ where $n < 4$.  

55
2.4.2.3 Form factor

The form factor, $P(q)$, gives information about the size and shape of particles or macromolecules in solution, and describes the single particle scattering. In this section, all form factors will be presented in the normalized form. For $n$ scatterers in volume $V_p$, the form factor represents the spatial density-density correlation function, or pair correlation function $P(r)$, summed or integrated over the volume of the scattering object. The form factor depends on the properties of the individual scatterers, but does not account for their locations, and is therefore a measure of the scattering amplitude. Mathematically, the amplitude of the single particle form factor, $F(q)$, is the Fourier transform of the spatial density distribution, or $P(r)$, given by [11,12]:

$$F(q) = \int_{V} P(r)e^{iq\cdot r}dr$$ (2.21)

where $P(r)$ is the probability of finding a scatterer at distance $r$ (from a reference point) within the volume. The integral is performed over the whole particle volume, $V_p$, and normalized to that volume. The single particle form factor is then defined as the square of the amplitude:

$$P(q) = \langle |F(q)|^2 \rangle$$ (2.22)

In a system with a collection of particles, the scattering intensity is given by Equation 2.9, which is simplified to Equation 2.11 if the average particle form factor is used. While the WLM solutions are polydisperse, using the form factor of the average particle shape and size to calculate the contributions to the overall scattering cross-section is a reasonable assumption [14].

While the micelles in this work are both polydisperse and flexible, the WLMs behave like rods at length scales smaller than the persistence length, $l_p$. On this length scale, the WLMs are rigid, and SANS fitting to cylindrical models can help determine the important length scales. The most basic form factor that can be applied to WLM solutions is that of a
thin rod. Figure 2.25 defines the relevant angles for rod-like or cylindrical systems that are anisotropic. In Figure 2.25, the angle $\theta$ represents the angle between the major axis of the rod and $\mathbf{q}$. In the thin rod case, the rod of length $L$ is significantly longer than its radius, $R$, such that $L \gg R$. Here, as $R \to 0$, the scattering amplitude is defined as [11, 13]:

$$F_L(q, \theta) = 2 \frac{\sin\left(\frac{qL}{2} \cos \theta\right)}{qL \cos \theta} \tag{2.23}$$

Here, $F_L(q, \theta)$ is the scattering amplitude along the rod, also known as the longitudinal component.

Figure 2.7: Orientation of a rigid rod, with angle $\theta$ defined as the angle between $\mathbf{q}$ and the axis of the cylinder. Reprinted from reference [11].

For oriented thin rods, Equation 2.22 applies, such that the form factor $P(q)$ is simply the square of Equation 2.23. However, in the case of randomly oriented rods, which applies to the WLM solutions at rest, the normalized form factor $P(q)$ must be orientationally averaged:

$$P_{rod}(q) = -\frac{1}{2} \int_{-1}^{1} |F_L(q, \theta)|^2 \sin \theta d\theta = -\frac{1}{2} \int_{-1}^{1} \left[\frac{\sin\left(\frac{qL}{2} \cos \theta\right)}{qL \cos \theta}\right]^2 \sin \theta d\theta \tag{2.24}$$
Integrating gives the form factor for randomly oriented thin rods in solution [11, 12]:

\[
P_{\text{rod}}(q) = \frac{2}{qL} \int_0^{\frac{qL}{2}} \frac{\sin(x)}{x} dx - \frac{4\sin^2(qL)}{(qL)^2}
\] (2.25)

The form factor approximation for WLMs becomes more accurate as contributions to the form factor from both the length and radius are considered. Unlike in Equation 2.22, the form factor amplitude for the cylinder takes into account the scattering amplitudes from both the cylinder length, \(F_L(q, \theta)\), and radius, \(F_R(q, \theta)\), such that:

\[
F(q, \theta) = F_L(q, \theta)F_R(q, \theta)
\] (2.26)

Here, \(F_L(q, \theta)\) is the scattering amplitude along the rod, given by Equation 2.23 above, and \(F_R(q, \theta)\) is the scattering amplitude perpendicular to the rod. Again using the angle between the cylinder axis and \(q\), the scattering amplitude for the perpendicular component is defined by [11]:

\[
F_R(q, \theta) = 2J_1(qR\sin\theta)\frac{qR\sin\theta}{qR\sin\theta}
\] (2.27)

where \(J_1\) is the cylindrical Bessel function of the first kind. Combining the length and radius contributions as given by Equation 2.26 gives:

\[
F_{\text{cylinder}}(q, \theta) = \left[2 \sin\left(\frac{qL}{2}\cos\theta\right)\right] \left[2J_1(qR\sin\theta)\frac{qR\sin\theta}{qR\sin\theta}\right]
\] (2.28)

for an oriented cylinder. For cylinders with random orientation in solution, the form factor is orientationally averaged over all configurations such that:

\[
P_{\text{cylinder}}(q) = -\frac{1}{2} \int_{-1}^{1} |F_{\text{cylinder}}(q, \theta)|^2 \sin\theta d\theta
\] (2.29)

Interestingly, the absolute scattering intensity for oriented cylinders may actually be
lower than randomly oriented cylinders, as shown by the angular-dependence of the scattering amplitude given by Equation 2.28. An example of this can be seen in Chapter 3, Section 3.4. This decrease in the overall intensity is perhaps counter-intuitive for two reasons. First, when the WLM cylinders are oriented, the micelles are specifically aligning and organizing along the flow direction, which leads to a higher intensity in the sector average (averaging methods will be discussed in Section 2.4.3). However, the overall intensity in the measurement plane is lower due to the scattering amplitude given in 2.28. Second, the scattering invariant must be constant as given by Equation 2.15. However, because only one plane is actually measured using SANS, it is not possible to calculate $I(q)$ over all configurations. Therefore, the lower intensities seen in oriented WLM solutions are not in violation of the scattering invariant and are actually predicted based on Equation 2.28.

The flexible cylinder model is an extension of the cylindrical form factor, which takes into account excluded volume effects [17]. The flexible cylinder model incorporates the idea that a long, wormlike chain can be broken into smaller segments that are locally stiff ($l_p$). The flexible cylinder model does not include inter-micellar interactions, and gives similar results to the cylinder model when used in WLM solutions in the high-$q$ limit. Additional improvements to the flexible cylinder model, including the addition of interactions, were made by Chen et al. [18] specifically for WLM solutions.

2.4.2.4 Structure factor

The structure factor, $S(q)$, gives information about the interactions of an ensemble of scattering object within a medium. In the dilute limit, $S(q) \rightarrow 1$, such that only the form factor is measured. The structure factor is the direct Fourier transform of the space correlation function, and it depends on the relative positions of different pairs of scatterers. Specifically, the coherent scattering portion of $S(q)$ is the Fourier transform in space of the pair distribution function between scattering objects, $g(r_{12})$, where $r_{12} = r_1 - r_2$ is the distance between
the centers of two scattering objects. The structure factor is given by [11,12]:

\[ S(q) = 1 + \int_V e^{i\mathbf{q} \cdot \mathbf{r}_{12}} g(\mathbf{r}_{12}) d\mathbf{r}_{12} \]  

(2.30)

as the Dirac peak at the origin of the structure factor is not experimentally accessible, the contribution is normally subtracted giving:

\[ S(q) = 1 + \int_V e^{i\mathbf{q} \cdot \mathbf{r}_{12}} [g(\mathbf{r}_{12}) - 1] d\mathbf{r}_{12} \]  

(2.31)

The structure factor at vanishing \( q \), \( S(q \to 0) \), is related to the normalized osmotic compressibility of the fluid. In the case of repulsive interactions, \( S(0) \) is less than one, whereas attractive interactions lead to a value of \( S(0) \) greater than one. As such, the structure factor and pair distribution function are related to the interaction potential between objects. The pair distribution function, \( g(\mathbf{r}_{12}) \), is typically calculated using liquid state theory and the Ornstein-Zernike equation [19]:

\[ h(r_{12}) = g(r_{12}) - 1 = c(r_{12}) + n_p \int c(r_{13})[g(r_{23}) - 1] dr_{23} \]  

(2.32)

where \( c(r) \) is the direct correlation function, which is related to the potential of mean force between particles. Determining \( c(r) \) requires a closure approximation, such as the commonly used Percus-Yevick closure [11].

### 2.4.3 SANS data reduction

All neutron scattering experiments were performed at either the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg,
MD or the Institut Laue-Langevin (ILL) in Grenoble, France. The measured scattering intensity is given by [11]:

\[ I_s(q) = I_0(\lambda)T(\lambda)d\frac{d\Sigma(q)}{d\Omega}d\Omega \]

where \( I_0(\lambda) = \phi(\lambda)A_2\varepsilon(\lambda)t \) \hspace{1cm} (2.33)

where \( I_0(\lambda) \) is the incident neutron beam current (empty beam transmission), \( \phi(\lambda) \) is the neutron flux on the sample, \( d \) is the sample thickness, \( A_2 \) is the illuminated sample area, \( T(\lambda) \) is the transmission of the sample, \( \varepsilon(\lambda) \) is the detector efficiency, and \( t \) is the counting time. The scattered intensity is then reduced to the absolute form, where the macroscopic scattering cross-section is given by:

\[ d\Sigma(q) = \frac{I_s(q)}{I_0(\lambda)T(\lambda)d\Omega}d\Delta\Omega \] \hspace{1cm} (2.34)

NIST raw data was reduced to an absolute scale using Equation 2.34 in IgorPro using NIST standards, and by also accounting for background (blocked beam scattering), empty cell scattering, and detector efficiency [20]. ILL raw data was reduced in the Grasp Matlab software accounting for the same factors.

There are several ways to reduce and analyze SANS data. Figure 2.8 illustrates each method on the 0.01% wt NaTos solution, where anisotropic scattering data is shown for effect. In Figure 2.8, the 2-D scattering data is shown on the left, and the resulting reduced intensity curve is shown on the right. Figure 2.8a shows the standard circular average method. Here, all of the 2-D SANS data is used to obtain the 1-D curve. When the scattering in the sample is isotropic, there is no difference between the resulting intensity \( I(q) \) between the circular average and sector average methods. Figure 2.8b shows the sector average method, where a small portion of the scattering is chosen over which to reduce the data. In this case, the sector average is in the vertical direction, which is the direction of the increased intensity on the 2-D pattern. The resulting 1-D intensity curve from the sector average in this direction is therefore higher than in the circular average. Note that as the corners of the detector
are not used in this average, the accessible $q$ range is smaller, as seen from the 1-D curve. Figure 2.8c also shows a sector average, but this time in the horizontal direction, where $I(q)$ decreases. Finally, Figure 2.8d shows the annular average over a fixed $q$-range, referred to as $q^*$. This annular average is used to calculate the order parameter, and will be discussed further in Section 2.6.1.

2.4.4 Static SANS Experimental details

The primary static SANS measurements were taken at the NCNR on the NG-7 30 m SANS instrument. Static SANS measurements were taken using the 10CB sample environment at the NCNR, with temperature control from a Julaba circulating bath. Samples were measured in 2 mm quartz cells, with temperature set to 35 $^\circ$C ± 0.1 $^\circ$C. Samples equilibrated at 35 $^\circ$C were loaded into the quartz cells at least two hours prior to the SANS measurements. The loaded quartz sample cells were held at 35 $^\circ$C in an oven before being placed in the 10CB fixture. The samples were allowed to equilibrate for 20 minutes in the 10CB fixture before measuring the reported data. Test SANS spectra taken during the equilibration period showed no significant differences to the equilibrium spectra.

For the primary samples used in this work (0.01% wt NaTos through 0.25% wt NaTos solutions), the magnitude of the measured scattering vector, $q$, ranged from 0.001 Å$^{-1}$ to 0.5 Å$^{-1}$ using detector distances of 15.3 m (lens), 4 m and 1 m. Neutron guides, which are used to improve the flux to the sample, were used at the 4 m (5 guides) and 1 m (8 guides) configuration. Smearing effects from neutron guides will be discussed further in Chapter 3, Section 3.4.4. The neutron wavelength, $\lambda$, was 6 Å at 4 m and 1 m, and 8.4 Å at 15.3 m. The wavelength spread (FWHM), $\Delta\lambda/\lambda$, was 11.5% for both wavelengths. These results are reported in Chapter 4, Figure 4.2. Additional measurements on higher branching levels (0.185% wt NaTos through 0.50% wt NaTos solutions) were also performed on NG-7, where the results are reported in Chapter 4, Figure 4.3. Here, $q$ ranged from 0.001 Å$^{-1}$ to 0.55 Å$^{-1}$ using detector distances of 15.3 m (lens, no guides), 13 m (1 guide), 4 m (5 guides) and 1 m (8 guides). At 13 m, 4 m, and 1 m, $\lambda = 6$ Å and $\lambda = 8.09$ Å at 15.3 m, with $\Delta\lambda/\lambda = 11.5%$ for both wavelengths. Static measurements were also taken in all
Figure 2.8: Methods of reducing and analyzing SANS data. (a) The standard circular average method averages the 1-D curve from all 2-D data. In the case of isotropic scattering, the circular average gives the same result as the sector averages in (b) and (c). (b) Sector average in the vertical direction. When the anisotropy is in the direction of the sector average, $I(q)$ increases. (c) Horizontal sector average, where $I(q)$ decreases. (d) Annular average over a fixed $q$-range, used to calculate the order parameter. Data shown from the 0.01% wt NaTos solution.
flow devices (rheometer, 1-2 shear cell) before flow-SANS measurements, with excellent reproducibility between configurations (see Section 2.6.2 below, Appendix E).

2.5 Small angle neutron scattering (SANS) under flow

2.5.1 Motivation

Small angle neutron scattering (SANS) under flow, commonly known as rheo-SANS or flow-SANS, combines microstructural SANS measurements with an applied deformation field in order to measure flow-induced structures in complex fluids. Such methods enable a robust characterization of the microstructure and flow properties of surfactant wormlike micelle (WLM) solutions. The set-up of a flow- or rheo-SANS experiment differs from the traditional static SANS measurement, which is illustrated in Figure 2.5. The development of new sample environments enables the flow-induced microstructure to be measured in the three planes of shear: the flow-vorticity (1-3), flow-gradient (1-2) and gradient-vorticity (2-3) planes. Advances in neutron collection and data analysis have improved the temporal resolution of time-dependent responses, significantly reducing the time required to perform such measurements. Theoretical advances in constitutive modeling and the stress-SANS rule now permit the development and testing of structure-property relationships. Such methodologies have allowed flow instabilities, such as shear and vorticity banding, and shear-induced structural transitions to be identified in WLM solutions. Additional sample environments have enabled the study of WLMs under extensional and Poiseuille flows, in addition to flows in microfluidic devices.

2.5.2 Sample environments for SANS under flow

Rheo-SANS methods have been used to determine the flow-induced structure of a variety of soft materials since the 1980s [21]. The term ‘rheo-SANS’ often implies SANS measurements which are performed in either a concentric cylinder Couette or parallel plate geometry during an imposed shear deformation, which may or may not involve simultaneous rheological measurements. Rheo-SANS methods enable the material microstructure to be probed in the three shear planes, which are illustrated in Figure 2.9: the 1-3 (flow-vorticity
or velocity-vorticity) plane, the 2-3 (gradient-vorticity or velocity gradient-vorticity) plane, and the 1-2 (flow-gradient or velocity-velocity gradient) plane. The projections of the material microstructure onto each shear plane may be measured using a variety of SANS sample environments. In addition to illustrating each of the three shear planes, Figure 2.9 shows a sample scattering pattern from each plane that results from shear-induced alignment, where WLMs typically align in the direction of the flow. These flow-induced microstructural rearrangements can be quantified using a segmental order parameter or alignment factor, which will be discussed in Section 2.6.1 below.

The current rheo-SANS sample environments are depicted in Figure 2.10, and additional details of the geometries and sample cells can be found below. When the rheometer configurations shown in Figure 2.10a are used for the 1-3 and 2-3 plane scattering experiments, simultaneous rheology is recorded throughout the duration of the SANS measurement [22]. Measurements in the flow-gradient (1-2) plane (Figure 2.10b) are much more difficult, and as such, are restricted to SANS measurements during flow without simultaneous rheology [23,24]. Table 2.1 below summarizes the available geometries for rheo- or flow-SANS experiments, and the relevant configuration parameters, where the rheo-SANS geometries are specific to the NCNR. Here, the aspect ratio, \( \Gamma \) is defined as \( \Gamma = \frac{L}{H} \), and the gap to radius ratio, \( \varepsilon \) is defined as \( \varepsilon = \frac{H}{R_1} \), where \( H \) is the gap size, \( L \) is the height of the bob, and \( R_1 \) is the inner radius of the concentric cylinder Couette geometry. Table 2.1 includes the rheometer configurations for the Anton-Paar instrument at the NCNR; it does not include the geometry for the TA Instruments ARES G2 dielectric rheo-SANS configuration, which is currently being developed.

### 2.5.3 Rheo-SANS in the 1-3 (flow-vorticity) plane

#### 2.5.3.1 Background on rheo-SANS

Most SANS measurements of WLMs under flow are performed in the 1-3 (flow-vorticity) shear plane (Figure 2.10a). Currently, these 1-3 plane experiments are performed using a rheometer outfitted with a quartz or titanium Couette cell centered in the neutron beam line [22]; however, initial experiments were performed using several custom-made
Figure 2.9: An illustration of the three shear planes accessible by SANS. In order to access the 2-3 flow-vorticity (a) and 1-3 flow-vorticity (b) planes, a rheometer is aligned in the neutron beam. To access the 1-2 flow-gradient plane (c), a sample environment has been developed through a collaboration between the Institut Laue-Langevin (ILL, France), the National Institute of Standards and Technology Center for Neutron Research (NCNR, USA), and the University of Delaware (UD, USA). The micelles align along the direction of shear flow in each plane, and sample WLM scattering patterns are provided for each plane.
Couette shearing apparati [21, 25–28]. As WLMs tend to align in the flow direction upon shearing, the resulting increase in SANS anisotropy is symmetric along the vorticity direction (Figure 2.9). The resulting 2-D SANS pattern under shear is a convolution of the shear-induced material microstructure across the Couette cell gap and an angle of alignment cannot be determined due to the symmetry imposed by the method. WLM solutions often exhibit spatially-dependent flow properties, such as shear banding [29], which cannot be resolved with these gap-averaged 1-3 plane measurements. However, spatially-resolved measurements along the vorticity direction may be performed using 1-3 plane rheo-SANS, which are useful in the detection of flow instabilities such as vorticity banding [30,31]. Most experiments in the 1-3 plane use an Anton-Paar MCR stress-controlled rheometer with a concentric-cylinder Couette geometry (Figure 2.10) [22]. Additionally, a TA Instruments ARES-G2 strain-controlled rheometer with a concentric-cylinder Couette geometry is now available at the NCNR for 1-3 plane measurements [32]. A summary of the rheo-SANS available geometries (Anton-Paar) can be seen in Table 2.1.
Table 2.1: Configuration parameters for rheo- and flow-SANS, where $\epsilon$ is the gap-to-radius ratio, $\epsilon = H/R_1$, and $\Gamma$ is the aspect ratio, where $\Gamma = L/H$.

<table>
<thead>
<tr>
<th>Type</th>
<th>Material</th>
<th>Dimensions</th>
<th>$\epsilon$</th>
<th>$\Gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2 shear cell</td>
<td>aluminum</td>
<td>$R_1 = 25.5$, $R_2 = 26.5$ mm</td>
<td>0.039</td>
<td>5</td>
</tr>
<tr>
<td>1-2 shear cell</td>
<td>stainless steel</td>
<td>$R_1 = 25.5$, $R_2 = 26.5$ mm</td>
<td>0.039</td>
<td>5</td>
</tr>
<tr>
<td>1-2 shear cell</td>
<td>magnetic coupling - SS, Al, or Ti</td>
<td>$R_1 = 25.5$, $R_2 = 26.5$ mm</td>
<td>0.039</td>
<td>5</td>
</tr>
<tr>
<td>Rheometer</td>
<td>quartz</td>
<td>$R_1 = 24$, $R_2 = 25$ mm</td>
<td>0.042</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 24$, $R_2 = 25$ mm</td>
<td>0.042</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 13.5$, $R_2 = 15$ mm</td>
<td>0.111</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 14$, $R_2 = 15$ mm</td>
<td>0.071</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 14.5$, $R_2 = 15$ mm</td>
<td>0.034</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 13.5$, $R_2 = 14.5$ mm</td>
<td>0.074</td>
<td>36</td>
</tr>
<tr>
<td>Rheometer</td>
<td>titanium</td>
<td>$R_1 = 14$, $R_2 = 14.5$ mm</td>
<td>0.036</td>
<td>36</td>
</tr>
</tbody>
</table>

2.5.3.2 Experimental details

The rheo-SANS experiments in the 1-3 (flow-vorticity) plane were conducted at the NCNR on either the NGB 30m SANS or NGB 10m SANS instruments [22]. An Anton-Paar MCR-502 stress-controlled rheometer (used in strain-controlled mode) with a concentric-cylinder Couette geometry was used for all experiments. The rheometrical geometry was composed of a titanium moving inner cylinder and stationary outer cup as previously stated. All studies were performed with a gap size of 1 mm unless otherwise noted. The three main geometries used in this work are a) $R_1 = 13.5$ mm, $R_2 = 14.5$ mm, $\epsilon = 0.074$, $\Gamma = 36$; b) $R_1 = 14$ mm, $R_2 = 15$ mm, $\epsilon = 0.071$, $\Gamma = 36$; and c) $R_1 = 24.0$ mm, $R_2 = 25.0$ mm, $\epsilon = 0.042$, $\Gamma = 36$. A summary of all SANS rheometer configurations can be seen in Table 2.1. Samples were conditioned in the rheometer for 10 minutes at 35 °C to achieve thermal equilibrium; repeated frequency sweeps were performed after the equilibration time to ensure reproducibility. Rheology was verified to be independent of instrument and geometry. A solvent trap filled with D$_2$O was utilized to provide a saturated atmosphere and to limit sample evaporation. Two vertically-oriented beam apertures were placed prior to the rheometer to minimize spatial smearing that results from the rheometer curvature. The apertures limit
the scattering volume to a small region where the flow direction, beam direction, and slit orientation are mutually orthogonal, with the beam and flow directions spanning the horizontal plane. A 5 mm x 20 mm source aperture was positioned at the end of the neutron guides. A sample aperture (2 mm x 20 mm slit) was centered approximately 3 inches prior to the quartz windows of the rheometer. Select experiments were repeated with a 3 mm x 20 mm source aperture and no significant resolution effects were observed. See Chapter 3, Section 3.4 for a discussion of the slit dimension effects. In the Chapter 3 studies, the third configuration ($R_1 = 24.0$ mm, $R_2 = 25.0$ mm, $\varepsilon = 0.042$, $\Gamma = 36$) was used.

For the 10m SANS experiments, the neutron wavelength, $\lambda$, was 5 Å with a wavelength spread $\Delta \lambda / \lambda = 12.0\%$. A detector distance of 5.2 m was used to cover a q-vector ranging from 0.008 Å$^{-1}$ to 0.10 Å$^{-1}$. Results were corroborated with select rheo-SANS experiments using a Couette geometry with a 1.0 mm gap ($R_1 = 14.0$ mm; $R_2 = 15.0$ mm; $\Gamma = 36$; $\varepsilon = 0.071$). The detector distance of 4.3 m and the neutron wavelength, $\lambda$, of 5 Å ($\Delta \lambda / \lambda = 12.0\%$) covered a q-vector ranging from 0.01 Å$^{-1}$ to 0.12 Å$^{-1}$. For the 30m SANS experiments, $\lambda = 6\AA$ with a wavelength spread $\Delta \lambda / \lambda = 13.1\%$. Two detector distances (8 m, 1.65 m) were used to cover a q-vector ranging from 0.006 Å$^{-1}$ to 0.2 Å$^{-1}$.

### 2.5.4 Flow-SANS in the 1-2 (flow-gradient) plane

#### 2.5.4.1 Background

To access the 1-2 (flow-gradient) plane with SANS methods, the Couette cell must be designed to lie horizontal with its rotation axis parallel to the beam. To accommodate such measurements, a sealed, short aspect ratio 1-2 plane shear cell was recently designed [23, 24], which can be seen in Figure 2.10b. This orientation enables obtaining spatially-resolved information across the Couette gap, which has proven useful in the detection of shear banding flow instabilities [1,2,33–36]. The 1-2 shear cell is a short Couette (5mm path length) as described by Gurnon et al. [24]. The cell consists of a rotating inner cylinder ($R_1 = 25.5$ mm) and an outer stationary cylinder ($R_2 = 26.5$ mm) such that the gap width is 1.0 mm, the resulting aspect ratio, $\Gamma = L/H = 5$ and the gap to radius ratio, $\varepsilon = H/R = 0.039$. Temperature control is maintained by a flow-through port within the cell that is connected to
a water bath. A stepper motor is used to translate a cadmium beam aperture across the gap, providing spatial resolution. The 1-2 plane shear cell is currently available at the NCNR and the ILL.

### 2.5.4.2 Experimental details

Flow-SANS experiments in the 1-2 (flow-gradient) plane of shear were conducted at both the NCNR and ILL. All experiments were performed in a short gap Couette cell (5mm path length) as previously described [23, 24]. The shear cell consists of a rotating inner cylinder \( R_1 = 25.5 \text{ mm} \) and an outer stationary cylinder \( R_2 = 26.5 \text{ mm} \) such that the gap width is \( 1.0 \text{ mm}, \Gamma = 5 \) and \( \varepsilon = 0.039 \). Temperature control is maintained by using a flow-through port within the cell that is connected to a heated water bath (\( 35 \degree C \pm 0.1 \degree C \) for all experiments). Two cadmium beam slits are placed prior to the front wall of the shear cell. The first is a 5 mm slit oriented horizontally which constrains the measured region to one where the flow is essentially vertical. The second slit is oriented vertically, and has a width based on desired spatial resolution. A stepper motor is used to translate the slit across the gap, providing spatial resolution. The motor is calibrated by taking empty cell transmission measurements across the cell gap. The edges of the gap are identified by the large changes in the number of transmitted neutrons from the aluminum to the fluid (air) in the empty cell [23,24], which can be seen in Figure 2.11. Empty cell and sample transmission measurements were taken at each spatial position across the gap. Samples were allowed to equilibrate for a minimum of 30 minutes after loading, and multiple static measurements were taken during the equilibration period to identify any structural changes. Any bubbles were removed from the cell before the start of each experiment.

**Low and high branching - steady shear SANS:** For the low branching (0.01% wt NaTos) and high branching (0.10% wt NaTos) solutions, the primary flow-SANS experiments were performed at NIST using the NG-7 30m SANS instrument. All NIST experiments were performed with a 0.1 x 3 mm straight secondary beam slit. Measurements were taken at several positions across the gap, ranging from \( r/H = 0.1 \) to \( r/H = 0.9 \). The main experiments were performed using an aluminum shear cell with magnetic coupling, with one
aluminum window and one quartz window to view the sample. Steady-shear scattering experiments were performed with a detector distance of 8 m and 6 Å neutrons for a minimum of one hour. The measured scattering vector, q, ranged from 0.005 Å\(^{-1}\) to 0.05 Å\(^{-1}\) with ∆λ/λ = 11.5%. Complimentary steady-shear experiments were conducted in a titanium shear cell for a minimum duration of one hour at a detector distance of 8 m with 6 Å neutrons and a wavelength spread of ∆λ/λ = 11.5%. The q-range in those experiment covered the range 0.007 Å\(^{-1}\) to 0.05 Å\(^{-1}\). Select experiments on the 0.01% wt NaTos solution were performed on the D-22 SANS instrument at ILL. Experiments were performed at a detector distance of 11.2 m with 6 Å neutrons and a wavelength spread of ∆λ/λ = 10%. A 0.3 mm wide curved slit was used for these experiments. Experiments were performed at two positions located near the inner (r/H = 0.3) and outer wall (r/H = 0.7) of the shear cell. Steady-shear experiments were conducted for 10 minutes covering a q-range of 0.0044 Å\(^{-1}\) to 0.065 Å\(^{-1}\). Repeated experiments at a detector distance of 17.6 m yielded identical results within error, indicating that the decrease in resolution from 17.6 m to 11.2 m was insignificant.

**Mild branching - steady shear & LAOS SANS:** For the mildly branched solution (0.05% wt NaTos), the flow-SANS experiments were performed at ILL on the D-22 SANS instrument at a detector distance of 11.0 m with an 8.0 m rectangular collimation (40 x 55 mm), 6 Å neutrons, and a wavelength spread of ∆λ/λ = 10%. LAOS experiments were
performed at two gap positions \((r/H = 0.25\) and 0.75\) with a 0.3 mm wide curved slit for five conditions (see Chapter 7 Figures 7.13, 7.14, and 7.15), and five gap positions \((r/H = 0.15, 0.35, 0.5, 0.65, 0.85)\) with a 0.1 mm wide curved slit (conditions 1 and 2, see Chapter 7 Figures 7.6 and 7.8). Steady shear experiments were conducted using the 0.1 mm curved slit for a minimum of 10 minutes. All experiments covered a \(q\)-range of 0.0048 \(\text{Å}^{-1}\) to 0.068 \(\text{Å}^{-1}\), consistent with previous work on these solutions [1]. Sample transmission measurements were taken at each gap position; gap position did not significantly affect sample transmission. The sample was allowed to equilibrate after loading, and several static measurements were repeated throughout the course of the experiment to ensure that no permanent changes to the sample resulted from shear. LAOS experiments were repeated at each gap position to ensure that the steady alternance structure was measured, and to ensure that the sample had not been subjected to bubbling, evaporation, or irreversible changes from shear.

The data in conditions one (0.1 mm slit) was recorded in the ILL ‘list mode’ where each neutron is time stamped (see Section 3.3.2 for more details). This provides the greater temporal resolution seen in these conditions (more data points and alignment factors per \(t/T\)) versus the conditions taken in ‘kinetic mode.’ Significantly longer count times were also used in the list mode experiments, leading to the lower uncertainty reported in the alignment factors seen in Chapter 7. The data in the other five conditions was taken with a 0.3 mm slit and was recorded using the ILL ‘kinetic mode.’ In this mode, the temporal bin width is chosen in advance, leading to the fewer alignment factor points per cycle in these tests. Due to time constraints, the experiments were performed for significantly less time, which leads to the higher uncertainty in the alignment factor calculations. The neutron count at each position for the latter five experiments is approximately one-third of the neutron count at each position for the primary two conditions. To ensure that the temporal resolution did not affect the results, the data from conditions one and two was re-processed with the same temporal bin width as the latter conditions; no significant differences in alignment were observed. Finally, one short trial of condition 1 \((r/H = 0.15)\) was recorded in kinetic mode; no significant differences were observed between this trial and the trials in list mode. The reproducibility of the LAOS stress response is discussed below in Section 2.6.4 below.
Low branching - LAOS SANS: For the low branching solution (0.01% wt NaTos), the LAOS flow-SANS experiments were performed at ILL on the D-22 SANS instrument at a detector distance of 11.0 m with an 8.0 m rectangular collimation (40 x 55 mm), 6 Å neutrons, and a wavelength spread of $\Delta \lambda / \lambda = 10\%$. LAOS experiments were performed at multiple gap positions with a 0.1 mm wide curved slit for several conditions. All experiments covered a q-range of 0.007 Å$^{-1}$ to 0.066 Å$^{-1}$, consistent with previous work on these solutions [1]. Sample transmission measurements were taken at each gap position; gap position did not significantly affect sample transmission. The sample was allowed to equilibrate after loading, and several static measurements were repeated throughout the course of the experiment to ensure that no permanent changes to the sample resulted from shear.

2.5.5 Summary of all SANS experiments

Table 2.2 below summarizes all of the SANS experiments performed, both under flow and static, for reference. Geometry and experiment type details are provided.

Table 2.2: Summary of all performed SANS experiments

<table>
<thead>
<tr>
<th>Date</th>
<th>Instrument</th>
<th>Geometry</th>
<th>Experiment type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2013</td>
<td>NIST NG7</td>
<td>rheometer</td>
<td>steady shear, LAOS</td>
</tr>
<tr>
<td>6/2013</td>
<td>ILL D22</td>
<td>1-2 shear cell</td>
<td>steady shear, LAOS</td>
</tr>
<tr>
<td>11/2013</td>
<td>NIST NG7</td>
<td>rheometer</td>
<td>steady shear, LAOS</td>
</tr>
<tr>
<td>1/2014</td>
<td>NIST NG7</td>
<td>magnetic 1-2 shear cell</td>
<td>steady shear</td>
</tr>
<tr>
<td>3/2014</td>
<td>NIST NG3</td>
<td>rheometer</td>
<td>steady shear</td>
</tr>
<tr>
<td>6/2014</td>
<td>NIST NGB30</td>
<td>rheometer</td>
<td>steady shear, LAOS, startup</td>
</tr>
<tr>
<td>9/2014</td>
<td>NIST NGB30</td>
<td>1-2 shear cell</td>
<td>LAOS</td>
</tr>
<tr>
<td>9/2014</td>
<td>NIST NGB10</td>
<td>rheometer</td>
<td>steady shear, startup</td>
</tr>
<tr>
<td>1/2015</td>
<td>NIST NGB10</td>
<td>rheometer</td>
<td>startup, LAOS</td>
</tr>
<tr>
<td>6/2015</td>
<td>NIST NG7</td>
<td>rheometer</td>
<td>steady shear, shear vorticity banding</td>
</tr>
<tr>
<td>6/2015</td>
<td>ILL D22</td>
<td>1-2 shear cell</td>
<td>steady shear, LAOS</td>
</tr>
<tr>
<td>8/2015</td>
<td>NIST NG7</td>
<td>rheometer</td>
<td>startup, NaCl WLMs</td>
</tr>
<tr>
<td>9/2015</td>
<td>NIST NGB30</td>
<td>1-2 shear cell</td>
<td>startup</td>
</tr>
<tr>
<td>1/2016</td>
<td>NIST NGB30</td>
<td>1-2 shear cell</td>
<td>startup</td>
</tr>
<tr>
<td>5/2016</td>
<td>NIST NGB30</td>
<td>1-2 shear cell</td>
<td>startup</td>
</tr>
<tr>
<td>6/2016</td>
<td>ILL D22</td>
<td>1-2 shear cell</td>
<td>LAOS</td>
</tr>
<tr>
<td>10/2016</td>
<td>NIST NGB30</td>
<td>rheometer</td>
<td>startup</td>
</tr>
</tbody>
</table>
2.6 Analysis of anisotropic scattering data

2.6.1 Shear-induced microstructural rearrangements

Wormlike micelles tend to show strong alignment in the flow direction during shear flow [37], as well as a variety of other flows, including extension [38], pipe flow [39–41], and contraction slit flows [42, 43]. Several metrics are commonly used to quantify these microstructural rearrangements. Early works compared differences in the absolute scattering intensity, $I(q)$, under flow in the 1-3 flow-vorticity plane with contour plots of the 2-D intensity [44–47], or with sector-averages of $I(q)$ in the perpendicular (vorticity) and parallel (flow) directions, $I(q_{\perp})$ and $I(q_{\parallel})$, respectively [48–52]. Later, order parameters used in the analysis of liquid crystal microstructures were incorporated into the analysis of shear-induced WLM microstructures. These parameters quantify the measured microstructural rearrangements based on scattering anisotropy. The commonly used metrics include the $P_2$ orientation parameter [53–55] and the scalar ‘alignment factor,’ $A_f$, [23, 30, 56, 57] with the angle of alignment of the primary eigenvector, $\phi_0$. Note that in the case of 1-3 and 2-3 plane rheo-SANS, $\phi_0$ cannot be measured due to the symmetry imposed by the method, whereas $\phi_0$ can be determined in 1-2 plane measurements. In general, as the microstructure for a WLM can be described by a second order tensor formed by a dyadic product of an end-to-end vector, $Q$, as $<Q Q>$, measurements in all three planes of flow are necessary to fully characterize the microstructure under flow [34]. As SANS probes microstructure on length scales from the nanometer to the micron, the predominant source of flow-induced anisotropy in the SANS spectra is segmental alignment. As segmental alignment is also the primary source of elastic stress in the flowing WLM solution, and this elasticity can also be represented by $<Q Q>$, a formal ‘stress-SANS’ rule [34] can be derived for WLMs in direct analogy to the stress-optical rule [58].

The anisotropy parameters are calculated from the scattered intensity in the $q^{-1}$ (rod-like segment) scattering regime. The rod-like scattering regime is usually chosen to focus on segmental alignment of WLMs. However, it is not uncommon for $P_2$ or $A_f$ to be calculated as a function of $q$-position [56]. A value of zero represents a system that is, on average, isotropic and non-aligned, whereas a value of one is the theoretical perfectly aligned state.
corresponding to a nematic order of thin, rigid rods. The scalar $P_2$ orientation parameter is calculated by the integral:

$$P_2 = \int_0^{\pi} f(\theta) P_2(\theta) \sin(\theta) d\theta$$  \hspace{1cm} (2.35)

where $f(\theta)$ is the projection of the normalized orientation distribution function (ODF) onto the shear plane (intensity distribution), and $\theta$ is the azimuthal angle with respect to the flow direction.

While the calculations are different, $P_2$ is roughly equivalent to the alignment factor, defined as [56]:

$$A_f(q^*) = \frac{\int_0^{2\pi} I(q^*, \phi) \cos(2(\phi - \phi_0)) d\phi}{\int_0^{2\pi} I(q^*, \phi) d\phi}$$  \hspace{1cm} (2.36)

where $I(q^*)$ is the intensity over a small fixed $q$-range, $q^*$, and $\phi$ is the azimuthal angle and $\phi_0$ is the azimuthal angle of maximum intensity which corresponds to the average orientation angle (see Figure 2.12). The $\cos(2(\phi - \phi_0))$ term is a result of the symmetry that arises in the anisotropic scattering from rod or wormlike objects.

In this work, we report the degree of microstructural rearrangements using the alignment factor and orientation angle ($\phi_0$) specified by Equation 2.36. Note that in the case of 1-3 plane rheo-SANS measurements, the true orientation angle cannot be determined due to the symmetry imposed by the method, and accordingly the value is fixed at $\phi_0 = 90^\circ$. In Figure 2.12, the region $q^*$ and angle $\phi$, and the resulting intensity distribution, can be seen for a sample 2-D scattering pattern from 1-2 plane SANS. For the purpose of the alignment factor calculation, we define the angle $\phi = 0^\circ$ as the angle at $90^\circ$ to the flow direction. In Figure 2.12, $\phi = 0^\circ$ is along the gradient direction on the right hand side, and increases in the counter-clockwise direction ($\phi = 90^\circ$ corresponds to the flow direction). Near perfect flow-alignment corresponds to $\phi_0 \approx 0^\circ$, as the direction of the scattering (increased intensity) that
results from micellar alignment is oriented at 90° from the flow direction. A detailed discussion of the error associated with this calculation and the effect of the SANS configuration on this calculation will be discussed in Chapter 3.

Figure 2.12: Defining parameters for alignment factor calculation. (L) 2-D SANS pattern from 1-2 plane measurements, where the region $q^*$ of rod-like scattering is shown between concentric circles. The angle $\phi = 0^\circ$ along the gradient direction, and $\phi = 90^\circ$ along the flow direction. Near perfect flow-alignment corresponds to $\phi_0 \approx 0^\circ$, as the direction of increased intensity due to micellar alignment is oriented at 90° from the flow direction.

The aforementioned stress-SANS rule was developed to determine the polymeric stress from the alignment factor [34], based on the Giesekus-diffusion (G-D) model. Using the alignment factor and the azimuthal angle of maximum intensity, the stress-SANS rule is given by:

$$\tau_{12,p} = G_0(CA_f)^{1/2} \sin(2\phi_0)$$  \hspace{1cm} (2.37)

$$N_{1,p} = 2G_0(CA_f)^{1/2} \cos(2\phi_0)$$  \hspace{1cm} (2.38)

where $\tau_{12,p}$ is the polymeric shear stress, $N_{1,p}$ is the polymeric first normal stress difference,
$G_0$ is the plateau modulus and $C$ is the stress-SANS coefficient, a constant determined on a per-system basis.

Several works have used the stress-SANS rule to successfully predict the polymeric stress when compared to the measured shear stress; however this relationship breaks down in the event of highly non-linear flows [24, 34–36]. While the stress-SANS coefficient, $C$, is a constant, a shear-rate dependent stress-SANS coefficient has shown promise in relating the alignment factor and stress in such non-linear flows [24]. A variety of other empirical relationships between the order parameter and shear rate or viscosity have been developed [59, 60], displaying power law and exponential dependences, respectively.

**2.6.2 SANS reproducibility and determining $q^*$ for alignment factor calculation**

Before determining the q-region, $q^*$, over which to calculate the alignment factor, the absolute scattering of each sample at rest first was compared between configurations. These absolute scattering profiles were shown to be independent of facility, instrument and sample environment from repeated experiments, by performing static SANS measurements prior to each experiment under flow (see Figure 2.13). Further, the absolute scattering profiles were insensitive to multiple sample preparations, as different experiments were often performed with different sample preparations. The static microstructures for all solutions discussed in this work were isotropic between the scattering planes measured, and were independent of sample cell and configuration. The good agreement between the static scattering of each sample in the static quartz cells, rheometer configurations, and the 1-2 shear cell helps verify the absence of significant multiple scattering due to different cell path lengths or other unintended geometrical effects. This agreement is vital when calculating the alignment factor from Equation 2.36, as small differences in the absolute intensity or background in the SANS results can drastically affect the calculated $A_f$ value. The uncertainty associated with this calculation and effects from different configurations are discussed in Chapter 3.

Figure 2.13 below shows the comparison of the static structure measured for both the low branched 0.01% wt NaTos solution and the highly branched 0.10% wt NaTos solution.
between the standard quartz cells, two rheometer configurations with different path lengths, and the 1-2 shear cell. The static quartz cells and first rheometer configuration have path lengths of 2 mm, the second rheometer configuration has a path length of 1 mm, and the 1-2 shear cell has a path length of 5 mm, which result in overall transmissions of $T \approx 0.8$, 0.9, and 0.6 for the 2 mm, 1 mm and 5 mm configurations, respectively. The scattering shown in Figure 2.13 shows excellent agreement in both samples across all configurations, validating that the static material structure is independent of plane and sample cell. The reproducibility across sample configurations and sample preparations for all WLM solutions can be seen in Appendix B.

After verifying reproducibility between configurations, $q^*$ for the alignment factor calculations was selected, which is specific to each sample. The alignment factor is normally chosen in the $q^{-1}$, or rod-like scattering, region of the 1-D scattering. In this region, the alignment factor corresponds to the segmental alignment of the WLMs. As each sample has a different persistence length, $l_p$, where the material is locally stiff, the $q^*$ region varies slightly between samples. However, the results presented in this work are fairly insensitive
to the selection of $q^*$, which can be seen in Figure 2.14 below. Further, the trends presented in this work are qualitatively consistent across samples whether $q^*$ is chosen individually for each sample, or held constant across all samples. In samples containing an interaction peak, this $q^{-1}$ regime is estimated and occurs near the interaction peak, as a clear $q^{-1}$ region is obscured by the influence of the interaction peak. An example of this $q^{-1}$ region can be seen for the 0.05% wt NaTos solution in Figure 2.14 below. The $q^{-1}$ region is shown between the dotted lines in Figure 2.14 (L), whereas the chosen q-range for the $A_f(q)$ calculation, $q^*$, is highlighted in light blue (see Equation 2.36). This $q^*$ range is always equal to or less than the full range of $q^{-1}$, and is chosen as the range within the $q^{-1}$ region where the alignment factor is constant and attains its maximum value. Determination of the $q^*$ range is discussed further in Chapter 3. The $q^*$ region for the remaining WLM solutions can be found in Appendix B.

The $q^*$ region in the 2-D scattering pattern for the 0.05% wt NaTos solution is shown in the top inset of Figure 2.14 for a Weissenberg number of $Wi = 75$ at a gap position of $r/H = 0.15$. The q-range spans $q^* = 0.0199 - 0.0278 \text{ Å}^{-1}$. The bottom (L) inset shows a sample azimuthal intensity distribution, $I(q^*, \phi)$, used in the alignment factor calculation (Equation 2.36) from the SANS data for $Wi = 75$ at $r/H = 0.15$, which is used to calculate the alignment factor. The bottom (R) inset shows the alignment factor calculation over the full $q^{-1}$ region, using bins of small q-width (designated by the x-error bars). The results are mostly within error of each other. In Figure 2.14 (R), the 1-2 plane $A_f$ is calculated for the steady shear condition $Wi = 75$ using three different q-ranges within the $q^{-1}$ regime (R). At four of the five gap positions, the alignment is not dependent on the q-range chosen. At $r/H = 0.15$, the calculated alignment is similar between all q-ranges, indicating that the choice of q-range within the $q^{-1}$ regime does not significantly affect the results.

### 2.6.3 Alignment factor calculations

The alignment factor for all experiments was calculated in either the GRASP software (all ILL experiments), or in Igor with the NIST macros (all NIST experiments) as given by Equation 2.36. Both programs were modified to calculate the alignment factor upon data reduction (see Chapter 3, Section 3.3). The alignment factor was always calculated over the
specific $q^*$ range for each sample, shown in Appendix B, where the azimuthal bin size, $b$, ranged from 2.5 to 10° to determine $I(q^*, \phi)$. The choice of the optimal angular bin size depends on the total number of counts in the particular trial and the configuration used, which will be discussed further in Chapter 3. Generally, the azimuthal bin size was chosen to minimize the uncertainty associated with the calculation, which depends on the neutron count, detector efficiency and resolution, among other factors. The uncertainty in the alignment factor is calculated based on the uncertainty around each value of the intensity in $I(q^*, \phi)$, which can be seen in the inset of Figure 2.14 and is reported as one standard deviation of that particular intensity. The alignment factor calculation involves an integral in the numerator and denominator, which in practicality, are calculated as a summation approximating the integral. The uncertainty is then calculated in two steps, where the upper and lower integrals are approximated by:

$$A_f(q^*) \approx \frac{\sum_{n=1}^{360/b} I(q^*, \phi = nb) \cos(2(\phi - \phi_0))}{\sum_{n=1}^{360/b} I(q^*, \phi = nb)} \approx \frac{\sum_{n=1}^{360/b} I_n \cos(2(\phi - \phi_0))}{\sum_{n=1}^{360/b} I_n}$$  \hspace{1cm} (2.39)
where the azimuthal bin size, \( b \), is in degrees. There were no significant differences in the calculated ‘true’ alignment from the integral and ‘approximate’ alignment from the summation, giving credence to simplifying the calculation in this way. As the bins are evenly spaced, multiplying the top and bottom sums by the degree width is unnecessary, as these quantities will cancel in all calculations. Then simplifying:

\[
X = \frac{360}{b} \sum_{n=1}^{360/b} x_n = \frac{360}{b} \sum_{n=1}^{360/b} I(q^*, \phi = nb) \cos(2(\phi - \phi_0))
\]

\[
Y = \frac{360}{b} \sum_{n=1}^{360/b} y_n = \frac{360}{b} \sum_{n=1}^{360/b} I(q^*, \phi = nb)
\]

such that the uncertainty in \( X \) and \( Y \) are given by:

\[
\delta X = \sqrt{(\delta x_1)^2 + (\delta x_2)^2 + \ldots (\delta x_{360/b})^2}
\]

\[
\delta Y = \sqrt{(\delta y_1)^2 + (\delta y_2)^2 + \ldots (\delta y_{360/b})^2}
\]

(2.41)

The alignment factor and associated uncertainty are then approximated by:

\[
A_f \approx \frac{X}{Y} \quad \text{and} \quad \frac{\delta A_f}{A_f} \approx \sqrt{\left(\frac{\delta X}{X}\right)^2 + \left(\frac{\delta Y}{Y}\right)^2}
\]

(2.42)

The alignment factor was always calculated using more than one bin size to confirm that the calculated value did not depend on azimuthal width for the \( b = 2.5 \) to 10° range. The reported uncertainty decreases with higher \( b \) values because the uncertainty around the reported intensity decreases with the increasing neutron counts. However, lower \( b \) values give the summation that is the closest approximation to the true integral, which is an important trade-off to keep in mind when performing the alignment factor calculations. Over the \( b = 2.5 \) to 10° range, the alignment factor calculation was nearly identical in all of our calculations, giving confidence in the accuracy of the calculation method.
2.6.4 Repeatability of LAOS structural response in time

To demonstrate that the LAOS response during 1-2 plane SANS was that of the steady alternance state, the measurements were repeated at the same gap position at two to three different time points after the start of LAOS. This ensures that the material response does not change in time, and that the material does not degrade during the course of the experiment. These multiple measurements per gap position also ensure that proper statistics are recorded to calculate the alignment factor. The individual SANS measurements are then added together to obtain a final SANS pattern for each time point during the oscillation. The alignment factor curves shown in Figures 7.6 and 7.8 are calculated from this final pattern at each time point.

Figure 2.15: Individual LAOS SANS trials at $r/H = 0.15$ for condition 2. Despite hours of time between individual measurements, the alignment factor response is not significantly different between trials. The individual trials are then added together to calculate the alignment factors shown in Figures 7.6 and 7.8.

An example of this analysis is shown in Figure 2.15 for the De=0.58, Wi=75 condition at the inner wall. The measurements at this condition were taken over a total of 20.5 hours, without stopping the oscillation in between measurements. Below, the three trials recorded for $r/H = 0.15$ are shown, where the individual trials are performed over a 16h+
period of time. As this state is the most aligned of all trials between conditions one and two, any changes to the material or instabilities in the system would be most detectable at this condition and position. As Figure 2.15 clearly shows, the LAOS response is stable and repeatable over this extremely long period of time, which verifies the steady alternance state and the observed over-orientation. Shorter trials at this condition taken in ‘kinetic mode’ prior to this extended trial confirm that the response is repeatable between multiple trials.

2.7 Solution dynamics
2.7.1 Neutron spin echo (NSE)

2.7.1.1 Background

Neutron spin echo (NSE) spectroscopy is an inelastic, often referred to as ‘quasi-elastic,’ time-of-flight neutron scattering technique. In small angle neutron scattering (SANS), which is an elastic neutron scattering technique, the energy transfer (or change in velocity of the neutrons) is assumed to be negligible. In NSE, however, the change in neutron velocity is measured to detect the system dynamics. In addition to resolving $\vec{q}$ (as given in Section 2.4.1), in NSE, the energy $\vec{E}$ or frequency $\vec{\omega}$ is also resolved ($\vec{E} = \hbar \vec{\omega}$) where $[11, 61–63]$,

$$\vec{E} = \vec{E}_s - \vec{E}_i$$
$$\vec{\omega} = \vec{\omega}_s - \vec{\omega}_i$$

where $\vec{E}_i$ and $\vec{\omega}_i$ are the energy and frequency of the incident beam and $\vec{E}_s$ and $\vec{\omega}_s$ are the energy and frequency of the scattered beam, respectively. Here, the dynamic structure factor, $S(q, E)$ or $S(q, \omega)$, is a function of the energy transfer, which is the Fourier transform of the space-time correlation function; the SANS structure factor measures only the space correlation function. The incoherent portion of the structure factor is the Fourier transform of the self correlation function in space-time, whereas the coherent portion of the structure factor is the Fourier transform of the pair correlation function in space-time. NSE therefore provides a measure of the density-density correlation via the intermediate scattering function (ISF), $I(q, t)$, which is a function of the momentum transfer, $q$, and time, $t$. As neutron spin echo is
conducted in the time-domain, the intermediate scattering function is the Fourier transform of \( S(q, \omega) \). The normalized intermediate scattering function (NISF) measured via NSE is given by:

\[
\frac{I(q, t)}{I(q, 0)} = \frac{e^{-iq[r_i(t) - r_j(0)]}}{e^{-iq[r_i(0) - r_j(0)]}}
\] (2.44)

Neutron spin echo takes advantage of the magnetic properties of neutrons. Neutrons have a spin, \( \vec{S} \) of magnitude \( S = \frac{1}{2} \) and a magnetic moment. When placed into a magnetic field, \( \vec{B} \), the neutron experiences torque from the field perpendicular to its spin direction (vectors bolded for clarity):

\[
\mathbf{T} = \mathbf{S} \times \mathbf{B}
\] (2.45)

The torque on the neutron leads it to precess via Larmor precession, with the Larmor frequency \( \omega_L \):

\[
\frac{d\mathbf{S}}{dt} = \gamma [\mathbf{S} \times \mathbf{B}]
\]

\[
\omega_L = \gamma B
\] (2.46)

where \( \gamma \) is the neutron gyromagnetic ratio, \( 1.832 \cdot 10^8 \) s\(^{-1}\)T\(^{-1}\). The total precession angle, \( \phi \), then depends on the time, \( t \), the neutron spends in the magnetic field, given by:

\[
\phi = \omega_L t = \frac{\gamma}{\nu} \int \mathbf{B} \cdot d\mathbf{l}
\] (2.47)

where \( \nu \) is the neutron velocity and \( \int \mathbf{B} \cdot d\mathbf{l} \) is the field integral, where the magnetic coil is of length \( l \). In NSE at the NCNR, the neutrons pass through two parallel magnetic fields of magnitude \( B_1 \) and \( B_2 \) prior to and after interacting with the sample, respectively. These fields can either be oriented parallel and have the neutron spins flipped before interacting with the sample, or they can be oriented in the opposite direction. This process is described below and is depicted in Figure 2.16. If the neutron changes energy when it scatters, the phases
before and after scattering will be different, such that [62,63]:

\[
\phi_1 - \phi_2 = \gamma \int B dl \left( \frac{1}{v_1} - \frac{1}{v_2} \right)
\]  

(2.48)

which assumes that \( \int B_1 \cdot dl_1 = \int B_2 \cdot dl_2 \). Conversely if the scattering is elastic, a polarization echo is obtained, meaning that the precession angle of all neutrons is the same at the echo point. The polarization, \( \langle P \rangle \), actually measured during an experiment is the ensemble average over all precession angles:

\[
\langle P \rangle = \langle \cos(\phi_1 - \phi_2) \rangle
\]

(2.49)

As the polarization measures the difference between \( \phi_1 \) and \( \phi_2 \), the individual velocities \( v_1 \) and \( v_2 \) are also not measured individually. Using the equations of motion and a first-order Taylor expansion, then combining with Equation 2.48,

\[
h \omega = m(v_1^2 - v_2^2) \approx m \bar{v} dv
\]

\[
\phi_1 - \phi_2 = \frac{\gamma dv}{v^2} \int B \cdot dl
\]

\[
\phi_1 - \phi_2 = \frac{\gamma h \omega}{mv^3} \int B \cdot dl
\]

(2.50)

Finally, the time \( t \) can be defined in terms of known quantities using de Broglie \( (p = mv = h/\lambda) \):

\[
t = \frac{\phi_1 - \phi_2}{\omega} = \frac{m^2 \gamma \lambda^3}{2\pi h^2} \int B \cdot dl
\]

(2.51)

There are several manipulations used in NSE measurements to detect the velocity change in the neutrons detailed in Equation 2.48 that take advantage of these known magnetic properties [61]. The NSE manipulations can be seen in Figure 2.16 for the setup at the NCNR. Neutrons in the incoming beam first pass through a velocity selector, but still have different velocities. This leads to a loss of polarization or de-phasing of the spins over
time. The spin polarizer orients all of the spins along the propagation direction, and then the neutron beam then passes through a $\pi/2$ flipper, which orients the neutron spin to spin up. This orients the neutrons in the direction perpendicular to the magnetic field, $B_1$, such that they precess in the direction toward the sample. The neutrons then encounter a magnetic precession coil of field $B_1$ and precess via Larmor precession as given by Equations 2.45 and 2.46. The neutrons then pass through a $\pi$ flipper, and then interact with the sample. The neutrons exchange energy with the atoms moving in the sample, which alters their velocity distribution. The $\pi$ flipper is necessary to flip the spins such that a phase difference can be detected between $B_1$ and $B_2$ if they are oriented parallel (Equation 2.48). The neutrons then pass through another precession coil of field $B_2$, which is oriented in the same direction as $B_1$. The neutrons then pass through another $\pi/2$ flipper which re-orients them, pass through a polarizer, and hit the detector.

![Diagram of neutron spin echo experiment](image)

Figure 2.16: Schematic of a neutron spin echo (NSE) spectroscopy experiment. Reprinted from the NIST Center for Neutron Research, reference [61]. This sequence enables detecting small changes in neutron velocities, as amplified using the echo condition.

Neutron spin echo measurements are particularly useful in studying WLM solutions, because the measurements enable the *segmental* dynamics of the worms to be probed. Further, the NSE accessible $q$-range is similar to that of SANS, unlike dynamic light scattering.
which access significantly longer length scales (lower q-values) than in SANS. The similar q-range between NSE and SANS allows the dynamics to be examined on the length scales corresponding with the measured SANS structure.

2.7.1.2 Experimental details

Neutron spin echo measurements were performed at the NCNR on the NG-A instrument using 4 mm quartz-windowed cells. Several wavelengths and Fourier times, $\tau$, were used to cover the full scattering vector: $\lambda = 8$ Å ($0.12 < q < 0.14$ Å$^{-1}$, $0.2 \leq \tau \leq 40$ ns), $\lambda = 11$ Å ($0.06 < q < 0.12$ Å$^{-1}$, $0.5 \leq \tau \leq 100$ ns), $\lambda = 15$ Å ($0.02 < q < 0.06$ Å$^{-1}$, $1 \leq \tau \leq 200$ ns), and $\lambda = 17$ Å ($0.01 < q < 0.025$ Å$^{-1}$, $1 \leq \tau \leq 300$ ns). Charcoal was used as the resolution standard for the $\lambda = 15$ Å experiments, and carbosilica was used for the remaining experiments. A summary of these configurations can be seen in Table 2.3 below.

To validate the longest wavelength and Fourier time measurements performed at the NCNR to date ($\tau > 250$ ns, $\lambda = 17$ Å), we overlap the q-region of the measurements with the $\lambda = 15$ Å measurements for comparison. Data was reduced using NIST standards and accounting for the D$_2$O solvent in the DAVE software. Data was fit in the DAVE PAN 1-D fitting module. The detector at each configuration was divided into multiple sectors to access different q-positions. Data was fit to a stretched exponential function with three fit parameters: amplitude ($a$), decay constant (1/$\Gamma$), and stretch exponent ($\beta$). Initial fitting was performed with no fixed parameters, where $a \approx 1$ for all fits across all configurations, and $\beta$ did not vary significantly within each configuration. These $\beta$ values are used in the paired t-test results, as any error associated with the edges of the detector is constant across samples. Final $\Gamma$ results were calculated from subsequent fits, where $\beta$ was held constant within each configuration to account for higher associated errors at the detector edges. Results did not significantly differ between fitting methods.
Table 2.3: Summary of NSE configurations. * symbol indicates follow-up experiments using different sample preparations and configurations.

<table>
<thead>
<tr>
<th>Scattering vector $q$ (Å⁻¹)</th>
<th>Wavelength $\lambda$ (Å)</th>
<th>Beam x</th>
<th>Beam y</th>
<th># Fourier times</th>
<th>FT range (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.018</td>
<td>17</td>
<td>13.66</td>
<td>14.95</td>
<td>13</td>
<td>0.68 - 290</td>
</tr>
<tr>
<td>0.025</td>
<td>15</td>
<td>13.66</td>
<td>15.02</td>
<td>12</td>
<td>1.1 - 200</td>
</tr>
<tr>
<td>0.05</td>
<td>15</td>
<td>13.66</td>
<td>15.02</td>
<td>12</td>
<td>1.1 - 200</td>
</tr>
<tr>
<td>0.08</td>
<td>11</td>
<td>13.63</td>
<td>15.14</td>
<td>13</td>
<td>0.15 - 100</td>
</tr>
<tr>
<td>0.11</td>
<td>11</td>
<td>13.63</td>
<td>15.14</td>
<td>13</td>
<td>0.15 - 100</td>
</tr>
<tr>
<td>0.14</td>
<td>8</td>
<td>13.73</td>
<td>14.43</td>
<td>13</td>
<td>0.07 - 40</td>
</tr>
<tr>
<td>0.018*</td>
<td>17</td>
<td>14.60</td>
<td>16.67</td>
<td>9</td>
<td>8.7 - 300</td>
</tr>
<tr>
<td>0.010*</td>
<td>17</td>
<td>14.60</td>
<td>16.67</td>
<td>9</td>
<td>8.7 - 300</td>
</tr>
</tbody>
</table>

2.7.2 Dynamic light scattering (DLS)

2.7.2.1 Background

Dynamic light scattering is useful to probe larger-scale structural relaxations than those detectable by NSE, such as relaxations of the chain and entangled or branched network. DLS has a lower accessible scattering vector, $q$, and very wide range of accessible delay times, $t$, depending on the instrument used. In the limit of small angles, the scattering vector, $q$, is related to the angle, $\theta$ by:

$$ q = \frac{4\pi n_0}{\lambda} \sin\left(\frac{\theta}{2}\right) $$  \hspace{1cm} (2.52)

where $\lambda$ is the wavelength of light, and $n_0$ is the refractive index of the medium. For the experiments on the WLMs, $n_0 = 1.3284$ for D₂O at 35 °C.

Dynamic light scattering is based on the concept that the Brownian motion of colloids or particles causes fluctuations in the scattering. Here, the timescale of motion is dependent on the particle size, temperature and viscosity of the surrounding medium. This concept is valid in the dilute limit. As the solution concentration is increased, interparticle or intermicelle interactions as is the case here, will begin to affect the scattering. DLS uses a digital
correlator to measure the intensity-intensity autocorrelation function, or second-order autocorrelation function, $g_2(t)$, given by [64]:

$$g_2(t) = \frac{1}{T} \int_0^T I(t^*)I(t^* + t)dt$$  \hspace{1cm} (2.53)$$

where $I$ is the intensity of the scattered light. Measurements of $g_2(t)$ are converted to the first-order electric field autocorrelation function, $g_1(t)$, via the Siegert relation [64]:

$$g_2(t) = 1 + C[g_1(t)]^2$$  \hspace{1cm} (2.54)$$

where $C$ is a correction factor dependent on the geometry and laser alignment. Note $C$ is normally denoted as $\beta$, however, $C$ is used for clarity as the stretch exponent here is denoted by $\beta$. The first-order autocorrelation function, given by:

$$g_1(t) = \frac{1}{T} \int_0^T E(t^*)E(t^* + t)dt$$  \hspace{1cm} (2.55)$$

where $E$ is the electric field of the scattered light. For monodisperse, Brownian particles, $g_1(t)$ decays exponentially as:

$$g_1(t) = e^{-\Gamma(q)t}$$

where $\Gamma(q) = q^2D$  \hspace{1cm} (2.56)$$

where $\Gamma(q)$ is the relaxation rate and $D$ is the diffusion coefficient.

Dynamic light scattering is traditionally used to examine diffusive dynamics. However, often in polymeric solutions, two relaxation modes are observed in DLS. The origin of the primary relaxation mode measured in DLS for polymeric or WLM solutions is generally well accepted and has been attributed to a translational diffusion of chain segments [65,66]. For pure translational diffusion, the relaxation rate, $\Gamma(q)$, should scale linearly as $q^2$ with no y-intercept, as previously reported in semi-dilute polymers and WLMs [66–68]. A non-zero y-intercept indicates the presence of rotational diffusion in addition to translational diffusion.
2.7.2.2 Experimental details

Dynamic light scattering measurements were performed in the Soft Matter Laboratory at the Institut Laue-Langevin using an ALV Static and dynamic light scattering instrument. The ALV CGS-3 Compact Goniometer System (ALV GmbH, Langen, FRG) uses a helium-neon (HeNe) laser with $\lambda = 632.8$ nm, with a 3.125 ns shortest sampling time. Cylindrical glass cuvettes ($d = 10$ mm) were used for all measurements and were filled with approximately 2.5 mL of sample; all samples were filtered before loading to remove any dust that could affect the results. The temperature was held constant at $35^\circ \pm 0.1^\circ$ C for all measurements. To minimize turbulence from the toluene bath, samples were allowed to equilibrate for 20 minutes after being placed in the measurement holder before measuring. Experiments were performed over the angle range $25^\circ \leq \theta \leq 150^\circ$, corresponding to a q-range of $0.000571 \leq q \leq 0.00255$ Å$^{-1}$, using $n_0$ for D$_2$O at 35 °C as given above. Background from the toluene bath and D$_2$O solvent was accounted for. Measurements were performed in triplicate for a minimum of 60 s, for a total minimum time of 180 s. Measurements of the second-order autocorrelation function, $g_2(t)$, were converted to the first-order autocorrelation function, $g_1(t)$, via the Siegert relation. The value of the stretch exponent $\beta$ used for the fitting is determined by the value at which the plot of $g_1(t)$ versus $q^2 t^\beta$ collapses for all angles.

Results were corroborated across instruments and sample preparations using two additional DLS instruments at the University of Delaware. A Brookhaven Instruments green laser system ($\lambda = 532$ nm, $45^\circ \leq \theta \leq 130^\circ$) was used at several angles. Additionally, a Brookhaven Zeta Phase Analysis Light Scattering (ZetaPALS) red laser system ($\lambda = 658$ nm, $\theta = 90^\circ$) was used at one angle.
References


Chapter 3
DEVELOPMENT OF INSTRUMENTATION AND DATA ANALYSIS METHODS

3.1 Introduction

An important element of this dissertation is the development of new techniques and data analysis methods in regard to small angle neutron scattering (SANS) experiments. This chapter will discuss these advances, which can be broken down into two main aims. The first aim focuses on improving the temporal resolution of SANS experiments, in theory and in practice. One disadvantage of neutron scattering when compared to x-ray scattering, for example, is the significantly lower flux that is obtained in SANS experiments. These advances in time-resolved analysis seek to mitigate some of the issues associated with low neutron flux, namely the poor time-resolution of the resulting SANS data. The improvements in time-resolved analysis are discussed in the context of time-dependent structural responses detected by SANS, which in the case of wormlike micelles (WLMs), can result from time-dependent deformations. However, these methods can be used to look at other time-dependent processes, such as kinetics, which will be discussed below.

In the following, the theoretical aspects of time-resolved data processing will be examined. A deconvolution protocol is presented, which was developed for obtaining material responses from time-resolved small-angle scattering data. This protocol is published in reference [1]. This data is not limited to SANS experiments, but could also come from light (SALS) or x-rays (SAXS). Previously used methods convolve material responses with information from the procedure used to group data into discrete time intervals, known as binning. Here, enhanced signal resolution can be obtained by using methods of signal processing to analyze time-resolved scattering data. The method is illustrated for a time-resolved rheo-SANS measurement of a complex, structured surfactant solution under oscillatory shear flow.
We show how the underlying material response can be clearly decoupled from the binning procedure. This method greatly reduces the experimental acquisition time, by approximately one-third for the aforementioned rheo-SANS experiment. Then, the implementation of this procedure at two reactor facilities, the NIST Center for Neutron Research (NCNR) and Institut Laue-Langevin (ILL), will be discussed.

The second aim in this chapter focuses on the SANS experimental set-up and how the chosen SANS configuration ultimately affects the resolution of the measured microstructural rearrangements. Specifically, the chosen experimental configuration affects the resolution of the intensity distribution, or orientation distribution function (ODF), of the material under shear which is projected on to each plane. This intensity distribution, \( I(q^*, \phi) \), is ultimately used to calculate the alignment factor calculation from Equation 2.36. The chosen configuration to perform the SANS experiments ultimately determines the experimental resolution, and the can greatly affect the accuracy of the measured intensity distribution. Here, the configurational effect on the \( A_f \) calculation is examined by varying important SANS parameters that change the experimental resolution. These parameters include the detector distance, the number of guides or collimation, and the width of the slits used for the rheometer or 1-2 shear cell set-ups. As discussed in Chapter 2, Section 2.6.2, the static microstructure must be independent of sample environment and configurations to obtain an accurate calculation of the alignment factor. However, although the static 1-D SANS data may be independent of configuration, additional considerations must be taken into account when performing the annular average that gives the intensity distribution, \( I(q^*, \phi) \). These configuration and resolution effects are examined in-depth, such that the optimal configuration can be chosen for all experiments. Further, \( I(q^*, \phi) \) represents the ODF of the WLMs under shear, meaning that more information about the material structure can be gained by examining \( I(q^*, \phi) \) in addition to \( A_f \) (see Chapter 5, Figure 5.6). However, to get useful and accurate information about \( I(q^*, \phi) \), the configuration resolution effects must be well understood.
3.2 Time-resolved neutron scattering analysis

3.2.1 Motivation

The study of soft matter is a multidisciplinary and active area of research that often includes materials with time-dependent structures, resulting from self-assembly, phase transitions or an external excitation, such as a shear or electromagnetic field. Accessing structural information on the relevant length scales in soft matter science can be achieved through light, x-ray, or neutron scattering. During a scattering experiment, a beam of particles of a specified wavelength is directed onto the material of interest. This elastic scattering is collected at a detector that records the spatial position of the particle and the time of acquisition. Scattering from stationary or steady-state materials provides microstructural information about the quiescent or locally time-independent state; thus the material properties can be represented by the time-average over the experimental period, \( T \). However, there has been a recent increase of interest surrounding time-resolved scattering experiments, where materials such as biological macromolecules [2, 3], gels [4–6], vesicles and membranes [7–9], polymers and polymer crystal phases [10, 11], and micelle solutions [12–15] have been investigated. The structure of materials responding to an applied excitation should not be analyzed by this simple time-average of the scattering, as the time-dependent nature of the response cannot be discerned. Accordingly, the development of new methods to analyze time-dependent scattering data is essential to both accurately and efficiently determine the true temporal material response.

Time-dependent scattering is often analyzed by an averaging procedure known as ‘binning.’ The binning procedure groups the scattering information into fixed intervals (bins) of duration \( t_w \), referred to as the bin width. Here, the material response is examined on a timescale much shorter than that of the full experiment, \( t_w \ll T \). By dividing the scattered particles into discrete time bins, the material properties are averaged over \( t_w \) and are assumed to be relatively constant within the bin. For example, in a scattering experiment of 30-minute duration (\( T = 30 \text{ min} \)), researchers may choose to examine the structural changes after every minute (\( t_w = 1 \text{ min} \)). In this case, the average material structure per one-minute time bin is analyzed.
In order for such analysis to be performed, the detector must time-stamp each detected particle in addition to recording its spatial position. Figure 3.1 shows an example data set, where the X and Y position on the detector and the time of detection for each scattering event are shown in three dimensions for a typical small angle neutron scattering (SANS) experiment. The red data points in Figure 3.1 represent neutrons scattered during a cycle of an oscillatory shear experiment of period $T$, so that the time axis is normalized as $t/T$. The spatial and temporal dependence of the scattering events leading to this detector response, as shown in Figure 3.1, is indicative of the continuously varying dynamics inherent to the system of interest.

Figure 3.1: Example time-resolved neutron scattering experiment of period $T$, where the detector records the spatial X and Y positions, and time of detection, for each scattered neutron. Each red dot represents an individual scattering event. The standard binning method for an oscillatory shear experiment groups neutrons registered within an interval of time, $t_w$, together (indicated by colored and black lines), forming a single scattering pattern with temporal resolution $t_w$. Here, $t_w = T/10$. Note the two temporal ends of the figure are joined, such that $t/T = 0 = 1$.

In the **standard binning method**, three dimensional spatially- and temporally-resolved data are reduced to a sequence of two-dimensional patterns, where the detector response to the scattering is grouped into non-overlapping time bins of duration $t_w$. As shown in Figure
3.1, the detected scattering events are binned with $t_w = T/10$ (between black or colored lines) to form a total of ten scattering patterns over the experiment period, $T$. By using the standard binning method, all derived material properties have an equal temporal resolution and precision of $t_w$. The temporal precision of the binned data is determined by the bin width, $t_w$, whereas the temporal resolution is determined by the time step between consecutive bins, which in the standard binning method is also $t_w$. Any properties that are changing on time scales faster than $t_w$ cannot be detected. The scattering patterns shown result from the data binned between each set of colored lines and contain information about the material properties during that specific portion of the oscillation. In the previous example of a 30-minute scattering experiment with a bin width of one-minute, the standard binning method would result in 30 total bins each of duration one minute. Any structure changes occurring faster than one minute would not be detected using this method.

3.2.2 Processing time-dependent scattering

The data binning procedure is analogous to applying a moving average to a time series, as they both result in smoothed, time-averaged data. However, unlike in the moving average procedure, the data binning procedure is necessary to examine time-resolved data, as the material response cannot be elucidated without data processing. The goal of the time-resolved data analysis, therefore, is to resolve the underlying material response. In the context of time-resolved scattering experiments, the coarse-grained binning procedure is necessary to reduce the dimensionality of the data for analysis. In many cases, the binned data is referred to as being the ‘true’ material response, which is not accurate because the binned data depends on the choice of bin width. The true material response should be independent of the analysis method. By applying an ever-widening bin-width to the same experimental data, the finer features of the response will be ‘averaged out’ until eventually the bin is the same width as the period. Thus to determine the true material response, the method of analysis should account for, and remove, artifacts associated with the coarse graining procedure.
3.2.3 Convolution and deconvolution

Suppose that the underlying material response of interest, \( m(t) \), is continuous and is represented by time-resolved elastic scattering data. The material response of interest could be the intensity or position of a particular peak, for example, or some integral function of the pattern such as an alignment factor or order parameter. These responses necessarily change as a function of real time throughout the experiment, and may be brought about from external forces such as shear or temperature change. This time-dependent response, \( m(t) \), is not to be confused with the instrument resolution function or the material scattering function, which are defined in the inverse space domain. These functions are inherent to the instrument and the scattering data and are convolved in the inverse space domain, resulting in the instrument-smeared signal that is recorded during a scattering experiment. The function \( m(t) \) therefore describes the time-dependent nature of the instrument-smeared signal; the following procedure does not attempt to alter or correct the signal based on instrument smearing. We also note that a finite wavelength distribution of neutrons in SANS experiments introduces time smearing of the response and this is not explicitly considered here, such that the method may require additional considerations for experiments performed with a broad distribution of incident velocities, such as in a spallation neutron experiment. The scattering data is grouped into time bins, \( b(t,t_w) \), of duration \( t_w \), which is defined by the boxcar function at a time, \( t \),

\[
b(t,t_w) = \frac{1}{t_w} H \left( -t - \frac{t_w}{2} \right) - \frac{1}{t_w} H \left( -t + \frac{t_w}{2} \right)
\]

(3.1)

where

\[
H(t) = \int_{-\infty}^{t} \delta(s) \, ds
\]

(3.2)

is the Heaviside step function, and \( \delta(s) \) is the Dirac delta function. The use of this bin function ensures that all neutrons inside the bin are counted with equal weighting, while those outside are ignored. The binned data, referred to as \( c(t) \), is equivalent to the area overlap between the material response and the bin as a function of the amount that the bin is
translated,
\[ c(t) = \int m(t')b(t - t', t_w) \, dt'. \]  
(3.3)

Equation 3.3 is more concisely written as
\[ c(t) = m(t) \otimes b(t, t_w) \]  
(3.4)

where \( \otimes \) is the convolution operator. Equation 3.4 therefore explicitly states that the binned data is the convolution of the material response and the bin. A representation of the convolution in terms of the scattering data looks like can be seen in Figure 3.2.

Figure 3.2: Visual representation of the convolution in terms of scattering data. On the left is the boxcar function in terms of the time bin, \( t_w \), which is convolved with the scattering data (middle) to produce the observed scattering data, shown here for the 1-2 plane (right).

In order to obtain the material response \( m(t) \), from the convolved data, \( c(t) \), a deconvolution must be applied. According to the convolution theorem, the Fourier transform of a convolution is equal to the product of the Fourier transforms. Denoting the Fourier transform operator as \( \mathcal{F} \), and the Fourier transform of a time domain function by a change of variable and capitalization, the theorem states that
\[ \mathcal{F} \{ c(t) \} = C(\omega) = \mathcal{F} \{ m(t) \otimes b(t, t_w) \} = M(\omega) \cdot B(\omega, t_w). \]  
(3.5)

In order to bin the data, a value of \( t_w \) in Equation 3.3 is chosen. Accordingly, \( b(t, t_w) \) and \( B(\omega, t_w) \) in Equations 3.4 and 3.5 are fully known. Given the form of the bin, as defined in
Equation 3.1, the Fourier transform is the well-known sinc function,

$$\mathcal{F}\{b(t,t_w)\} = B(\omega,t_w) = \frac{2\sin\left(\frac{t_w\omega}{2}\right)}{t_w\omega}$$ (3.6)

which is also illustrated in Figure 3.3a. As the sinc function contains negative lobes, a wide chosen bin width for data analysis can lead to data inversion, which is illustrated in Figure 3.3b.

No assumptions, other than continuity in time, are made about the form of \(m(t)\) or \(M(\omega)\). To remove any artifacts associated with the binning procedure, the Fourier transform of the convolved (binned) data can be divided by the known Fourier transform of the bin,

$$M(\omega) = \frac{C(\omega)}{B(\omega,t_w)}. \quad (3.7)$$

The deconvolution, obtained by applying the inverse Fourier transform, results in replication of the material response unaffected, in principle, by any effects of the binning procedure,

$$\mathcal{F}^{-1}\{M(\omega)\} = \mathcal{F}^{-1}\left\{\frac{C(\omega)}{B(\omega,t_w)}\right\} = m(t). \quad (3.8)$$

Figure 3.3: Sinc function and data inversion issues. (a) Standard sinc function. The negative lobes of the function can lead to issues in data inversion, where an example is shown in (b). (b) Sample data, ‘M,’ which when binned at a bin width of \(t_w\), leads to inversion.

The differences between the binning procedure and the full deconvolution process
are illustrated for a time-periodic material response in Figure 3.4(a) and Figure 3.4(b), respectively, for bins of different sizes on a simulated data set. Only the first half of the period is shown in Figure 3.4 for clarity. The simulated material response (black, Figure 3.4(a) and (b)) is constructed of odd harmonics of equal magnitude up to and including the 29th harmonic. The simulated response was convolved with different time windows to obtain the results in Figure 3.4(a); these results were then deconvolved by the same time window in Figure 3.4(b).

The results in Figure 3.4(a) represent the material response that is obtained when different bin sizes are chosen to process the data. For convenience, the bin duration, $t_w$, is expressed as an even integer fraction of the period of oscillation, $T$, such that $t_w = T/N$. Here, the temporal resolution is approximately continuous through $t/T$, whereas the temporal precision is determined by the bin width, $T/N$. Larger integers thus correspond to shorter bins, better approximating the underlying material response. Clearly, the results of binning alone are dependent on the bin size, as significantly different responses are seen with changing $N$. In Figure 3.4(b), the data from Figure 3.4(a) is deconvolved to obtain the true material response. The result of the deconvolution is completely independent of the bin size, a property required of the material response.

As seen from the data in Figure 3.3b and Figure 3.4a, the negative lobes of the sinc function can lead to data inversion if too large of a bin width is chosen. For example, the sample data in Figure 3.3b resembles the shape of an ‘M,’ with two peaks and a single valley. After convolving the data with a bin width, $t_w$, of the same width as the ‘M’ feature, the signal now contains a single peak in the region of the valley, thereby inverting this feature. The same qualitative trend can be seen in Figure 3.4a, where the inversions are most apparent when the widest bin widths are used. By applying the deconvolution process, the data inversion is eliminated (Figure 3.4b), thereby motivating its use when the feature size of a response is unknown.

On the basis of the data displayed in Figure 3.4, a bin as wide as half of the period, $T/2$, can be used, in theory, to accurately determine the material response via deconvolution. Such analysis has clear implications in the length of time required to carry out a
time-resolved scattering experiment. In many studies where binning is used, bin widths on the order of $T/30$ are employed to provide a reasonable balance between temporal resolution and experiment duration[6, 15]. If a constant number of scattering events per bin is desired (normally around 100,000 – 250,000 or greater, depending on the information sought by the researcher), then scattering events sufficient to fill bins of width $T/2$ can be collected 15 times faster than the number of scattering events required to fill bins of width $T/30$. However, experimental limitations and noise in the data limit the practical bin size that can be applied to reduce scattering time, which will be discussed in the next section.

Figure 3.4: The results of binning only (a) and binning and deconvolving (b) time-resolved sample data set from bins of width $T/N$, where $T$ is the period of oscillation and $N$ is an even integer. Only the first half of the oscillation is shown for clarity. The solid black line indicates the underlying material function, and the colored lines indicate the results of the two procedures. Only by deconvolution can the true material response be determined without artifacts from the analysis.

3.2.4 Discretization

The formalism above in support of deconvolution assumes continuous functions and transforms. Practically, the underlying continuous material response can only be measured discretely, and therefore, the ‘true’ deconvolved signal must also be discrete. The integrals in Equations 3.3 and those involved in the transforms in Equations 3.5 and 3.8 are therefore
replaced by sums. While the arguments remain the same, the application of the ideas requires refinement when dealing with discretely-measured data. The primary concerns when deconvolving discrete data are associated with Fourier transformation and inverse Fourier transformation, which can be affected by noise, time-step size, and bin-width. Additionally, the binned data must be processed in a specific manner to implement the deconvolution procedure. In the standard binning method, the temporal precision and temporal resolution are the same because the bins are non-overlapping in time. Accordingly, the binned material response cannot be deconvolved because there exists only one data point per bin width. The binning procedure can be modified to allow the bins to ‘slide’ at a certain time step, \( t_s \), where \( t_s << t_w \). In this method, referred to as the **sliding binning method**, the bins overlap in time so that neutrons are counted multiple times, but only once per bin. Implementing the **sliding binning method** greatly increases the temporal resolution of the binned signal (by a factor of \( n = t_w/t_s \)), thus enabling better deconvolution. In the previous example of a 30-minute scattering experiment with a bin width of one-minute, the sliding binning method increases the total bin number by \( 30n \). A chosen value of \( n=5 \) would result in 150 total bins, each of duration one minute (illustrated in Figure 3.5). Note that the appropriate choice of \( n \) is dependent on the data set, and larger \( n \)-values are often required for wider bin widths. This numerical example, given in step 1. of Figure 3.5, uses the sliding binning method to achieve five-fold improved temporal resolution over the standard binning method. Figure 3.5 also helps to visualize the full procedure, from the data processing to the final deconvolution step. A sample procedure and Matlab commands are provided as a practical example, which addresses issues such as noise and bin width effects (which will be discussed below).

### 3.2.5 Noise effects

The deconvolution process provides a pathway for dramatically reducing the acquisition time for a time-resolved scattering experiment by using larger bin sizes. However, noise effects limit the practical bin width that can be applied to a data set to obtain an accurate deconvolved signal. Fourier transforming discrete data requires division by the number of points in the time domain signal, and inverse Fourier transformation requires multiplication
Figure 3.5: Flow chart illustrating the data processing and deconvolution procedure, with a Matlab example for reference. Steps 2. to 4. correspond to equations discussed in the text, whereas step 1. is performed in the scattering reduction software. Step 3a. allows the user to determine the optimal truncation frequency for the inverse transform.
by the number of points in the frequency domain signal. The signal-to-noise ratio (SNR) of an experimentally-measured signal can be increased by truncating the spectrum in the frequency domain. Truncating the frequency spectrum is almost always necessary based on the noise level and the error associated with experimental data (step 3a., Figure 3.5). In time-periodic experiments, the truncation frequency can be estimated by examining the magnitude of the noise in the Fourier transform of the time-averaged data, which is most apparent at high frequencies. Truncating the full spectrum thereby removes a significant amount of noise from the signal. The inverse Fourier transform then only uses the frequencies that are above the level of the noise to reconstruct the discrete true signal. In data sets where the noise amplitude is higher than that of a frequency that contributes to the signal, the feature resulting from that frequency cannot be resolved in the true signal. Figure 3.6 examines the effect of noise on the deconvolution procedure for different bin widths and different truncation frequencies.

The signals in Figure 3.6 are calculated by deconvolving the time-average of the original signal featured in Figure 3.4 with different levels of added noise. These calculations are the same as those performed in Figure 3.4; however noise was added to the time-averaged signal before performing the deconvolution, such that the results are no longer analytically defined. Gaussian-distributed zero-mean white noise was generated in Matlab, where one standard deviation of the noise amplitude was equal to 0.1%, 0.25% or 0.5% of the mean amplitude of the time-averaged signal. Figure 3.6 clearly shows the effect of noise on the deconvolved signal at different bin widths ($T/2$, $T/10$, $T/32$), and of truncating the full Fourier spectrum at different frequencies, ranging from the full frequency spectrum (no truncation) to $1/32$ of the full spectrum (number of frequencies used to construct the original signal). As seen in Figure 3.6, the closer the truncation frequency is to the number of frequencies used to generate the signal, the more noise is filtered, leading to a smoother signal. However, the end of the Convolution and deconvolution section illustrated a case where a bin width of $T/2$ can reduce the time that would currently be taken to acquire data sufficient for bins of width $T/30$ by a factor of 15. However, as Figure 3.6 shows, there are limitations in the bin width that should be chosen when performing an experiment. Bins of width $T/32$ handle
the noise the best, as the smaller bin width leads to sharper features in the time-averaged signal, which results in a high signal-to-noise ratio. Using bins of $T/32$, the deconvolution result after truncation is nearly unaffected by the increasing noise level within the range examined. However, the effect of the added noise is pronounced at bins of $T/2$, where even the truncated deconvolution results greatly differ from the expected original signal. Smaller bin widths are optimal in the deconvolution procedure for several reasons. The width of the sinc function in frequency space is inversely proportional to the bin width in real time, meaning that smaller bin widths cover a wider frequency range. The number of roots in the sinc function also increases with wider bin sizes in the same frequency range, leading to more information loss with wider bins. Lastly, the amplitude of the sinc function at high frequencies is larger when the bin size is smaller, leading to a higher signal-to-noise ratio when the deconvolution is performed. However, by truncating the spectrum at all bin widths, the deconvolution result becomes closer to that of the original signal. The truncation of the frequency spectrum is important to perform during this procedure (Figures 3.5 and 3.6) such that only the frequencies with amplitudes significantly above the level of the noise are used to reconstruct the discrete true signal.

3.2.6 Time-step and bin-width effects

A fundamental result in the field of information theory, often referred to as the Nyquist-Shannon sampling theory states that

If a function $x(t)$ contains no frequencies higher than $B$ Hz, it is completely determined by giving its ordinates at a series of points spaced $1/(2B)$ s apart.

The sampling theorem sets the upper limit on the angular frequencies that can be determined by the Fourier transformation of discretely-measured data. The upper frequency limit of the band, denoted by $B$, and the size of the time step, $t_s$, are therefore related by:

$$B = \frac{\pi}{t_s}. \quad (3.9)$$

The frequency response of the bin function defined in Equation 3.1 decays with angular frequency as $\frac{2}{t_s \omega}$ as shown in Equation 3.6. In the deconvolution, the Fourier transform of
Figure 3.6: Binning and deconvolution of noisy data at different bin (time) widths. Noise levels of 0.1, 0.25 and 0.5% were added to the time-average of the original signal from bin widths of $T/2$, $T/10$ and $T/32$. The full frequency spectrum transform always returns noisy data. However, truncating the Fourier transforms (denoted as a fraction of the full spectrum) removes noise from the signal so that the true signal is more closely approximated. The original signal (black) has frequencies corresponding to $1/32$ of the full Fourier transform. The true signal at $1/32$ of the full transform is best approximated using bins of $T/32$, and deviates significantly with increasing bin size. Data is shifted vertically for visual aid.
the convolved data is therefore divided by a number less than or equal to one. It is possible to set a value on how much the frequency response has decayed by truncating the response at a particular frequency. If we refer to the amplitude of the sinc function as $L$:

$$L = \frac{2}{t_w \omega}$$

(3.10)

The frequency that solves Equation 3.10 can be readily equated with the upper frequency of the band from Equation 3.9 to give a relation between the step size, the bin width, and the desired amplitude of the sinc function,

$$\frac{2}{L t_w} = \frac{\pi}{t_s} \Rightarrow \frac{t_w}{t_s} = \frac{2}{\pi L}.$$  

(3.11)

This result states that if one wishes to probe frequencies as high those required to decay the sinc function to 5% of the zero-frequency value, such that $L = 0.05$, then $\frac{t_w}{t_s} = \frac{40}{\pi} \approx 12.73$. This requires the step size to be thirteen times smaller than the bin width. However, often times the experimental scattering signal decays much faster than that of the sinc function.

In oscillatory shear experiments, for example, the stress response is highly indicative of the scattering signal. The higher order harmonics present in the Fourier transform of the stress response are a good estimate of the higher order harmonics present in the structural response. In many of these experiments, it is more realistic to restrict the sinc function to $15 - 20\%$ of the zero-frequency value, where the frequency of the sinc function is near that of the data truncation frequency (determined using step 3a. in Figure 3.5). At $15 - 20\%$ of the zero-frequency value, a step size of $t_s = t_w/3$ or $t_w/5$ is often sufficient; however, the optimal step size is dependent on the data set and bins of large $t_w$ may require finer step sizes.

In addition to the amplitude, the phase of the sinc must also be considered to determine which frequencies will be irretrievably lost during the deconvolution. As $\sin(\omega) = 0$ when $\omega = n\pi \forall n \in \mathbb{Z}$, frequencies equal to $\frac{n\pi}{t_w}$ will be eliminated from the deconvolved function. Practically speaking, the deconvolution will be undefined when the discrete Fourier transform (DFT) of the time window contains zeros, as the DFT of the time-averaged data is
divided by that of the window function. As mentioned in Figure 3.5, the number of points for the transform can be carefully chosen to avoid such complications. Note that the chosen number of points for the transform, k, should be greater than or equal to the number of slices. By doing so, the transform will be padded with zeros (Matlab), as opposed to prematurely truncating the spectrum.

### 3.2.7 Experimental results and accessibility

The standard and proposed analysis techniques are compared using a time-resolved large amplitude oscillatory shear (LAOS) rheo-SANS experiment taken at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The experiment was performed on a previously characterized [16, 17] mildly branched wormlike micellar solution with an applied strain amplitude $\gamma_0 = 225$ and angular frequency $\omega = 0.2 \text{ rad} \cdot \text{s}^{-1}$. Scattering was measured in the 1,3 flow-vorticity plane of shear. One material property that is directly calculated from binned neutron data, which therefore may represent $c(t)$, is the alignment factor. The scalar alignment factor is a measure of shear-induced anisotropy and is defined by the spatial average on the detector, given by Equation 2.36. Figure 3.7 shows the results for the standard binning method, the sliding binning method, and the full deconvolution (translated for visual aid). First, the alignment factor was calculated for each of the thirty, non-overlapping bins (red) using the standard binning method ($t_w = t_s = T/30$). The sliding binning method (gray) was performed on the same data set using overlapping bins with a step size five-fold smaller than the bin width ($t_w = T/30$, $t_s = T/150 = t_w/5$), yielding a five-fold improvement in the temporal resolution and 150 total bins. While a value of $n=5$ (as seen in Figure 3.5) provides sufficient temporal resolution to perform the deconvolution for bins of width $T/30$ in this experiment, larger values of $n$ may be required when the chosen bin size is larger than $T/30$.

The experimental data processed using the sliding bin method (gray) was deconvolved to elicit the true (discretized) material response (black). The discrete nature of the standard binning method, which leads to poor temporal resolution, is apparent in Figure

114
3.7, whereas the sliding binning method presents improved temporal resolution. The sliding bin curve (gray) exhibits small oscillations in the alignment factor signal, suggestive of a higher frequency material response, that are not seen with the standard binning method. While portions of the sliding bin curve could be interpolated from the standard bin points, the existence of the higher frequency oscillations in the material structure and the position and value of the maximum alignment would not be resolvable via interpolation. The deconvolved signal (black) displays sharper oscillations in $A_f$ that reflect the true response. The residuals in Figure 3.7 highlight the improvements to feature sharpness and quality obtained by deconvolution. While the sliding bin method and the deconvolution yield similar results, there are distinct differences between the two steps. A comparison of the sliding bin method versus the deconvolution can be seen in Figure 3.8a. As a check, the deconvolved data was re-smeared with the same bin width; the sliding bin curve was recovered (Figure 3.8b).

Figure 3.7: LAOS experimental results from a mildly branched WLM solution at $\omega = 0.2$ rad·s$^{-1}$ and $\gamma_0 = 225$. The time-periodic 1-3 plane alignment factor ($A_f$), $c(t)$, is binned into 150 bins of width $t_w = T/30$ ($t_s = t_w/5$). The standard binning method (red) is compared to the sliding binning method (gray) and the full deconvolution (black). Small oscillations in the $A_f$ signal from $0.45 \leq t/T \leq 0.65$ are not resolved via the standard method. Residuals show the impact of deconvolution, where the deconvolved signal exhibits sharper, more pronounced oscillations that represent the true response. Error bars span $t_w$. 

115
In Figure 3.9, we examine the higher frequency oscillations in the alignment factor and compare the deconvolved, true alignment (black) to the measured shear stress (blue). The alignment factor oscillations clearly correspond to similar oscillations in the measured shear stress. These features cannot be resolved using the standard binning method due to poor temporal resolution and limited number of points, making it more difficult to derive information from the stress-SANS rule [18], or other empirical relationships. Simply reducing the bin size will not improve the situation, as the statistical accuracy of the data decreases correspondingly. The improved temporal resolution and feature clarity gained from the deconvolution provide a more direct and accurate pathway to quantitatively link the structural alignment to the measured bulk rheological properties. The deconvolution process also provides a method for reducing total experiment time required to achieve a given accuracy in scattering experiments. However, the noise level ultimately limits the resolution that can be obtained. Similar to the results shown in Figure 3.6, the experimental deconvolution results for this data set are insensitive to bins of width $T/20$ compared with $T/30$ (data not shown), leading to a reduction in scattering (data acquisition) time of one-third.

In additional oscillatory shear conditions, we found that the deconvolution results were also unaffected by the reduction in bin width from $T/30$ to $T/20$ (data not shown). Depending on the features present in the signal, further time reduction can be obtained by implementing larger bin sizes. The time-averaged signal in Figure 3.7b. has two small oscillations on the order of $T/10$ in the alignment factor and stress signal: one from $0.45 \leq t/T \leq 0.55$ and the other from $0.55 \leq t/T \leq 0.65$. Therefore, when a bin size on the order of $T/10$ is used, the magnitude of the Fourier transform at these frequencies is roughly equivalent to the noise, making an accurate deconvolution difficult to perform. As the material stress response contains complementary features to the alignment factor response, the appropriate bin width can be estimated by examining the width of the stress response features and then choosing a smaller bin size. By decreasing the bin size from $T/10$ to $T/20$, the deconvolution was successfully performed for this data set.

In summary, we have shown a procedure to determine the true, underlying material response from a time-periodic signal given discrete data points, such as the alignment factor.
Figure 3.8: Direct comparison of the sliding bin method with (a) the deconvolved data, which shows sharper features than the sliding bin method; and (b) the deconvolved data re-smeared with the time bin, $t_w = T/30$. As expected, re-smearing the data leads to a recovery of the sliding bin data.

calculated from neutron events. This is accomplished by rigorously deconvoluting the scattering data, which is unavoidably operated on by a sliding boxcar function in time during data processing. When applied to a particular time-resolved data set, the proposed sliding bin method gives the same temporal precision as the standard bin method, while greatly improving the temporal resolution. The full deconvolution procedure yields the true material response, which is unobtainable using binning alone. This procedure is general and can be applied to many forms of time-periodic scattering data.

3.3 Implementation of time-resolved analysis at ILL and the NCNR

3.3.1 Motivation

In order to take advantage of the time-resolved analysis presented above in Section 3.2, the sliding bin method described in Section 3.2.1 had to be enacted at both the NIST Center for Neutron Research (NCNR) and the Institut Laue-Langevin (ILL). The sliding bin method itself does not require the time-resolved scattering data to be time-periodic; the
method can simply be used to improve the *temporal resolution* of the experiment. Periodicity is only required for the deconvolution procedure performed in Matlab, which improves the *temporal precision* of the experiment. Therefore, the sliding bin method can be used to greatly improve the temporal resolution of transient measurements like shear startup, in addition to oscillatory measurements like large amplitude oscillatory shear (LAOS). The implementation of the sliding bin method varied between the ILL and the NCNR, and is described below for each facility.

3.3.2 **ILL time-resolved analysis**

3.3.2.1 **List mode versus kinetic mode**

Until recently, the method of taking time-resolved scattering data at the ILL was referred to as ‘kinetic mode.’ During the summer of 2015, new capabilities were finalized to collect and analyze this data, referred to as ‘list mode,’ thanks to help from Miguel Gonzalez in the Computing for Science division at ILL. Now, kinetic mode and list mode are the two
main methods of obtaining time-resolved neutron scattering data. Both modes can be used
for oscillatory data (such as large amplitude oscillatory shear) or for stream data (such as
shear startup). In list mode, each neutron is time stamped. This process enables the user
to gain greater temporal resolution from the experiments, as the data can be processed at
any chosen time width, and for any number of slices. An example of time-resolved data
collected in list mode is shown later in Chapter 7 (Figures 7.6 and 7.8), where there are more
data points and alignment factors during the course of the oscillation cycle, $t/T$, than are
reported using a kinetic mode experiment. In list mode, the bins may overlap, such that the
temporal resolution can exceed the temporal precision. In kinetic mode, the neutrons are
binned according to a temporal bin width chosen in advance, where the temporal resolution
and precision are identical because the bins do not overlap. These experiments can be seen
in Chapter 7 (Figures 7.13, 7.14, and 7.15), where significantly fewer points per cycle are
reported because the number of points was pre-determined by the experimental input. In
kinetic mode, the data is recorded as a nexus (.nxs) file, which can be directly read into
the GRASP software for reduction. The nexus file has a depth equal to the number of bins
selected before the experiment, so that each bin can be examined individually. However,
the bin width can never be changed after the data is collected, so any material responses
occurring on a time scale faster than the bin width is lost. In list mode, the data is recorded as
a list (.lst) file. A nexus file of the total scattering from the experiment is also generated with
the list file, but this file does not have temporal resolution. The list file must be processed in
the large array manipulation program (LAMP) software, from which is exported as a nexus
file that can be read directly into GRASP. This processing step will be described in Section
3.3.2.2 below. The method of data binning in a ‘kinetic mode’ experiment can always be
recovered from a list mode file by choosing a fixed time width and no overlapping bins in
LAMP. As such, there is no real disadvantage to taking files in list mode, except for the
slightly longer processing time ($\sim 30$ s to $2$ min depending on the file size) needed to divide
the file into bins and export the processed file in the LAMP software, discussed below in
Section 3.3.2.2.

In addition to the improved temporal resolution, there is another advantage for taking
files in list mode as opposed to kinetic mode. In list mode for oscillatory shear data, the cycles can be examined during different times in the experiment file. For example, if a list mode experiment was performed for one hour, the file could be analyzed during the first twenty minutes, or the second twenty minutes, and so on, for whatever desired time-width less than the one hour experiment duration. This feature is useful when dealing with shear banding or other transient responses, as the phase or amplitude of the LAOS responses may change in time as the material responds to the startup of flow. If these files are taken in kinetic mode, the average response over time is reported, and it is assumed that the response is that of the ‘steady alternance state.’ However, in list mode, this assumption no longer has to be made; instead it can be verified (or not) by analyzing the data at different time points during the cycle. This verification process was used frequently when analyzing the LAOS data discussed in Chapter 7.

3.3.2.2 Large array manipulation program (LAMP) list mode processing

List mode files are processed in the large array manipulation program (LAMP) software provided by the ILL, which can be seen in Figure 3.10a. Working with Miguel Gonzalez, this ‘Event file analysis’ module of the program was brought online in the summer of 2015 (Figure 3.10b) and can be found on the ILL website. The new LAMP program module for processing time-resolved data must be used with the main LAMP program shown in Figure 3.10a. When LAMP is started, the working path and data path can be specified in the main program; all processed files are exported to the working path so it is not necessary to specify a data path. To access the new processing module, the code ‘event_file’ is entered in the manipulations section, seen on the bottom left of Figure 3.10a. Before loading an event file, the ‘Use trigger?’ and time delay box must be specified (Figure 3.10b). In LAOS, the ‘sample’ trigger option must be used, and the delay time is specified as a time slightly shorter than the full cycle length, $T$, to account for any variation in the cycle time or triggering. All times entered in the event file analysis panel must be in ms. No delay time is required for stream files; here, the ‘Use trigger?’ option is set to ‘no.’ The list mode file can then be loaded as the input file. The time per slice box sets the temporal precision or bin width, $t_w$. 

120
and the number of slices input sets the temporal resolution. In Figure 3.10b, the bin width is 598.66 ms, which corresponds to $T/30$. The number of slices is set to 60, which gives a temporal resolution that is 2-fold greater than the temporal precision, $n = 2$. The data is binned by selecting the ‘bin’ button, and the data slices can be displayed in the main LAMP frame (Figure 3.10a) by selecting ‘show’ — > ‘bin details’ from the panel in Figure 3.10b. Finally, the data is exported to a nexus file that can be read into GRASP for reduction by selecting the ‘export binned data’ option. Like in the kinetic mode files, the exported nexus file has a depth equal to the number of slices chosen, such that each bin can be analyzed individually.

3.3.3 NCNR time-resolved analysis: improved Igor codes and capabilities

3.3.3.1 New Igor reduction codes for SANS

The data reduction programming at the NCNR was developed in Igor by Kline [19]. Unlike at ILL, the time-resolved SANS files at the NCNR are only taken in one format, known as an event mode file (.hst). Similar to the ILL list mode experiments, a file of the total scattering from the experiment is also generated with the event mode experiment file, known as a VAX file, but this file contains no time-resolved information. Event mode files are recorded similarly to list mode files, where each neutron is time-stamped. The event mode data must then be processed using the Event Data portion of the NCNR Igor macros, where the file can be divided into multiple slices and each slice can be exported as a VAX file for reduction. Unlike the ILL list mode data which is exported as a single nexus file, each slice from the NCNR event mode data is exported as its own file, making the reduction process more time-consuming and labor intensive. To address this problem, the NCNR Igor codes have been modified to make data reduction and alignment factor calculation simpler and more efficient.

Three codes have been developed to modify and simplify the current NCNR time-resolved data processing for SANS reduction. These codes can be copied and pasted into the NCNR Igor macros [19] to enact the ‘sliding bin method’ described above. Additionally, the codes allow one to specify a q-range for the alignment factor calculation, and whether the
Figure 3.10: New LAMP program module for processing time-resolved data. (a) The main LAMP interface, where the working path and data path can be specified. Upon starting LAMP, ‘event_file’ is entered in the manipulations section (bottom left) to open the ‘Event file analysis’ module. (b) To perform the event file analysis, a list mode file is selected from the working path specified in (a), as the input file. Before loading the file, the ‘Use trigger?’ and time delay box must be specified. For LAOS files, the ‘Use trigger?’ is set to sample; for stream files, it is set to no. For LAOS files, the time delay (min delay in ms) should be set to a time slightly shorter than the cycle time to account for cycle variation; no delay time is needed for stream files. The bin width is entered in the time/slice box (here 598.66 ms = 0.59866 s per slice) and the temporal resolution is set by the number of slices. Here, the time/slice corresponds to \( \frac{T}{30} \), but the number of slices = 60, such that the temporal resolution is 2-fold greater than the temporal precision, \( n = 2 \).
alignment factor should be calculated for flow-SANS or rheo-SANS (fitting $\phi_0$ vs. $\phi_0 = 0$). After the NCNR macros are loaded, the procedure windows to be modified can be found under Windows $\rightarrow$ Procedure Windows. The three procedure windows to replace are the event mode processing panel (EventModeProcessing.ipf), the multiple reduce panel (MultipleReduce.ipf) and the circular and sector average panel (CircSectAve.ipf). To replace each panel, unlock the code and delete the current code, paste each code below, and then compile the code before closing the panel.

### 3.3.3.2 Event Mode Processing

Changes to the event mode processing panel allow the sliding bin method to be enacted. In the original NCNR protocol, the user could only choose the number of bins, and from there, the bin width was calculated discretely. To implement the sliding bin method, the event mode processing panel was modified, as seen in Figure 3.11. In the original panel, only the ‘max time’ and ‘number of slices’ inputs were available, such that the bin width was defined by $t_w = \frac{\text{max time}}{\text{number of slices}}$ (see Figure 3.1 above). In the new panel, there are three inputs: ‘slice width of period,’ ‘max time,’ and ‘number of slices.’ In this panel, the bin width is now defined as $t_w = \frac{\text{max time}}{\text{slice width of period}}$, which sets the temporal precision. Then, the temporal resolution is defined by the ‘number of slices’ option, which is generally chosen as an integer multiple, $n$, of the ‘slice width of period’ input. In Figure 3.11, the ‘number of slices’ is 8-fold higher than the ‘slice width of period’ input ($n = 8$), meaning that the temporal resolution is now improved by 8-fold from using the sliding bin method. To obtain the standard binning method using the new panel, the inputs of ‘number of slices’ and ‘slice width of period’ are set equal to each other.

While the processing mode is set to oscillatory in Figure 3.11, the same procedure can be used in stream mode. Stream mode should be selected for all non-oscillatory time-dependent deformations using this method, including shear startup. There is one minor difference between the stream mode processing and oscillatory mode processing. In both modes, $t_w = \frac{\text{max time}}{\text{slice width of period}}$; however, the time step varies between the two modes. In oscillatory mode, $t_s = \frac{\text{max time}}{\text{number of slices}}$. This spacing occurs because
the bins centered at points near the end of the cycle require the binning to ‘wrap around.’ In this case, neutrons from the beginning of the cycle are added to a particular bin. For example, in a cycle of length $T$ and bin width $T/10$ where $n = 2$, the first bin will be centered at $T/20$ but the final bin will be centered at $T$. This means that the range of the final bin spans $19T/20$ to $21T/20 = T/20$, which is why the neutrons from the cycle start are added to this bin. In stream mode, however, there is no cycle; the user only has a single stream of data. Therefore, the bins in stream mode cannot ‘wrap around’ as they do in oscillatory mode. In this case, then, $t_s = \text{max time}/(\text{number of slices} + n)$. This results because the first and last bins in stream mode must be centered at $t_w/2$ and $T - t_w/2$, respectively.

![Figure 3.11: New event mode processing panel for implementing the sliding bin method. The original panel included the ‘max time’ and ‘number of slices’ inputs only. The ‘slice width of period’ corresponds to the bin width, and the ‘number of slices’ can now be chosen as a multiple of the slice width. Here, $n = 8 =$ number of slices/slice width of period.](image)

3.3.3.3 Multiple Reduce

The multiple reduce panel speeds up data processing by allowing multiple files to be reduced at the same time. This feature is especially important when processing time-resolved data, which may be binned into hundreds of slices. The new multiple reduce panel can be seen in Figure 3.12. In the original multiple reduce panel, the only available inputs
were the ‘file number list’ and ‘protocol,’ as seen in Figure 3.12. In the new panel, there are additional options that are then printed in a pop-up window labeled ‘Files and Factors’ (see left of Figure 3.12). When reducing multiple files, either the ‘Flow $A_f$’ or ‘Rheo $A_f$’ box can be checked to perform the alignment factor calculation, given by Equation 2.36. When ‘Flow $A_f$’ is selected, the angle of increased intensity, $\phi_0$, is fit and printed into the ‘Files and Factors’ table along with the alignment factor. When ‘Rheo $A_f$’ is selected, $\phi_0$ is automatically set to 90° due to the symmetry imposed by the method. In this case, just the alignment factor value is printed (see example table in Figure 3.12). In addition to the alignment factor and/or angle, the SANS run number and run label are also printed in the table. To specify the q-range ($q^*$) over which to calculate the alignment factor, the ‘Set Q’ button can be used, where the center of the q-range (in $\AA^{-1}$) is specified, along with a q-width, where $\Delta q$ is defined from the q-center to the end of the q-range. The $\Delta q$ here is specified in $\AA^{-1}$, unlike in the Averaging panel (discussed below) where it is specified in pixels. The choice of $\Delta q$ in $\AA^{-1}$ was made to ensure that the same $q^*$ was used across experiments with different configurations, as the number of pixels varies when the sample-to-detector distance is changed.

Figure 3.12: New multiple reduce panel for improved processing of time-resolved data. The ‘Flow $A_f$’ and ‘Rheo $A_f$’ boxes were added to allow the alignment factor (and $\phi_0$ for flow-SANS) to be calculated during data reduction. The ‘Set Q’ button allows the $q^*$ range to be specified. The file number and label, as well as calculated values, are all printed after reduction in the ‘Files and Factors’ table.
3.3.3.4 Annular and Sector Averaging

Finally, the annular averaging and sector averaging panel (CircSectAve.ipf) allows the intensity distribution, \( I(q^*, \phi) \), to be examined over a specified \( q^* \) for a reduced file. In the averaging panel, \( q^* \) is defined by entering the center of the \( q \)-range and a \( q \)-width in pixels, as seen in Figure 3.13b. Note that the number of pixels that constitutes \( q^* \) is a function of the experiment sample-to-detector distance. This process creates an annulus around the particular scattering file, shown in Figure 3.13c, where the middle green circle is the ‘\( q \)-center.’ Here, the \( q \)-width is the total width of the \( q \)-range in pixels (total width between blue lines in Figure 3.13c), not the half-width defined above for the Multiple Reduce panel. In the original averaging panel, after the \( q \)-range was defined, \( I(q^*, \phi) \) could be displayed (Figure 3.13d) by pressing ‘Do average,’ and had to be saved by checking the ‘save to disk’ box in Figure 3.13b. However, this method is inconvenient if several \( q \) ranges are used to examine multiple \( I(q, \phi) \) before selecting the final \( q^* \) over which to define \( I(q^*, \phi) \) and to calculate the alignment factor. In this process, the alignment factor would need to be calculated for each \( I(q, \phi) \), which requires saving and renaming each file, and then calculating the value for each particular \( q \) input.

In the new averaging panel, some of these issues have been addressed. Now, when the \( q \)-center and \( \Delta q \) are specified and ‘Do average’ is selected, the values for \( I(q^*, \phi) \) and the associated error for each point are printed in a table labeled ‘Intensity Distribution’ (Figure 3.13a). Additionally, the value of the alignment factor, \( A_f \), is printed in the command window, which can be seen in Figure 3.13e. Along with \( A_f \), the calculated values for the integral in the numerator and denominator of Equation 2.36 are printed below \( A_f \). Printing these three values helps the user select an accurate \( q^* \) range, because the user can directly observe how the alignment factor input integrals and resulting calculation change over each selected \( q \)-range.
Figure 3.13: New averaging panel for determination of $q^*$ region and associated error in alignment factor calculation. a) Printed values of the angle, $\phi$, $I(q, \phi)$ (labeled aveint), and uncertainty associated with the intensity at each angle (sigave); values are used to calculate the uncertainty in $A_f$. b) Average panel, where the q-center is specified in Å$^{-1}$ and $\Delta q$ in pixels. c) Visual representation of the specified q-annulus (between the blue concentric circles) on the 2-D scattering pattern; q-center is shown by the green middle circle. d) $I(q, \phi)$ output as specified by the q-center and $\Delta q$ inputs. e) Printout of the calculated $A_f$ and upper and lower integral values.
3.4 Analysis of SANS configuration parameters

3.4.1 Motivation

When analyzing shear-induced microstructural rearrangements between multiple sample preparations, experiment locations (NCNR, ILL, or other), instruments and configurations, the factors that affect the calculation of the alignment factor (Equation 2.36) must be well-understood such that results between trials are reproducible. In Section 2.6.2 and Appendix B, the absolute scattering intensity of each sample (with the same level of branching) was shown to overlay regardless of the preparation, acquisition location, configuration, and so forth, but only the 1-D reduced scattering curve was examined. Here, it will be shown that even minor changes in the 1-D scattering curve or the resolution of a particular configuration can have a significant effect on the 2-D data, which is subsequently used to calculate the alignment factor. Small changes in the absolute intensity ultimately affect the background of the intensity distribution, \( I(q^*, \phi) \), which propagates and leads to significant differences in the calculated value of \( A_f \). Understanding how these differences ultimately affect the measured responses of the WLMs, and choosing the optimal configuration for SANS experiments, enables results to be reproduced and firm conclusions to be drawn across experiments.

To illustrate the magnitude of the effect that small changes in the background may have on the alignment factor calculation, Figure 3.14 shows sample data from the low branching solution (0.01% wt NaTos). All data reported in this section was taken on this 0.01% wt solution during 1-3 (flow-vorticity) plane rheo-SANS experiments unless specifically noted. Experiments were performed on the NCNR NGB-30 m SANS instrument at a wavelength and spread of \( \lambda = 6 \, \text{Å} \) and \( \Delta \lambda / \lambda = 13.1\% \). Figure 3.14a shows the 1-D reduced curves for the sample at rest and at \( \dot{\gamma} = 45 \, \text{s}^{-1} \) at a configuration using one guide and a detector distance of 12 m, plus the 1-D curves for the \( \dot{\gamma} = 45 \, \text{s}^{-1} \) data with an added background of 1 unit (+1 cm\(^{-1}\)) and a subtracted background of -1 unit (-1 cm\(^{-1}\)). As seen in Figure 3.14a, the intensity of the simulated \( \dot{\gamma} = 45 \, \text{s}^{-1} \) data is either within the uncertainty of the true intensity data, or just outside of the uncertainty. As the intensity of the data at rest is significantly higher than all three of the curves under shear, the choice of using a background value of \( \pm 1 \, \text{cm}^{-1} \) to examine changes to the alignment factor is a reasonable choice. Note that as previously
discussed in Chapter 2, shearing the WLMs leads to flow-alignment of the micelles, so it is expected that the absolute intensity of the WLMs decreases under shear.

![Figure 3.14](image)

Figure 3.14: Sample data for the 0.01% wt NaTos solution illustrating the effect of the background on the absolute intensity, intensity distribution, $I(q^*, \phi)$, and resulting $A_f(q^*)$ calculation. Data is shown for a configuration of 1 guide and a detector distance of 12 m, at a shear rate of $\dot{\gamma} = 45 \text{ s}^{-1}$ for a trial of 300 s. (a) 1-D absolute scattering intensity for the sample at rest and under shear with different backgrounds. While the intensities of the shear data (□) and simulated data (● = +1, △ = −1) are close to, if not within, uncertainty of one another in the $q^*$ region, the absolute intensity for data at rest is significantly higher. (b) $I(q^*, \phi)$ for the shear and simulated data. Despite the three distributions appearing nearly identical, the calculated $A_f$ values are not within uncertainty.

In Figure 3.14b, the intensity distribution, $I(q^*, \phi)$, is shown for the data at $\dot{\gamma} = 45 \text{ s}^{-1}$, and the simulated data with the same added or subtracted background of 1 unit (1 cm$^{-1}$). The three intensity distributions look nearly identical, however, the shift in the background has a significant effect on the alignment factor calculation. In fact, the effect is large enough that the calculated alignment factors for the three distributions are not within the uncertainty of one another. It is important to note that the uncertainty reported in this dissertation in regard to the alignment factor stems from the uncertainty around the intensity distribution at each point (see Section 2.6.3) and does not encompass all sources of uncertainty. For example, when the number of points in $I(q^*, \phi)$ is decreased, the uncertainty due to the measured intensity also decreases because there are more neutron counts per angular bin. However,
when the number of points is decreased, the uncertainty associated with the integral approximation (Chapter 2, Section 2.6.3) increases because there are fewer points; this uncertainty is much more difficult to quantify. Therefore, the value of the alignment factor in Figure 3.14b is reported to three significant digits for illustrative purposes, but in reality, the true value of the alignment factor cannot be determined to the accuracy of three significant digits.

Figure 3.14 helps illustrate the importance of understanding how configurational changes affect the recorded 2-D scattering and the associated resolution, as even minor changes in $I(q^*, \phi)$ lead to statistically different values of the alignment factor. This effect has important implications when results are compared between different facilities and instruments, configurations, and scattering planes. For example, despite the fact that all data is reduced to an absolute standard, the instruments at the NCNR and the ILL will have different associated backgrounds, resolution, detector efficiency, and smearing. Thus the instrument configuration plays an important role because the resolution and number of pixels in a certain q-range changes based on the detector distance and number of guides. Further, the slits used in front of the rheometer or shear cell, and at the source aperture, also contribute to the orientational and spatial smearing. Finally, the effect on the background between scattering planes is especially important, as agreement between the 1-2 and 1-3 plane results for a particular example suggests that the orientation distribution function (ODF) is uniaxial, whereas results that do not agree suggest a non-uniaxial ODF. For example, if minor variations in the background contribute to an observed difference in the alignment and/or orientation angle, when such differences do not actually exist, one may conclude incorrectly that the ODF is not uniaxial and that structural differences exist between planes. Fully resolving these effects thus motivates the results reported in the following sections, which were used to select the optimal SANS configurations for the experiments reported in this dissertation.

3.4.2 Reproducibility between repeated trials and effect on $A_f$

First, it was necessary to confirm that the microstructural response to shear was not affected by time or aging in the WLM solutions. This confirmation ensures that any observed differences in the background or alignment factor calculation discussed above are not an
effect of evaporation, aging, or any other changes to the sample over the experiment duration. Here, we examine the intensity distribution, \( I(q^*, \phi) \), and its reproducibility over time. As shown in Figure 2.15 previously, the alignment factor response over long times (24 h+) appears stable for LAOS experiments, suggesting that these WLM solutions and the shear-induced microstructural response is quite stable both under shear and over repeated trials. However, it was also important to verify that \( I(q^*, \phi) \) was reproducible over multiple trials and did not significantly change over the long experiment duration. Figure 3.15 confirms the solution stability between steady shear trials taken 11 hours apart during SANS steady shear and relaxation experiments. The experiments were performed at a detector distance of 8 m, with one guide, where the source aperture at the nozzle was 5 mm and the sample aperture in front of rheometer was 2 mm (see Figure 3.20 for a diagram of these slits). Here, the sample shear rate was \( \dot{\gamma} = 45 \text{ s}^{-1} \), where the two trials were recorded over 300 s each, where \( t_{\text{start}} = 360 \text{ s} \) and \( t_{\text{end}} = 660 \text{ s} \) after the startup of shear. Trials discussed throughout this analysis (Section 3.4) were performed with a minimum rest time of 180 s between consecutive runs unless otherwise noted.

Figure 3.15: Reproducibility of the microstructural response to shear between steady shear trials, as represented by \( I(q^*, \phi) \). The trials were taken 11 hours apart from one another, for 300 s each. The calculated alignment factor, \( A_f \), between trials is identical between two significant digits, confirming that the WLM response is not affected by shear, evaporation, aging, or other effects during the duration of the SANS experiments.
As seen in Figure 3.15, the shear-induced intensity distribution \( I(q^*, \phi) \) is nearly identical between the two trials; notably, the background level does not change over time. The calculated alignment factor between trials is equal within two significant digits. These results are clearly within the calculated uncertainty of one another (\( \delta A_f = 0.005 \) for both trials), unlike the sample data shown in Figure 3.14. As previously mentioned, the true value of the alignment factor cannot be determined to the accuracy of three significant digits, but is shown here based on the calculations alone. Therefore, as long as the sample is given adequate time to relax between trials, the long duration of SANS experiments does not appear to significantly affect the reported results. Although the experiments were performed at the same shear rate, the data in Figure 3.15 is not equal to the data in Figure 3.14 above. The data in Figure 3.14 was collected after 360 s of shearing at \( \dot{\gamma} = 4.2 \text{ s}^{-1} \) before increasing the shear rate to \( \dot{\gamma} = 45 \text{ s}^{-1} \), and this solution has an associated hysteresis.

### 3.4.3 Effect of detector distance

The detector distance chosen for an experiment can drastically change the calculated alignment and other quantities, due to differences in resolution and the absolute scattering intensity. Figure 3.16 shows the differences in the scattering intensity that result from different resolutions and detector distances for the 0.01% wt NaTos solution at rest (rheometer configuration). All configurations used one guide, and had an aperture of 8 mm and a slit of 5 mm. In Figure 3.16a, the data at each configuration appears to agree fairly well. Toward the lower end of a q-range that each detector distance can access, however, the resolution becomes poor. For example, the absolute intensity of the data from the 1.65 m configuration (which can be seen better in Figure 3.16b) is significantly lower than that of the other configurations in the region of the interaction peak. As the detector distance increases, the absolute intensity in the interaction peak area gets higher, due to the better resolution. At a detector distance of 8 m and higher, the scattering in the peak area is unaffected by the detector distance.
Figure 3.16: Effect of the detector distance and associated resolution on the 1-D absolute intensity of the 0.01% wt NaTos solution at rest. (a) 1-D absolute intensity for distances 1.65 to 8 m. The absolute intensity of the scattering from the 8 m configuration is clearly higher than the other configurations. (b) The absolute intensity of the scattering from the 8 m to 13 m configurations is identical within uncertainty. The absolute intensities for the shorter detector distances (< 4m) are evidently lower than in the longer distances.

These results are not surprising when the q-resolution for each configuration is examined, referred to as $\sigma_Q/Q$, where the q-standard deviation, $\sigma_Q$, is given by [20]:

$$\sigma_Q = \frac{2\pi}{\lambda L_2} \sigma_r \quad (3.12)$$

where $\sigma_r$ is the spatial standard deviation, or the standard deviation of the neutron beam size at the detector, and $L_2$ is the sample-to-detector distance. At the start of the q-range in the 1.65 m configuration (high q-values), $\sigma_Q/Q = 5.3\%$, whereas at the lowest q-value within the range, $q = 0.017 \, \text{Å}^{-1}$, the resolution worsens to $\sigma_Q/Q = 19.4\%$. As $q = 0.017 \, \text{Å}^{-1}$ occurs in the region of the interaction peak, the lower absolute intensity in this region seen in Figure 3.16 is the result of the increasingly poor resolution at this detector distance. With increasing detector distance, $\sigma_Q/Q$ across the accessible q-range actually becomes worse; for the 13 m configuration used here, $\sigma_Q/Q = 6.2\%$ and 28\% for the high and low-q value resolutions, respectively. While an increasing $L_2$ serves to decrease $\sigma_Q$, the beam size is larger and the q-values are lower at longer detector distances, which ultimately increases $\sigma_Q/Q$. However,
as increasing the detector distance changes the accessible q-range, the absolute intensity in the region of the interaction peak increases due to better resolution with increasing detector distance (until 8 m). The absolute scattering intensity is indistinguishable between detector distances of 8 m and 13 m, shown in Figure 3.16b. The wavelength spread also affects $\sigma_Q/Q$, but because the wavelength spread is held approximately constant across all experiments, this effect will not be discussed further.

The small differences in 1-D absolute scattering intensity that result from the configuration detector distance are more noticeable when the 2-D data is examined. Of particular interest is the effect on the intensity distribution, $I(q^*,\phi)$, which is obtained via annular average of the 2-D data in the $q^*$ annulus. The intensity distribution directly affects the calculated value of the alignment factor, as given by Equation 2.36. Figure 3.17 examines the intensity distribution under shear for the 0.01% wt NaTos solution for two shear rates: 4.2 (Figure 3.17a, b) and 45 s\(^{-1}\) (Figure 3.17c, d). The experiment shown in Figure 3.17 was performed by shearing the WLMs for 360 s at $\dot{\gamma} = 4.2$ s\(^{-1}\), immediately increasing the shear rate to $\dot{\gamma} = 45$ s\(^{-1}\), and shearing for an additional 360 s. The $I(q^*,\phi)$ distributions shown in Figure 3.17a and b were collected at $\dot{\gamma} = 4.2$ s\(^{-1}\) from $t_1 = 60$ to $t_2 = 360$ s, whereas $I(q^*,\phi)$ in Figure 3.17c and d were collected at $\dot{\gamma} = 45$ s\(^{-1}\) from $t_1 = 60$ to $t_2 = 360$ s after the shear rate increase, or $t_1 = 420$ to $t_2 = 720$ s total experiment time. As the sample did not have a rest period between shear rates, the results in Figure 3.17 cannot be compared to those in Figure 3.15. In Figure 3.17, the intensity distribution is calculated over the same $q^*$ range for all detector distances. Differences in the measured $I(q^*,\phi)$ can result for several reasons. First, the number of pixels over the same $q^*$ is significantly lower at shorter detector distances than in longer ones. Next, the lower absolute scattering intensity seen from the 1-D curves in Figure 3.16 for the shorter detector distances can lead to a lower background in the measured $I(q^*,\phi)$. Finally, the quality and sharpness of the measured distribution depends on the number of scattering counts in the region of $q^*$. At longer detector distances where the count rates are lower (for an equal number of guides), poor statistics can lead to noisy data and a noisy measured $I(q^*,\phi)$. The uncertainty in the alignment factor calculation discussed in Section 2.6.3 only takes into account the uncertainty in the intensity distribution, which
addresses the poor statistics. However, uncertainty in the alignment factor due to the first
two reasons are not accounted for by this simple uncertainty calculation.

Figure 3.17: Effect of the detector distance on the resolution of the microstructural response
to shear, as represented by $I(q^*, \phi)$ for two shear rates: $\dot{\gamma} = 4.2$ s$^{-1}$ (a, b) and $\dot{\gamma} = 45$ s$^{-1}$ (c, d).
Distances 1.65 to 6 m are shown in (a, c), and 6 to 13 m are shown in (b, d). For both shear
rates, longer detector distances lead to sharper intensity distributions and higher calculated
values of $A_f$. Higher $A_f$ values are obtained at longer distances despite the lower background
values at shorter detector distances, which serves to artificially increase the value of $A_f$ (see
Figure 3.14b). The low background is most drastic in $I(q^*, \phi)$ from at 1.65 m, where the 1-D
absolute intensity is the lowest due to poor q-resolution.

Figure 3.17a and b shows $I(q^*, \phi)$ for $\dot{\gamma} = 4.2$ s$^{-1}$ for detector distances of 6 m and
less (a) and 6 m and greater (b). In Figure 3.17a, the intensity distribution at 1.65 m is sig-
nificantly different than the other distributions. Most notably, the distribution appears to be
shifted downwards as compared to the other distributions. This shift in the distribution is a
result of the poor q-resolution in the $q^*$ regime at 1.65 m. The peaks in the distribution at 1.65 m are not as sharp as the peaks for the 3 m and higher detector distances. In addition to the poor q-resolution, this peak smearing occurs because there are only three pixels across the range of $q^*$ at 1.65 m. At a detector distance of 13 m, for example, thirteen pixels cover $q^*$. With fewer pixels, the intensity smearing becomes worse, leading to peaks that are not well-defined for configurations with few pixels. The pixel effect can be seen better for the 1.65 m configuration in Figure 3.17c at $\dot{\gamma} = 45$ s$^{-1}$. Here, the intensity around the peaks is much lower than in the other configurations and has a much higher associated uncertainty due to the low number of pixels included in the annular average of $I(q^*, \phi)$. Despite significant differences in $I(q^*, \phi)$ in Figure 3.17a and b at $\dot{\gamma} = 4.2$ s$^{-1}$, the calculated value of the alignment factor is roughly equal between all detector distances ($A_f = 0.04$ to 0.05). Two factors lead to this result: the lower backgrounds of $I(q^*, \phi)$ in the shorter detector distances artificially increase $A_f$, while the lower absolute intensities at these distances serve to decrease $A_f$. However, this result is only observed at low $A_f$ values; the calculated $A_f$ between configurations varies more significantly as the shear rate increases (see Figure 3.17c, d).

As seen in Figure 3.17, the effect of the detector distance depends on the applied shear rate or the overall degree of orientation. As the detector distance is increased from 1.65 m in Figure 3.17 a and b ($\dot{\gamma} = 4.2$ s$^{-1}$), the background of $I(q^*, \phi)$ gets noticeably higher because the 1-D absolute intensity at these detector distances is higher. The peaks also sharpen with increasing detector distance, because of the larger number of pixels used in the determination of $I(q^*, \phi)$. However, at $\dot{\gamma} = 45$ s$^{-1}$ (Figure 3.17 c, d), the effect of the background is less noticeable, while the differences in peak sharpness are more apparent. These trends can be explained by the increasing alignment in the WLMs with increasing shear rate. As the WLM segments align further (independent of configuration), the background decreases and the peak intensity increases. Therefore, as the shear rate is increased, the effect of background level on $I(q^*, \phi)$ between configurations effect is minimized, while differences in the peak intensity with configuration are magnified. At higher shear rates, the peak smearing effects are more substantial than the background effects, which can be seen by the calculated value of the alignment factor at $\dot{\gamma} = 45$ s$^{-1}$ (Figure 3.17 c, d). Whereas at $\dot{\gamma} = 4.2$ s$^{-1}$, $A_f$ was
nearly independent of configuration, at $\dot{\gamma} = 45 \text{ s}^{-1}$, $A_f$ continually increases with increasing detector distance. In fact, $A_f$ is more than 50% greater at 13 m than at 1.65 m. The large variation in the calculated $A_f$ at higher shear rates illustrates why the configuration must be chosen carefully for each experiment to ensure reproducibility. However, there are trade-offs involved when choosing the optimal detector distance. The scattering count rate at 6 m is over double that of the 13 m configuration, and the calculated alignment factor at 6 m is within 10% of the value calculated at 13 m. Additionally, any experiments done at 13 m will have significantly poorer temporal resolution due to this low count rate. The configuration at 13 m is not ideal for another reason: as the beam was not perfectly centered on the detector at this configuration, part of the $q^*$ region was cut off at the $\phi = 0^\circ$ and $\phi = 90^\circ$ portions of the detector. This leads to a $I(q^*, \phi)$ that is not perfectly symmetric in Figure 3.17d. To optimize temporal resolution, counting time, and accuracy of the alignment factor calculation, the optimal detector distance was chosen to be 8 m for this particular rheo-SANS experiment. In this configuration, $q^*$ within the center of the q-range, which is a good rule-of-thumb when selecting configurations. This 8 m configuration, seen previously in Figure 3.15, will be used in the majority of the trials in the following sections.

3.4.4 Effect of the number of guides

Neutron guides can be used to improve the flux of the incident neutron beam hitting the sample, which increases the sample scattering count rate. In time-resolved neutron scattering experiments, the use of guides significantly improves the temporal resolution by increasing the number of counts per unit time at all times in the experiment. Neutron guides essentially work as mirrors for neutrons, which help reflect and focus the neutron beam to maximize the neutrons that interact with the sample. The guides cannot perfectly focus the beam, however, such that increasing the number of guides also increases the beam size. With a larger beam size, the accessible q-range is sometimes altered because some of the low q-values can be eliminated by the presence of the large beam. For example, in an 8 m configuration, shown in Figure 3.18a for one and four guides, the accessible q-range is altered by the guides. While using one guide, the accessible range is 0.0055 to 0.0554 Å$^{-1}$,
whereas this range shortens to 0.0072 to 0.0554 Å⁻¹ while using four guides. As the use of guides also increases the q-smearing of the experiment due to the larger beam, the magnitude of this effect on the alignment factor and other quantities had to be elucidated.

Figure 3.18: Effect of the number of guides, width of slits, and associated resolution on the 1-D absolute intensity of the 0.01% wt NaTos solution at rest. (a) 1-D absolute intensity for distances 1.65 to 8 m at one and four guides. The absolute intensity of the scattering does not appear to be altered by the use of one vs. four guides. (b) The 8 m configuration is examined with different sized apertures (at nozzle) and slits (front of rheometer). The absolute scattering intensity at rest does not appear to be altered by the aperture or slit size.

As the number of guides is increased, the q-resolution $\sigma_Q/Q$ worsens (Equation 3.12) for the same accessible q-range, because the beam size increases. If the number of guides changes the accessible q-range, $\sigma_Q/Q$ at the lowest q-value will actually decrease, because the lowest q-value has increased, and then subsequently increase as the number of guides is increased over that same q-range. The effect of the number of guides on $\sigma_Q/Q$ is fairly small; for the 8 m configuration with one guide shown in Figure 3.15 and in Figure 3.18a, $\sigma_Q/Q= 5.7\%$ and 25.9\% for the maximum and minimum q-values, respectively. Increasing to two guides, $\sigma_Q/Q= 5.8\%$ and 27.9\%, before decreasing at 3 guides due to a change in the q-range. In Figure 3.18a, the 8 m configuration is shown with 4 guides, which has resolutions of $\sigma_Q/Q= 6.1\%$ and 26.2\% for the high and low q-values.

In configurations at the same detector distance but with a different number of guides, such as those shown in Figure 3.18a for 8 m, only the q-resolution $\sigma_Q/Q$ should change.
The number of pixels over which to determine \( I(q^*, \phi) \) and calculate the alignment factor remains the same because the distance is not changing; therefore, the q-smearing in relation to the number of guides should be the only relevant quantity for this analysis. Figure 3.19 seems to confirm this. In Figure 3.19, the distribution \( I(q^*, \phi) \) is examined for the 0.01% wt NaTos solution at a shear rate of \( \dot{\gamma} = 26.4 \text{ s}^{-1} \), for three 8 m configurations (with one, four or five guides) with the same slit and aperture widths as in the conditions above (slit = 5 mm, aperture = 8 mm). The distributions shown in Figure 3.19a are those of the steady state \((t_1 = 600 \text{ s and } t_2 = 780 \text{ s after shear startup})\), where the alignment factor remains steady in time when \( t > 600 \text{ s} \). The two distributions in Figure 3.19b were taken over a longer time \((t_1 = 420 \text{ s and } t_2 = 780 \text{ s after shear startup})\) to double the total number of counts. The higher number of counts in the distributions in Figure 3.19b serves to minimize the uncertainty, such that the differences between the two extreme configurations could be clearly identified.

The steady state curves shown in Figure 3.19a for the one, four and five guide configurations show that the number of guides does not affect the background of the intensity distribution, \( I(q^*, \phi) \). In fact, the steady state distributions nearly overlay between the three configurations until the regions of the maximum intensity. In these regions (near \( \phi = 90^\circ \) and \( \phi = 270^\circ \)), the peak intensity is maximum in the one guide configuration. As the q-resolution worsens with the number of guides, the four and five guide configurations show slightly lower maximum intensities around the peaks. While the four and five guide configurations are nearly identical, the peaks are slightly lower in the five guide configuration. Clearly, as the number of guides increases, the peak-smearing worsens, leading to lower calculated values of the alignment factor. However, this peak smearing effect is not that large in magnitude; the alignment calculated from the one guide configuration is only 10% higher than that calculated from the configurations with four and give guides.

The two most extreme configurations (one and five guides) were then examined further, which can be seen in Figure 3.19b. The number of counts in these curves was over twice that of the curves in Figure 3.19a. Once again, the background level is unchanged by the number of guides in the configuration. As the number of counts in the distributions in Figure 3.19b is doubled, the uncertainty around each point in \( I(q^*, \phi) \) is much lower than in
Figure 3.19a. Significant differences between the two extreme configurations are apparent, as the peak height for the one guide configuration is over 3 cm\(^{-1}\) higher than in the five guide configuration. This leads to an alignment factor that is larger for the one guide configuration, but once again, the value of \(A_f\) between configurations is within 10%.

![Figure 3.19: Effect of the number of guides on the resolution of \(I(q^*, \phi)\) for the 0.01% wt NaTos solution at \(\dot{\gamma} = 26.4 \text{ s}^{-1}\).](image)

(a) Steady state intensity distributions for configurations with 1, 4 or 5 guides at 8 m. The background is unchanged by the number of guides, but increasing the number of guides decreases the peak intensity of \(I(q^*, \phi)\), thereby decreasing \(A_f\). (b) As there is little difference between the 4 and 5 guide configurations in (a), the 1 and 5 guide configurations are compared for a longer duration of time (\(\Delta t = 360 \text{ s}\)). Similar to the result seen in (a), the 5 guide configuration leads to a lower value of \(A_f\) because of peak-smearing, leading to a lower peak intensity than in the 1 guide configuration.

3.4.5 Effect of the aperture and rheometer slit width

In both the 1-3 plane rheo-SANS and 1-2 plane flow-SANS experiments discussed in this dissertation, a source aperture and sample slit must be used. In this section, the effect of the dimensions of these slits will be discussed for the 8 m sample-to-detector distance. The placement of the source aperture and sample slit can be seen for a standard rheo-SANS configuration in Figure 3.20. Both of these slits can be easily altered in an experiment to decrease the spatial smearing in a measurement, which can result from the curvature of the rheometer. The source aperture is in place to confine the beam to a narrow height and width,
and $w$, respectively (Figure 3.20a). After the neutrons pass through the velocity selector, the source aperture, which is placed at the nozzle shown in Figure 3.20, blocks neutrons at the edges the beam. This aperture thus narrows the beam to certain dimensions, from which the resolution and smearing can be determined.

Figure 3.20: Placement of the source aperture and sample slit for a standard rheo-SANS configuration. The black boxes detail the full cadmium slit piece, whereas the smaller rectangles inside specify the slit location and dimensions. In (a), the source aperture and nozzle are highlighted, where the actual aperture height, $h$, and width, $w$, are specified by the yellow rectangle. The back side of the sample slit is shown in blue. Photos adapted from reference [21].

The neutron beam has a triangular wavelength distribution (see Figure 3.21). In addition to narrowing the beam to smaller dimensions by blocking some of the incoming neutrons, smaller source apertures may also slightly reduce the wavelength spread, $\Delta \lambda / \lambda$, as the blocked neutrons may come from the tail ends of the distribution. However, smaller source apertures also reduce the overall flux hitting the sample, which presents a challenge for samples at low concentrations. For example, reducing the source aperture from $w_{\text{aperture}} = 8$ mm to $w_{\text{aperture}} = 5$ mm in these experiments reduced the overall count rate by $\approx 25\%$ for the 8 m, one guide configuration. In certain experiments, the smearing effects discussed below
may be a necessary tradeoff to gain 25% higher flux.

Figure 3.21: Triangular wavelength distribution for the neutron beam, where $\lambda$ is the wavelength and $\Delta \lambda$ is the wavelength spread. Reprinted from reference [20].

In the 1-3 plane rheometer configuration, the primary use for the sample slit is to confine the scattering volume to the region where the flow direction is primarily orthogonal to the beam direction and the vertical direction. The differences in the sample slit configuration for the 1-2 shear cell will be discussed in the next section. This region is highlighted in blue Figure 3.20a and b; this region in relation to the flow direction can be seen in Figure 2.10. As the Anton-Paar geometries used in the rheo-SANS experiments have a height of 36 mm, the height of the rheometer slit is usually held constant at $h_{slit} = 20$ mm to eliminate end effects. Therefore, the width, $w_{slit}$, of the rheometer slit is usually the length scale that is adjusted in these experiments. The use of larger slit widths increases the scattering volume, and thereby scattering count rate, but will also increase spatial smearing. The increase or decrease in scattering volume roughly scales with the increase or decrease in count rate. For example, a reduction in width from $w_{slit} = 5$ mm to $w_{slit} = 2$ mm led to a 2.67-fold reduction in count rate, which corresponded to a 2.5-fold reduction in the scattering volume for the 8 m and one guide configuration. The true width of the region where the flow direction is mutually orthogonal to the beam direction and the vertical is a line of infinitesimal width; therefore any non-zero width of the rheometer slit leads to smearing in space from the rheometer curvature.
The optimal aperture and slit widths should thus be selected to minimize orientational and q-smearing, while maximizing the scattering count rate, which will be further discussed below. At rest, the aperture and slit width do not affect the 1-D absolute scattering intensity, as seen in Figure 3.18b.

To understand the effect of the aperture, differing source apertures were examined for the 0.01% wt NaTos solution. As seen in Figure 3.22a, the intensity distribution $I(q^*, \phi)$ and calculated alignment factor differ when the aperture size is changed. For the wide aperture and wide slit configuration ($w_{aperture} = 8$ mm, $w_{slit} = 5$ mm), the background of the intensity distribution is significantly higher than in the two configurations where both slits are smaller ($w_{aperture} = 5$ mm, $w_{slit} = 2$ mm). The wider source and sample slits lead to an alignment factor that is about 10% lower than for narrower slits. As compared to the narrow slit configurations, the wide slit configuration measures more orientational smearing from the rheometer slit, and more spatial smearing from the aperture. The maximum intensity of the wide slit configuration is about equal to that of the configuration with four guides but narrower slits, suggesting that the wider slits lead to a peak smearing that is similar to the peak smearing seen when the number of guides is increased. When the two narrow slit configurations are compared in Figure 3.22a, the effect of the guides is similar to that observed in Figure 3.19, as the background does not change but the peak intensity is smeared and has a lower absolute intensity for the higher guide configuration. The calculated alignment factor is the same between the one and four guide configurations even though the peak intensity is higher in the one guide configuration and the background is the same between both configurations. This is likely an effect of the noise associated with $I(q^*, \phi)$ for the one guide configuration, however, which results from the low count rates and total scattering counts when the narrow slit and aperture are used.

After a certain reduction in width, there is no apparent added benefit of further reducing the source aperture. Figure 3.22b shows this is the case when reducing the aperture size from 5 mm to 3 mm, where there is no noticeable effect on the intensity distribution. The slight difference in the alignment factor calculation is within the uncertainty ($\pm 0.006$),
suggesting that the difference in the calculation is simply due to the low count rates and uncertainty in $I(q^*, \phi)$. Whereas the reduction from $w = 8$ mm to $w = 5$ led to a 25\% reduction in overall counts, the reduction in width from $w = 5$ mm to $w = 3$ mm had no effect on the overall count rate. This helps explain why there is no observable effect on the scattering when this additional reduction is implemented. From these results, it appears that 5 mm is the ideal width of the source aperture.

Figure 3.22: Effect of the width of the source aperture (at nozzle) and sample slit (in front of rheometer) on the resolution of $I(q^*, \phi)$. (a) When the source aperture is decreased from 8 mm to 5 mm, and the slit size is reduced from 5 mm to 2 mm, the effect of the number of guides seen above in Figure 3.19 is minimized. The background is higher in the wide slit configuration ($w_{\text{aperture}} = 8$ mm, $w_{\text{slit}} = 5$ mm) than in the two narrow slit configurations, leading to a lower value of $A_f$. (b) The source aperture is changed from 5 mm to 3 mm with no noticeable change in $I(q^*, \phi)$. $A_f$ is slightly larger for the 3 mm configuration, however, this is likely due to poor statistics and not a true structural change, as the intensity distributions are nearly identical.

Based on Figure 3.22a, it appears that reducing the rheometer slit size helps to decrease the background and orientational smearing in $I(q^*, \phi)$. Figure 3.23a further supports this notion, where the resulting $I(q^*, \phi)$ for the 0.01\% wt NaTos solution at $\dot{\gamma} = 45$ s$^{-1}$ is compared for two different slit sizes, 5 mm and 2 mm. While the intensity distributions in Figure 3.23a are quite similar, the maximum intensity is slightly higher in the 2 mm configuration, and the background is slightly higher in the 5 mm configuration. This higher background is
a direct result of the orientational smearing that occurs with a wider rheometer slit, as curvature effects start to become important and will add to the background. Once again, the effect of this smearing is relatively minor, as the alignment from the 2 mm configuration is only 10% higher than from the 5 mm configuration. It should be noted that the horizontal beam divergence through the path length of the rheometer is on the order of 10% to 20% of the sample slit width. These calculations for different configurations can be seen in Appendix D.

Figure 3.23: Effect of the width of the sample slit (in front of the rheometer) on $I(q^*, \phi)$ (a) While the distributions are similar, the narrow slit (2 mm) provides a lower background and lower orientational smearing as compared to the wide slit (5 mm) configuration for 1 guide. This results in an alignment factor that is 10% higher in the narrow slit case. (b) The same effect is observed in the configurations with 4 guides. The alignment factor is only 5% higher in the narrow slit case with 4 guides.

3.4.6 Effect of slit dimensions for 1-2 shear cell

In the 1-2 shear cell configuration, there is an additional slit in addition to the source aperture and sample slit used in the rheometer configuration. This third ‘translating slit,’ along with the slit that is placed prior to the shear cell, can be seen in Figure 3.24, where the slit placed prior to the shear cell will be referred to as the ‘stationary slit.’ The stationary slit is placed in the region encompassed by the black square in Figure 3.24, where the actual dimensions of the slit are highlighted in the smaller rectangle, with specified height, $h$, and
width, $w$. The translating slit is highlighted with the longer, red rectangle and left-pointing arrow in Figure 3.24. This slit is curved to match the curvature of the center of the shear cell gap ($r/H = 0.5$). During an experiment, the translating slit is translated to the left to overlay with the stationary slit, which further confines the region of accessible scattering.

Figure 3.24: Shear cell configuration with the stationary and translating slits. The stationary slit region is encompassed by the black square, where the actual slit dimensions are within the smaller blue rectangle, where $h$ is the slit height and $w$ is the width. The translating slit is highlighted by the red rectangle and arrow, where the width is significantly smaller than the width of the stationary slit to further confine the scattering volume.

While the stationary slit confines the scattering dimensions to those encompassing the flow-direction, the translating slit determines the width of the gap that is probed for each scattering experiment. For example, the width of the 1-2 shear cell gap is $H = 1$ mm, so a translating slit of width $w = 0.1$ mm probes 1/10th of the gap during each measurement. The smaller the width of the translating slit, the finer the spatial resolution. While the rheometer slit normally ranges from $w = 2$ to 5 mm by $h = 20$ mm, the stationary shear cell slit is much smaller, as the height of the region encompassing the flow-direction is significantly shorter. The dimensions of the stationary slit are approximately $w = 2$ mm by $h = 1$ to 5 mm. As gap
width of the shear cell is \( H = 1 \) mm, the translating slit width usually ranges from \( w = 0.05 \) to 0.3 mm.

To probe the effect of the slit configuration on the resolution of the data collected from the 1-2 shear cell, both the 0.01\% wt and 0.05\% wt NaTos solution were examined. There are considerable differences in the parameters that must be optimized in 1-2 plane versus 1-3 plane SANS measurements. In the 1-2 shear cell configurations, the total scattering volume is significantly smaller than in the rheometer configurations. For an average rheometer configuration, the slit is \( w = 5 \) mm by \( h = 20 \) mm, with a 1 mm gap on either side of the rheometer, for an approximate scattering volume of \( V \approx 200 \) mm\(^3\). For the 1-2 shear cell configuration with the largest scattering volume, where the translating slit is not used, the largest dimensions are 1 x 5 x 5 mm, for an approximate scattering volume of \( V \approx 25 \) mm\(^3\). In a more typical configuration, the dimensions are 0.1 x 5 x 5 mm (\( V \approx 2.5 \) mm\(^3\)), meaning that optimizing the count rate and total number of counts is extremely important in the 1-2 shear cell configurations. In these configurations, smearing effects from the factor previously mentioned may be a worthwhile trade-off to maximize the count rate and temporal resolution, and to minimize experiment time.

To examine the effect of the translating slit width, steady shear measurements were performed on the 0.01\% wt NaTos solution at seventeen slit positions across the gap, \( r/H \) for three slit widths: 0.05, 0.1 and 0.25 mm. The data is presented such that the translating slit is centered around the reported \( r/H \). For example, at \( r/H = 0.25 \), the 0.25 mm slit covers the spatial region from \( r/H = 0.125 \) to 0.375, whereas the 0.05 mm slit covers a much smaller spatial region, from \( r/H = 0.225 \) to 0.275. From the vastly different spatial regions covered, it would appear as though the spatial smearing between the finest and largest slit should be significant. The measurements were performed in rapid succession (no sample reloading) at a shear rate of \( \dot{\gamma} = 45 \) s\(^{-1}\) after an initial startup time of ten minutes to allow the sample to reach its steady state. The sample was allowed to rest for 300 s between subsequent trials. The measured positions were approximately the same for each slit width, where the positions for the 0.05 mm slit did not overlap in space, but the positions for the other two widths did overlap. The resulting calculated alignment factors for these experiments can be
seen in Figure 3.25a. In addition, results from trials at different times and facilities, with two different sample preparations of the 0.01% wt NaTos solution, are reported in Figure 3.25a.

Figure 3.25: Effect of the width of the translating slit on $I(q^*, \phi)$ and $A_f$ for the 0.01% wt NaTos solution at $\dot{\gamma} = 45 \text{s}^{-1}$. The dimensions of the stationary slit were 2x5 mm for all experiments. (a) $A_f$ as a function of gap position, $r/H$ for different slit widths and different facilities. The slit width appears to have little effect on $A_f$, even when the width increases five-fold from 0.05 to 0.25 mm. (b) $I(q^*, \phi)$ is nearly identical between trials at the NCNR and ILL with slit widths of 0.1 and 0.3 mm, respectively. $A_f$ is within the uncertainty, as shown for the gap position $r/H = \cdots$ from the curve in (a). $A_f$ appears to be independent of the translating slit width for this configuration, indicating that spatial smearing is not significant.

As seen in Figure 3.25a, the spatial smearing associated with larger slit widths appears to have little effect on the calculated alignment factor. It should be noted that the horizontal beam divergence through the path length of the 1-2 shear cell is on the order of 10% of the width of the translating slit, which is relatively minor. The calculations of the beam divergence can be seen in Appendix D. The calculated value of $A_f$ appears to be fairly independent of the sample preparation, facility, or width of the translating slit. This result is rather surprising, especially near the inner wall, where the structure changes significantly with increasing gap position. While significant changes in $A_f$ are not seen in this 0.01% wt NaTos solution, it is possible that the smearing would become more significant in a sample that showed a more pronounced form of shear banding. In this situation, smearing in space could become very significant in spatial regions near or encompassing the shear band interface. The agreement between the calculated values of $A_f$ between slit sizes and sample
preparations is perhaps not surprising when the intensity distributions, \( I(q^*, \phi) \), between two different sample preparations and facilities are examined in Figure 3.25b. The translating slit width in the ILL configuration was three times wider than in the NCNR configuration, yet \( I(q^*, \phi) \) and the resulting value of \( A_f \) are within the uncertainty of one another. While the calculation of the alignment factor can be affected artificially by multiple factors discussed in this chapter, the agreement in \( I(q^*, \phi) \) across sample preparations, facilities, and slit widths is rather remarkable and speaks to the reproducibility of the SANS experiments.

To examine the effect of the stationary slit height, \( h \), from Figure 3.24, steady shear measurements were performed with different stationary slit heights on the 0.05\% wt NaTos solution at \( \dot{\gamma} = 45 \text{ s}^{-1} \). The stationary slit width was held constant at \( w = 2 \text{ mm} \), which does not confine the scattering volume because the gap is only 1 mm wide. However, the stationary slit height does confine the scattering volume, and was chosen as \( h = 1, 3, \) or 5 mm. Figure 3.26a shows a comparison of \( I(q^*, \phi) \) between two configurations at the NCNR with an equal translating slit width \( (w = 0.1 \text{ mm}) \) and stationary slit heights of either \( h = 1 \) or 3 mm, and a configuration at the ILL with dimensions of \( w = 0.3 \text{ mm} \) and \( h = 5 \text{ mm} \). The NCNR experiments were performed on the same sample, whereas a new sample preparation was used in the ILL trial. As seen in Figure 3.26a, the intensity distributions are again nearly identical between the three configurations. Here, \( I(q^*, \phi) \) for the ILL configuration is rather sharp and well-defined, as the scattering volume from this configuration is at least five times larger than in the other configurations. The uncertainty around the intensity distribution is the lowest in this configuration, because the larger slits allow for a higher total number of counts for the same experiment duration. The two NCNR configurations, in comparison, show \( I(q^*, \phi) \) that are extremely noisy due to the low count rates that result from the smaller slit sizes. As the count time was held constant between the two NCNR configurations, the intensity distribution from the \( h = 1 \text{ mm} \) configuration has considerable noise and a higher associated uncertainty in the calculated alignment factor from the three-fold reduction in scattering volume associated with the smaller slit height.

Similar to the results seen for the 0.01\% wt NaTos solution (Figure 3.25), the results
Figure 3.26: Effect of the width of the stationary slit and translating slit on $I(q^*, \phi)$ and $A_f$ for the 0.05% wt NaTos solution. The dimensions are specified as translating slit width x shear cell slit height (the two smallest dimensions). (a) $I(q^*, \phi)$ and $A_f$ are nearly identical between facility and choice of slit at the inner wall for $\dot{\gamma} = 45 \text{ s}^{-1}$. (b) $A_f$ was calculated across the gap for the two NIST configurations, where the translating slit was identical (0.1 mm) between the two. The $A_f$ calculation is independent of the height of the shear cell slit, indicating that spatial smearing is not significant.

for the 0.05% wt NaTos solution seem fairly insensitive to the stationary slit height, translating slit width, and experimental facility. As the intensity distributions appear to be independent of the configuration, the larger slit configurations may be ideal to maximize the total number of counts. This tradeoff appears to have minimal effect on the calculated value of the alignment factor, as seen in Figure 3.26b, which compares $A_f$ across the gap for the two NCNR configurations. In all cases, the calculated $A_f$ values are equal within the uncertainty. This result suggests that a larger stationary slit height, like $h = 3$, or even $h = 5$ mm, is the most beneficial configuration to maximize the scattering volume while measuring accurate results. However, when more precise spatial information is required, like in a shear banding sample which shows large changes in $A_f$ with increasing gap position, a smaller translating or stationary slit size may be preferred. However, in both of these WLM solutions (0.01% and 0.05% wt NaTos), the samples exhibited shear banding and the slit dimensions had no noticeable effects in any measured trial. Additional calculations of the beam divergence can be seen in Appendix D.
3.4.7 Discussion on configuration effects

In this analysis, the effect of the sample-to-detector distance, aperture and slit dimensions, and collimation (number of guides) was examined primarily for the 0.01% wt NaTos solution, with some follow-up experiments on the 0.05% wt solution. The results between the two solutions were qualitatively consistent, and were consistent across multiple sample preparations, suggesting that these are general effects versus sample specific effects. Of all of the configurational variables, choosing the optimal sample-to-detector distance appears to be the most important variable for an accurate determination of the alignment factor and intensity distribution, $I(q^*, \phi)$ (Figures 3.16 and 3.17). Increasing this distance ultimately increases the number of pixels that constitute $q^*$, giving a more accurate determination of $I(q^*, \phi)$. However, very long distances may truncate the $q^*$ region, which is not ideal. Therefore, the chosen detector distance should encompass $q^*$ in the middle of the accessible q-range, to balance the increasing number of pixels but decreasing flux with increasing detector distance.

In relation to the effect of the detector distance, all of the other configurational effects are fairly minor, and alone, appear to contribute to a change in the alignment factor of roughly 10% or less. Should several smearing parameters be used (numerous guides, wide slits), then these effects may compound to result in errors larger than 10%. However, it appears that optimizing certain parameters serves to lessen the impact of other parameters. For example, in Figure 3.23, the use of four guides versus one guide has a relatively minor effect (the alignment factors are nearly identical) when the rheometer slit is narrow ($w_{slit} = 2$ mm), perhaps because other orientational smearing effects are eliminated. However, this increase in guides from one to four doubles the flux, which is a significant advantage for a relatively minor penalty in terms of the smearing. The effect of the number of guides is slightly larger when the wider rheometer slit ($w_{slit} = 5$ mm) is used. Therefore, in experiments where the flux must be optimized, the optimal configuration may be that of narrow source apertures and sample slits and multiple guides, which minimize orientational smearing effects while producing a reasonable flux.

Interestingly, the width of the translating and stationary slits for the 1-2 shear cell
experiments had little observable effects on the WLM response (Figures 3.25, 3.26). This result was surprising, as the width of the translating slit determines the proportion of the gap that is probed during each experiment and was expected to have a significant impact. As the 1-2 shear cell experiments have significantly lower flux than the 1-3 plane rheometer experiments, the uncertainty in the calculations due to low number of counts may play a role in these observations. Longer experiment durations could answer this question definitively. However, as neutron beam time is limited, these results suggest that the ideal configuration is one that maximizes the stationary slit height \((h = 5 \text{ mm})\) and provides reasonable spatial resolution via the translating slit width. While a translating slit width of \(w = 0.25 \text{ mm}\) may be too large when examining certain shear banding samples, for example, this slit width is perfectly reasonable in the case of shear thinning or mildly shear banding solutions (Figure 3.25). Additionally, it seems that a reduction in slit width from \(w = 0.1\) to \(w = 0.05 \text{ mm}\) has little added benefit, and is quite detrimental because the flux is halved. Based on the results presented above, it appears that a translating slit width in the \(w = 0.1\) to \(w = 0.25 \text{ mm}\) range is optimal.

3.5 Conclusions

In this chapter, the optimal methods for performing neutron scattering experiments were discussed in regard to: 1) time-resolved data analysis (Section 3.2), 2) time-resolved data collection (Section 3.3), and 3) experimental configuration and set-up (Section 3.4). All three of these factors are extremely important in improving the resolution and repeatability of SANS experiments, whether in regard to time resolution (Sections 3.2, 3.4) or spatial and orientational resolution (Section 3.4). Outlining these methods helps to explain and standardize the results presented in the remainder of this thesis; these methods are also of utility for future work in terms of planning experiments and analyzing time-resolved data.

In regard to time-resolved data analysis (Section 3.2), an improved method of analyzing time-resolved elastic scattering data was shown to increase the precision of the functions derived from scattering information, while significantly decreasing the data acquisition time. The developed deconvolution procedure greatly improves the temporal resolution and the
resulting accuracy of the calculated material response to an external excitation. Sample data sets with and without noise and SANS measurements taken during large amplitude oscillatory shear show that the experiment time can be reduced by one-third or more, depending on the time scale of the features. The improved accuracy and precision of the deconvolved signal features enable the scattering signal to be quantitatively linked to the measured rheology for the development of structure-property relationships. Time-resolved data collection (Section 3.3) allows the user to apply the ideas discussed in Section 3.2 to real neutron scattering data. Methods to implement the ‘sliding bin method’ were enacted at the ILL and NCNR. These new programs and codes can improve the temporal resolution to any degree as chosen by the user; the results shown in this work use a five- to ten-fold improvement for practical purposes (see Chapters 6, 7). Note that the temporal precision is not affected by the sliding bin method; the full deconvolution procedure in Matlab must be performed to do so. In addition to implementing the sliding bin method, the new Igor codes used to analyze the NCNR data greatly improve data processing time, which can be laborious with time-resolved SANS data that involves analysis of hundreds, if not thousands, of data slices. The new programs simultaneously printing the alignment factor and orientation angle during data reduction, and also enable $q^*$ to be determined easily from the annular average panel (Figures 3.12, 3.13).

The effect of different experiment configurations on the collected neutron scattering data was discussed in Section 3.4. The variables examined, including the sample-to-detector distance, collimation or number of guides, source aperture dimensions, and sample slit dimensions, all have an impact on the measured intensity distribution $I(q^*, \phi)$, which is used to calculate the alignment factor, $A_f$ (Equation 2.36). These effects were discussed across multiple sample preparations, facilities, and instruments, to draw firm conclusions which could be used to determine the optimal experimental configuration. Of all factors, the sample-to-detector distance had the greatest impact on the measurable and calculated parameters. As long as the chosen detector distance enclosed $q^*$ near the center of the accessible $q$-range, the smearing around $I(q^*, \phi)$ and associated errors in the calculated parameters were minimized. The collimation and aperture and slit dimensions combined had a lesser impact than
the sample-to-detector distance. While spatial and orientational smearing were detected with more guides or wider slits, the decrease in the calculated $A_f$ was always on the order of 10% or less. By optimizing certain variables, like decreasing the slit or aperture widths, the effect of other parameters like the number of guides was minimized (Figure 3.23). These results provide extensive guidelines for planning future experiments, where tradeoffs between the orientational and spatial smearing and count rate must be considered. Finally, the results also provide a basis for understanding any inconsistencies in the collected data or calculated alignment factors between experiments that may have been performed with different configurations.
References


Chapter 4

EQUILIBRIUM STATIC AND DYNAMIC PROPERTIES

4.1 Introduction

As discussed in Chapter 1, a goal of this research is to establish by experiment the influence of micellar branching on the rheological behavior of WLMs. To address this, the branching levels in the model WLM solutions must be established. In this chapter, the equilibrium properties of model solutions of mixed cationic and anionic wormlike micelles (WLMs) are explored using a combination of static and dynamic characterization tools. Specific focus is paid to the differences in WLM solutions with varying levels of the added salt sodium tosylate (NaTos), which can induce branching in WLM solutions. Here, solutions with varying levels of branching are compared to discern what features can be attributed to branching versus other solution properties, like the solution ionic strength and the resulting electrostatic interactions. These WLMs from mixed cationic and anionic surfactants were first studied by Koehler et al. [1], and have been previously well-characterized in water [1–3]. Determining and quantifying branching in WLM solutions has been a long-standing scientific challenge for several reasons. One main reason is that the branching is induced by the addition of a hydrotropic, or penetrating, salt such as sodium tosylate. The addition of salt modifies the inter-micelle interactions, making scattering models that predict branching of little utility, as the low-\( q \) scattering region is influenced by the electrostatic interactions. Here, the branched structure that results with salt addition is confirmed with the use of cryo-transmission electron microscopy (cryo-TEM), and differences in the static small angle neutron scattering (SANS) with increasing branching are explored. Cryo-TEM is one of the few direct visualization methods that can help identify branch points, and is commonly used to justify branching in WLM solutions [4–9]. However, resolving branch
points using cryo-TEM is still difficult due to the fact that concentrations in the semi-dilute regime are required for branching to occur [2,8,10].

Measurements of the equilibrium dynamical properties of the model WLM solutions are also discussed in this chapter. Linear viscoelastic rheology (LVE) and scattering methods such as neutron spin echo (NSE) and dynamic light scattering (DLS) are performed to help understand the solution dynamics. In this chapter and in Chapter 5, results are first presented as a comparison between the low and highly branched solutions to shed light on characteristic differences that result from branching. Then, results from the mildly branched solution are presented and compared. The mildly branched solution results are presented separately for clarity, as a detailed experimental study of this solution and a comparison to constitutive modeling predictions are shown later in Chapters 5 and 7. Finally, any additional results from higher branching levels are presented. The results from the Sections 4.2 and 4.3 are published in references [9,11].

4.2 Structure confirmation

The equilibrium structure of the WLMs was confirmed using two methods: cryo-TEM and static SANS. The primary goal of these experiments was to confirm that wormlike micelles were forming in solution as opposed to other structures, and to identify branching with added salt. The secondary goal was to confirm that the wormlike structures were equivalent to those probed by Schubert et al. [2], from which this work is based. Frequent comparisons are made back to these works [2,12] to provide a basis for the future rheology and SANS experiments under flow.

4.2.1 Cryo-transmission electron microscopy (cryo-TEM)

Cryo-TEM was performed on solutions with a fixed surfactant concentration \( (C_D = 1.5\% \text{ wt}) \) and various salt concentrations to visualize the effect of salt concentration on the structure: low (0.01% wt NaTos), high (0.10% wt NaTos), and very high salt (0.15% wt NaTos). Here, the surfactant concentration lies on the boundary of the dilute and semi-dilute regimes \( (C_D = C^* \approx 1.5\% \text{ wt}) \), as noted by a change in the micellar scaling laws at
this concentration [2, 12]. As opposed to inducing structural changes (such as branching) by changing the surfactant concentration, the structure of these solutions is controlled by a change in the concentration of added salt. By holding the surfactant concentration constant, changes in the properties can be attributed to changes in branching level as opposed to concentration changes. A qualitative distinction between the resulting structures is observed in Figure 4.1, where the 0.01% wt NaTos (a, red) and 0.10% wt NaTos (b, blue) worm-like micelles are compared. Additional images of these two solutions, along with images of the 0.15% wt NaTos solution, can be seen in Appendix E.

Figure 4.1: Comparison between CTAT/SDBS worm-like micellar solutions with a fixed surfactant concentration ($C^* \approx C_D = 1.5\%$ wt) with low salt (a, 0.01% wt NaTos, red) and high salt (b, 0.10% wt NaTos, blue). (a) Chains are highly linear. The inset provides a larger scale view of the long, linear structures apparent throughout the sample. (b) Micelles have identifiable branch points, as indicated by the arrows, and form a variety of junctions, loops, and other structures. The inset shows the larger scale morphology that contrasts the linear micelles observed in the (a) inset.

Figure 4.1a (red) shows the 0.01% wt NaTos solution containing linear micelles and no observable branch points. In contrast, the 0.10% wt NaTos solution shown in Figure 4.1b (blue) shows a high probability of finding a branch point along a contour, and contains a
variety of loops and branch points. While the concentration makes it difficult to differentiate between branch points and overlapping micelles, the white arrows point to clear loops or three-fold junctions where overlap does not occur. These junctions and other irregular structures are also observed in the very high salt (0.15% wt NaTos) solution (Appendix E), and become more prevalent with the addition of the hydrotropic salt. The structures are consistently observed across multiple images from different grid locations. These results are consistent with the findings of Schubert et al. [2], where branching was proposed with increasing hydrotropic salt content. While all samples undergo the same preparation and imaging conditions, flow-aligned structures are observed in the linear system (0.01% wt NaTos) that are absent in the samples of higher salt content. This alignment is difficult to avoid and is enforced by the micellar topologies: the linear structures align more easily than those containing branch points or network-like structures that introduce steric effects.

The insets show the larger-scale structural differences, where long thread-like micelles (a) and interconnected structures (b) are observed. The micellar diameter, $d_{cs}$, was estimated to be between 40 Å and 50 Å for all samples using ImageJ analysis on multiple images. Micellar diameter was not a function of salt concentration within the precision obtainable by cryo-TEM. The diameter measurements agreed with the cross-sectional radius of 21.4 Å ($d_{cs} = 42.8$ Å) determined by Schubert et al. [2] via static SANS. Additionally, Schubert et al. [2] calculated the contour length of the micelles to be on the order of several microns, which was supported with additional cryo-TEM images. Qualitatively, the number of branch points is much higher in the 0.10% wt NaTos sample (and 0.15% wt NaTos sample) than in the 0.01% wt NaTos sample. Although these and additional images in Appendix E show the formation of branch points with added NaTos, due to the limited contrast and the tendency of the samples to shear align with the cryo-TEM grid, no quantitative relationships between NaTos content and structure have been developed.

4.2.2 Static small angle neutron scattering (SANS)

Static small angle neutron scattering measurements were performed to determine the equilibrium structures and micellar length scales of the WLMs with varying salt content [2].
SANS results were used to calculate the micellar radius using several models, which was then quantitatively compared to the cryo-TEM estimates and the length scales determined by [2]. Figure 4.2 (top) shows the 1-D azimuthally-averaged SANS measurements for salt concentrations ranging from 0.01% wt to 0.25% wt NaTos, in the full q-range from 0.001 Å⁻¹ to 0.5 Å⁻¹ corresponding to real space dimensions on the order of 10 Å to 6000 Å. The 1-D scattering for more highly branched solutions (0.185% wt - 0.50% wt NaTos) can be seen in Figure 4.3. A 2-D isotropic scattering pattern for the low salt system (0.01% NaTos, red) and high salt system (0.10% NaTos, blue) are shown in Figure 4.2 (top) to highlight the differences in the scattering between the two samples, which will be compared frequently throughout this dissertation. The scattering from the mild salt solution (0.05% wt NaTos) is also highlighted in the bottom of the figure, as this solution is examined extensively throughout this work.

At rest, all 2-D patterns are isotropic with regard to angle, indicating no net micellar orientation. In the low salt system, there is a strong interaction peak that appears in the 2-D pattern as an intensity ring at \( q \approx 0.02 \text{ Å}^{-1} \). In real space, this q-value corresponds to a correlation length on the order of 300 Å, given by:

\[
\xi = \frac{2\pi}{q_{\text{max}}},
\]

which is indicative of the preferred inter-micellar separation distance arising from the electrostatic repulsions between micellar segments. This correlation length is not to be confused with the hydrodynamic correlation length, which is associated with the mesh size, \( \xi_{M} \), for entangled wormlike micelles. This estimate of \( \xi \approx 300 \text{ Å} \) is in good agreement with expect scaling of the inter-micelle spacing with the volume fraction, \( \phi \), and cross-sectional radius, \( r_{cs} \), for semi-dilute WLMs [1]:

\[
\xi = r_{cs}(\frac{\pi}{\phi})^{1/2},
\]

which also yields \( \xi \approx 300 \text{ Å} \) (determination of \( r_{cs} \) is discussed below). As the intensity is
isotropic, the sample is also isotropic with no net alignment of the micellar segments. With increasing salt concentration, the electrostatic interactions are progressively screened and the interaction peak is dampened. In the 2-D scattering of the 0.10% wt NaTos system, the mitigation of the interaction peak is evident, as the ring structure is no longer visible.

As seen from Figure 4.2 (bottom), the equilibrium microstructure of the mildly branched solution (0.05% wt NaTos) falls in between that of the low (0.01% wt NaTos) and high (0.10% wt NaTos) branched solutions. In Figure 4.2 (bottom), the dotted vertical lines denote $q^*$, the region across which the alignment factor is calculated (Equation 2.36). A mild interaction peak occurs at $q \approx 0.02 \, \text{Å}^{-1}$ from a partial, but incomplete screening of electrostatic interactions with salt addition. This interaction peak is seen clearly in both the 2-D scattering pattern, which displays a faint ring, and the 1-D scattering curve from Figure 4.2 (bottom). While the interaction peak remains at the same q-position for all samples, it is significantly more pronounced in the solution with low branching seen above in Figure 4.2. As the q-position does not change with added salt, screening the electrostatic interactions does not change the preferred inter-micelle distance (Equation 4.1). This result is expected based on the scaling from Equation 4.2, as all solutions are composed of the same total surfactant concentration with only minor changes in salt concentration ($\phi \approx \text{constant}$) and $r_{cs}$ is comparable across samples (see below).

The 1-D scattering of the 0.15% wt NaTos solution is also highlighted (purple + symbol) in Figure 4.2 (top) to show the structural similarities between this sample and the 0.10% wt NaTos solution. The similarity in the SANS between these two samples is supported by the cryo-TEM results which show comparable features (see Appendix E). At the maximum salt concentration shown in Figure 4.2 ($C_s = 0.25\%$ wt), and at all salt concentrations shown in Figure 4.3, the interaction peak has completely disappeared. In Figure 4.3, the 0.25% wt and 0.50% wt NaTos solutions are highlighted because they will be discussed in Section 4.4 on solution dynamics below. Further, the slope of the scattering curves at low q-values increases with added salt once the interaction peak has disappeared (Figure 4.3 inset). Generally, an increasing slope in the low-\textit{q} regime indicates an increasing fractal dimension, $d_f$, which is expected with increasing branching. However, due to the strong electrostatic
Figure 4.2: Top: 1-D azimuthally-averaged static SANS for CTAT/SDBS WLM solutions with a range of salt (0.01% wt NaTos) to (0.25% wt NaTos). 2-D scattering patterns are highlighted for the low salt (0.01% wt NaTos, red) and high salt system (0.10% wt NaTos, blue). The strong interaction peak at low salt concentration manifests itself as a ring in the 2-D scattering pattern (red), whereas the electrostatic interactions are screened at high salt concentrations (blue), leading to the disappearance of the interaction peak. The 0.15% wt NaTos 1-D scattering is also shown (purple) to highlight the structural similarities between the 0.15% wt and 0.10% wt sample, in qualitative agreement with the cryo-TEM results.

Bottom: Static SANS of the 0.05% wt NaTos solution, where the static 2-D pattern from the 1-2 shear cell is shown and the faint ring leads to the mild interaction peak in the 1-D scattering. The color scheme difference in the SANS patterns reflects data taken at ILL vs. NIST above.
interactions in this series of WLMs, the true value of $d_f$ (which could help quantitatively
determine the amount of branching in the system) cannot be determined. Although scat-
tering models exist for three-fold junctions, such models cannot be used accurately, as it is
unknown to what degree the low-$q$ slope increases due to branching versus to what degree
the slope increases simply due to the screening of electrostatic repulsions with added salt.
Finally, the high-$q$ scattering ($q \geq 0.04$ Å$^{-1}$) for all samples collapses onto one curve (in
both Figure 4.2 top and Figure 4.3), indicating that the basic cylindrical structure of the mi-
celles does not change with added salt. This result implies that with salt addition, only the
branching level is altered, not the fundamental wormlike structure. To determine micellar
length scales, scattering models for a cylinder and flexible cylinder were fit to the data in the
high-$q$ region beyond the influence of the interaction peak. As expected, both models yielded
similar results and all cross-sectional radii, $r_{cs}$, ranged from 20.2 Å to 21.3 Å across all salt
concentrations (0.01% wt - 0.50% wt NaTos). Using the simpler Guinier approximation for
the form factor (Chapter 2, Equation 2.16) and then relating $r_{cs}$ to the cross-sectional radius
of gyration, $R_{g,cs}$ by Equation 2.19 yields $r_{cs} = 21.2$ Å to 21.9 Å, in good agreement with
the Guinier analysis of Schubert et al. [2] where $r_{cs} = 21.2$ Å to 21.6 Å. As expected, the
cross-sectional radius of the micelles slightly decreases with increasing salt concentration,
due to screened repulsions that decrease the effective headgroup size.

4.3 Micellar properties as a function of added salt

4.3.1 Relaxation time and zero-shear viscosity

The material relaxation time, $\tau_R$, and the zero-shear viscosity, $\eta_0$, of the WLMs over
the range of added salt (0.0% wt - 0.25% wt NaTos) were examined as a function of salt
concentration and the ratio of the concentrations of the ions, which self-assemble to form
the micelles. SDBS and NaTos dissociate to form negatively charged ions and CTAT forms
positively charged ions in solution. The material relaxation time is determined as the inverse
of the cross-over frequency, $\omega_c$, the angular frequency at which $G'$ and $G''$ are equal in the
linear viscoelastic regime (Equation 1.25). The zero-shear viscosity and an estimate of the
shear relaxation time, $\tau_v$, were determined by fitting the Cross Model (Equation 4.3) [13] to
Figure 4.3: Static SANS measurements for very highly branched solutions. The 0.25% (black) and 0.50% (blue) wt NaTos solutions are highlighted, as they are discussed further in the section on solution dynamics.

the steady shear data:

\[
\eta(\dot{\gamma}) = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1 + (\dot{\gamma}/\tau_v)^m}
\]

(4.3)

where \(\eta_\infty\) is the high shear viscosity and the exponent \(m = N + 1\) and ranges between 1.0 and 1.3, where \(N\) is the power law index. The steady shear results to which the Cross Model was fit will be discussed further based on branching level in Chapter 5. The zero-shear viscosity determined by the steady shear rheology was also compared to the complex viscosity, \(\eta^\ast(\omega)\), measured via frequency sweeps in the linear viscoelastic regime (see Section 4.3.2 below). The frequency sweep data can be fit similarly using the Cross Model. At low frequencies in the terminal regime, where \(\eta^\ast(\omega)\) enters a plateau region, \(\eta^\ast(\omega \to 0)\) is expected to equal \(\eta_0\). The zero-shear viscosity and \(\eta^\ast(\omega \to 0)\) were in good agreement for all WLM solutions, as expected.

For the surfactant concentration used here \((C_D = 1.5\% \text{ wt CTAT/SDBS in 97/3 wt ratio})\), Schubert et al. [2] indicated that \(\eta_0\) and \(\tau_R\) of the micelles decrease monotonically as
a function of increasing salt concentration over the range of $C_s = 0$ to 0.25% wt NaTos. Figure 4.4a confirms this trend in both $\eta_0$ and $\tau_R$. However, while we see the same qualitative trends, the results cannot be compared on a quantitative basis due to the isotopic substitution; Schubert et al. [2] used water, whereas we use D$_2$O as the solvent. A discussion of this isotopic substitution and a comparison of the rheological properties between samples prepared in water versus D$_2$O can be seen in Appendix F.

Figure 4.4: Zero-shear viscosity, $\eta_0$, and rheological relaxation time, $\tau_R$, as a function of salt concentration (a) and ion concentration ratio (b). Both parameters are decreasing functions of salt and ion ratio, indicating that the system has surpassed the commonly-observed first viscosity maximum in WLM systems. The range of salt concentration is limited such that a second viscosity maximum is not observed. The associated error in both metrics determined in samples with multiple preparations is smaller than the symbol size.

At $C_D = 1.5\%$ wt, the micelles are very long, even at low salt concentrations, as evidenced by the cryo-TEM images. Accordingly, the commonly-observed viscosity maximum is effectively shifted to negative salt concentrations at this concentration of mixed surfactant. The viscosity maximum is only observed at lower surfactant concentrations with increasing salt concentration at the 97/3 weight ratio of CTAT/SDBS [1,2]. The decreases in $\eta_0$ and $\tau_R$ with increasing ion concentration ratio scale with similar dependences, and are comparable to the viscosity and relaxation time trends reported by Sachsenheimer et al. [14] for related WLM solutions, including CTAB/NaSal (Figure 4.4b). The observed trends are qualitatively
similar to those of the CTAB/NaSal solutions between the two observed viscosity maxima (as a function of ion concentration), which is expected given the functional and structural similarities between both surfactants and salts [14]. In our work, a second viscosity maximum is not observed, which is likely due to the limited range of salt concentrations examined.

### 4.3.2 Linear viscoelastic regime (LVE) rheology

The linear viscoelastic rheology of the samples (0.01% - 0.25% wt NaTos) was measured to determine characteristic differences with added salt and to estimate characteristic length and time scales. Results were compared to an extended Maxwell (Oldroyd-B) model as previously performed [15, 16]. As seen in Figure 4.5a, the crossover frequency, $\omega_c$, increases with increasing salt content. As the relaxation time, $\tau_R$, is the inverse of the crossover frequency (Equation 1.25), $\tau_R$ of the high salt (0.10% wt NaTos) sample is an order of magnitude shorter than that of the low salt case (0.01% wt NaTos). The LVE rheology in Figure 4.5 shows that the value of the moduli at the crossover point, or crossover modulus $G_c(\omega_c)$, is not significantly affected by low levels of salt. However, $G_c$ increases significantly at high salt content, as observed in the 0.185% and 0.25% wt NaTos samples. This increase in the crossover modulus with increasing salt content is explored further in the discussion (Section 4.3.3, see Figure 4.7).

The low frequency LVE data shown in Figure 4.5 for the WLMs is dominated by changes in the relaxation time due to the addition of hydrotropic salt but is otherwise qualitatively similar. A Cole-Cole representation of the LVE data can be seen in Figure 4.6, where the data at low frequencies appears to be independent of added salt content. As salt concentration increases, the Deborah number ($De = \omega \tau_R$) at which deviations from Maxwellian behavior occur decreases, as seen in Figure 4.5b, where the dynamic moduli are normalized by $G_c$ and the frequency by $\omega_c$. For example, the Deborah number of the $G''$ minimum at high frequency decreases systematically with added salt. The slope of the plateau in $G'$ gradually increases with added salt until the $G'$ plateau essentially disappears when $C_s \geq 0.185\%$ wt NaTos. These deviations in LVE behavior are in agreement with results from Khatory et al. [17], where the deviations from Maxwellian behavior in the Cole-Cole representation
of the data increase significantly as the salt concentration increases. As observed by Khatory et al. [17], the deviations from semi-circular behavior shown in Figure 4.6 are apparent at high salt concentrations.

Figure 4.5: Dynamic moduli, $G'$ and $G''$, as a function of salt (0.01% - 0.25% wt NaTos). (a) The low salt system is a nearly perfect Oldroyd-B fluid, with the exception of a slight upturn in $G'$ in the plateau region. With increasing NaTos, the upturn in $G'$ at $\omega > \omega_c$ becomes significant; the 0.25% wt NaTos sample has no plateau over the measured $\omega$. (b) Deviations from the Oldroyd-B model with NaTos are more apparent when the moduli are normalized by the crossover modulus, $G_c$.

Table 4.1 provides a summary of the differences in the length and time scales between the two samples, determined from rheology and SANS data. Fits to the steady shear rheology will be discussed further in Chapter 5. Also included are estimates of length scales that can be derived from fits to SANS data or by micellar scaling laws outlined in Chapter 1, Section 1.3. These length scales include the persistence length $l_p$, mesh size $\xi_M$, entanglement length $l_e$, and contour length $L_c$. While these scaling laws described in Section 1.3 are most applicable to nonionic, linear micelles, the values are on the same order of magnitude as results from light scattering and other methods employed by Schubert et al. [2], which are shown for comparison. It is to be noted that the majority of their measurements were performed in samples in water (as opposed to D$_2$O) as the solvent, which can result in rheological differences [18]. Interpretation of these length scales for the high salt sample is to
be cautioned as the theories do not explicitly account for topological changes that may result from adding salt. While it is difficult to derive quantitative information from cryo-TEM, these predictions appear to be in line with observations from the images. The repeatability of the LVE response used to calculate these values can be seen in Appendix G.

Figure 4.6: Cole-Cole representation of LVE data, $G''/G_c$ vs. $G'/G_c$, normalized by the crossover modulus. Deviations from Maxwell behavior (semi-circular response) are observed at high salt contents, which may result from branching.

The micellar length scales were also calculated for the mildly branched solution (0.05% wt NaTos), which can be seen in Table 4.2. The values compare favorably to the calculations, SANS fits [9], and length scales (Schubert et al. [2]) for the low and highly branched solutions seen in Table 4.1. The cross-sectional radius, $r_{cs}$, was 20.8 Å using the flexible cylinder model, which lies between the calculated radii in solutions with less salt (21.3 Å) and more salt (20.4 Å) [9]. The slight decrease in cross-sectional radius with added salt is expected, as screening around the surfactant headgroups leads to a smaller effective headgroup size.

4.3.3 Discussion: salt effect on WLM topology and LVE rheology

Topological changes observed in the cryo-TEM in addition to the rheological changes observed with added salt strongly suggest that branching is induced as hydrotropic salt is
Table 4.1: Characteristic length and time scales of low and high salt (0.01%, 0.10% wt NaTos) WLMs

<table>
<thead>
<tr>
<th>Variable</th>
<th>Method</th>
<th>Low salt</th>
<th>High salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_c$ (rad · s$^{-1}$)</td>
<td>LVE rheology</td>
<td>0.18</td>
<td>2.6</td>
</tr>
<tr>
<td>$\tau_R$ (s)</td>
<td>LVE rheology</td>
<td>5.6</td>
<td>0.39</td>
</tr>
<tr>
<td>$\eta_0$ (Pa·s)</td>
<td>Steady shear rheology</td>
<td>34</td>
<td>2.6</td>
</tr>
<tr>
<td>$\eta_\infty$ (Pa·s)</td>
<td>Extended Maxwell model</td>
<td>N/A</td>
<td>0.027</td>
</tr>
<tr>
<td>N</td>
<td>Steady shear rheology</td>
<td>0</td>
<td>0.15</td>
</tr>
<tr>
<td>$G'_N$ (Pa)</td>
<td>LVE rheology</td>
<td>7.4</td>
<td>7.2</td>
</tr>
<tr>
<td>$G''_{\text{min}}$ (Pa)</td>
<td>LVE rheology</td>
<td>0.80</td>
<td>0.96</td>
</tr>
<tr>
<td>$\tau_{\text{break}}$ (s)</td>
<td>LVE rheology/scaling laws</td>
<td>0.13</td>
<td>0.03</td>
</tr>
<tr>
<td>$\tau_{\text{rep}}$ (s)</td>
<td>LVE rheology/scaling laws</td>
<td>230</td>
<td>4.9</td>
</tr>
<tr>
<td>$r_{cs}$ (Å)</td>
<td>cryo-TEM</td>
<td>20 - 25</td>
<td>20 - 25</td>
</tr>
<tr>
<td>$r_{cs}$ (Å)</td>
<td>SANS flexible cylinder model</td>
<td>21.3</td>
<td>20.4</td>
</tr>
<tr>
<td>$r_{cs}$ (Å)</td>
<td>SANS, Schubert et al. [2]</td>
<td>21.4 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>$\xi_M$ (Å)</td>
<td>scaling laws</td>
<td>830</td>
<td>840</td>
</tr>
<tr>
<td>$\xi_M$ (Å)</td>
<td>Schubert et al. [2]</td>
<td>~900 - 1000 (in H$_2$O)</td>
<td></td>
</tr>
<tr>
<td>$l_e/L_c$</td>
<td>scaling laws</td>
<td>0.091</td>
<td>0.133</td>
</tr>
<tr>
<td>$l_e$ (Å)</td>
<td>scaling laws</td>
<td>730</td>
<td>1700</td>
</tr>
<tr>
<td>$l_e$ (Å)</td>
<td>Schubert et al. [2]</td>
<td>N/A</td>
<td>2050 (in H$_2$O)</td>
</tr>
<tr>
<td>$L_c$ (Å)</td>
<td>scaling laws</td>
<td>8,100</td>
<td>13,000</td>
</tr>
<tr>
<td>$L_c$ (Å)</td>
<td>Schubert et al. [2]</td>
<td>N/A</td>
<td>21,000 (in H$_2$O)</td>
</tr>
<tr>
<td>$l_p$ (Å)</td>
<td>SANS cylinder model</td>
<td>1000</td>
<td>300</td>
</tr>
<tr>
<td>$l_p$ (Å)</td>
<td>rheo-optics, Schubert et al. (2003)</td>
<td>850 (0.05% NaTos)</td>
<td>310 (in H$_2$O)</td>
</tr>
</tbody>
</table>

added, as concluded by Schubert et al. [2]. The cryo-TEM micrographs show the presence of branch points in the higher salt solutions, whereas no branch points are observed in the images of the low salt solution. The observed deviations from Maxwellian behavior at high frequency in the LVE rheology with added salt can also be attributed to branching, and such deviations are often observed in branched polymers [19]. The branching arising from added hydrotropic salt is in agreement with many other works on branched micelles using similar surfactant systems [2,8,14] and is often used to explain the decrease in relaxation time and zero shear viscosity with increasing salt concentration in WLMs.
Table 4.2: Average characteristic properties of the 0.05% wt NaTos WLM solution

<table>
<thead>
<tr>
<th>Property</th>
<th>Notation</th>
<th>Method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relaxation time</td>
<td>( \tau_r ) (s)</td>
<td>LVE rheology</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>Zero-shear viscosity</td>
<td>( \eta_0 ) (Pa·s)</td>
<td>Cross model</td>
<td>9.5 ± 1.0</td>
</tr>
<tr>
<td>High shear viscosity</td>
<td>( \eta_\infty ) (Pa·s)</td>
<td>Oldroyd-B model</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>High shear viscosity</td>
<td>( \eta_\infty ) (Pa·s)</td>
<td>Cross model</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Power law index</td>
<td>N</td>
<td>Steady shear rheology</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Critical shear rates</td>
<td>( Wi_1, Wi_2 )</td>
<td>Startup rheology, model fits</td>
<td>2.6 ± 0.6, 100 ± 10</td>
</tr>
<tr>
<td>Plateau modulus</td>
<td>( G_N^0 ) (Pa)</td>
<td>LVE rheology</td>
<td>6.4 ± 0.4</td>
</tr>
<tr>
<td>Minimum loss modulus</td>
<td>( G_{min}'' ) (Pa)</td>
<td>LVE rheology</td>
<td>0.76 ± 0.07</td>
</tr>
<tr>
<td>Breakage time</td>
<td>( \tau_{break} ) (s)</td>
<td>LVE rheology/model fits</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Reptation time</td>
<td>( \tau_{rep} ) (s)</td>
<td>LVE rheology/model fits</td>
<td>40 ± 5</td>
</tr>
<tr>
<td>Mesh size</td>
<td>( \xi_M ) (Å)</td>
<td>model fits</td>
<td>870 ± 20</td>
</tr>
<tr>
<td>Entanglement length</td>
<td>( l_e ) (Å)</td>
<td>model fits</td>
<td>890 ± 40</td>
</tr>
<tr>
<td>Contour length</td>
<td>( L_c ) (Å)</td>
<td>model fits</td>
<td>7500 ± 500</td>
</tr>
<tr>
<td>Cross-sectional radius</td>
<td>( r_{cs} ) (Å)</td>
<td>SANS flexible cylinder model</td>
<td>20.8 ± 0.4</td>
</tr>
<tr>
<td>Persistence length</td>
<td>( l_p ) (Å)</td>
<td>Schubert et al. [2] (in H$_2$O)</td>
<td>850 ± 10</td>
</tr>
</tbody>
</table>

As expected from Schubert et al. [2], the WLM zero-shear viscosities are monotonically decreasing functions of salt concentration between 0% wt NaTos and 0.25% wt NaTos, confirming that the samples in this work are at or beyond the viscosity maximum observed for increasing surfactant concentrations. With increasing salt, branch density increases, which reduces the effective micellar contour length controlling reptation and provides additional stress relief mechanisms, thereby decreasing the relaxation time. By reducing both the breakage and reptation times, the zero-shear viscosity also decreases. As such, the branches may hinder shear thinning, as evidenced by the increase in the power law index of the 0% wt and 0.01% wt NaTos samples of \( N = 0 \) to \( N = 0.3 \) for the 0.25% wt NaTos sample. While linear chains can easily separate and stratify, branches provide physical barriers to flow alignment and shear thinning, which may lead to a decrease in the power law index. This phenomenon will be discussed further in Chapter 5.

In contrast to deviations in the LVE rheology attributed to branching in polymers [19], the low frequency LVE for the WLMs is qualitatively similar between branching (salt) levels. This observation is in accordance with the arguments presented by Granek and Cates
[20] regarding the stress relaxation mechanisms in the fast-breaking limit, where a micelle need only reptate a small fraction of its tube because the tube is constantly breaking and reforming. The low frequency data are therefore subject to many more breakage and recombination events than are the high frequency data, leading to a single Maxwellian relaxation time. For the Maxwell model, the zero-shear viscosity is proportional to the plateau modulus, \( G^0_N \) (Equation 1.40), so the nearly constant ratio of \( \eta_0 / \tau_R \) across samples suggests the modulus remains fairly constant, which is reasonable given that the surfactant content is constant across all samples. Experimentally, \( G^0_N \) is roughly equivalent for samples at low salt content, with deviations at higher levels of branching (high salt) where WLM behavior is no longer Maxwellian. Despite significant deviations from Maxwellian behavior at high salt concentration, the modulus values \( G^0_N \) and \( G''_{\text{min}} \) (based on model fits) were not greatly increased by branching between the low (0.01% wt NaTos) and high (0.10% wt NaTos) salt samples. Similarly, Figure 4.7 shows that the crossover modulus, \( G_c \), is relatively insensitive to added salt (branching) until \( C_s > 0.15\% \) wt NaTos. The increase in \( G_c \) at higher salt concentrations can be explained by the development of connected network-like structures. In addition to providing relevant length and time scales, the LVE data can also be used to predict the first normal stress difference, \( N_1 \), in the low frequency and shear rate regimes using Laun’s rule, which will be discussed further in Chapter 5, Section 5.11.

While strictly applicable to linear, nonionic systems, the scaling laws and estimated length and time scales presented in Table 4.1 provide a reasonable estimate for comparing the two samples with different levels of branching. As expected from the increasing scission energy with added salt, the contour length of the branched system (high salt) was significantly higher than that of the mainly linear system (low salt). However, the reptation time decreases because the “effective length” of the branched micelles becomes the distance between branch points, which is probabilistically expected to decrease with increasing salt concentration. Fitting the SANS cylinder model gives a reasonable estimate of the micelle persistence length for both samples when compared to rheo-optical measurements of Schubert et al. [2]; however, these values should be viewed with caution as fitting was performed past the interaction peak only and the fits are extrapolated to q-values below those measured.
Figure 4.7: Crossover modulus, $G_c$, as a function of salt concentration (branching level). Error bars are calculated for samples with multiple preparations. $G_c$ is more sensitive to sample preparation than $\eta_0$ or $\tau_R$. The crossover modulus significantly increases when network-like structures become prevalent.

4.4 Solution dynamics

4.4.1 Motivation

Dynamic measurements have proven useful in differentiating between topologies in both polymeric systems and wormlike micelles [9, 21, 22] due to differences in chain dynamics. Unlike in polymeric systems, the branches in WLMs are not chemically bound. As discussed above, branching is most commonly induced by salt addition or changes in temperature and concentration. As shown in Section 4.2.2, traditional static SANS methods cannot be used to detect branching, as the branching effect is convoluted by the changes in ionic strength, concentration or temperature. However, branching in WLMs is thought to provide additional stress relief mechanisms due to the presence of sliding branch points, such that an array of relaxation modes may be expected in highly branched or network-like micelles as discussed in Section 4.3.2 above [8, 9]. The expected differences in the solution dynamics based on branching level suggest that dynamic measurements like neutron spin echo (NSE) and dynamic light scattering (DLS) may be more successful in identifying branching than static SANS. Accordingly, PGSE-NMR diffusion measurements have been successfully used...
to confirm the presence of branching in reverse micellar solutions of lecithin and oil [10,23],
and significant deviations from Maxwellian behavior were observed at high frequencies in
the branched solutions (as was the case for the branched solutions in Section 4.3.2 above).
These PGSE-NMR methods have been the only direct measurement and confirmation of
branching in WLM solutions due to the difficulty of measuring branching [8]. Here, NSE
and DLS measurements are used to determine signatures that reflect underlying topological
differences in the WLM series characterized in the above sections. It should be noted that
salt addition makes the formation of branch points more favorable due to the screening of
electrostatic interactions [9, 14, 24], meaning that electrostatic interactions may also have a
separate impact on the solution dynamics. As NSE has been successfully used to distin-
guish free chains from cross-linked chains in polymer networks [25], it is expected that these
results can be extended to characterize polymeric branching.

4.4.2 Theory

Neutron spin echo has been previously used to detect the fast segmental dynamics
of wormlike micelles [26, 27]. The intermediate scattering function, \( S(q,t)/S(q,0) \) can be
obtained using NSE, as shown by Seto et al. [26] and fit using the model of Zilman and
Granek [28] (Equation 4.4):

\[
\frac{I(q,t)}{I(q,0)} \frac{S(q,t)}{S(q,0)} = \exp(-\Gamma(q)t^{\beta})
\]

where \( \beta = 3/4 \) for a wormlike chain, and \( \beta = 2/3 \) for a flexible membrane [28]. \( \Gamma(q) \) is the
relaxation rate, which is related to the segmental diffusion coefficient, \( D_G \) by:

\[
\Gamma(q) = D_G q^{2/\beta}
\]

For solutions of wormlike chains, \( \Gamma(q) \propto q^{8/3} \), whereas \( \Gamma(q) \propto q^{3} \) for a flexible membrane.

In previous NSE experiments on WLMs, including those on a similar cationic sur-
factant (CTAB) system with added salt, a stretch exponent of \( \beta = 3/4 \) was observed, as
is expected for a wormlike chain. Notably, the CTAB solutions exhibited Maxwell-like
behavior \[27\] in the linear viscoelastic (LVE) rheology. This trend indicates that these solutions contain little if any branching, as high levels of branching lead to strong deviations from Maxwellian behavior in the LVE rheology \[8, 9, 17, 29, 30\], which is also the case for branched polymers \[21, 22, 31\]. As shown above in Section 4.3.2, solutions with low levels of branching display Maxwell-like behavior, while the more highly branched solutions strongly deviate in the high frequency regime, suggesting that the dynamic relaxation may differ between branching levels.

Neutron spin echo measurements are particularly interesting in these WLM solutions to probe the segmental dynamics of the worms, which correspond with the length scales measured by SANS in Section 4.2.2 above. However, the branched WLMs here are particularly long and entangled, with persistence lengths \((l_p)\) on the order of microns that increase with branching level, as confirmed by cryo-TEM and estimates from scaling laws (see Tables 4.1, 4.2 above). Dynamic light scattering is then useful to probe the larger scale relaxations of the chain and entangled or branched network, due to the lower accessible scattering vector, \(q\), and wide range of accessible delay times, \(t\). In semi-dilute polymer and WLM solutions, two relaxation modes are commonly observed in DLS and other dynamic scattering measurements when the chains are entangled or topologically constrained \[32–39\]; only one, fast relaxation mode is typically observed in unentangled or dilute solutions \[34, 35\]. The first-order autocorrelation function, \(g_1(t)\), from the DLS measurements can be fit using a double, stretched exponential as is commonly performed in WLM and polymer solutions \[34, 38–40\]:

\[
g_1(t) = A_1 \exp\left(-\Gamma_1(q)t^{\beta_1}\right) + (1 - A_1) \exp\left(-\Gamma_2(q)t^{\beta_2}\right)
\]

where the stretch exponent, \(\beta_1\), of the fast relaxation rate, \(\Gamma_1\), is typically \(\beta_1 = 1\) for entangled polymers, and the slow relaxation rate, \(\Gamma_2\), shows a stretch exponential of \(\beta_2 < 1\). In the DLS regime, purely diffusive dynamics are expected. Here, the first-order autocorrelation function is related to the translational and rotational diffusion coefficients in a single exponential
decay by:

\[ g_1(t) \approx \exp[-(q^2 D_t - 6 D_r)t] \] (4.7)

where \( D_t \) is the translational diffusion coefficient and \( D_r \) is the rotational diffusion coefficient. In the diffusive regime, \( \Gamma(q) \) is related to the measured, apparent diffusion coefficient, \( D_{app} \) by:

\[ \Gamma(q) \propto D_{app} q^2 \] (4.8)

The plot of \( \Gamma(q) \) versus \( q^2 \) is linear for pure diffusion. Using Equations 4.7 and 4.8, there is no y-intercept in the plot of \( \Gamma(q) \) vs. \( q^2 \) in the case of purely translational diffusion, and the slope is equal to \( D_{app} \), or \( D_t \), the translational diffusion coefficient. When rotational diffusion is also present, the y-intercept is finite and corresponds to \( 6D_r \). The plot of \( \Gamma(q)/q^2 \) versus \( q^2 \) will be constant when rotation is not present. Note that the apparent diffusion coefficient is related to the diffusion coefficient at infinite dilution, \( D_0 \), by:

\[ D_{app} = D_0 (1 + k_D c + ..) \] (4.9)

where \( c \) is the concentration in solution, and \( k_D \) is the diffusion second virial coefficient. When \( D_{app} \) is plotted versus \( c \), a linear region of the plot indicates that \( D_{app} \) is affected by interactions in the system. The low concentration, constant region of this curve indicates infinite dilution and gives the true value of \( D_0 \). As the WLM solutions studied here are in the semi-dilute regime and electrostatic interactions are present, we measure \( D_{app} \) as opposed to \( D_0 \) with these experiments. However, diluting these WLMs solutions also changes the physical structure of the micelles, making an accurate determination of \( D_0 \) difficult.

The fast relaxation mechanism in semi-dilute polymeric solutions has been attributed to cooperative, translational diffusion of the short chain segments or blobs between entanglement points [39, 41]. In the case of pure diffusion, the relaxation rate of the fast relaxation mode should scale linearly as \( q^2 \), as previously reported in semi-dilute polymers and WLMs [27, 32, 39]. Conversely, the origins of the slow relaxation mechanism have been widely
debated, although much of the recent work also attributes this relaxation to a diffusive mode [36–39, 41, 42]. Recent studies point to a slow, self-diffusion type of relaxation mode that results from hindered motions of interacting or entangled chains [34, 38–40], which may reflect long-range correlated fluctuations, like those from the internal motion of a transient network [35–38, 40, 42, 43]. The scaling of this relaxation mode can vary, but is generally as $q^2$, provided that the distance $1/q$ is greater than the radius of gyration, $R_g$ [38, 41].

The rheological measurements presented in Section 4.3.2 above and calculations based on scaling laws (Tables 4.1, 4.2 above) show differences in the stretching and breakage of micelles based on branching level, in agreement with trends in branched polymers [21, 22]. Accordingly, it is expected that the diffusion coefficients, stretch exponents and relaxation rates may differ based on level of branching and network formation.

### 4.4.3 Sample characterization: LVE and SANS

Linear viscoelastic (LVE) rheology was performed on the specific sample preparations used for the NSE and DLS experiments, to confirm the differences reported in Section 4.3.2 above in the relaxation spectra of the wormlike micelles based on branching level (Figure 4.8(a)) [9]. Here, we refer to the 0.01% wt NaTos solution as ‘low branching,’ the 0.25% wt NaTos solution as ‘highly branched,’ and the 0.50% wt NaTos solution as a ‘branched network.’ The 0.25% wt NaTos ‘highly branched’ solution is not to be confused with the 0.10% wt NaTos solution from Sections 4.2 and 4.3 above (sometimes referred to as high branching); this name is qualitative and will only be used in regard to the 0.25% wt NaTos solution in this section on dynamics. As the crossover frequency increases with branching, the relaxation times decrease accordingly, where for the low branching, highly branched and network-like solutions $\tau_R = 6, 0.02, \text{ and } 0.007 \text{ s}$, respectively. The modulus at the crossover point, $G_c$, is denoted by the star symbols in Figure 4.8(a). As shown above in Figure 4.7, the observed increase in $G_c$ with branching results from the formation of branch points and network-like structures. Figure 4.8(a) also shows that the low branching solution exhibits Maxwell-like (Oldroyd-B model) behavior with a single minimum in $G''$ at high frequencies. Clear deviations from this behavior are seen in the two more highly branched solutions,
where most notably $G'$ does not exhibit a high frequency plateau.

Figure 4.8: LVE rheology (a) and SANS (b) characterization of the low branched (0.01%, red △), highly branched (0.25%, black □) and branched network (0.50%, blue ◦) solutions. (a) LVE results confirm a decrease in $\tau_R$, increase in $G_c$(•), and deviations from Maxwell behavior with branching. (b) While differences in structure result at low q-values due to electrostatic interactions (see insets), at high-q values, the cylindrical structure between samples is identical.

A comparison of the SANS spectra between the three solutions can be seen in Figure 4.8(b). As seen in Figure 4.8(b), the scattering at high q-values ($q > 0.03$ Å$^{-1}$), or short length scales ($d < 200$ Å), is nearly identical between samples; this confirms the results reported in Section 4.2.2 above. The cross-sectional radius, $r_{cs}$, of the micelles was fit using the flexible cylinder model in this high q-region, yielding $r_{cs} = 21.0 \pm 0.1$ Å for all solutions, in good agreement with the calculated values from Section 4.2.2 and the cryo-TEM measurements presented above (Section 4.2.1). This result and the collapse of all curves at high q-values indicates that salt addition and branching does not affect the cylindrical nature of the micelles or the cross-sectional size at the salt concentrations examined in this study. At mid to low q-values ($q < 0.03$ Å$^{-1}$), however, the scattering diverges due to differences in the electrostatic interactions that result from adding salt. In Figure 4.8(b), an interaction peak is observed in the low branched solution at $q = 0.02$ Å$^{-1}$ which appears as a ring in the 2-D scattering (bottom inset), due to repulsions between the cationic head groups. As salt is added to induce branching, these interactions are screened, which leads to a gradual disappearance of the
interaction peak and increase in the scattering intensity at low q-values. These differences in electrostatic interactions between samples with different levels of branching come to play an important role in the observed differences in the solution dynamics, which will be discussed further below.

4.4.4 Segmental dynamics via neutron spin echo (NSE)

Neutron spin echo measurements are particularly useful in WLM solutions, as they probe the segmental dynamics of the solutions on the same length scales probed by SANS. By fitting the neutron spin echos across the detector, the normalized intermediate scattering function (NISF), \( \frac{I(q,t)}{I(q,0)} \) can be determined for a particular scattering vector, \( q \). Once \( \frac{I(q,t)}{I(q,0)} \) is determined, it is fit using the stretched exponential function given by:

\[
\frac{I(q,t)}{I(q,0)} = A \exp\left(\frac{-C(q)t}{\beta}\right)
\]

(4.10)

where \( A \) is the amplitude which should equal 1, and \( C \) is the decay constant in seconds. The value of \( C \) and the uncertainty from the fit in Equation 4.10 is then converted to \( \Gamma(q) \) from Equation 4.4 above by \( \Gamma(q) = \frac{1}{C(q)} \) and \( \delta \Gamma = \Gamma \delta C / C = \delta C / C^2 \).

The normalized intermediate scattering functions obtained from NSE and the associated fits for select \( q \)-values are shown in Figure 4.9. Figure 4.9 compares only the two solutions which are the most distinct in terms of branching for clarity: the low branching and branched network solutions. In Figure 4.9, the intermediate scattering functions that decay quickly (short Fourier times) correspond to small length scales (high \( q \)-values). Conversely, the intermediate scattering functions that have only partially decayed (long Fourier times) correspond to large length scales and low \( q \)-values. As seen in Figure 4.9, the intermediate scattering function for the fastest relaxations (high \( q \)-values) is nearly identical between the two samples. This result is not surprising, as high \( q \)-values measure the dynamics on the length scale of the micellar cross-section and basic cylinder, which is unchanged with added salt. As longer length-scale relaxations are probed, the normalized intermediate scattering functions start to differ between the three solutions. At the lowest \( q \)-values, the relaxations...
are the slowest, and significant differences can be seen between the branching levels. While the results are not shown, the data for the 0.25% NaTos highly branched solution will be discussed further in Section 4.4.10.

![Normalized intermediate scattering functions (NISFs)](image)

**Figure 4.9:** Normalized intermediate scattering functions (NISFs) for the low branching (0.01% wt, solid symbol, dotted line) and branched network (0.50% wt, open symbol, solid line) solutions. At high $q$-values (short Fourier times), the NISFs are identical within uncertainty. As the $q$-values decrease, subtle but significant changes are seen in the NISFs.

Fits to Equation 4.4 are used to determine the relaxation rate, $\Gamma(q)$, and stretch exponent, $\beta$ for all three solutions, which can be seen in Figure 4.10. In Figure 4.10a, the expected scaling for segmental dynamics of a wormlike chain, $\Gamma(q) \propto q^{8/3}$, is denoted. At short length scales (high $q$-values, $q > 0.12$ Å$^{-1}$), $\Gamma(q)$ is independent of branching level within the experimental uncertainty (Figure 4.10a). Just as the absolute scattering intensities collapsed onto the same curve in SANS in this region (Figure 4.8b), the calculated $\Gamma(q)$ collapse onto the same curve at these short length scales. In this region, $\Gamma(q)$ scales as $q^{8/3}$ for all samples, as is expected for a wormlike chain. This result is not surprising, as at this length scale, the samples are cylindrical and wormlike as determined by SANS. The calculated segmental diffusion coefficient, $D_G$, between the three solutions is also identical within
the experimental uncertainty; these values are provided in Table 4.3. Here, the value of $D_G$ is similar to that previously reported for similar CTAB WLM solutions (here $D_G \approx 0.06$ vs. $D_G \approx 0.05 \text{ nm}^{8/3} \cdot \text{ns}^{-1}$) [27]. As the $q$-value is decreased ($q < 0.1 \text{ Å}^{-1}$), deviations from this scaling become apparent, which is expected as diffusive motion and the network-like properties of the systems become important. The uncertainty in each calculated $\Gamma(q)$ is fairly small in this $q$-range, and is usually smaller than the size of the data points (Figure 4.10a). The value of $\Gamma(q)$ is relatively insensitive to changes in $\beta$ and the amplitude, such that fixing $\beta$ to the average value across the configuration $q$-range, or setting the amplitude to $A = 1$ from Equation 4.10 has no effect (within the uncertainty) on the value of $\Gamma(q)$. The insensitivity of $\Gamma(q)$ to these fitting parameters gives high confidence in the reported results.

Conversely, the calculated value of $\beta$ is much more sensitive to the fitting procedure, and has a fairly high associated uncertainty. To address this, a paired t-test can be used to compare the values of $\beta$ between samples. In a particular configuration, the measured $q$-positions are constant across samples because the detector does not move. Within each configuration, the detector can be divided into multiple bins of different $q$-position. Therefore, within one configuration, the $q$-bins are identical across samples, resulting in each sample having a single $I(q,t)/I(q,0)$ and therefore $\beta$ for each $q$-bin. As such, the pairing can be done for $\beta$ between samples based on identical $q$-value. The t-tests are performed as follows, where $d$ is a vector of the differences in stretch exponents, vector $x$, at each $q$-value between two samples:

$$d_1 = x_{0.50\% \text{NaTos}} - x_{0.25\% \text{NaTos}}$$
$$d_2 = x_{0.50\% \text{NaTos}} - x_{0.01\% \text{NaTos}}$$
$$d_3 = x_{0.25\% \text{NaTos}} - x_{0.01\% \text{NaTos}}$$

The true mean of $d$, $\mu_d$, is then used to define the null ($H_0$) and alternative ($H_1$) hypotheses.
using a two-tailed test as:

\[ H_0 : \mu_d = 0 \]
\[ H_1 : \mu_d \neq 0 \]

(4.12)

Using the paired t-test in the same \( q \)-region (\( q > 0.12\text{Å}^{-1} \)), the calculated value of \( \beta \) was also found to be independent of branching (\( p > 0.5 \) in all tests). Further, the value of \( \beta \) was near the expected value for a wormlike chain at these \( q \)-positions, where \( \beta \approx 3/4 \) for all bins. As both \( \Gamma(q) \) and \( \beta \) are sample-independent in this region, the results suggest similar dynamics on the basic cylindrical and cross-sectional length scales, \( r_{cs} \), between samples with different levels of branching. These results are not surprising considering that the SANS results showed no structural differences in this region based on branching (Figure 4.8b).

![Figure 4.10: WLM relaxation rate, \( \Gamma(q) \), as a function of \( q \). (a) \( \Gamma(q) \) across the full \( q \)-range. \( \Gamma(q) \) and \( \beta \) are statistically identical at high \( q \), where the scaling \( \Gamma(q) \propto q^{8/3} \) holds. (b) As \( q \) decreases, significant differences in \( \Gamma(q) \) and \( \beta \) are observed (solid points, \( q < 0.02\text{Å}^{-1} \)). Trends continue to lower \( q \) (open symbols, second experiment), but uncertainty is higher from using fewer Fourier times.](image)

Figure 4.10: WLM relaxation rate, \( \Gamma(q) \), as a function of \( q \). (a) \( \Gamma(q) \) across the full \( q \)-range. \( \Gamma(q) \) and \( \beta \) are statistically identical at high \( q \), where the scaling \( \Gamma(q) \propto q^{8/3} \) holds. (b) As \( q \) decreases, significant differences in \( \Gamma(q) \) and \( \beta \) are observed (solid points, \( q < 0.02\text{Å}^{-1} \)). Trends continue to lower \( q \) (open symbols, second experiment), but uncertainty is higher from using fewer Fourier times.

As \( q \) decreases, the slope of the relaxation rate versus \( q \) decreases from the 8/3 scaling (Figure 4.10a). This trend indicates that diffusive modes become important at longer length scales. In the case of pure diffusion, \( \Gamma(q) \propto q^2 \). Interestingly, in the intermediate-\( q \) range
(0.02 < q < 0.08 Å⁻¹), statistically significant differences in β are observed between samples, using the paired t-tests described above (p < 0.05). These differences in β appear to correspond to minor structural changes detected in the SANS spectra on these length scales. However, the relaxation rates in this region are statistically identical, suggesting that the minor structural differences on these length scales do not affect the overall relaxation rate, but that β is sensitive to the such structural differences. At the longest length scales and lowest q-values, additional long Fourier times were added to increase the accuracy of the calculated Γ(q) and β. Validation of these low-q experiments was required, as the long wavelengths and Fourier times had not previously been used on the NCNR NSE instrument; this is discussed below in Section 4.4.5.2. At these q-values (q < 0.02 Å⁻¹) and Fourier times (τ ≤ 290 ns), statistically significant differences are observed in both β and Γ(q) for the low branching (0.01% wt NaTos) and branched network (0.50% wt NaTos) solutions. For Γ(q), each data point is outside of the uncertainty of the other (solid symbols, Figure 4.10b), whereas a paired t-test was used for β (p < 0.05). Due to time limitations, only these two samples were probed in this region. A close-up of this low-q data can be seen in Figure 4.10b. The data in Figure 4.10b shown in solid symbols corresponds to the same experiment as the higher q data; the open symbols represent a second, follow-up experiment in the low-q region. Unfortunately due to the low flux and long counting times required in the low-q configurations, and the few Fourier times that were used in the second experiment (9 FT vs. 13 FT in the original experiment), the uncertainty is fairly high in these data.

As the sample with low branching contains little to no branch points, we expect a stretch exponent of β = 3/4, as predicted by Zilman and Granek [28] for a worm-like chain, across the appropriate q-range. Conversely, in the branched network solution, we only expect a stretch exponent of β=3/4 on the smallest length scales that represent the micelle cylinder, or roughly the persistence length l_p. At length scales longer than this, or those around the mesh size ξ_M, we expect a transition to lower values of β due to the high density of branch points. On the mesh size length scale, a value of β near the expected value of β = 2/3 for flexible membranes would be reasonable, as the branched network solution is behaving as
a single, interconnected network. Figures 4.11 and 4.12a appear to confirm this hypothesis, where significant differences are observed in the stretch exponents between samples on longer length scales \( q = 0.018 \text{Å}^{-1} \), real space \( d \approx 350 \text{Å} \).

Figure 4.11: Comparison of the low-\( q \) (\( q = 0.018 \text{Å}^{-1} \)), long Fourier time (\( \tau = 290 \text{ns} \)) NISFs for the low branched (red) and branched network (blue) solutions. Fits to the data show significant differences in \( \beta \), where the low branched \( \beta = 0.771 \pm 0.053 \) is within error of the theoretical \( \beta = 3/4 \) for a wormlike chain, and the branched network solution \( \beta = 0.628 \pm 0.047 \) is within error of the expected value for membranes, \( \beta = 2/3 \).

As seen in Figure 4.11, the low branching solution \( \beta = 0.72 \) is in line with \( \beta = 3/4 \), which is reasonable due to its long persistence length, 350 Å < \( l_p \). In the network-like solution, \( \beta = 0.63 \), which is closer to the expected \( \beta = 2/3 \) for a flexible membrane. The persistence length of these WLM solutions is known to decrease with branching because the electrostatic interactions are screened, which is verified by our calculations (Tables 4.1, 4.2) and the work of Schubert et al. [2]. The persistence length for the 0.25% wt NaTos solution was previously determined to be \( l_p \approx 200 \text{Å} \) by Schubert et al. [2], indicating that \( l_p \) of our branched network solution (0.50% wt NaTos) should be even less than 200 Å. In the case of the branched network solution, the persistence length is clearly smaller than the length scale probed at \( q = 0.018 \text{Å}^{-1} \), \( l_p < 350 \text{Å} \). Therefore, the stretch exponent of \( \beta = 0.63 \) is measuring the network-like length scale, where the interconnections of the network lead to similar dynamics as in a flexible membrane. The fits for the stretch exponent in the low-\( q \)
region are robust, as seen in Figure 4.12a for the 0.01% wt NaTos solution. Figure 4.12a shows four intermediate scattering functions and fits for $\beta$ in the low-$q$ region, which all encompass $\beta = 3/4$ within the uncertainty for the solution with low branching.

While Figure 4.11 shows the NISFs for only one $q$-position, these differences in stretch exponent at low-$q$ values persist across the whole low-$q$ region. It should also be noted that these differences in $\beta$ continue to even lower $q$-values ($q \approx 0.01 \text{Å}^{-1}$), which approaches the length scale of the mesh size for the 0.01% wt NaTos solution (Table 4.1). However, the stretch exponent for this solution does not decrease to the $\beta = 2/3$ value observed for the network-like solution. Therefore, the differences in $\beta$ observed between the two solutions appear to be a result of the difference in branching level, not simply a difference in the measured length scale.

### 4.4.5 Validation of NSE parameters

#### 4.4.5.1 Comparison between NSE configurations

As briefly discussed above, it is important to verify the fits to the intermediate scattering functions across multiple configurations, especially in the low-$q$ region where the neutron wavelengths are longer and multiple scattering can be an issue. Figure 4.12a shows multiple intermediate scattering functions and fits for the low branched solution (0.01% wt NaTos) in this regime, over two different configurations: a 17 Å configuration centered at $q = 0.018 \text{Å}^{-1}$ and 15 Å centered at $q=0.025 \text{Å}^{-1}$. In Figure 4.12a, the stretch exponent fits for all four normalized intermediate scattering functions are within the uncertainty of the theoretical $\beta = 3/4$ for a wormlike chain, demonstrating the robustness of the stretch exponent fit within this regime. The uncertainty around the fits in the 17 Å configuration is lower because these measurements extend to longer Fourier times ($\tau_{\text{max}} = 290$ ns vs. $\tau_{\text{max}} \leq 200$ ns for the 15 Å configuration), which improves the accuracy of the calculation. This low-$q$ region is on the length scales at which contributions from branching are expected, as it accesses the network-like length scale of the highly branched and branched network solutions. The low-$q$ data also approaches the length scale of the mesh size, $\xi_M$, for the low branching solution. Interestingly, the interaction peak that results in the low branched solution occurs...
at \( q = 0.02 \text{ Å}^{-1} \). Thus it is perhaps unsurprising that the deviations in the sample behavior starts to occur at this \( q \)-position. While the interactions are highly screened in the highly branched and branched network solutions, the electrostatic repulsions at the micellar surface in the low branched solution aid in cooperative diffusion. This deviation at low-\( q \) may also be an electrostatic effect, which carries into the dynamic light scattering (DLS) regime, and will be discussed further below in Sections 4.4.8 and 4.4.9.

![Graph](image)

Figure 4.12: NISFs for low-\( q \) configurations (\( q < 0.03 \text{ Å}^{-1} \)) for the 0.01% wt NaTos solution. (a) NISFs from 17 Å (red, blue) and 15 Å (pink, green). Additional Fourier times at 17 Å result in a smaller uncertainty in \( \beta \) than at 15 Å. All fits agree with the expected \( \beta = 3/4 \), within uncertainty. (b) NISFs at \( q \approx 0.02 \text{ Å}^{-1} \): 17 Å centered at \( q = 0.018 \text{ Å}^{-1} \) vs. 15 Å at \( q = 0.025 \text{ Å}^{-1} \). The additional Fourier times at 17 Å lead to a smaller uncertainty in \( \beta \), which is closer to \( \beta = 3/4 \).

### 4.4.5.2 Long Fourier time and long \( \lambda \) measurements

To validate the low-\( q \) and long Fourier time measurements, Figure 4.12b shows the comparison in the normalized intermediate scattering function in the low branched solution between two configurations, shown at \( q \approx 0.02 \text{ Å}^{-1} \): 15 Å centered at \( q = 0.025 \text{ Å}^{-1} \) vs. 17 Å centered at \( q = 0.018 \text{ Å}^{-1} \). Not only are the relaxation rates similar, but the uncertainty around the fit to the stretch exponent in the 17 Å configuration is less than half of the uncertainty associated with the 15 Å configuration fit due to the additional measured Fourier times. Further, the fit stretch exponent value of \( \beta = 0.774 +/- 0.066 \) at 17 Å is closer to the theoretical
value of $\beta = 3/4$ for a wormlike chain. As these samples are still fairly dilute, and the neutron transmission, $T$, was always $T > 0.4$ at these long wavelengths using 4 mm sample cells. Because of this, these results are not surprising, as the multiple scattering effects that result when moving between the two configurations are fairly insignificant. Still, measuring the NSE response at these two configurations and observing the similarity in the data at approximately equal $q$-positions helps to verify the accuracy of the long wavelength, low-$q$ position measurement.

4.4.5.3 Spatial bin size resolution and accuracy

In NSE experiments, the detector is divided into arbitrary bins over which to analyze the data. Generally, the number of bins over which to divide the detector is chosen based on optimizing the uncertainty in the associated parameters from the fit. An example of this binning procedure and an extended discussion about the uncertainty associated with binning the NSE data can be seen in Appendix H. However, the uncertainty in the fits of $\Gamma(q)$ and $\beta$ in the fit to the normalized intermediate scattering function (NISF), $I(q,t)/I(q,0)$, is reported based on the total number of neutron counts in a particular bin. For each Fourier time, the detector is divided into sub-regions, which each produce an echo that is fit and is averaged into the points that compose $I(q,t)/I(q,0)$. Changing the bin size does not change the uncertainty in the fits to the echoes, it only affects the number of echoes that are then averaged to generate each point in $I(q,t)/I(q,0)$. Therefore, when a larger number of sub-regions on the detector are used, there are more neutron counts and more echoes that are incorporated into each point in $I(q,t)/I(q,0)$, decreasing the reported uncertainty around the fit at each point. This phenomena is outlined Figure 4.13a, where the largest bin size occurs when the detector is divided into five bins, and the smallest bin size occurs when the detector is divided into nine bins. The calculated uncertainty around the fit in the nine bin NISF is substantially larger than in the five bin NISF, despite the fact that the two curves are nearly identical. The fits to the curves produce identical values of $\beta$ and $C$ (Equation 4.10) within the uncertainty. Similar results are seen in Figure 4.13b, where bin widths of two, five and eight detector slices are compared across incrementally changing $q$-positions. Here,
the decay constant $C$ was expected to increase monotonically with decreasing $q$-position (decreasing $\Gamma(q)$ with decreasing $q$), which is observed and is independent of the number of detector slices used.

![Figure 4.13](image.png)

Figure 4.13: Comparison of the NISFs and fit when the detector is sliced into multiple bins of different widths. (a) NISFs for the same $q$-position ($q \approx 0.018 \text{Å}^{-1}$) when the detector is sliced into 5, 7, or 9 bins produce the same decay constant, $C$ (Equation 4.10) and $\beta$ within the uncertainty. The uncertainty is highest at the smallest bin width (9 bins) (b) Fits to $C$ and $\beta$ are reasonable and follow expected trends regard of bin size for the $q$-range $0.015 < q < 0.021 \text{Å}^{-1}$.

While the reported uncertainty accurately captures the uncertainty in the intensity based on neutron statistics, it does not take into account the spatial smearing that can occur when multiple echoes are averaged into one point. For example, the data from the eight bin configuration in Figure 4.13b has a lower spatial smearing than the data from the two bin configuration. The lower spatial smearing results because fewer sub-regions of the detector are used in the eight bin data, meaning that the sub-regions that are used have a much smaller range of $q$-position (see Appendix H). In the eight bin configuration, the sub-regions range from $q=0.0140 \text{Å}^{-1}$ to $q=0.0181 \text{Å}^{-1}$, for an average $q$-value of $q=0.0160 \text{Å}^{-1}$. The sub-regions for the two bin data completely encompass the range of the eight bin data, $q=0.0127 \text{Å}^{-1}$ to $q=0.0182 \text{Å}^{-1}$, for an average $q$-value of $q=0.0154 \text{Å}^{-1}$. The spatial smearing effect seems minimal in the data reported in Figure 4.13, as the reported trends are as expected.
in this $q$-range. However, the large range of $q$-positions may result in significant spatial smearing in certain configurations. This is especially true for data in which only one bin is used (see Appendix H); one bin data was not used in the reported results because of this smearing. Therefore, configurational effects can increase the uncertainty in terms of the spatial smearing, which is unreported in the uncertainty calculation and must be considered when analyzing NSE data.

4.4.6 Diffusive dynamics via dynamic light scattering (DLS)

Dynamic light scattering (DLS) measurements show more distinct differences in the solution dynamics based on branching level than are observed in the NSE measurements. The DLS results are presented as the normalized, first-order autocorrelation function, denoted as $g_1(t)$ versus the delay time, $t$ for each particular angle, $\theta$, corresponding to a $q$-range as specified by Equation 2.52. While spectra from select angles are shown in this section, the full, angle-dependent relaxation spectra can be seen for all three solutions in Appendix I. Select angular spectra, $g_1(t)$ vs. $t$, for the 0.50% wt NaTos (branched network) solution can be seen in Figure 4.14 below across the full angular spectrum from $\theta = 25^\circ$ to $150^\circ$.

As seen in Figure 4.14 below, there are two clear decay functions indicating two distinct relaxation mechanisms in the spectra at each angle. The presence of two relaxation modes in these WLM solutions is not surprising, given the vast evidence of a fast and slow relaxation mode in many entangled polymer solutions and macromolecular solutions in the semi-dilute regime [34, 36–38, 40]. As these solutions are semi-dilute and have significant interactions between micelles, the dilute limit assumptions no longer hold, and the presence of multiple relaxation modes is a function of the inter-micelle interactions. Both relaxation mechanisms are observed in each of the three WLM solutions. We refer to the first decay seen in Figure 4.14 (and seen in the spectra for all samples) as the fast relaxation mechanism, denoted by $\Gamma_1(q)$ and characterized by stretch exponent $\beta_1$ (Equation 4.6). The second decay, referred to as the slow relaxation mechanism, is named as $\Gamma_2(q)$ and is characterized by $\beta_2$. 

190
Figure 4.14: DLS angular spectra of the normalized, first-order correlation function, $g_1(t)$, vs. the delay time, $t$, as a function of scattering angle, $\theta$, for the network-like, 0.50% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all $\theta$.

In Figure 4.14, the slow relaxation mode shows a significantly more stretched response in comparison to the fast relaxation mode, especially at high angles where the presence of the slow relaxation mode is most pronounced. This observation suggests that $\beta_1 > \beta_2$, as the lower the stretch exponent, the more stretched the decay function; a value of $\beta = 1$ returns the standard exponential decay. Interestingly, the stretch exponent $\beta_2$ appears to increase with decreasing angle, as the decay function appears to sharpen. With decreasing angle, the presence of the slow relaxation mode is less distinguishable than at high angles, due to this apparent increase in $\beta_2$. The quantitative trends in the stretch exponents $\beta_1$ and $\beta_2$ with changing angle will be discussed further in Section 4.4.7 below. The same angle-dependent relaxation spectra presented in Figure 4.14 for the 0.50% wt NaTos solution are shown for the highly branched, 0.25% wt NaTos solution in Figure 4.15, and for the low branching, 0.01% wt NaTos solution in Figure 4.16. The full relaxation spectra for both solutions can be seen in Appendix I.

In Figure 4.15, both the fast and slow relaxation modes are distinct at all angles in the 0.25% wt NaTos solution, unlike in the 0.50% wt NaTos solution where the slow relaxation mode was difficult to discern at low angles. The fast relaxation mode appears
Figure 4.15: DLS spectra \( g_1(t) \) vs. \( t \) for the highly branched, 0.25% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all \( \theta \); the slow mode is more pronounced (smaller \( \beta_2 \)) than at 0.50% wt NaTos.

to undergo a more rapid decay in the 0.25% wt NaTos solution across the angular range, suggesting that \( \Gamma_{1.0.25\%}(q) > \Gamma_{1.0.50\%}(q) \). Further, the slow relaxation mode appears to be stretched over longer times in the 0.25% wt vs. 0.50% wt NaTos solution, indicating that the stretch exponent \( \beta_2 \) is lower in the 0.25% wt NaTos solution. However, the relaxation spectra in Figure 4.15 are qualitatively similar to those presented in Figure 4.14. In both WLM solutions, \( \beta_2 \) appears to increase with decreasing angle, making the slow relaxation mode less pronounced with decreasing \( \theta \) (decreasing \( q \)). From Figures 4.14 and 4.15, it also appears as though the amplitude of the slow relaxation mode decreases with decreasing angle. These quantitative trends, along with quantitative differences between the WLM solutions, will be discussed in Section 4.4.9. An additional comparison of the relaxation spectra between solutions can be seen in Appendix I for select angles.

The slow relaxation mode is the most pronounced in the solution with the lowest branching, 0.01% wt NaTos, as seen in Figure 4.16, and is prominent at all angles. By examining Figure 4.16, it can be inferred that the value of \( \beta_2 \) is the lowest in this solution, as the slow mode covers three decades of delay times at some angles. As observed in the two branched solutions, it also appears that \( \beta_2 \) increases with decreasing angle (decreasing \( q \)). However, unlike in the other two solutions, it appears as though the slow relaxation mode
becomes more pronounced with decreasing \( \theta \) and that the amplitude of the slow mode actually increases as \( \theta \) is decreased, which will be discussed further in Section 4.4.7. Finally, from comparing Figure 4.16 to Figures 4.14 and 4.15, it is clear that the 0.01% wt NaTos solution exhibits the most rapid decay of all three solutions in the fast mode. As the relaxation rate measured from NSE was also the largest for this solution at low \( q \)-values, it appears as though the statistically significant differences in \( \Gamma(q) \) observed in NSE carry into the DLS regime.

### 4.4.7 DLS data fitting

As shown by Equation 4.6, there are five parameters that need to be fit when analyzing the DLS data to extract the relaxation rates for the fast and slow relaxation mode, \( \Gamma_1(q) \) and \( \Gamma_2(q) \). Standard equations for fitting bimodal data, like the double exponential fit, showed poor fits to the WLM data versus the double stretched exponential function given in Equation 4.6, which is commonly used in soft materials and entangled systems [34, 38–40]. The CONTIN algorithm is a possible option, but as there are only two modes in the DLS data, the double stretched exponential is sufficient, simpler, and physically meaningful. The method of cumulants would also be inappropriate, as the method is designed for...
polydisperse, but monomodal systems. While Equation 4.6 provided the best fits to the data, the double stretched exponential equation requires multiple variables to be fit, which may or may not be constant across the $q$-range accessed by DLS. These parameters include two stretch exponents ($\beta_1, \beta_2$), one constant indicating the relative amplitudes of the fast and slow mode ($A_1, A_1 = 1 - A_2$), and then two relaxation rates ($\Gamma_1(q), \Gamma_2(q)$) which will vary at each $q$-position. When possible, the number of variables to fit at each $q$-position should be minimized. By examining Figures 4.14, 4.15, and 4.16, it is clear that the proportion of the fast relaxation mode to the slow mode ($A_1$ to $A_2$) changes with angle, $\theta$. This phenomenon can be seen more clearly in Figures 4.17, 4.18, and 4.19 below. Therefore, $\Gamma_1(q), \Gamma_2(q)$, and $A_1$ will change with changing $q$-position or $\theta$. However, the stretch exponents may be constant across $q$ values, and the data presented in Figures 4.17 and 4.18 help to address this.

Figure 4.17: Scaling of $\beta_1$ for the 0.50% wt NaTos solution on a linear-log (a) and log-log (b) scale. To determine $\beta_1$, $g_1(t)$ vs. $q^2 t^{\beta_1}$ should collapse wrt the fast mode. Here, $\beta_1 = 1$ and the curves collapse well. As $\theta$ decreases, $\beta_2$ and the fast mode amplitude, $A_1$, increase, as seen by the sharper decay in the slow mode.

In entangled polymer systems, $\beta_1$ is often fixed to a value of $\beta_1 = 1$. Due to the similarity of the entangled WLMs to entangled polymer solutions, the choice of $\beta_1 = 1$ was a practical starting point. However, the neutron spin echo data was fit to a stretch exponent that was less than one at the lowest $q$-range measurable for all samples; the differences observed in the NSE data continued into the DLS regime as seen by Figure 4.20. Therefore, the assumption that $\beta_1 = 1$ had to be validated for each WLM solution. In these dynamic
measurements, whether NSE, DLS, or other, the plot of the normalized decay function \( g_1(t) \), \( I(q,t)/I(q,0) \), etc.) should scale with \( q^2 t^\beta \) provided that \( \beta \) is constant across the accessed \( q \)-region. If \( \beta = 1 \), then the normalized functions simply scale as \( q^2 t \).

Figures 4.17 and 4.18 show the plot of \( g_1(t) \) versus \( q^2 t \) for the 0.50% wt and 0.25% wt NaTos solutions, respectively, in both a linear-log (a) and log-log (b) scaling. Both of these WLM solutions show similar scalings. As seen in Figures 4.17 and 4.18, the normalized curves for these highly branched solutions collapse with regard to the fast relaxation mechanism when plotted by \( q^2 t \). This collapse of \( g_1(t) \) versus \( q^2 t \) indicates that \( \beta_1 = 1 \) is the appropriate value of the first stretch exponent for the highly branched WLM solutions, as is expected for this type of entangled system. Figures 4.17 and 4.18 also suggest that the value of \( \beta_2 \) is not constant as the \( q \)-position or \( \theta \) is changed, as the curves do not collapse in the region of the slow relaxation mechanism. With regard to the slow relaxation mechanism, the decay becomes sharper with decreasing \( q \)-position (decreasing \( \theta \)); this trend has been previously observed in WLMs [43] and other soft matter systems [38,44]. Similarly, it appears that the amplitude of the slow relaxation mode, \( A_2 \), decreases with decreasing angle. As \( \beta_2 \) increases, the slow relaxation mode becomes less pronounced and therefore the contribution to the total amplitude from the slow mode also decreases.
Figure 4.19: Scaling of $\beta_1$ for the 0.01% wt NaTos solution on a linear-log (a) and log-log (b) scale. Using $\beta_1 = 1$ leads to a near, but not perfect, collapse of $g_1(t)$ vs. $q^2t^{\beta_1}$ wrt the fast mode. With decreasing $\theta$, $\beta_2$ increases but $A_2$ increases as the slow mode becomes more pronounced.

Figure 4.19 shows the $g_1(t)$ versus $q^2t$ for the 0.01% wt NaTos solution. In contrast to the two branched solutions, the normalized relaxation curves for the low branching solution do not collapse perfectly with regard to the fast relaxation mode when plotted by $q^2t$, although the scaling appears to be close to $q^2t$. However, the amplitude of the slow relaxation mode, $A_2$, also increases with decreasing angle, whereas $A_2$ decreased with angle in the other solutions. While $g_1(t)$ versus $q^2t$ does not collapse as well as the other systems, it is difficult to tell if this is an effect of the increasing $A_2$ value with decreasing angle, or if in fact $\beta_1 = 1$ is not the appropriate value of the first stretch exponent. As the value of $\beta_1 = 1$ does lead to a near collapse of the data, we choose $\beta_1 = 1$ to fit the data for this solution for consistency. Fitting the data using $\beta_1 < 1$ for this solution gives the same qualitative trends, giving confidence to our interpretation of the data. As aforementioned, in the 0.01% wt NaTos solution, the amplitude of the slow relaxation mode clearly increases with decreasing angle, which is in contrast to the behavior for the two branched solutions. Interestingly, $\beta_2$ increases with decreasing angle in all cases, which has been observed previously in WLM solutions [43]. In this work, Buhler et al. [43] saw a slight increase in the amplitude of the slow mode with decreasing angle for a similar CTAB WLM solution, which is consistent with the behavior...
of the low branching solution. This trend has also been observed in polyelectrolyte solutions [45], and in polymer solutions depending on the solvent quality [39,44]. However, it is also common in soft materials to see the amplitude of the slow mode decrease with decreasing angle [38,44].

It is difficult to explain the difference in behavior in the low branched versus the two highly branched solutions with regard to the angular dependence of the slow mode amplitude, $A_2$. One explanation could be the difference in ionic strength and electrostatic interactions between the solutions. The solution with low branching has very strong electrostatic interactions, whereas in the two highly branched solutions, these interactions are largely screened. The amplitude of the slow mode has a strong dependence on the amount of added salt in polyelectrolyte and polymer solutions [36,46], which could be a contributing factor here. Another explanation, which may be coupled to ionic strength effects, is the difference in length scales between the low branching and highly branched solutions. As the solutions have dramatically different electrostatic interactions, this includes both physical and interaction-based length scales. As reported in Table 4.1 and discussed above in Section 4.4.4, the low branching solution has a much longer persistence length than in the two branched solutions. From the LVE rheology shown in Figure 4.8 and scaling rules presented in Chapter 1, Section 1.3, it can be inferred that the length scales in the two highly branched solutions are fairly similar, whereas the low branched solution has a larger mesh size, $\xi_M$. Specifically, Equation 1.38 shows that the mesh size is inversely related to the plateau modulus, so the increase in $G_0^N$ with branching shown in Figure 4.8 is associated with a decrease in the mesh size. While the branched solutions have longer overall contour lengths than in the low branching solution, the relevant length scale in these solutions (especially to the slow mode) becomes the distance between branch points, which is associated with the mesh size [2] and is significantly smaller for the branched solutions. Therefore, the motions of the micellar network may be probed over the full DLS $q$-range in the highly branched solutions, but longer length scales may be required to probe these dynamics for the low branched solution. As such, it is reasonable to hypothesize that the slow relaxation mode becomes more prominent at lower angles (lower $q$-values) in the low branched solution because the lower
angles correspond to longer length scales, where the dynamics of the entangled network can be probed.

It is important to note that if we fit the data and fix none of the parameters, similar qualitative results are obtained. However, the data near the ends of the $q$-range seems to be more affected by the multitude of variables that can be fit and slightly deviates from the expected trends. Further, by fixing no variables, it appears that $\beta_1$ slightly increases with decreasing $q$-position (decreasing $\theta$) while $\beta_2$ stays roughly constant until the ends of the $q$-range are encountered. However, the theory and data shown in Figure 4.18 suggest that it is really $\beta_1$ that should be constant and that $\beta_2$ should change with $q$. Clearly, the fast relaxation mode data can collapse onto one curve by selecting $\beta_1 = 1$, whereas the slow relaxation mode data never collapses with a fixed choice of $\beta_2$. Further, fixing $\beta_2$ to an average value while fixing $\beta_1 = 1$ leads to poor fits across much of the $q$-range. Based on this analysis, it appears as though $\beta_1$ is a $q$-independent parameter, whereas the remaining variables ($\beta_2, A_1, A_2$) are all $q$-dependent variables that must be fit at each angle.

4.4.8 Quantitative DLS results and link to NSE

As discussed in Section 4.4.4 above and shown in Figure 4.10, the differences in the segmental dynamics determined via neutron spin echo between the levels of branching begin to become significant around $q = 0.02 \text{ Å}^{-1}$. At $q$-values lower than this, statistically significant differences in the relaxation rate, $\Gamma(q)$ and stretch exponent, $\beta$, are seen; these differences grow as the $q$-value is further decreased and longer length scales are accessed. Interestingly, the low branched solution (0.01% wt NaTos) had a significantly larger relaxation rate in this NSE regime, despite having significantly longer rheological relaxation times. As $q = 0.02 \text{ Å}^{-1}$ corresponds to the location of the interaction peak in the low branched solution, which results from the repulsive interactions around the micellar head groups, it was assumed that these relaxation rate differences were influenced by different levels of electrostatic screening in the WLM solutions. These differences carry over into the DLS regime, which can be seen in Figure 4.20a for all three solutions. Figure 4.20a only shows the DLS results for the fast relaxation mechanism, $\Gamma_1(q)$. As was the case in the NSE measurements
at low-\(q\), the relaxation rate is the largest in the solution with the lowest level of branching; this phenomenon will be discussed further in Section 4.4.9 below. The results in Figure 4.20a suggest that the trends in the segmental dynamics are reflective of the fast relaxation mode, as opposed to the slow mode where the trends with regard to branching level are opposite.

Figure 4.20: Comparison of NSE and DLS. (a) Differences in the low-\(q\) NSE data are more distinguishable via DLS, and are likely a result of the solution electrostatics. (b) While the low branching solution exhibits the fastest ‘fast mode’ (\(\Gamma_1(q)\)), it also exhibits the slowest ‘slow mode’ (\(\Gamma_1^+(q)\)). Error bars in the DLS data are the standard deviation calculated from multiple trials.

In the slow relaxation mechanism, the trends are reversed from the fast relaxation mechanism, meaning that the most highly branched solution exhibits the fastest ‘slow’ mode. This trend is not surprising given the solution relaxation times, and from the fact that the slow relaxation mode, very broadly, stems from inter-micelle interactions [38]. The origins of the slow relaxation mode will be discussed further in Section 4.4.9 below. The 0.50\% wt NaTos solution has a relaxation time that is nearly 10\(^3\) faster than in the low branched, 0.01\% wt NaTos solution, but is only two-fold faster than in the 0.25\% wt NaTos solution. The difference in the relaxation times is largely an effect of the screened electrostatic interactions and the sliding branch points that can relieve stress in solutions with higher salt content. As the branched network solution has the fastest relaxation time, the slow mode results appear to reflect the differences in relaxation time between solutions and the screening of interactions that occurs with added salt. While the slow mode has traditionally been associated with
reptation, it should be noted that recent studies suggest that the slow mode is not associated
with reptation itself [38, 39, 41], but rather with the interactions that govern the relaxation
time and network behavior.

Purely diffusive solution behavior is indicated when the relaxation rate measured via
DLS, \( \Gamma(q) \) scales as \( q^2 \), as given by Equation 4.8 above. As seen in Figure 4.20, both the
fast and slow relaxation mechanisms scale with \( q^2 \), indicating that both modes are purely
diffusive. The calculated apparent diffusion coefficients for both modes, \( D_1 \) and \( D_2 \) can be
seen in Table 4.3. Interestingly, this scaling does not appear to be affected by the different
\( \theta \)-dependent trends in scattering amplitude (\( A_1 \) and \( A_2 \)) between the WLM solutions. It is not
surprising that both the fast and slow mode exhibit purely diffusive behavior, as deviations
from the \( q^{8/3} \) scaling expected for segmental dynamics began well within the NSE regime
(\( q < 0.1 \ \text{Å}^{-1} \)), as seen in Figure 4.10a. However, the notable difference here is that the stretch
exponent \( \beta_2 \) does not affect the scaling of the slow mode relaxation rate with \( q \) (Equation
4.8), whereas in the NSE regime, the stretch exponent does affect \( \Gamma(q) \) (Equation 4.5). The
plot of \( \Gamma(q) \) versus \( q^2 \) can be seen in Figure 4.21a for the fast mode and Figure 4.21b for the
slow mode. For all solutions, the y-intercept is nearly zero for both modes, indicating purely
translational, as opposed to rotational, diffusion in this regime (\( D_0 = D_t \)). These curves are
used to calculate the diffusion coefficient for each mode where the intercept is fixed to zero,
which are reported in Table 4.3.

Table 4.3: Calculated diffusion coefficients from NSE and DLS for the 0.01%, 0.25%, and
0.50% wt NaTos WLMs. \( D_G \) is the segmental diffusion coefficient from the high-\( q \) NSE data
where \( \Gamma \propto q^{8/3} \); \( D_1 \) and \( D_2 \) are the diffusion coefficients calculated from DLS corresponding
to the fast and slow relaxation mode, respectively. The associated uncertainty gives the 95%
confidence interval.

<table>
<thead>
<tr>
<th>Sample, % wt NaTos</th>
<th>( D_G \times 10^{-17}, \ \text{m}^{8/3} \text{s}^{-1} )</th>
<th>( D_1 \times 10^{-11}, \ \text{m}^2 \text{s}^{-1} )</th>
<th>( D_2 \times 10^{-14}, \ \text{m}^2 \text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>5.96 ± 0.10</td>
<td>10.1 ± 0.1</td>
<td>5.87 ± 0.18</td>
</tr>
<tr>
<td>0.25</td>
<td>5.81 ± 0.10</td>
<td>2.44 ± 0.02</td>
<td>58.4 ± 1.1</td>
</tr>
<tr>
<td>0.50</td>
<td>5.97 ± 0.08</td>
<td>1.72 ± 0.01</td>
<td>127.3 ± 2.0</td>
</tr>
</tbody>
</table>
4.4.9 Interpretation of DLS results

Evidence of the fast relaxation mode being that of cooperative diffusion is supported by a number of studies on these phenomena in entangled polymeric solutions [32, 35, 38]. Specifically, in non-entangled, semi-dilute polymer solutions, only a cooperative diffusion mode is detected, whereas in entangled solutions, both a cooperative and slow mode are seen. While the low branched solution is dominated by the cooperative diffusion mode based on strong electrostatic interactions, the slow mode relaxation rate is the fastest in the most highly branched solution. It may be counterintuitive that the solution with the lowest ionic strength exhibits the largest apparent diffusion coefficient for the fast relaxation mode, as the Stokes-Einstein-Sutherland equation suggests that $D$ should be smallest in the low branching solution where the hydrodynamic radius, $r_h$, is the largest:

$$D = \frac{k_BT}{6\pi\eta r_h}$$

(4.13)

where $r_h$ is typically associated with the radius of gyration. However, it has been well documented that increasing the solution ionic strength in polymers and polyelectrolytes serves to decrease the magnitude of $D_1$ when the polymer or polyelectrolyte concentration is held
constant [45,47–49]. In these charged WLM solutions, the Stokes-Einstein-Sutherland equation should not be used. However, as a baseline, using Equation 4.13 and the cross-sectional radius of gyration determined by Equation 2.19 gives \( D = 1.6 \cdot 10^{-10} \text{m}^2\cdot\text{s}^{-1} \), which is similar to \( D_1 \) for the 0.01% wt NaTos solution in Table 4.3. Using a segmental radius of gyration associated with the persistence length (Equation 2.27, where \( L = l_p \)), gives a value of \( D_1 \) from Stokes-Einstein-Sutherland that is orders of magnitude lower than the value reported in Table 4.3 for the 0.01% wt NaTos solution. However, for the 0.25% wt and 0.50% wt NaTos solutions, the Stokes-Einstein-Sutherland values of \( D_1 \) are on the same order of magnitude as those in Table 4.3. One explanation for this phenomenon is that the dynamics are coupled between the micelles and the counterion cloud, where \( D_1 \) is actually the sum of the cooperative diffusion coefficient and the contribution from the coupling [49]. In the low branching solution, this coupling would greatly increase \( D_1 \), whereas the coupling effects are relatively minor in the more highly branched solutions where most of the interactions are screened.

While the nature of the slow mode has been long-debated, as discussed in Section 4.4.2 above, the trends in the slow mode based on branching level are not unexpected, as studies generally suggest that this mode results from hindered motions of interacting or entangled chains [38]. Explicitly in WLM solutions, this slow relaxation mode has shown to reflect long-range correlated fluctuations, like those from the internal motion of a transient network [36–38]. In polyelectrolyte solutions, adding salt results in an increasing magnitude of \( D_2 \) [47,49], as is observed in these WLM solutions. An increase in \( D_2 \) with added salt is counter-intuitive, as the slow mode is associated with large aggregates of many chains or motions of a network, and electrostatic repulsions should prevent aggregation and therefore the slow mode. However, dipole-dipole interactions from the counterion cloud can lead to aggregate-like structures in low salt solutions [49]. The relative impact of the counterion cloud and the dipole interactions on the dynamics of these WLM solutions may explain the differences in the slow mode trends observed between the low and high branching solutions.

When comparing the branched network solution to the low branching solution, there are two distinct differences. First, the electrostatic interactions are screened in the network-like solution, which addresses the contribution to the slow mode from interacting chains.
These interactions are correlated long-range and serve to slow the dynamics of the entangled, low branching micelles, where the dipole-dipole interactions mentioned above may play a role [49]. However, Muthukumar [49] could not explain the slow mode behavior by these interactions alone, and suggested that entanglement effects and cross-link density also play a role in the slow mode behavior. Second, the network-like solution is not entangled in the same way as the low branching solution. In highly branched solutions, the entanglement length and distance between branch points are not well separated [2, 12] and the motion of branch points may eliminate entanglements. As branching increases and interconnected structures form, the WLMs become more similar to a membrane than to an entangled solution. Branch points can slide to relieve stress or to relieve entanglements, decreasing hindrance to motion that contributes to the slow relaxation mode [38]. Therefore, the contribution to the slow mode from such entanglements and hindered motions is reduced at high branching levels. As the slow relaxation mode is not well understood, it is difficult to quantify the contributions to the slow mode from the electrostatic interactions versus the branching, although both are thought to play a role [49]. In general, these two effects are hard to de-couple, as the branching results from changing the ionic environment. However, from the work that has been reported on the slow relaxation mode, it is reasonable to conclude that both the differences in electrostatic interactions and in branching level contribute to the observed differences in the slow mode between samples.

4.4.10 Discussion: Solution dynamics

In both the neutron spin echo and dynamic light scattering measurements, the behavior of the two branched solutions (0.25% wt NaTos, 0.50% wt NaTos) was similar, whereas the behavior of the linear solution (0.01% wt NaTos) was quite different. These differences in dynamics appear to be the result of differences in the electrostatic interactions as well as differences in the branching level between solutions. Because the branching is induced by changing the electrostatic interactions in the system, it is difficult to de-couple these effects. As mentioned above, the difference in relaxation time is $10^3$ between the network-like and low branching solution, but is only two-fold different in the case of the highly branched and
network-like solutions. Clearly, the initial screening of the interactions has the largest effect on the relaxation time and the solution dynamics, as the difference in salt content between the 0.01% wt and the 0.25% wt NaTos solution and the 0.25% wt and 0.50% wt NaTos solution is nearly the same. However, there is little difference in the relaxation time and solution dynamics from both NSE and DLS between the 0.25% wt and 0.50% wt NaTos solutions, whereas the differences in the relaxation time and dynamics of the 0.01% wt NaTos solution compared to the other two solutions are quite significant. This trend is particularly noticeable in the DLS data shown in Figure 4.20b. The relaxation rate for both the fast mode and the slow mode between the two branched solutions are very similar in magnitude; when compared to the other two solutions, the relaxation rate for the fast mode of the low branched solution is nearly an order of magnitude higher, and the relaxation rate for the slow mode is nearly an order of magnitude lower. The similarities between the 0.50% wt NaTos solution and 0.25% wt NaTos solution are also observed in the low-\(q\) regime of the NSE measurements, shown in Figure 4.22.

Figure 4.22: Comparison of the NSE low-\(q\) results for the two highly branched solutions, 0.25% wt NaTos and 0.50% wt NaTos. Nearly identical NISFs are obtained between the two samples, confirming the similarity between the two solutions and the presence of highly branched, network-like features.

As seen in Figure 4.22, the low-\(q\) normalized intermediate scattering function (NISF)
and fit to the NISF between the two solutions is nearly identical. In Figure 4.22, the 0.25% wt NaTos solution has four fewer Fourier times than the 0.50% wt NaTos solution, due to an early reactor shutdown at the NCNR. Having the four fewer Fourier times makes accurate calculation of the relaxation rate $\Gamma(q)$ and the stretch exponent $\beta$ difficult, which is why this data is not included in the NSE data shown in Figure 4.10. However, Figure 4.10 does clearly show the similarity between the 0.50% wt and 0.25% wt NaTos dynamic response at the shorter Fourier times, indicating that the 0.25% wt NaTos solution is also significantly different than the low branching solution at low $q$-values. This result is not surprising, as the ‘highly branched’ and ‘network-like’ denominations for the samples are purely qualitative, and these two solutions most likely have similar, and very high, levels of branching. Re-examining the LVE rheology for the low salt WLM solutions (Figure 4.7) versus these higher salt solutions (Figure 4.8) supports this hypothesis. As seen in Figure 4.7, the crossover modulus $G_c$ only slightly increases with added salt, until a significant amount of branching and interconnections are formed in the system ($C_S \geq 0.185$% wt NaTos). In Figure 4.8, the crossover modulus for the 0.01% wt NaTos solution is significantly lower than both the 0.25% wt and 0.50% wt NaTos solutions, as is expected for a solution with low branching. However, in Figure 4.8, the crossover modulus is roughly the same between the two highly branched solutions. As the two highly branched solutions have similar values of the crossover modulus, it is likely that the branching levels and network-like qualities of the two solutions are also similar.

While it is difficult to understand the electrostatic effects versus the branching effects, the neutron spin echo results do provide significant insight. As the stretch exponent is an indicator of the micellar morphology, the measurements of $\beta$ should not be affected by the differences in electrostatic interactions between the systems. Examining the value of $\beta$ across the NSE $q$-range indicates precisely the behavior that we expect from these systems. At short length scales, all of the WLM solutions behave the same in both $\beta$ and $\Gamma(q)$, indicating that the same wormlike structure is observed across solutions. At much longer length scales, where NSE probes length scales on the order of the mesh size, $\xi_M$, we see significant differences in the solution dynamics. While the differences in $\Gamma(q)$ may be attributed to the
electrostatics, the significant differences in $\beta$ give firm evidence of the morphological differences. The solution with low branching always acts like a wormlike chain throughout all NSE length scales, whereas the branched, network-like micelles starts to behave more like a flexible membrane when these longer length scales are probed. As aforementioned, detecting branching in WLM solutions has been a long-standing and difficult challenge [8]. While previously branching in WLMs could only be detected by PGSE-NMR diffusion measurements [10,23], neutron spin echo now provides a new method that branching can be identified by.

4.5 Conclusions

In this chapter, the equilibrium static and dynamic properties of mixed cationic and anionic wormlike micellar solutions with various amounts of added salt were characterized. The addition of salt to these WLM solutions is known to induce branching, and the effects are magnified when penetrating salts are used. A wealth of measurements detailed in this chapter support the conclusion that branch points are formed as the hydrotropic salt sodium tosylate (NaTos) is added to these WLM solutions at a fixed surfactant concentration of $C_D = 1.5\%$ wt. These measurements explored the static and dynamic signatures of branching in these solutions; additional non-equilibrium signatures will be discussed in the remaining chapters.

The static properties of the solutions with different levels of added salt were first explored. Cryo-transmission electron microscopy (TEM) measurements identified the presence of branch points at high salt concentrations; no branch points were observed at the lowest salt concentration. As cryo-TEM cannot exclude the presence of branch points, the solution with no observable branch points is qualitatively referred to as the solution with ‘low branching.’ Static small angle neutron scattering (SANS) measurements were then used to calculate the basic length scales of the micelles, in good agreement with the prior work of Schubert [2,12]. At high-$q$ values, the SANS data collapsed onto the same curve regardless of added salt, indicating that adding salt does not change the basic, cylindrical structure of the micelles and instead alters the branching level. With increasing salt content, the low-$q$ slope of the static SANS curves also increased, due to the screening of electrostatic interactions. A true fractal dimension could not be determined from the static SANS, as the low-$q$ slope can
increase both from the screening of electrostatic interactions and the formation of branch points. Therefore, static SANS cannot be used to distinguish branching in these charged WLM solutions, as the differences in the SANS spectra result from the electrostatic interactions. If branching effects are present in the static SANS spectra, they cannot be de-coupled from the electrostatic effects.

The dynamic properties of the solution were also probed, using both rheology and scattering techniques. As adding salt to the WLM solutions screens the electrostatic interactions, the relaxation time decreased with increasing salt content. While the WLM solutions with low amounts of added salt showed Maxwell-like (Oldroyd-B fluid) behavior in the linear viscoelastic (LVE) rheology, the LVE spectra of the high salt solutions showed deviations similar to those observed in branched polymers. These deviations may indicate a spectrum of relaxation times is more appropriate for branched WLMs, as opposed to the single relaxation time that accurately captures the behavior of Maxwell fluids. At low to mild salt concentrations, the salt addition did not appear to greatly affect the LVE rheology, except for increasing the crossover frequency and decreasing relaxation time. At high salt concentrations, however, the crossover and plateau moduli increased in magnitude, signifying the presence of branch points and interconnected structures. These signatures of branching were then confirmed using the dynamic measurements neutron spin echo (NSE) and dynamic light scattering (DLS). Specifically, NSE measurements on length scales relevant to the branched network dynamics revealed similar dynamics to those of a flexible membrane.

Identifying the effects of branching versus those of the electrostatic interactions in the system is challenging, as the branching in the systems is induced by changing the ionic environment. In both the static and dynamic properties, contributions from the electrostatic interactions and branching likely played a role, but de-coupling these effects was not possible in most cases. While the branching effect and electrostatic effect are inherently intertwined, dynamic neutron spin echo measurements helped to identify structural differences between samples with different levels of branching by way of the stretch exponent. Neutron spin echo is just the second experimental method (outside of cryo-TEM) besides PGSE-NMR to verify
branching in these WLM solutions, making it a useful tool for future investigations. Individually, the measurements presented in this chapter do not unequivocally support branching in these WLM solutions. However, when combined, these methods give strong evidence of branching in the WLMs, and provide both static and dynamic signatures to help identify micellar branching in the future.
References


Chapter 5

STRUCTURE AND RHEOLOGY: STEADY SHEAR

5.1 Introduction

In Chapter 4, static and dynamic equilibrium properties of mixed cationic and anionic WLMs were examined to determine signatures of micellar branching and topological changes. In this and the remaining dissertation chapters, the non-equilibrium properties of the WLMs are explored using a combination of rheological and neutron scattering techniques. The aim of these chapters is to establish non-equilibrium signatures of microstructure changes with added salt. In this chapter, the steady shear rheological properties are explored as a function of added salt. Additional evidence is provided to demonstrate that adding sodium tosylate (NaTos) to these solutions changes the morphology, resulting in branched micelles. As in Chapter 4, we discuss what rheological and structural features can be attributed to branching versus other solution properties. In terms of the steady shear rheology, shear banding and shear thinning are discussed, which are both commonly observed spatially-dependent flow phenomena in WLMs. As mentioned in Chapter 4, the power law index, $N$, increases with added salt (and branching). This trend suggests that shear banding may disappear in solutions with high branching levels, which we explore with steady shear measurements. For clarity, only the steady state, steady shear measurements are presented in this chapter. Time-dependent steady shear startup measurements are discussed in Chapter 6, which also helps to distinguish shear thinning from shear banding.

To complement the rheological results, steady shear flow-small angle neutron scattering measurements are taken in two shear planes, the 1-3 (flow-vorticity) and 1-2 (flow-gradient) planes. The 1-3 plane measurements do not provide spatial resolution and instead give a gap-averaged structure under shear. These measurements help to determine an average degree of micellar orientation as a function of shear rate and branching level. The 1-2
plane measurements, on the other hand, do provide spatial resolution. The 1-2 plane data corroborates the interpretation of the rheological data in terms of shear banding versus shear thinning, as the spatially-dependent structure can be observed across the concentric cylinder Couette gap. In this chapter and throughout this dissertation, the alignment factor (orientation parameter) determined via SANS measurements is denoted by ‘1-3 $A_f$’ and ‘1-2 $A_f$’ for the alignment factor in the 1-3 plane and 1-2 plane, respectively. In this chapter, as in Chapter 4, the results are first presented as a comparison between the low and highly branched solutions, which are published in references [1,2]. Then, results are presented for the mildly branched solution (published in reference [3]). Finally, results from all other branching levels are presented, where some results have been published in reference [4]. Again, the results for the mildly branched solution are presented separately for clarity due to extensive work on this solution presented in Chapters 6 and 7.

5.2 Shear thinning in wormlike micelles

Shear thinning is a commonly observed flow phenomenon in wormlike micelles. In shear thinning solutions, the viscosity decreases with increasing shear rate. In wormlike micelles, this decrease in the viscosity is associated with flow-alignment of the wormlike chains, which produces less resistance to flow. A typical shear thinning velocity profile can be seen in Figure 5.1, where the shear rate, $\dot{\gamma}$, is the derivative of the velocity with respect to the gap position. Shear thinning is often described by the Cross model [5], described in Chapter 4, Equation 4.3, or by the power law fluid model. The power law model for the shear stress, $\sigma$, and the viscosity, $\eta$, in terms of the shear rate, $\dot{\gamma}$, is defined as:

$$\sigma(\dot{\gamma}) = K \dot{\gamma}^N$$
$$\eta(\dot{\gamma}) = K \dot{\gamma}^{N-1}$$

(5.1)

where $N$ is the power law index and $K$ is the consistency. A value of $N = 1$ corresponds to a Newtonian fluid, $N < 1$ to a shear thinning fluid, and $N > 1$ to a shear thickening fluid. The power law model is more simplistic and is the basis for the Cross model. The power
A law model does not account for the low shear rate Newtonian plateau ($\eta_0$) or high shear rate Newtonian plateau ($\eta_\infty$) in the viscosity as is observed in the Cross model (Equation 4.3); rather the Cross model at intermediate shear rates reduces to the power law model.

The degree of shear thinning in a material can be characterized by the power law index, such that an increasing value of $N$ indicates a lesser degree of shear thinning. As described in Chapter 4, the power law index of the WLMs in this study increases with increasing salt content. Accordingly, the WLMs show a lesser degree of shear thinning with added salt. In an extreme case of shear thinning, known as shear banding, the power law index increases to a minimum value of $N = 0$ (or $N \approx 0$). In shear banding, the flow becomes unstable; this phenomenon will be discussed further below in Section 5.3. A comparison of a shear banding versus a shear thinning velocity profile can be seen in Figure 5.1. The major difference between shear thinning and shear banding materials is that shear thinning solutions exhibit a continuous velocity profile across the Couette gap, whereas shear banding materials exhibit a discontinuity in the velocity profile that arises from the instability.

![Illustration of the velocity profiles corresponding to shear banding (a) and shear thinning (b) across a Couette geometry gap. The shear banding profile is discontinuous with regard to velocity, whereas the shear thinning velocity profile is continuous.](image)

Figure 5.1: Illustration of the velocity profiles corresponding to shear banding (a) and shear thinning (b) across a Couette geometry gap. The shear banding profile is discontinuous with regard to velocity, whereas the shear thinning velocity profile is continuous.

As seen in Figure 5.1a, the shear rate for a shear thinning fluid, which is defined as the gradient of the velocity, decreases across the Couette geometry gap. As the velocity profile is continuous across the Couette gap, the shear rate profile is also continuous with
respect to the gap position in shear thinning solutions. As the viscosity is a function of
the micelle microstructure and the applied shear rate, both the micelle viscosity and shear-
induced structure are also a function of the gap position. For a concentric cylinder Couette
gap, the shear rate at the inner and outer wall can be determined by [6]:

\[
\dot{\gamma}_R = \frac{2\Omega_i}{N(1 - \kappa^2/N)}
\]

\[
\dot{\gamma}_o = \frac{-2\Omega_i}{N(1 - \kappa^{-2}/N)}
\]

(5.2)

where \(R_i\) and \(R_o\) are the inner and outer Couette radii, respectively, \(\kappa = R_i/R_o\), and \(\Omega_i\) is
the rotation rate of the inner cylinder. The power law index can also be defined in terms of
the torque, as \(N = \frac{d\ln M_i}{d\ln \Omega_i}\) where \(M_i\) is the torque at the inner wall. One caveat to Equation
5.2 is that \(N\) must be constant over the shear rate range from the inner to the outer wall,
which is normally a good assumption. Equation 5.2 assumes an inner rotating cylinder and
stationary outer cylinder; however, in the case of a stationary inner cylinder and rotating
outer cylinder, \(\Omega_i\) is simply replaced with \(\Omega_o\). In this chapter, the location in the gap is
denoted by \(r/H\), where \(H = R_o - R_i\), and \(r = R - R_i\). Unlike in shear thinning solutions,
shear banding solutions exhibit a discontinuous velocity profile, and therefore, discontinuous
shear rate profile across the Couette gap. As shear banding fluids are defined in the limit as
\(N \to 0\), Equation 5.2 is no longer valid. These intricacies associated with shear banding will
be discussed further below.

5.3 Shear banding in wormlike micelles

Wormlike micelles are a commonly used model system for studying non-linear flow
phenomena and flow instabilities such as shear banding [7–9]. Linear WLMs tend to exhibit
shear banding under steady shear deformation. Shear banding is a phenomenon where the
flow exhibits spatial heterogeneities and organizes into macroscopic bands of high shear rate
(low viscosity) and low shear rate (high viscosity). Shear banding is an extreme case of shear
thinning, where the measured power law index, \(N\), is zero or close to zero. Shear banding
is illustrated in Figure 5.1b, where the velocity profile across the gap is discontinuous in a
shear banding system. The discontinuity in the velocity profile leads to the two (or more) distinct bands shown in Figure 5.1b. In contrast to the shear thinning velocity profile, where the shear rate continuously changes across the Couette gap, in shear banding each band has a distinct shear rate that is approximately constant across each band. Shear banding occurs in systems that have an underlying non-monotonic constitutive equation [10, 11]. However, shear banding has also been observed in models of entangled polymers and in WLMs that exhibit monotonic flow curves [12, 13]. Accordingly, the steady shear flow curve of most shear banding WLMs can be described by three regions: the low shear rate Newtonian regime (region I), shear banding regime (region II), and the regime at shear rates in excess of the shear banding regime (region III). This three region flow curve is also applicable to shear thinning micelles. In this case, region II is a strongly shear thinning regime, and region III is designated by an upturn in the stress that corresponds to a change in the power law index.

By altering the WLM solution composition or temperature, morphological changes such as branching can be induced and controlled. Branching in WLMs has shown the potential to alter or eliminate the shear banding behavior of the solution, as the apparent ‘stress plateau’ increases in slope with increasing branching [4]. However, as mentioned above, shear banding has been predicted in models of entangled solutions with monotonic flow curves and is expected in cylindrical Couette geometries [12–14], and has been observed experimentally in WLMs with an apparent positive power law index [13, 15, 16]. Further, there is a significant effect of temperature on the formation and stability of shear bands [17], which makes isolating the effect of branching difficult if temperature is used as the method to control branching. An alternative is to vary the branching by adding salt. However, this method modifies the electrostatic interactions in the system, which may be equally convoluting.

Shear banding has been verified experimentally in polymeric and micellar systems using a variety of experimental methods. Rheo-optical flow birefringence [9, 18] and rheo-nuclear magnetic resonance (rheo-NMR) measurements [19, 20] were some of the first methods used to observe shear banding in WLM solutions. Direct imaging methods, such as particle tracking velocimetry (PTV), have shown the formation of transient and steady shear
bands [15, 21]. Scattering methods including flow-small angle neutron, light or x-ray scattering (flow-SANS, flow-SALS, flow-SAXS) are also commonly used when determining signatures of shear banded flow [22–25]. Berret et al. [22] first used rheo-SANS in the flow-vorticity (1-3) plane to estimate the width of the shear bands in a WLM solution. Spatially-resolved SANS measurements in the flow-gradient (1-2) plane were later used to detect shear banding [1,16,24,26,27]. In these works, shear banding was confirmed by a large decrease in micelle segmental alignment across the concentric-cylinder Couette cell gap; an example of this behavior can be seen from the 2-D scattering patterns shown in Figure 5.2. The discontinuous material alignment as a function of increasing gap position led to a high ‘alignment band’ and low ‘alignment band’ that corresponded to the high shear rate and low shear rate bands, respectively. These 1-2 plane methods will be used to validate shear banding versus shear thinning in this chapter for the present WLM series with added salt. Helgeson et al. [26] used a combination of flow-SANS and rheo-PTV to determine a critical alignment factor and angle at the shear band interface, which has shown to be applicable to other shear banding WLM solutions [27]. In highly shear thinning, non-shear banding materials, the alignment slowly and gradually decreased as a function of gap position [1, 26, 28] and did not meet the critical values necessary for shear banding set forth by Helgeson et al. [26]. Several phenomena have been commonly observed in shear banding materials, including slow transients, the formation of shear-induced structures, and oscillating rheological responses [13,29,30], which may include elastic turbulence and fluctuations of the shear band interface [17,31,32]. These rheological characteristics and experimental techniques are detailed in a review by Manneville [33]. As many of these responses indicating shear banding pertain to time-dependent phenomena, they will be discussed in further detail in Chapter 6.

5.4 Theory: shear banding

The underlying nonmonotonic constitutive equation that describes shear banding wormlike micelles is illustrated in Figure 5.3. Figure 5.3 illustrates the three region flow curve described above, for a fluid with zero slope or a positive slope in the shear banding regime. The low shear rate Newtonian region (region I) is indicated by curve $AB (N = 0)$ or
Figure 5.2: Concentric cylinder Couette flow resulting in shear banding. Bands of distinct velocity, viscosity and structure (via SANS, inset) are observed.

$AB'$ $(N > 0)$ in Figure 5.3. The nonmonotonic portion of the curve is denoted with dashed lines $(CE)$, and is bound by two shear rates, $\dot{\gamma}_c_1$ and $\dot{\gamma}_c_2$. The region II unstable plateau is indicated by curves $BF$ or $BF'$. Finally, the stable, high shear rate region III is indicated by $FG$ or $FG'$. Many constitutive models will predict this nonmonotonic behavior in the stress versus shear rate curve, and several have been used to describe shear banding. In the simplest, Cates and co-workers used a theory of breakage and recombination for nonionic micelles to extract critical parameters for the onset of shear banding under steady shear deformation based on the Doi-Edwards model [7, 34, 35]. In this ‘toy model,’ a zero slope in the region II plateau is assumed. For a given plateau modulus, $G^0_N$, and material relaxation time, $\tau_R$, the critical stress, $\sigma_1$, and shear rate, $\dot{\gamma}_1$ or $Wi_1$, for the onset of shear banding are illustrated in Figure 5.3 and are predicted by Equation 5.3:

$$\sigma_1 = 2/3G^0_N \quad \dot{\gamma}_1 = 2.6/\tau_R \quad \text{or} \quad Wi_1 = 2.6$$  

(5.3)

While derived from a simple theory, Equation 5.3 provides a basis for examining the shear banding WLMs discussed in this work. Deviations from this ‘toy model’ may result in the case of charged or branched micelles, where this model is no longer strictly applicable.
Koshy et al. [37] showed that the scaling of $G_N^0$ with concentration is stronger in regimes where branching is not expected, which may lead to discrepancies in the critical shear rate and stress predictions. Additionally, Fardin et al. [17] demonstrated that solution temperature and composition can affect these critical stress and shear rate values.

It is widely accepted that the band width in the shear banding regime increases linearly with applied shear rate, as shown by several theoretical and experimental works [7,14,16,19]. The applied shear rate, $\dot{\gamma}$ or $Wi$, is comprised of the proportion of the material in the high shear rate band ($\dot{\gamma}_2$, $Wi_2$) and the portion in the low shear rate band ($\dot{\gamma}_1$, $Wi_1$):

$$\dot{\gamma} = (1 - \alpha)\dot{\gamma}_1 + \alpha\dot{\gamma}_2 \quad \text{or} \quad Wi = (1 - \alpha)Wi_1 + \alpha Wi_2$$

(5.4)

where $\alpha$ is the fraction of the material within the high shear rate, or ‘high shear,’ band, $\dot{\gamma}_1$ or $Wi_1$ is the shear rate at the onset of region II, and $\dot{\gamma}_2$ or $Wi_2$ is the shear rate at the onset of region III. In this chapter, we use both a shear rate basis and Weissenberg number basis ($Wi = \tau_R \dot{\gamma}$) to discuss our results; the $Wi$ basis allows us to compare the WLMs on a dimensionless basis, accounting for the differences in micellar relaxation time with added salt. In many micellar and polymeric solutions, Equation 5.4 successfully describes the shear banding behavior of the system [38, 39]. Experiments have shown that in some solutions, the average shear rate in the high and low shear bands increases with increasing applied shear rate; however, these changes are fairly small [15,16]. In all of these works, the linear relationship between shear rate and band width was confirmed.

It should be noted that $\dot{\gamma}_1$ and $\dot{\gamma}_2$ correspond to the average shear rate within the shear bands in experimental systems. Figure 5.1b illustrates shear banding in the ideal case, such that only one shear rate is observed in either band. This idealized case is the one described by the theory of Cates and co-workers [7,34,35]. Here, the velocity profile and shear rate are truly discontinuous across the shear band interface. In this case, $\dot{\gamma}_1$ and $\dot{\gamma}_2$ are the only shear rates observed throughout the fluid, regardless of the applied shear rate. The shear stress is the same (and constant) in the two bands, which leads to a steady-state stress selection that is independent of the initial conditions or flow history. Finally, this model is not sufficient
to resolve a unique shear stress, as there can be a range of total shear stresses where two shear rates may be locally stable [11]. This result implies that the curve BF shown in Figure 5.3 cannot be determined using this model. Practically speaking, this idealized case is not observed in WLM solutions, as the solutions have a finite width, diffuse interface between the shear bands. This finite width interface leads to a locally varying shear rate within both the high shear rate and low shear rate bands [15,21]. A constant shear rate across the band would also imply that the structure within the each band is independent of the gap position, which has not been observed in shear banding WLMs [1,3,16,26,27].

Figure 5.3: Schematic flow curves for shear banding WLMs, with homogeneous constitutive curve ACEG. BF shows the stress selection and steady shear banded flow curve from stress or rate diffusion models. B’F’ shows the steady shear banded flow curve for systems with concentration coupling, or those in measured in a concentric cylinder Couette geometry. The three regions of the flow curve are indicated below the plot. Reprinted with minor revisions with permission from reference [14] from Springer-Verlag (see Appendix P).

In order to accurately describe experimental systems and to resolve a unique stress along the flow curve (curve BF, Figure 5.3), constitutive models such as the Giesekus or Johnson-Segalman model have been adapted to include non-local terms in the equations of motion, which take the form of a non-local dependence of the extra stress [11,40–43]. A gradient diffusion term is added to the constitutive equation in either the extra stress or the
shear rate, resulting in two different forms of the diffusion coefficient, $D$. While the physical basis of the stress diffusion and rate diffusion terms is debated, proposed mechanisms include hydrodynamic interactions, particle diffusion, and Frank elasticity from semiflexibility [42,43]. Helgeson et al. [16] showed a structural basis for this stress diffusion, where gradients in WLM microstructure between the high and low shear rate bands leads to spatial gradients in the polymeric stress. When polymeric stress diffusion is used, the selected stress must be calculated numerically; in the shear rate diffusion models, the selected stress can be calculated more easily [11,40]. In the polymeric stress diffusion models, the stress selection can be solved for a stationary interface, such that a unique shear stress plateau ($BF$ in Figure 5.3) is obtained in the nonmonotonic portion of the flow curve (dotted lines in Figure 5.3) for the nominal imposed shear rates [11,43]. In this case, the width of the interface between the shear bands, $l$, is given by [43]:

$$l = \sqrt{D \tau_R}$$  \hspace{1cm} (5.5)

In both of the aforementioned cases, the stress plateau in the flow curve corresponding to the shear banded state (region II) was assumed to have a zero slope ($N = 0$). However, as mentioned above, WLMs have been shown to shear band even with small, positive slopes in region II [13, 15, 16]. This positive slope can either be a result of flow-concentration coupling and/or the use of a cylindrical Couette geometry [12,14,42]. For this case of shear banding, the steady shear banding flow curve is described by $B'F'$ in Figure 5.3. The positive slope in the case of cylindrical Couette geometries arises because the shear stress across the Couette gap is inversely related to the square of the radius, leading to a decrease in shear stress with increasing gap position [6]. Regardless of whether the inner or outer cylinder is rotating, this geometrical bias leads to the formation of the high shear rate band near the inner cylinder [44]. Therefore, in a cylindrical Couette geometry, the value of $N$ can be close to, but not exactly, zero. In models that include concentration coupling parameters, an increase in the banding stress is observed with increasing concentration [11,14], which has accurately described the behavior of WLMs far from the isotropic-to-nematic transition.
Significant positive slopes in region II attributed to flow-concentration coupling have been observed in experiments on semi-dilute solutions far above the overlap concentration \((C \gg C^*)\), or in concentrated solutions \([13, 17]\). As the WLM solutions examined in this work are much closer to the overlap concentration \((C \approx C^*)\), we do not expect significant positive slopes in region II for solutions that exhibit shear banding.

5.5 Low vs. highly branched solutions: rheology and microstructure

To examine the shear thinning versus shear banding phenomena in the WLM solutions discussed in this work, a comparison of the flow behavior between the ‘low’ and ‘high’ salt solutions is presented in this section. The low salt solution corresponds to 0.01% wt NaTos, and the high salt solution refers to the 0.10% wt NaTos solution. Results are first presented based on salt content, and then the case is made for the low and high salt solutions corresponding to low and highly branched solutions as the section progresses. Results from the mild salt solution (0.05% wt NaTos) and higher salt solutions \((C_s > 0.10\% \text{ wt NaTos})\) are presented in Sections 5.7 and 5.9, respectively.

5.5.1 Steady shear rheology

To compare the specific effects of added salt on the shear rheology, the steady-state viscosity and stress were compared both at equivalent shear rates (Figure 5.4a) and Weissenberg numbers (Figure 5.4b) for the 0.01% wt NaTos and 0.10% wt NaTos samples. Here, the Weissenberg number, \(Wi\), is the product of the shear rate and the material relaxation time, \(Wi = \tau R \dot{\gamma}\). Figure 5.4 shows shear thinning behavior in both samples, where the zero-shear viscosity, like the relaxation time, decreases by an order of magnitude with an order of magnitude increase in added salt content. Results were fit by the Cross Model (Equation 4.3) to yield \(\eta_{0,\text{low salt}} = 34 \text{ Pa} \cdot \text{s}\) and \(\eta_{0,\text{high salt}} = 2.6 \text{ Pa} \cdot \text{s}\) (Table 4.1).

Figure 5.4 shows that while the difference in stress between the two samples is a nonmonotonic function of shear rate, the stress is always higher in the high salt case at an equivalent \(Wi\). Ultimately, this trend in the stress is a result of the shear thinning response and how it differs in the two solutions. Whereas both samples shear thin, the degree of shear
thinning is mitigated by adding salt, which can be observed by the slope in the viscosity curves of $k = -1$ in the low salt system (red) and $k = -0.85$ in the high salt system (blue). This translates to a power law index of $N = 0$ in the low salt sample and $N = 0.15$ in the high salt sample using the power law model described in Equation 5.1 above. The power law index $N = 0$ applies to the stress plateau in the low salt sample (red), which spans a wide range of shear rates ($Wi = 1$ to $Wi \approx 300$). As mentioned in Section 5.4 above, a true value of $N = 0$ is not possible in cylindrical Couette geometries; here $N = 0$ is accurate to two significant digits. The stress plateau in the low salt solutions is strongly suggestive of shear banding at these shear rates. At low shear rates ($\dot{\gamma} \approx 0.2 \text{ s}^{-1}, Wi \approx 1$), an apparent nonmonotonic region of the flow curve is observed, which also strongly suggests shear banding as indicated by the nonmonotonic flow curve illustrated in Figure 5.3. Although this region of the flow curve appears to be stable based on complementary startup measurements for ten minutes or longer (discussed further in Chapter 6), this behavior is likely metastable and not representative of the true flow curve [29]. If longer times were measured, the resulting curve should reach the steady state described by curve $BF$ in Figure 5.3. This nonmonotonic behavior and the resulting hysteresis is also discussed for the WLM solutions prepared in water in Appendix F. Beyond the shear banding region, the viscosity in the low salt sample begins to approach its minimum, high rate value, $\eta_\infty$. The high rate viscosity should not be confused with the

Figure 5.4: Steady-shear flow curve of the low (0.01% wt NaTos) and high salt (0.10% wt NaTos) solutions on an absolute scale (a) and Weissenberg number scale (b).
solvent viscosity, $\eta_s$, that is often used in Oldroyd-B fluids, as $\eta_{\infty} \gg \eta_s$.

In the high salt sample (blue in Figure 5.4), the stress maintains a positive slope throughout region II. Region II covers a much smaller range of shear rates ($1 \leq Wi \leq 40$), and the larger power law index is indicative of a strongly shear thinning, as opposed to shear banding, solution. The nonmonotonic behavior observed at the onset of region II in the low salt solution is not observed in the high salt solution, again suggestive of shear thinning. At high shear rates and Weissenberg numbers, the high salt system shows reproducible shear thickening behavior. The shear thickening is highly repeatable amongst additional sample preparations and is also observed in samples with higher salt concentrations, which will be discussed further in Sections 5.6.3 and 5.9.1. Upon shear startup, it is well known that shear banding can take hundreds of seconds to develop in a worm-like micellar solution [24,29,45]. In the low salt sample, the steady-state stress response is observed only after 100 s, at minimum, for the shear rates in the stress plateau, which is consistent with shear band formation. Conversely, the steady-state stress response in the high salt solution is achieved rapidly after shear startup ($< 10s$) for all shear rates shown, in accordance with behavior typical of samples that exhibit simple shear thinning. This startup behavior will be discussed further in Chapter 6.

5.5.2 1-3 plane small angle neutron scattering (SANS)

As the rheological results suggest different mechanisms of shear thinning between the low (0.01% wt NaTos) and high (0.10% wt NaTos) salt samples, structural SANS measurements were performed to compare the flow-induced structures of the micelles at equivalent absolute shear rates. The results will be discussed on a Weissenberg number basis in Section 5.6.1. Rheo-SANS measurements were taken in the 1-3 (flow-vorticity) plane at nominal applied shear rates along the steady shear flow curves, which are shown in Figure 5.5. Under shear flow, micellar segments align in the flow direction [4,24,46], and these microstructural rearrangements are quantified by a scalar alignment factor [47] calculated from the 2-D SANS shown in Figure 5.5, given by Equation 2.36. Note that in the case of 1-3 plane rheo-SANS, the orientation angle from the alignment factor calculation, $\phi_0$, is
zero due to the symmetry imposed by the method. The intensity distribution, \( I(q^*, \phi) \), is a projection of the material orientation distribution function (ODF) onto a particular scattering plane \([48]\), which can potentially be used to distinguish micellar morphologies and will be discussed further below. Here, the underlying material intensity distribution is directly used to calculate the alignment factor, as opposed to fitting the intensity or orientation distribution function (ODF) to a particular model before the parameter is derived and calculated as is often done \([48]\). In micelles with varying topologies, a single orientation distribution, such as the commonly used Maier-Saupe potential for nematic liquid crystals \([47,49,50]\), may not be adequate to describe all systems.

Figure 5.5 shows the scattering and alignment as a function of shear rate for the 0.01% and 0.10% wt NaTos samples. The aligned 2-D scattering patterns vary significantly between the two samples due to the presence of the interaction peak in the 0.01% wt NaTos sample; however, this difference should not affect the \( A_f \) calculation because the \( q^* \) region is defined in the vicinity of the interaction peak for the 0.01% wt NaTos solution (Appendix B). Figure 5.5 specifically emphasizes the 1-3 plane alignment factor and stress at shear rates within the flow curves where the samples exhibit a high degree of shear thinning. Despite differences in the steady-shear rheology between the samples, the alignment factors follow the same trend with increasing shear rate. The high salt sample has consistently lower values of the alignment factor until the viscosity upturn (shear thickening) is encountered. This trend is also observed in samples with higher salt content \([4]\), where the alignment factor is lower at the same absolute shear rate than in low salt WLMs, until a critical shear rate is reached where the alignment factor for all WLM solutions collapses onto the same curve. Here, the alignment is independent of viscosity, stress, shear rate, and sample.

To explore the shear thickening behavior of the high salt solution further, two points of roughly equal alignment between the two solutions are highlighted in Figure 5.5. The first set of points examined correspond to shear rates in the shear banding or shear thinning regime, while the second set correspond to rates greater than that of the observed shear thickening response. In the first pair of alignment factors, where \( A_f \approx 0.3 \), the nominal shear rates for equal alignment differ, as \( \dot{\gamma}_{\text{low salt}} = 45 \text{ s}^{-1} \) and \( \dot{\gamma}_{\text{high salt}} = 90 \text{ s}^{-1} \). As shear thickening
Figure 5.5: Alignment factor and 1-3 plane 2-D scattering patterns of the low (0.01% wt NaTos, red) and high salt (0.10% wt NaTos, blue) solutions at multiple shear rates across the steady shear flow curve. The mechanism of anisotropy clearly differs between the two series of scattering patterns due to the presence of the interaction peak in the low salt sample and its absence in the high salt sample. The resulting $1 - 3 A_f$ is lower in the high salt case until the viscosity upturn. Two points of equal $A_f$ between solutions are highlighted for further discussion: one before and one after the viscosity upturn in the high salt solution.
occurs, the alignment factors approach the same value with increasing shear rate \((1-3 A_f \approx 0.55)\), as shown by the second pair of alignment factors \((\dot{\gamma}_{\text{low salt}} = \dot{\gamma}_{\text{high salt}} = 420 \text{ s}^{-1})\). Figure 5.6 shows the orientation distribution function and the 1-D scattering of the low and high salt samples at these two points of equal alignment. The intensity distributions are normalized to provide a fair comparison of the samples. Sector-averaged scattering (see Figure 2.8b) was performed in the anisotropy (vorticity) direction to determine the structure of the material aligning in the flow direction, which is common practice when analyzing anisotropic or flow-aligned scattering data [16, 51]. In highly aligned samples, there is little to no scattering along the flow axis above background so the sector-average method focuses only on the aligned material. Because the intensity distribution is a projection of the overall material orientation, any changes to the intensity distribution result from changes to the ODF and the underlying material structure.

Figure 5.6a shows the intensity distribution of the low and high salt samples at \(\dot{\gamma} = 45 \text{ s}^{-1}\) and \(\dot{\gamma} = 90 \text{ s}^{-1}\), respectively \((1-3 A_f \approx 0.3)\). Despite having the same alignment factor values, the intensity distribution of the low salt sample is much sharper than that of the high salt sample, reflecting different underlying orientation distribution functions. The sector-averaged scattering in the vorticity direction (Figure 5.6b) for both the low and high salt sample yields nearly identical scattering to its static structure. The change in the absolute intensity between the static and shear-induced structures results from the sector average method described in Figure 2.8a and b, where a larger fraction of the material is in the flow direction under shear as compared to the sample at rest, leading to a higher absolute intensity. Between Figure 5.6a and c, clear differences in the intensity distribution and the 1-D sector-averaged scattering can be observed in the high salt sample after the onset of shear thickening. When \(\dot{\gamma} = 420 \text{ s}^{-1}\), both samples have the same alignment factor \((1-3 A_f \approx 0.55)\) and nearly identical normalized intensity distributions. The shape of the intensity distribution with angle remains the same for the low salt case, and is the same at all shear rates for this sample, resulting from a similar underlying ODF and material structure. Conversely, the intensity distribution for the high salt sample becomes much sharper than its original form, indicative of a change in structure. At shear rates higher than the shear thickening onset, a
similar ODF is observed in the high salt sample as in the low salt sample (Figure 5.6c). A change in structure is also detected in the 1-D sector-averaged SANS (Figure 5.6d), where the peak at $q = 0.022 \text{ Å}^{-1}$ that is not present in the high salt sample under static conditions now appears at high shear rates. In the direction of anisotropy, the structure of the high salt sample is now similar to the static structure of the low salt sample, and is quite dissimilar to its own static structure. Interestingly, the first shear rate at which this peak appears in the scattering is at the onset of shear thickening ($\dot{\gamma} = 185 \text{ s}^{-1}$); thus the rheological shear thickening can be linked to a change in the SANS structure of the high salt sample. Note that there are no permanent changes to the material structure, which reverts to its static form upon the cessation of shear.

We note that the 1-3 alignment factor can only provide SANS information that is convolved in space (across the Couette gap) as a function of the shear rate. When the alignment factor for the low salt sample is compared to the stress within the stress plateau, it is observed that the alignment factor increases steadily as the shear rate increases, despite the nearly constant stress. This likely corresponds with an increasing alignment and proportion of material within the high shear rate band with increasing shear rate. However, as the trends between the two systems are fairly similar, to truly resolve the nature of the material structure and flow properties across the gap, 1-2 plane structural measurements are necessary to gain spatial resolution. These measurements can definitively determine the presence of shear banding or shear thinning in the two solutions.

### 5.5.3 1-2 plane SANS

Spatially-resolved, 1-2 plane flow-SANS measurements were performed at identical shear rates in order to distinguish spatially-dependent flow properties including shear banding. Measurements were taken at applied shear rates of $\dot{\gamma} = 15$, 26.4 and 45 s$^{-1}$, which represent three shear rates within the stress plateau (low salt) or stress gradient (high salt) regions of the flow curves. Figure 5.7 displays the alignment and scattering patterns at an applied shear rate of $\dot{\gamma} = 45 \text{ s}^{-1}$ for five positions across the gap taken with a narrow, straight slit (0.1 mm). The alignment factor for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ and $\dot{\gamma} = 15 \text{ s}^{-1}$ are also shown at three gap
Figure 5.6: Normalized intensity distribution (a,c) and sector-averaged 1-D SANS in the anisotropy direction (b,d) for the low and high salt samples before (a,b) and after shear thickening (c,d), corresponding to the bolded points from Figure 5.5. (a) For equal $A_f$, the intensity distribution of the low salt sample is much sharper than the high salt sample, reflecting the micellar orientation and topology. (B) The SANS structure for the high salt sample under shear is nearly identical to the static high salt structure (blue line). (c) Both samples have equal $A_f$ and nearly identical intensity distributions. This structural change is detected in the 1-D SANS (d), where the sector average scattering from the high salt system under strong flow is nearly identical to that of the low salt system (red line). In contrast, the structure for the low salt system under shear shows increased flow alignment but the correlation peak maintains its position with increasing rate.
Additional measurements were taken on the 0.01% NaTos sample using a wider, 0.3 mm slit (○) at the Institut Laue-Langevin (ILL), and a different configuration at the NIST Center for Neutron Research (NCNR, ▽) to demonstrate the reliability of the method.

The alignment for the low salt sample (red, Figure 5.7a) shows interesting features suggestive of shear banding that are absent in the high salt sample (blue, Figure 5.7b). As seen in Figure 5.7a, at $r/H \geq 0.5$ in the low salt solution, all of the alignment factors and respective scattering patterns appear identical for each shear rate. This “alignment banding,” evidenced by the constant alignment in the outer portion of the gap, is strongly suggestive of shear banding. The discontinuous change in $A_f$ from the inner to the outer wall is reminiscent of the discontinuous velocity profile observed in shear banding systems (Figure 5.1b). In the low shear rate band, it is expected that the micelles are entangled and will not substantially align within the band. The 2-D scattering patterns shown below the figure at $\dot{\gamma} = 45 \, \text{s}^{-1}$ also support the presence of shear banding, as these patterns do not change in the outer half of the gap. Consequently, the underlying intensity distribution which is used to calculate the alignment factor is identical in all three measurements. As the intensity distribution is a projection of the orientation distribution function of the material and changes based on the material microstructure, these measurements indicate that the same structure is present in the outer half of the gap. This alignment banding also implies the absence of shear thinning within the low shear band, which agrees with the PTV measurements of Helgeson et al. [16] that show little change in material structure across the low shear band for a related system. The decrease in alignment with increasing gap position in the high shear rate band, however, is consistent with shear banding systems that have a finite interface width (see Section 5.4). In solutions with a finite interface, the shear rate is expected to decrease across the high shear rate band, leading to the lower observed alignment with increasing gap position.

Conversely, the behavior of the high salt sample (blue, Figure 5.7b) exhibits a gradual decrease in alignment as a function of gap position. A weak, continuous gradient in alignment is evident in the 2-D scattering patterns, where the sample becomes nearly isotropic close to the outer wall. This behavior is expected from a material that exhibits continuous shear thinning, as the decreasing shear rate with increasing gap position should correspond
Figure 5.7: Alignment factor and 1-2 plane SANS 2-D patterns at $\dot{\gamma} = 45$, 26.4 and 15 s$^{-1}$ in the 0.01% wt (a) and 0.10% wt NaTos (b) solutions. Symbols denote different experiments: NCNR with 0.1 mm straight slit (□), NCNR with 0.1 mm curved slit (▽), and ILL with 0.3 mm curved slit (⋄). Inset: relative location of shear rates along flow curve. Shear banding is supported in the low salt system, where $A_f$ is constant at $r/H \geq 0.5$ at all rates. Conversely, the 1-2 plane $A_f$ provides evidence of shear thinning only in the high salt system, as $A_f$ continually decreases across the gap at all rates. The equivalent 1-3 plane $A_f$ is shown by ×. Dotted lines for visual aid only.
to a lower degree of segmental alignment with increasing gap position in such materials. In fact, here the alignment factor appears linearly related to the gap position, in stark contrast to the discontinuous behavior observed in the low branching solution. The results also agree with visual observations from Helgeson et al. [26] comparing shear banding and non-shear banding solutions. In their work, there was a significant change in alignment and visual scattering from the inner to the outer wall in the shear banding CTAB sample, in accordance with the scattering from our low salt sample. However, the non-banding CTAB sample showed little difference in the scattering across the gap, in agreement with the scattering from our high salt solution. The 1-3 alignment factor for each sample at each of the three shear rates is noted with the “×” symbol in Figure 5.7. While often (incorrectly) assumed that the 1-3 alignment factor represents an “average” alignment across the gap, the 1-3 alignment factor here is clearly below the average for the 1-2 plane alignment. Any inference that could be made about the gap behavior from the 1-3 plane alignment factor would fail to identify differences between the two samples due to their similar 1-3 plane alignment trends. The 1-2 plane SANS data, however, show strong evidence to support the shear banding and shear thinning in the low and high salt WLM systems, respectively.

5.6 Discussion: low vs. highly branched solutions

5.6.1 Salt effect on SANS

To further address the interpretation of 1-3 plane rheo-SANS data, we revisit the flow curves and alignment factors in Figure 5.8, shown now on a Weissenberg number scale. Despite the differences in the steady state flow curves between the two samples with different levels of branching, similar trends are observed for the 1-3 plane alignment factors. In Figure 5.8, both samples show a nearly linear region of alignment as a function of Weissenberg number (or shear rate). The derivative of the alignment factor with respect to shear rate is higher in the 0.01% wt NaTos sample, whereas the derivative of the alignment factor with respect to Weissenberg number is higher in the 0.10% wt NaTos sample. This result is surprising considering the 0.01% wt NaTos solution exhibits shear banding, whereas the 0.10% wt NaTos solution exhibits shear thinning only. Quantitatively, this should result
in a higher stress-SANS coefficient (analog to the stress-optical coefficient, Equation 2.37) in the branched solution (high salt) than in the linear solution (low salt) because the 1-3 plane and 1-2 plane alignment for the branched solution is lower than for the linear solution while the resulting stress is higher. The difference in the stress-SANS coefficient between the two solutions may be an indicator of branching; however, we cannot draw definitive conclusions because the shear banding in the 0.01% wt NaTos solution may also impact the value of the stress-SANS coefficient. The 1-3 plane SANS shown in Figures 5.5 and 5.8 results indicate that branching inhibits flow alignment on a scale of absolute shear rate, whereas the opposite trend is observed based on Weissenberg number. This result is verified in solutions with higher levels of added salt, which will be discussed in Sections 5.8.1 and 5.9.2 below, indicating that branching promotes flow alignment on a Weissenberg number scale, but suppresses flow alignment based on absolute shear rate.

While both samples in Figure 5.8 show a linear increase in the 1-3 plane alignment with increasing shear rate, this alignment results from different mechanisms. In the high salt sample, the alignment increases in the shear thinning region. For the low salt (and mild salt) sample to show the same alignment trend during shear banding, the material in the high shear band must be continuously evolving toward an increasingly aligned, or nematic-like state with increasing shear rate. Furthermore, the linearity of the fit to the alignment data with increasing shear rate implies that the relative width of the bands should increase linearly with shear rate, in agreement with many recent results [13,16,52]. As the change in shear rate is small, a small change in the band width is expected. As the number of 1-2 plane gap positions measured is limited, the change in width of the bands cannot be quantified by the SANS measurements. Interestingly, the rheo-SANS alignment factor is proportional to the 1-2 plane inner wall alignment factor ($r/H = 0.13$) for the three shear rates investigated in the 1-2 plane experiments. However, the relationship is not a simple proportion or linear function when the rheo-SANS $A_f$ in the low salt solution is correlated to the average 1-2 $A_f$ across all five gap positions. This curious relationship can be understood by examining the intensity distribution from the 1-3 plane SANS, which is a projection of the overall orientation distribution function (ODF) of the material onto the 1-3 plane [48].
plane ODF is a convolution in space of several gap-dependent ODFs, and thus has a similar maximum intensity as the 1-2 plane inner wall ODF, superimposed with contributions from less aligned states with lower intensities. The lower aligned states raise the background in the 1-3 plane ODF, leading to lower alignment. With increasing rate, the background rises slightly while the maximum intensity rises greatly, leading to a near proportionality between the 1-3 $A_f$ and 1-2 plane inner wall $A_f$.

Figure 5.8: 1-3 alignment factor and stress of the low salt (0.01% wt NaTos) and high salt (0.10% wt NaTos) solutions on a Weissenberg number scale. Both samples show nearly linear increases in alignment with increasing $Wi$ or shear rate.

The comparison of the 1-3 and 1-2 plane data, and the strong correlation between the 1-3 and 1-2 plane alignment factor at the inner wall, provides important insight into the three-dimensional structure of branched WLMs under flow. As previously mentioned, the 1-3 plane alignment factor does not represent an average alignment across the velocity gradient, as observed in Figure 5.7, suggesting that the micellar ODF is not uniaxial. Furthermore, both samples displayed highly similar alignment trends under 1-3 plane SANS, indicating that analyzing the 1-3 plane data alone may provide potentially misleading information. While the 1-3 plane alignment factor failed to identify differences in the gap behavior, the
1-2 plane data shows strong evidence to support the different mechanisms of shear thinning and shear banding in the low and highly branched WLM systems, respectively. Because the two samples share 1-3 plane alignment trends, no information about the flow behavior across the gap can be accurately inferred from the 1-3 plane data. The conclusions drawn from the 1-3 and 1-2 plane data highlight the importance of spatially-dependent information for confirmation of flow properties, as opposed to deducing the properties via 1-3 plane measurements.

To ensure that the observed trends are a result of the topological differences in the WLMs, as opposed to viscosity differences, we examine effect of viscosity on the alignment factor. Figure 5.9 shows the 1-3 plane alignment factor as a function of the measured viscosity between the low and high salt solutions. In Figure 5.9a, the results are shown for the specific samples used in this study, performed on NIST NG-3 with a large Couette geometry ($R_1 = 24.0$ mm, $\Gamma = 36$, $\varepsilon = 0.042$).

![Figure 5.9: 1-3 $A_f$ vs. viscosity for the low and high salt samples using different sample preparations, geometries, and beamlines. Dotted lines are for visual aid. (a) Results reported in Figure 5.5, on NG-3. (b) Additional trials on NGB-10. The different $A_f$ measured for samples of the same viscosity strongly suggests that topological differences lead to the observed $A_f$ trends. At a critical shear rate, $A_f$ becomes independent of solution viscosity.](image)

In Figure 5.9b, results are shown from follow-up tests using new samples, on the NGB-10 instrument, with a smaller Couette geometry ($R_1 = 13.5$ mm, $\Gamma = 36$, $\varepsilon = 0.074$).
Despite differences in sample batch, beamline, and geometry, the trends are nearly identical between the trials, giving further confidence in the method. Figure 5.9 shows clearly that at the same viscosity, the two solutions align to different degrees until a maximum alignment is reached. At a critical shear rate (as shown in Figures 5.5 and 5.8), the alignment becomes independent of viscosity, shear rate, and stress. As the microstructural rearrangements show a different and complex dependence on shear rate, stress, and viscosity between the two samples, the alignment is greatly affected by topological differences like branching.

### 5.6.2 Interpretation of 1-2 plane SANS results

A recent review by Lerouge and Berret [13] details the structural transitions and instabilities that are commonly observed in WLM solutions. The time- and spatially-dependent nature of such flow instabilities must be considered when interpreting the 1-2 and 1-3 plane SANS results. In the 0.01\% wt NaTos, the power law index of $N \approx 0$ indicates shear banding, and the plateau spans a wide range of Weissenberg numbers, ranging from $Wi = 1$ to $Wi \approx 300$. As noted by Lerouge and Berret [13], shear banding flow can be geometry-dependent and also can be affected by Taylor-like vortices and elastic instabilities at high Weissenberg and elastic Taylor numbers. Such instabilities are often localized within the high shear band and the onset occurs at a critical Taylor number (see Appendix J), which is based on the measurement geometry [53]. The Taylor number for the purely inertial case is given by [54]:

$$ Ta = \left( \frac{H}{R_i} \right)^{1/2} Re = \varepsilon^{1/2} Re \quad (5.6) $$

where $Re$ is the Reynolds number, and $Ta_c \approx 41$. In the purely elastic case, Taylor number is given as [53,54]:

$$ Ta = \left( \frac{H}{R_i} \right)^{1/2} Wi = \varepsilon^{1/2} Wi \quad (5.7) $$

where $Wi$ is the Weissenberg number, and $Ta_c$ is estimated to fall between 6 and 30 depending on the model or sample used [6,54,55] (see Section 5.6.3.1). It should be noted that inertial instabilities cannot occur in the ARES G2 geometry, where the outer cup rotates.
As seen in Figure 5.9, the structural and viscosity results in the low salt solution appear to be independent of a nearly two-fold increase in $\varepsilon$, and the resulting flow curves are independent of geometry, suggesting that the shear banding is relatively insensitive to geometry. Furthermore, selected tests in the 1-2 shear cell were repeated on two additional occasions (Figure 5.7), yielding similar results. Therefore, the time-averaged structure and alignment in the shear banded state are highly repeatable in the low salt solution. However, due to the limited spatial resolution of the 1-2 plane SANS (slit size = 0.1 mm), few gap positions measured (5), and time-averaging of the SANS data, we cannot detect specific instabilities during shear banding, such as interface fluctuations, vortices, or turbulent bursts within the high shear band. Follow-up studies using 1-2 plane SANS measurements during shear startup, which can detect these time-dependent phenomena, will be discussed in Chapter 6. Regardless of the possible instabilities at play, the highly reproducible time-averaged scattering gives confidence in the interpretation of the SANS results that indicate shear banding in the low salt solution. One technique that can be used to resolve such flow instabilities is the simultaneous rheometry and ultrafast ultrasonic imaging detailed by several recent works [13,54,56], which provides complementary information to SANS.

In the 0.10% wt NaTos solution, $N = 0.15$ indicates shear thinning. We note that Adams and Olmsted [12] have shown that it is possible for models of entangled polymers to display shear banding without exhibiting a true stress plateau, and that flow-concentration coupling and the use of cylindrical Couette geometries can lead to a positive value of $N$ in shear banding systems [14, 44]. However, as the surfactant concentration in these WLM solutions is low ($C_D = 1.5\%$ wt) and on the border of the dilute and semi-dilute regime ($C^* \approx 1.5\%$ wt), it is unlikely for the high salt sample to shear band while exhibiting a positive sloping constitutive equation. Only in solutions well within the semi-dilute or concentrated regimes would this be expected [13]. Further, the maximum elastic Taylor number, $Ta$, achieved in the 1-2 shear cell for this sample ($\dot{\gamma} = 45 \text{ s}^{-1}$) is less than 3.5 (Equation 5.7), well below the critical $Ta_c$ for elastic instability [6, 55], giving confidence in the shear thinning interpretation of the 1-2 shear cell results for the high salt solution. Additional details can be found in Appendix J, along with considerations of other macroscopic instabilities.
5.6.3 High salt solution - shear thickening structural transition

Shear thickening at high shear rates is commonly observed in WLM solutions, and is often attributed to a structural transition and/or elastic turbulence [13, 56, 57]. Shear thickening that leads to a highly aligned or birefringent shear-induced structure is well-documented in WLM solutions in the dilute regime or near the overlap concentration ($C_D \leq C^*$) [13]. Elastic turbulence, resulting in a transition to a bi-stable state followed by fully turbulent flow, has been associated with semi-dilute WLM solutions ($C_D \gg C^*$) that are 10-fold more concentrated than the present system. Recently, Fardin et al. [57] showed that in very dilute WLM solutions, the structural transition occurred alongside elastic turbulence. The following rheological results, along with the structural changes observed in the 1-3 plane SANS in the shear thickening regime of the high salt solution (Figure 5.6), suggest that a structural transition occurs in this regime resulting in a highly ordered, anisotropic state.

5.6.3.1 Rheology

In this particular system (CTAT/SDBS, 97/3 weight ratio), shear thickening has been observed at similar concentrations ($C_D = 0.5\%$ wt) near $\dot{\gamma} = 100$ s$^{-1}$ [58], which was attributed to a structural transition. Koehler et al. [58] note that the shear thickening is common at surfactant concentrations near $C^*$, which is the surfactant concentration used here ($C^* \approx C_D = 1.5\%$ wt). This behavior has also been attributed to a structural transition in other studies of CTAT and related wormlike micelles [59–61]. As the shear thinning behavior begins at higher rates with increasing surfactant concentration [58] and the critical rate of shear thickening increases with concentration in systems of pure CTAT in D$_2$O [13], it is expected that shear thickening from a structural transition would also occur at $C_D=1.5\%$ wt, at $\dot{\gamma} > 100$ s$^{-1}$. Furthermore, the high salt solution exhibits its maximum alignment in the shear thickening regime, suggestive of a strong degree of structural order. The shear thickening response observed in the high salt sample is reproducible over different sample preparations and rheometer configurations, and is also observed in solutions with higher salt concentrations (see Section 5.9.1). Figure 5.10 shows the similarity in the flow curves between two different sample preparations (a) and two rheometer configurations (b). The onset of shear
thickening is seemingly independent of configurational changes that affect the critical inertial and elastic Taylor numbers for elastic turbulence. However, as Fardin et al. [57] have shown that shear induced structure formation can occur together with elastic turbulence in dilute WLM solutions, elastic turbulence alongside the structural transition in the high salt solution cannot be ruled out. As the curvature of the Couette geometry is similar between the two configurations shown in Figure 5.10b ($\varepsilon = 0.084$ vs. 0.074), additional measurements using different curvatures are merited to determine if significant elastic turbulence is present. Conversely, inertial instabilities are extremely unlikely in all conditions (see Appendix J).

The elastic Taylor number at the onset of shear thickening in the high salt sample was calculated for the geometries used in this work (see Appendix J). The range of resulting Taylor numbers is between $12 \leq Ta \leq 20$. For comparison, in other shear thinning WLMs ($N = 0.45$) where both inertia and elasticity are important, the onset of inertioelastic instability occurs at an elastic $Ta_c = 22$ [54]. The elastic $Ta_c = 22$ is greater than that expected by the Upper Convected Maxwell model ($Ta_c \approx 6$), but agrees well with predictions that take shear thinning into account [55], where $Ta_c \approx 30$ [6]. Using the rheological properties of the high salt solution ($N = 0.85$), Larson et al. [55] predicts $Ta_c$ is orders of magnitude higher than is encountered during shear thickening (see Appendix J); however, no experimental results on very highly shear thinning WLMs are available to verify this result. Regardless, at $Ta_c = 33$, [54] saw only small deviations from the base flow ($\delta v = 0.06$), indicating that if turbulence is present at the shear thickening onset, only minor deviations from the base flow would be expected.

Another characteristic observed when shear thickening is accompanied by elastic turbulence is a substantial change in the level of fluctuations in the steady shear stress response in time. Recent work by Fardin et al. [56] shows that for a 10-fold more concentrated, shear banding CTAB/NaNO$_3$ system in the semi-dilute regime, the stress fluctuations in the laminar flow region immediately preceding the turbulent transition are on the order of 3%, whereas in the thickening “bi-stable” regime, these fluctuations grow as high as 30%. Finally, in the fully turbulent regime, the fluctuations settle to around 15% but are still significantly larger than those observed in the laminar regime. Near the shear thickening regime
Figure 5.10: Repeatability of shear thickening in the 0.10% wt NaTos solution over different geometries and sample preparations. (a) Flow curves from two samples are nearly identical, including the shear thickening response. The first curve (solid, 1) was determined by a flow sweep up test, whereas the second curve (open, 2) was determined by startup measurements. (b) Flow curves from the ARES G2 ($\epsilon = 0.084$) and MCR 502 ($\epsilon = 0.074$) used for SANS. Shear thickening is preserved despite differences in geometry, instrument, and sample.

In the high salt solution, long-time startup tests were performed in both the ARES G2 and the MCR 502. Unlike in the CTAB/NaNO$_3$ system, the fluctuations in the stress response at the shear rates surrounding the shear thickening regime do not change significantly with shear rate, and are on the order of 3.5% or less (see Appendix J). Because shear thinning increases the $Ta_c$ for elastic turbulence, the shear thickening is not dependent on geometry, and the stress fluctuations are minor, we believe that the structural transition occurs without significant elastic turbulence or deviations from the base flow. However, due to limited previous work on non-shear banding, highly shear thinning WLMs, we cannot rule out more substantial contributions to the shear thickening from elastic turbulence. Regardless, the interpretation of our results in the context of a shear thickening structural transition would not change, as Fardin et al. [57] has shown that such a transition to a highly-ordered, anisotropic state and elastic turbulence can occur together. Additional details and calculations can be seen in Appendix J.
5.6.3.2 1-3 plane SANS

As mentioned previously, shear thickening is also observed in samples with higher degrees of branching (higher NaTos concentrations). We propose that this shear thickening structural transition corresponds to the point at which branches begin to break, leading to an alignment of highly ordered linear chains. As the steric hindrance to alignment is removed when branches break, the aligned chains should obtain the maximum degree of alignment at and beyond these shear rates. Fittingly, $A_f$ remains constant with increasing shear rate after this proposed breakage point, which is observed in Figures 5.5 and 5.8. Figure 5.6 provides further evidence to support this notion of branch breakage, as clear changes to the orientation distribution function and the SANS structure of the high salt sample occur after the shear thickening onset. Branch breakage should lead to alignment of linear chains and similar ODF between the two samples, which is the result observed in Figure 5.6.

The observed differences in the ODFs between the two samples can be explained by topological differences. Before the shear thickening region, the intensity distribution of the low salt (low branching) sample is much sharper than the high salt (high branching) sample, even when the alignment is equal. In the low salt sample, the alignment results from only linear chains, leading to a sharp, narrow Poisson-like ODF. Conversely, in the high salt sample, the “backbones” of the chains may align, but the many branches and junctions may extend outwards from the main chain, resulting in a wider distribution that is well-described by the Maier-Saupe distribution. The branched structures flow with the “backbones” and therefore do not align perfectly in the flow direction. The alignment factor in the highly branched case therefore has contributions to the $\cos(2\phi)$ term from many partially aligned branches, whereas the low branched structure has contributions from primarily fully flow-aligned chains. This difference in mechanism of alignment enables the branched structure to have the same value of alignment from a less steep orientation distribution. While the shape of the intensity distribution remains constant for the low salt case at all shear rates studied, the intensity distribution for the high salt sample changes in the shear thickening region, indicative of changing structure that may result from branch breakage. Fittingly, at shear rates higher than the shear thickening onset, a similar structure and ODF is observed in the
high salt sample as in the low salt sample. Similar phenomena are observed in samples with higher levels of salt (branching), with SANS structural changes directly corresponding with shear thickening in the steady-shear flow curve [4]. The shear rate at which shear thickening is observed increases with branching level. If branch breakage contributes to the structural transition, this would be expected due to the faster breakage time that results from increasing salt content.

The observed changes in the material orientation distribution function emphasize the importance of using several metrics when quantifying anisotropy in flow-induced structures. A metric such as the alignment factor that makes no assumptions about the underlying ODF is helpful to describe the overall alignment, as the ODF is shear rate-dependent. However, examining the shape of the ODF provides additional insight into the alignment mechanism and material structure. By utilizing the ODF in the analysis of anisotropy, we gain information that is otherwise lost by the use of a single order parameter. The ODF analysis paired with the sector averaged SANS confirms that the material structure changes at the shear rates surrounding shear thickening, supporting a structural transition from branch breakage.

5.6.4 The Cox-Merz rule and Laun’s rule

In addition to providing relevant length and time scales, the linear viscoelastic (LVE) regime data discussed in Chapter 4, Section 4.3.2 can also be used to predict the first normal stress difference, \( N_1 \), in the low frequency and shear rate regime using the Cox-Merz rule and Laun’s rule [62, 63]. The Cox-Merz rule links the complex viscosity measured in an LVE test, \( \eta^* \), to the steady shear viscosity, given by [62]:

\[
|\eta^*(\omega)| = \eta(\dot{\gamma})|_{\dot{\gamma}=\omega}
\]  

(5.8)

The Cox-Merz rule has been widely applicable to polymer melts, and both semi-dilute and concentrated polymer solutions, making it of potential use to the semi-dilute WLMs in this work. However, the Cox-Merz rule is also known to fail in solutions with a deformation-dependent microstructure, potentially limiting the applicable shear rate regime here [64].
Paired with the Cox-Merz rule, Laun’s rule can then be used to predict $N_1$, by [63]:

$$N_{1,Laun}(\dot{\gamma})|_{\omega=\dot{\gamma}} \cong 2G'(\omega)\left\{1 + \left(\frac{G'(\omega)}{G''(\omega)}\right)^2\right\}^{0.7} \tag{5.9}$$

It should be noted that these two rules are empirical relationships, so observed differences in terms of the low versus high branching systems should be interpreted with caution. Laun’s rule and the Cox-Merz rule are used to reconstruct the stress and viscosity data to determine the range of accuracy in the $N_1$ predictions; these results can be seen in Figure 5.11a and Figure 5.11b for the 0.01% wt and 0.10% wt NaTos solutions, respectively.

![Figure 5.11](image)

Figure 5.11: Prediction of $N_1$, $\sigma$ and $\eta$ using Laun’s rule and the Cox-Merz rule from $\sigma^*$ and $\eta^*$ for the 0.01% wt (a) and 0.10% wt NaTos (b) solutions. Quantitatively accurate predictions are shown in the dark, solid lines. The rules provide reasonable values for a larger range of shear rates in the linear case, exceeding the inverse of the material relaxation time. The estimates deviate from the measured values before the inverse of the relaxation time in the branched case.

As seen in Figure 5.11, Laun’s rule is reasonable to shear rates lower than the inverse of the relaxation time in the linear system (based on the stress and viscosity), but is only accurate to shear rates slightly under this value in the highly branched system. It should be noted that $N_1$ could not be measured independently, so the results should be interpreted with caution. These deviations correspond to a smaller window of Weissenberg numbers where the two rules apply for the branched solution. This trend may be a signature of branching, as
the Cox-Merz rule fails when the microstructure of a solution rearranges under shear [64]. Branching leads to higher flow alignment on the basis of Weissenberg number (Figure 5.8), which suggests that the microstructure starts to rearrange significantly at lower $Wi$, and rearranges more at equivalent $Wi$. This branching effect is likely at the root of the smaller shear rate window where the two rules are applicable in the case of the 0.10% wt NaTos solution, which is also supported by evidence from orthogonal superposition measurements (OSP) (see Appendix K). While performed on samples at a higher concentration, the OSP measurements show a more significant breakdown of network-like structures, as indicated by $G_N^0$ and $G_c$, for the branched solutions at equivalent $Wi$. The breakdown of these branched structures becomes significant at lower $Wi$ in the branched solutions, in line with the failure of Laun’s rule and the Cox-Merz rule here. The OSP measurements also support the hypothesis of branch breakage discussed in Section 5.6.3.2 above. By taking additional SANS measurements in the low shear rate regime, the stress-SANS rule [16] and Laun’s rule can potentially be used to differentiate between branching levels by linking the micellar alignment to the expected stress response and normal stress differences. Finally, this analysis can be extended to solutions with higher levels of branching to see if the branching is a feasible explanation for the observed differences in the applicable range of these empirical rules.

5.6.5 Summary: low vs. high branching

The results presented in this section give strong evidence of two phenomena associated with adding salt to the mixed cationic and anionic WLMs. First, by analyzing the 1-3 plane SANS results and the resulting orientation distribution functions, different topologies are obtained in the solutions with different amounts of added salt. The 1-3 plane differences between solutions are maintained when the results are compared on a basis of viscosity or stress, further supporting microstructural differences between samples. These non-equilibrium results are in agreement with the cryo-TEM and other methods presented in Chapter 4 that suggested branch formation with added sodium tosylate. These microstructure differences are likely at the root of differences observed in the Cox-Merz and Laun’s rule between the solutions. Second, adding salt appears to lead to the disappearance of shear
bANDING in the WLM solutions. The solution with low salt, and thereby low branching, exhibited shear banding as evidenced by the rheology and 1-2 plane SANS results. Conversely, shear thinning only was observed in the high salt, highly branched solution. While it is unclear if the shear banding is eliminated by the branching, changes in viscosity, or differences in electrostatic interactions, each of these changes is associated with salt addition. Therefore, we expect similar trends based on added salt when other WLM solutions are examined, which will be presented in the remainder of the chapter.

5.7 Mildly branched solution: rheology and microstructure

In Section 5.5 above, shear banding was observed in the 0.01% wt NaTos solution where the power law index was approximately zero. This shear banding behavior was eliminated in the 0.10% wt NaTos solution, where the power law index increased to $N = 0.15$. In the section below, we examine the 0.05% wt NaTos solution, referred to as ‘mildly branched,’ which should fall between the low and highly branched solutions in terms of microstructure and flow behavior. As the power law index of the mildly branched solution should fall in between the shear thinning and shear banding solutions discussed in Section 5.5 above, this solution could feasibly exhibit either behavior, which will be explored below.

5.7.1 Steady shear rheology

The steady shear flow curve for the mildly branched solution (0.05% wt NaTos) is shown in Figure 5.12, where the stress is normalized by the plateau modulus, $G^0_N$, and the viscosity is normalized by the zero-shear viscosity, $\eta_0$. The log-log slope of the viscosity is $k = -0.93$ for this solution, which results in a power law index of $N = 0.07$. This value is in between the values of $N$ observed for the low and highly branched solutions. As the steady shear rheology of the mildly branched solution falls in between that of the low and highly branched solutions, either shear banding or shear thinning could be possible in this solution. To help determine if the solution shear bands, the steady shear flow curve in Figure 5.12 is compared alongside a model flow curve from the Vasquez-Cook-McKinley (VCM) model [65, 66]. The VCM model predicts shear banding in wormlike micelles under both steady
shear and large amplitude oscillatory shear (LAOS) by explicitly accounting for breakage and reformation events between short and entangled species. The similarity between the VCM model sample flow curve shown in Figure 5.12 and the mildly branched solution flow curve strongly suggests shear banding. More details of the model and the shear banding predictions are given in Chapter 7. The flow curve in Figure 5.12 is divided into three regions typically observed in WLM solutions, as estimated by the dotted lines: the low shear rate Newtonian regime (region I), shear banding regime (region II), and the regime at shear rates in excess of the shear banding regime (region III).

![Figure 5.12: Steady shear flow curve for the 0.05% wt NaTos solution. Regions I, II and III are estimated using Equation 5.3 and the Bingham model past region II. The * indicates the maximum Wi for the majority of the LAOS measurements discussed in Chapter 7. Similar features are observed between the experimental data and the VCM model flow curve (digitized from Zhou et al. [65]).](image)

While the power law index in this solution is non-zero, shear banding is both possible [12, 65] and predicted for banding in a cylindrical Couette device [42]. Additionally, the steady shear flow curve shown in Figure 5.12 was determined via startup measurements; the time for the stress response to reach steady state after startup is several minutes, and is longer near the beginning of region II. This long transient strongly suggests that this solution shear bands, and is consistent with the trends seen in other shear banding WLMs [24, 29, 30, 33].
The breakage and recombination model of Cates and Candau [34] (Equation 5.3) yields a critical stress, \( \sigma_1 = 2/3 G_0^0 \), of 4.03 Pa, which corresponds to a measured critical shear rate of \( W_i^1 = 1.1 \); however, the theoretical critical shear rate is \( W_i^1 = 2.6 \). This discrepancy between the measured and theoretical critical shear rate may be explained by possible branching in the system, as it has been shown previously that the scaling of \( G_0^0 N \) is stronger when branching is not present [37]. Further, the ionic nature of the system, and solution temperature and composition, may play a role [17]. The data past the shear banding regime were fit to the Bingham fluid model, as performed by Salmon et al. [38], yielding \( \sigma = 4.1 + 0.04 W_i \). Using this model, we estimate \( W_{i2} = 100 \). The flow curve in Figure 5.12 is similar to that used in the VCM model predictions [65], providing a quantitative comparison for our experimental results. While differences exist, especially at low \( W_i \), this is likely an effect of the larger gap-to-radius ratio used in their work; we expect better agreement at equal ratios [66].

The shear startup measurements used to corroborate the flow curve reveal rich transients as the stress evolves toward steady state shear banding. Hu et al. [21] analyzed the transient velocity profiles of shear banding wormlike micelles using PTV, and related the behavior back to the features observed in the startup rheology. The PTV confirmed steady state shear banding for conditions when shoulders and other non-linear features were observed in the time-dependent startup stress response, similar to the features originally documented by Grand et al. [29]. When we examine the stress responses of our solution upon startup at shear rates in the shear banding regime, we observe these same features indicative of steady state shear banding: large stress overshoots, shoulders, undershoots and secondary overshoots before the stress reaches its steady state value. The stress transients also persist for hundreds of relaxation times at shear rates within the shear banding regime, again in agreement with experimental signatures of shear banding [24,29,30] and modeling predictions [66]. A more detailed study of this time-dependent startup rheological behavior is presented in Chapter 6.

### 5.7.2 1-3 plane SANS

As the steady shear rheological results were indicative of shear banding in the mildly branched solution, 1-3 plane SANS measurements were performed to look for signatures
of shear banding and branching. From the fits to the rheology, the shear banding regime (region II) encompasses $Wi_1 = 2.6$ to $Wi_2 = 100$, such that region III covers all $Wi > 100$. The 1-3 plane alignment factor versus shear rate is shown in Figure 5.13 for two rheometer configurations. The 1-3 plane alignment increases steadily with shear rate until $Wi = 250$, at which point the measured alignment becomes independent of applied shear rate, as was observed in the low and highly branched solutions. As $Wi = 250$ is well within region III, the constant alignment with increasing shear rate in this region indicates that the material across the gap is nearly uniform. Note that the flow direction is in the horizontal direction with respect to the scattering patterns seen in Figure 5.13. While the results reported in Figure 5.13 are the steady state values, the measurements were performed with temporal resolution to capture the startup behavior. In all experiments, at least $200\tau_R$ was required for the alignment factor to reach steady state, consistent with expectations for a shear banding sample [24]. Clear alignment is observed when $Wi = 25$ (a), as evidenced by the increased intensity in the vorticity direction ($z$-direction). However, in addition to this alignment, an isotropic background ring is observed at $q \approx 0.02 \text{ Å}^{-1}$, where the interaction peak is located (red/purple). The pronounced lobes (yellow) superimposed with this isotropic ring have been interpreted as a signature of shear banding by Berret et al. [22], as the 1-3 plane scattering is a convolution of the spatially-dependent scattering across the gap. A nearly isotropic portion of the scattering is also observed at $Wi = 75$, near the end of region II (Figure 5.13b). The intensity of the isotropic portion (purple) is much lower and the intensity of the lobes (yellow/red) is much higher at this shear rate, indicating a larger proportion of material within the high shear band. This result is expected, as calculations of the band width as a function of Weissenberg number from Equation 5.4 indicate roughly three-fold more material in the high shear band at this rate.

The highest shear rate shown in Figure 5.13 is well within region III ($Wi = 250$, c), where no shear banding is expected. There is no evidence of the isotropic ring in the scattering, where a highly aligned, butterfly-like pattern is observed. When the results shown in Figure 5.13 are compared to the 1-3 plane results for the low and highly branched solutions
(Figure 5.5), the shear banding solution (low branching) exhibited a similar isotropic contribution to the scattering during shear banding, further suggesting shear banding in the mildly branched solution. This isotropic contribution to the scattering was not observed in the shear thinning, highly branched solution.

Figure 5.13: 1-3 plane $A_f$ as a function of applied $Wi$. Excellent agreement is obtained between two rheometer configurations and sample preparations. $A_f$ increases with $Wi$ until $Wi = 250$, at which $A_f$ becomes shear rate independent. Scattering patterns are shown for $Wi = 25$ (region II, a), $Wi = 75$ (end of region II, b) and $Wi = 250$ (region III, c). Evidence of shear banding is seen in (a) and (b), as the anisotropy is superimposed with an isotropic ring in the flow direction; however this ring disappears at $Wi = 250$.

5.7.3 1-2 plane SANS

Alignment banding is an indicator of shear banding. Hence, spatially-resolved 1-2 plane measurements were performed at applied shear rates in regions II and III: $Wi = 14$, 25, 44, 63 and 75 (region II), 97 (border of region II and III), 130 and 247 (region III). Figure 5.14 shows the 2-D scattering patterns and 1-2 plane alignment factor, referred to as 1-2 $A_f$ in all figures, as a function of gap position, $r/H$, and shear rate. Scattering patterns are shown for three shear rates: $Wi = 25$ (region II), $Wi = 75$ (end of region II), and $Wi = 247$ (region III). Note that the flow direction is in the vertical direction with respect to the
scattering patterns, as opposed to in the horizontal direction as seen in the 1-3 plane patterns. As the alignment factor is a function of local shear rate [1], lines between points are for visual aid only, because the shear rate may change across the band and is not always a linear function of gap position. One trend is immediately apparent in the spatially-dependent alignment factor for the shear rates within region II. While the inner wall alignment factor, \( A_f(r/H = 0.15) \), steadily increases with increasing applied shear rate, the outer wall alignment factor, \( A_f(r/H = 0.85) \), remains fairly constant and near zero. Visually, this results in nearly isotropic scattering patterns at \( r/H = 0.85 \) when \( Wi = 25 \) and 75 (Figure 5.14). The large drop in \( A_f \) with increasing \( r/H \), which is clearly seen in the 2-D patterns, indicates a discontinuous alignment profile. This trend in alignment is expected, as the shear rate profile is discontinuous across the gap [21] and is similar to the alignment trends seen in other shear banding WLM solutions [27]. Conversely, for shear thinning (region III), the material structure is similar across the gap, as evidenced by the 2-D scattering patterns when \( Wi = 247 \). In region II, the slope of the alignment factor between \( r/H = 0.15 \) and \( r/H = 0.5 \) is roughly equal despite the increasing applied shear rate. This indicates a similar shear rate profile in the high shear band with increasing applied shear rate, which is expected based on Equation 5.4. The critical alignment factor at the shear band interface, \( A_f^* \), determined by Helgeson et al. [26] is \( A_f^* = 0.18 \), which indicates that the alignment in the high and low shear bands should be above and below \( A_f^* \), respectively, which agrees well with our region II results.

As expected from the rheology, \( Wi = 75 \) is still well within the banding regime. The outer wall alignment is similar to that of the other shear rates within the banding regime and is less than \( A_f^* \). At \( Wi = 97 \), the outer wall alignment is noticeably higher than that of the lower shear rates but still below \( A_f^* \), and the alignment factor profile is nearly linear. In previous work by Helgeson et al. [16] and Gurnon et al. [27], the alignment factor (and velocity profile) became increasingly linear as region III was approached, indicating that \( Wi = 97 \) is near the onset of region III. When \( Wi = 130 \), the alignment at the outer wall (\( A_f = 0.2 \)) is significantly higher than in the region II shear rates, and is above \( A_f^* \). Further, the alignment factor across the gap appears to have a convex shape, similar to alignment trends at the onset of region III observed by Helgeson et al. [16] and Gurnon et al. [27]. Lastly, at
Figure 5.14: Steady shear results: 1-2 plane alignment factor and scattering patterns as a function of gap position, $r/H$, and applied shear rate, $Wi$. 2-D patterns are shown for $Wi = 25$ (region II), $Wi = 75$ (end of region II) and $Wi = 247$ (region III). Significant decreases in $A_f$ from the inner to outer wall are most prevalent for $Wi$ well within region II. In and near region III, the alignment factor decreases more linearly with gap position. The estimated width of the high shear band, $\alpha$, is shown in the legend. Dotted lines are for visual aid only.
$Wi = 247$, $A_f \geq 0.40$ at all gap positions. The outer wall alignment is 70% of the inner wall alignment, suggesting that a highly ordered material has filled the gap, and that the material is near its maximally aligned state. These trends in the alignment confirm that the onset of region III is between $Wi = 97$ and $Wi = 130$, and are in good agreement with the critical shear rate estimates of $Wi_1 = 2.6$ and $Wi_2 = 100$.

These 1-2 plane results support shear banding. At $Wi = 25$, the lobes observed in the 1-3 plane pattern clearly result from the pronounced lobes evident in the 1-2 plane measurements at $r/H = 0.15$ (Figure 5.14). The isotropic portion of the 1-3 plane scattering results from the nearly isotropic 1-2 plane scattering from the low shear rate band at $Wi=25$ ($r/H = 0.5, 0.85$) in Figure 5.14. The isotropic portion of the 1-3 plane scattering observed at $Wi = 75$ is also corroborated by the 1-2 plane measurements, where the nearly isotropic ring is seen at the outer wall ($r/H=0.85$). At $Wi=247$, the scattering patterns are very highly aligned for both the 1-2 plane and 1-3 plane measurements, confirming the absence of shear banding during both measurements.

Using the critical shear rates and Equation 5.4, the proportion of material within the high shear band, $\alpha$, was estimated (legend of Figure 5.14). Note that $\alpha$ was not significantly impacted by choice of $Wi_1 = 2.6$ versus $Wi_1 = 1.1$. At $Wi = 75$, the proportion of material within the high shear band was estimated to be 75%, whereas at $Wi = 97$, 97% of the material was in the high shear band. These $\alpha$ values agree well when the alignment factor near the calculated band interface is compared to $A_f^*$. When $Wi \leq 75$, the outer wall alignment factor ($r/H = 0.85$) is fairly independent of the applied shear rate, suggesting that the shear rate within the low shear band is roughly equivalent at these applied shear rates. Conversely, the higher outer wall alignment at $Wi = 97$ at may indicate an increase in the average shear rate in the band [16,27].

The calculated band width of 75% at $Wi = 75$ also agrees well with time-resolved 1-2 plane SANS data at $Wi = 75$. These measurements, performed at steady state, are able to detect the presence or absence of fluctuations in the material response, as measured by the alignment factor (see discussion below, Section 5.8.3). The alignment factor at $r/H = 0.15$, 0.35 and 0.50 is nearly constant in time and does not exhibit fluctuations. The alignment at
\( r/H = 0.65 \) and \( 0.85 \), however, exhibits fluctuations. These fluctuations are likely the result of the proximity of the measurement to the shear band interface, and fluctuations of the shear band interface and oscillating rheological responses that can result in shear banding fluids [17, 31–33]. As both positions exhibit alignment fluctuations, the shear band interface is inferred to be between \( r/H = 0.65 \) and \( 0.85 \), in good agreement with the calculated \( \alpha = 0.75 \).

While we are below the critical Taylor number for elastic turbulence \( (Ta_c \approx 22 – 30) \) in the shear banding regime [6, 54, 57], interface fluctuations are to be expected in shear banding WLMs and vortices in the vorticity direction are also possible [31,32]. However, due to the low concentration, small gap-to-radius ratio of the shear cell, high temperature, and small amplitude of the alignment factor oscillations, it is likely that any undulations of the band interface are also of small amplitude [17].

The predictions of \( \alpha \) shown in Figure 5.14 are also in good agreement with the observed orientation angle, \( \phi_0 \), which can be seen in Figure 5.15 for shear rates within region II. As seen in Figure 5.15, the value of \( \phi_0 \) depends on the applied shear rate and gap position, where a discontinuity in \( \phi_0 \) is observed between the inner and outer wall positions. This discontinuity in the micellar orientation appears to correspond with the transition between the high shear rate and low shear rate bands. As such, two lines are shown for visual aid: the dotted red line indicates the maximum \( \phi_0 \) observed in the high shear rate band, whereas the dash-dot blue line shows the minimum orientation angle for the low shear rate band. The maximum value of \( \phi_0 \) in the high rate band is about \( 5^\circ \), whereas the minimum \( \phi_0 \) in the low rate band is around \( 10^\circ \). The gap positions where \( \phi_0 \) transitions from the high rate to the low rate band (based on shear rate) are consistent with the predictions of \( \alpha \) above. While the orientation angle between the two bands appears to be discontinuous, a higher degree of spatial resolution would be required to determine if these estimates of \( \phi_0 \) for the high and low rate bands are accurate and if \( \phi_0 \) is truly discontinuous between bands.

The orientation angle has previously been used as an indicator of shear banding. In addition to establishing a critical alignment factor at the shear band interface, Helgeson et al. [26] also determined a critical orientation angle at the interface. In these studies, the critical orientation angle \( \phi_0^* = 17^\circ \pm 2^\circ \) at the band interface [16,26]. While the critical orientation
Figure 5.15: 1-2 plane orientation angle, $\phi_0$, vs. $r/H$. The dotted line corresponds to the maximum $\phi_0$ observed in the high shear rate band ($\phi_{0,\text{high}} \leq 5^\circ$), and the dash-dot line to the minimum $\phi_0$ in the low shear rate band ($\phi_{0,\text{low}} > 10^\circ$). A discontinuity in $\phi_0$ is observed between the bands, indicative of the discontinuous structure, orientation, and velocity profile in shear banding solutions.

angle appears to be lower in the mildly branched solution ($5^\circ < \phi_{0}^* < 10^\circ$ based on Figure 5.15), the results are qualitatively similar. The quantitative differences in critical orientation angle between the WLMs here and in the work of Helgeson et al. [26] are not surprising given the solutions here are significantly less concentrated. Further, the mildly branched solution shows smaller increases in the orientation angle with increasing $r/H$ within the high shear rate band than in the solutions studied by Helgeson et al. [26], which helps to explain the lower observed value of $\phi_{0}^*$. For the region III shear rates, the measured $\phi_0$ was less than $4^\circ$ at all gap positions, in good agreement with previous observations [16,26].

5.8 Discussion: mildly branched solution

5.8.1 1-3 plane SANS

In Section 5.5.2 above, it was hypothesized that branching leads to suppressed flow alignment on an absolute shear rate scale, but enhanced flow alignment on a Weissenberg number scale in terms of the 1-3 plane alignment factor. However, this hypothesis could not be validated by comparing two WLM solutions alone. In Figure 5.16 below, the 1-3 plane
alignment factor for the mildly branched solution is added to the comparison between the low and highly branched solutions. Perhaps not surprisingly, the 1-3 plane results for the mildly branched solution fall in between the results for the low and highly branched solutions on both an absolute shear rate and Weissenberg number scale. As was the case in the other two solutions, after a critical shear rate, the alignment factor reached a maximum value after which point $A_f$ was shear rate independent. As seen in Figure 5.16, the maximum value of the alignment factor for all three solutions is roughly equivalent. The slightly lower maximum alignment seen in the mildly branched solution is likely a result of the configurational effects discussed in Chapter 3, Section 3.4, as the low and highly branched solution data were taken during the same experiment and configuration, whereas the mildly branched solution data is from a different experiment and configuration. This equivalent high rate alignment further supports the notion of branch breakage and structure change after the critical shear rate discussed above in Section 5.5.2 (Figure 5.6), because after the critical rate, the micelles orient to the same degree regardless of branching level. This maximum micelle alignment, paired with the collapse of the WLM orientation distribution functions at maximum alignment (Figure 5.6), suggests that the underlying microstructures are similar after the critical point. As mentioned in Section 5.6.4, deviations from the Cox-Merz and Laun’s rules were observed at lower Weissenberg numbers for the branched WLM solution than in the linear WLM solution. These differences were attributed to changes in the shear-induced microstructure, which began at lower $Wi$ for the 0.10% wt NaTos solution. The results presented in Figure 5.16 further support this hypothesis because the microstructure appears to align further on a Wi basis with increasing branching.

5.8.2 Mechanism of flow-alignment and shear banding: low vs. mild branching

While the 1-2 plane alignment factor and orientation angle results for the mildly branched solution presented in Figures 5.14 and 5.15 indicate shear banding in this solution, these results show different trends than observed in the low branching solution (Figure 5.7a). In the mildly branched solution, the alignment factor in the low shear rate band was close to zero, and the orientation angle in the low shear rate band was significantly larger than in the
Figure 5.16: $1-3A_f$ of the 0.01% wt, 0.05% wt, and 0.10% wt NaTos solutions on a shear rate (a) and Weissenberg number (b) scale. As $A_f(\dot{\gamma})$ and $A_f(Wi)$ show opposite trends between the low and high salt solutions, it is unsurprising that the alignment of the mild salt solution falls between the two in both cases.

High shear rate band ($\phi_{0,\text{low}} > 10^{\circ}$). These features are considered to be structural signatures of shear banding, and are similar to those observed in related shear banding WLMs [16,24,26,27,67]. In the low branching solution, the alignment factor shows a different trend (Figure 5.7a). Instead of near-zero alignment in the low shear rate band, the low shear rate band exhibits an ‘alignment band’ of significant, non-zero alignment when $r/H > 0.5$. Unlike in the mildly branched solution, the alignment in the low shear rate band increases with increasing shear rate. Further, the material in the low shear rate band has a low orientation angle at $\dot{\gamma} = 45 \text{ s}^{-1}$ ($\phi_{0,\text{low}} \approx 2^{\circ}$), as can be seen from the 2-D scattering patterns in Figure 5.7a. Interestingly, $\phi_{0,\text{low}}$ is roughly constant across the low shear rate band in this solution, and decreases with shear rate ($\phi_{0,\text{low}} \approx 11^{\circ}$ at $\dot{\gamma} = 15 \text{ s}^{-1}$). These differences persist when the two solutions are compared at the same dimensionless shear rate, as shown for $Wi \approx 80$ in Figure 5.17. The discontinuity in the alignment factor from the inner to outer wall clearly indicates that the low branching solution exhibits shear banding; however, the differences in alignment and orientation angle suggest that the mechanism of shear banding may differ between the two solutions.

The observed differences in the shear banding of the two solutions may be a result of
differences in branching level, or differences in the electrostatic interactions in the system. The small amount of added salt between the low and mildly branched solutions serves to decrease the zero-shear viscosity by a factor of four between the two solutions. As such, the electrostatic interactions between the two solutions are significantly different despite the small difference in amount of added salt. The higher zero-shear viscosity in the 0.01% wt NaTos solution results in a significantly higher elasticity number, $El$, in this solution at equivalent Weissenberg numbers. The elasticity number is given by [68]:

$$El = \frac{Wi}{Re}$$

$$El = \frac{Wi}{\rho \Omega_R R_i H / \eta_0}$$

$$El = \frac{\tau_R \eta_0}{\rho H^2}$$ (5.10)

where $Re$ is the Reynolds number, $H$ is the gap width, and $\rho$ is the fluid density, which is approximately equal between WLM solutions. As $El$ is independent of the applied shear rate, only $\eta_0$ and the geometry are important. The four-fold higher value of $\eta_0$ and $\tau_R$ in the 0.01% wt NaTos solution results in a roughly eight-fold higher elasticity number. As shear
banding is often coupled with elastic instabilities [13,17], the difference in $El$ may account for some of the differences in the mechanism of shear banding between the two solutions. The mechanism of shear band formation in each solution will be explored in Chapter 6.

### 5.8.3 Shear banding and interface fluctuations

To address the possibility of elastic flow instabilities and interface fluctuations discussed in Section 5.7.3, time-resolved 1-2 plane SANS measurements were taken at $Wi = 75$. The measurements started upon shear startup, with the 1-2 shear cell slit translating between positions without ceasing shear, so these measurements are essentially probing any steady state fluctuations in the alignment factor that could correspond with interface fluctuations. The material response reached steady state within $t \approx 350$ s, in good agreement with time-resolved rheo-SANS measurements at $Wi = 75$, and remained at steady state at all longer times. The alignment factor measurements are shown in Figure 5.18. The startup of shear began when the slit was located at $r/H = 0.15$ (inner wall). The $\Delta t$ of 900 s for $r/H = 0.15$ corresponds to an absolute time starting at $t = 0$ s and ending at $t = 900$ s. As seen in Figure 5.18, the dotted vertical line when $r/H = 0.15$ indicates the time for the material response to reach steady state after the startup of shear (350 s). At $r/H = 0.15$, at absolute times greater than 350 s, the alignment factor is fairly constant with no significant fluctuations. There are also only minor fluctuations of the alignment factor when $r/H = 0.35$. The absolute time of the experiment at $r/H = 0.35$ corresponds to $t = 3600$ s to $t = 4500$ s after shear startup. Similarly, at $r/H = 0.50$, there are only minor fluctuations of the alignment factor during the measurement. The absolute time of the experiment at $r/H = 0.50$ corresponds to $t = 1800$ s to $t = 2700$ s after shear startup.

At $r/H = 0.65$, a different trend in the steady-state alignment factor is observed than at the previous three gap positions. Here, the alignment factor exhibits weak fluctuations at steady-state that are similar to those observed in the 1-3 plane alignment factor at steady-state (data not shown). These fluctuations are likely a result of the shear banding response, which can lead to fluctuating rheological responses and/or a fluctuating shear band interface. The absolute time of the experiment at $r/H = 0.65$ corresponds to $t = 2700$ s to $t = 3600$ s after
shear startup. At \( r/H = 0.85 \), a similar fluctuating alignment factor response is observed, with even more pronounced fluctuations than are observed at \( r/H = 0.65 \). The absolute time of the experiment at \( r/H = 0.85 \) corresponds to \( t = 900 \) s to \( t = 1800 \) s after shear startup. As the steady-state alignment factor response fluctuates at both \( r/H = 0.65 \) and \( r/H = 0.85 \), it is likely that the shear band interface is located in between these two gap positions. With the 0.1 mm slit, the \( r/H = 0.65 \) position covers \( r/H = 0.6 \) to 0.7 and \( r/H = 0.85 \) covers \( r/H = 0.8 \) to 0.9, so we infer that the interface is between \( r/H = 0.7 \) and 0.8. This proposed interface location is in good agreement with the calculation of \( \alpha = 0.75 \) at \( Wi = 75 \).

![Figure 5.18: 1-2 plane \( A_f \) fluctuations based on \( r/H \) after shear startup at \( Wi = 75 \). The dotted vertical line at \( r/H = 0.15 \) indicates the time after startup until steady state is reached. The alignment in time is fairly constant at \( r/H \leq 0.5 \); fluctuations occur at \( r/H = 0.65, 0.85 \), indicating proximity to the shear band interface.](image)

Finally, it should be noted that even large fluctuations in the alignment factor may not correspond with large fluctuations in the position of the shear band interface. Specifically in shear banding WLMs, Ito et al. [69] recently showed using crossed-Nicol flow-birefringence that even large fluctuations in the stress and structure lead to very little change in the position...
of the shear band interface. In these experiments, the shear band interface could be precisely located by a change in the birefringence color, as opposed to traditional experiments where only a bright and dark phase can be identified. While minor fluctuations of the interface position occurred, the average position of the shear band interface remained constant. From digitizing the data of Ito et al. [69] to get an estimate of these fluctuations, for a fluctuation in the stress of 23%, only a 4% fluctuation in the interface location was observed. The solutions used by Ito et al. [69] were similar to the solutions here, and consisted of CTAB and sodium salicylate (NaSal). Further, in these branched solutions, the stress fluctuations observed during shear banding are significantly smaller than the ones reported by Ito et al. [69]. As the measured structure and alignment from SANS are directly related to the polymeric shear stress (Equation 2.37), it is likely that the observed fluctuations in the alignment factor do not result in significant fluctuations in the position of the shear band interface.

5.8.4 Summary: mild branching

The results presented in this section indicate that the mildly branched solution exhibits shear banding under steady shear deformation, as predicted by the similar VCM model flow curve shown in Figure 5.12 above. Both the power law index, $N$, and the 1-3 plane alignment are in between the values for the low and highly branched solutions presented in Section 5.5. While the mildly branched solution exhibited shear banding and long transience in the stress and microstructure, the solution did not exhibit the nonmonotonic behavior observed in the flow curve of the 0.01% wt NaTos solution, which suggests that the underlying constitutive equation of this solution is monotonic. The 1-2 plane alignment factor and orientation angle during shear banding were in agreement with results from similar shear banding WLMs [16,24,26,27,67]. However, the properties of this solution show significant differences to the properties of the low salt sample. These differences in the rheology and flow-alignment between the low and mildly branched solutions suggest that the mechanism of shear banding may differ between the two solutions.
5.9 High branching levels: rheology and microstructure

In Sections 5.5 and 5.7 above, shear banding was observed under steady shear deformation in the low and mildly branched solutions (0.01% wt and 0.05% wt NaTos). In the highly branched solution (0.10% wt NaTos), no shear banding was observed under steady shear. These results are not surprising, given that the power law index, \( N \), increases with increasing added salt (increasing branching). However, as shear thinning was only observed in one branched WLM solution, additional solutions with higher branching levels were investigated to verify the results. These solutions will be discussed in this section, where in all cases the level of added NaTos is \( C_s > 0.10\% \) wt NaTos. While the data on these more highly branched solutions is not as extensive as the previous results, it provides evidence to further confirm that shear banding disappears at high branching levels.

5.9.1 Steady shear rheology

In this section, the steady shear rheology of highly branched solutions is examined. The WLM solutions consist of the following salt concentrations, in \% wt NaTos: 0.125, 0.15, 0.185, and 0.25. For reference, cryo-TEM images of the 0.15% wt NaTos solutions can be seen in Appendix E. Figure 5.19 shows the steady shear flow curves for the 0.125% wt and 0.15% wt NaTos solutions. As seen in Figure 5.19a, the 0.125% wt NaTos solution shows a slightly lower degree of shear thinning than the 0.10% wt NaTos solution discussed in Section 5.5.1 above. Here, the power law index increases from the value of \( N = 0.15 \) for the 0.10% wt NaTos solution to \( N = 0.18 \) for the 0.125% wt NaTos solution. The same trend is observed in the 0.15% wt NaTos solution in Figure 5.19b, where \( N \) increases further to \( N = 0.20 \). By examining these higher salt solutions, it becomes obvious that \( N \) gradually increases with added salt, even beyond what was observed in the 0.10% wt NaTos solution previously.

In Figure 5.19b, the same apparent shear thickening behavior observed in the 0.10% wt NaTos solution is also observed in the 0.15% wt NaTos solution. To verify this behavior, startup measurements were taken across the flow curve to supplement the flow sweep measurements. Single measurements were taken at low shear rates, whereas measurements were
Figure 5.19: Steady shear flow curves for the 0.125% wt NaTos (a) and 0.15% wt NaTos (b) WLM solutions. \( N \) increases from \( N = 0.15 \) in the 0.10% wt NaTos solution to \( N = 0.18 \) and \( N = 0.2 \) for the 0.125% wt and 0.15% wt NaTos solutions, respectively. In (b), shear startup measurements are used to corroborate the flow curve and verify the reproducibility of the observed high rate shear thickening.

taken in duplicate or triplicate near the shear thickening region. In all cases, the startup behavior was repeatable between trials, and was consistent with the data taken via flow sweep. As was the case in the 0.10% wt NaTos solution, this shear thickening behavior is extremely reproducible and most likely corresponds to the breakage of the WLM branches and other structures. In the 0.10% wt NaTos solution, this shear thickening corresponded to the critical shear rate of maximum alignment measured by 1-3 plane SANS, where the orientation distribution function and 1-D SANS structure reflected a change in the underlying microstructure (Section 5.5.2). Shear thickening behavior at high shear rates is common in WLMs in this concentration regime and has been associated with a structural transition, providing further evidence of a structural change [58–61]. This shear thickening behavior is also reproducible across sample preparations and instruments. Simultaneous rheology was recorded during 1-3 plane SANS measurements on this solution, which was performed using the Anton-Paar MCR502 with a different sample preparation. The reproducibility of the flow curve and the shear thickening behavior can be seen in Appendix L. The shear thickening behavior of this solution is also discussed by Rogers et al. [4].

Figure 5.20a and 5.20b shows the flow curves for the 0.185% wt and 0.25% wt NaTos
solutions, respectively. Measurements were taken both via flow sweep and with startup experiments. Figure 5.20 shows that $N$ continues to increase with added salt content and micellar branching. Here, $N$ increases further from the values calculated for the 0.125% wt and 0.15% wt NaTos solutions to $N = 0.24$ and $N = 0.30$ for the 0.185% wt and 0.25% wt NaTos solutions, respectively. No shear thickening is observed in either case, due to limited Weissenberg number range that can be probed on the ARES G2 rheometer for these solutions. At the high shear rates that would correspond to the $Wi$ where shear thickening was observed in the 0.10% wt and 0.15% wt NaTos solutions, the sample is ejected from the rheometer and an accurate measurement cannot be obtained. A summary of the steady shear results based on branching level can be seen in the discussion in Section 5.10 below.

![Figure 5.20: Steady shear flow curves for the 0.185% wt NaTos (a) and 0.25% wt NaTos (b) WLM solutions. $N$ increases with branching to $N = 0.24$ and $N = 0.30$ for the 0.185% wt and 0.25% wt NaTos solutions, respectively. Shear startup measurements are used to corroborate the flow curve in both cases.](image)

5.9.2 1-3 plane SANS

For the 0.15% wt and 0.25% wt NaTos solutions, 1-3 plane SANS measurements were taken to further examine the rheological behavior. The steady shear flow curves for the two solutions are compared in Figure 5.21a on a shear rate scale, and Figure 5.21b on a Weissenberg number scale. As seen in Figure 5.21a, the shear stress at equivalent shear rates is initially higher in the 0.15% wt NaTos solution. At higher shear rates ($\dot{\gamma} > 90 \text{ s}^{-1}$), the shear
stresses become similar in magnitude between samples at the same shear rate. The dotted vertical lines in Figure 5.21 correspond to shear rates at which the 2-D SANS patterns are shown, where the 0.15% wt NaTos solution patterns are in the first row (purple box), and the 0.25% wt NaTos solution patterns are in the second row (black box). Interestingly, in Figure 5.21b, the stress for the 0.25% wt NaTos solution is always higher than that in the 0.15% wt NaTos solution across the entire measured Wi range. In some 1-3 plane experiments, simultaneous rheology was recorded during measurements; a comparison of the measured rheological properties during rheo-SANS to the flow curves presented in Section 5.9.1 can be seen in Appendix L. Excellent agreement is observed between instruments and sample preparations.

Figure 5.21c shows the 1-3 plane alignment factor as a function of shear rate, and Figure 5.21d shows the results as a function of Weissenberg number. As was the case for the lesser branched solutions, branching again appears to mitigate flow alignment on an absolute shear rate scale, but magnify alignment on a Weissenberg number scale. Despite similar stresses between the solutions on a shear rate scale when \( \dot{\gamma} > 90 \text{ s}^{-1} \), the 1-3 plane \( A_f \) is always higher in the 0.15% wt NaTos solution until the critical rate is exceeded. This trend is apparent when the 2-D scattering patterns shown in Figure 5.21 are examined; the 0.15% wt NaTos solution clearly shows a higher degree of anisotropy until \( \dot{\gamma} = 2000 \text{ s}^{-1} \), where the 1-3 \( A_f \) is equivalent between samples. On the Weissenberg number scale, the shear stress and alignment are always greater in the 0.25% wt NaTos solution until the critical rate. After the critical shear rate, the maximum alignment is reached, which is roughly equal between the two solutions. In the 0.15% wt NaTos solution, two different sample preparations were measured during different experiments, with different configurations on different instruments. In the first configuration, a 1.5 mm Couette gap was used on the NG-B 10 m SANS instrument, for a gap-to-radius ratio of \( \varepsilon = 0.11 \). The detector distance was 4.3 m with a neutron wavelength of \( \lambda = 5 \text{ Å} \). In the second configuration, a 1.0 mm gap was used on the NG-3 30 m SANS instrument (now NG-B 30 m), for a gap-to-radius ratio of \( \varepsilon = 0.07 \). The detector distance was 10 m with a neutron wavelength of \( \lambda = 6 \text{ Å} \).
Figure 5.21: Shear stress (a,b) and $1-3 A_f$ (c,d) for the 0.15% wt and 0.25% wt NaTos high salt solutions on a shear rate scale (a,c) and Weissenberg number scale (b,d). (a,c) On a shear rate scale, the shear stress and $1-3 A_f$ are generally higher in the 0.15% wt NaTos solution until the critical shear rate. 2-D SANS patterns are shown for the shear rates indicated by dotted lines, with the 0.15% wt NaTos solution in the first row (purple box). (b,d) Using $Wi$, the shear stress and $1-3 A_f$ are consistently larger for the 0.25% wt NaTos solution. (c,d) For the 0.15% wt NaTos solution, two sample preparations were examined using different geometries; good agreement was observed between the trials.
Section 3.4, differences in the calculated alignment factor are expected between the two trials. Nevertheless, as seen in Figure 5.21, the configuration and sample preparation have a fairly minor effect on the calculated $A_f$, and good agreement is observed between trials. Note that the scattering patterns for the 0.15% wt NaTos solution shown in Figure 5.21 are from the NG-B 10 m instrument, as the configuration was similar to that used for the 0.25% wt NaTos solution, which was also taken on NG-B 10 during a different experiment.

In both trials for the 0.15% wt NaTos solution, the alignment has achieved its maximum value by the time $\dot{\gamma} = 1000 \text{ s}^{-1}$. However, it does appear that the shear rate at the onset of maximum alignment (critical shear rate, $\dot{\gamma}_c$) is lower in the configuration with the Couette gap of 1 mm. In the data using the 1.5 mm Couette gap, this critical shear rate is in the range of $\dot{\gamma}_c = 850$ to 1000 s$^{-1}$ when the uncertainty in the calculation is taken into account. In the 1 mm configuration, the alignment has reached a maximum by the time $\dot{\gamma} = 1000 \text{ s}^{-1}$ is reached; however, the alignment in this configuration as a function of shear rate is higher than in the 1.5 mm configuration in this region. The next shear rate measured below $\dot{\gamma} = 1000 \text{ s}^{-1}$ in this configuration is $\dot{\gamma} = 575 \text{ s}^{-1}$, which is the shear rate immediately prior to the observed shear thickening in this solution shown in Figure 5.19b. At $\dot{\gamma} = 575 \text{ s}^{-1}$, the maximum alignment has not been reached; however, if the trend higher alignment in the 1 mm configuration continued, we would estimate that the critical shear rate is lower here than in the 1.5 mm configuration. In fact, the alignment follows a power-law dependence on the shear rate prior to $\dot{\gamma} = 1000 \text{ s}^{-1}$, which is violated at $\dot{\gamma} = 1000 \text{ s}^{-1}$. Using this power-law relationship and the average value of $A_f$ when $\dot{\gamma} \geq 1000 \text{ s}^{-1}$ (to account for uncertainty in the calculation) to predict the critical shear rate, we find $\dot{\gamma}_c = 620 \text{ s}^{-1}$. If the value of $A_f(\dot{\gamma} = 1000 \text{ s}^{-1})$ is used, $\dot{\gamma}_c = 700 \text{ s}^{-1}$. Both calculations are in good agreement with the onset of shear thickening presented in Figure 5.19b, where the measurements were taken in a Couette of similar curvature ($\varepsilon = 0.08$). The gap and curvature effect on the onset of different flow regimes in wormlike micelles is well-documented, so it is not surprising that different critical shear rates are observed between the two configurations.

As discussed above in Section 5.5.2, the highly branched 0.10% wt NaTos solution showed lower levels of alignment than the 0.01% wt NaTos solution on an absolute shear
rate basis despite the higher measured shear stresses along the flow curve at these shear rates (Figure 5.5). As the alignment factor is related to the polymeric stress (Equation 2.37), we hypothesized that the underlying microstructure differences in the branched versus linear systems led to a difference in the stress-SANS rule coefficient. However, the differences in alignment as a function of stress could not be definitively linked to microstructure differences because of the shear banding instability in the 0.01% wt NaTos solution, which could convolute the interpretation. As both the 0.15% wt NaTos and 0.25% wt NaTos solutions are thought to exhibit shear thinning, the same analysis can be performed here to draw stronger conclusions. In Figure 5.22, the 1-3 plane alignment factor as a function of the measured shear stress is shown for the 0.15% wt and 0.25% wt NaTos solutions. The 2-D SANS patterns are also shown for three points of equal shear stress between the two solutions.

![Figure 5.22: 1-3 $A_f$ as a function of shear stress and 2-D scattering patterns for the 0.15% wt and 0.25% wt NaTos solutions. Both 1-3 plane experiments for the 0.15% wt NaTos solution are included. The 1-3 $A_f$ is always greater for equivalent shear stresses in the 0.15% wt NaTos before $\dot{\gamma}_c$ (patterns a, b). After $\dot{\gamma}_c$, the 1-3 $A_f$ and associated shear stress are similar between solutions (pattern c).](image)

The 1-3 plane alignment factor is significantly higher at equal shear stresses in the 0.15% wt NaTos solution than in the 0.25% wt NaTos solution for all measured stresses.
before the critical shear rate. The stark differences in alignment at these stresses are visually apparent in the 2-D scattering patterns (Figure 5.22a, b). After the critical rate, the alignment factor and associated shear stresses are roughly equal between the two solutions, which can also be seen in the 2-D patterns (Figure 5.22c). These results are in agreement with those presented in Figure 5.5, as the solution with the lower level of branching in each case exhibits a higher degree of flow alignment for the equivalent shear stress. As both of the solutions shown in Figure 5.22 exhibit shear thinning, these results provide a stronger case for microstructure changes leading to a distinct stress-SANS coefficient for each solution. Further, Figure 5.22 shows that the observed changes in the alignment factor between the WLMs cannot trivially be attributed to differences in the shear stress.

5.9.3 1-2 plane SANS

Besides particle tracking velocimetry (PTV), 1-2 plane SANS measurements are the strongest evidence to indicate shear thinning versus shear banding in these WLM solutions because of the provided spatial resolution. Here, 1-2 plane measurements were also taken on the 0.15% wt NaTos and 0.25% wt NaTos solutions. Based on the rheological results and increasing power law index with added salt, it is expected that both of these solutions will exhibit shear thinning under steady shear deformation as opposed to shear banding. Further, the 0.15% wt NaTos solution is very similar to the 0.10% wt NaTos solution both in terms of the static scattering (see Chapter 4, Figure 4.2) and the structure as imaged by cryo-TEM (Appendix E), giving further reason to expect shear thinning in this solution.

The 1-2 plane, steady shear results for the 0.15% wt NaTos solution can be seen in Figure 5.23. For this solution, three shear rates were probed: 45, 575, and 1000 s\(^{-1}\). These shear rates correspond to Weissenberg numbers of \( Wi = 4.5, 57.5, \) and 100, respectively \((\tau R \approx 0.1 \text{ s})\). Figure 5.23a, the 1-2 plane alignment factor is shown for the three shear rates as a function of the gap position, \( r/H \). As seen in Figure 5.23a, the 1-2 plane \( A_f \) shows a slow and gradual decrease in magnitude as a function of increasing gap position. The continuous decrease in \( A_f \) is indicative of the continuous velocity profile exhibited by shear thinning systems (Figure 5.1a), as opposed to shear banding systems (Figure 5.1b). The results seen
in Figure 5.23a are quite similar to those observed for the 0.10% wt NaTos solution, shown in Figure 5.7b. This result is not surprising given the aforementioned similarities between the two solutions. In fact, the alignment factor shown in Figure 5.23a is almost linear with respect to the gap position, which is similar to the behavior observed in the 0.10% wt NaTos solution (Figure 5.7b). This linear behavior is a far cry from the discontinuous changes in the alignment factor profile seen for the shear banding, 0.01% wt and 0.05% wt NaTos solutions (Figures 5.7a and 5.14, respectively). Although the shear rates examined in Figure 5.23 are far apart in magnitude, the corresponding Weissenberg numbers ($Wi = 4.5, 57.5, 100$) all fell in the shear banding regime for the 0.01% wt and 0.05% wt NaTos solutions, giving further confidence in our interpretation of shear thinning for this solution.

Figure 5.23: 1-2 alignment factor, $A_f$, and orientation angle, $\phi_0$, for the 0.15% wt NaTos high salt solution. The continuous change in $A_f$ and $\phi_0$ across the gap indicate shear thinning, similar to the 0.10% wt NaTos solution.

As mentioned above in Section 5.5.2 from 1-3 plane results between the low and highly branched solutions, branching appears to mitigate flow alignment on an absolute shear rate scale. Comparing Figures 5.23a and 5.7b seems to confirm this trend. The alignment of both the 0.10% wt and 0.15% wt NaTos solutions was measured at a shear rate of $\dot{\gamma} = 45\; \text{s}^{-1}$, and the alignment of the 0.15% wt NaTos solution was lower at all gap positions. However, if the results are normalized on a Weissenberg number basis, it appears as though these trends would reverse, as was the case in Section 5.6.1. While there is no direct comparison of the
two samples based on $Wi$, the alignment at $\dot{\gamma} = 45 \text{ s}^{-1}$ is only slightly lower in the 0.15% wt NaTos solution versus the 0.10% wt NaTos solution, but $Wi$ for the 0.15% wt NaTos solution is only $Wi = 4.5$ versus $Wi = 18$ in the 0.10% wt NaTos solution.

The orientation angle as a function of shear rate for the 0.15% wt NaTos solution can be seen in Figure 5.23b. As expected for a shear thinning solution, the orientation angle decreases continuously with respect to gap position at $\dot{\gamma} = 45 \text{ s}^{-1}$. This trend is in contrast to the results seen in Figure 5.15 for the shear banding, 0.05% wt NaTos solution, where a discontinuous change in $\phi_0$ with gap position was observed in the shear banding regime. At the two higher shear rates, the orientation angle is significantly smaller and is nearly zero at all gap positions, suggesting that the WLMs at these shear rates are almost perfectly aligned with the flow direction. However, there does appear to be a minor increase in the orientation angle towards the outer wall at $\dot{\gamma} = 575 \text{ s}^{-1}$, as is expected for shear thinning solutions. These alignment factor and orientation angle results suggest that $\dot{\gamma} = 575 \text{ s}^{-1}$ occurs before the critical shear rate of maximum alignment (and shear thickening) discussed in Sections 5.5.2 and 5.9.1, which is in good agreement with the 1-3 plane measurements. The increase in the magnitude of $A_f$ from $\dot{\gamma} = 575 \text{ s}^{-1}$ to $\dot{\gamma} = 1000 \text{ s}^{-1}$ also suggests that $\dot{\gamma} = 575 \text{ s}^{-1}$ is before the critical rate, and is consistent with the increase in magnitude of the 1-3 $A_f$ between these two shear rates. At $\dot{\gamma} = 1000 \text{ s}^{-1}$, the orientation angle is essentially constant with gap position, suggesting that this shear rate is in excess of the critical rate and the WLMs are maximally aligned, in agreement with previous measurements by Gurnon et al. [67] and the 1-3 plane $A_f$ results. These observations are also consistent with the steady shear flow curve for the 0.15% wt NaTos solution shown in Figure 5.19b, where $\dot{\gamma} = 575 \text{ s}^{-1}$ was immediately prior to the shear thickening behavior and $\dot{\gamma} = 1000 \text{ s}^{-1}$ was beyond the observed shear thickening. Finally, the results from each of the three shear rates are consistent with shear thinning as opposed to shear banding, based on the critical values of $A_f$ and $\phi_0$ set forth by Helgeson et al. [26] for shear thinning and shear banding solutions.

The 1-2 plane, steady shear results for the more highly branched, 0.25% wt NaTos solution can be seen in Figure 5.24. In this solution, several shear rates were measured only at the inner wall: $\dot{\gamma} = 90, 180, 225, \text{ and } 270 \text{ s}^{-1}$. Two shear rates were probed at both the inner
and outer walls: \( \dot{\gamma} = 45 \) and \( 315 \text{ s}^{-1} \), and one shear rate was probed across the gap, \( \dot{\gamma} = 135 \text{ s}^{-1} \). The shear rates of 45, 135, and 315 s\(^{-1}\) correspond to Weissenberg numbers of \( Wi = 0.75, 2.3, \) and 5.3, respectively (\( \tau_R \approx 0.017 \text{ s} \)). Figure 5.24a shows the 1-2 plane alignment factor for all shear rates as a function of gap position. As was observed in the 0.15% wt NaTos solution, the 1-2 plane alignment shows a continuous decrease as a function of gap position at \( \dot{\gamma} = 135 \text{ s}^{-1} \), indicative of shear thinning. The alignment factor as a function of gap position also shows a roughly linear dependence in this solution.

Figure 5.24: 1-2 alignment factor, \( A_f \), and orientation angle, \( \phi_0 \), for the 0.25% wt NaTos high salt solution. The continuous change in \( A_f \) and \( \phi_0 \) across the gap indicate shear thinning, similar to the 0.10% wt NaTos solution.

While the data shown in Figure 5.24a at \( \dot{\gamma} = 45 \) and \( 315 \text{ s}^{-1} \) only covers two gap positions, the differences in alignment between the inner and outer wall also support shear thinning as opposed to shear banding. The alignment factor at the inner and outer wall at \( \dot{\gamma} = 45 \text{ s}^{-1} \) are very similar in magnitude, and the difference in \( A_f \) between the inner and outer walls at \( \dot{\gamma} = 315 \text{ s}^{-1} \) is consistent with the results from the 0.10% wt and 0.15% wt NaTos solution. Additionally, in Figures 5.7b and 5.23a, the slope of \( A_f \) vs. \( r/H \) increases with shear rate for shear thinning solutions. If linear behavior is assumed at \( \dot{\gamma} = 45 \) and \( 315 \text{ s}^{-1} \), the same trend would hold for the 0.25% wt NaTos solution. Figure 5.24b shows the orientation angle as a function of shear rate and gap position for the 0.25% wt NaTos solution, which also support the conclusion of shear thinning. At \( \dot{\gamma} = 135 \text{ s}^{-1} \), the orientation...
angle shows a gradual increase with gap position; this trend is also observed at $\dot{\gamma} = 45$ and $315 \text{ s}^{-1}$. As seen in Figure 5.24b, the orientation angle at the inner wall also appears to decrease with shear rate, which is confirmed in Figure 5.25.

![Figure 5.25: 1-2 $A_f$ (a) and orientation angle, $\phi_0$, (b) at the inner wall ($r/H = 0.167$) for the 0.25% wt NaTos solution as a function of shear rate.](image)

Results for the alignment and orientation angle at the inner wall only ($r/H = 0.167$), as a function of shear rate, can be seen in Figure 5.25. In Figure 5.25a, the alignment factor at the inner wall shows a nearly linear increase in magnitude with shear rate. This result is not surprising given the linear increase in the 1-3 plane $A_f$ with shear rate for the 0.01% wt and 0.10% wt NaTos solutions (Section 5.5.2). As the 1-3 plane $A_f$ is a convolution in space across the gap of the 1-2 plane $A_f$, the largest contributions to the 1-3 plane $A_f$ are those from the inner wall positions where the WLMs are the most aligned. As such, a similar increase in alignment with shear rate is expected between the 1-3 $A_f$ and the 1-2 $A_f$ at the inner wall. Figure 5.25b shows a decrease in the orientation angle with shear rate, which appears to flatten off at high shear rates. The decrease in $\phi_0$ with shear rate is consistent with results from other WLMs presented above, where $\phi_0$ approaches zero at high Weissenberg numbers. While $\phi_0$ appears to reach an asymptotic value once $\dot{\gamma} \geq 225 \text{ s}^{-1}$, it is unlikely that $\phi_0$ reaches a minimum that is non-zero based on results from other branching levels. As these three shear rates correspond to very similar $Wi (Wi = 3.8, 4.5, \text{ and } 5.3)$, and fairly low
values of \( Wi \), it is likely that \( \phi_0 \) would further decrease as the shear rate is increased. A larger shear rate range would be needed to determine definitively whether \( \phi_0 \) for the 0.25\% NaTos solution approaches zero, as is observed in the other WLM solutions.

5.10 Discussion: all branching levels

Several trends were observed in the steady shear rheology and steady shear SANS in the 1-2 and 1-3 planes for the WLMs based on the amount of added salt, and by consequence, amount of branching in the solution. These results are summarized and discussed for all branching levels below.

5.10.1 Steady shear rheology

The steady shear rheological results for all branching levels are summarized in Figure 5.26. In Figure 5.26a, the flow curves are compared based on absolute shear rate. At low shear rates in the Newtonian plateau (region I), the shear stress is higher for the solutions with lower salt contents, \( C_s \). For shear rates near the end of region II and into region III (\( \dot{\gamma} \approx 50 - 100 \text{ s}^{-1} \)), the shear stresses for most of the solutions approach similar values. The flow curve for the 0.01\% wt NaTos solution is the exception to this trend, which has significantly lower shear stresses in region II. Across region II where \( N \approx 0 \), the average shear stress is \( \sigma = 3.2 \pm 0.2 \text{ Pa} \), whereas the other solutions have average shear stresses over twice as large for the same region. While an upturn in the stress is observed at \( \dot{\gamma} > 50 \text{ s}^{-1} \), the shear stress for the 0.01\% wt NaTos solution does not reach the same magnitude as the shear stresses for the other solutions within the measured range. While it is feasible that the shear stresses in this solution would continue increasing to the magnitude of the other solution stresses at higher shear rates, a different measuring geometry would have to be used, as the solution becomes unstable and foams at shear rates higher than those in the presented range.

When the flow curves are examined on the basis of Weissenberg number in Figure 5.26b, different trends are observed versus those seen in Figure 5.26a. As seen in Figure 5.26b, the region I Newtonian regime for all solutions essentially collapses onto a single curve when the solutions are examined based on \( Wi \). As \( Wi \) increases into region II, the
shear stress becomes higher with increasing $C_s$. This result is expected based on the increase in $N$ with $C_s$, which is clearly seen by the increase in the slope of the shear stress vs. $Wi$ with $C_s$ in Figure 5.26b. The shear stresses for the 0.01% wt NaTos solution are still significantly lower than in the other solutions, which are much closer in magnitude.

![Graph](image)

Figure 5.26: Steady shear flow curves as a function of added salt, $C_s$ (% wt NaTos) on a shear rate (a) and Weissenberg number (b) basis. (a) The shear stress, $\sigma$, is higher in region I for low $C_s$; in regions II and II, $\sigma$ is similar in magnitude when $C_s > 0.01$% wt NaTos. (b) $\sigma, N$ increase with NaTos based on $Wi$.

Examining the steady shear results for all WLMs on a basis of shear rate and $Wi$ helps to interpret the SANS results more easily. The results based on a shear rate scale are perhaps difficult to understand in regions I and II, because these regions of the flow curves coincide with different shear rates and do not overlap. However, these results show a near collapse of the flow curves at high shear rates (region III), which helps to explain the collapse of the alignment factor at high shear rates. In region III after the critical rate for each solution, the values of the stress are roughly equal regardless of added salt. This further supports the notion of a structural transition and branch breakage at high rates. If all WLM solutions have equal shear stresses and viscosities, the underlying microstructure should also be roughly equal. This notion implies that at high rates, all WLM structures are similar and the maximum alignment in region III results from an alignment of linear chains. The Weissenberg number results presented in Figure 5.26b provide a clear basis for understanding the steady
shear trends in regions I and II. In region I, the results are nearly identical across samples, which is expected for samples with similar linear rheological properties. In region II, the shear stress monotonically increases for increasing $C_s$. By examining the WLM solutions using both bases, a clearer understanding of the flow phenomena is obtained.

5.10.2 Empirical relationship for the power law index

As shown above in Figure 5.26b, and as discussed throughout this chapter, the steady shear results clearly show an increase in the power law index, $N$, with increasing added salt concentrations. These steady shear results summarized for all branching levels can be seen in Figure 5.27 in terms of the power law index, where an empirical relationship is developed to link the salt concentration to $N$. Figure 5.27a shows the relationship between added salt and $N$ in terms of the weight percent of added salt, whereas Figure 5.27b shows the data in terms of the molar ratio of anionic to cationic species in each solution. These two bases were chosen, as they were used for the comparisons of the zero-shear viscosity and relaxation time presented in Chapter 4, Section 4.3.1. For each solution, $N$ was calculated based on the power law fluid model (Equation 5.1), over a shear rate range in region II where $N$ was not dependent on the applied shear rate. The minimum $Wi$ used for the calculations was roughly equivalent between branching levels for consistency; the maximum $Wi$ was larger in solutions of low $C_s$, as region II covers a larger range of $Wi$ in these solutions. In each case, a quadratic empirical relationship is developed, that describes the data well over the salt concentration range studied. Note that these relationships cannot be used to extrapolate $N$ for added salt contents lower than 0.01% wt NaTos, as this would result in a negative power law index, which is non-physical. We assume that $N \approx 0$ when $C_s \leq 0.01$% wt NaTos.

5.10.3 1-3 plane comparison: all branching levels

As discussed in Sections 5.6.1 and 5.8.1 above, added salt and branching appeared to lead to a decrease in the flow-alignment based on shear rate, but an increase in alignment based on Weissenberg number. The 1-3 plane alignment factor results for all salt concentrations are summarized in Figure 5.28 below, on a basis of shear rate (a) and Weissenberg
Figure 5.27: Power law index, $N$, as a function of added salt in terms of $C_s$ (% wt NaTos) (a) and in $R$, the ratio of the molarity of anionic species to cationic species. Empirical relationships are developed in each case that describe the data well.

number (b). As was the case for the 0.01% wt through 0.10% wt NaTos solutions, the trends in alignment are confirmed across all branching levels. For the 0.15% wt NaTos solution, the data is shown for the configuration with the smaller curvature, $\varepsilon$, which is most similar to the configurations used for the other samples; however, the data from the larger gap configuration also follows the observed trends in $A_f$ with branching level. For all branching levels, the maximum alignment obtained is approximately equal. Differences in geometry can impact the maximum flow alignment (Figure 5.21), and the configuration can impact the calculation of $A_f$ (see Chapter 3, Section 3.4). While the reported error bars are calculated from the uncertainty in the intensity distribution, the true uncertainty stems from factors like the geometry and configuration. Accordingly, the maximum $A_f$ in Figure 5.28 can be assumed to be equal when all of these factors are factored into the uncertainty.

The shear stress in region II increases on a $Wi$ basis with increasing salt content $C_s$ (see Figure 5.26b), which helps to partially explain why the 1-3 plane alignment factor is always greater for higher branching levels in region II on a $Wi$ scale. In region II, an increase in the shear stress leads to an increase in the 1-3 plane alignment, which is expected based on
the stress-SANS rule (Chapter 2, Equation 2.37) [16]. However, the higher shear stress associated with higher branching levels at equal $Wi$ does not fully explain this trend in the 1-3 $A_f$. As seen in Figure 5.22, on the basis of equal stress, solutions with lower branching levels actually align further. The same analysis extended to all branching levels can be seen in Figure 5.29 below, where the alignment for equal stresses is highest at low branching levels. This result is consistent with the results shown between the low and highly branched solutions in Figure 5.5, where lower alignment was observed in the highly branched solution at equal shear rates despite higher shear stresses. We hypothesized that microstructural differences lead to this trend, which in turn results in a higher value of the stress-SANS coefficient with increasing branching (Equation 2.37). Clearly, the results in Figure 5.29 indicate that the stress-SANS coefficient must increase as branching increases. Therefore, for the 1-3 $A_f$ to increase with branching on a $Wi$ scale, the stresses for increasing $C_s$ must be significantly larger on a $Wi$ scale than for low $C_s$.

This phenomenon can be better explained when the 1-3 plane $A_f$ in Figure 5.28b is examined further. In Figure 5.28b, the difference in the magnitude of $A_f$ between branching levels is quite small at low $Wi$ (near the start of region II). As $Wi$ increases further into region II, the difference in the magnitude of $A_f$ between solutions of different branching levels also
increases. When the flow curves are re-examined in Figure 5.26b on the Wi basis, the cause of this behavior becomes clear. At low Wi, high Cs solutions have only slightly higher shear stresses than the low Cs solutions, leading to 1-3 A_f values that are similar in magnitude. As the WLM solutions align further for equal stresses when Cs is lower, the 1-3 A_f should be roughly equal between samples in this region. As Wi increases, the difference in the magnitude of the shear stress between low and high Cs solutions also increases because the power law index increases with Cs. Accordingly, in region II, larger differences in A_f are observed with increasing Wi until the critical shear rate is reached. After the critical shear rate, the stress, viscosity, and microstructure of all solutions are approximately equal.

Figure 5.29: 1-3 A_f as a function of shear stress for WLM solutions of all branching levels. A_f for equal stress is highest at low branching levels, indicating that the stress-SANS coefficient (Equation 2.37) increases with branching.

5.11 Conclusions

In this chapter, the non-equilibrium, steady shear properties of mixed cationic and anionic wormlike micellar solutions with various amounts of added sodium tosylate (NaTos) were explored with the goal of developing signatures of micellar branching. The addition of NaTos to these solutions leads to WLM branching, which is supported by rheological, structural, and dynamic measurements reported in this chapter and in Chapter 4. In this chapter
specifically, shear banding and shear thinning non-equilibrium flow phenomena were examined for the branched WLMs using steady shear rheology and steady shear flow-small angle neutron scattering (flow-SANS) in two shear planes. Both shear thinning and shear banding are spatially-dependent flow phenomena that are commonly observed in WLM solutions (Figure 5.1). Steady shear rheological characterization suggests that shear banding is eliminated at high levels of branching, as seen by the increase in the power law index, $N$, with branching (Figures 5.4, 5.12, 5.26, 5.27). This observation is supported by spatially-resolved 1-2 (flow-gradient) plane SANS measurements on solutions with different branching levels. In the solution with low branching (0.01% wt NaTos), a discontinuous change in the alignment factor from the inner to the outer wall is observed (Figure 5.7a), reminiscent of the discontinuous velocity profile observed in shear banding systems (Figure 5.1b). ‘Alignment banding’ is observed in the outer half of the gap, indicative of shear banding in this solution. In the mildly branched solution, different trends in the shear-induced alignment are observed (Figure 5.14). The alignment trends in this solution are also indicative of shear banding, consistent with the VCM model flow curve (Figure 5.12). While a discontinuous change in $A_f$ is observed from the inner to the outer wall, near-zero alignment was observed in the low shear rate band. These results are similar to the structural results seen from other shear banding WLM solutions [16, 24, 26, 27, 67]. The different mechanisms of flow alignment in the two solutions suggest that the solutions may exhibit different mechanisms of shear banding (Figure 5.17), which may be a result of differences in the branching level and/or solution elasticity (Equation 5.10). The mechanism of shear banding will be explored further in Chapter 6 for each solution.

The 1-2 plane results also verify that the shear banding observed in the WLMs with low to mild branching levels is not observed when significant branching is present (Figure 5.7a, 5.23, 5.24). While branching is associated with the disappearance of shear banding, it is likely that branching is not the sole contributing factor to the elimination of the shear banding phenomena. As seen in Figure 5.26, region II encompasses a smaller shear rate range with increasing branching, meaning that adding salt moves the zero-shear viscosity closer to the high rate viscosity. While branch points may physically hinder flow alignment
and can slide to prevent extreme breakage during shear, the proximity of $\eta_0$ to $\eta_\infty$ with added salt could also contribute to $N$ increasing with branching. Further, as these solutions greatly differ in ionic strength, electrostatic interactions, relaxation time, and zero-shear viscosity, (which determine the solution elasticity, Equation 5.10), any of these factors could play a significant role in the disappearance of shear banding with increasing branching.

In the steady shear rheology of solutions with high branching levels, shear thickening occurs at high shear rates in region III (Figures 5.4, 5.19). We attribute this behavior to a structural transition, which is commonly observed in WLMs in this concentration regime. A structural transition during shear thickening is supported with SANS measurements in the 1-3 plane. A new method of analyzing the effects of branching in wormlike micelles and possible branch breakage is proposed using the scattering intensity distribution, or orientation distribution function (ODF) from the 1-3 plane measurements (Figure 5.6). Examining the ODF provides more information about the underlying material structure than alignment factor analysis alone. The widening of the micellar ODF under flow with increasing salt concentration supports increasing branch density. At equal shear rates, branched micelles flow-align less than their linear counterparts, despite higher shear stresses (Figures 5.5, 5.28). Using Equation 2.37, this leads to a unique stress-SANS coefficient for each branching level. This behavior persists until a critical shear rate is reached, which is dependent on the level of added salt and branching. This critical shear rate corresponds to the shear thickening observed in the rheology. At the critical rate, the ODFs of the branched micelles become comparable to those observed for the linear WLMs, suggesting an alignment of linear chains that results from branch breakage. Sector-averaged SANS under flow confirms that the micellar structure is different at rates in excess of the critical value (Figure 5.6). A multi-technique experimental approach, combining nonlinear rheology and flow-SANS in different shear planes has enabled us to link micellar microstructure and topology to the macroscopic flow properties of WLM solutions, providing a more complete data set for further rigorous testing of microstructure-based constitutive equations, which will be discussed further in Chapter 7.
References


Chapter 6

STRUCTURE AND RHEOLOGY: SHEAR STARTUP

6.1 Introduction

In Chapter 5, the non-equilibrium properties of mixed cationic and anionic WLMs were examined to determine how added salt and topological changes affect the steady shear flow properties. Only the steady shear properties were investigated; no time-dependent measurements were examined. The natural extension of the work in Chapter 5 is to therefore examine the time-dependence of the material properties that leads to the observed shear thinning or shear banding under steady state conditions. Accordingly, in this chapter, both the rheological and neutron scattering investigations conducted in Chapter 5 are extended to include the time-dependent flows. Specifically, transient shear startup deformations are examined, so the time-dependent behavior that leads to the steady state can be determined for each WLM solution. One specific goal of this chapter is to understand how the rheology and microstructure of WLM solutions that shear band versus those that shear thin evolve in time to reach such different steady flow behaviors. Additionally, as discussed in Chapter 5, a different form of alignment is observed for these two classes of shear banding solutions under steady shear. Hence, another goal of this chapter is to determine how the rheology and shear-induced microstructures in each solution evolve differently in time to reach distinct shear banded states. In addition, we seek to understand if, and how, different mechanisms of shear banding are present in the two solutions. As in Chapters 4 and 5, we discuss what rheological and structural features can be attributed to branching versus other solution properties, especially in the context of shear banding and its underlying mechanisms.
In addition to performing time-dependent startup rheological measurements, in this chapter, time-dependent flow-small angle neutron scattering measurements are also performed. Once again, these measurements are taken in two shear planes, the 1-3 (flow-vorticity) and 1-2 (flow-gradient) planes. While the 1-3 plane measurements do not provide spatial resolution, these measurements can be taken with temporal resolution, which enables us to understand the evolution of the microstructure to the steady state. In these time-dependent flows, 1-3 plane measurements are often extremely useful, due to the improved neutron flux associated with these, as opposed to the 1-2 plane, measurements (see Chapter 3, Section 3.4). The 1-3 plane measurements give an estimate of the structural transient associated with shear startup, which enables the 1-2 plane measurements to be more focused. The 1-2 plane measurements in this chapter provide both spatial and temporal resolution, meaning that the structure and alignment can be determined as a function of time after shear startup, and as a function of gap position. As the structure can be determined as a function of space and time, the 1-2 plane data is used to determine the structural mechanisms behind the observed shear banding in the low (0.01% wt NaTos) and mildly (0.05% wt NaTos) branched solutions. In this chapter, the results are first presented for the low branching solution, followed by the results for the mildly branched solution so that the differences in the shear banding mechanisms can be compared. Due to the volume of data, the solutions are presented sequentially for clarity. Finally, the results for all other branching levels, which exhibit shear thinning, will be discussed. Parts of this chapter are published in reference [1].

6.2 Rheological signatures of shear banding

Transient shear startup measurements are often used to support a hypothesis of shear banding in WLMs, as shear banding solutions often exhibit rich transients as the stress evolves toward steady state shear banding. Hu et al. [2] analyzed the transient velocity profiles of shear banding and shear thinning wormlike micelles using particle tracking velocimetry (PTV) measurements [2,3]. Hu et al. [2] then related certain features of the startup behavior back to shear banding versus shear thinning behavior in WLM solutions, for solutions with no discernible wall slip. In the solutions examined by Hu et al. [2], certain features
were considered signatures of shear banding, and the stress response could be divided into five distinct stages, which are illustrated in Figure 6.1a. These features include a large, sharp stress overshoot upon shear startup, followed by a shoulder-like feature immediately following the overshoot. In stage I shown in Figure 6.1a, Hu et al. [2] observed approximately linear velocity profiles with a rapidly increasing stress (stress overshoot). In stage II, which occurs directly following the stress overshoot and into the shoulder region, the velocity profile becomes dramatically nonlinear. At certain locations within the gap \(0.15 \leq r/H \leq 0.5\), the material has a lower velocity than the material close to the outer wall \((r/H > 0.5)\), indicating elastic recoil. Hu et al. [2] interpret these velocity profiles in the context of transient shear banding, in agreement with the modeling efforts of Fielding and co-workers [4, 5].

After the shoulder, a stress undershoot and another ‘secondary’ overshoot are observed (see inset of Figure 6.1a). In this stage three, the shear rate becomes more inhomogeneous across the gap. Finally, in stage IV, the low shear rate band and the band interface becomes visible. The low shear rate band grows and expands toward the inner wall, before the stress settles to its steady state value in stage V.

Stress overshoots are still observed in shear thinning polymers and WLMs, where the stress overshoot in WLMs corresponds to micellar breakage. However, in the shear thinning solutions, the stress overshoots are significantly more rounded than in the shear banding solutions. Importantly, while the undershoot and secondary overshoot are also present in the shear thinning solutions studied by Hu et al. [2], the shoulder feature in their stage II region of the startup curve is unique to the shear banding solutions (see Figure 6.1a). The secondary overshoot observed in the stress responses corresponds to the time at which the low shear band becomes discernible, which is illustrated in the inset in Figure 6.1a. The transient PTV measurements of [2] provide a useful first guide to interpreting the bulk rheological behavior in the context of shear band formation. It is important to note that the PTV measurements of Hu et al. [2] correspond to shear banding solutions that exhibit no wall slip. Wall slip is often observed in shear banding solutions, which may fuel different behavior than in shear banding solutions where no slip occurs [6–10].

The PTV measurements of Hu et al. [2] confirmed steady state shear banding for
conditions when shoulders and other nonlinear features were observed in the time-dependent startup stress response, similar to the features originally documented by Grand et al. [11]. Another common feature of shear banding solutions is a long transient in the startup stress response, which may persist for hundreds of relaxation times at shear rates within the shear banding regime. The longest transients are expected at the onset of region II, which has been observed experimentally [11–14] and predicted by models [15]. In addition to the features described by Hu et al. [2], another common feature of a shear banding response is a metastable plateau region in the startup stress, which is illustrated in Figure 6.1b. Here, the stress appears stable after the secondary overshoot (Figure 6.1b, i), but after long times, the stress suddenly decreases (ii) to steady state (iii) [13]. In comparison, shear thinning solutions exhibit much faster transients in relative $\tau_R$, giving another basis to interpret the startup responses.

Figure 6.1: Features of the startup stress response indicative of shear banding at shear rates well within (a) and at the onset of (b) region II. Note that region II refers to the shear banding regime in the three-region, steady shear flow curve. (a) Five stages of the startup response determined by Hu et al. [2]. Linear velocity profiles are observed in I, that become highly nonlinear in II when elastic recoil is observed. In III, a shoulder-like region and stress undershoot are followed by a secondary overshoot (inset). The secondary overshoot marks the onset of IV, where the shear band interface becomes discernible. In V, steady state shear banding occurs. (b) Near the onset of region II, a metastable plateau region is observed (i), which is followed by a sharp decrease in stress (ii), and the steady state stress (iii).
6.3 Mechanisms of shear banding

The mechanism of shear band formation in WLM solutions has been debated in the literature. Berret [12] proposed that upon shear startup, a nematic-like phase near the inner rotating cylinder nucleates and grows outward. However, transient particle tracking velocimetry (PTV) measurements by Hu and co-workers [2, 3] suggest that the material across the gap disentangles upon startup and breaks, enters a long lived metastable shear thinning state, and finally settles into shear bands with the material in the outer shear band re-entangling. This mechanism of shear banding proposed by Hu and Lips [3] is referred to as the ‘disentangle, re-entangle’ mechanism, which is illustrated in Figure 6.2. Both works used a CPyCl/NaSal solution in brine; however Berret [12] studied a 12% wt solution, whereas Hu and co-workers used a 5.9% wt solution [2, 3]. Using time-resolved SANS measurements in the 1-2 plane, López-Barrón et al. [14] were able to resolve this debate and confirm the mechanism of shear band formation in a 6% wt CPyCl/NaSal solution [16–18].


In order to make precise, time-resolved SANS measurements upon shear startup, López-Barrón et al. [14] used an acquisition trigger synched with the SANS instrument and 1-2 shear cell motor to begin data collection immediately upon shear startup. SANS results were also compared to time-resolved small angle light scattering (SALS) measurements during shear band formation. For the shear startup experiments, two shear rates were selected: one prior to onset of shear banding regime and one in the shear banding regime. Prior to shear banding, a small stress overshoot was observed in the rheology, and both the stress...
and 1-2 plane alignment factor evolved steadily in time to steady state values. As the flow is homogeneous at this shear rate, little change in the structure was observed upon startup. The steady state alignment factor value of $A_f = 0.07$ and angle of $\phi_0 = 21.7^\circ$ were both below the critical values expected for shear banding, $A_f^* = 0.18$ and $\phi_0^* = 17^\circ$ [19], confirming homogeneous flow. The stress-SANS rule was then used to calculate the shear stress and normal stress differences, which compared favorably to the measured values.

Significantly different behavior was observed in the shear banding regime, where SANS measurements were taken at the moving inner Couette cylinder ($r/H = 0.2$) and the outer stationary cylinder ($r/H = 0.8$). A large stress overshoot was seen in the rheology at this shear rate, which corresponded to nearly isotropic scattering. However, immediately following the stress overshoot, the scattering became highly anisotropic at both the inner and outer walls. During the course of the startup experiment, the material at the inner wall (high shear band) remained highly aligned but did not significantly change in structure. However, the material at the outer wall (low shear band) evolved in time from highly aligned micelles to entangled, minimally aligned micelles. These results confirm the mechanism of shear banding presented by Hu and co-workers [2,3] by showing that the WLM solution disentangles and aligns upon startup, and the low shear band eventually settles and re-entangles. On longer length scales, SALS measurements showed butterfly-type patterns, indicated density fluctuations and longer length scale order. Once again, the stress-SANS rule was used to calculate the shear and normal stresses; however, the stress-SANS coefficient used was an order of magnitude higher than had been used in the homogeneous flow calculations. With the adjusted stress-SANS coefficient, favorable values were obtained using values from either band prior to the onset of shear banding. After the onset of shear banding, only the calculated values from the high shear band were reasonable, confirming the breakdown of the stress-SANS rule for highly non-linear flows.

The relaxation of the homogeneous and shear banded state was also probed at the same shear rates. In the homogeneous state, both the stress and alignment factor relaxation were exponential, as predicted by the Maxwell model. In the shear banded state, however,
the stress relaxation was fit to two exponential decays while the alignment factor was described by a single exponential decay after a lag time. The initial, extremely fast decay in stress corresponded to a disappearance of the butterfly-pattern in the SALS measurements and therefore relaxation of the density fluctuations on the micron scale. During this relaxation period, no change or relaxation was seen in the alignment factor value. Once the stress entered the second, slower relaxation process, the measured stress and alignment factor decayed commensurately. Thus the combination of rheological, SALS and 1-2 plane SANS measurements enabled the separation of relaxation processes and shear band formation mechanism to be determined.

6.4 Mechanism of shear banding: low vs. mild branching

Based on the alignment factor results presented in Chapter 5, the low and mildly branched solutions appear to exhibit different mechanisms of shear banding. As mentioned in Chapter 5, in traditional shear banding systems, the band width of the high shear rate band should increase linearly with applied shear rate, as given by Equation 5.4 [20–23]. From the 1-2 plane SANS results in Chapter 5, it is clear that the shear banding in the mildly branched (0.05% wt NaTos) solution follows this lever rule (see Figure 5.14). However, when examining the results for the solution with low branching (0.01% wt NaTos) in Figure 5.7, it appears that the band width remains nearly constant with shear rate. While the spatial resolution of the measurement is not precise enough to verify the exact location of the shear band interface, a measurable change in the location of the interface is expected based on the large change in Weissenberg number between the probed shear rates ($Wi \approx 80$ to $Wi \approx 250$ between $\dot{\gamma} = 15$ and 45 s$^{-1}$).

Another difference between the two systems is observed based on the magnitude of the alignment factor. As shown in Chapter 5, there are large visual differences in the 2-D SANS patterns for the low branching and mildly branched solutions. Both solutions exhibit a large and discontinuous change in alignment with increasing gap position in the shear banding regime. However, the mildly branched solution shows little to no alignment at the outer wall in the shear banding regime. This alignment does not increase with increasing...
shear rate, and is consistent with SANS results from other shear banding wormlike micelle systems [14,17–19,23]. The degree of alignment and the measured orientation angle in the mildly branched solution are in good agreement with the critical values of $A_f$ and $\phi_0$ set forth by Helgeson et al. [23] for shear banding WLMs. The results for the mildly branched solution suggest that the mechanism of shear banding is similar to the ‘disentangle, re-entangle’ mechanism [2,3,14]. Conversely, for the low branching solution, an ‘alignment band’ that is non-zero in magnitude corresponds to the low shear rate band, and is observed at all shear rates. However, in contrast to the behavior of the mildly branched solution, the alignment in the alignment band increases with increasing shear rate. At $\dot{\gamma} = 45 \text{ s}^{-1}$, the alignment in the low alignment band is $A_f \approx 0.2$, which is larger than the critical value of $A_f$ set forth by Helgeson et al. [23]. The distinct behavior in the low branching solution suggests that it may not follow the ‘disentangle, re-entangle’ mechanism. In Chapter 5, we hypothesized that the differences in shear banding may be a result of the differences in electrostatic interactions and solution elasticity between the two samples (Equation 5.10). Wall slip and elastic instabilities can occur at high shear rates and lead to different shear banding behavior than is observed at low shear rates or in lower elasticity solutions [6–10,24]. The results presented in this chapter will be discussed further in the context of these flow behaviors.

6.5 Shear startup: low branching solution

As the low branching solution exhibits anomalous flow alignment (Chapter 5), we first examine this solution using the startup rheology and structural response in two shear planes to determine the shear banding mechanism. Additional trials from startup rheology measurements and startup SANS measurements can be found in Appendix M.

6.5.1 Startup rheology

As the low branching solution (0.01% wt NaTos) exhibited an alignment band that was distinct from the alignment seen in the mildly branched solution (0.05% wt NaTos), shear startup rheological measurements were first performed to determine signatures of the shear banding response which may differ between the two solutions. Startup measurements
were taken in triplicate to determine the shear rates at which the startup stress response was reproducible. For reference, the approximate steady shear flow curve determined from the startup measurements is shown in Figure 6.3. Figures 6.4 and 6.5 correspond to low shear rates near the onset of region II (at steady state), Figure 6.6 corresponds to shear rates well within region II (at steady state), and Figure 6.7 corresponds to shear rates near the onset of region III (at steady state). In Figures 6.4, 6.6, and 6.7, the average stress response is shown for each shear rate, where the error bars correspond to the standard deviation of the stress between the three trials. Additional trials that explore the unique behavior near the onset of region II are shown in Appendix M. In Figure 6.8, the three individual trials are shown for several shear rates, to demonstrate the reproducibility of the startup responses. The steady shear startup measurements reveal rich transients as the stress evolves toward steady state shear banding, and the features of the stress response are dependent on the shear rate region.

The flow curve shown in Figure 6.3 is nearly identical to the flow curve reported in Chapter 5, Section 5.5.1 for the steady shear case. The effect of the Couette curvature and gap-to-radius ratio on the flow curve is discussed in Appendices L and M. At low shear rates, near the onset of the shear banding regime ($\dot{\gamma} = 0.1 \text{ s}^{-1}$) an overshoot in the stress is observed, indicating that the steady state has not been reached in this region of the curve. Hour long startup trials in this region of the flow curve are shown in Appendix M. Beyond this shear rate and up to $\dot{\gamma} = 4.2 \text{ s}^{-1}$, the stress is nearly constant with increasing shear rate. When $\dot{\gamma} > 4.2 \text{ s}^{-1}$, a small upturn is observed in the flow curve, which would generally indicate the onset of region III. However, as shown in Chapter 5, Section 5.5.3, shear banding is observed at shear rates between $\dot{\gamma} = 15$ and $45 \text{ s}^{-1}$. The results from Chapter 5 suggest that the entrance into region III is more likely near the second upturn in the flow curve, which is observed at a shear rate of $\dot{\gamma} = 90 \text{ s}^{-1}$. The inset in Figure 6.3 is shown on a linear scale to showcase the uncertainty in the stress response; the error bars are the standard deviation of the stress response at steady state, which exhibits fluctuations in the shear banding regime.

Hu et al. [2] analyzed the transient velocity profiles of shear thinning and shear banding wormlike micelles using PTV, and related the behavior back to the features observed in the startup rheology. In their work, the velocity profile was approximately linear at all times.
Figure 6.3: Startup flow curve for the 0.01% wt NaTos solution. The overshoot at $\dot{\gamma} = 0.1 \text{ s}^{-1}$ indicates that steady state has not been reached. Inset shown on a linear-log scale to show the uncertainty in stress at high $\dot{\gamma}$. Dotted lines are for visual aid only; the thick dashed line corresponds to the anticipated steady state behavior at the onset of region II.

when no stress overshoot was observed, showed transient shear banding when rounded stress overshoots and undershoots were observed, and showed steady state shear banding when shoulders and other non-linear features were observed in the time-dependent startup stress response, $\sigma^+(t, \dot{\gamma})$. Using the work of Hu et al. [2] as a basis, we can examine the features of the transient stress response. The startup measurements for the low branching solution can be seen in Figure 6.4 below for low shear rates at and above the start of the shear banding regime ($0.5 \leq \dot{\gamma} \leq 10.5 \text{ s}^{-1}$). In this solution, the first shear rate shown in Figure 6.4, $\dot{\gamma} = 0.5 \text{ s}^{-1}$, corresponds to a Weissenberg number of $Wi \approx 3.5$, which is above the critical shear rate for shear banding for the toy model of Cates and co-workers of $Wi_1 = 2.6$ [20, 25, 26] (see Chapter 5, Equation 5.3). Accordingly, shear banding is expected at this shear rate.

The features in the stress response at the lowest shear rates ($\dot{\gamma} = 0.5, 1, 2.5 \text{ s}^{-1}$) are more closely examined in Figure 6.5. The stress responses at these shear rates exhibit different features as the shear rate is increased further into region II. In Figure 6.5a, the stress overshoot at $\dot{\gamma} = 0.5 \text{ s}^{-1}$ contains features that are not observed at any other shear rate within the shear banding regime. Immediately following the stress overshoot, the stress response exhibits a broad shoulder, which is followed by a sharp decrease in the stress that has a
Figure 6.4: Stress response as a function of time after shear startup for the 0.01% wt NaTos solution for shear rates near the onset of region II. A close-up of the responses in (a) is shown in (b), such that the nonlinear features of the response can be seen more easily. Error bars are the standard deviation of three measurements. Nonlinear features, including stress overshoots, shoulders, undershoots, and secondary overshoots are observed.

nearly discontinuous slope. A minor, second shoulder is then observed which leads into a stress undershoot and a secondary overshoot. After the secondary overshoot, the stress response slowly decreases until a steady state is reached after approximately $300\tau_R$ ($t \approx 1800$ s, data not shown). The long stress transient observed when $\dot{\gamma} = 0.5$ s$^{-1}$ is typical in shear banding solutions, especially near the onset of region II where the longest transience is expected [11, 12, 14]. When the shear rate is increased to $\dot{\gamma} = 1$ s$^{-1}$, the broad shoulder immediately following the stress overshoot has disappeared, and the stress undershoot is of a lower magnitude. While a secondary overshoot is never observed, as the stress is continuously increasing over the 1200 s experiment duration, indicating that the stress response has not achieved its steady state value and a secondary overshoot could be observed at long times. Finally, when $\dot{\gamma} = 2.5$ s$^{-1}$, a pronounced shoulder following the stress overshoot is observed, in line with the observations of Hu et al. [2] for shear banding solutions. The first stress undershoot is of a greater magnitude than in the previous two shear rates, and the stress response exhibits several secondary overshoots and undershoots which are reproducible between trials. These features are again in qualitative agreement with the findings of Hu et al. [2].
As the shear rate is nominally increased, certain features of the stress response become more pronounced, which can be seen in the enlarged view of the response in Figure 6.4b. As expected, the magnitude of the stress overshoot increases with increasing shear rate, indicating a larger degree of micellar breakage upon shear startup that may lead to shear banding [4]. The shape of the stress overshoot also becomes sharper with increasing shear rate, and the overshoot occurs at earlier times following startup, indicating that micellar breakage is primarily dependent on the magnitude of the acquired strain. In entangled polymer solutions with different architectures, Snijkers et al. [27] saw the same decrease in the location (in time) of the stress overshoot upon shear startup; however, the shape of the stress overshoot was similar between shear rates [27, 28]. This difference suggests that the change in shape of the WLM stress response with increasing shear rate is a result of the breakage, which is not present in entangled polymer solutions. The shoulder following the primary stress overshoot also becomes more pronounced with shear rate (Figure 6.4b). This shoulder feature turns into a minor stress overshoot and secondary overshoot above $\dot{\gamma} = 4.2$ s$^{-1}$, which is immediately followed by a significant stress undershoot. Finally, the oscillations in the stress response following the stress undershoot become very pronounced when
\( \dot{\gamma} \geq 4.2 \text{ s}^{-1} \). Such oscillating rheological responses and fluctuations are common signatures of shear banding in WLM solutions [12,29–31]. These oscillations are highly reproducible, and can be seen based on individual trials for these shear rates in Figure 6.8a.

The startup rheological results for the three shear rates used in the primary 1-2 plane flow SANS experiments can be seen in Figure 6.6, where \( \dot{\gamma} = 15, 26.4, \text{ and } 45 \text{ s}^{-1} \). The magnitude of the stress overshoot continues to increase with shear rate, and the stress overshoot again becomes sharper and narrower with shear rate. At each shear rate, stress overshoot, shoulders, stress undershoots, and following secondary overshoots are consistent with the features discussed by Hu et al. [2] for shear banding WLMs. As was the case in Figure 6.4, significant oscillations are observed in the steady state stress response, consistent with other shear banding WLMs. Once again, these oscillating responses are reproducible in both magnitude and the period of oscillation (Figure 6.8). The features of the stress response are the most unique at the highest shear rate, where \( \dot{\gamma} = 45 \text{ s}^{-1} \). The shape of the stress response is at this shear rate is the sharpest and narrowest in width, and is distinct from the general shape observed at the lower rates. After the stress overshoot, multiple shoulder-like features are observed. Finally, the amplitude of the steady state oscillations appears to increase at this shear rate, which can be seen in the inset of Figure 6.3 and is further explored in Figure 6.8b. The change in the features of the startup stress response at \( \dot{\gamma} = 45 \text{ s}^{-1} \) suggests that this shear rate is at the onset of a different flow regime, where either shear banding behavior becomes more dominated by elastic instabilities, or is eliminated and region III is entered.

Finally, we examine shear rates greater than \( \dot{\gamma} = 45 \text{ s}^{-1} \). At these shear rates near the onset of region III, the features of the stress response are markedly different from those presented in Figure 6.6. The startup stress response for three shear rates when \( \dot{\gamma} \geq 60 \text{ s}^{-1} \) can be seen in Figure 6.7, which appear to be on the border of regions II and III. As seen in Figure 6.7a, the shape of the stress overshoot becomes sharper and narrower at these high rates when compared to the stress overshoots seen at the lower rates in Figure 6.6, and is similar to the shape observed at \( \dot{\gamma} = 45 \text{ s}^{-1} \). The magnitude of the stress overshoot continues to increase with increasing shear rate. At all three shear rates shown in Figure 6.7, the stress response contains the same shoulder-like features observed at the lower shear rates, which were also
Figure 6.6: Startup stress response at shear rates within the shear banding regime corresponding to the 1-2 plane flow-SANS measurements. Error bars represent the standard deviation of three startup measurements. A close-up of the responses in (a) is shown in (b), such that the nonlinear features of the response can be seen more easily. The shape of the stress response at $\dot{\gamma} = 45 \text{ s}^{-1}$ is distinct from the response at all lower shear rates.

observed by Hu et al. [2] for shear banding solutions. Interestingly, this shoulder region appears to collapse onto the same curve for the three shear rates, which can be seen more clearly in Figure 6.7b. However, two major differences in the stress response features are observed at these high shear rates. First, the steady state stress response becomes increasingly chaotic with increasing shear rate. The three individual startup trials shown in Figure 6.8c demonstrate this behavior clearly. While the stress response between multiple trials always reaches the same steady state value, these chaotic fluctuations in the response are expected at high Weissenberg numbers from elastic turbulence that can occur in conjunction with shear banding [9, 29, 32–34]. Second, the presence of a stress undershoot and secondary overshoot disappears at the highest shear rate when $\dot{\gamma} \geq 90 \text{ s}^{-1}$. As seen in Figure 6.7, when $\dot{\gamma} \geq 60 \text{ s}^{-1}$, a clear undershoot follows the stress overshoot, followed by a secondary overshoot. The behavior at $\dot{\gamma} \geq 60 \text{ s}^{-1}$ is similar to when $\dot{\gamma} \geq 45 \text{ s}^{-1}$ (Figure 6.6); however, the secondary overshoot is less pronounced (see Figure 6.8). When the shear rate is further increased to $\dot{\gamma} \geq 75 \text{ s}^{-1}$, only a small undershoot and secondary overshoot are observed. The disappearance of these features may indicate that the onset of region III has been surpassed. As the
stress is still nearly constant in this region, shear banding may still occur. Therefore, another possible explanation is that the solution elasticity and elastic instabilities may play a larger role on the shear banding behavior in this region. Interestingly, in all startup trials for this solution, the location of the stress overshoot in time is greater than the calculated breakage time ($\tau_{\text{break}} \approx 0.13$ s, Table 4.1).

![Figure 6.7](image)

Figure 6.7: Startup stress response at shear rates near the onset of region III. A close-up of the responses in (a) is shown in (b), such that the chaotic responses can be seen more easily. Error bars represent the standard deviation of three startup measurements.

The individual startup trials for the shear rates shown in Figures 6.4, 6.6 and 6.7 above are shown in Figure 6.8a, b, and c below, respectively. In Figure 6.8a and b, highly reproducible stress responses are observed between each of the three trials, where $\dot{\gamma} \leq 45$ s$^{-1}$. In all cases, the amplitude and period of the fluctuations in the stress response is essentially constant between repeated trials. As mentioned previously, the amplitude of the oscillations appears to increase when $\dot{\gamma} = 45$ s$^{-1}$ (Figure 6.8b). However, the largest fluctuations observed when $\dot{\gamma} = 45$ s$^{-1}$ are less than 6.5% of the average value. These fluctuations are not significantly larger than in the lower shear rates on a relative basis, where the fluctuations are roughly 5%; the absolute magnitude is only larger based on the higher stress at $\dot{\gamma} = 45$ s$^{-1}$.

In similar WLM solutions, Fardin et al. [32] observed stable stress fluctuations on the order of 3% of the average stress in the region exiting the stress plateau, which corresponded to a laminar flow regime. These fluctuations are similar in magnitude to the stress
fluctuations observed in this system for the shear rates shown in Figure 6.8a and b. However, in Figure 6.8c, the observed stress fluctuations are larger than at the lower shear rates. Further, significant deviations from azimuthal flow and elastic turbulence are expected due to the large Taylor number \( Ta > 100 \) at each of these shear rates [35]. When \( \dot{\gamma} = 60 \text{ s}^{-1} \), the stress response fluctuations are still reproducible between trials, but the amplitude of the fluctuations is larger (maximum \( \approx 8\% \) of average) and varies more in time. At \( \dot{\gamma} = 75 \text{ s}^{-1} \), the stress response fluctuations are similar in magnitude and amplitude between trials, but do not always share the same phase. The amplitude of the fluctuations is similar to when \( \dot{\gamma} = 60 \text{ s}^{-1} \). Finally, when \( \dot{\gamma} = 90 \text{ s}^{-1} \), the fluctuations in the stress response are completely chaotic and are not reproducible between trials; only the average stress at steady state is reproducible between trials at this shear rate. While the amplitude of the majority of the oscillations is below 15\%, the fluctuations are as large as 25\% to 30\% during each trial, indicating significant elastic turbulence. The work of Fardin et al. [32] again provides a useful comparison, as in the ‘transition’ region into region III, the stress fluctuations were as high as 30\% and were unstable in amplitude, reflective of significant elastic turbulence. Past the transition region, the fluctuations settled and became stable in amplitude, but were larger than before the transition, on the order of 15\%. Based on the work of Fardin et al. [32] and the observed stress responses in Figure 6.8c, it appears as though \( \dot{\gamma} = 90 \text{ s}^{-1} \) is within the transition region to region III. Based on the shape of the stress response and the fluctuations when \( \dot{\gamma} = 60 \text{ and} \)
75 s⁻¹, these shear rates are likely close to, but not within, the transition region.

6.5.2 Startup 1-3 plane SANS

To complement the startup rheological measurements, startup 1-3 plane SANS measurements were performed. The 1-3 plane measurements are analogous to the startup rheology in the sense that both measurements provide results indicative of the bulk rheological or structural properties. Accordingly, the presence of nonlinear features such as overshoots, undershoots, and oscillating responses can be examined in the 1-3 plane $A_f$. As rheo-SANS measurements provide increased flux versus the 1-2 plane measurements, the experiments can be performed more quickly, and a variety of shear rates can be examined. The gap-to-radius ratio, $\varepsilon$, for these experiments is $\varepsilon = 0.071$ versus $\varepsilon = 0.084$ for the startup rheology measurements. In these experiments, the structure at each shear rate was measured upon shear startup for twenty minutes. Three repeated trials were performed and added together to give the structural response reported in this section. Each bin for these measurements corresponding to a calculated alignment factor is 24 seconds long, with 150 bins calculated over the 1200 second experiment duration. Additional bins of 10 second intervals are shown for the first 50 seconds of the experiment. The behavior presented in this section is reproducible over sample preparations, rheometer configurations, and SANS instruments. Results for additional shear rates and individual trials can be seen in Appendix M, as well as results from additional experiments. The impact of the Couette geometry and gap-to-radius ratio on the shear banding startup response is also explored in Appendix M.

The 1-3 plane alignment factor for these startup trials can be seen in Figure 6.9 for the shear rates corresponding to the stress responses shown in Figure 6.4. These shear rates are near the onset of shear banding in the low branching solution. Accordingly, a long transient in the structural response, which is similar to the long stress transient, is observed at all shear rates and is indicative of shear banding. Results are shown on a log-log and log-linear scale for clarity, as changes in $A_f$ in time may be easier to see on different scales. As seen in Figure 6.9, while the steady state alignment is low, a significant startup alignment and transient is observed at shear rates as low as $\dot{\gamma} = 2.5$ s⁻¹. The maximum alignment upon shear startup
at this shear rate is seven-fold higher than the steady state alignment. At each shear rate, oscillations in the $A_f$ response are observed that mirror the oscillations in the transient stress response. The similarity in the responses indicates that the degree of orientation fluctuates in time in the shear banded state. The largest decrease in the degree of orientation is observed when $t < 200$ seconds after shear startup. This decrease in orientation corresponds to the stress overshoot and subsequent stress undershoot in the stress response, so $A_f$ is expected to show significant decreases here by the stress-SANS rule (Equation 2.37). The $A_f$ response also shows a local minimum in the region of the stress undershoot, again indicating that the structural response reflects many of the features of the stress response.

![Figure 6.9: 1-3 plane $A_f$ as a function of time after shear startup at shear rates near the onset of region II, on a log-log (a) and log-linear (b) scale. A long transient in $A_f$ is observed at all rates, and is consistent with the long transient in the stress response that indicates shear banding. The maximum startup $A_f$ is several-fold larger than the steady state values.](image)

The 1-3 plane alignment factor as a function of time after shear startup can be seen in Figure 6.10 for the same shear rates used in the 1-2 plane experiments; the results are shown on a log-log (a) and log-linear scale (b) for clarity. In the 1-2 plane experiments, only the steady shear structure is measured for $\dot{\gamma} = 90$ and $150$ s$^{-1}$, whereas the startup structure is measured for $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$. As seen in Figure 6.10, a long transient is observed in the structural responses at $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$. Despite that long transients are expected closer to the onset of region II, the $A_f$ response at $\dot{\gamma} = 15$ s$^{-1}$ appears to exhibit a faster
transient than at \( \dot{\gamma} = 45 \text{ s}^{-1} \), as the \( A_f \) at \( \dot{\gamma} = 45 \text{ s}^{-1} \) does not appear to exhibit its steady state until \( t > 900 \text{ s} \), where repeatable oscillations are observed. However, as \( A_f \) is much lower at \( \dot{\gamma} = 15 \text{ s}^{-1} \), it is possible that the structure at this shear rate also takes this long to reach steady state, and the fluctuations are harder to resolve based on the difficulty in calculating \( A_f \) accurately when \( A_f \) is low. Accordingly, the transient corresponding to the large initial decrease in \( A_f \) upon shear startup when \( t \leq 300 \text{ seconds} \) is roughly the same between shear rates. This transient is on the same time scale as the stress takes to reach steady state in the rheological measurements shown in Figure 6.6. Immediately following this region, \( A_f \) at \( \dot{\gamma} = 45 \text{ s}^{-1} \) exhibits a significant undershoot, reflecting the stress response (Figure 6.6).

Figure 6.10: 1-3 plane \( A_f \) as a function of time after shear startup, on a log-log (a) and log-linear (b) scale. A long transient in the \( A_f \) response is consistent with shear banding when \( \dot{\gamma} \leq 90 \text{ s}^{-1} \). At \( \dot{\gamma} = 150 \text{ s}^{-1} \), the fast structural transient indicates little to no shear banding.

A faster transient in the alignment factor response is observed when \( \dot{\gamma} = 90 \) and 150 s\(^{-1} \), which is expected based on the stress responses shown in Figure 6.7. However, the features of the structural response and the transient when \( \dot{\gamma} = 90 \text{ s}^{-1} \) are similar to those shown at lower shear rates, suggesting that shear banding may still occur at this shear. When \( \dot{\gamma} = 150 \text{ s}^{-1} \), however, the transient in the \( A_f \) response has nearly disappeared. This result is consistent with the steady shear results, which showed that \( A_f \) has reached its maximum value at this shear rate. As a highly aligned structure is expected to fill the gap when \( \dot{\gamma} = 150 \text{ s}^{-1} \), little to no transience is expected. The long transient in the \( A_f \) response upon shear
startup, similar to the long stress transient, appears to be a signature of shear banding that can be used to identify when shear banding is present in a particular system.

6.5.3 Startup 1-2 plane SANS

The 1-2 plane startup SANS measurements were only performed on the select shear rates shown in Figure 6.6 based on time limitations: $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$. These shear rates correspond to the three shear rates examined under steady shear presented in Chapter 5, Section 5.5.1. However, interesting startup rheological behavior was observed at higher shear rates (Figure 6.7), which suggests that the shear banding behavior may be eliminated, or that it is strongly influenced by significant fluctuations and elastic instabilities. As such, 1-2 plane steady shear measurements were also performed at $\dot{\gamma} = 90$ and $150$ s$^{-1}$, to determine if the shear banding behavior disappeared at high rates. The steady state 1-2 plane alignment factor as a function of gap position for these five shear rates can be seen in Figure 6.11a.

![Figure 6.11](image)

Figure 6.11: Steady state 1-2 plane alignment factor for the 0.01% wt NaTos solution as a function of gap position, $r/H$. (a) Measurements taken at the end of shear startup. An upturn in alignment at the outer wall is most apparent at $\dot{\gamma} = 90$ and $150$ s$^{-1}$, suggesting the presence of a third shear band. (b) The presence of a third band is further suggested by separate measurements at $\dot{\gamma} = 45$ s$^{-1}$, where the upturn is also observed.

As seen in Figure 6.11a, the results for $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$ are nearly identical in both magnitude and shape to the results shown in Figure 5.7 in Chapter 5. As additional gap
positions are used in the measurements shown in Figure 6.11a, the alignment band at these three shear rates, which indicates shear banding, is even more pronounced. As was the case in the previous results, the width of the high shear rate band does not appear to increase significantly with increasing shear rate, in contrast to the lever rule predictions (Equation 5.4). During a separate experiment, the 1-2 plane $A_f$ was measured continuously across the gap at $\dot{\gamma} = 45 \text{ s}^{-1}$, in order to determine the features of the response with better spatial resolution; this measurement is shown in Figure 6.11b. Interestingly, a new feature is observed when the $A_f$ response is examined in Figure 6.11b. The alignment band is still present across the gap; however, near the outer wall, an increase in alignment is observed. This increase in alignment when $r/H > 0.8$ is larger than the calculation uncertainty, suggesting that the material at the outer wall is experiencing a higher shear rate than in the middle of the gap. When the 1-2 plane results at high shear rates are examined in Figure 6.11a, a similar feature in the $A_f$ response across the gap is observed. At both $\dot{\gamma} = 90$ and $150 \text{ s}^{-1}$, the alignment factor at the gap position closest to the outer wall is significantly higher than $A_f$ in the middle of the gap. While anomalous, this phenomenon again suggests that the material at the outer wall is experiencing a higher shear rate than in the middle of the gap. Interestingly, the alignment band structure observed when $\dot{\gamma} \leq 45 \text{ s}^{-1}$ is still observed at these higher two shear rates. The alignment band is much smaller and less pronounced when $\dot{\gamma} = 150 \text{ s}^{-1}$, suggesting that minimal if any shear banding is occurring at this shear rate, which is consistent with the 1-3 plane results. However, the pronounced alignment band when $\dot{\gamma} = 90 \text{ s}^{-1}$ suggests that the rheological results shown in Figure 6.7 do not indicate the end of the shear banding regime, but rather a new regime of shear banding that is influenced strongly by elastic instabilities and turbulence. The presence of shear banding when $\dot{\gamma} = 90 \text{ s}^{-1}$ is also consistent with the 1-3 plane results, which showed a long transient in the structural response for this shear rate.

The 1-2 plane alignment factor was then examined as a function of time after shear startup at several gap positions at $\dot{\gamma} = 15 \text{ s}^{-1}$. In order to sufficient neutron counts to calculate the structure and alignment factor, multiple trials were performed for each shear rate, which are then added together to determine the time-dependent material response. As the rheology measurements shown in Figure 6.8b were reproducible in terms of the observed stress.
response and oscillations in the response for the three shear rates measured with 1-2 plane SANS, the startup trials are also expected to be reproducible. The 1-2 plane alignment factor at the seven gap positions measured at $\dot{\gamma} = 15 \text{s}^{-1}$ can be seen in Figure 6.12a. A schematic indicating the location of each position within the gap, the steady state $A_f$ value, and the approximate location of the shear band interface can be seen in Figure 6.12b. The steady state value shown in Figure 6.12b is determined at the end of the 900 second experiment.

Figure 6.12: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 15 \text{s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.

At all gap positions shown in Figure 6.12a, an extremely long transient in the alignment factor response is observed. At the position closest to the inner wall ($r/H = 0.1$), $A_f$ does not reach its steady state value until 200 to 300 seconds after shear startup. This transient in the alignment factor response is in good agreement with the startup measurements shown in Figure 6.6, where the stress response takes approximately 300 seconds to reach the steady state. The alignment factor at $r/H = 0.1$ reaches a maximum value of $A_{f,\text{max}} = 0.47$ at the start of the experiment, which reduces to $A_{f,\text{steady}} = 0.20$ at steady state. Interestingly, at the following gap position ($r/H = 0.2$), the $A_f$ response takes around 350 seconds to reach steady state. An even larger change in the alignment factor is observed, where $A_{f,\text{max}} = 0.42$ and is three times larger than the steady state value, $A_{f,\text{steady}} = 0.14$. The
transient in the alignment factor response appears to increase with increasing gap position. For \( r/H = 0.3, 0.45 \) and 0.6, \( A_f \) does not reach its steady state value for over 500 seconds. Finally, at the outer two gap positions (\( r/H = 0.8, 0.9 \), the steady state \( A_f \) is not achieved until the end of the experiment, where \( t = 900 \) s. The largest difference in the maximum \( A_f \) and steady state \( A_f \) appears to occur at the positions closest to the shear band interface, where \( r/H = 0.3 \) and \( r/H = 0.45 \). The alignment band seen in Figure 6.12b consists of the four outer gap positions, where \( r/H \geq 0.45 \), at which the longest \( A_f \) transience are seen. In Figure 6.12a, the alignment at these four positions clearly meets at the same value at \( t = 900 \) s. Once the steady state is reached, oscillations in \( A_f \) are observed that are reminiscent of the oscillations in the stress response observed in Figures 6.6 and 6.8.

While the transient observed at the inner wall is in agreement with the startup stress response, the outer wall transient is about three-fold longer than the inner wall transient. This discrepancy between the transient at the inner and outer walls is not unexpected, as the ‘disentangle, re-entangle’ mechanism suggests that the material at the outer wall must slowly re-arrange and re-entangle in time, unlike the material at the inner wall which remains highly aligned [2, 3, 14]. However, an interesting trend is observed when the outer wall alignment is examined as a function of time after shear startup. At \( r/H = 0.8 \) and \( r/H = 0.9 \), the alignment factor is significantly lower than in the other two positions composing the alignment band when \( t \leq 500 \) s. At times greater than 500 seconds, the alignment at the outer wall increases in time, and eventually reaches the same magnitude observed at \( r/H = 0.45 \) and \( r/H = 0.6 \), forming the alignment band. This result appears to contradict the ‘disentangle, re-entangle’ mechanism, as the alignment at the outer wall is expected to decrease in time, not increase [14]. This interesting and anomalous behavior at the outer wall may explain differences in the mechanism of shear banding that are expected between this solution and the solution with mild branching.

Similar trends in the 1-2 plane alignment factor response are observed when the shear rate is increased to \( \dot{\gamma} = 26.4 \text{ s}^{-1} \), which can be seen in Figure 6.13a. As seen in Figure 6.13a, a clear alignment band is observed at the end of the experiment (\( t = 1200 \) s), where the alignment at the four outer gap positions is nearly identical; the steady state values can be
seen in Figure 6.13b. While close in magnitude, the alignment at \( r/H = 0.3 \) is distinctly higher than in the alignment band. Steady state oscillations in \( A_f \) are observed at all gap positions. As expected, raising the shear rate increases the maximum alignment upon shear startup and at steady state for this solution. At this shear rate, the alignment at the inner wall \((r/H = 0.1, 0.2)\) reaches steady state after approximately 400 seconds, which is longer than the stress transient \((t \approx 300 \text{ s})\). The transient continues to increase in time with increasing gap position, consistent with the results at \( \dot{\gamma} = 15 \text{ s}^{-1} \). At the outer wall, the steady state alignment values are not achieved until approximately 1100 seconds, suggesting that the 900 second experiment time at \( \dot{\gamma} = 15 \text{ s}^{-1} \) may not be sufficient to capture the true steady state response. The transient at each of the gap positions seems to be similar between the two shear rates. At \( r/H = 0.9 \), \( A_f \) again appears to increase at long times, as opposed to the decrease that is expected from the typical ‘disentangle, re-entangle’ mechanism. This growth of \( A_f \) in time will be explored further in the discussion (Section 6.6).

As was also observed at the lower shear rate, \( A_f \) seems to decrease in magnitude most significantly from startup to steady state at positions near the shear band interface (Figure 6.13). The maximum alignment factor at \( r/H = 0.45 \) is \( A_{f,\text{max}} = 0.48 \), which is over five-fold larger than the steady state value, \( A_{f,\text{steady}} = 0.09 \). While the five-fold decrease in the alignment factor is quite significant, the magnitude of the stress overshoot to the steady state stress is even more significant at 15-fold larger (\( \sigma_{\text{startup}} = 70.4 \text{ Pa} \) vs. \( \sigma_{\text{steady}} = 4.5 \text{ Pa} \)). While the structure and polymeric stress response are linked through the stress-SANS rule (Chapter 2, Equation 2.37), the difference in the magnitude of the startup stress versus the startup \( A_f \) suggests that the alignment factor cannot fully account for the measured startup stresses. The stress overshoot is associated with elastic stresses and yielding phenomena [4, 5, 36], which helps to explain this discrepancy. The stress-SANS rule accounts only for the polymeric stress, and breaks down in the limit of highly nonlinear behavior [23], which has been observed in other shear banding WLM solutions [14, 18].

The 1-2 plane alignment for the final shear rate, \( \dot{\gamma} = 45 \text{ s}^{-1} \), can be seen in Figure 6.14a. In Figure 6.14a, the steady state \( A_f \) oscillations are more pronounced than in the previous two shear rates. This behavior is in good agreement with the startup rheology
Figure 6.13: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.

results, which showed more pronounced fluctuations at this shear rate (see Figures 6.6, 6.8). For all gap positions, the $A_f$ transient is at least 400 seconds, and appears to increase with increasing gap position. For the three measured shear rates, the length of the $A_f$ transient does not appear to significantly differ, which is also consistent with the startup rheology measurements. As expected, a clear alignment band is again observed when $r/H \geq 0.45$.

The largest decrease in the measured $A_f$ occurs near the shear band interface identified in Figure 6.14b. The maximum $A_f$ at $r/H = 0.45$ of $A_{f,max} = 0.52$ is three times larger than the steady state value, $A_{f, steady} = 0.17$. This three-fold decrease in the alignment factor corresponds to a 27-fold decrease in the startup to steady state stress ($\sigma_{\text{start}} = 134.7 \text{ Pa}$ vs. $\sigma_{\text{steady}} = 4.9 \text{ Pa}$). As the maximum attainable value of $A_f$ is $A_f = 1$, a 27-fold change in the steady state $A_f$ could never be observed upon startup. However, it should be noted that the minimum time resolution for the SANS measurements is ten seconds. If the same time is used for the stress comparison, only a 1.7-fold higher stress value is seen from the steady state value at $t = 10 \text{ s}$. This comparison suggests that the alignment factor may be more sensitive to changes in the structure than the bulk measured stress. When the other shear rates are examined at $r/H = 0.45$, the stress is only 1.5 times higher at $t = 10 \text{ s}$ versus the
five-fold change in $A_f$ when $\dot{\gamma} = 26.4 \, s^{-1}$. While at $\dot{\gamma} = 15 \, s^{-1}$, the stress is 2.6 times higher than the steady state when $t = 10 \, s$, $A_f$ is five times its steady state value, again suggesting that $A_f$ is more sensitive to changes in the material properties than the bulk rheology.

![Figure 6.14: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 45 \, s^{-1}$ and (a) as a function of time after shear startup (b) at steady state, where the approximate location of the shear band interface is depicted.](image)

An interesting phenomenon is observed when $A_f$ in the alignment band is more closely examined (Figure 6.14). Once again, the alignment at the outer wall, especially when $r/H = 0.9$, increases after long times. Surprisingly, when $t \geq 300$ seconds, the alignment at $r/H = 0.9$ is significantly larger than at the preceding gap positions, $r/H = 0.6$ and $r/H = 0.8$. After about 500 seconds, the alignment slowly starts to decrease again, and reaches its steady state value around 900 seconds. The larger degree of alignment observed at $r/H = 0.9$ during these times in the experiment is consistent with the anomalous upturn in $A_f$ at the outer wall seen in Figure 6.11b at $\dot{\gamma} = 45 \, s^{-1}$, and in Figure 6.11a for $\dot{\gamma} = 90$ and 150 $s^{-1}$. These results again suggest that the material near the outer wall is somehow experiencing a higher shear rate than the material closer to the middle of the gap, causing a higher degree of orientation. This anomalous behavior will be explored further in the discussion (Section 6.6).
The alignment factor response does not appear to change significantly between shear rates. While the alignment increases with increasing shear rate, the same qualitative banded structure is observed at all rates. In all cases, the 1-2 plane alignment exhibits a longer transient at the outer wall versus the inner wall. This $A_f$ transient is near the order of the stress transient at the inner wall, but is significantly longer at the outer wall. Further, when the alignment factor at $t = 10$ seconds is compared to the steady state $A_f$, a larger difference is seen than when the stress at $t = 10$ seconds is compared to the steady state stress. These two observations suggest that the alignment factor may be a more sensitive measure of when the material response reaches steady state than the measured stress response. Finally, steady state oscillations in $A_f$ are observed at all rates and are consistent with the rheological measurements. These oscillating responses are reproducible between multiple trials, and suggest that the features of the startup rheological behavior can be linked to observed structural changes.

6.6 Discussion: low branching solution

6.6.1 Structural mechanism of shear banding

The goal of the startup 1-2 plane measurements was to determine the mechanism of shear banding for the low branching solution, and to compare this mechanism to the mechanism of shear banding for the mildly branched solution. While the 1-2 plane alignment factor shown in Figures 6.12, 6.13, and 6.14 showed interesting trends in time after startup and demonstrated anomalous behavior at the outer wall, it is difficult to determine a mechanism of shear banding from that analysis alone. To determine how the shear bands form during shear startup, the 1-2 plane alignment factor can be examined in a different manner, instead as a function of gap position at multiple times following the start of shear. Analyzing the alignment factor in this manner is similar to analyzing the time-dependent velocity profile during shear startup. An example this analysis can be seen in Figure 6.15 for $\dot{\gamma} = 26.4$ s$^{-1}$. By analyzing the alignment factor profile at different time points after shear startup as a proxy for the time-dependent velocity profile, the formation of and changes to the shear banded structure can be determined. Particle tracking velocimetry measurements are shown
below in Section 6.6.2, verifying that the time-dependent 1-2 plane alignment factor is a good substitute for the velocity profile when the velocity profile is not available.

Figure 6.15: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ and time after shear startup. (a) Highly shear thinning behavior is observed at early times. (b) The shear bands begin to form. (c) The material at the outer wall re-entangles and settles; the shear band interface is pronounced. An alignment band is formed at the outer wall. $A_f$ at $r/H = 0.9$ is lower than at the other positions. (d) $A_f$ in the alignment band increases in magnitude. (e) $A_f$ in the alignment band begins to settle. (f) An approximate steady state is reached.

Examining the time-dependent alignment factor profiles in Figure 6.15 helps to elucidate the mechanism of shear banding. In Figure 6.15a, an alignment factor profile suggestive of highly shear thinning wormlike micelles is observed. This profile is measured at $t = 25$ seconds after shear startup, and is in agreement with the early stages of the disentangle, re-entangle mechanism, where homogeneous alignment is expected (see Figure 6.2b). In Figure 6.15b, a highly shear thinning state is still present after 50 seconds. A small kink in the $A_f$ response is observed between $r/H = 0.3$ and $r/H = 0.45$, indicating the formation of the shear band interface, which is illustrated in Figure 6.2c. After 100 seconds, the shear band interface is highly pronounced (Figure 6.15c). The material at the outer wall has re-entangled and settled in accordance with the shear banded state described in Figure 6.2d for
the disentangle, re-entangle mechanism. A clear alignment band is formed near the outer wall; however, $A_f$ at $r/H = 0.9$ is significantly lower than at the other positions that compose the steady state alignment band. In Figure 6.15c, it appears as though the alignment at $r/H = 0.9$ acts independently of the alignment between $r/H = 0.45$ and $r/H = 0.8$, suggesting the possible presence of a third shear band. At 250 seconds following shear startup (Figure 6.15d), the alignment at the inner wall ($r/H = 0.1, 0.2,$ and 0.3) has not significantly changed from when $t = 100$ s, indicating that an approximate steady state has been reached at the inner wall. However, $A_f$ in the alignment band increases in magnitude at all positions, but most significantly when $r/H = 0.9$. This increase in alignment signifies that the material is becoming more oriented, contrasting the disentangle, re-entangle mechanism where $A_f$ in the low shear rate band should continuously decrease after the shear bands have formed. In Figure 6.15e, $A_f$ in the alignment band begins to settle in time after 500 seconds, slowly decreasing in magnitude. Finally, after 850 seconds, an approximate steady state is reached (Figure 6.15f). While only shown for one shear rate in Figure 6.15, this new ‘disentangle, re-entangle, re-align’ mechanism is observed for all three shear rates examined with 1-2 plane SANS. These results can be seen for $\dot{\gamma} = 15$ s$^{-1}$ and $\dot{\gamma} = 45$ s$^{-1}$ in Figure 6.16.

Figure 6.16: Gap-dependent 1-2 plane $A_f$ at different time points (in seconds) after shear startup at (a) $\dot{\gamma} = 15$ s$^{-1}$, and (b) $\dot{\gamma} = 45$ s$^{-1}$. ‘Re-alignment’ is observed at both rates.

At all shear rates, the ‘re-alignment’ of the material in the outer half of the gap is the most pronounced when closest to the outer wall, as seen in Figures 6.15 and 6.16. In each
case, the homogeneous shear thinning state is observed at early times, which slowly evolves to a shear banded structure. Interestingly, the alignment at the inner wall appears to reach its steady state more quickly at $\dot{\gamma} = 45$ s$^{-1}$ versus $\dot{\gamma} = 15$ s$^{-1}$, which can be seen when $A_f$ at $t = 50$ seconds in Figure 6.16 is compared. Despite this faster transience at the inner wall when $\dot{\gamma} = 45$ s$^{-1}$, the outer wall transience occurs on roughly the same time scale for both shear rates. When $\dot{\gamma} = 45$ s$^{-1}$, an upturn in alignment near the outer wall is observed for several time points, which is similar to the upturn seen in the steady shear results in Figure 6.11. This upturn suggests that the material at the outer wall may be responding differently than the material between $r/H = 0.45$ and $r/H = 0.8$, possibly forming a third shear band.

As seen in Figure 6.16, the final steady state for both shear rates has an alignment that is clearly larger than the minimum value, which occurs at earlier time points. The minimum $A_f$ at these earlier times appears to coincide with the stress undershoot observed in the startup rheology (Figure 6.6). The increase in alignment in time at the outer wall can be seen for each shear rate below in Figure 6.17. As $A_f$ at $r/H = 0.9$ is initially lower than $A_f$ in the center of the gap, the re-aligning of the micelles in time leads to the increased alignment at $r/H = 0.9$, and the steady state alignment band near the outer wall of the Couette. If a third shear band is present, as is suggested by the upturn in the alignment factor near the outer wall, the band either disappears when the flat alignment band is formed at long times, or it shifts to larger $r/H$ out of the detection range, and exists closer to the outer wall.

![Figure 6.17](image)

Figure 6.17: 1-2 plane $A_f$ at the outer wall as a function of time after shear startup at (a) $\dot{\gamma} = 15$ s$^{-1}$, (b) $\dot{\gamma} = 26.4$ s$^{-1}$, and (c) $\dot{\gamma} = 45$ s$^{-1}$. At all shear rates, $A_f$ ‘re-aligns’ and increases in time after reaching its minimum value.
6.6.2 Particle tracking velocimetry (PTV) measurements

The steady shear alignment factor results shown in Figure 6.11 paired with the time-
dependent behavior of the material at the outer wall suggests that a three band structure may possibly be formed in this solution. The presence of three bands has been seen before under steady shear for highly elastic WLMs at high Weissenberg numbers in concentric cylinder Couette flow [6–9], and is also predicted by constitutive models for certain boundary conditions [37]. Note that shear banding in a cone-and-plate geometry is expected to form three bands [38]. The three banded state observed by Manneville [9] occurred at fairly long times after shear startup, and corresponded to the presence of significant fluctuations, driven by elastic instabilities and wall slip. As shown by Equation 5.10 in Chapter 5, the elasticity number for the low branching WLMs is significantly higher than in the mildly branched solution, where $E_l_{\text{low}} \approx 1.7 \cdot 10^5$ and $E_l_{\text{mild}} = 1.2 \cdot 10^4$ in the ARES G2 rheometer. The presence of a three banded structure would explain the observed differences in flow alignment between the low branched solution, and the mildly branched solution which exhibits more traditional shear banding behavior [14,17–19,23,39].

In order to verify the hypothesis about a potential three banded structure and/or wall slip in the low branching solution, particle tracking velocimetry (PTV) measurements were performed. All PTV measurements were performed by Peng Cheng at the University of California, Santa Barbara. The gap-to-radius ratio of the PTV measurements is slightly smaller than in the 1-2 shear cell ($\varepsilon = 0.029$ vs. $\varepsilon = 0.039$), which must be taken into account when interpreting the results. The velocity profile for the 0.01% wt NaTos solution at $\dot{\gamma} = 45$ s$^{-1}$ can be seen in Figure 6.18, where the profile was measured twenty minutes after shear startup to allow the sample to reach its equilibrium state. The velocity at each position is normalized by the velocity applied at the inner wall, $v_0$. As hypothesized based on the 1-2 plane SANS results, the presence of a three band structure is observed in Figure 6.18. The location of the interface of the third band appears to occur around $r/H \approx 0.9$, which is approximated by the dotted vertical line. As the third band is extremely close to the outer wall, it is not surprising that the SANS results detected only small changes in alignment at $r/H = 0.9$. Using the 1-2 plane alignment factor results to identify the location of the band
interface compares favorably with the interface location identified with PTV.

Figure 6.18: Velocity profile for the 0.01% wt NaTos solution at $\dot{\gamma} = 45 \text{ s}^{-1}$. Three distinct shear bands can be identified, where the lowest shear rate is in the second band. Profile measurements were taken twenty minutes after shear startup. Dotted lines are approximate and for visual aid only.

When the shear rate in each band is examined in Figure 6.18, the shear rate is the greatest at the inner wall, as determined by the slope of the velocity profile. The shear rate in the second, middle band is actually lower than the shear rate observed in the third band, near the outer wall. These results are consistent with the results of Manneville [9], who also saw the lowest shear rate in the middle band. When the velocity profile is examined at the inner wall, the measured velocity is lower than the applied velocity ($v_y/v_0 < 1$), indicating the presence of wall slip. Although the wall slip is fairly small, the presence of wall slip leading to a three banded state is also consistent with the findings of Manneville [9]. While velocity profiling was not performed at $\dot{\gamma} = 90$ and $150 \text{ s}^{-1}$, the behavior at these shear rates is likely similar to the behavior at $\dot{\gamma} = 45 \text{ s}^{-1}$ based on the similarities in the startup rheology. With increasing shear rate, the prominence of wall slip and elastic instabilities is expected to increase, which explains the more chaotic behavior observed in the rheology at higher shear rates. More significant wall slip and instabilities could lead to a larger, more pronounced third band at the outer wall. As the third band has a larger shear rate than the middle band,
the upturn in \( A_f \) observed at these higher rates can be explained by the presence of this third band. Velocity profiles for two additional shear rates, \( \dot{\gamma} = 8.5 \) and \( 26.4 \text{ s}^{-1} \), can be seen in Figure 6.19. These profiles were also measured twenty minutes after startup, which may not be sufficient to reach steady state at the lower shear rates. Regardless, the velocity profiles show the presence of three bands in all cases. The shear band interfaces are in fairly close proximity regardless of shear rate, in good agreement with the 1-2 plane \( A_f \) results. The degree of wall slip appears to be the same between the three conditions, which is consistent with the similarities in the startup rheology measured for these rates. As the startup stress responses were significantly more chaotic when \( \dot{\gamma} = 90 \text{ s}^{-1} \), it is reasonable to assume that a larger degree of slip would be observed at these high rates, despite the similar degree of slip observed at the rates shown in Figure 6.19.

![Figure 6.19: Velocity profile for the 0.01% wt NaTos solution at \( \dot{\gamma} = 8.5, 26.4, \) and \( 45 \text{ s}^{-1} \). Three distinct shear bands can be identified in all three cases, and the same degree of wall slip is observed for each shear rate. Profile measurements were taken twenty minutes after shear startup, which may not be sufficient for the profile to reach steady state.](image)

The work of Manneville [9] also helps to explain the ‘re-alignment’ stage of the shear banding mechanism observed in this solution. In their work, Manneville [9] saw a near-zero velocities in the low shear rate band at early times upon startup. With time, the near-zero velocities rose in magnitude, forming the middle band. As the velocity profile in the middle band has a finite slope, the shear rate in this band is larger than in a traditional shear banding
system, where the shear rate in the low shear rate band is close to zero. This finite shear rate in the middle band leads to the non-zero alignment band in this solution during shear banding, as opposed to the near-zero alignment observed in typical shear banding WLMs.

6.7 Shear startup: mildly branched solution

In the low branching solution, a distinct shear banding mechanism was identified that is driven by wall slip and elastic instabilities. The results presented in Chapter 5 for the mildly branched solution are in good agreement with previous SANS results following the ‘disentangle, re-entangle’ mechanism [2,3,14]. However, to verify this mechanism of shear banding in the mildly branched solution, the same startup rheology and structural measurements for this solution are performed in this section. These measurements are compared to the results from the low branching solution, and are used to confirm the mechanism of shear banding in this solution. Additional trials for this solution can be seen in Appendix M.

6.7.1 Startup rheology

After analyzing the stress responses of the 0.01% wt NaTos solution, startup rheological measurements were also performed for the mildly branched solution (0.05% wt NaTos) to determine if any signatures of the shear banding response differed between the two solutions. Startup measurements were also taken in triplicate for this solution. For comparison purposes, the steady state flow curve is shown in Figure 6.20. In Figures 6.21, 6.22, and 6.23 below, the average stress response is shown for each shear rate, where the error bars correspond to the standard deviation of the stress between the three trials. Figure 6.21 corresponds to shear rates near the onset of region II, Figure 6.22 corresponds to shear rates well within the shear banding regime (region II), and Figure 6.23 corresponds to shear rates at the onset of region III and in region III. As was the case in the low branching solution, the features of the shear startup response are dependent on the shear rate regime examined.

A steady shear flow curve was determined from the startup measurements, which can be seen in Figure 6.20. The inset in Figure 6.20 is shown on a linear-log scale so that the fluctuations in the stress response (error bars) can be seen more clearly. The flow curve is
similar to the flow curve reported in Chapter 5, Section 5.7 for the steady shear case. Unlike in the low branching solution, the flow curve determined from the startup measurements is monotonically increasing, which suggests that the startup measurements have accessed the steady state at all shear rates. When $\dot{\gamma} \geq 60 \text{ s}^{-1}$, a small upturn is observed in the flow curve, which indicates the onset of region III. We predicted the onset of region III at $\dot{\gamma} = 60 \text{ s}^{-1}$ in Chapter 5, Section 5.7, so the resulting flow curve here is in good agreement with these previous measurements. We again use the work of Hu et al. [2] as a basis for comparing the features of the transient stress response in this solution. The startup measurements for shear rates at the onset of region II can be seen in Figure 6.21 below ($2 \leq \dot{\gamma} \leq 8.5 \text{ s}^{-1}$). The first shear rate shown in Figure 6.21, $\dot{\gamma} = 2 \text{ s}^{-1}$, corresponds to a Weissenberg number of $Wi \approx 3.3$. This shear rate is above the critical shear rate we previously determined for this solution in Chapter 5, so shear banding is expected at this shear rate. This dimensionless shear rate is also above the critical shear rate for shear banding for the toy model of Cates and co-workers of $Wi_1 = 2.6$ [20,25,26] (Equation 5.3).

![Figure 6.20: Startup flow curve for the 0.05% wt NaTos solution, which is similar to the steady shear curve shown in Chapter 5. Inset shown on a linear-log scale to show the fluctuations in the stress response at high $\dot{\gamma}$.](image)

When the stress response of the mildly branched solution is examined at the lowest shear rate ($\dot{\gamma} = 2 \text{ s}^{-1}$), a distinct feature is observed that is not observed in the low branching
solution at approximately the same Weissenberg number (Figure 6.4, \( \dot{\gamma} = 0.5 \text{ s}^{-1} \)). In Figure 6.21, the startup stress response slowly and monotonically decreases toward steady state between \( t = 15 \) and \( t = 200 \) seconds, forming a metastable plateau-like region. At \( t = 200 \) s, the stress sharply decreases and finally flattens out to the steady state value around \( t = 350 \) s. The time of 350 seconds corresponds to \( 210 \tau_R \), meaning that if both solutions exhibited this type of response on a similar dimensionless time scale, the stress response would have to be measured for over 2,000 seconds in the low branching solution. Longer time measurements of the startup behavior of the 0.01% wt NaTos solution indicate that a similar behavior is observed after long times; therefore, the stress response shown in Figure 6.4 has not yet reached steady state. This sharp decrease in the stress after a period of slow relaxation in a plateau-like region is also observed at the two other shear rates shown in Figure 6.21, and is a clear signature of shear banding. At each shear rate shown in Figure 6.21, a stress overshoot is followed by an undershoot and secondary overshoot; however, no shoulder-like feature is observed at these shear rates. As was the case in the low branching solution, the stress overshoot increases in magnitude with increasing shear rate, and the location (in time) of the overshoot decreases with increasing shear rate.

Figure 6.21: Stress response as a function of time after shear startup for the 0.05% wt NaTos solution for shear rates near the onset of region II. Error bars are the standard deviation of three trials. Nonlinear features including stress overshoots, undershoots, secondary overshoots, and a metastable plateau region are observed.
In Figure 6.22, the startup stress response is examined for three shear rates well within region II, which correspond to the shear rates used in the 1-2 plane measurements. These three shear rates are the same absolute shear rates used for the 1-2 plane measurements in the mildly branched solution: \( \dot{\gamma} = 15, 26.4 \) and \( 45 \) s\(^{-1}\). The behavior between \( \dot{\gamma} = 15 \) s\(^{-1}\) versus \( \dot{\gamma} = 26.4 \) and \( 45 \) s\(^{-1}\) slightly differs. When we examine the stress response of the mildly branched solution upon shear startup at \( \dot{\gamma} = 26.4 \) and \( 45 \) s\(^{-1}\), nearly identical features are observed to those reported by the shear banding solutions of Hu et al. [2] (Figure 6.22). These features include a large stress overshoot followed by a shoulder, an undershoot and another overshoot before the stress settles to its steady state value. A sharp stress overshoot and multiple, dominant shoulder-like features are observed at these two shear rates, that are significantly less pronounced at \( \dot{\gamma} = 15 \) s\(^{-1}\). While the stress undershoot has almost disappeared when \( \dot{\gamma} = 45 \) s\(^{-1}\), the undershoot is more pronounced at the lower shear rates in Figure 6.22 (\( \dot{\gamma} = 15 \) and 26.4 s\(^{-1}\)). While the undershoot and secondary overshoot are also present in the shear thinning solutions studied by Hu et al. [2], the shoulder feature in their ‘stage II’ region of the startup curve is unique to the shear banding solution. The secondary overshoot observed in the stress responses corresponds to the time at which the low shear band becomes discernible, according to [2]. The stress response and secondary overshoot shown in Figure 6.22 can be compared to the gap-dependent alignment factor profiles below to determine if the onset of shear banding is consistent with this feature. In the stress responses shown in Figure 6.22, the length of time of \( \tau_R \) has elapsed at the shoulder region of the stress response, indicating that the material can begin to relax and form shear bands in this regime. This point in time corresponds to the onset of ‘stage III,’ where the velocity profile begins to become significantly inhomogeneous across the gap [2]. In this region, the material takes approximately 120\( \tau_R \) to relax to its steady state stress. The transient PTV measurements of [2] provide a useful first guide to interpreting the bulk rheological behavior in the context of shear band formation.

The startup rheological measurements shown in Figure 6.22 for the mildly branched solution share many of the same features as in the low branching solution. In both cases, the stress overshoot occurs earlier in time and becomes sharper with increasing shear rate.
Figure 6.22: Stress response as a function of time after shear startup for shear rates within region II, which are used in the 1-2 plane measurements. Error bars are the standard deviation of three trials. The stress overshoot becomes sharper and more pronounced with increasing shear rate; the stress undershoot and secondary overshoot become less pronounced with rate.

The prominence of the stress undershoot becomes less pronounced near the onset of region III in both cases, but in this same region, the shoulder-like regions become more dominant, and multiple shoulder-like features are observed. These features are all consistent with the findings of Hu et al. [2] and seem to be consistent across shear banding systems. One major difference in the responses is observed between the low and mildly branched solutions. In the low branching solution, the stress response shows consistent, reproducible oscillations once the steady state is reached. These oscillations are not observed in the mildly branched solution. This difference provides insight into the different mechanisms of shear banding in each case. Oscillating stress responses are often observed in WLM solutions that have high solution elasticity, and can result from elastically-driven phenomena, turbulence, and interface fluctuations [12,29–34]. The screened electrostatic interactions in the mildly branched solution lead to a lower zero-shear viscosity, which helps to explain some of these differences. The lower $\eta_0$ in the mildly branched solution leads to a solution elasticity that is an order of magnitude lower (Equation 5.10), and therefore the absence of some of the traditional elastic-dominated phenomena.

Finally, we examine shear rates greater than $\dot{\gamma} = 45$ s$^{-1}$ in Figure 6.23. Our previous
calculations of $W_{i_2}=100$ ($\dot{\gamma} = 60 \text{ s}^{-1}$) is in good agreement with our findings in the startup rheology. At $\dot{\gamma} = 60 \text{ s}^{-1}$, the features of the stress response are very similar to when $\dot{\gamma} = 45 \text{ s}^{-1}$, with slightly larger fluctuations observed. At $\dot{\gamma} = 45 \text{ s}^{-1}$, the average and maximum fluctuations were less than 2% and 4%, respectively. At $\dot{\gamma} = 60 \text{ s}^{-1}$, the average fluctuations are around 4% of the steady state stress, with occasional fluctuations as large as 12%, so we conclude that that this shear rate is right at the border of the transition into region III. At the two shear rates in region III ($\dot{\gamma} = 75$ and 90 s$^{-1}$), however, the fluctuations of the stress response are significantly larger, in good agreement with the observations of Fardin et al. [32] for the ‘transition’ into region III.

Figure 6.23: Stress response as a function of time after shear startup for shear rates at and above the onset of region III. Error bars are the standard deviation of three trials. The shape of the stress overshoot does not change significantly with rate; fluctuations in the stress response increase with increasing shear rate.

As seen in Figure 6.23a, the shape of the stress overshoot is sharper and narrower at these high rates when compared to the stress overshoots seen at the lower rates in Figures 6.22 and 6.21, and is similar to the shape observed at $\dot{\gamma} = 45 \text{ s}^{-1}$. The magnitude of the stress overshoot continues to increase with increasing shear rate. The stress responses shown in Figure 6.23 contain multiple shoulder-like features; however, the stress undershoots immediately preceding the steady state stress have completely disappeared above $\dot{\gamma} = 60 \text{ s}^{-1}$. 

329
This disappearance of the stress undershoot may indicate the absence of shear banding. Interestingly, a sharp stress undershoot is observed at each of the three shear rates at much earlier times following the stress overshoot (Figure 6.23b). As mentioned above, the steady state stress response becomes increasingly chaotic with increasing shear rate, where very pronounced fluctuations are seen at $\dot{\gamma} = 75$ and $90 \, \text{s}^{-1}$. The steady state value of the stress response between multiple trials are the same; however the trials are not reproducible in terms of the fluctuations, in good agreement with the results of Fardin et al. [32] in the transition region. When $\dot{\gamma} = 75 \, \text{s}^{-1}$, the average fluctuations are around 10%, and occasional chaotic fluctuations on the order of 20% are observed. While most fluctuations are on the order of 15% of the steady state stress response, at $\dot{\gamma} = 90 \, \text{s}^{-1}$, the largest fluctuations are roughly 30%, again in good agreement with previous work [32]. The large fluctuations and the disappearance of some features described by Hu et al. [2] for shear banding indicates that the onset of region III has occurred. As was the case for the low branching solution, in all startup trials, the location of the stress overshoot in time is greater than the calculated breakage time ($\tau_{\text{break}} \approx 0.07 \, \text{s}$, Table 4.2).

### 6.7.2 Startup 1-3 plane SANS

Startup 1-3 plane SANS measurements were performed to complement the rheological measurements, and to provide a basis of comparison with the low branching solution. Despite the faster transient in the rheology in the mild branching solution versus the low branching solution, the structure at each shear rate was measured for twenty minutes, except in the case of the highest rates in region III which were measured for fifteen minutes. Three repeated trials were performed and added together to give the structural response reported in this section; the reproducibility of individual trials is shown in Appendix M. The 1-3 plane alignment factor for shear rates near the onset of region II are shown in Figure 6.24 below, where $\dot{\gamma} = 3.6, 4.2$ and $8.5 \, \text{s}^{-1}$. As seen in Figure 6.24, the $A_f$ response exhibits a gradual decrease in alignment over the course of the experiment, which is most noticeable when $\dot{\gamma} = 8.5 \, \text{s}^{-1}$. At $\dot{\gamma} = 8.5 \, \text{s}^{-1}$, the $A_f$ response reaches steady state after approximately 600 seconds, which is longer than the 350 second transient seen in the rheological stress response (Figure
6.22). A longer transient in the $A_f$ response versus the startup stress response was also observed in the low branching solution, again suggesting that the structural measurements are a better indicator of the true material steady state. The longer structural transient implies that the microstructural rearrangements that occur on these long time scales do not significantly affect the measured stress response.

Figure 6.24: 1-3 plane alignment factor as a function of time after startup for the 0.05% wt NaTos solution at shear rates near the onset of region II on a (a) log-log and (b) log-linear scale for clarity. A long, gradual transient is observed at each of the three shear rates, similar to the stress response shown in Figure 6.22.

Startup measurements were also performed for the shear rates well within region II, which can be seen in Figure 6.25. The three lowest shear rates were used in the 1-2 plane experiments: $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$. The 1-3 $A_f$ is also shown at $\dot{\gamma} = 90$ and $150$ s$^{-1}$ for comparison to the low branching solution. When the startup response for the three shear rates shown in Figure 6.25 is compared to equal shear rates for the low branching solution, significant differences in the time dependent response are observed. In Figure 6.25, a long and gradual transient in $A_f$ is observed, which is significantly less pronounced than the $A_f$ transient observed in the low branching solution. However, when comparing the $A_f$ responses, the differences in Weissenberg number and relaxation time must be considered. The first data point shown in the responses in Figure 6.25 occurs at $6\tau_R$ for the mildly branched solution, but corresponds to less than $2\tau_R$ in the low branching solution. Accounting for the
differences in relaxation time, a less dramatic transient is still observed in the case of mild branching, as a significant decrease in $A_f$ is still observed when $t > 6 \tau_R$ (Figure 6.10). At these three shear rates, the nearly flat portion of the $A_f$ response starting at $t = 10$ s until $t = 100$ s (Figure 6.25) appears to correspond to a similar portion of the $A_f$ response when $t > 100$ s in the low branching solution (Figure 6.10).

Figure 6.25: 1-3 plane $A_f$ as a function of time after startup at shear rates well within region II and into region III on a (a) log-log and (b) log-linear scale for clarity. A long, gradual transient is observed that is distinct in shape from the pronounced transient observed in the low branching solution.

The transient in the 1-3 plane $A_f$ becomes significantly faster at the shear rates in region III. When $\dot{\gamma} = 90$ and 150 s$^{-1}$, the alignment reaches its steady state in less than 200 seconds. At $\dot{\gamma} = 225$ s$^{-1}$, no transient in the alignment factor is observed; this data can be seen in Appendix M. For the mildly branched solution, the $A_f$ transient becomes faster with increasing shear rate even within the shear banding regime. This behavior is expected because at lower shear rates, the width of the low shear rate band is larger (Equation 5.4). With increasing shear rate, less of the material must relax and re-entangle in the low shear rate band, leading to this faster transient with increasing rate. However, the $A_f$ transient is approximately equal in time between $\dot{\gamma} = 15, 26.4$ and 45 s$^{-1}$ for the low branching solution, which reflects the different mechanism of shear banding. Because the shear banding is
elastically-driven in the low branching case, and the width of the three bands is similar between shear rates (Figure 6.19). Accordingly, the time for the shear bands to evolve to steady state is nearly shear rate-independent for the low branching solution. Regardless of length, the presence of the long transient in $A_f$ appears to be a good indicator of shear banding, which will be verified using a non-shear banding sample in Section 6.9.2 below.

### 6.7.3 Startup 1-2 plane SANS

The 1-2 plane startup SANS measurements were performed on the select shear rates shown in Figure 6.22, which are the same shear rates used for the low branching solution: $\dot{\gamma} = 15, 26.4$ and $45$ s$^{-1}$. To enable comparison to the results presented in Chapter 5, Section 5.7.3, the steady state 1-2 plane alignment factor as a function of gap position for these three shear rates can be seen in Figure 6.26. As seen in Figure 6.26, the results are nearly identical in both magnitude and shape to the previous results (Figure 5.14), giving confidence in the comparison. As additional gap positions are used in the measurements shown in Figure 6.26, the location of the shear band interface can be more easily identified. The width of the high shear rate band increases approximately in accordance with the lever rule (Equation 5.4), as was the case with the results shown in Chapter 5. The 1-2 plane results shown in Figure 6.26 are in good agreement with the ‘disentangle, re-entangle’ mechanism [2,3,14], and are similar to the SANS results seen in typical shear banding WLM solutions [14,17–19,23].

The time-dependent, 1-2 plane startup measurements for the mildly branched solution are first explored at the lowest shear rate, $\dot{\gamma} = 15$ s$^{-1}$. In this solution, we expect the longest transient in the alignment factor response to correspond with the lowest shear rate, as was the case for the 1-3 plane results shown in Figure 6.25. The 1-2 plane $A_f$ as a function of time after shear startup can be seen in Figure 6.27a for six gap positions. A schematic depicting the relationship between each measurement and the gap position can be seen in Figure 6.27b, where the steady state $A_f$ values are shown by the symbols. In Figure 6.27b and in the results for the other shear rates, the shear band interface location is depicted based on the critical values of $A_f$ for shear banding set forth by Helgeson et al. [23], which was used to determine the location of the interface and the width of the high shear rate band, $\alpha$, in
Figure 6.26: Steady shear 1-2 plane $A_f$ for the 0.05% wt NaTos solution as a function of gap position, $r/H$, taken at the end of shear startup measurements. Results are consistent with the steady shear results presented in Chapter 5, Section 5.7.3. An increase in the width of the high shear rate band is observed with increasing shear rate (Equation 5.4).

Chapter 5, Section 5.7.3. While startup measurements were not performed at $r/H = 0.15$, a steady shear measurement was taken to help identify the location of the shear band interface.

At the two positions closest to the inner wall shown in Figure 6.27 ($r/H = 0.05, 0.25$), the shape of the alignment factor response is similar to the shape observed in the 1-3 plane measurements. A nearly flat and then convex portion of the $A_f$ response is observed before a dramatic decrease is seen when $t > 40$ seconds, which continues until approximately 100 seconds. The shape of the $A_f$ response is distinct from the response seen in the low branching solution (Figures 6.12, 6.13, and 6.14), even when the differences in relaxation time or Weissenberg number are taken into account. The shear rate of $\dot{\gamma} = 45$ s$^{-1}$ for the mildly branched solution is at approximately the same Weissenberg number as $\dot{\gamma} = 15$ s$^{-1}$ for the low branching solution. The alignment factor response at the outer wall exhibits a different shape, where the decrease upon startup is concave in nature. The initial decrease in the value of $A_f$ at the outer wall is more consistent with the results in the low branching solution, which is surprising based on the different shear banding mechanisms. While the alignment factor at most of the gap positions reaches a magnitude similar to the steady state magnitude after 200 seconds, the true steady state response is not achieved until approximately 500
seconds. These results are in good agreement with the 1-3 plane results at $\dot{\gamma} = 15 \text{ s}^{-1}$, which also exhibited a transient on the order of $t = 500$ seconds. Finally, small oscillations in the $A_f$ response are observed in the 1-2 plane measurements here, and also in the 1-3 plane experiments. Although these oscillating responses were not observed in the measured stress, these results are not unusual for shear banding systems. One explanation of these differences is the change in geometry between the different measurements, which can greatly affect the shear banding response based on the gap width [37] but also the Couette height.

Figure 6.27: 1-2 plane $A_f$ for the 0.05% wt NaTos solution as a function of time after shear startup at $\dot{\gamma} = 15 \text{ s}^{-1}$ (a) and corresponding steady state $A_f$ as a function of gap position (b). The location of the shear band interface is depicted for visual aid using the critical values set forth by Helgeson et al. [23].

The 1-2 plane measurements were performed for additional gap positions at $\dot{\gamma} = 26.4 \text{ s}^{-1}$, where the results for the eleven positions can be seen in Figure 6.28a. Once again, a depiction of the gap position can be seen in Figure 6.28b, where the steady state $A_f$ values are shown by the symbols and the location of the shear band interface is estimated for visual aid. As seen in Figure 6.28a, a long and pronounced transient is observed at this shear rate, especially near the shear band interface. The alignment factor decays much more significantly at the positions near the interface ($r/H = 0.3$ to $r/H = 0.55$) as opposed to the positions near the inner wall. Near the inner wall, a long transient in $A_f$ is still observed, but
a large decrease in the magnitude is not observed as it is toward the outer wall. Similar to
the results when $\dot{\gamma} = 15 \text{ s}^{-1}$, the $A_f$ relaxation at early times takes on a convex shape near
the inner wall, and exhibits a concave response closer to the outer wall. At nearly all gap
positions, pronounced oscillations in the alignment factor are observed once the steady state
value is reached. While not observed in the stress response, this type of unstable behavior
may be promoted by the use of the short-path length Couette for the 1-2 shear cell. These
oscillations in the 1-2 plane $A_f$ and the shape of the startup response near the outer wall are
similar to the behavior exhibited by the low branching solution.

![Figure 6.28](image_url)

**Figure 6.28:** 1-2 plane $A_f$ as a function of time after shear startup at $\dot{\gamma} = 26.4 \text{ s}^{-1}$ (a) and
corresponding steady state $A_f$ as a function of gap position (b). The location of the shear
band interface is estimated for visual aid.

When the shear rate is increased to $\dot{\gamma} = 45 \text{ s}^{-1}$, the alignment factor transient is sig-
nificantly faster at all gap positions. These results are consistent with the trends in the 1-3
plane SANS (Figure 6.25) and the startup stress response (Figure 6.22), and can be seen in
Figure 6.29a. The steady state alignment and a depiction of the shear band interface can be
seen in Figure 6.29b, where the width of the high shear rate band has clearly increased with
increasing shear rate. At this shear rate, only two gap positions measured fall within the
low shear rate band. As seen in Figure 6.29a, little to no transient in $A_f$ is observed at the
positions within the high shear rate band. A small increase in $A_f$ at early times is seen at the
two innermost gap positions. This increase in alignment is in good agreement with stage IV of the disentangle, re-entangle mechanism, where the shear rate in the high shear rate band increases in time. The alignment in the low shear rate band continuously evolves to a state of lower alignment, reflecting the re-entangling of the micelles. As was the case for the lower shear rates, the $A_f$ response at all gap positions exhibits steady state fluctuations.

Figure 6.29: 1-2 plane $A_f$ as a function of time after shear startup at $\dot{\gamma} = 45 \text{ s}^{-1}$ (a) and corresponding steady state $A_f$ as a function of gap position (b). The location of the shear band interface is estimated for visual aid.

6.8 Discussion: mildly branched solution

6.8.1 Structural mechanism of shear banding

The goal of the startup 1-2 plane measurements was to confirm the disentangle, re-entangle mechanism of shear banding for the mildly branched solution, and to then compare this mechanism to the mechanism in the low branching solution. Here, we perform the same analysis as in the low branching solution to determine the structural mechanism of shear banding from the 1-2 plane SANS measurements. In Figure 6.30, we analyze $A_f$ as a function of gap position at multiple times following the start of shear for $\dot{\gamma} = 26.4 \text{ s}^{-1}$. We can then compare this analysis to the time-dependent velocity profile measurements of Hu et al. [2] during shear startup, to either confirm the ‘disentangle, re-entangle’ mechanism or...
identify a separate shear banding mechanism. The analysis is performed at $\dot{\gamma} = 26.4 \, s^{-1}$ due to the wealth of gap positions measured at this shear rate.

Examining the time-dependent alignment factor profiles in Figure 6.30 helps to elucidate and confirm the disentangle, re-entangle mechanism in the mildly branched solution. In Figure 6.30a, the shear band interface has already started to form when $t = 15$ seconds. When the startup rheology at this shear rate is examined (Figure 6.22), the onset of stage IV is expected at $t \approx 10$ seconds, where the secondary stress overshoot occurs. According to Hu et al. [2], stage IV corresponds to the point at which the shear band interface can be identified, which is in good agreement with the $A_f$ results shown in Figure 6.30a. At this time, the low shear rate band consists of the three gap positions where $r/H \geq 0.65$. After 25 seconds (Figure 6.30b), the alignment in the low shear rate band decreases, while the alignment in the high shear rate band increases from the initial alignment. These changes in alignment are also consistent with stage IV described by Hu et al. [2], where the shear rate in the high shear rate band continues to increase in time, while the shear rate in the low rate band decreases in time. Using the critical value of $A^*_f = 0.18$ set forth by Helgeson et al. [23], the low shear rate band now includes four gap positions, where $r/H \geq 0.55$, and the location of the interface occurs between $0.5 < r/H < 0.55$. This growth in width of the low shear rate band is also observed by Hu et al. [2].

In Figure 6.30c, the $A_f$ profile is measured at $t = 50$ seconds after shear startup. The alignment in the low shear rate band continues to decrease and the width of the low shear rate band continues to expand, in good agreement with the disentangle, re-entangle mechanism. In Figure 6.30c, five gap positions are now included in the low shear rate band, where $r/H \geq 0.5$. The shear band interface is now located between $0.3 < r/H < 0.5$. After 100 seconds, the alignment in the five outer gap positions has further decreased, and is well below $A^*_f$ at all positions (Figure 6.30d). The alignment at $r/H = 0.3$ has decreased significantly from when $t = 50$ s, and is now only slightly larger than the critical value ($A_f = 0.22$ vs. $A^*_f = 0.18$). This decrease in alignment suggests that the shear band interface has moved further to the left and is now closer to $r/H = 0.3$. In Figure 6.30e, the alignment factor at both the inner and outer bands starts to settle to steady state. An approximate steady
state is seen in Figure 6.30f, where the low and high shear rate bands are well separated. At all locations within the low shear rate band, the alignment factor is far below $A_f^*$, where $A_f < 0.1$. At all time stages shown in Figure 6.30, the alignment factor results are in excellent agreement with the disentangle, re-entangle mechanism and the observations of Hu et al. [2] using PTV. These results, along with the results from the low branching solution, confirm that the startup alignment factor can be used as a proxy for PTV measurements to determine the shear banding mechanism in WLM solutions. While only shown for one shear rate in Figure 6.30, the disentangle, re-entangle mechanism is observed for all three shear rates examined with 1-2 plane SANS.

![Figure 6.30: 1-2 plane $A_f$ for $\dot{\gamma} = 26.4 \text{ s}^{-1}$ as a function of $r/H$ and time after shear startup.](image)

(a) The low shear band has started to form, including three positions where $r/H \geq 0.65$. (b) The alignment in the low shear rate band decreases, while the high shear rate band alignment increases. (c) The material at the outer wall re-entangles and settles, further decreasing in $A_f$. The location of the shear band interface moves to lower $r/H$. (d) The location of the band interface continues shifting to lower $r/H$, consistent with the disentangle, re-entangle mechanism. (e) $A_f$ in both bands begins to settle. (f) An approximate steady state is reached, where the interface is located between $0.3 < r/H < 0.5$.

The results shown in Figure 6.30 can be seen for the other two shear rates in Figure 6.31. As seen in Figure 6.31a, similar features of the $A_f$ response are observed at $\dot{\gamma} = 15 \text{ s}^{-1}$.
The low shear rate band increases in width in time, in good agreement with the disentangle, re-entangle mechanism. After 250 seconds, an approximate steady state is reached, where the shear band interface occurs before $r/H = 0.25$. The results at $\dot{\gamma} = 45 \text{ s}^{-1}$ are seen in Figure 6.31b. While only minor changes in the $A_f$ profile are seen in time, the alignment in the low shear rate band and near the band interface decreases in time, indicating that the low shear rate band becomes larger in width over time.

![Figure 6.31: Time-dependent 1-2 plane $A_f$ for (a) $\dot{\gamma} = 15 \text{ s}^{-1}$ and (b) $\dot{\gamma} = 45 \text{ s}^{-1}$. (a) The location of the shear band interface continuously moves to the left, indicating a growth of the low shear rate band. (b) A faster transient is observed at higher rates. Results at both shear rates are consistent with the disentangle, re-entangle mechanism.](image)

6.8.2 Shear banding mechanism: low vs. mild branching

The 1-2 plane SANS results, paired with particle tracking velocimetry measurements, confirm a different mechanism of shear banding between the low and mildly branched solutions. At all shear rates measured with 1-2 plane SANS, the low branching solution exhibits a three band structure, whereas the mildly branched solution exhibits two shear bands at all times and follows the disentangle, re-entangle mechanism. The same 1-2 plane $A_f$ comparison from Figure 5.17 shown in Chapter 5 based on Weissenberg number for the steady shear results is shown again in Figure 6.32 based on the startup results. The additional gap
positions used in the startup measurements provide a clearer difference between the two solutions. As seen in Figure 6.32, the mildly branched solution achieves a significantly higher degree of alignment at nearly every gap position for the same Weissenberg number. This result is consistent with the steady shear results in Chapter 5 that showed that branching amplifies alignment on the basis of Weissenberg number. The location of the shear band interface is also distinctly different between solutions. In the low branching solution, the interface appears to occur around \( r/H = 0.4 \), whereas the interface occurs closer to \( r/H = 0.75 \) for the mildly branched solution. These differences are not surprising based on the fact that the low branching solution does not obey the lever rule for shear banding (Equation 5.4).

![Figure 6.32: Steady shear 1-2 plane \( A_f \) for the 0.01% wt and 0.05% wt NaTos solutions at equivalent Weissenberg numbers, \( Wi \approx 80 \), taken at the end of shear startup measurements.](image)

As previously discussed, the difference in the shear banding behavior appears to be the result of differences in the solution elasticity. Elastic instabilities and interface fluctuations can lead to wall slip the resulting three band structure in the low branching solution [6–9]. The magnitude of the elasticity number, \( El \), is over an order of magnitude larger in the low branching solution. As \( El \) is dependent on the zero-shear viscosity and relaxation time, the difference in the solution elasticity is the result of the differences in electrostatic interactions but also branching. As discussed in Chapter 1, many studies have shown that significant branching is often already present in WLM solutions at the viscosity maximum.
A significant reduction in the zero-shear viscosity is seen between these two solutions because the electrostatic interactions are screened. However, the screening of these interactions is also inherently linked to branching, as branching becomes more significant as the interactions are screened. Further, screening the electrostatic interactions serves to decrease the relaxation time, but the relaxation time is also decreased by the presence of branch points that can slide to relieve stress. The theory of Lequeux [40] presented in Chapter 1, Section 1.5 for branched micelles does not consider the relative role of electrostatic interactions, which makes the determination of the relative contributions to $E_l$ of the screened interactions versus the presence of branch points difficult. In Chapter 8, the recommendations for future work discusses this conflict further, and potential ways to elucidate the effect of charge and electrostatic interactions on the shear banding behavior.

6.9 Shear startup: higher branching levels

As signatures of shear banding were identified from the startup stress and structural responses in the low and mildly branched solutions, signatures of shear thinning are examined in this section for more highly branched solutions. The results presented in this section mostly focus on the 0.10% wt NaTos solution; however, results from additional branching levels can be seen in Appendix M.

6.9.1 Startup rheology

The startup stress response for the low and mildly branched solutions was analyzed to determine signatures of shear banding. To determine which of the identified features is actually a feature of shear banding, the results must be compared to a non-shear banding sample. To do this, startup rheological measurements were also performed on the highly branched, 0.10% wt NaTos solution. While a prominent stress overshoot is often associated with shear banding [4, 5], breakage in wormlike micelles can lead to a stress overshoot without steady state shear banding. Therefore, it is important to identify which rheological characteristics are truly unique to the shear banding solutions.
The startup stress responses for the highly branched solution can be seen in Figure 6.33. While Figure 6.33 shows trials for only 300 seconds, additional long-time trials can be seen in Appendix M. The trials shown in Appendix M also cover higher shear rates up to $\dot{\gamma} = 575 \text{ s}^{-1}$. The stress response are presented in the same groupings as for the low and mildly branched solution, where the shear rates near the onset of region II can be seen in Figure 6.33a and b, the shear rates well within region II can be seen in Figure 6.33c and d, and the shear rates at or beyond region III can be seen in Figure 6.33e and f. As discussed in Chapter 5, Section 5.10, the onset of region II varies between samples, but the high shear rate behavior is fairly similar between solutions. In Figure 6.33a and b, the stress response for the highly branched solution greatly differs from the shear banding solutions shown in Figures 6.4 and 6.21. While stress overshoots are still present, the stress overshoots are small in magnitude and rounded in shape, which is consistent with the description provided by Hu et al. [2] for shear thinning solutions. As seen clearly in Figure 6.33b, stress undershoots are also observed, which are small in magnitude; no secondary overshoot is observed after the stress undershoots. In the corresponding shear rates in the shear banding solutions, secondary overshoots are always observed, even at low shear rates. Additionally, the shoulder-like features described by Hu et al. [2] for shear banding solutions are not observed. The stress response reaches its steady state value less than three seconds after shear startup ($\approx 7 \tau_R$). The time of $7 \tau_R$ to steady state is again consistent with shear thinning as opposed to shear banding, as the mildly branched solution took approximately $210 \tau_R$ to reach steady state at shear rates in the same region. As was the case for the other two solutions, the location in time of the stress overshoot decreases with increasing shear rate.

In Figure 6.33c and d, the startup stress response for the shear rates well within region II are examined. In the shear banding solutions, these stress responses exhibited increasingly sharp stress overshoots, shoulder-like features and long transience. As seen in Figure 6.33, the shape of the stress overshoot is still fairly wide until $\dot{\gamma} = 45 \text{ s}^{-1}$. At this point, the stress overshoot sharpens, but all features of the stress response are still rounded. As was the case in the shear thinning solutions of Hu et al. [2], the stress response exhibits an overshoot, undershoot, and secondary overshoots; however, the shoulder-like features that Hu et al. [2]
Figure 6.33: Stress response as a function of time after startup for the 0.10% wt NaTos solution. (a,b) The stress response near the onset of region II exhibits a rounded stress overshoot and at higher rates, a minor stress undershoot. No secondary overshoot is observed. (c,d) At the three shear rates well within region II, the rounded stress overshooots and undershoots are still observed. Secondary overshoots are also observed, but no shoulder-like features are present. (e,f) At the highest rates in region III, shoulder-like features are finally observed but are distinct from those in the shear banding solutions. At all shear rates, the stress response reaches its steady state value in $t \leq 5$ s ($t \leq 12\tau_R$).
specifically note to distinguish the shear banding systems are not observed. These shoulder-like features are observed at the three identical shear rates for the shear banding solutions. Finally, the transient in the stress response is still fast in this solution, where the stress reaches steady state in less than four seconds ($10\tau_R$). For the corresponding region II shear rate for the mildly branched solution, approximately $120\tau_R$ passes before the steady state is reached.

Finally, the startup stress response for the shear rates at and beyond region III are shown in Figure 6.33e and f. In Figure 6.33e and f, the stress response finally exhibits a shoulder-like feature following the stress overshoot when $\dot{\gamma} = 60 \text{ s}^{-1}$. However, this feature is followed by a very small local minimum in the stress (Figure 6.33f), as opposed to a large, global minimum in the stress as is observed for shear banding solutions after the shoulder. At $\dot{\gamma} = 75$ and $90 \text{ s}^{-1}$, the stress response also features a shoulder-like response, however, this feature is significantly broader and rounder than in the shear banding solutions. All observed secondary overshots and undershoots are rounded in nature and small in magnitude, which is again in contradiction with the features seen for the shear banding solutions. The stress response in all cases reaches steady state in five seconds or less, which corresponds to $12\tau_R$.

As was the case for the other two solutions, in all startup trials, the location of the stress overshoot in time is greater than the calculated breakage time ($\tau_{\text{break}} \approx 0.03 \text{ s}$, Table 4.1). Interestingly, the time for the stress to reach its steady state value increases with shear rate for the highly branched solution, but decreases with shear rate for the low and mildly branched solutions, which may be an additional signature of shear thinning versus shear banding.

### 6.9.2 Startup 1-3 plane SANS

A long transient in the startup stress response is associated with shear banding in the low and mildly branched solutions. As shown above, a rather fast stress transient is observed in the highly branched solution, which only exhibits shear thinning. To determine if a fast structural transient was also observed in the highly branched solution, 1-3 plane startup SANS measurements were performed. These measurements were only performed one time to verify the absence of transience unlike in the shear banding solutions, where the trials were repeated three times. As such, the results are noisy due to poorer statistics.
While the results for this specific experiment pertain to only one trial, they are reflective of the general behavior of this solution, as repeated experiments on the same branching level yield results similar to those shown below in Figure 6.34.

The 1-3 plane alignment factor for the shear startup experiments can be seen for shear rates within regions II and III in Figure 6.34. While the responses are noisy, a time-dependent structural response is not observed in response to the startup of shear at any of the shear rates. Instead, the value of $A_f$ is approximately constant in time with a certain degree of noise. The fluctuations in $A_f$ are of the same magnitude between all shear rates, which suggests that the small fluctuations result from a low number of counts as opposed to a change in structure. The structural response is in good agreement with the startup stress response, as no significant fluctuations in the stress response are observed up to shear rates of $\dot{\gamma} = 90 \text{ s}^{-1}$ (Figure 6.33). The results from Figure 6.34 are consistent with results from other shear rates, and other experiments on the same solution, where no transient in the startup stress response is observed. These additional results, and results for other branching levels, can be seen in Appendix M.

![Figure 6.34](image.png)

Figure 6.34: 1-3 plane $A_f$ for the 0.10% wt NaTos solution as a function of time after startup for shear rates well within region II and region III on a (a) log-log and (b) linear-linear scaling. $A_f$ exhibits some fluctuations due to poor statistics. No time dependence is observed at startup, indicating shear thinning.
6.9.3 Startup 1-2 plane SANS

As the 1-3 plane measurements showed little to no transience for the highly branched solution, only select shear rates were chosen for the startup 1-2 plane measurements. As was done for the two shear banding solutions, the steady shear alignment factor was recorded for the three common shear rates: $\dot{\gamma} = 15, 26.4, \text{ and } 45 \text{ s}^{-1}$. The steady shear alignment from this experiment can be seen for those three rates in Figure 6.35. As expected, the results are in excellent agreement with the results presented in Chapter 5, Section 5.5.3. Of these three shear rates, startup measurements were only performed at $\dot{\gamma} = 15 \text{ s}^{-1}$ and $\dot{\gamma} = 45 \text{ s}^{-1}$ to verify the absence of transience. Additionally, steady shear and startup measurements were performed at $\dot{\gamma} = 60 \text{ s}^{-1}$ so verify that shear banding was not observed at higher Weissenberg numbers ($Wi = 23$); these results can also be seen in Figure 6.35. As seen by the similarity to the previous results and the similarity of the $A_f$ response at $\dot{\gamma} = 60 \text{ s}^{-1}$ to $\dot{\gamma} = 45 \text{ s}^{-1}$, no shear banding is observed for this solution.

![Figure 6.35: Steady shear 1-2 plane $A_f$ for the 0.10% wt NaTos solution as a function of gap position, $r/H$, taken at the end of shear startup measurements. Results are consistent with the steady shear results presented in Chapter 5, Section 5.5.3. No shear banding is observed.](image)

The startup measurements at all shear rates were only performed for 300 seconds, due to the fast transience observed in the startup rheology for this sample (Figure 6.33). The 1-2 plane alignment factor for the $\dot{\gamma} = 15 \text{ s}^{-1}$ trials can be seen in Figure 6.36a and b, where

347
five gap positions are measured. As seen in Figure 6.36a and b, no transient or startup effects are seen in the alignment factor response. The fluctuations observed in $A_f$ at this shear rate are more likely to be a result of poor statistics and few repetitions than true oscillations in the $A_f$ response, as $\dot{\gamma} = 15 \text{ s}^{-1}$ is a fairly low Weissenberg number for this solution and the fluctuations are fairly random unlike in the shear banding solutions. Further, the calculation of $A_f$ becomes less accurate when $A_f$ is low. While the stress response reaches steady state quickly in this solution, structural transience were observed in the two shear banding solutions beyond the time of the stress transient, which does not occur here. The absence of a structural transient again indicates shear thinning as opposed to shear banding.

Figure 6.36c and d shows the 1-2 $A_f$ results when the shear rate is raised to $\dot{\gamma} = 45 \text{ s}^{-1}$; here, only three gap positions are measured. Once again, no transient is observed in the $A_f$ response. The fluctuations in $A_f$ here are smaller due to the larger magnitude of $A_f$, which reduces uncertainty in the calculation. Finally, in Figure 6.36e and f, the 1-2 $A_f$ is shown at $\dot{\gamma} = 60 \text{ s}^{-1}$ for three gap positions. The alignment factor here shows similar behavior to when $\dot{\gamma} = 45 \text{ s}^{-1}$, and is essentially constant in time. The oscillations in the $A_f$ response are more likely to be true oscillations here than at $\dot{\gamma} = 15 \text{ s}^{-1}$ based the proximity of this condition to region III and the higher degree of alignment used to calculate $A_f$. The absence of a structural transient here versus in the results for the two shear banding solutions suggests that the time-dependent $A_f$ can be used as a guideline to determine when shear banding versus shear thinning is expected in a particular solution.

### 6.9.4 Summary: high branching

As seen from the startup rheology and SANS results, the stress and structure of WLM solutions reach steady state quickly after startup when shear banding is not present. In the startup rheology, the steady state stress was achieved in five seconds or less for shear rates up to $\dot{\gamma} = 90 \text{ s}^{-1}$, which corresponds to $12 \tau_R$. Equivalent stress responses in the shear banding solutions often taken hundreds of relaxation times before steady state is reached. The shape and sequence of features in the stress response was unique for this solution and was in good agreement with the observations of Hu et al. [2] for shear thinning solutions. The features
Figure 6.36: 1-2 plane $A_f$ as a function of time after startup at (a,b) $\dot{\gamma} = 15 \text{ s}^{-1}$, (c,d) $\dot{\gamma} = 45 \text{ s}^{-1}$, and (e,f) $\dot{\gamma} = 60 \text{ s}^{-1}$ on a (a,c,e) log-log and (b,d,f) linear-linear scale. No transience or shear banding is observed at any shear rate. The fluctuations in $A_f$ when $\dot{\gamma} = 60 \text{ s}^{-1}$ may be due to the proximity to region III.
of the stress responses in the shear banding regime were similar between the low and mildly branched solution. In the structural response, as represented by the alignment factor, no transient was observed in response to shear startup at any of the measured shear rates. In the shear banding solutions, a transient longer than the stress transient was observed in $A_f$, suggesting that this transient can help identify shear banding versus shear thinning in WLM solutions. At high shear rates near or in region III, some fluctuations in the $A_f$ response were observed in the 1-2 plane measurements, which is may expected due to the presence of stress fluctuations once region III is reached [32]. The results from the highly branched solution are useful for comparison to the shear banding solutions, and help us determine key features of the startup behavior that lead to shear banding.

6.10 Discussion: all branching levels

In this chapter, startup stress and structural signatures of shear banding and shear thinning were identified based on branching level. The similarities and differences in these startup responses are discussed in this section.

6.10.1 Signatures of shear banding vs. shear thinning

The combination of nonlinear rheology with flow-small angle neutron scattering allows us to determine signatures of shear banding and shear thinning in these WLM solutions. The identified rheological signatures of shear banding are consistent with previous works [11–14]. Near the onset of region II, transients on the order of hundreds of relaxation times are identified in the two shear banding solutions. In the same region, a transient of less than $10\tau_R$ was observed for the shear thinning, highly branched solution. The startup rheology results also confirm the work of Hu et al. [2] for a different surfactant and a lower concentration, suggesting that their proposed stages of shear band formation may be universal for WLMs. Shear thinning and shear banding solutions contain many of the same features in shear startup measurements, including stress overshoots, undershoots and secondary overshoots. However, Hu et al. [2] discussed that the main difference between the startup behavior for shear thinning and shear banding solutions was a shoulder-like region
following the stress overshoot in the case of shear banding. We confirm this behavior in our solutions, as significant shoulder regions are observed in region II for the two shear banding solutions. A shoulder-like region is only observed at the onset of region III in the shear thinning solution. Further, the stress overshoots and other features of the startup response are significantly more rounded in the shear thinning solution, which is also consistent with the description by Hu et al. [2].

In addition to the difference in the shoulder feature described by Hu et al. [2], we also identify other differences between the shear banding and shear thinning solutions. These differences are in relation to the order and magnitude of the features observed in the startup stress response. When the startup responses for the highly branched solution are examined, the magnitude of the stress overshoot appears to be smaller than in the low and mildly branched solutions. Even when compared at equivalent Weissenberg number, the magnitude of the stress overshoot to the steady state stress is smaller in the highly branched solution, which will be discussed below in Section 6.38. The sequence of nonlinear features also varies when the shear thinning solution is compared to the shear banding solutions. For the highly branched solution where the shoulder-like feature is observed (region III), the feature is immediately followed by a very small local minimum in the stress. In the shear banding solutions, the shoulder is always followed by a global minimum in the stress, which is often large in magnitude. In the shear thinning solution, all observed secondary overshoots and undershoots are rounded in nature and much smaller in magnitude than in the shear banding solutions. Finally, in our shear thinning solution, the time for the stress to reach steady state increases with shear rate. The stress and structure evolve more quickly to steady state with increasing shear rate in the shear banding solutions.

Finally, we identify structural transients that are indicative of shear banding using 1-3 plane and 1-2 plane SANS measurements. In the shear banding solutions, a long and discernible structural transient is observed in both planes. A longer transient is seen at gap positions near the outer wall in the 1-2 plane measurements, where the material at the outer wall rearranges more slowly before the steady state is achieved. As the 1-3 plane measurements represent the average structure across the gap, the small structural changes at the outer
wall in time are difficult to detect. Regardless, the transient in $A_f$ in both planes is often longer than the transient in the measured stress response. As the stress overshoot is often an order of magnitude larger than the steady state stress, transients in the stress at long times and of lower magnitudes are often hard to detect by comparison. Conversely, the alignment factor only ranges from zero to one, and does not measure the large elastic stresses that lead to the overshoot. Accordingly, micellar alignment is observed directly after the stress overshoot; micellar alignment is not observed at the overshoot itself [14]. As the alignment factor only measures segmental alignment, as opposed to the total shear stress, $A_f$ is a more sensitive measure of when steady state flow has been achieved. No structural transient is observed at any shear rate in either plane for the highly branched solution. Even when the results are normalized based on the material relaxation time, the behavior in the highly branched solution is significantly faster than in the shear banding solutions. The absence of the structural transient can therefore be used as an indicator of shear thinning as opposed to shear banding.

6.10.2 Particle tracking velocimetry: low vs. high branching

To confirm shear thinning in the highly branched solution, particle tracking velocimetry (PTV) measurements were performed at a single shear rate. The measured velocity profile at $\dot{\gamma} = 45 \text{ s}^{-1}$ can be seen in Figure 6.37 with a comparison to the profile for the low branching solution. As seen in Figure 6.37, unlike in the low branching solution, no wall slip is observed at the inner wall in the highly branched solution. The velocity profile across the gap is nearly linear, indicating shear thinning. Interestingly, the velocity profile for the low branching solution in the third shear band falls onto the same curve as the profile for the highly branched solution. The similar behavior of the two solutions in this region near the outer wall again signifies that the shear banding fluctuations in the low branching solution are driven by instabilities in the middle band as opposed to the outer band, in agreement with the work of Manneville [9].
6.10.3 Shear startup to determine micellar morphology

As discussed in Section 6.9.1, the stress overshoots at low Weissenberg numbers for the highly branched solution seemed to be lower in magnitude and more rounded than in the solutions with lower branching. In entangled polymer solutions, the polymer morphology has shown to have a significant effect on the startup rheology in terms of this stress overshoot \[27, 28\]. In these works, the ratio of the viscosity or stress at the maximum value (overshoot region) upon startup to the steady state viscosity or stress was dependent on the chain length and architecture, when the values were compared on a Weissenberg number basis. To examine if the startup rheology could also be used as an indicator of morphology in WLMs, we performed the same analysis using solutions with different levels of branching: 0.01%, 0.10% and 0.25% wt NaTos. These three solutions are chosen for clarity, and due to the large difference in salt content between each solution. The startup responses for the 0.25% wt NaTos solution are similar to those observed in the 0.10% wt NaTos solution, and can be seen in Appendix M. As seen in Figure 6.38, distinct trends in the ratio of the maximum startup viscosity to the steady state viscosity are also observed in these WLM solutions based on branching level.
Figure 6.38: Ratio of the overshoot (maximum) to steady state viscosity as a function of $Wi$ and branching level. As is observed in entangled polymers, the ratio of the overshoot to steady state viscosity or stress is a signature of solution morphology. The ratio decreases with branching, suggesting branching mitigates breakage upon startup.

In Figure 6.38, the ratio of the startup viscosity (or stress) to the steady state value is the largest in the case of low branching at low Weissenberg numbers. This overshoot behavior is slowly mitigated with the introduction of branching in the WLMs. The stress overshoot in WLM solutions corresponds to elastic phenomena and micellar breakage that may lead to shear banding [4, 5]. If this ratio is mitigated by branching, less breakage is occurring in the branched systems, which may hinder shear banding. The reduction in breakage may stem from several factors. In very branched and network-like systems, like in the 0.25% wt NaTos solution, branching may physically prevent breakage due to the presence of interconnections. In polymers, branching can mitigate the stress overshoot for these reasons [41], so it is not unreasonable to suggest a similar phenomenon here. Additionally, sliding branch points may prevent breakage as well. Under shear startup, if a branch point can slide to reduce stress as opposed to breaking, the resistance to flow will be lower and the stress and viscosity overshoot will be mitigated. The reduction in breakage is also supported by orthogonal superposition measurements, which are shown in Appendix K. The OSP measurements show a slower decrease of the WLM relaxation time with branching for equivalent
6.11 Conclusions

In this chapter, the investigations into the non-equilibrium, steady shear properties of mixed cationic and anionic wormlike micellar solutions discussed in Chapter 5 were continued by including time-dependent measurements of the stress and microstructure upon shear startup. Specifically, in this chapter the shear banding and shear thinning phenomena identified in Chapter 5 based on branching level were examined further to understand how the flow behavior evolves in time. To do this, shear startup rheology was performed for long times to detect signatures of shear banding. Startup flow-SANS measurements in two shear planes complement the rheological results. In Chapter 5, the mechanism of flow alignment was shown to differ between the low and mildly branched solutions, suggesting a different mechanism of shear banding. One goal of this chapter was to identify and understand the different mechanisms of shear banding between the low and mildly branched solutions using the time-dependent startup responses. Using a combination of rheology, particle tracking velocimetry (PTV), and flow-SANS, distinct shear banding mechanisms are identified between the solutions. These differences are a result of wall slip and elastic instabilities, which are amplified in the low branching solution based on the high solution elasticity (Equation 5.10).

At all shear rates measured with 1-2 plane SANS and PTV, the low branching solution exhibits a three band structure. In this form of shear banding, the lowest shear rate is observed in the middle band, whereas a higher shear rate is observed closer to the outer wall. Using the 1-2 plane SANS measurements as a proxy for time-dependent PTV measurements, a ‘disentangle, re-entangle, re-align’ mechanism of shear banding is proposed. The time-dependent, 1-2 plane $A_f$ is shown to be a good substitute for PTV, when the technique is not available. Conversely, the mildly branched solution exhibits two shear bands at all times and follows the disentangle, re-entangle mechanism [2, 3, 14]. Wall slip and
elastic instabilities often lead to distinct shear banding behavior versus when no wall slip is present [6–10]. The resulting three band structure in the low branching solution is the result of such behavior, as wall slip was confirmed with PTV measurements. The elasticity number is an order of magnitude larger in the low branching versus mildly branched solution, which magnifies these elastically-driven phenomena. Further, the majority of the measurements on the low branching solution are taken at significantly higher Weissenberg numbers than in the mildly branched solution, where significant effects from elastic turbulence are likely (especially near the onset of region III). Separating the effects of branching versus the electrostatic interactions on the observed shear banding mechanism is difficult because the two solution properties are inherently linked. The solution elasticity depends on the zero-shear viscosity and relaxation time, both of which decrease with branching and screened interactions. Screening the electrostatic interactions decreases the relaxation time, but sliding branch points also decrease $\tau_R$. In Chapter 8, recommendations to isolate the effect on shear banding from branching and electrostatics are discussed further.

The startup rheology and SANS results are also used to determine signatures of shear banding and shear thinning. The five stage process described by Hu et al. [2] for shear band formation in WLMs describes the startup behavior of the low and mildly branched solution well, despite the different mechanisms of shear band formation. The main difference in the startup rheology between the two solutions was that the low branching solution exhibits steady state fluctuations in the stress response that are not seen in the mildly branched case. Long transients in the stress response, and in the alignment factor response in both shear planes, indicate the formation of shear bands. The alignment factor response, especially in the 1-2 plane, often shows a longer transient than in the startup stress response. As rheology can only measure the bulk flow properties, the spatially-resolved structural measurements are a better indicator of the true material steady state. These spatially-resolved SANS measurements are more sensitive to small changes in structure that occur near the outer wall of the Couette gap, which may be drowned out in a bulk measurement. Fast transients were observed in the stress and structure responses at all shear rates for the highly branched, shear thinning solution. The startup stress responses for the highly branched solution are distinct
from those observed during shear banding, and are in good agreement with the results for shear thinning solutions identified by Hu et al. [2]. The differences in the startup stress and structure in this solution versus the shear banding solutions persist even when differences in the relaxation times are accounted for. The measurements on the highly branched solution confirm that the absence of a pronounced transient in the structural response is indicative of shear thinning as opposed to shear banding.

Finally, we examine if the ratio of the stress and viscosity overshoot to the steady state values can be used to detect differences in micellar branching. In polymer solutions, chain architecture has a significant impact on the startup response [27, 28], and polymeric branching is known to mitigate the stress overshoot [41]. Similar to polymer solutions, the stress and viscosity overshoot are dampened with branching, on a basis of equal Weissenberg number. We attribute this behavior to branch sliding, which may prevent breakage, and physical interconnections, which can also prevent micellar breakage. As significant breakage leads to shear banding in WLM solutions, it is possible that the smaller degree of breakage upon shear startup helps to prevent shear banding at high branching levels. While nonlinear rheology allows us to identify signatures of shear banding phenomena, it is only with flow-SANS measurements that new structural mechanisms of shear banding are identified based on branching level. The structural indications of shear banding are confirmed with particle tracking velocimetry, and provide more information than can be gained by the velocity profiles alone. Accordingly, the time-dependent 1-2 plane alignment can be used as a substitute for PTV when the method is not available, which will be discussed further in the context of large amplitude oscillatory shear (LAOS) deformations in Chapter 7.
References


Chapter 7

STRUCTURE AND RHEOLOGY: LARGE AMPLITUDE OSCILLATORY SHEAR (LAOS)

7.1 Introduction

In Chapter 6, the transient, non-equilibrium properties of mixed cationic and anionic WLMs were examined to determine signatures of micellar branching and shear banding from shear startup measurements. Chapter 6 was an extension of the steady shear rheological results presented in Chapter 5, where the time-dependent rheology and microstructure of the WLMs under a steady deformation was investigated. In this chapter, these investigations into the time-dependent, non-equilibrium properties of the WLMs continue. Specifically, in this chapter the behavior of the WLMs under oscillatory shear, specifically, large amplitude oscillatory shear (LAOS), is examined. Unlike in steady shear and shear startup, where the applied shear rate is not time-dependent, the applied shear rate in LAOS deformations is continuously changing in time. Furthermore, LAOS involves flow reversals. One goal of this chapter is to determine the WLM response to dynamic deformations such as LAOS, and to then relate the observed dynamic behavior back to the steady shear behavior discussed in Chapter 5. As was the case in Chapters 5 and 6, a combination of rheological and neutron scattering techniques are used to determine both structural and rheological signatures of the WLMs under dynamic LAOS deformations. Another aim of this chapter is to extend the investigations into shear banding and shear thinning discussed in Chapter 6 to time-dependent deformations such as LAOS. Shear banding under LAOS deformations is predicted, but has limited experimental verification.

In this chapter, the rheological properties under LAOS are explored as a function of added salt for three solutions: the low (0.01% wt NaTos), mild (0.05% wt NaTos), and highly branched (0.10% wt NaTos) solutions. As the most significant results pertain to the mildly
branched solution, these results are presented first, followed by the low branching solution, and finally the highly branched solution. As shear banding is observed in the low and mildly branched solutions under steady deformations, we address the possibility of shear band formation under LAOS for these two solutions. In the highly branched solution, we seek to confirm that the shear thinning behavior observed under steady shear is also observed under LAOS. As was done in Chapters 5 and 6, flow-small angle neutron scattering measurements are taken in two shear planes, the 1-3 (flow-vorticity) and 1-2 (flow-gradient) planes, under LAOS deformations to complement the measured rheology. The 1-3 plane measurements give insight to the gap-averaged structure under shear, and can detect the phase of the time-dependent alignment factor response under LAOS. These measurements also help to determine how the average degree of micellar orientation is affected by changing the frequency and amplitude of the LAOS deformation. The 1-2 plane measurements provide spatial resolution that enables the determination of shear thinning versus shear banding phenomena in the WLMs. In contrast to steady shear, under LAOS there are no clear rheological signatures of shear banding; therefore, 1-2 plane SANS measurements are one of the only currently available methods to determine whether shear banding under LAOS occurs. Results presented for the mildly branched solution are published in reference [1]; other parts of this chapter are published in reference [2].

7.2 Background

The natural extension for investigations into wormlike micelle (WLM) rheology and microstructure is to move from steady and step transient deformations to time-periodic measurements in the nonlinear regime, such as large amplitude oscillatory shear (LAOS). In oscillatory shear deformations, illustrated in Figure 7.1a, the applied strain, $\gamma$, is sinusoidal and the applied strain rate, $\dot{\gamma}$, is co-sinusoidal, as given by Equations 2.1 and 2.2 in Chapter 2. Oscillatory shear experiments in WLMs allow for the separation of elastic and viscous contributions to the stress response by systematically varying the frequency and amplitude of the applied deformation. At sufficiently small strain amplitudes, the resulting stress response, $\sigma$, is sinusoidal in time and the material response is said to be within the linear viscoelastic
regime (LVE), given by Equation J.1.

An example of a classical elastic, viscous and viscoelastic response can be seen in Figure 7.1a. The stress response of a purely viscous (Newtonian) fluid is in phase with the applied strain rate, as governed by Newton’s Law:

$$\sigma = \eta \dot{\gamma} \quad \text{or} \quad \sigma(t) = \eta \dot{\gamma}(t)$$

(7.1)

where $\eta$ is the viscosity, and the response of a pure elastic (Hookean) solid is in phase with the applied strain, as given by Hooke’s Law:

$$\sigma = G\gamma \quad \text{or} \quad \sigma(t) = G\gamma(t)$$

(7.2)

where $G$ is the modulus.

While these responses are often examined in the time domain, they can also be examined in the deformation domain, where the stress response is examined as a function of either the strain or the shear rate. In the deformation domain (Figure 7.1b), this translates to a straight line in the elastic projection of the 3-D Lissajous-Bowditch diagram (top) for an elastic solid (Equation 7.2), and a straight line in the viscous projection (bottom) for a viscous fluid (Equation 7.1). A viscoelastic fluid displays an elliptical response. Reviews of experimental methods and analysis for LAOS provide detailed information [3,4].

LAOS responses can be categorized by the dimensionless groups applicable to the solution. The Deborah number ($De = \tau_R \omega$) and Weissenberg number ($Wi = \tau_R \dot{\gamma}$) are the dimensionless frequency and shear rate that characterize the applied oscillation, respectively, where $\tau_R$ is the material relaxation time. Under LAOS, the stress response is time-periodic, but no longer sinusoidal. However, aspects of this analysis may still be used to interpret LAOS microstructural responses, as seen in Figure 7.1c. Here, at a high Deborah number (top), the alignment factor of the WLM solution throughout the oscillation is in phase with the magnitude of the applied strain and has a similar shape, indicating elastic-like behavior. Conversely, at a much lower Deborah number (bottom), the alignment factor phase and
shape are similar to the magnitude of the applied strain rate, indicating fluid-like behavior. The ideas presented in Figure 7.1b and 7.1c have been used along with other methods to interpret the stress and microstructure response of WLMs under LAOS, which will be discussed below.

Figure 7.1: Oscillatory shear applied deformations and analysis. a) The applied strain and strain rate are sinusoidal and co-sinusoidal in time (top), and the resulting linear regime stress responses in time (bottom). A response in phase with the strain is a classical elastic response, and with the rate is a viscous response; phase shifted responses are viscoelastic. b) Elastic (top) and viscous (bottom) Lissajous-Bowditch curves of the linear stress responses, where the stress is analyzed in terms of the strain and the strain rate. The linear responses represent classical elastic (top) and viscous (bottom) behaviors. c) Microstructure or alignment factor responses that display elastic (top) and viscous (bottom) behavior through the oscillation. In each case, the alignment factor closely follows the phase and shape of the magnitude of the applied deformation, as $A_f$ is a positive scalar quantity. In this WLM solution, the $A_f$ response is elastic at high $De$ and viscous at low $De$ for the same maximum shear rate, as is expected.
7.3 Shear banding under LAOS

The majority of the experimental work surrounding shear banding has focused on shear banding under steady shear flow (see Chapters 5, 6), which includes the majority of flow-small angle neutron scattering (flow-SANS) work [5–8]. Shear banding and related flow instabilities have been widely predicted under dynamic flows such as large amplitude oscillatory shear (LAOS) [9–12], which will be discussed further in section 7.4 below. Constitutive models have been used to identify Deborah number and Weissenberg number conditions for transient or steady shear banding in concentric-cylinder Couette flow during LAOS [9, 10]. Other works have suggested shear banding or similar instabilities under LAOS by showing that a material may act simultaneously as a fluid and elastic solid during LAOS, depending on the gap position [11,12].

Recent experiments have probed LAOS conditions where shear banding may occur; however, experimental verification of shear banding under LAOS is limited. In entangled polymer solutions, shear banding was observed under high frequency deformations for several Deborah numbers greater than one [13–15]. However, these results were debated by Li et al. [16], who used the same solutions to show that significant edge effects may have induced the shear banding. In other studies on wormlike micelles under LAOS, shear banding was concluded at low Deborah and Weissenberg numbers at the onset of non-linearity [17]. In all of these works, rheo-PTV was used to confirm shear banding using a cone and plate geometry. The model predictions of Adams and Olmsted [9] and Zhou et al. [10] are for concentric-cylinder Couette flow, and this difference in geometry from the experimental works may have a significant effect on the flow behavior and shear banding. To date, experimental work examining shear banding under LAOS in a concentric-cylinder Couette geometry is limited. Additionally, the previously cited works have only examined two regimes: high frequency (high De) or low frequency, low shear rate (low De and Wi). Thus the higher Weissenberg number conditions where shear banding may be present, as predicted by Zhou et al. [10], have not been verified, nor has any work used a method other than rheo-PTV to identify dynamic shear banding.

Lastly, recent experimental work by Gurnon et al. [18] examining WLMs under
LAOS was unable to verify the predictions of the Vasquez-Cook-McKinley (VCM) model used by Zhou et al. [10]. Surprisingly, Gurnon et al. [18] did not observe shear banding at any condition, but rather were able to access metastable homogeneous states conceptually predicted by the constitutive equation. Specifically, in the condition predicted to show LAOS shear banding by the VCM model ($De = 2.3$ and $Wi = 23$), the alignment factor was greater than the critical value for shear banding [5,6] at nearly every time point within the oscillation at both positions. The changes in alignment between the inner and outer wall were minor, indicative of shear thinning in region III. The differences in the underlying flow curves between the VCM model test solution and the experimental WLM solution are likely the cause of this discrepancy, as the solution used by Gurnon et al. [18] also did not show shear banding under steady shear at $Wi = 23$. In the other two conditions, the alignment factor was always below the critical condition throughout the oscillation, confirming the absence of shear banding during LAOS despite these conditions showing shear banding under steady shear. These latter conditions, in conjunction with the VCM model predictions, suggest that the presence of LAOS shear banding is dependent on the applied frequency and amplitude. Gurnon et al. [18] also used the stress-SANS rule to reconstruct the stress from the alignment factor in each condition. The stress reconstruction yielded favorable results to the measured stress for the majority of the oscillation cycle at low Weissenberg numbers; however, the stress reconstruction at the highest Weissenberg number showed significant deviations. Consistent with the results for steady shear at the corresponding maximum dynamic shear rate, a shear-rate dependent stress-SANS coefficient that was an order of magnitude larger than calculated at low $Wi$ was required to give reasonable results. Again, complementary rheo-light scattering results demonstrated longer length scale fluctuations were evident at the highest stress states, which corresponded to length scales not probed by SANS. Gurnon et al. [18] concluded that LAOS deformation enabled the exploration of metastable states of homogeneous flow that were inaccessible under steady shear where shear banding occurs.
7.4 Model predictions of shear banding under LAOS

While significant theoretical work has been dedicated to steady shear banding, modeling efforts to predict shear banding under large amplitude oscillatory shear have been limited. Adams and Olmsted [9] used the Rolie-Poly (RP) model with a convected constraint release (CCR) term, and predicted $De$ and $Wi$ values where inhomogeneous and homogeneous flow were expected under LAOS in the range of $1 \leq De \leq 100$ and $5 \leq Wi \leq 100$. Similar work by Carter et al. [19] and Fielding [20] predicted shear banding under LAOS for fluids with non-monotonic and monotonic underlying constitutive equations using the RP model with a CCR term. However, in this model, shear banding is predicted up to infinite shear rates under LAOS given a small applied frequency. Carter et al. [19] also extended the work of Moorcroft and Fielding [21] to show that stress overshoots in the LAOS response may lead to transient banding. Finally, Zhou et al. [10] used the Vasquez-Cook-McKinley (VCM) model to predict shear banding under LAOS with specific model parameters, and compared their results with a simpler, limiting case of the model. Unlike the RP model that attributes shear banding to flow-induced micellar alignment [22], the VCM model explicitly accounts for micellar breakage that leads to shear banding [23,24]. Using this breakage term solves the low frequency issues in the RP model [19, 20], and shear banding under LAOS is only predicted at shear rates that exhibit shear banding under steady shear. Zhou et al. [10] examined a broad range of $De$, $Wi$, and critical strain ($\gamma_{0,c}$) conditions and identified where shear banding may occur covering the range $0.1 \leq De \leq 25$, $0.1 \leq Wi \leq 500$ and $1 \leq \gamma_{0,c} \leq 1000$, yielding similar results for both cases of the model. Recent modeling work by Germann et al. [25] connects much of the observed behavior under LAOS to a model that explicitly includes shear-induced micellar breakage. The model predictions of Adams and Olmsted [9] and Zhou et al. [10] assumed concentric-cylinder Couette flow, thus 1-2 plane shear cell measurements of WLMs under LAOS provide a more useful comparison with these theoretical results than the cone and plate measurements.
7.5 **Large amplitude oscillatory shear: mildly branched solution**

Large amplitude oscillatory shear experiments for the mildly branched solution are presented below. As this solution is known to exhibit shear banding under steady shear deformation, it is reasonable to believe that shear banding could be observed under LAOS for select applied frequencies and strain amplitudes, despite the limited experimental verification. The LAOS conditions discussed in this section are chosen based on modeling predictions of LAOS shear banding, and results are then compared back to modeling efforts described in Section 7.4. These results are published in reference [1].

7.5.1 **Vasquez-Cook-McKinley (VCM) model and mildly branched solution**

As mentioned in Section 7.4 above, the Vasquez-Cook-McKinley model is designed specifically for entangled wormlike micelles that can break and recombine [10, 24, 26]. The widely used Rolie-Poly model was initially developed to model linear entangled polymers, and does not account for breakage and recombination events that can occur in WLMs. Based on all of the models mentioned in Section 7.4 that predict shear banding under LAOS, the VCM model is the most reasonable to use when examining shear banding in the WLM solutions used in this work. The VCM model is self-consistently derived from kinetic network theory [24], and accurately captures the coupling between the microstructure and the macroscopic flow behavior [10]. The model explicitly accounts for breakage and reformation events that can lead to shear banding by the use of two species: long, entangled chains and short chains. The one concern of the VCM model is that the model is not thermodynamically consistent; however, recent work correcting this deficiency shows that the VCM model yields reasonable predictions for the LAOS flows of concern here [25].

In the work of Zhou *et al.* [10], a flow curve for a model fluid was published which accompanied the predictions of shear banding under LAOS. As discussed in Chapter 5, the mildly branched solution was chosen as a model sample to test the VCM model predictions of shear banding under LAOS due to the similarities between the experimental flow curve and the model flow curve. A comparison of these flow curves can be seen in Chapter 5, Figure 5.12. As mentioned above, experimental works that have attempted to identify shear banding
under LAOS have only probed two regimes: high frequency ($De > 1$), and low frequency, low shear rate (low $De$ and $Wi$). As higher Weissenberg number conditions predicted to shear band by Zhou et al. [10] have not been experimentally verified, we focus on high $Wi$ in this study. Several of the LAOS experiments presented in this chapter are performed at the same dimensionless shear rate, $Wi = 75$. In Figure 5.12, $Wi = 75$, is highlighted for reference.

### 7.5.2 Revisiting linear viscoelastic regime (LVE) rheology

To determine the appropriate Deborah and Weissenberg numbers for the LAOS experiments, we revisit the linear rheology of the mildly branched solution to determine characteristic time scales. As the level of branching at this salt concentration (0.05% wt NaTos) is mild, the linear viscoelastic data was fit with the Oldroyd-B model, where $G''$ is augmented with a high rate viscosity to account for Rouse modes at higher frequencies. As seen in Figure 7.2, the results compare favorably with the model, indicating that mild branching does not significantly affect the LVE behavior.

![Figure 7.2: Dynamic moduli $G'$ (□) and $G''$ (△) of the 0.05% wt NaTos WLM solution. The Oldroyd-B model fit is shown by solid line. The two Deborah numbers that will be examined by LAOS section are highlighted in red ($De = 0.17$, $\omega = 0.1 \text{ rad} \cdot \text{s}^{-1}$) and blue ($De = 0.58$, $\omega = 0.35 \text{ rad} \cdot \text{s}^{-1}$).](image)

---

371
The largest deviations are seen in high frequencies: a true plateau modulus, $G_N^0$, is not achieved as $G'$ displays a mild slope, and the location of $G''_{min}$ is incorrectly predicted. Deviations at low frequency are also seen in $G'$. As LAOS shear banding has been previously studied in entangled polymers at $De > 1$, we focus on $De < 1$. The frequencies $De = 0.17$ and $De = 0.58$ are highlighted, where the primary LAOS experiments were performed. Using the LVE data, the crossover frequency, $\omega_c = 0.6 \text{ rad} \cdot \text{s}^{-1}$, resulting in $\tau_R = 1.7 \text{ s}$. For reference, Table 4.2 provides an estimate of the average length and time scales of the solution and uncertainties for multiple sample preparations, determined from rheology, SANS, and model fits [27–32]. The value of the persistence length, $l_p$, was determined by Schubert et al. [32] via flow-birefringence measurements for the sample prepared in water, which should be comparable to that of the current system prepared in D$_2$O [33].

7.5.3 LAOS rheology

LAOS measurements were performed at many Deborah and Weissenberg number combinations; select results are shown in the Pipkin diagram of the elastic Lissajous-Bowditch curves ($\sigma$ vs. $\gamma$) in Figure 7.3 (top) and viscous Lissajous-Bowditch curves ($\sigma$ vs. $\dot{\gamma}$) in Figure 7.3 (bottom). We focus on $0.17 \leq De \leq 0.75$ and $64 \leq Wi \leq 113$, where the shapes of the elastic and viscous Lissajous-Bowditch projections are fairly similar. The stress responses share many of the same features, including stress overshoots that lead to secondary loops in the viscous Lissajous-Bowditch projections, followed by local stress undershoots and secondary overshoots. While it is difficult to tell from the Pipkin diagrams, many of the LAOS stress overshoots and undershoots are similar to those observed in the stress response to shear startup [8, 34]. The elastic Pipkin diagram shows that with increasing $De$ at constant $Wi$, the stress overshoot gradually disappears. This overshoot is an indication of micellar breakage, which often leads to shear banding [21]. We postulate that at sufficiently high frequencies, shear banding will cease or a non-breakage shear banding mechanism will occur, in agreement with the predictions of Zhou et al. [10]. However, as the stress responses within our range share qualitatively similar features, the possibility of shear banding during LAOS is difficult to determine from the shear stress alone. See Appendix N for a direct
comparison of LAOS conditions, and Chapter 2 for reproducibility studies (Section 2.6.4), and the uncertainty associated with the features (Section 2.3.4).

The portions of the Pipkin diagram corresponding to the primary SANS experiments are highlighted in Figure 7.3 (condition one: $De = 0.17$, $Wi = 75$; condition two: $De = 0.58$, $Wi = 75$), where a large stress overshoot is observed in both cases. A comparison of the stress responses for each condition can be seen in Figure 7.4. The overshoot appears more pronounced when $De = 0.17$; however, the magnitude of the stress overshoot (maximum stress during the cycle) is smaller at this condition ($23.2 \pm 0.2$ vs. $28.6 \pm 0.2$ Pa). The other major difference between the curves is accentuated in the elastic Pipkin diagram (Figure 7.4). At $De = 0.17$, the stress response after the overshoot appears relatively constant and is nearly flat with decreasing strain, whereas at $De = 0.58$, the stress is continuously evolving. Finally, the stress response at $De = 0.17$, $Wi = 75$ is nearly in phase with the applied shear rate, indicating that the response is primarily shear rate-dependent. At $De = 0.58$, $Wi = 75$, the stress response is also primarily shear rate-dependent but shows a slight phase shift. This phase shift indicates that the stress response is more elastically-dominated than in the first condition, leading to a larger stress overshoot. These features are not surprising, as the frequency is three-fold that of the first condition, and the LVE elastic modulus at this frequency is an order of magnitude larger than that of the first condition.

The dominant stress overshoot at both conditions gives credence to the ‘sequence of physical processes’ approach of Rogers and co-workers for analyzing LAOS, as the cycle is dominated by fluid-like behavior in both conditions when $De < 1$, but also contains elastic contributions [4,35–37]. These classical behaviors are outlined in Figure 7.4 for conditions one and two, where the red portions of the curve correspond to elastic-like behavior, and the blue portions of the curves correspond to fluid-like behavior. As seen in Figure 7.4, the stress overshoot represents purely elastic behavior as observed by the linear response in the stress versus strain curve in the overshoot region, which is governed by Hooke’s Law (Equation 7.2). The offset from the origin in the LAOS curves represents the strain from equilibrium [37], which is similar to behavior observed in the Bingham model [36]. From the stress overshoot region, a local modulus and yield strain for each condition can be calculated [35].
Figure 7.3: Pipkin diagrams of the Lissajous-Bowditch projections: (top) Elastic ($\sigma(t)$ vs $\gamma(t)$) and (bottom) viscous ($\sigma(t)$ vs $\dot{\gamma}(t)$). The bolded red and blue spectra correspond to the conditions explored using flow-SANS.
Figure 7.4: Lissajous-Bowditch projections of the LAOS stress response for (a) condition one ($De = 0.17$, $Wi = 75$), and (b) condition two ($De = 0.58$, $Wi = 75$). Red outlined portions of the curves denote elastic-like behavior, where a linear relationship in $\sigma$ vs. $\gamma$ is observed. The micelles break and yield after this stress overshoot. Blue outlined curves denote fluid-like behavior, where a linear relationship in $\sigma$ vs. $\dot{\gamma}$ is observed, indicating viscous flow after micelle breakage. While the classic elastic and viscous behaviors are observed in both conditions, the behaviors are more pronounced in condition one.
After the stress overshoot, a linear portion of the stress versus the shear rate curve is observed indicating viscous flow, as governed by Newton’s Law (Equation 7.1). Therefore, the presence of the stress overshoot can be interpreted as an elastic type of yielding, after which the micelles break and flow. While both conditions exhibit the classic elastic- and fluid-like phenomena during the course of the oscillation cycle, these behaviors are more pronounced in condition one. However, the presence of stress overshoots may lead to transient and steady state shear banding in polymers and WLMs due to breakage [21]; thus we anticipate that the more prominent overshoot, and thereby higher degree of breakage, when $De = 0.58$ should lead to more pronounced shear banding.

### 7.5.4 LAOS 1-2 plane flow-SANS

#### 7.5.4.1 Design of experiments

Seven experimental conditions were chosen to test the VCM model predictions [10]: five within the predicted shear banding regime and two outside of the predicting shear banding regime. While the specific parameters used in their work differ from our conditions, the flow curves are similar (Figure 5.12). Our experimental LAOS conditions are compared to the VCM model predictions in Figure 7.5. Five of the seven conditions are predicted to shear band under LAOS, and six of the seven displayed steady shear banding at equivalent shear rates. Two primary conditions were explored in great detail ($De = 0.17$, $Wi = 75$ and $De = 0.58$, $Wi = 75$) using five gap positions, while the remaining five conditions were examined at two gap positions. The additional experiments were performed on conditions ranging between $0.17 \leq De \leq 0.75$ and $64 \leq Wi \leq 113$, where the alignment factor was examined as a function of gap position, $r/H$, and normalized cycle time, $t/T$. The map of these conditions can be seen in Figure 7.5 below. For all conditions, when $t/T = 0$ and $0.5$, the applied strain is zero ($\gamma = 0$) and the magnitude of the shear rate, $|\dot{\gamma}|$, is at a maximum. Conversely, when $t/T = 0.25$ and $0.75$, $\dot{\gamma} = 0$ and $|\gamma|$ is at a maximum. As the alignment factor measures the degree of micellar alignment, which is independent of shear direction, we compare the alignment with the magnitude of the strain or shear rate when analyzing SANS results. Additional
details on the reproducibility of these results can be seen in Chapter 2, Section 2.6.4. These conditions are summarized in Table 7.1.

![Figure 7.5: Comparison of experimental LAOS conditions with VCM model predictions (open circles). Equal strain amplitudes are shown by color, Wi by symbol, and De by open/closed symbols. All but two conditions are predicted to shear band under LAOS. Alignment banding is observed for conditions marked by □. VCM predictions are digitized from [10].](image)

Table 7.1: LAOS conditions and parameters for the 0.05% wt NaTos solution.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>De, Wi</th>
<th>ω, rad·s⁻¹</th>
<th>γ₀</th>
<th>γ₀, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.17, 75</td>
<td>0.1</td>
<td>450</td>
<td>45</td>
</tr>
<tr>
<td>2</td>
<td>0.58, 75</td>
<td>0.35</td>
<td>128.5</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>0.33, 75</td>
<td>0.2</td>
<td>225</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>0.50, 64</td>
<td>0.3</td>
<td>128.5</td>
<td>38.6</td>
</tr>
<tr>
<td>5</td>
<td>0.50, 113</td>
<td>0.3</td>
<td>225</td>
<td>67.5</td>
</tr>
<tr>
<td>6</td>
<td>0.67, 85</td>
<td>0.4</td>
<td>128.5</td>
<td>51.4</td>
</tr>
<tr>
<td>7</td>
<td>0.75, 96</td>
<td>0.45</td>
<td>128.5</td>
<td>57.8</td>
</tr>
</tbody>
</table>

7.5.4.2 Primary experiments: De = 0.17, Wi = 75 and De = 0.58, Wi = 75

The primary LAOS conditions, De = 0.17, Wi = 75 and De = 0.58, Wi = 75, have the same shear rate amplitude so the impact of frequency on shear banding could be investigated. In these two conditions (as well as De = 0.33, Wi = 75), the increase in frequency results in a
decrease in the strain amplitude $\gamma_0$ to hold the Weissenberg number amplitude ($Wi_0 = \gamma_0 \omega$) constant at 75. In latter experiments, the strain amplitude $\gamma_0$ was held constant while the frequency was increased, thereby increasing the maximum shear rate, $Wi_0$. In the final two experiments, the frequency was held constant, while the strain amplitude and thereby shear rate were increased. The results from the two primary conditions can be seen below, where $De = 0.17, Wi = 75$ is referred to as ‘condition 1’ and $De = 0.58, Wi = 75$ is referred to as ‘condition 2.’

7.5.4.3 LAOS Condition 1, $De = 0.17, Wi = 75$

In condition one, the sample is expected to exhibit primarily fluid-like behavior throughout the oscillation as $De \ll 1$. Figure 7.6(a) shows the spatially-dependent alignment factor during the LAOS cycle, where the shape and phase of the response at all gap positions mirrors the magnitude of the applied shear rate. The alignment is at a maximum at the maximum shear rate ($t/T = 0, 0.5$). A comparison of the alignment and the stress response can be seen in Figure 7.10, where both responses are nearly in phase with the applied shear rate, indicating predominantly viscous behavior through the cycle. Interestingly, the alignment does not appear to be influenced by the applied strain despite the large stress overshoot in the rheology, and shows no response to this stress overshoot (Figure 7.10). We note that structural changes in the stress overshoot region may occur on larger length scales than accessible by SANS, thus we limit our comparison of the shear-induced structures under LAOS to segmental alignment. Larger-scale structural rearrangements can be detected via rheo-SALS and may result from shear-induced de-mixing [18,34].

As seen in Figure 7.6(a), the alignment factor decreases rapidly and monotonically as a function of gap position at all times, which is highlighted during specific portions of the cycle in Figure 7.6(b). The minimum alignment occurs roughly at times of zero shear rate and maximum strain, which further indicates that the material does not respond to the applied strain on the segment length scale at this condition. The profiles in Figure 7.6(b) indicate LAOS shear banding, as the outer wall alignment at multiple $t/T$ is significantly lower than the inner wall alignment, and is below the steady shear critical value of $A_f^* =$
Figure 7.6: (a) 1-2 plane $A_f$ as a function of cycle time, $t/T$, and gap position, $r/H$, at $De = 0.17$, $Wi = 75$. The shape and time-dependence of $A_f$ closely tracks that of $|\dot{\gamma}|$. (b) 1-2 $A_f$ as a function of gap position at select $t/T$ as indicated in (a). The alignment factor as a function of gap position decreases significantly when $A_f > 0$, leading to a similar mechanism of shear banding as is observed under steady shear.

0.18. This trend in the alignment is fairly insensitive to $t/T$, showing the persistence of the shear banded state through the cycle. The steady decrease in the alignment factor with gap position is similar to the steady shear trends near the end of region II, $Wi \geq 63$. Further into region II ($Wi < 63$), the alignment decreases more significantly and discontinuously near the shear band interface. Thus, shear banding at this LAOS condition is similar to steady shear banding between $Wi = 63$ and 75 (see Discussion, Section 7.6).

The evolution of the orientation angle during the cycle, which can be seen in Figure 7.7, also supports the interpretation of shear banding. The change in sign in the orientation angle corresponds to the reversal of the flow direction during LAOS. As was the case for the steady shear data, the value of $\phi_0$ near the inner wall is similar between positions, whereas the orientation angle near the outer wall is significantly lower. As seen in Figure 7.7, the orientation angle at the inner three gap positions ($r/H = 0.15, 0.35, 0.5$) is similar and clustered together throughout the oscillation cycle, which we interpret as the high shear rate band. The material in the outer two gap positions ($r/H = 0.65, 0.85$) is significantly less
oriented, forming the low shear rate band. While the material in the low shear rate band under LAOS is slightly more oriented than under steady shear, there is still a significant change in orientation angle between the high and low rate bands.

![Figure 7.7: Orientation angle, $\phi_0$, as a function of cycle time, $t/T$, and gap position, $r/H$, at $De = 0.17$, $Wi = 75$. Based on $\phi_0$, the three inner positions ($r/H = 0.15, 0.35, 0.5$) appear to cluster together to form the high shear rate band, whereas $r/H = 0.65, 0.85$ form the low shear rate band.](image)

7.5.4.4 LAOS Condition 2, $De = 0.58$, $Wi = 75$

As condition two is at a higher frequency than condition one, the sample is expected to show signatures of both viscous and elastic-like behavior during the cycle. The 1-2 plane alignment can be seen in Figure 7.8(a), where local extrema are observed as a function of time at all gap positions. Similar to condition one, the segmental alignment at all gap positions is in phase with the measured stress response (Figure 7.10), and is primarily in phase with the applied shear rate. However, in contrast to condition one, at this higher frequency, significant overshoot behavior is evident in the alignment factor after the shearing direction is reversed ($\dot{\gamma} = 0$ at $t/T = 0.25, 0.75$). The local extrema in the alignment factor response are reflective of the local curvature changes in the stress response at this condition (Figure 7.10). While the stress response exhibits a large stress overshoot and local curvature
changes in time that resemble secondary undershoots and overshoots, a true undershoot and secondary overshoot are not observed as seen in condition one (Figure 7.10).

Figure 7.8: (a) 1-2 plane $A_f$ at $De = 0.58$, $Wi = 75$. At all $r/H$, $A_f$ is in phase with the stress response and roughly in phase with $|\dot{\gamma}|$. As the shape of $A_f$ contains local extrema, $A_f$ is a function of both $|\gamma|$ and $|\dot{\gamma}|$. (b) 1-2 plane $A_f$ at select $t/T$ indicated in (a). $A_f$ is more discontinuous across the gap than in condition one, indicating shear banding that is also fairly independent of $t/T$.

The alignment factor is not at a global maximum when $t/T \approx 0$ and 0.5 in this condition, but is instead at a local maximum. The maximum alignment factor is observed when $t/T \approx 0.36$, the location of the stress overshoot (Figure 7.10). Even though $De < 1$, this relationship between the structure and the stress overshoot (and thereby the applied strain) shows that during portions of the cycle, the applied strain and the elastic-like properties of the material are predominant contributions to the shear-induced structure. Similar to condition one, the alignment in Figure 7.8(b) decreases monotonically as a function of gap position; however, when $r/H \leq 0.5$, the material forms a distinct, highly aligned band, and for $r/H > 0.5$, another clear alignment band is discernible (Figure 7.8(b)). Between $r/H = 0.5$ and 0.65, there is a distinct drop in the magnitude of the alignment between bands, which is similar to the drop in alignment in the steady shear banding regime (region II). This discontinuity indicates the presence of dynamic shear bands and the location of the shear band interface,
which will be explored further in the Discussion, Section 7.6. These discontinuous alignment trends are fairly independent of $t/T$, again indicating the persistence of shear banded structure through the cycle.

As was the case in condition one, the orientation angle during the cycle in condition two also supports the interpretation of shear banding, which can be seen in Figure 7.9. Once again, the orientation angle near the inner wall forms a cluster of similar values throughout all time points in the cycle. The high shear rate band is interpreted as the inner three gap positions, $r/H = 0.15, 0.35, 0.5$. Interestingly, in Figure 7.9, the orientation angle at these three inner positions is nearly identical throughout the cycle, indicating that the fluid behaves very similarly at all three positions. This result is not surprising considering that the alignment for these three positions is closer in magnitude than in condition one, forming a clear high shear rate alignment band. In the low shear rate band ($r/H = 0.65, 0.85$), the orientation angle is significantly lower. The material in the outer two gap positions is less oriented, and the values of $\phi_0$ during the cycle also appear to cluster together, unlike in the low shear rate band in condition one. Again, this result is not surprising given the similar magnitude of the alignment factors at these two gap positions. These differences in the orientation angle between condition one and two seem to reflect the different mechanisms of alignment that are observed during each cycle.

### 7.5.4.5 Comparison of LAOS results between conditions 1 and 2

Both conditions one and two appear to exhibit LAOS shear banding, in line with the VCM model predictions [10]. A comparison of the alignment and shear stress for both conditions can be seen in Figure 7.10. The condition one maximum alignment is observed at the maximum shear rate ($t/T \approx 0.5$). As $De \ll 1$, this result is not surprising; however, the maximum stress occurs when $t/T = 0.31$. This discrepancy is interesting, as the stress-SANS rule directly relates segmental alignment and angle ($1-2 A_f, \phi_0$) and the polymeric stress, $\sigma_{12,p}$ [6]. In this solution, the segments are nearly flow aligned such that the angle of alignment cannot be well-resolved from the 1-2 plane LAOS data. In condition two, the maximum alignment coincides with the maximum stress, suggesting an elastic-like response.
Figure 7.9: Orientation angle, $\phi_0$, as a function of $t/T$ and $r/H$ at $De = 0.58$, $Wi = 75$. As in condition one, the three inner positions appear to form the high shear rate band, whereas the outer two form the low shear rate band.

upon flow reversal during the LAOS cycle. This behavior precedes viscous alignment behavior, where a local alignment maximum is observed at the maximum shear rate, which is similar to that observed at lower frequency in condition one. The local alignment maximum also corresponds with an inflection point in the stress response.

In condition two, where the alignment factor shows an undershoot and secondary overshoot, the stress response after the overshoot displays the shoulder-like features described by [34] for shear startup leading to steady state shear banding. The shape of the alignment factor is simple in condition one due to the dominance of fluid-like behavior during the cycle and long cycle time; whereas the shape of the alignment becomes more complicated for condition two, where the frequency is over three times greater, leading to a faster cycle time and a more dominant role of the material elasticity. This is further exemplified when the LAOS stress at $Wi = 75$ is compared to the steady shear stress in these conditions. In condition one, the LAOS stress is lower than the steady shear stress, as the long period allows the material to relax throughout the cycle. In condition two, the faster cycle time leads to incomplete material relaxation, and thus a higher LAOS stress than steady shear stress at $Wi = 75$. The higher average stress throughout the cycle in condition two ultimately leads to
a higher average 1-2 plane alignment factor during the cycle.

7.5.4.6 Comparison of LAOS results with steady shear

To further analyze the shear banding under LAOS, the alignment in both conditions was compared to the steady shear alignment. In Figure 7.11, the 1-2 plane alignment factor is shown for all conditions when $Wi = 75$ ($t/T = 0.5$ for LAOS conditions). In condition one ($De = 0.17$, $Wi = 75$), the alignment is slightly less than or equal to the steady shear alignment at all gap positions. Conversely, the alignment in condition two is significantly greater than the steady shear alignment, referred to as ‘over-orientation’ as previously termed by Rogers et al. [38]. The maximum alignment for condition two ($r/H = 0.36$) exhibits similar trends in over-orientation, and larger degrees of over-orientation are observed at the outer wall than at the inner wall. In condition one, the similarity of the alignment factor profile with the steady shear profile suggests a similar type of shear banding, where a small portion of the material is in the low shear band. The similar behavior is not surprising when the LAOS stress response is analyzed. Between the point of zero stress ($\sigma(t/T) = 0$) and maximum stress ($\sigma_{max}(t/T)$), the elapsed time is nearly $2\tau_R$ ($\Delta t_1 = 3.20$ s, $\tau_R = 1.67$ s), allowing the material to partially relax during this time. The long cycle time ($T = 62.8$ s) leads to a slow increase in the
applied shear rate during the cycle, allowing additional material relaxation. This results in a smaller maximum stress than in condition two (23.2 vs. 28.6 Pa). After the stress overshoot, greater than \(7\tau_R\) elapse before the maximum shear rate is reached, giving the material time to relax to a nearly steady state structure. At \(t/T = 0.5\), the shear stress in the LAOS cycle is less than the steady state stress despite \(Wi = 75\) (Figure 7.10), which leads to the lower LAOS alignment than steady shear alignment observed in Figure 7.11. The alignment profile in condition one shows a more noticeable discontinuity than the steady shear profile, where the largest difference in alignment occurs at \(r/H = 0.65\). The discontinuous profile resembles those when \(Wi < 75\) under steady shear, suggesting that the ‘effective’ LAOS gap-averaged shear rate at \(t/T = 0.5\) is between 64 < \(Wi < 75\).

Figure 7.11: 1-2 plane \(A_f\) at three conditions: \(Wi = 75\) steady shear (□); condition one at \(Wi = 75\) (○); and condition two at \(Wi = 75\) (△). The condition one \(A_F\) is similar, but less than, the steady shear \(A_f\). Condition two exhibits ‘over-orientation,’ where the 1-2 \(A_f\) is always greater than that of steady shear. Over-orientation is more pronounced near the outer wall, in the low shear band.

The significant differences in the alignment factor profile in condition two versus steady shear suggest a different mechanism of LAOS shear banding than seen in condition one. The over-orientation at \(t/T = 0.5\) is nearly identical to the over-orientation at \(t/T = 0.36\) (global maximum), showing the persistence of the shear banded state throughout the
cycle. The large decrease in alignment and clear discontinuity between \( r/H = 0.5 \) and \( r/H = 0.65 \) indicates that the shear band interface lies between these two gap positions, and that the proportion of material within the high shear band is smaller in this condition \((0.5 < \alpha < 0.65)\) than for steady shear \((\alpha \approx 0.75)\). However, as the 1-2 alignment factor is a function of shear rate, the effective shear rate within the low shear band must also be higher at this condition. This fits accordingly with the higher stress observed in this condition versus steady shear at \( Wi = 75 \) (Figure 7.10). For condition two, the elapsed time between zero stress and the maximum stress is on the order of the relaxation time, \( \Delta t_1 = 1.69 \text{ s} \approx \tau_R = 1.67 \text{ s} \). Thus, the material has less time to relax than in condition one, resulting in a larger stress overshoot. After the stress overshoot, \( Wi = 75 \) is reached in \( 1.4\tau_R \), allowing little additional time for structure relaxation. Shear stresses during the cycle that are higher than the steady shear stress \((\sigma = 7.7 \text{ Pa})\) lead to the observed over-orientation at both \( t/T = 0.36 \) \((\sigma = 14 \text{ Pa})\) and \( t/T = 0.5 \) \((\sigma = 11 \text{ Pa})\). Condition two therefore leads to a structural metastable shear banded state that is not accessible under steady shear. The chosen Deborah and Weissenberg numbers allow sufficient material relaxation for shear bands to form, but prevent full structure relaxation, resulting in over-orientation. As the over-orientation is more pronounced at the outer wall, the results support the disentangle re-entangle mechanism of shear banding [8], where the material must relax and re-entangle after startup to form the low shear band. With insufficient time for full relaxation and re-entanglement, the low shear band material is trapped in a metastable state of higher alignment.

The difference in the shear banding behavior between conditions one and two can be further explained when the alignment between the two conditions is directly compared. Figure 7.12 shows the alignment factor as a function of gap position for both conditions, where condition one \((De = 0.17, Wi = 75)\) is shown with solid lines and condition two \((De = 0.58, Wi = 75)\) is shown by data points. In Figure 7.12, the alignment in regions of increasing shear rate magnitude \((0.25 \leq t/T \leq 0.5, 0.75 \leq t/T \leq 1)\) is significantly different between the two conditions, resulting from the differences in cycle time and material relaxation during LAOS. A different trend, however, is observed when the regions of decreasing shear rate magnitude are examined. In these regions \((0 \leq t/T \leq 0.25, 0.5 \leq t/T \leq 0.75)\), the alignment factor
is nearly identical between the two conditions at $r/H = 0.15$, but deviates with increasing $r/H$. This suggests that the material at the outer wall must relax much further than at the inner wall during shear banding, again in line with the ‘disentangle re-entangle’ mechanism of shear banding [8].

Figure 7.12: 1-2 plane $A_f$ as a function of $t/T$ and $r/H$ for both conditions. Condition one ($De = 0.17$, $Wi = 75$) is shown with solid lines whereas condition two ($De = 0.58$, $Wi = 75$) is shown with data points. With decreasing $|\dot{\gamma}|$ ($0 \leq t/T \leq 0.25$, $0.5 \leq t/T \leq 0.75$), $A_f$ is similar between conditions at $r/H = 0.15$ and 0.35. When $r/H \geq 0.5$, the alignment factor deviates, suggesting a different mechanism of shear banding.

When $r/H \geq 0.5$, the magnitude of alignment greatly differs. In fact, the alignment at $r/H = 0.5$ for condition two (upward triangles) is now nearly identical to the alignment of condition one at $r/H = 0.35$. Further, the alignment for condition two at $r/H = 0.65$ (downward triangles) and 0.85 (diamonds) in this region now nearly identically follows the condition one alignment at $r/H = 0.5$ and 0.65, respectively. The different alignment trends between the conditions enable us to identify different mechanisms of shear banding under LAOS, despite qualitatively similar LAOS stress responses. Condition two exhibits more significant shear banding and a metastable structural state, whereas condition one is able to access stresses below those of the measured steady shear flow curve. These results highlight the importance of using spatially-dependent structure measurements, as shear banding
under LAOS could be anticipated from the predictions of Zhou et al. [10], but elucidating the mechanism of shear banding requires knowledge of the spatiotemporally varying local microstructure in the bands.

### 7.5.5 Additional conditions to validate VCM model predictions

Additional flow-SANS experiments under LAOS were performed to determine the effect of frequency and shear rate on LAOS shear banding (Figure 7.5), and to further validate the VCM model predictions [10]. These experiments were performed using a wider slit (0.3 mm) and were taken at only two gap positions ($r/H = 0.25$ and 0.75). A comparison of the Lissajous-Bowditch curves for all conditions can be seen in Appendix N. Figure 7.13 shows the shear stress and 1-2 plane alignment factor for $De = 0.33$, $Wi = 75$, a frequency between conditions one and two. Not surprisingly, the alignment factor is roughly in phase with the shear rate and follows the phase of the stress response. The maximum alignment occurs when $t/T = 0.5$, similar to condition one; however, evidence of the stress overshoot is observed in the alignment factor, where a local maximum is observed at $t/T \approx 0.34$. For comparison purposes, we interpolate the steady shear alignment factor at $r/H = 0.25$ and 0.75 at $Wi = 75$ to be 0.42 and 0.12, respectively. The maximum LAOS alignment is 0.45 and 0.25, respectively. Therefore, over-orientation is minimal at the inner wall, but significant at the outer wall. This result lies between the two initial conditions, and the intermediate deformation frequency gives the material more time to relax during the cycle than in condition two. However, a metastable shear banded state still results because the material cannot relax fully, in line with VCM model predictions (Figure 7.5).

Next, the strain amplitude from condition two was held constant while the frequency was lowered to obtain a shear rate amplitude well within region II ($De = 0.50$, $Wi = 64$). Experiments were also performed at $De = 0.50$, $Wi = 113$ to see if shear banding could be induced in region III. The alignment factor and stress for both conditions are shown in Figure 7.14. The response of the alignment factor is similar between the conditions, and the global maxima in the alignment factor reflect the presence of large stress overshoots in the LAOS stress response. The magnitude of the alignment factor at both gap positions is greater at
Figure 7.13: 1-2 plane $A_f$ and shear stress for $De = 0.33$, $Wi = 75$. The alignment during the oscillation contains features of conditions one and two, including an overshoot and maximum alignment when $t/T = 0.5$.

$Wi = 113$; however, the stress overshoot has a larger magnitude at $Wi = 64$. With only two gap positions, it is difficult to precisely determine shear banding; however, shear banding is likely at $Wi = 64$ due to the similarity in frequency and amplitude to condition two, the shear rate $Wi = 64$ being well within region II, and the presence of a large stress overshoot. Additionally, a distinct drop in the alignment factor is observed between gap positions, and the alignment at the outer wall ($r/H = 0.75$) is near the critical value of $A_f^*$. Minimal over-orientation occurs at the inner wall, whereas significant over-orientation occurs at the outer wall. Shear banding is unlikely when $Wi = 113$. Despite the lower stress overshoot than at $Wi = 64$, the material is highly aligned at both gap positions. The maximum alignment under LAOS at the outer wall is greater than 0.4 and is two-thirds that of the maximum inner wall alignment, suggesting that the shear-induced aligned state has filled the gap. The over-orientation is significant, as the maximum alignment at both gap positions is greater than the steady shear alignment at both $Wi = 113$ and $Wi = 247$. The large amplitude and fast cycle time leads to a metastable structural state in region III. The predictions of Zhou et al. [10] show $De = 0.50$, $Wi = 64$ as shear banding and $De = 0.50$, $Wi = 113$ as non-shear banding (Figure 7.5), in line with our interpretation of the data.

Finally, two conditions were probed where the strain amplitude was held at that of
condition two while the frequency was increased, such that $De = 0.67$, $Wi = 84$ and $De = 0.75$, $Wi = 95$. Both conditions result in shear rate amplitudes that correspond to minimal shear banding under steady shear ($0.03 < \alpha < 0.25$), according to our calculations. The results, shown in Figure 7.15, are not surprising. A high degree of over-orientation is achieved at both the inner and outer walls for both conditions, indicating that the aligned structure has filled the much of, if not all of, the gap. As the oscillation period is faster than that of condition two and the shear rate is higher in both conditions, the material cannot relax sufficiently during the cycle to form shear bands. As measurements were taken at only two positions, we cannot eliminate the possibility of shear banding but the maximum alignment is so large at the outer wall in both cases that shear banding is highly unlikely. While $De = 0.67$, $Wi = 84$ was predicted to shear band by Zhou et al. [10], $De = 0.75$, $Wi = 95$ was predicted to be outside of the banding regime. As both of these conditions are on the border of the predicted shear banding and non-shear banding regions and the flow curves differ slightly between experiment and prediction (Figure 5.12), we again obtain good experimental agreement with the VCM model predictions.
Figure 7.15: 1-2 plane $A_f$ and shear stress for conditions where $\gamma_0 = 128.5$. (L) $De = 0.67$, $Wi = 84$. (R) $De = 0.75$, $Wi = 95$. While the magnitude of the alignment differs, the qualitative trends indicate a metastable structural state in region III.

### 7.6 Discussion: mildly branched solution

Table 7.2 gives a comparison of the LAOS conditions, including the maximum stress and corresponding $t/T$, the yield strain, the time elapsed from zero stress to the maximum stress ($\Delta t_1$), the time elapsed from the stress overshoot to $t/T = 0.5$ ($\Delta t_2$), the maximum over-orientation ratio ($A_{f,\text{max}}^{\text{LAOS}}/A_{f,\text{steady shear}}$) at two gap positions, the stress ratio ($|\sigma_{\text{LAOS}}^{\text{avg}}/\sigma_{SS}|$), and the position $t/T$ of maximum cycle alignment. While showing slight frequency- and amplitude-dependence, the strain acquired between the point of zero shear rate and the stress overshoot is approximately 32 strain units at all conditions, suggesting that this value corresponds to an upper bound on the amount of strain that can be acquired prior to stable flow, such that $\gamma_{\text{yield}} = 32.3 \pm 3.1$ [36]. This is typically associated with static yielding, and is referred to here as a yield strain above which flow begins. Using the local modulus analysis approach [35], where the derivative of the shear stress with respect to the strain is calculated as an instantaneous modulus, the value of $G'$ in the stress overshoot region for all conditions was also nearly identical: $G'_{\text{local}} = 1.2 \text{ Pa} \pm 0.1 \text{ Pa}$. This local elastic modulus corresponds to the elastic modulus obtained in the LVE regime when $De = 0.5$. Therefore, a rheological analysis alone makes differentiating between LAOS shear banding and shear
thinning difficult. In all of the LAOS conditions probed on a basis of Deborah and Weissenberg number, three conditions showed significant over-orientation and are interpreted as non-shear banding: $De = 0.5, Wi = 113$ (no steady shear banding); $De = 0.67, Wi = 85, De = 0.75, Wi = 96$. In these conditions, the over-orientation ratio (O-O) at the inner wall was 1.5 or greater, whereas this ratio was 1.3 or less in the shear banding conditions. At the outer wall, the over-orientation ratio was 3.0 or greater, provided that the condition showed steady shear banding. This ratio was 2.9 or less for the LAOS shear banding conditions. These ratios for the degree of over-orientation are similar to those observed in a similar frequency range by Rogers et al. [38] in the 1-3 plane (O-O $\approx 1.8$); however, LAOS shear banding could not be elucidated from their 1-3 plane measurements. Using the absolute value of the stress during LAOS, a stress ratio was calculated over the steady shear stress, $|\sigma_{LAOS}|_{avg}/\sigma_{SS}$. The ratio was 1.20 or below for LAOS shear banding, and was 1.23 and above for non-shear banding, provided that the condition showed steady state shear banding. These results provide guidelines for LAOS shear banding, assuming steady shear banding as a pre-requisite: O-O($t/T = 0.25$) $\leq 1.3$, O-O($t/T = 0.75$) $\leq 2.9$ and $|\sigma_{LAOS}|_{avg}/\sigma_{SS} \leq 1.20$. Similarly, for conditions that showed steady shear banding, the cycle times of the stress overshoot and maximum alignment (if not at max $Wi$) were greater for the conditions that did not shear band. The magnitude of the stress overshoot had no impact on the LAOS shear banding.

Table 7.2: 0.05% wt NaTos LAOS time scales and properties across conditions. Alignment factors for calculation of the maximum cycle over-orientation (O-O) were interpolated when necessary.

| De  | Wi  | $\Delta t_1$ (s) | $\Delta t_2$ (s) | $\sigma_{max}$ (Pa) | $\eta_{yield}$ | $t/T(\sigma_{max}; A_f_{max})$ | O-O($t/T = 0.25; 0.75$) | $|\sigma_{LAOS}|_{avg}/\sigma_{SS}$ |
|-----|-----|-----------------|-----------------|------------------|----------------|-----------------|-----------------|-----------------|
| 0.17 | 75  | 3.20            | 12.06           | 23.2 ± 0.2       | 29.1 ± 1.9    | 0.31 : 0.50    | 0.9 : 0.7       | 0.87            |
| 0.33 | 75  | 2.27            | 4.47            | 25.3 ± 0.2       | 30.5 ± 1.4    | 0.34 : 0.50    | 1.1 : 2.1       | 1.00            |
| 0.5  | 64  | 1.96            | 2.82            | 28.1 ± 0.5       | 31.5 ± 1.0    | 0.38 : 0.36    | 1.3 : 2.9       | 1.13            |
| 0.58 | 75  | 1.69            | 2.36            | 28.6 ± 0.2       | 33.3 ± 1.1    | 0.39 : 0.36    | 1.1 : 2.1       | 1.20            |

|                | 0.5  | 1.47            | 3.39            | 26.7 ± 0.4       | 32.4 ± 1.4    | 0.36 : 0.35    | 1.6 : 2.3       | 1.16            |
| Non-shear banding | 0.67 | 1.52            | 1.96            | 27.4 ± 0.3       | 34.2 ± 1.1    | 0.40 : 0.37    | 1.5 : 3.0       | 1.23            |
|                | 0.75 | 1.28            | 1.85            | 25.2 ± 0.4       | 35.4 ± 1.1    | 0.41 : 0.39    | 1.7 : 3.1       | 1.25            |

In non-shear banding conditions, $\Delta t_1$ is less than that of the material relaxation time.
(τ_R = 1.67 s), which explains the high degree of over-orientation. In the latter two conditions, \( \Delta t_2 \) was on the order of the relaxation time, leading to minimal relaxation after the stress overshoot. When the imposed shear conditions correspond to Deborah and Weissenberg numbers of 0.5 and 113, respectively, a pronounced shoulder is reached after the overshoot that leads to the over-orientation in an elapsed time less than that of the relaxation time. As the material does not have time to sufficiently relax throughout the oscillation in all of these conditions, it remains in a highly aligned, metastable state across the gap during LAOS. As \( \Delta t_1 \) and \( \Delta t_2 \) increase, the material has more time to relax through the cycle and the degree of over-orientation decreases. The only condition where over-orientation was not observed was \( De = 0.17, Wi = 75 \), where the maximum alignment during LAOS was equal to, or less than, that of the steady state. In most conditions where over-orientation was observed, little over-orientation was seen at the inner wall and significant over-orientation was seen at the outer wall. When \( \Delta t_1 \) is nearly equal to that of the relaxation time and \( \Delta t_2 \) is greater than the relaxation time, over-orientation and shear banding occur simultaneously. A long \( \Delta t_1 \) allows the material to relax partially before the stress overshoot (\( De = 0.17, 0.33 \)), leading to a lower maximum stress. From the results, it is clear that inducing shear banding under LAOS is a delicate balance between the applied Deborah and Weissenberg numbers. If the Deborah number was between 0.17 and 0.58, shear banding was observed under LAOS if the shear rate amplitude was within region II. At higher Deborah numbers in region II and shear rate amplitudes in region III, shear banding was not observed. The interpretation of shear banding and non-shear banding in all of our results agrees well with the predictions of Zhou et al. [10] based on Deborah and Weissenberg number. While Adams and Olmsted [9] did not probe conditions where the Deborah number was less than one, these experimental results appear consistent with their predictions based on the Weissenberg number range for shear banding at a Deborah number of one. These results also suggest that any level of branching at this salt concentration does not significantly affect the shear banding behavior.

In summary, shear banding under LAOS was investigated for the mildly branched wormlike micelle solution, which had steady shear rheology similar to that employed by the VCM model (see Chapter 5, Section 5.12), with the goal of testing the model predictions.
of LAOS shear banding. The conditions imposed under LAOS greatly affect the existence and type of shear banding near the onset of region III. We find alignment banding indicative of shear banding for a range of frequencies and amplitudes which are consistent with VCM model predictions. At $De = 0.17$ and $Wi = 75$, the maximum alignment as a function of gap position mirrors the steady shear alignment values, indicating a similar shear banding behavior between LAOS and steady shear. At $De = 0.58$ and $Wi = 75$, the maximum alignment under LAOS surpasses that of steady shear, termed ‘over-orientation.’ This over-orientation results from the shorter period of oscillation, which does not give the material sufficient time to relax within the cycle, making the shear banding more pronounced. Further increasing the frequency while keeping the shear rate amplitude constant leads to non-shear banded, metastable structural states in region III. These results have helped experimentally verify predictions of shear banding under LAOS using a mechanistic model that includes shear-induced micellar breakage, and can be used for the improvement of theoretical models.

7.7 LAOS shear banding: low branching solution

As shear banding under LAOS was experimentally verified in Couette flow for the first time using the mildly branched solution, similar measurements were performed on the low branching solution, which exhibits shear banding under steady shear. The aim of these measurements was two-fold. The first goal was to verify if shear banding under LAOS was also observed for the low branching solution (0.01% wt NaTos). As different mechanisms of shear banding are observed between the low and mildly branched solutions under steady shear (Chapters 5, 6), the second goal was to determine if different mechanisms of shear banding were also observed under LAOS for this solution. As two distinct mechanisms of shear band formation under LAOS were identified in the mildly branched solution, the approach for the low branching solution was to use a variety of Deborah and Weissenberg numbers to test if the mechanism of shear banding was dependent on the applied conditions.


7.7.1 Design of experiments

To answer the proposed questions about LAOS shear banding in the low branching solution, ten conditions of different Deborah and Weissenberg numbers were chosen, which are detailed in Table 7.3. It should be noted that the crossover frequency of the sample used to conduct the LAOS experiments was $\omega_c = 0.1 \text{ rad\cdot s}^{-1} (\tau_R = 10 \text{ s})$, which was used to calculate $De$ and $Wi$. In six of the ten conditions, the maximum shear rate during LAOS was $\dot{\gamma}_0 = 45 \text{ s}^{-1}$. This shear rate amplitude was chosen because it corresponds to a steady shear condition where shear banding is most pronounced in this solution (see Chapters 5, 6), and particle tracking velocimetry (PTV) measurements showed a clear formation of three shear bands under steady shear (Chapter 6, Section 6.6.2). The velocity profiles measured in Chapter 6 helped explain the different mechanisms of shear banding observed between the low and mildly branched solution. The wealth of the steady shear results and the interesting steady shear behavior at this shear rate made this shear rate amplitude of interest for the LAOS experiments. Choosing this amplitude would also help in the interpretation of the LAOS results, as we did not have the capabilities to perform PTV measurements during LAOS. Lastly, using this shear rate amplitude enables comparisons back to the mildly branched solution on an absolute frequency and shear rate scale. The results could not be compared on a $De$ and $Wi$ basis due to low frequency limitations on the 1-2 shear cell.

As seen in Table 7.3, a much larger range of Deborah and Weissenberg number conditions were studied in the low branching solution than in the mildly branched solution. As we only studied a narrow range of $De$ and $Wi$ in the 0.05% wt NaTos solution, the effects of significantly changing the frequency and amplitude were never examined, motivating the choice of conditions shown in Table 7.3. While six of the conditions share the same maximum shear rate, conditions one, four, nine and ten probe lower shear rates. Conditions nine and ten have the same frequency as condition three, and were added after anomalous behavior was observed in condition three. In condition one, the same strain amplitude as used in condition three was probed, in order to elucidate the effects of lowering the frequency on the LAOS response. In conditions four and nine, the shear rate is approximately the same as in
Table 7.3: LAOS parameters for the 0.01% wt NaTos solution. The nomenclature from the first and second columns is used to refer to each condition.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>De, Wi</th>
<th>ω, rad·s⁻¹</th>
<th>γ₀</th>
<th>γ₀, s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>≈ 1,295 (0.92, 295)</td>
<td>0.092</td>
<td>321</td>
<td>29.5</td>
</tr>
<tr>
<td>2</td>
<td>1,450</td>
<td>0.1</td>
<td>450</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>1.4,450</td>
<td>0.14</td>
<td>321</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>2,300</td>
<td>0.2</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>2,450</td>
<td>0.2</td>
<td>225</td>
<td>45</td>
</tr>
<tr>
<td>6</td>
<td>3,450</td>
<td>0.3</td>
<td>150</td>
<td>45</td>
</tr>
<tr>
<td>7</td>
<td>4.2,450</td>
<td>0.42</td>
<td>107.5</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>9,450</td>
<td>0.9</td>
<td>50</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>1.4,300</td>
<td>0.14</td>
<td>215</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>1.4,400</td>
<td>0.14</td>
<td>286</td>
<td>40</td>
</tr>
</tbody>
</table>

condition one. Here, the effects of increasing the frequency and lowering the strain amplitude will be examined. In all conditions, the Weissenberg number under LAOS corresponds to a shear banding condition under steady shear.

7.7.2 LAOS rheology

LAOS measurements were performed at the Deborah and Weissenberg number combinations given in Table 7.3. In each LAOS condition, several parameters are changed, while one parameter constant for comparison to other conditions. In these experiments, either the Weissenberg number amplitude, \( Wi₀ \), is held constant, the Deborah number, \( De \), is held constant, or the strain amplitude \( γ₀ \), is held constant. This design of experiments allows us to elucidate the effects on the LAOS response of \( Wi₀ \), \( De \), and \( γ₀ \). The results compared on a basis of Weissenberg number amplitude can be seen in Figure 7.16, where the elastic Lissajous-Bowditch projections can be seen in Figure 7.16a,c and the viscous Lissajous-Bowditch projections can be seen in Figure 7.16b,d.

In Figure 7.16a and b, the Lissajous-Bowditch projections are shown for the three conditions for which the shear rate amplitude of the deformation was \( Wi₀ ≈ 300 \). The three stress responses are very similar between the conditions and share many of the same features.
All conditions exhibit prominent stress overshoots, which lead to secondary loops in the viscous Lissajous-Bowditch projections. As seen in Figure 7.16a, the stress overshoot becomes less prominent with increasing $De$, which leads to a lower magnitude of the stress overshoot and less pronounced secondary loops that consist of smaller areas in the viscous projections shown in Figure 7.16b. This trend suggests that the stress overshoot gradually disappears with increasing frequency, which was also the case in the mildly branched solution. The stress overshoot is an indication of micellar breakage that can lead to shear banding [21], as was seen in the mildly branched solution under LAOS. Using the sequence of physical processes approach, the dominant stress overshoot in these three conditions suggests that the cycles are dominated by fluid-like behavior, but still have significant elastic contributions to the stress [4, 35–37]. In the stress overshoot region, a local modulus and yield strain for each condition can be calculated [35], which, by visual inspection, is similar between these three conditions based on the slopes from the elastic Lissajous-Bowditch projections in the stress overshoot region (Figure 7.16a). The calculated values are shown in Table 7.4. After the stress overshoot, the micelles break and flow, as seen by the linear portions of the stress versus shear rate curves (Figure 7.16b). While the three conditions exhibit the classic elastic-and fluid-like phenomena during the course of the oscillation cycle, these behaviors are the most pronounced when the Deborah number is the lowest, which suggests that the classical behaviors are better separated at low frequencies.

In Figure 7.16c and d, the Lissajous-Bowditch projections are shown for the six conditions where $Wi_0 = 450$. The features of the stress responses gradually change as the frequency is increased, where $De = 1$ has the largest strain amplitude, and the strain amplitude gradually decreases with increasing $De$ (Figure 7.16c). At low $De$, the stress responses are similar to those observed at $Wi_0 \approx 300$, and exhibit significant stress overshoots and secondary loops in the viscous Lissajous-Bowditch projections. As was the case when $Wi_0 \approx 300$ (Figure 7.16a, b), as $De$ is increased, the stress overshoot gradually becomes less pronounced and lower in magnitude. As a result, the secondary loops in the viscous Lissajous-Bowditch projections enclose a much smaller area with increasing $De$ until the secondary loops completely disappear when $De = 9$. A very small region is enclosed in the
Figure 7.16: LAOS stress response of the 0.01% wt NaTos solution based on equivalent Weissenberg number (shear rate) amplitude, \( Wi_0 \), in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) \( Wi_0 \approx 300 \). The stress overshoot becomes less pronounced and lower in magnitude as De is increased, which leads to a decreasing enclosed area in the secondary loops of the viscous projections. (c,d) \( Wi_0 = 450 \). The same behaviors are observed as in (a,b); however, the stress overshoot has nearly disappeared when De = 4.2 and has fully disappeared when De = 9. The disappearance of the overshoot indicates that micellar breakage is limited, which may mitigate shear banding or lead to a different shear banding mechanism.
secondary loops when $De = 4.2$, indicating that the stress overshoot has nearly disappeared at this frequency. As was hypothesized for $Wi_0 \approx 300$, the stress overshoot gradually disappears with increasing frequency (which was also the case in the mildly branched solution). Again, the stress overshoot is an indication of shear banding based on micellar breakage [21], so shear banding is possible in the conditions where a stress overshoot is observed. We postulate that high frequencies, like in $De = 9$, $Wi = 450$, shear banding will cease or a non-breakage shear banding mechanism will occur due to the absence of the stress overshoot. Shear banding has been observed at some of these higher frequencies in polymer solutions using a cone and plate geometry [13–15]; however, these results have been debated based on edge fracture and edge effects [16]. While we observed minor slip in this solution under steady shear which can lead to shear banding, the use of the concentric cylinder Couette geometry mitigates concerns over edge fracture.

Again using the sequence of physical processes approach, the stress overshoot in five of the six conditions shown in Figure 7.16c and d suggests that the cycles are dominated by fluid-like behavior, but still have significant elastic contributions to the stress [4,35–37]. In the stress overshoot region, a local modulus and yield strain for each condition can again be calculated [35], based on the linear portion of the elastic Lissajous-Bowditch projections in the stress overshoot region (Figure 7.16c). The calculated values are shown in Table 7.4. Immediately following the stress overshoot, the micelles exhibit a type of yielding leading to breakage and viscous flow (linear portions of viscous Lissajous-Bowditch projection, Figure 7.16d). As was the case when $Wi_0 \approx 300$, the majority of the conditions shown in Figure 7.16c and d exhibit classic elastic- and fluid-like behaviors during the course of the cycle, but these behaviors are the most pronounced when the Deborah number is the lowest.

Figure 7.17 compares the LAOS conditions on a basis of equivalent frequency, or Deborah number. In Figure 7.17a and b, the Lissajous-Bowditch projections are shown for three conditions at which $De = 1.4$. As the change in Weissenberg number amplitude is fairly small between the three conditions ($Wi_0 = 300$ to 450), the three responses share many of the same qualitative features, including pronounced stress overshoots and secondary loops.
in the viscous projections. As seen in Figure 7.17a, the stress overshoot is a complex function of \( W_i \), where the stress overshoot is smallest in magnitude when \( W_{i_0} = 300 \). However, increasing \( W_{i_0} \) from 400 to 450 does not further increase the magnitude of the stress overshoot. This trend was also observed in amplitude sweeps on the mildly branched solution, suggesting there is a maximum value of the stress overshoot that can be obtained in the LAOS experiments. As previously mentioned, predominantly fluid-like behavior is expected for these conditions, but we still expect significant elastic contributions to the flow behavior based on the stress overshoot region. Once again, the local modulus is similar between these three conditions based on the slopes from the elastic Lissajous-Bowditch projections in the stress overshoot region (Figure 7.17a, Table 7.4). Interestingly, after the micelles break and flow, equivalent LAOS stresses are observed for a significant portion of the response in the region where \( \gamma \approx 0 \). The equivalent stresses in this region suggest that after the micelles break and flow, they achieve a similar degree of relaxation at this point during the cycle. Continuing along the curve, when \( \gamma > 0 \), a lower stress is achieved when \( W_{i_0} = 300 \), suggesting the micelles relax further in this condition during the cycle than in the other two.

In Figure 7.17c and d, the Lissajous-Bowditch projections are compared for two conditions where \( De = 2 \). Again the change in Weissenberg number amplitude is fairly small (\( W_{i_0} = 300 \) and 450), so the two responses are fairly similar. In Figure 7.17a, the magnitude of the stress overshoot slightly increases with \( W_i \), but the increase is lower than observed in Figure 7.17a and b for the same change in \( W_{i_0} \). Again, predominantly fluid-like behavior is expected for these conditions, but the classic elastic and viscous-like behaviors are less pronounced than in Figure 7.17a and b due to the higher frequency. The local modulus is similar between the two conditions, and after the micelles break and flow, equivalent LAOS stresses are observed before \( \gamma = 0 \), which is earlier in the cycle than observed in Figure 7.17a and b. The equivalent stresses suggest a similar degree of relaxation at this point during the cycle; however, when \( W_i = 300 \), lower LAOS stresses are observed with increasing \( \gamma \), suggesting a more significant degree of relaxation in this condition.

Finally, Figure 7.18 compares the LAOS conditions on a basis of equivalent strain amplitude, \( \gamma_0 \). In Figure 7.18a and b, the Lissajous-Bowditch projections are shown for two
Figure 7.17: LAOS stress response based on equivalent Deborah number, $De$, in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) $De = 1.4$. While all curves are similar in shape, the magnitude of the stress overshoot is not a simple function of $Wi_0$. Nearly equivalent local moduli are seen in all conditions; equal LAOS stresses are observed at the maximum shear rate ($\gamma = 0$). (c,d) $De = 2$. Similar behaviors are observed as in (a,b). The LAOS stresses are nearly equal when $\gamma = 0$, but are actually equal at strains closer to the stress overshoot than in (a,b).
conditions where $\gamma_0 = 321$. Here, the change in both Deborah and Weissenberg number is small between the two conditions, which leads to similar behavior in the stress overshoot and secondary loops. As seen in Figure 7.18a, the stress overshoot is larger when $De$, and therefore, $Wi_0$, are smaller. The stress overshoot is more pronounced when $De$ is smaller, which leads to a steeper slope in the elastic projection in the overshoot region. The steeper slope signifies that the local modulus is larger when $De \approx 1$. Unlike in Figure 7.17, equivalent LAOS stresses are observed here at the maximum strain, which suggests that similar microstructures may be observed at this point in the cycle. In Figure 7.18c and d, similar behaviors are observed as in Figure 7.18a and b. Here, $\gamma_0 = 150$, and the classic elastic-and fluid-like behaviors are less pronounced than in Figure 7.18a and b, due to the higher frequencies of deformation. As was the case above, the stress overshoot is more pronounced and the local modulus is larger when $De$ is smaller. Again, the equivalent LAOS stresses are observed at the maximum strain, which suggests that the micelles respond similar to deformation in this region.

A comparison of the phases of the stress response for all of the conditions can be seen in Figure 7.19. At low $De$, the phase is closest to that of a viscous fluid, indicated by the dotted lines in Figure 7.19. As $De$ in increased, the responses shift away from fluid-like behavior, indicating the presence of elastic-like behavior. When $De = 9$, the response is nearly in phase with the applied strain. The calculated local modulus, $G'_{\text{local}}$, yield strain, $\gamma_{\text{yield}}$, and magnitude of the stress overshoot or maximum stress, $\sigma_{\text{max}}$ can be seen in Table 7.4 below for all of the conditions. A yield strain and local modulus are not calculated for condition eight, where there is no stress overshoot in the rheology. Unlike in the mildly branched solution, the local moduli shown in Table 7.4 are lower than observed in the LVE rheology for the same $De$.

In Table 7.4, the calculated values confirm the visual trends discussed above. First, with increasing frequency, the local modulus decreases. This trend is seen visually in Figures 7.16, 7.17, and 7.18, where the slope of the elastic Lissajous-Bowditch projections in the region of the stress overshoot is smaller with increasing frequency. For the same $De$, a larger local modulus is observed at lower $Wi_0$. Next, the yield strain increases with frequency
Figure 7.18: LAOS stress response based on equivalent strain amplitude, $\gamma_0$, in terms of the elastic (a,c) and viscous (b,d) Lissajous-Bowditch projections. (a,b) $\gamma_0 = 321$. The two curves are similar in shape, but the prominence and magnitude of the stress overshoot is greater at lower frequency. A steeper slope in (a) in the region of the stress overshoot when $De \approx 1$ indicates a larger local modulus. The LAOS stresses are equal at the maximum strain. (c,d) $\gamma_0 = 150$. Similar behaviors are observed as in (a,b), where the stress overshoot is more pronounced at lower $De$, and a larger local modulus is observed. The LAOS stresses are equal at the maximum strain.
Figure 7.19: LAOS stress response for all conditions. The dotted vertical lines indicate the phase of a viscous fluid response. As $De$ increases, the phase of the response shifts more toward elastic-like behavior.

Table 7.4: LAOS local modulus, $G'_{\text{local}}$, yield strain, $\gamma_{\text{yield}}$, and magnitude of the stress overshoot, $\sigma_{\text{max}}$ for the 0.01% wt NaTos solution, when applicable.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>$De, Wi$</th>
<th>$G'_{\text{local}}, \text{ Pa}$</th>
<th>$\gamma_{\text{yield}}$</th>
<th>$\sigma_{\text{max}}, \text{ Pa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\approx 1.295 (0.92, 295)$</td>
<td>0.48</td>
<td>43.0±2.0</td>
<td>14.3±0.1</td>
</tr>
<tr>
<td>2</td>
<td>1,450</td>
<td>0.32</td>
<td>59.7±2.7</td>
<td>14.2±0.1</td>
</tr>
<tr>
<td>3</td>
<td>1.4,450</td>
<td>0.27</td>
<td>65.9±1.6</td>
<td>13.2±0.1</td>
</tr>
<tr>
<td>4</td>
<td>2,300</td>
<td>0.33</td>
<td>50.5±1.4</td>
<td>12.0±0.1</td>
</tr>
<tr>
<td>5</td>
<td>2,450</td>
<td>0.25</td>
<td>69.5±2.0</td>
<td>12.0±0.1</td>
</tr>
<tr>
<td>6</td>
<td>3,450</td>
<td>0.19</td>
<td>84.7±1.7</td>
<td>12.0±0.1</td>
</tr>
<tr>
<td>7</td>
<td>4.2,450</td>
<td>0.16</td>
<td>94.0±1.3</td>
<td>11.7±0.1</td>
</tr>
<tr>
<td>8</td>
<td>9,450</td>
<td>N/A</td>
<td>N/A</td>
<td>12.6±0.1</td>
</tr>
<tr>
<td>9</td>
<td>1.4,300</td>
<td>0.39</td>
<td>46.2±2.2</td>
<td>12.6±0.1</td>
</tr>
<tr>
<td>10</td>
<td>1.4,400</td>
<td>0.31</td>
<td>57.1±2.1</td>
<td>13.3±0.1</td>
</tr>
</tbody>
</table>

for the same $W_{i0}$. This result is not surprising, considering that the location of the stress overshoot shifts to later $t/T$ with increasing $De$ (Figure 7.19), meaning that more strain is required before the micelles break and flow. Finally, with decreasing strain amplitude for equal $W_{i0}$, the stress overshoot slowly decreases in magnitude (Figure 7.16). However, once the stress overshoot has disappeared, the maximum stress does not have to decrease, as $\sigma_{\text{max}}$ at $De = 9$ is larger than in many other conditions.
7.7.3 LAOS 1-3 plane SANS

To complement the rheological results, 1-3 plane SANS measurements were performed on the 0.01% wt NaTos solution. The goal of the rheo-SANS measurements was to determine the dependence of the structural response, i.e. the alignment factor, on the applied frequency and amplitude. By changing the dimensionless frequency and amplitude, we can determine the effect of these parameters on the magnitude of the alignment factor during the oscillation cycle, and the phase of the alignment factor response. It should be noted that in these experiments, the crossover frequency slightly differed from the LAOS rheology and 1-2 plane SANS measurements. Here, $\omega_c = 0.14$ rad·s$^{-1}$, such that $\tau_R = 7$ s. As such, results should be interpreted accordingly. This difference in crossover frequency and relaxation time had no effect on the steady shear results; in Chapter 3, Section 3.4.6 the alignment results are compared from samples with crossover frequencies ranging from $\omega_c = 0.10$ to 0.18 rad·s$^{-1}$. However, as the Deborah and Weissenberg numbers are determined based off of the crossover frequency, these differences may affect the LAOS results. In the results for this section, the frequency and amplitude of the applied deformation will be reported for clarity in addition to the $De$ and $Wi$, which are calculated based on $\omega_c = 0.14$ rad·s$^{-1}$.

The three conditions performed using 1-3 plane SANS that are most relevant to the 1-2 plane measurements are the following Deborah numbers, where $Wi = 321$ in each case: $De = 1, 3, 9$. At $De = 1, Wi = 321$, the frequency is $\omega = 0.14$ rad·s$^{-1}$, and the amplitude is $\gamma_0 = 321$. This condition is identical in absolute terms to condition three in Table 7.3, and is close in dimensionless terms to condition one. When $De = 3, Wi = 321$, the same absolute frequency is used as in condition seven, and the same dimensionless frequency as condition six, where the maximum shear rate in the cycle is the same between all three conditions. Finally, at $De = 9, Wi = 321$, the dimensionless frequency is the same as in condition eight, and the maximum absolute shear rate is also identical. Based on the phase of the stress response at each condition (Figure 7.19), fluid-like behavior is expected when $De = 1$, and elastic-like behavior is expected when $De = 9$, with $De = 3$ falling some where in between the first two conditions. The 1-3 plane alignment factor during the course of the oscillation cycle can be seen in Figure 7.20 for these three conditions.
Figure 7.20: LAOS 1-3 plane $A_f$ for three conditions where $Wi = 321$ and $De = 1, 3, 9$. Nearly fluid behavior is observed when $De = 1$ and nearly elastic behavior is observed when $De = 9$; the phase of the response when $De = 3$ falls in between. The magnitude of the $A_f$ response is not affected between $De = 1$ and $De = 3$ but decreases when $De = 9$.

In Figure 7.20, $De = 1, Wi = 321$ exhibits predominantly fluid-like behavior, as is expected based on the rheology. The minima in the alignment factor are symmetric, and occur at $t/T = 0.29$ and $t/T = 0.79$, whereas a perfect fluid response corresponds to minima at $t/T = 0.25$ and $t/T = 0.75$. Conversely, when $De = 9$, nearly elastic behavior is observed, where the $A_f$ minima occur when $t/T = 0.43$ and $t/T = 0.93$. For a perfect elastic solid, these minima would correspond to $t/T = 0.5$ and $t/T = 0$. The phase of the response at $De = 3$ falls between that of the first two conditions. Here, the alignment minima correspond to $t/T = 0.35$ and $t/T = 0.85$. As expected, the phase of the alignment factor responses shown in Figure 7.20 roughly correspond to the phase of the stress responses reported in Figure 7.19 for the related conditions. Interestingly, the maximum magnitude of the alignment factor is not affected by increasing the frequency from $De = 1$ to $De = 3$. The stress responses for both of these conditions exhibit prominent stress overshoots, corresponding to micellar breakage and flow. Accordingly, a large degree of alignment is expected in these conditions. Interestingly, the alignment factor reaches a maximum in these two conditions in the region near the stress overshoot (before $t/T = 0.5$); however, no distinct local maxima are observed as were observed for the mildly branched solution. As $De = 9$ does not exhibit
a stress overshoot, the micelles are not expected to break and flow. Instead, the micelles respond to the applied strain, and we hypothesize that at this condition, the micelles simply stretch and rearrange to align, breaking minimally. As such, a lower degree of orientation is expected at higher frequencies like $De = 9$. While the response was only measured for thirty minutes at $De = 9$, $Wi = 321$, no change in the phase of $A_f$ was observed from the first to second halves of the experiment, which becomes important for the 1-2 plane measurements.

As $De = 1$, $Wi = 321$ was not perfectly in phase with the applied shear rate, an additional experiment was performed with an even lower frequency, where $De = 0.48$, $Wi = 321$. The results for this condition can be seen in Figure 7.21, where the magnitude and phase of the response in this condition are compared to the original three conditions shown in Figure 7.20. In Figure 7.21, it is apparent that the phase of the $A_f$ response when $De = 0.48$ is even closer to fluid behavior, where the minima in $A_f$ are observed when $t/T = 0.27$ and $t/T = 0.77$. The magnitude of the alignment when $De = 0.48$ is the same as when $De = 1$ and $De = 3$, which is not surprising because micellar breakage are flow are still expected in this condition. One final experiment was performed at $De = 9$, $Wi = 3210$ to probe the effect of raising the Weissenberg number on the structural response; these results are also seen in Figure 7.21. Two distinct effects are observed in this condition. As the shear rate is increased by an order of magnitude, the magnitude of $A_f$ doubles from the previous conditions. Additionally, the alignment factor response is not in phase with the previous condition when $De = 9$; instead the response shifts to the left and has a similar phase to when $De = 3$. This change in the phase of the response illustrates that in addition to the applied frequency, the relative magnitude of the Deborah and Weissenberg numbers, $De : Wi$, contributes to the $A_f$ response. Unlike in the other conditions, a distinct local maximum in $A_f$ is observed in the final condition. As the shear rate is increased ten-fold in this condition, the local maximum corresponds to the stress overshoot and micellar breakage and flow.

From the rheo-SANS results, several conclusions can be drawn. First, the phase of the stress response is a good indicator of the phase of the structural response, as represented by the alignment factor. Increasing the frequency gradually shifts the phase of the stress response, and concurrently shifts the phase of the alignment factor response. Increasing the
Figure 7.21: LAOS 1-3 plane $A_f$ for $De = 0.48, Wi = 321$ and $De = 9, Wi = 3210$, with the conditions from Figure 7.20. The phase when $De = 0.48$ is closer to fluid behavior than when $De = 1$. When $Wi$ is increased 10-fold when $De = 9$, the magnitude of $A_f$ doubles. The phase of the $A_f$ response also shifts to the left, and is similar to when $De = 3$. This response illustrates that the relative magnitude of $De : Wi$ contributes to the phase of $A_f$.

Shear rate for the same Deborah number clearly increases the magnitude of the alignment factor. However, increasing the Deborah number for the same Weissenberg number does not always mitigate the alignment. A similar degree of alignment was observed between $De = 0.48$ and $De = 3$. A decrease in alignment was only observed when the Deborah number was drastically increased to $De = 9$, which corresponds to a disappearance in the stress overshoot in the rheology. As the stress overshoot corresponds to micellar breakage, vastly increasing the Deborah number serves to mitigate micellar breakage. Finally, a stress overshoot in the rheology is not always reflected in the alignment factor response. Distinct local maxima in the $A_f$ response reflective of the stress overshoot were only observed at extremely high shear rates. While the rheo-SANS measurements were performed on a slightly different sample than the 1-2 plane measurements, the conclusions drawn from the 1-3 plane results can be used to help interpret the 1-2 plane data.
7.7.4 LAOS 1-2 plane flow-SANS

The 1-2 plane SANS results for the conditions outlined in Table 7.3 are presented below. Additional information on these conditions can be seen in Appendix O. In most cases, five or more gap positions are examined, but in some measurements, only two positions could be recorded due to time limitations. Results are presented in order of listing in Table 7.3.

7.7.4.1 Condition one: $De \approx 1, Wi = 295$

In condition one, a low Deborah number and a high Weissenberg number are examined, corresponding to $De = 0.92$, $Wi = 295$. For comparisons to other conditions, we denote this condition as $De \approx 1$. Here, the frequency and amplitude are $\omega = 0.092$ rad s$^{-1}$ and $\gamma_0 = 321$, respectively, for a maximum shear rate of $\dot{\gamma}_0 = 29.5$ s$^{-1}$. As mentioned above, this condition shares the same strain amplitude and the same $De$ as the $De = 1, Wi = 321$ rheo-SANS experiment. Under steady shear, shear banding was observed for this shear rate. While Deborah numbers of this magnitude were not examined in the mildly branched solution, shear banding was observed in the mildly branched solution for a similar ratio of $De : Wi$, so it would be reasonable to observe shear banding in this LAOS condition. Additionally, based on the rheological and 1-3 plane results, and the ratio of $De : Wi$ being very low, primarily fluid-like behavior is expected at this condition.

The 1-2 plane alignment factor results can be seen for condition one in Figure 7.22a for six gap positions, denoted by $r/H$. As was expected, the 1-2 plane $A_f$ is nearly in phase with the applied shear rate, indicating fluid-like behavior during the course of the oscillation cycle. As the Deborah number is close to one, the $A_f$ response is not perfectly in phase with the rate, indicating some elastic-like behavior. The symmetric minima in $A_f$ are observed in the range of $t/T = 0.27 - 0.28$ and $t/T = 0.77 - 0.78$, whereas the minima in the shear rate occur at $t/T = 0.25$ and 0.75. The phase of the $A_f$ response is consistent with the phase of the stress response, which corresponds to $t/T = 0.27$ and $t/T = 0.77$. The phase of the alignment factor response appears to be consistent between the inner and outer walls, as was the case for the mildly branched solution.
In Figure 7.22a, fairly typical behavior is observed in the alignment factor response near the inner wall \((r/H = 0.125 \text{ through } 0.325)\), where the magnitude of \(A_f\) decreases with increasing gap position. Despite the prominent stress overshoot in the rheology, there is little evidence of the overshoot in the \(A_f\) response. While \(A_f\) appears to exhibit a local maxima near \(t/T = 0.36\) and 0.86 for each gap position, the amplitude of the maximum is quite small. This behavior is similar to the behavior observed for the mildly branched solution, where in condition one, there was no evidence of the stress overshoot in the \(A_f\) response (Figure 7.6), and in condition three, a weak overshoot in the \(A_f\) response was observed (Figure 7.13). In the mildly branched solution, the absence of a strong alignment factor overshoot was observed at lower Deborah numbers than presented here \((De = 0.17 \text{ for condition } 1, De = 0.33 \text{ for condition three})\). However, the ratio of \(De : Wi\) for this condition is in between the ratio of \(De : Wi\) for conditions one and three in the mildly branched solution. As the behavior shown here in Figure 7.22a in regard to the alignment overshoot is also in between that of conditions one and three for the mildly branched solution, this suggests that the metric
for determining when certain features appear in the $A_f$ response may not be a function of $De$, but instead, of the relative magnitude of $De$ to $Wi$, i.e., the strain.

The magnitude of the alignment factor response decreases further with increasing gap position from $r/H = 0.325$ to 0.525. From $r/H = 0.525$ to 0.825, the alignment factor response is similar in magnitude at all positions and clusters together in an ‘alignment band’ similar to what was observed under steady shear. This outer wall alignment band is indicative of shear banding under LAOS at this condition, and suggests that the mechanism of shear banding under LAOS may be similar to the mechanism of shear banding under steady shear for this solution. As the magnitude of the alignment at $r/H = 0.525$ is larger than in the other two positions, this suggests that this position is at or near the shear band interface. A similar mechanism of LAOS shear banding and steady shear banding was also observed in the mildly branched solution (condition 1, see Section 7.5.4.3), which suggests that the steady shear behavior can help explain the LAOS behavior for certain $De$ and $Wi$.

An interesting trend is observed when the alignment profiles are examined more closely. Despite the alignment band, the magnitude of the alignment at $r/H = 0.525$ is slightly larger than the alignment at $r/H = 0.675$ at nearly all times in the cycle, which is not surprising based on the steady shear results. However, the magnitude of the alignment when $r/H = 0.825$ appears to be slightly larger than at $r/H = 0.675$, and is closer in magnitude to the response at $r/H = 0.525$. This slight increase in $A_f$ at the outer wall is reminiscent of the steady shear behavior, where a slight increase in the outer wall alignment was also observed (which can be seen in Figure 7.22b). When compared to the PTV velocity profiles, it was concluded that this slight increase in alignment corresponded to material aligning in the third band, which was at a higher shear rate than in the second, central band. Based on the results in Figure 7.22a, it is difficult to definitively determine whether or not the alignment at the outer wall is truly higher than in the previous gap position. However, should this be the case, the LAOS results are consistent with the steady shear results, which showed a three banded structure.

The alignment factor profiles at select $t/T$ (indicated by the vertical lines in Figure 7.22a) can be seen in Figure 7.22b. The alignment factor profiles are also compared to the
steady shear profiles at \( Wi = 264 \) and \( Wi = 450 \) to show the similarity in the shear banding response between LAOS and steady shear. Throughout the time points during the cycle shown in Figure 7.22b, the shear banded state is persistent, and always resembles the shape of the steady shear profiles. While the magnitude of \( A_f \) changes depending on \( t/T \), the shape and the presence of the alignment band remain essentially the same throughout \( t/T \); the response appears to be vertically shifted at different time points in the cycle. Interestingly, the maximum alignment in the alignment band reaches the value of the steady shear case (\( Wi = 264 \)), but never surpasses this value. The alignment at the inner wall, however, does exhibit over-orientation and surpasses the steady shear value. The observed over-orientation at the inner wall but not the outer wall is contrary to the trends observed in the mildly branched solution, where over-orientation was observed at all gap positions and was more significant at the outer wall. In the mildly branched solution, the over-orientation was more significant at the outer wall because the shear banding was driven by a slow re-entanglement of the WLMs in the low shear rate band, and the WLMs did not always have sufficient time to fully relax during the oscillation. Accordingly, this difference in over-orientation again suggests that a different mechanism of LAOS shear banding is present in this solution than in the mildly branched solution.

The behavior at the outer wall (\( r/H = 0.825 \)) was explored further for multiple points in time during the experiment. These results can be seen in Appendix O, where the total measurement time for the outer wall position was 2.5 hours. From the start of the experiment until \( \Delta t = 3.5 \) hours, the response at the outer wall does not appear to change in the magnitude or the phase of the alignment factor. Therefore, the magnitude of the alignment at \( r/H = 0.825 \) appears to be a stable feature of the LAOS stress response. This alignment is also compared to two individual trials at \( r/H = 0.675 \) in Appendix O, which are also identical in phase and magnitude between trials. Should the alignment at this outer wall position corresponded to a third shear band, these results indicate that the presence of this band is stable throughout the course of the experiment.
7.7.4.2 Condition two: $De = 1, Wi = 450$

Condition two was next examined, which has nearly the same frequency as in condition one. Here, $De = 1, Wi = 450$, corresponding to a frequency and amplitude of $\omega = 0.1$ rad·s$^{-1}$ and $\gamma_0 = 450$, respectively, for a maximum shear rate of $\dot{\gamma}_0 = 45$ s$^{-1}$. Based on the steady shear banding at this shear rate, and the results from condition one, LAOS shear banding is also expected in this condition. The phase of the stress response is nearly identical between conditions one and two, where the zeros in the stress are observed at $t/T = 0.27$ and $t/T = 0.77$ in each case. In this condition, there is a small ratio of $De : Wi$, so primarily fluid-like behavior is expected. The 1-2 plane alignment factor results can be seen for condition two in Figure 7.23. As the measurements for this condition were taken over the course of nine hours, the average results are presented in Figure 7.23a, whereas the results from individual one-hour time trials are presented in Figure 7.23b. No significant differences are observed between the responses for multiple trials, indicating that this LAOS response is stable over the nine-hour experiment time.

Similar to condition one, the 1-2 plane $A_f$ seen for condition two in Figure 7.23 is nearly in phase with the applied shear rate, again indicating fluid-like behavior. In both of these conditions, the $A_f$ response is not perfectly in phase with the rate, indicating some elastic phenomena during the course of the oscillation cycle. The phase of the alignment factor response is nearly identical to that of condition one, and is the same between the inner and outer walls. Here, the minimum $A_f$ is observed around $t/T = 0.28$ and $t/T = 0.78$, which is similar to condition one. The phase of the $A_f$ response is consistent with the phase of the stress response, which corresponds to $t/T = 0.27$ and $t/T = 0.77$. The similarity of the response to condition one is expected, as the two conditions share essentially the same frequency, and only differ in the maximum attainable shear rate during the cycle. Accordingly, the alignment at each comparable gap position is higher in condition two, due to the higher maximum shear rate.

Despite the large stress overshoot in the rheology, there is again little evidence of the overshoot in the $A_f$ response for this condition. In fact, while the outer four gap positions
Figure 7.23: 1-2 plane \( A_f \) during the LAOS cycle for the 0.01% wt NaTos solution for \( De = 1, Wi = 450 \) (a) the cycle average response, (b) hour-long trials during the experiment. Similar results are obtained between trials, indicating the response is stable over the course of the experiment. An alignment band occurs when \( r/H \geq 0.675 \), where \( A_f \) is indistinguishable between positions. \( A_f(r/H = 0.525) \) is similar in magnitude to the alignment band, suggesting that \( r/H = 0.525 \) is near the shear band interface.

\( (r/H \geq 0.325) \) show inflection points in the region of the stress overshoot, the inner most position \((r/H = 0.125)\) is the only position that exhibits a true local maxima in the \( A_f \) response. As we hypothesized that the relevant quantity for determining features in the alignment response is the ratio of \( De : Wi \), and \( De : Wi \) here is smaller than in condition one, it is not surprising that the local maxima in the \( A_f \) response here are either less pronounced here or non-existent. As \( De : Wi \) in this condition is approximately equal to the ratio for the mildly branched solution in condition one, we expect little to no evidence of the stress overshoot in the alignment factor response. The results for this condition give additional evidence that the Deborah to Weissenberg number ratio, \( 1/\gamma_0 \), is what determines the features of the structural response, as opposed to the Deborah number alone.

The 1-2 plane alignment factor during the LAOS cycle decreases steadily from the inner wall until \( r/H = 0.675 \), but does not change in magnitude between \( r/H = 0.675 \) and 0.875 (Figure 7.23). These trends in \( A_f \) can be better seen in Figure 7.24, where select \( t/T \) are shown in Figure 7.24a from which \( A_f \) is shown as a function of gap position in
Figure 7.24b. As was the case in condition one, the alignment during the course of the cycle for the outer two positions forms an ‘alignment band’ indicative of LAOS shear banding. However, here unlike in condition one, the alignment at $r/H = 0.675$ is indistinguishable from the alignment at $r/H = 0.825$. This outer wall alignment band is again suggestive that the mechanism of shear banding under LAOS may be similar to the mechanism of shear banding under steady shear. Interestingly, alignment banding was only observed in this condition for the outer two most gap positions, as opposed to the outer three most positions that composed the alignment band in condition one. However, the alignment at $r/H = 0.525$ in this condition is still close in magnitude to the alignment when $r/H \geq 0.675$, suggesting that $r/H = 0.525$ near the shear band interface.

Figure 7.24: 1-2 plane $A_f$ for $De = 1$, $Wi = 450$ where select $t/T$ are shown by the dotted lines in (a), for which the $A_f$ profiles are shown as a function of $r/H$ in (b), along with the steady shear profile for $Wi = 450$. Clear alignment banding is observed throughout the cycle, which is similar to the steady shear banding at $Wi = 450$.

In Figure 7.24b, the alignment banding can be seen more clearly during the course of the oscillation cycle. The alignment band is clearly visible at each $t/T$, indicating the persistence of the shear banded state during the cycle. As was the case in condition one, alignment factor again appears to maintain a similar shape throughout the cycle. The alignment at the maximum shear rate ($t/T = 0.5$) is slightly higher at all gap positions than in steady shear at $Wi = 450$. However, the alignment in the alignment band is almost within the uncertainty of
the steady shear value, whereas the observed over-orientation increases with decreasing \( r/H \).

As was the case in condition one, there is little to no over-orientation in the low shear rate band, but high degrees of over-orientation in the high shear rate band. This again suggests a different mechanism of LAOS shear banding in the low branched solution versus the mildly branched solution, which showed the smallest degree of over-orientation in the high shear rate band.

### 7.7.4.3 Condition three: \( De = 1.4, Wi = 450 \)

Condition three is similar to condition two in terms of the applied deformation. Here, the frequency is increased and the strain amplitude is decreased such that \( De = 1.4, Wi = 450 \), corresponding to a frequency and amplitude of \( \omega = 0.14 \, \text{rad} \cdot \text{s}^{-1} \) and \( \gamma_0 = 321 \), respectively. For this condition, the maximum shear rate is \( \dot{\gamma} = 45 \, \text{s}^{-1} \). Based on the results from condition two and similarity to that condition, we expect to see LAOS shear banding in this condition. Again, in this condition, the ratio of \( De : Wi \) is small and the phase of the stress response is close to the applied shear rate (Figure 7.19), so primarily fluid-like behavior is expected. However, an interesting response was observed when the 1-2 plane alignment factor was analyzed for this condition, which can be seen in Figure 7.25. In Figure 7.25, the phase of the alignment factor response at the outer wall appears to change in time. The change in the phase of the alignment factor response does not appear to be a startup effect. The measurements for this condition were taken over the course of eighteen hours and the behavior persists throughout the experiment. To further explore this behavior, followup experiments were performed at the same \( De \) in conditions nine and ten.

Unlike in condition two, the alignment factor responses shown in Figure 7.25 for \( r/H = 0.725 \) and \( r/H = 0.825 \) are not stable in time. However, an alignment band indicative of shear banding appears to form between the two positions, indicated by the similar magnitude of \( A_f \) seen in Figure 7.25a and b. As seen in Figure 7.25a, the phase of the alignment factor response at the outer wall (\( r/H = 0.825 \)) shifts in time to the left, where the symmetric \( A_f \) minima occur at earlier cycle times \( t/T \). The symmetric minima in the \( A_f \) responses are approximated by the dotted lines in Figure 7.25 for clarity. As the phase shifts to the left,
Figure 7.25: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 450$ for different times in the experiment at two gap positions: $r/H = 0.825$ (a) and $r/H = 0.725$ (b). (a) The phase of the $A_f$ response clearly shifts in time to the left. (b) The $A_f$ response starts with the same phase as in (a) and then the phase shifts to the left, before reversing and shifting to the right.

the alignment factor response becomes closer in phase to the applied shear rate, indicating fluid-like behavior. The change in the phase of the alignment factor response is slow and occurs over many hours, as the responses shown in Figure 7.25a are in one-hour time intervals. Between the first ($t = 3 - 4$ h) and second trials ($t = 5 - 6$ h), a significant shift occurs, where the $A_f$ minima start at $t/T = 0.3$ and $t/T = 0.7$, but end perfectly in phase with the applied rate, $t/T = 0.25$ and $t/T = 0.75$. The magnitude and shape of the response does not appear to change in time, only the phase of the response appears to change. No indicators of this behavior were observed during rheology measurements; however, the results shown in Figure 7.25a suggest that rheology would have to be measured for hours to see this effect.

In Figure 7.25b, the phase of the alignment factor response is shown for another outer wall position ($r/H = 0.725$). As seen in Figure 7.25b, very little change in the alignment factor response is observed over the first 2.5 hours of the experiment. When the position is re-measured at later times ($t = 6 - 7$ h), the alignment factor response shows the same shifts in time to the left as were seen at $r/H = 0.825$. From $t = 0 - 1.5$ hours, the $A_f$ minima are found at $t/T = 0.3$ and $t/T = 0.7$, whereas the minima have shifted to $t/T = 0.225$
and $t/T = 0.725$ when seven hours have passed. These minima now are observed prior to the minima of pure fluid behavior, which occur at $t/T = 0.25$ and $t/T = 0.75$. As the measurement from $t = 6-7$ hours was taken immediately following the final measurement in Figure 7.25a, where the $A_f$ minima were at $t/T = 0.25$ and $t/T = 0.75$, it appears as though the material behaves uniformly between these two gap positions and phase of the alignment factor response is consistent across the gap positions near the outer wall. The magnitude of the $A_f$ response decreases from $t = 2.5$ hours to $t = 6$ hours, but does not further decrease for the remaining twelve hours of the experiment. This change in the magnitude of $A_f$ is likely associated with shear startup and the structure evolving to steady state.

Interestingly, between $t = 7$ and $t = 9$ hours, the phase of the alignment factor response reverses direction and starts to shift to the right, where the minima in the $A_f$ response after nine hours are at $t/T = 0.265$ and $t/T = 0.765$. This shifting and reversing of the alignment factor response is repeatable and persists for the entire 18 hours of the experiment, which can be seen in more detail in Figures 7.26 and 7.27 below. Throughout the course of the experiment, it appears as though the phase of the response shifts to the left until the $A_f$ minima come slightly before the shear rate minima, at which point the phase of the response reverses and shifts toward minima at higher $t/T$. While the response is unstable in time, the phase shifting and reversals are highly repeatable during the course of the experiment, and are repeatable in a followup experiment performed to verify the behavior. The location of the $A_f$ minima over the course of the experiment ranges from $t/T = 0.22$ and $t/T = 0.72$ to $t/T = 0.33$ and $t/T = 0.83$. The zeros in the stress response for this condition, which typically correspond with $A_f$, fall between these extrema at $t/T = 0.277$ and $t/T = 0.777$.

The phase shift of the alignment factor response and the reversal of the direction of the phase shift is explored further in Figure 7.26 below. In Figure 7.26a, half-hour trials are shown at the outer wall, where $r/H = 0.725$. The response shown in Figure 7.25b from $t = 8-9$ hours is broken into two trials, where the phase shifts to the right between time points. At the next point in time where this position is measured ($t = 17$ h), the response is shifting to the left, and continues shifting to the left after 18 hours. Figure 7.26b shows the shift in phase of the alignment factor response between consecutive measurements for three gap
positions near the outer wall: $r/H = 0.725, 0.825, 0.875$. These measurements span several hours from $t = 15.5$ to $t = 18$ hours. In Figure 7.26b, the $A_f$ response shifts continuously to the left, regardless of the gap position. Here, the location of the $A_f$ minima shifts from $t/T = 0.33$ and $t/T = 0.83$ at $t = 15.5$ hours to $t/T = 0.24$ and $t/T = 0.74$ at $t = 17.5$ hours. As suggested by the results shown in Figure 7.25, the results shown in Figure 7.26b again suggest that the material near the outer wall behaves uniformly between gap positions, and that phase of the alignment factor response is the same between gap positions near the outer wall for equal times in the experiment. However, the magnitude of the alignment factor response closest to the outer wall ($r/H = 0.875$) is larger than when $r/H = 0.725$, suggesting the presence of a third shear band. Despite the poor statistics used to calculate $A_f$ when half-hour trials are used, the alignment in both trials at $r/H = 0.875$ is larger than in both trials when $r/H = 0.725$ for most $t/T$ (outside of the calculation uncertainty) when the phases are aligned. This difference in the magnitude of $A_f$ again supports the presence of three shear bands, in line with the steady shear results and the results presented in condition one.

Figure 7.26: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 450$ for different experiment times at three gap positions: $r/H = 0.725$ (a,b), $r/H = 0.825$ (b), $r/H = 0.875$ (b). (a) The phase of the $A_f$ response shifts in time regardless of experiment time. The response moves to the right before reversing and moving to the left. (b) $A_f$ at all $r/H$ appears to shift in unison. The phase moves continuously in time to the left regardless of $r/H4$. Despite the poor statistics associated with 0.5 hour trials, $A_f$ at $r/H = 0.875$ is clearly larger than at $r/H = 0.725$. 

419
Interestingly, the phase shift in the alignment factor response appears to occur only in the low shear rate band, which can be seen in Figure 7.27. In Figure 7.27a, three half-hour trials are shown for the two inner gap positions: $r/H = 0.125$ and $r/H = 0.325$. As seen in Figure 7.26 above, half-hour trials were sufficient to see significant phase shifts in the conditions near the outer wall. However, as seen in Figure 7.27a, at the two inner wall positions, no phase shift is observed over the three trials for either position. This observed trend at the inner wall does not appear to be a function of the total experiment time, or the system reaching a steady state. As seen in Figure 7.26b, the gap positions measured immediately following these trials still exhibited phase shifts. The alignment factor for the gap positions shown in Figure 7.27b also exhibits phase shifts, and these measurements were taken immediately following the inner wall experiments. The measurements at time points on either side of the inner wall measurements cannot definitively be used to determine that phase shifts do not occur at the inner wall; however, these measurements strongly suggest that the alignment factor phases in the low shear rate band shift continuously throughout the course of the experiment, and little if any phase shifts are observed at the inner wall.

Figure 7.27: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 450$ at different experiment times at the inner wall (a) and near the outer wall (b). (a) In the high shear rate band ($r/H = 0.125, 0.325$), the phase of the $A_f$ response does not appear to shift in time. (b) When $r/H = 0.475$, the phase of the $A_f$ response shifts to the left in time. At $r/H = 0.625$, the $A_f$ response shifts to the right; experiments were taken immediately prior to the $r/H = 0.475$ data. Dotted lines which indicate the response phases are for visual aid.
In Figure 7.27b, three half-hour trials are shown for two gap positions in or near the low shear rate band: \( r/H = 0.475 \) and \( r/H = 0.625 \). As the alignment when \( r/H = 0.475 \) is slightly higher than at \( r/H = 0.625 \), this gap position is likely at or near the shear band interface. At \( r/H = 0.475 \), minor phase shifts occur between each half-hour trial, and all phases shift to the left. Conversely, the experiments at \( r/H = 0.625 \) were performed immediately prior to the \( r/H = 0.475 \) experiments, and exhibit substantial phase shifts to the right. These measurements shed light on two important details. First, it appears as though the material within the low shear rate band and the subsequent responses are shifting in sync across the band. From \( t = 9 \) to \( t = 10.5 \) hours, the response shifts continuously to the right (\( r/H = 0.625 \)), and from \( t = 10.5 \) to \( t = 12 \) hours, the response appears to reverse and shifts continuously to the left (\( r/H = 0.475 \)). The responses shown in Figure 7.27b seem to confirm the behavior suggested by the continuous phase shifts between positions shown in Figure 7.26b. Next, Figure 7.27b also suggests that the alignment factor response of the material in the high shear rate band may not exhibit phase shifts, as was suggested by Figure 7.27a. While significant phase shifts are observed between each half-hour trial when \( r/H = 0.625 \), the observed phase changes when \( r/H = 0.475 \) are smaller. As \( r/H = 0.475 \) is near the shear band interface, the smaller observed phase shifts support the hypothesis that the response of the WLMs in the high shear rate band does not exhibit phase changes. This finding initially appears to contradict previous findings that suggest elastic instabilities and turbulence occur in the high shear rate band \([39–41]\), as we expect the observed phase shifts to be a result of elastic instabilities, wall slip, and/or turbulence. However, when interpreted in the context of a three banded state, these results are sensible based on the work of Manneville et al. \([42]\). Manneville et al. \([42]\) saw the largest fluctuations in behavior in the middle shear band, where the lowest shear rate was observed. The existence of the three banded state and these fluctuations was a result of wall slip and elastic instabilities. As the largest fluctuations were seen in the lowest shear rate band, it is not surprising that this behavior is observed if a three banded state is present under LAOS.

The presence of three shear bands under LAOS is further supported when the alignment factor profiles are examined for all gap positions. The 1-2 plane alignment factor as
a function of cycle time, \( t/T \), for seven gap positions can be seen in Figure 7.28a. In Figure 7.28a, results at each gap position are shown for measured times during the experiment where the phases are similar between positions. As the results in Figures 7.27b and 7.26b suggest that the phases of the alignment factor responses shift together in time, choosing responses with similar phases allows us to examine the alignment factor profiles across the gap accurately. The seven gap positions shown in Figure 7.28a give a clear picture of the shear banding under LAOS. As was the case in the previous two conditions, the alignment factor response at the outer wall \( (r/H = 0.625, 0.725, 0.825) \) forms an ‘alignment band’ indicative of shear banding. As was seen in Figure 7.26b, the alignment when \( r/H = 0.875 \) is similar in magnitude, but slightly higher, than in the alignment band. As the alignment at \( r/H = 0.875 \) is greater than in the alignment band outside of the calculation uncertainty, the presence of a third shear band is strongly suggested. The presence of a third shear band under LAOS is similar to the results seen in condition one, and to the steady shear results, giving credence to this conclusion. As the alignment when \( r/H = 0.475 \) is only slightly larger than in the alignment band, and the phase of the response exhibits only minor phase shifts, we conclude that \( r/H = 0.475 \) is at or near the shear band interface.

In Figure 7.28b, the alignment factor is shown as a function of gap position for select cycle times, \( t/T \), denoted by the dotted vertical lines in 7.28a. The presence of the alignment band is persistent throughout the oscillation cycle, giving strong evidence of shear banding. The shapes of the alignment factor profiles are very similar to the shape of the alignment factor under steady shear at \( Wi = 450 \), indicating a similar form of shear banding. The upturn in alignment at \( r/H = 0.875 \) is nearly identical to the upturn observed under steady shear at the outer wall (which corresponds to the third shear band), strongly suggesting the presence of a third band. Unlike in the mildly branched solution, the shape of the \( A_f \) profile does not significantly change during the course of the cycle. The maximum alignment in the outer half of the gap \( (r/H > 0.5) \) is slightly higher than under steady shear at the maximum shear rate, indicating very little over-orientation in the outer two bands. As was the case in conditions one and two, the over-orientation becomes more significant near the inner wall.
Figure 7.28: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 450$ for experiment times where the $A_f$ phases are roughly equivalent at all $r/H$. (a) An alignment band is formed between $r/H = 0.625$ and 0.825, indicative of shear banding. $A_f(r/H = 0.475)$ is similar in magnitude to the alignment band, suggesting it is near the shear band interface. $A_f(r/H = 0.875)$ is greater than in the alignment band, giving evidence of a third shear band. (b) $A_f(r/H)$ for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 450$ are shown for comparison. Shear banding and the presence of a third band are suggested throughout the cycle.

7.7.4.4 Condition four: $De = 2$, $Wi = 300$

In condition four, $De = 2$, $Wi = 300$, which corresponds to a frequency and amplitude of $\omega = 0.2 \text{ rad}\cdot\text{s}^{-1}$ and $\gamma_0 = 150$, respectively, for a maximum shear rate of $\dot{\gamma}_0 = 30 \text{ s}^{-1}$. Condition four has nearly the same Weissenberg number as condition one ($Wi = 300$ vs. $Wi = 295$) allowing us to make comparisons between the two. Further, condition four shares the same frequency as condition five, and the same strain amplitude as condition six. In condition four, the frequency is over twice that of condition one, which exhibited LAOS shear banding. As seen in Figure 7.19, the phase of the stress response is further shifted from fluid-like behavior in this condition than in the previous three, but is still nearly rate-aligned. Additionally, the ratio of the $De : Wi$ is still small in this condition, so fluid-like behavior is still expected. Specifically, the $De : Wi$ ratio here is in between the ratio of conditions two and three for the mildly branched solution, which both showed primarily fluid-like behavior and local maxima in the alignment factor response.

The 1-2 plane alignment factor during the oscillation cycle is shown for condition
Based on the shifts in the phase of the alignment factor response observed in condition four at the outer wall, multiple trials were recorded at the outer wall throughout the course of this experiment. No phase shifts were observed over roughly six hours of measurement at the outer wall; these results can be seen in Appendix O. At the inner most gap position ($r/H = 0.125$), a prominent maximum in the alignment factor is observed in the region of the stress overshoot; a local maximum is observed at this time in the cycle for the other gap positions. The phase of the response is still similar to that of the applied shear rate, indicating fluid-like behavior. Here, the minima in the alignment factor response are slightly shifted from conditions one and two, where $t/T \approx 0.3$ and $t/T \approx 0.8$, which is expected from the increased frequency in this condition. The phase of the alignment factor response is similar, but not identical, to that of the stress response, where the zeros are observed at $t/T = 0.28$ and $t/T = 0.78$. The magnitude and phase of the $A_f$ response are not surprising based on comparisons to the mildly branched solution. As this condition falls in between conditions two and three for the mildly branched solution in terms of $De:Wi$, fluid-like behavior and local maxima were expected in the alignment factor response.

Figure 7.29: 1-2 plane $A_f$ for $De = 2$, $Wi = 300$. (a) An alignment band is formed between $r/H = 0.675$ and 0.825, where $A_f$ is nearly identical throughout the cycle. $A_f(r/H = 0.525)$ is similar in magnitude to the alignment band, suggesting that $r/H = 0.525$ is near the shear band interface. (b) $A_f$ as a function of $r/H$ for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 264$ and $Wi = 450$ are shown for comparison.
The 1-2 plane alignment factor decreases monotonically in magnitude from the inner wall until \( r/H = 0.675 \). As was observed in condition two, the magnitude of \( A_f \) between \( r/H = 0.675 \) and 0.875 does not change (Figure 7.29a). As was the case in all previous conditions, the alignment during the course of the cycle for the outer two positions forms an ‘alignment band’ indicating shear banding under LAOS. Like in condition two, the alignment at \( r/H = 0.675 \) is virtually identical to the alignment at \( r/H = 0.825 \). As was the case in the prior conditions, the alignment at \( r/H = 0.525 \) is only slightly larger than in the outer two gap positions, suggesting that this position is close to the shear band interface. The outer wall alignment band again suggests a similar mechanism of shear banding between LAOS and steady shear. The alignment banding can be seen more clearly in Figure 7.29b, where the gap-dependent alignment factor is shown for select \( t/T \) indicated by the dotted vertical lines in Figure 7.29a. While the shear-banded state is persistent throughout the oscillation cycle, an interesting trend is observed when the alignment factor profiles are compared to the steady shear profiles. The alignment in the low shear rate band does not reach the value of the steady shear alignment, whereas the alignment in the high shear rate band exhibits a high degree of over-orientation.

Condition four shares the same Weissenberg number as condition one, and many features of the structural response are similar. While the magnitude of the alignment factor response is slightly larger in condition four at the inner wall, the magnitude of the outer wall responses is actually slightly lower in condition four. This suggests that increasing the frequency between conditions one and four serves to increase the alignment in the high shear rate band, but decrease the alignment in the low shear rate band. While the magnitude of the outer wall alignment is not significantly lower in condition four, this comparison suggests that increasing the frequency may mitigate some of the wall slip and instabilities that lead to the three banded state under steady shear. This hypothesis is supported by the higher observed alignment in the high shear rate band, as a higher alignment is expected when slip is eliminated. While alignment banding is only observed in this condition for the outer two most gap positions, the difference in magnitude between the responses at \( r/H = 0.525 \) and \( r/H = 0.675 \) is similar between conditions one and four. This result suggests that the
shear band interface is near $r/H = 0.525$ for both conditions, and may occur at the same gap position. While there was evidence of a third shear band in condition one, no evidence of this behavior is observed in condition four. Due to the presence of the alignment band, it is likely that the three banded state still occurs in this condition. However, the equal alignment between the two outer conditions here again supports that increasing the frequency mitigates some of the instabilities that lead to the formation of the three banded state.

7.7.4.5 Condition five: $De = 2, Wi = 450$

Condition five and condition four share the same frequency, but the amplitude is increased such that $De = 2, Wi = 450$. This condition corresponds to a frequency and amplitude of $\omega = 0.2 \text{ rad}\cdot\text{s}^{-1}$ and $\gamma_0 = 225$, respectively, for a maximum shear rate of $\dot{\gamma}_0 = 45 \text{ s}^{-1}$. Due to the large number of gap positions investigated in condition four, only three gap positions were measured here: $r/H = 0.325, 0.675, \text{ and } 0.825$. As the last two positions have formed the alignment band in the previous conditions ($r/H = 0.675, 0.825$), only one additional position near the inner wall was needed to determine if shear banding occurs under LAOS in this condition. When compared to condition four, the ratio of $De : Wi$ decreases because the Weissenberg number gets larger while the Deborah number remains constant.

As seen in Figure 7.19, the zeros in the stress response are identical to in condition four, at $t/T = 0.28$ and $t/T = 0.78$. Accordingly, fluid-like behavior is again expected, and local maxima are also expected in the alignment factor response. Here, $De : Wi$ is nearly identical to condition three in the mildly branched solution, so similar behavior is expected. While the experiment was only performed over two hours, no phase shifts in the alignment factor response were observed at the outer wall (see Appendix O for more details).

The 1-2 plane alignment factor for the three measured gap positions in condition five can be seen as a function of time during the LAOS cycle, $t/T$, in Figure 7.30. As expected, mild local maxima in the alignment factor response are observed. As the strain amplitude and overall shear rate are increased here from condition four, it is not surprising that the alignment factor here is always greater than in condition four for equivalent gap positions. As in all previous conditions, the alignment factor response at $r/H = 0.675$ and
0.825 is identical within the calculation uncertainty during the course of the cycle, forming an alignment band or the low shear rate band. Unlike in the previous conditions, the phase of the stress response is slightly earlier than the phase of the alignment factor response, where the symmetric minima in \( A_f \) occur roughly at \( t/T = 0.31 \) and \( t/T = 0.81 \). The alignment factor overshoot \( (t/T \approx 0.43) \) is also delayed from the stress overshoot \( (t/T = 0.88) \) in the rheology, which could be an effect of sample preparation or difference in geometry.

Figure 7.30: 1-2 plane \( A_f \) during \( t/T \) for \( De = 2, Wi = 450 \). A clear alignment band indicative of shear banding occurs for positions \( r/H = 0.675 \) and 0.825, where \( A_f \) is identical within the uncertainty throughout \( t/T \).

While alignment banding is observed both in this condition and in condition four, the magnitude of the alignment in the alignment band greatly differs. In fact, the alignment within the band in condition five is nearly twice that of condition four, while the shear rate was only increased by 50%. These results are consistent with the steady shear results, however, which showed a nearly two-fold increase in the 1-2 plane alignment factor when the shear rate was increased from \( \dot{\gamma} = 26.4 \text{ s}^{-1} \) to \( \dot{\gamma} = 45 \text{ s}^{-1} \). Here, the maximum alignment in the alignment band is equal to that under steady shear, whereas a small degree of over-orientation is observed at \( r/H = 0.325 \). The similarity of the shear banding response in all conditions up until this point suggests that changing the frequency and shear rate within this range does
not affect the type of shear banding observed under LAOS, but rather, the magnitude of the alignment within the bands.

7.7.4.6 Condition six: $De = 3, Wi = 450$

Only two gap positions were measured in condition six, where $De = 3$ and $Wi = 450$. These measurements were performed to determine if the structural response would shift in phase as the frequency is increased, which occurs with the stress response. Here, the frequency and amplitude are $\omega = 0.3 \text{ rad}\cdot\text{s}^{-1}$ and $\gamma_0 = 150$, respectively, for a maximum shear rate of $\dot{\gamma}_0 = 45 \text{ s}^{-1}$. From Figure 7.19, the zeros in the stress response are observed at $t/T = 0.29$ and $t/T = 0.79$, which still corresponds to primarily fluid-like behavior. Condition six shares the same Weissenberg number as the majority of the other conditions, and shares a strain amplitude with condition four. Although the Deborah number here is fairly high, the Weissenberg number is too, giving this condition the same $De : Wi$ ratio as in condition four. Despite the high $De$, it is reasonable to expect fluid-like behavior like in condition four based on the $De : Wi$ ratio and the phase of the stress response.

The 1-2 plane alignment factor results can be seen for condition six in Figure 7.31. The alignment factor results do not appear entirely two-fold symmetric throughout the course of the oscillation cycle, which is required for a stable LAOS experiment. The measured rheology shows no signs of asymmetry, thus these slight asymmetries are likely a result of the short experiment time for this condition. All trials for condition six were performed in two hours total, versus several hours in the other conditions. The results should be interpreted loosely due to these asymmetries. In Figure 7.31, the alignment factor response during the course of the oscillation is still close to the phase of the applied shear rate, indicating fluid-like behavior. While it is difficult to determine the exact location of the minima in the alignment factor due to the asymmetries, we can estimate the values as $t/T = 0.32$ and $t/T = 0.82$. While the minima in the shear rate correspond to $t/T = 0.25$ and $t/T = 0.75$, the response is still primarily rate-aligned. The minima in $A_f$ occur at later cycle times ($t/T$) than the zeros in the stress response. Interestingly, this response appears to be further...
phase shifted from fluid-like behavior than in condition four, despite the identical $De : Wi$ and similar zeros in the stress response.

Figure 7.31: 1-2 plane $A_f$ during $t/T$ for $De = 3, Wi = 450$ for two gap positions. $A_f$ does not appear fully two-fold symmetric for $r/H = 0.675$.

Increasing the frequency while holding the strain amplitude constant serves to increase the overall alignment in condition six versus in condition four, by about 50% for each gap position. As the response in condition six is still primarily fluid-like, increasing the frequency serves to increase the overall shear rate, as opposed to preventing flow-alignment, which may result at very large frequencies when the material acts as an elastic solid. However, the increase in alignment observed from condition four to condition six is much smaller than the increase observed from condition four to condition five, despite the same change in shear rate. From condition four to condition five, the alignment over doubled at the outer wall and increased by more than 50% at $r/H = 0.325$. Clearly, increasing the frequency in this regime has some mitigating effects on the alignment versus simply increasing the strain amplitude.

While the alignment factor results do not appear fully symmetric, this is most likely an effect of the short experiment time as opposed to a true asymmetry. To confirm this, the results at the outer wall were divided into smaller sections of time to examine the symmetry.
of the response, and if possible phase shifts occurred; these results can be seen in Appendix O. No phase shift is observed at the outer wall over the measured period of time, which covers 1.5 hours of the two hour total experiment.

7.7.4.7 **Condition seven: De = 4.2, Wi = 450**

Four gap positions were measured for condition seven, where \( De = 4.2 \) and \( Wi = 450 \). As in the previous measurements, this condition was performed to determine if the structural response would shift in phase as the frequency is increased, which is the case for the stress response. Here, the frequency and amplitude are \( \omega = 0.42 \text{ rad}\cdot\text{s}^{-1} \) and \( \gamma_0 = 107.5 \), respectively, for a maximum shear rate of \( \dot{\gamma}_0 = 45 \text{ s}^{-1} \). The zeros in the stress response are observed at \( t/T = 0.31 \) and \( t/T = 0.81 \) (Figure 7.19), which still corresponds to primarily fluid-like behavior but represents a large phase shift from the other responses. Here, the Deborah to Weissenberg number ratio is much higher than in previous conditions, which suggests that this condition may exhibit different behavior than the other conditions. The 1-2 plane alignment factor for two gap positions measured during this condition is shown in Figure 7.32a. Interestingly, the inner wall response \((r/H = 0.325)\) appears fluid-like, whereas the outer wall response \((r/H = 0.675)\) appears elastic-like.

Interestingly, the magnitude of the alignment factor response at both gap positions shown in Figure 7.32 appears larger than in conditions five and six, which is counter-intuitive because the frequency is increased and the strain amplitude is decreased. This result offers a counter-example to the trends seen between conditions four through six, where increasing the strain amplitude increased the alignment further than increasing the frequency did. The measurement at the inner wall shown in Figure 7.32a was taken from the startup of LAOS for one half hour. The outer wall measurement was taken from 0.5 to 1 hour after startup, which may help explain the observed phase shift in the responses. As \( De = 4.2 \) is a fairly high Deborah number, it is not surprising to observe an elastic-like material response; however, it appears that there is a long transient upon shear startup before the steady alternance state is reached. Figure 7.32b supports this idea of a long transient, where the alignment factor response at \( r/H = 0.675 \) is shown for three time points after the start of the oscillation:
Figure 7.32: 1-2 plane $A_f$ during the LAOS cycle for $De = 4.2$, $Wi = 450$. (a) The first two measurements at the inner and outer wall, where the outer wall phase appears shifted from the inner wall phase. (b) The phase of the $A_f$ response at the outer wall, which gradually shifts in time. The minima in the $A_f$ response for each time point are indicated by the dotted vertical lines.

0.5 to 1 hour, 1 to 1.5 hours, and 1.5 to 2 hours. Between the first two time points, the phase of the $A_f$ response shifts further toward that of an elastic solid, which can be seen by the dotted vertical lines in Figure 7.32 which indicate the two-fold symmetric minima in the $A_f$ response. Between 1.5 and 2 hours, the response shifts slightly further, such that it is perfectly in phase with the magnitude of the applied strain, indicating purely elastic behavior.

The shift in the phase of the alignment factor response also occurs at the inner wall. This behavior suggests that the response between the inner and outer walls is not actually out of phase, but rather the responses shift in time in sync. The alignment factor response as a function of time during the experiment can be seen in Figure 7.33 for the two inner wall positions, $r/H = 0.125$ and $r/H = 0.325$. The minima in the alignment factor, which are two-fold symmetric, are indicated with the dotted vertical lines in Figure 7.33. As seen in Figure 7.33a, the phase of the response shifts nearly 45° when $r/H = 0.325$ from the startup of the LAOS experiment until $t = 2.5$ hours, which is indicated by a change in the $t/T$ location of the alignment minima of roughly $\Delta t/T = 0.125$. After 2.5 hours, the response is nearly perfectly in phase with the applied strain. The alignment at $r/H = 0.125$ is measured immediately following the second measurement at $r/H = 0.325$. Here, the phase is shifted
slightly further but the responses are nearly in phase with one another. Interestingly, the shape and magnitude of the alignment factor do not appear to change in time, only the phase of the response. There are no signatures from the rheology of this behavior; however, as the phases shift slowly in time, the LAOS stress response would likely have to be measured for hours to detect this behavior.

Figure 7.33: 1-2 plane $A_f$ as a function of time at the inner wall when $De = 4.2$, $Wi = 450$. (a) The $A_f$ response at $r/H = 0.325$ shifts significantly from startup to $t = 2.5$ hours. $A_f$ at $r/H = 0.125$ is further shifted and nearly perfectly in phase with the applied strain. (b) Both positions exhibit nearly perfect elastic-like responses. The minima in the $A_f$ response for each time point are indicated by the dotted vertical lines.

In Figure 7.33b, the alignment factor responses are shown for later times in the experiment than in Figure 7.33a. The dotted lines are kept from Figure 7.33a for comparison of the phases. The phase of each response appears further shifted from in Figure 7.33b, but not by a significant amount. For the inner-most position, $r/H = 0.125$, the response appears that it has shifted beyond the phase of purely elastic behavior (black vertical lines). As the measurements in Figure 7.33b are taken at the end of the experiment, it is unclear if the phases of the alignment factor response will continue shifting, which would indicate a transition back toward fluid-like behavior, or if the response has reached steady state at this point, which is $t = 5.5$ hours after the startup of LAOS. However, the most significant phase shift occurs within the first thirty minutes of shearing, and the phase shifts are relatively minor at
longer times, suggesting that an approximate steady state has been reached by the end of the experiment.

The 1-2 plane alignment factor can be seen for the four measured gap positions in Figure 7.34a, where the measurements were performed consecutively to probe roughly equal times in the experiment between gap positions. In Figure 7.34a, the phases of the responses at each gap position are similar. Unlike in Figure 7.32a, where the phases appeared to be shifted between the inner and outer walls, this indicates that the material across the gap shifts together in time, and the alignment factor responses are actually not phase shifted based on gap position. Further, the alignment factor response at $r/H = 0.675$ has not shifted further from the response shown in Figure 7.32b, again suggesting that an approximate steady state has been reached by the end of the experiment. Despite that the responses in Figure 7.34a exhibit strain-dependent alignment, unlike the rate-dependent alignment in the previous conditions, an alignment band is still observed in the outer two gap positions. The alignment band is again indicative of shear banding, where gap-dependent alignment factor profiles at several $t/T$ shown by dotted lines in Figure 7.32a are shown in Figure 7.32b.

Figure 7.34: 1-2 plane $A_f$ when $De = 4.2$, $Wi = 450$. (a) $A_f$ at $r/H$ is recorded consecutively to probe similar time points in the experiment; the response phases are similar. Dotted lines indicate times examined in (b). (b) $A_f$ profiles at select $t/T$, and the corresponding steady shear $A_f$. The alignment band in the outer two gap positions and the magnitude of the alignment during the cycle is similar to that observed in steady shear.
In Figure 7.32b, the alignment factor profiles as a function of gap position for condition seven are compared to the steady shear alignment factor profile at $Wi = 450$ ($\dot{\gamma} = 45 \text{ s}^{-1}$). No over-orientation is observed in this LAOS condition if the alignment is compared to the steady shear case at the maximum shear rate ($Wi = 450$), as was done for the previous conditions and the mildly branched solution. However, in this condition, the alignment factor responds to the applied strain and not the applied rate. When $t/T$ is near the maximum strain, then slight over-orientation is observed in the LAOS condition. Interestingly, at these cycle times, the over-orientation only occurs at the inner wall. At the outer wall, the alignment is identical within the calculation uncertainty to the steady shear alignment. The trend in the over-orientation is contrary to what was observed in the mildly branched solution, where over-orientation was significant at all gap positions, again suggesting a different mechanism of LAOS shear banding between the two systems. The alignment band is persistent throughout the LAOS cycle, suggesting a persistent shear banded structure during the oscillation. At all time points shown in Figure 7.34b, the $A_f$ response across the gap is similar to the steady shear alignment in shape and magnitude. Even at cycle times where $A_f$ is lower in magnitude than in steady shear ($t/T = 0.4, 0.5$), the response appears to be vertically shifted from the steady shear case, such that the banded structure remains in tact. These time-dependent alignment factor profiles help to confirm shear banding in this condition, and suggest that the mechanism of LAOS shear banding is similar to steady shear banding.

7.7.4.8 Condition eight: $De = 9, Wi = 450$

As elastic-like behavior was observed in condition seven, elastic-like behavior is again expected for condition eight, where the frequency is increased to $De = 9, Wi = 450$. In this condition, the frequency is $\omega = 0.9 \text{ rad} \cdot \text{s}^{-1}$ and the strain amplitude is $\gamma_0 = 50$, resulting in a maximum shear rate of $\dot{\gamma}_0 = 45 \text{ s}^{-1}$. Condition eight corresponds to a roughly two-fold increase in the frequency from condition seven, and a two-fold decrease in the strain amplitude. Here, the Deborah number to Weissenberg number ratio is the highest for all conditions by a significant amount. The zeros in the stress response occur at $t/T = 0.39$ and $t/T = 0.89$.
(Figure 7.19). The 1-2 plane alignment factor results can be seen for condition eight in Figure 7.35. In Figure 7.35a, the alignment factor is shown for measurements performed in the first 2.5 hours of the 5-hour experiment, whereas the results from the second 2.5 hours of the experiment are shown in comparison to the first half in Figure 7.35b.

![Figure 7.35: 1-2 plane $A_f$ during the LAOS cycle for $De = 9, Wi = 450$. The first measurements at each $r/H$ are shown in (a), whereas the second round of measurements at each $r/H$ are shown for comparison in (b). The phase of the $A_f$ response at each position gradually shifts in time toward more elastic behavior.](image)

As seen in Figure 7.35a, the 1-2 plane alignment factor results from the first half of the experiment are nearly in phase with the applied strain. Here, the minima in the alignment factor are at $t/T = 0.41$ and $t/T = 0.91$, whereas the minima in the applied strain are at $t/T = 0.5$ and $t/T = 0 = 1$. These initial minima in $A_f$ are near the zeros measured in the stress response. Interestingly, at the three outer positions in this condition, where $r/H \geq 0.525$, there is very little alignment. Unlike in the other conditions, these positions do not form an alignment band, but rather the alignment decreases with increasing gap position. These three positions still appear to form a low shear rate band (Figure 7.36); however, unlike in the previous conditions, this low shear rate band has the near-zero alignment that is expected for a typical shear banding solution [5–8,18]. The alignment factor profiles at different time points during the cycle can be seen in Figure 7.36b, where the selected values of $t/T$ are
indicated by the dotted lines in Figure 7.36a. The trend in the outer wall alignment factor in this condition suggests that the material still shows shear banding under LAOS in this condition, which is clear from the $A_f$ profiles in Figure 7.36; however, the mechanism of shear banding changes. A change in the shear banding mechanism in this condition is not surprising given the differences in the alignment factor phase. When the wormlike micelles exhibit a highly elastic response, the micelles are stretching and re-orienting to align because the material is acting as an elastic solid; the micelles are not truly flowing as they are in lower frequency conditions. Accordingly, a much lesser degree of alignment is expected in the low shear rate band if the micelles are simply stretching, as opposed to flowing, in this condition.

Figure 7.36: 1-2 plane $A_f$ for $De = 9, Wi = 450$ with cycle times indicated by dotted lines (a) that are used to show the alignment profiles during the cycle in (b). A comparison to the steady shear alignment is also shown in (b). A clear banded structure is apparent throughout the oscillation, that differs in the type of banding from steady shear.

When the LAOS orientation is compared to the steady shear condition at equivalent shear rates ($t/T = 0.5$), the LAOS alignment is clearly lower than in the steady shear case at $Wi = 450$ (Figure 7.36). However, as this condition responds to the applied strain instead of the shear rate, over-orientation is observed if the full cycle is examined, which can be seen in Figure 7.36 for several $t/T$. The observed over-orientation only occurs in the high shear rate band, as the low shear rate band exhibits a low degree of alignment that is similar to other shear banding WLMs. The low degree of alignment in the low shear rate band suggests
that the material in this condition exhibits only two shear bands. The trademark of the three banded state in this solution is the non-zero ‘alignment band’ that forms in the outer half of the gap, which corresponds to the lowest shear rate, middle band (see Chapter 6, Section 6.6.2). The three banded state is confirmed under steady shear and is likely observed in the first five LAOS conditions, but not in this condition. This three banded state is associated with a small degree of slip at the inner wall (see Chapter 6, Section 6.6.2) and potential elastic flow instabilities from the high applied Weissenberg numbers. However, in this condition, the fast oscillation cycle leads to an elastic response as opposed to viscous flow that is associated with these instabilities. Further, the smaller strain amplitude in this condition may mitigate wall slip. For these reasons, we hypothesize a two-banded structure under LAOS in this condition, and a different mechanism of LAOS shear band formation.

In Figure 7.35b, the alignment factor response from the second half of the experiment is compared to the response from the first half of the experiment. As was the case in condition seven, the phase of the alignment factor response gradually shifts in time to become closer to the response of an elastic solid. Additional information detailing this continuous phase shift of the alignment factor response can be seen in Appendix O. In the second half of the experiment, the minima in the alignment factor are observed at \( t/T \approx 0.47 \) and \( t/T \approx 0.97 \), meaning the alignment factor is nearly perfectly in phase with the applied strain. The alignment of the material when \( r/H \geq 0.525 \) remains close to zero, confirming that this new shear banding mechanism is that of the steady state. Analyzing the response between the two time trials allows us to determine when the steady alternance state is reached. An in-depth analysis can be seen in Appendix O. A change in the phase of the response between the two trials is observed at \( r/H = 0.675 \), where the first trial occurs 1.5 to two hours after shear startup, and the second trial occurs four to 4.5 hours after startup. At \( r/H = 0.525 \), however, no change in the magnitude or phase of the \( A_f \) response is observed between the two trials, spanning two to 2.5 hours after startup and 4.5 to five hours after startup. From this analysis, we can conclude that the response is not at the steady alternance state as of \( t = 1.5 \) hours, but does reach steady state after \( t = 2 \) hours. The alignment factor always maintains the same magnitude during the process of phase shifting. As such, the shear banding profiles shown
in Figure 7.36b are still applicable to the steady state response; the $t/T$ values corresponding to each profile will just slightly shift in time.

### 7.7.4.9 Condition nine: $De = 1.4$, $Wi = 300$

After exploring conditions one through eight, additional experiments were performed at $De = 1.4$ to probe the interesting phase shift behavior that was observed during the course of the oscillation cycle in condition three. In conditions nine and ten, we probe $De = 1.4$ and $Wi = 300$ and $Wi = 400$, respectively. In condition nine, the strain amplitude is lowered to $\gamma_0 = 215$, such that the maximum shear rate is $\dot{\gamma}_0 = 30 \text{s}^{-1}$. This maximum shear rate is identical to the maximum shear rate in conditions one and four, where a rheological comparison can be seen in Figure 7.16. As seen from the stress response shown in Figure 7.19, fluid-like behavior is expected in this condition, where the zeros in the stress response are seen at $t/T = 0.270$ and $t/T = 0.770$. This phase of the stress response is similar but not identical to the phase in condition three, where $t/T = 0.277$ and $t/T = 0.777$. The ratio of the Deborah and Weissenberg numbers, $De : Wi$, is larger than in condition three, so local maxima in the alignment factor response are expected.

Figure 7.37a shows the average 1-2 plane alignment factor during the cycle for condition nine at five gap positions. As expected, local maxima are observed in the alignment factor response, near cycle times where the stress overshoot is observed (see Figure 7.19). In Figure 7.37a, a clear alignment band is formed at the outer wall where $r/H = 0.675$ and $r/H = 0.825$. As was observed in condition three, the magnitude of the alignment factor response when $r/H = 0.525$ is very similar to the magnitude of the alignment in the alignment band. This similarity suggests that $r/H = 0.525$ is either at or near the shear band interface. Interestingly, the minima in the alignment factor response are observed at approximately $t/T = 0.31$ and $t/T = 0.81$, which is significantly later in the cycle than the zeros in the stress response.

In Figure 7.37b, the alignment factor profiles as a function of gap position at select $t/T$ for condition nine are compared to the steady shear alignment factor profiles at $Wi = 264$ and $Wi = 450$. The chosen $t/T$ are indicated by the dotted vertical lines in Figure 7.37b. The
1-2 plane alignment factor decreases monotonically from the inner wall until \( r/H = 0.675 \) at all cycle times. For certain cycle times shown in Figure 7.37b, there is a slight increase in the magnitude of \( A_f \) when \( r/H = 0.825 \) that is outside of the experimental uncertainty. However, the magnitude of \( A_f \) between \( r/H = 0.675 \) and \( r/H = 0.875 \) does not change within the calculation uncertainty for the majority of the cycle. As was the case in many of the prior conditions, the alignment at \( r/H = 0.525 \) is only slightly larger than in the outer two gap positions, suggesting that this position is close to the shear band interface. The outer wall alignment band and the slight upturn in alignment at \( r/H = 0.875 \) again suggests a three banded structure under LAOS, which was also inferred by the results in condition three. As seen by the alignment factor profiles in Figure 7.37b, the shear-banded state is persistent throughout the oscillation cycle, and the shape of the \( A_f \) response is similar to the steady shear response at most cycle times. Interestingly, when the alignment factor profiles are compared to the steady shear profiles, the alignment in the low shear rate band never exceeds the value of the alignment when \( Wi = 264 \). However, while no over-orientation is observed in the low shear rate band, significant over-orientation is observed near the inner wall. The observed over-orientation appears to increase with decreasing gap position, which
was also the case in many prior conditions.

In condition nine, the same behavior as in condition three is observed, where phase shifts in the alignment factor response are seen near the outer wall. This behavior persists during the entire experiment, as was the case in condition three. The behavior is also repeatable over multiple trials, where results from a second experiment can be seen in Appendix O. The alignment factor response at different time points in the experiment can be seen in Figure 7.38a for the outer wall \(r/H = 0.675\) and in Figure 7.38b for the inner wall \(r/H = 0.125, 0.325\). As seen in Figure 7.38a, the phase of the alignment factor response at the outer wall shifts in time to the left, where the symmetric \(A_f\) minima occur at earlier cycle times \(t/T\). The minima in the \(A_f\) responses are approximated by the dotted lines in Figure 7.38 for clarity. Between the first \((t = 0 - 1\, \text{h})\) and third trials \((t = 2 - 3\, \text{h})\), a small shift occurs, where the \(A_f\) minima start at \(t/T = 0.31\) and \(t/T = 0.71\), but end at \(t/T = 0.28\) and \(t/T = 0.78\). This small shift near the experiment startup is expected based on the results in condition three, where little change in phase was observed for the first 2.5 hours of the experiment. The magnitude and shape of the response does not appear to change in time, only the phase of the response appears to change. Between the third and fourth trials, the response reverses and shifts to the right. A more significant shift in the phase of the alignment factor response is observed, where the symmetric minima in \(A_f\) move from approximately \(t/T = 0.28\) and \(t/T = 0.78\) to \(t/T = 0.33\) and \(t/T = 0.83\).

In Figure 7.38b, the alignment factor response is shown in time for the two inner wall positions. As was the case in condition three, no observable change in phase is detected when \(r/H = 0.125\). In both conditions, this gap position is well within the high shear rate band. Interestingly, small phase changes are observed when \(r/H = 0.325\), which were not observed in condition three. Between the first two time points shown in Figure 7.38b, the phase of the response shifts to the right, whereas between the second two time points, the response reverses and shifts to the left. Measurements between the time points shown in Figure 7.38b confirm this trend in the alignment factor phase when \(r/H = 0.325\), but are not included for clarity. The phase shifts at \(r/H = 0.325\) that are observed in condition nine may be a result of the location of the shear band interface, or the magnitude of the
alignment factor. In condition three, the alignment at $r/H = 0.325$ is significantly larger than in condition nine, and it is significantly larger than in the alignment band, meaning the gap position is far away from the shear band interface. Conversely, in condition nine, the micelles are not as well aligned at $r/H = 0.325$. While this position is still higher in alignment than in the alignment band, the magnitude of the alignment at this position is closer to that in the alignment band than in condition three. This result suggests two possible explanations, which are not mutually exclusive. Strongly aligned micelles may be more stable, and thus do not exhibit phase shifts. If this was the case, the lower degree of orientation in this condition would explain the phase shift behavior. Additionally, $r/H = 0.325$ may be closer to the shear band interface in this condition than in condition three. If this were the case, it would explain why the alignment at $r/H = 0.325$ is closer to that of the alignment band for this condition. As the shear band interface is diffuse and has a finite width, the closer a gap position is to the interface, the more likely the phase shift behavior will be observed.
7.7.4.10 Condition ten: $De = 1.4$, $Wi = 400$

Condition ten is the final condition, where we probe $De = 1.4$ and $Wi = 400$. Here, the strain amplitude is increased from condition nine to $\gamma_0 = 286$, such that the maximum shear rate is $\dot{\gamma}_0 = 40 \text{ s}^{-1}$. Condition ten is the only condition with this maximum shear rate. From Figure 7.19, fluid-like behavior is again expected in this condition; the zeros in the stress response are seen at $t/T = 0.270$ and $t/T = 0.770$, which is identical to condition nine. Here, the $De : Wi$ ratio is also larger than in condition three, so local maxima in the alignment factor response are expected. Three separate experiments were performed using condition ten; two will be discussed in this section, and the results from the third trial can be seen in Appendix O. The first trial was performed for 9.5 hours, the second for 16 hours, and the third for 2.5 hours. Between all trials, the alignment factor responses were of equal magnitude; the phase of the response simply differs between trials.

In all three trials, the alignment factor response exhibited significant shifts in time during the course of the experiment. Figure 7.39a shows the 1-2 plane alignment factor as a function of gap position for the first trial in condition ten. As significant phase differences between gap positions occurred during this experiment, the responses shown in Figure 7.39a are shifted such that each gap position has the same phase. The true phases are shown in Figures 7.40 and 7.41 below; shifting the phases allows the alignment factor profiles to be determined in Figure 7.39b. As was the case in conditions three and nine, the alignment factor response in this condition shifts in time across the gap equally, so shifting the responses is necessary to obtain an accurate picture of the gap-dependent alignment factor in Figure 7.39b. In Figure 7.39a, local maxima in the $A_f$ response are observed at multiple gap positions, as is expected based on the ratio of $De : Wi$. As is the case for the majority of the other conditions, an alignment band is formed between $r/H = 0.675$ and $r/H = 0.825$ that indicates shear banding. At $r/H = 0.525$, the response is similar in magnitude to the alignment band, suggesting that this position is near the shear band interface. Nearly identical features of the 1-2 $A_f$ response are observed in the second trial, which is reported in Figure 7.43.

In Figure 7.39b, the alignment factor profiles for different $t/T$ (dotted lines in Figure 7.39a) are shown as a function of gap position, along with the steady shear profiles for
$Wi = 264$ and $Wi = 450$. It should be noted that the gap-dependent alignment factors shown in Figure 7.39b are representative of the different structures observed during the cycle in this condition, as the shape and magnitude of the $A_f$ response does not change in time. However, the assigned $t/T$ for each profile is arbitrary as the phases shift in time; this value of $t/T$ simply corresponds to the location indicated in Figure 7.39a, which is only the true $t/T$ for certain times during the experiment. The shear banded structure during LAOS shown in Figure 7.39b is reminiscent of the steady shear structure when $Wi = 450$. In fact, the LAOS structures are nearly identical to $Wi = 450$ at $t/T = 0.1$ and $t/T = 0.5$ despite the fact that $Wi_0 = 400$. As steady shear measurements were not performed at $Wi = 400$, the degree of over-orientation cannot be precisely determined. However, it can be inferred based on the comparison to $Wi = 450$ that little to no over-orientation is observed at the outer wall. Over-orientation is observed at the inner wall, as the LAOS $A_f$ when $t/T = 0.5$ is larger than the steady shear result, which is measured at a higher shear rate.

Figure 7.39: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$. (a) The $A_f$ responses are shifted so the phases are aligned at all $r/H$. (a) An alignment band is formed between $r/H = 0.625$ and 0.825, indicative of shear banding. $A_f(r/H = 0.475)$ is similar in magnitude to the alignment band, suggesting it is near the shear band interface. (b) $A_f$ as a function of gap position for select $t/T$ denoted by dotted lines in (a). Steady shear results for $Wi = 264$ and $Wi = 450$ are shown for comparison. Banded structures similar to the steady shear profiles are observed throughout the cycle.

The phase of the alignment factor response was next examined for the first trial. The
alignment factor at the outer wall \((r/H = 0.675)\) is examined as a function of time after the start of LAOS in Figure 7.40. The alignment factor response for three half-hour trials after shear startup can be seen in Figure 7.40a. In each trial, the phase of the alignment factor response shifts to the right in time, meaning that the minimum value of \(A_f\) is observed at later cycle times \(t/T\). Over the course of the two hour measurement, the minima in \(A_f\) shift from approximately \(t/T = 0.295\) and \(t/T = 0.795\) to \(t/T = 0.36\) and \(t/T = 0.86\). In Figure 7.40b, the alignment factor is shown again at \(t = 1.5\) h, and for two later times within the cycle. As was the case in conditions three and nine, the phase of the alignment factor response begins to shift in the reverse direction around 2.5 hours after the start of the experiment. After four hours of shearing, the phase of the alignment factor response is nearly the same as at the start of the experiment, where the minima are observed at \(t/T = 0.31\) and \(t/T = 0.81\). Throughout the duration of the first trial, the phase of alignment factor response across the gap shifts between exhibiting minima at approximately \(t/T = 0.295\) and \(t/T = 0.295\) (starting phase) to approximately \(t/T = 0.38\) and \(t/T = 0.88\) (maximum phase). Essentially, the alignment factor response oscillates continuously between the starting phase and the maximum phase, and never appears to reach an equilibrium state. In this trial, the starting phase exhibits the earliest minima in the \(A_f\) response, which indicates that the phase of the response initially shifts to the right. Interestingly, in trials two and three, the starting phase exhibits the latest minima in the \(A_f\) response such that the initial phase shifts to the left, which will be discussed further below.

In conditions three and nine, the alignment factor response at the inner wall \((r/H = 0.125, 0.325)\) exhibited little to no change in phase. However, in these conditions, the majority of the measurements were performed at the outer wall as opposed to the inner wall, giving only a small window of time over which to examine the response. In trial one, the alignment factor response at the inner wall was examined over a wide range of times during the experiment, which can be seen in Figure 7.41a for three gap positions: \(r/H = 0.125, 0.225, 0.325\). In Figure 7.41a, the alignment factor response does not change phases within the half-hour time trials recorded for each gap position. As was the case in conditions three and nine, half-hour long trials were sufficient to observe phase shifts at the outer wall, but not at the inner
Figure 7.40: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times when $r/H=0.675$. (a) The phase shifts to the right between $t = 0$ and $t = 2$ hours. (b) After $t = 2$ hours, the phase of the $A_f$ response reverses and shifts to the left. Dotted vertical lines estimate the phases of the $A_f$ response.

The measurements performed at $r/H = 0.125$ and $r/H = 0.325$ were taken between $t = 4$ to $t = 6$ hours after the start of the experiment, and the responses share the same phase. However, the alignment factor response at $r/H = 0.225$ has a significantly different phase than in the other two positions. In Figure 7.41b, the measurements for the other gap positions at times leading up to the measurement at $r/H = 0.225$ are shown. As seen in Figure 7.41b, the phase of the $A_f$ response shifts to the right regardless of gap position.

As the trials at $r/H = 0.225$ were not performed until $t = 8.5$ to $t = 9.5$ hours after the start of the experiment, the results suggest a different conclusion than in conditions three and nine. In conditions three and nine, the lack of observable phase change at the inner wall was attributed to the phase shifts primarily occurring the in the low shear rate band. While it is possible that the responses in conditions three and nine exhibit different behavior than here in condition ten, it is unlikely as this condition falls in between those two conditions. Instead, it is more likely that the phase shifts occur at all gap positions, but are more difficult to detect at the inner wall or that the phase of the response changes more slowly at the inner wall. One possible explanation is that the material closest to the outer wall travels a farther physical
distance during each oscillation cycle. When the phase of the alignment factor response changes, it is more apparent at these outer wall positions. Another explanation could have to do with elastic instabilities in the middle band. As previously mentioned, Manneville et al. [42] saw the largest fluctuations in the middle of the three shear bands in WLMs under steady shear. If the phase shifts are a result of these large fluctuations and instabilities in the middle band, the phase shift behavior must propagate from the middle band outward, and could be dampened at other gap positions in the process.

The second trial in condition ten was performed to more closely examine the behavior at the inner wall and to determine if significant phase shifts were present. The 1-2 plane alignment factor at the inner wall ($r/H = 0.325$) for trial two can be seen in Figure 7.42a. As was the case in trial one, and in conditions three and nine, no change in the phase of $A_f$ is observed between the three half-hour trials spanning $t = 0$ to $t = 1.5$ hours after shear startup. However, after two hours of shearing, a small shift in the phase at $r/H = 0.325$ is observed. Unlike in trial one, the first phase shift occurs to the left, such that the minima in the $A_f$ response occur at earlier cycle times, $t/T$. In trial three (see Appendix O), the primary phase
shift also occurs to the left. As was the case in previous trials and conditions, the magnitude of the $A_f$ response does not appear to change in time; only the phase of the response appears to change. Figure 7.42b shows the 1-2 plane alignment factor at the outer wall, where the measurements were performed directly after the inner wall measurements shown in Figure 7.42a. For the first trial shown in Figure 7.42b, the phase of the alignment factor response is similar to the final inner wall phase shown in Figure 7.42a. These results once again signify that when the phases of the response change, they change across the gap concurrently. In Figure 7.42b, the phase of the alignment factor response shifts continuously to the left. The initial minima in $A_f$ observed in Figure 7.42a occur at $t/T = 0.295$ and $t/T = 0.795$ (starting phase), whereas the minima of the final trial shown in Figure 7.42b occur at $t/T = 0.22$ and $t/T = 0.72$. Interestingly, the starting phase in both trials one and two is the same; however, the direction of the phase shifts in time are different. The starting phase for trial three is also the same as trials one and two (see Appendix O), which indicates that the response is always identical at early times during the experiment.

Figure 7.42: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times for trial two when: (a) $r/H = 0.325$, and (b) $r/H = 0.675$. (a) At the inner wall, no phase shift is observed in $A_f$ from $t = 0$ to $1.5$ h. A small, left shift is observed between $t = 1.5$ to $2$ h. (b) At the outer wall, the phase of the response shifts continuously to the left. At $t = 2$ h, the phase at the outer wall and inner wall are nearly equal. Dotted vertical lines estimate the phases of the $A_f$ response.
After examining the early-time behavior in trial two, the gap was scanned continuously in time during the experiment such that each of the six gap positions was measured consecutively. Each gap position was measured three times such that the alignment factor response can be broken down into three sub-trials, which can be seen in Figure 7.43, where panels a, b, and c correspond to each sub-trial. In each sub-trial, the measurement starts at a gap position of $r/H = 0.825$ and moves toward the inner wall until $r/H = 0.125$ is reached; each gap position is measured for one half-hour. After measurement at $r/H = 0.125$, the slit is moved back to the outer wall and the process is repeated. The magnitude and shape of the alignment factor for each sub-trial shown in Figure 7.43 are nearly identical to the results seen in Figure 7.39 for trial one, which indicates that only the phase of the alignment factor response is affected during repeated experiments. In Figure 7.43a, the phase of the $A_f$ response shifts continuously to the left, which is a continuation of the behavior shown in Figure 7.42; the phase shift has not yet reversed directions. The minima in the alignment factor response at the latest time point in Figure 7.43a ($r/H = 0.125$) occur approximately at $t/T = 0.2$ and $t/T = 0.7$.

![Figure 7.43: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ for all gap positions for three continuous trials of three hours each. (a) The phase shifts to the left in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.2$ and $t/T = 0.7$. (b) The phase reverses and shifts to the right in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.27$ and $t/T = 0.77$. (c) The phase one again reverses and shifts to the left in time, where the minima in $A_f$ at $r/H = 0.125$ are approximately at $t/T = 0.22$ and $t/T = 0.72$.](image)

In Figure 7.43b, the results from the second sub-trial exhibit significant phase shifts from in the first trial. The minima in the $A_f$ response at the earliest time point ($r/H = 0.825$)
are at larger \( t/T \) than when \( r/H = 0.125 \) in sub-trial one, indicating that the direction of the phase shift has reversed. During the entirety of sub-trial two, the alignment factor response shifts to the right. When \( r/H = 0.125 \), the minima in the alignment factor response are observed at \( t/T = 0.27 \) and \( t/T = 0.77 \). In sub-trial two, the response has not yet returned to the starting phase. However, in sub-trial three (Figure 7.43c), the response at the outer-most gap position returns to the starting phase. From \( r/H = 0.825 \), the phase of the alignment factor response again reverses direction. For the remainder of sub-trial three, the response shifts continuously to the left. At the final time measured in Figure 7.43c, the minima in \( A_f \) are observed at \( t/T = 0.22 \) and \( t/T = 0.72 \). From these trials and the measurements shown in Figure 7.42, the range of the phase shifts can be determined. Here, the starting phase represents the largest cycle times where the \( A_f \) minima are observed (\( t/T = 0.295 \) and \( t/T = 0.795 \)). The phase of the alignment factor response oscillates continuously between the starting phase, and the minimum phase, which occurs at \( t/T = 0.2 \) and \( t/T = 0.7 \). The range of observed phases in this trial is similar to the range observed in trial one.

Finally, the alignment at the inner wall (\( r/H = 0.125 \)) was measured further to examine the change in phase as a function of time. These results can be seen in Figure 7.44a, where the first trial shown is the last trial in sub-trial three. In Figure 7.44a, the alignment factor is identical in magnitude and phase for the three half-hour trials spanning \( t = 13 \) to \( t = 14.5 \) hours, which initially suggests that the response at the inner wall has reached a steady state. However, the response at the inner wall is re-measured at \( t = 15 \) hours, and a small phase shift to the left is observed. This behavior is in agreement with outer wall measurements (\( r/H = 0.675 \)) seen in Figure 7.44b. In Figure 7.44b, the response at the outer wall shifts to the left until \( t = 15 \) hours, and this phase shift continues when \( r/H = 0.125 \). At \( t = 15.5 \) hours, the phase of the response at the outer wall reverses directions. Figure 7.44a clearly helps to resolve the behavior at the inner wall, and suggests that any inner wall phase shifts must be measured over a longer period of time than those at the outer wall. Although phase shifts at the outer wall may be observed between half-hour measurements, these shifts may not be observed at the inner wall for up to two hours. These measurements help to clarify the behavior in conditions three and nine. Clearly, the phase shifts are most
detectable at the outer wall; however, the phase at the inner wall still changes slowly in time. As suggested earlier, the phase shift behavior may be dampened at the inner wall, but it most likely never fully disappears.

Figure 7.44: 1-2 plane $A_f$ for $De = 1.4$, $Wi = 400$ at different experiment times when (a) $r/H = 0.125$, and (b) $r/H = 0.675$. (a) The phase of the alignment factor response at the inner wall does not change over a 1.5h time frame, similar to results seen in conditions three and nine. (b) At the outer wall, the phase shifts to the left before reversing and shifting to the right. Dotted vertical lines estimate the phases of the $A_f$ response.

It remains unclear why measurements for the same LAOS condition can exhibit phase shifts in opposite directions. As previously mentioned, all three trials performed had the same starting phase, where the alignment factor minima were observed at $t/T \approx 0.3$ and $t/T \approx 0.8$. It should be noted that this behavior was also observed in condition nine. In the second trial for condition nine shown in Appendix O, the phase shifts occur primarily to the left, resulting in $A_f$ minima at $t/T < 0.25$ and $t/T < 0.75$. The phase shifts discussed in the text for condition nine occur primarily to the right. One possible explanation is that inhomogeneities in the fluid may trigger the phase shift behavior, and may favor one direction or the other. This phenomena does not appear to be a result of aging either, as trial three shown in Appendix O was actually performed first, followed by trial one and finally trial three. The direction of the phase shift alternated between each trial, making again an unlikely source for the observed differences.
7.8 Discussion: low branching solution

7.8.1 Phase of the alignment factor response

By slightly altering the frequency and strain amplitude of the applied LAOS deformation, different structural responses were observed in the ten conditions examined for the low branching solution. As seen from the phase of the stress response shown in Figure 7.19 for all conditions, we expected the alignment factor response to shift toward more elastic-like behavior as the Deborah number was increased. However, the phase of the 1-2 plane alignment factor response did not always coincide with the measured stress response. These differences are likely a result of different sample preparations, different measuring times, and the different geometries of the 1-2 shear cell versus the ARES G2 rheometer. While generally slight differences in geometry should not significantly affect the results, shear banding phenomena are known to depend on the geometry [43]. The phase shift behavior observed in some conditions may be specific to the 1-2 shear cell, which is a short, sealed Couette device. Further, the long duration measured during SANS versus during the rheological measurements likely contributes to some of the differences in the phase behavior.

Of the ten conditions, only the conditions at $De = 1.4$ (conditions three, nine and ten) appeared to exhibit changes in the phase of the alignment factor response that were reversible in time. The two conditions at the highest frequencies exhibited phase shifts in time, which appeared to reach a steady state and were not reversible. However, it should be noted that the experiments at $De = 1.4$ were performed for much longer durations than in some other cases, so this behavior cannot be entirely ruled out. To understand this behavior better, we revisit the conditions surrounding condition three: conditions one, two, and four. In condition two ($De = 1, Wi = 450$), the experiment was performed for nine hours. The experiment files were divided into small increments to check for phase shifts, but no evidence of this behavior was observed (see Figure 7.23). In the conditions at $De = 1.4$, significant phase shift behavior was observed before nine hours, which strongly suggests that the response in condition two is stable. While condition one was only measured for six hours, this condition is likely stable if condition two is stable, based on the lower frequency and Weissenberg number. In condition four, where $De = 2$, the measurement was only performed for 6.5 hours, which
may not be long enough to observe an unusual behavior in the phase responses. However, the phase shifts in conditions three, nine and ten were detected within this time range. Further, multiple measurements at the same gap position spanning the entire experiment showed no sign of phase shifts in the $A_f$ response, again indicating that the response is likely stable. A comparison of the $A_f$ responses for conditions one, two, and four at the inner wall can be seen in Figure 7.45.

Figure 7.45: 1-2 plane $A_f$ during $t/T$ at $r/H = 0.125$ for three conditions: $De \approx 1$, $Wi = 295$, $De = 1$, $Wi = 450$, and $De = 2$, $Wi = 300$. Dotted vertical lines correspond to the phases of the responses. As $De$ is increased, the phase of the $A_f$ response shifts further from fluid-like behavior.

An interesting trend is observed when the phases of conditions one, two and four are compared to the starting phase of condition ten (see Figure 7.45). In condition ten at early times in the experiment, the minima in the alignment factor response were always observed at $t/T = 0.295$ and $t/T = 0.795$. While defining the starting phase with three significant digits may seem inappropriate, each of the three trials had a phase starting at exactly this cycle time. In Figure 7.45, the alignment factor responses and the phase of the response are shown for the inner wall for conditions one, two, and four. As seen in Figure 7.45, the phase of conditions one and two is below the starting phase of condition ten ($A_f$ minima at earlier $t/T$), whereas the phase of condition four is above the starting phase of
condition ten. While it seems unlikely, a response with a starting phase in between the phases of conditions two and four may be inherently unstable. The inner wall alignment for conditions two and four is higher throughout much of the cycle than in conditions three and nine, which correspond to equivalent Wi, which may be a stabilizing factor. Additional investigation would be needed to determine the role of the starting phase on the stability of the structural response. The starting phases for conditions nine and three are identical to condition ten, which further supports this hypothesis. As seen in Figure 7.45, the phase of the alignment factor response appears to increase with frequency, which is expected based on the rheological results. However, the phase of the stress response of conditions one and two are identical in the rheology, and the stress response for condition four is not nearly as shifted as the corresponding alignment factor response. However, these differences are observed at many of the conditions, and may simply be a result of geometrical or sample preparation differences.

7.8.2 Conditions where $De = 1.4$

The conditions at which the Deborah number was 1.4 were the only conditions that we observed to exhibit reversible phase shift behavior in terms of the alignment factor response during the experiment duration. As the strain amplitude change between these conditions was not very large, this similar behavior observed between conditions was expected, which is why conditions nine and ten were measured to verify the phase shift behavior. A comparison of the inner wall results ($r/H = 0.125$) between conditions three, nine and ten can be seen in Figure 7.46. The results are not perfectly in phase because the measurements are taken at different times during the experiment. The starting phase for all conditions is identical, which is not surprising based on the measured stress responses. The zeros in the stress response for condition three are at slightly higher $t/T$ than in conditions nine and ten ($t/T = 0.277, 0.777$ vs. $t/T = 0.27, 0.77$); however, all conditions are very similar. The curves shown in Figure 7.46 are similar in terms of the features observed during the cycle, and the $A_f$ for each condition essentially collapses onto the same curve for most parts of the
cycle (when the phases are aligned). The major difference in the alignment between the conditions is only in the magnitude, where $A_f$ is greatest when the strain amplitude is the largest. The structural response in these three conditions differs in shape and magnitude versus the surrounding similar conditions that do not exhibit phase changes, which may give insight to the observed phase shift behavior.

![Graph showing $A_f$ during $t/T$ at $r/H = 0.125$ for three conditions when $De = 1.4$: $Wi = 300$, $Wi = 400$ and $Wi = 450$, corresponding to strain amplitudes of $\gamma_0 = 215$, 286, 321, respectively.]

7.8.3 **Alignment factor at equivalent $Wi$**

In the mildly branched solution, the alignment at the maximum shear rate during LAOS was compared to the alignment under steady shear at an equivalent shear rate. This comparison helped to elucidate the different mechanisms of LAOS shear banding seen in the mildly branched solution. The same analysis was performed for the low branching solution, with the goal of gaining additional insight into the mechanism of shear banding under LAOS. However in most LAOS conditions, very similar behavior was observed during the course of the oscillation cycle in terms of the alignment banding, which made elucidating different mechanisms of shear banding formation difficult. The alignment factor response was first examined at the maximum shear rate ($t/T = 0.5$) for conditions where the maximum shear
rate, $Wi_0$, was equivalent. A comparison of the alignment across the three LAOS conditions where $Wi_0 \approx 300$ can be seen in Figure 7.47 (conditions one, four, and nine), along with the steady shear alignment at $Wi = 264$ and $Wi = 450$. As seen in Figure 7.47, the gap-dependent alignment factor for all three conditions at the maximum shear rate is essentially identical within the calculation error, except at the inner wall where condition one is slightly lower. The similarity in the responses between conditions is not entirely surprising, given the proximity of the Deborah numbers. However, virtually no difference is seen between any of the conditions, and an equivalent change in $De$ in the mildly branched solution did produce different results. This difference in behavior between the low and mildly branched solutions again confirms the different mechanisms of shear banding under steady shear and LAOS.

![Figure 7.47: 1-2 plane $A_f$ when $t/T = 0.5$ ($Wi = 300$) for the three conditions where $Wi_0 \approx 300$: $De = 1, 1.4, 2$. At all gap positions, $A_f$ is approximately identical between conditions. Dotted lines are for visual aid only.](image)

The LAOS responses shown in Figure 7.47 are nearly identical to the steady shear results in the outer half of the gap. The magnitude of the alignment factor when $r/H > 0.5$ is equivalent to the steady shear values when $Wi = 264$, which is near the rate amplitude of $Wi_0 = 300$. This comparison clearly confirms that over-orientation is not observed in the outer half of the gap under LAOS in these three conditions. As the shape and magnitude of $A_f$ in this region is identical to the steady shear case, a similar mechanism of shear band
formation is proposed. As discussed earlier, evidence of a third shear band was observed in conditions one and three, and the behavior in conditions four and nine is similar to these two conditions. Further, the alignment band under LAOS in all three conditions is similar to the steady shear alignment band that indicated a three band state (see Chapter 6, Section 6.6.2), which strongly suggests that a three band structure is present under LAOS. Interestingly, at the inner wall, a large degree of over-orientation is observed. The degree of over-orientation appears to increase as the gap position decreases, which is the opposite trend observed in the mildly branched solution, where the over-orientation was the smallest at the inner wall. These differences in behavior again show that the mechanism of LAOS shear banding between the two solutions is much different, as was the case for steady shear.

The same comparison in Figure 7.47 is shown for the remaining experiments where $Wi_0 = 450$ in Figure 7.48 below. In Figure 7.48, the alignment factor profiles are shown at the maximum shear rate for all conditions ($t/T = 0.5$), but the profiles are also shown at the maximum strain ($t/T = 0.25$) for conditions seven and eight, which exhibited strain-dependent alignment. The steady shear results at $Wi = 450$ are also shown for comparison.

Figure 7.48: $A_f$ when $t/T = 0.5$ for the conditions where $Wi_0 = 450$: $De = 1, 1.4, 2, 4.2,$ and 9. $A_f(t/T = 0.25)$ is also shown for conditions 7 and 8, which exhibited strain-dependent alignment. In conditions 2, 3, and 5, $A_f$ is approximately identical between conditions. Dotted lines are for visual aid.
As was the case when $Wi_0 = 300$, all conditions show $A_f$ profiles that are similar in shape to the steady shear profile regardless of magnitude, except in condition eight. In conditions two, three, and five, the alignment factor is essentially identical at all gap positions, and exhibits a prominent alignment band. The similarity of the LAOS behavior to the steady shear behavior again suggests that three shear bands form under LAOS in these conditions. Even though condition seven exhibits alignment that responds to the applied strain, a clear alignment band is still present at the maximum shear rate when $t/T = 0.5$. However, the alignment band and overall alignment are significantly larger when $t/T = 0.25$. Surprisingly, the alignment when $t/T = 0.25$ is identical to the alignment in conditions two, three, and five when $t/T = 0.5$, which suggests that the mechanism of shear banding is not affected by the strain-dependent alignment in condition seven. As the response of condition seven shifts toward elastic-like behavior in time, this result implies that upon LAOS startup, the micelles still break and flow. This breakage enables the WLMs to form shear bands via a similar mechanism to conditions two, three and five. These interesting observations shows that within the range of frequencies examined ($De = 1$ to $De = 4.2$), the magnitude of the alignment factor does not depend on the applied frequency or strain amplitude for equivalent Weissenberg numbers. These results are also in agreement with the rheo-SANS results from three different Deborah numbers ($De = 0.48, 1, 4$), which shown that the maximum alignment was not affected by increasing $De$ (see Section 7.7.3). As was the case when $Wi_0 = 300$, there is little over-orientation observed at the outer wall for $De = 1$ to $De = 4.2$, but the degree of over-orientation increases as the gap position decreases.

The 1-3 plane results in Section 7.7.3 also showed that the magnitude of $A_f$ decreased when $De$ was further increased to $De = 9$. We hypothesized that the lower degree of orientation resulted from the micelles re-orienting and stretching with the deformation as opposed to breaking and flowing. In this hypothesis is the inherent assumption that this re-orienting and stretching results in a lower maximum orientation than the breakage mechanism. However, when the results in Figure 7.48 are examined more closely, an unexpected result is observed. At $t/T = 0.25$, which corresponds to the maximum alignment for the $De = 9$ condition, the same degree of alignment is observed at the inner wall as in all other conditions. When the
alignment factor profiles for $De = 9$ are compared back to the other conditions, the lower degree of orientation in the 1-3 plane $A_f$ does not result from a lower maximum alignment at the inner wall, but rather a lower alignment in the outer half of the gap, corresponding to the low shear rate band. This comparison disproves our initial hypothesis and suggests several explanations. First, the degree of micellar orientation may not be limited by the small applied strain amplitude in certain systems. While it was assumed that small strain amplitudes would limit the amount of total alignment, this may not be the case above a certain threshold. The strain amplitudes used in each of these conditions are extremely large, and although the strain amplitude of $\gamma_0 = 50$ when $De = 9$ is small relative to the other conditions, it is still a significant amplitude. If the frequency is further increased while the strain amplitude is further decreased, there may be a condition at which the maximum alignment under LAOS becomes lower. Another explanation is that upon LAOS startup, the micelles still break when $De = 9$. The shorter, more mobile micelles can then align to the same degree when they are being stretched at high frequencies. Additional experiments at higher $De$ would need to be performed to determine which of these explanations is more likely.

In condition eight, a different mechanism of shear banding is observed than in the other conditions. At equivalent shear rates, the LAOS alignment is clearly lower than in the steady shear case. However, significant over-orientation is observed at the inner wall if the LAOS results at $t/T = 0.25$ are compared to the steady shear results. In the low shear rate band, over-orientation is never observed, as the alignment is close to zero. Condition eight is the only condition to exhibit near-zero alignment in the outer half of the gap, which suggests that the material in this condition has only two shear bands. As the indication of the three banded state is a non-zero alignment band that forms in the outer half of the gap, a three band structure is not likely to be present here. The alignment factor profiles for this condition suggest a type of shear banding that is similar to in the mildly branched solution and other standard shear banding systems. As previously mentioned, if the smaller strain amplitude in this condition mitigates breakage and wall slip, a disappearance of the three banded state would be expected. For these reasons, we conclude that a different mechanism of LAOS shear banding in this condition results in a two-banded structure.
7.8.4 LAOS results in the context of steady shear

To further interpret the LAOS results, the LAOS stress response is examined in the context of the steady shear stress response. The steady shear flow curve and the states probed by LAOS are shown in Figure 7.49, where the LAOS stress at the maximum shear rate is compared to the steady shear stress at the equivalent shear rate in (a), and the root-mean-square average LAOS stress, $\sigma^*$, is shown in (b). As seen in Figure 7.49a, the LAOS stress is larger than the steady shear stress at all conditions except when $De = 9, Wi = 450$. At $De = 9, Wi = 450$, the LAOS stress is approximately equal to the steady shear stress. In the mildly branched solution, the observed over-orientation in the structure under LAOS was the result of higher LAOS stresses at the maximum shear rate. As nine of the ten conditions shown by Figure 7.49 exhibit higher LAOS stresses, the over-orientation in the low branching solution also appears to be a result of larger LAOS stresses. However, in the low branching solution, this over-orientation occurs at the inner wall as opposed to the outer wall for the mildly branched solution. In Figure 7.49b, $\sigma^*$ is always higher than the steady shear stress.

In Figure 7.49a, the proximity of the LAOS stress to the steady shear stress in condition eight helps to interpret the different mechanism of shear banding in this condition. All other conditions exhibit over-orientation at the inner wall, and little or no over-orientation at the outer wall, which results in an average alignment that is higher than in steady shear for the equivalent shear rate. However, in condition eight, over-orientation is still observed at the inner wall, but a near-zero alignment is observed near the outer wall. This leads to an average alignment under LAOS that is comparable to the steady shear alignment. As the LAOS stress and steady shear stress are comparable when $De = 9$, we also expect these steady shear and LAOS alignment values to be comparable. This mechanism of comparable alignment is distinct from condition one in the mildly branched solution, where the average LAOS alignment was also similar to the steady shear alignment. In that case, $A_f$ was comparable at each gap position for steady shear and LAOS. In this condition, both over-orientation and ‘under-orientation’ are observed at different gap positions, which average to the steady shear value.

The comparison of the LAOS stress to the steady shear stress in Figure 7.49a also
Figure 7.49: Steady shear stress and (a) stress at the equivalent, maximum shear rate during LAOS, and (b) the root-mean-square average LAOS stress, $\sigma^*$, for the low branching solution. The larger LAOS stresses in both cases help explain the observed over-orientation. In (a), when $De = 9$, the steady shear and LAOS stresses are approximately equal.

helps interpret the over-orientation reported in Figures 7.47 and 7.48. When $Wi \approx 300$, the LAOS stress slowly increases with $De$ (Figure 7.49). The lower LAOS stress at $De \approx 1, Wi = 295$ leads to inner wall over-orientation that is less significant than when $De = 1.4$ or $De = 2$ (Figure 7.47). Further, the average LAOS stress for this condition is substantially lower than in the other conditions (Figure 7.49b, Table 7.5). Conversely, the LAOS stress for $De = 1.4$ and $De = 2$ are within the uncertainty of one another when $Wi = 300$, which results in alignment factors that are also equal within the uncertainty at the maximum shear rate (Figure 7.47). When the results at $Wi = 450$ shown in Figure 7.49 are compared, an interesting trend is observed. Despite the increase in the LAOS stress with increasing $De$, little to no change in $A_f$ at the maximum shear rate is seen (Figure 7.48). In fact, when $De = 4.2$, the LAOS stress is significantly higher than in the other conditions, yet a lower alignment is seen at the maximum shear rate. Equal alignment to the other conditions is only observed when the profile is examined at the maximum strain instead of the maximum shear rate (Figure 7.48). This phenomenon can be explained by the evolution of the stress overshoot with increasing $De$. As the location of the stress overshoot shifts to larger $t/T$ with increasing $De$, the LAOS stress reported in Figure 7.49 for $De = 4.2$ is near the overshoot value. However, because the
stress overshoot is small in this case, the micelles do not exhibit a large degree of breakage and flow alignment when $t/T = 0.5$. Instead, the micelles respond to the strain, which leads to a maximum $A_f$ that is comparable to the other conditions. However, the average stress and $\sigma^*$ are roughly the same between conditions, which can be seen in Figure 7.49b, and in Table 7.5. As the average LAOS stress is nearly equivalent between all conditions when $Wi = 450$, this analysis suggests that the maximum attainable cycle alignment is dependent on the average cycle stress, as opposed to the LAOS stress at the maximum shear rate.

Table 7.5: LAOS average and root-mean-square average stress, $\sigma^*$, for the 0.01% wt NaTos solution. Averages are calculated using the absolute value of the cycle stress.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>$De, Wi$</th>
<th>$\sigma_{average}, \text{Pa}$</th>
<th>$\sigma^*, \text{Pa}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 295</td>
<td>6.02</td>
<td>6.80</td>
</tr>
<tr>
<td>2</td>
<td>1, 450</td>
<td>6.30</td>
<td>7.06</td>
</tr>
<tr>
<td>3</td>
<td>1.4, 450</td>
<td>6.38</td>
<td>7.16</td>
</tr>
<tr>
<td>4</td>
<td>2, 300</td>
<td>6.22</td>
<td>6.97</td>
</tr>
<tr>
<td>5</td>
<td>2, 450</td>
<td>6.55</td>
<td>7.33</td>
</tr>
<tr>
<td>6</td>
<td>3, 450</td>
<td>6.41</td>
<td>7.27</td>
</tr>
<tr>
<td>7</td>
<td>4.2, 450</td>
<td>6.49</td>
<td>7.42</td>
</tr>
<tr>
<td>8</td>
<td>9, 450</td>
<td>6.56</td>
<td>7.68</td>
</tr>
<tr>
<td>9</td>
<td>1.4, 300</td>
<td>6.45</td>
<td>7.13</td>
</tr>
<tr>
<td>10</td>
<td>1.4, 400</td>
<td>6.35</td>
<td>7.10</td>
</tr>
</tbody>
</table>

7.8.5 Summary: low branching

By examining a wide range of frequencies and shear rates under LAOS, different mechanisms of shear banding were able to be identified in the low branching solution. These shear banding mechanisms are distinct from the two shear banding mechanisms identified in the mildly branched solution. In conditions with low Deborah and high Weissenberg numbers, a similar mechanism of shear banding is observed to in the steady shear case discussed in Chapter 6. Here, an ‘alignment band’ of significant and non-zero alignment is observed in the outer half of the gap. In the steady shear case, this phenomenon corresponded to the formation of a structure with three shear bands. While there is only evidence of this third band
in conditions one and three, from particle tracking velocimetry measurements under steady shear (Chapter 6, Section 6.6.2), we expect the width of the third shear band near the outer wall to be quite small. Accordingly, it is unlikely for us to be able to detect this third band in the LAOS measurements unless the measurement is taken extremely close to the outer wall. However, the similar ‘alignment banding’ observed in the first five conditions under LAOS suggests that the three banded structure is also observed under LAOS deformations.

A different trend in the LAOS alignment in seen in condition eight. Here, the applied Deborah number is an order of magnitude higher than in condition one, where the evidence of three bands was observed. The high Deborah number in this condition leads to an elastic response during LAOS, and near-zero alignment in the low shear rate band, similar to what was observed in the mildly branched solution. As the high Deborah number in this condition mitigates flow and instead allows the material to act as an elastic solid, the micellar breakage and flow associated with elastic instabilities and the three banded state may be eliminated. The significantly lower strain amplitude may also mitigate wall slip, leading to a standard shear banded state with two bands as opposed to a three banded state.

7.9 LAOS shear thinning: highly branched solution

After confirming shear banding under LAOS in the low and mildly branched solution, the nonlinear oscillatory shear behavior of the highly branched (0.10% wt NaTos) solution was investigated under LAOS. The VCM model predictions of Zhou et al. [10] suggest that shear banding under steady shear is a pre-requisite for shear banding under LAOS. As this solution has sufficient branching such that shear banding is not observed under steady shear, shear banding under LAOS is not expected for this solution. Nevertheless, we seek to confirm this hypothesis and investigate the LAOS behavior of more highly branched solutions to determine signatures of branching.

7.9.1 Sample characterization: 0.10% wt NaTos

The 0.10% wt NaTos solution that was used for the 1-2 plane LAOS experiments slightly differs from the solution used for the steady shear and shear startup investigations.
In this section, we present a comparison between the two solutions to help better understand the observed LAOS results. We will refer to the solution presented in Chapters 4 through 6 as the ‘original’ 0.10% wt NaTos solution, and this new sample as the ‘new’ or ‘LAOS’ 0.10% wt NaTos solution. In addition to static SANS and rheological results, we will briefly present 1-3 and 1-2 plane steady shear results for this new 0.10% wt NaTos solution. It should be noted that many of the relevant rheology and 1-3 plane LAOS measurements were performed on the ‘original’ sample, which will be noted when the results are presented. These results are a supplement to the 1-2 plane results, and show similar features despite the differences in sample preparation.

Figure 7.50 shows the static SANS comparison between the original and new 0.10% wt NaTos solutions. As seen in Figure 7.50, the 1-D scattering curves for the original sample at rest in the three different configurations is nearly identical between configuration and sample preparation. These solutions show a clear low-$q$ slope, indicating the disappearance of the interaction peak which was observed in the lower salt solutions. The LAOS 0.10% wt NaTos sample has a nearly flat slope at low $q$-values and still exhibits a slight interaction peak. The 1-D curve from the 1-2 shear cell is in good agreement with the 1-D curve for the LAOS sample from the 1-3 plane SANS rheometer configuration. For reference, the 0.075% wt NaTos solution from the 1-3 plane configuration is also shown, which is similar in structure to the new 0.10% wt NaTos solution. The faint interaction peak in the new 0.10% wt NaTos solution, and its similarity in structure to the 0.075% wt NaTos solution, suggests that this new solution has a true salt concentration in between that of the 0.075% wt and 0.10% wt NaTos solutions.

The LVE rheology of the new 0.10% wt NaTos solution also suggests that its true salt content is in between 0.075% wt and 0.10% wt NaTos; see Appendix G for a comparison of the LVE spectra. In the original solution, the crossover frequency was $\omega_c=2.6$ rad·s$^{-1}$, resulting in a relaxation time of $\tau_R=0.4$ seconds. In this new solution, the crossover frequency is significantly lower, such that $\omega_c=1.8$ rad·s$^{-1}$ and $\tau_R=0.5$ seconds. Interpolating based on the LVE rheology data presented as a function of salt concentration in Chapter 4, Figure 4.4, we estimate an effective salt concentration for this solution of $C_s \approx 0.088$% wt NaTos.
Figure 7.50: Comparison of 0.10% wt NaTos ‘original’ sample used for previously reported experiments (blue) vs. the solution for the LAOS experiments. The LAOS sample has a longer relaxation time and a similar structure to the 0.075% wt NaTos solution, suggesting it has an effective salt content less than the original 0.10% wt NaTos solution.

Steady shear 1-3 plane SANS measurements also support that the new solution has a lower effect salt content. A comparison of the 1-3 plane SANS results for the original and new samples can be seen in Figure 7.51 on an absolute shear rate basis. As seen in Figure 7.51, the new LAOS sample has a higher 1-3 plane alignment factor across the shear rate spectrum until the critical shear rate is reached. As was discussed extensively in Chapter 5 (see Section 5.10), higher alignment is observed in the 1-3 plane on an absolute shear rate basis (until the critical shear rate) for solutions with lower salt concentrations. Accordingly, the higher 1-3 plane $A_f$ for the new versus the original sample shown in Figure 7.51 supports our estimate of the new solution salt concentration of $C_s \approx 0.088\%$ wt NaTos. While the new solution appears to have a lower salt concentration than the original 0.10% wt NaTos solution, this new solution does not appear to exhibit shear banding under steady shear deformation. Steady shear startup measurements on this solution taken during 1-3 plane SANS showed a fast transient in the stress response before reaching steady state, unlike in the low and mildly branched solutions. No structural transient was observed in the 1-3 plane $A_f$ measurements for this solution (which were taken with time-resolution), indicating that this
new solution and the original 0.10% wt NaTos solution both exhibit shear thinning under steady shear.

![Image](image.png)

Figure 7.51: Comparison of the 1-3 plane $A_f$ for the 0.10% wt NaTos ‘original’ sample and the ‘new’ LAOS sample. The higher 1-3 $A_f$ in the new LAOS sample suggests it has a lower effective salt concentration, which is consistent with our estimates based on the rheology and static SANS.

The absence of shear banding in the new 0.10% wt NaTos solution suggested by the startup stress and 1-3 plane alignment factor response is corroborated with 1-2 plane measurements. These 1-2 plane measurements were taken for several shear rates, at two gap positions ($r/H = 0.3, 0.7$) before the LAOS measurements were performed. The 1-2 plane alignment results, and a comparison to the alignment from the original sample, can be seen in Figure 7.52. The 1-2 plane alignment for the new solution is higher than the alignment of the original solution at each shear rate and gap position. The alignment for the new solution at $r/H = 0.7$, however, is only slightly higher than the original solution alignment. At $r/H = 0.3$, the new solution alignment becomes significantly higher than the original solution alignment for the same shear rate. This difference in the alignment of the two solutions becomes more pronounced as the shear rate is increased.

In shear thinning solutions, inferring that the 1-2 $A_f$ is a linear function of gap position is a good assumption (see Chapter 5, Section 5.9.3). While there are only two $A_f$ values
for each shear rate in the new solution data, if we assume linear behavior, the slope between points is larger in the new solution at equivalent shear rates. This higher slope suggests a higher degree of shear thinning in the new versus the original solution, which is consistent with our estimated effective $C_s$ for this solution, and the previous rheological results which show that the power law index increases with added salt (see Chapter 5, Section 5.10). This trend is observed even if the difference in the relaxation time and resulting Weissenberg number between the solutions is accounted for. The slope of the 1-2 $A_f$ versus gap position at $\dot{\gamma} = 26.4$ s$^{-1}$ for the new solution ($Wi = 15$) is larger than in the original solution at $\dot{\gamma} = 45$ s$^{-1}$, where $Wi = 17$. This Weissenberg number comparison further validates that $N$ should be lower in the new solution versus the original. Using the empirical relationship developed in Chapter 5 Section 5.10, we estimate that $N = 0.13$ for the new 0.10% wt NaTos solution, versus $N = 0.15$ for the original solution.

Figure 7.52: Comparison of the 1-2 plane $A_f$ for the 0.10% wt NaTos ‘original’ sample and the ‘new’ LAOS sample. The higher 1-2 $A_f$ in the new LAOS sample further supports that it has a lower effective salt concentration. Dotted lines are for visual aid only.
7.9.2 LAOS rheology

As the ‘new’ 0.10% wt NaTos solution was used extensively for 1-2 and 1-3 plane measurements, sufficient sample could not be recovered to perform the LAOS rheological measurements. The LAOS stress responses presented in this section are performed on the original sample preparation shown in Figure 7.50 (□ symbol). The LAOS measurements presented here directly correspond to the 1-3 plane LAOS measurements shown below in Section 7.9.3. While the sample preparations differ between the 1-2 plane and 1-3 plane experiments, the solution properties are fairly similar and the results should be compared and interpreted accordingly. In the results presented in this and the following sections, the reported Deborah and Weissenberg numbers \( (De, Wi) \) are based on the ‘new’ solution so that results can be compared to the other branching levels. Table 7.6 summarizes the LAOS parameters, and the \( De \) and \( Wi \) based on both solutions. The condition in which \( De = 0.85, Wi = 25 \) will be referred to as \( De \approx 1, Wi = 25 \) to enable comparisons to the solution with low branching.

Table 7.6: LAOS conditions and parameters for the 0.10% wt NaTos solution. The nomenclature from the first and second columns (new solution) will be used to refer to each condition throughout the text.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>( De, Wi_{\text{new}} )</th>
<th>( \omega, \text{rad s}^{-1} )</th>
<th>( \gamma_0 )</th>
<th>( \gamma_0, \text{s}^{-1} )</th>
<th>( De, Wi_{\text{original}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \approx 1,25 ) (0.85, 25)</td>
<td>1.53</td>
<td>30</td>
<td>45.9</td>
<td>0.6, 18</td>
</tr>
<tr>
<td>2</td>
<td>7.5, 25</td>
<td>13.8</td>
<td>3.33</td>
<td>45.9</td>
<td>5.4, 18</td>
</tr>
<tr>
<td>3</td>
<td>2.5, 8.3</td>
<td>4.6</td>
<td>3.33</td>
<td>15.3</td>
<td>1.8, 6</td>
</tr>
<tr>
<td>4</td>
<td>0.08, 25</td>
<td>0.14</td>
<td>321</td>
<td>45</td>
<td>0.05, 18</td>
</tr>
</tbody>
</table>

The LAOS rheology from condition one \( (De \approx 1, Wi = 25) \) can be seen in Figure 7.53 as Lissajous-Bowditch projections. Figure 7.53a shows the elastic projection in terms of the stress vs. the strain, and Figure 7.53b shows the viscous projection (stress vs. shear rate). A significant stress overshoot is observed in the elastic projection (Figure 7.53a), which leads to secondary loops in the viscous projection (Figure 7.53b). As this response was measured on the original sample, the original \( De, Wi \) from Table 7.6 can be used to compare the results to the Pipkin diagram of the mildly branched solution presented in Figure 7.3. When compared,
the LAOS stress responses for the mildly branched solution has a milder stress overshoot that results in more rounded secondary loops in the viscous projection. The sharp secondary loops observed in the 0.10% wt NaTos solution, however, consist of significantly less area in the overall stress response, which means that the stress overshoot region covers a smaller portion of the cycle in the 0.10% wt NaTos solution. This observation supports the results in Chapter 6, which showed that branching mitigates the stress overshoot under shear startup deformations.

LAOS stress responses from conditions two ($De = 7.5$, $Wi = 25$) and three ($De = 2.5$, $Wi = 8.3$) are compared in Figure 7.54 in terms of the Lissajous-Bowditch projections. While the maximum shear rate in condition two is three times that of the maximum rate in condition three, both conditions share the same strain amplitude ($\gamma_0 = 3.33$). As condition one and condition two share the same maximum shear rate, this choice of conditions allows us to compare the relative effects of the frequency and strain amplitude on the LAOS stress and structural responses. No stress overshoot is observed in either condition two or three, which is expected. The stress overshoot is associated with micellar breakage and flow, and as these conditions are at relatively high Deborah numbers, significant breakage is not expected. While the two stress responses are similar, condition two exhibits a more elastic-like
response (Figure 7.54a). A straight line in the stress versus strain curve indicates a Hookean solid response, and the smaller area carved out in the elastic projection for condition two indicates that it is closer to this ideal solid behavior than condition three. This behavior is not surprising given that the applied frequency is three times larger in condition two, and is within the plateau region of the LVE rheology (Chapter 4, Figure 4.5). These results can also be compared to the Pipkin diagram of the mildly branched solution presented in Figure 7.3. However, as the LAOS stress responses for both the mild and highly branched solutions lack distinctive features at these conditions, no discernible differences could be identified between the solutions.

Figure 7.54: Lissajous-Bowditch representation of the stress response for two conditions: $De = 2.5$, $Wi = 8.3$, and $De = 7.5$, $Wi = 25$. Reported values of $De$ and $Wi$ are based on the new 0.10% wt NaTos solution. (a) Elastic representation, $\sigma$ vs. $\gamma$, and (b) viscous representation, $\sigma$ vs. $\dot{\gamma}$.

### 7.9.3 1-3 plane LAOS SANS

To complement the rheological results, 1-3 plane SANS measurements were taken for conditions one, three and four listed above in Table 7.6; an error in the triggering electronics prevented the condition two data from being analyzed. As mentioned before, the 1-3 plane measurements for conditions one and three and the LAOS stress response for conditions one through three correspond to the original sample. The 1-3 plane alignment factor as a function of time during the oscillation cycle, $t/T$, can be seen for condition one ($De \approx 1$, $
Wi = 25) in Figure 7.55, along with the corresponding LAOS stress during the cycle. As seen in Figure 7.55, the 1-3 plane alignment factor response is nearly perfectly in phase with the stress response, and is nearly in phase with the applied shear rate (\( \dot{\gamma} = 0 \) at \( t/T = 0.25, 0.75 \)). This response suggests that the material acts primarily as a fluid during the course of the oscillation cycle.

In Figure 7.55, the maximum alignment during the cycle roughly corresponds with the maximum shear rate. Interestingly, the alignment appears to exhibit a reproducible local maximum before the maximum stress (\( t/T = 0.38, 0.88 \)). This local maximum is outside of the calculated uncertainty, as \( \delta A_f < 0.007 \) in this region and is smaller than the point size for the majority of the cycle. This local maximum appears to correspond with an inflection point in the stress response, which can be seen better in the elastic Lissajous-Bowditch projection in Figure 7.53a, at \( \gamma \approx 1500\% \). Another local maximum appears to coincide with the maximum stress, which is also reproducible during the cycle. Other local maxima and inflection points in the \( A_f \) response correspond with inflection points and features of the stress response during the course of the oscillation cycle. Finally, the maximum alignment during LAOS for
this condition is slightly larger than the corresponding steady shear value, and is outside of the calculated uncertainty, where $A_{f,SS} = 0.147 \pm 0.003$ and $A_{f,LAOS} = 0.172 \pm 0.006$.

The 1-3 plane alignment factor during the oscillation cycle and associated LAOS stress can be seen for condition three ($De = 2.5, Wi = 8.3$) in Figure 7.56. Unlike in condition one, the 1-3 plane alignment factor response is nearly in phase with the applied strain ($\gamma = 0$ at $t/T = 0, 1$). The phase of the alignment factor response also agrees well with the measured stress response, which suggests that the material acts primarily as an elastic solid during the course of the cycle. In Figure 7.56, an interesting upturn and local maximum in the alignment factor response is observed from $t/T = 0.375$ to 0.5 and $t/T = 0.875$ to 1. To verify the validity of this feature in the $A_f$ response, the first half and second half of the LAOS experiment file were analyzed separately, which can be seen in Appendix O. The feature is persistent during both halves of the experiment, but there appears to be a slight phase shift in the data from the first half of the data to the second half. This feature could result if there is a phase shift in the $A_f$ response from the inner to the outer wall of the Couette, for example, which can be verified with 1-2 plane measurements. As was the case in condition one, the maximum alignment factor observed during the cycle in condition two is roughly that of the steady shear value; in both cases, $A_f \approx 0.06$. As condition two exhibited stronger elastic features in the LAOS rheology than condition three, we expect the 1-3 plane results for condition two would also show elastic-like behavior.

Finally, the 1-3 plane results for condition four ($De = 0.08, Wi = 25$) can be seen in Figure 7.57. These measurements were taken so the results could be compared to the 0.01% wt NaTos solution on an absolute deformation basis. In this condition, the absolute frequency and shear rate are identical to the $De = 1, Wi = 321$ 1-3 plane experiment from the low branching solution, where $\omega = 0.14 \text{ rad} \cdot \text{s}^{-1}$, $\gamma_0 = 321$, and $\dot{\gamma}_0 = 45 \text{ s}^{-1}$. Results from two trials are shown in Figure 7.57 to demonstrate the repeatability and phase stability of the response, which was unstable for the same condition in the low branching solution. These results also give insight into the effect of dramatically lowering the frequency on the micellar structural response. As seen in Figure 7.57, the 1-3 plane alignment factor is perfectly in phase with the applied shear rate ($\dot{\gamma} = 0$ at $t/T = 0.25, 0.75$), suggesting fluid behavior during
Figure 7.56: 1-3 plane $A_f$ and LAOS stress during $t/T$ at $De=2.5$, $Wi=8.3$. The $A_f$ response is in phase with the stress and is nearly in phase with the applied strain, indicating elastic-like behavior.

As seen by comparing Figures 7.57 and 7.20, the magnitude of the alignment factor in this condition is roughly half that observed in the low branching solution for the same conditions (denoted $De = 1, Wi = 321$ in Figure 7.20). As was the case in steady shear, this
Figure 7.57: 1-3 plane $A_f$ and LAOS stress during $t/T$ at $De = 0.08$, $Wi = 25$. The $A_f$ response is in phase with the applied shear rate, indicating fluid behavior.

suggests that branching mitigates flow alignment on an absolute shear rate scale, or in this case, when the LAOS conditions are identical on an absolute (as opposed to dimensionless) basis. While $De = 1$, $Wi = 321$ was not perfectly rate-aligned in the low branching solution, the response of the highly branched solution does show perfect rate alignment. This rate alignment results because the Deborah number is an order of magnitude lower for the highly branched solution than in the low branched solution for the same condition, meaning that fluid behavior is expected. Finally, fluid behavior is supported when the maximum LAOS and steady shear alignment are compared. In Figure 7.57, the maximum LAOS alignment occurs at the maximum shear rate, and the value of $A_f$ is equal to the steady shear $A_f$. These equivalent alignment values suggest that the WLMs behave in this LAOS condition as they would under steady shear at the same rate, in line with the Cox-Merz rule discussed in Chapter 5, Section 5.11.
7.9.4 1-2 plane LAOS SANS

For the 0.10% wt NaTos solution, 1-2 plane SANS measurements were taken for two conditions at equivalent Weissenberg numbers (conditions one and two) and two at equivalent strain amplitudes (conditions two and three). These measurements were performed at two gap positions \((r/H = 0.3, 0.7)\) using a 0.3 mm curved slit. In condition one, a low dimensionless frequency and moderate shear rate was used, giving \(De \approx 1\) and \(Wi = 25\). Based on the 1-3 plane results and results from the other WLM solutions at this dimensionless frequency, we expect the solution to exhibit fluid-like behavior in this condition. In the second condition, a high dimensionless frequency was examined, where \(De = 7.5\). As the frequency is significantly higher here for the same shear rate, and based on the rheology and 1-3 plane results, we expect elastic-like behavior in this condition. The 1-2 plane alignment factor results for these two LAOS conditions can be seen in Figure 7.58. As expected from the LAOS stress response, in the first condition (Figure 7.58a), the alignment factor response is in phase with the applied strain rate, indicating fluid-like behavior. Conversely, in Figure 7.58b, the alignment factor response is nearly perfectly in phase with the applied strain, indicating elastic-like behavior which is also consistent with the rheology.

![Figure 7.58](image)

Figure 7.58: 1-2 plane \(A_f\) during the LAOS cycle for the 0.10% wt NaTos solution for (a) \(De \approx 1, Wi = 25\) and (b) \(De = 7.5, Wi = 25\).

In Figure 7.58a, the maximum alignment occurs roughly around the maximum shear
rate \((t/T = 0.5)\). A significant degree of alignment is observed at both the inner and outer walls. The inner and outer wall \(A_f\) response are in phase with one another and are similar in magnitude, indicating shear thinning in this condition. The opposite trend is observed in Figure 7.58b. Here, the maximum alignment is observed near the maximum strain \((t/T = 0.25, 0.75)\). The alignment at the inner and outer walls for this condition is less than one-third that of the first condition, despite the equivalent applied shear rate. This decrease in alignment at between \(De = 1\) and \(De = 7.5\) for the same \(Wi\) was not observed in the low branching solution over a similar change in \(De\). The alignment factor response is roughly in phase between the inner and outer walls, and the magnitudes are similar, as was observed in the first condition. These features indicate that the WLMs exhibit shear thinning at this condition as well as the first. The results in Figure 7.58b also demonstrate the role of the strain amplitude in determining the degree of micellar alignment. In Figure 7.58b, the strain amplitude is much lower than in Figure 7.58a, because the frequency is higher. The increase in the frequency leads to a lesser degree of flow alignment and an elastic-like response in this condition. In the mildly branched solution, increasing the frequency and decreasing the strain amplitude served to increase the maximum alignment between conditions one and two (see Figure 7.10). However, this result is clearly only applicable within a small window of frequency and amplitude combinations, as both conditions for the mildly branched solution had stress responses that still exhibited stress overshoots. Here, when \(De\) is increased by a factor of nine, the strain amplitude is decreased by a factor of nine hold the shear rate constant. At these low strain amplitudes, the micelles cannot break and flow, as evidenced by the lack of stress overshoot in the rheology (Figure 7.54). Instead, the micelles respond to deformation as an elastic solid and simply stretch and align as the strain is increased. Interestingly, when the amplitude is held constant but the frequency is reduced (condition three), fluid-like behavior is observed again. The maximum alignment at the inner wall between conditions two and three is nearly identical; however, the alignment factor responses are completely out of phase.

Despite that the 1-2 plane and 1-3 plane results are from different sample preparations, the samples are still similar in terms of the flow properties and the results can be
loosely compared. In condition one, the 1-2 plane results are consistent with the 1-3 plane results in terms of the phase of the response. Although the LAOS rheology was performed on the original sample and not the new sample, the shape and features of the 1-2 plane results are in excellent agreement with the LAOS stress response. The greatest difference between the 1-2 plane and 1-3 plane results is the magnitude of the alignment factor and the degree of over-orientation. While the 1-3 plane alignment is expected to be lower than the 1-2 plane alignment at the inner wall due to gap averaging, in this case, the 1-2 plane alignment at the outer wall is still significantly higher than the 1-3 plane alignment. The differences in the magnitude of the alignment are most likely a result of the different sample preparations, as the new sample is expected to align further than the original sample (see Figures 7.51, 7.52).

While the steady shear and LAOS alignment were similar in the 1-3 plane for the original sample, the 1-2 plane results showed large degrees of over-orientation. The differences in over-orientation here are likely a result of the relative Deborah and Weissenberg numbers for each experiment. While denoted \( De \approx 1, Wi = 25 \) for clarity, the 1-3 plane deformation for the original sample actually corresponds to \( De = 0.6, Wi = 18 \) as noted in Table 7.6. This change in dimensionless groups has two effects on the observed over-orientation. First, the dimensionless shear rate is lower in the 1-3 plane measurements. As observed for the mildly branched solution, the degree of over-orientation appears to increase with shear rate (Table 7.2). Next, the dimensionless frequency is lower. As seen by the results for the mildly branched solution in Table 7.2, within a small window of frequencies, the degree of over-orientation increases as the frequency is increased. The largest degrees of over-orientation in the mildly branched solution were observed when the frequency and shear rate were highest. As such, the comparison of the results here with those of the mildly branched suggests that both the lower dimensionless frequency and shear rate in the 1-3 plane experiments lead to the lower degrees of over-orientation versus the 1-2 plane experiments.

In condition three \((De = 2.5, Wi = 8.3)\), the 1-2 plane and 1-3 plane results are in better agreement in terms of the magnitude of the alignment factor. However, the phase of the alignment factor response is not in agreement between measurements, and the responses appear to have opposite phases. This may explain the anomalous feature observed in the
1-3 plane results shown in Figure 7.56), as the 1-3 plane $A_f$ is a convolution in space of the micellar structure across the gap. The 1-2 plane measurements were taken over a two hour period of time, whereas the 1-3 plane measurements were only taken over one half hour. As seen in Appendix O, the phase of the 1-3 plane response appears to be shifting in time. Should this response continue to shift in time, it is feasible that the 1-3 and 1-2 plane responses would agree. If this were the case, it would suggest that over the course of many LAOS cycles, the material would undergo a type of yielding under LAOS that would eventually lead to flow during the oscillation cycle. Finally, although there are no 1-2 plane results for condition four, it is likely that the 1-2 plane response would resemble the 1-3 plane results. As seen at $De = 0.17, Wi = 75$ for the mildly branched solution, the stress overshoot had no impact on the alignment factor response, and the 1-2 plane results for this condition resemble the 1-3 plane results for condition four. Therefore, as condition four has an even lower Deborah and Weissenberg number ($De = 0.08, Wi = 25$), it is likely that the 1-2 plane results would resemble the measured 1-3 plane results.

7.9.5 Discussion: high branching

In order to better understand the LAOS results, the LAOS stress response is examined in the context of the steady shear stress response. The flow curve measured during rheo-SANS and the states probed by LAOS are shown in Figure 7.59. In Figure 7.59, the LAOS stress at the maximum shear rate, and the root-mean-square average LAOS stress, $\sigma^*$, are compared to the steady shear stress at the equivalent shear rate. As seen in Figure 7.59, the LAOS stress at the maximum rate is only larger than the steady shear stress when $De \approx 1, Wi = 25$ (condition 1). However, $\sigma^*$ is equal to or greater than the steady shear stress in all three conditions. In condition one, the LAOS stress at the maximum rate is over five-fold higher than the steady shear stress, which leads to the pronounced over-orientation. When $De = 7.5$ for the same Weissenberg number (condition 2), the maximum LAOS stress is three-fold lower than the steady shear stress, which explains the drastic decrease in the maximum $A_f$ and the absence of over-orientation. In condition two, $\sigma^*$ is equivalent to the steady shear stress, so based on the Rutgers-Delaware rule, an equal alignment under steady
shear and LAOS would be expected. However, as the LAOS alignment is much lower than in steady shear, the material behavior does not follow this empirical rule.

Figure 7.59: Steady shear stress (from rheo-SANS) and the stress at the equivalent, maximum shear rate during LAOS for the highly branched solution. The larger LAOS stress at $De \approx 1, Wi = 25$ explains the observed over-orientation.

The proximity of the LAOS stress to the steady shear stress shown in Figure 7.59, along with the LAOS cycle average stresses given in Table 7.7, help to interpret the observed over-orientation. At $De = 2.5, Wi = 8.3$ (condition 3), the LAOS stress at the maximum shear rate is much closer to the steady shear stress than when $De = 7.5, Wi = 25$ (condition 2). Accordingly, the steady shear alignment is only 30% higher than the maximum LAOS alignment in this condition, whereas the steady shear alignment is 220% higher when $De = 7.5$. In condition three, $\sigma^*$ sits above the steady shear flow curve, so this ‘under-orientation’ is not expected based on the Rutgers-Delaware rule. The maximum stress and average cycle stresses (see Table 7.7) between conditions two and three are nearly identical. As was the case in the low branching solution, the similar average LAOS stress results in a maximum LAOS alignment that is also similar between conditions 2 and 3. Comparing these LAOS results to steady shear in Figure 7.59 helps clarify the LAOS results in the context of steady shear, and in relation to one another.
Table 7.7: LAOS average and root-mean-square average stress for the 0.10% wt NaTos solution. Averages are calculated using the absolute value of the cycle stress.

<table>
<thead>
<tr>
<th>Condition #</th>
<th>De, Wi</th>
<th>( \sigma_{\text{average}}, \text{Pa} )</th>
<th>( \sigma^*, \text{Pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1, 25</td>
<td>32.3</td>
<td>43.7</td>
</tr>
<tr>
<td>2</td>
<td>7.5, 25</td>
<td>13.6</td>
<td>15.1</td>
</tr>
<tr>
<td>3</td>
<td>2.5, 8.3</td>
<td>13.0</td>
<td>14.4</td>
</tr>
</tbody>
</table>

7.10 Discussion: all branching levels

While certain behaviors during LAOS are common across samples, the majority of the results are sample-specific. In all cases, the phase of the rheological stress response is a fairly good predictor of the phase of the alignment factor response. However, the features in the stress response are not always observed in the \( A_f \) response, especially at low Deborah numbers. Shear banding is observed in the low and mildly branched solutions, whereas shear thinning is seen in the highly branched solution. Despite shear banding in the mildly branched solution and shear thinning in the highly branched solution, the two samples show similar behavior at certain conditions. For example, decreasing the Deborah number in the region where \( De < 1 \) results in a lower degree of flow alignment. In the low branching solution, equal magnitudes of the flow alignment are observed between \( De = 0.48 \) and \( De = 3 \). This difference suggests that either the low branching solution does not follow the same trend at the other two systems, or that lower frequencies would have to be probed to see this effect. In the mild and highly branched solutions, a large degree of over-orientation is observed near the outer wall; the over-orientation is less pronounced at the inner wall. Once again, these trends are not observed in the low branching solution, which shows little to no over-orientation at the outer wall.

While shear banding was observed in the low and mildly branched solutions, different mechanisms of shear band formation are observed in each case. Shear thinning only is observed in the highly branched solution. Each WLM system exhibits a similar behavior under LAOS as is observed under steady shear for at least some conditions. For example, the mildly branched solution shows a similar form a shear banding under LAOS to the shear
banding under steady shear for low Deborah numbers. In the low branching solution, a three banded structure is hypothesized under LAOS for all but one condition. This three banded structure is the same structure that results under steady shear deformations for this solution, which results from wall slip and possible elastic instabilities in the solution. As was the case with steady shear, the differences in LAOS shear banding behavior can be partially attributed to the different electrostatic interactions and solution elasticity between the low and mildly branched solutions. In the mildly branched solution, small adjustments to the applied frequency and amplitude greatly affect the presence and type of shear banding that is seen. Conversely, in the low branching solution, a new mechanism of shear banding is not observed until the frequency is increased by a factor of nine. Here, the same type of shear banding is observed when the frequency is increased by greater than four-fold. In the mildly branched solution, a two-fold increase in the frequency is enough to change the mechanism of shear banding, which suggests that the observed shear banding under LAOS is much more sensitive to frequency in the mildly branched solution than in the low branching solution.

Interestingly, increasing the Deborah number from $De = 1$ to $De = 9$ does not affect the maximum observed alignment in the low branching solution under LAOS; this change only affects the magnitude of the alignment at the outer wall, in the low shear rate band. The maximum observed alignment appears to be a function of the average cycle stress. Conversely, in the highly branched solution, significantly lower alignment for the same Weissenberg number is seen when $De$ is increased over a similar range. These differences in the alignment factor magnitude likely result from the different mechanisms of flow alignment associated with shear banding versus shear thinning. Finally, the degree and mechanism of over-orientation is distinct between solutions. While the mild and highly branched solutions show the largest degree of over-orientation at the outer wall, the low branching solution exhibits little to no over-orientation in this region. Instead, the low branching solution only exhibits over-orientation near the inner wall. When compared based on equivalent Deborah numbers, the over-orientation in the highly branched solution is significantly higher at both the inner and outer walls when $De = 1$ for the same maximum shear rate. In the highly branched solution, the outer wall over-orientation at $De = 1, Wi = 25$ is over two-fold greater
than in steady shear, and the inner wall alignment is over 1.5 times the steady shear value. In the low branching solution when $De = 1, Wi = 450$, little to no over-orientation is seen at the outer wall, while the inner wall over-orientation is roughly 1.3 times the steady shear value. However, no over-orientation is observed when $De = 7.5$ for the highly branched solution, and the alignment is far below the steady shear value. This behavior is predicted by the LAOS stress response, which is lower than the steady shear stress at the equivalent $Wi$. Conversely, when $De = 9$ for the low branching solution, the maximum LAOS alignment is 20% larger than the steady shear value. As distinct mechanisms of flow alignment occur in each system, we cannot make general assumptions about the flow alignment or over-orientation across $De$ and $Wi$ between samples; instead, the LAOS stress response is a better tool to predict the alignment behavior.

7.11 Conclusions

In this chapter, the investigation into the non-equilibrium properties of mixed cationic and anionic wormlike micellar solutions with various amounts of added sodium tosylate (NaTos) was continued using large amplitude oscillatory shear (LAOS) dynamic deformations. In this chapter specifically, shear banding and shear thinning flow phenomena were examined for the branched WLMs under these dynamic deformations using a combination of rheological and flow-small angle neutron scattering techniques. As was discussed in Chapters 5 and 6, high branching levels are associated with the disappearance of shear banding under steady shear deformations. In this chapter, we sought to confirm shear banding and shear thinning in the various WLM solutions examined. Using SANS measurements, it was confirmed that high branching levels are also associated with a disappearance of shear banding under LAOS deformations. Prior to the work presented in this chapter, experimental work confirming LAOS shear banding was limited. However, by using 1-2 (flow-gradient) plane flow-SANS, we successfully identified shear banding under LAOS for the first time in concentric cylinder Couette flow. These initial measurements were performed on the mildly branched solution (0.05% wt NaTos), and were used to test the Vasquez-Cook-McKinley
(VCM) model predictions of shear banding under LAOS. In this solution, the applied frequency and amplitude of the LAOS deformation greatly impacts the existence and type of shear banding that is observed. At low frequencies, the maximum alignment under LAOS as a function of gap position mirrors the steady shear alignment values, indicating a similar shear banding behavior between LAOS and steady shear. Conversely, as the frequency is raised, the maximum alignment under LAOS surpasses that of steady shear, which we refer to as ‘over-orientation.’ The over-orientation results from the shorter oscillation cycle, which does not give the material sufficient time to relax, making the shear banding more pronounced. Our results are in excellent agreement with the VCM model predictions, and can be used for the improvement of similar theoretical models. Guidelines to predict LAOS shear banding in future conditions for this solution were developed, using the degree of over-orientation and features of the LAOS stress response.

After LAOS shear banding was confirmed in the mildly branched solution, additional LAOS measurements were performed in the low branching solution (0.01% wt NaTos) to determine if shear banding could be verified. As was the case in steady shear for the low branching solution (see Chapters 5, 6), ‘alignment banding’ indicative of shear banding was observed in the outer half of the gap in almost all LAOS conditions. The observed alignment banding under steady shear corresponds to a three banded structure (Chapter 6, Section 6.6.2), which we propose is also the mechanism of shear banding under LAOS. The three banded structure in the low branching solution is a result of the high applied Weissenberg numbers, minor wall slip, and possible elastic instabilities that can arise from the high solution elasticity and strong electrostatic interactions (Equation 5.10). The alignment banding mechanism of LAOS shear banding is distinct from the two mechanisms observed in the mildly branched solution. At the highest Deborah number probed, a different and more traditional form of shear banding is observed in the low branching solution, where only two shear bands are present.

The 1-2 plane LAOS results also verify that shear banding is not observed when significant branching is present. As the solution electrostatic interactions seem to contribute to different shear banding mechanisms between the low and mildly branched solutions under
both steady shear and LAOS, it is likely that branching is not the sole contributing factor to the elimination of the shear banding phenomena under LAOS. As was the case under steady shear, applying the same absolute conditions to the WLMs under LAOS ($\omega, \gamma_0$) led to a lower observed flow alignment with increasing branching. While increasing the Deborah number by an order of magnitude did not affect the maximum LAOS alignment in the low branching solution for the same Weissenberg number, the highly branched solution showed significantly lower alignment when $De$ was increased over a similar range. These differences in the magnitude of the alignment may have to do with the shear banding observed in the low branching solution, and shear thinning observed in the highly branched solution. Finally, the degree and mechanism of over-orientation was distinct between solutions. While the mild and highly branched solutions showed the largest degree of over-orientation at the outer wall, the low branching solution exhibited little to no over-orientation in this region. Instead, the low branching solution only exhibited over-orientation near the inner wall. The differences in branching, but also the differences in the solution elasticity and electrostatic interactions, play a significant role in the different LAOS behaviors observed in these WLM solutions.
References


Chapter 8
CONCLUSIONS AND OUTLOOK

8.1 Introduction

Wormlike micelles are ubiquitous in a wide variety of applications ranging from cosmetic products, to soaps and paints, and oil and energy recovery fluids. WLMs are also commonly used as a model system for studying polymers and polyelectrolytes, and for studying nonlinear flow phenomena and instabilities such as shear banding. Despite the vast use of WLMs in both industry and academic research, relatively little is known about how underlying topological differences affect the flow properties. Inducing micellar branching provides a microstructural pathway to alter and optimize the flow properties for targeted applications. Branched WLMs are also attractive as a model system for studying polymeric branching, which has been a long-standing scientific and technological challenge. However, branching in WLMs has been relatively unexplored, and the effect of branching on the flow properties and flow instabilities is not well understood.

This dissertation addressed two broad aims. The first aim was to advance instrumentation and analysis methods within rheology and neutron scattering for use within the broader scientific community. The second aim was to develop an understanding of how the microstructure of soft materials is coupled to the resulting flow properties. Developing these structure-property relationships is the first step toward the ultimate goal of designing materials with optimal flow properties \textit{a priori}. To narrow these aims, surfactant wormlike micelles with different underlying topologies, i.e., different levels of branching were chosen as a model system. The overall goal of this dissertation was to understand the fundamental role of micellar topology and branching on the resulting shear flow properties and flow-induced microstructures of wormlike micelle solutions. To accomplish this goal, one major
objective was to develop quantitative structure-property relationships that link the micellar microstructure, and in particular the degree of micellar branching, to the macroscopic flow properties. A second major objective was to develop new techniques and analysis methods in neutron scattering and rheology that would enable the characterization of these branched WLM solutions under transient flows.

The model system of mixed cationic and anionic wormlike micelles used in this work have been previously well-characterized at rest [1–3]. To build on this work, we sought to understand the interplay between the WLM topology, nonlinear rheological behavior, flow-induced microstructure, and solution dynamics. Of particular focus was the effect of branching on the linear and nonlinear rheology, including steady shear, shear startup, and large amplitude oscillatory shear (LAOS), and the effect of branching on the flow-induced microstructure under these deformations. By using a combination of advanced methods in rheology and neutron scattering, significant progress has been made toward understanding these flow-structural relationships, and toward developing quantitative and qualitative metrics by branching can be understood. These results provide a microstructural basis for understanding and engineering WLM solutions with specific rheological properties for targeted applications.

### 8.2 Equilibrium structure and rheology

The mixed cationic and anionic WLM solutions extensively studied by Schubert et al. [1] provide a model system to study micellar branching in terms of the microstructure and flow behavior. In order to interpret the nonlinear behavior of these WLM solutions, the equilibrium behavior first had to be well understood. First, branched structures with salt addition were confirmed using cryo-TEM. Over multiple images and different grid locations, no branch points were ever observed in the 0.01% wt NaTos solution. Branch points were easily identified for the 0.10% wt and 0.15% wt NaTos solutions in multiple images. Understanding the impact of salt addition on the micelle structure was also important. In static SANS measurements, the high-$q$ regions of the curves collapsed for all branching levels. This result confirms that adding sodium tosylate to the WLM solutions does not fundamentally alter the
cylindrical structure of the micelle. Instead, salt addition alters only the branching level, enabling fair comparisons between solutions. However, branching cannot be determined from static SANS alone, as electrostatic interactions also affect the scattering at low $q$-values. A schematic of the effect of adding NaTos to the solutions is shown in Figure 8.1. The WLMs transition from linear and entangled, to branched and entangled, to finally an interconnected network.

Figure 8.1: Illustration of branch formation in WLMs by adding NaTos. The WLMs transition from long and entangled species (a) to branched and entangled species (b), and finally, an interconnected network (c).

Measurements of the linear viscoelastic rheology are indicative of micellar branching, and confirm that the WLM solutions are beyond the first viscosity maximum observed in WLM solutions with added hydrotropic salt [4, 5]. Decreases in the relaxation time and zero-shear viscosity with added salt are consistent with the work of Schubert et al. [1], and other experimental works involving micellar branching [4–8], as well as theory [9]. The decreases in $\eta_0$ and $\tau_R$ are accompanied by increases in the plateau modulus, $G_N^0$, which is consistent with increasing branch density and increasing overall contour length, $L_c$ [4–6, 10]. Our calculations of the micellar length scales from this data support this conclusion, where an increase in $L_c$ is observed with added salt. The increases in the plateau and crossover moduli at high salt concentrations correspond to a change in the scaling of $\eta_0$ and $\tau_R$ with added salt, indicating the formation of interconnected, branched structures. Deviations from Maxwellian behavior are also observed at high branching levels, similar to the deviations observed in branched polymers [11–13]. While the mechanisms leading to the deviations
in the relaxation spectra are different between branched WLMs and branched polymers, these deviations suggest that a spectrum of relaxation times may result when significant interconnections are present.

These results provide a quantitative understanding of how the micellar length and time scales are impacted by the addition of hydroscopic salt, and thereby branching. The inability to determine the degree of branching from static SANS measurements exemplifies how the solution branching is inherently linked to the presence or absence of significant electrostatic interactions. However, changes in the scaling of rheological properties indicate when significant branching is present, providing a starting point by which to interpret the nonlinear properties. The increase in the plateau modulus and the changes to the LVE rheology with added salt provide physical evidence of branching that is independent of the electrostatic interactions. The full characterization of the equilibrium structure, rheology, and relevant length scales provides a basis for understanding the role of branching on the solution dynamics and nonlinear flow properties.

8.3 Dynamic equilibrium properties

To rationally design stable materials with optimal flow properties, the interplay between the solution microstructure, dynamics, and rheology must be understood. The presence of significant electrostatic interactions in solution can fundamentally alter the solution stability, both in regard to the equilibrium dynamics, and the nonequilibrium flow properties. While the segmental dynamics of linear WLMs have been probed [14, 15], the impact of branching on these dynamics has yet to be explored. Further, the role of solution electrostatic interactions and micellar branching on the diffusive dynamics is not well understood. Finally, identifying micellar branching in solution has been a long-standing scientific challenge, where the only direct measurements of branching have been performed using PGSE-NMR [16,17].

Here, the combination of neutron spin echo (NSE) and dynamic light scattering (DLS) is used for the first time to understand the impact of micellar branching on the solution dynamics. The WLM segmental dynamics are found to be independent of branching
level on length scales corresponding to the basic micelle cylinder, confirming the SANS results that show that salt addition does not fundamentally alter the cylindrical nature of the micelles. However, at longer length scales, significant micellar branching leads to fundamentally different dynamic behavior, where the structural parameter, $\beta$, reflects dynamics similar to flexible membranes. At these longer length scales, faster segmental dynamics are observed for the linear WLMs, which results from differences in electrostatic interactions.

The differences in relaxation rate at low-$q$ values from NSE carry over into the dynamic light scattering regime. The DLS measurements confirm that the differences in relaxation rate stem from the WLM interactions in solution, and that the diffusive dynamics are dominated by the solution ionic environment. The DLS results establish that the diffusive dynamics are coupled between the micelles and the counterion cloud surrounding the micelles, and the measured diffusion coefficient results from the cooperative diffusion coefficient and the contribution from the coupling $[18]$. The impact of the counterion cloud on the dynamic properties is significantly decreased in highly screened, highly branched micelles. This result provides a basis for understanding the nonlinear flow phenomena and instabilities, which will ultimately be impacted by the electrostatic interactions and counterion cloud. Additionally, two relaxation modes are observed that reflect the entangled nature of the WLMs in solution. The slow relaxation mode stems from hindered motions of interacting or entangled chains $[19]$, which becomes significantly faster when branching is present. While the counterion cloud and dipole-dipole interactions may play a role in the slow mode, the entirety of the slow mode behavior cannot be attributed to these interactions alone; rather entanglement effects become important $[18,19]$. While the relative contribution of branching versus electrostatic interactions is hard to de-couple, it is reasonable to conclude that both factors contribute to the observed differences in the slow mode based on branching level.

While it has been difficult to separate the electrostatic effects versus the branching effects on the solution dynamics, these new neutron spin echo results provide significant insight into differences in micellar morphology. As the measurement of $\beta$ is not affected by the differences in electrostatic interactions, this quantity provides a measure of solution branching that is independent of the ionic environment. The identified structural differences
demonstrate the utility of NSE measurements in determining solution morphology, making NSE just the second experimental method to verify branching in WLMs.

8.4 Steady shear: shear banding vs. shear thinning

Shear banding is a flow instability that is commonly observed in wormlike micelle solutions. While a wealth of literature is devoted to understanding shear banding phenomena [20], little is known about the role of the underlying topology on the development of this behavior [21]. Further, while constitutive models may explicitly account for micellar breakage and reformation events that lead to shear banding [22–25], current efforts focus on linear WLM solutions. Shear thinning is also commonly observed in WLM solutions, and the differences between shear thinning and shear banding can be difficult to discern from shear rheology alone. The presence of shear thinning versus shear banding is known to be affected by changes in solution composition, temperature, and measurement geometry [26]; however, the explicit effects of branching on shear banding phenomena are yet to be explored.

In this dissertation, the combination of nonlinear rheology and flow-small angle neutron scattering (flow-SANS) measurements in two shear planes provides a comprehensive picture of the role of added salt and branching on the flow-induced microstructure and flow properties of WLM solutions. With increasing salt and branching, the power law index, $N$, increases. An empirical relationship is developed to link the amount of added salt to the resulting power law index; this empirical relationship can be useful for formulating WLMs with specific flow properties. At high levels of branching and added salt ($C_s \geq 0.10\%$ wt NaTos), a disappearance of shear banding in favor of shear thinning is observed. The transition between shear banding versus shear thinning in the WLM solutions corresponds to the change in scaling of $\eta_0$ and $\tau_R$ with added salt. This result provides a quantitative link between the equilibrium rheology and the nonequilibrium flow properties, and suggests that the equilibrium properties can be used to predict the nonlinear behavior. While branching is associated with the disappearance of shear banding, the differences in electrostatic interactions and the counterion cloud, relaxation time, and zero-shear viscosity may also play a significant role.
The flow-induced microstructure is also distinct between branching levels. In the 1-3 plane, branching mitigates flow alignment on an absolute shear rate scale, but magnifies alignment on a Weissenberg number scale. Calculations using Laun’s rule and the Cox-Merz rule explain this behavior, where deviations at earlier $Wi$ are seen in the case of branching. These deviations are the result of the larger degree of microstructure rearrangements for equivalent $Wi$ when branching is present. The deviations based on branching level from these empirical rules are supported by orthogonal superposition measurements, which show a faster breakdown of branched versus linear structures with increasing shear rate on an equivalent $Wi$ scale. Using OSP, we develop new metrics for evaluating the nonlinear viscoelasticity of WLMs, based on relative changes to the plateau and crossover moduli, as well as the relaxation time. As OSP measurements can only be interpreted outside of the shear banding regime where electrostatic interactions are not significant, the results provide a true structural signature of branching that is unaffected by the solution electrostatic interactions.

The empirical rules paired with the OSP measurements suggest that branched structures break down with shear. This branch breakage with shear is confirmed by analyzing the orientation distribution function (ODF) from the 1-3 plane SANS experiments, which links the shear-induced microstructure to measured rheological phenomena. The ODFs under shear are dependent on branching level; this new analysis is used to differentiate between micellar topologies for the first time. Rounder and wider ODFs are observed for branched systems, reflecting the partial alignment of branched structures as opposed to the alignment of linear chains. While branching is associated with lower flow alignment on an absolute shear rate scale, after a critical shear rate, the alignment between all branching levels collapses onto the same curve. This critical shear rate corresponds to a shear thickening rheological response at high shear rates in the branched WLMs. At this point, the ODFs also collapse, indicating that the alignment beyond the critical rate results from the alignment of linear chains in all solutions. This ODF analysis presents a new method to identify structural differences in branched WLMs, and links the measured rheological behavior to physical microstructure changes.

The mildly branched solution exhibits shear banding flow behavior that is consistent
with theory [27–29] and previous experimental results on shear banding WLMs [30–32]. From the 1-2 plane structural information, the critical shear rates for shear banding are determined, which are consistent with VCM model predictions that incorporate micellar breakage [23]. Using a simple lever rule, the width of the high shear rate band, $\alpha$, is accurately predicted from the 1-2 plane structural data. The alignment factor near the calculated band interface is in good agreement with critical values set forth by Helgeson et al. [30]. As Helgeson et al. [30] used a different and significantly more concentrated WLM solution, the results suggest that this critical orientation is universal in shear banding WLMs. Discontinuous changes in the orientation angle across the gap are shown to be a good indicator of shear banding and the location of the band interface. These results suggest that 1-2 plane SANS can be used as an alternative to particle tracking velocimetry (PTV) measurements to both determine the presence of shear banding and the location of the shear band interface.

A distinct form of flow alignment is identified in the low branching solution during shear banding using 1-2 plane SANS. In contrast to the behavior observed for the mildly branched solution, the alignment in the low shear rate band exhibits a significant degree of order that is independent of gap position. This ‘alignment band’ behavior is not consistent theory or the lever rule. The unusual flow alignment behavior suggests that a different mechanism of shear banding is present in the low branching solution, which may be a result of differences in the branching level and solution elasticity. This distinct mechanism of flow alignment demonstrates the utility of using spatially-resolved 1-2 plane SANS measurements as opposed to rheology or 1-3 plane measurements alone. Only with the spatially-resolved measurements can different forms of shear banding between the low and mildly branched solution be identified and explored. While PTV measurements can identify shear banding, the structural basis of shear banding can be attained only with SANS measurements.

This multi-technique experimental approach, combining nonlinear rheology and flow-SANS in different shear planes enables us to link micellar microstructure and topology to the macroscopic flow properties of WLM solutions. The ODF analysis explicitly links the
rheological flow properties to specific structural changes and branch breakage. SANS measurements in the 1-2 plane provide both spatial information and structural information, making them more desirable than rheology or particle tracking methods alone. The steady shear results provide a data set for testing microstructure-based constitutive equations, such as the VCM model [23] and its thermodynamically correct GCB variant [25], that explicitly account for micellar breakage. The results also provide a platform for incorporating micellar branching into these constitutive models.

8.5 Shear startup and the mechanism of shear band formation

The steady shear results suggest two different mechanisms of shear banding exist between the low and mildly branched solutions. However, most theoretical works involving shear banding predict a similar, two-banded state whether the solution has an underlying constitutive curve that is non-monotonic or monotonic [20, 22, 23, 27–29]. Nonetheless, the location of the band interface can depend on the geometry and applied boundary conditions, where three banded states may be observed [33].

Using a combination of rheology, particle tracking velocimetry (PTV), and flow-SANS, distinct shear banding mechanisms are identified between the low and mildly branched solutions. We propose new analyses of the 1-2 plane structural information to gain similar information to time-dependent PTV measurements. Here, the 1-2 plane, time- and spatially-dependent alignment factor is used as a proxy for PTV to confirm that the mildly branched solution exhibits shear banding following the disentangle, re-entangle mechanism [31, 34, 35]. The microstructural evolution is tracked in time as a function of gap position (similarly to PTV) to verify this shear banding mechanism. Conversely, the low branching solution exhibits a three band structure at all measured shear rates. We use the time- and spatially-dependent $A_f$ to propose a new ‘disentangle, re-entangle, re-align’ mechanism of shear banding. Excellent agreement is obtained between the location of the shear band interfaces determined via 1-2 plane SANS and via PTV. These results suggest that the time-dependent, 1-2 plane $A_f$ is an accurate, and more perhaps desirable, substitute for PTV, as
additional structural information is gained via SANS. While nonlinear rheology allows signatures of shear banding to be identified, it is only with flow-SANS that new microstructure-based mechanisms of shear banding are identified for each branching level. These structural results also provide a data set for the improvement of current and future microstructure-based constitutive models that predict shear banding.

The SANS structural results suggest that the different mechanisms of shear banding are a result of wall slip and elastic instabilities, which is confirmed with PTV measurements. These phenomena often lead to distinct shear banding behavior versus when no wall slip is present [36–40]. These behaviors are amplified in the low branching solution based on the high degree of elasticity. As the solution elasticity is a function of the relaxation time and zero-shear viscosity, which is inherently linked to branching, it is unclear what role the branching has on the shear banding mechanism. However, high branching levels lead to a lower solution elasticity, which inevitably helps to mitigate the shear banding instability.

The combination of startup rheology and SANS is used to establish clear rheological and structural signatures of shear banding versus shear thinning. The five stage process described by Hu et al. [35] for shear band formation in WLMs describes the startup rheological behavior of the low and mildly branched solution well, despite the different mechanisms of shear band formation. These rheological similarities demonstrate the utility of time- and spatially-resolved structure measurements, as no clear rheological signatures of the different banding mechanisms can be determined. However, long transients in the stress and structural response indicate the formation of shear bands, whereas fast transients in the stress and structural response are indicative of shear thinning. These differences in response persist even when the solution relaxation times are accounted for, suggesting that the duration of these transients is a good indicator of the steady state flow behavior. The alignment factor, especially in the 1-2 plane, shows a longer transient than the startup stress in shear banding solutions. As rheology is a bulk measurement, the time- and spatially-resolved structure is a more sensitive measure of when the steady state has been achieved. The features of the startup stress response for shear thinning solutions are distinct from those observed during shear banding in magnitude, shape and sequence. Our findings are in good agreement with
results for shear thinning and shear banding solutions identified by Hu et al. [35], despite differences in WLM concentration and surfactant. These similarities suggest that the features of stress response for shear thinning and shear banding WLMs may be universally applicable.

Finally, parallels between branched WLMs and branched polymer solutions are established, where the startup rheology is used as an indicator of morphology [41, 42]. The ratio of the stress and viscosity overshoot to the steady state values is indicative of micellar branching. High branching levels mitigate this overshoot, as is the case in branched polymers [43]. To our knowledge, this is the first use of shear startup measurements to successfully differentiate between topologies in wormlike micelles. We attribute this behavior to a mitigation of micellar breakage, which may result from branch sliding and physical interconnections. The reduced breakage upon shear startup helps to prevent shear banding at high branching levels. While branching is not solely responsible for the disappearance of shear banding at high salt concentrations, these measurements provide evidence that branching plays a substantial role in reducing shear banding. This finding is further confirmed by the OSP measurements, which show a slower decrease in the relaxation time under shear when branching is present. As the relaxation time decreases from breakage and a shortening of the micelles, this breakage is restricted when branching is present. Analysis of these startup responses provide a much needed link between the chain architecture and the resulting flow properties.

8.6 Mild branching: shear banding under LAOS and VCM model predictions

The natural extension of the shear banding investigations under steady shear is to examine shear banding under large amplitude oscillatory shear (LAOS). Shear banding under LAOS and related instabilities have been widely predicted [23, 25, 44, 45], but experimental verification is lacking. The agreement between the steady shear properties of the mildly branched solution and the VCM model predictions [23] provides an optimal solution for examining shear banding under LAOS. Accordingly, the explicit objective was to either confirm or deny the presence of LAOS shear banding based on the VCM model predictions,
by examining conditions both inside and outside of the predicted shear banding regime that exhibit qualitatively similar LAOS stress responses.

Using 1-2 plane flow-small angle neutron scattering (flow-SANS), shear banding under LAOS in concentric cylinder Couette flow is verified experimentally for the first time. Importantly, these results confirm the central role of shear-induced breakage and reformation on triggering the shear banding instability. The conditions imposed under LAOS greatly affect the existence and type of shear banding near the onset of region III. Two distinct mechanisms of shear band formation under LAOS are identified by analyzing the time and stress scales measured via nonlinear rheology. These distinct structural mechanisms leading to shear banding could not be identified without the structural information provided by SANS, again demonstrating the utility of the 1-2 plane measurements over other methods. At low Deborah numbers, the material has sufficient time to relax during the oscillation cycle, resulting in a similar shear banding behavior under LAOS and steady shear. When the frequency is increased, the maximum alignment under LAOS surpasses that of steady shear, termed ‘over-orientation.’ This over-orientation results from the shorter time scales during the cycle, which lead to incomplete material relaxation and more pronounced shear banding. Further increasing the frequency at a constant shear rate amplitude leads to non-shear banded, metastable structural states in region III.

Our 1-2 plane SANS results for the mildly branched solution are in excellent agreement with the VCM model predictions, where six of the seven conditions tested agree with the model. Over-orientation and shear banding are independent phenomena. Based on the SANS results, an ‘over-orientation ratio’ is developed as a guideline to predict when LAOS shear banding will occur. Finally, using the SANS results as a basis, the LAOS stress responses are re-visited. Despite qualitative similarities, features of the LAOS stress response can be used to predict LAOS shear banding. We also identify features of the stress response that are important in the determination of shear banding versus those which are not. Two distinct LAOS time scales, as well as the location during the cycle \( (t/T) \) of the stress overshoot, are influential factors in determining shear banding. Additionally, the yield strain and
the ratio of the LAOS stress to the steady shear stress are important. Interestingly, the magnitude of the stress overshoot and the value of the local modulus in the overshoot region have no impact on whether shear banding occurs. This analysis combining the structural SANS results with the LAOS stress response allows us to develop predictive structure-property relationships for future determinations of LAOS shear banding.

The 1-2 plane SANS measurements enable us to experimentally validate VCM model predictions of LAOS shear banding for the first time, and can be used for the improvement of other theoretical models. New mechanisms of shear band formation under LAOS are identified based on an analysis of time scales and the features of the stress response. Finally, quantitative structure-property relationships to predict LAOS shear banding in the future are developed from the LAOS stress response and degree of over-orientation in the 1-2 plane measurements. By better understanding of the physical basis and mechanisms behind the flow behavior, from both theory and experiments, complex flows like LAOS are interpreted and understood. Developing quantitative metrics like the degree of over-orientation and the LAOS stress analysis directly links the structure measured by SANS to the measured rheological flow properties. Further, the degree of over-orientation and LAOS stress analysis connect the steady shear flow properties to the dynamic flow properties. These results clearly illustrate that WLMs, and soft materials in general, respond differently to steady and dynamic deformations. For example, steady shear banding is required, but does not predict, when LAOS shear banding occurs. This dynamic flow behavior has implications for practical applications, where complex dynamic flows are involved. These results also lay the groundwork for understanding the dynamic flow properties in the context of steady shear.

8.7 LAOS responses based on branching

Identifying shear banding under LAOS in the mildly branched solution raised several questions in regard to the LAOS behavior of the other WLM solutions. As shear banding is also observed in the low branching behavior under steady shear, a natural continuation of this work is to probe the behavior of the low branching solution under LAOS. Under steady shear, the low branching solution does not follow the lever rule or agree with the VCM model
predictions due to the presence of an elastically-driven three band structure. This complex shear banding structure complicates the interpretation of LAOS, and at present, there is no constitutive model for comparison. In addition to shear banding, another objective was to understand the impact of branching on the LAOS flow behavior.

The combination of spatially-resolved, 1-2 plane SANS measurements and advances in time-resolved data collection allow new mechanisms of LAOS shear banding to be identified in the low branching solution. An ‘alignment band’ form of LAOS shear banding is observed in nearly all conditions that is reminiscent of the steady shear alignment. We propose that the mechanism of LAOS shear banding is similar to steady shear, where three shear bands are observed. The presence of the third band is detected in certain conditions, verifying this mechanism. The alignment banding mechanism of LAOS shear banding is distinct from the two mechanisms observed in the mildly branched solution, and may respond to the applied shear rate or the applied strain. While three shear bands are expected in cone-and-plate geometries and have been observed near the onset of nonlinearity under LAOS [46], the mechanism identified here is distinct and has not been reported in the literature. List mode data collection at the Institut Laue-Langevin enables two sub-categories of LAOS shear banding to be identified: stable and unstable. In most conditions, the phase of the LAOS response is stable in time after an equilibration period. However, in certain conditions, the phase of the response changes throughout the experiment, continuously oscillating around a central value. While the cause of this instability is not yet understood, this behavior could not be identified without spatially- and temporally-resolved 1-2 plane SANS, as we find no rheological indicators of such behavior.

At the highest Deborah number, only two shear bands are present, and the alignment in the low shear rate band is close to zero. Our results suggest that the faster oscillation cycle and lower amplitude used in this condition mitigate the wall slip and elastic instabilities that lead to the three band state. Interestingly, increasing the frequency does not mitigate the maximum alignment in the 1-2 plane, as might be expected based on an assumption of micellar breakage leading to shear banding. Instead, increasing the frequency lowers alignment in the outer band. The lower alignment observed in 1-3 plane measurements at
high frequencies is not a result of a lower maximum alignment, but rather a lower outer wall alignment. These results also suggest that the wall slip and instabilities observed at lower frequencies may mitigate alignment in the highest shear rate band, which is not surprising given that elastic instabilities are associated with turbulence and a loss of order.

As was the case in steady shear, high branching levels are associated with a disappearance of shear banding under LAOS, suggesting that steady shear banding is a pre-requisite for LAOS shear banding. Based on the same absolute conditions ($\omega$, $\gamma_0$), a lower degree of alignment is observed when branching is present, in agreement with the steady shear observations. Branching promotes over-orientation at low Deborah numbers, but dampens over-orientation when $De$ is increased. Therefore, we cannot establish a universal behavior for the degree of over-orientation based on branching level. However, we find that the degree of alignment and over-orientation is predicted by the LAOS stress response. Despite equivalent Weissenberg numbers, the maximum stress under LAOS is five-fold larger when $De = 1$ versus $De = 7.5$ in the highly branched solution, which leads to a nearly five-fold increase in the maximum LAOS alignment. The LAOS stress at equal $Wi$ is larger than steady shear when $De = 1$, resulting in over-orientation, but is less than steady shear when $De = 7.5$, leading to ‘under-orientation.’ The maximum alignment under LAOS is nearly identical for $De = 7.5, Wi = 25$ and $De = 2.5, Wi = 8.3$, which have similar maximum LAOS stresses. This analysis links the measured rheological stress response to the LAOS structural phenomena, and provides a platform for interpreting LAOS in the context of steady shear.

8.8 Advances in SANS data collection and analysis

A major goal of this dissertation was to use a combination of neutron scattering and rheological methods to help better understand the flow-structural properties of branched WLMs. The development of new techniques, data collection procedures, and data analysis methods to help achieve this goal are presented in Chapter 3, where three main objectives were established. The first objective was to develop a theoretical framework to understand and improve smearing issues associated with analyzing time-resolved SANS data. The second objective was to implement this framework at neutron scattering facilities, to combat
some issues associated with low neutron flux. The third objective focused understanding and optimizing on the experimental set-up for proper and reproducible measurements.

New methods of time-resolved data analysis are developed, which improve the temporal resolution of SANS experiments. In the standard method of time-resolved analysis at the NIST Center for Neutron Research (NCNR) and at the Institut Laue-Langevin (ILL), the neutron scattering data is binned into discrete, non-overlapping time bins. By minimizing the bin width for better temporal precision, neutron counts are sacrificed. To surmount this issue, we develop the sliding bin method, where the bins can overlap in time. In a large amplitude oscillatory shear (LAOS) experiment, the standard procedure is to use thirty non-overlapping bins in time. By implementing the sliding bin method, better temporal resolution is achieved without sacrificing temporal precision. For the same bin width, now any number of bins can be chosen, such that the temporal resolution can be improved by several-fold, or even an order of magnitude. From the sliding bin method, a deconvolution procedure is developed. The binning procedure inherently smears the data in time. For time-periodic data, the deconvolution procedure ‘de-smears’ the data by removing the effect of the time bin.

The sliding bin method was implemented at the ILL and in the Igor codes at the NCNR, where the NCNR codes have been requested by and shared with other facility users. Additionally, a Matlab routine to perform the deconvolution has been developed. In the updates to the NCNR Igor codes, the user can now select the bin width, and the number of total slices, to improve the temporal resolution of the data slices without sacrificing statistics or temporal precision. While to some this improvement may seem trivial, all of the LAOS data reported in Chapter 7 was analyzed using 120 slices, which is four-fold higher than the original method and requires no additional effort than the standard procedure. An example of the original method can be seen in Figure 8.2 below. The improved temporal resolution allows features like the local maxima and minima in $A_f$ to be determined precisely, which cannot be done using only thirty bins (see Figure 8.2). Additionally, the 1-2 plane studies of the unstable, phase shifting LAOS responses in the low branching solution would not be possible without this method for two reasons. First, the minima in the $A_f$ response cannot be accurately determined if only thirty points per cycle are used, which can be seen in Figure
Second, and more importantly, the sliding bin method implemented at the ILL is done in list mode. Prior list mode, kinetic mode files were taken hours apart from one another, and phase shifts have been observed between positions (Figure 8.2). In kinetic mode, the data cannot be re-binned or divided into smaller time slices, such that any phase shifts occurring in time at the inner and outer wall cannot be detected. With list mode, the time file can be sub-divided, so any time during the experiment can be accessed. Had the data in Figure 8.2 been recorded in list mode, the WLM LAOS responses could be unambiguously interpreted.

Figure 8.2: 1-2 plane $A_f$ at two gap positions during LAOS, where list mode is not used and phase shifts are observed between the two positions. In both cases, the inner wall was measured first. (a) Initial experiments on the 0.01% wt NaTos solution. (b) Initial experiments on the 0.05% wt NaTos solution.

The sliding bin method allows the user to obtain any desired temporal resolution. The greatest improvements in resolution are gained between the standard binning method and the sliding bin method. While the deconvolution improves the temporal precision further, the effects are relatively minor in comparison to implementing the sliding bin method when the standard $T/30$ bin size is used. The deconvolution procedure is most useful in time-limited experiments, where a much wider bin width can be used ($T/15$, $T/20$) and the response can be deconvolved. For long experiment times, processing the data using two different bin widths can help determine the smearing effects. For example, if the data is processed using $T/30$ and $T/60$, and no differences are seen in the $A_f$ response, the deconvolution
The analysis of the startup data shown in Chapter 6 provides an even stronger justification for using the sliding bin method. As the startup data is not time-periodic, the deconvolution procedure cannot be used. In Chapter 6, the number of total slices used in the first 100 seconds of the experiment is an order of magnitude larger than in the standard binning method, which provides excellent temporal resolution. Slicing the data into different bin widths in this region helps to resolve and understand the startup response. To calculate \( A_f \) accurately when the material is highly aligned requires fewer neutrons than when the material is poorly aligned. As such, bin widths as small as ten seconds can be used at the start of the experiment. When compared to 30 second time bins in the same region, significant smearing is observed in the larger bin size. However, slicing the data using multiple time bins allows us to compare the overlap between results. When the 10 second bins and the 30 second bins share the same response, we can transition to using larger bins to reduce the observed noise in the response. To obtain the temporal resolution shown in Chapter 6, the measurement time would need to be an order of magnitude larger. Instead of a one to two hour experiment, ten to twenty hours would be required for each measurement. Therefore, the sliding bin method is an invaluable tool for measurements where fine temporal resolution is required, providing an order of magnitude improvement in the temporal resolution for little additional effort. By implementing the sliding bin method and deconvolution procedure, enhanced signal resolution is obtained by using methods of signal processing to analyze time-resolved scattering data, providing a tool for the broader scientific community.

The final objective focused on the SANS experimental set-up and how the chosen SANS configuration affects the resolution of the measured microstructural rearrangements. As SANS time is limited, the configuration must be optimized to maximize the neutron flux while minimizing smearing effects, while also ensuring reproducible results between instruments and scattering facilities. We systematically examined the effect of the detector distance, collimation, and the width of the slits used for flow-SANS to conclude that the
sample-to-detector distance has the greatest impact on the measurable structure and calculated parameters. As long as the chosen detector distance encloses \( q^* \) near the center of the accessible q-range, the smearing around \( I(q^*, \phi) \) and associated errors in the calculated parameters are minimized. The collimation and aperture and slit dimensions combined have a lesser impact than the sample-to-detector distance, and are on the order of 10% or less. By optimizing certain variables, like decreasing the slit or aperture widths, the effect of other parameters, like the number of guides, is minimized. Therefore, we find that we can optimize the experiments by using reasonable slit widths and a large number of guides to increase the flux, as the increase in the number of guides has a minimal effect once the slit smearing is minimized. These results establish the critical role of the experiment configuration on the interpretation of the SANS results, and provide extensive guidelines for planning future flow-SANS experiments. Finally, the results provide a basis for understanding any inconsistencies in the collected data or calculated alignment factors between experiments that may have been performed with different configurations.

8.9 Recommendations for future work

While significant progress was made in this dissertation toward understanding the effect of branching on the flow properties of WLMs, many questions remain unanswered. Specifically, separating the impact of branching versus electrostatic interactions is essential to fully understand these results. Along these lines, understanding the specific impact of charge on shear banding is an interesting future direction. Exploring the effect of branching on extensional and other flows would bring a comprehensive understanding to the branching effect. Finally, recommendations for improving flow-SANS experiments are given.

8.9.1 Separating the impact of electrostatic interactions and branching

In WLM solutions, the most common way to induce branching is via the addition of a screening salt or hydrotropic salt. Salt addition screens the electrostatic interactions around the micellar head groups, and increases the overall ionic strength in solution. This salt addition results in a decrease in the relaxation time and zero-shear viscosity of the WLMs,
ultimately affecting the solution elasticity. As branching in WLM solutions is inherently linked to the screening of electrostatic interactions, understanding the effects of physical branches versus screened charges on the flow behavior and dynamics is difficult. To resolve this issue, two approaches can be taken. First, branching can be induced by methods other than adding salt. Second, the specific impact of charge on shear banding can be elucidated.

8.9.1.1 Inducing branching via alternative methods

The effect of micellar branching versus changes in the ionic environment could not be separated in many aspects of this work, as branching is induced by adding a screening salt. The salt addition dramatically alters the electrostatic interactions in the WLM solutions, therefore changing the solution relaxation time and zero-shear viscosity. Branching may also be induced by raising the temperature, although the increase in temperature will also serve to decrease $\tau_R$ and $\eta_0$. These effects made it difficult to discern which flow phenomena are an effect of the different branching levels versus which are an effect of the ionic environment, and most likely, both factors play a role.

One method of solving this problem is to induce branching without altering the ionic environment, or without significantly changing the relaxation time. A possible route for doing this involves the use of WLM and nanoparticle mixtures, where micelle-nanoparticle junctions that act as physical cross-links between micelles [47]. In this work, Helgeson et al. [47] added cationic nanoparticles to WLM solutions, which greatly increased the zero-shear viscosity and other viscoelastic properties. In order to separate the branching effects using a system like this, a suitable control sample would need to be formulated, where only linear chains are observed. Schubert et al. [1] showed that the addition of a screening salt (NaTos) versus a hydroorganic salt (NaCl) had different effects on the solution properties, and most likely branching. WLMs with added NaTos and NaCl could also be formulated in a manner to match $\tau_R$ and $\eta_0$ between samples; however, this would lead to a different overall ionic strength of solution as more NaCl would need to be added to achieve the same properties. A precise method of quantifying branching would also be required to establish differences between the solutions.
Another solution that some researchers have used is to compare WLMs with the same zero shear viscosity on either side of the first viscosity maximum. While this would be infeasible in this system, as the viscosity maximum is already surpassed, it is a reasonable first step. However, using this strategy presents its own unique problems. Specifically, the WLMs are in the growth phase before the viscosity maximum, which essentially results in a comparison between more rod-like micelles and long and entangled micelles. As such, it would be difficult to understand what effects are the result of the difference in length versus the differences in branching. However, a more reasonable solution may be to compare WLMs with the same zero-shear viscosity at the bottom of the first viscosity maximum to the start of the second viscosity maximum. As the WLMs are already sufficiently long at this point, this solution may be more useful in understanding branching effects. Finally, increasing the surfactant concentration is another method to induce branching; however, separating the concentration effects from branching effects would present unique challenges.

8.9.1.2 The effect of charge on shear band formation

Outside of wormlike micelles, shear banding flow instabilities are also common in polymers and self-assembled solutions, viruses and biological materials, and colloidal dispersions and glasses [20,48–50]. Shear banding occurs in both steady and dynamic flows under a wide range of flow conditions and geometries, including microchannel and pipe flows [48, 49]; thus, understanding and controlling this flow instability is of commercial value. The microscopic mechanisms behind shear banding are thought to include concentration gradients, topological changes, entanglement or breakage effects, or changes in charge or association [20]. Despite the vast shear banding literature, experimental verification of these proposed mechanisms is limited. Accordingly, the role of the solution ionic strength and charge distribution on shear banding has yet to be elucidated. In addition to helping to separate the effects of branching and the electrostatic interactions discussed in this dissertation, the impact of charge on the solution stability is of fundamental scientific interest, as nearly all flowing soft materials are locally charged. While ionic strength plays an important role,
minor changes in macromolecular surface charge also have a significant impact on the viscosity, interactions, and function. Therefore, the role of the charge distribution and location along the macromolecule is of equal importance, illustrated in Figure 8.3. By understanding the fundamental role of charge on instability formation, materials can be characterized and tailored to withstand deformations encountered in manufacturing, transport and use.

Figure 8.3: Possible surface charge profiles in ionic WLM solutions. (a) Uniform (b) Uniform distribution of hydrotropic counterion salt (c) Uniform counterion at higher ratio (d) Non-uniform counterion.

Using model systems, factors that have previously confounded charge effects on shear banding can be controlled: concentration, shape, and macromolecular flexibility. These properties can alter the shear banding mechanism [20,48], thus the role of charge may be dependent on the mechanism. These proposed investigations can be broken down into two categories: flexible self-assembled systems, and stiff to semi-flexible rod-like suspensions. In the first group, well-characterized ionic surfactants can be used. Via the addition of simple and hydrotropic counterion salts, the effects of ionic strength, surface charge, charge distribution, and salt valence can be examined using a careful design of experiments and ANOVA style analysis, while controlling for length via temperature or other stimuli. In the latter group, shorter rod-like particles, such as viruses, shear band via isotropic-to-nematic (I-N) transition [50]. Here, surface charge can be controlled via polar media or surface coatings [51]. Experimentally identifying concentration gradients that may result during I-N
shear banding is also of interest, to corroborate significant computational efforts that have predicted this behavior.

Quantifiable rheological and structural ‘charge-dependent’ signatures of shear banding can be developed. When shear banding results, additional measurements can be performed to determine the role of charge on the stability of the banded state [48], which can be compared to theory. Using a careful design of experiments and statistical analysis, the significant and possibly synergistic variables surrounding charge and shear banding can be determined. The ultimate goal would be to develop universal, dimensionless flow stability criteria based on, but not limited to, ionic strength, charge distribution, counterion ratio, flexibility, concentration, and size.

8.9.2 Beyond shear: extensional rheology

As orthogonal superposition rheology (OSP) measurements proved useful in identifying characteristics of branching, other non-shear rheological methods may be useful in the determination of branching as well. Extensional rheology has shown to be useful in differentiating between micelles with different levels of branching [6]. At very high branching levels, the Trouton ratio of the extensional to shear viscosity (\(Tr = \eta_E/\eta_0\)) is expected to reach the Newtonian value of \(Tr = 3\). Capillary breakup extensional rheometry (CaBER) measurements may be useful to help quantify the level of branching in solution. In CaBER measurements, the solution is filled between two plates, which are quickly pulled apart to form a filament. The extensional relaxation time, \(\tau_E\), can be determined from the filament lifetime in the elastocapillary thinning regime by [52]:

\[
\frac{R(t)}{R_0} \approx \left( \frac{G_N^0 R_0}{2\sigma} \right)^{1/3} \exp\left( -\frac{t}{3\tau_E} \right)
\]  

(8.1)

where \(R_0\) is the initial filament radius, and \(\sigma\) is the surface tension. From this, the extensional viscosity can be determined by [52]:

\[
\eta_E = \frac{\sigma}{\dot{\varepsilon} R} = \frac{\sigma}{-2dR(t)/dt}
\]  

(8.2)
where $\dot{\varepsilon}$ is the extensional rate. We have not performed surface tension measurements, so these quantities from Equations 8.1 and 8.2 must be estimated. However, preliminary CaBER results can be seen in Figure 8.4 below for the low and highly branched solutions (0.01% wt and 0.10% wt NaTos) over multiple trials. As seen in Figure 8.4, the filament lifetime is significantly longer in the low branching solution. Using Equations 8.1 and 8.2, similar results to Sachsenheimer et al. [6] are seen. For the low branching solution, we estimate an extensional viscosity of $\eta_E \sim O(10^5)$ in the elastocapillary thinning regime, leading to a Trouton ratio of $Tr \sim O(10^4)$. For the highly branched solution, we find $\eta_E \sim O(10^3)$ and $Tr \sim O(10^3)$. As these Trouton ratios are still quite large, additional CaBER measurements on more highly branched systems may prove interesting.

![Figure 8.4: CaBER results from multiple trials for the: (a) 0.01% wt and (b) 0.10% wt NaTos solutions. Dotted vertical lines indicate the elastocapillary regime used to calculate the extensional relaxation time and viscosity.](image)

### 8.9.3 Improving SANS experiments

While substantial progress was made toward improving the temporal resolution of SANS experiments, additional modifications to the existing sample environments can be made. Suggestions for data collection procedures are also discussed below.
8.9.3.1 Time-resolved data collection

As shown in Figure 8.2 above, materials often exhibit responses that are unexpected or unknowingly time-dependent. Recording neutron scattering data with time-resolution at the NCNR (event mode) and ILL (list mode) is relatively painless and takes little extra effort on the part of the user. Further, SANS time is limited and experiments cannot often be repeated. Accordingly, it is recommended that neutron scattering data always be recorded with time-resolution, whether or not time-dependent phenomena are expected. Chapter 3 and Section 8.8 above discuss justifications to collecting data in this manner. Information can be lost when the time-dependent data is not recorded, and time-resolved can be recorded effortlessly. In fact, the time-resolved files at the NCNR and at the ILL do not needed to be processed and sliced unless the user chooses to do so; separate files of the total SANS data are always recorded. This recommendation is especially applicable to the LAOS measurements, shown in Figure 8.2 above and discussed in Chapter 7. While list mode was not available for the data shown in Figure 8.2, had it been available, the data could be clearly interpreted. When data is taken with time-resolution, it can always be re-examined if unexpected results are obtained; if not, the experiment must be repeated or the results are inconclusive.

8.9.3.2 Use of encoder for 1-2 plane LAOS experiments

At the ILL, a program within the Nomad control software allows the user to observe the waveform output, to ensure a sinusoidal deformation is applied by the motor for the 1-2 shear cell during LAOS. At the NCNR, the current 1-2 shear cell motor does not work as well as at the ILL in terms of applying a perfect sinusoid. Currently at the NCNR, the applied waveform cannot be seen during the LAOS experiments. The stepper motor moves in an approximate waveform, where often a true sinusoid is not obtained. As a result, a response with a ‘flat top’ may be observed which can be seen in Figure 8.5, which corresponds to the non-perfect wave output from the NCNR motor. By using an encoder to measure the waveform output, the waveform can be seen immediately to evaluate the deformation. Further, any drift of the motor position can be seen in time, which provides additional useful information.
Figure 8.5: 1-2 plane $A_f$ under LAOS ($De = 1, Wi = 321$) for the 0.01% wt NaTos solution for thirty minute trials using the NCNR 1-2 shear cell. A flat, instead of rounded, response is seen, which reflects the non-sinusoidal waveform applied by the motor.

### 8.10 Outlook

The rheology and flow-small angle neutron scattering (flow-SANS) methods and results discussed in this dissertation demonstrate some of the valuable insights gained about the broad range of shear-induced microstructural changes coupled with, and responsible for, the nonlinear steady and dynamic rheology of branched wormlike micellar systems. As with polymers, entangled WLM solutions exhibit strong flow-alignment, resulting in shear thinning and shear banding. However, shear-induced topological changes manifest a much richer flow behavior, including shear thickening and branch breakage, as well as shear-induced breakage leading to shear banding. Throughout, flow-SANS provides critical and unique structural information about micellar orientation on length scales of direct relevance to the macroscopic rheology. Importantly, this range of microstructural responses to an imposed shear flow often drive instabilities, the simplest of which, stable shear banding, can be resolved by spatiotemporal resolution afforded by advances in 1-2 plane sample environments. Coupling rheology with SANS and allied methods such as particle image velocimetry is critical for mapping the local kinematics as well as the local microstructure in such structured flows. Advancing this to include more complex flows such as extensions, contractions and
expansions will be invaluable for tailoring WLM solutions for applications. This thesis establishes many qualitative and quantitative structure-property relationships, but the wealth of chemistries and commensurate WLM topologies merits much future work.

Advances in constitutive equation modeling that can capture not only the elastic stresses of entropic nature, but also topological changes including branching, breakage, and micellar growth will be required to fully understand the complex WLM behavior. Non-linear coupling with the flow kinematics in rheologically relevant geometries can be expected to lead to a wealth of instabilities of mechanical and thermodynamic nature. While shear banding can find utility for some applications, for others, suppressing shear banding and related instabilities may be critical. Thus, better understanding the role of branching and the underlying mechanism of nonlinear coupling can be used to control WLM rheology and ultimately, such instabilities. Finally, engineering WLM solutions for specific applications will benefit from robust constitutive models that capture the wealth of WLM physical behaviors and topological differences afforded by their self-assembled nature.
References


### Appendix A

**NOMENCLATURE AND ACRONYMS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-2</td>
<td>flow-gradient</td>
</tr>
<tr>
<td>1-2 $A_f$</td>
<td>1-2 (flow-gradient) plane alignment factor</td>
</tr>
<tr>
<td>1-3</td>
<td>flow-vorticity</td>
</tr>
<tr>
<td>1-3 $A_f$</td>
<td>1-3 (flow-vorticity) plane alignment factor</td>
</tr>
<tr>
<td>$A_f$</td>
<td>alignment factor</td>
</tr>
<tr>
<td>$\beta$</td>
<td>stretch exponent</td>
</tr>
<tr>
<td>$C_D$</td>
<td>surfactant concentration</td>
</tr>
<tr>
<td>$C_s$</td>
<td>salt concentration</td>
</tr>
<tr>
<td>$C^*$</td>
<td>overlap concentration</td>
</tr>
<tr>
<td>$De$</td>
<td>Deborah number</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
</tr>
<tr>
<td>$E_c$</td>
<td>endcap formation energy</td>
</tr>
<tr>
<td>$E_e$</td>
<td>electrostatic contribution to scission energy</td>
</tr>
<tr>
<td>$E_{sciss}$</td>
<td>scission energy</td>
</tr>
<tr>
<td>$g_1(t)$</td>
<td>first-order autocorrelation function</td>
</tr>
<tr>
<td>$G'$</td>
<td>storage modulus, elastic modulus</td>
</tr>
<tr>
<td>$G''$</td>
<td>loss modulus, viscous modulus</td>
</tr>
<tr>
<td>$G_c$</td>
<td>crossover modulus</td>
</tr>
<tr>
<td>$G_0$</td>
<td>plateau modulus</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Couette aspect ratio</td>
</tr>
<tr>
<td>$\Gamma(q)$</td>
<td>relaxation rate</td>
</tr>
<tr>
<td>$I(q)$</td>
<td>absolute scattering intensity</td>
</tr>
<tr>
<td>$I(q,t)$</td>
<td>intermediate scattering function</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>gap-to-radius ratio</td>
</tr>
<tr>
<td>$\eta_0$</td>
<td>zero-shear viscosity</td>
</tr>
<tr>
<td>$\eta_\infty$</td>
<td>infinite rate viscosity</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>shear strain</td>
</tr>
<tr>
<td>$\gamma_0$</td>
<td>strain amplitude</td>
</tr>
<tr>
<td>$\dot{\gamma}_0$</td>
<td>shear rate amplitude</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>shear rate</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant, $1.381 \times 10^{-23}$ J/K</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye screening length</td>
</tr>
<tr>
<td>$l_B$</td>
<td>Bjerrum length</td>
</tr>
<tr>
<td>$L_c$</td>
<td>contour length</td>
</tr>
<tr>
<td>$l_e$</td>
<td>entanglement length</td>
</tr>
<tr>
<td>$L_m$</td>
<td>length between branch points</td>
</tr>
<tr>
<td>$l_p$</td>
<td>persistence length</td>
</tr>
<tr>
<td>$N$</td>
<td>power law index</td>
</tr>
<tr>
<td>$\xi_M$</td>
<td>mesh size</td>
</tr>
<tr>
<td>$P(q)$</td>
<td>form factor</td>
</tr>
<tr>
<td>$p$</td>
<td>packing parameter</td>
</tr>
<tr>
<td>$r_{cs}$</td>
<td>cross-sectional radius</td>
</tr>
<tr>
<td>$R_g$</td>
<td>radius of gyration</td>
</tr>
<tr>
<td>$S(q)$</td>
<td>structure factor</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>shear stress</td>
</tr>
<tr>
<td>$\tau_{\text{break}}$</td>
<td>breakage time</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>relaxation time</td>
</tr>
<tr>
<td>$\tau_{\text{rep}}$</td>
<td>reptation time</td>
</tr>
<tr>
<td>$\theta$</td>
<td>scattering angle</td>
</tr>
<tr>
<td>$\phi_0$</td>
<td>orientation angle, azimuthal angle of greatest intensity</td>
</tr>
<tr>
<td>$\phi$</td>
<td>volume fraction OR azimuthal angle</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency</td>
</tr>
<tr>
<td>$\omega_c$</td>
<td>crossover frequency</td>
</tr>
<tr>
<td>$q$</td>
<td>scattering wave vector</td>
</tr>
<tr>
<td>$Wi$</td>
<td>Weissenberg number</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>CaBER</td>
<td>capillary breakup extensional rheometry</td>
</tr>
<tr>
<td>CPyCl</td>
<td>cetylpyridinium chloride</td>
</tr>
<tr>
<td>cryo-TEM</td>
<td>cryo-transmission electron microscopy</td>
</tr>
<tr>
<td>CTAB</td>
<td>cetrimonium bromide</td>
</tr>
<tr>
<td>CTAT</td>
<td>cetyltrimethylammonium tosylate</td>
</tr>
<tr>
<td>DLS</td>
<td>dynamic light scattering</td>
</tr>
<tr>
<td>flow-SANS</td>
<td>flow-small angle neutron scattering</td>
</tr>
<tr>
<td>ILL</td>
<td>Institut Laue-Langevin</td>
</tr>
<tr>
<td>I-N</td>
<td>isotropic-to-nematic</td>
</tr>
<tr>
<td>LAMP</td>
<td>large array manipulation program</td>
</tr>
<tr>
<td>LAOS</td>
<td>large amplitude oscillatory shear</td>
</tr>
<tr>
<td>LVE</td>
<td>linear viscoelastic regime</td>
</tr>
<tr>
<td>NaOL</td>
<td>sodium oleate</td>
</tr>
<tr>
<td>NaSal</td>
<td>sodium salicylate</td>
</tr>
<tr>
<td>NaTos</td>
<td>sodium tosylate</td>
</tr>
<tr>
<td>NCNR</td>
<td>NIST Center for Neutron Research</td>
</tr>
<tr>
<td>NISF</td>
<td>normalized intermediate scattering function</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NESE</td>
<td>neutron spin echo</td>
</tr>
<tr>
<td>OSP</td>
<td>orthogonal superposition</td>
</tr>
<tr>
<td>PGSE-NMR</td>
<td>pulsed gradient nuclear magnetic resonance</td>
</tr>
<tr>
<td>PTV</td>
<td>particle tracking velocimetry</td>
</tr>
<tr>
<td>rheo-SANS</td>
<td>rheo-small angle neutron scattering</td>
</tr>
<tr>
<td>SANS</td>
<td>small angle neutron scattering</td>
</tr>
<tr>
<td>SAOS</td>
<td>small amplitude oscillatory shear</td>
</tr>
<tr>
<td>SDBS</td>
<td>sodium dodecylbenzenesulfonate</td>
</tr>
<tr>
<td>SIPS</td>
<td>shear induced phase separation</td>
</tr>
<tr>
<td>WLM</td>
<td>wormlike micelle</td>
</tr>
</tbody>
</table>

Table A.2: Acronyms
Appendix B

ALIGNMENT FACTOR Q-RANGE FOR EACH SAMPLE

The $q^*$ region used to calculate the alignment factor from Equation 2.36 is a range within the $q^{-1}$ scattering regime for each wormlike micelle solution, over multiple configurations and sample preparations. Within $q^*$, the value of $A_f$ remains constant. The magnitude of $A_f$ is the largest in the $q^*$ region. In each of the figures below, the $q^{-1}$ region is highlighted in blue (or the equivalent region when an interaction peak occurs); the chosen $q^*$ is highlighted in pink. The scattering for the 0.01% wt and 0.05% wt NaTos solutions can be seen in Figure B.1, for the 0.10% wt and 0.15% wt NaTos solutions in Figure B.2, and for the 0.25% wt NaTos solution in Figure B.3. For all solutions, excellent agreement is observed between configurations and sample preparations.

Figure B.1: Static scattering of the 0.01% wt (a) and 0.05% wt (b) NaTos solutions across multiple configurations. The interaction peak region is shown in blue; $q^*$ is shown in pink. In (b), the lower peaks for NGB10 configurations are a result of the instrument resolution and closer detector distance.
Figure B.2: Static scattering of the 0.10% wt (a) and 0.15% wt (b) NaTos solutions across multiple configurations. The $q^{-1}$ region is highlighted in blue; $q^*$ is highlighted in pink.

Figure B.3: Static scattering of the 0.25% wt NaTos solution across multiple configurations. The $q^{-1}$ region is highlighted in blue; $q^*$ is highlighted in pink.
Appendix C

AMPLITUDE SWEEPS TO DETERMINE THE LINEAR VISCOELASTIC REGIME OF THE WLM SOLUTIONS

For the 0.25% wt NaTos solution (prepared in water) shown in Figure C.1, we examine frequencies at the ends of the relaxation spectra in multiples of the relaxation time $\tau_R$, where the Deborah number, $De$, is the normalized frequency ($De = \omega / \omega_c$). This process helps to identify the ideal strain amplitude, $\gamma_0$, to use across the entire frequency range for a frequency sweep. Figure C.1 presents the range $0.1 \leq De \leq 10$ to cover a wide range of the LVE spectra. As seen in Figure C.1, strain amplitudes up to about $\gamma_0 = 30\%$ appear to be in the linear regime, even at $De = 10$. The same general behavior shown in Figure C.1 for the 0.25% wt NaTos solution was observed for the remainder of the samples prepared in water. The ideal amplitude range to be used for experiments on the solutions in water was determined to be $5 \leq \gamma_0 \leq 20\%$ for LVE experiments.

Figure C.1: Amplitude sweep for the 0.25% wt NaTos solution (in water) to determine the linear viscoelastic regime across the relevant frequency range, where $\omega_c \approx 4.5$ rad·s$^{-1}$. (a) $\omega = 0.45$ rad·s$^{-1}$, well below the crossover frequency $\omega_c$ where $De = 0.1$ (b) $\omega = 10$ rad·s$^{-1}$, near $\omega_c$ where $De = 2.2$ (c) $\omega = 45$ rad·s$^{-1}$, well above $\omega_c$ where $De = 10$

The same analysis is performed for the D$_2$O solutions. As seen in Figure C.1, amplitudes within the LVE window become smaller with increasing frequency. Therefore, we
focus on the high frequency response for the D$_2$O solutions, although amplitude sweeps were also performed at low Deborah numbers to determine a minimum amplitude where a strong rheometer signal could be obtained. Figure C.2 shows the high frequency amplitude sweeps for the 0.10% wt NaTos solution in D$_2$O. While many conditions show a large range of strain amplitudes within the LVE window, we use $\gamma_{0,max} = 20\%$. The value of $\gamma_{0,max} = 20\%$ was chosen because at $\omega = 30$ and 32 rad·s$^{-1}$, the LVE window appears shortened to $\gamma_{0,max} = 30\%$ due to changes in $G''$. However, at these frequencies, the transducer is transitioning into a new torque regime (transducer switches from medium to high mode). This produces unreliable data in the LVE spectrum. Further into the high torque regime at higher frequencies, the LVE window appears much larger, despite the increased frequency. This suggests that the LVE window in the relevant frequency range for this solution is actually well beyond $\gamma_{0,max} = 30\%$; however, we still use $\gamma_{0,max} = 20\%$ to be cautious. The same trends are observed in the other WLM solutions prepared in D$_2$O, confirming that the range $5 \leq \gamma_0 \leq 20\%$ is appropriate for all LVE experiments on these solutions.

![Figure C.2: Amplitude sweep at high frequencies for the 0.10% wt NaTos solution (D$_2$O).](image)

(a) $\omega = 20$ to 32 rad·s$^{-1}$. At $\omega = 30$ and 32 rad·s$^{-1}$, the LVE window is small due to changes in $G''$. Responses at these frequencies are likely inaccurate, as the transducer torque range changes and produces unreliable data. (b) $\omega = 34$ to 40 rad·s$^{-1}$; the LVE window appears wider than in (a) despite higher $\omega$. 

528
Appendix D

CALCULATIONS OF THE BEAM DIVERGENCE FOR RHEO- AND FLOW-SANS EXPERIMENTS

In the following calculations, we consider the smearing effects from the beam divergence on the 1-2 shear cell configuration. The equations to determine the instrument smearing were developed by Barker and Pedersen [1]; while the equations were developed for circular apertures, the effects can be divided into the horizontal and vertical components for rectangular slits. Several quantities discussed in Chapter 3, Section 3.4, among others, are important for the smearing, where a schematic can be seen in Figure D.1. The size of the source and sample apertures (slits), the source-to-sample-aperture distance, and the sample-aperture-to-detector distance are all important. Here, we calculate both the umbra and penumbra sizes.

Figure D.1: Relevant length scales for SANS instrumental smearing. Note that $L_1$ extends before the source aperture at the nozzle, such that collimation effects are accounted for. Reprinted from reference [2].
There are two major differences in our calculations versus the quantities shown in Figure D.1. In this case, the sample-aperture-to-detector distance is replaced with the distance between the sample aperture and the back edges of the rheometer or shear cell, to determine the beam size at the time of exit. Additionally, \( L_1 \) extends before the source aperture at the nozzle of the SANS instrument, such that collimation effects are accounted for. To understand the beam smearing, the sizes of the source and sample aperture are projected onto the detector plane. Two quantities are defined, where \( D_1 \) is the beam diameter if the sample slit is infinitesimal in size, and \( D_2 \) is the beam diameter if the source aperture is infinitesimal in size. These parameters can be calculated by [1]:

\[
D_1 = \frac{2S_1L_2}{L_1} \\
D_2 = \frac{2S_2(L_1 + L_2)}{L_1}
\]

where \( S_1 \) is the source slit half-width (or radius of a circular aperture), and \( S_2 \) is the sample slit half width. The larger the number of guides, the smaller \( L_1 \) becomes.

\[
2A_1 = \frac{\text{abs}(D_1 - D_2)}{2} \\
2A_2 = \frac{D_1 + D_2}{2}
\]

\( A_1 \) and \( A_2 \) define the beam profile shape as a trapezoid, where the full width at the bottom will be \( 2A_2 \) (penumbra) and the full width of the top of the trapezoid is \( 2A_1 \) (umbra).

In our experiments, typically five guides are used, which gives \( L_2 = 7.97 \) m in the NIST configuration. At ILL, an 8 m collimation is typically used, so using this distance is appropriate. In the results shown in Chapter 3, Section 3.4, several source slits were used: 8x20 mm, 5x20 mm, and 3x20 mm. Using these slits, \( S_1 \) is always 10 mm in the vertical, and either 4, 2.5, or 1.5 mm in the horizontal. With the standard round slit, the beam size has a radius of 25.4 mm. The slit confining the vertical direction is placed directly onto the shear cell \( (h = 1, 3, 5 \text{ mm}, S_{2, vert} = 0.5, 1.5, \text{ or } 2.5 \text{ mm}) \). The width of the front of the shear...
Table D.1: Beam divergence for different slit configurations on the 1-2 shear cell. The * indicates the standard configuration for the 1-2 shear cell used in this work.

<table>
<thead>
<tr>
<th># guides, $L_2$ (m)</th>
<th>Source aperture, mm x mm</th>
<th>Slit x and y, mm x mm</th>
<th>$2A_{1,x}$ mm</th>
<th>$2A_{2,x}$ mm</th>
<th>$2A_{1,y}$ mm</th>
<th>$2A_{2,y}$ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 7.97</td>
<td>round, $R = 25.4$</td>
<td>0.1 x 5</td>
<td>0.029</td>
<td>0.229</td>
<td>4.93</td>
<td>5.09</td>
</tr>
<tr>
<td>4, 9.52</td>
<td>round, $R = 25.4$</td>
<td>0.1 x 5</td>
<td>0.008</td>
<td>0.208</td>
<td>4.94</td>
<td>5.07</td>
</tr>
<tr>
<td>1, 14.17</td>
<td>round, $R = 25.4$</td>
<td>0.1 x 5</td>
<td>0.028</td>
<td>0.173</td>
<td>4.96</td>
<td>5.05</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>round, $R = 25.4$</td>
<td>0.3 x 3</td>
<td>0.172</td>
<td>0.430</td>
<td>2.92</td>
<td>3.09</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>5 x 20</td>
<td>0.1 x 5</td>
<td>0.080</td>
<td>0.121</td>
<td>4.96</td>
<td>5.06</td>
</tr>
<tr>
<td>*5, 7.97</td>
<td>5 x 20</td>
<td>0.1 x 5</td>
<td>0.088</td>
<td>0.113</td>
<td>4.98</td>
<td>5.04</td>
</tr>
<tr>
<td>4, 9.52</td>
<td>5 x 20</td>
<td>0.1 x 5</td>
<td>0.090</td>
<td>0.111</td>
<td>4.98</td>
<td>5.03</td>
</tr>
<tr>
<td>1, 14.17</td>
<td>5 x 20</td>
<td>0.1 x 5</td>
<td>0.093</td>
<td>0.107</td>
<td>4.99</td>
<td>5.02</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>5 x 20</td>
<td>0.3 x 5</td>
<td>0.280</td>
<td>0.322</td>
<td>4.96</td>
<td>5.06</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>5 x 20</td>
<td>0.3 x 5</td>
<td>0.288</td>
<td>0.313</td>
<td>4.98</td>
<td>5.04</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>8 x 20</td>
<td>0.1 x 5</td>
<td>0.067</td>
<td>0.134</td>
<td>4.96</td>
<td>5.06</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>8 x 20</td>
<td>0.1 x 5</td>
<td>0.080</td>
<td>0.121</td>
<td>4.98</td>
<td>5.04</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>3 x 20</td>
<td>0.1 x 5</td>
<td>0.088</td>
<td>0.113</td>
<td>4.96</td>
<td>5.06</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>3 x 20</td>
<td>0.1 x 5</td>
<td>0.093</td>
<td>0.108</td>
<td>4.98</td>
<td>5.04</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>8 x 20</td>
<td>0.3 x 5</td>
<td>0.258</td>
<td>0.334</td>
<td>4.96</td>
<td>5.06</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>8 x 20</td>
<td>0.3 x 5</td>
<td>0.280</td>
<td>0.321</td>
<td>4.98</td>
<td>5.04</td>
</tr>
</tbody>
</table>

The beam from this placement to the windows is 0.3 inches, for a total path length of 5 mm plus 0.3 in, $L_2 = 12.62$ mm in the vertical direction [3]. The translating slit sits an additional 0.3 inches in front of the vertical slit, such that $L_2 = 20.24$ mm in the horizontal direction [3]. The translating slit is either of width 0.1 or 0.3 mm, such that $S_{2,\text{horiz}} = 0.05$ or 0.15 mm. The beam divergence in the horizontal direction is the most important, as the shear cell gap is only 1 mm wide; however, the divergence in both directions is calculated. The results for different configurations are shown in Table D.1.

As seen in Table D.1, the small width of the shear cell slits and source slits leads to little divergence over the shear cell path length. Reducing the source aperture from the standard, large aperture to a narrower, rectangular slit essentially reduces the smearing by 50%. Even with a large number of guides, the beam is never larger than 0.14 mm in width by the time of exit from the shear cell when the narrower apertures are used. The total smearing in the horizontal direction is roughly 10% of the slit width, for both the 0.1 mm and 0.3 mm wide translating slits. The smearing in the y-direction is always negligible to the total slit height. As seen by these calculations, increasing the number of guides appears to be the best way to increase the flux to the sample, while producing little extra smearing in
Table D.2: Beam divergence for different slit configurations on the rheometer. The * indicates the typical 1-3 plane configuration.

<table>
<thead>
<tr>
<th># guides, $L_2$ (m)</th>
<th>Source aperture, mm x mm</th>
<th>Slit x and y, mm x mm</th>
<th>$2\Delta_{1,x}$ mm</th>
<th>$2\Delta_{2,x}$ mm</th>
<th>$2\Delta_{1,y}$ mm</th>
<th>$2\Delta_{2,y}$ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>5, 7.97</td>
<td>round, $R = 25.4$</td>
<td>2 x 10</td>
<td>0.029</td>
<td>0.229</td>
<td>4.93</td>
<td>5.09</td>
</tr>
<tr>
<td>4, 9.52</td>
<td>round, $R = 25.4$</td>
<td>2 x 10</td>
<td>0.008</td>
<td>0.208</td>
<td>4.94</td>
<td>5.07</td>
</tr>
<tr>
<td>1, 14.17</td>
<td>round, $R = 25.4$</td>
<td>2 x 10</td>
<td>0.028</td>
<td>0.173</td>
<td>4.96</td>
<td>5.05</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>round, $R = 25.4$</td>
<td>5 x 10</td>
<td>0.172</td>
<td>0.430</td>
<td>2.92</td>
<td>3.09</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>5 x 20</td>
<td>2 x 10</td>
<td>1.85</td>
<td>2.34</td>
<td>9.51</td>
<td>11.46</td>
</tr>
<tr>
<td>*5, 7.97</td>
<td>5 x 20</td>
<td>2 x 10</td>
<td>1.91</td>
<td>2.21</td>
<td>9.70</td>
<td>10.89</td>
</tr>
<tr>
<td>4, 9.52</td>
<td>5 x 20</td>
<td>2 x 10</td>
<td>1.93</td>
<td>2.17</td>
<td>9.75</td>
<td>10.75</td>
</tr>
<tr>
<td>1, 14.17</td>
<td>5 x 20</td>
<td>2 x 10</td>
<td>1.95</td>
<td>2.12</td>
<td>9.83</td>
<td>10.50</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>5 x 20</td>
<td>5 x 10</td>
<td>5.00</td>
<td>5.49</td>
<td>9.51</td>
<td>11.46</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>5 x 20</td>
<td>5 x 10</td>
<td>5.00</td>
<td>5.30</td>
<td>9.70</td>
<td>10.89</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>8 x 20</td>
<td>2 x 10</td>
<td>1.71</td>
<td>2.49</td>
<td>9.51</td>
<td>11.46</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>8 x 20</td>
<td>2 x 10</td>
<td>1.82</td>
<td>2.30</td>
<td>9.70</td>
<td>10.89</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>3 x 20</td>
<td>2 x 10</td>
<td>1.95</td>
<td>2.24</td>
<td>9.51</td>
<td>11.46</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>3 x 20</td>
<td>2 x 10</td>
<td>1.97</td>
<td>2.15</td>
<td>9.70</td>
<td>10.89</td>
</tr>
<tr>
<td>7, 4.87</td>
<td>8 x 20</td>
<td>5 x 10</td>
<td>4.85</td>
<td>5.63</td>
<td>9.51</td>
<td>11.46</td>
</tr>
<tr>
<td>5, 7.97</td>
<td>8 x 20</td>
<td>5 x 10</td>
<td>4.91</td>
<td>5.39</td>
<td>9.70</td>
<td>10.89</td>
</tr>
</tbody>
</table>

space across the shear cell gap.

The same calculations can be performed for the 1-3 plane rheometer configurations. Based on the specification from Anton-Paar [4], we can estimate $L_2$ as 237 mm using a cup diameter of 30 mm. As the rheometer configurations involve wider slits and a longer $L_2$, the divergence is worse in these configurations, which can be seen in Table D.2. However, in the standard configuration, we still see approximately a 10% smearing. The same source slits are used for the rheometer experiments, and either a 5 mm or 2 mm by 10 mm sample slit is used. The smearing is on the order of 10 to 20% for each configuration. As seen in Table D.2, the smearing that results in these configurations is mostly due to the larger sample slit. While the source slit has some effect, it is relatively minor in comparison to the sample slit effect.
References


Appendix E
ADDITIONAL CRYO-TEM MICROGRAPHS

While performing cryo-TEM, multiple images were taken for each sample in different grid locations and at different magnifications. Additional images for the 0.01% wt NaTos (low branching, red) solution and 0.10% wt NaTos solution (high branching, blue) are shown in the top two rows of Figure E.1 to validate the trends reported in the main paper. To further confirm the qualitative branching trends observed between the 0.10% wt NaTos solution and 0.01% wt NaTos solution, cryo-TEM was also performed on a 0.15% wt NaTos solution (very high branching). The 0.15% wt NaTos solution is highlighted in purple to correspond to the purple 1D scattering shown in Figure 2 of the main paper. Results are shown in the bottom row (purple) of Figure E.1, where the 0.15% wt NaTos solution exhibits structures similar to those observed in the highly branched case (0.10% wt NaTos), including loops and three-fold junctions. Conversely, the three images of the 0.01% wt NaTos solution confirm that the self-assembled morphology of this sample is of a linear, wormlike micelle.

When compared, the images at the lowest magnification (right hand column) show qualitative differences between the branching levels on longer length scales: the low branched sample appears predominantly linear, whereas the two branched solutions appear network-like. While branching is a dynamic process and not all micelles may be branched at all times, these results confirm increasing branching with increasing salt concentration.
Figure E.1: Cryo-TEM images of the low branching (0.01% wt NaTos, top red), high branching (0.10% wt NaTos, middle blue) and very high branching (0.15% wt NaTos, bottom purple) solutions. Images were taken at different magnifications and grid locations. The 1D static scattering of the 0.15% wt NaTos solution is also highlighted in purple in the static SANS plot Chapter 4. Similar to the 0.10% wt NaTos solution, a variety of irregular structures, junctions and loops are observed in the 0.15% wt NaTos solution; however, the 0.01% wt NaTos solution shows primarily linear structures in all images.
Appendix F

COMPARISON OF WLM RHEOLOGY IN WATER VS. D$_2$O

The isotopic substitution between water and deuterium oxide has been extensively explored for WLM solutions [1]. The micellar growth and associated length scales are not significantly affected by this substitution; the difference in persistence length, $l_p$, is on the order of 10% [1]. However, we see significant differences in the relaxation spectra and zero-shear viscosity between these CTAT/SDBS WLM solutions in water versus D$_2$O. It should be noted that the WLM solutions examined by López-Barrón and Wagner [1] were those of CTAB, which is structurally similar to CTAT. However, these solutions were significantly more concentrated than the current solutions, and were near the isotropic-to-nematic (I-N) transition, where micellar growth scales differently (Equation 1.15). Therefore, the comparisons between our work with the solutions in D$_2$O versus those previously characterized in water [2,3] should be interpreted with caution, as the WLMs here are in a different concentration regime than those examined previously by López-Barrón and Wagner [1]. Here, we examine the behavior of the WLMs in water versus D$_2$O. It should be noted that the experiments in water were performed at 25 °C, whereas the solutions in D$_2$O were performed at 35 °C. Using D$_2$O instead of water as the solvent increases the Krafft temperature of the micelles by about 10% in similar systems [1], which we observe to be the case here as well. As 25 °C is very close to the Krafft temperature for the D$_2$O WLMs, we could not perform the measurements at 25 °C. However, the effect of temperature here appears to be minor in comparison to the isotopic substitution, as determined via temperature sweeps on the solutions in D$_2$O.

Despite the fact that viscosity of D$_2$O is 23% higher than that of water and the heat capacity is 12% higher, the zero-shear viscosity of the WLMs in water versus D$_2$O is about an order of magnitude higher. This is partially a result of the lower temperature, which
serves to increase the viscosity, but it cannot fully account for the differences. As noted by López-Barrón and Wagner [1] and Helgeson [4], the WLMs should become stiffer in D$_2$O versus water, but this does not serve to increase the zero-shear viscosity. We also see an increase in the crossover frequency, $\omega_c$, in D$_2$O versus water of about an order of magnitude, which leads to an order of magnitude decrease in the relaxation time. This result is consistent with the work of Helgeson [4], which showed that the I-N transition was shifted toward lower temperatures for samples in D$_2$O, as decreasing the temperature increases the material relaxation time. Therefore, despite the increased stiffness of the micelles in D$_2$O, the relaxation time always decreases for the solutions in D$_2$O versus water for the same amount of added salt.

Figure F.1 shows the rheological results for the highly branched, 0.25% wt NaTos solution in water. Figure F.1a shows the linear viscoelastic regime (LVE) rheology for this solution, which shows stark contrasts to the 0.25% wt NaTos solution in D$_2$O presented in Chapter 4, Sections 4.3 and 4.3.2. Table F.1 compares the relevant quantities between the water and D$_2$O solutions. The zero-shear viscosity of the 0.25% wt NaTos WLM solution in water is roughly 10-fold larger than for the solution in D$_2$O (1.2 vs. 0.17 Pa·s), which is seemingly counter-intuitive because the micelles are more flexible in water. This corresponds to an order of magnitude faster relaxation time for the D$_2$O solutions. However, the cross-over modulus, $G_c$, is about two-fold higher for the solutions in D$_2$O, which is supported by the increased stiffness of the micelles in the deuterated solvent [1,4]. A power law index, $N$, of $N = 0.19$ is observed in the solution (Figure F.1b), and there is no evidence of hysteresis or shear banding. The value of $N$ here is lower than in the D$_2$O solution. However, it is unclear as to whether this is a solvent effect or temperature effect, as lowering the temperature in these solutions also lowers the power law index.

The differences in magnitude of the cross-over modulus increase with added salt, which may be a result of differences in the branching level in the solutions. An increase in $G_c$ with added salt can be attributed to increasing branching, due to the formation of network-like structures. In the water solutions, $G_c$ increases from 2.0 Pa to 2.6 Pa from 0.01% wt NaTos to 0.25% wt NaTos, which is an 30% increase in modulus. For the solutions in D$_2$O,
The crossover frequency, $\omega_c$, is $\omega_c = 4.6 \text{ rad}\cdot\text{s}^{-1}$, such that $\tau_R = 0.22 \text{ s}$. The crossover modulus is $G_c = 2.6 \text{ Pa}$, which is about half that of the solution in D$_2$O; the zero-shear viscosity is $\eta_0 = 1.2 \text{ Pa}\cdot\text{s}$, which is about 10-fold higher than for the D$_2$O solution.

However, the modulus increases from 3.0 Pa to 4.8 Pa, a 60% increase. This suggests that the branching may be more pronounced in the solutions in D$_2$O versus water at 0.25% wt NaTos. The salt addition may also affect the micellar growth differently in water versus D$_2$O. The salt addition in D$_2$O has no effect on the modulus between the 0.01% wt and 0.05% wt NaTos solutions. We believe this is because the micelles are already very long and are not forming significant interconnected networks at 0.05% wt NaTos (which would serve to increase the modulus). However, in water, the modulus increases 10% from 2.0 Pa to 2.2 Pa between these two salt concentrations. If branching were not at play, another explanation could be that the micelles are continuing to grow and entangle in the water solutions, leading to higher modulus values with added salt. The temperature difference between the WLM series could also have an effect on the modulus.

Figure F.2 shows the rheological results for the low branching, 0.01% wt NaTos solution in water. As seen from Figure F.2a, the crossover frequency for the solution in water is an order of magnitude lower than in D$_2$O, as was the case for the other WLM solutions in water. Here, this results in a relaxation time of $\tau_R = 54 \text{ s}$, which is significantly longer than the $\tau_R = 5.6 \text{ s}$ for the D$_2$O solution. As the solution in D$_2$O shows extremely long transience in the steady shear rheology, an even longer transience is expected for the solution.
in water. The flow curves of the solutions in water (Figure F.2) and D$_2$O (see Figure 5.4) also share some of the same features that are indicative of this long transience, including a metastable portion of the flow curve. This metastable region appears as an overshoot in the low shear rate regime during the transition from region I to region II (Newtonian to shear thinning or shear banding). The flow curve overshoot and metastable state is a signature of shear banding [5], which can be assumed for both the solution in water and in D$_2$O.

![Flow curve and frequency sweep](image)

Figure F.2: Frequency sweep (a) and flow curve (b) for the 0.01% wt NaTos solution in water. (a) Here, $\omega_c = 0.019 \text{ rad} \cdot \text{s}^{-1}$, such that $\tau_R = 54 \text{ s}$. The crossover modulus is $G_c=2.0 \text{ Pa}$, compared to 3.0 Pa for the solution in D$_2$O; the zero-shear viscosity is $\eta_0 = 230 \text{ Pa} \cdot \text{s}$, which is about 7-fold higher than for the D$_2$O solution. (b) An artificial power law index of $N \approx 0.06$ can be determined from the end of the flow curve beyond the metastable regime; points along the flow curve were collected after 300 s. However, the true $N$ should be determined from the steady state flow curve which requires much longer wait times.

In Figure F.2b, the steady shear flow curve is presented, however, this flow curve is likely not that of the steady state. In taking the flow sweep, 250 s was left as an equilibration time between consecutive, increasing shear rates with a 50 s averaging time for each data point. While this equilibration time would be sufficient for the solution in D$_2$O at most shear rates, the solution in water has a significantly longer (10-fold) relaxation time. Further, in the solution prepared in D$_2$O, there is longer than a twenty minute transient in regions near the beginning of the flow curve, so it is likely that the solution in water would need an order of magnitude longer (200 min) equilibration time between points, which is not practical from a measurement perspective. Therefore, the steady shear flow curve presented in Figure F.2
is most likely not that of the steady state, but instead accesses metastable states along the flow curve. An artificial power law index of $N \approx 0.06$ can be determined from the higher shear rates, but this is likely not the power law index of the steady state. Additionally, the power law index shown in Table F.1 for the 0.01% wt NaTos solution in D$_2$O ($N \approx 0$) was taken from a different region of the flow curve, so these two values are not comparable. In the D$_2$O solution, we calculate the value of $N \approx 0$ from the region immediately following the metastable ‘stress overshoot’ region of the flow curve. If we were to compare this same region for the solution in water seen in Figure F.2b, the region exhibits a significant slope where $N = 0.28$. As the power law index increases with increasing salt content and $N = 0.19$ for the 0.25% wt NaTos solution, $N = 0.28$ is also not the true power law index. This slope and the true power law index will be significantly lower at steady state when sufficient equilibration time is allowed between points.

Finally, Figure F.3 shows the rheological results for the 0.05% wt NaTos solution in water, which falls in between the two solutions already discussed. As was the case in the other solutions, Figure F.3a shows that the crossover frequency is ten-fold lower for the solution in water than in D$_2$O, which results in $\tau_R = 14$ s (vs. $\tau_R=1.7$ s for the D$_2$O solution). The flow curves of the solutions in water (Figure F.3b) and D$_2$O (see Figure 5.12) do not share same features as was the case in the 0.01% wt NaTos solutions. In Figure F.3b, the solution clearly shows a metastable portion of the flow curve and overshoot in the low shear rate regime, indicative of shear banding [5]. While the 0.05% wt NaTos solution in D$_2$O also exhibits shear banding (see Chapter 5, Section 5.7), its flow curve does not show this metastable branch. However, the solution in D$_2$O still shows long transience in the steady shear rheology, so we again expect a longer transience for the solution in water. This longer transience is likely an effect of the longer relaxation time that results from the isotopic substitution and the difference in temperature between the systems, as lower temperatures lead to more pronounced shear banding [6,7]. In Figure F.3b, the steady shear flow curve is presented. While this flow curve more closely approximates the steady state than the curve in Figure F.2b for the 0.01% wt NaTos solution, we still expect that this is not the true flow curve. We explore the transience and hysteresis in the flow curve further below in Figure F.4.
In this flow sweep, 45 s was left as an equilibration time between consecutive, increasing shear rates with a 15 s averaging time for each data point, for a total time of one minute per shear rate. This equilibration time is sufficient for the solution in D$_2$O; however, it cannot capture the long transience at transition between region I and region II in the solution in water. Therefore, the steady shear flow curve presented in Figure F.3 may be that of the steady state at high shear rates near region III, but accesses metastable states at lower shear rates.

Figure F.3: Frequency sweep (a) and flow curve (b) for the 0.05% wt NaTos solution in water. (a) Here, $\omega_c = 0.07$ rad·s$^{-1}$, such that $\tau_R = 14$ s. The crossover modulus is $G_c = 2.2$ Pa, compared to 3.0 Pa for the solution in D$_2$O; the zero-shear viscosity is $\eta_0 = 65$ Pa·s, which is about 6-fold higher than for the D$_2$O solution. (b) $N \approx 0.10$ is determined from the higher shear rates; points along the flow curve were collected after 60 s. The true $N$ should be determined from the steady state flow curve which requires much longer wait times.

An artificial power law index of $N \approx 0.10$ can be determined from the higher shear rates (Figure F.3b), but this was not taken in the same region as the power law index shown in Table F.1 for the 0.05% wt NaTos solution in D$_2$O ($N \approx 0.07$). Using the same region near the start of region II to calculate $N$ for the solution in water, the region exhibits a larger slope giving $N = 0.15$. Interestingly, this value of $N$ is lower than the value of $N$ seen for the 0.01% wt NaTos solution in water in the same region. As the power law index increases with increasing salt content, this result indicates that the flow curve shown in Figure F.3b for the 0.05% wt NaTos solution in water is closer to the true flow curve than that shown
in Figure F.2b for the 0.01% wt NaTos solution. The result further confirms that neither of these calculated values of $N$ is the true power law index, which should be taken from the start of region II and will be lower steady state. Interestingly, the value of $N = 0.1$ is accurate to one significant digit in short-time measurements of this region of the flow curve (Figure F.4). While it is possible that the slope in this region would change based on the true steady state flow curve, these results seem to indicate that a relative steady state has been reached at higher shear rates for this solution, which will be discussed further below.

Table F.1: Comparison of rheological properties for WLMs in H$_2$O vs. D$_2$O, labelled by the % wt NaTos in each solution followed by the solvent. Note that the power law index, $N$, could not be calculated from the steady state flow curves for the solutions in water, so these values should be interpreted with caution.

<table>
<thead>
<tr>
<th>Property</th>
<th>0.01% H$_2$O</th>
<th>0.01% D$_2$O</th>
<th>0.05% H$_2$O</th>
<th>0.05% D$_2$O</th>
<th>0.25% H$_2$O</th>
<th>0.25% D$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_c$ (rad·s$^{-1}$)</td>
<td>0.019</td>
<td>0.18</td>
<td>0.07</td>
<td>0.6</td>
<td>4.6</td>
<td>60</td>
</tr>
<tr>
<td>$\tau_R$ (s)</td>
<td>54</td>
<td>5.6</td>
<td>14</td>
<td>1.7</td>
<td>0.22</td>
<td>0.017</td>
</tr>
<tr>
<td>$\eta_0$ (Pa·s)</td>
<td>230</td>
<td>34</td>
<td>65</td>
<td>11</td>
<td>1.2</td>
<td>0.17</td>
</tr>
<tr>
<td>$G_c$</td>
<td>2.0</td>
<td>3.0</td>
<td>2.2</td>
<td>3.0</td>
<td>2.6</td>
<td>4.8</td>
</tr>
<tr>
<td>$N$</td>
<td>0.06</td>
<td>0</td>
<td>0.10</td>
<td>0.07</td>
<td>0.19</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Figure F.4 explores the hysteresis and time-dependence of the recorded flow curve for the 0.05% wt NaTos solution in water. In Figure F.4a, the flow curve is compared for three trials. In the first trial, a 10 second equilibration time and 5 second averaging time was used, for a total time of 15 seconds per shear rate. In the second trial, the same times were used, but the step size between shear rates was smaller (10 vs. 5 points per decade). The third trial shown is the 45 second delay time and 15 second averaging time presented above in Figure F.3b. In Figure F.4a, the largest metastable or ‘stress overshoot’ region of the flow curve is seen in the first trial. This result is unsurprising and has been observed previously [5], as this trial used the shortest equilibration time and had the largest jump in shear rate between consecutive points. Thus, we expect this flow curve to be the furthest from the steady state curve [5]. The stress in this region drops in trial two, simply by using smaller shear rate jumps; the smaller change in shear rate allows the WLMs to relax more, leading to lower
stresses closer to the steady state values. Finally, the overshoot region is further minimized in the third trial by greatly increasing the equilibration time.

Figure F.4: Flow curve time dependence and hysteresis for different acquisition times for the 0.05% wt NaTos solution in water. (a) Three trials- 1. 10 s equilibration time, 5 s averaging time, 5 points per decade; 2. 10 s/5 s/10 ppd; 3. 45 s/15 s/10 ppd. The behavior at low shear rates (start of region II) approaches that of the steady state as longer equilibration times are used. (b) Two trials - 45 s/15 s/10 ppd versus 60 s/15 s/10 ppd. The two trials are nearly identical, indicating that significantly longer equilibration times are required near the start of region II. The high rate behavior and calculated power law index $N$ is similar between all trials.

In Figure F.4b, we compare the third trial to an even longer trial, with a 60 second delay time and 15 second averaging time. Here, the flow curve does not seem to be significantly affected by the longer wait time. While the stress in the overshoot region appears lower in the fourth trial, it is difficult to tell whether this difference is outside of the instrumental uncertainty. To access the true steady state flow curve, significantly longer equilibration times would have to be used. Finally, as mentioned above, the high shear rate region of the flow curves shown in Figure F.4 appears to be fairly independent of the condition, where $N \approx 0.1$ in all trials. This observation is consistent with behavior commonly seen in shear banding WLMs, which reach steady state faster with increasing shear rate. While significantly longer wait times may need to be used to access the true flow curve, it appears as though the high rate behavior is at least close to that of the steady state.
References


Appendix G

RHEOLOGICAL RESPONSE OF WLMS BETWEEN REPEATED SAMPLE PREPARATIONS

Here, we show the repeatability of the rheology, specifically the linear viscoelastic regime (LVE) frequency sweeps, between sample preparations. The calculations of the micellar length scales reported in the text use an average of the parameters extracted from the LVE data across the multiple sample preparations. One of the main differences observed over time in preparing the WLM solutions is the magnitude of the dynamic moduli, $G'$ and $G''$. In samples made early on in this dissertation work, the dynamic moduli, and the plateau moduli, were slightly higher. This trend may be the result of using a new batch of surfactant, specifically the CTAT. Surfactants are known to vary batch to batch; the original CTAT used in this work was much older and was leftover from Beth Schubert. This difference in the primary surfactant could lead to stiffening or aging, which could slightly change the LVE results. Additionally, when a new batch of SDBS was ordered, it was observed that the crossover frequency of the solutions decreased slightly. For the 0.01% wt NaTos solution, the crossover frequency for the early samples ranged from $\omega_c = 0.14 - 0.18 \text{ rad}\cdot\text{s}^{-1}$, whereas for the new samples, the range was $\omega_c = 0.10 - 0.12 \text{ rad}\cdot\text{s}^{-1}$. This changed the relaxation time from an average of $\tau_R = 5.6$ to 7.1 s for the early samples, to $\tau_R = 8.3$ to 10 s for the later samples. As the SDBS is ordered from TCI and is only 95% pure, small differences in the SDBS may affect the results. The lower crossover frequencies did not appear to affect the rheological and SANS results when trials were repeated, but these differences are noted in the text when applicable. For consistency, the calculations of micellar length scales presented in the text use the average of the samples prepared before any reagents were re-ordered.

Figure G.1a shows the LVE spectra between multiple sample preparations and instruments for the 0.01% wt NaTos solution. The data taken on the MCR instrument at the ILL
is boxed; these results generally differ the most from the other trials and may be a result of improper instrument calibration or the difference in geometry used. Figure G.1b shows the spectra for the 0.05% wt NaTos solution. All spectra were taken on the ARES G2; good agreement is seen for all sample preparations.

Figure G.1: LVE spectra of the 0.01% wt (a) and 0.05% wt (b) NaTos solutions between multiple sample preparations and instruments. Good agreement is seen in all sample preparations.

In Figure G.2a, the LVE spectra are shown for the 0.10% wt NaTos solution, and in Figure G.2b, the spectra are show for the 0.15% wt NaTos solution. All spectra were taken on the ARES G2. Good agreement is seen for all sample preparations. Only two spectra were taken for the 0.15% wt NaTos solution because the sample was used infrequently.

The repeatability of both the LVE spectra and the steady shear flow curve are shown for the 0.25% wt NaTos solution in Figure G.3a and b, respectively. Once again, the ILL results are boxed, and show the largest deviation from the other measurements. As the deviations shown in Figure G.3 are most significant at high frequencies, this is most likely a result of the instrument calibration or contributions from inertia. As seen in Figure G.3b, excellent agreement is seen in the steady shear flow curve despite differences in the LVE rheology; the most significant differences are observed in the low shear rate Newtonian plateau.

The 0.10% wt NaTos solution had some variation in sample preparation, which could
Figure G.2: LVE spectra of the 0.10% wt (a) and 0.15% wt (b) NaTos solutions between multiple sample preparations and instruments. Good agreement is seen in all sample preparations.

Figure G.3: LVE spectra (a) and steady shear flow curves (b) of the 0.25% wt NaTos solution between multiple sample preparations and instruments. The spectrum taken at the ILL on an Anton-Paar MCR rheo-SANS rheometer is boxed and varies the most from the other sample preparations. Despite the larger variation in the LVE spectra than in other solutions, the steady shear flow curves in (b) are not significantly different between trials.
have been the result of imperfect mixing when the samples were prepared and shipped immediately to the ILL in France. While most samples showed excellent reproducibility, there was some variation in the samples prepared for ILL experiments and subsequently used for 1-3 plane SANS versus the remaining 0.10% wt NaTos solutions, as detailed in Chapter 7. A comparison of the ‘original’ sample used in the results from Chapters 4 through 6 and the ‘new’ sample used for LAOS can be seen in Figure G.4. As seen in Figure G.4, the original sample has a higher crossover frequency ($\omega_c = 2.6$ vs. 1.8 rad·s$^{-1}$), which results in a faster relaxation time ($\tau_R = 0.4$ vs. 0.5 s). The LVE spectra are similar between the two solutions; the new solution has a slightly higher crossover modulus, but the value of $G_c$ is within the window of crossover moduli observed between different sample preparations for the original 0.10% wt NaTos solution.

Figure G.4: LVE spectra of the two 0.10% wt NaTos solutions: the original sample used for Chapters 4 through 6, and the new sample used for LAOS measurements (Chapter 7). The new sample has a slightly lower crossover frequency ($\omega_c = 1.8$ vs. 2.6 rad·s$^{-1}$), resulting in a longer relaxation time ($\tau_R = 0.5$ vs. 0.4 s).
Appendix H

NEUTRON SPIN ECHO DETECTOR DIVISION AND UNCERTAINTY

In neutron spin echo experiments, the detector is divided into the number of bins specified by the user over which to analyze the data. An example of this detector division can be seen in Figure H.1, where the bins are divided by the blue vertical lines in the figure. This process can be rather arbitrary and is generally chosen based on the number of neutron counts and the associated uncertainty in the fits of the echoes, and ultimately, the normalized intermediate scattering functions (NISFs), $I(q,t)/I(q,0)$ with bins of different widths. However, while a larger bin width leads to a lower uncertainty in the calculated fits of the NISF a larger bin width also leads to a larger spatial smearing. Figure H.1 shows the detector division at a centered $q$-position of $q = 0.08$ Å$^{-1}$ using 15 Å neutrons, for one Fourier time, $\tau = 0.155$ ns. The highlighted box in the center of the detector shown in Figure H.1 corresponds to a $q$-position of $q = 0.0770$ Å$^{-1}$. In each detector bin, the $q$-position reported for $I(q,t)/I(q,0)$ is an average of all of the detector boxes within that $q$-range. In the case of Figure H.1, the reported $q$-position for that detector central slice is $q = 0.0788$ Å$^{-1}$; however, the range of $q$-positions based on the detector boxes is $q = 0.0757$ Å$^{-1}$ to $q = 0.0834$ Å$^{-1}$. This range of $q$-positions used to generate the average $I(q,t)/I(q,0)$ for the average $q$-value thus leads to a spatial smearing that is difficult to quantify. Similarly, if the detector is not divided at all for the same data (1 bin), the reported average $q$-position for $I(q,t)/I(q,0)$ is $q = 0.0784$ Å$^{-1}$, which is nearly identical to the $q$-position of the center bin when the detector is divided into five bins. Here, the minimum and maximum $q$-values on the detector correspond to $q = 0.0639$ Å$^{-1}$ to $q = 0.0928$ Å$^{-1}$, which is a significantly wider range than in the five bin case. However, in the one bin case, the calculated uncertainty associated with $I(q,t)/I(q,0)$ and the fit to the relaxation rate and stretch exponent would be lower than in the case of five detector bins because of the higher neutron counts, and despite a very large
spatial smearing. To address some of this spatial smearing, Figure 4.13 in the text compares
the NISFs from different detector bin widths to help validate and help understand some of
the issues with calculating the uncertainty in the data from different bin widths.

Figure H.1: Division of the detector in a typical NSE experiment, shown for the $q$-position
$q = 0.08 \text{ Å}^{-1}$. Here, the detector is divided in to 5 slices; however only 3 slices produce nor-
malized intermediate scattering functions $I(q,t)/I(q,0)$, because the detector is masked for
the entirety of the two end bins. The highlighted box in the center of the detector corresponds
to $q = 0.0770 \text{ Å}^{-1}$.

These clear issues with spatial smearing in NSE are difficult to quantify and are often
not considered or reported. To better understand the associated uncertainty with the fits
to the NISF, Figure H.2 below shows a typical spin echo that is fit within the reduction
software. Figure H.2 shows the echo for the highlighted blue box on the detector in the
middle slice shown in Figure H.1. Each detector box produces an echo like the one shown in
Figure H.2, meaning that changing the bin width does not affect the quality of this fit; it only
affects the number of these fits used to generate the average $I(q,t)/I(q,0)$. Keep in mind
that this detector box corresponds to one $q$-position at only one Fourier time that composes
$I(q,t)/I(q,0)$. Therefore, in the case of the data divided into five spatial bins, 44 echoes
are used to generate one point in the $I(q,t)/I(q,0)$ curve, at the Fourier time $\tau = 0.155
\text{ ns}$ shown here. In the case of only one bin, now 104 echoes are fit to produce that single
point on the $I(q,t)/I(q,0)$ curve, reducing the calculated uncertainty in this data point. This
effect is seen in Figure 4.13a in the text, as the calculated uncertainty around the fits with the smaller bin sizes (largest bin is 5, smallest bin is 9) is substantially higher than in the largest bin size. However, the large range of $q$-positions used in the one bin configuration again serves to increase the uncertainty in terms of the spatial smearing, which is unreported in the uncertainty calculation. Therefore, the reported uncertainty is only that based on the neutron counts, and not the spatial smearing that may result.

![Figure H.2: Example fit to an echo from the detector bin highlighted in Figure H.1, where $q = 0.0770 \, \text{Å}^{-1}$.](image)

Figure H.2: Example fit to an echo from the detector bin highlighted in Figure H.1, where $q = 0.0770 \, \text{Å}^{-1}$. 
Appendix I

FULL ANGULAR DLS SPECTRA FOR WLM SOLUTIONS

In the text, the dynamic light scattering (DLS) experimental spectra were shown for select angles for clarity, ranging from $\theta = 25^\circ$ to $150^\circ$, for the three solutions used in the dynamic experiments: 0.01%, 0.25% and 0.50% wt NaTos. These DLS spectra show the normalized, first-order autocorrelation function, $g_1(t)$, versus the delay time, $t$, for each solution. Here, the complete DLS spectra are shown for the three solutions, where $5^\circ$ angular steps were used from $\theta = 90^\circ$ to $150^\circ$ and $2.5^\circ$ angular steps were used from $\theta = 25^\circ$ to $87.5^\circ$. In some solutions, the data for angles at the ends of the spectra were particularly noisy or had a low correction factor ($C$ from Equation 2.54 where $C < 0.7$; $C = 1$ is ideal); those spectra were not included. The branched network, 0.50% wt NaTos solution had the highest $C$ values across the spectrum ($C \approx 1$ at all $\theta$); this data can be seen in Figure I.1.

Figure I.1: Full DLS angular spectrum of the normalized, first-order correlation function, $g_1(t)$, vs. the delay time, $t$, for the branched network, 0.50% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all angles.

Figure I.1 shows the normalized $g_1(t)$ versus the delay time for the 0.50% wt NaTos solution, on both a linear-log (a) and log-log (b) scaling for clarity. Both the fast and slow
relaxation mode are observed at all angles and are fairly well-separated. While the shape of the fast relaxation mechanism, indicative of the stretch exponent $\beta_1$, appears to be constant across the angular range, the shape of the slow relaxation mode, indicative of $\beta_2$, appears to sharpen with decreasing angle. This phenomenon is discussed further in terms of the data fitting in Section 4.4.7 in the text. A similar plot of the full relaxation spectra for the 0.25% wt NaTos solution can be seen in Figure I.2. The same qualitative trends are observed in terms of $\beta_1$ and $\beta_2$ in this solution. In comparison to the branched network solution shown in Figure I.1, the slow relaxation mechanism in Figure I.2 appears to be slower and stretched over more delay times. This indicates that $\beta_2$ for the 0.25% wt NaTos solution is, on average, lower than for the 0.50% wt NaTos solution.

![Figure I.2: Full DLS spectra $g_1(t)$ vs. $t$ for the high branching, 0.25% wt NaTos solution in linear-log (a) and log-log scaling (b). Two relaxation modes are visible at all $\theta$; however, the slow mode appears to have a more stretched response (lower stretch exponent, $\beta_2$) vs. the branched network solution shown in Figure I.1.](image)

Figure I.3 shows $g_1(t)$ versus $t$ for the low branching, 0.01% wt NaTos solution, on both a linear-log (a) and log-log (b) scaling for clarity. Both the fast and slow relaxation mode are observed at all angles; the modes are the most separated and distinct for this solution versus the two branched solutions. As in the other two solutions, the shape of the slow mode, indicative of $\beta_2$, appears to sharpen with decreasing angle. However, unlike in the other two solutions, the slow mode becomes more pronounced and appears to have a larger amplitude, $A_2$, with decreasing angle in the 0.01% wt NaTos solution. This phenomenon is
discussed further in terms of the data fitting in Section 4.4.7 in the text. In comparison to the two branched solutions shown in Figures I.1 and I.2, the slow mode is significantly more stretched and pronounced in the 0.01% wt NaTos solution, indicating that \( \beta_2 \) is the lowest in this solution.

![Figure I.3: Full DLS spectra](image)

Figure I.3: Full DLS spectra \( g_1(t) \) vs. \( t \) for the low branching, 0.01% wt NaTos solution in a linear-log scaling (a) and log-log scaling (b). Two relaxation modes are visible at all angles; however, the slow relaxation mechanism here appears to have the most pronounced and stretched response (lower stretch exponent, \( \beta_2 \)) vs. the two branched solutions.

In Figure I.4, select angular spectra are shown for the three WLM solutions. The spectra are shown for three angles, \( \theta = 27.5^\circ, 50^\circ, \) and \( 125^\circ \), on a linear-log (a) and log-log (b) scale for clarity. The first decay, or fast relaxation mode, in Figure I.4 corresponds to \( \Gamma_1(q) \), whereas the second decay, or slow relaxation mode, corresponds to \( \Gamma_2(q) \). Both \( \Gamma_1(q) \) and \( \Gamma_2(q) \) increase with increasing angle.

As is seen in Figure I.4, the low branching (0.01% wt NaTos) clearly exhibits the fastest relaxation for the first mode by a significant amount. From Figure I.4, it is also apparent that the slow relaxation mode is the most prominent in the relaxation spectra of the 0.01% wt NaTos solution. While the two relaxation modes are distinct in all three solutions, the two modes are the most well-separated in the low branching solution. Further, the amplitude of this slow mode appears to increase with decreasing angle, unlike in the other two solutions. This indicates that the constants \( A_1 \) and \( A_2 \) from Equation 4.6 are significantly different for this solution, as \( A_1 \) and \( A_2 \) are nearly equal at low angles. The contributions from the slow
Figure I.4: Comparison of DLS spectra across WLM solutions on a linear-log (a) and log-log (b) scale at $\theta = 27.5^\circ$, $50^\circ$, and $125^\circ$. While the 0.01% wt NaTos solution exhibits the fastest primary relaxation mode ($\Gamma_1(q)$), it also exhibits the slowest secondary relaxation mode, $\Gamma_2(q)$. The branched network solution (0.50% wt NaTos) has the fastest of the second, slow relaxation mode.

mode in the two more branched solutions are significantly smaller. Note that the values of $A_1$ and $A_2$ are normalized such that $A_1 + A_2 = 1$. 

555
Appendix J

CONSIDERATIONS SURROUNDING ELASTIC FLOW INSTABILITIES AND ELASTIC TURBULENCE

J.0.1 Calculations from rheometrical geometries

Significant work by Lerouge and Berret [1], Fardin et al. [2], and Perge et al. [3], among many others, analyzes macroscopic instabilities and turbulence in WLM solutions. We consider both inertial and elastic instabilities by calculating the inertial and elastic Taylor numbers for the results presented based on geometry. The inertial Taylor number is defined as $\text{Ta}_{\text{inertial}} = (d/R_i)^{0.5} Re$, where $Re$ is the Reynolds number. The critical Taylor number for inertial instability is $\text{Ta}_{\text{inertial}} = 41$ [4]. In the results presented, inertial Taylor numbers are as follows for the high salt solution: $\text{Ta}_{\text{inertial}} < 0.1$ in the 1-2 shear cell and $\text{Ta}_{\text{inertial}} < 1$ in the ARES G2. The inertial Taylor numbers for the low salt solution are $\text{Ta}_{\text{inertial}} < 0.01$ in the 1-2 shear cell and $\text{Ta}_{\text{inertial}} < 0.1$ in the ARES G2. As all of these Taylor numbers are significantly less than 41, we rule out inertial instabilities.

The critical condition or the elastic Taylor number, $Ta$, for the onset of elastic instability is defined as $Ta = (d/R_i)^{0.5} Wi$ [5]. For the Upper Convected Maxwell Model, $Ta_c \approx 6$, although when fluid rheology is taken into account, shear thinning greatly increases the critical condition [5]. Experimentally, in other shear thinning WLMs ($N = 0.45$) where both inertia and elasticity are important, the onset of inertoelastic instability occurred at an elastic $Ta_c = 22$ [3]. The elastic $Ta_c = 22$ agrees well with the predictions of [5] for $N = 0.45$. At $Ta_c = 33$, [3] saw small deviations from the base flow, where $\delta v = 0.06$. According to the predictions of [5], the critical condition for solutions with a power law index $N = 0.7$ is $Ta_c \approx 500$, and an exponential increase in critical condition is seen with shear thinning index. Experimentally, in shear thinning polymer solutions, they saw an onset of instability 20 to 45% lower than the predicted values, giving a minimum $Ta_c = 220$ when $N = 0.7$. 

556
However, no experimental work has been performed on more highly shear thinning WLM solutions similar to our solutions, where $N = 0.85$.

In the high salt, 0.10% wt NaTos solution, we have calculated the elastic Taylor number in various geometries and instruments (ARES G2, MCR501 and 1-2 shear cell) to verify the interpretation of our results. In the 1-2 shear cell, the three shear rates examined result in elastic Taylor numbers in the range of $1 \leq Ta \leq 3.5$, which are well below model predictions and experimental results \cite{3, 5}. Therefore, in the 1-2 shear cell, we do not expect any elastic turbulence in the high salt solution. At the onset of the shear thickening regime, $12 \leq Ta \leq 20$ depending on the geometry used (see Methods for geometry details). The Taylor number at the end of the shear thickening regime ranges from $25 \leq Ta \leq 45$ based on geometry. According to the predictions and experimental results on shear thinning polymer solutions performed by Larson et al. \cite{5}, it appears that the shear thickening regime is below the critical condition for elastic instability. However, the results from Perge et al. \cite{3} that show only small deviations from the base flow up to $Ta = 33$ gives confidence that the flow will not be significantly affected by turbulence should elastic instabilities arise in this regime.

In the shear banding, 0.01% wt NaTos solution, the stress plateau spans $Wi = 1$ to $Wi \approx 300$. Due to the high Weissenberg numbers across the stress plateau, the elastic Taylor number in the 1-2 shear cell results ranges from $15 \leq Ta \leq 50$. While we cannot discern elastic instabilities during shear banding using our SANS methods, elastic turbulence may be present in the high shear band due to the high Weissenberg numbers. However, $Ta = 15$ at the first shear rate in the 1-2 shear cell, which is less than the transition of $Ta_c = 22$ observed in the work of Perge et al. \cite{3}. While the other two shear rates in the 1-2 shear cell are above $Ta_c = 22$, the trends observed that indicate shear banding are the same at all three shear rates. Furthermore, 1-2 shear cell results for this sample at $Ta = 9$ (data not shown) also show the same alignment trend, giving further evidence that the presence or absence of elastic instabilities does not affect the interpretation of the 1-2 plane SANS.

We also consider endwall and Ekman layer effects due to the short aspect ratio of the 1-2 shear cell ($\Gamma = 5$). For a Newtonian fluid, the RMS error of the Couette velocity profile $u(r,z)$ for $\Gamma=5$ is $\approx 0.01$ in comparison to the infinite cylinder profile \cite{6}. Larson
et al. [5] among others found that shear thinning in viscoelastic fluids generally increases the critical dimensionless groups for the onset of instabilities or deviations from the expected flow, giving evidence that this RMS value is on the correct order of magnitude (and thus fairly insignificant). While the shear cell is a short cylinder, the stationary end walls minimize the size and strength of the Ekman vortices as compared with moving endwalls [7,8]. Paired with the low shear rates in used in the 1-2 plane studies and resulting inertial Taylor numbers, the resulting Ekman layer should not interact with the primary flow and the axial and radial components of the velocity gradient should be effectively zero [7,8].

J.0.2 Shear thickening of the highly branched solution

To address the possibility of elastic turbulence in the shear thickening regime of the 0.10% wt NaTos solution, long time startup measurements were performed to determine the fluctuations of the stress response in time. For a shear banding CTAB solution in the semi-dilute regime (10-fold more concentrated than our solutions), Fardin et al. [2] observed stress fluctuations on the order of 3% in the laminar, highly aligned region exiting the stress plateau, where the aligned structures are expected to fill the entire gap. These fluctuations were stable in the amplitude over the course of one hour. In the “transition” region (stress upturn, shear thickening may occur), the stress never appears stable in time. The fluctuations were as high as 30%, and the most significant deviations began in less than 20 minutes (unstable in amplitude). Past the “transition” region, the fluctuations settled (stable in amplitude) but were larger, on the order of 15%. Using these regimes as a guide, the stability of the 0.10% wt NaTos solution at and around the shear thickening transition was assessed using startup measurements in both the ARES G2 (strain controlled) and the NIST MCR 501 rheometer (stress controlled operating in strain controlled mode), the results of which are shown in Table J.1. Measurements in the ARES G2 were performed for 30 minutes, and measurements in the MCR501 were performed for 20 minutes during SANS measurements. The fluctuations around the mean value of the stress at a variety of shear rates (before, at and after the shear thickening transition) are reported for both instruments in Table J.1.

These long-time startup tests show that the fluctuations are stable in amplitude over
Table J.1: Stress fluctuations in the shear thickening regime for the branched 0.10% wt NaTos solution

<table>
<thead>
<tr>
<th>$\dot{\gamma}$ (s$^{-1}$)</th>
<th>ARES G2 $\Delta \sigma$ (%)</th>
<th>MCR 501 $\Delta \sigma$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.19</td>
<td>2.50</td>
</tr>
<tr>
<td>185</td>
<td>3.30</td>
<td>3.07</td>
</tr>
<tr>
<td>225</td>
<td>3.01</td>
<td>3.54</td>
</tr>
<tr>
<td>275</td>
<td>2.97</td>
<td>2.64</td>
</tr>
<tr>
<td>325</td>
<td>2.90</td>
<td>2.84</td>
</tr>
<tr>
<td>375</td>
<td>3.49</td>
<td>2.96</td>
</tr>
<tr>
<td>420</td>
<td>3.43</td>
<td>2.82</td>
</tr>
<tr>
<td>450</td>
<td>N/A</td>
<td>2.98</td>
</tr>
<tr>
<td>500</td>
<td>3.48</td>
<td>2.67</td>
</tr>
<tr>
<td>575</td>
<td>3.54</td>
<td>2.36</td>
</tr>
<tr>
<td>650</td>
<td>N/A</td>
<td>2.23</td>
</tr>
</tbody>
</table>

the course of the test ($t>10s$) and are roughly the same between the two instruments. The fluctuations in the recorded stress are similar to those observed in the laminar flow regime (maximum 3.54% for each instrument) from [2], and are also independent of shear rate. As expected for a WLM system undergoing a structural transition during shear thickening, the fluctuations around the stress are detectable, but not large. These results further support that the shear thickening likely corresponds to a structural transition that is not significantly affected by elastic turbulence. Interestingly, the stress of the 0.10% wt NaTos solution is unstable over long times beginning at $\dot{\gamma} \geq 2000$ s$^{-1}$. It is likely that elastic turbulence begins to significantly affect the flow at these higher shear rates.
References


Appendix K

ORTHOGONAL SUPERPOSITION RHEOLOGY (OSP)

Orthogonal superposition (OSP) measurements were performed on the WLMs with different levels of branching to determine signatures of branching via the nonlinear viscoelasticity. In the OSP measurements, the surfactant concentration was 4% wt and the solutions were prepared in water instead of D₂O; all samples are referred to by the weight fraction of added salt. While the surfactant concentration is higher here than used for the samples in the text, we see a similar decrease in the zero-shear viscosity and relaxation time with salt addition, indicating a similar formation of branched structures with added salt. As OSP is a relatively new rheological method, our goal was to develop new metrics to understand the OSP response, that would in turn help distinguish features of branching. In the OSP measurements discussed below, the dynamic moduli, $G'$ and $G''$, were measured in the orthogonal direction while the WLMs were sheared. This type of measurement allows us to examine how the linear viscoelastic response of the WLMs changes once shear is applied and the microstructure of the solution changes. It should be noted that OSP spectra cannot be accurately recorded on shear banding fluids.

Figure K.1 below shows an example of the changes in the relaxation spectra that occur under shear, for the 0.10% wt NaTos solution (a) and the 0.125% wt NaTos solution (b). The spectra shown in Figure K.1 are representative of the qualitative trends observed for all WLM solutions measured. Several key changes to the spectra under shear are observed. In particular, the crossover frequency, $\omega_c$, increases with increasing shear rate, indicating that the resulting relaxation time ($\tau_R = 1/\omega_c$) decreases with shear rate. Additionally, the crossover modulus, $G_c$, and the plateau modulus, $G_0^N$, also decrease with increasing shear rate. These decreases are indicative of a breakdown of entanglements and network-like structures, and at high shear rates, a shortening of the micelles. Accordingly, a loss of entanglements and
micellar breakage leads to the faster relaxation times that are observed based on the increases in $\omega_c$. It should be noted that shear banding was observed when $C_s = 0.01$ and 0.05% wt NaTos, so accurate measurements could not be obtained.

![Figure K.1: Dynamic moduli, $G'$ and $G''$, under shear measured by OSP for the (a) 0.10% wt, and (b) 0.125% wt NaTos solutions. The crossover frequency increases with shear rate, indicating a decrease in $\tau_R$. The plateau modulus, $G_0^N$, also decreases with shear.](image)

Based on the results presented in Figure K.1, new metrics were developed to evaluate the nonlinear viscoelasticity of the WLMs and to understand the branching effect. The four metrics that appear to be affected by shear include $G_c$, $G_0^N$, $\omega_c$, and $\tau_R$. As each WLM solution has different starting values of these quantities, the changes occurring during shear had to be normalized based on the original values from the LVE spectrum. Accordingly, the following normalizations were used for analyzing the results. In terms of the plateau and crossover moduli, the orthogonal moduli can be normalized by the original LVE values. The normalized crossover modulus and plateau modulus are given by $G_{c,\perp}/G_{c,\parallel}$ and $G_{0,N,\perp}/G_{0,N,\parallel}$, where the $\parallel$ subscript indicates the LVE modulus. The crossover frequency and relaxation time are also normalized by the LVE values, as $\omega_{c,\perp}/\omega_{c,\parallel}$ and $\tau_{R,\perp}/\tau_{R,\parallel}$.

Using these metrics, the analysis of the orthogonal dynamic moduli can be seen in Figure K.2 based on the changes to the crossover frequency and crossover modulus. As seen in Figure K.2, a faster breakdown of branched versus linear structures is observed, as the normalized crossover modulus decreases faster at equivalent Wi with increasing branching.
Significant deviations from the LVE values appear to occur at earlier $Wi$ at higher branching levels, which is consistent with the Laun’s rule calculations in Section 5.11 in the text. A larger decrease in the plateau modulus, $G_0^N$, is also seen with branching, although there are difficulties in determining this quantity accurately, which will be discussed below. We also see a slower increase in $\omega_c$ with branching. A slower increase in $\omega_c$ leads to a slower decrease in $\tau_R$ with branching. This finding supports the conclusions drawn in Chapter 6, where branching appears to prevent breakage leading to shear banding. On first inspection, it may appear that effects of branching on $G_c$ and $\tau_R$ are contradictory. The prevention of breakage suggested by the slower decrease in $\tau_R$ seems to contradict the faster breakdown of branched structures with shear, from the decrease in $G_c$. However, branching leads to an increase in $G_c$ and $G_0^N$ in the LVE rheology due to the formation of network-like structures. The faster breakdown of these branched structures simply implies that more interconnections and branches can be broken when the branching level is higher.

![Figure K.2: Normalized crossover frequency, $\omega_c$, and crossover modulus, $G_c$, during shear, measured via OSP. A faster breakdown of network-like structures, indicated by $G_c$, occurs with branching. Branching also appears to mitigate breakage, causing a slower decrease in $\tau_R$ with shear.](image)

In Figure K.2, the change in the crossover modulus is examined to determine the breakdown of network-like structures, as opposed to the plateau modulus. Based on the
scalings presented in Chapter 1, $G_c$ and $G_N^0$ should scale in the same manner for Maxwell fluids, so analysis of either quantity should yield the same results. If the plateau modulus was used, however, the analysis would become more complicated. As the relaxation time under shear changes based on branching level, the frequency location of the plateau modulus should shift to higher frequencies. As the accessible $Wi$ range is small at high frequencies, it is difficult to determine the plateau modulus accurately. If $G_N^0$ is compared at the same frequency despite the changes in $\omega_c$, the results could be convoluted by the different scaling of $\omega_c$ with branching level for equivalent $Wi$. As $\omega_c$ and $G_c$ can always be easily determined, the analysis of these quantities is more straightforward, making these two metrics a better choice from which to draw conclusions.

Finally, we establish an orthogonal Weissenberg number, $Wi_\perp$, which is given by $Wi_\perp = \tau_{R,\perp} \dot{\gamma}$. As the relaxation time decreases with shear, the orthogonal Weissenberg number is always lower than the standard $Wi$ determined based on LVE rheology. This orthogonal Weissenberg number can help improve the accuracy of calculations of the onset of elastic and other instabilities. These calculations rely on the material relaxation time at rest to determine the instability onset. However, once significant breakage and micellar alignment occurs, the relaxation time of the material greatly decreases, which we verify with the OSP measurements shown in Figure K.1. Defining $Wi_\perp$ gives a new and more accurate basis by which to calculate these numbers in the future. This change in the WLM relaxation time with shear also helps to explain why the onset of instabilities are seen at significantly higher $Wi$ than expected based on theory and current calculations.
Appendix L

COMPARISON OF FLOW CURVES FROM 1-3 PLANE SANS AND RHEOLOGY

Simultaneous rheology was recorded during some 1-3 plane rheo-SANS experiments; early rheo-SANS measurements did not have the capability to record the rheology concurrently due to the experimental set-up. These results shown below are compared to the original flow curves reported in the text, which were measured on the ARES G2 instrument. All rheo-SANS rheology measurements were performed on an Anton-Paar MCR instrument. In addition to comparing the results across instruments, these results also compare different sample preparations. In the two most commonly used rheo-SANS concentric cylinder Couette geometries (see Chapter 2, Table 2.1 for a list of configurations), the gap-to-radius ratios are $\epsilon = 0.071$ and $\epsilon = 0.074$ versus $\epsilon = 0.084$ for the ARES G2 geometry. As these ratios are fairly similar, we expect good agreement between the rheo-SANS and rheology measurements.

Figure L.1 shows the 1-3 plane results vs. the ARES G2 results for the 0.15% wt NaTos solution. Two 1-3 plane experiments are shown from two different sample preparations. In Figure L.1, excellent agreement is obtained between the 1-3 plane measurements (purple, ◦) and the ARES G2 measurements for the same sample preparation, despite different curvatures. The startup measurements in both instruments give the same results as the steady shear flow curve. The 1-3 plane measurements are performed on an Anton-Paar MCR 502, so the difference in instrument is also negligible. Another sample preparation used in 1-3 plane experiments is shown in Figure L.1 by the × symbol. Good agreement between the sample preparations is observed. The shear thickening at high rates is preserved in the rheo-SANS experiments, and occurs in both sample preparations, again indicating the reproducibility of this phenomenon. This phenomenon is also reproducible in the 0.10% wt NaTos solution, which can be seen below in Figure L.2. The power law index, $N$, calculated
from both experiments (for the same sample preparation) is identical within two significant digits. While having simultaneous rheology is always desirable, the repeatability of the rheological results here gives added confidence to the interpretation of the 1-3 plane data when simultaneous rheology could not be recorded.

Figure L.1: Flow curves for the 0.15% wt NaTos WLM solution for two sample preparations and instruments. Flow sweep and startup measurements were taken on the ARES G2; 1-3 SANS flow curves were taken on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparation and instrument, including the shear thickening. $N$ is identical within two significant digits for the ARES G2 and 1-3 plane (purple, ◦) measurements.

Figure L.2 shows the 1-3 plane results for the highly branched, 0.10% wt NaTos solution for two separate experiments on different sample preparations. The SANS instrument also varies between the trials. The ARES G2 results for the 0.10% wt NaTos solution on two different sample preparations are shown for in Figure L.2 comparison. As seen in Figure L.2, good agreement is obtained between the two 1-3 plane experiments and the two ARES G2 measurements, despite different curvatures and different sample preparations. The curvatures for the two 1-3 plane experiments are nearly equivalent, where $\varepsilon \approx 0.07$ in each case. The shear thickening at high rates is also observed in both of the rheo-SANS experiments, as was the case in the 0.15% wt NaTos solution. The reproducibility of these results once again
gives confidence to any data from experiments recorded when rheological measurements could not be taken during SANS.

Figure L.2: Comparison of flow curves for the 0.10% wt NaTos WLM solution for two sample preparations for SANS, and two additional sample preparations for rheometry on the ARES G2. The two 1-3 SANS flow curves were taken during experiments on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparation and instrument, including in the shear thickening region. All four trials exhibit the shear thickening behavior.

The flow curve was also verified during SANS for the 0.01% wt NaTos solution. As this solution exhibits pronounced shear banding and a non-monotonic constitutive equation, even small changes to the instrument and curvature can affect the shear banding behavior [1, 2]. The effect of the curvature on the shear banding behavior is discussed further in Appendix M. In Figure L.3, the resulting flow curves from four rheo-SANS experiments are shown, alongside the original flow curve taken on the ARES G2, which is reported in Chapter 5, Section 5.5.1. Here, $\varepsilon$ is the gap-to-radius ratio. Good agreement is seen between the four SANS trials, and the trial on the ARES G2. In the trials where $\varepsilon = 0.074$ and $\varepsilon = 0.111$, experiments were performed on a sample from the same preparation batch, during the same SANS experiment, to test the effect of the curvature, $\varepsilon$, on shear banding in this solution. By using the same sample preparation and instrument configuration, the curvature effects can be
elucidated. As seen by comparing the results between $\varepsilon = 0.074$ and $\varepsilon = 0.111$, the slope of the stress plateau slightly increases when the curvature increases. The steady shear stress is nearly identical, but slightly higher when $\varepsilon = 0.111$, at $\dot{\gamma} = 2 \text{ s}^{-1}$. However, the difference in the measured shear stress grows larger with shear rate between the two configurations, resulting in an increasing power law index, $N$, with increasing $\varepsilon$. These results also suggest that the onset of region III may occur sooner in geometries where the gap-to-radius ratio is larger, which is discussed further in Appendix M.

![Figure L.3](image)

Figure L.3: Flow curves for the 0.01% wt NaTos WLM solution for multiple sample preparations for SANS; the ARES G2 curve reported in Chapter 5, Section 5.5.1 is shown for reference. All 1-3 SANS flow curves were taken on the Anton-Paar MCR 502. The curves show excellent agreement between sample preparations, instruments, and curvatures. The trials where $\varepsilon = 0.074$ and $\varepsilon = 0.111$ were performed on a sample from the same batch in the same experiment to examine the effect of $\varepsilon$. The power law index, $N$, increases with increasing $\varepsilon$.

The increase in $N$ with $\varepsilon$ is also observed in the other 1-3 plane trials shown in Figure L.3. The stress measured from the 1-3 plane trials where $\varepsilon$ exhibits the plateau that is closest to $N = 0$. The largest plateau slope is observed at $\varepsilon = 0.111$. An increase in $N$ is expected when $\varepsilon$ is increased because of the larger stress gradients that occur across the gap. These results are also not surprising in the context of other works on shear banding [3,4]. Increasing the gap-to-radius ratio is known to lead to less stable shear banding in solution [1–4], and the larger increase in the stress at high shear rates is indicative of elastic turbulence in region
III (see Chapter 6, Section 6.5.1). Nevertheless, the results for all rheo-SANS experiments share the same qualitative features and yield similar results in terms of the alignment factor. The effect of the curvature on the alignment factor is discussed further in Appendix M.
References


Appendix M

ADDITIONAL STARTUP TRIALS

M.1 0.01% wt NaTos

M.1.1 Startup rheology

Long-time, startup rheological measurements were performed on the low branching solution. The goal of these measurements was to understand the startup behavior at low shear rates, before, at, and beyond the onset of region II. Another goal of these measurements was to determine if the metastable plateau region identified at the onset of region II in the mildly branched solution was also observed in the low branching solution. In the solution used for these startup measurements, $\omega_c = 0.18 \text{ rad} \cdot \text{s}^{-1}$, which is equivalent to the sample used in the Chapter 5, Section 5.5 results. This crossover frequency is slightly higher than the crossover frequency of the sample used for the startup measurements, $\omega_c = 0.12 \text{ rad} \cdot \text{s}^{-1}$.

The startup measurements for shear rates before and at the onset of region II can be seen in Figure M.1. In Figure M.1a, shear rates are shown corresponding to Weissenberg numbers of $Wi = 0.44$ to $Wi = 0.69$. Although these shear rates are below the predicted values for the onset of shear banding by the toy model of Cates and co-workers, $Wi_1 = 2.6$ [1–3] (see Chapter 5, Equation 5.3), extremely long transience and metastable states appear to occur at these Weissenberg numbers lower than unity. It should be noted that the toy model critical predicted stress for the onset of shear banding for this solution does not occur until region III, suggesting that this model is inappropriate for this particular, highly charged solution. Interestingly, the maximum stress observed during startup actually decreases when the shear rate is increased between $\dot{\gamma} = 0.1$ and $0.125 \text{ s}^{-1}$. Additional shear rates before and at the onset of region II can be seen in Figure M.1b. Here, the Weissenberg numbers range between $Wi = 0.69$ to $Wi = 1.11$. Once again, the maximum stress during startup...
decreases when the shear rate is increased between $\dot{\gamma} = 0.125$ and $0.158$ s$^{-1}$. At shear rates in excess of $\dot{\gamma} = 0.158$ s$^{-1}$, the maximum observed stress increases with shear rate. In Figure M.1b, long transients are also observed in the stress response, but the shape of the stress response changes. When $\dot{\gamma} \geq 0.158$ s$^{-1}$, stress undershoots and metastable-like regions are observed in the stress responses, similar to those observed by Hu et al. [4]. While the stress response appears nearly constant after the undershoot at these shear rates, the stress slowly and gradually decreases in time. This metastable plateau region is similar to that observed in the mildly branched solution. No stress undershoots are observed at the lower shear rates. This observed change in shape of the stress response between $\dot{\gamma} = 0.125$ and $0.158$ s$^{-1}$ may be indicative of a transition between transient shear banding upon shear startup that is not indicative of the steady state, to steady state shear banding.

Figure M.1: Startup stress response for the 0.01% wt NaTos solution at low shear rates before or at the onset of region II. In this solution, $\omega_c = 0.18$ rad·s$^{-1}$. (a) Despite $Wi < 1$, long transience in the stress response is observed. The transient is more pronounced with increasing shear rate. (b) Long transients still occur at each rate, where $Wi$ ranges from 0.69 to 1.11. Interestingly, the magnitude of the maximum stress decreases between $\dot{\gamma} = 0.1$ and $0.125$ s$^{-1}$ in (a), and between $\dot{\gamma} = 0.125$ and $0.158$ s$^{-1}$ in (b).

The startup stress response for shear rates at the onset of region II, and just beyond the onset of region II, can be seen in Figure M.2. In all cases, the maximum stress observed during startup increases with shear rate. Figure M.2a shows shear rates corresponding to
Weissenberg numbers of $Wi = 1.11$ to $Wi = 2.22$. In the mildly branched solution, the shear banding onset was around $Wi = 2.6$. Once again, long transience and metastable states appear to occur at these Weissenberg numbers. The long, flat metastable plateau region evolves to a shoulder-like feature with increasing shear rate. For all four shear rates shown in Figure M.2a, the transient appears to last longer than the one hour measurement time. The same nonlinear features discussed in Chapter 6 are seen here, including stress overshoots, undershoots, secondary overshoots, and shoulders. In Figure M.2b, the Weissenberg numbers range between $Wi = 2.22$ to $Wi = 4.44$. At all shear rates, a long and gradual decrease in the stress response is seen in time, which corresponds to a shoulder-like feature. Once again, the transience of the stress response appears to be longer than the measurement time.

Figure M.2: Startup stress response at low shear rates at and beyond the onset of region II. (a) $1.11 \leq Wi \leq 2.22$. The metastable plateau region evolves to a shoulder-like feature with increasing rate. (b) $2.22 \leq Wi \leq 4.44$. Long transients still occur at each rate. In both (a) and (b), the stress transient appears to be longer than the measurement time, which is one hour for most shear rates.

Finally, the stress responses shown in Figure M.3 are at shear rates well within region II. In Figure M.3a, the startup response for Weissenberg numbers between $Wi = 4.44$ to $Wi = 8.77$ can be seen, where a long transient and shoulder-like region is observed for each rate. As was the case in the mildly branched solution, at $\dot{\gamma} = 1.58 \text{ s}^{-1}$, a sharp drop in the magnitude of the stress response is seen after long times, indicating steady state. In Figure
M.3b, the shoulder-like region of the response gets smaller with increasing shear rate. The shear rates in Figure M.3b correspond to $Wi = 8.77$ to $Wi = 17.56$. At the highest shear rate ($\dot{\gamma} = 3.16 \text{ s}^{-1}$), steady state oscillations are observed in the stress response. These oscillations are similar to those discussed in Chapter 6 at shear rates within the same region. These results give more insight to the startup behavior and long transience near the onset of region II, and confirm similar startup features between the low and mildly branched solutions.

Figure M.3: Startup stress response at low shear beyond the onset of region II. (a) $4.44 \leq Wi \leq 8.77$. The shoulder-like feature evolves more quickly with increasing rate. When $\dot{\gamma} = 1.58 \text{ s}^{-1}$, a sharp drop in $\sigma$ is seen after long times, indicating steady state. (b) $8.77 \leq Wi \leq 17.56$. Shoulder-like features still occur at each rate. At $\dot{\gamma} = 3.16 \text{ s}^{-1}$, oscillations in the steady state response are observed, similar to those reported in Chapter 6.

M.1.2 1-3 plane SANS: additional shear rates

For clarity, the results from all shear rates were not shown in Chapter 6, Section 6.5.2. During the experiments from which the data is presented, three additional shear rates were performed: $\dot{\gamma} = 60, 225$, and $420 \text{ s}^{-1}$. As was the case for the results shown in Section 6.5.2, the measurements for these three shear rates were performed in triplicate. The resulting 1-3 plane alignment factor as a function of time after shear startup can be seen in Figure M.4 for these shear rates. As seen in Figure M.4, the 1-3 plane $A_f$ exhibits a long transient when $\dot{\gamma} = 60 \text{ s}^{-1}$, indicative of shear banding. The shape of the transient is quite similar
to when $\dot{\gamma} = 45 \text{ s}^{-1}$, which is shown for reference, suggesting that a similar mechanism of shear banding is present. At $\dot{\gamma} = 225$ and $420 \text{ s}^{-1}$, little to no transient is observed in the $A_f$ response. The two responses are nearly identical in shape and magnitude, indicating that the solution has reached its maximally aligned state at these shear rates; these results are in good agreement with those presented in Chapter 5, Section 5.5.2. As was the case for the high shear rates shown in Chapter 6, Section 6.5.2, only minor fluctuations in the steady state $A_f$ are observed when the material is maximally aligned.

Figure M.4: 1-3 plane $A_f$ as a function of time after shear startup on a log-log (a) and log-linear (b) scale. At $\dot{\gamma} = 60 \text{ s}^{-1}$, a long transient in the $A_f$ response is consistent with shear banding and is similar to when $\dot{\gamma} = 45 \text{ s}^{-1}$. When $\dot{\gamma} \geq 225 \text{ s}^{-1}$, the fast structural transient indicates little to no shear banding.

M.1.3 1-3 plane SANS: effect of the curvature, $\varepsilon$

As discussed in Chapter 6 and in Appendix L, shear banding phenomena are greatly impacted by the curvature of the concentric cylinder Couette geometry, specifically, the gap-to-radius ratio $\varepsilon$ [5, 6]. While SANS measurements have been performed using different geometries (Chapter 2, Section 2.2; Appendix L), it is difficult to directly elucidate the impact of $\varepsilon$ when different sample preparations and SANS configurations are used (see Chapter 3, Section 3.4). Accordingly, in our final 1-3 plane experiment, studies on the effect of $\varepsilon$ were performed. In these studies, a large sample of the 0.01% wt NaTos solution was prepared.
such that a new sample from the same preparation could be used in each configuration. By using the same sample preparation, geometry differences can be elucidated, while aging or shear effects are eliminated by using a fresh sample. For these studies, two geometries were used; the SANS configuration was held constant. In both geometries, a 30 mm diameter cup was used. For the first geometry, a 28 mm diameter bob was used, resulting in a gap-to-radius ratio of $\varepsilon = 0.071$; these results are reported in Chapter 6, Section 6.5.2. In the second geometry, the bob diameter was 27 mm, resulting in a 1.5 mm gap vs. the 1.0 mm gap in the first geometry, and $\varepsilon = 0.111$. Due to time limitations, the measurements in the second geometry were performed only up to $\dot{\gamma} = 60 \text{ s}^{-1}$; these results can be seen below in Figures M.5 and M.6. All measurements were performed in triplicate, except for those in the second geometry at $\dot{\gamma} = 4.2, 8.5$ and $60 \text{ s}^{-1}$, which were performed in duplicate.

Figure M.5: 1-3 plane $A_f$ for the 0.01% wt NaTos solution in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup near the onset of region II, on a log-log (a) and linear-linear (b) scale. Long, pronounced transients in $A_f$ are observed at all shear rates.

Figure M.5 shows the 1-3 plane alignment factor as a function of time after shear startup in the second geometry, where $\varepsilon = 0.111$. The shear rates examined in Figure M.5 are near the onset of region II. In Figure M.5, a pronounced, slow transient is observed in the $A_f$ response at all shear rates. As was the case for the results in the first geometry, shown in Chapter 6, Section 6.5.2, the time duration of the $A_f$ transient does not significantly change with increasing shear rate. At all shear rates, this transient lasts for approximately
200 seconds before the steady state is reached. Small oscillations in the steady state $A_f$ response are also observed. Similar behavior is observed at higher rates well within region II, where the 1-3 $A_f$ response can be seen in Figure M.6. Once again, the $A_f$ transient is around 200 to 300 seconds at all shear rates. Interestingly, large oscillations in the steady state $A_f$ are observed when $\dot{\gamma} \geq 26.4$ s$^{-1}$, which are similar to the 1-2 plane results discussed in Chapter 6, Section 6.5.3. These oscillations are reproducible between trials, which will be discussed further in Section M.1.4 below. At all shear rates shown in Figure M.6, the maximum alignment upon startup is similar, unlike at lower rates (Figure M.5).

![Figure M.6: 1-3 plane $A_f$ in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup, at shear rates well within region II, on a log-log (a) and linear-linear (b) scale. Long transients in $A_f$ are observed at all shear rates. Pronounced steady state oscillations in $A_f$ are observed when $\dot{\gamma} \geq 26.4$ s$^{-1}$.](image)

In order to elucidate the effects of changing the gap-to-radius ratio, the alignment factor results were compared between geometries at equivalent shear rates. A comparison of the 1-3 $A_f$ at shear rates near the onset of region II can be seen in Figure M.7 below, where the results are shown on a linear-linear scale in a-d, and on a log-log scale in e-h. In Figure M.7, the $A_f$ results between the two geometries are similar at all shear rates. Subtle differences in the first 100 seconds of startup are observed at the lowest shear rates, $\dot{\gamma} = 2.5$ and 4.2 s$^{-1}$ (Figure M.7a,e and b,f respectively). However, at $\dot{\gamma} = 4.2$ s$^{-1}$, only two trials were performed in the second geometry, so these differences may be a result of experimental noise. The results shown for $\dot{\gamma} = 2.5$ s$^{-1}$ between geometries are more likely to reflect true
differences in the $A_f$ response, as three trials were performed in each case, and differences in the WLM response are expected near the onset of region II when the geometry and curvature are changed [6]. The results are nearly identical between geometries at $\dot{\gamma} = 8.5$ and 10.5 s$^{-1}$.

Figure M.7: Comparison of the startup 1-3 plane $A_f$ between geometries at shear rates near the onset of region II, on a linear-linear (a-d) and log-log (e-h) scale. The shear rate is equivalent in the vertical direction and increases from left to right. The small gap geometry ($\varepsilon = 0.071$) is always shown in front. Results are similar between geometries at all rates.

Differences in the $A_f$ response between the geometries are more pronounced when the shear rate is raised. The 1-3 $A_f$ at shear rates well within region II are shown in Figure M.7 below for both geometries. In Figure M.8, the differences in the $A_f$ response between geometries become more pronounced with increasing shear rate. Only subtle differences are observed in the first 100 seconds after startup at the lowest shear rate, $\dot{\gamma} = 15$ s$^{-1}$ (Figure M.8a,e). When $\dot{\gamma} = 26.4$ s$^{-1}$, the 1-3 plane $A_f$ exhibits a more gradual, prolonged response in the small gap geometry ($\varepsilon = 0.071$). In the large gap geometry ($\varepsilon = 0.111$), the decrease in $A_f$ over time occurs more rapidly. The $A_f$ response when $\dot{\gamma} \geq 26.4$ s$^{-1}$ exhibits an undershoot in the large gap geometry that is reminiscent of the stress undershoot observed in the rheology measurements (Chapter 6, Section 6.5.1). Despite differences in the $A_f$ startup response, the steady state $A_f$ is identical between geometries when $\dot{\gamma} = 26.4$ s$^{-1}$.

Interestingly, when $\dot{\gamma} \geq 45$ s$^{-1}$, the resulting steady state 1-3 plane $A_f$ is lower in the
large gap geometry ($\varepsilon = 0.111$) than in the small gap geometry ($\varepsilon = 0.071$). A comparison of the steady state $A_f$ between geometries can be seen in Figure M.9, where the error bars represent the standard deviation of the $A_f$ fluctuations. The lower observed alignment with the larger geometry gap is in good agreement with the results from the 0.15% wt NaTos solution presented in Chapter 5, Section 5.9.2. As was the case when $\dot{\gamma} = 26.4 \text{ s}^{-1}$, the 1-3 plane $A_f$ exhibits a more gradual decrease in the small gap geometry when $\dot{\gamma} \geq 45 \text{ s}^{-1}$. At these shear rates, the transient in $A_f$ is significantly longer in the small gap geometry; a sharp and rapid decrease in $A_f$ over time occurs in the large gap geometry. Despite the steady state oscillations in $A_f$ when $\dot{\gamma} \geq 45 \text{ s}^{-1}$ that lead to a large uncertainty, the alignment in the small gap geometry is statistically larger at these two shear rates (Figure M.9). The steady state oscillations are reproducible, which will be shown in Section M.1.4 below. This result is not surprising for two reasons. First, the stress gradient is larger across the gap in the large gap geometry, which should lead to a lower overall alignment. Additionally, increasing the gap-to-radius ratio is known to lead to less stable shear banding in solution [5–8]. Less stable shear banding may be accompanied by interface fluctuations and elastic turbulence, which
may decrease the overall ordering of the micelles; the fluctuations in $A_f$ for the larger gap geometry suggest the shear banding is less stable. As discussed in Appendix L, the stress increases in this region of the flow curve for the large gap geometry, suggesting that the onset of region III occurs at lower shear rates. This hypothesis is supported by the pronounced $A_f$ fluctuations in this geometry, as fluctuations can be a signature of region III behavior.

Figure M.9: Comparison of the steady state 1-3 plane $A_f$ between geometries. Error bars are the standard deviation of the steady state $A_f$, which are larger when $\epsilon = 0.111$ due to fluctuations at steady state. When $\dot{\gamma} \geq 26.4 \text{ s}^{-1}$, the steady state $A_f$ is larger for $\epsilon = 0.071$.

Finally, these results suggest that the $A_f$ fluctuations become more pronounced as the shear banding becomes less stable. In Chapter 6, Section 6.5.3, the 1-2 plane results exhibited steady state fluctuations in $A_f$ that were significantly less pronounced in the 1-3 plane measurements. This result was surprising, as the 1-2 shear cell has a smaller gap-to-radius ratio than the small gap geometry ($\epsilon = 0.039$ vs. $\epsilon = 0.071$). The smaller fluctuations in the small gap 1-3 plane measurements may be a result of dampening that occurs from taking a gap-averaged measurement. Additionally, the 1-2 shear cell is a short gap Couette, where the aspect ratio is only $\Gamma = 5$. The short nature of the Couette may lead to unstable behavior, as the infinite cylinder assumption behind unidirectional flow may be violated. Further, both ends of the 1-2 shear cell are sealed, unlike in a traditional geometry where one
surface is exposed to the air. The difference in the endwall behavior and Ekman layer effects may lead to the development of different instabilities (see Appendix J).

**M.1.4 1-3 plane SANS: individual trials**

In Chapter 6, Section 6.5.2, the 1-3 plane alignment factor was given as the sum of three individual trials. While rheology measurements suggest that these trials are reproducible (Section 6.5.1), select individual SANS trials were analyzed to confirm the reproducibility of the response. Individual trials were also analyzed for the second, larger gap geometry discussed above. The largest fluctuations are expected at higher shear rates within region II, or within region III (Section 6.5.1). Accordingly, the three trials for the two highest shear rates in the banding regime were analyzed for each geometry, where \( \dot{\gamma} = 26.4 \) and 45 s\(^{-1}\). The 1-3 plane \( A_f \) results for these two shear rates can be seen in Figure M.10 for the small gap geometry, where the results were presented in Section 6.5.2. In Figure M.10a, the 1-3 plane \( A_f \) at \( \dot{\gamma} = 45 \) s\(^{-1}\) is nearly identical between the three trials, demonstrating the reproducibility of the experiment. The local minima and maxima are clearly repeatable between individual trials. Due to poor statistics that result from analyzing individual trials, some noise is observed in the responses; the combined \( A_f \) presented in Chapter 6 is shown via the transparent points, which reduces this noise.

![Figure M.10: 1-3 plane \( A_f \) over repeated trials from the results shown in Chapter 6, Section 6.5.2 (\( \varepsilon = 0.071 \)) as a function of time after shear startup. The \( A_f \) response is reproducible between trials.](image-url)
A similar reproducibility between trials is seen at $\dot{\gamma} = 26.4 \text{ s}^{-1}$ (Figure M.10b). Once again, $A_f$ is similar between the three trials, especially in the 100 seconds immediately following shear startup. At long times ($t > 750 \text{ s}$), the magnitude of the fluctuations in $A_f$ is similar between the trials; however, these fluctuations are not perfectly in phase as they are at shorter times. As such, the fluctuations for the combined trial (transparent black points) are slightly dampened at these long times, but still visible. Small shifts in the location of the fluctuations in the stress response were also observed in the rheology (Chapter 6, Section 6.5.1), so these results are expected.

As aforementioned, the analysis of individual trials was also performed in the larger gap geometry, where $\varepsilon = 0.111$. The 1-3 plane $A_f$ for these measurements is shown in Figure M.11a for $\dot{\gamma} = 45 \text{ s}^{-1}$, and in Figure M.11b for $\dot{\gamma} = 26.4 \text{ s}^{-1}$. As seen in Figure M.11a, the alignment factor response to shear startup is still highly reproducible in the larger gap geometry. However, as was the case in the small gap geometry (Figure M.10b), the magnitude of the fluctuations is always similar in magnitude, but the phase is not always perfectly aligned. When the fluctuations are not in phase, the magnitude of the $A_f$ fluctuations is slightly dampened ($500 \leq t \leq 750 \text{ s}$). However, throughout the majority of the experiment, the responses are in phase and the oscillations in $A_f$ are always highly reproducible. Therefore, any oscillations in the average startup $A_f$ response reported in Chapter 6 may be dampened, but are true features of the response. The $A_f$ response between trials at $\dot{\gamma} = 26.4 \text{ s}^{-1}$ is nearly identical, where the fluctuations are in phase throughout the experiment duration. As higher shear rates lead to more chaotic responses, more reproducible results are expected as the shear rate is lowered. As both geometries show excellent reproducibility of the response between trials, and fewer fluctuations are expected as the shear rate is lowered, these results give confidence in the accuracy and reproducibility of the combined trials presented in Chapter 6.

M.1.5 1-3 plane SANS: additional trials

Additional 1-3 plane SANS measurements were taken on the 0.01% wt NaTos solution in a geometry with a smaller gap-to-radius ratio, $\varepsilon$, than reported in Chapter 6, Section 6.5.2. Here, $\varepsilon = 0.042$ versus $\varepsilon = 0.071$ in Chapter 6; a different sample preparation and
Figure M.11: 1-3 plane $A_f$ for three trials in the second geometry ($\varepsilon = 0.111$) as a function of time after shear startup for (a) $\dot{\gamma} = 45 \text{ s}^{-1}$, and (b) $\dot{\gamma} = 26.4 \text{ s}^{-1}$. The pronounced steady state oscillations in $A_f$ when $\dot{\gamma} \geq 26.4 \text{ s}^{-1}$ are reproducible.

仪器使用的方法与上述在第M.1.3和M.1.4节中讨论的方法不同。因此，应小心比较前后的结果。图M.12中的2-3平面取向因子可以用于三种剪切速率，分别为：4.2、15和45 s\(^{-1}\)。在每一种剪切速率下，进行了两项试验。如图M.12所示，对于每一种剪切速率，都取得了极好的一致结果。在图M.12a和b中，对于$\dot{\gamma} = 4.2 \text{ s}^{-1}$，最大的性能下降发生在前100秒，但$A_f$并不明显达到稳定状态。虽然样本制备不同，但$A_f$的暂态特征与图M.7中其他两个几何体显示的特征相似。在$\dot{\gamma} = 15 \text{ s}^{-1}$时，观察到一个更明显的$A_f$暂态，该图M.12c和d中可以看到。$A_f$在每一种实验中都逐渐下降。$A_f$在$\dot{\gamma} = 15 \text{ s}^{-1}$时稍高，这是因为$\varepsilon$的较大下降。最后，在$\dot{\gamma} = 45 \text{ s}^{-1}$时，可以观察到图M.12e和f中的1-3平面$A_f$的快速而明显的下降。在稳态$A_f$中只有轻微的波动。
Figure M.12: Startup 1-3 plane $A_f$ for the 0.01% wt NaTos solution, in a geometry where $\varepsilon = 0.042$. Results are shown on a log-log (a,c,e) and linear-linear (b,d,f) scale for clarity. The shear rates examined are: $\gamma = 4.2$ (a,b), 15 (c,d), and 45 s$^{-1}$. Two trials were recorded for each shear rate; excellent agreement in obtained between trials. The $A_f$ transient lasts hundreds of seconds in each case.
than in either of the geometries with larger gap-to-radius ratios (Figure M.8). As was the case when the two geometries were compared in Section M.1.3, at $\dot{\gamma} = 45$ s$^{-1}$, the steady state $A_f$ is significantly larger when the gap-to-radius ratio is smaller. While the sample preparations differ, these results are likely due to geometrical differences as opposed to differences in the sample itself. In Section M.1.3, the shape, length, and magnitude of the $A_f$ response were similar between geometries near the onset of region II, which is also the case when the results in Figures M.12 and M.7 are compared. However, with increasing shear rate, the magnitude of the steady state $A_f$ and length of the transient shown in Figure M.12 follow the same trends as discussed in Section M.1.3: a larger $A_f$ and longer transient are observed when $\varepsilon$ is lower. Based on the results from the three geometries, we conclude that larger gap-to-radius ratios result in less stable shear banding that is accompanied by fluctuations in the steady state structure, which leads to a lower overall alignment at steady state.

M.1.6 1-2 plane SANS: additional shear rates

The shear rates examined in Chapter 6, Section 6.5.3 using 1-2 plane SANS measurements are those well within region II and near the onset of region III for the low branching solution: $\dot{\gamma} = 15, 26.4,$ and 45 s$^{-1}$. However, based on the rheological results shown above in Section M.1.1 and in Chapter 6, Section 6.5.1, the onset of region II occurs at shear rates significantly lower than unity, where $\dot{\gamma} \approx 0.1$ s$^{-1}$. Accordingly, 1-2 plane SANS measurements were also performed at these lower shear rates, which are shown below for $\dot{\gamma} = 2.5$ and 10.5 s$^{-1}$. In the particle tracking velocimetry (PTV) results shown in Chapter 6, Section 6.6.2, a three band structure was observed at shear rates as low as $\dot{\gamma} = 8.5$ s$^{-1}$. Accordingly, these results can help confirm these findings and explore if the presence of three shear bands occurs at lower shear rates.

The 1-2 plane alignment factor results for $\dot{\gamma} = 10.5$ s$^{-1}$ are shown in Figure M.13a below. The 1-2 $A_f$ results are shown on a log-log and linear-linear scale in Figure M.14. Individual trials for the inner wall position can be seen in Section M.1.7 below. As seen in Figure M.13a, the long transient in the startup response observed in the higher shear rates reported in Section 6.5.3 are preserved when the shear rate is lowered. A clear shear banded
structure is observed at this shear rate, despite the relatively low levels of alignment at steady state. A large undershoot in the $A_f$ response at the two outer wall positions ($r/H > 0.67$) is also observed at the higher shear rates, which corresponded with the presence of a third shear band. This undershoot can be clearly seen on a log-log scaling in Figure M.14a. The end of this undershoot region ($t > 300$ s) indicates the time at which the three banded structure becomes relatively stable.

In order to examine the three band structure, two positions near the outer wall that are fairly close together are examined: $r/H = 0.86$ and $r/H = 0.91$. As seen in the startup results in Figure M.13a, and the steady state response in Figure M.13b, the presence of the third shear band can be clearly seen. The steady state alignment at these two positions is significantly higher than when $r/H = 0.48$ and $r/H = 0.67$, where the error bars shown in Figure M.13b are calculated based on the fluctuations in the steady state $A_f$ response. The larger alignment at these positions can be clearly seen on a linear-linear scale in Figure M.14b. In the cartoon depiction of the shear band interfaces shown in Figure M.13b, three clear shear bands are shown, where the location of the third shear band is in good agreement with the PTV results for a similar shear rate, $\dot{\gamma} = 8.5$ s$^{-1}$.
As was performed for the higher shear rates reported in Chapter 6, Section 6.5.3, the structural mechanism of shear banding was also examined at $\dot{\gamma} = 10.5 \text{ s}^{-1}$. As large changes in the magnitude of the structural response occur for long times at this shear rate, the mechanism can be closely examined. The time-dependent, 1-2 plane alignment factor is shown as a function of gap position in Figure M.15. In Figure M.15a, the response at early times ($t \leq 50 \text{ s}$) is shown in five second increments. Interestingly, despite the fairly uniform gap-dependent $A_f$ at early times, the behavior at the outer two gap positions which eventually form the third shear band ($r/H = 0.86, 0.91$) is distinct at times as early as five seconds after shear startup. Until $t = 45 \text{ s}$, the alignment at these outer two positions is dramatically lower and forms a sharp interface with the other positions. When $t > 45 \text{ s}$, the alignment at these outer two positions finally increases and becomes larger than the alignment at positions in the middle of the gap. In Figure M.15a, the interface between the inner and middle band also becomes more distinct in time. At all positions, the alignment factor steadily and monotonically decreases in time. In Figure M.15b, the magnitude of $A_f$ at the outer wall is fairly constant in time, whereas $A_f$ at the inner wall continuously decreases; these results are consistent with the results at other shear rates (Section 6.5.3). Finally, in Figure M.15c, the alignment factor at all gap positions slightly fluctuates around a near steady-state value. These fluctuations are the result of the time-dependent fluctuations.
in $A_f$, which are shown clearly in Figure M.14b. In the black bolded points, the $A_f$ response at the approximate steady state (end of the experiment) is shown, where three shear bands are evident.

Figure M.15: Gap-dependent 1-2 plane $A_f$ at different time points after shear startup, indicated in seconds, at $\dot{\gamma} = 10.5$ s$^{-1}$. ‘Re-alignment’ is observed in time. Distinct behavior near the outer wall and the development of the third shear band is apparent even from early times.

The 1-2 plane alignment factor as a function of time after shear startup for $\dot{\gamma} = 2.5$ s$^{-1}$ is shown in Figure M.16a below; results on a log-log and linear-linear scale are shown in Figure M.17. As is the case for the shear rates presented in Chapter 6, Section 6.5.3 and in Figure M.13a above, a long transient in the startup alignment factor is still observed when the shear rate is further lowered. Once again, a clear alignment banded structure is observed at this shear rate, which appears to include the outer four gap positions shown in Figure M.16a. Despite the extremely low levels of alignment at steady state, shear banding is still expected at this shear rate based on the rheological results, which is depicted by the schematic in Figure M.16b. As seen in Figures M.16b and M.17, the average alignment at $r/H = 0.29$ is slightly larger than at the outer three gap positions, indicating this position is near the shear band interface. Due to the limited number of gap positions probed, the presence of three shear bands versus two cannot be confirmed with these measurements. The error bars shown in Figure M.16b are calculated based on the fluctuations in the steady state $A_f$ response. A large undershoot in the $A_f$ response at the three outer wall positions ($r/H \geq 0.48$) is seen, which is similar to the behavior observed at the higher shear rates. This undershoot can be seen more clearly in Figure M.17a.
Interestingly, at this low shear rate, evidence of the stress overshoot is observed in the $A_f$ response. At all gap positions shown in Figure M.16a, an increase in $A_f$ is observed at all gap positions ($t \leq 10$ s) before the dramatic decrease in magnitude. This behavior is likely to be captured here, as opposed to the higher shear rates, because the stress overshoot occurs at longer times which are accessible by SANS at the lowest shear rates (see rheology results in Chapter 6, Section 6.5.1; Section M.1.1 above). Interestingly, this overshoot occurs at the longest times near the inner wall ($t \approx 10$ s) and shorter times at the outer wall ($t \approx 6$ s). Similarly, the initial decrease in the magnitude of the $A_f$ response has the longest transient at the inner wall ($r/H = 0.1$), which can be seen most clearly in Figure M.17a. Here, the initial decrease in $A_f$ occurs until $t \approx 200$ seconds, after which a small undershoot in the alignment factor is seen. This time decreases with increasing gap position, where the alignment undershoot at $r/H = 0.48$ occurs around $t = 80$ seconds, and the undershoot at the outer wall ($r/H = 0.86$) occurs around $t = 60$ seconds. Interestingly, at long times ($t \approx 800$ s), the alignment factor at the inner wall ($r/H = 0.1$) decreases in magnitude, after the value of $A_f$ appeared to reach a steady state around $t = 300$ seconds. This decrease in $A_f$ after long times may correspond with the metastable plateau region of the stress response at low shear rates, which also exhibits a decrease in magnitude at long times.
The structural mechanism of shear banding was also examined at $\dot{\gamma} = 2.5\ s^{-1}$ by tracking the gap-dependent alignment factor at different times after shear startup, which can be seen in Figure M.18. In Figure M.18a, the startup alignment factor response is examined in five second intervals. From $t = 10$ seconds to $t = 50$ seconds, the magnitude of $A_f$ continually decreases in time for all gap positions. However, the alignment near the inner wall decreases the most significantly in time. After 50 seconds, the inner wall alignment continues to decrease significantly in time, whereas the outer wall alignment reaches an approximate steady value (Figure M.18b). At long times (Figure M.18c), an approximate steady state is reached at all gap positions. The alignment factor at each gap position fluctuates around this approximate steady state after the large decrease in alignment at the inner wall at $t \approx 800$ seconds. This approximate steady state is indicated by the bolded, black points in Figure M.18c. At this point in time, the clear alignment band is observed.

The 1-2 plane alignment factor was also measured for three gap positions at a shear rate expected to be outside of the shear banding regime: $\dot{\gamma} = 150\ s^{-1}$. The time- and spatially-dependent alignment factor can be seen for this shear rate in Figure M.19a. As seen in Figure M.19a, little to no transient in the $A_f$ response is observed at each gap position. Interestingly, the alignment at the outer wall ($r/H = 0.9$), on average, is larger than in the middle of the gap ($r/H = 0.6$). This behavior is similar to the behavior for the shear rates that exhibited a

Figure M.17: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 2.5\ s^{-1}$ as a function of time after shear startup on a (a) log-log and (b) linear-linear scale for clarity.
third shear band. However, the fluctuations in the $A_f$ response are significantly larger at this shear rate, which is expected based on its proximity to region III. Further, at many points in time, the alignment at both gap positions is equal in magnitude. Despite this behavior, as seen by the steady state $A_f$ shown in Figure M.19b and by the steady state results shown in Chapter 6, Section 6.5.3, little to no shear banding is observed at this shear rate. The material appears to be near its maximally aligned state, as the magnitude of the alignment at all three gap positions is similar. This near maximal alignment is consistent with the 1-3 plane $A_f$ results presented in Chapter 5, Section 5.5.2.

Figure M.19: 1-2 plane $A_f$ as a function of gap position for $\dot{\gamma} = 150$ s$^{-1}$ and (a) as a function of time after shear startup (b) at steady state. Shear banding does not appear to occur.
M.1.7 1-2 plane SANS: individual trials

In Chapter 6, Section 6.5.3, the 1-2 plane alignment factor presented was the sum of six or more individual trials. Select individual SANS trials were analyzed to confirm the reproducibility of the results, which are shown in Figure M.20. For clarity, in Figure M.20, individual trials are shown at the inner wall only \((r/H = 0.1)\) for \(\dot{\gamma} = 10.5 \text{ s}^{-1}\). Trials at the inner wall show the largest degree of alignment, so any changes between trials are the more apparent at this position. Further, at \(\dot{\gamma} = 10.5 \text{ s}^{-1}\), only four trials were used at each position, which can be easily interpreted. The results are shown on a log-log scale in Figure M.20a and on a linear-linear scale in Figure M.20b for clarity. In Figure M.20, the 1-2 plane \(A_f\) at \(\dot{\gamma} = 10.5 \text{ s}^{-1}\) is nearly identical between the four trials, demonstrating the reproducibility of the experiment. While fairly minor differences in \(A_f\) at early times after startup \((t < 70 \text{ s})\) are observed in Figure M.20a for the first trial, the linear scaling shown in Figure M.20b shows that these differences are negligible. The shoulder-like feature in the \(A_f\) response upon startup \((20 < t < 60 \text{ s})\), as well as local minima and maxima, are clearly repeatable between individual trials. Due to poor statistics that result from analyzing individual trials, some noise is observed in the responses; the combined \(A_f\) presented above in Section M.1.6 is shown via the transparent points. However, the fluctuations and oscillations between trials are generally reproducible (Figure M.20b), and are not the result of noise. At certain points in time, the phases of the individual responses are not perfectly in phase, such that the fluctuations in the combined trial are slightly dampened in magnitude from the individual trials. Accordingly, the observed fluctuations in the combined results presented in Chapter 6, Section 6.5.3 should also be reproducible, and are possibly dampened from the actual magnitude of the fluctuations in the individual trials.

M.2 0.05% wt NaTos

M.2.1 1-3 plane startup: additional shear rates

In addition to the shear rates shown in Chapter 6, Section 6.7.2, startup measurements were also performed on the mildly branched solution at several additional shear rates. These shear rates include \(\dot{\gamma} = 60, 75, 225\) and \(420 \text{ s}^{-1}\). These results can be seen in Figure M.21;
results from $\dot{\gamma} = 90$ and $150$ s$^{-1}$ that were previously reported are shown for comparison. As seen in Figure M.21, no transient is observed in the $A_f$ response once $\dot{\gamma} \geq 225$ s$^{-1}$. The absence of a transient indicates that the WLMs are at the maximally aligned state at this shear rate, which is in good agreement with the steady shear results presented in Chapter 5, Section 5.7.2. Interestingly, the WLMs appear to achieve a higher degree of alignment at $\dot{\gamma} = 225$ s$^{-1}$ than at $\dot{\gamma} = 420$ s$^{-1}$. However, the alignment at $\dot{\gamma} = 420$ s$^{-1}$ is equivalent to the alignment at $\dot{\gamma} = 150$ s$^{-1}$ at steady state. Despite the equivalent alignment at these two shear rates, the alignment factor at $\dot{\gamma} = 150$ s$^{-1}$ shows a short transient, while at $\dot{\gamma} = 420$ s$^{-1}$, little to no $A_f$ transient is observed. This result suggests that effects from turbulence or elastic instabilities may slightly decrease the alignment at extremely high shear rates. At the lower shear rates shown in Figure M.21, the average alignment at steady state increases with increasing shear rate, as expected; however, the steady state alignment at $\dot{\gamma} = 60, 75$, and $90$ s$^{-1}$ is similar in magnitude.

M.2.2 1-3 plane startup: individual trials

As three separate SANS experiments were performed for each shear rate shown in the results in Chapter 6, Section 6.7.2, the individual trials had to be verified to be reproducible. Here, the results from individual trials are shown for two shear rates within the shear banding
Figure M.21: 1-3 plane $A_f$ as a function of time after startup at shear rates in region III on a (a) log-log and (b) log-linear scale for clarity. No transient is observed when $\dot{\gamma} \geq 225$ s$^{-1}$.

regime: $\dot{\gamma} = 26.4$ and 45 s$^{-1}$. In this solution, the onset of region III occurs at $\dot{\gamma} = 60$ s$^{-1}$. The 1-3 plane alignment factor for the three trials for $\dot{\gamma} = 45$ s$^{-1}$ is shown below in Figure M.22, where the combined $A_f$ curve is shown by the black transparent points. As seen in Figure M.22, the results between the three trials are similar and indicate the reproducibility of the individual trials. While the alignment for trial two is slightly higher than in the other two trials, the same features and oscillations in the response are observed across trials. Unlike in the low branching solution, the fluctuations in the $A_f$ response are more chaotic in the mildly branched solution. While the response is generally reproducible, some of the fluctuations are dampened in the combined trial where the individual trials are not perfectly in phase.

The three trials for a lower shear rate, $\dot{\gamma} = 26.4$ s$^{-1}$ are shown below in Figure M.23, where again, the combined alignment factor curve is shown by the black transparent points. At this shear rate, the fluctuations in the $A_f$ response are more pronounced than at $\dot{\gamma} = 45$ s$^{-1}$. These fluctuations are more reproducible at this lower shear rate because it occurs further from the onset of region III. The behavior in the individual trials shown in Figure M.23 is, in general, more reproducible than at the higher shear rate shown in Figure M.22, and in each trial, the magnitude of the $A_f$ response is similar. This reproducibility between trials leads to more pronounced fluctuations in the combined alignment factor curve, and a combined curve that is more representative of the individual trials than at $\dot{\gamma} = 45$ s$^{-1}$. Regardless,
Figure M.22: 1-3 plane $A_f$ as a function of time after startup for three trials where $\dot{\gamma} = 45$ s$^{-1}$. While the magnitude of the $A_f$ response slightly differs between trials, the features of the response are all preserved.

The results from individual trials are fairly reproducible at both shear rates, confirming that the combined curves shown in Chapter 6, Section 6.7.2 are representative of the underlying alignment factor response at each shear rate.

Figure M.23: 1-3 plane $A_f$ as a function of time after startup for three trials at $\dot{\gamma} = 26.4$ s$^{-1}$. The magnitude and fluctuations of the $A_f$ response are reproducible between the three trials.
M.3 Highly branched: 0.10% wt NaTos

M.3.1 Startup rheology

The startup rheology for the highly branched solution shown in Chapter 6, Section 6.9.1 was performed for 300 seconds. These startup trials exhibited a transient of $t \leq 5$ seconds at all shear rates. However, in the shear banding solutions, metastable regions of the stress response are observed at certain shear rates that appear to be at steady state, when in fact a long transient occurs. To verify the absence of long transients at all shear rates in the high branching solution, additional, long time startup measurements were performed. These trials were performed for 1800 seconds, and can be seen in Figure M.24 for shear rates between $\dot{\gamma} = 1$ and $90 \text{ s}^{-1}$. At each shear rate, the stress response reaches steady state in $t \leq 5 \text{ s}$, confirming the fast evolution of the response. This transient is on the order of the estimated reptation time ($\tau_{rep} \approx 4.9 \text{ s}$, see Chapter 4, Table 4.1).

![Figure M.24: Startup stress response in regions II and III for the 0.10% wt NaTos solution for 1800 s, on a log-log (a) and linear-linear (b) scale. At all shear rates, a fast transient is observed ($t \leq 5 \text{ s}$). The features of the stress response are similar to those shown in Chapter 6, Section 6.9.1, verifying that these stress response features are independent of sample preparation.](image)

The features of the stress response observed in Figure M.24a are similar to those shown in Chapter 6, Section 6.9.1 for the highly branched solution, despite different sample
preparations. Rounded stress overshoots and undershoots are observed, and the shoulder-like features that indicate shear banding (region II) in the low and mildly branched solutions are only observed near or in region III. The shoulder-like region occurs during times that encompass the material relaxation time ($\tau_R \approx 1.7$ s, Chapter 4, Table 4.1). Figure M.24b clearly shows that the stress response does not change in value throughout the long experiment duration. The long time responses confirm the fast transients, but also that the solution is stable to long-time deformations and does not exhibit aging. These results are in good agreement with the SANS results, which show that the structure does not change over many hours or age over repeated measurements despite the long duration of the experiments. The startup stress response for additional shear rates in region III can be seen in Figure M.25 and M.26.

![Figure M.25](image)

Figure M.25: Long-time startup stress response in region III on a log-log (a) and linear-linear (b) scale for the highly branched solution. A fast transient is observed at all shear rates ($t \leq 10$ s). The fluctuations in the steady state response increase with increasing shear rate until $\dot{\gamma} = 185$ s$^{-1}$, as is expected in region III [9].

In Figure M.25, the startup stress response in region III is examined, where the resulting Weissenberg number range is $48 \leq Wi \leq 125$. As is the case for the other startup measurements (Figure M.24), the stress response rapidly evolves to steady state in ten seconds or less for all shear rates in Figure M.25. However, the observed fluctuations in the stress response significantly increase in magnitude with increasing shear rate until $\dot{\gamma} = 185$
s\(^{-1}\), which is best illustrated on a linear scale (Figure M.25b). However, as discussed in Appendix J, these fluctuations are only 3.1% of the steady state value. Only small fluctuations in the stress response are observed in region II; the largest fluctuation at \(\dot{\gamma} = 90\) s\(^{-1}\) is merely 0.05% of the steady state value. When the shear rate is increased to \(\dot{\gamma} = 125\) s\(^{-1}\), the average and maximum fluctuations are 0.29% and 0.76% of the steady state value, respectively. While the fluctuations are the largest at \(\dot{\gamma} = 185\) s\(^{-1}\), large fluctuations are also observed at the highest shear rates probed (144 \(\leq Wi \leq 221\)), which are shown in Figure M.26.

Figure M.26: Startup stress response at long times for shear rates well within region III for the highly branched solution, in a log-log (a) and linear-linear (b) scale. At all shear rates, a fast transient is observed \((t \leq 10\) s\)). The fluctuations in the steady state response are \(\approx 2\%\) of the average value for all shear rates.

In Figure M.26, similar features upon shear startup are observed as in Figure M.25. Interestingly, in Figure M.25, the maximum stress in the stress overshoot continues to increase with increasing shear rate, whereas in Figure M.26, the maximum stress is equal between all shear rates. As the stress overshoot occurs at very short times, where few points are measured, additional measurements would have to be performed to determine if the magnitude of the overshoot is truly constant at these shear rates. At all shear rates, however, the stress overshoot occurs at times longer than the breakage time \((\tau_{\text{break}} \approx 0.03\) s, Chapter 4, Table 4.1\)). In Figure M.26, the stress response reaches steady state is approximately 10 seconds or less. As seen in Figure M.26b, the fluctuations in the stress response appear
to become smaller in time; however, the stress response is always stable. These long-time startup measurements again confirm the absence of long transients in the highly branched solution, which can be used as an indicator of shear thinning in WLM solutions.

M.4 Network-like: 0.25% wt NaTos

M.4.1 Startup rheology

The features observed in the shear thinning, 0.10% wt NaTos solution discussed in Chapter 6, Section 6.9.1 and discussed above were verified on the more highly branched, 0.25% wt NaTos solution. The startup measurements for this solution can be seen in Figure M.27, where rounded stress overshoots and undershoots are observed. Sharp overshoots and shoulder-like features are not observed across the shear rate range measured. Only a limited range of Weissenberg numbers could be probed for this sample, as the sample is ejected from the rheometer at high shear rates. As such, the startup comparison shown in Chapter 6 could only be determined for low $Wi$.

Figure M.27: Startup stress response for the network-like, 0.25% wt NaTos solution. Fast transients, along with rounded overshoots and undershoots, are observed, similar to the 0.10% wt NaTos solution.
References


Appendix N

NORMALIZED LISSAJOUS-BOWDITCH PROJECTIONS OF LAOS CONDITIONS FOR MILDLY BRANCHED SOLUTION

As previously noted, the LAOS stress responses across the seven conditions probed using flow-SANS appear qualitatively similar based on the Lissajous-Bowditch projections from Figure 7.3. The shear stress measured under LAOS for all conditions is shown below in Figure N.1. The Lissajous-Bowditch projections are compared on a normalized basis in order to identify common features of the material response between conditions. The stress response is normalized by the maximum stress (stress at the overshoot), and the strain and shear rate are normalized by the maximum strain and shear rate amplitude, respectively. The elastic Lissajous-Bowditch projections (L) display strong stress overshoots that result in secondary loops in the viscous Lissajous-Bowditch projections (R).

Figure N.1: Elastic (L) and viscous (R) Lissajous-Bowditch projections for the LAOS conditions featured, on a normalized strain, shear rate and stress scale. Similar qualitative features are seen in the projections in all conditions, despite significant differences in the shear banding behavior.
One of the biggest differences in the curves is the magnitude of the normalized stress overshoot. At \( Wi = 75 \), the magnitude of the normalized stress overshoot decreases with increasing Deborah number. When \( De = 0.58, Wi = 75 \) and \( De = 0.50, Wi = 64 \), nearly identical normalized Lissajous-Bowditch curves result, which is not surprising considering the similar mechanism of shear banding. However, when \( De = 0.50, Wi = 113 \), the magnitude of the normalized stress overshoot is roughly the same, but the material does not shear band. The most significant difference in the Lissajous-Bowditch projection in this condition is the location of the stress overshoot, which occurs at a higher magnitude of the normalized strain. When \( De > 0.58 \), the normalized stress overshoot remains of similar magnitude and location as at \( De = 0.58 \), despite that these conditions do not show shear banding. Another distinct difference between the projections of the different conditions is the slope of the normalized stress vs. strain in the region directly following the overshoot. While the lower Deborah numbers show slow changes (low slope), the higher Deborah number conditions show a more drastic decrease in the normalized stress vs. strain (high slope). Again, many of the higher Deborah number conditions show similar normalized responses in this region, despite significant differences in shear banding behavior under LAOS. These qualitative similarities in the Lissajous-Bowditch projections between the shear banding and non-shear banding conditions shows the importance of using spatially-resolved measurements when determining and interpreting dynamic shear banding.
Appendix O

TIME DIVISIONS OF LAOS SCATTERING DATA

O.1 Low branching solution: 0.01% wt NaTos

O.1.1 Condition one: $De \approx 1$, $Wi = 295$

As condition three exhibited reversible phase shifts in the alignment factor response, the remaining conditions were examined as a function of time over the duration of the experiment to determine whether similar phase shifts occurred. The 1-2 plane results at the outer wall ($r/H = 0.825$) for condition one can be seen as a function of the experiment time in Figure O.1a. As seen in Figure O.1a, the phase of the alignment factor response does not change over the 3.5 hours of the experiment that were measured at the outer wall.

Figure O.1: 1-2 plane $A_f$ at the outer wall during the LAOS cycle for $De \approx 1$, $Wi = 295$. The phase of the $A_f$ response does not appear to shift in time, and the response remains the same through multiple measurements. (a) $r/H = 0.825$, (b) $r/H = 0.675$, with a comparison to $r/H = 0.825$. $A_f$ at $r/H = 0.825$ is larger at many $t/T$, suggesting the presence of a third band.
While the statistics are poor due to using half-hour trials, the shape and phase of the $A_f$ response also do not appear to change during the experiment duration in Figure O.1a. In Figure O.1b, similar results are shown for $r/H = 0.675$. The phase and shape of the response are not a function of experiment time. The alignment factor at $r/H = 0.825$ for one representative time point is also shown in Figure O.1b. The phase of all three responses is identical. Further, although the statistics are fairly poor from the short trial time, the alignment during much of the cycle when $r/H = 0.825$ is larger than when $r/H = 0.675$. This higher alignment suggests the presence of a third shear band under LAOS, which is similar to the mechanism of shear banding seen under steady shear for this solution.

O.1.2 **Condition four: $De = 2, Wi = 300$**

The same analysis performed for condition one was also performed for condition four, to check for the presence of phase shifts in the alignment factor response. The 1-2 plane alignment factor for half-hour trials during the course of the experiment can be seen for the outer wall positions ($r/H = 0.675, 0.825$) in Figure O.2a. As seen in Figure O.2a, the phase of the alignment factor response is identical between all trials at the outer wall, regardless of time during the experiment, or gap position. These trials at the outer wall span several hours of the experiment, from $t = 0.5$ to $t = 5.75$ hours, which suggests that the phase of the alignment factor response is stable over this time period. As was the case in the outer wall trials in condition one, the magnitude and shape of the alignment factor response at $r/H = 0.675$ also appears to be independent of experiment time, suggesting that this response is the response of the steady alternance state.

A similar result is observed when the $A_f$ response at the inner wall ($r/H = 0.325$) is measured in time, which can be seen in Figure O.2b. In Figure O.2b, the response at the inner wall is measured from the start of the experiment, and covers a time range up until $t = 3.5$ hours. As was observed at the outer wall, the shape and the magnitude of the alignment factor response do not significantly change over the three trials shown in Figure O.2b. The results shown at the inner wall are also completely in phase with the response at $r/H = 0.125$, which is measured from $t = 3.5 - 4.5$ hours (data not shown). These time
trials again suggest that the response in condition two is stable, or is at least stable over the 6.5 hour duration of the experiment that was measured.

![Figure O.2: 1-2 plane $A_f$ for $De = 2$, $Wi = 300$ across the duration of the experiment. (a) At the two outer wall positions ($r/H = 0.675, 0.825$), the phase of the $A_f$ response does not appear to shift in time. (b) Near the inner wall ($r/H = 0.325$), the phase of the response is also stable.

O.1.3 Condition five: $De = 2$, $Wi = 450$

As only three gap positions were measured in condition five, the experiment measuring time spanned only two hours. While this measurement time is fairly short, phase changes were observed in conditions three, nine, and ten nearly immediately after the start of shear. Accordingly, the trials for condition five were also examined in time to check for phase shifts. These time trials can be seen in Figure O.3 for the two outer wall positions, $r/H = 0.675$ and $r/H = 0.825$. While the data is not shown in Figure O.3, the phase of the response at the inner wall is identical to the phase of the outer wall data. As seen in Figure O.3, the phase of the response at the outer wall does not change over the 1.5 hour long measuring time. The magnitude and the shape of the alignment is essentially identical across all three trials, regardless of the gap position. These time trials give additional evidence of the alignment band, as the structure throughout the experiment is truly equal, and reproducible, between trials.
Figure O.3: 1-2 plane $A_f$ at two outer wall positions for $De = 2$, $Wi = 450$. The phase of the $A_f$ response does not appear to shift in time over the two-hour experiment.

O.1.4 **Condition six:** $De = 3$, $Wi = 450$

As was the case in condition five, the experiment time for condition six was rather short. In this condition, only two gap positions were measured, $r/H = 0.325$ and $r/H = 0.675$, for a total of a two hour experiment. As discussed in the text, the alignment factor response during the course of the oscillation cycle did not appear entirely symmetric in this condition, which is required for a stable LAOS experiment. In a LAOS experiment, the only thing that changes over the applied deformation is the direction of shear; the magnitude and shape of the applied shear rate remain constant. As the material alignment is a scalar function, and the material does not respond to the direction of shear, the alignment factor response should always be two-fold symmetric for these experiments.

The $A_f$ response at the inner wall in condition six was nearly symmetric, but the outer wall response deviated further from the expected two-fold symmetry. We had several hypotheses to explain the break in symmetry. First, the loss of symmetry could be a result of poor measurement statistics, which is probably the most likely case. Next, the triggering and binning procedure is not perfect, as each cycle may have a slightly different ending time due to limits in the equipment precision. Finally, a loss of symmetry could be observed if the
phase of the alignment factor response is changing in time. While the first two hypotheses could not be verified, we could compare individual time trials of the alignment factor at the outer wall, which can be seen in Figure O.4. Interestingly, the slight asymmetry is observed in all three time trials; however, the phase, shape, and magnitude of the alignment factor response does not change in time. The asymmetry is most pronounced at the minima in the \( A_f \) response, which are not equal in magnitude. This particular effect suggests an issue in data processing, and bad events and outlier cycles may need to be removed from the data set to fix these issues. Poor statistics and low neutron flux can also exacerbate these effects.

![Figure O.4: 1-2 plane \( A_f \) at \( r/H = 0.675 \) for \( De = 3, Wi = 450 \). The phase of the \( A_f \) response does not appear to shift in time over the two hour experiment.](image)

**O.1.5 Condition eight: \( De = 9, Wi = 450 \)**

The phase shifts of the alignment factor response in condition eight can be better seen in Figure O.5 for the two positions at the inner wall, where \( r/H = 0.125 \) is shown in (a), and \( r/H = 0.325 \) is shown in (b). As seen in Figure O.5, the alignment factor response continually shifts in time to become more in line with the applied strain, where the minima correspond to \( t/T = 0, 0.5, 1 \). Even in ten minute increments (Figure O.5a), the phase of the response is changing, suggesting that the phase change is a continuous process until the
steady state is reached. At all time points in the experiment, the measured phase of the $A_f$ response shifts to the right. At no point during the experiment is evidence of a left shift observed, suggesting that the phase shifts irreversibly to the right to reach steady state.

Figure O.5: 1-2 plane $A_f$ at the inner wall for $De = 9$, $Wi = 450$ as a function of experiment time. (a) $r/H = 0.125$. The phase of the $A_f$ response shifts in time before becoming nearly in phase with the applied strain. (b) $r/H = 0.325$. $A_f$ shifts continuously in time before reaching steady state.

Time trials for two outer wall positions can be seen in Figure O.6, which are used to determine when the response reaches steady state. In Figure O.6a, the response is shown at $r/H = 0.675$, where the two time trials span 1.5 to 2 hours after the start of shearing, and 4 to 4.5 hours after the start of shear. While the responses are noisy, there is a clear shift in phase between the two experiments, indicating that the response is not at steady state after 1.5 hours of shearing. In Figure O.6b, the response is shown at $r/H = 0.525$, where the two trials span 2 to 2.5 hours after the start of shearing, and 4.5 to 5 hours after the start of shear. Unlike in Figure O.6a, the responses are much less noisy, thanks to the higher alignment at this position. There is no apparent phase shift between the two trials, and the symmetric alignment maxima and minima can be determined (indicated by dotted vertical lines). As the phase and alignment between the two experiments is similar, we can conclude that the steady alternance state is achieved around 2 hours after the startup of shear.
Figure O.6: 1-2 plane $A_f$ at the outer wall for $De = 9$, $Wi = 450$. (a) The phase of the $A_f$ response appears to shift in time between the measurement at 1.5 to 2h and 4 to 4.5h at $r/H = 0.675$. (b) The phase and response of $A_f$ appears steady between the two measurements, indicating steady state has been reached after 2h.

**O.1.6 Condition nine: $De = 1.4$, $Wi = 300$**

In condition nine, the same anomalous phase shift behavior as in condition three was observed. A second, short trial was performed in condition nine to verify the phase shift behavior was reproducible. In this experiment, the response was only measured for two hours; 1.5 of those hours was measured at the outer wall. The other half hour measurement was performed at $r/H = 0.325$; the data is not shown. The 1-2 plane alignment factor from the second trial can be seen in Figure O.7 for $r/H = 0.675$ for three half-hour measurements during the experiment. As seen in Figure O.7, an immediate and significant phase shift is observed between each of the three trials, which span $t = 0.5$ hours to $t = 2$ hours. While the data is not shown, the phase for the measurement taken at $t = 0.5$ hours has shifted to the left of the initial phase measured from $t = 0$ to $t = 0.5$ hours at the inner wall. Interestingly, the phase from $t = 0$ to $t = 0.5$ hours has minima at $t/T$ larger than $t/T = 0.25$ and $t/T = 0.75$. However, in each of the three trials shown in Figure O.7, the phase shifts continuously to the left such that the minima in $A_f$ occur at times significantly earlier than $t/T = 0.25$ and $t/T = 0.75$. This trend in the direction of the phase shift is different than observed in the
trial in the text, where the shift minima were primarily at \( t/T \) larger than \( t/T = 0.25 \) and \( t/T = 0.75 \). However, differences in the shift direction were observed between multiple trials in condition ten, so this behavior is not out of the ordinary. It is unclear what factors determine which direction the phase shifts.

![Figure O.7: 1-2 plane \( A_f \) at the outer wall \((r/H = 0.675)\) during the LAOS cycle for \( De = 1.4, Wi = 300 \) for a repeated experiment. The phase of the \( A_f \) response shifts significantly in time over the two hour experiment. Dotted lines correspond to the symmetric minima in the \( A_f \) response.](image)

**Condition ten: \( De = 1.4, Wi = 400 \)**

Finally, despite the two trials reported in the text, a third trial was performed in condition ten to verify the phase shift behavior. In this experiment, the response was only measured for 2.5 hours; two of those hours were measured at the outer wall. The results from the third trial can be seen in Figure O.8 for \( r/H = 0.675 \) for the four half-hour trials. While not shown in Figure O.8, the starting phase at the inner wall \((r/H = 0.325)\) was the same as in the two trials shown in the text, where the minima in \( A_f \) were observed at \( t/T = 0.295 \) and \( t/T = 0.795 \). As seen in Figure O.8, a significant left shift in the \( A_f \) response is observed for each of the four trials. The initial left shift of the response is similar to the shift observed in trial two, but is the opposite direction from the shift observed in trial one. Phase shifts
that occurred in opposite directions were also observed in condition nine. As was the case in trial two of condition nine, the minima in the $A_f$ response shift from the starting phase continuously to the left such that the minima in $A_f$ occur at times significantly earlier than $t/T = 0.25$ and $t/T = 0.75$ by the end of the trial.

Figure O.8: 1-2 plane $A_f$ at the outer wall ($r/H = 0.675$) during the LAOS cycle for $De = 1.4$, $Wi = 400$ for a repeated experiment. The phase of the $A_f$ response shifts significantly in time over the 2.5 hour experiment. Dotted lines correspond to the symmetric minima in the $A_f$ response.

O.2 High branching solution: 0.10% wt NaTos

In the 1-3 plane measurements, the alignment factor response for $De = 2.5$, $Wi = 8.3$ showed an anomalous feature right before the maximum shear rate ($t/T = 0.5, 1$). In these regions, a small upturn in the alignment factor was observed, which can be seen in Figure O.9. Visually, this feature looks as though the alignment factor is a superposition of responses with different phases across the gap. If the phase of the alignment factor response changes in time, then it is also possible that this feature is the result of multiple response phases across the gap. To examine whether the alignment factor phase changes as a function of time during the experiment, the overall experiment for this condition was divided into two halves, which are shown in Figure O.9. As seen in Figure O.9, the phase of the $A_f$ response
is furthest to the left in the first half of the experiment. In the second half of the experiment, the phase has shifted slightly to the right. This observed phase change, while only examined over one half hour, suggests that the measured response here is not at steady state. As these 1-3 plane results have the opposite phase of the 1-2 plane results for the same condition, it is possible that the phase of this response continues to shift in time until it reaches steady state, at which point the phases of the two experiments could be the same.

Figure O.9: 1-3 plane $A_f$ during $t/T$ at $De = 2.5$, $Wi = 8.3$. The $A_f$ response for the whole experiment is shown in black, for the first 900 s in pink, and for the final 900 s in blue. Fairly good agreement is observed between the trials.
Appendix P

PERMISSIONS FOR FIGURE AND ARTICLE REPRINTING

Below are the required permissions for reprinted figures. Government sources do not require permissions to reprint; these figures are noted and the source is cited in the relevant chapter. For reprinted publications, all co-authors are aware that the articles are reprinted in this dissertation. Two first-author publications (references [1, 2]) are printed in the Journal of Rheology (AIP Publishing). For these references, permissions are not required to reprint in a dissertation, as given by the AIP website [3]:

“Q: May I include my AIP Publishing article in my thesis or dissertation? AIP Publishing permits authors to include their published articles in a thesis or dissertation. It is understood that the thesis or dissertation may be published in print and/or electronic form and offered for sale on demand, as well as included in a university’s repository. Formal permission from AIP Publishing is not needed. If the university requires written permission, however, we are happy to supply it.”

Two first-author publications (references [4, 5]) are printed by the Royal Society of Chemistry (RSC). Permissions are not required for reprinting in a thesis, as per the RSC website [6]:

“Author reusing their own work published by the Royal Society of Chemistry: You do not need to request permission to reuse your own figures, diagrams, etc, that were originally published in a Royal Society of Chemistry publication. However, permission should be requested for use of the whole article or chapter except if reusing it in a thesis. If you are including an article or book chapter published by us in your thesis please ensure that your co-authors are aware of this.”
Figure P.1: Permissions for reprinting Figure 1.1. Figure reprinted (adapted) with permission from reference [7]. Copyright 2003 American Chemical Society.

Figure P.2: Permissions for reprinting Figure 1.2. Figure reprinted (adapted) with permission from reference [8]. Copyright 1994 American Chemical Society.
Figure P.3: Permissions for reprinting Figure 5.3 from reference [10]. From: the European physical journal. E, Soft matter by European Physical Society ; Societa italiana di fisica. Reproduced with permission of SPRINGER-VERLAG in the format Thesis/Dissertation via Copyright Clearance Center.
Figure P.4: Permissions for reprinting Figure 6.2. Reprinted figure with permission from reference [9]. Copyright 2014 by the American Physical Society.
References


