RHEO-SANS
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ACNS  2008

Session C, 1:45 Monday;  Poster PC1.1, Matt Helgeson, Monday pm.
CO-AUTHORS

- Dr. Matt Liberatore (CSM)
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- Dennis Kalman
- Matt Reichert
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- Dr. Paul Butler (NCNR-NIST:)

NJW ACNS TUTORIAL
RHEO_SANS
Presentation Overview

Processing & Applications

Microstructure

Chixotropic Rheology
University of Delaware
1743
UD Rheology Labs

RHEO-SANS, RHEO-SALS, DLS, FQELS, HFQCR, DWS, microrheology
Center for Neutron Science
www.cns.che.udel.edu

• Development of national educational tools, courses, methods
• Eric Kaler & NJW
• Darrin Pochan
• Kristi Kiick
• Thomas Epps III
• Raul Lobo
• Millicent Sullivan
Outline

• Motivation for Rheo-SANS
• Previous attempts at reconstruction of 3-D structure and rheology
• Previous 1-2 shear plane measurement device designs
• New 1-2 shear plane SANS cell
• Calibration
• Examples:
  – Wormlike Micelles
  – Multilamellar Vesicles
WHY RHEO-SANS*?

- Structural information on complex fluids in the size range 1nm~1 micron both at rest and under flow conditions
- Access to rheological properties not accessible in a mechanical rheometer
- Contrast matching in SANS enables probing individual components in a mixture

* Rheology concurrent with small angle neutron scattering
Rheo-Optics and Rheo-SANS

1. RHEOLOGY is both a property measurement and a scientific method for interrogating materials.

2. Rheology alone may not be sufficient to understand the connections between molecular properties and bulk properties.
Rheology: Definitions:

Newton’s Law of Viscosity: \( \tau = \eta \dot{\gamma} \)

Energy dissipated per unit volume:
\[
E = \eta (\dot{\gamma})^2
\]

<table>
<thead>
<tr>
<th>Substance</th>
<th>Approximate Viscosity (Pa·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>(10^{40})</td>
</tr>
<tr>
<td>Molten Glass</td>
<td>(10^{12})</td>
</tr>
<tr>
<td>Molten Polymers</td>
<td>(10^3)</td>
</tr>
<tr>
<td>Honey</td>
<td>1</td>
</tr>
<tr>
<td>Water</td>
<td>(10^{-3})</td>
</tr>
<tr>
<td>Air</td>
<td>(10^{-5})</td>
</tr>
</tbody>
</table>
General Shear Behavior

\[ \tau = \tau_y + K \gamma \]

- \( n = 1 \), Newtonian
- \( n < 1 \), pseudoplastic
- \( n > 1 \), dilatant
Viscoelastic Behavior of Fluids

For systems with a yield stress, \( G'(w>0)=G_0 \)

Glassy, solid like behavior

\[
\frac{G''}{G'} = \tan \delta
\]

Viscoelastic behavior of a Maxwell Element
Drag flows: Couette geometry

M. Couette (1890)
Drag flows: Couette geometry

Concentric cylinders, inner one rotating: \( \omega \)

1. Steady, laminar, isothermal flow
2. Negligible gravity and end effects
3. Symmetric in \( \theta \)
4. \( v_r=v_z=0 \) and \( v_\theta=r\omega \)

Equations of motion:

\[
\begin{align*}
    r: & \quad 1 \frac{\partial (r \sigma_{rr})}{\partial r} - \frac{\sigma_{\theta \theta}}{r} = -\rho \frac{v_\theta^2}{r} \\
    \theta: & \quad \frac{\partial (r^2 \sigma_{r\theta})}{\partial r} = 0 \\
    z: & \quad \frac{-\partial p}{\partial z} + \rho g = 0
\end{align*}
\]
Drag flows: Couette geometry

Boundary conditions
1. \( v_\theta = R_i \omega \) at \( R_i \)
2. \( v_\theta = 0 \) at \( R_o \)

Shear stress

\[
\begin{align*}
\theta: \quad & \frac{\partial (r^2 \sigma_{r\theta})}{\partial r} = 0 \quad \rightarrow \quad \sigma_{r\theta} = \frac{C}{r^2} \\
\sigma_{r\theta}(R_o) \cdot (2\pi \cdot R_o \cdot L) &= \frac{M}{R_o}
\end{align*}
\]

Macosko, “Rheology”
Scattering angle $\propto 1/\text{Length}$

Plateau intensity, overall length

Bending due to flexibility, persistence length

"-1" slope, rigid rods

Micelle diameter

Intensity

(light)

(SANS)

(USANS)

“q” scattering angle
Rheo-SANS Investigation

NIST, NG-7, stress control rheometer
Shear Cell, Rheo-SANS

Couette shear cell at D11, ILL, Grenoble
Designed by Peter Lindner
Shear Cell, **Rheo-SANS**
Shear Cell, Rheo-SANS
Small Angle Neutron Scattering

\[ \mathbf{q} = \frac{4\pi n}{\lambda_0} \sin \left( \frac{\theta}{2} \right) \]

Isabelle Grillo 2000-08-07
SANS Beamline NIST
Rheo-SANS (1-3, 2-3 plane)
Anton Paar UDS w/ Couette Cell
Rheo-SANS instrument
Rheo-SANS Couette Cell
Rheo-SANS examples

• Immiscible polymer blends- droplet size, shape, orientation in simple shear flow
• Measuring the nonequilibrium structure of a shearing colloidal suspension
• Shear Banding in Worm-Like Micelles
Resolving 3-D structure from 1-3 and 2-3 plane SANS data:

**FIG. 12.** On-axis SANS images for B615 at shear rates a) 1.9 s$^{-1}$, b) 3.9 s$^{-1}$ c) 7.8 s$^{-1}$, and d) 11.7 s$^{-1}$. The contours are on a log-scale, and are on the same scale for all images.

**FIG. 13.** Off-axis SANS images for B615 at shear rates a) 1.9 s$^{-1}$, b) 3.9 s$^{-1}$ c) 7.8 s$^{-1}$, and d) 11.7 s$^{-1}$. The contours are on a log-scale, and are on the same scale for all images.

**FIG. 14.** SANS measured ellipsoid parameters versus shear rate. Aspect ratio for blends B615 (▼), B610 (■), B605 (●). Minor axis for blends B615 (▲), B610 (□) and B605 (○). Tilt angle for blends B615 (▲), B610 (□), and B605 (○), with representative error bar.
Resolving 3-D structure from 1-3 and 2-3 plane SANS data: Kernick & Wagner, JOR 43(3), 521-549, (1999)

**FIG. 17.** Equivalent radius versus stress from SANS for blends B615 (▽), B610 (■), B605 (◇), B110 (▲). Also included is the size from the static measurement (figure 11) as a function of previous stress for B610 (—) and B110 (・・・).
Production of nanofibers by shear processing TLCP blends

Figure 5. POM picture of recovered TLCP fibers in the 30 wt % blend after PBT matrix dissolution. Tested shear rate is 620 1/s.

Figure 11. SEM micrographs of freeze-fractured quenched extrudates for the 30 wt % blend sheared at (a) 822 and (b) 18000 1/s.

Correlation of the minor-phase orientation to the flow-induced morphological transitions in thermotropic liquid crystalline polymer/PBT blends
Van Eijndhoven-Rivera MJ, Wagner NJ, Hsiao B
COLLOIDS
Engineered Nanomaterials
e.g., "house paint"

Gels and Processing

Stable Dispersion

Aggregated Dispersion/Gel

$\Phi_{\text{max}} = 0$

Brownian Dynamics Simulation $\phi = 0.40$

$\Phi_{\text{max}} \sim 4 \ kT$

Simulations suggest that the final gel topology depends on the height of the energy barrier

M. Hütter, *J. Colloid Interface Sci.* **231** (2000)
Recent work on agglomerates

- Degussa Fumed Silica
- RHEO-USANS measurements of Structure
  (Peukert/Sommer/DuPont)
Comparison between Small Angle Neutron Scattering and Light Scattering experiments

goal:
- determine structure of the aggregates
- extract fractal dimension $d_F$

expected fractal dimension:
- $d_F = 2.1$ for reaction limited cluster cluster aggregation (RLCCA)

1 wt% Ludox TM50; 1M KNO₃; solvent: D₂O; t=672s

**Light Scattering:**
- slope: $-2.09 \pm 0.03$
- calculated theoretical line
  - slope = 2.0
  - $d_{agg} = 273$ nm

**Small Angle Neutron Scattering:**
- slope $= -1.96 \pm 0.01$
- $d_p = 36.274$ nm
- theoretical line for monodisperse spheres

$I(q)$ / cm$^{-1}$

$q$ / Å$^{-1}$
Fractal dimension for 5wt% Ludox at a salt concentration of 0.4 M KNO₃

Fractal dimension

Brownian motion:
- SANS
- Light Scattering
- Calculation

Turbulent shear:
- SANS

Reaction Limited Cluster
Aggregation

Reactivity Limited
Monomer Cluster
Aggregation

Fractal dimension vs. time

- $\gamma = 1000 \text{ s}^{-1}$
- $\gamma = 0 \text{ s}^{-1}$

Time / h

Fractal dimension
Hydrocluster Mechanism of Shear Thickening

**FIG. 5.** Snapshots of particles with LVF > 0.6 at Pe = 3000, the configurations are separated by unit strain. The flow direction is left to right and the shear gradient direction is top to bottom. The simulations were in a rectangular box.

John Melrose and Robin Ball, approximate SD simulations

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Scattering Examples

Spherically Symmetric

Anisotropic

Cluster

Crystalline
Shear Thickened Fluid Microstructure: *Ultra Small Angle Neutron Scattering (USANS)*

- Colloidal Silica
  - $d_{\text{DLS}}=577.2 \pm 41.2\text{nm}$
  - $d_{\text{SEM}}=510 \pm 19\text{nm}$
  - $d_{\text{USANS}}=520 \pm 52\text{nm}$
- Clarient PEG-200
  - $(\eta_0=42\text{cP})$
Flow-USANS Data, \( \phi=0.40 \)

- 1\textsuperscript{st} peak shifts to lower q and higher Intensity w/increasing shear
- 2\textsuperscript{nd} increasing magnitude w/shear at fixed q
- Agrees with Maranzano, but larger particles and lower rates
- Clustering and microstructure compression

Cluster size \( \sim 2\pi / q \sim 900 \text{nm} \)

\[ \text{Tick line} = \text{thickened state} \]
Flow-USANS Data, $\phi=0.52$

Cluster size $\sim 2\pi/q \sim 1000\text{nm}$

Thick lines = thickened state

$\eta\ (\text{Pa}\cdot\text{s})$

$\gamma\ (1/\text{s})$

$\phi=0.520\text{ Silica in PEG-200 (62.5\% wt)}$
Structure Measurements in the Plane of Shear (1-2)

Probing the 1-2 plane (velocity-vorticity)

- Maximum microstructure deformation and alignment is available in the 1-2 plane
- Shear banding, wall effects, etc.. Accessible only in 1-2 plane
1-2 SANS ISSUES

• Need for quantitative SANS
• Need for rheological measurement
• Need for gap resolution, shear banding and shear induced phase transitions
Burghardt and coworkers: *Macromolecules, Vol. 34, No. 19, 2001*

**Figure 3.** Schematic of annular cone and plate geometry used for X-ray measurements of fluid structure in the 1–2 plane. The cone angle has been exaggerated in this diagram; the actual cone angle is 5°.
Shear Flow Induced Transition from Liquid-Crystalline to Polymer Behavior in Side-Chain Liquid Crystal Polymers

L. Noirez and A. Lapp

FIG. 1. Section of the shear cell ring placed in a vertical position for the three-axis geometry defining the three axes \((\hat{\theta}, \hat{\phi}, \hat{\varphi})\). The scattering vector is defined by \(\vec{q} = \vec{k}_i - \vec{k}_f\), where \(\vec{k}_i\) is the incident beam and \(\vec{k}_f\) is the diffracted one.

FIG. 2. Schematic of the neutron scattering cell used for the observation of the vorticity plane with a typical neutron scattering pattern (\(\lambda = 3.5\,\text{Å},\,d = 2\,\text{m}\)) obtained with the H/D mixture in the smectic phase (\(T = 93\,\text{°C}\)) under a shear flow of 6 s\(^{-1}\). The upper part of the pattern corresponds to a shadow due to the upper rotating ring.
Design of the 1,2-plane shear cell
1-2 Plane SANS Setup

- Aluminum Couette
- 2.0 mm gap
- 10 mm path length

40 mM EHAC 300 mM NaSal

Flow gradient

+32 s⁻¹

-32 s⁻¹
1-2 Plane SANS Cell
1-2 Plane SANS Cell

Reduction of beam into a slit that can be translated across the gap.
# 1-2 Plane Cell Gap Positioning

![Graph showing data and calculated measure](image)

<table>
<thead>
<tr>
<th></th>
<th>Measures / mm</th>
<th>$\mu$ / mm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total thickness</td>
<td>21 Al</td>
<td>0.00497</td>
</tr>
<tr>
<td>Lower block</td>
<td>16 1:1 mixture of $H_2O/D_2O$</td>
<td>0.3689</td>
</tr>
<tr>
<td>Hole</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Bob</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Cover plate</td>
<td>5 NJW ACNS TUTORIAL</td>
<td></td>
</tr>
<tr>
<td>Thickness inside</td>
<td>6 RHEO_SANS</td>
<td></td>
</tr>
</tbody>
</table>
1-2 plane cell: End Effects

End effects in current cell geometry
Low turbidity (SANS) samples, the ends do not dominate signal
Isotropic at rest, so ends contribute little to observed anisotropy
Validation with birefringence and rheology
Flow 1-2 SANS

\[
\frac{I(q, \phi, \gamma)}{I(q, \phi, \gamma = 0)}
\]
40 % DISPERSION

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RHEO_SANS
RHEO_OPTICS: Stress-Optical Rules

• Polymers:

\[ \eta_{\text{thermo}} \gamma = \langle r_x r_y \rangle \]
\[ \Delta n'_{xy} = \langle r_x r_y \rangle \]
\[ \Delta n'_{xy} = C \eta_{\text{thermo}} \gamma \]

• Colloids:

\[ \eta_{\text{thermo}} \gamma \alpha \propto \langle P_{xy} \rangle \]
\[ \Delta n''_{xy} \propto \langle P_{xy} \rangle \]
\[ \Delta n''_{xy} = C \eta_{\text{thermo}} \gamma \]

Spherical Harmonic Functions for “3-D” Expansions

Expansion of nearest neighbor distribution in spherical harmonics

Measurements of the 3-D structure by “3-D sans” enables direct calculation of the components of the stress

Hydrodynamic component of the stress is calculated directly from the measured microstructure and the exact 2-body hydrodynamics interactions, many-body hydrodynamics are neglected.

\[ \tau_{\text{measured}} \sim 2.5 \times \tau_{\text{calculated}} \]
Siple Award
US Army Science Conference, 2002

"Advanced Armor Utilizing Shear Thickening Fluids", by Y. S. Lee, E. D. Wetzel, R. G. Egres Jr., N. J. Wagner
Ballistic Testing

3 layers Nylon, 800 fps

2 layers STF-Nylon, 800 fps
Rheo-SANS Conclusions

- Rheo-SANS is a powerful method to interrogate the nonequilibrium structure and structure-property relations in flowing systems and processing flows.
- Quantitative 1-2 Plane SANS is demonstrated
- Gap Resolution (0.1mm) is demonstrated
- Colloids: microstructure and rheo-SANS demonstrated in shear thinning and shear thickening regime.
- Wormlike-micelles: microstructure across gap in shear induced phase separation (SIPS) is quantified for the first time.

**MORE DEVELOPMENT WORK IN PROGRESS:**
- True Rheo-SANS in the 1-2 Plane
- concurrent flow visualization
- concurrent flow-SALS

Session C, 1:45 Monday; Poster PC1.1, Matt Helgeson, Monday pm.