Dynamics of Complex Polymer Fluids During Flow & Processing

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Topics

• Synchrotron studies of flow & processing
  – Experimental infrastructure & examples
    • Shear flow
    • Processing

• ERL: microfocus + coherence
  – Microfocus… 2 ideas
  – Coherence…
    • Homodyne scattering to measure velocity gradients?
How do we (currently) use synchrotron?

• High flux
  – Time-resolved studies of structural dynamics in ‘real time’
  – Closely coupled to detector issues
  – Potential of 3rd generation sources probably not yet maxed out

• ‘High’ energy (18 - 25 keV)
  – Expedient way to reduce absorption, enable novel instrumentation
In situ scattering: Shear flow

\[ \nu_1 = \gamma x_2 \]

"1" or "Flow" direction

"2" or "Gradient" direction

"3" or "Vorticity" direction

‘1-2 Plane’

‘1-3 Plane’
Rotating-disk shear cell: 1-3 plane

Linkam CSS-450 Shear Stage:

Annular cone & plate shear cell: 1-2 plane

Shear cell:

Representative setup:

LCP Structure

(a) Microscopic

\[ u = \text{test molecule orientation} \]

(b) Mesoscopic

\[ n = \text{director orientation} \]

\[ \Psi(n) \]

\[ S_m = \langle uu \rangle - \frac{I}{3} \]

\[ S_m = \langle nn \rangle - \frac{I}{3} \]

\[ \Psi(u) \]

Orientation Distribution Function

Order Parameter Tensor

Scalar Order Parameter

\[ \bar{S} \]
Lyotropic nematic PBG: 1-2 plane scattering patterns

PBG: Reversal in 1-2 Plane


(Larson-Doi ‘tumbling polydomain’ model)
Orientation ‘Trajectories’

ERL Idea #1

- Polydomain materials
  - LCPs
  - Block Copolymers

Large beams currently average over distribution of domain/grain orientations

*Microfocus to enable ‘single domain’ measurements? During shear?*
ERL Idea #1… Issues

• What about third dimension?

- Good opportunities for detailed mapping of domain/grain structure in thin samples (*e.g.* evolution during annealing)
- Possible *in situ* studies on thin *solids* during deformation?
- But, how to realize controlled flows on liquid samples?
Beyond shear:
Complex channel flows

- Materials processing often involves mixtures of shear & extension

- Extension can be much more effective than shear at aligning fluid microstructure

- ‘Slit-contraction’ and ‘slit-expansion’ flows: superposition of stretching on otherwise inhomogeneous shear flow
X-ray capable channel flow die

Interchangeable spacers define particular geometry:

Typical experiment:
Commercial LCP in channel flow

- Xydar commercial LCP
- Melt experiments at 350 C

1:4 slit-expansion flow: Bimodal orientation state

ERL Idea #2

- Complex fluids + microfluidics + microfocus x-ray scattering
- Combined effects of flow + confinement on complex fluids
- Liquid crystals, lyotropic surfactants, etc.
- Platform for extremely precious (e.g. small quantity) samples?

- Typical microfluidics… 10s of microns
- ERL microfocus… more than adequate (overkill?)
- Question: necessary to move towards ‘nanofluidics’ for interesting confinement effects?
Polymer Bicontinuous Microemulsions

• Bates & Lodge, U. Minnesota
• Symmetric blends of immiscible linear homopolymers with corresponding diblock
• M_w adjusted so T_{ODT} of pure diblock ~ T_c of pure binary blend
• Typical isopleth phase diagram:
Quiescent neutron scattering

- PEE-PDMS:
- Teubner-Strey model:

\[ S(q) \sim \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \]

Morkved et al., Faraday Disc. 112, 335 (1999)
Steady shear: PEE-PDMS


**Experiment:**

**Model:**

PS-PI Microemulsion: X-ray Photon Correlation Spectroscopy

- Beamline 8-ID
- Simon Mochrie, Yale

Speckle pattern

125°C
17 ms exposure
850 images/series

\[ g_2(\Delta t) = \frac{\langle I(t)I(t + \Delta t) \rangle}{\langle I(t)^2 \rangle} \]
PS-PI Microemulsion: X-ray Photon Correlation Spectroscopy

125°C

Increasing $q$…
PS-PI Microemulsion: X-ray Photon Correlation Spectroscopy

Dependence of Decay Time ($\tau$) on $q$

125°C

Direct probe of equilibrium dynamics at length scales of interest.
Coherent Scattering & Flow

Consider dilute spherical particles… (Berne & Pecora, Ch. 5)

Heterodyne correlation function (independent scattering):

\[ F_1(q, t) = \sum_{j=1}^{N} I_j \langle \exp \{ i q \cdot [r_j(t) - r_j(0)] \} \rangle = \sum_{j=1}^{N} I_j F_{sj}(q, t) \]

\[ G_s(R, t) = \langle \delta(R - [r_j(t) - r_j(0)]) \rangle \] (Probability of particle displacement \( R \) in time \( t \))

With no flow, \( G_s(R, t) \) satisfies diffusion equation…

\[ \frac{\partial}{\partial t} G_s(R, t) = D \nabla^2 G_s(R, t); \quad G_s(R, 0) = \delta(R) \]

Fourier transformation & solution gives:

\[ F_{sj}(q, t) = \exp(-q^2 Dt) \] Thus…

\[ F_1(q, t) \sim \exp(-q^2 Dt) \] (Heterodyne)

\[ F_2(q, t) = |F_1(q, t)|^2 \sim \exp(-2q^2 Dt) \] (Homodyne)
Added Flow…

$G_s(R,t)$ now satisfies convection-diffusion equation…

$$\frac{\partial}{\partial t} G_s + \nabla \cdot (\mathbf{V} G_s) = D \nabla^2 G_s; \quad G_s(R,0) = \delta(R)$$

For small scattering volume, linearize velocity field:

$$\mathbf{V} = \bar{\mathbf{V}} + \mathbf{\Gamma} \cdot \mathbf{R}$$

Mean velocity  Velocity gradient tensor

With only uniform velocity ($\mathbf{\Gamma} = 0$), solution becomes…

$$F_{sj}(\mathbf{q}, t) = \exp(i\mathbf{q} \cdot \bar{\mathbf{V}} t - q^2Dt)$$

Heterodyne spectrum shows Doppler shift: $F_1(\mathbf{q}, t) \sim \cos(q \cdot \bar{V} t)\exp(-q^2Dt)$

(Uniform flow has no effect on homodyne spectrum…)

(Recent work from Mark Sutton at APS Sector 8 demonstrates this in XPCS)
With velocity gradients...

*Homodyne* spectrum now is affected at leading order; under many conditions, this can dominate the measured correlation function.


\[
F_2(q, t) = \left| \int dR I(R) \exp\{-i q \cdot \Gamma \cdot R \} \right|^2
\]

Beam intensity profile  
Select various ‘projections’ of \( \Gamma \) depending on scattering geometry.

Correlation function shows *Gaussian* decay:

\[
F_2(q, t) \sim \exp(-q^2 \gamma^2 L^2 t^2)
\]

\( \gamma \) = characteristic deformation rate  
\( L \) = length scale of scattering volume

Allows measurement of velocity gradients provided…

\[
\tau_\gamma = \frac{1}{q \gamma L} \ll \tau_D = \frac{1}{q^2 D}
\]

(Note, as \( q \to 0 \), convection always dominates over diffusion, and will set time scale for decay of correlation function.)
Would this ever be interesting?

One possible application: ‘Shear-banding’ in complex fluids

Uniform shear:

- Localized band of high velocity gradient
- Constitutive instability and/or phase separation

Frequently found in solutions of wormlike micelles…

Concept: spatially-resolved, simultaneous measurements of structure via conventional SAXS and local velocity gradient via homodyne correlation function.

Can it work??
Reality check…

Correlation time: \[ \tau_\gamma = \frac{1}{q \gamma L} \]

Suppose \( q = 0.1 \text{ nm}^{-1} \) (typical SAXS)…

<table>
<thead>
<tr>
<th>( L = 100 \mu )</th>
<th>( L = 10 \mu )</th>
<th>( L = 1 \mu )</th>
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<tbody>
<tr>
<td>( \gamma = 1 \text{ s}^{-1}, \tau_\gamma = 10^{-4} \text{ s} )</td>
<td>( \gamma = 1 \text{ s}^{-1}, \tau_\gamma = 10^{-3} \text{ s} )</td>
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<td>( \gamma = 100 \text{ s}^{-1}, \tau_\gamma = 10^{-6} \text{ s} )</td>
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Competing objectives…
- want faster than intrinsic sample dynamics
- want high spatial resolution
- require coherence

Unknowns…
Maximum time resolution for XPCS? (detectors?) Effect of elongated scattering volume? If coherence imperfect, does coherence length replace \( L \)?
Summary

• *In situ* synchrotron scattering during flow yields detailed insights into microscopic origins of rheological properties of complex fluids

• Ideas…
  – Microfocus… single ‘domain’ dynamics?
    • Hard for flow…
  – Microfocus + microfluidics + complex fluids?
    • Should work; already possible?
  – Coherent scattering during flow?
    • Access to local velocity gradients from homodyne spectrum…
    • Many questions…
Real processing: *In situ* injection molding

Undulator Beamline 5ID-D of DND-CAT

16° trenches (on both the mold and wedge block) allow for scattered X-rays to readily exit the mold

Injection mold details

- Built-in Trenches (for X-ray Access)
- Wedge Block
- Mold Cavity
- 1-mm deep Al window (per side) – along mold centerline
- Assembled X-ray Mold & Wedge Block (side view)
- Tie Bars
Representative experiment: Injection molding of Vectra A®

Molding Parameters:

- Fill time = 4 sec
- $T_{\text{melt}} = 285$ °C
- $T_{\text{nozzle}} = 300$ °C
- $T_{\text{mold}} = 90$ °C

Data acquisition rate: 12 frames/sec

Video clip slowed down by factor of 2.4

Location along mold: 23 mm away from die entrance

PS-PI Microemulsion:
Structure during oscillatory shear

QuickTime™ and a decompressor are needed to see this picture.
PS-PI Microemulsion: Structure during oscillatory shear

PS-PI
125°C
50% strain

\[ \Delta \sin 2\chi \quad \Delta \cos 2\chi \]

\( f = 0.005 \text{ Hz} \)

\( f = 0.08 \text{ Hz} \)

Time (s)