Dynamics of Complex Polymer Fluids During Flow & Processing

Wesley Burghardt

Department of Chemical & Biological Engineering and Department of Materials Science and Engineering

Northwestern University

Evanston, IL

Topics

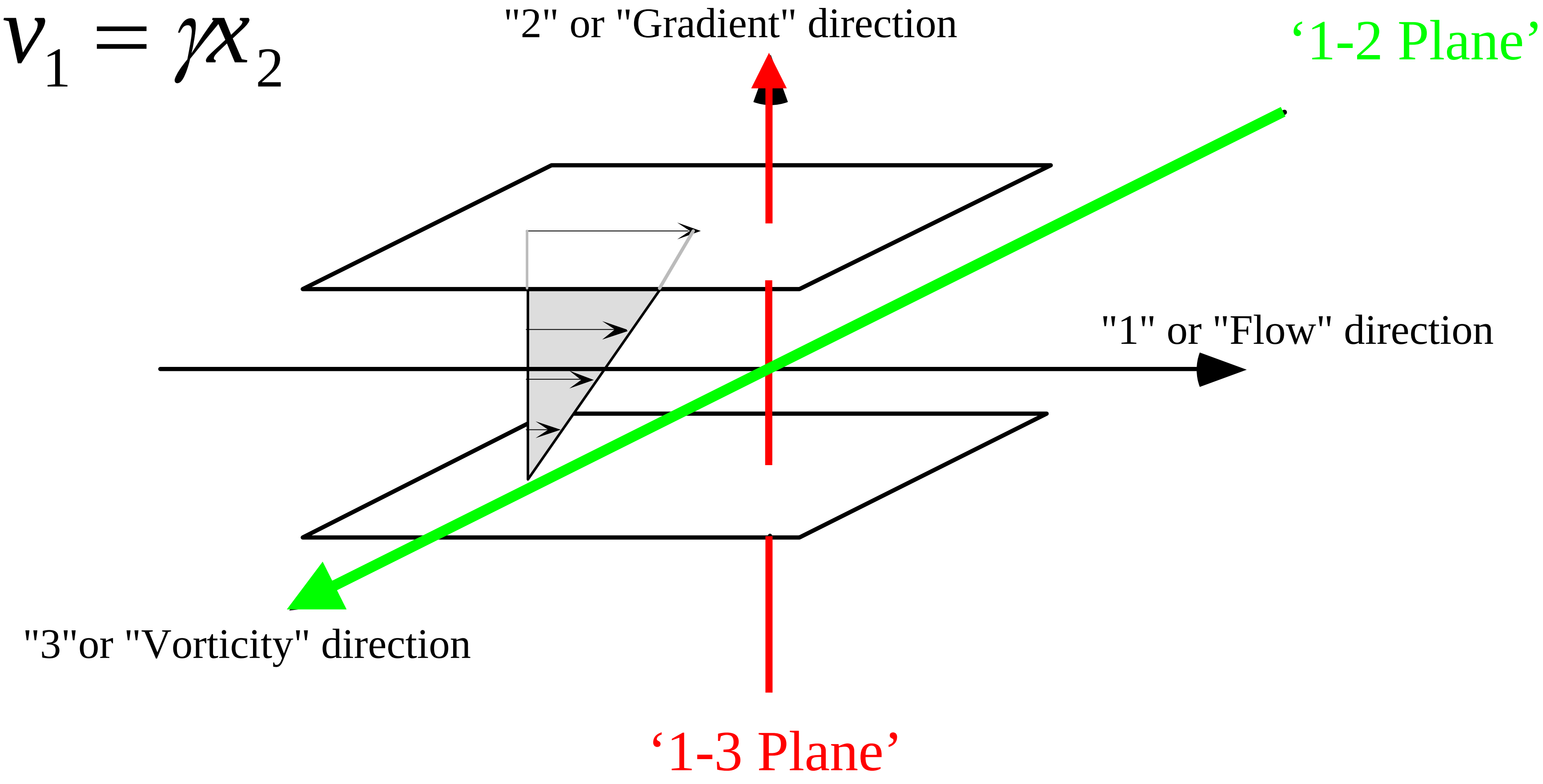
- Synchrotron studies of flow & processing
  - Experimental infrastructure & examples
    - Shear flow
    - Processing
- ERL: microfocus + coherence
  - Microfocus… 2 ideas
  - Coherence…
    - Homodyne scattering to measure velocity gradients?

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

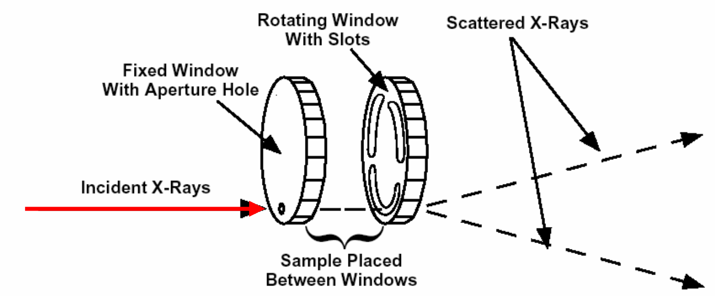
In situ scattering: Shear flow

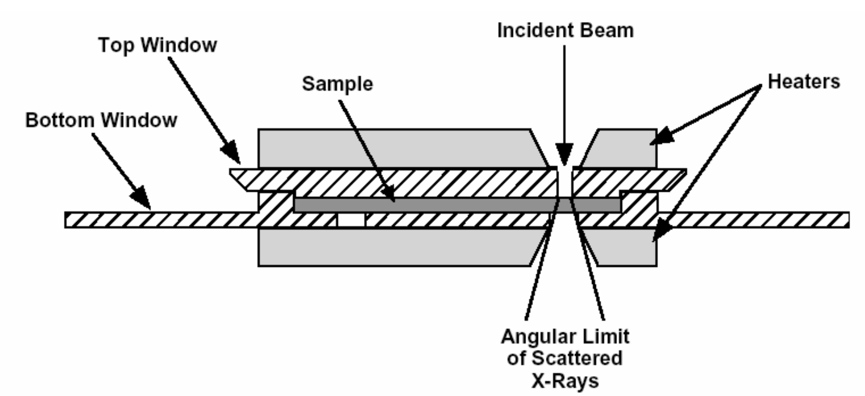
$$v_1 = \gamma x_2$$



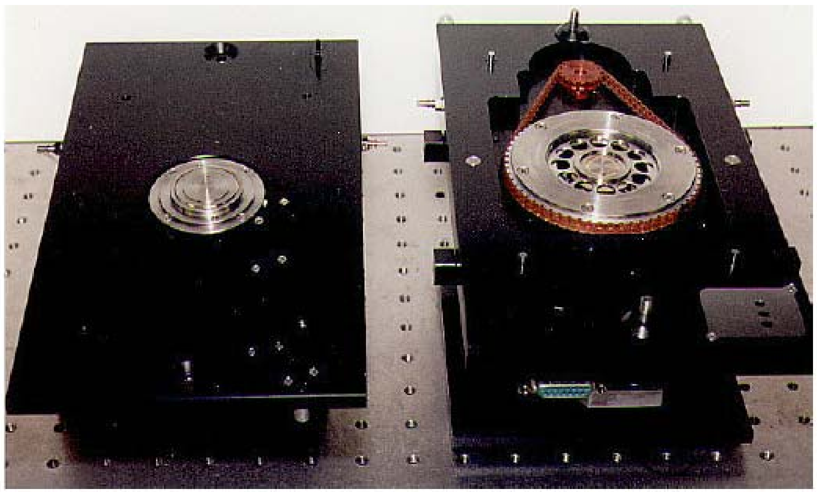
Rotating-disk shear cell:

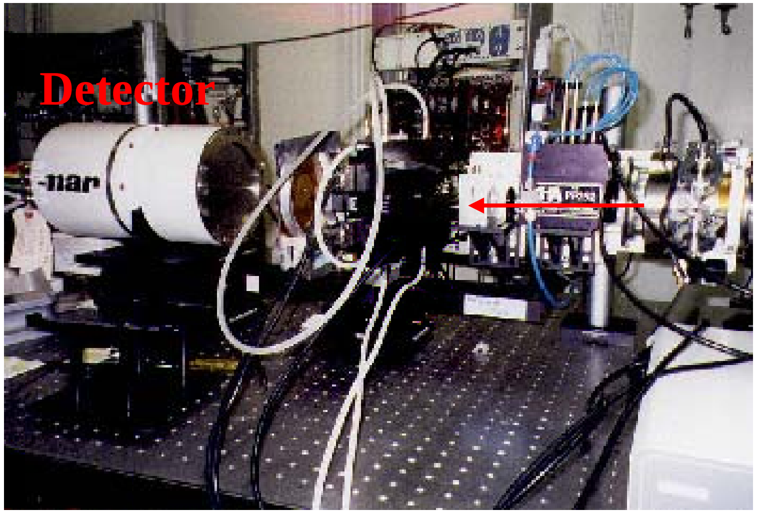
1-3 plane





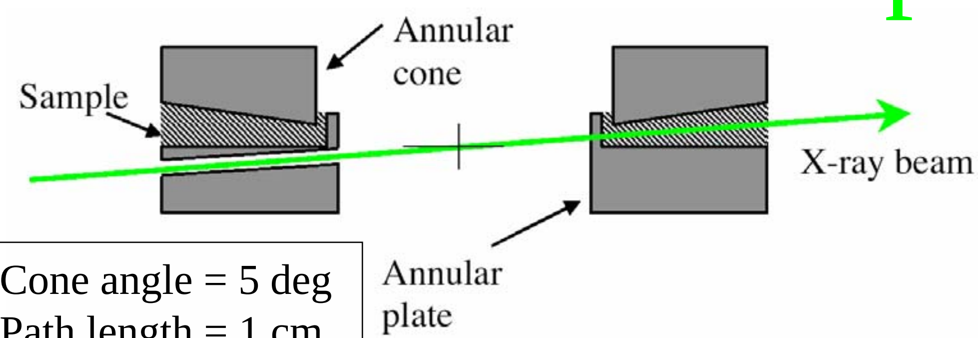
Linkam CSS-450 Shear Stage:



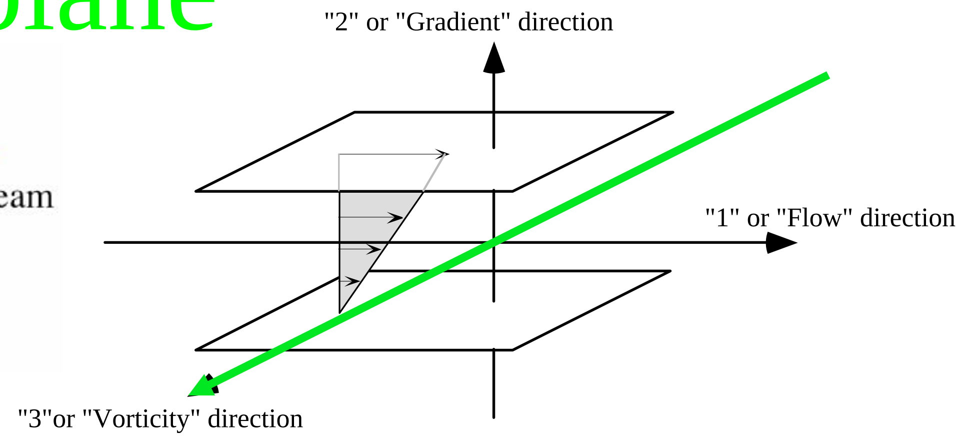


Ugaz & Burghardt, *Macromolecules*, **32**, 5581 (1998)

Annular cone & plate shear cell: 1-2 plane

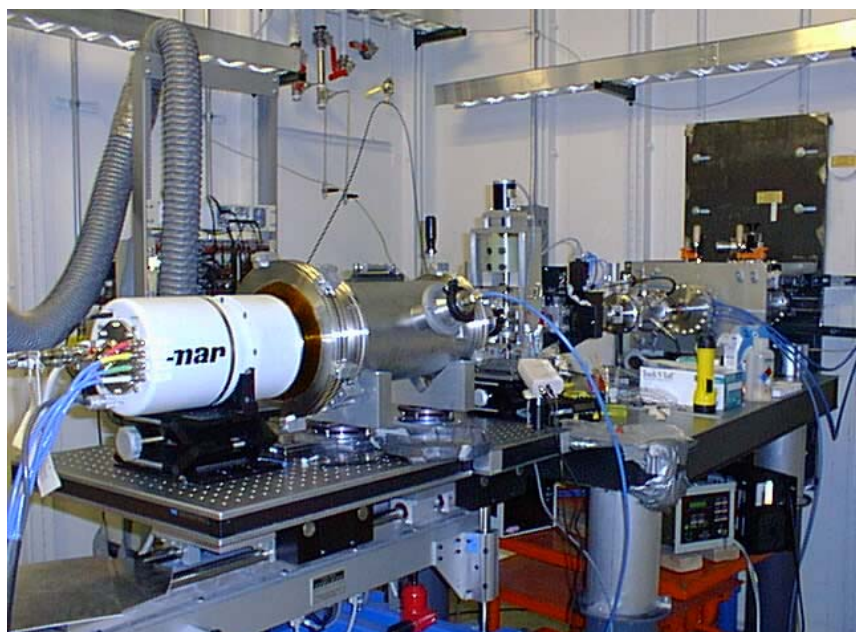


Cone angle = 5 deg
Path length = 1 cm



Shear cell:

Representative setup:



Caputo & Burghardt, *Macromolecules*, **34**, 6684 (2001).

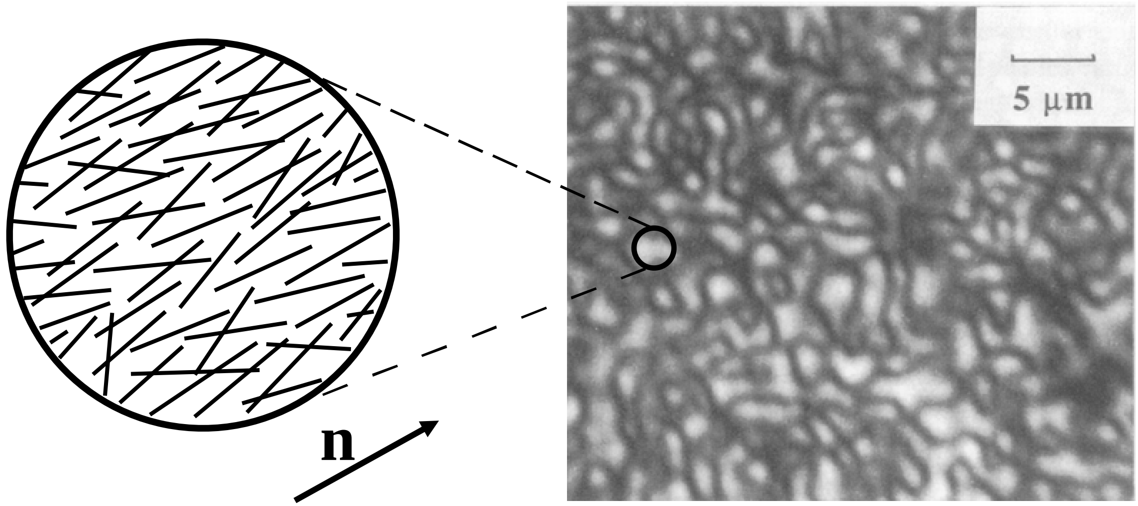
LCP Structure

(a) Microscopic

$\boldsymbol{u}$ = test molecule orientation

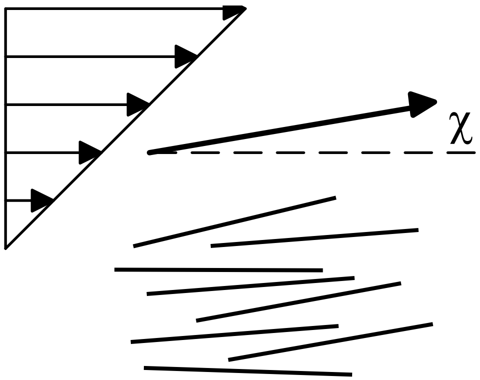
(b) Mesoscopic

$\boldsymbol{n}$ = director orientation

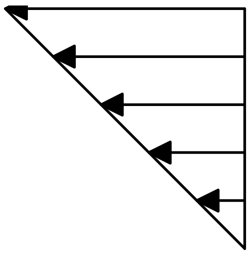


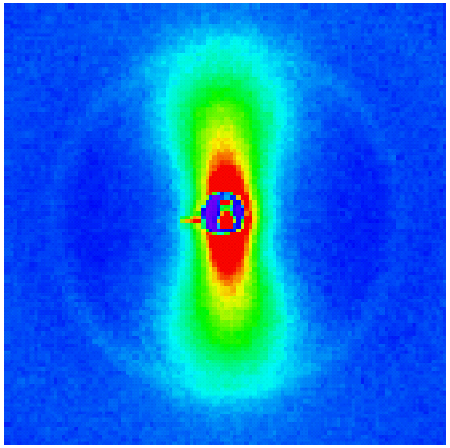
$\Psi(\boldsymbol{u})$	**Orientation Distribution Function**	$\bar{\Psi}(\boldsymbol{n})$
$\boldsymbol{S}_m = <\boldsymbol{uu}> - \boldsymbol{I}/3$	**Order Parameter Tensor**	$\bar{\boldsymbol{S}} = <\boldsymbol{nn}> - \boldsymbol{I}/3$
S_m	**Scalar Order Parameter**	$\bar{S}$

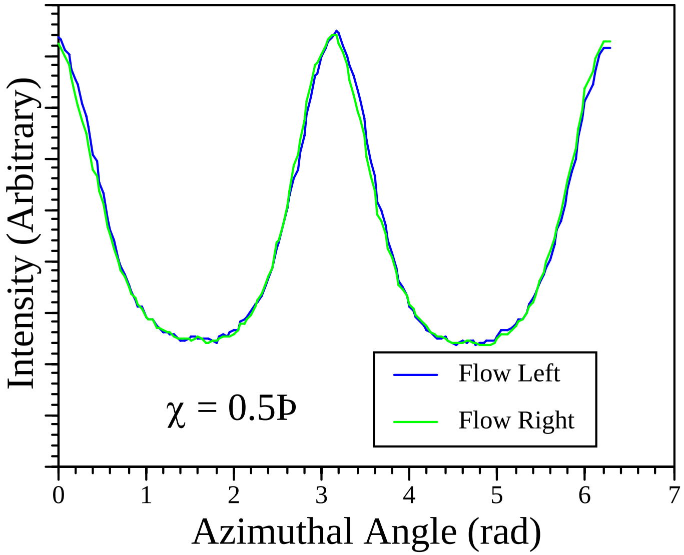
Lyotropic nematic PBG:
1-2 plane scattering patterns

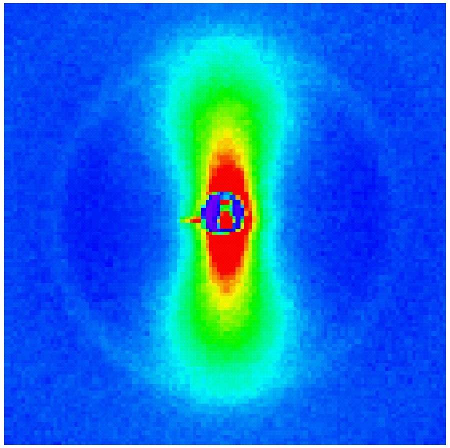


Shear Rate = 1 s^{-1}



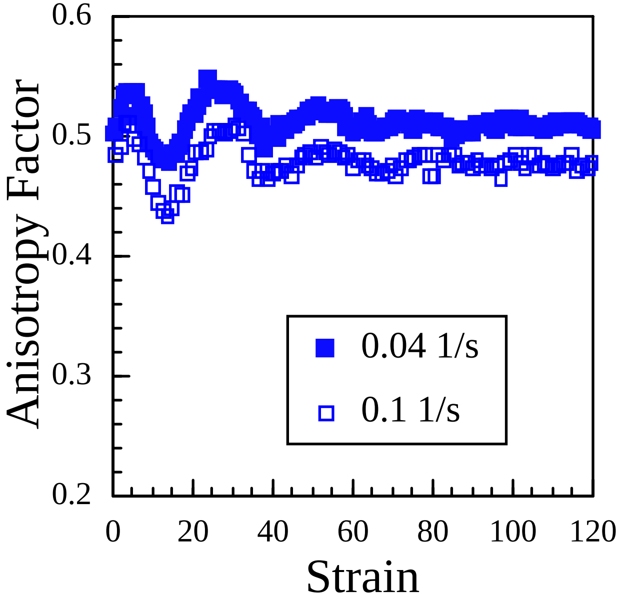


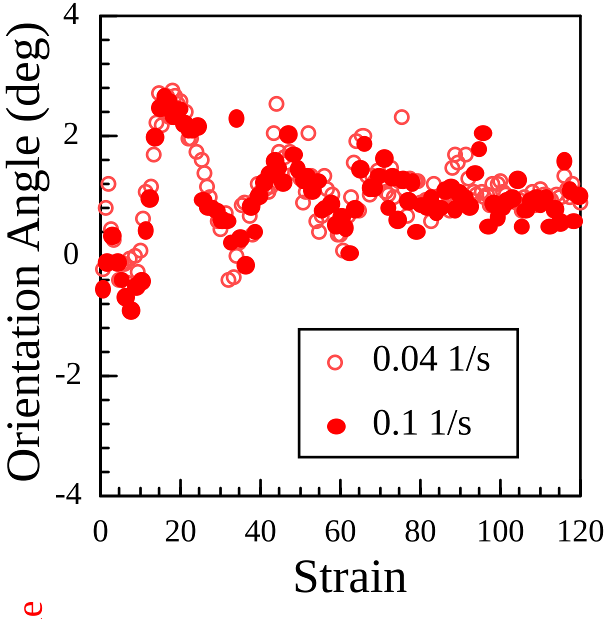


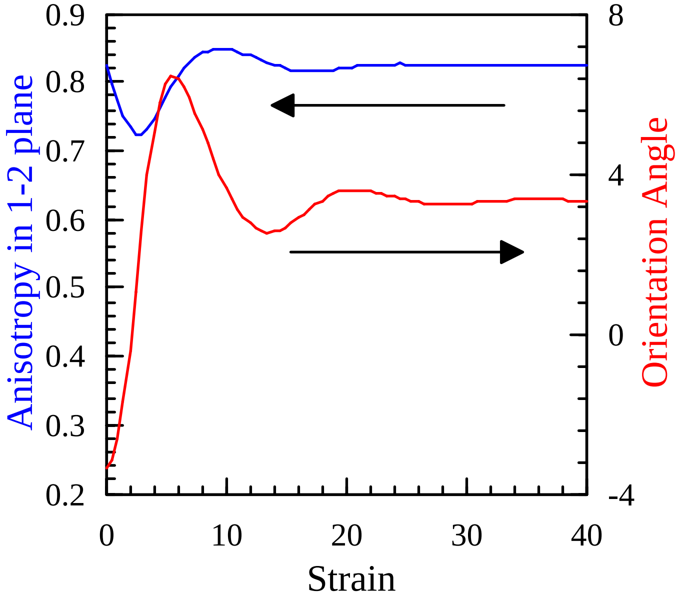


Caputo & Burghardt, *Macromolecules*, **34**, 6684 (2001).

PBG: Reversal in 1-2 Plane



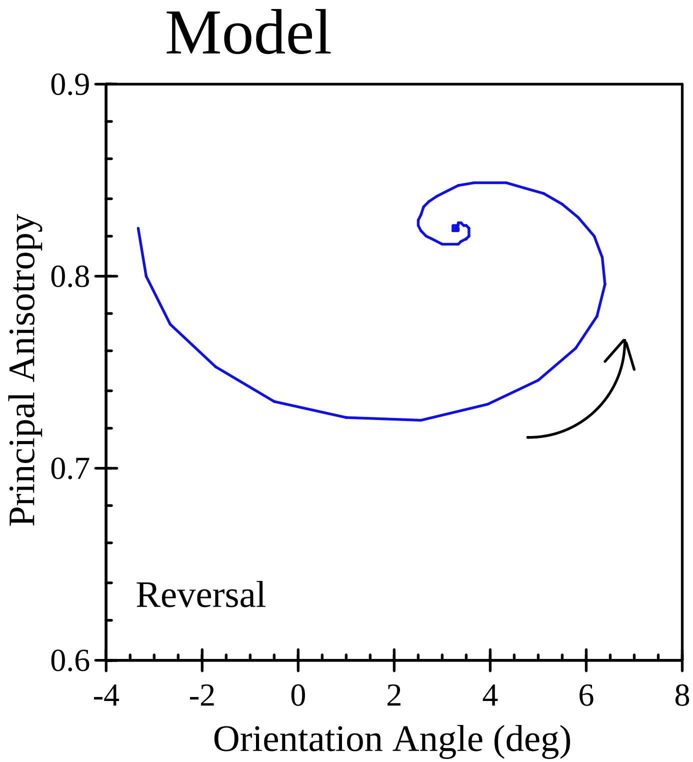


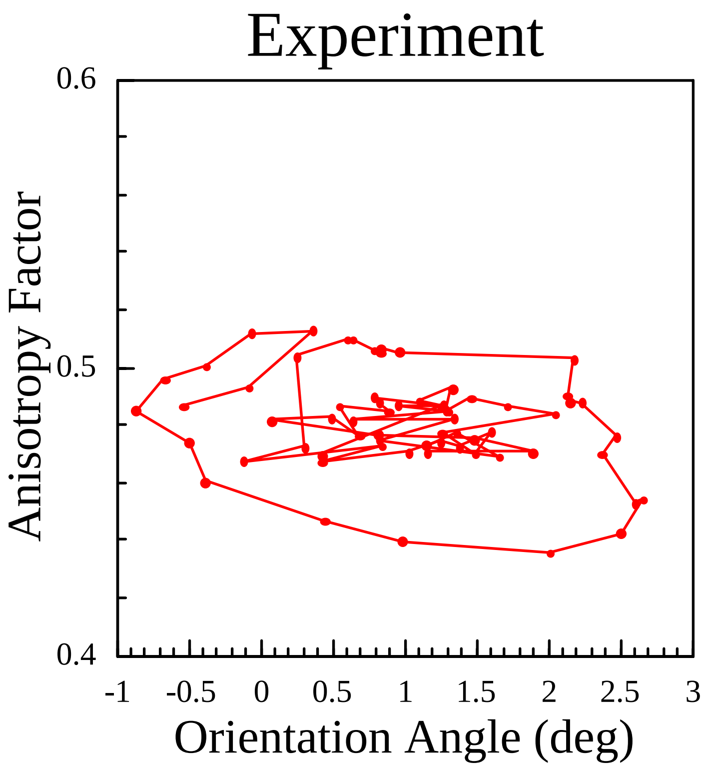


(Larson-Doi ‘tumbling polydomain’ model)

Caputo & Burghardt, *Macromolecules*, **34**, 6684 (2001).

Orientation 'Trajectories'

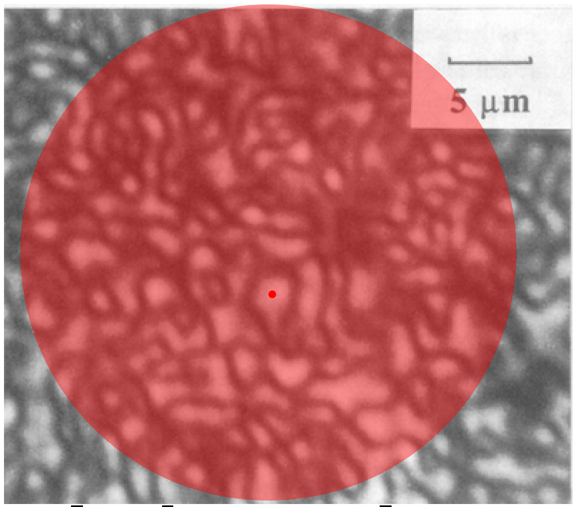




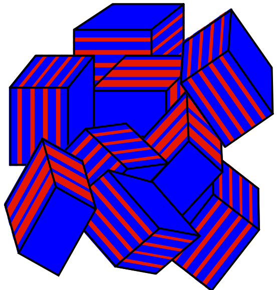
Caputo & Burghardt, *Macromolecules*, **34**, 6684 (2001).

ERL Idea #1

- Polydomain materials
  - LCPs



  - Block Copolymers

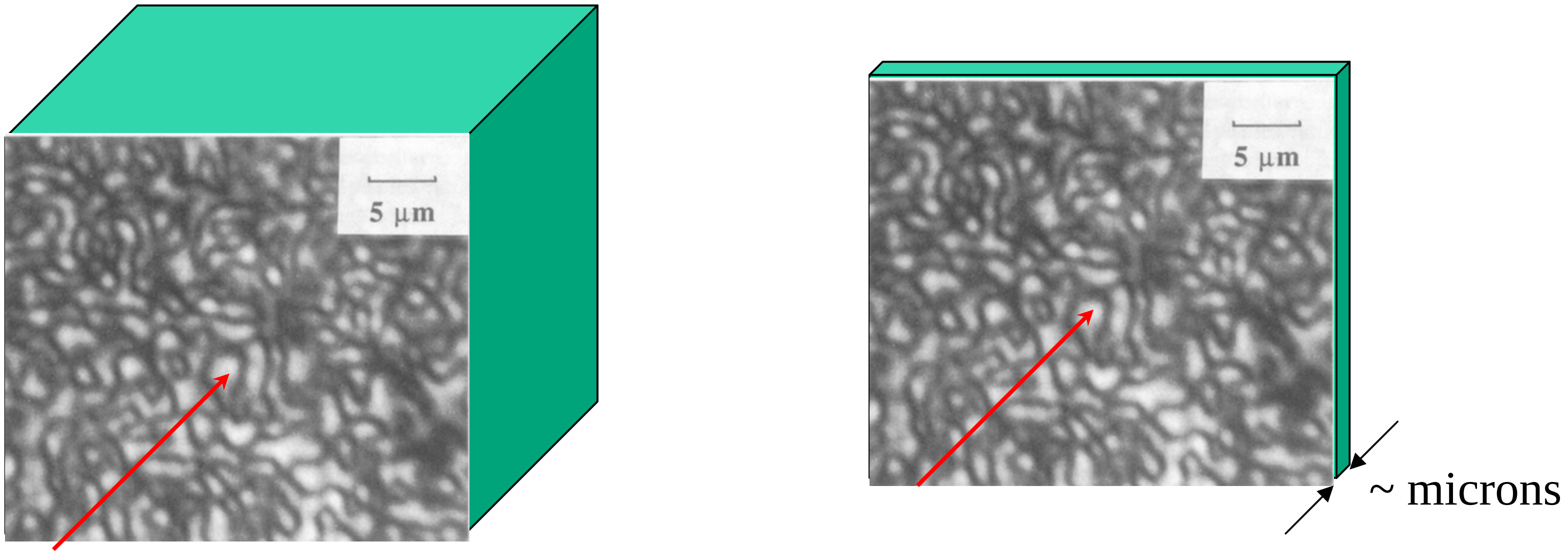


Large beams currently average over distribution of domain/grain orientations

Microfocus to enable 'single domain'measurements? During shear?

ERL Idea #1… Issues

- What about third dimension?



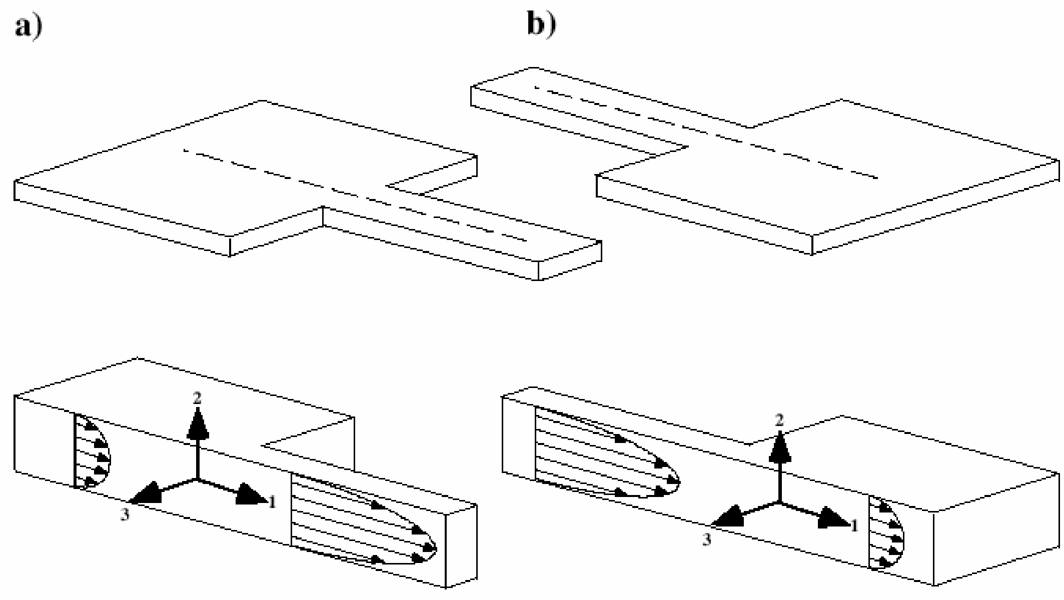
- Good opportunities for detailed mapping of domain/grain structure in thin samples (*e.g.* evolution during annealing)
- Possible *in situ* studies on thin *solids* during deformation?
- But, how to realize controlled flows on liquid samples?

Beyond shear: Complex channel flows

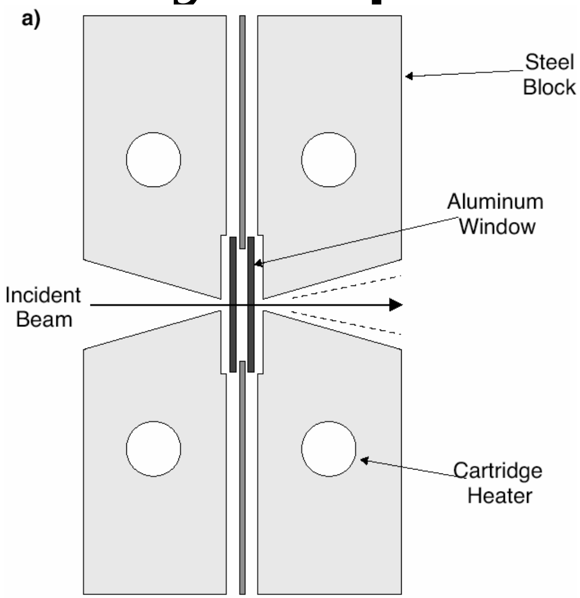
- Materials processing often involves mixtures of shear & extension

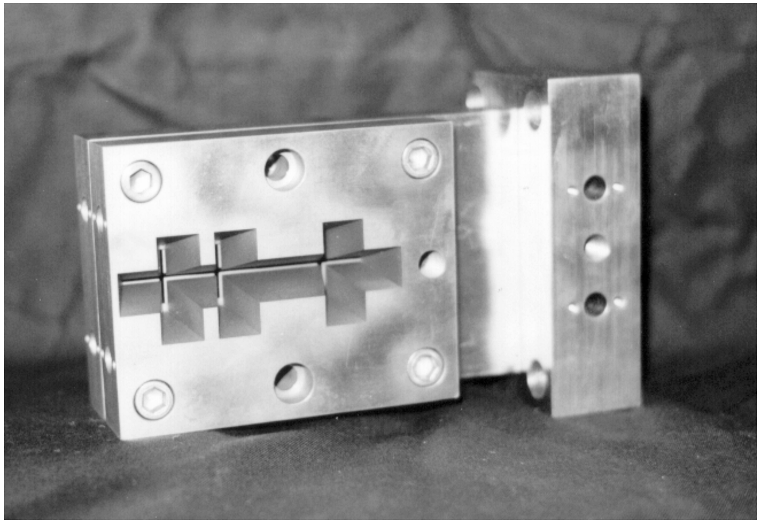
- Extension can be much more effective than shear at aligning fluid microstructure

- ‘Slit-contraction’ and ‘slit-expansion’ flows: superposition of stretching on otherwise inhomogeneous shear flow

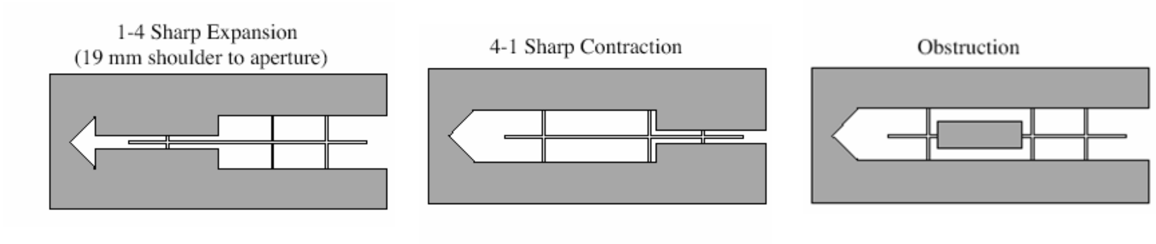


X-ray capable channel flow die



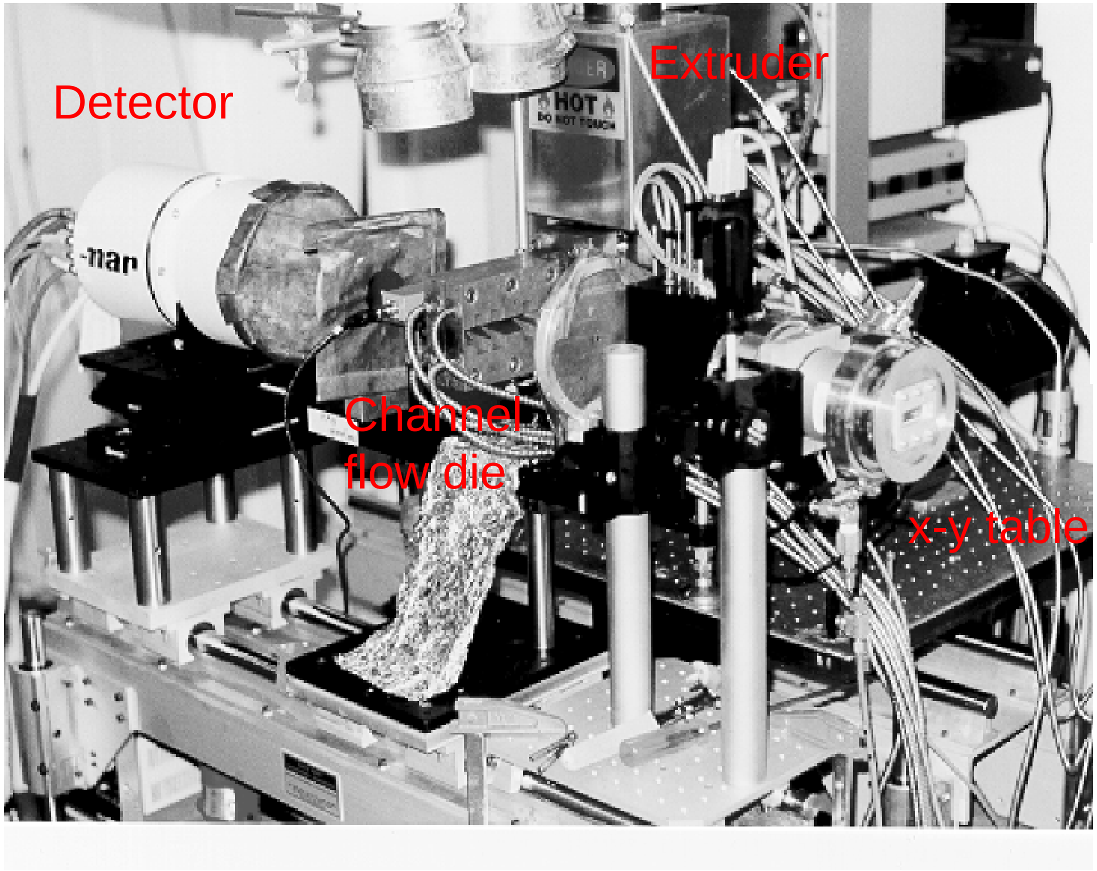


Interchangeable spacers define particular geometry:

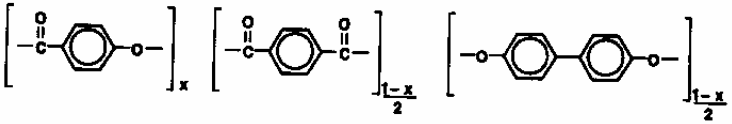


Cinader & Burghardt, *Macromolecules* **31**, 9099 (1998)

Typical experiment: Commercial LCP in channel flow



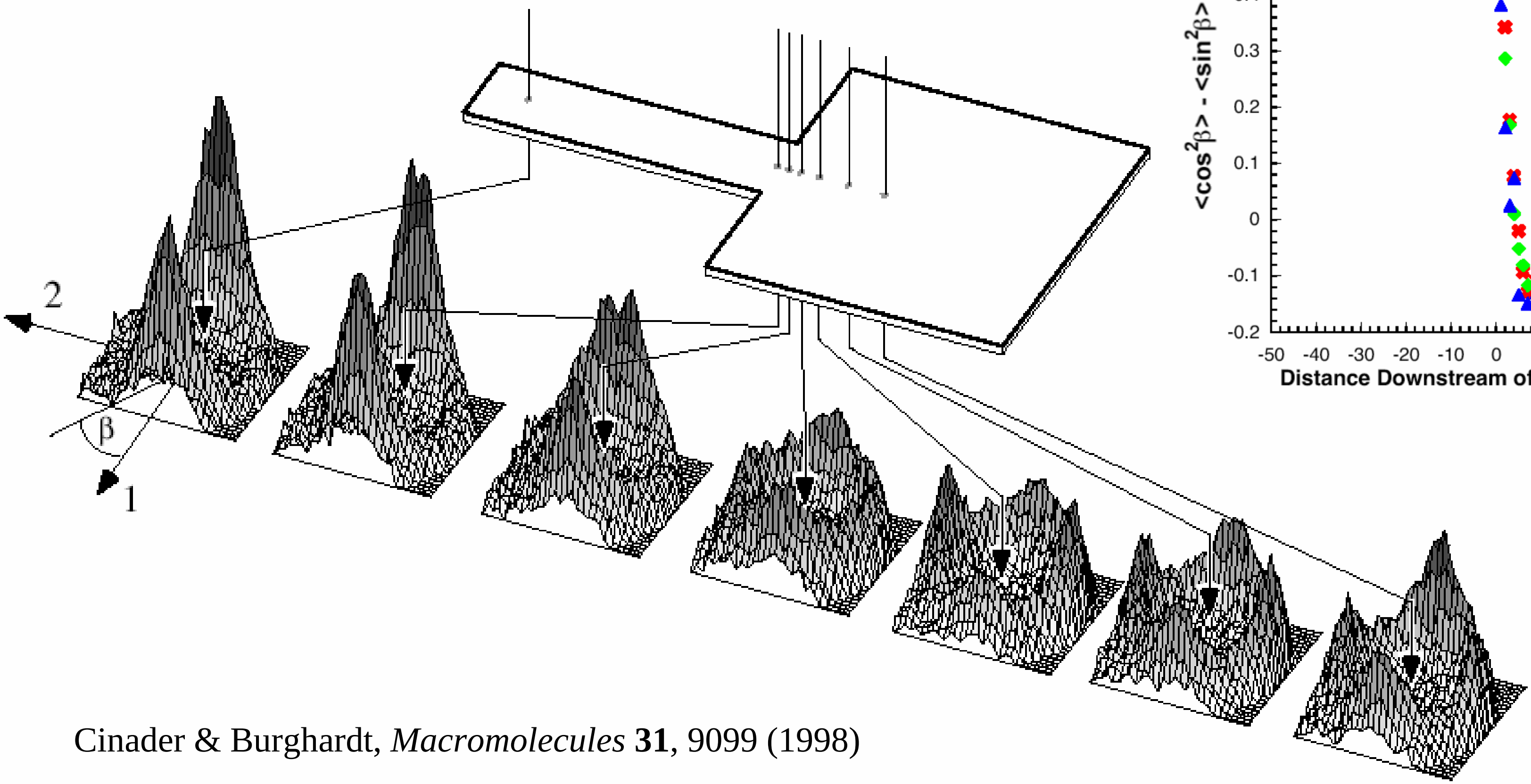
- Xydar commercial LCP

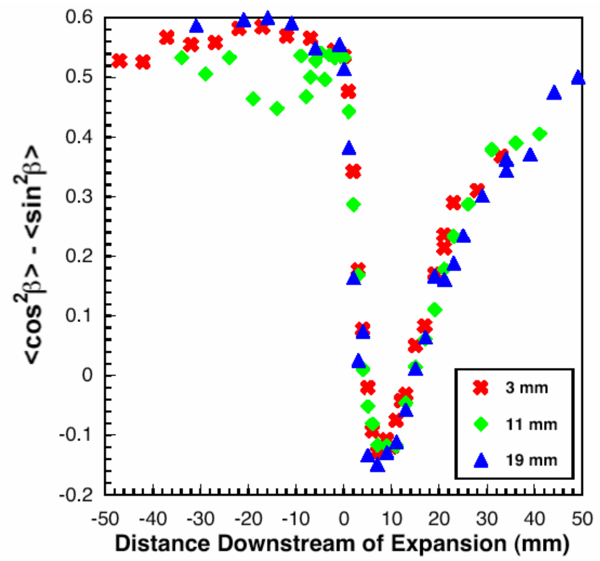


- Melt experiments at 350 C

Cinader & Burghardt, *Macromolecules* **31**, 9099 (1998)

1:4 slit-expansion flow: Bimodal orientation state





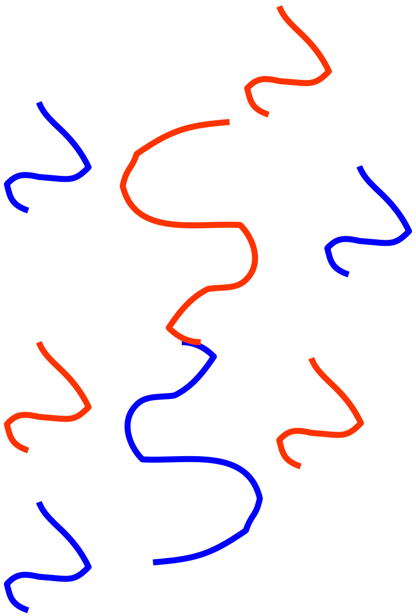
Cinader & Burghardt, *Macromolecules* **31**, 9099 (1998)

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?

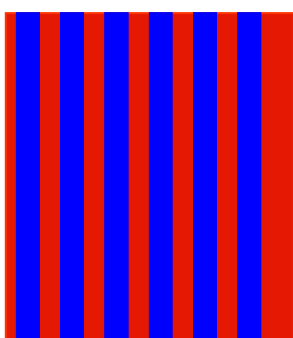
- Typical microfluidics… 10s of microns
- ERL microfocus… more than adequate (overkill?)
- Question: necessary to move towards ‘nanofluidics’ for interesting confinement effects?

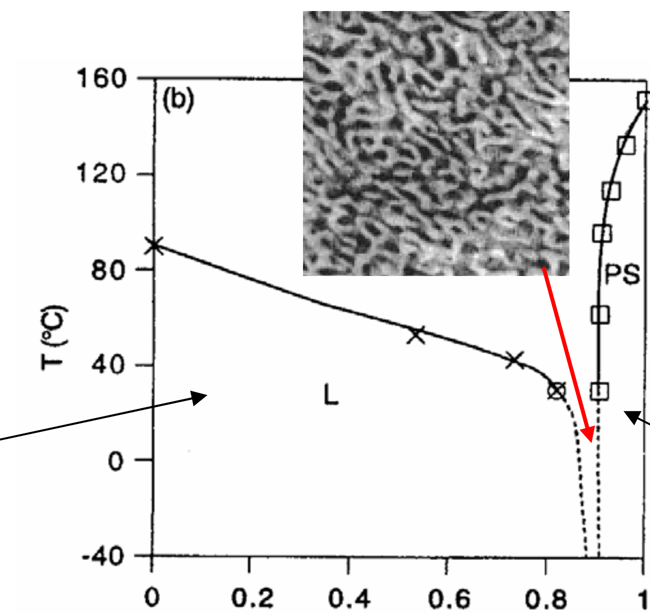
Polymer Bicontinuous Microemulsions



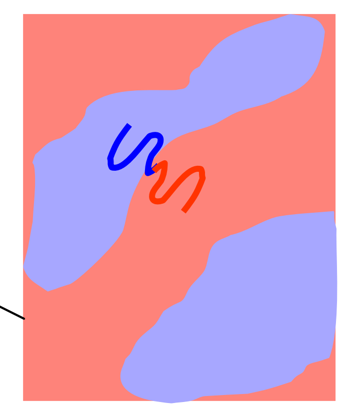
- Bates & Lodge, U. Minnesota
- Symmetric blends of immiscible linear homopolymers with corresponding diblock
- M_w adjusted so T_{ODT} of pure diblock ~ T_c of pure binary blend
- Typical isopleth phase diagram:

High BCP:



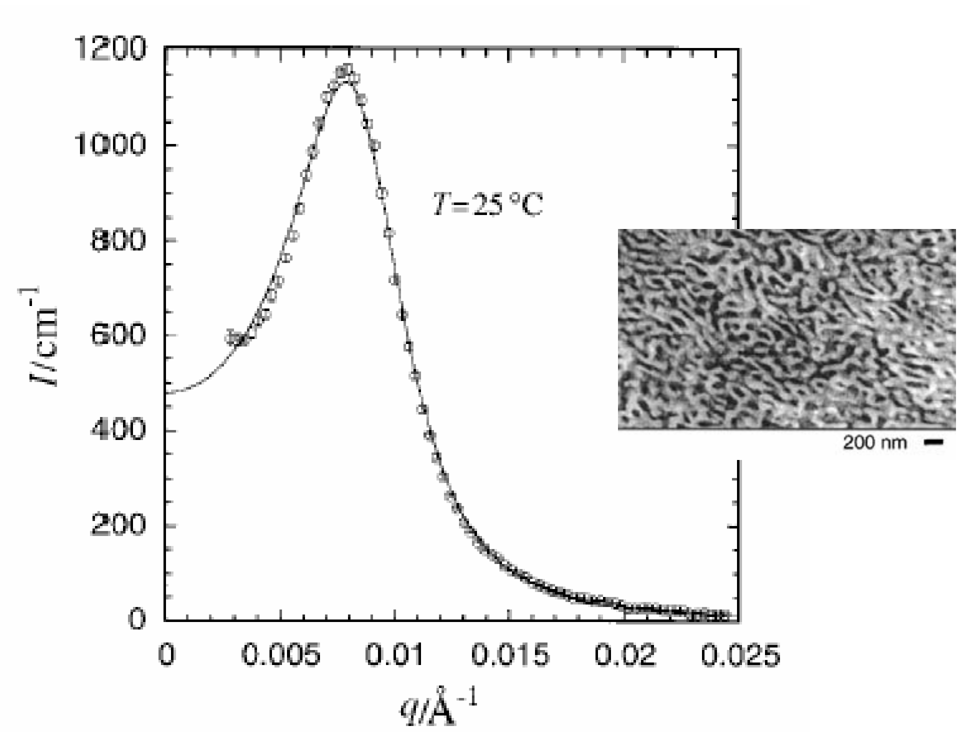


High homopolymer:



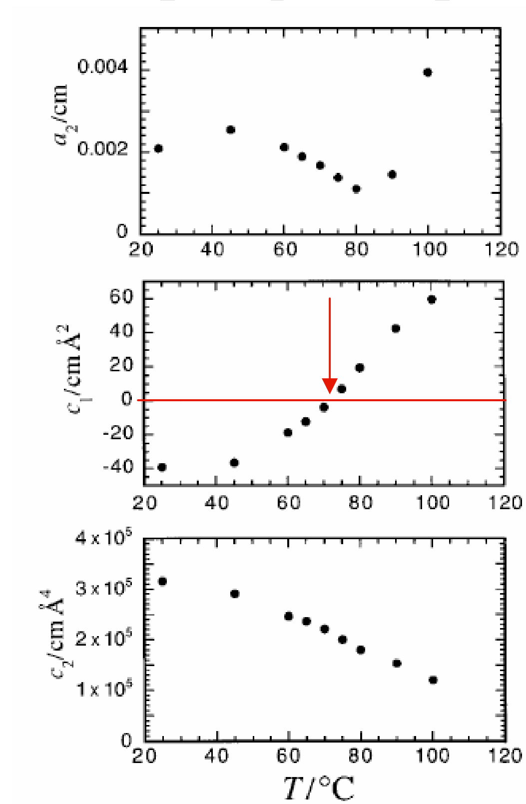
Quiescent neutron scattering

- 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)

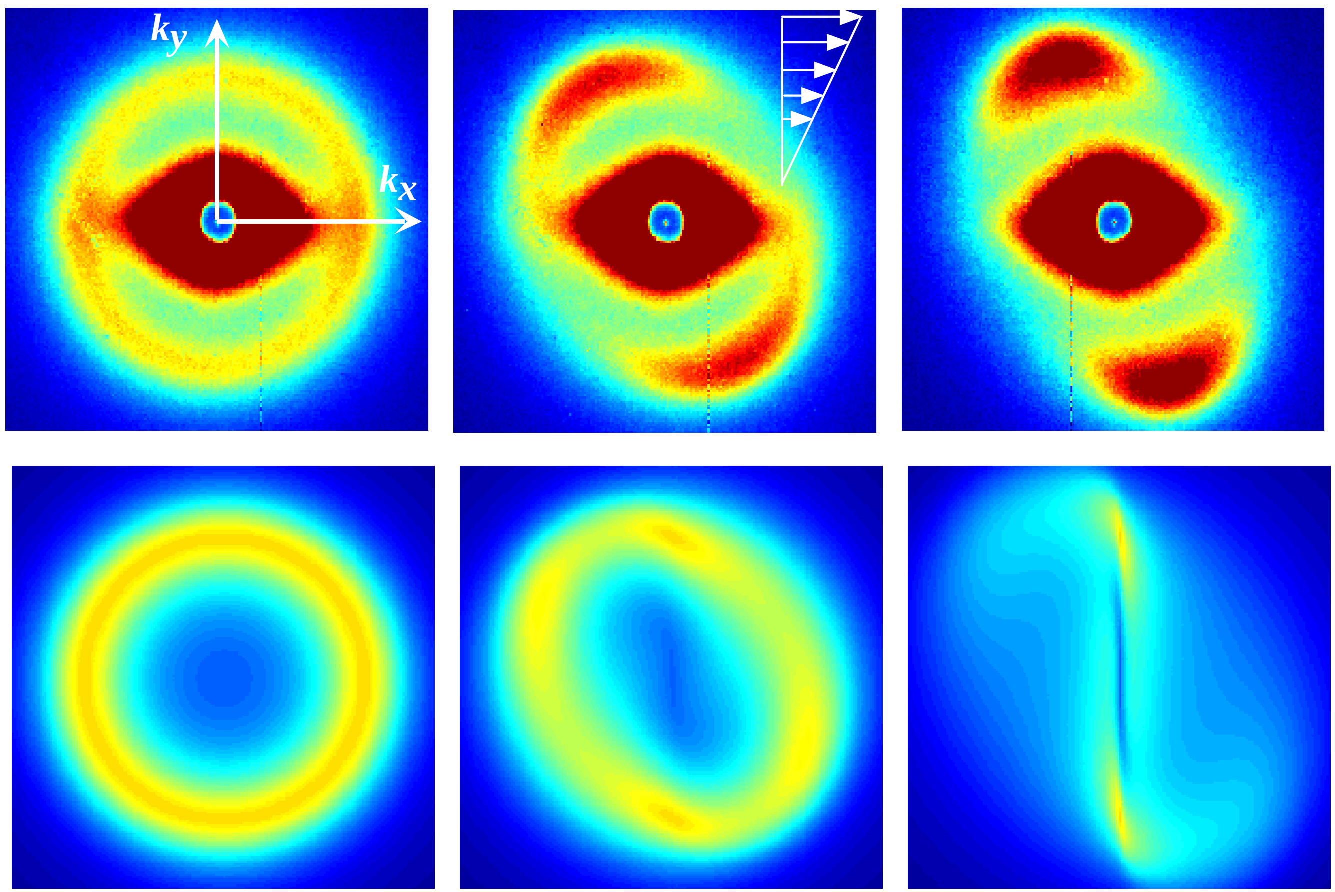
Steady shear: PEE-PDMS

Collaboration with T. P. Lodge & F. S. Bates, U. Minnesota

Caputo *et al.*, *Phys Rev. E*, **66**, 041401 (2002)

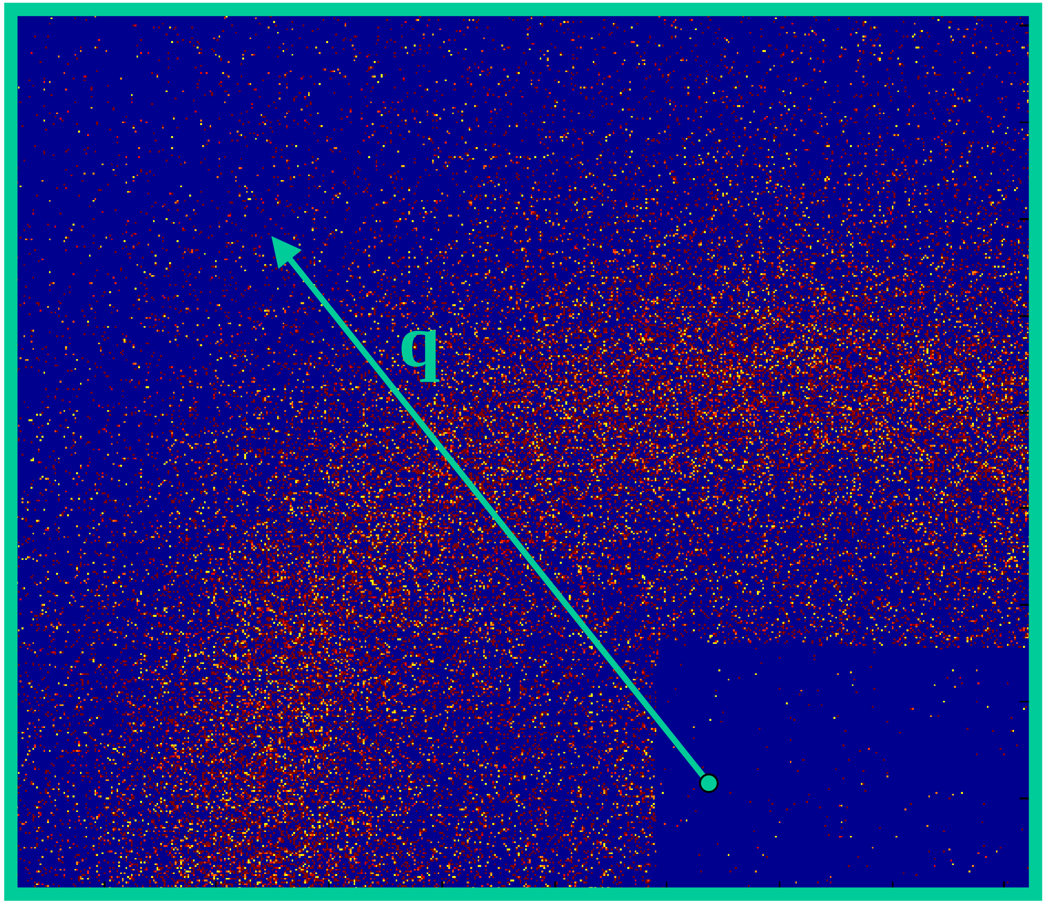
Experiment:

Model:



Model: Pätzold & Dawson, *Phys. Rev. E* **54**, 1669 (1996)

PS-PI Microemulsion:
X-ray Photon Correlation Spectroscopy



- Beamline 8-ID
- Simon Mochrie, Yale

Speckle pattern

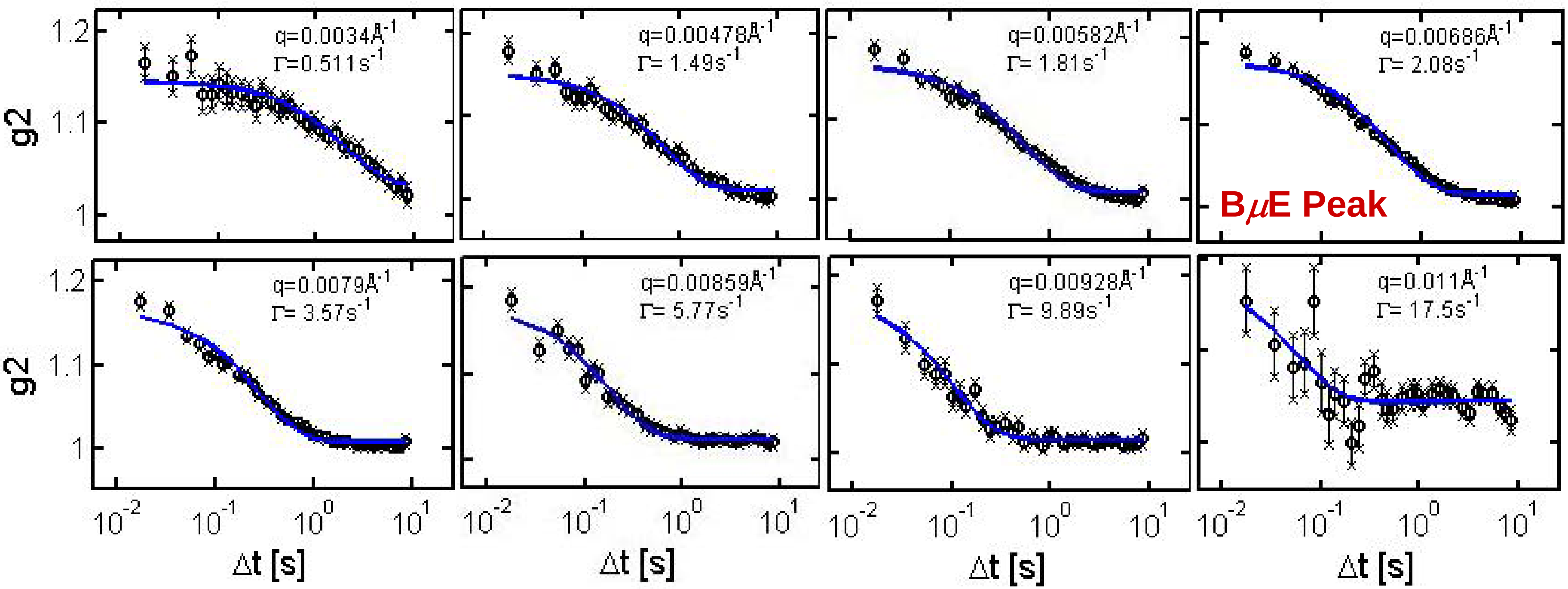
125˚C
17 ms exposure
850 images/series

$$g_2(\Delta t) = \frac{\langle I(t)I(t+\Delta t)\rangle}{\langle I(t)^2\rangle}$$

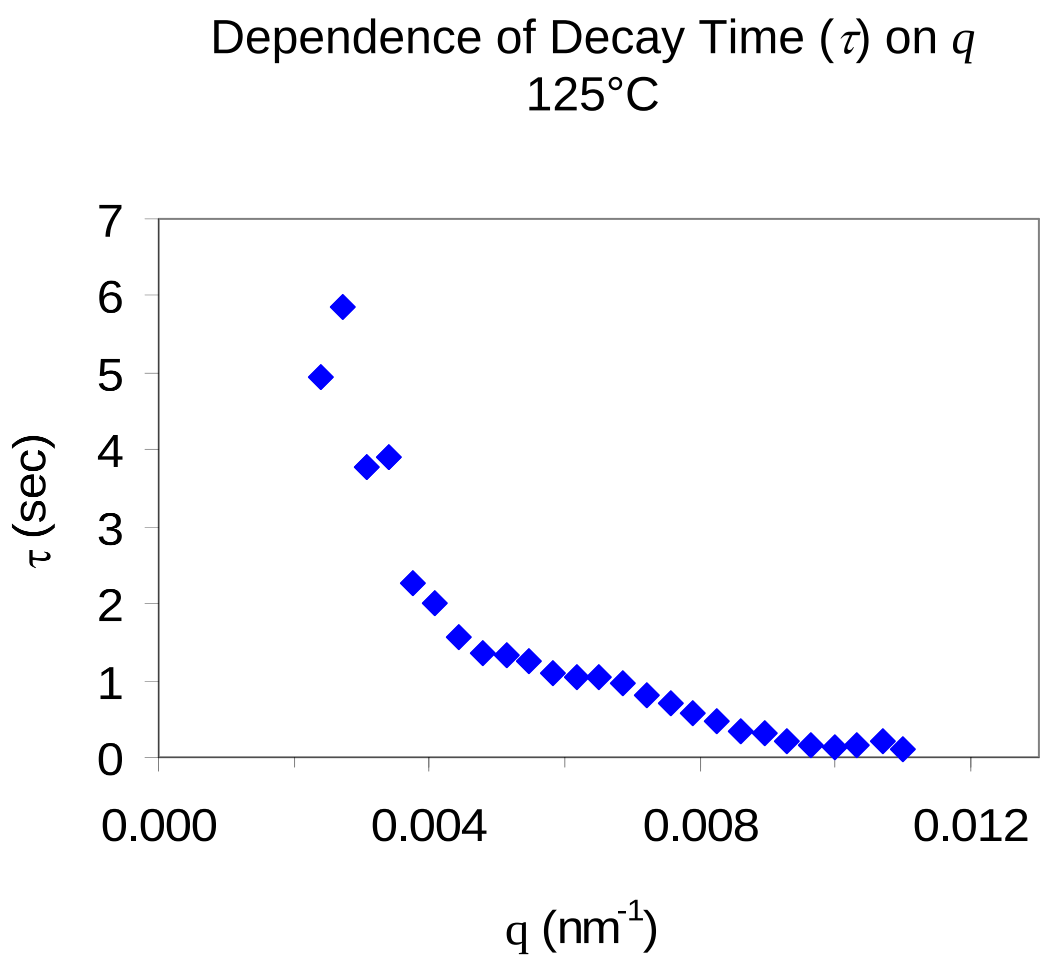
PS-PI Microemulsion:
X-ray Photon Correlation Spectroscopy

125˚C

Increasing *q*…



PS-PI Microemulsion: X-ray Photon Correlation Spectroscopy



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):

$$F_1(\mathbf{q},t) = \sum_{j=1}^{N} I_j \left\langle \exp\left\{i\mathbf{q}\cdot\left[\mathbf{r}_j(t)-\mathbf{r}_j(0)\right]\right\}\right\rangle = \sum_{j=1}^{N} I_j F_{sj}(\mathbf{q},t)$$

↕ Fourier transform pair

$$G_s(\mathbf{R},t) = \left\langle \delta(\mathbf{R} - \left[\mathbf{r}_j(t)-\mathbf{r}_j(0)\right]\right\rangle$$

(Probability of particle displacement **R** in time t)

With no flow, $G_s(\mathbf{R},t)$ satisfies diffusion equation…

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

Fourier transformation & solution gives:

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

Thus…

$$F_1(\mathbf{q},t) \sim \exp(-q^2 Dt)$$ (Heterodyne)

$$F_2(\mathbf{q},t) = \left|F_1(\mathbf{q},t)\right|^2 \sim \exp(-2q^2 Dt)$$ (Homodyne)

Added Flow…

$G_s(\mathbf{R},t)$ now satisfies *convection*-diffusion equation…

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

For small scattering volume, linearize velocity field:

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

Mean velocity

Velocity *gradient* tensor

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

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

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

(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.

Fuller & Leal, *JFM* **100**, 555-575 (1980):

$$F_2(\mathbf{q},t) = \left| \int d\mathbf{R} I(\mathbf{R}) \exp\{-i\mathbf{q}\cdot\mathbf{\Gamma}\cdot\mathbf{R}t\} \right|^2$$

Beam intensity profile

Select various 'projections' of Γ depending on scattering geometry.

Correlation function shows *Gaussian* decay:

$$F_2(\mathbf{q},t) \sim \exp(-q^2\gamma^2 L^2 t^2)$$

γ = characteristic deformation rate
L = length scale of scattering volume

Allows measurement of velocity gradients provided…

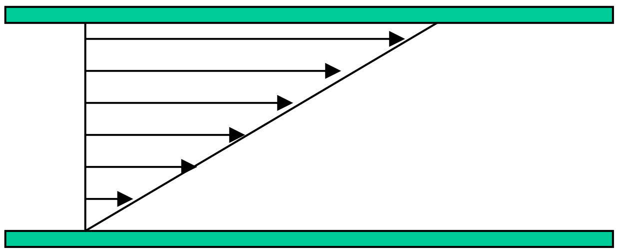
$$\tau_\gamma = \frac{1}{q\gamma L} << \tau_D = \frac{1}{q^2 D}$$

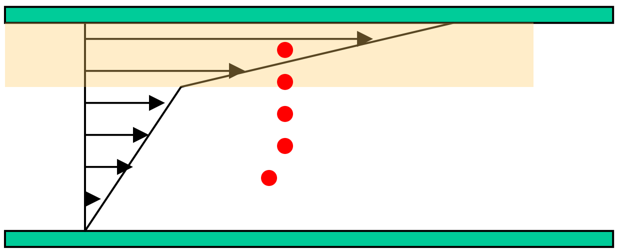
(Note, as $q \to 0$, convection always dominates over diffusion, and will set time scale for decay of correlation function.)

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 nm^{-1} (typical SAXS)…

<u>L = 100 μ</u>

$\gamma = 1\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-4}\ \mathrm{s}$

$\gamma = 100\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-6}\ \mathrm{s}$

<u>L = 10 μ</u>

$\gamma = 1\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-3}\ \mathrm{s}$

$\gamma = 100\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-5}\ \mathrm{s}$

<u>L = 1 μ</u>

$\gamma = 1\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-2}\ \mathrm{s}$

$\gamma = 100\ \mathrm{s}^{-1},\ \tau_\gamma = 10^{-4}\ \mathrm{s}$

<u>Competing objectives…</u>
- want faster than intrinsic sample dynamics
- want high spatial resolution
- require coherence

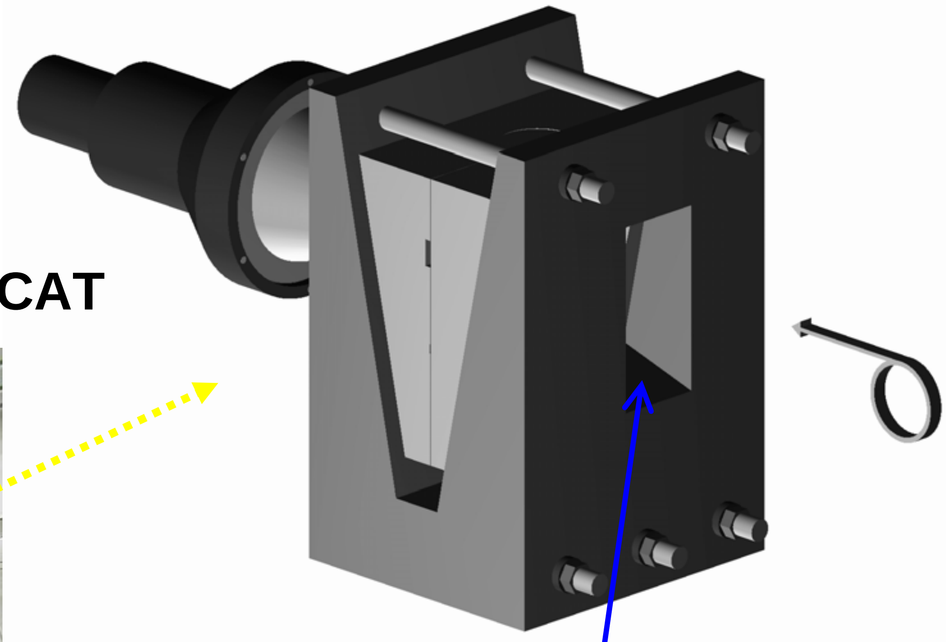
<u>Unknowns…</u>
Maximum time resolution for XPCS? (detectors?) Effect of elongated scattering volume? If coherence imperfect, does coherence length replace L?

Summary

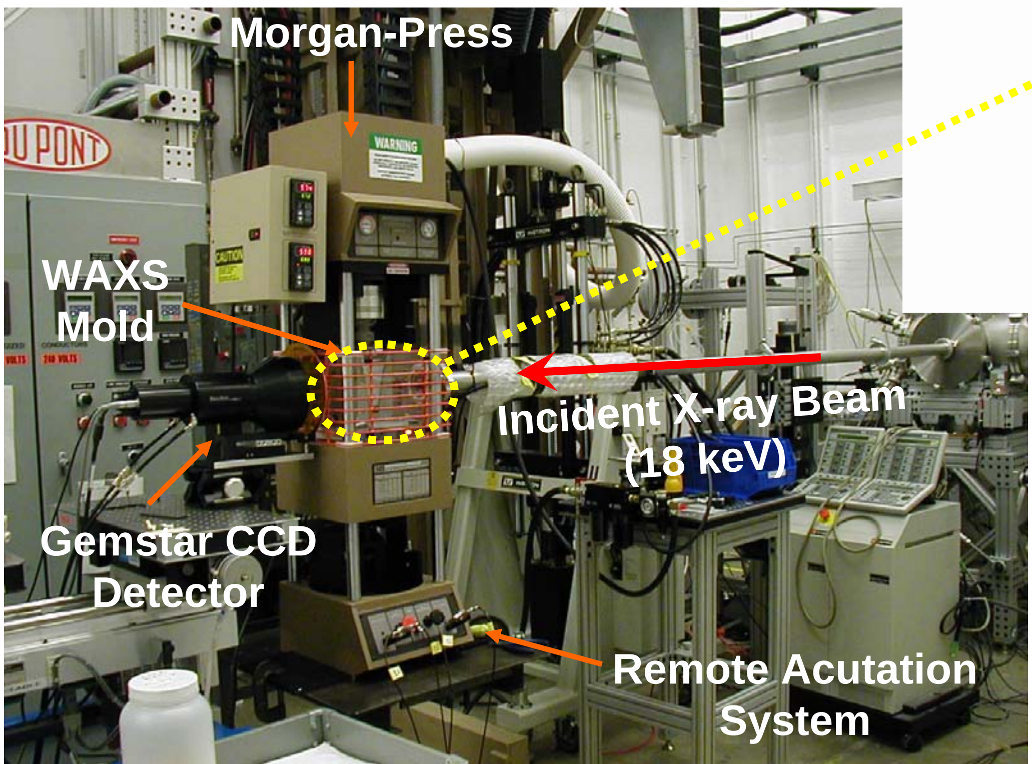
- *In situ* synchrotron scattering during flow yields detailed insights into microscopic origins of rheological properties of complex fluids
- Ideas…
  - Microfocus… single ‘domain’ dynamics?
    - Hard for flow…
  - Microfocus + microfluidics + complex fluids?
    - Should work; already possible?
  - Coherent scattering during flow?
    - Access to local velocity gradients from homodyne spectrum…
    - Many questions…

Real processing: *In situ* injection molding

WAXS Mold + Detector
(*Close up*)



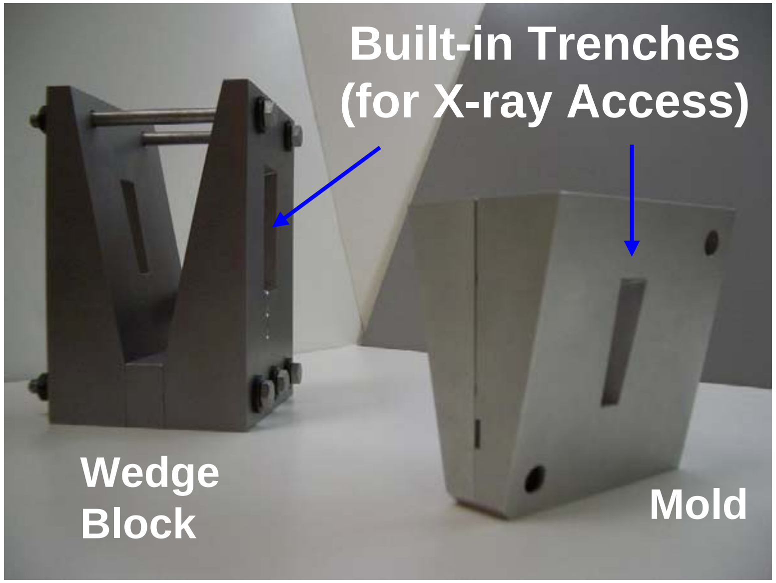
Undulator Beamline 5ID-D of DND-CAT

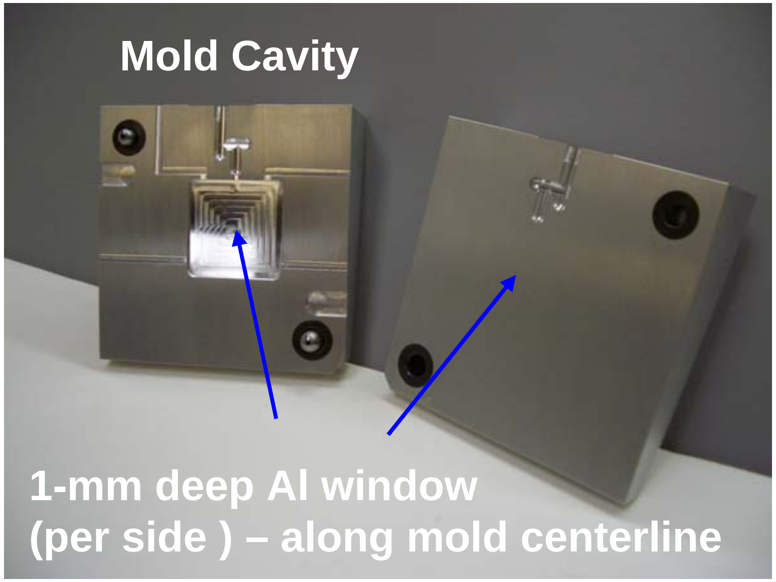


- 16^o trenches (on both the mold and wedge block) allow for scattered X-rays to readily exit the mold

Rendon & Burghardt, in preparation (2006)

Injection mold details

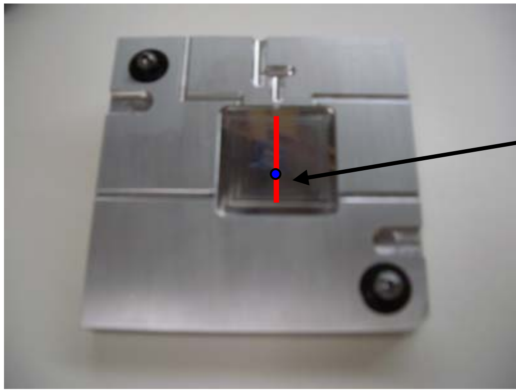




Assembled X-ray Mold
& Wedge Block
(side view)

Tie Bars

Representative experiment: Injection molding of Vectra A®



<u>Location along mold</u>:
23 mm away from die entrance

QuickTime™ and a
decompressor
are needed to see this picture.

Filling Direction

<u>Molding Parameters</u>:

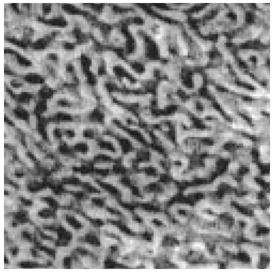
Fill time = 4 sec
T_{melt} = 285 ^oC
T_{nozzle} = 300 ^oC
T_{mold} = 90 ^oC

Data acquisition rate: 12 frames/sec
Video clip slowed down by factor of 2.4

Rendon & Burghardt, in preparation (2006)

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