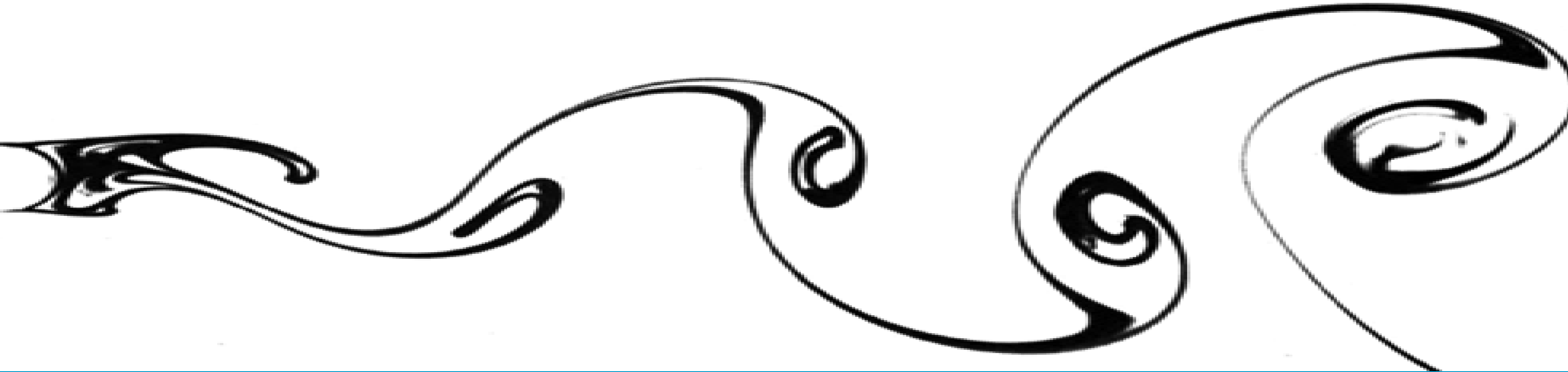

SANS Under Deformation and Flow: Principles and Measurements

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NCNR Summer School
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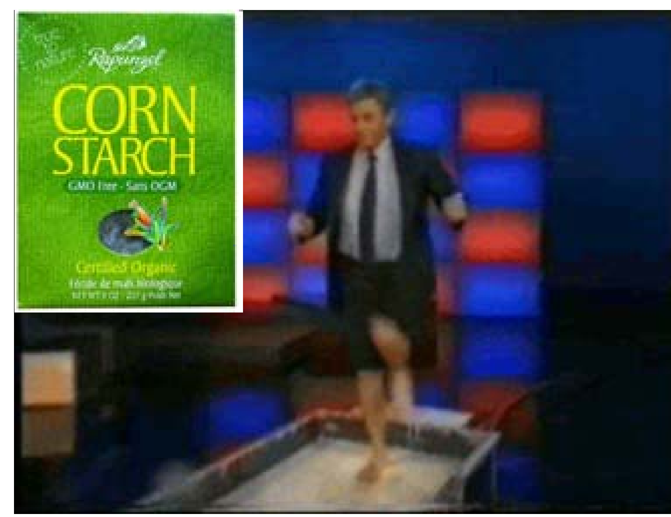
Why study microstructure under flow?

- Deformation changes microstructure
  - Many materials undergo drastic, sometimes irreversible changes when subjected to flow
  - Most "real world" materials are processed using flow, which can affect final material properties

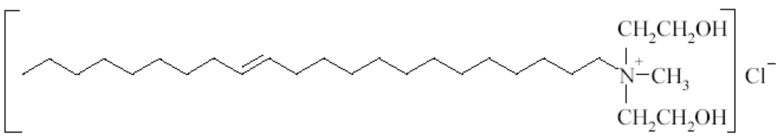
- Microstructure determines how a material will respond to mechanical force
  - Critical for design of process equipment
  - Many complex structured fluids do unexpected things when subjected to different types of flow…



Why study microstructure under flow?

- Example 2: shear-induced phase separation of surfactant solutions (Courtesy Matthew Liberatore, Colorado School of Mines)

Cationic Surfactant (EHAC):



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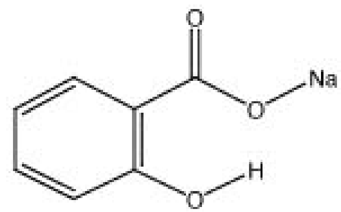
Salt (NaSal):



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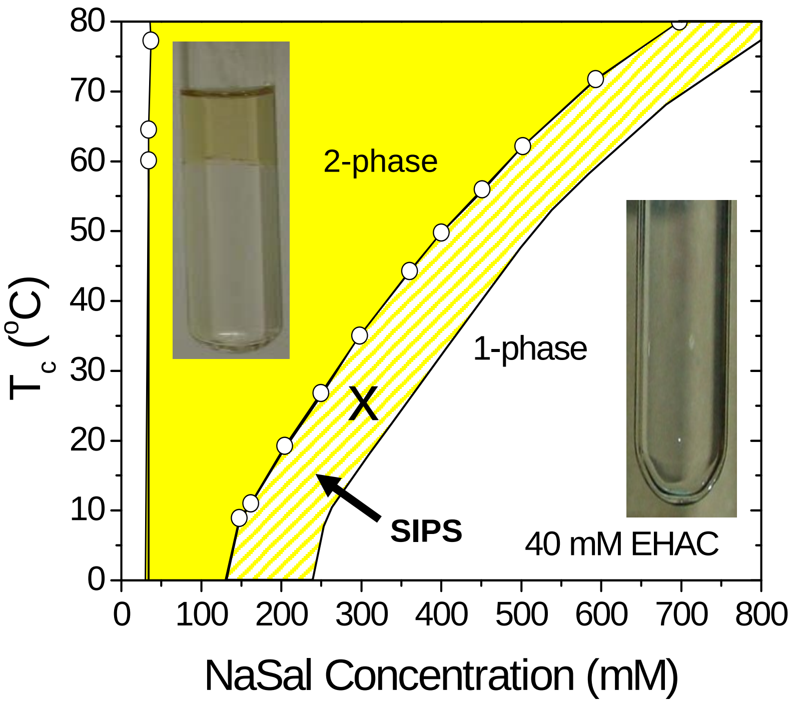
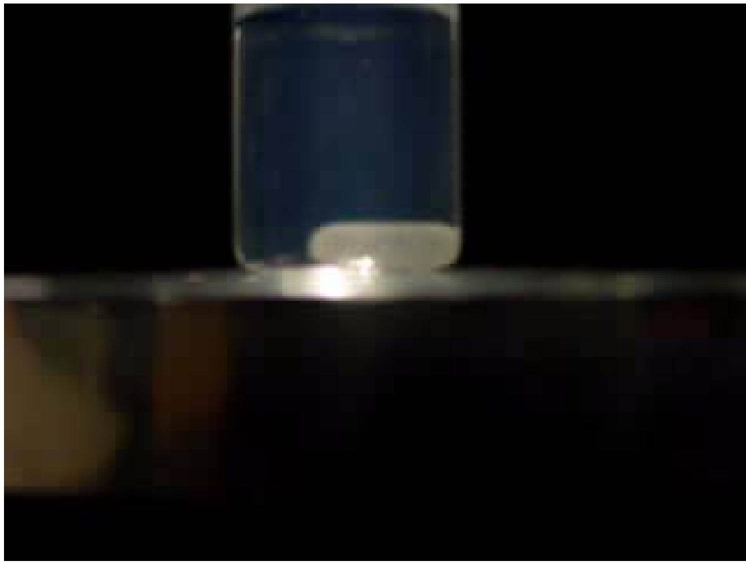
Wormlike micelles



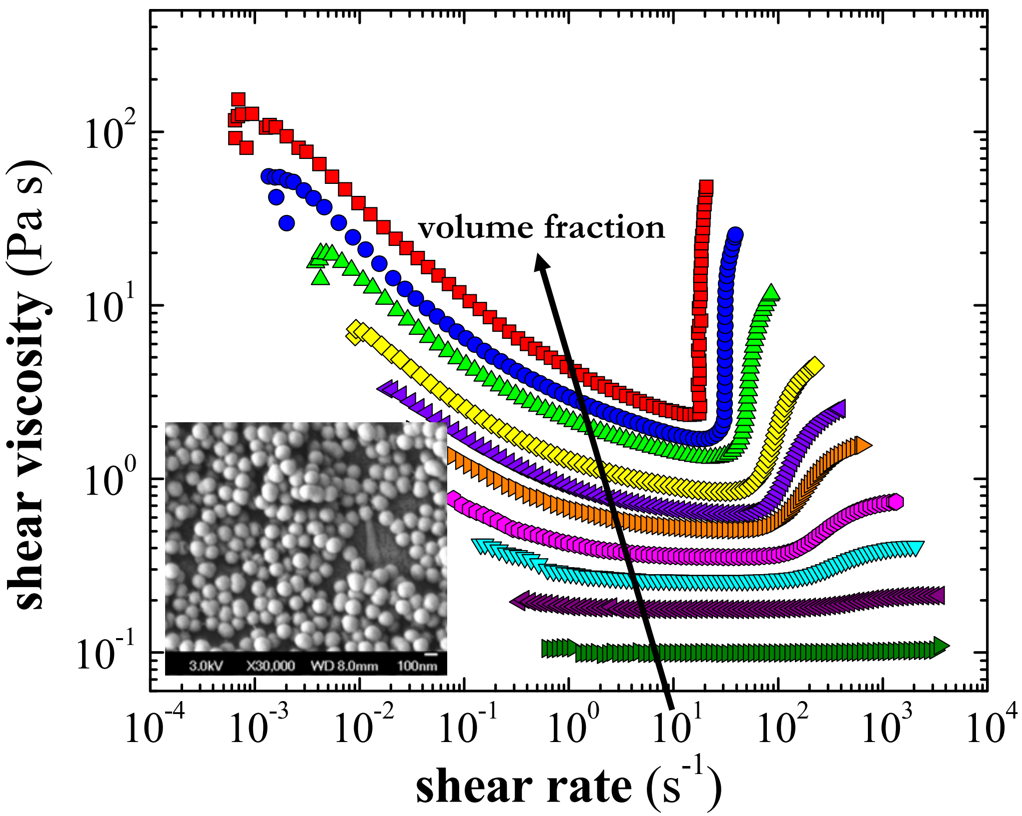
30 mM EHAC, 300 mM NaSal



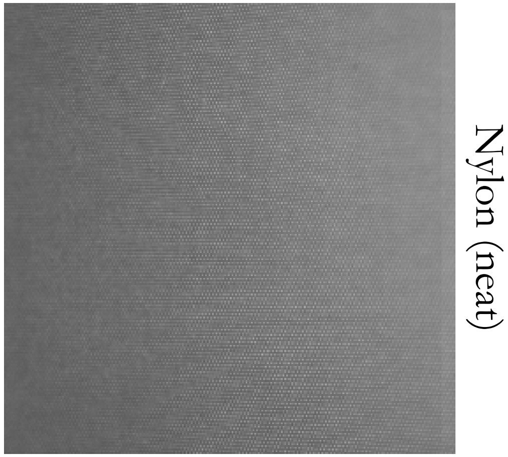
Why study microstructure under flow?

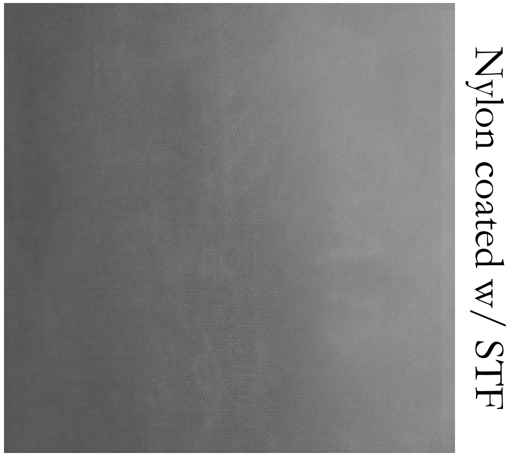
- Example 3: shear thickening in concentrated suspensions (courtesy Norm Wagner, University of Delaware)

SiO_2 spheres (a~120 nm) in PEG/EG



Ballistic impact ~300 m/s



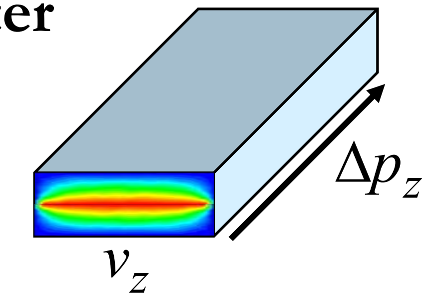


Outline

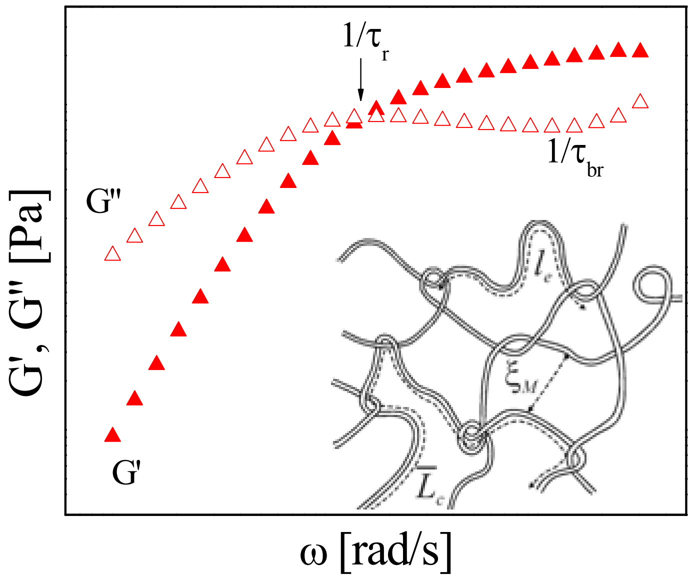
- **Rheology: a (brief) introduction**
- Measuring SANS under flow
- Scattering from flowing systems
- Practical applications

A 6-slide crash course in rheology…

- **Rheology: the study of deformation and flow of matter**
  - Rheology is an engineering tool: $$\rho \frac{D\mathbf{v}}{Dt} = \nabla p + \nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g}$$



  - Rheology is a spectroscopic method:



Objective: to understand the flow properties and behavior of complex fluids in terms of their microstructure.

- Gives insight into the physics of the fluid
- Informs engineering and decision making in material formulation and processing

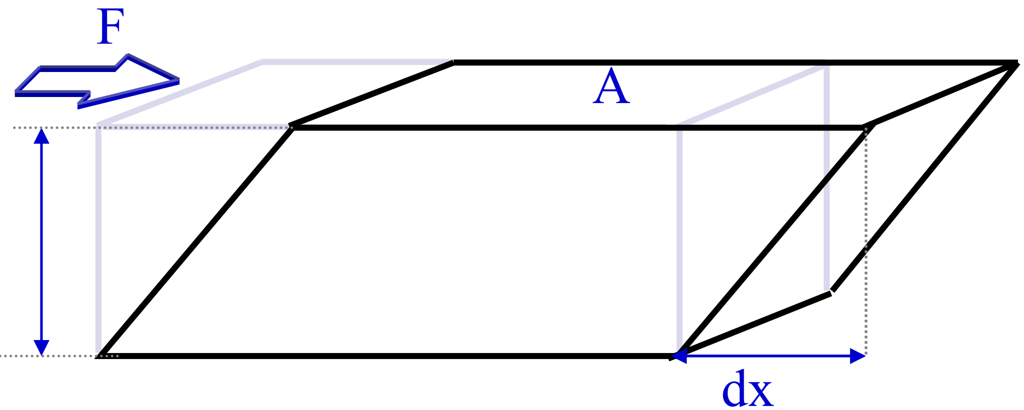
Describing deformation and stress

- The deformation tensor:

$$\mathbf{D} = \frac{1}{2}\left(\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}\right)$$

- The stress tensor:

$$\mathbf{T} = p\mathbf{I} + \boldsymbol{\tau}$$



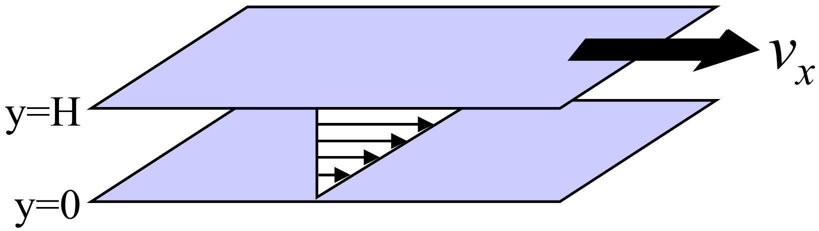
stress: $\mathrm{T} = \frac{F}{A}$ strain: $\gamma = \frac{dx}{dy}$

- A primary goal of rheology is to determine the relationship between deformation and stress within a material (the **constitutive equation**)

$$\boldsymbol{\tau} = f(\mathbf{D})$$

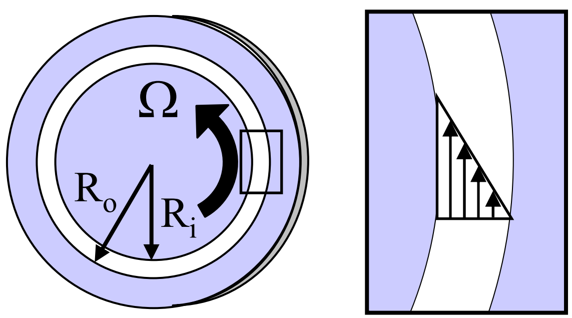
- Rheological measurements are typically performed in simple, **rheometric flows** where the **D** can be drastically simplified

- Sliding plates (planar drag):



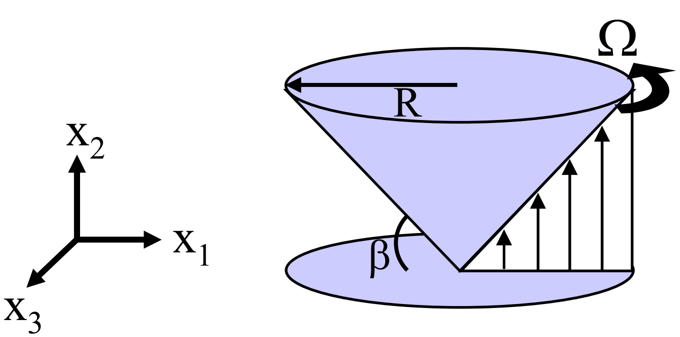
$$\dot{\mathbf{D}} = \begin{bmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \; \boldsymbol{\tau} = \begin{bmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{12} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}$$

- Concentric cylinders (Taylor-Couette):



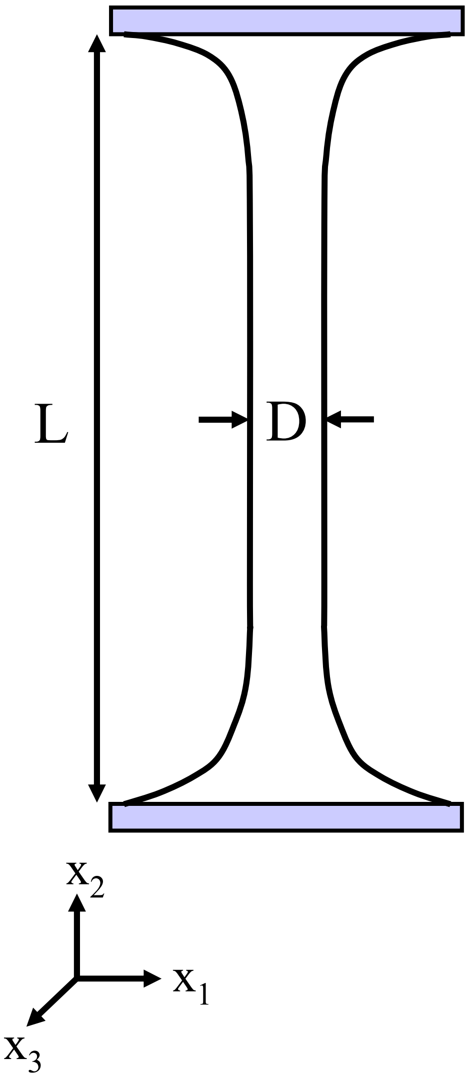
Geometry	$\{x_1, x_2, x_3\}$	Shear rate, $\dot{\gamma}$
Sliding plates	x, y, z	$\frac{v_x}{H}$
Couette	r, θ, z	$\frac{2\Omega}{1-(R_i/R_0)^2}$
Cone and plate	r, θ, ϕ	$\frac{\Omega}{\beta}$

- Cone and plate:



Rheometric flows: extensional deformation

- Filament stretching: (uniaxial extension)

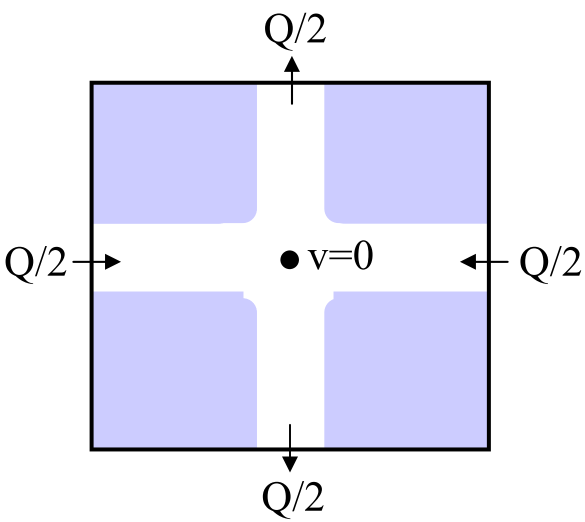


$$\dot{\mathbf{D}} = \begin{bmatrix} -\dot{\varepsilon} & 0 & 0 \\ 0 & -a\dot{\varepsilon} & 0 \\ 0 & 0 & (b+1)\dot{\varepsilon} \end{bmatrix}; \quad \boldsymbol{\tau} = \begin{bmatrix} \tau_{11} & 0 & 0 \\ 0 & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{bmatrix}$$

Geometry	**$\{x_1, x_2, x_3\}$**	**a, b**	**Extension rate, $\dot{\varepsilon}$**
Uniaxial	z, r, θ	1, 1	$\frac{d \ln L}{dt}$
Cross-slot	x, y, z	-1, -1	$\frac{Q}{D^2 H}$

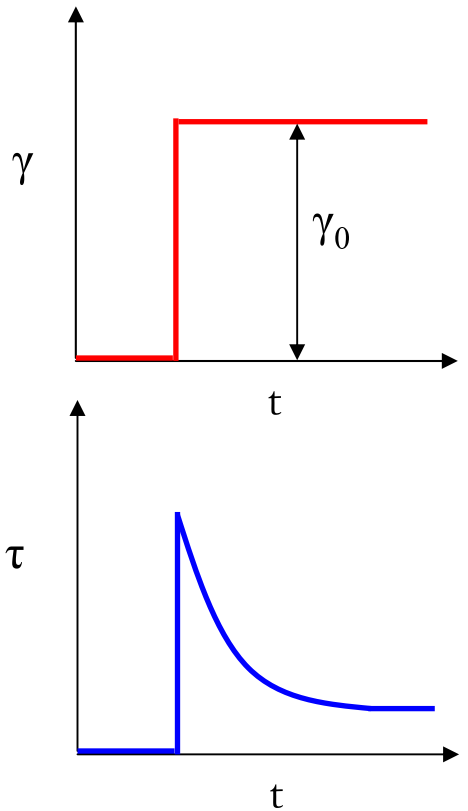
- Cross-slot (stagnation flow):

True extensional flows are difficult to achieve in practice.

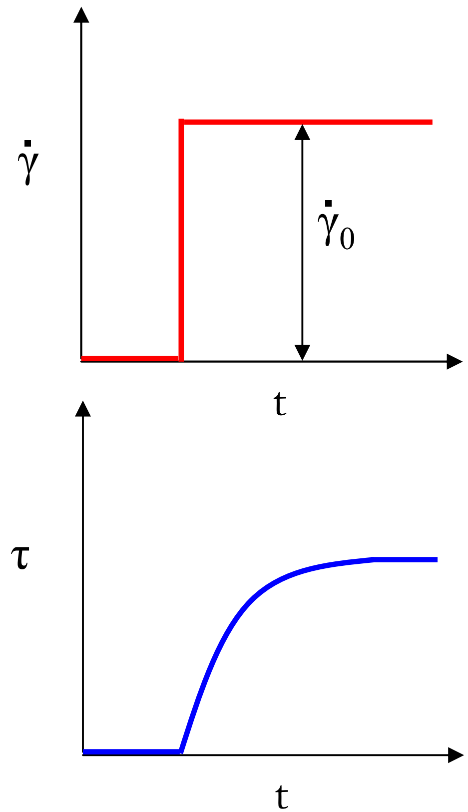


Rheological material functions (shear)

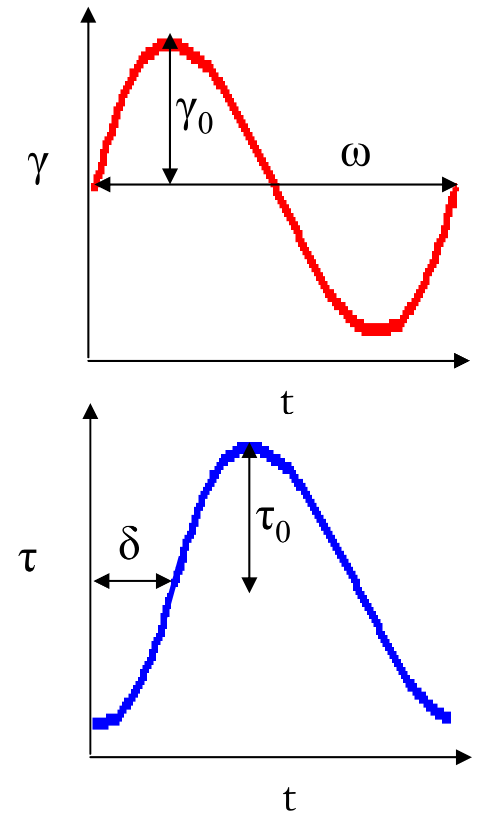
Step strain



Step rate



Small amplitude oscillation



Relaxation modulus:

$$G(t) = \frac{\tau(t)}{\gamma_0}$$

Shear viscosity:

$$\eta^+(t) = \frac{\tau(t)}{\dot{\gamma}_0} \quad \text{(Transient)}$$

$$\eta(\dot{\gamma}_0) = \lim_{t\to\infty} \eta^+(t) \quad \text{(Steady state)}$$

Dynamic moduli: G′, G″

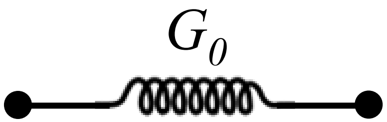
$$\left(G'^2 + G''^2\right) = \frac{\tau_0}{\gamma_0}$$

$$\frac{G'}{G''} = \tan\delta$$

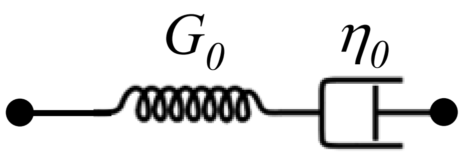
Simple constitutive models and behavior

Solids

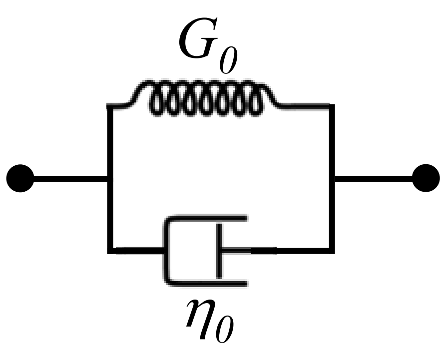
- Hookean solid: $\tau = G_0 \gamma$



- Maxwell fluid: $d\tau = G_0 e^{-t/\lambda} d\dot{\gamma}$

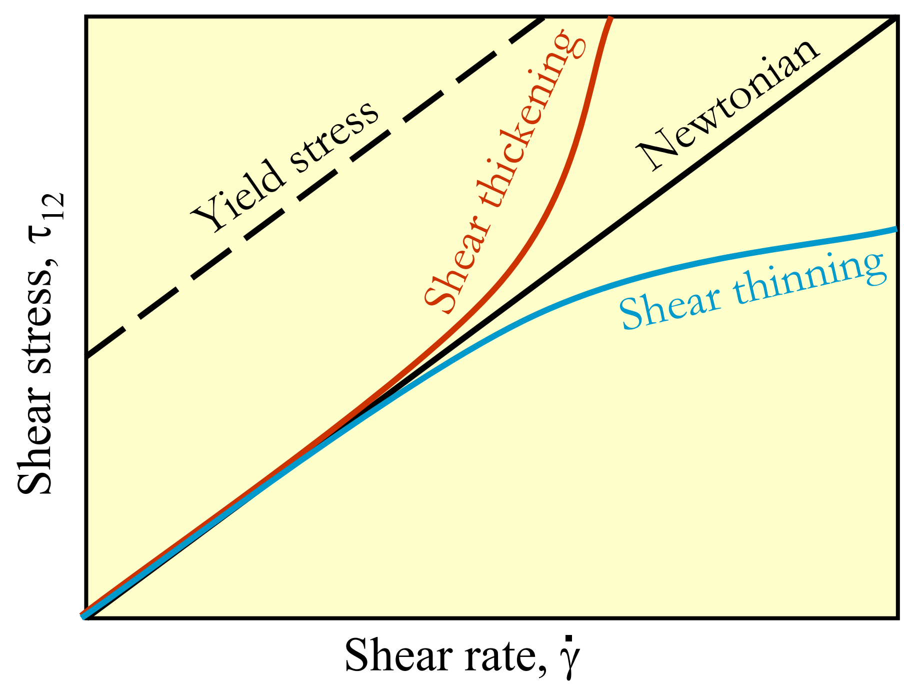


- Voigt fluid: $d\tau = G_0 d\gamma + \eta d\dot{\gamma}$



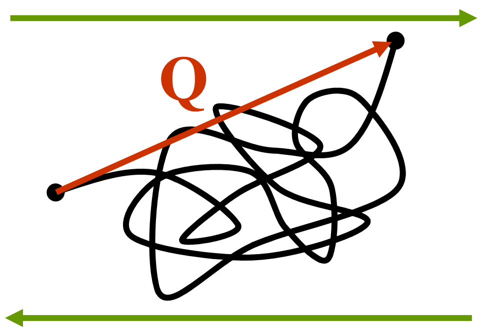
Liquids

- Newtonian liquid: $\tau = \eta \dot{\gamma}$
- Power law fluid: $\tau = \dfrac{\eta_0 \dot{\gamma}}{1 + (\lambda \dot{\gamma})^m}$
- Yield stress fluid: $\tau = \tau_y + k\dot{\gamma}^{-m}$



Structure-based constitutive models

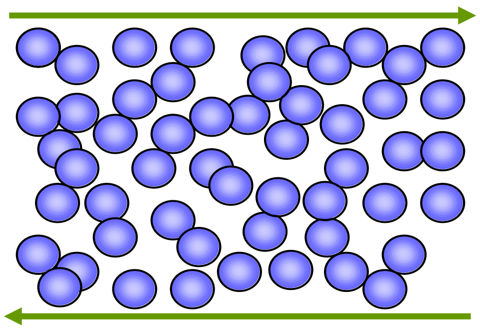
Polymers



- Kramers-Kronig: $\langle \mathbf{QQ} \rangle = \mathbf{I} + \boldsymbol{\tau}_p$
- Upper convected Maxwell:

$$\boldsymbol{\tau}_p^{(1)} = \left(\mathbf{I} + \frac{1}{G_0} \boldsymbol{\tau}_p \right) \cdot \boldsymbol{\tau}_p + G_0 \lambda \mathbf{D}$$

Suspensions



- Stokes-Einstein: $\frac{\eta}{\eta_s} = 1 + 2.5\phi + \ldots$
- Generalized Stokes-Einstein:

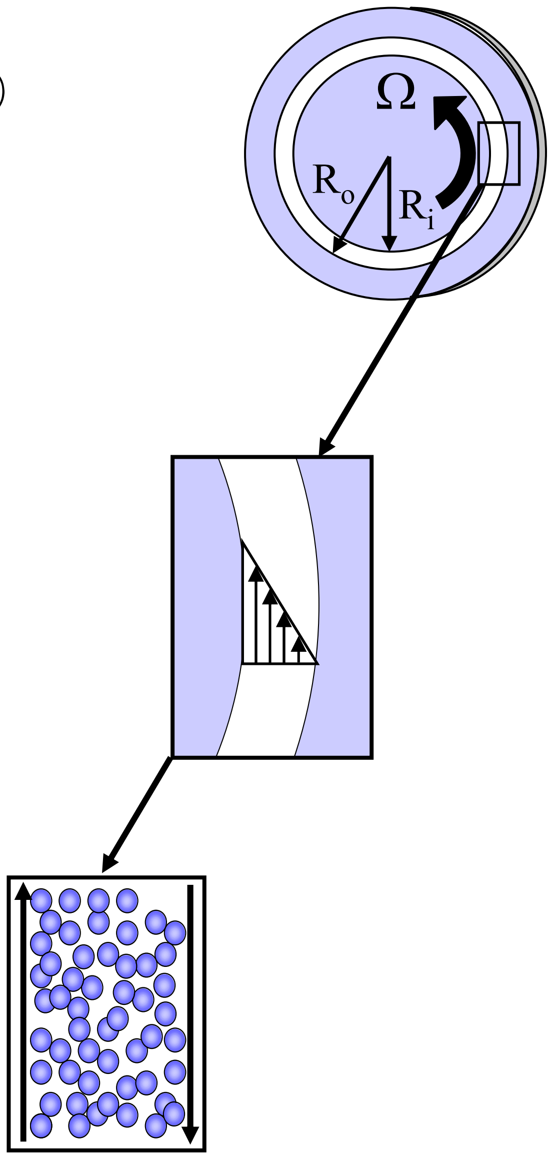
$$G^*(\omega) \propto \frac{\overbrace{i\omega \Im\left(\left\langle \Delta r^2(t) \right\rangle \right)}^{\text{Hydrodynamics}} \times \overbrace{S(q=0)}^{\text{Thermodynamics}}}{\pi a \eta_s}$$

Outline

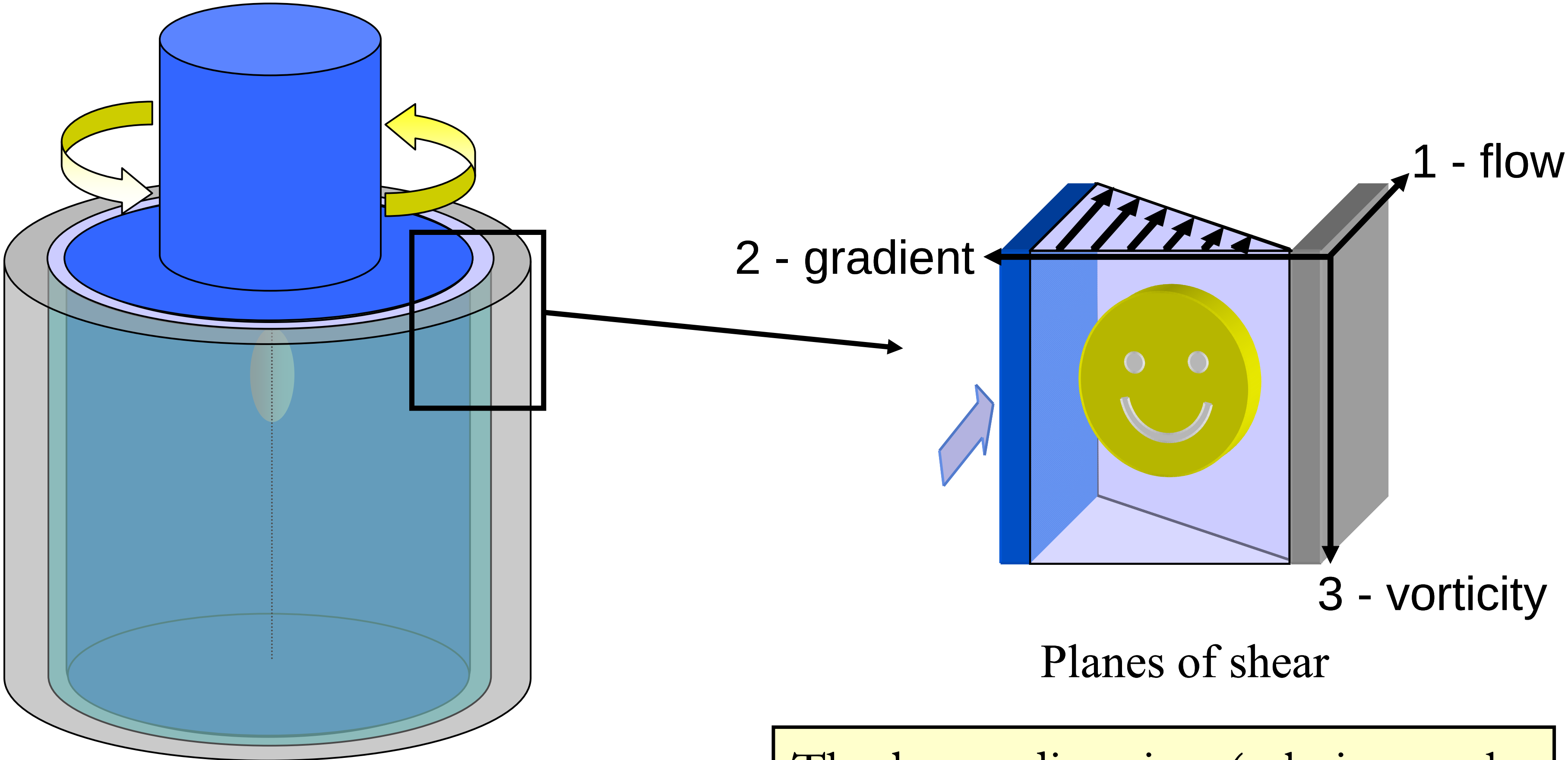
- Rheology: a (brief) introduction
- **Measuring SANS under flow**
- Scattering from flowing systems
- Practical applications

Flow environments for SANS

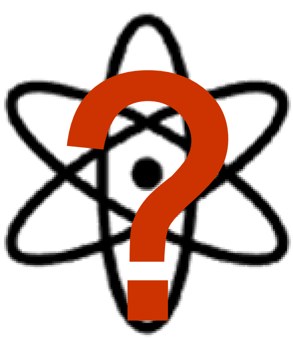
- Why flow-SANS/USANS?
  - Relevant length scale for most materials of interest (10-100 nm)
  - Easy to make flow environment transparent
  - Can accommodate optically turbid samples
- Requirements
  - Stable, steady flow over measurement time
  - Flow should be uniform across collimated beam area
  - Simultaneous rheological measurement (sometimes)
  - Temperature control
- Compatible flow geometries:
  - Steady shear: **Couette**
  - Steady extension: cross slot
  - Step strain: **Couette**, sliding plates
  - Oscillatory shear: **Couette**



Where do we put the beam?



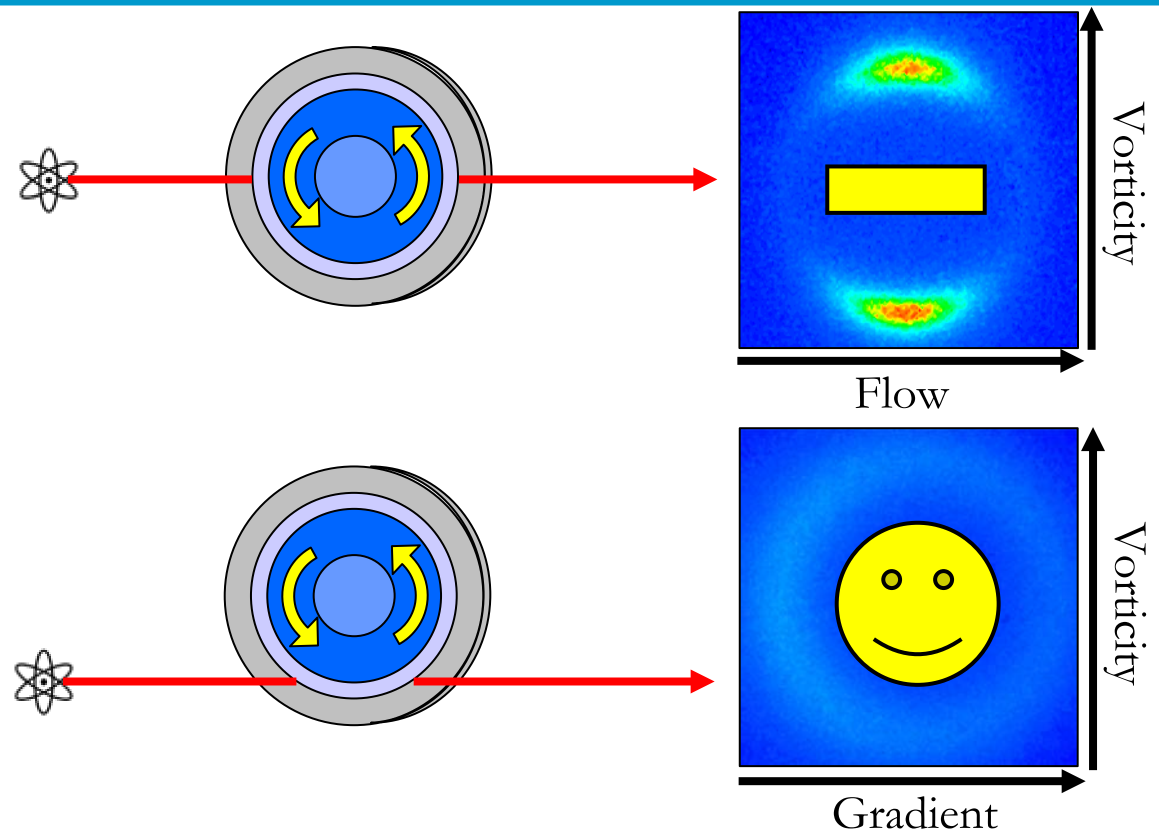
Planes of shear

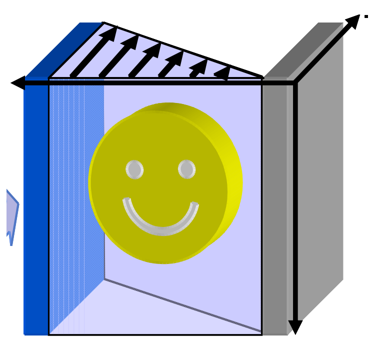


The beam direction (relative to the principal directions) will influence the observed scattering.

Where do we put the beam?

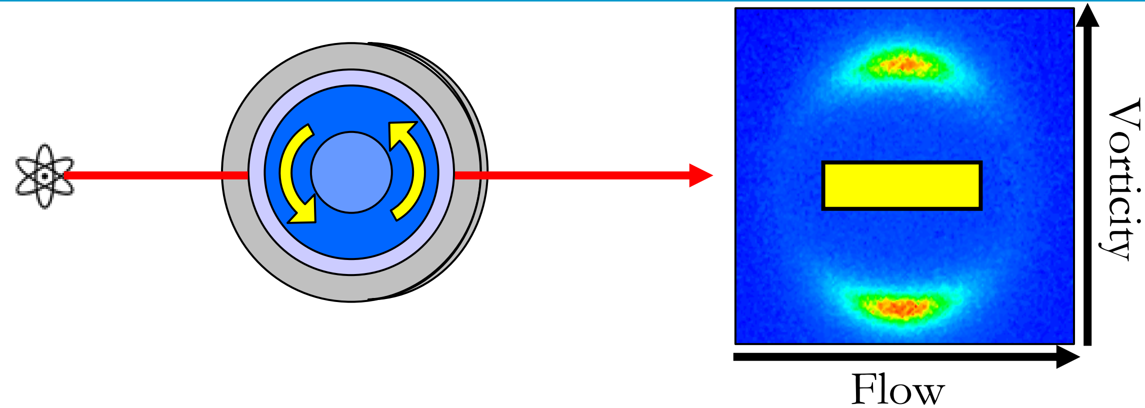
- 1-3 (flow-vorticity): "radial configuration"
- 2-3 (gradient-vorticity): "tangential configuration" in theory…



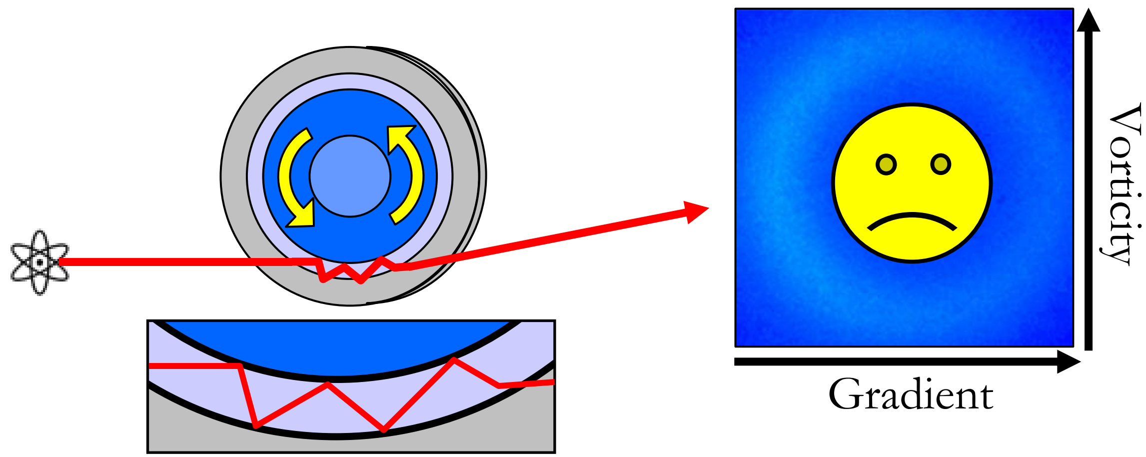


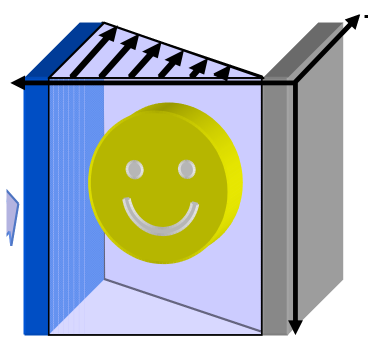
Where do we put the beam?

- 1-3 (flow-vorticity): "radial configuration"



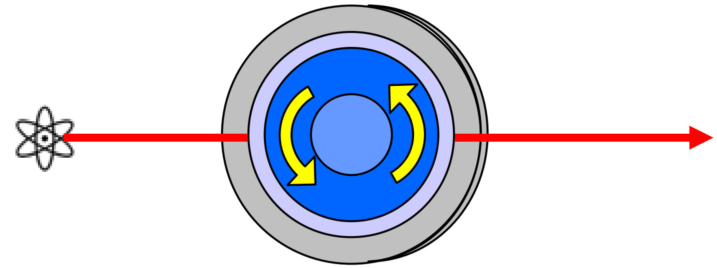
- 2-3 (gradient-vorticity): "tangential configuration" in theory… in practice

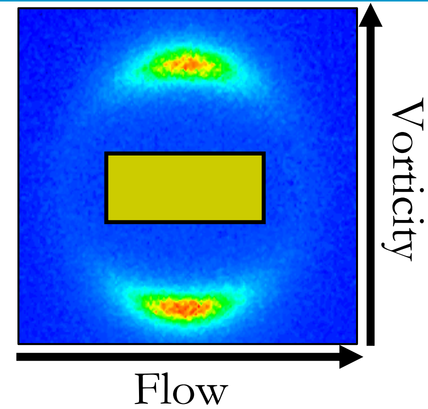




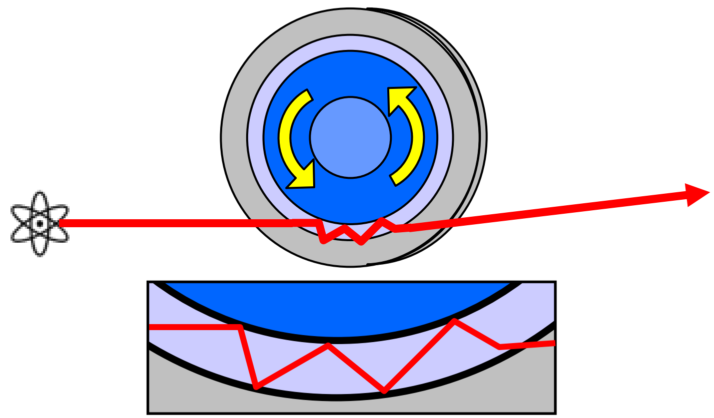
Where do we put the beam?

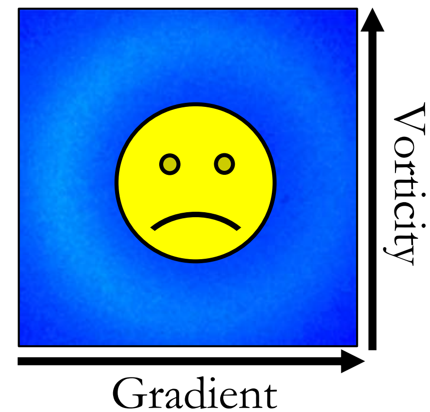
- 1-3 (flow-vorticity):
  “radial configuration”



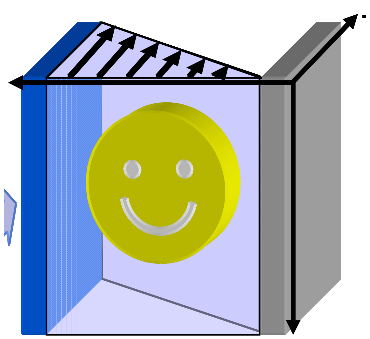


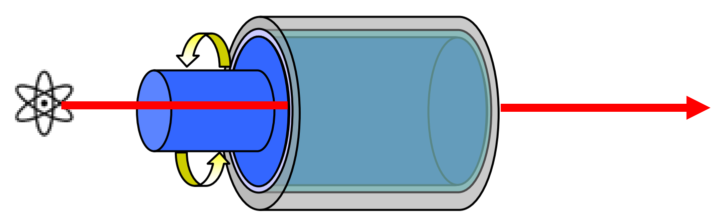
- 2-3 (gradient-vorticity):
  “tangential configuration”
  in theory…

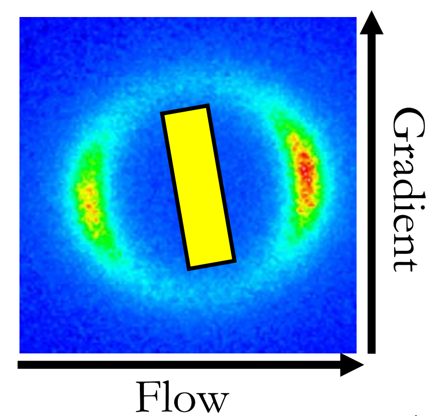




- 1-2 (flow-gradient):



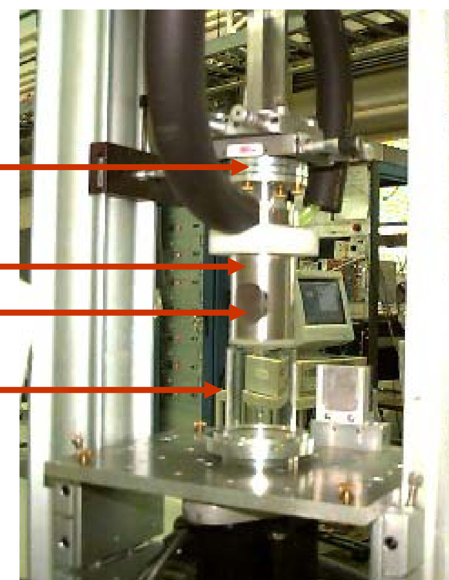




Flow-SANS environments at the NCNR

- Boulder Shear Cell (BSC)
  - Quartz inner cylinder, R_i = 59 mm, 60 mm
  - Quartz outer cylinder, R_0 = 61 mm
  - Sample volume: 10-15 mL
  - Temperature control
  - Available shear rates: 0-3890 s^{-1}\
  - **1-3 and 2-3 planes**

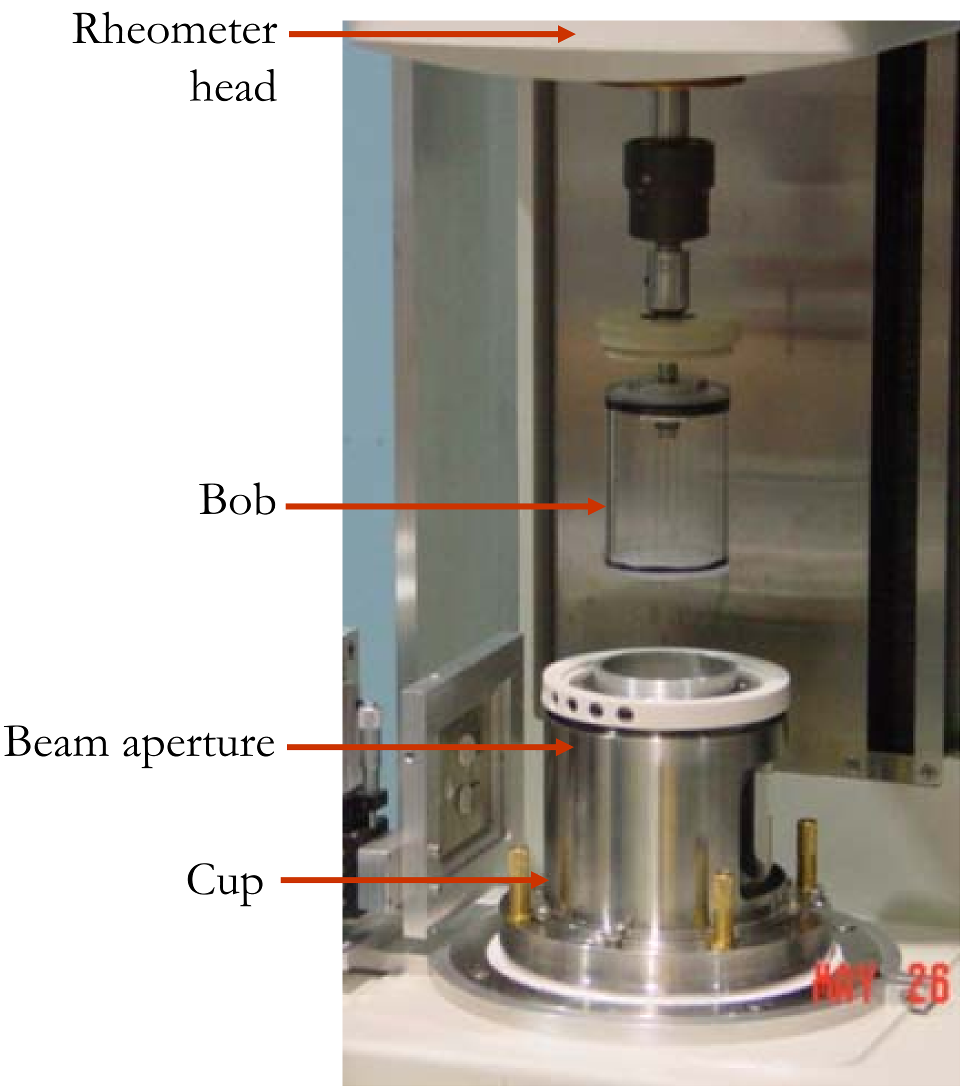
- Advantages
  - Control interface designed specifically for instrument control program
  - **Transparent for visual observation**



- Disadvantages
  - No online rheological measurement
  - No spatial resolution of signal
  - Relatively large sample volumes

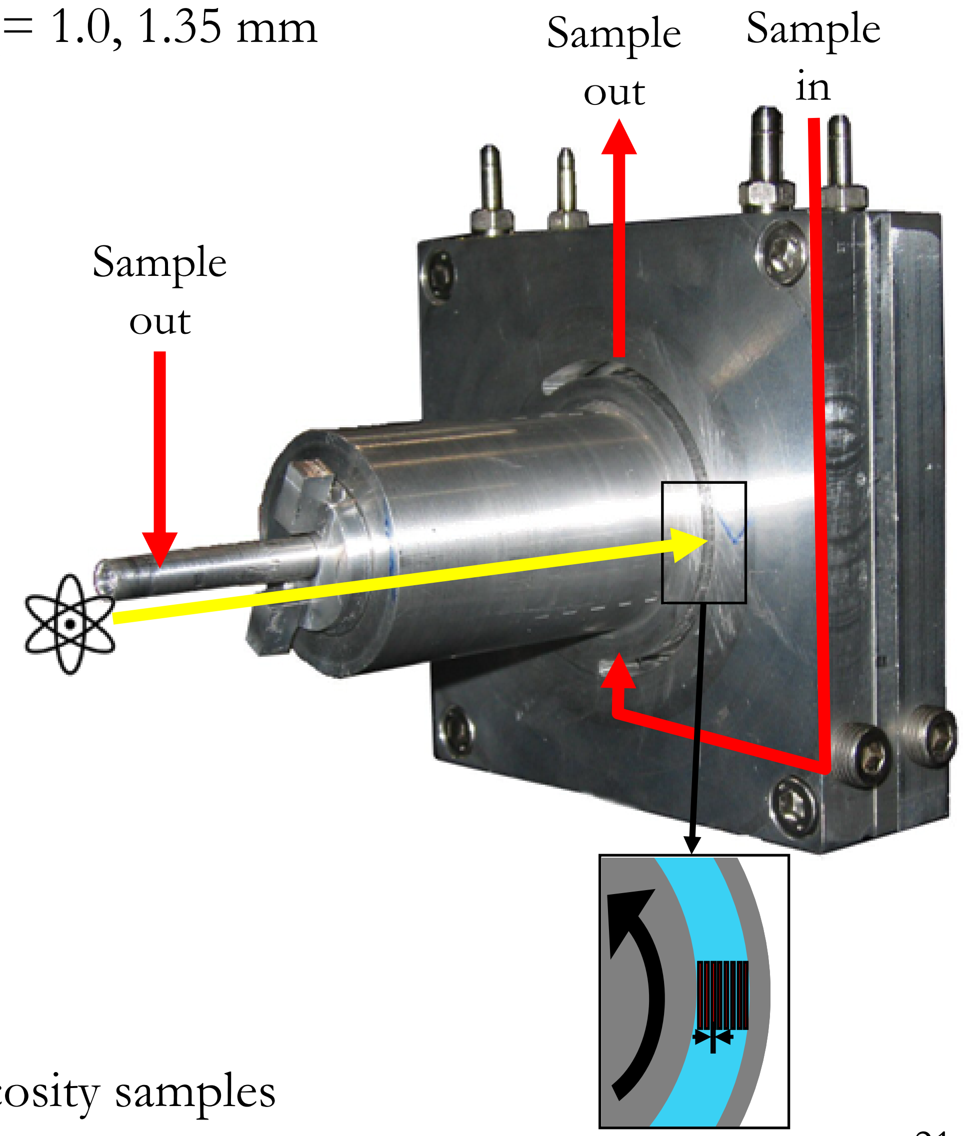
Flow-SANS environments at the NCNR

- Physica rheometer (Rheo-SANS)
  - Standard rotational rheometer
  - Quartz and titanium geometries
  - Sample volume: 5-10 mL
  - Available shear rates: 0-4800 s^{-1}
  - **1-3 and 2-3 planes**
- Advantages
  - **Online rheological measurement**
  - Sophisticated shear protocols
  - Relatively small sample size
- Disadvantages
  - No spatial resolution of signal
  - Relatively large sample volumes
  - Temperature control relatively sluggish



Flow-SANS environments at the NCNR

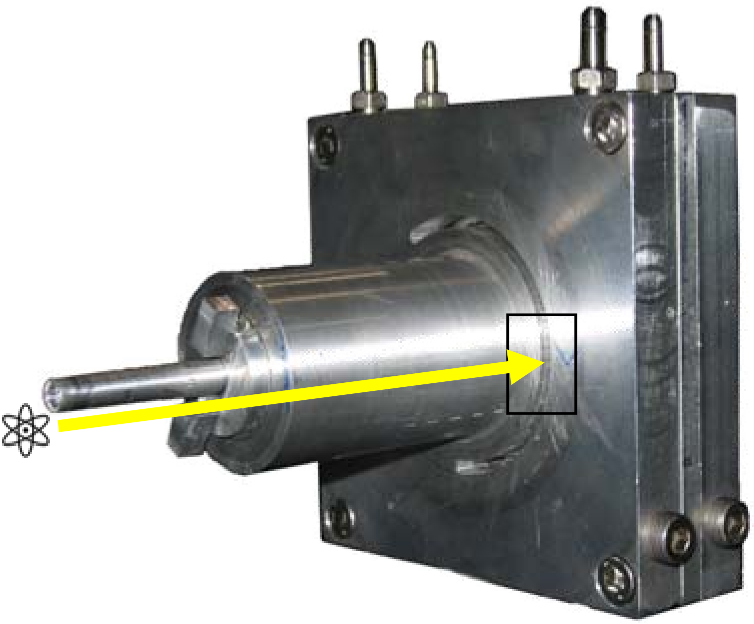
- Porcar shear cell (1-2 shear cell)
  - Aluminum inner/outer cylinders, R_o-R_i= 1.0, 1.35 mm
  - Sample volume: 10-15 mL
  - Available shear rates: 0-2380 s^{-1}
  - **1-2 plane**
- Advantages
  - **Only environment (anywhere!) capable of 1-2 plane measurements**
  - Spatial resolution within the gap
  - Relatively small sample size
- Disadvantages
  - No online rheological measurement
  - Requires strong sample scattering
  - Sample loading a problem for high viscosity samples

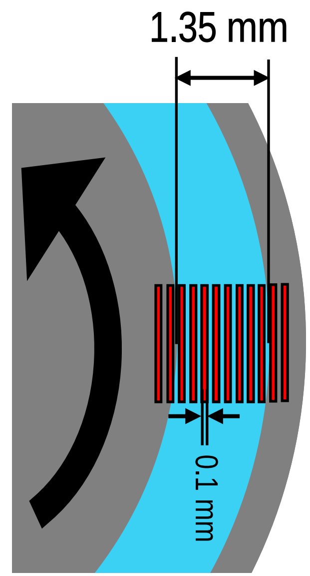


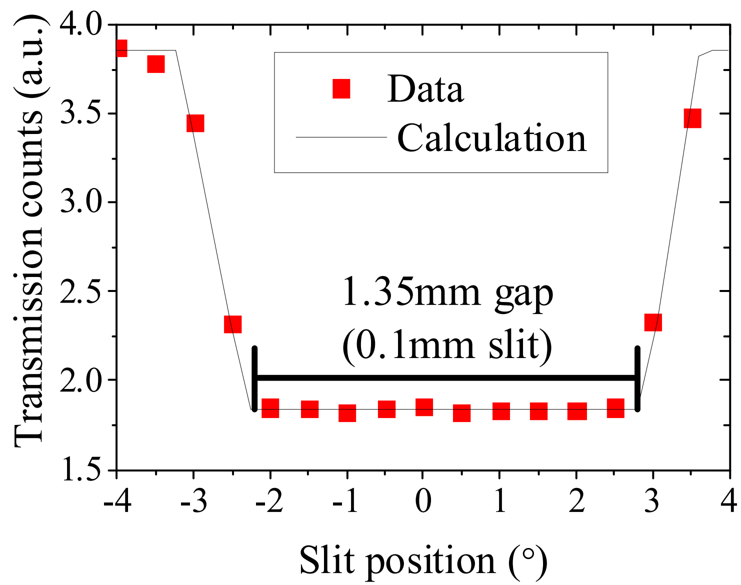
Calibrating the gap in the 1-2 shear cell

- Initial beam is collimated to a translating thin vertical slit (Available slit sizes: 0.1, 0.2, 0.5, 1.0 mm)

- Couette gap identified by performing a horizontal scan of the vertical slit

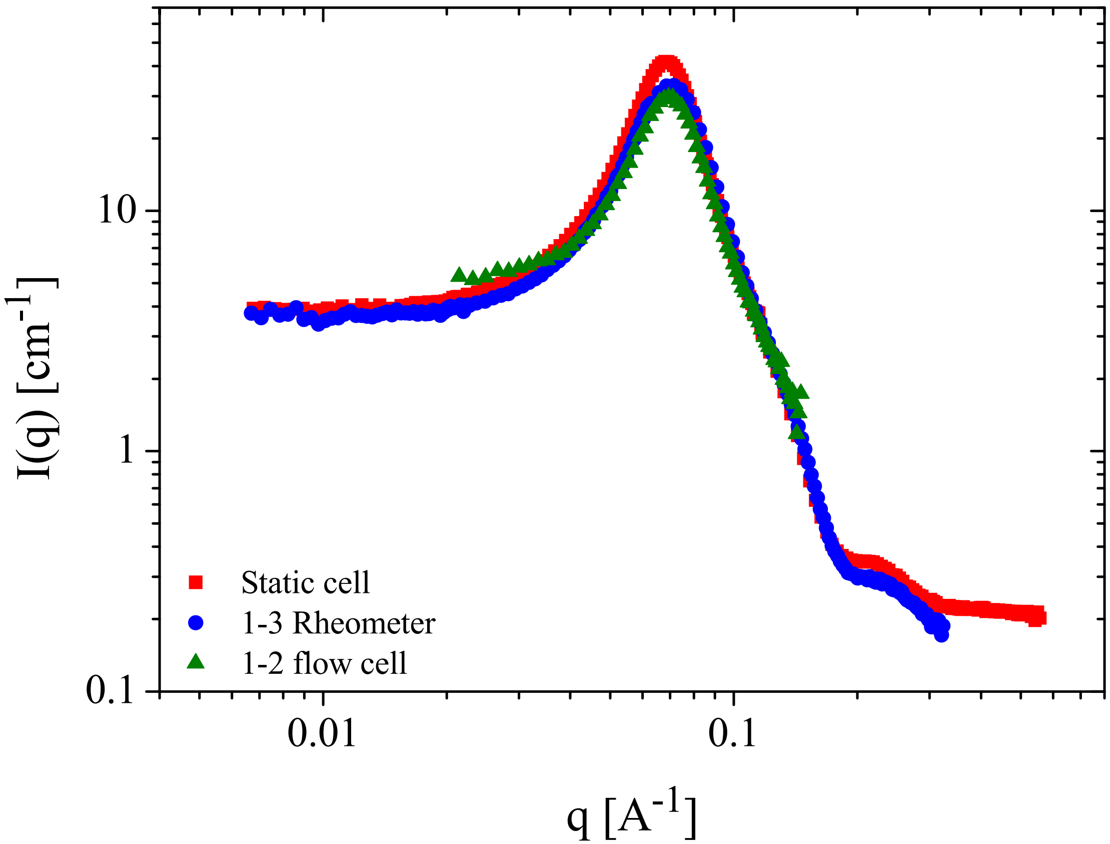


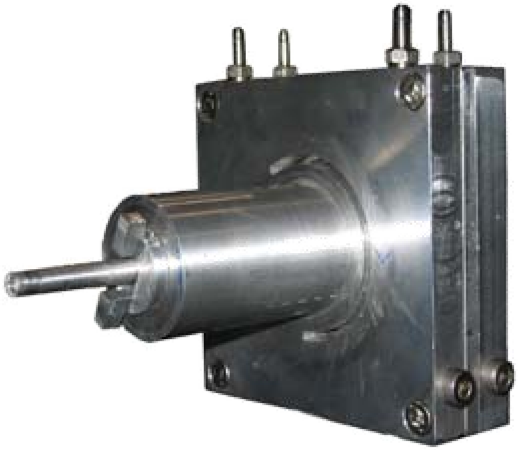




Sample scattering can be measured at up to 11 points within the gap.

Do the flow geometries influence sample scattering?

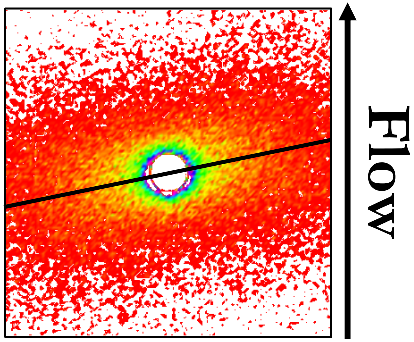




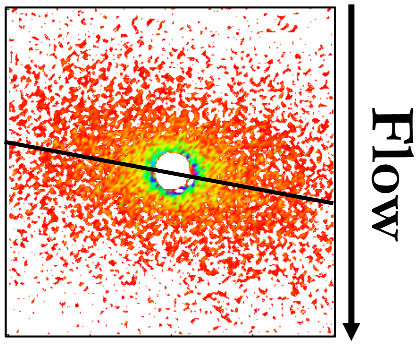
Variation in measured scattering is within typical sample to sample variability.

Designing and executing flow-SANS experiments

- Typical flow-SANS procedure
  - Install and align the flow environment, collimate neutron beam, calibrate the gap (instrument contact)
  - Perform a normal SANS measurement at rest in the flow environment
  - Design/program a shear protocol (instrument contact)
  - Perform measurement



+32 s^{-1}



-32 s^{-1}

- Things to consider/remember
  - Sample loading procedure
  - In what order will the shear protocol be performed?
  - Check sample integrity as often as possible (air bubbles, particle contamination)
  - Perform a measurement under reverse flow to ensure discount any instrument artifacts
  - **Don't forget normalization measurements! (empty cell, blocked beam)**

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- **Scattering from flowing systems**
- Practical applications

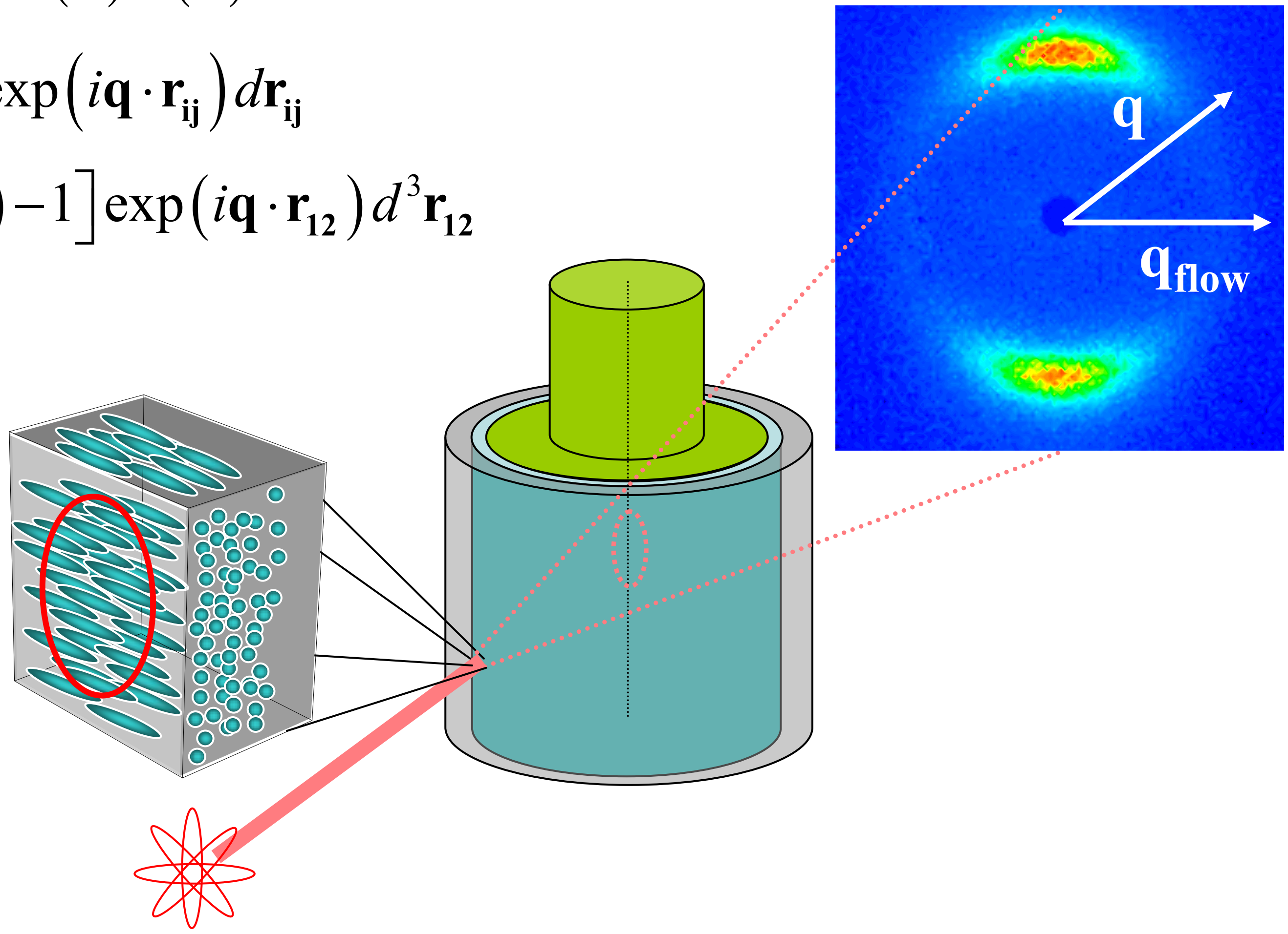
Scattering under flow = anisotropic scattering

- In general, the scattering of a structured fluid under shear will be anisotropic

$$I(\mathbf{q}) = (\Delta\rho_s)^2 N_p V_p^2 P(\mathbf{q}) S(\mathbf{q})$$

$$P(\mathbf{q}) = \int \left(p(\mathbf{r_{ij}}) \right)^2 \exp\left(i\mathbf{q}\cdot\mathbf{r_{ij}} \right) d\mathbf{r_{ij}}$$

$$S(\mathbf{q}) = 1 + \int \left[g(\mathbf{r_{12}}) - 1 \right] \exp\left(i\mathbf{q}\cdot\mathbf{r_{12}} \right) d^3\mathbf{r_{12}}$$



Scattering under flow = anisotropic scattering

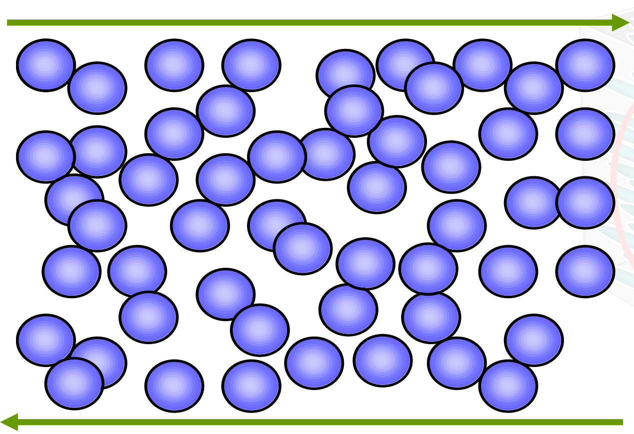
- In general, the scattering of a structured fluid under shear will be anisotropic… ***even for a suspension of spherical particles!***

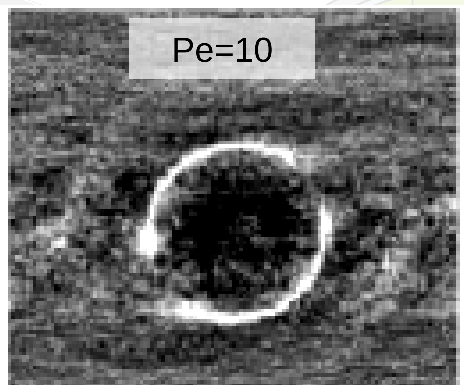
$$I(\mathbf{q}) = N_p V_p (\Delta\rho_s)^2 P(\mathbf{q}) S(\mathbf{q})$$

$$P(\mathbf{q}) = \int \left(p(\mathbf{r_{ij}})\right)^2 \exp\left(i\mathbf{q}\cdot\mathbf{r_{ij}}\right) d\mathbf{r_{ij}}$$

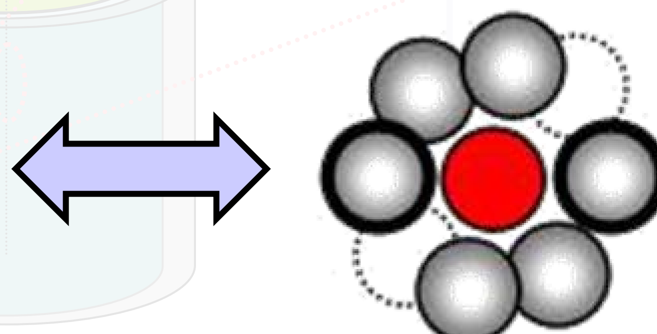
$$S(\mathbf{q}) = 1 + \int \left[g(\mathbf{r_{12}}) - 1\right] \exp\left(i\mathbf{q}\cdot\mathbf{r_{12}}\right) d^3\mathbf{r_{12}}$$

g(**r**) for spherical colloids



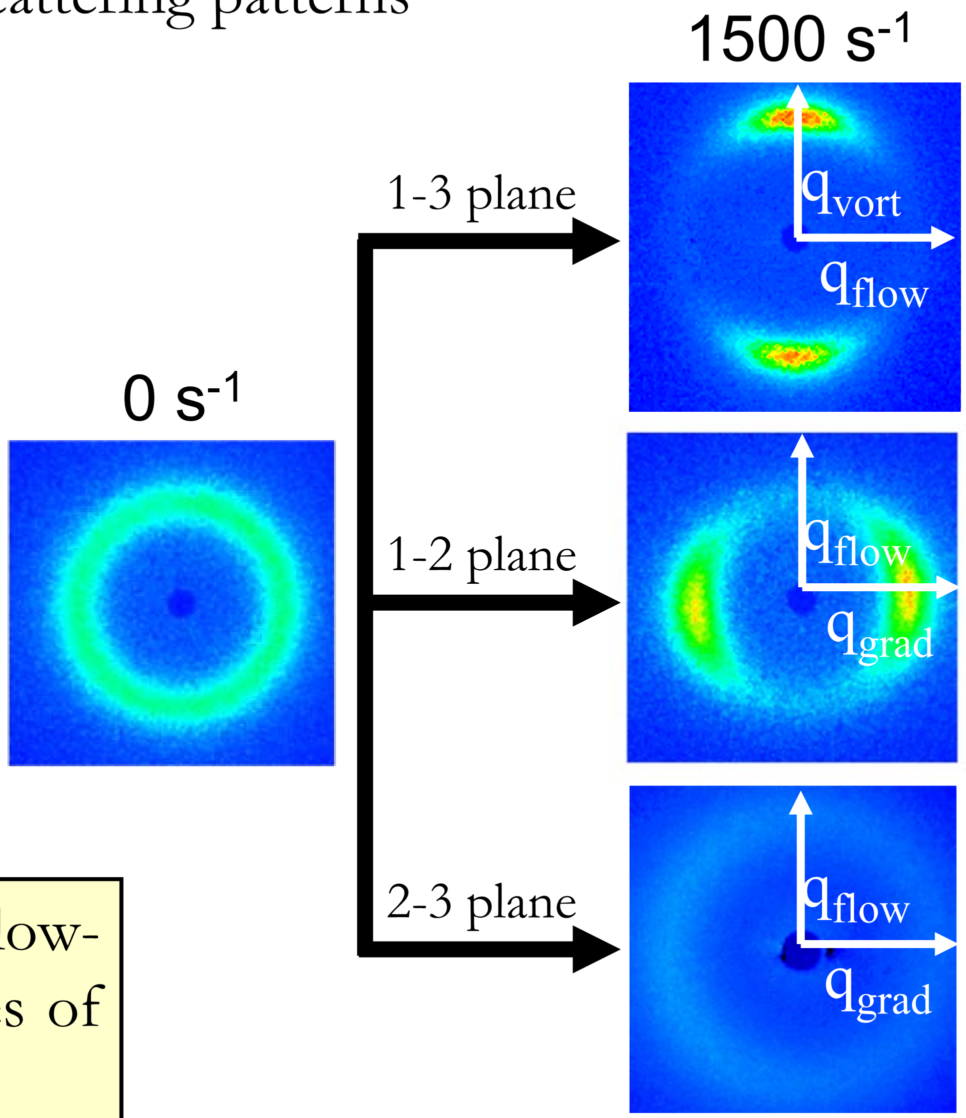


Foss and Brady, JFM 2000



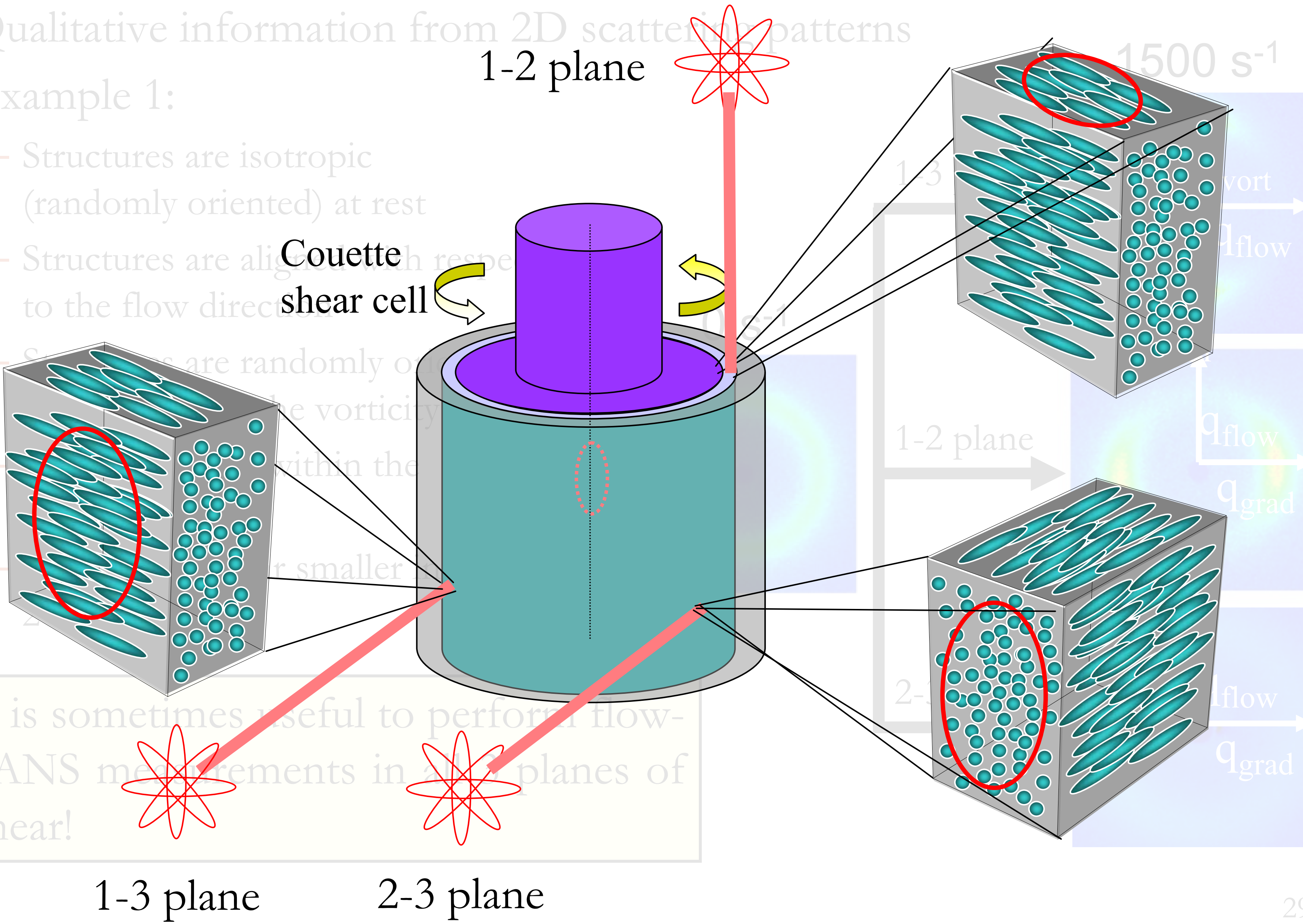
Dealing with anisotropic scattering

- Qualitative information from 2D scattering patterns
- Example 1:
  - Structures are isotropic (randomly oriented) at rest
  - Structures are aligned with respect to the flow direction
  - Structures are randomly oriented with respect to the vorticity direction
  - Orientation lies within the 1-2 plane
  - Structures appear smaller in the 2-3 plane



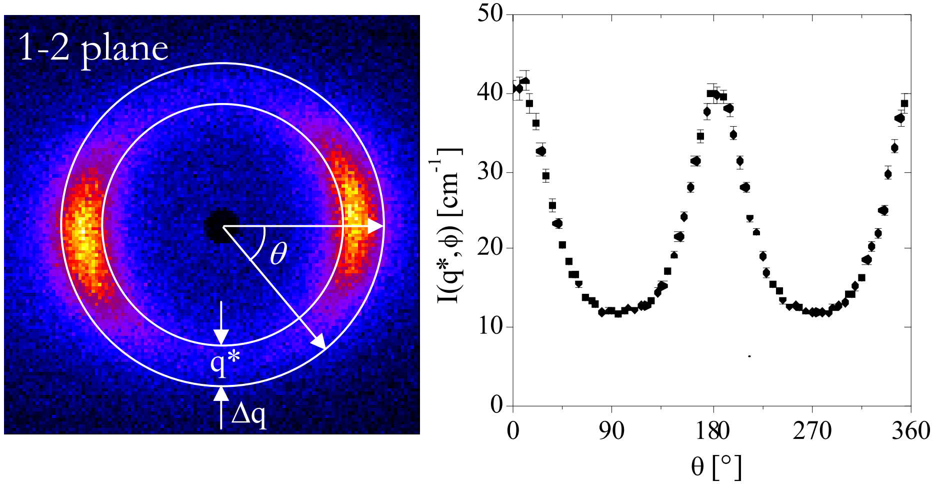
It is sometimes useful to perform flow-SANS measurements in all 3 planes of shear!

Dealing with anisotropic scattering



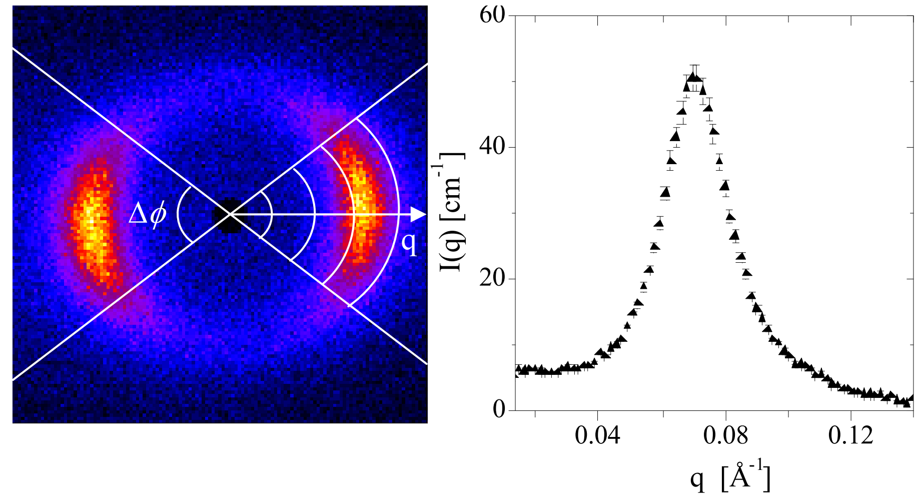
Data reduction of anisotropic scattering data

Annular (azimuthal) average



- Useful for determining alignment and orientation of structures at a specific length scale
- Annular averages at different q-values show how anisotropy varies with q
- **NOTE: flow-aligned structures will scatter at 90° relative to q_{flow}**

Sector average



- Useful for determining the structure of flow-aligned material
- Sector averages along the different directions (flow, gradient, vorticity) reveal the 3D structure of the fluid under flow

Analysis of anisotropic scattering data

- Sector-averaged data can be analyzed using the same methods as isotropic scattering data
  - Model-independent: Guinier, Porod, etc.
  - Model-dependent: shape, composition, interactions

$$I(q,\Delta\theta) \approx (\Delta\rho_s)^2 N_p V_p^2 P(q,\Delta\theta) S(q,\Delta\theta)$$

- Annular-averaged data can be analyzed by assuming the q-dependent and θ-dependent contributions to the scattering are factorizable

$$I(q^*,\theta) \approx I_{iso}(q^*)\hat{F}(\theta)$$

$$\underbrace{N_p V_p (\Delta\rho_s)^2 P_{iso}(q^*) S_{iso}(q^*)}$$

Hypothetical scattered intensity from an equivalent isotropic fluid

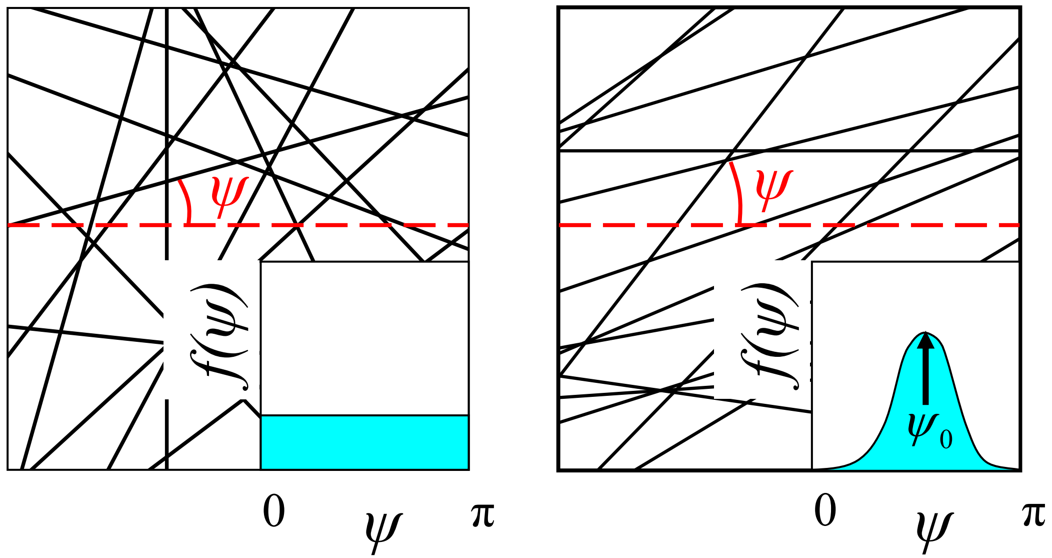
$$\hat{F}(\theta) = \int \left(f(\mathbf{u})\right)^2 \exp\left(i\hat{\boldsymbol{\theta}}\cdot\mathbf{u}\right) d\mathbf{u}$$

$\mathbf{u} \equiv$ Unit orientation vector

$f(\mathbf{u}) \equiv$ Orientational distribution function

Analysis of anisotropic scattering data

- Example: a fluid comprised of rigid rods



$$\cos\psi = \frac{\mathbf{u}\cdot\mathbf{n}}{|\mathbf{u}||\mathbf{n}|}$$

  – Orientation well-described by a Maier-Saupe type distribution

$$f(\psi) \propto P_2\left(\cos(\psi - \psi_0)\right); \; P_2(x) = \left(3x^2 - 1\right)/2$$

  – Assume the functional form of the distribution of scattering is similar to that of the real-space structure

$$\hat{F}(\theta) \propto \exp\left\{\alpha\left[P_2\left(\cos(\theta - \theta_0)\right) - 1\right]\right\}$$

Model-independent parameters

If we assume that any arbitrary orientation distribution with two-fold symmetry can be treated in a similar fashion, then we can define two moments of the anisotropic scattering pattern:

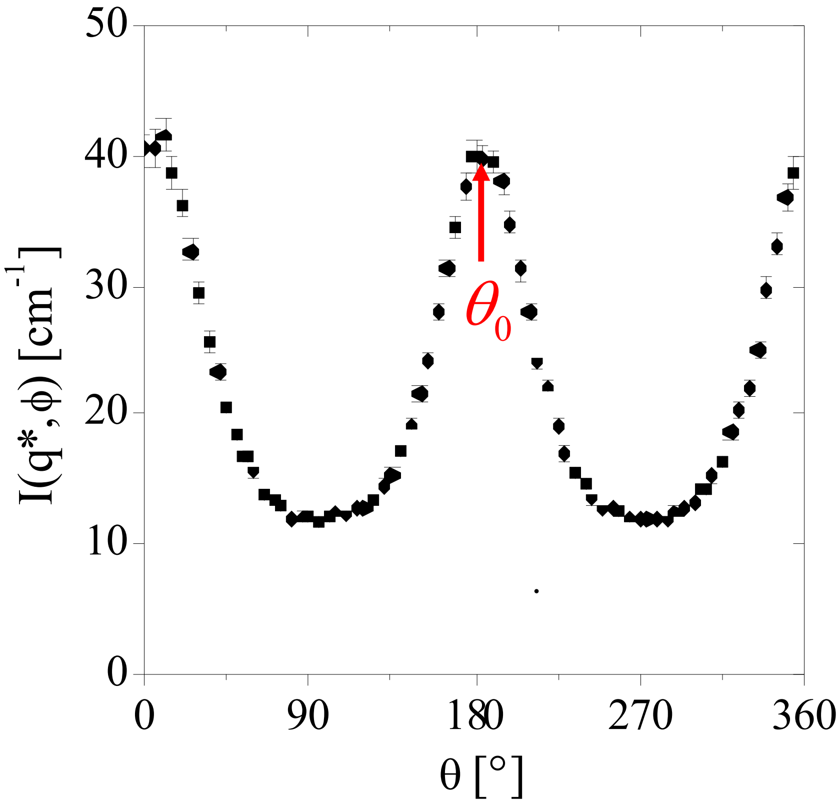
- $\theta_0(q^*) \equiv$ Average **orientation angle** at q^*

$$\theta_0(q^*): \left.\frac{\partial I(q^*,\theta)}{\partial\theta}\right|_{\theta=\theta_0} = 0, \quad \left.\frac{\partial^2 I(q^*,\theta)}{\partial^2\theta}\right|_{\theta=\theta_0} < 0$$

- $A_f(q^*) \equiv$ Structural **alignment factor** at q^*

$$A_f(q^*) = -\frac{\int_0^{2\pi} I(q^*,\theta)\cos\left[2(\theta-\theta_0)\right]d\theta}{\int_0^{2\pi} I(q^*,\theta)d\theta}$$

$$A_f = \begin{cases} 0 \Rightarrow \text{Isotropic} \\ 1 \Rightarrow \text{Fully aligned} \end{cases}$$

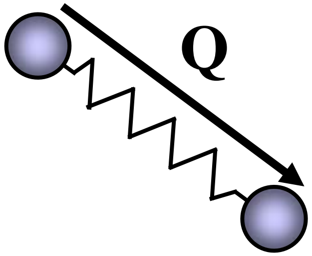


Relating rheology to structural anisotropy

- For certain kinds of materials, structural anisotropy can be used to directly compute the stresses within a fluid

Kramers relation: $\langle \mathbf{QQ} \rangle = \mathbf{I} + \boldsymbol{\tau}_{\mathbf{p}}$

Order tensor: $\mathbf{S} = \dfrac{\langle \mathbf{QQ} \rangle}{\operatorname{tr}\langle \mathbf{QQ} \rangle} - \dfrac{1}{3}\mathbf{I}$



- Example: the "stress-optic law" for polymers
  - Optical anisotropy arises from stretching of polymer chains relative to their equilibrium state

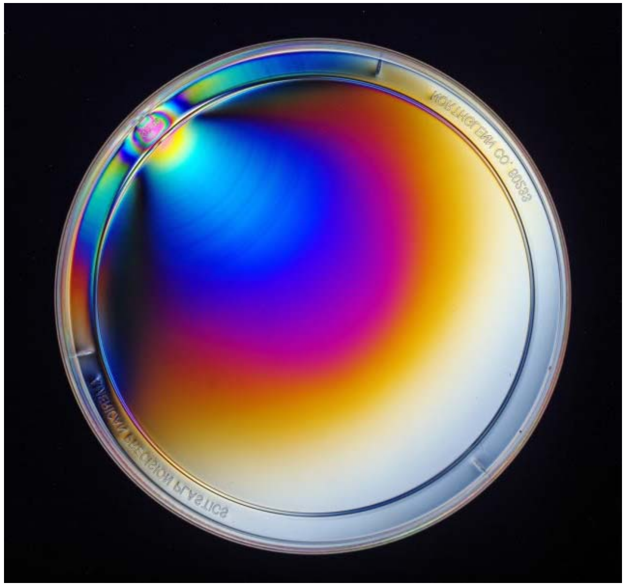
$$\mathbf{n} = C\mathbf{S}$$

$$S_{12} = \frac{\tau_{12}}{G_0} = \frac{1}{2C}\Delta n' \sin 2\chi$$

$$S_{22} - S_{11} = \frac{\tau_{22} - \tau_{11}}{G_0} = \frac{1}{C}\Delta n' \cos 2\chi$$

$\Delta n' \equiv$ birefringence (chain stretch)

$\chi \equiv$ extinction angle (chain orientation)



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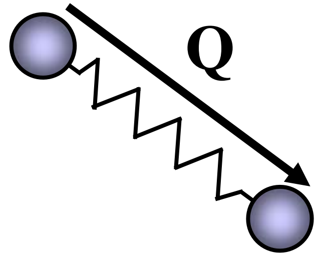

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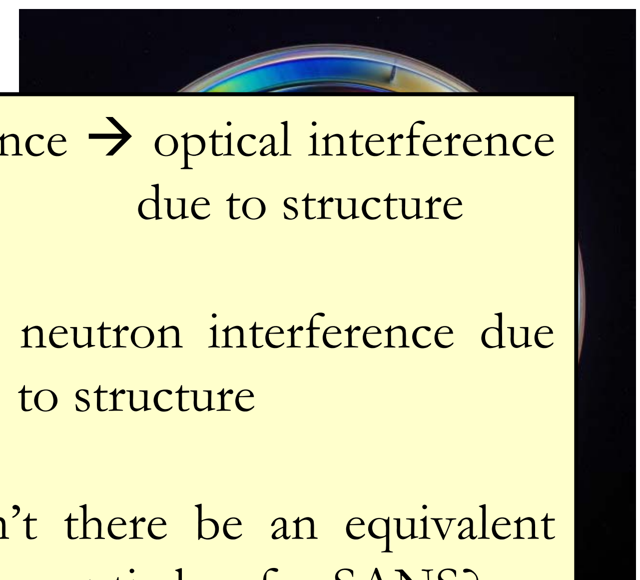


Birefringence → optical interference due to structure

SANS → neutron interference due to structure

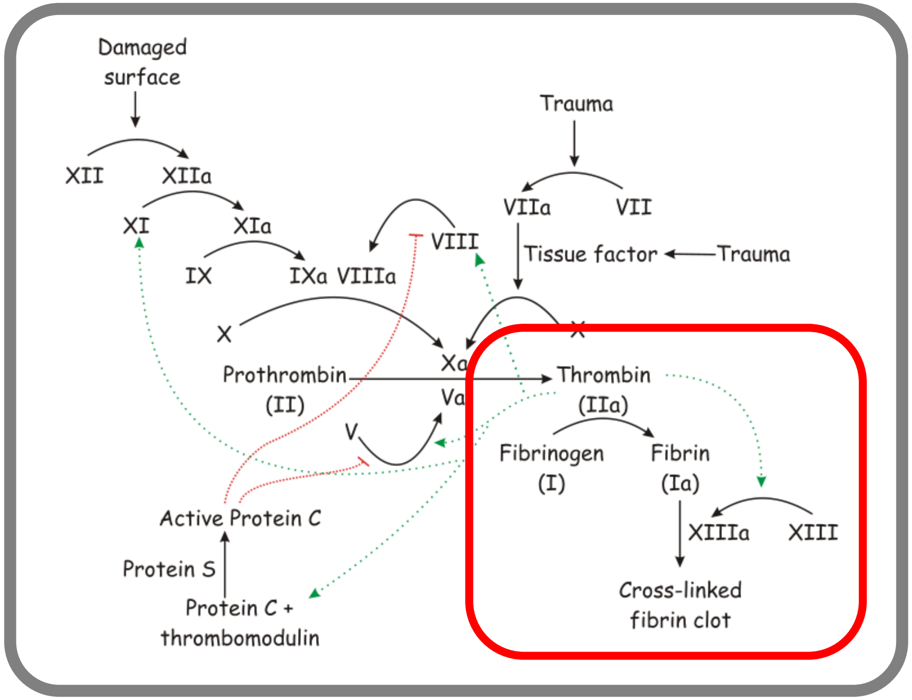
…shouldn't there be an equivalent to the stress-optic law for SANS?

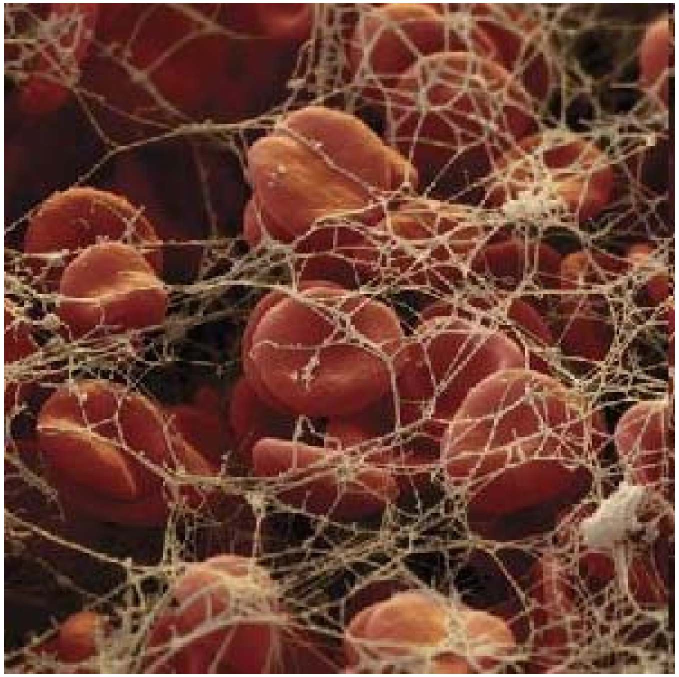
Outline

- Rheology: a (brief) introduction
- Measuring SANS under flow
- Scattering from flowing systems
- **Practical applications**

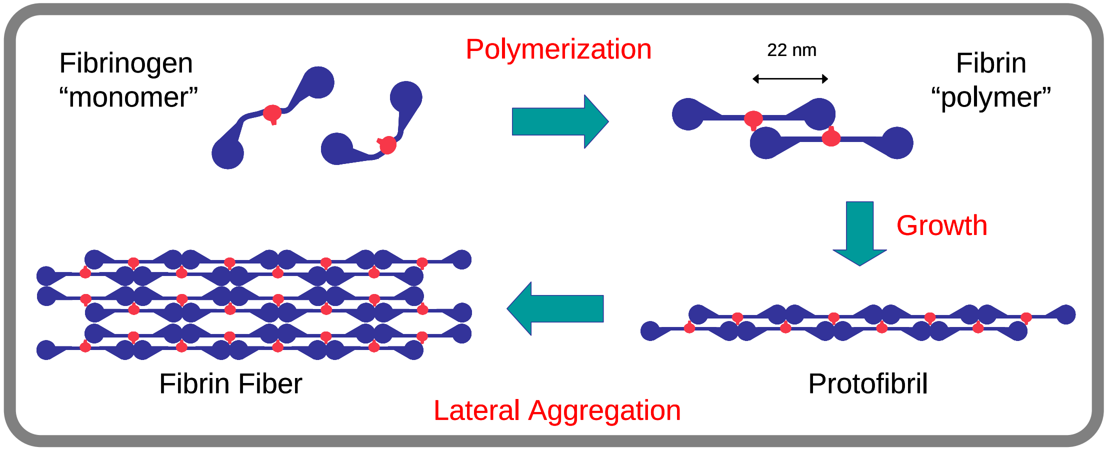
Formation of fibrin gels*

***Danilo Pozzo et al., University of Washington**



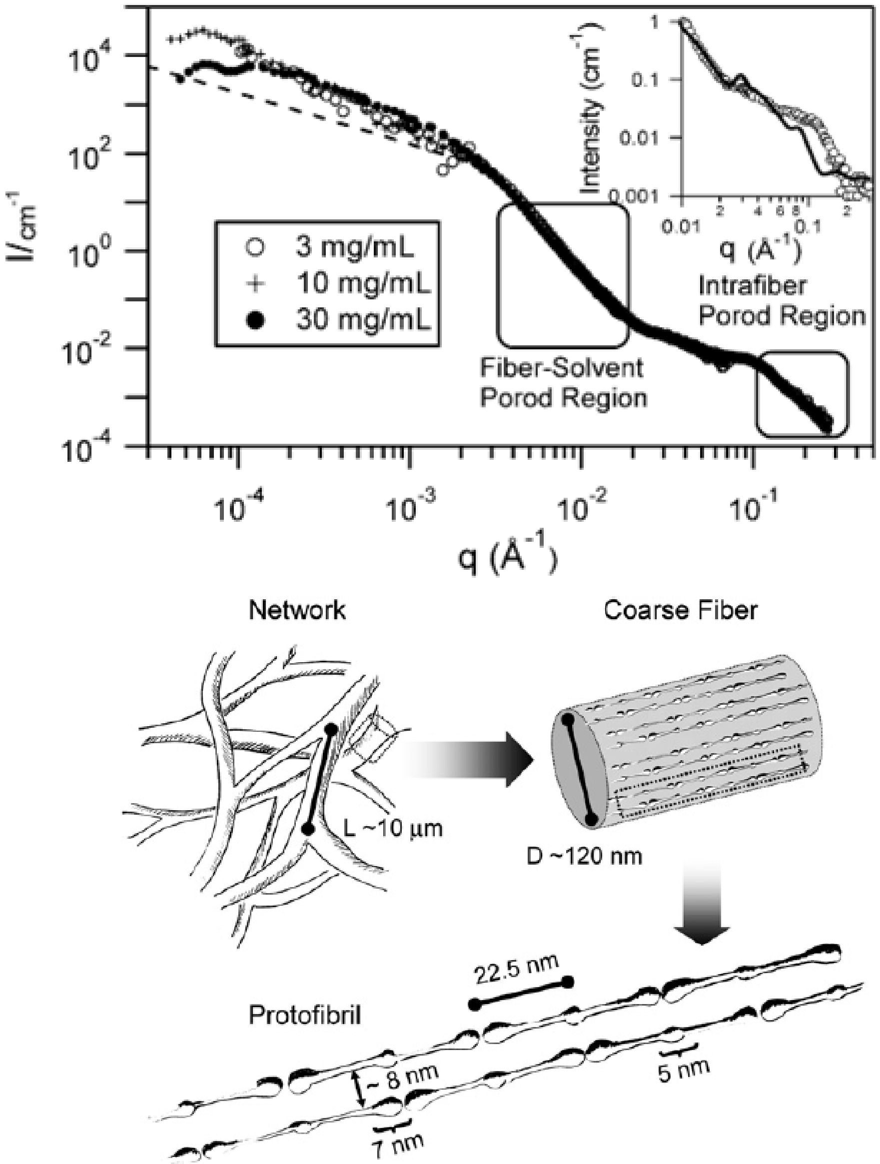


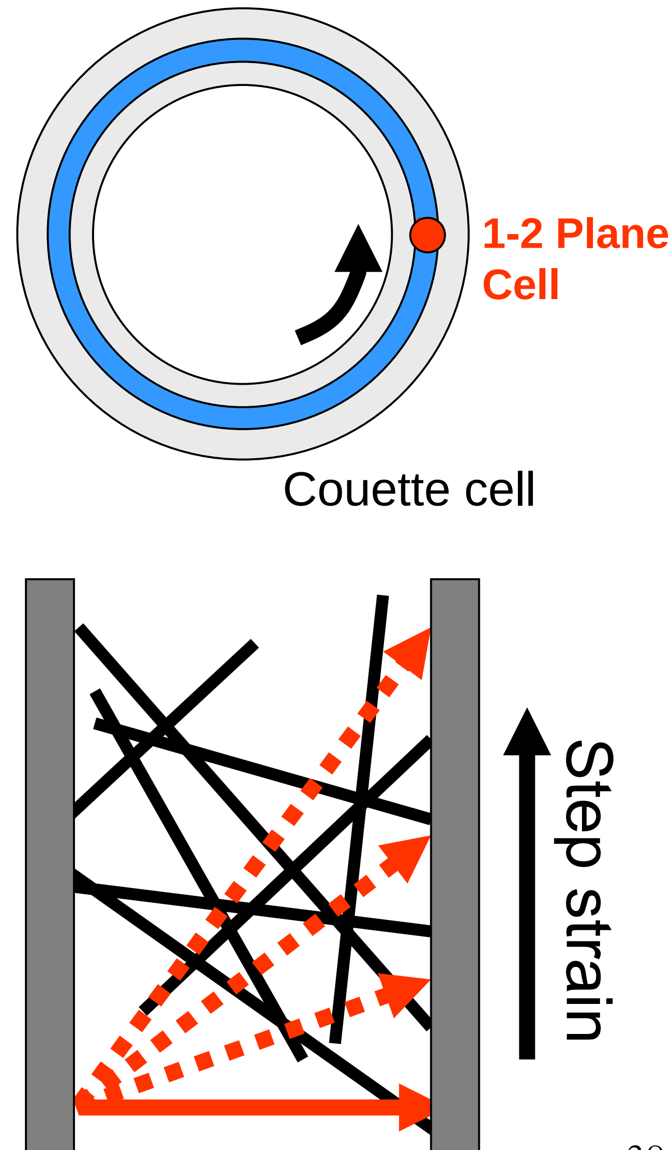
The structure of fibrin clots under shear deformation is important to understanding symptoms and treatment of atherosclerosis.



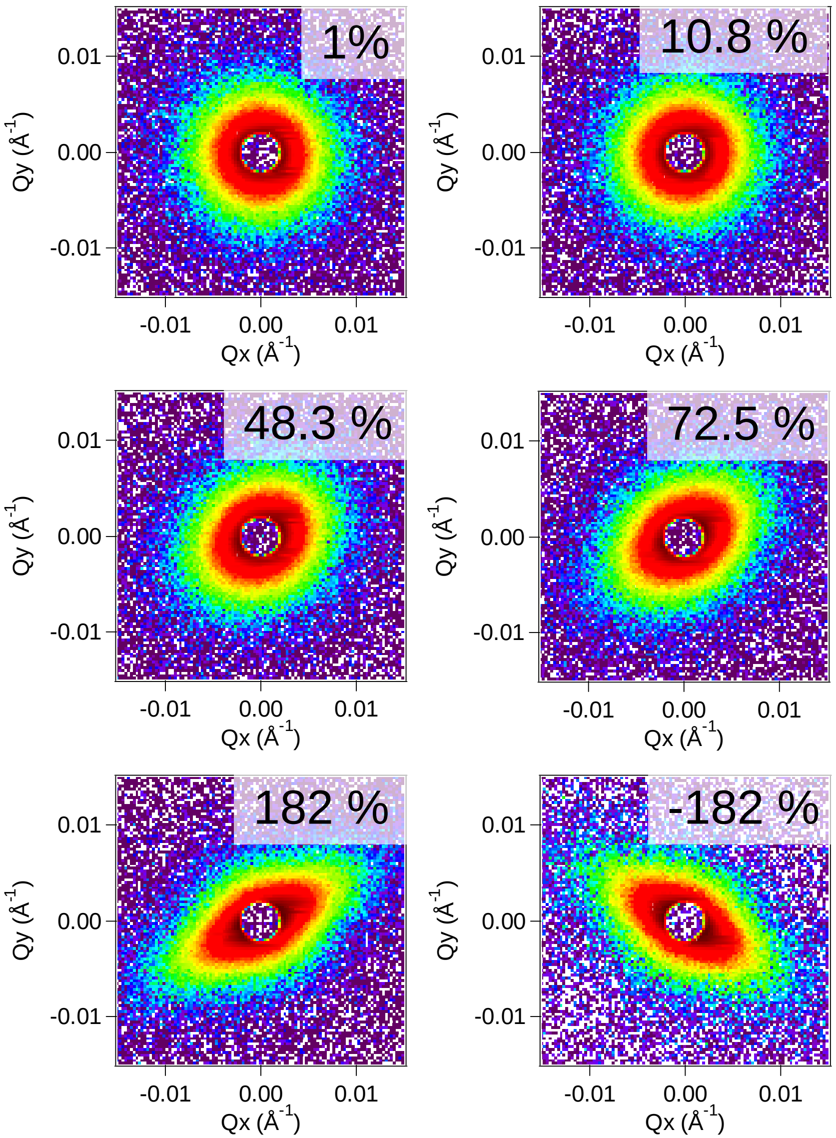
1-2 plane flow-SANS of fibrin gels

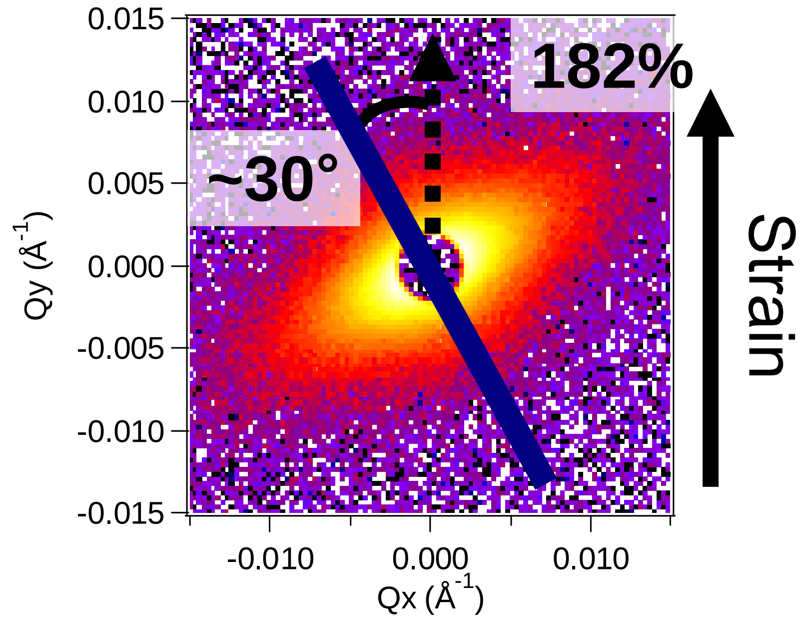
- Fibrin gel is formed *in situ* by mixing inside the Couette cell

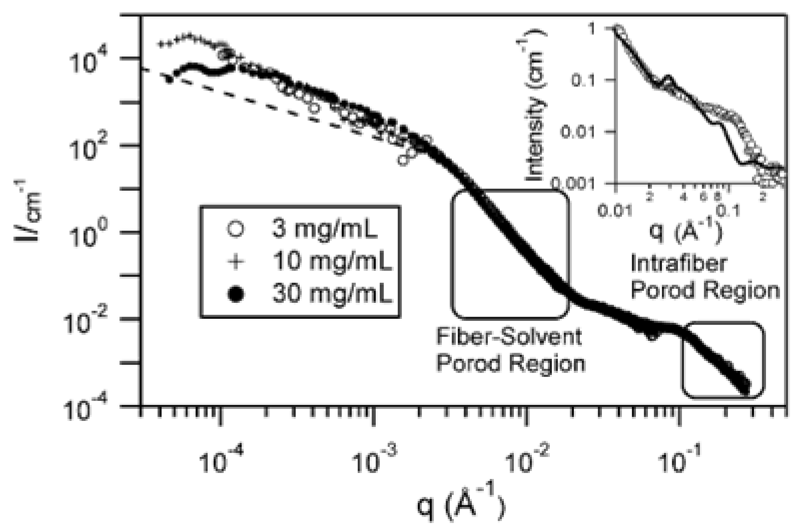




Fiber orientation under step strain



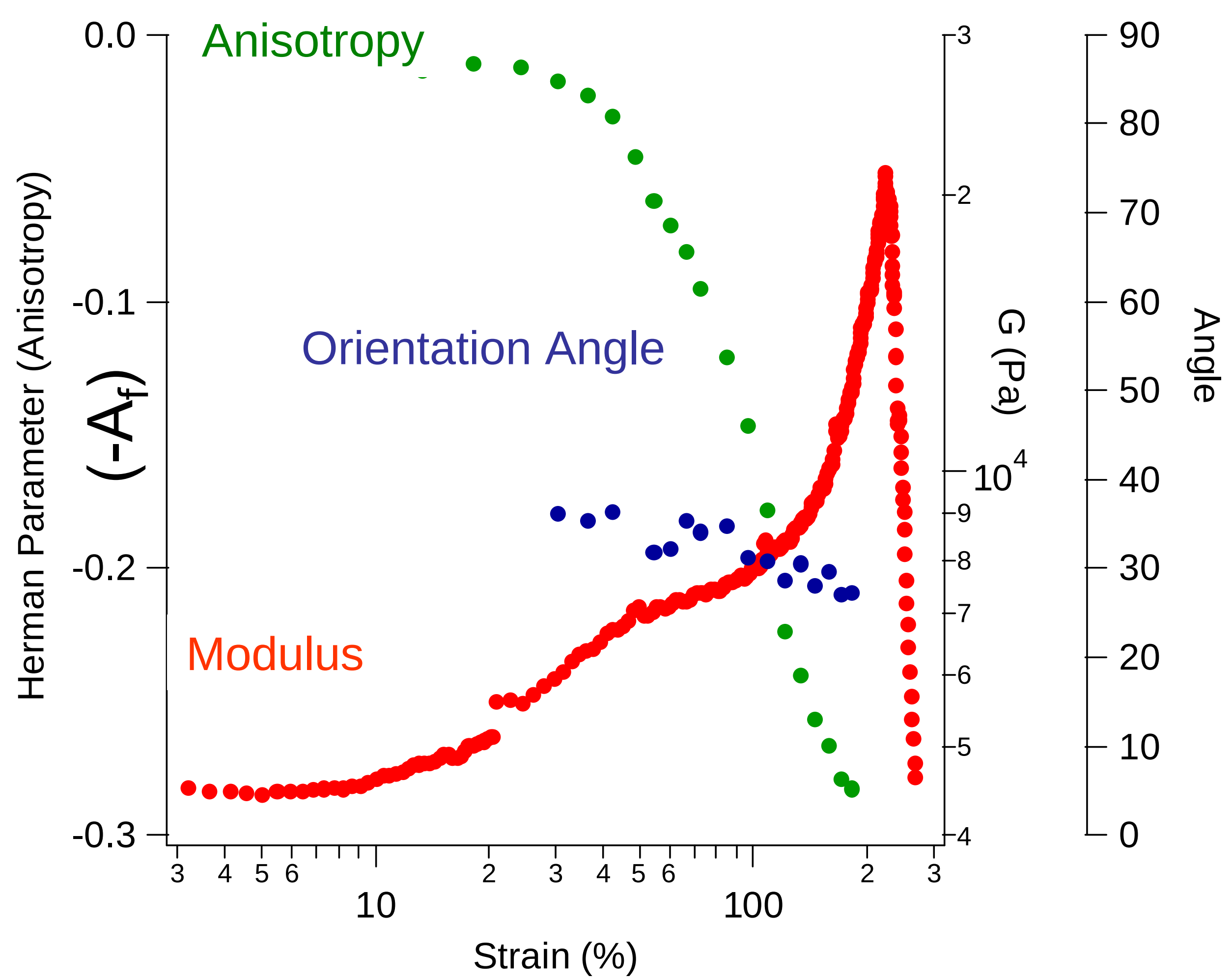




Fiber orientation is linked to gel rheology

Rheology: Linear elasticity → Strain hardening → Softening → Hardening

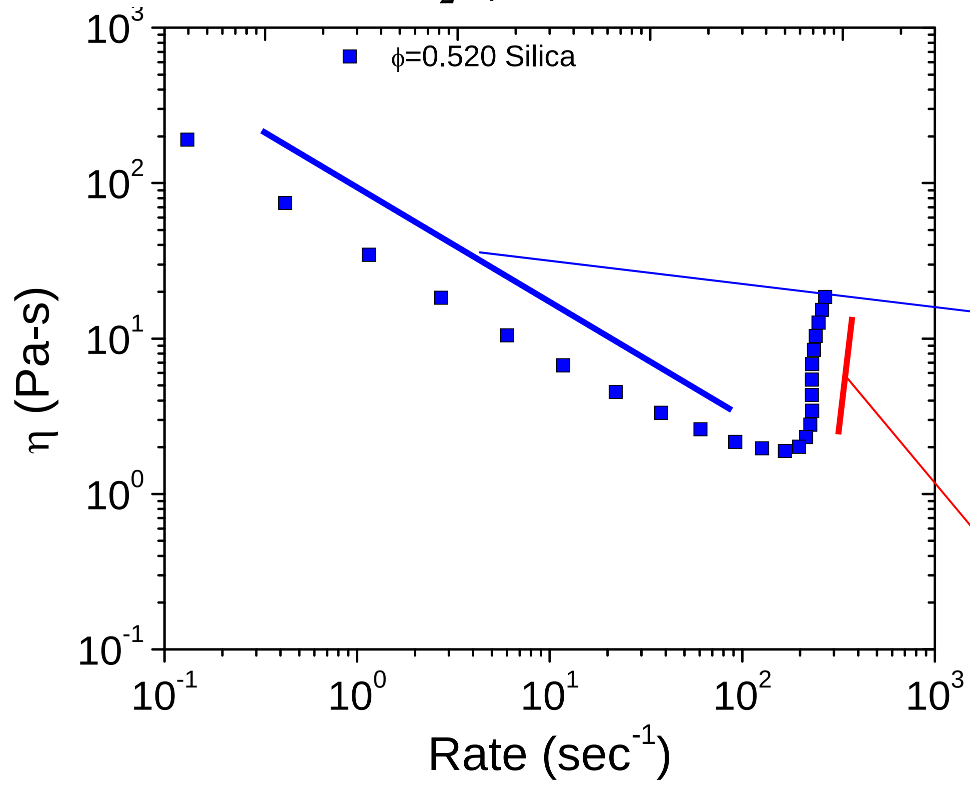
Structure: Equilibrium → Fiber stretching → Alignment → Limit of stretching



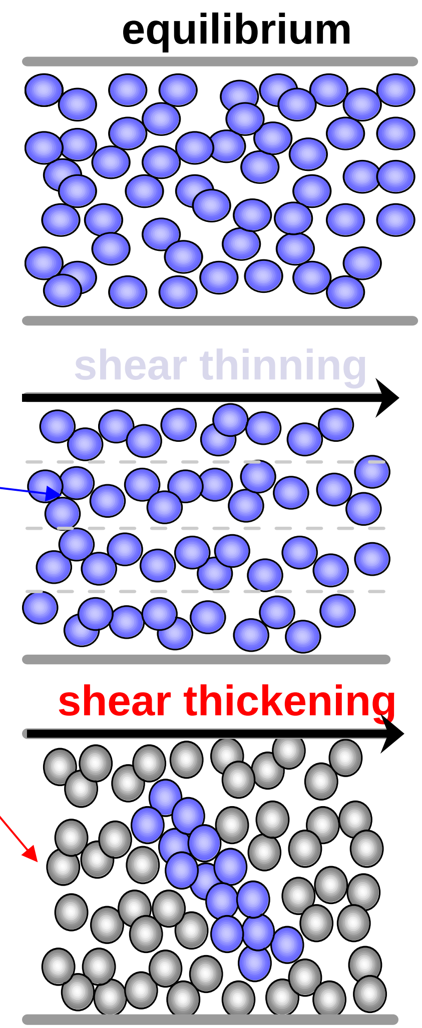
Shear thickening in colloidal suspensions*

***Norm Wagner et al., University of Delaware**

100 nm SiO_2, ϕ=0.52 in PEG/EG



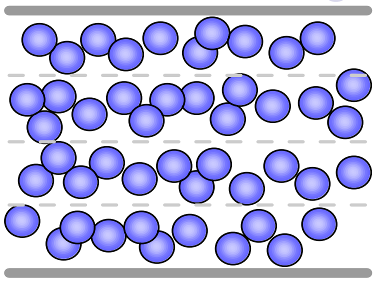
Hydroclusters increase viscosity

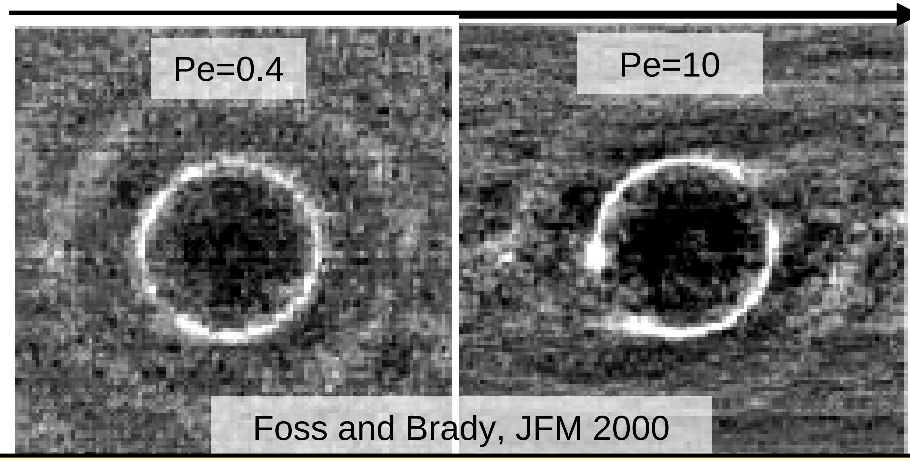


The proposed microstructural mechanisms of shear thickening in suspensions remain largely unconfirmed.

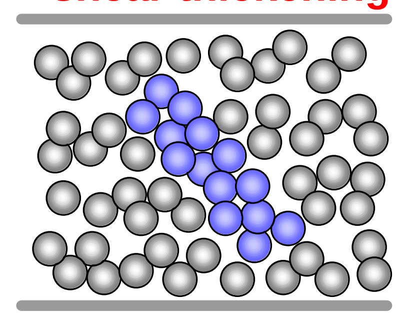
1-2 plane flow-SANS confirms hydrocluster formation

shear thinning

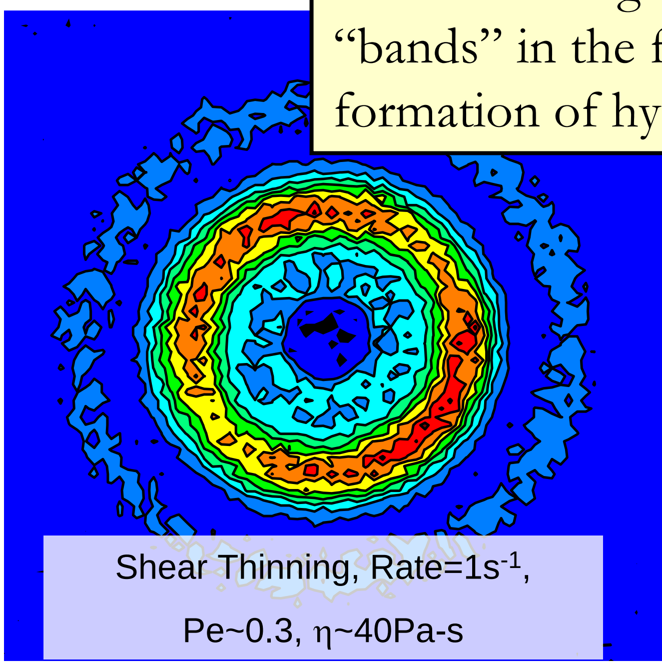


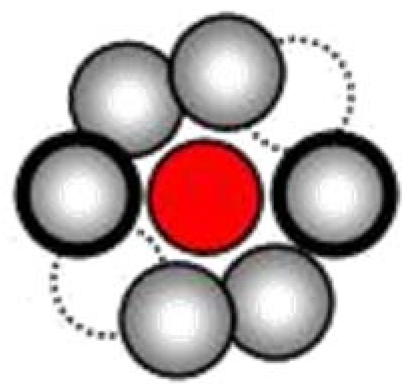


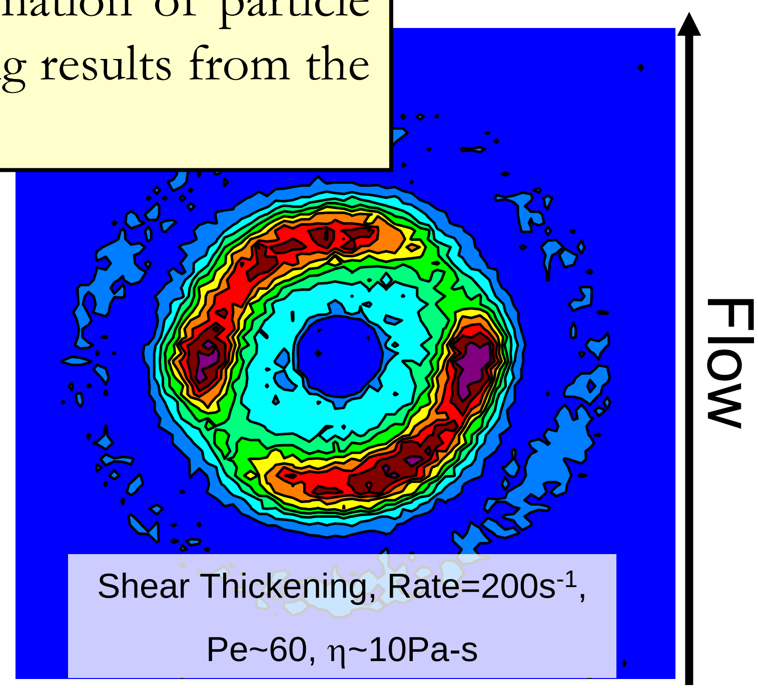
shear thickening



Shear thinning results from the formation of particle “bands” in the flow. Shear thickening results from the formation of hydroclusters.

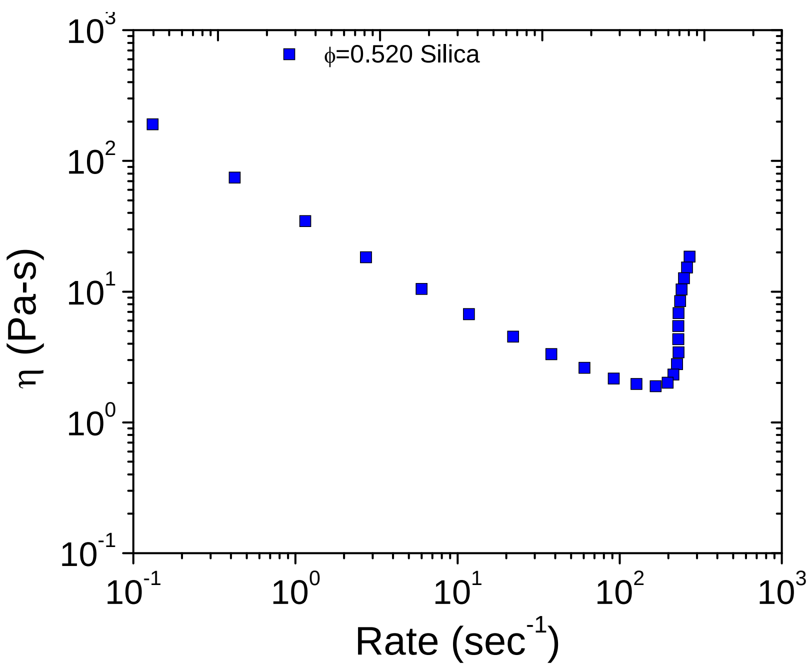


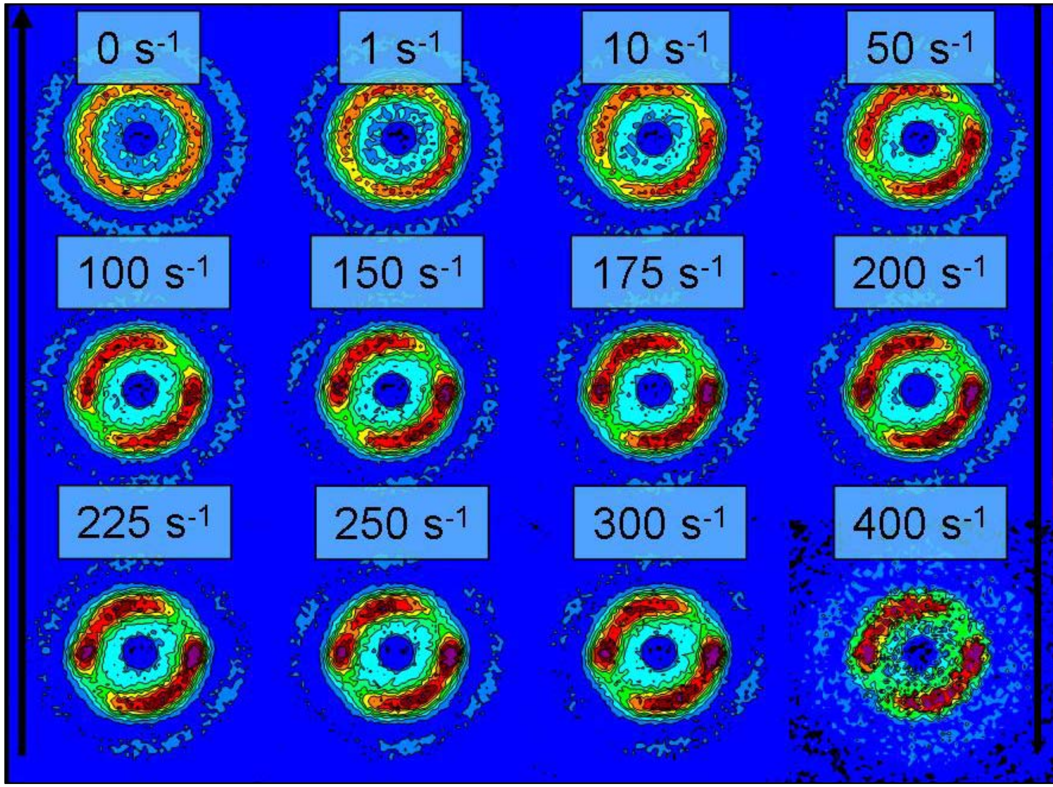




Note: 2D patterns have been rotated 90° in order to show “real” orientation.

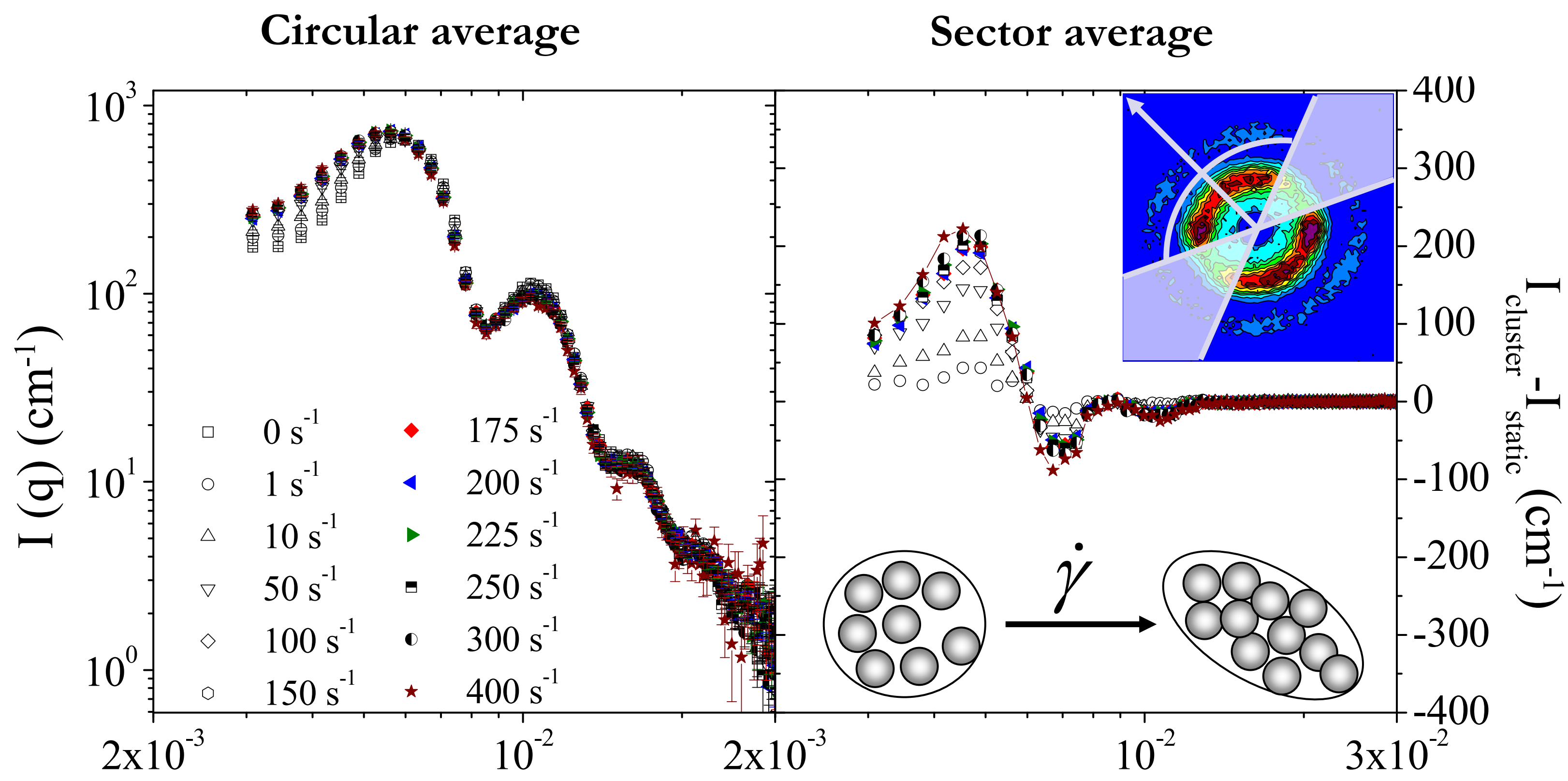
When do hydroclusters form?





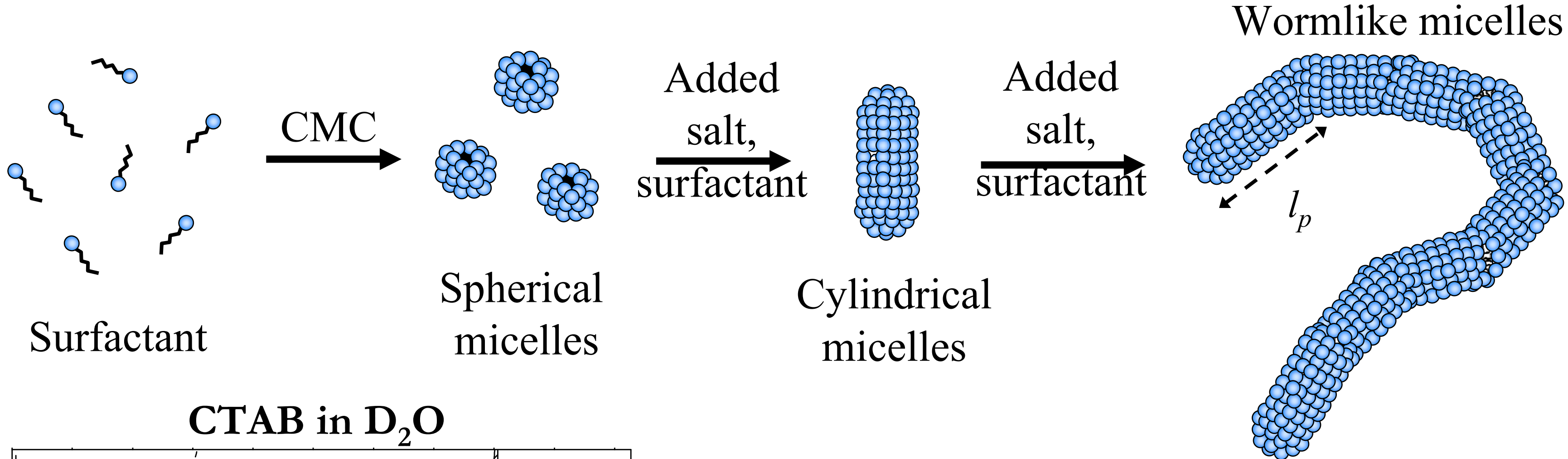
Flow-SANS reveals that hydrocluster formation occurs well before the onset of shear thickening (i.e. it is "masked" by the rheological effect of shear thinning).

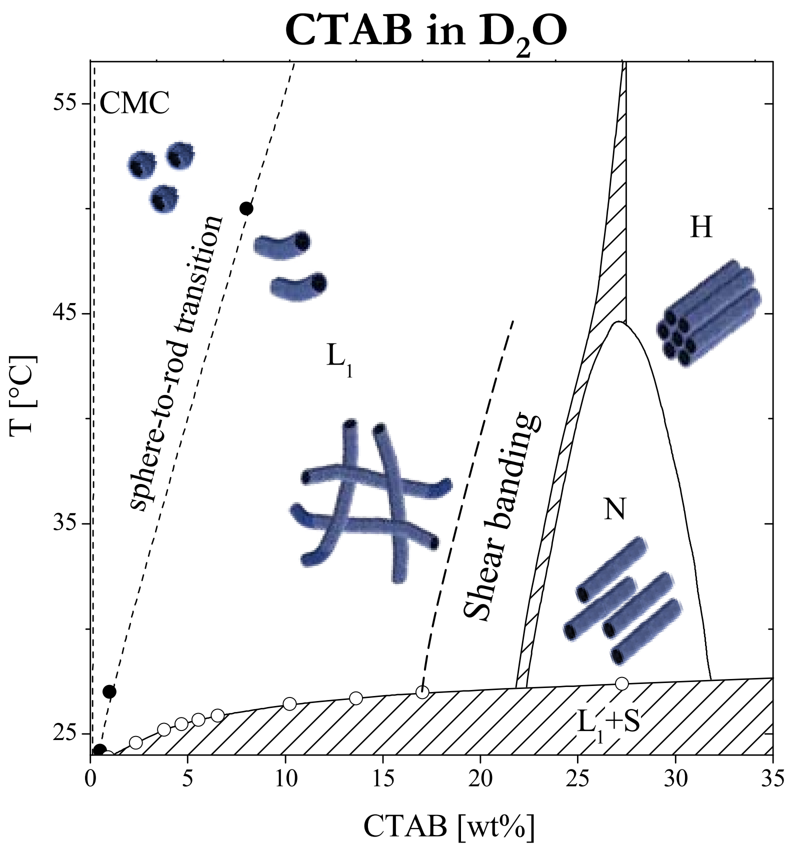
Evolution of hydroclusters



Sector averaging shows that clusters densify and become more anisotropic as the shear rate is increased.

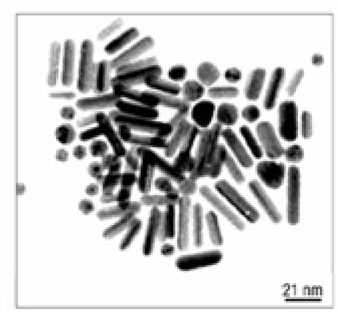
Wormlike micellar solutions (WLMs)





<u>Applications of wormlike micelles:</u>

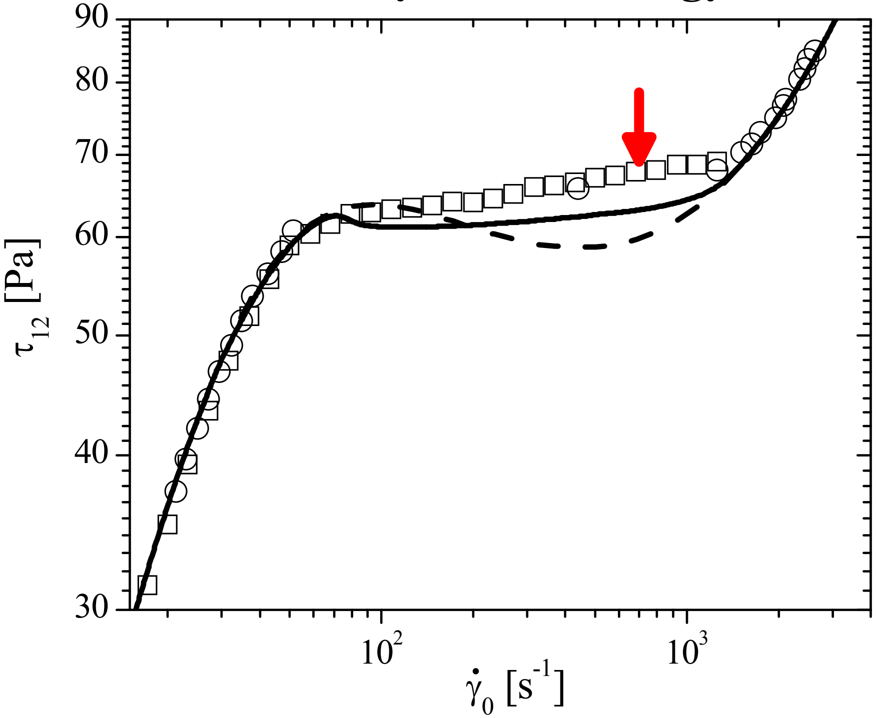
- Consumer products
- Enhanced oil recovery
- Drag reduction
- Nanotemplating



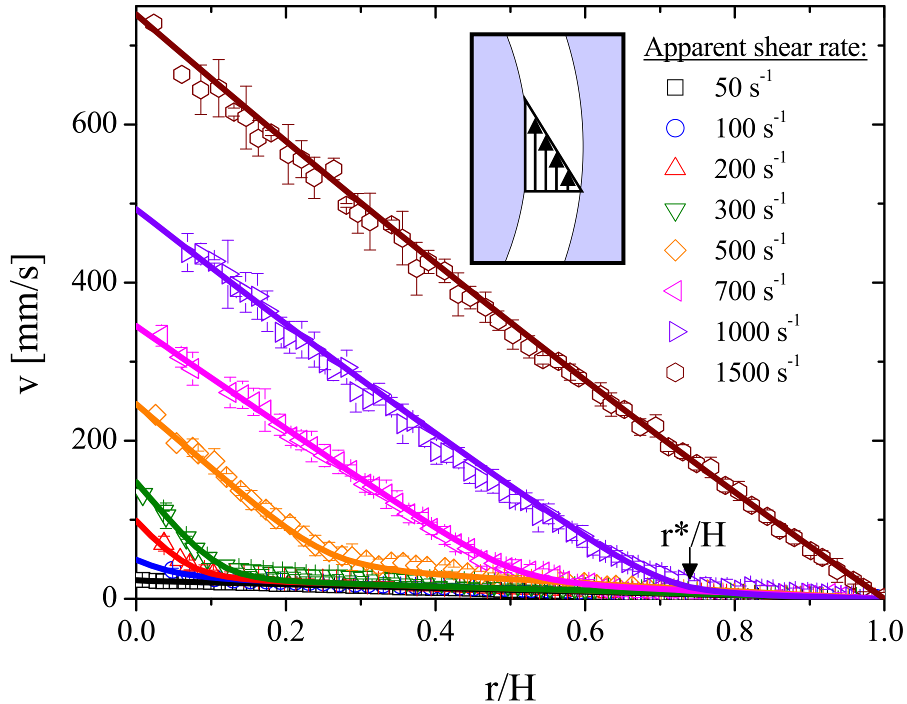
Shear

16.7 wt% CTAB in D_2O, 32°C

Steady shear rheology



Velocity profiles in Couette flow



- What is the mechanism of shear banding in this system?
- What are the microstructures of the high-shear and low-shear bands?
- Is shear banding a shear-induced phase separation? If so, is it first or second order?

… stay tuned for the group presentations!

Summary and Future outlook

- Numerous capabilities are available at NCNR for SANS measurements under shear flow
- Interpretation of flow-SANS data requires analysis of anisotropic scattering, frequently in multiple shear planes, to understand the 3D nature of the resulting structures
- Flow-SANS can provide unparalleled insight into the effect of macroscopic flow on fluid microstructure (and vice versa)
- Wish list for the future
  - **More users!**
  - Other flow geometries (extensional flow, pressure-driven flow)
  - Better analysis tools for anisotropic scattering

Acknowledgements

- NCNR User Group

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    Lionel Porcar
    Jeff Krzywon
    Andrew Jackson
    Andrea Hamill
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    Antonio Faraone

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- Danilo Pozzo, U. Washington
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… and you!