RHEO-SANS

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ACNS 2008

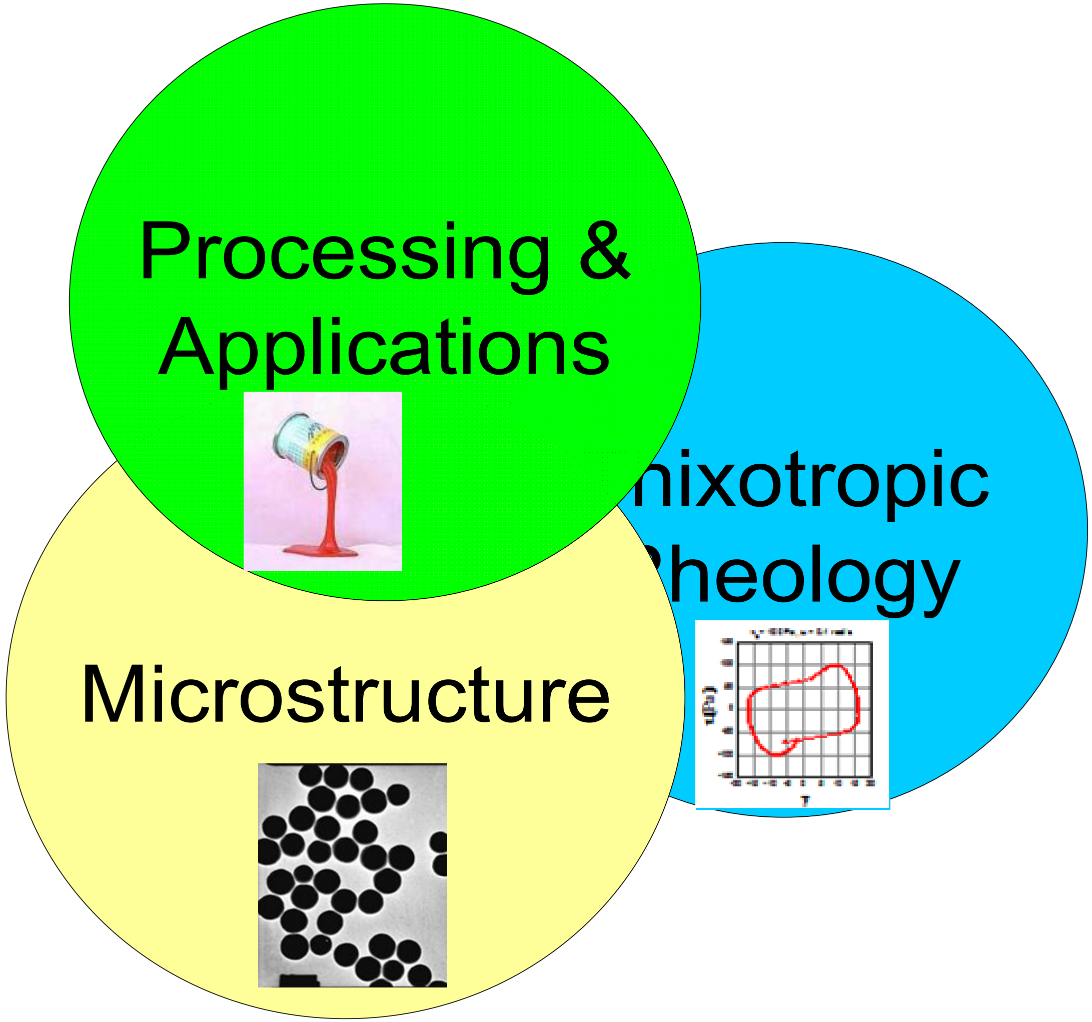
Session C, 1:45 Monday; Poster PC1.1, Matt Helgeson, Monday pm.

CO-AUTHORS

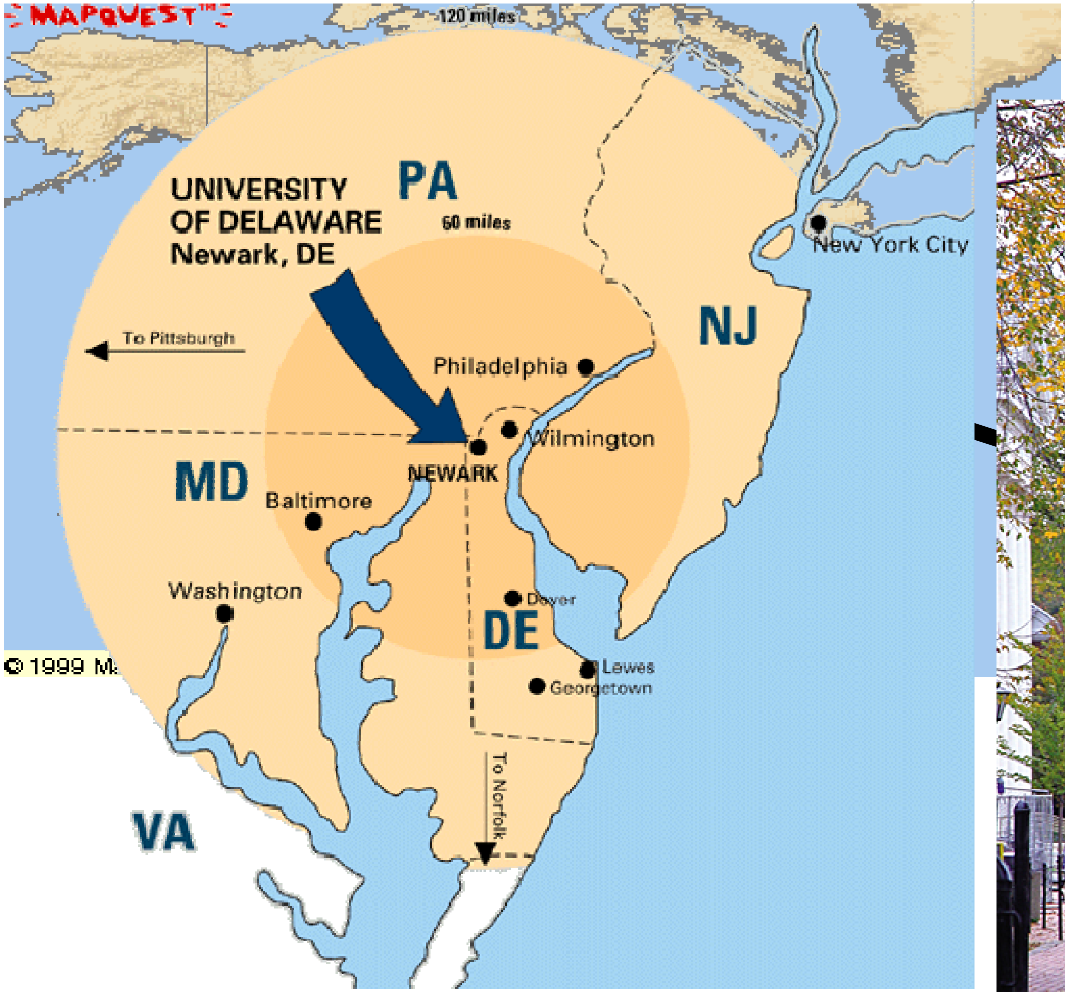
- Dr. Matt Liberatore (CSM)
- Dr. Florian Nettesheim (DuPont)
- Matt Helgeson
- Dennis Kalman
- Matt Reichert
- Dr. Lionel Porcar
- Dr. Paul Butler (NCNR-NIST:)

National Institute of Standards and Technology

Presentation Overview



University of Delaware 1743



UD Rheology Labs

RHEO-SANS, RHEO-SALS, DLS, FOQELS, HFQCR, DWS, microrheology

RHEO_SANS

Center for Neutron Science www.cns.che.udel.edu

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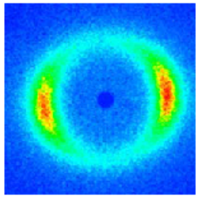
Chemical Engineering, all UD



Small Angle Neutron Scattering pattern from a flowing self-assembled surfactant system. The pattern indicates the molecular assembly and how the assembled structure aligns with the flow direction. The results are being used to engineer better surfactant systems for health care applications.

About CNS

The ***Center for Neutron Science*** at the University of Delaware is a cooperative agreement between the (UD) and the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR) to explore and develop new areas of neutron scattering science, with emphasis on strengths in complex fluids, macromolecular science, and condensed matter physics. This partnership will enhance the small angle neutron scattering (SANS) capabilities of the United States, and thereby, make them available to a large scientific user community. It also help train the next generation of neutron scientists and engineers for careers in support of the national nanotechnology initiative. SANS is a powerful probe of molecular and nanoscale structure, supramolecular order and dynamics, and can be used to monitor chemical and field-induced transformations. Because the technique requires a high-flux neutron source, SANS measurements are carried out at large national facilities, of which there are only four in the US. This cooperative agreement builds on the world-recognized expertise in SANS in the Departments of Chemical Engineering and Materials Science and Engineering at the University of Delaware and their long-standing scientific collaborations with the US' premier neutron scattering facility NCNR at NIST. The goals of the cooperative agreement include:

- the operation of SANS instrumentation at NCNR,
- exploration of new scientific applications of neutron scattering measurements,
- the development of new SANS instrumentation
- the development of new educational and training materials for use at UD, NIST and more broadly in support of the national neutron user community.

The project will include significant collaborative research with NIST scientists, and assisting visiting researchers at NCNR. A partnership between NIST and UD will help to develop novel experimental

http://www.cns.che.udel.edu/   10/17/2007

- 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

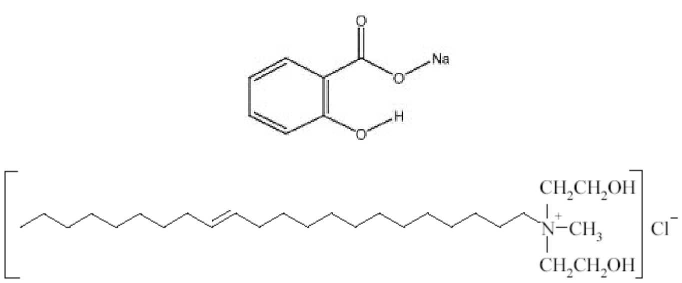
WHY RHEO-SANS*?

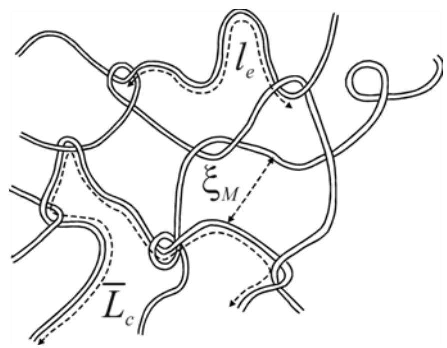
- Structural information on complex fluids in the size range 1nm~1 micron both at rest and under **flow** conditions
- Access to **rheological** properties not accessible in a mechanical rheometer
- Contrast matching in SANS enables probing individual **components** in a mixture

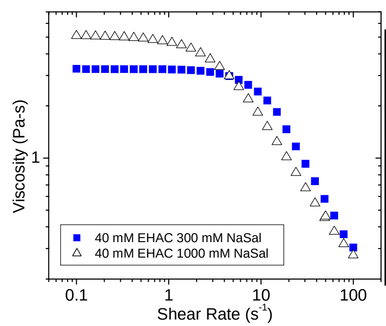
* Rheology concurrent with **s**mall **a**ngle **n**eutron **s**cattering

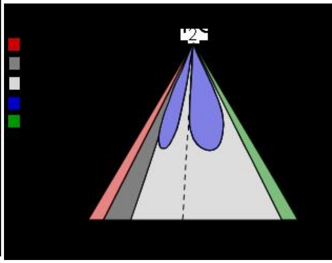
Rheo-Optics and Rheo-SANS

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.









Molecular Structure ⟷ Microstructure ⟷ Macroscopic observable properties

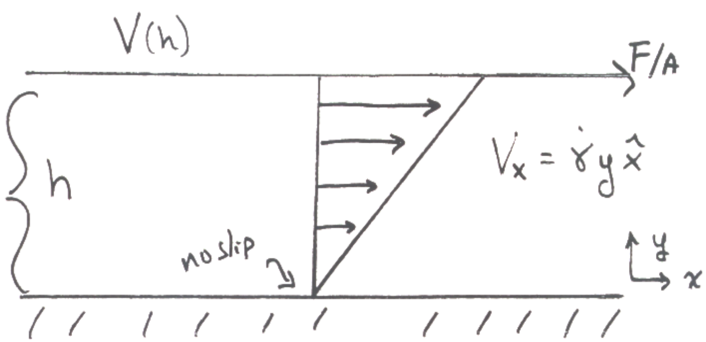
Rheology: Definitions:

Newton's Law of **Viscosity**: $\tau = \eta \dot{\gamma}$

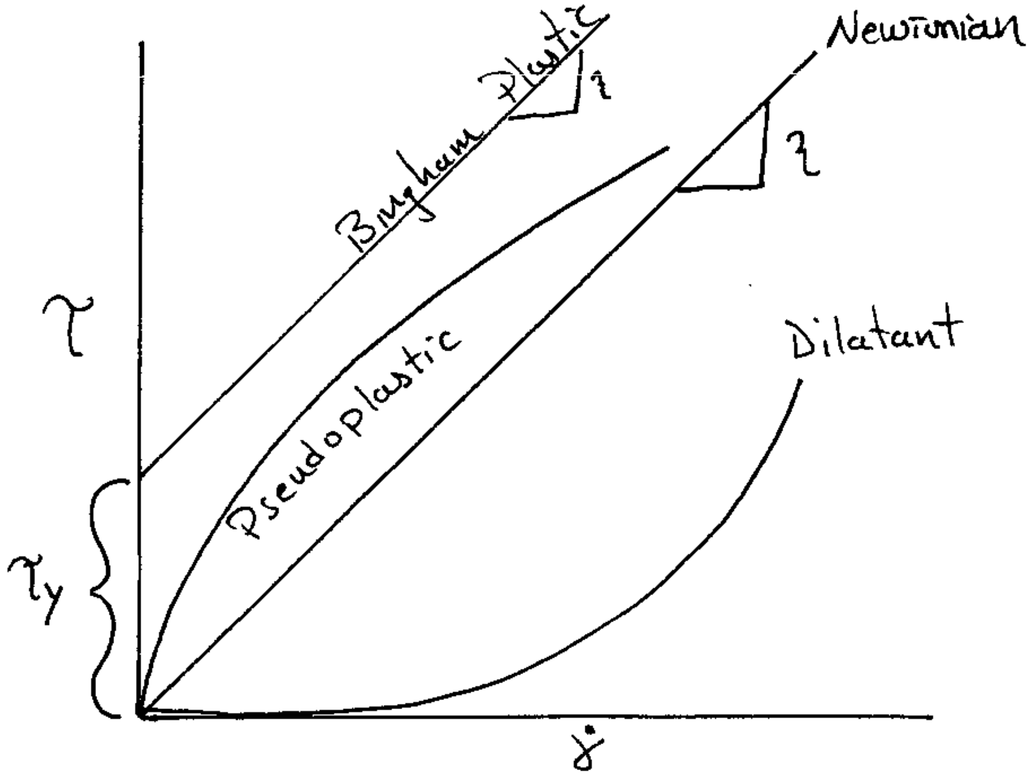
Energy dissipated per unit volume: $\dot{E} = \eta(\dot{\gamma})^2$

Typical Values of Viscosities

Substance	Approximate Viscosity (Pa·s)
Glass	10^{40}
Molten Glass	10^{12}
Molten Polymers	10^{3}
Honey	1
Water	10^{-3}
Air	10^{-5}



General Shear Behavior



Classifications of Rheological Behavior

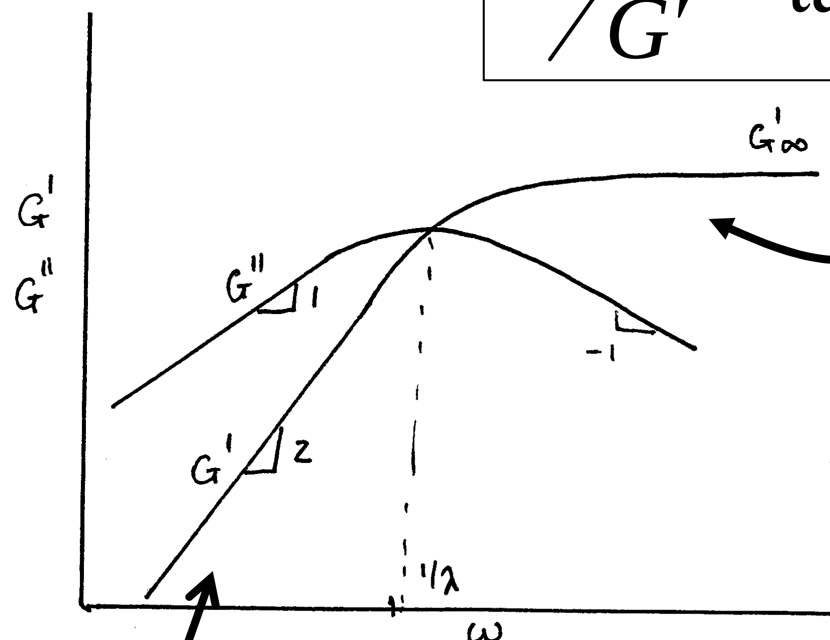
$$\tau = \tau_y + K \dot{\gamma}^n$$

n=1, Newtonian
n<1, pseudoplastic
n>1, dilatant

Viscoelastic Behavior of Fluids

$$G''/G' = \tan\delta$$

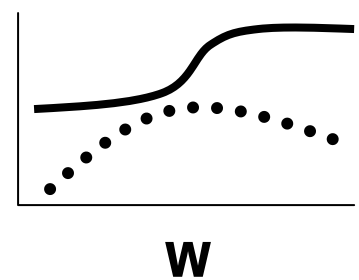
Glassy, solid like behavior



Viscoelastic behavior of a Maxwell Element

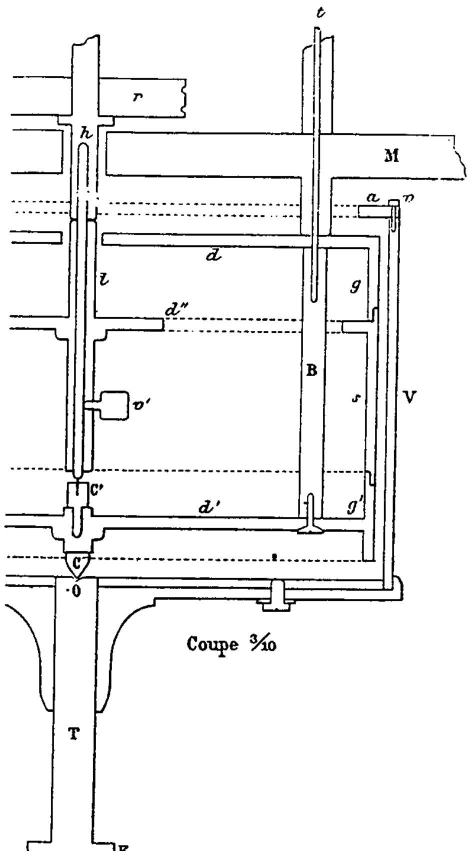
Liquid terminal regime

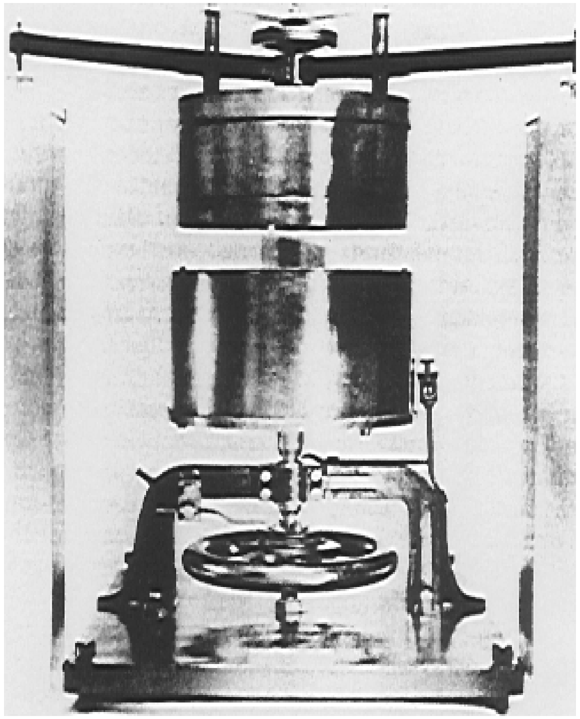
For systems with a yield stress, $G'(\mathbf{w} \Rightarrow 0) = G_0$



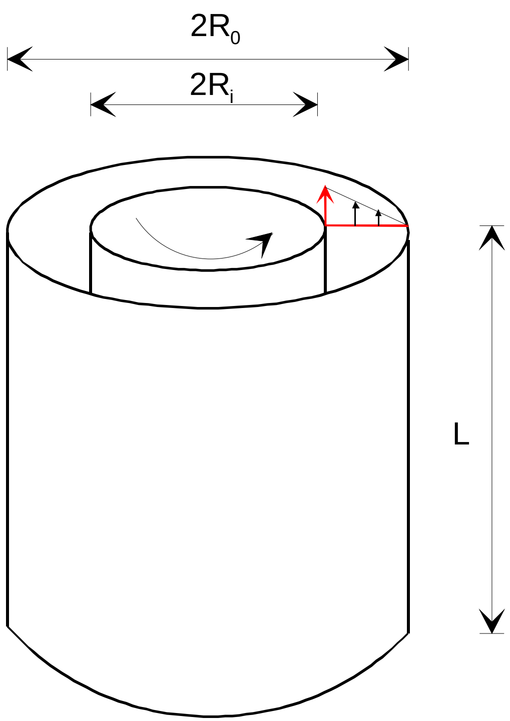
Drag flows : Couette geometry

M. Couette (1890)





Drag flows : Couette geometry



Concentric cylinders, inner one rotating : ω

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

Equations of motion:

$$r: \quad \frac{1}{r}\frac{\partial\left(r\sigma_{rr}\right)}{\partial r} - \frac{\sigma_{\theta\theta}}{r} = -\rho\frac{v_\theta^2}{r}$$

$$\theta: \quad \frac{\partial\left(r^2\sigma_{r\theta}\right)}{\partial r} = 0$$

$$z: \quad \frac{-\partial p}{\partial z} + \rho g = 0$$

Drag flows : Couette geometry

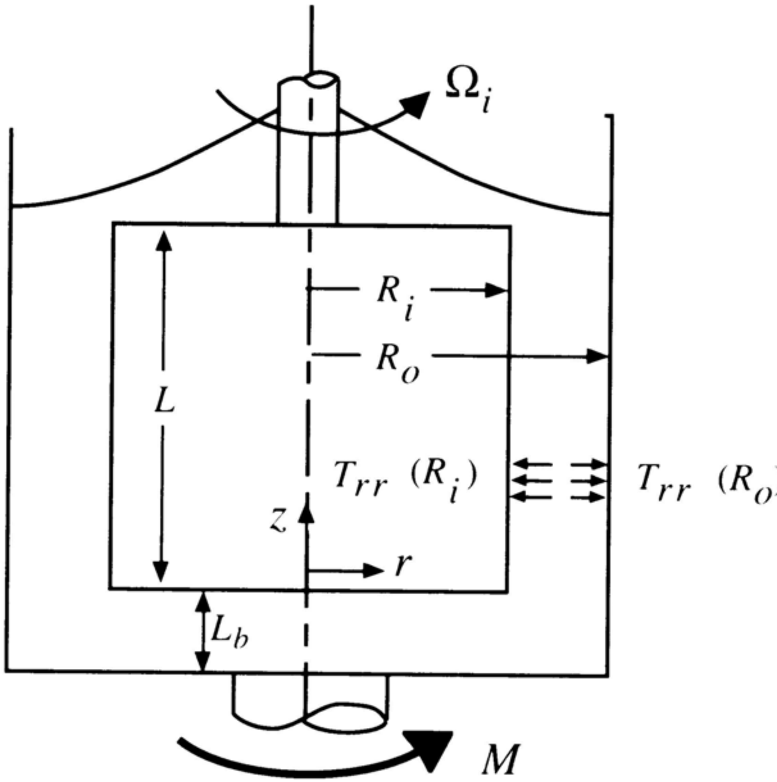
Boundary conditions
1. $v_\theta = R_i \omega$ at Ri
2. $v_\theta = 0$ at Ro

Shear stress

$$\theta: \quad \frac{\partial \left(r^2 \sigma_{r\theta} \right)}{\partial r} = 0 \quad \rightarrow \quad \sigma_{r\theta} = \frac{C}{r^2}$$

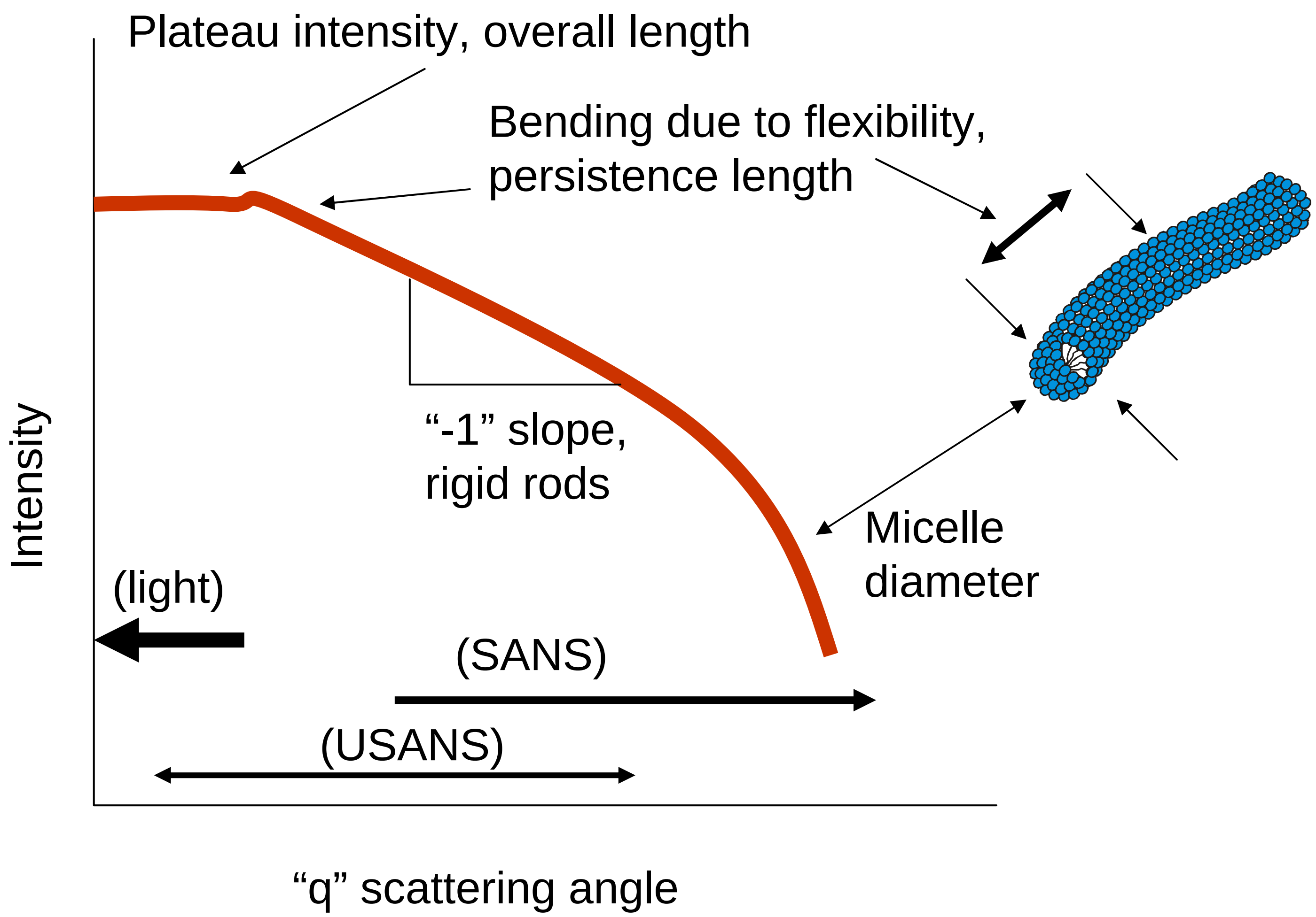
$$\sigma_{r\theta}(Ro) \cdot (2\pi \cdot Ro \cdot L) = \frac{M}{Ro}$$

$$\sigma_{r\theta} = \frac{M}{2\pi \cdot L \cdot r^2}$$



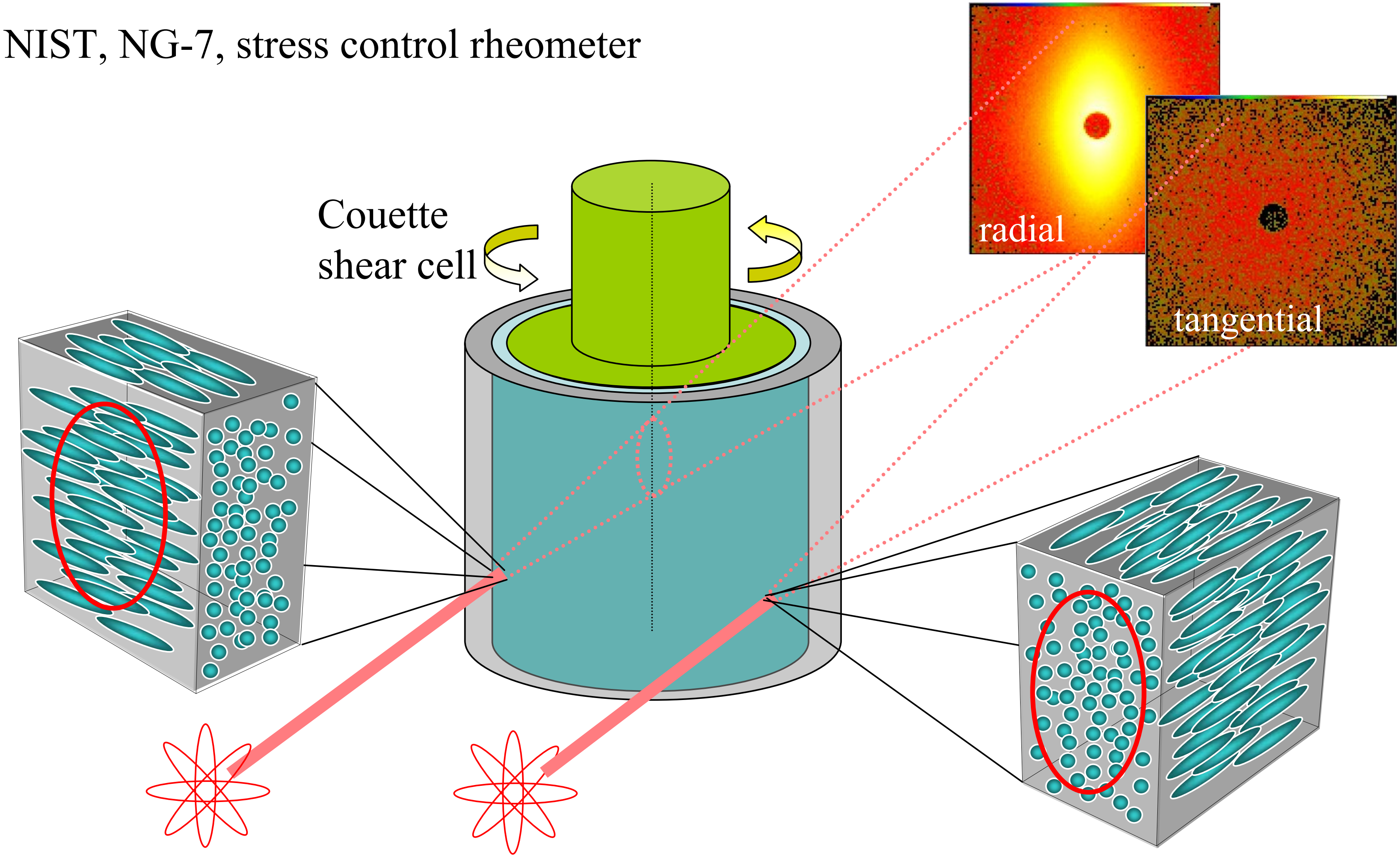
Macosko, “Rheology”

Scattering angle $\propto$ 1/Length

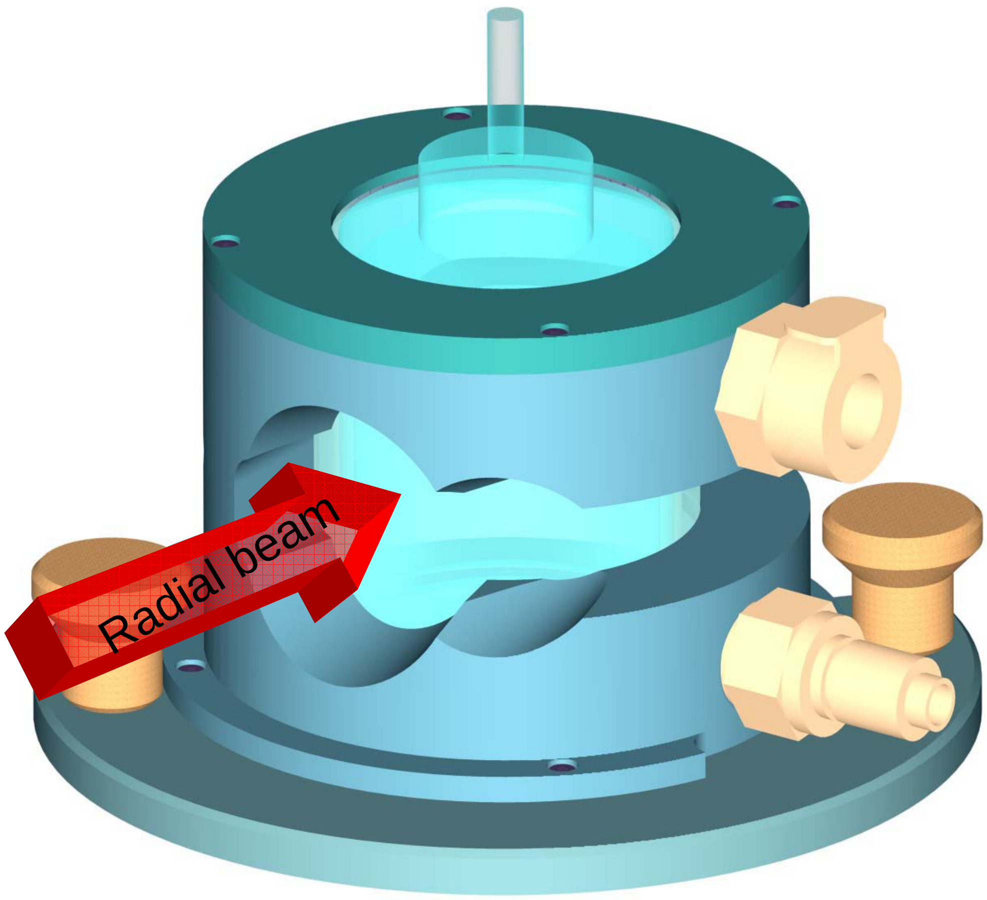


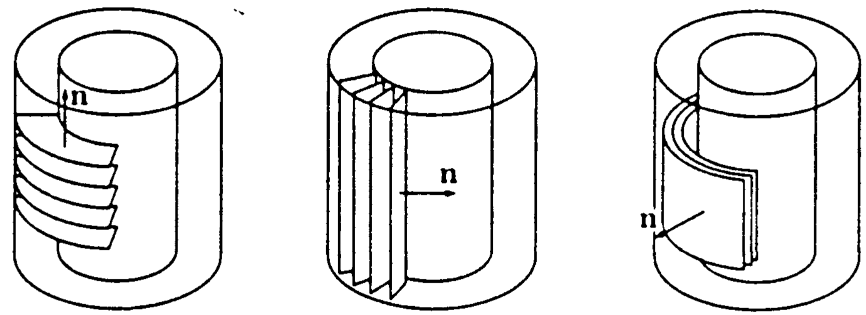
Rheo-SANS Investigation

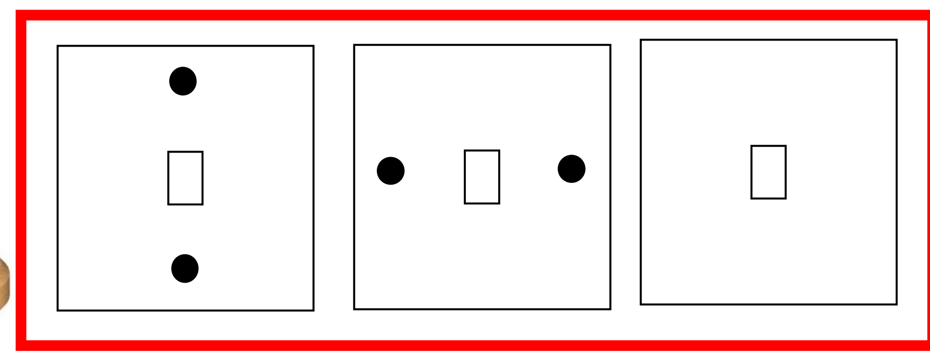
NIST, NG-7, stress control rheometer



Shear Cell, Rheo-SANS

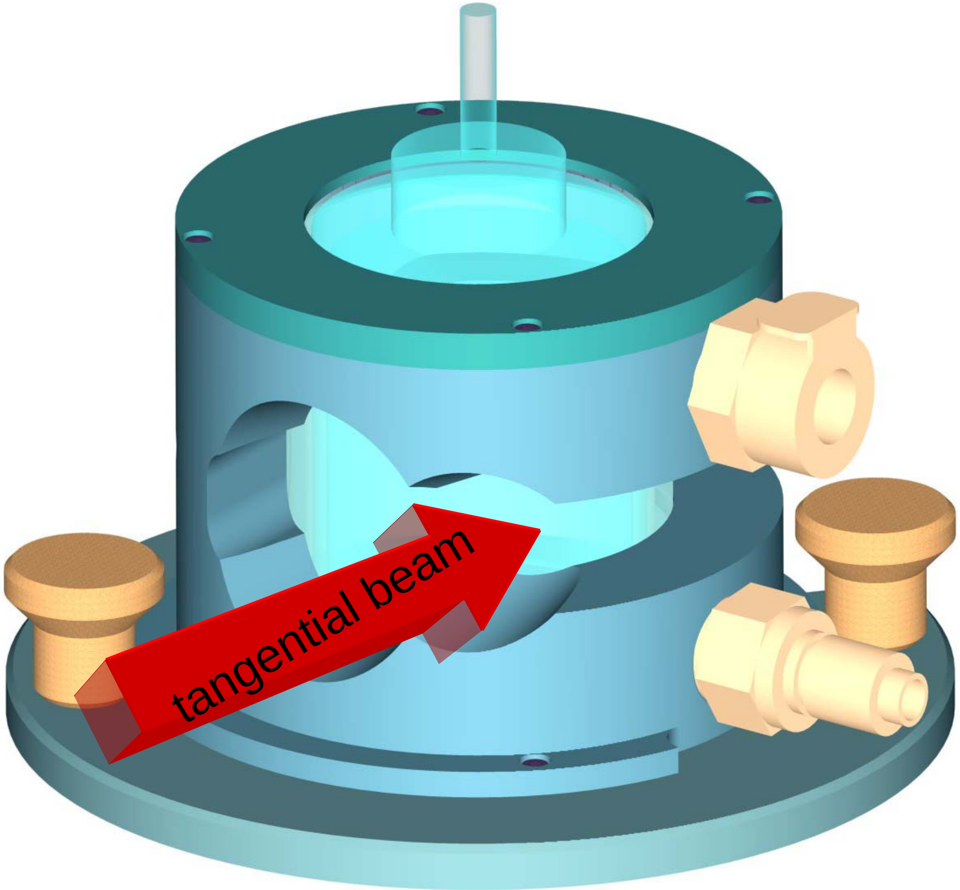


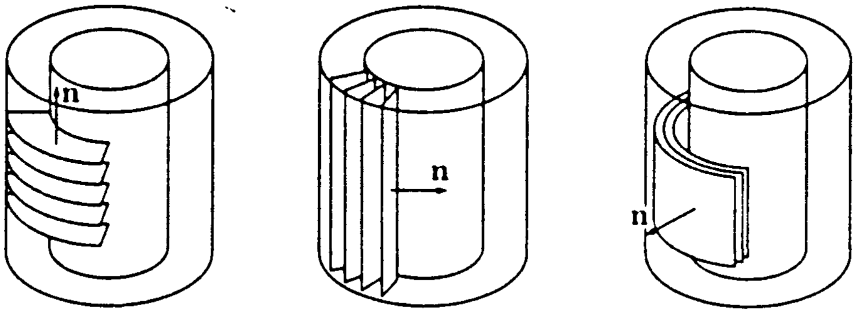


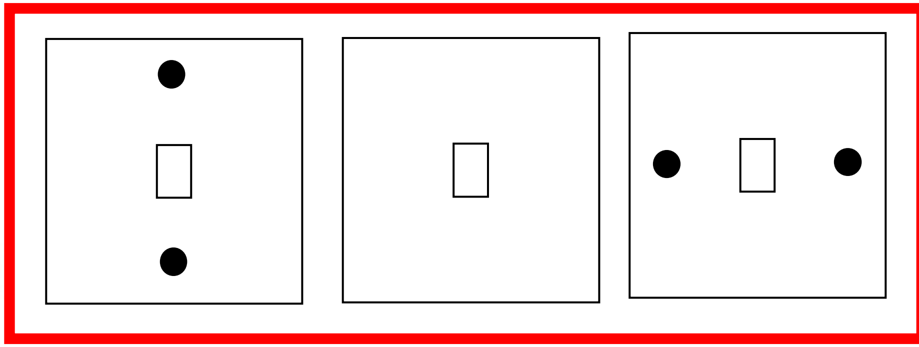


Couette shear cell at D11,
ILL, Grenoble
Designed by Peter Lindner

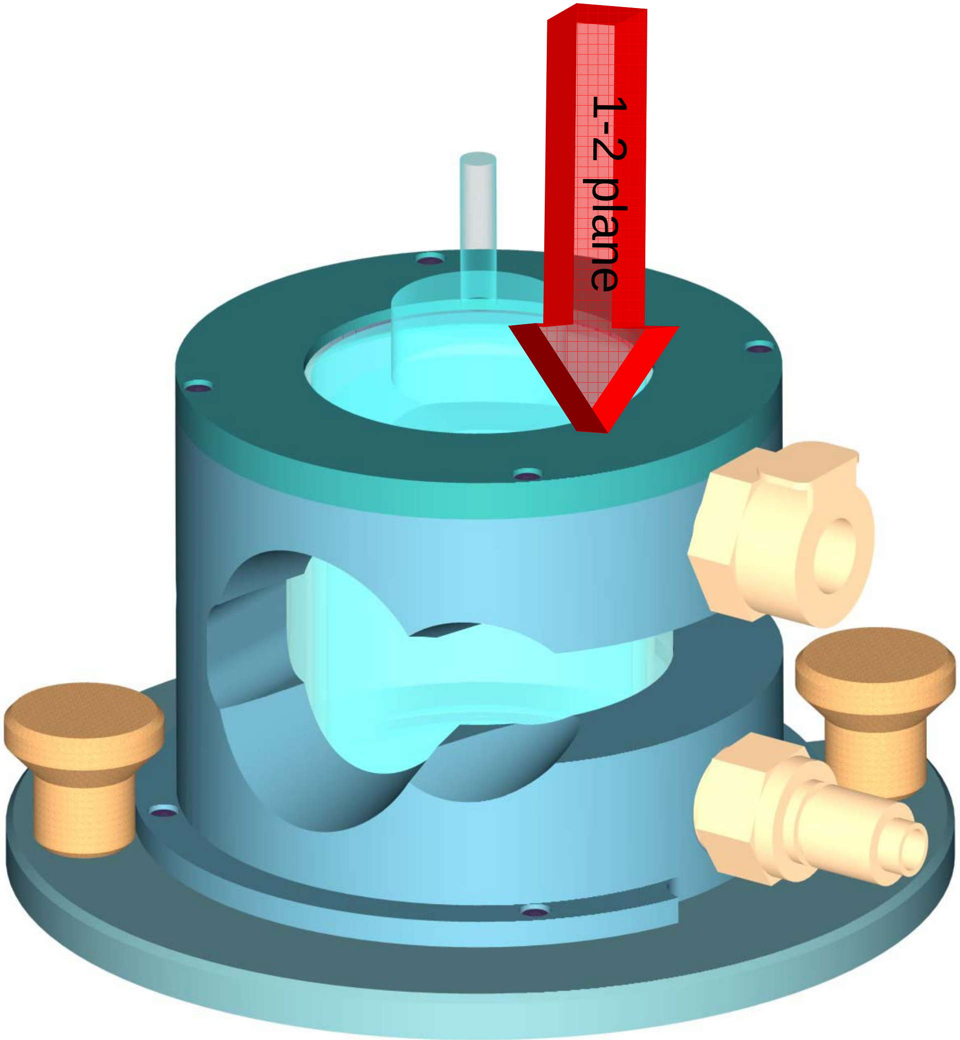
Shear Cell, Rheo-SANS

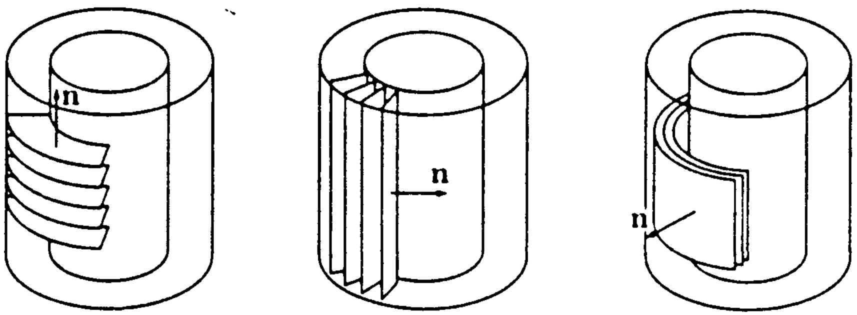


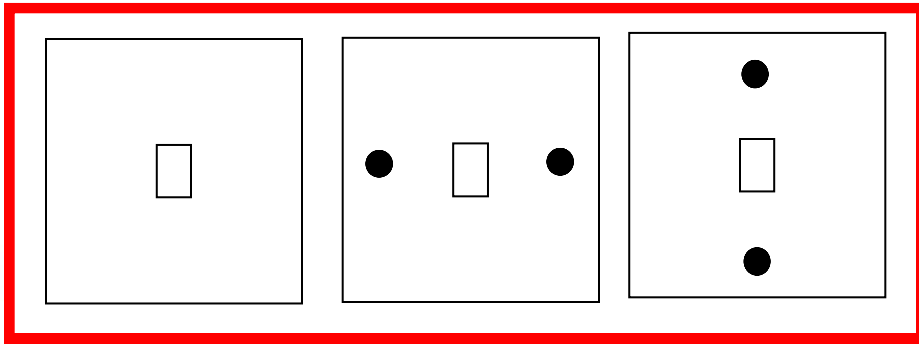




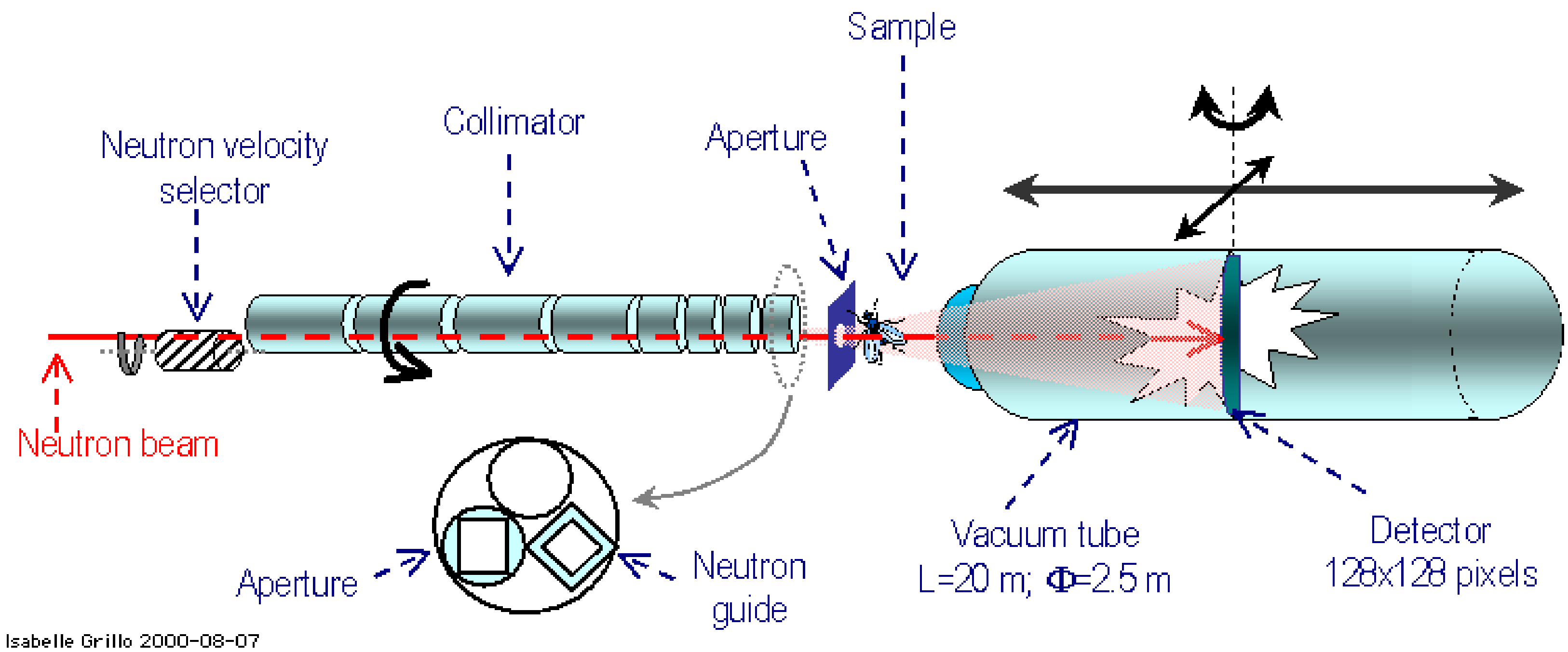
Shear Cell, Rheo-SANS







Small Angle Neutron Scattering



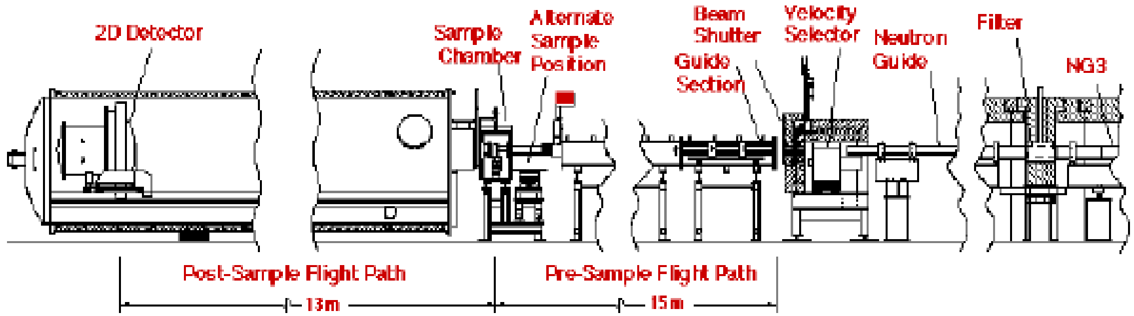
$$\vec{k}_i = \frac{2\pi n}{\lambda_0}$$

$$\vec{k}_s = \frac{2\pi n}{\lambda_0}$$

$$|\vec{q}| = \left|\vec{k}_s - \vec{k}_i\right|$$

$$|\vec{q}| = \frac{4\pi n}{\lambda_0}\sin\left(\frac{\theta}{2}\right)$$

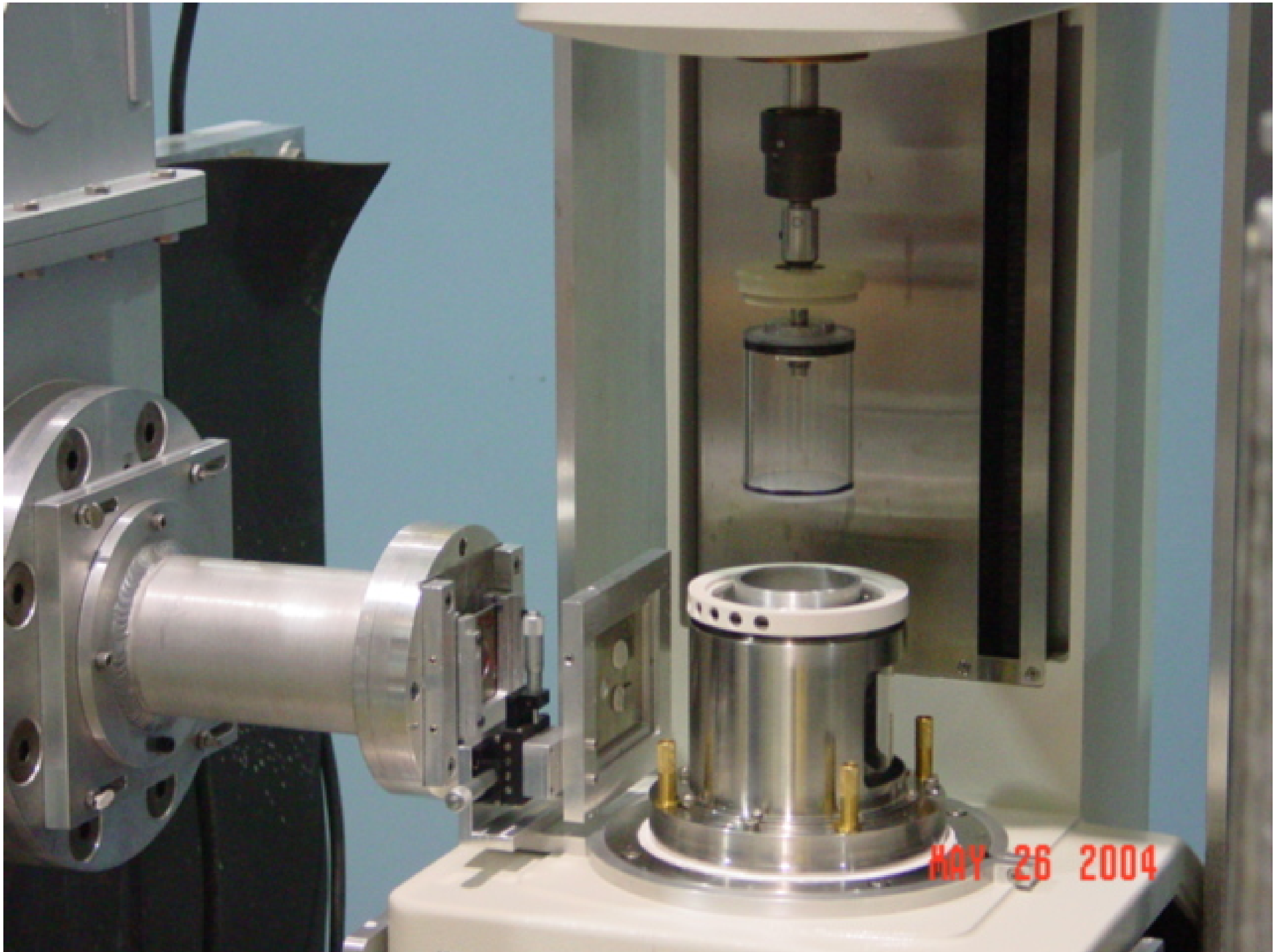
SANS Beamline NIST



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:

Kernick & Wagner, JOR 43(3), 521-549, (1999)

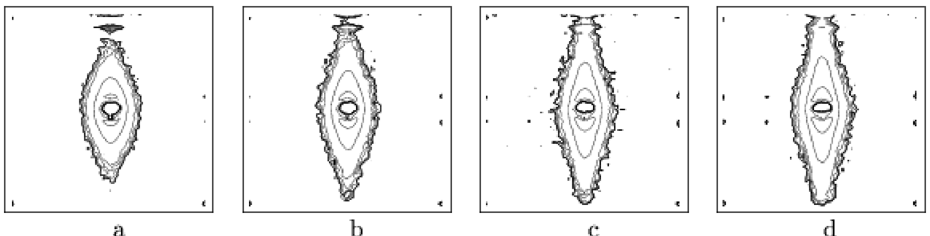


FIG. 12. On-axis SANS images for B615 at shear rates a) 1.9 s^{-1}, b) 3.9 s^{-1}c) 7.8 s^{-1}, and 11.7 s^{-1}. The contours are on a logscale, and are on the same scale for all images.

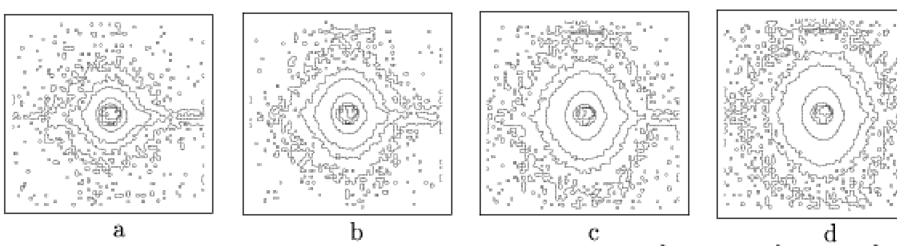
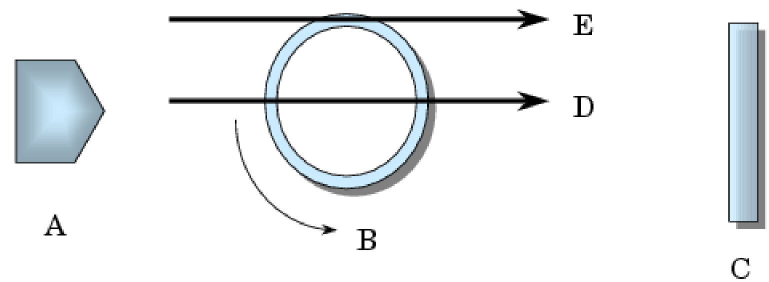


FIG. 13. Off-axis SANS images for B615 at shear rates a) 1.9 s^{-1}, b) 3.9 s^{-1}c) 7.8 s^{-1}, and 11.7 s^{-1}. The contours are on a logscale, and are on the same scale for all images.



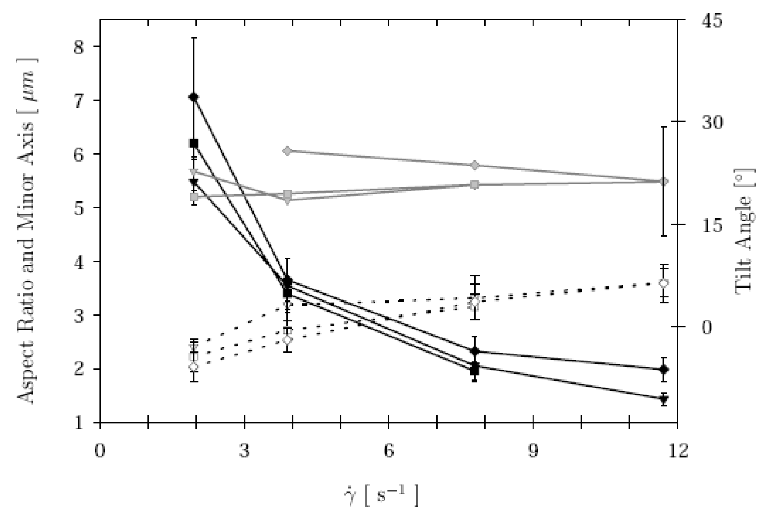
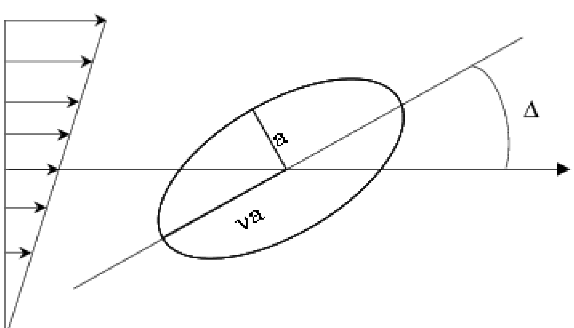


FIG. 14. SANS measured ellipsoid parameters versus shear rate. Aspect ratio for blends B615 (▼), B610 (■), B605 (◆). Minor axis for blends B615 (▽), B610 (□) and B605 (◇). Tilt angle for blends B615 (◭), B610 (▣), and B605 (◈), with representative error bar.



Resolving 3-D structure from 1-3 and 2-3 plane SANS data:

Kernick & Wagner, JOR 43(3), 521-549, (1999)

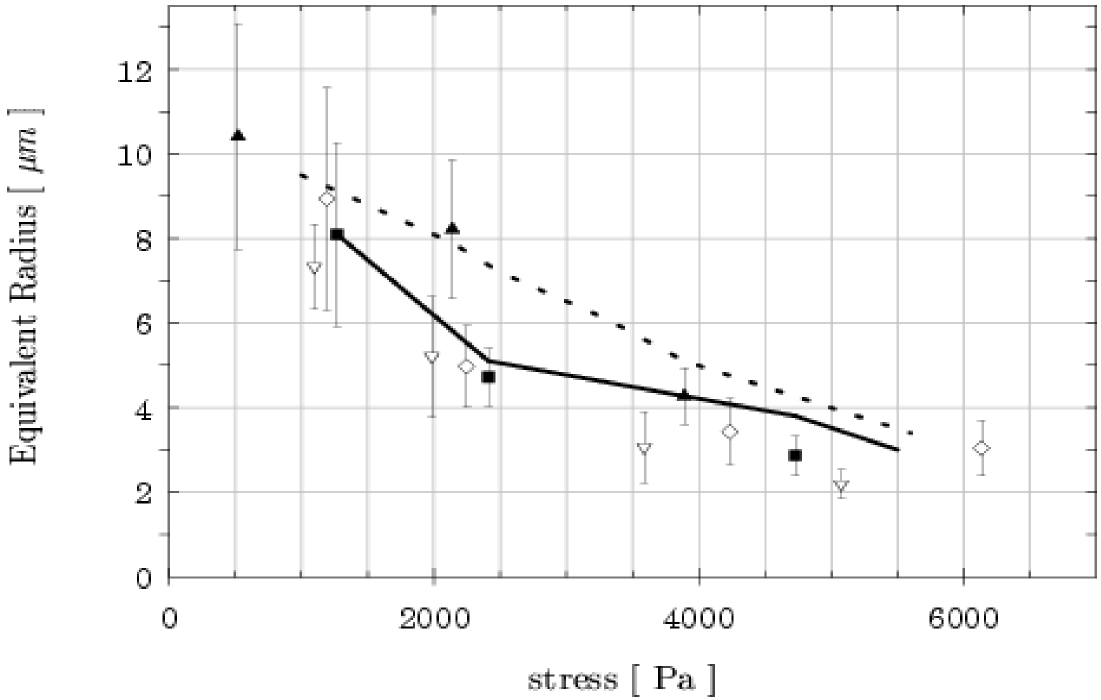
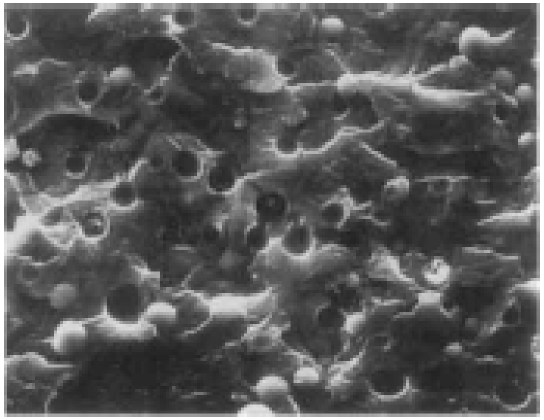


FIG. 17. Equivalent radius versus stress from SANS for blends B615 (▽), B610 (■), B605 (◇), B110 (▲). Also included is the size from the static measurement (figure 11) as a function of previous stress for B610 (—) and B110 (···).

Production of nanofibers by shear processing TLCP blends



Shear

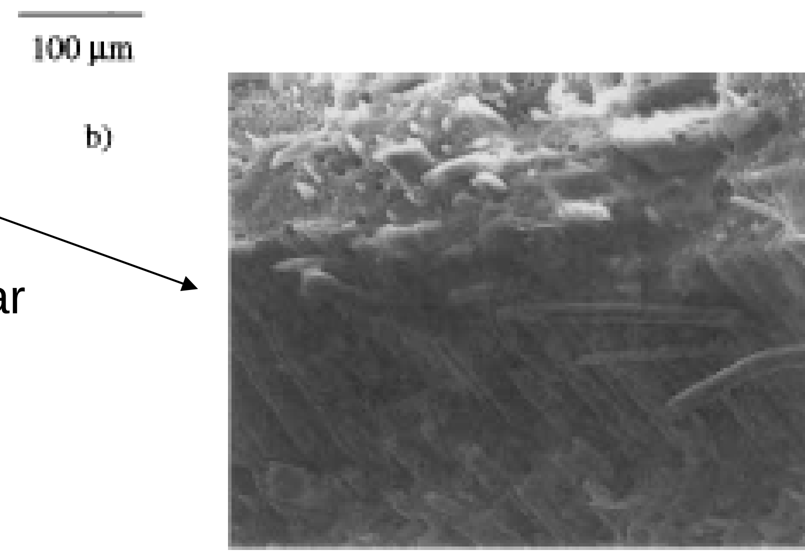


Figure 11. SEM micrographs of freeze-fractured quenched extrudates for the 30 wt % blend sheared at (a) 822 and (b) 18000 1/s.

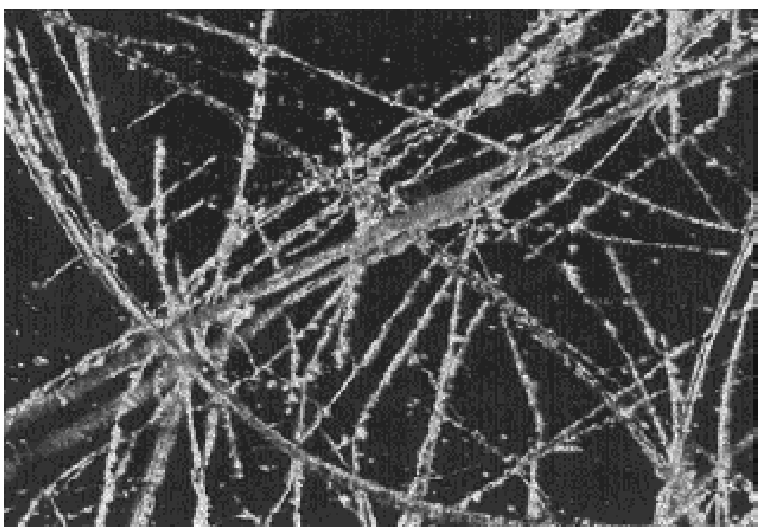
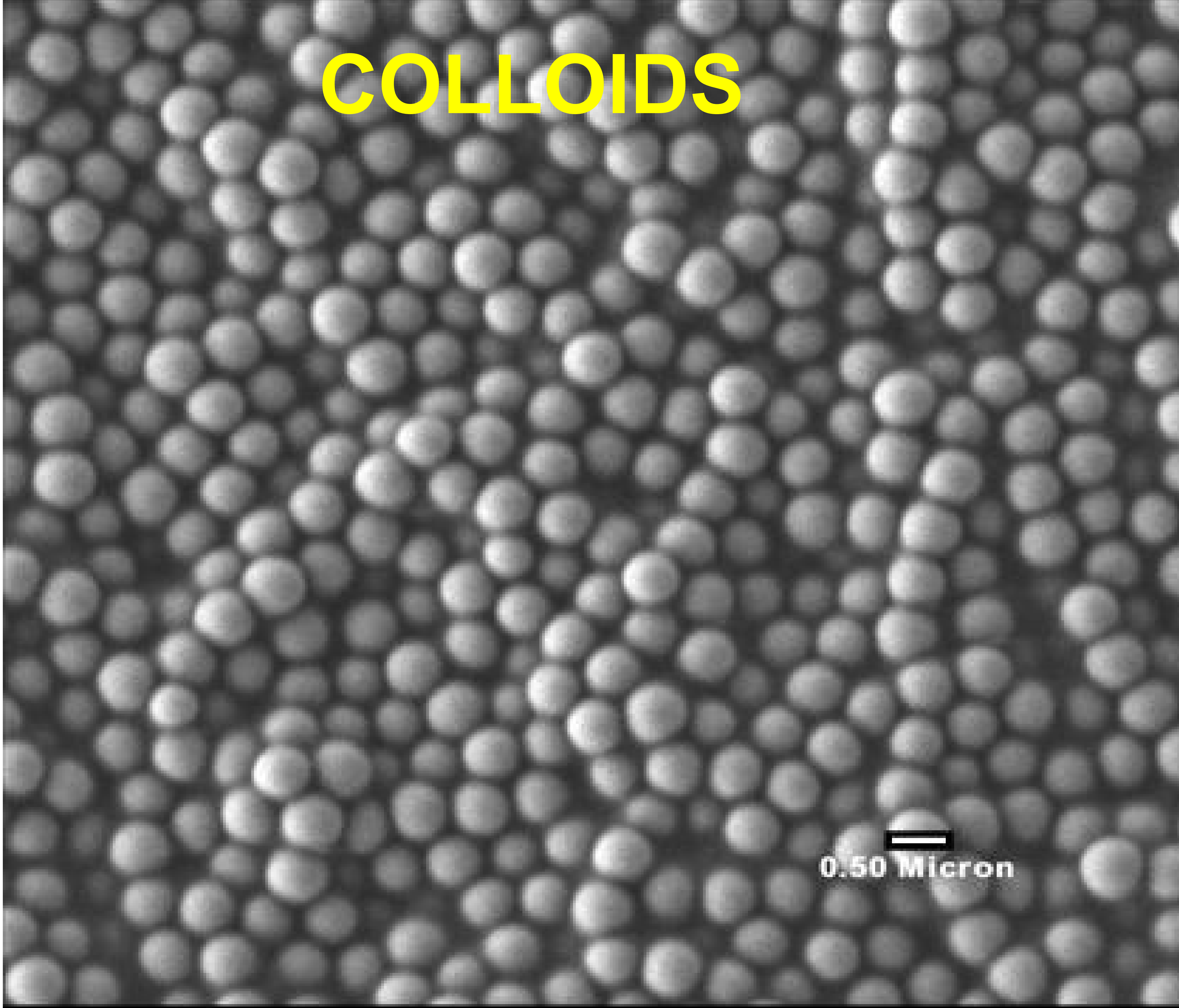


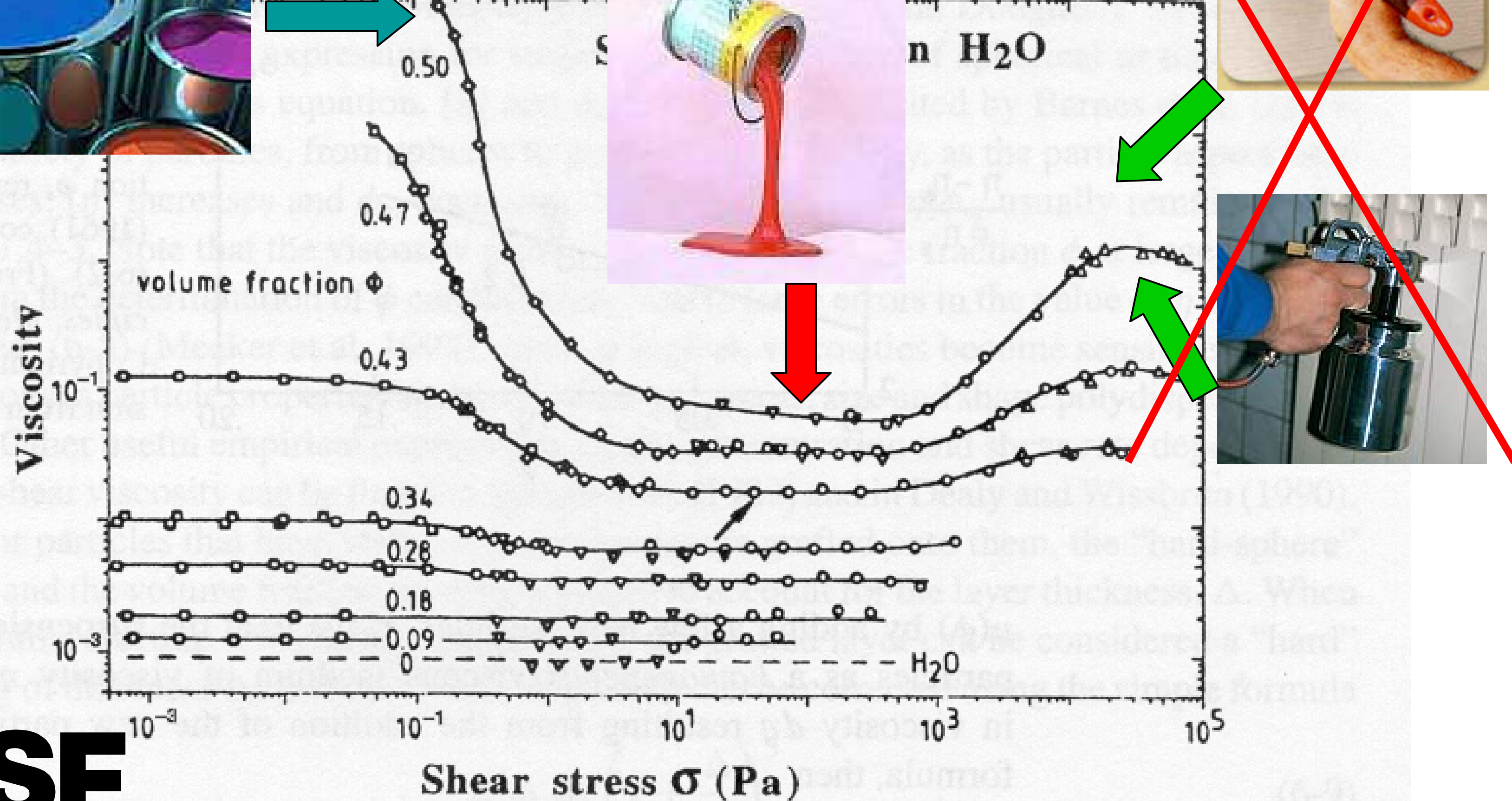
Figure 5. POM picture of recovered TLCP fibers in the 30 wt % blend after PBT matrix dissolution. Tested shear rate is 620 1/s.

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
JOURNAL OF POLYMER SCIENCE PART B-POLYMER PHYSICS 36(10): 1769-1780 (1998)

COLLOIDS



Engineered Nanomaterials e.g., “house paint”



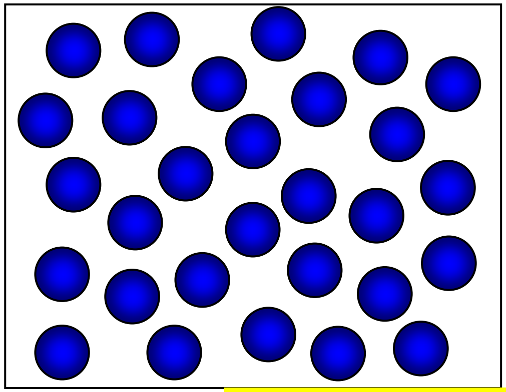
BASF

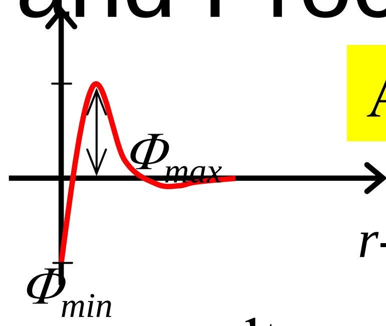
H. Martin Laun, ***Ang. Mak. Chem. 123/124*** (1984), 335.

RHEO_SANS

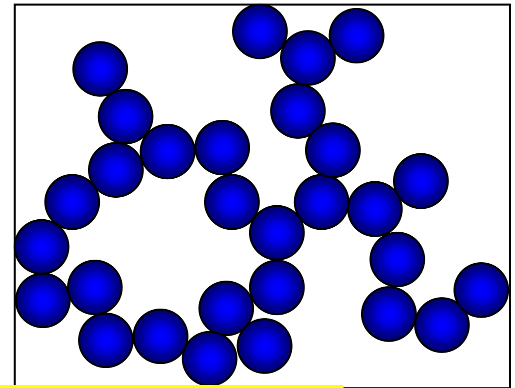
Gels and Processing

Stable Dispersion





Aggregated Dispersion/Gel

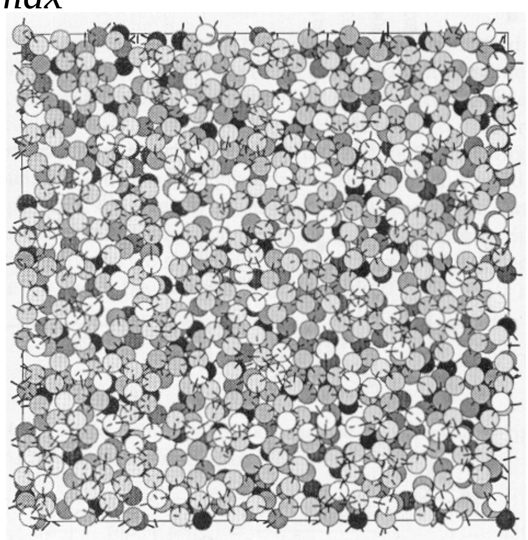


salt
pH
polymer

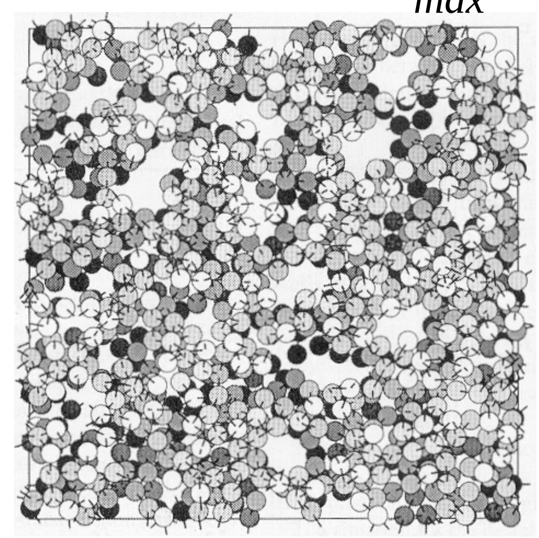
$\Phi_{max} = 0$

Brownian Dynamics Simulation $\phi = 0.40$

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



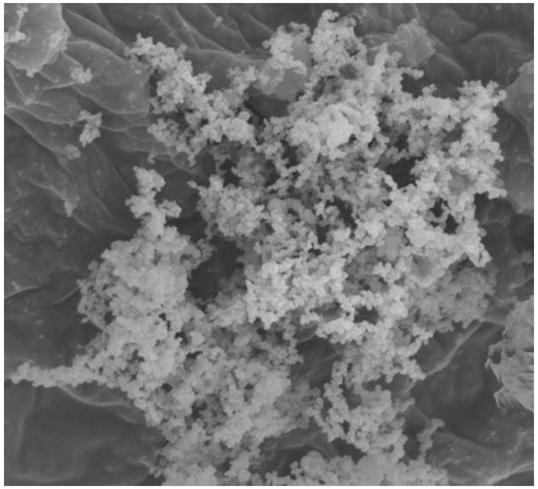
Simulations suggest that the final gel topology depends on the height of the energy barrier



M. Hütter, *J. Colloid Interface Sci*. **231** (2000)

Recent work on agglomerates

- Degussa Fumed Silica
- RHEO-USANS measurements of Structure (Peukert/Sommer/DuPont)



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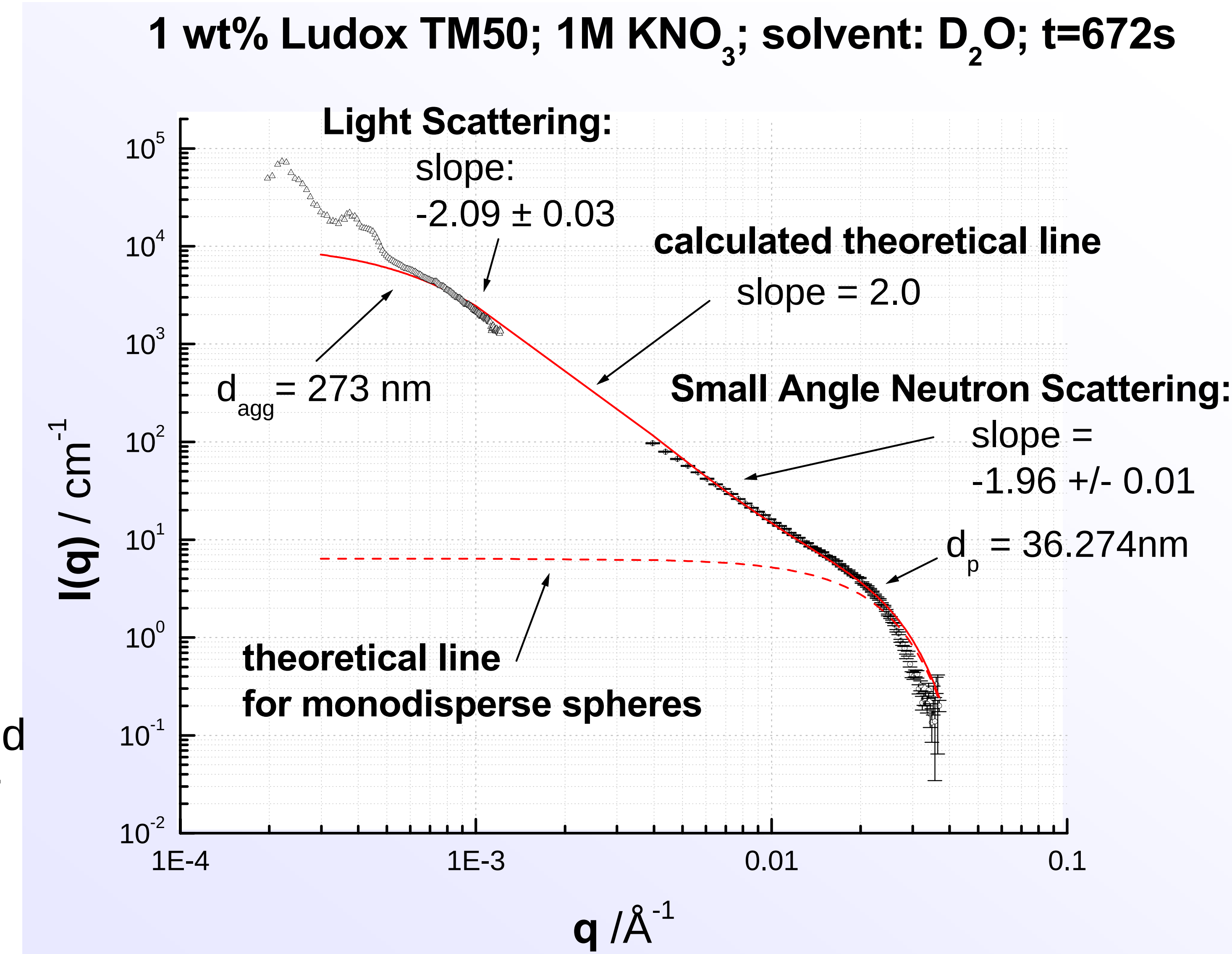
Comparison between Small Angle Neutron Scattering and Light Scattering experiments

goal:

- determine structure of the aggregates
- extract fractal dimension d_F

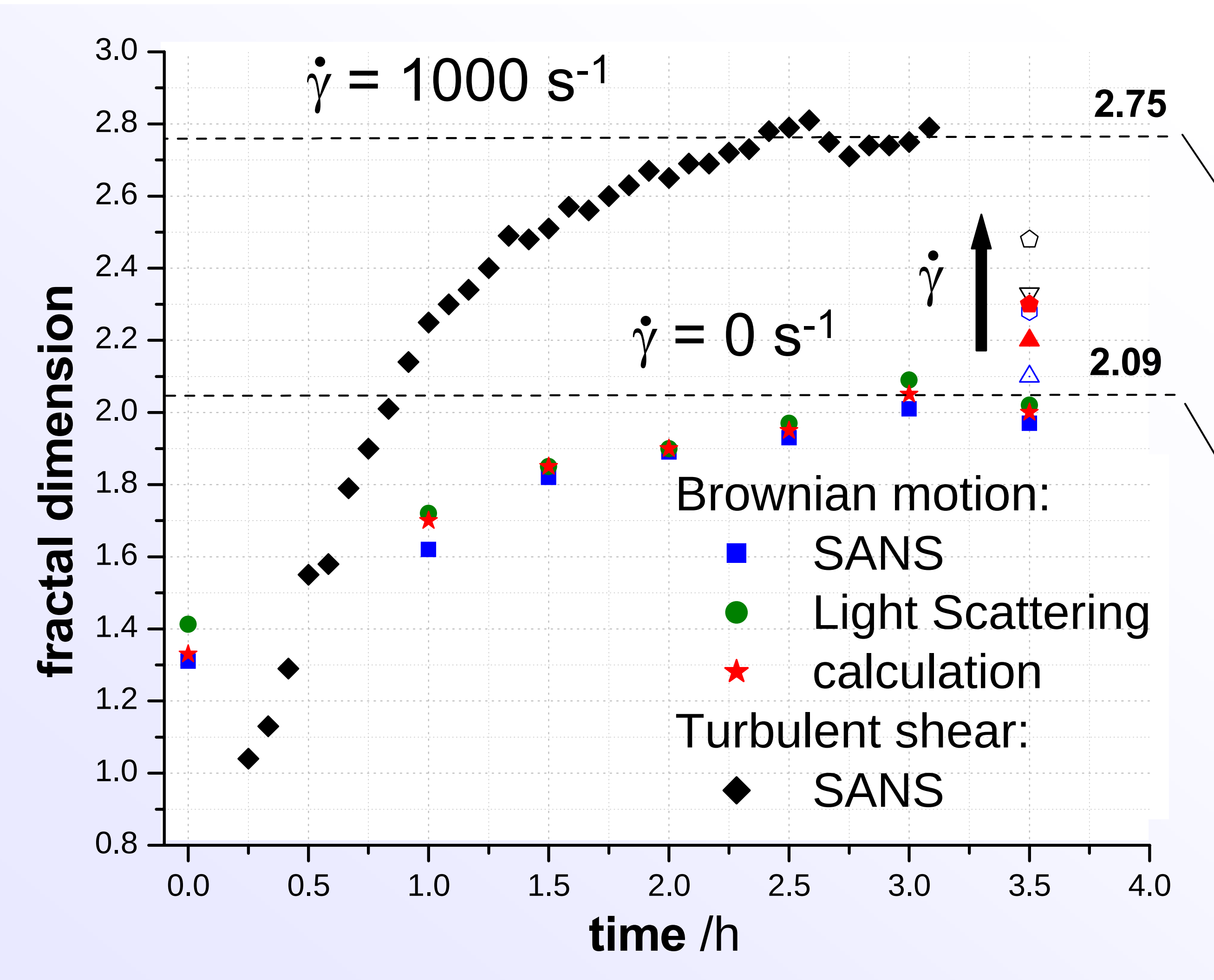
expected fractal dimension:

- d_F= 2.1 for reaction limited cluster cluster aggregation (RLCCA)

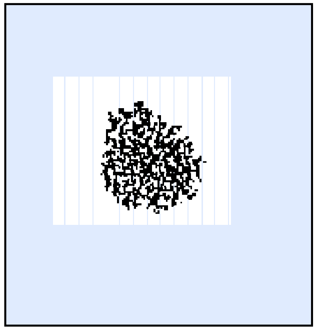


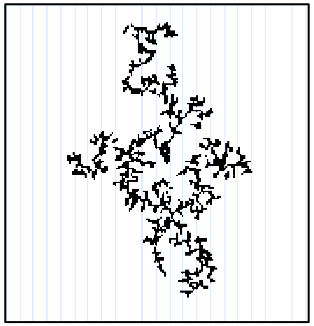
Fractal dimension for 5wt% Ludox at a salt concentration of 0.4 M KNO_3

dF



Reaction Limited Monomer Cluster Aggregation





Reaction Limited Cluster Cluster Aggregation

Hydrocluster Mechanism of Shear Thickening

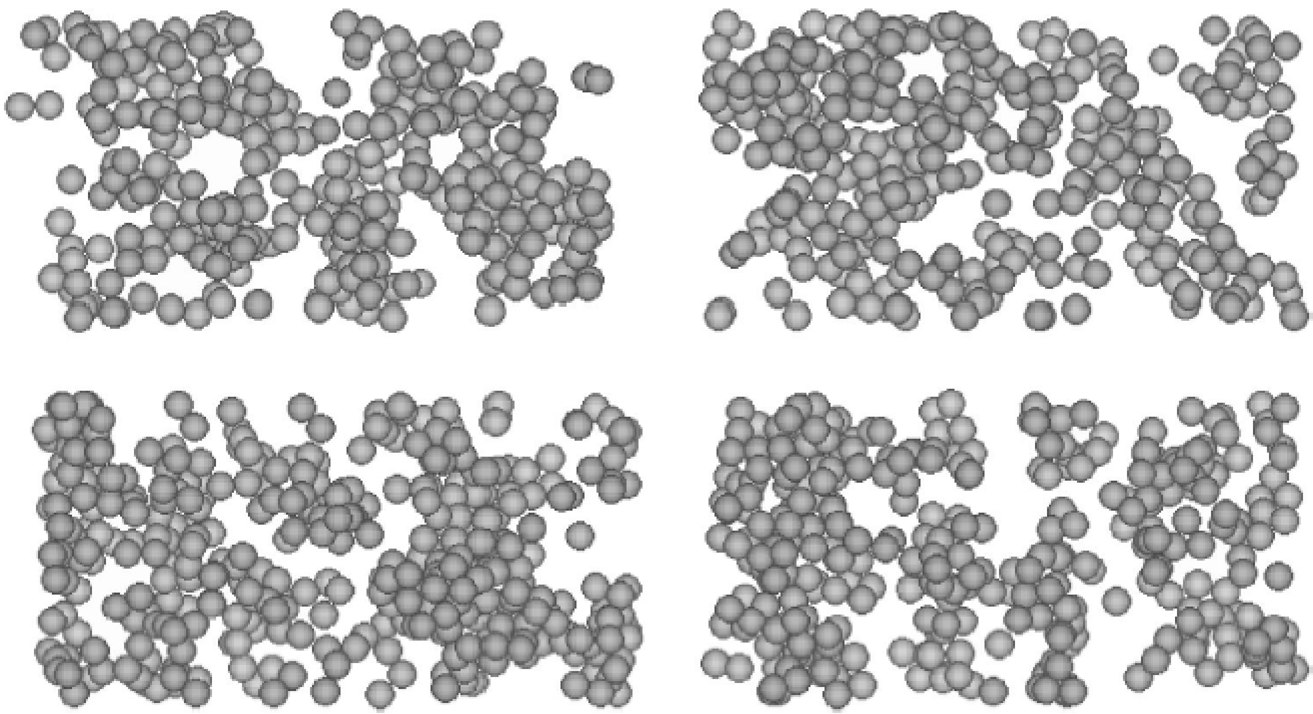
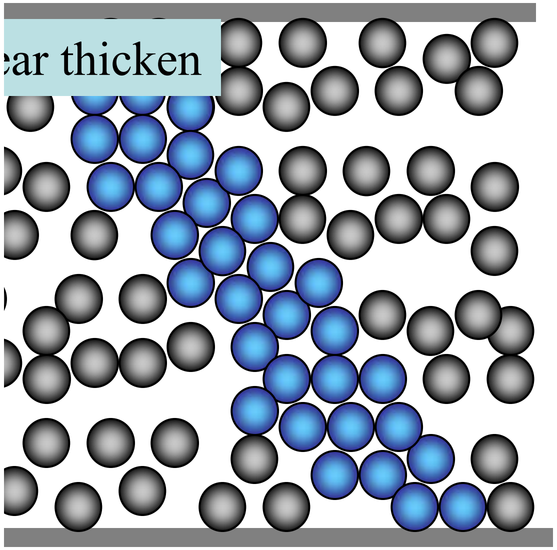
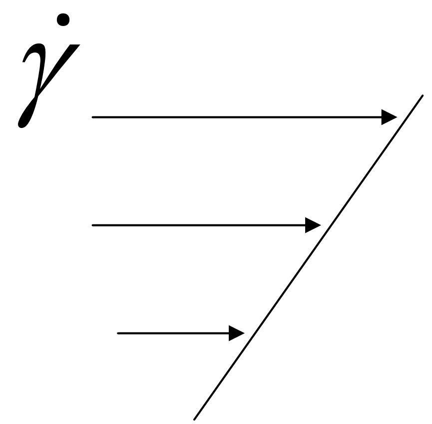
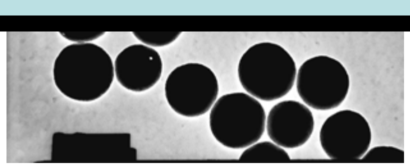


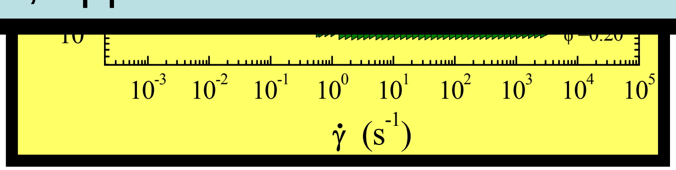
FIG. 5. Snapshots of particles with LVF > 0.6 at Pe = 3000, the configurations are separated by unit strain. The flow direction is left to right and the shear gradient direction is top to bottom. The simulations were in a rectangular box.



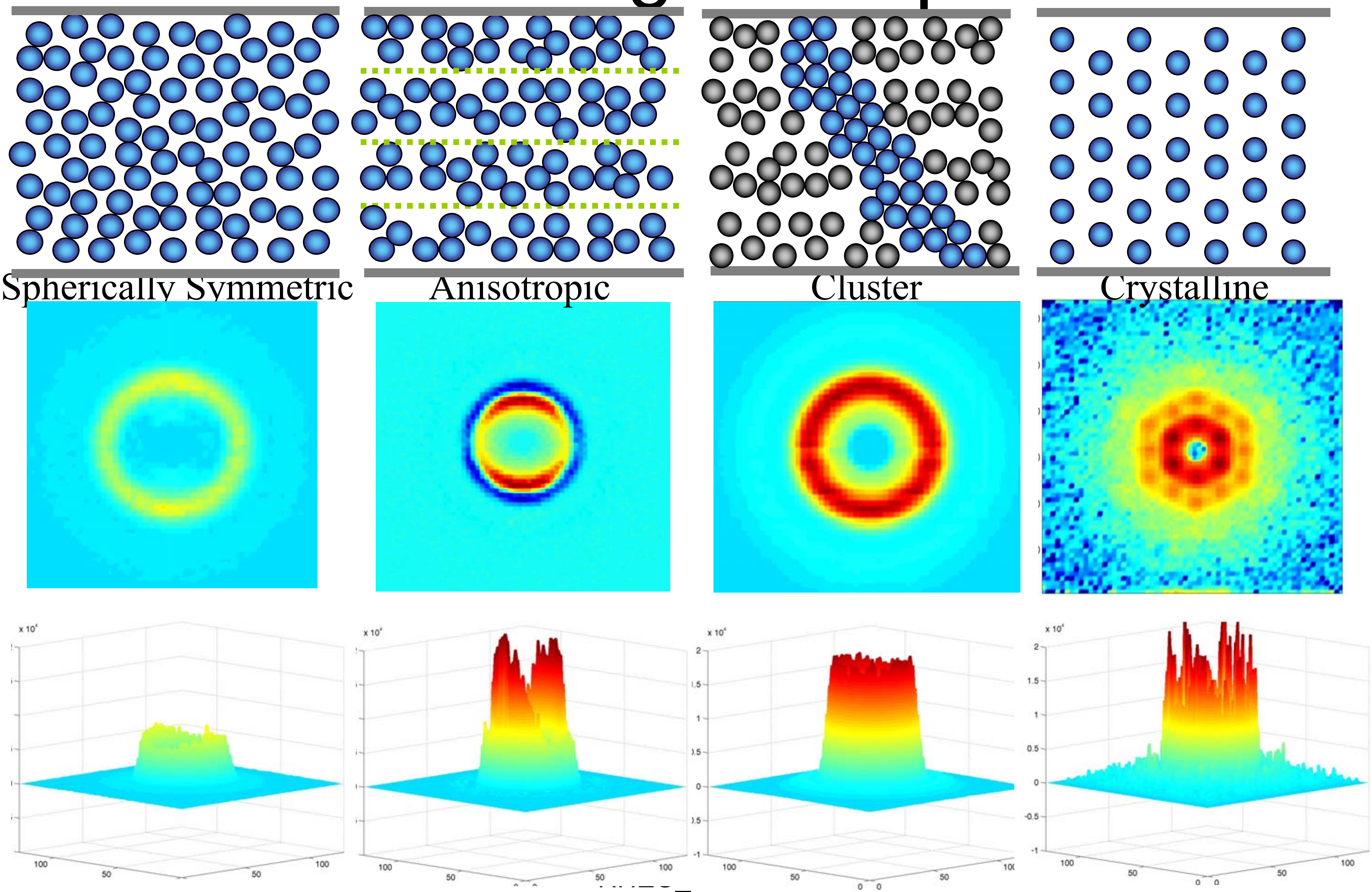


John Melrose and Robin Ball, approximate SD simulations



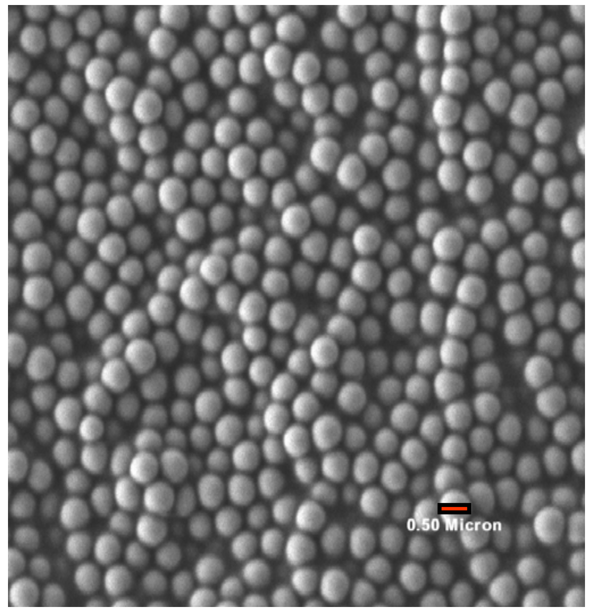


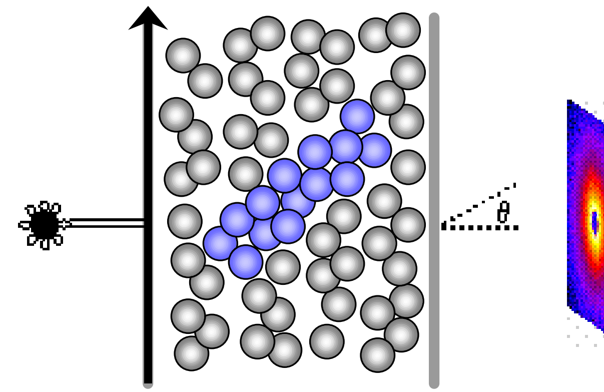
Scattering Examples



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

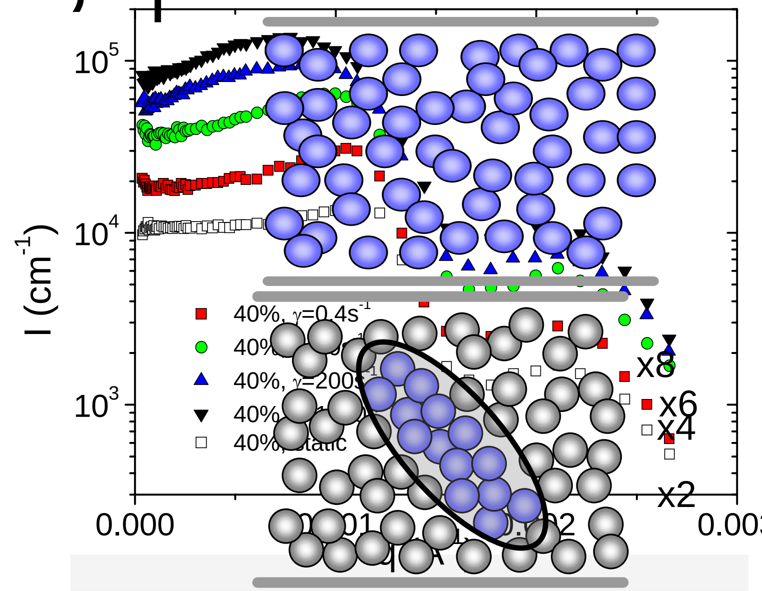
- Colloidal Silica
  - d_{DLS}=577.2 ± 41.2nm
  - d_{SEM}=510 ± 19nm
  - d_{USANS}=520 ± 52nm
- Clarient PEG-200
  - (η_0=42cP)

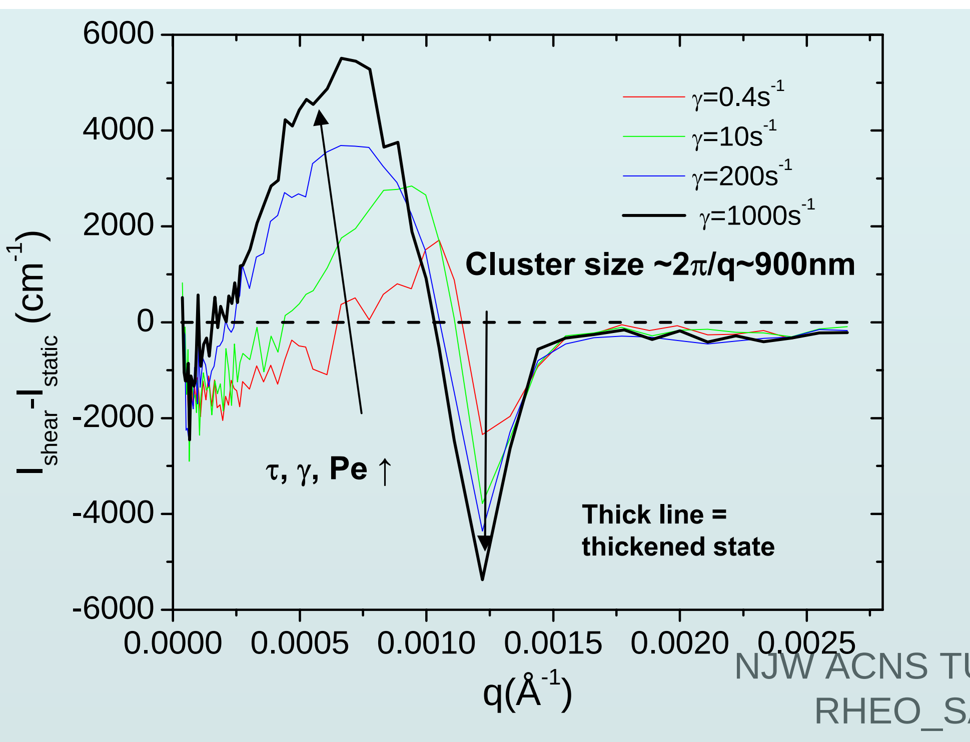


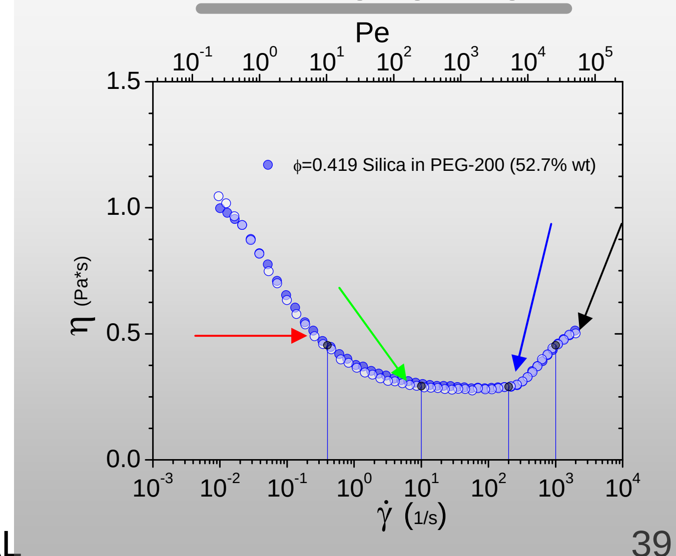


Flow-USANS Data, ϕ=0.40

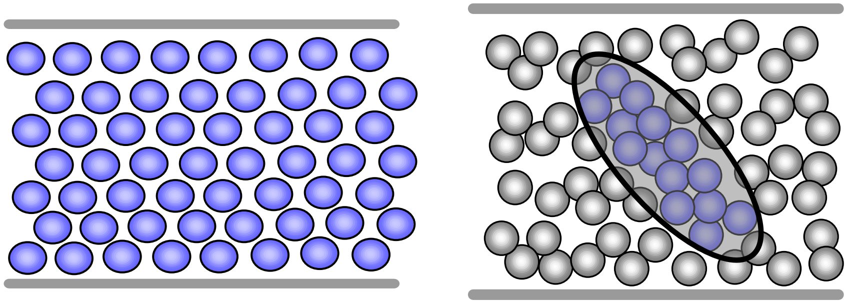
- 1^{st} peak shifts to lower q and higher Intensity w/increasing shear
- 2^{nd} increasing magnitude w/shear at fixed q
- Agrees with Maranzano, but larger particles and lower rates
- Clustering and microstructure compression

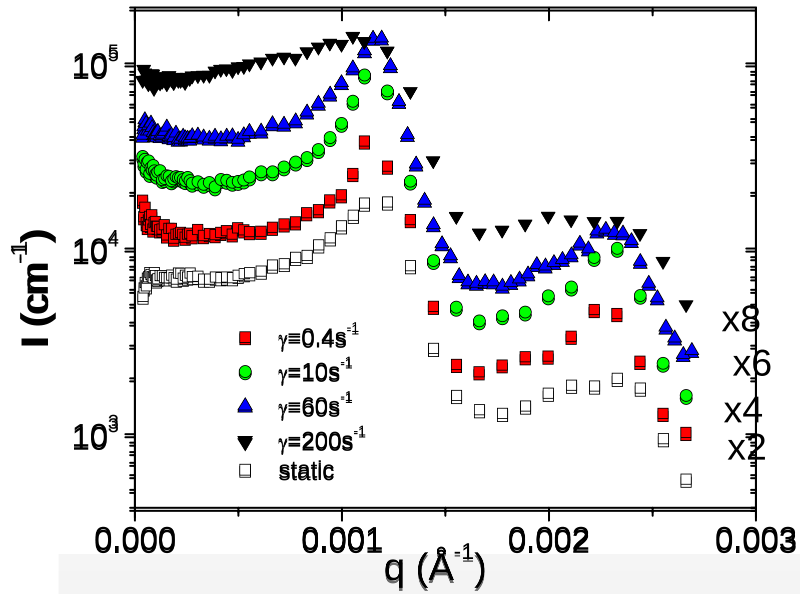


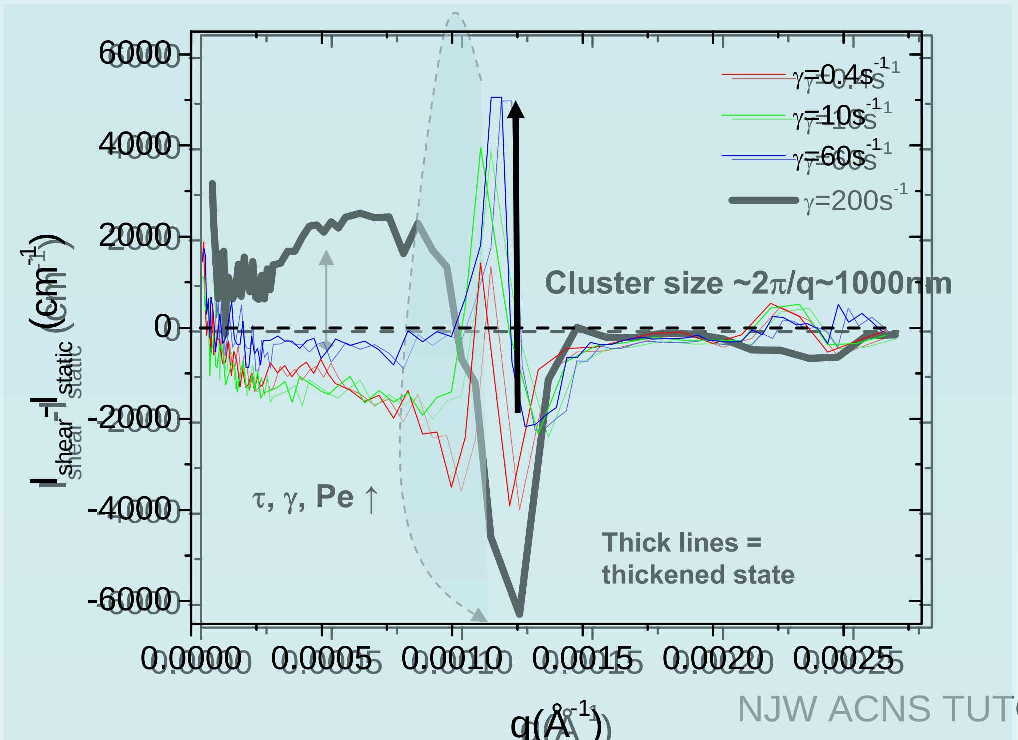


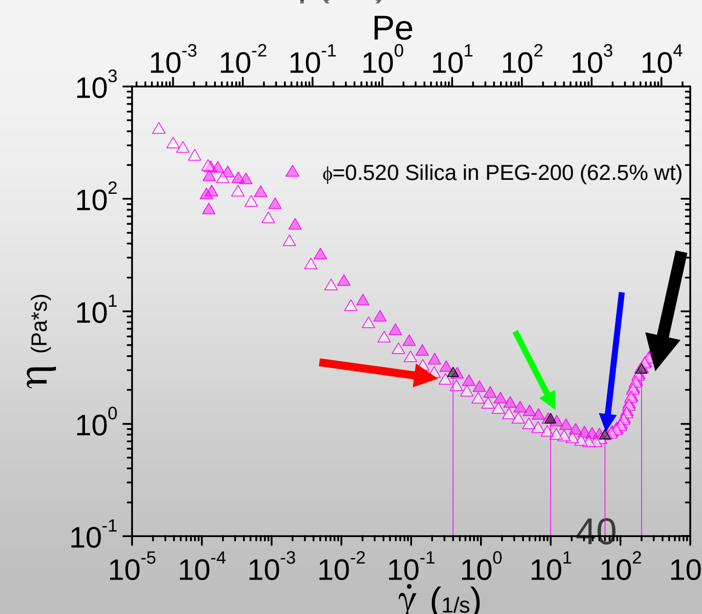


Flow-USANS Data, ϕ=0.52



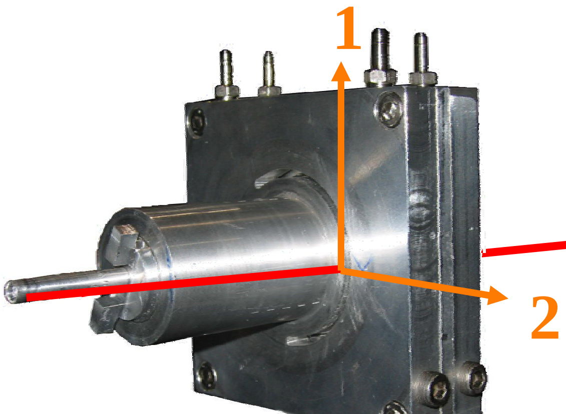


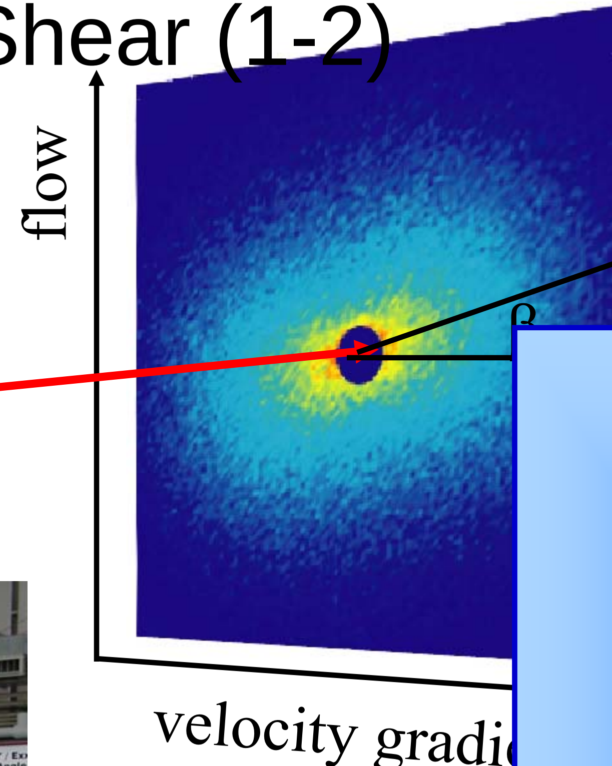


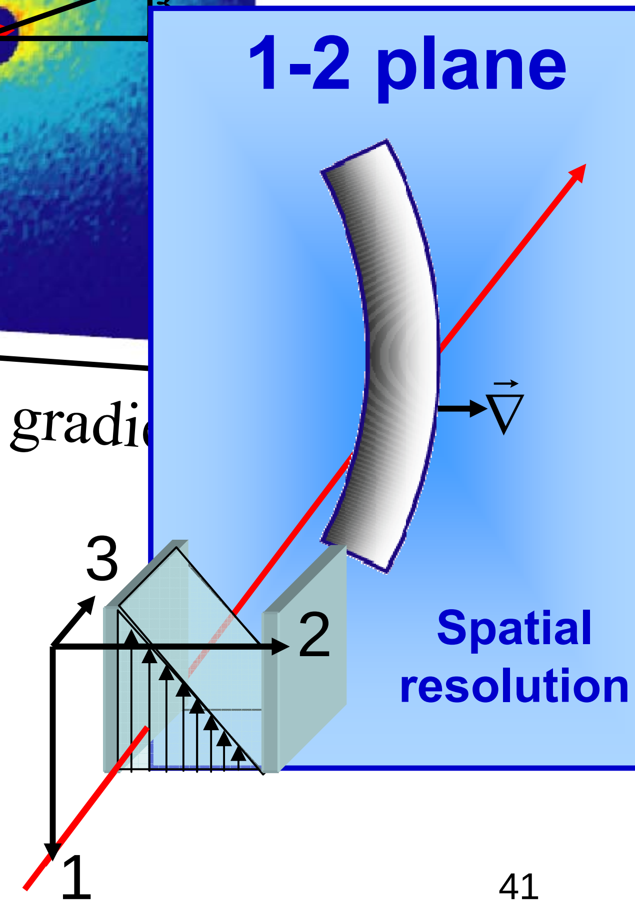


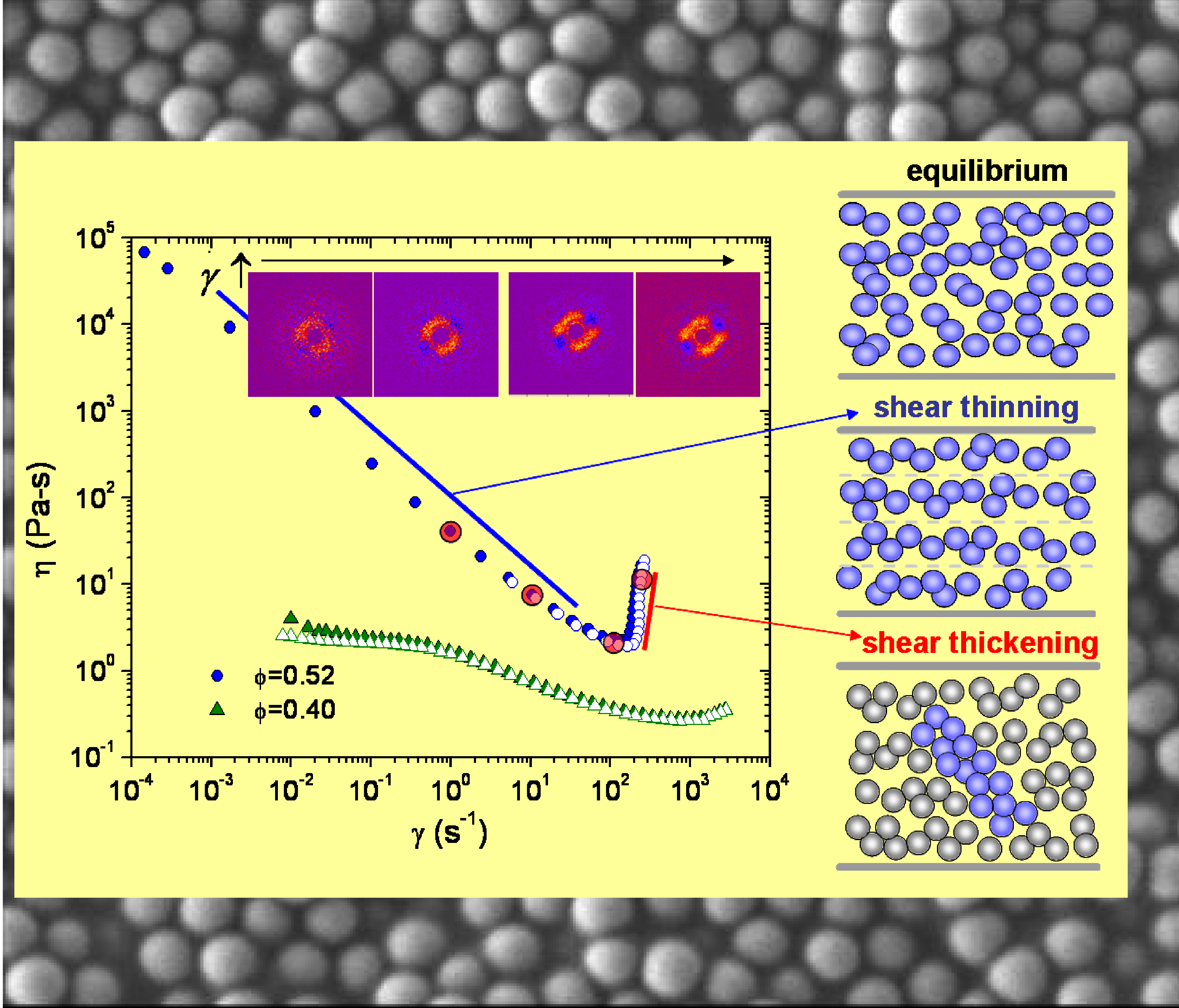
Structure Measurements in the Plane of Shear (1-2)

Liberatore et al. (2006) Phys. Rev. E **73**: 020504R



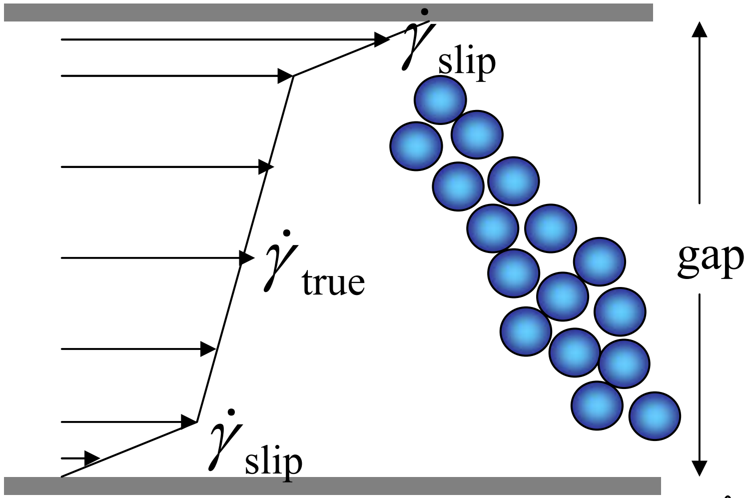


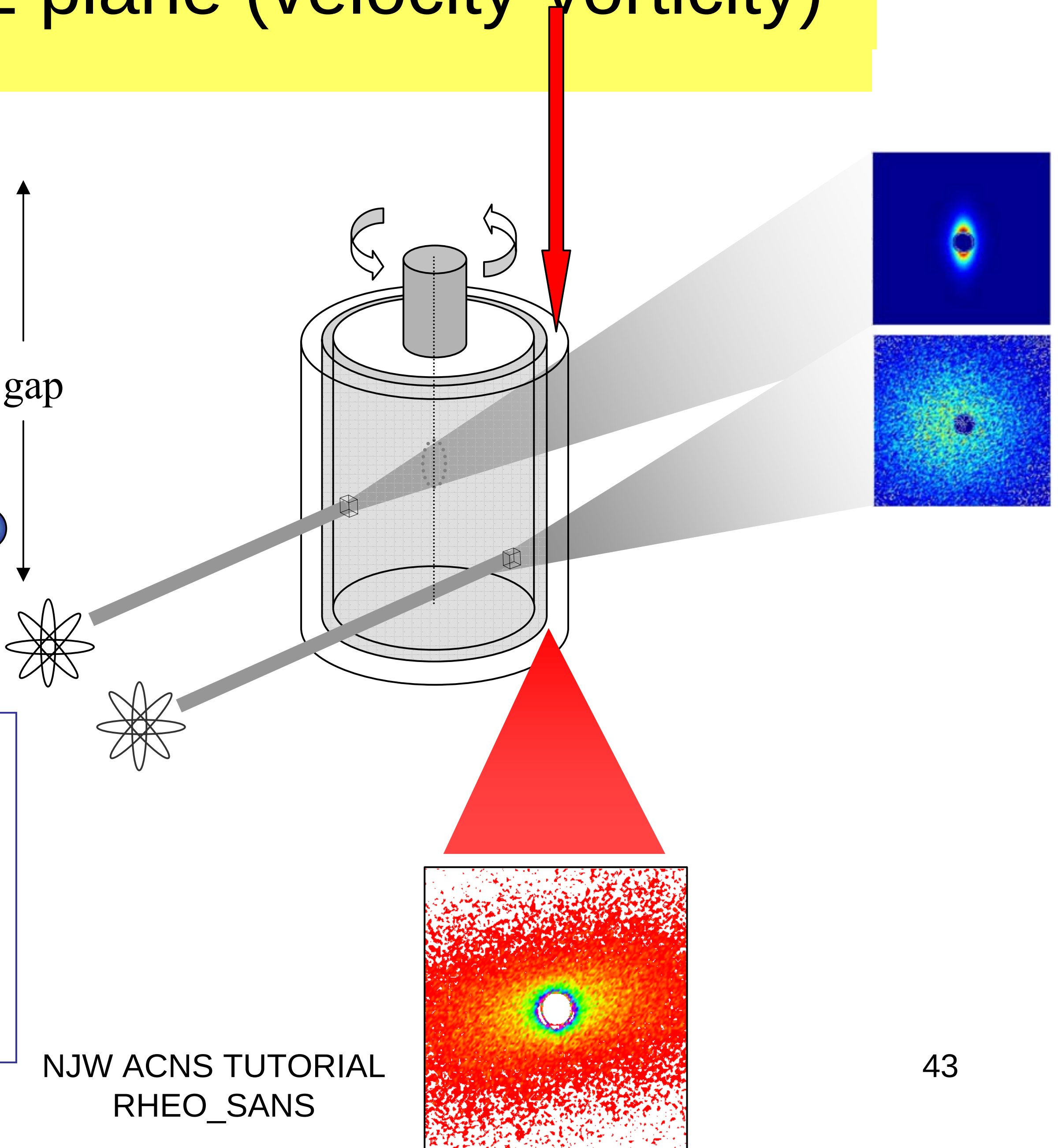




equilibrium
shear thinning
shear thickening
η (Pa-s)
γ (s^-1)
φ=0.52
φ=0.40
γ

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

1-2 X-RAY STUDIES

Burghardt and coworkers: *Macromolecules, Vol. 34, No. 19, 2001*

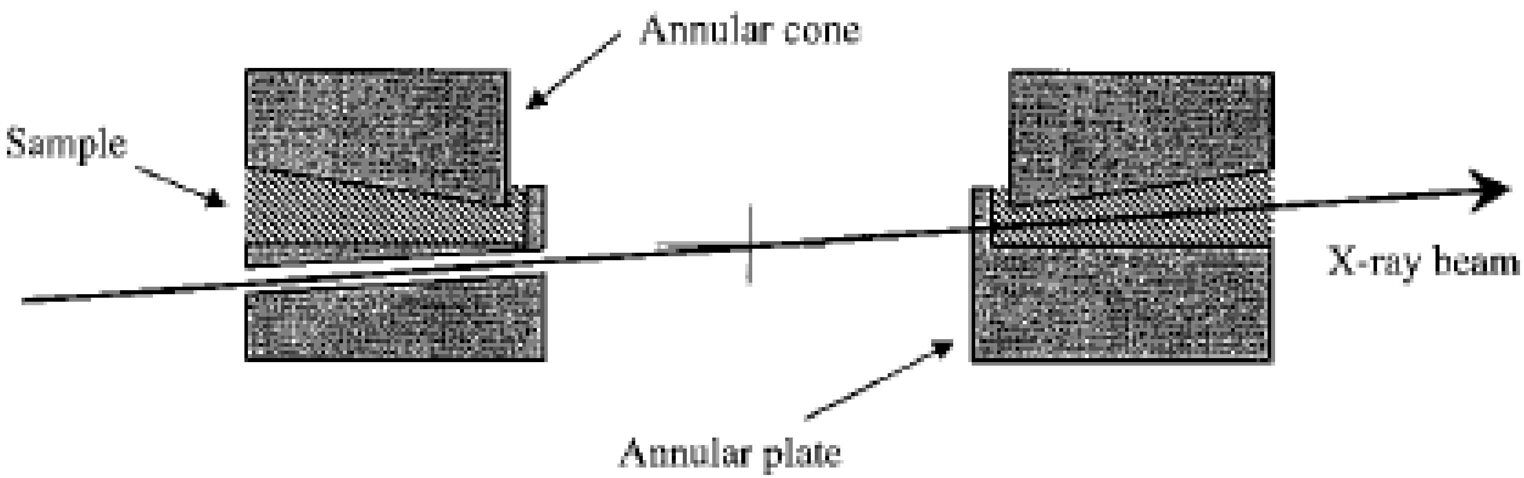


Figure 3. Schematic of annular cone and plate geometry used for X-ray measurements of fluid structure in the 1−2 plane. The cone angle has been exaggerated in this diagram; the actual cone angle is 5°.

1-2 SANS

VOLUME 78, NUMBER 1 PHYS I CAL RE V I EW LETTERS 6 JANUARY 1997

Shear Flow Induced Transition from Liquid-Crystalline to Polymer Behavior in Side-Chain Liquid Crystal Polymers L. Noirez and A. Lapp

VOLUME 78, NUMBER 1 PHYSICAL REV

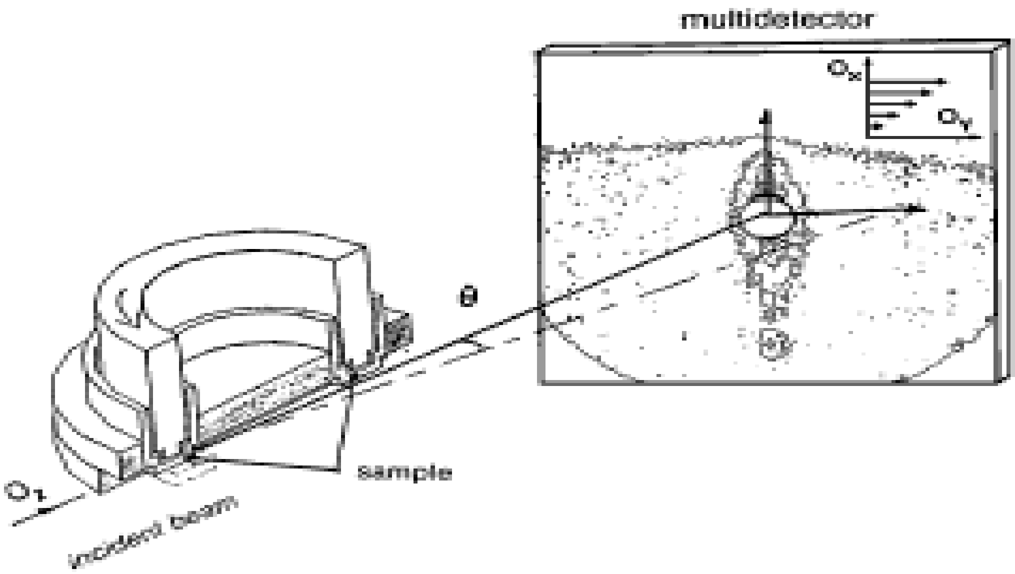


FIG. 2. Schematic of the neutron scattering cell used for the observation of the vorticity plane with a typical neutron scattering pattern ($\lambda = 3.5$ Å, $d = 2$ m) obtained with the H/D mixture in the smectic phase ($T = 93$ °C) under a shear flow of 6 s^{-1}. The upper part of the pattern corresponds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

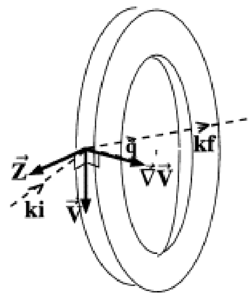
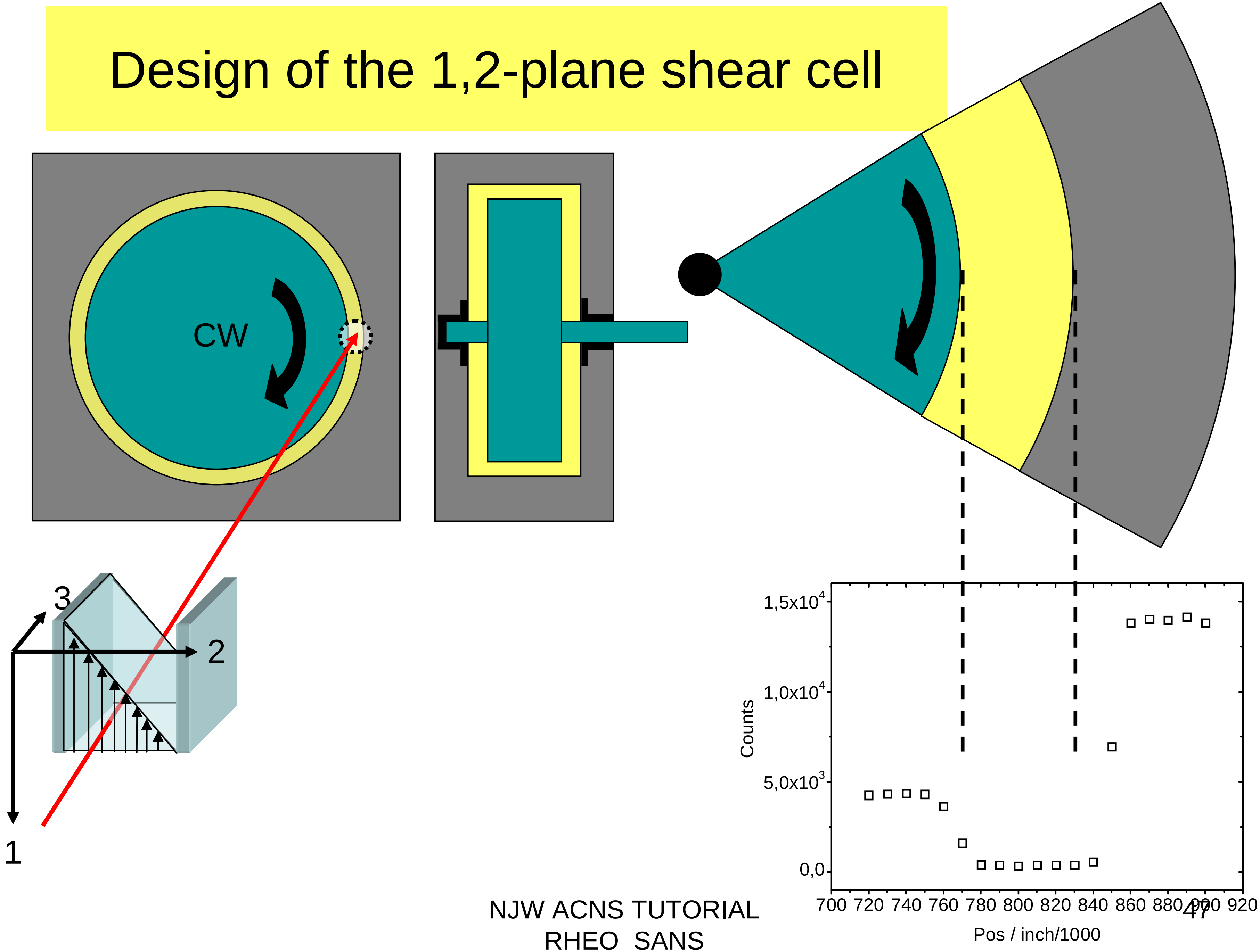


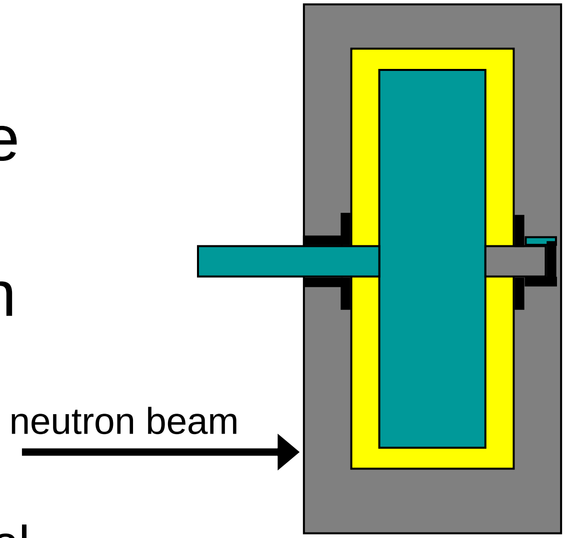
FIG. 1. Section of the shear cell ring (placed in a vertical position for the three-axis geometry) defining the three axes $(\vec{v}, \vec{\nabla}\cdot\vec{v}, \vec{z})$. The scattering vector is defined by $\vec{q} = \vec{k}_i - \vec{k}_f$, where $\vec{k}_i$ is the incident beam and $\vec{k}_f$ is the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

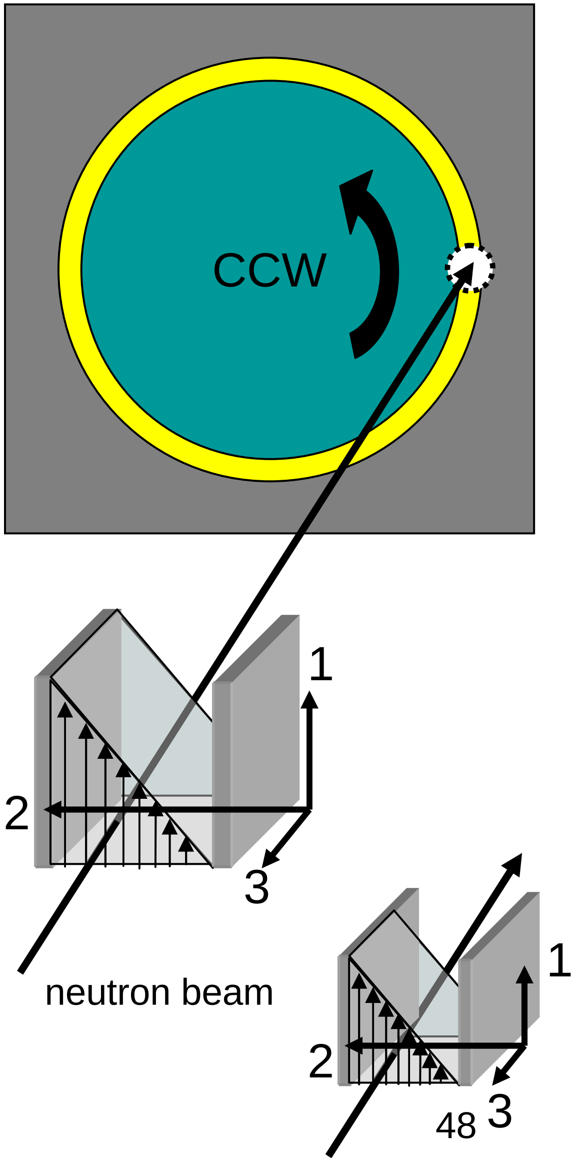
Design of the 1,2-plane shear cell



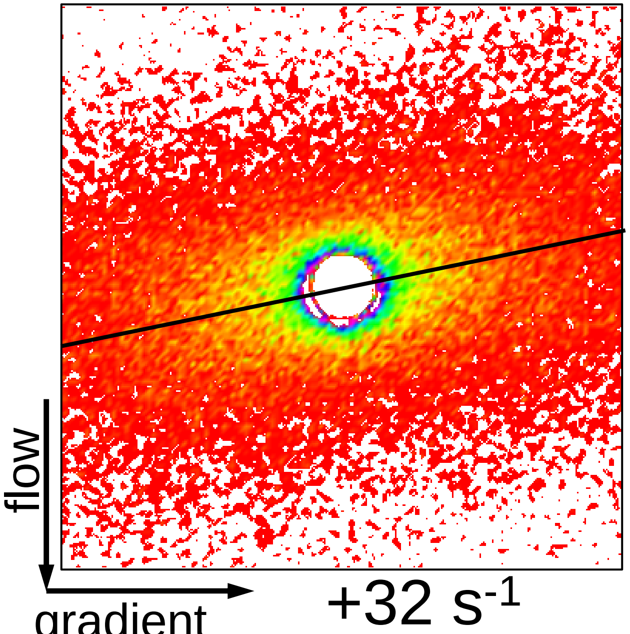
1-2 Plane SANS Setup

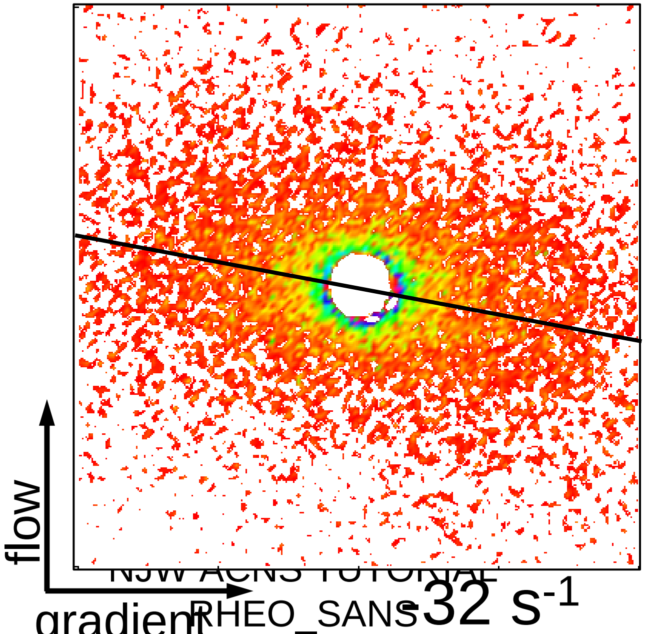
- Aluminum Couette
- 2.0 mm gap
- 10 mm path length



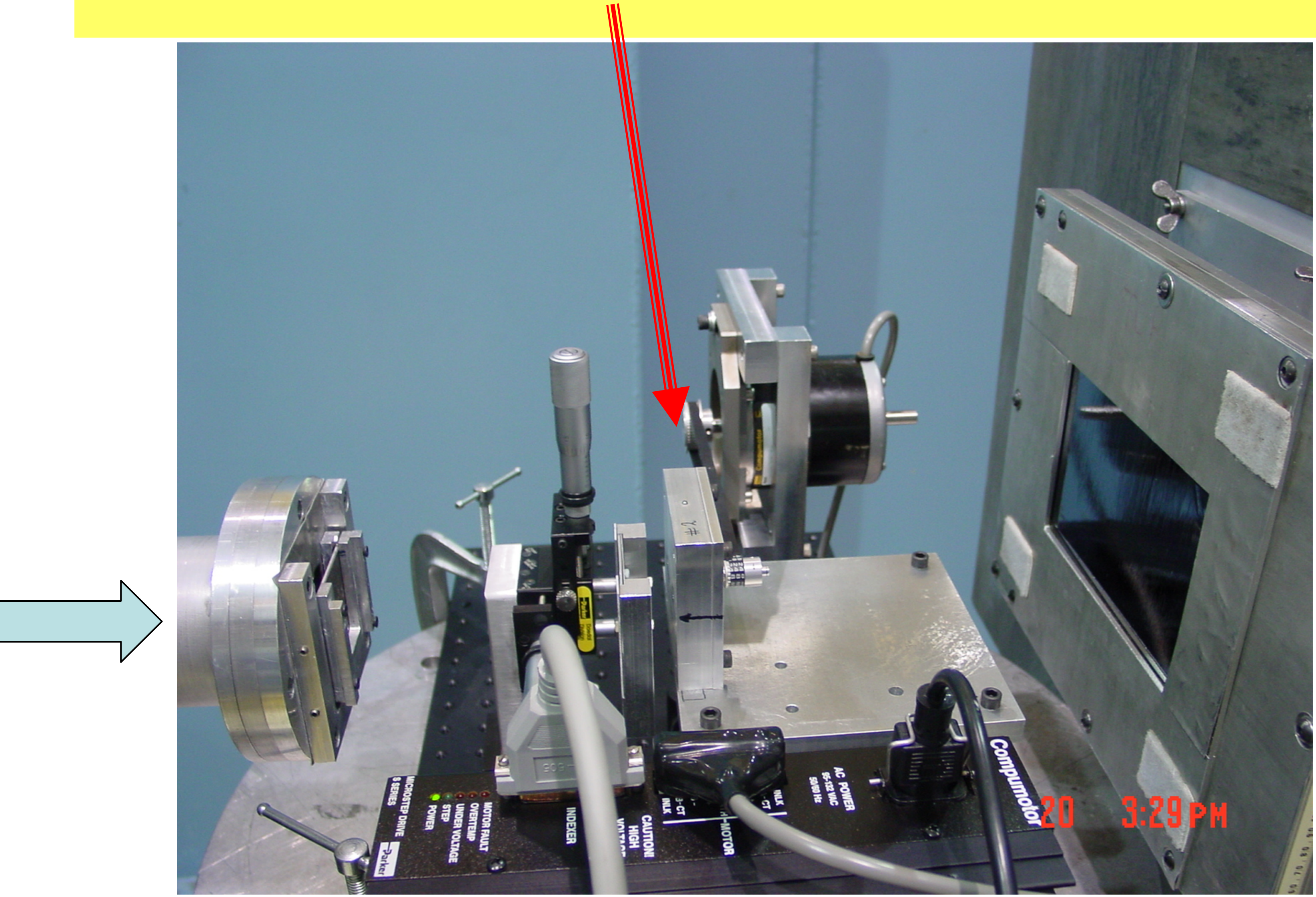


40 mM EHAC 300 mM NaSal

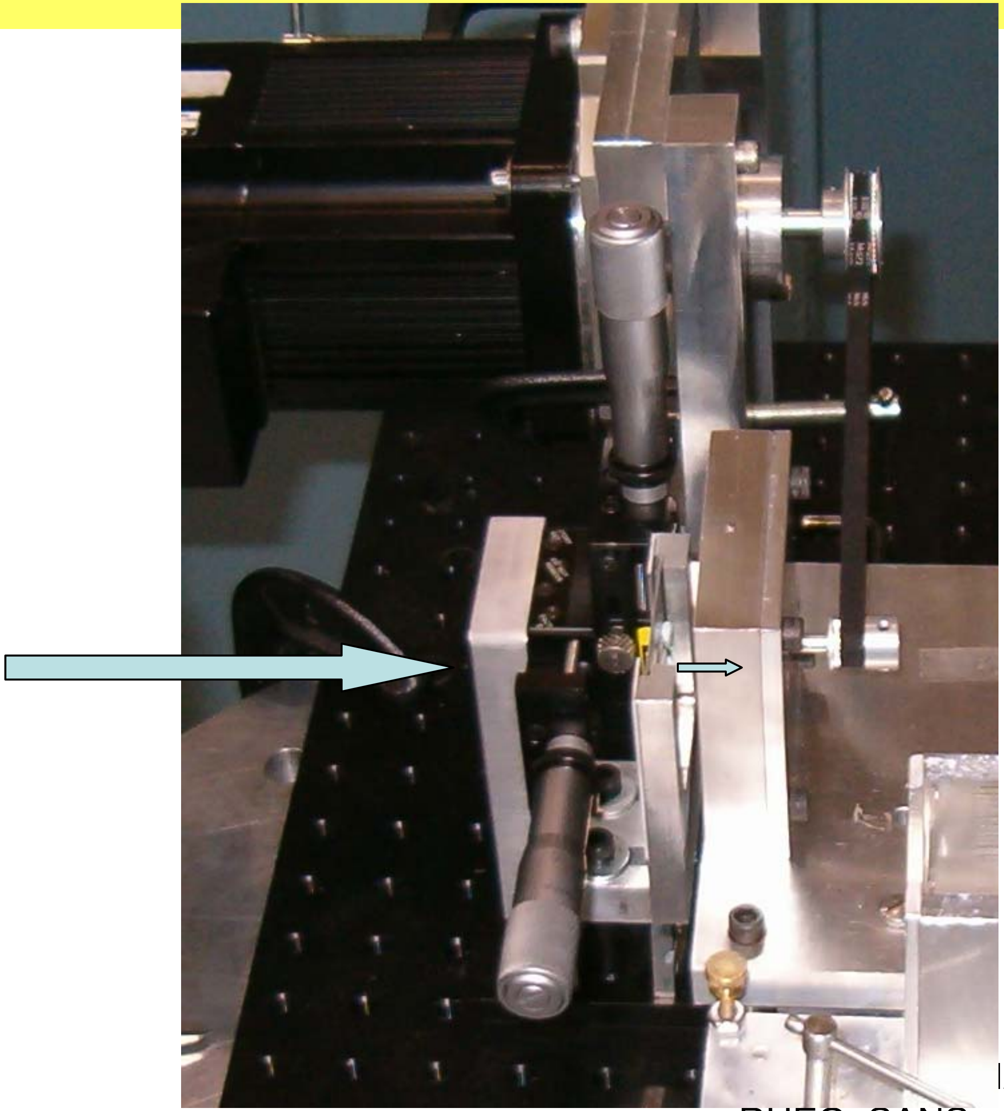


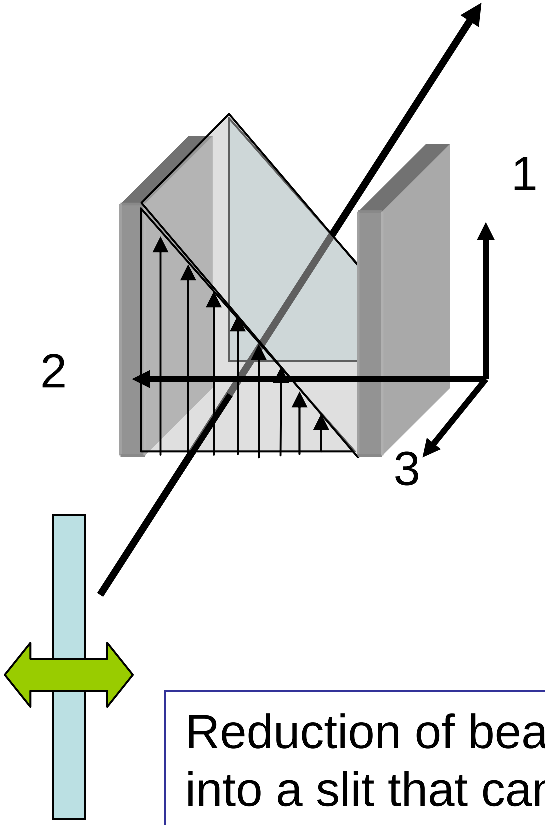


1-2 Plane SANS Cell



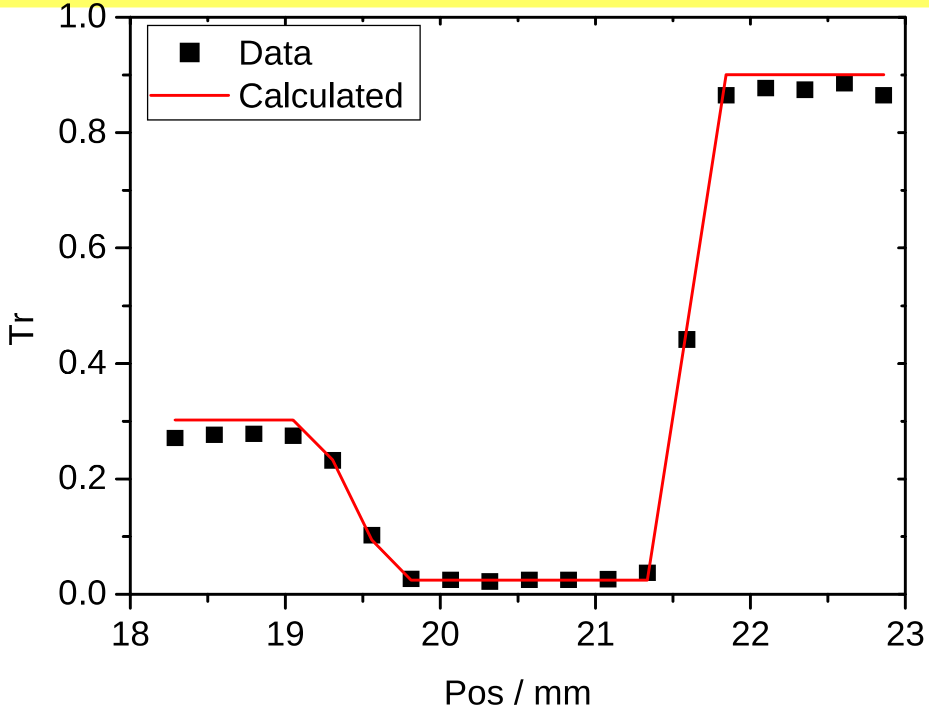
1-2 Plane SANS Cell





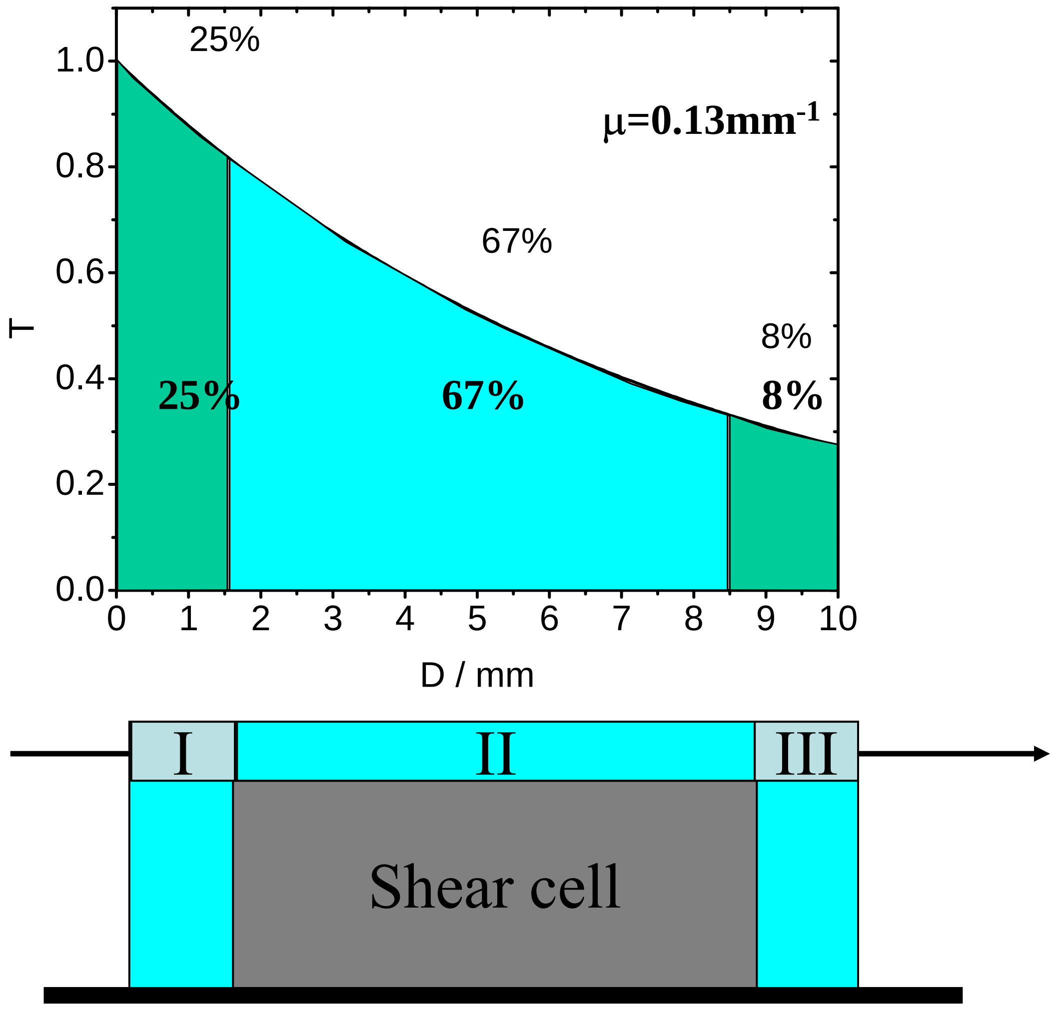
Reduction of beam into a slit that can be translated across the gap

1-2 Plane Cell Gap Positioning



	Measures / mm		μ / mm^{-1}
Total thickness	21	Al	0.00497
Lower block	16	1:1 mixture of H_2O/D_2O	0.3689
Hole	1		
Bob	7		
Cover plate	5		
Thickness inside	6		

1-2 plane cell: End Effects



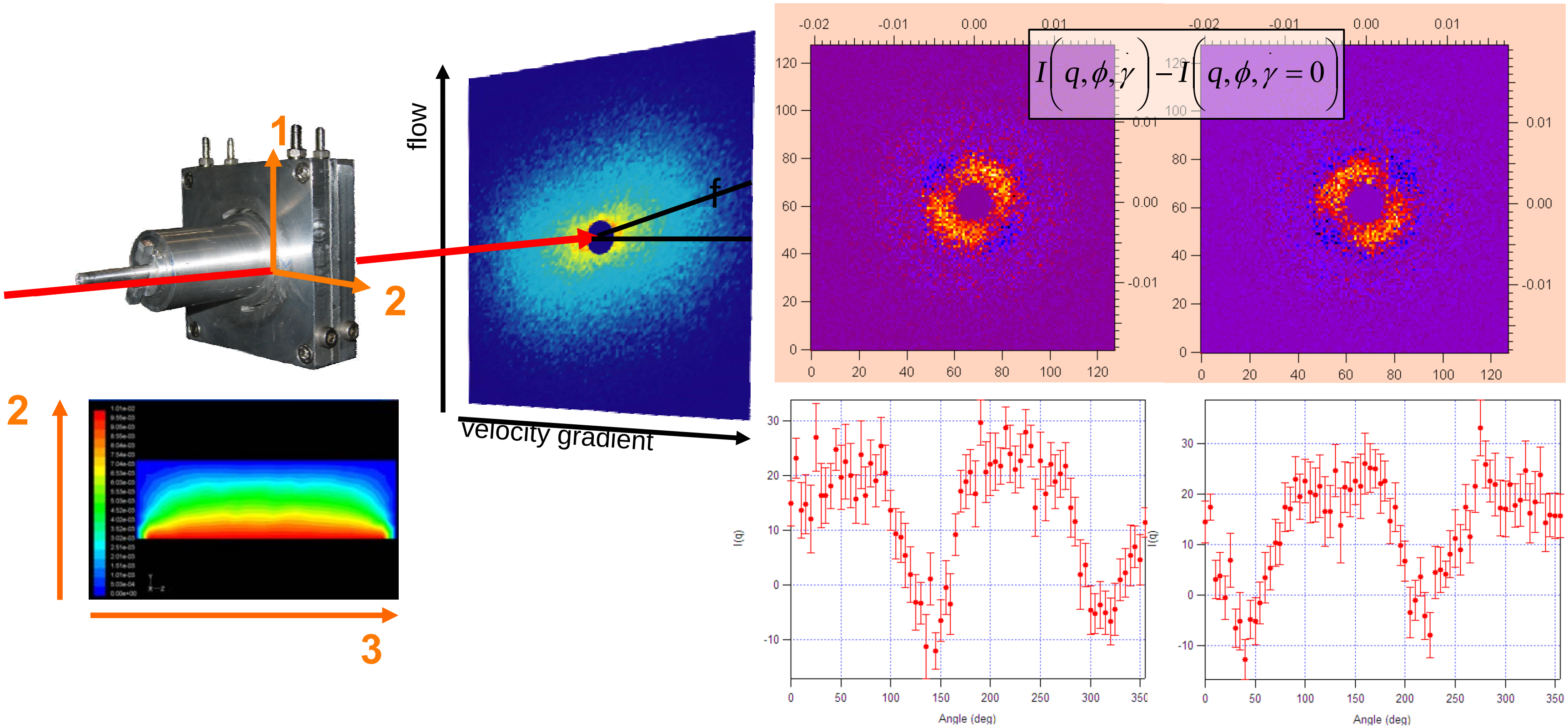
End effects in current cell geometry

Low turbidity (SANS) samples, the ends do not dominate signal

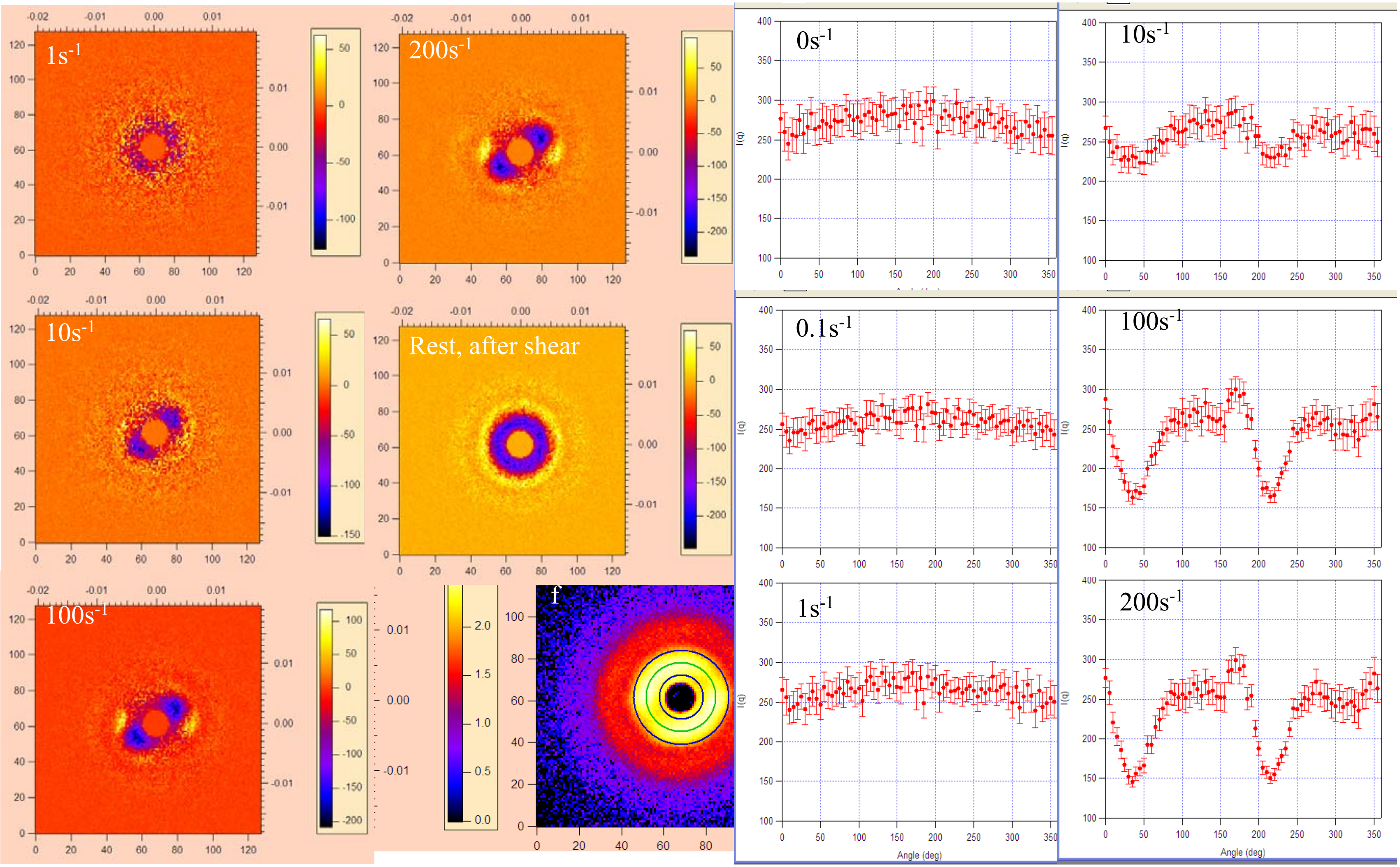
Isotropic at rest, so ends contribute little to observed anisotropy

Validation with birefringence and rheology

Flow 1-2 SANS

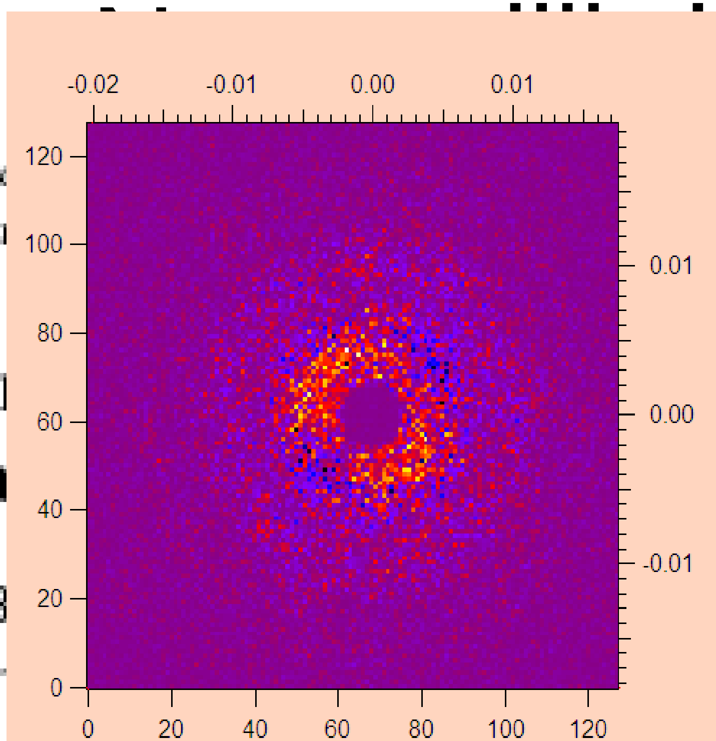

1
2
2
3
flow
velocity gradient
f
$I\left(q,\phi,\dot{\gamma}\right)-I\left(q,\phi,\dot{\gamma}=0\right)$
I(q)
Angle (deg)
I(q)
Angle (deg)

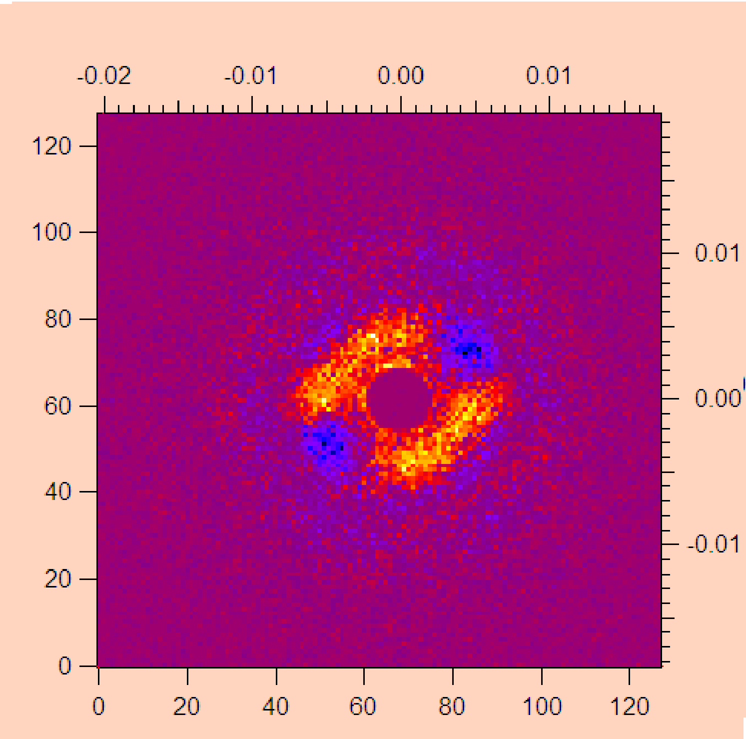
40 % DISPERSION



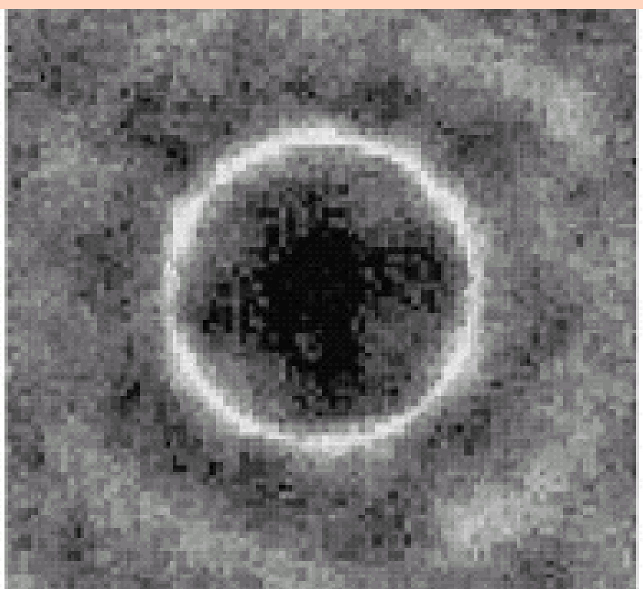
J. Fluid Mec
© 1997 Ca

Mic ... ions



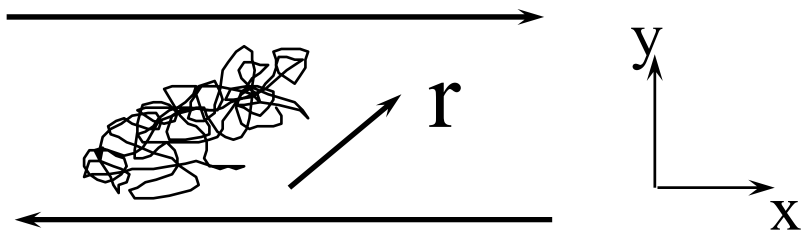


g(x, y)



RHEO_OPTICS: Stress-Optical Rules

- Polymers:

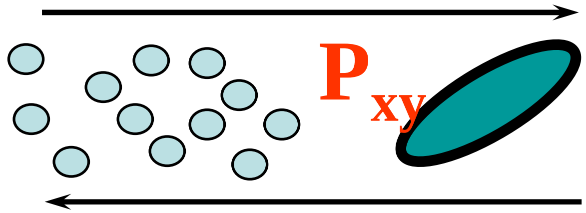


$$\eta^{thermo}\dot{\gamma} = \langle r_x \, r_y \rangle$$

$$\Delta n'_{xy} = \langle r_x \, r_y \rangle$$

$$\Delta n'_{xy} = C \, \eta^{thermo}\dot{\gamma}$$

- Colloids:



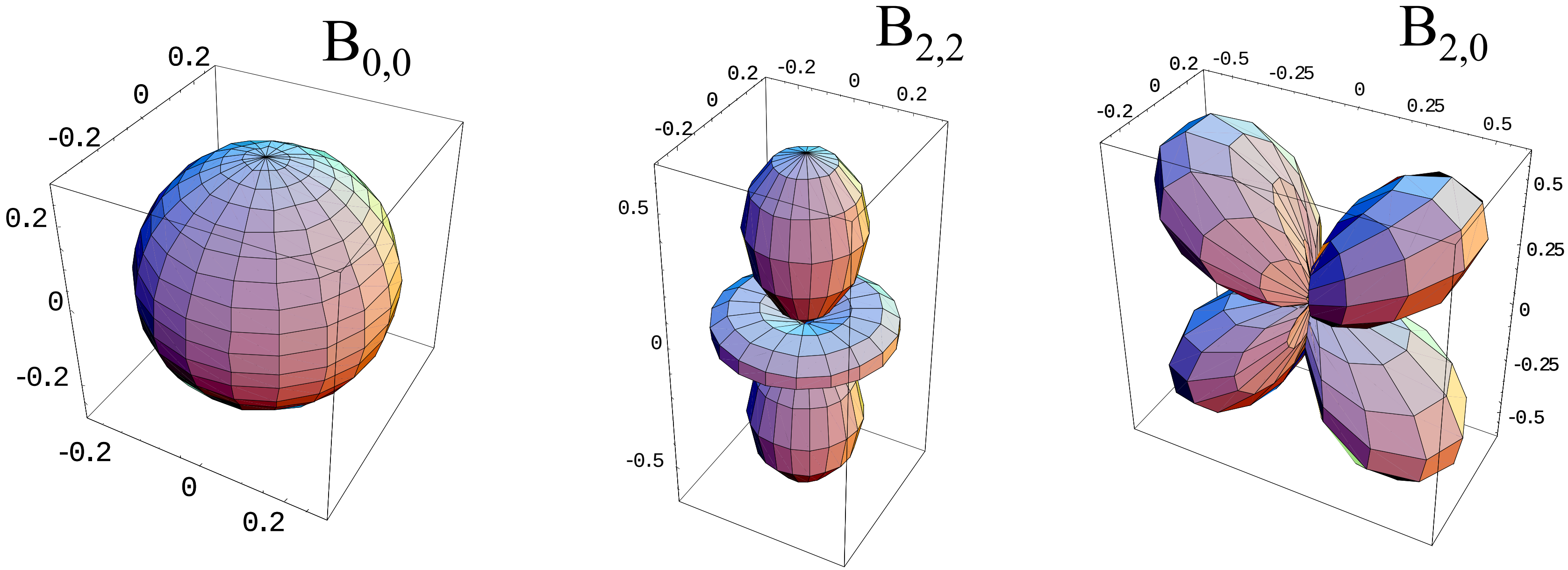
$$\eta^{thermo}\dot{\gamma} \, \alpha < P_{xy} >$$

$$\Delta n''_{xy} \, \alpha < P_{xy} >$$

$$\Delta n''_{xy} = C \, \eta^{thermo}\dot{\gamma}$$

"Optical Measurement of the Contributions of Colloidal Forces to the Rheology of Concentrated Suspensions", J. W. Bender and N. J. Wagner, J. Coll. Int. Sci., 172, pp. 171-184, 1995.

Spherical Harmonic Functions for “3-D” Expansions

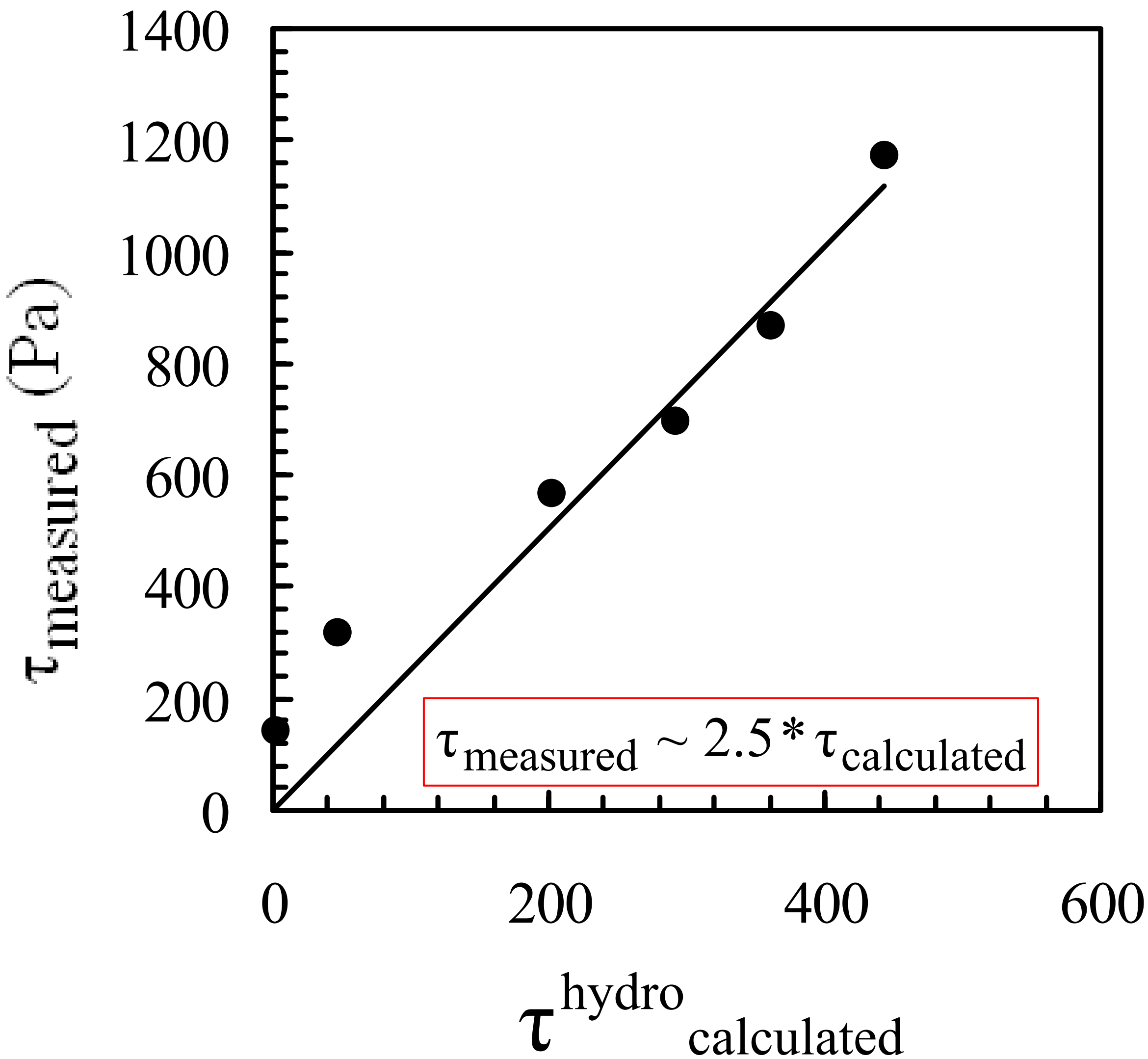


Expansion of nearest neighbor distribution in spherical harmonics

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

"Analysis of Nonequilibrium Structures of Shearing Colloidal Suspensions," N. J. Wagner & Bruce J. Ackerson, Journal of Chemical Physics, 97, pp. 1473-1483, 1992

Stress-SANS Relation

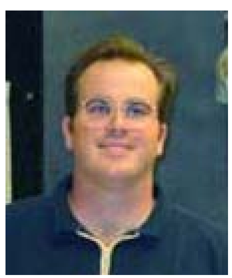


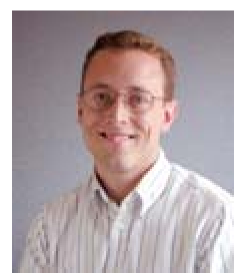
Hydrodynamic component of the stress is calculated directly from the measured microstructure and the exact 2-body hydrodynamics interactions, many-body hydrodynamics are neglected

"Flow-Small Angle Neutron Scattering Measurements of Colloidal Dispersion Microstructure Through the Shear Thickening Transition," by Brent J. Maranzano and Norman J. Wagner, J. Chem. Phys., 117, 10291-10302, 2002.

Siple Award
US Army Science Conference, 2002

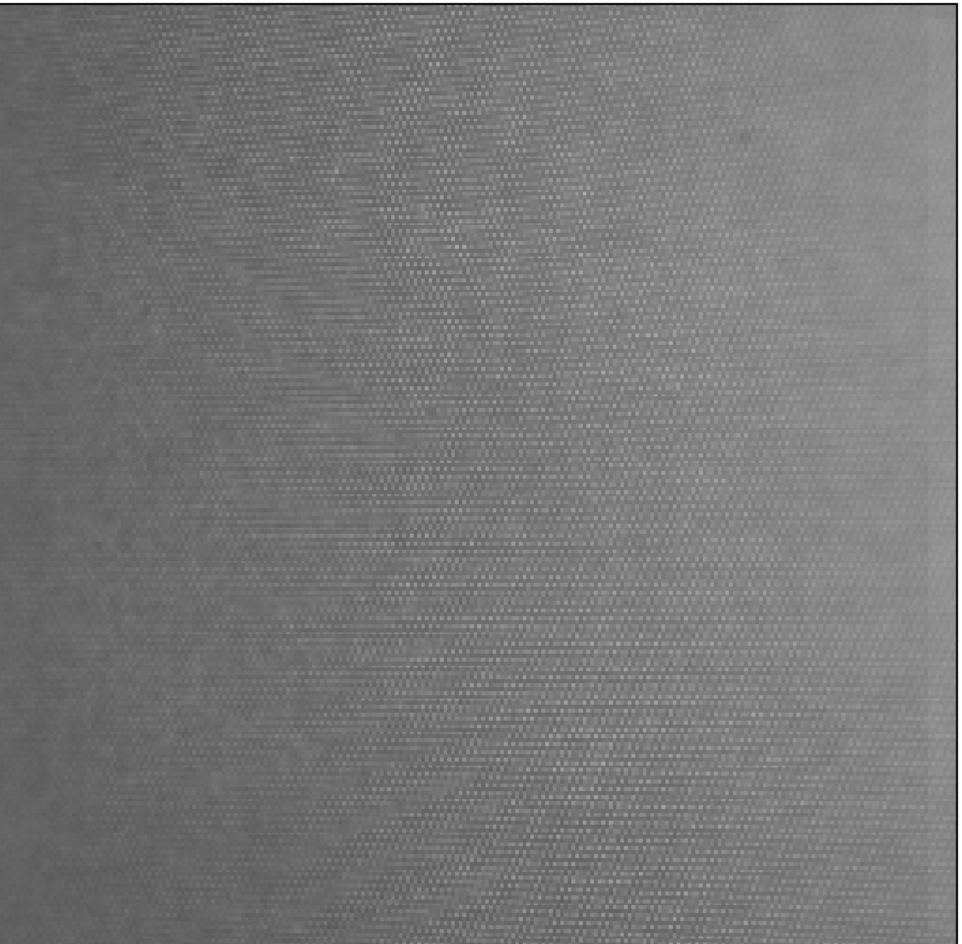
"Advanced Armor Utilizing Shear Thickening Fluids", by Y. S. Lee, E. D. Wetzel, R. G. Egres Jr., N. J. Wagner





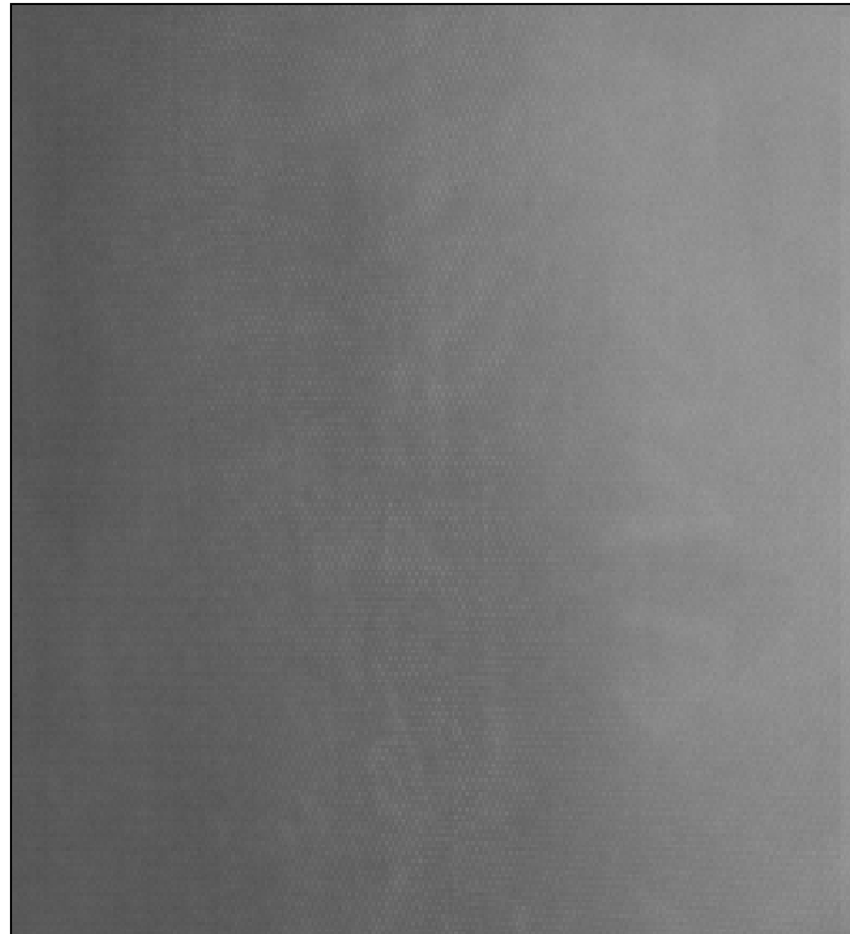
Ballistic Testing

3 layers Nylon, 800 fps



3 layers neat MD Nylon 800fps

2 layers STF-Nylon, 800 fps



2 layers STF-MD Nylon 800fps

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.