University of Delaware

Dynamic rheology and microstructure of concentrated, near hard-sphere colloidal dispersions under steady shear and LAOS via simultaneous rheometry and SANS measurements

A. Kate Gurnon

in collaboration with Norman J. Wagner, Lionel Porcar, Paul Butler, Aaron P. R. Eberle, P. Douglas Godfrin and Carlos Lopez-Barron

NCNR SANS school 06/20/2013

Acknowledgements

University of Delaware

- Doug Godfrin
- Carlos Lopez-Barron
- Jim Swan
- Dennis Kalman

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- Paul Butler
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- Lionel Porcar
- Kenny Honniball

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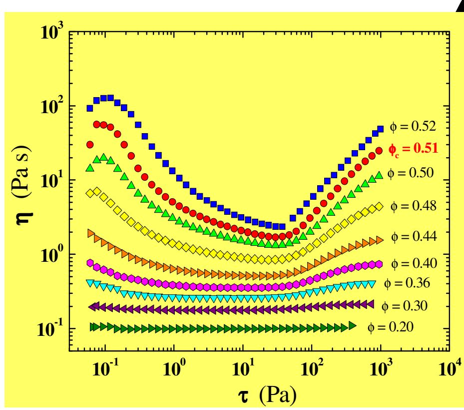
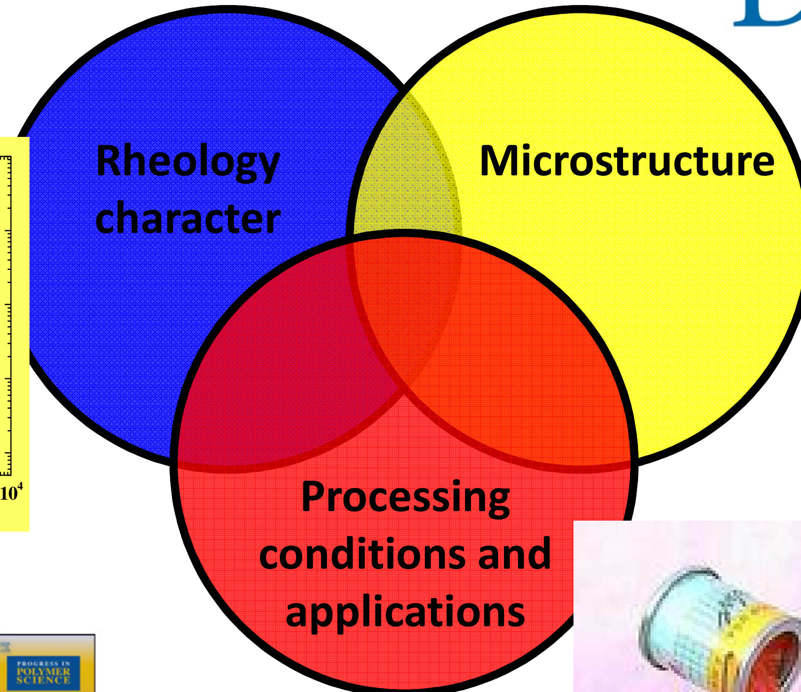
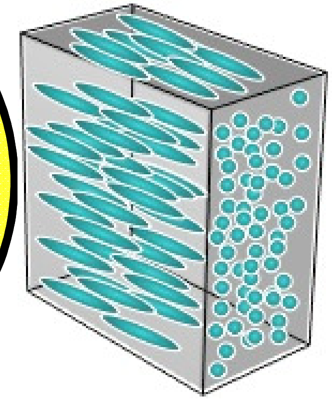
- NASA Delaware Space Grant Consortium (NASA Grant NNX10AN63H)
- Delaware Center for Neutron Science

Structure-property relationship: Why do we care?







Progress in Polymer Science 36 (2011) 1697–1753

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Progress in Polymer Science

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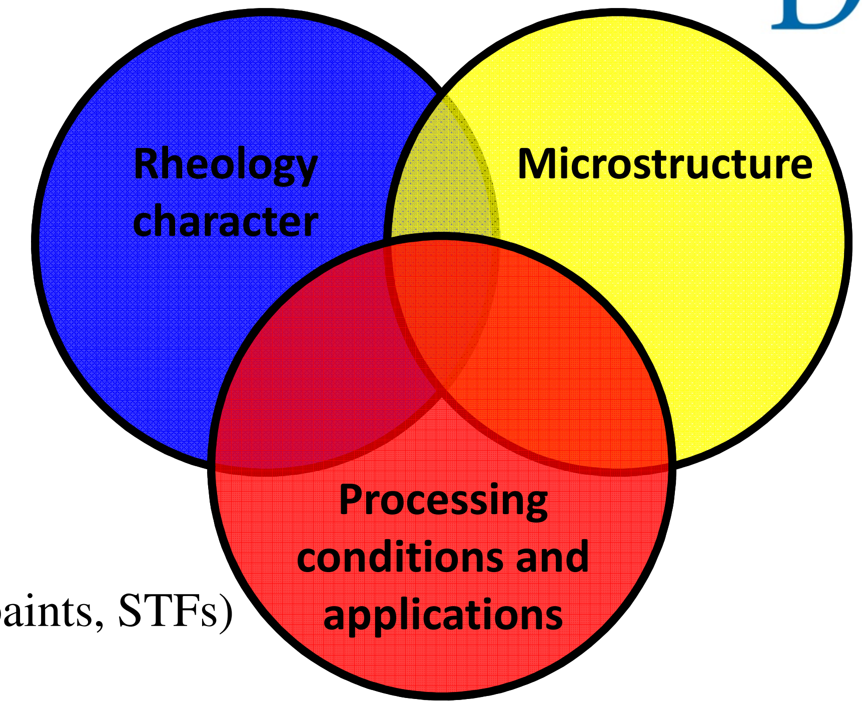
A review of nonlinear oscillatory shear tests: Analysis and application of large amplitude oscillatory shear (LAOS)

Kyu Hyun[a,*], Manfred Wilhelm[b], Christopher O. Klein[b], Kwang Soo Cho[c], Jung Gun Nam[d], Kyung Hyun Ahn[d], Seung Jong Lee[d], Randy H. Ewoldt[e], Gareth H. McKinley[f]

"…the use of complementary *in situ* microstructural probes…will help to more deeply connect the measured macroscopic response with the microstructural origin of nonlinear viscoelastic behavior." (March 2011)

Data: R. Egres, PHD UD

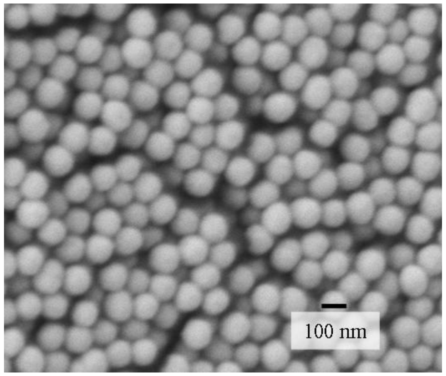
Structure-property relationship: Complex fluids



- Colloidal suspensions (coatings, paints, STFs)
- Gels
- Proteins (drug delivery)
- Biofilms
- Foams
- Personal hygiene (shampoos, soaps)
- Polymers (wormlike micelles)
- Emulsions
- Cosmetics (face wash, mascara, nail polish)
- Food processing (ketchup, cheese, butter, ice cream)
- …

Colloidal suspension: Shear Thickening Fluid

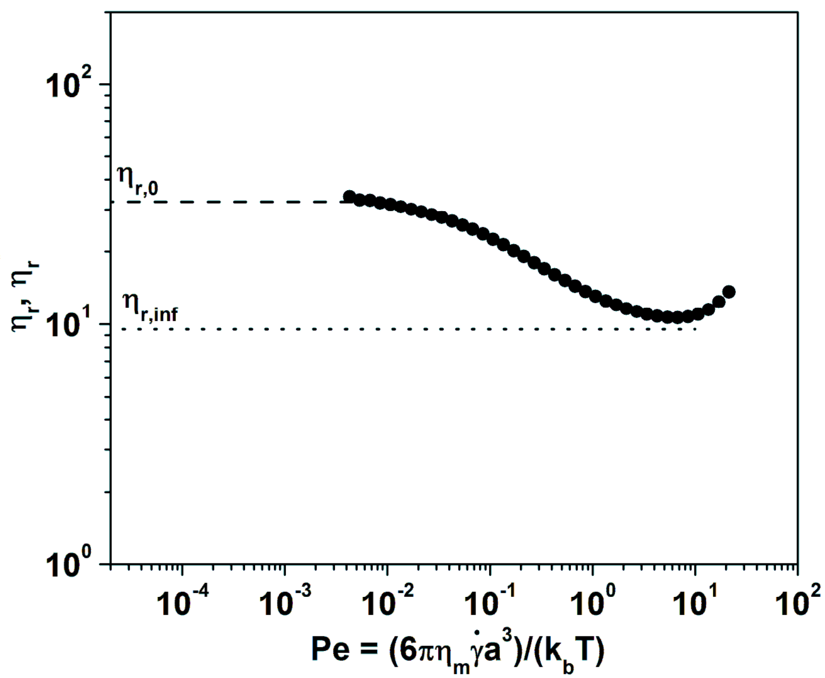
STF = SiO_2 particles + PEG-600/EG (30/70v)

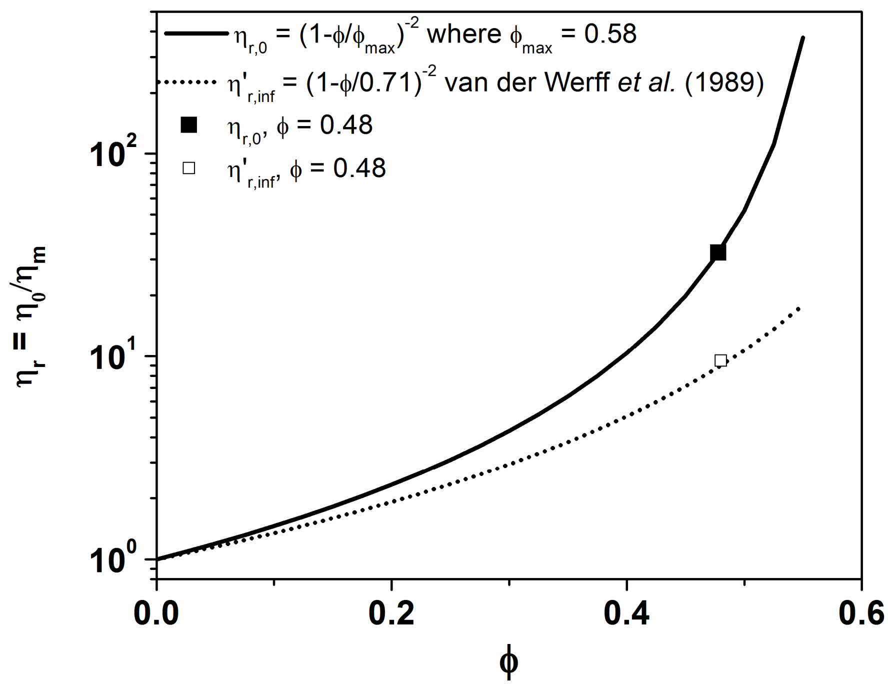


Particle Properties:
radius = 67.5 nm
$\rho_{particles}$ = 1.89 ±0.02 g/mL

Solvent Properties:
η = 0.043 Pa s
$\rho_{PEG-600}$ / ρ_{dEG} (30/70) = 1.201 g/mL

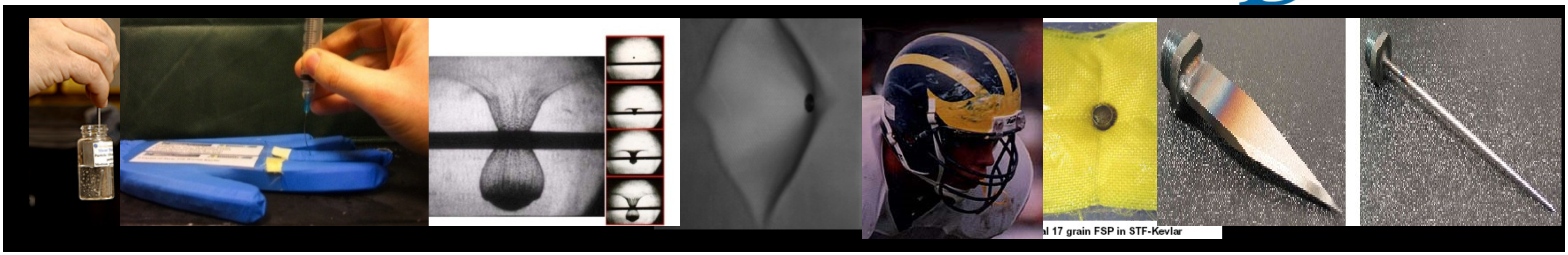
$$\phi_{\text{effective hard-sphere}} = 0.48$$

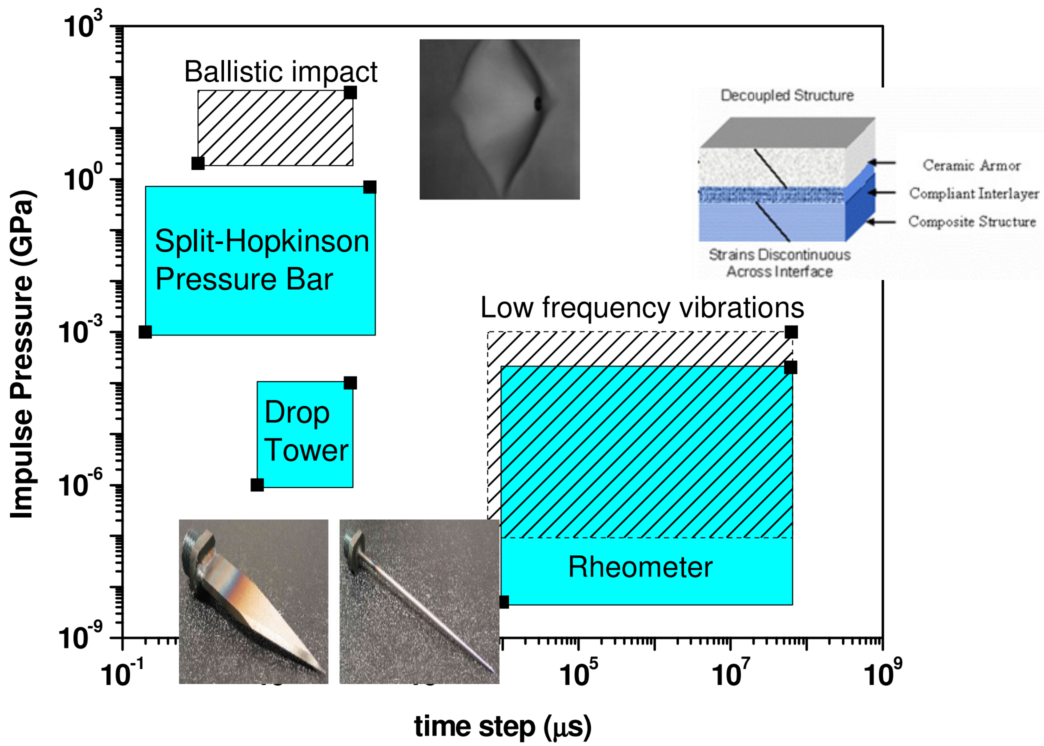




Z. Cheng *et al. Phys Rev E.* **65** (2002), 041405.
J. C. van der Werff and C. G. de Kruif. *J. Rheol.* **33**:3 (1989), 421-454.

Shear thickening fluids (STFs) applications: hometown hazards and out-of-this world peril





D. Kalman *et al. Applied Materials and Interfaces* 1**(11):** 2602-2612.
Davila and Chen *Appl Compos Mater* 7: 51-67 (1999)

Shear thickening fluids (STFs) applications: hometown hazards and out-of-this world peril

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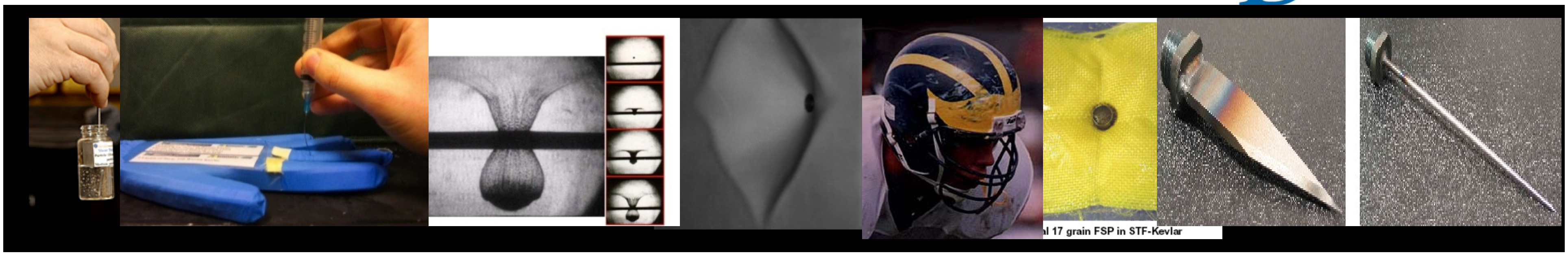
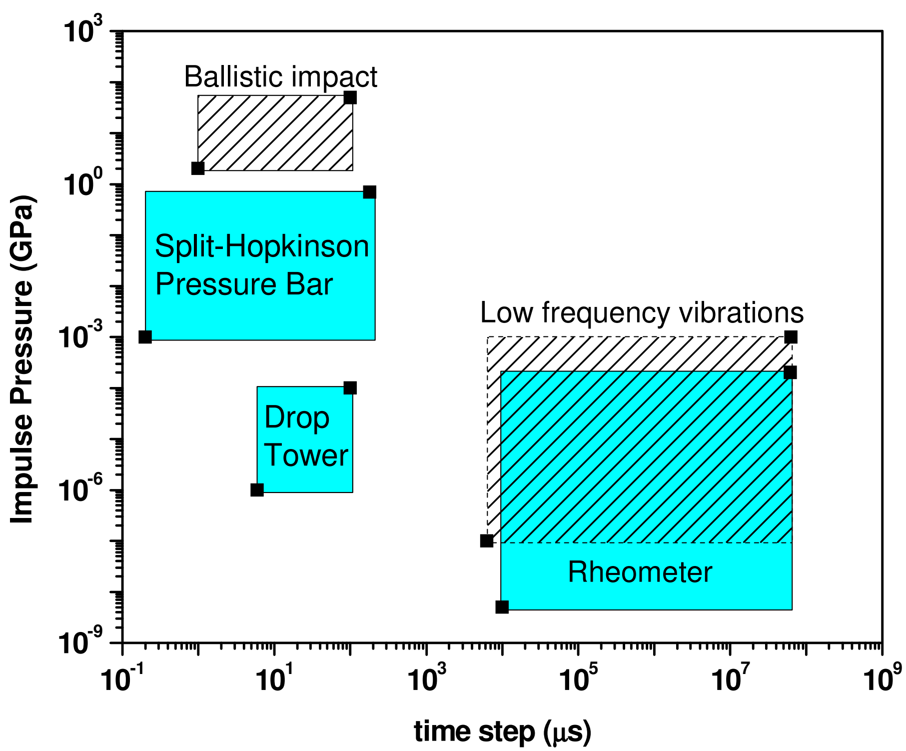
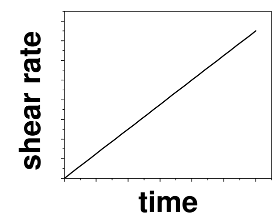
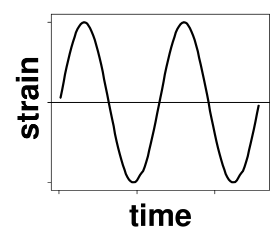


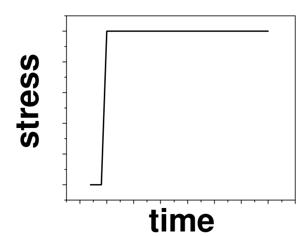




Steady shear deformation



Dynamic deformation



Transient deformation

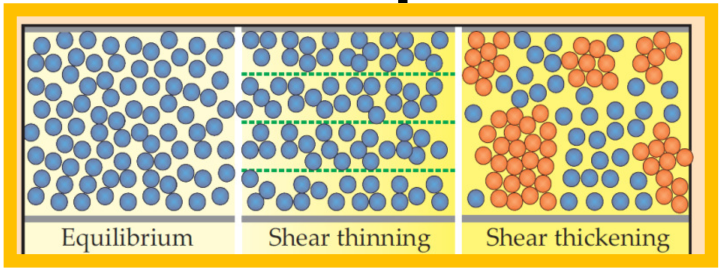
D. Kalman *et al. Applied Materials and Interfaces* 1**(11):** 2602-2612.
Davila and Chen *Appl Compos Mater* 7: 51-67 (1999)

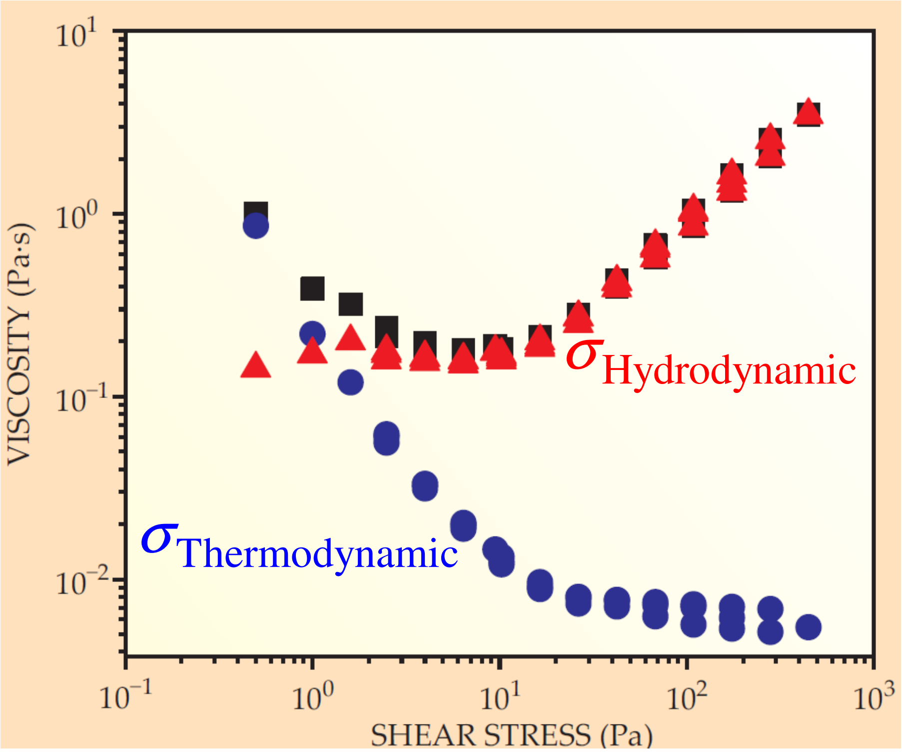
ILC DOVER *creating what's next*

COMPOSITE MATERIALS RESEARCH

NASA

Shear Thickening Fluids
and their response to steady shear



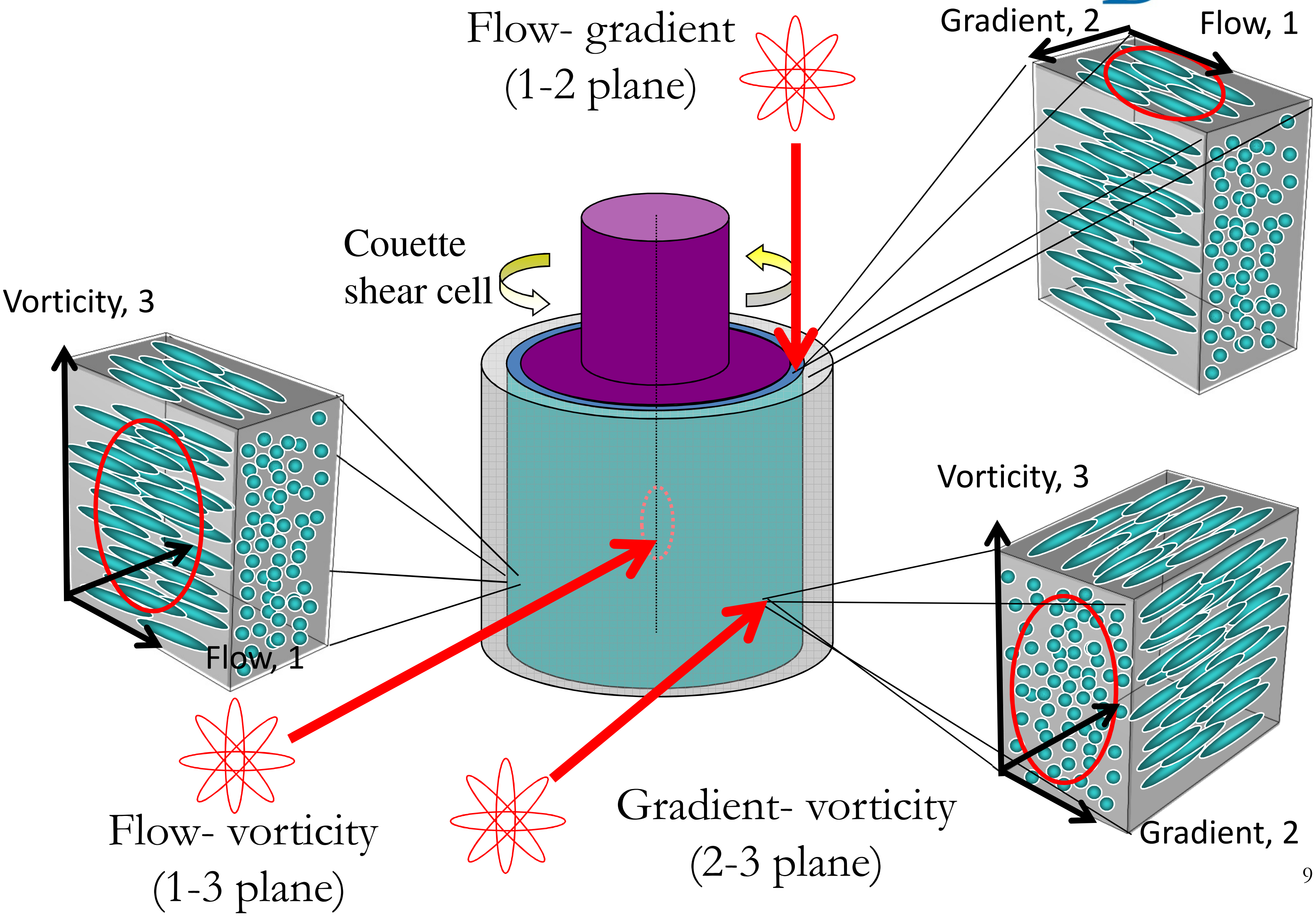


Hydrodynamic component associated with forces acting between particles due to motion through the suspending fluid.

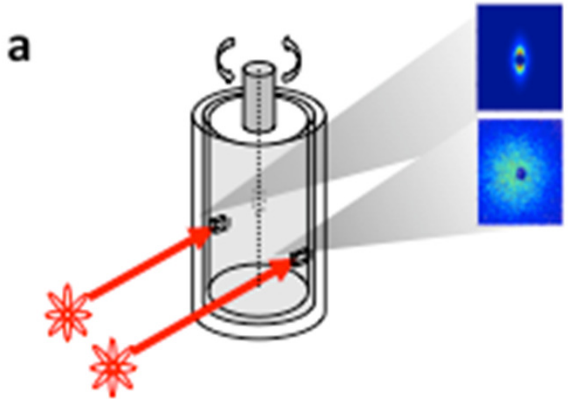
Thermodynamic component associated with the Brownian motion of the particles

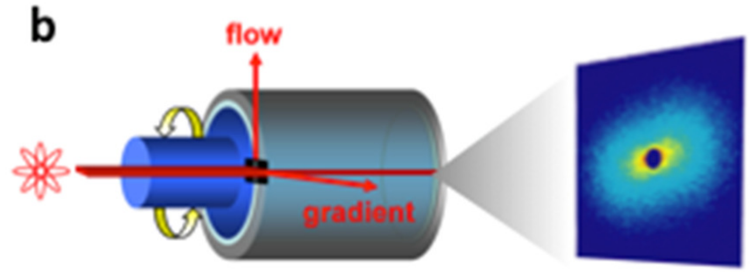
N. J. Wagner and J. F. Brady (2009). "Shear thickening in colloidal dispersions." *Physics Today* **62**(10): 27-32.
B. J. Maranzano and N. J. Wagner, *J. Chem. Phys.* **114,** 10514 (2001).
D. P. Kalman University of Delaware PhD Thesis, (2010).
J. Bender and N. J. Wagner *J. Rheol.* **40,** 899 (1996).

Complex fluids and shear flow: a 3D problem



Rheo-SANS & Flow-SANS

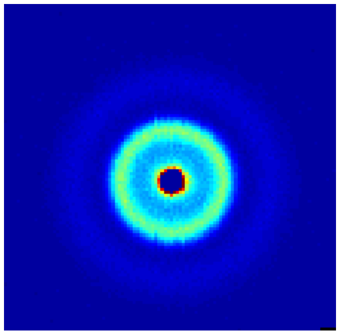


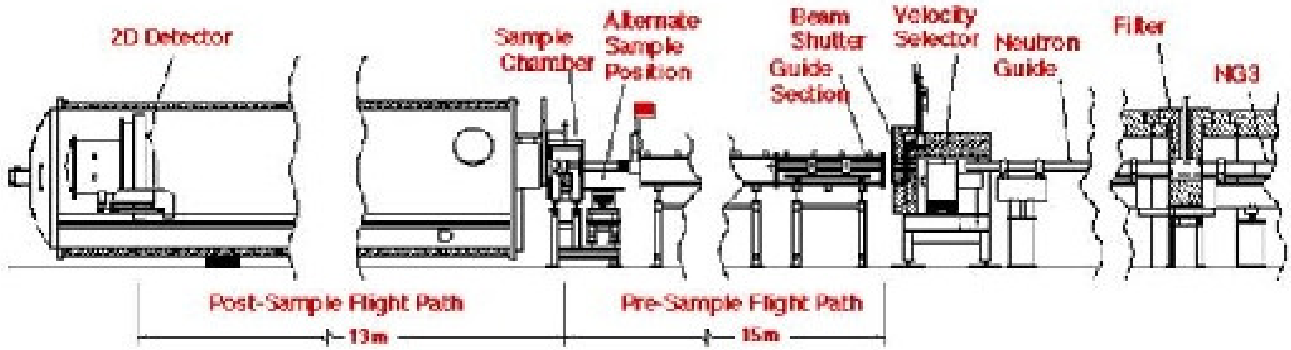


Aaron P.R. Eberle & Lionel Porcar . *Flow-SANS and Rheo-SANS.Applied to Soft Matter.* Curr. Opin. Coll. Int. Sci. **17** 33-43 (2012).
A. K. Gurnon *et al. Measuring material microstructure under flow using 1-2 plane flow-Small Angle Neutron Scattering.* Journal of Visual Experiments (accepted, 2013).

Small Angle Neutron Scattering Experiment

Detector



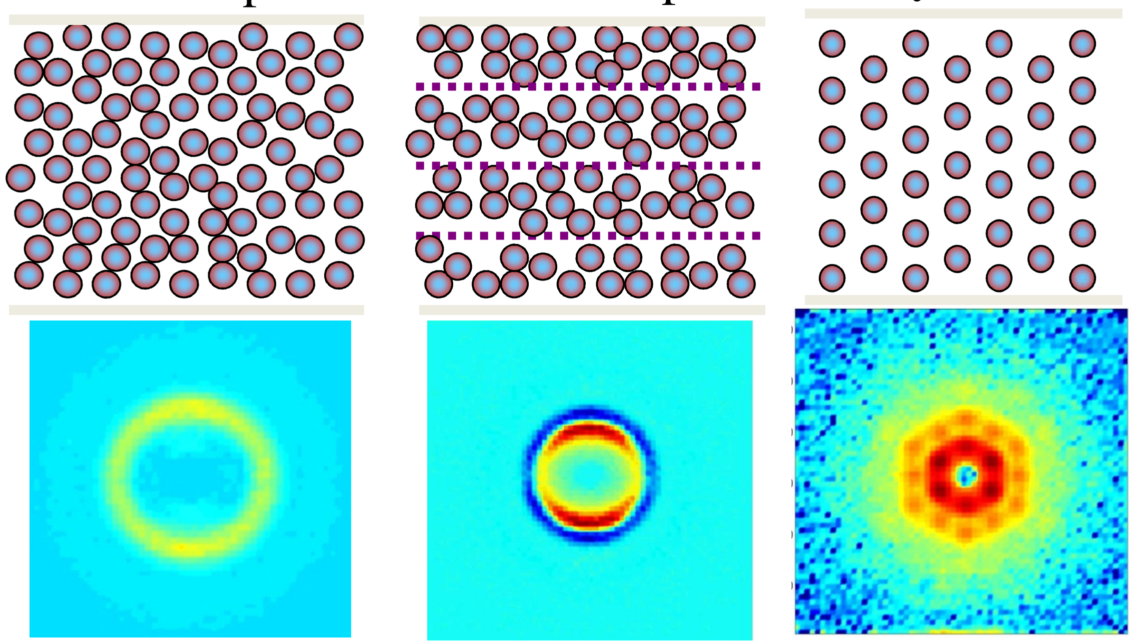


Scattering Examples

Random Suspension | Anisotropic | Crystalline

Real Space Structure:

Corresponding Scattering Pattern:

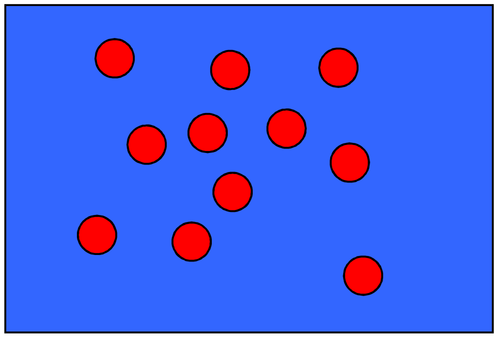


Liberatore et al. (2006) Phys. Rev. E **73**: 020504R

A. Eberle and L. Porcar (2012) *Current Opinion in Colloid and Interface Science* 17(**1**): 33-43.

What does Small Angle Neutron Scattering (SANS) measure?

$$I(q) = \phi V_p (\Delta\rho)^2 P(q) S(q)$$



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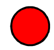
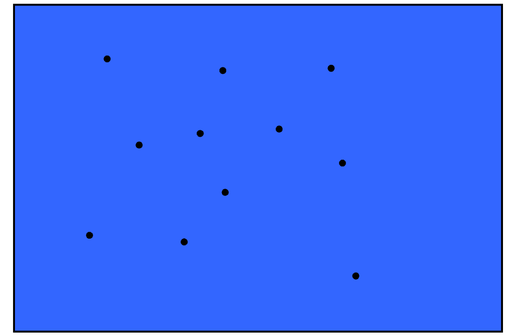
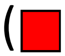
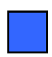
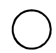
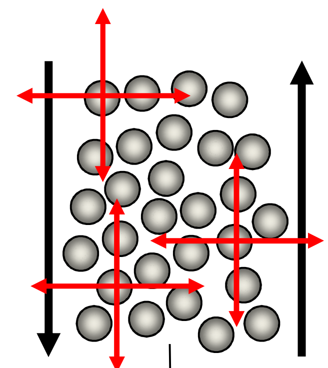


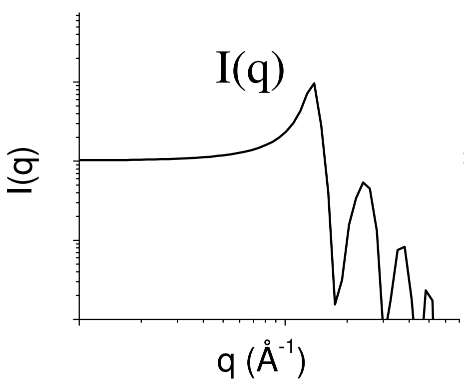
X



Adapted from slide by
Yun Liu at NIST

= ϕV_p ( - )^2 X  X





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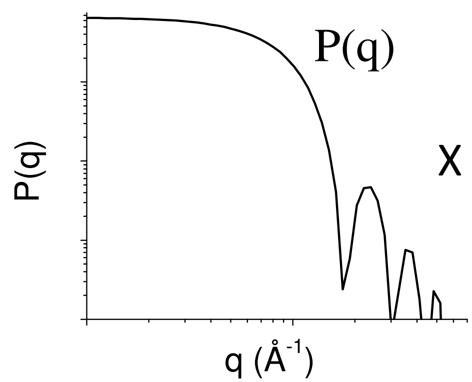
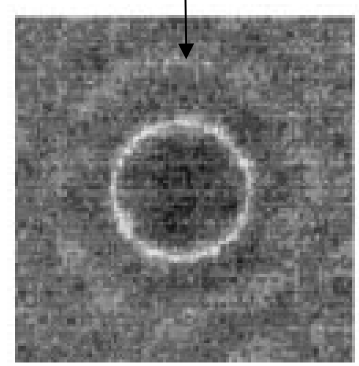
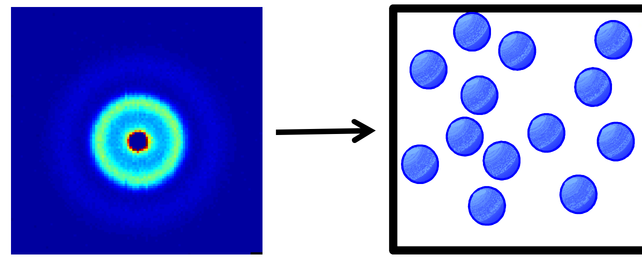
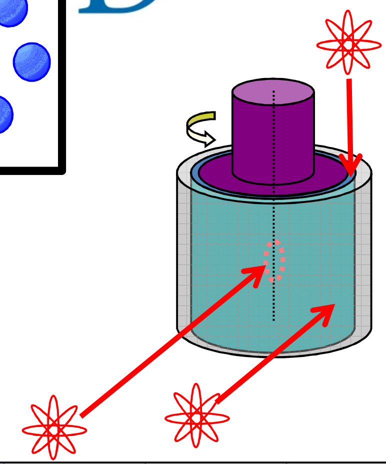


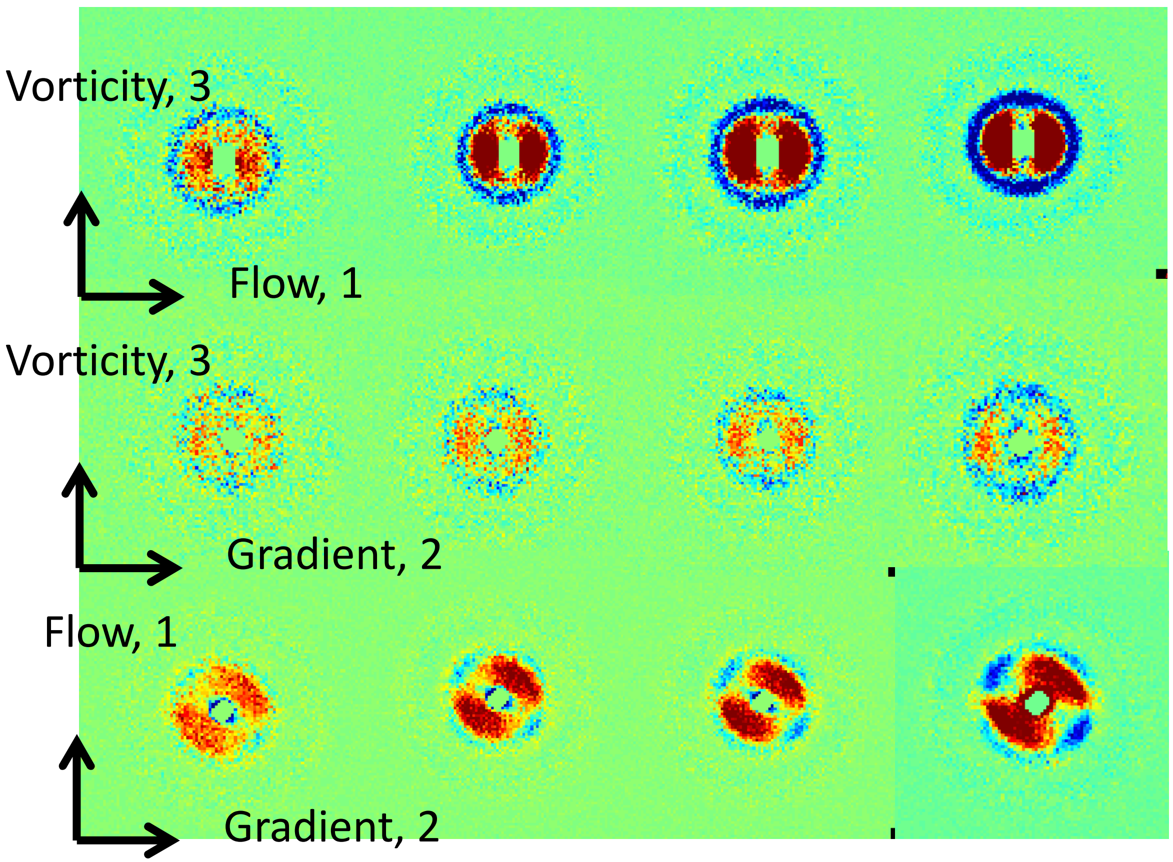
X

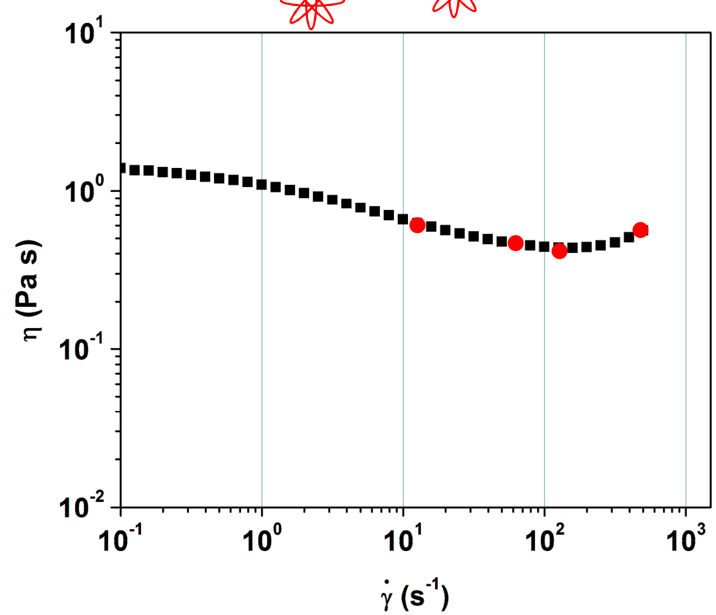


Measured 3-D microstructure in three planes of shear

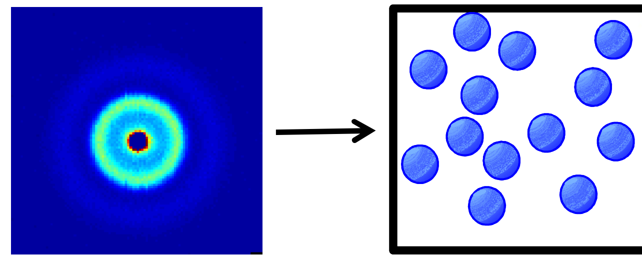




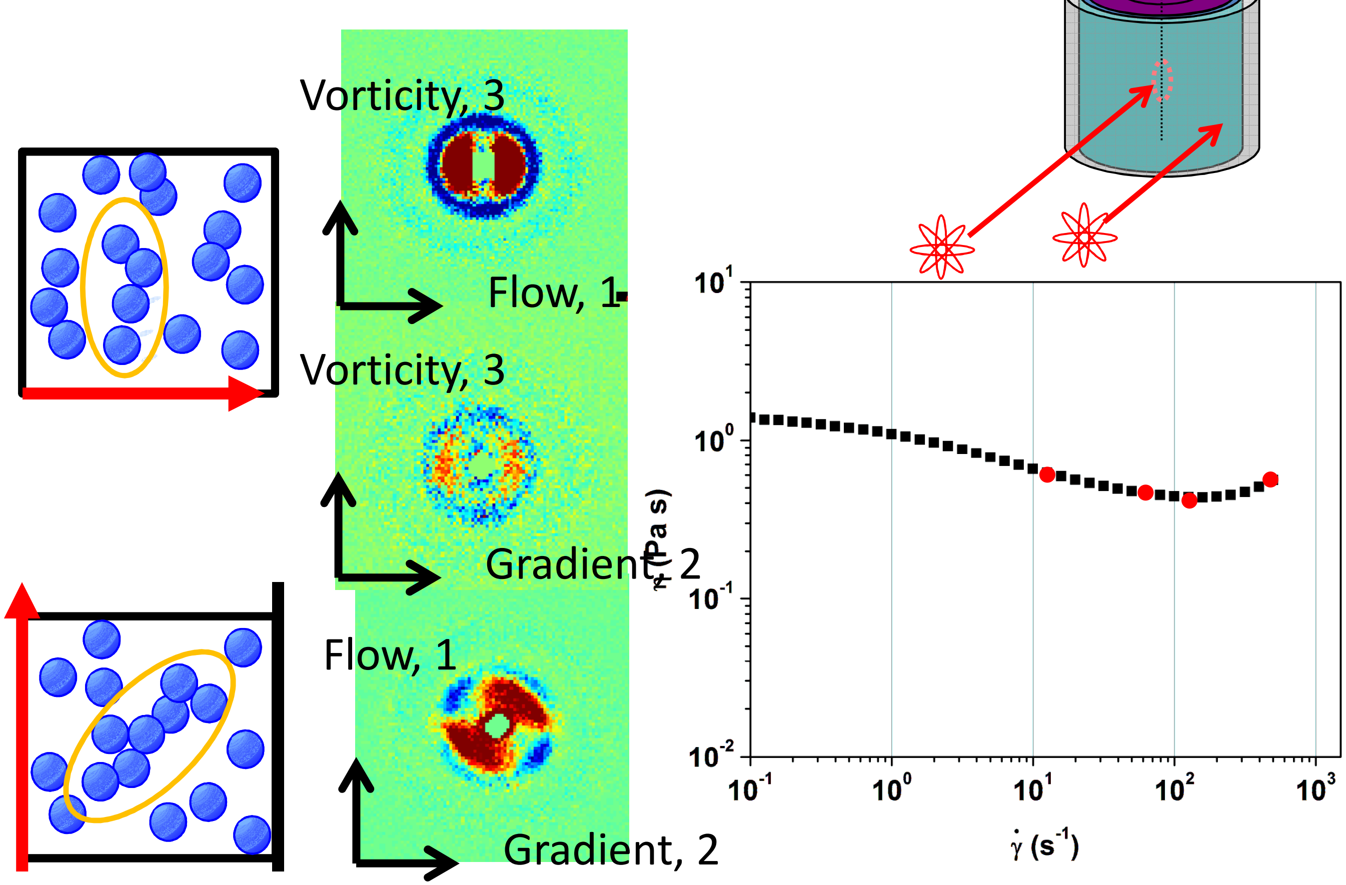




Measured 3-D microstructure in three planes of shear

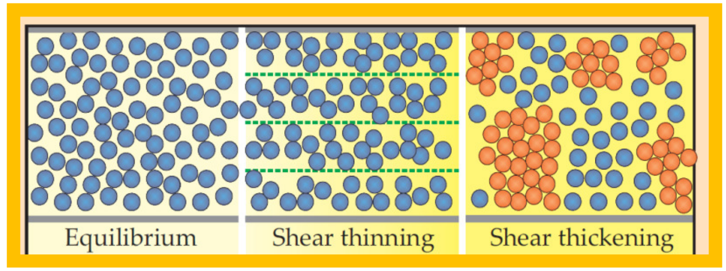


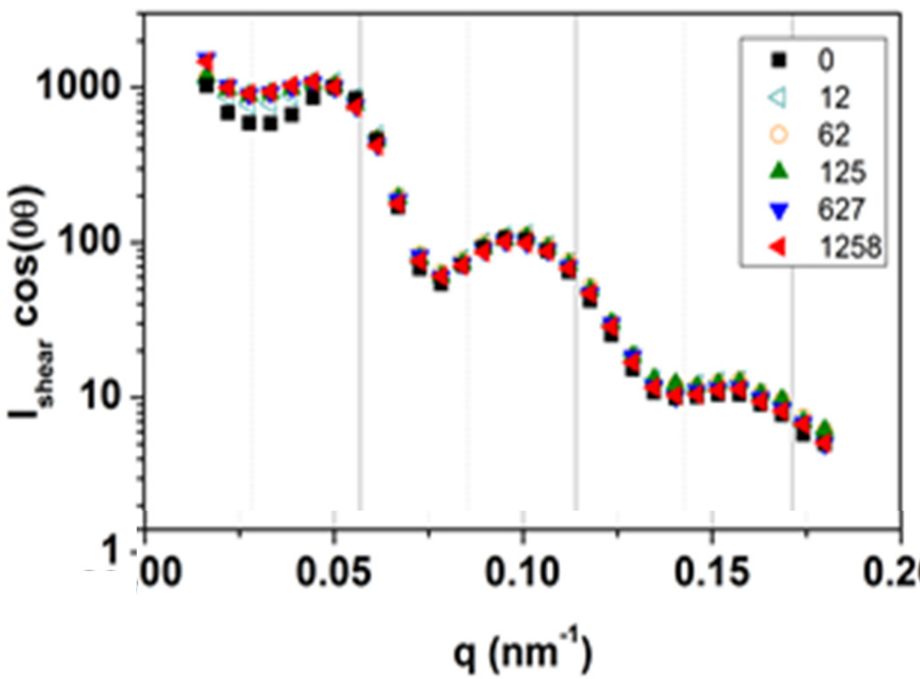
Anisotropy in pattern reflects a propensity for particles to align along the vorticity direction.

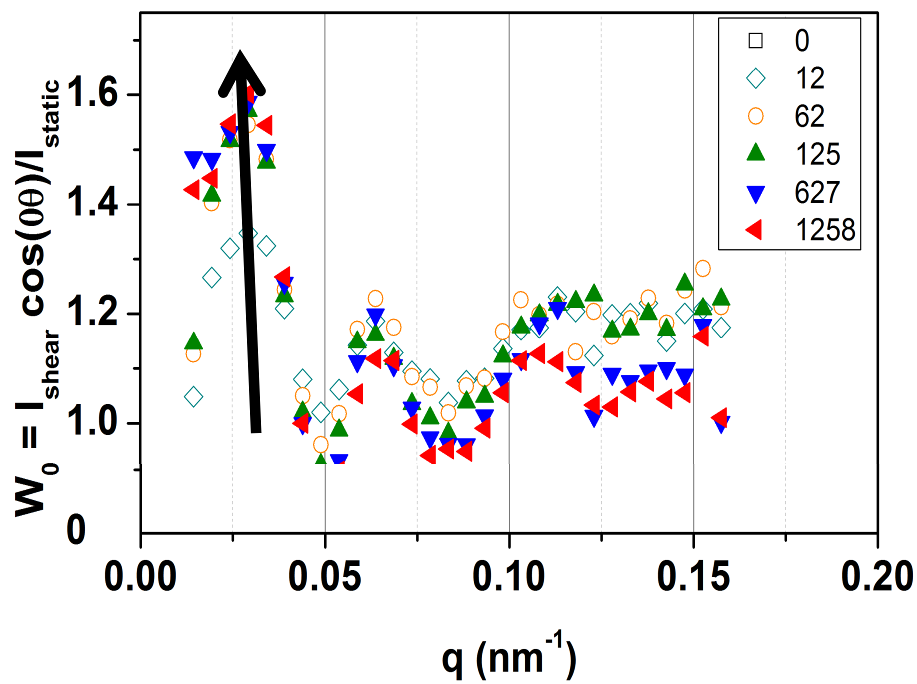


Reflects anisotropy in local microstructure along the compression axis.

Microstructural evidence of hydroclusters







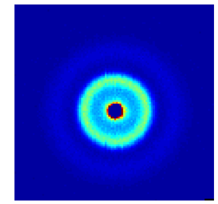
Defining the Stress-SANS rule:

Thermodynamic and hydrodynamic stresses

$$\underline{\underline{\sigma}} = \langle \underline{F}\,\underline{X} \rangle$$

$$g(r) \longrightarrow$$

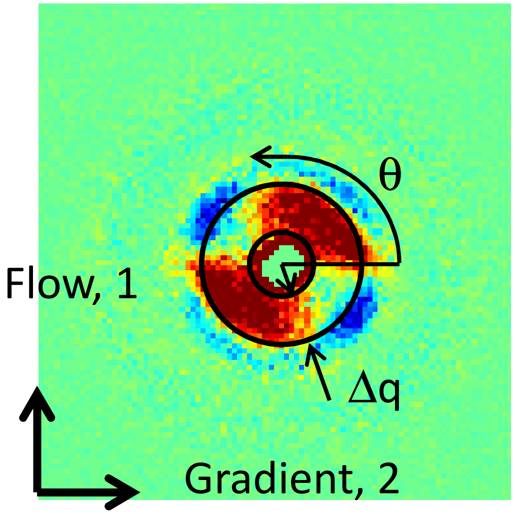
SANS

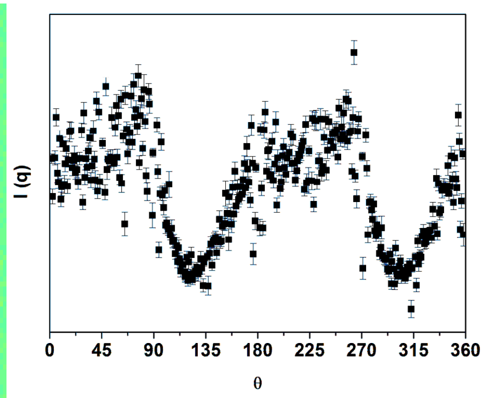


[1]N. J. Wagner and B. J. Ackerson, *J. Chem.* Phys. 97, 1473 (1992).
[2]B. J. Maranzano and N. J. Wagner (2002) *J. Chem. Phys.* **117,** 10291
[3]D. Kalman and N. J. Wagner, *Rheol Acta* (2009) **48**: 897-908.

Defining the Stress-SANS rule:

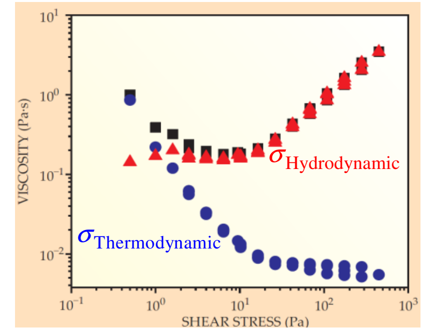
Thermodynamic and hydrodynamic stresses





$$\sigma = \left\langle \underline{F}\,\underline{X} \right\rangle$$

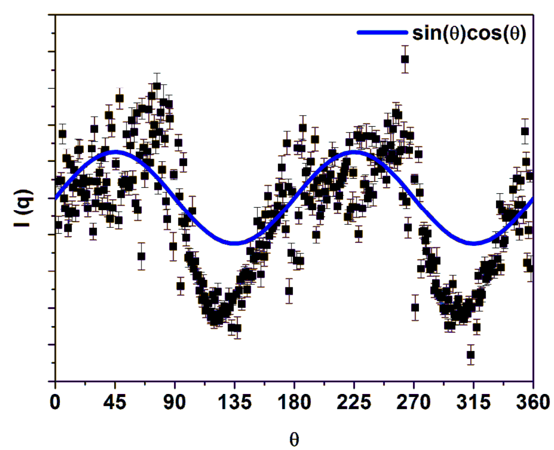
Different symmetries of the structure contribute differently to each of the stress components.

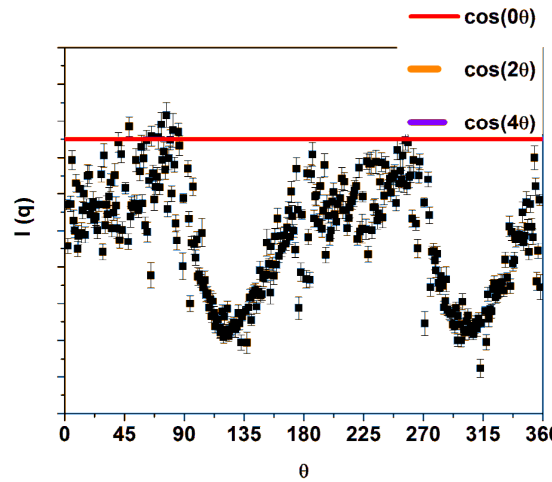


$$\sigma_{\text{total}} \propto \left\langle \underline{F}_{\text{thermodynamic}}\,\underline{X} \right\rangle + \left\langle \underline{F}_{\text{hydrodynamic}}\,\underline{X} \right\rangle$$

Two assumptions:

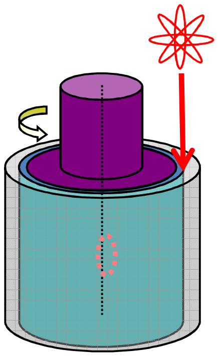
1. **The largest changes occur over Δq**
2. **To first order, the hydrodynamic stress is equal to the zeroeth moment of symmetry.**

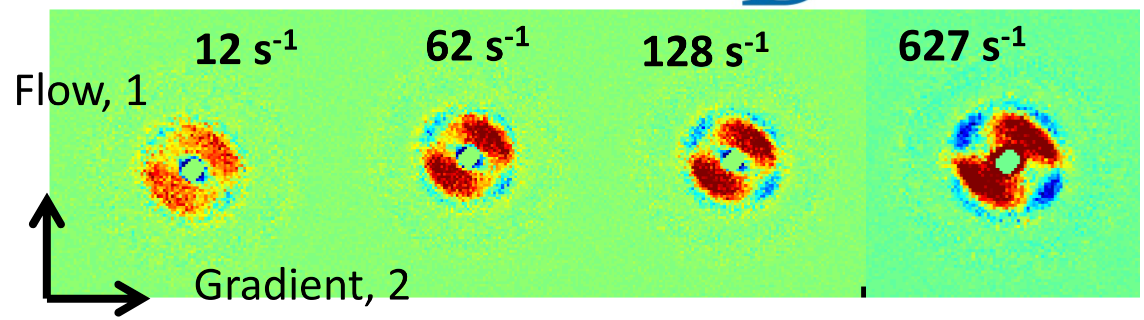


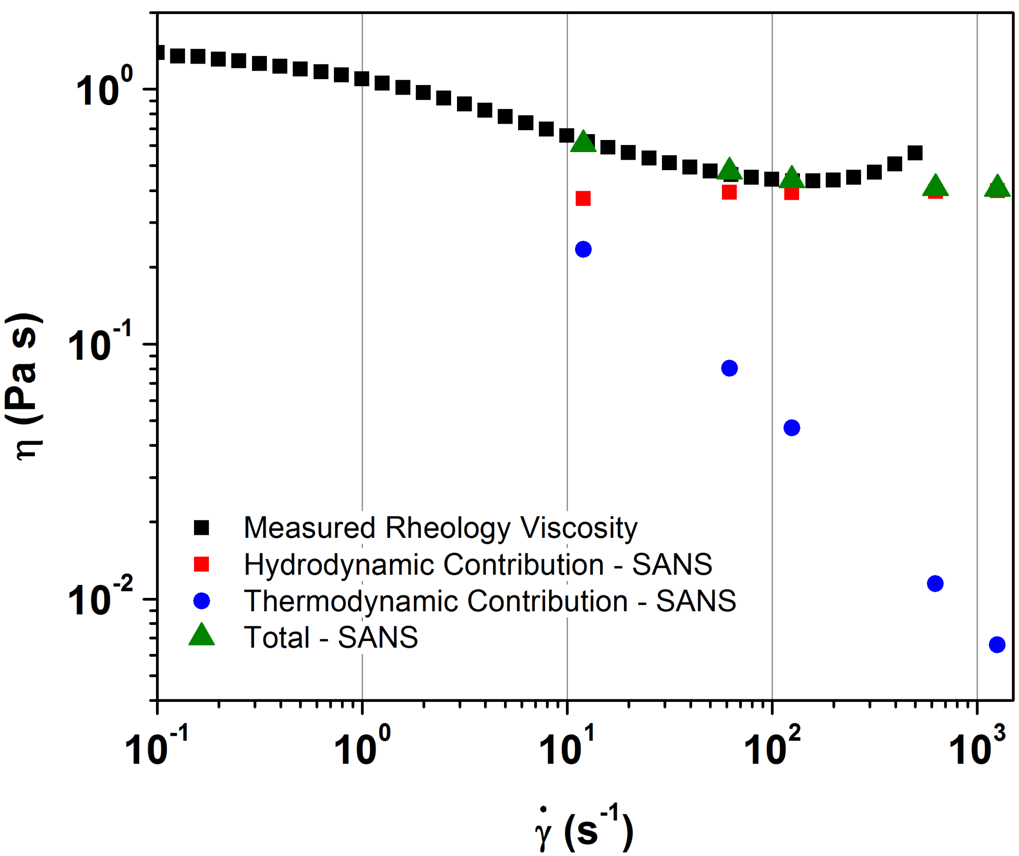


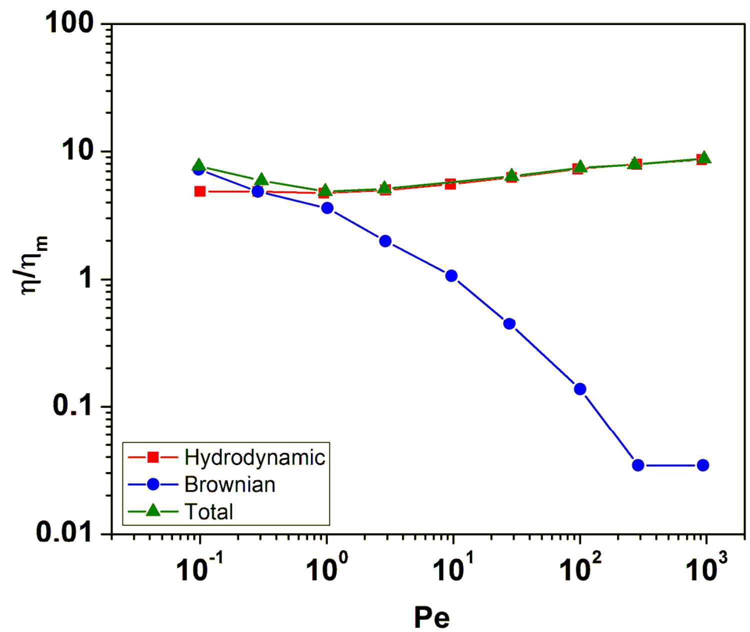
[1]N. J. Wagner and B. J. Ackerson, *J. Chem.* Phys. 97, 1473 (1992).
[2]B. J. Maranzano and N. J. Wagner (2002) *J. Chem. Phys.* **117,** 10291
[3]D. Kalman and N. J. Wagner, *Rheol Acta* (2009) **48**: 897-908.

Thermodynamic and hydrodynamic contributions to the total viscosity





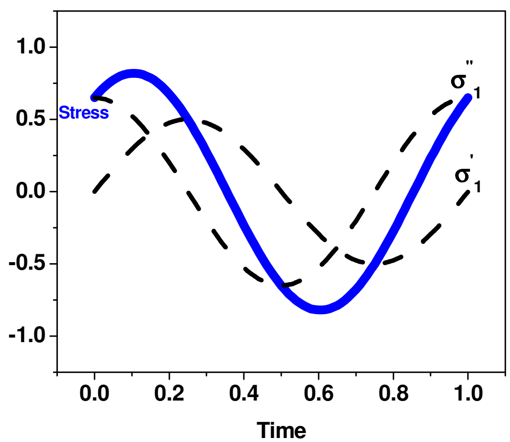


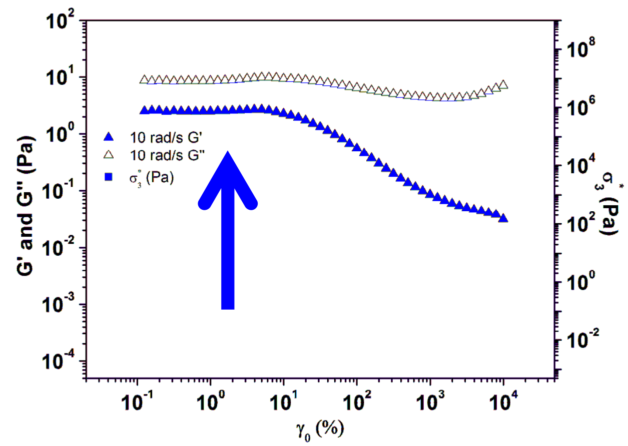


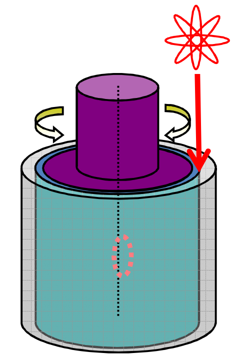
Accelerated Stokesian dynamics simulation results from A. J. Banchio and J. F. Brady. *J Chem Phys.* **118**:22 (2003),10323-32.

Nonlinear dynamic applications require nonlinear experiments: Large Amplitude Oscillatory Shear (LAOS)

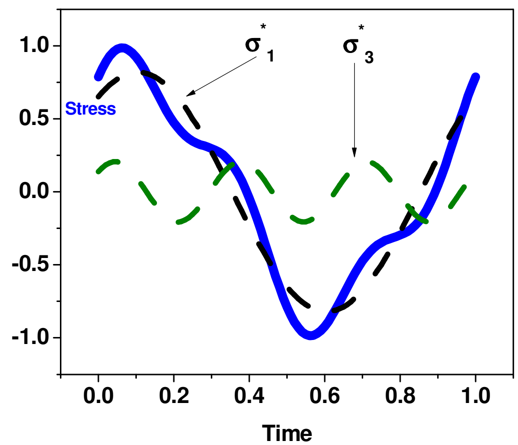
Linear Oscillatory Response

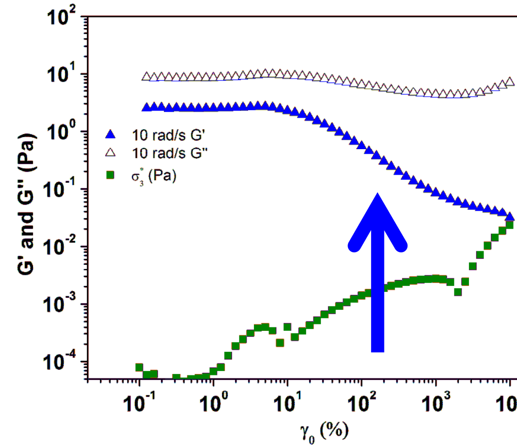


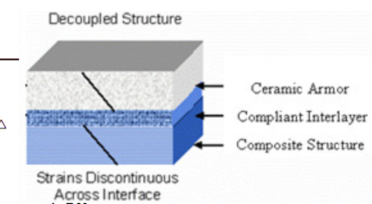


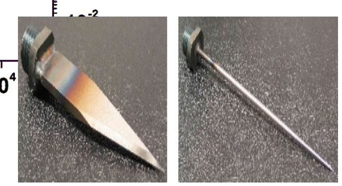


Nonlinear Oscillatory Response





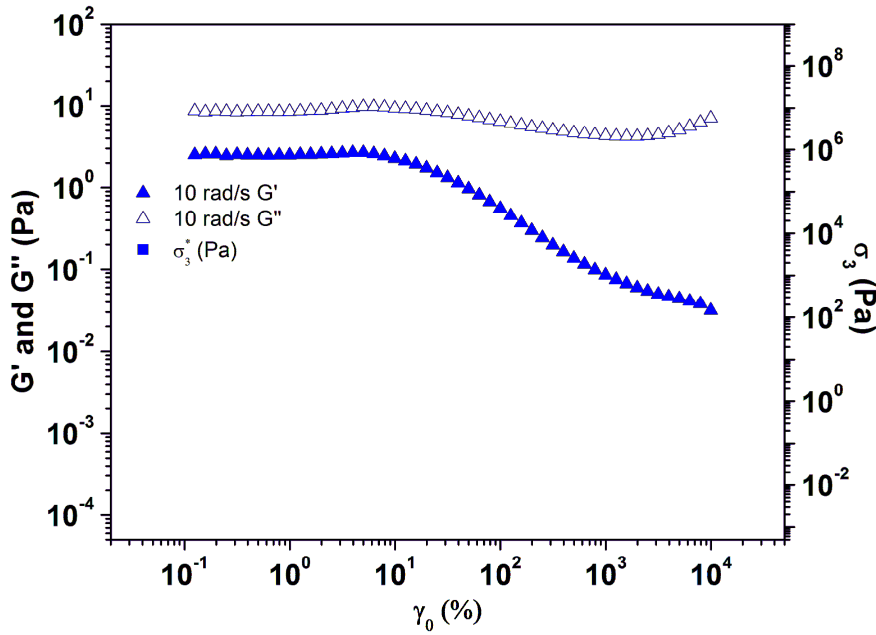


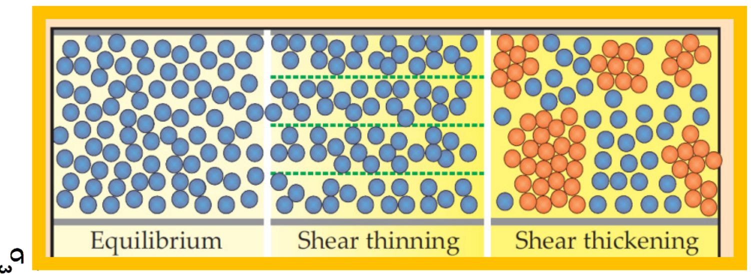


Nonlinear dynamic applications require nonlinear experiments: Large Amplitude Oscillatory Shear (LAOS)

1) During LAOS what are the thermodynamic and hydrodynamic contributions to the stress?

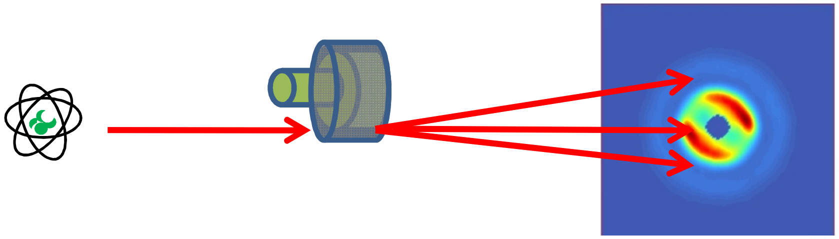
2) What is the microstructure?





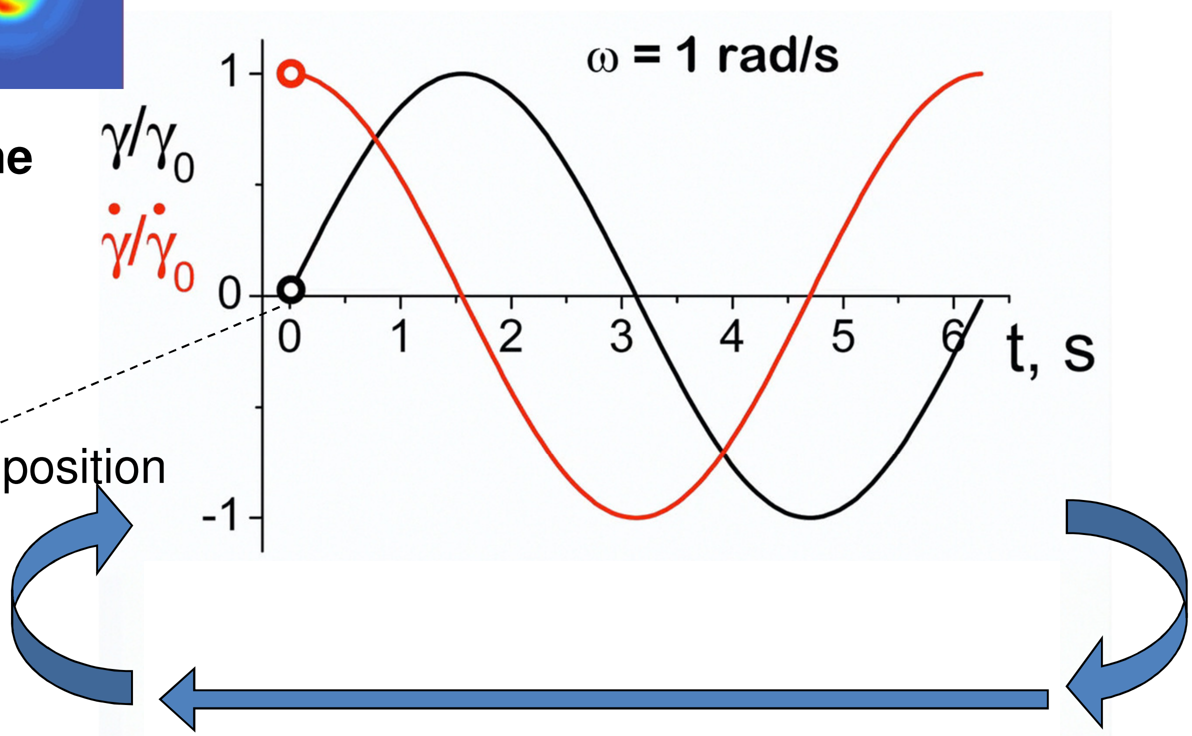
?

Time-resolved neutron scattering



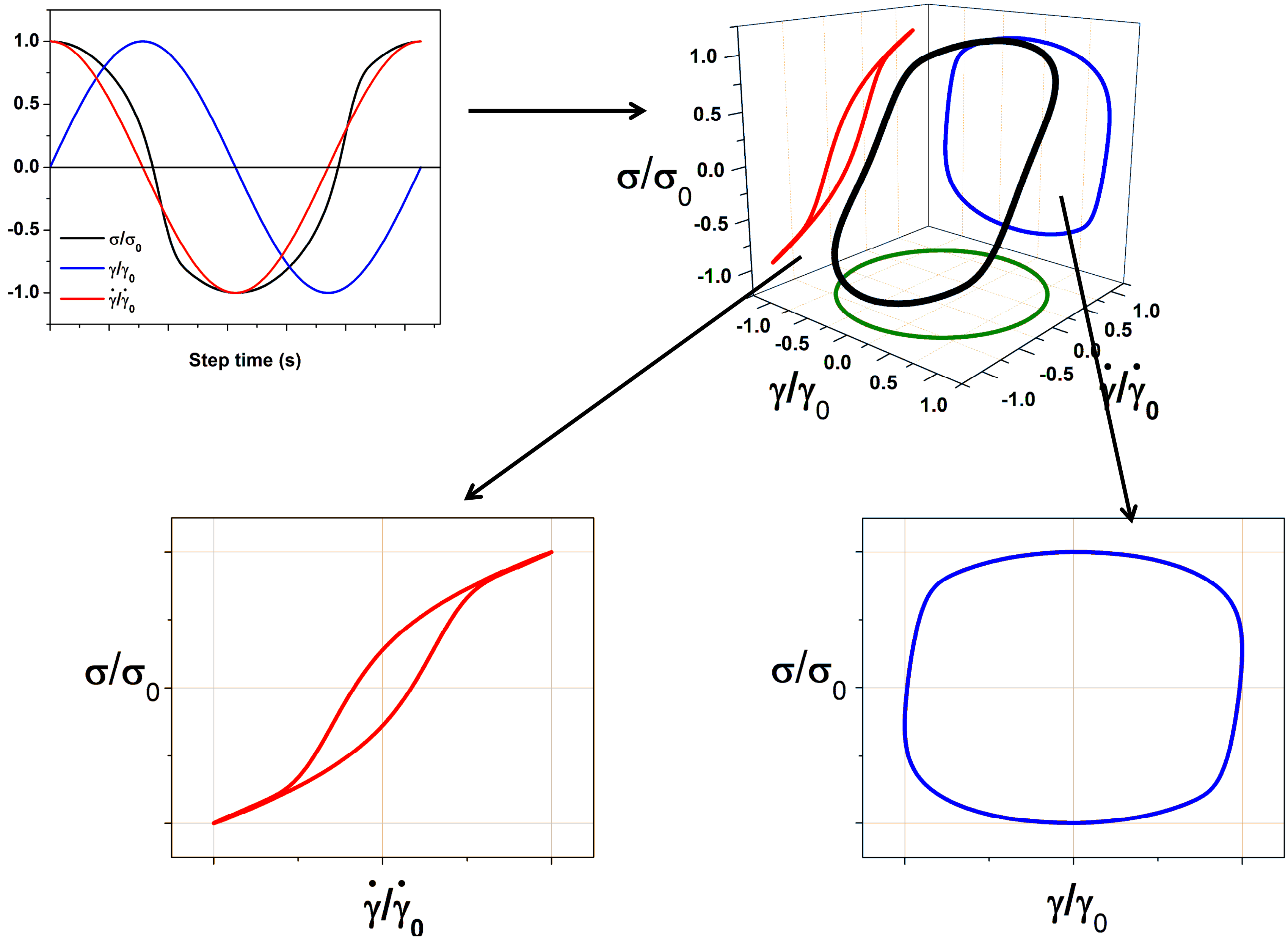
velocity- velocity gradient plane
LAOS time-resolved SANS

t=0 data acquisition trigger
in accordance with the motor position



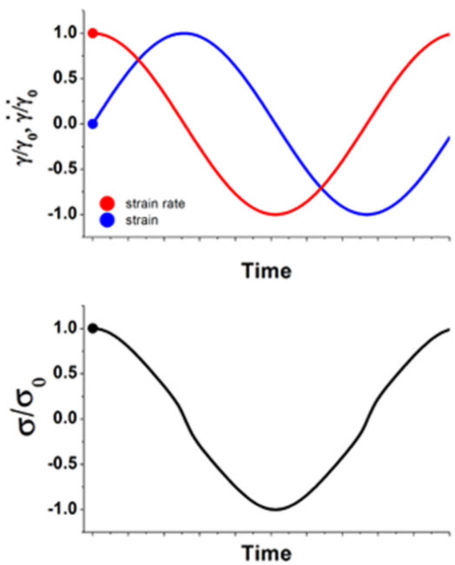
"Relaxation of a shear-induced lamellar phase measured with time resolved small angle neutron scattering", L. Porcar, W.A. Hamilton, P.D. Butler and G.G. Warr, *Physica B* **350**, e963 (2004)
Once upon a time: "Fast Relaxation of a Hexagonal Poiseuille Shear-induced Near-Surface Phase in a Threadlike Micellar Solution", W.A. Hamilton, P.D. Butler, L.J. Magid, Z. Han and T.M. Slawecki, *Physical Review E (Rapid Communications)* **60**, 1146 (1999)
C. Lopez-Barron *et al. Physical Review Letters,* 108, 258301 (2012).

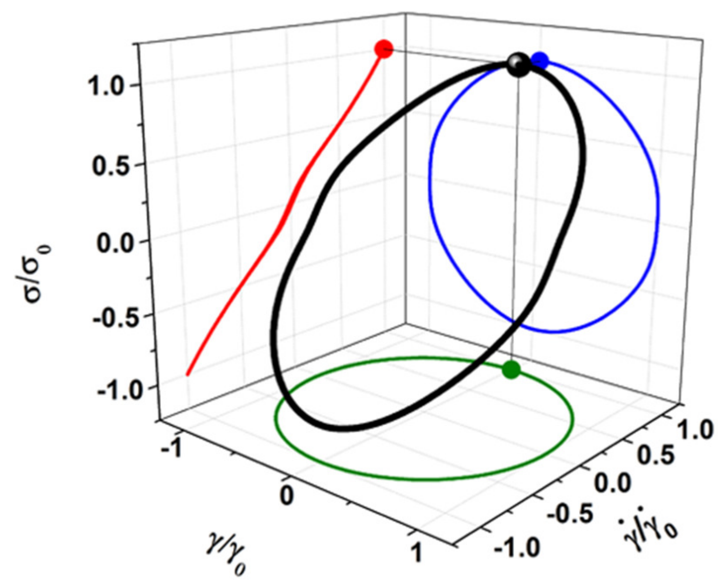
Deformation strain and strain rate frame of reference

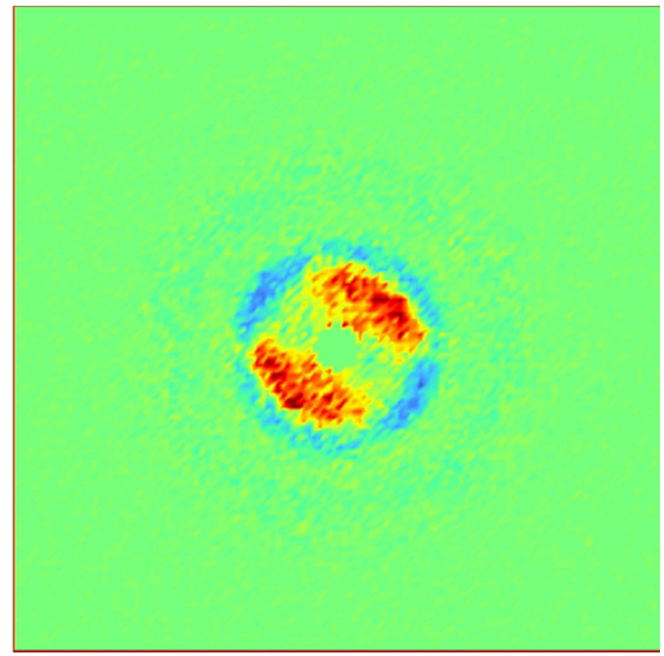


Evidence of a changing microstructure: 1-2 plane flow-SANS LAOS

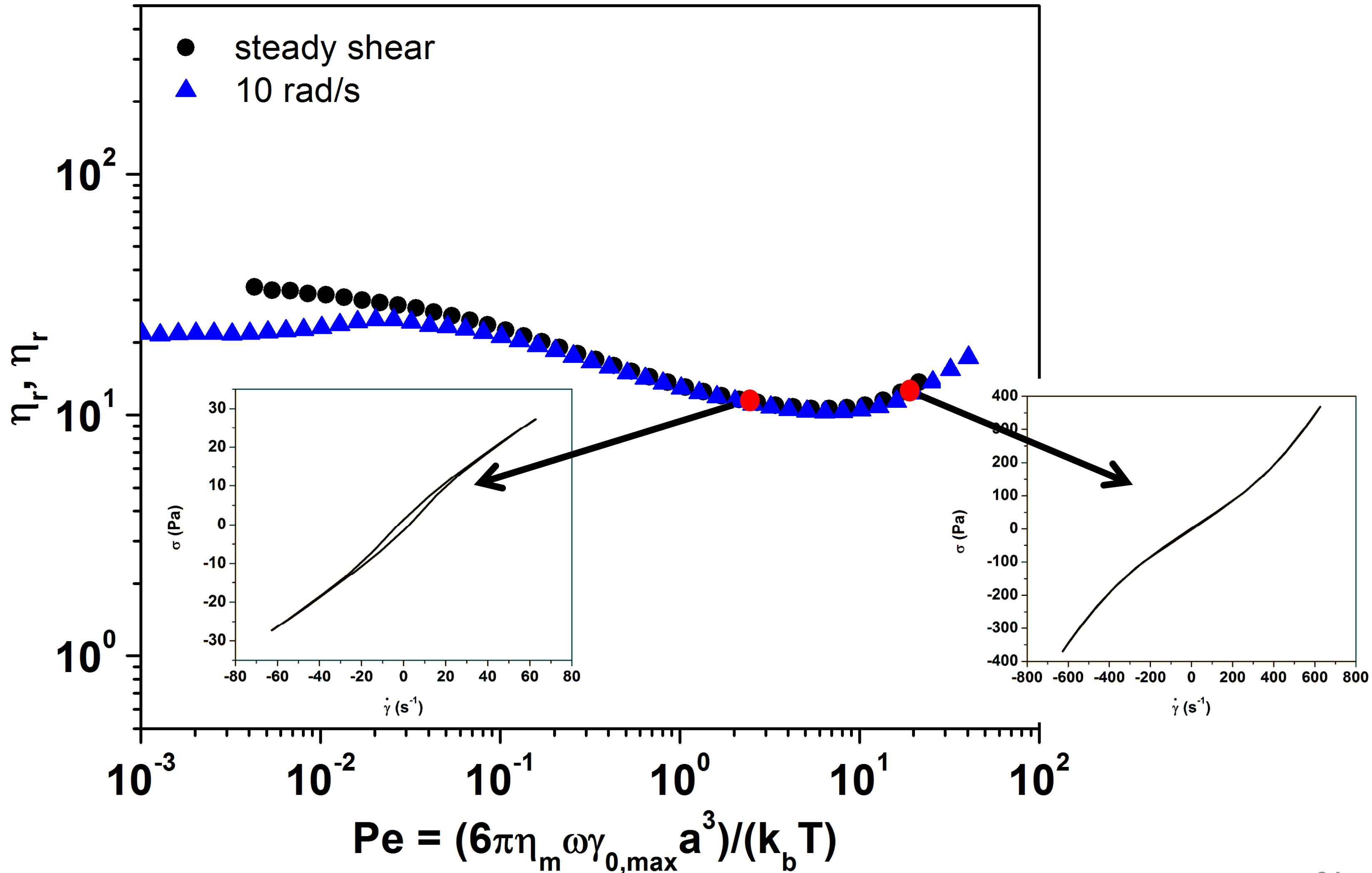
Pe = 12.5, LAOS – 10 rad/s and 3139%







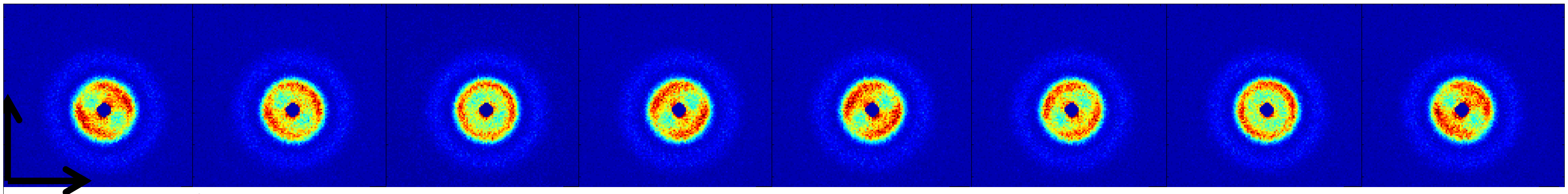
Two conditions, two different responses, one common viscosity



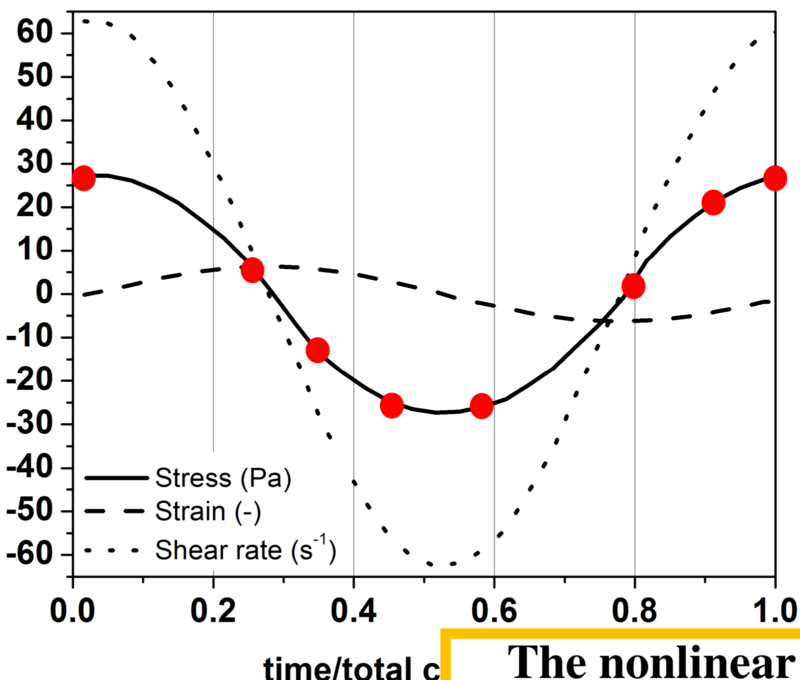
Implementing LAOS and the Stress-SANS rule

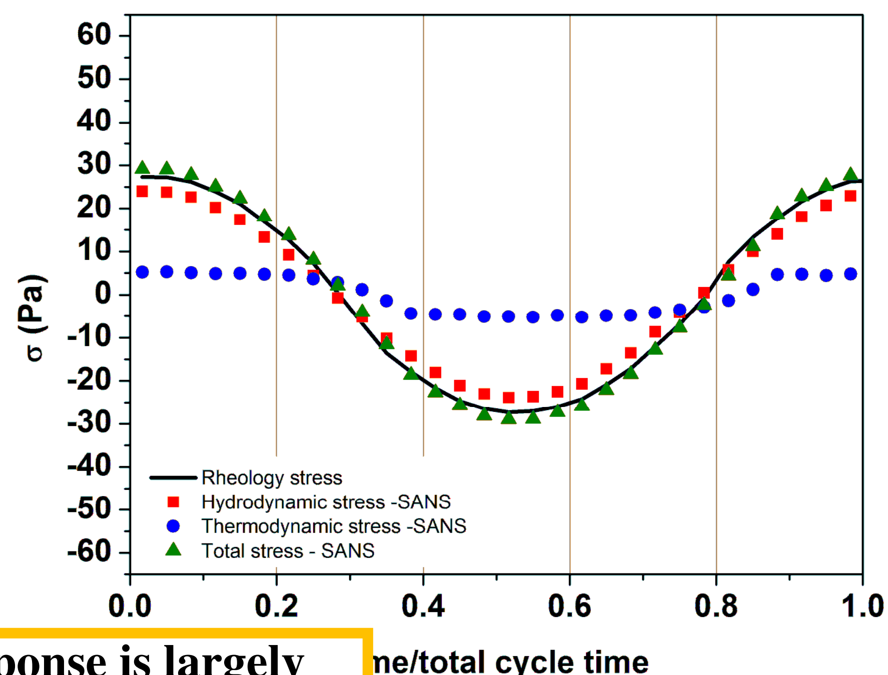
Pe = 2.5, LAOS – 10 rad/s and 627%

Flow, 1



Gradient, 2

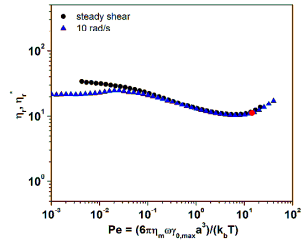




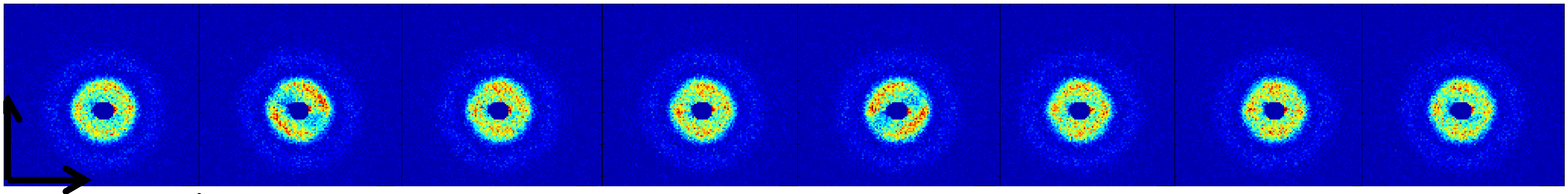
The nonlinear response is largely hydrodynamic in origin!

LAOS during shear thickening

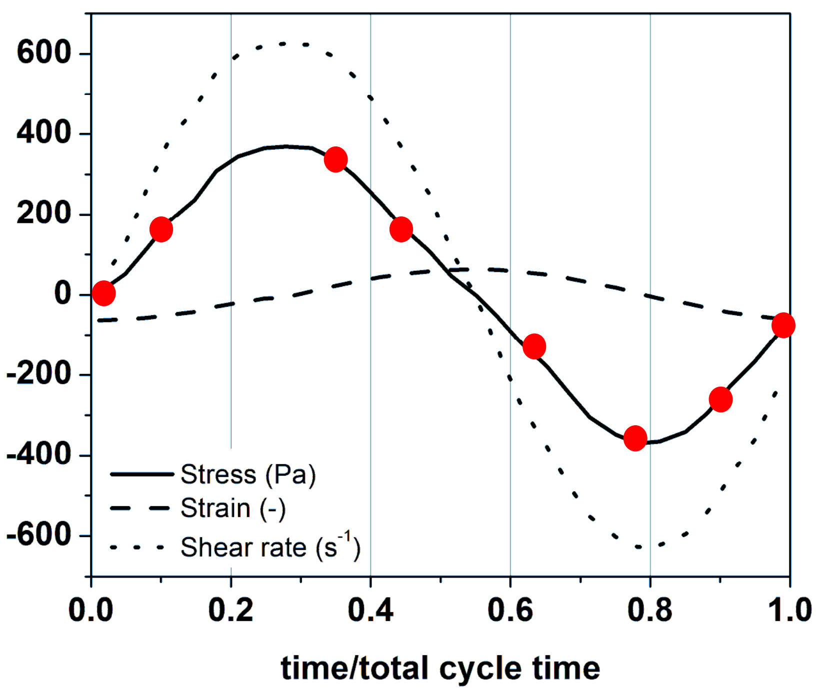
Pe = 25, LAOS – 10 rad/s and 6278%

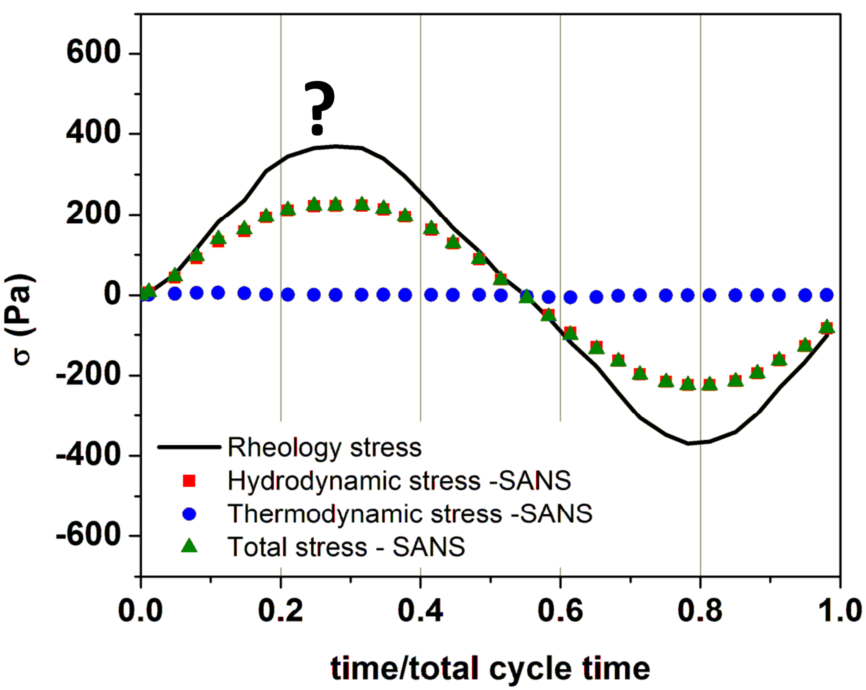


Flow, 1



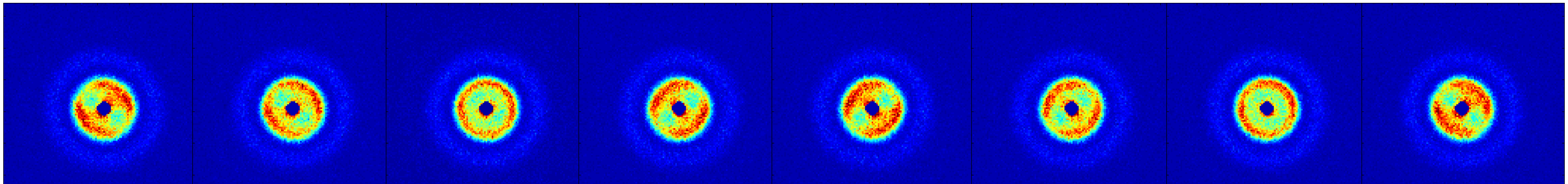
Gradient, 2



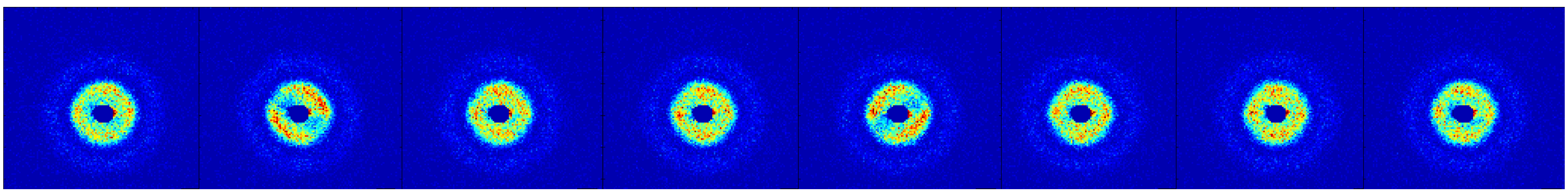


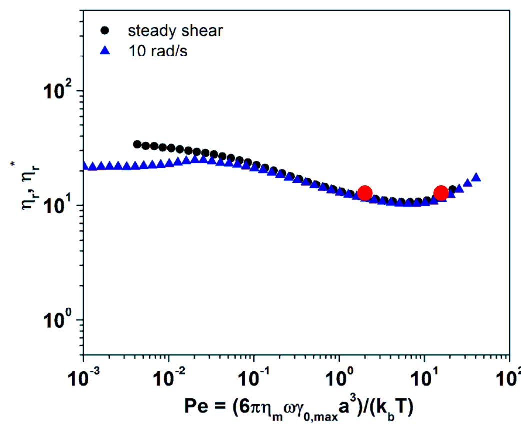
Equivalent complex viscosities, different structure, different stress

Shear Thinning, Pe = 2.5

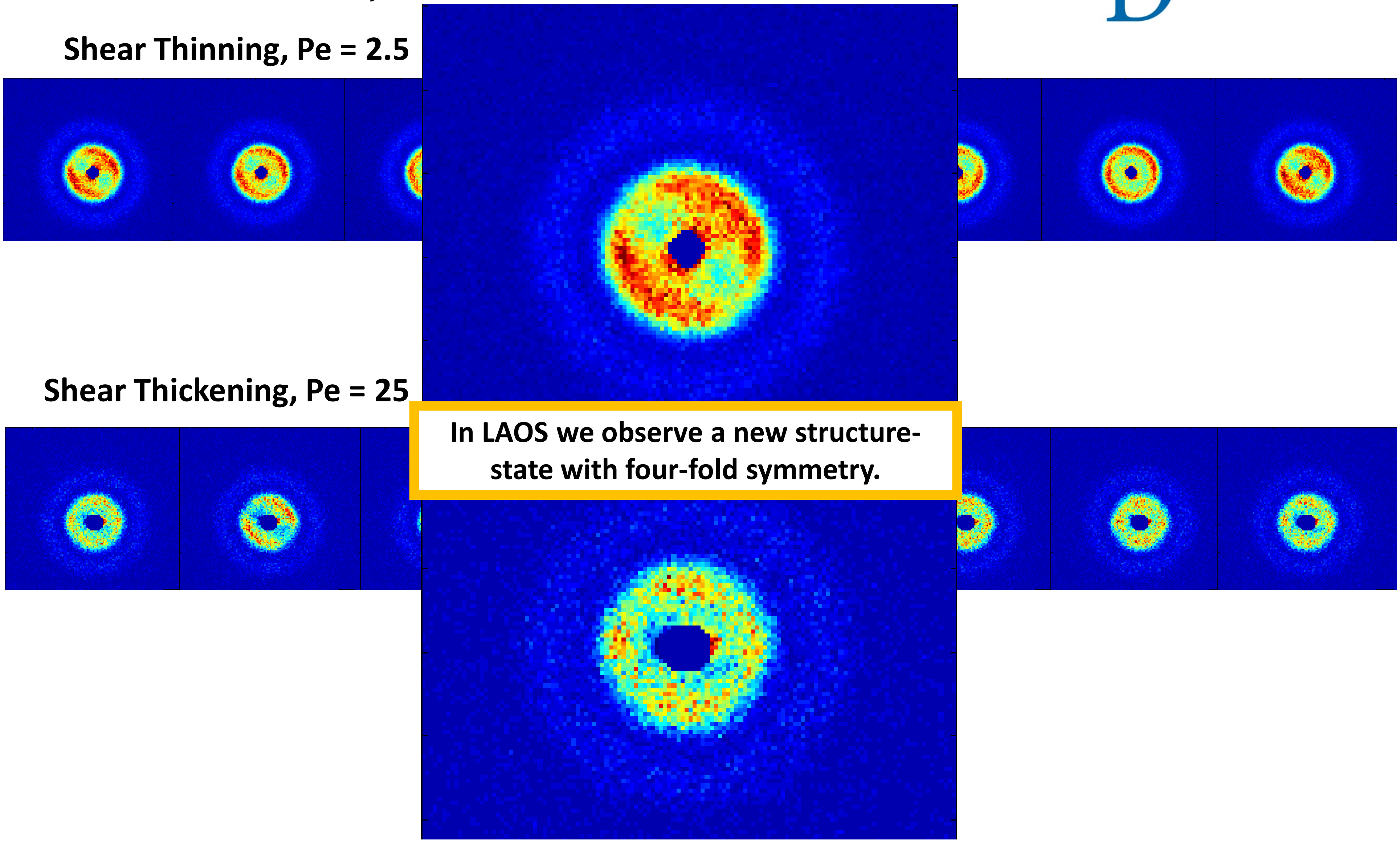


Shear Thickening, Pe = 25





Equivalent complex viscosities, different stress, different structure



E. Nazockdast, J.F. Morris. Journal of Fluid Mechanics **713**, 420-452. (2012).

Conclusions

1. Rheo-SANS and flow-SANS are instrumental measurements in decoupling the hydrodynamic and thermodynamic stress contributions during steady shear and LAOS

2. For the first time, under steady shear the three dimensional microstructure of a hard-sphere suspension has been measured

3. In LAOS, the hydrodynamic and thermodynamic stresses are successfully separated and defined for the dynamic response.

4. Only by utilizing time-resolved SANS is a new four-fold symmetry structure-state observed in the shear thickened state.

Future work

1. Understand how the new four-fold structure-state contributes to the total stress

2. Use the stress-SANS law to reconcile the discrepancy observed for the microstructure observed in the thickened state.

**The new LAOS-SANS experiment and shear cell instrumentation is now available for use at the ILL in Grenoble, France and at NCNR in Gaithersburg, MD.

Relevant rheo-and flow-SANS publications

A. K. Gurnon *et al. Measuring material microstructure under flow using 1-2 plane flow-Small Angle Neutron Scattering.* Journal of Visual Experiments (accepted, 2013).

Eberle, A. P. R. et al. Shear-induced anisotropy in nanoparticle gels with short-ranged interactions. Physical Review Letters submitted (2013).

Zemb, T. & Linder, P. Neutron, X-rays and Light. Scattering Methods Applied to Soft Condensed Matter. 552 (Elsevier Science, 2002).

Eberle, A. P. R. & Porcar, L. Flow-SANS and Rheo-SANS applied to soft matter. Current Opinion in Colloid & Interface Science 17, 33-43, doi:10.1016/j.cocis.2011.12.001 (2012).

Liberatore, M. W., Nettesheim, F., Wagner, N. J. & Porcar, L. Spatially resolved small-angle neutron scattering in the 1-2 plane: A study of shear-induced phase-separating wormlike micelles. Physical Review E 73, doi:10.1103/PhysRevE.73.020504 (2006).

Porcar, L., Pozzo, D., Langenbucher, G., Moyer, J. & Butler, P. D. Rheo-small-angle neutron scattering at the National Institute of Standards and Technology Center for Neutron Research. Review of Scientific Instruments 82, doi:10.1063/1.3609863 (2011).

Lopez-Barron, C. R., Porcar, L., Eberle, A. P. R. & Wagner, N. J. Dynamics of Melting and Recrystallization in a Polymeric Micellar Crystal Subjected to Large Amplitude Oscillatory Shear Flow. Physical Review Letters 108, 258301, doi:10.1103/PhysRevLett.108.258301 (2012).

Rogers, S., Kohlbrecher, J. & Lettinga, M. P. The molecular origin of stress generation in worm-like micelles, using a rheo-SANS LAOS approach. Soft Matter 8, 3831-3839, doi:10.1039/c2sm25569c (2012).

Relevant rheo-and flow-SANS publications continued…

Helgeson, M. E., Porcar, L., Lopez-Barron, C. & Wagner, N. J. Direct Observation of Flow-Concentration Coupling in a Shear-Banding Fluid. Physical Review Letters 105, doi:10.1103/PhysRevLett.105.084501 (2010).

Helgeson, M. E., Reichert, M. D., Hu, Y. T. & Wagner, N. J. Relating shear banding, structure, and phase behavior in wormlike micellar solutions. Soft Matter 5, 3858-3869, doi:10.1039/b900948e (2009).

Helgeson, M. E., Vasquez, P. A., Kaler, E. W. & Wagner, N. J. Rheology and spatially resolved structure of cetyltrimethylammonium bromide wormlike micelles through the shear banding transition. Journal of Rheology 53, 727-756, doi:10.1122/1.3089579 (2009).

Liberatore, M. W. et al. Microstructure and shear rheology of entangled wormlike micelles in solution. Journal of Rheology 53, 441-458, doi:10.1122/1.3072077 (2009).

Maranzano, B. J. & Wagner, N. J. Flow-small angle neutron scattering measurements of colloidal dispersion microstructure evolution through the shear thickening transition. Journal of Chemical Physics 117, 10291-10302, doi:10.1063/1.1519253 (2002).

Wagner, N. J. & Ackerson, B. J. Analysis of nonequilibrium structures of shearing colloidal suspensions. Journal of Chemical Physics 97, 1473-1483, doi:10.1063/1.463224 (1992).

Lopez-Barron, C., Gurnon, A. K., Porcar, L. & Wagner, N. J. Structural Evolution of a Model, Shear-Banding Wormlike Micellar Soution during Shear Start Up and Cessation Physical Review Letters submitted (2013).