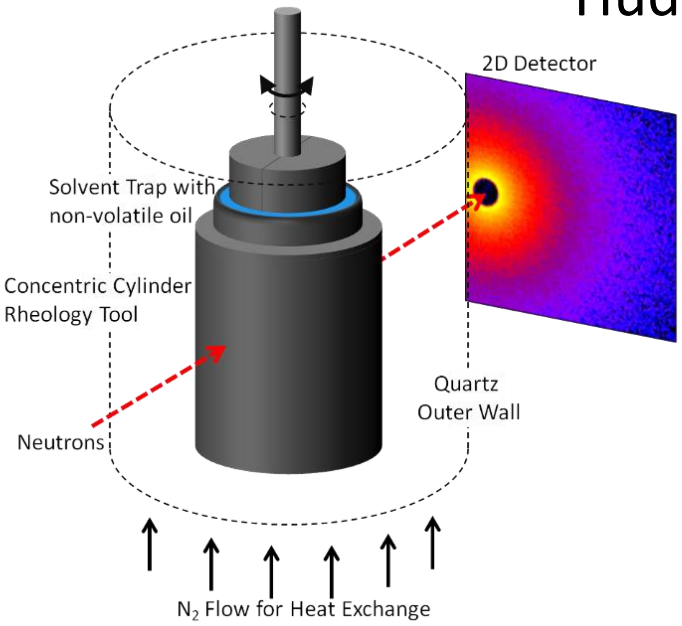
Suspension rheoSANS

RheoSANS @ NIST



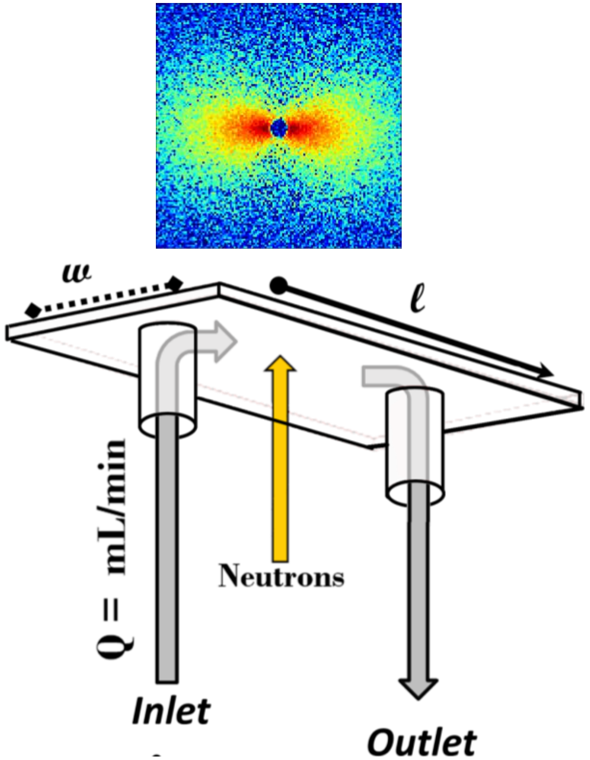
Hudson, Weigandt, Weston, Salipante, Seeman, Blair

Georgetown U., Physics

NIST Polymers and Complex Fluids Group

NIST Center for Neutron Research (NCNR)

μRheoSANS @ NIST



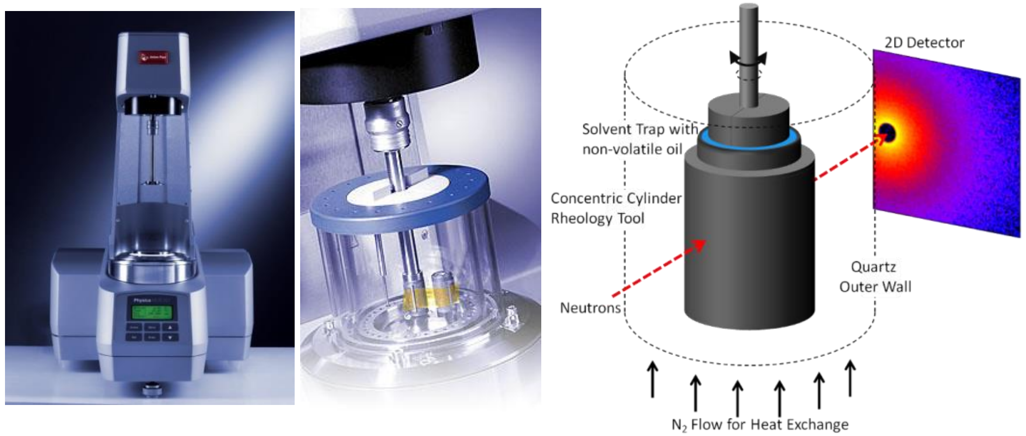
Outline

- rheoSANS
  - Dense vesicular emulsions
  - High shear rate
  - Rheologica Acta, in press, “Simultaneous slit rheometry and in situ neutron scattering”

Rheology

- Structure property relationships of fluids and viscoelastic solids.

RheoSANS

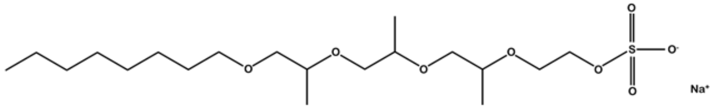


L. Porcar (NIST), J. Moyer (NIST), P. D. Butler (NIST), L. D. Pozzo (NIST, UW)
G. Langenbucher (Anton Paar)

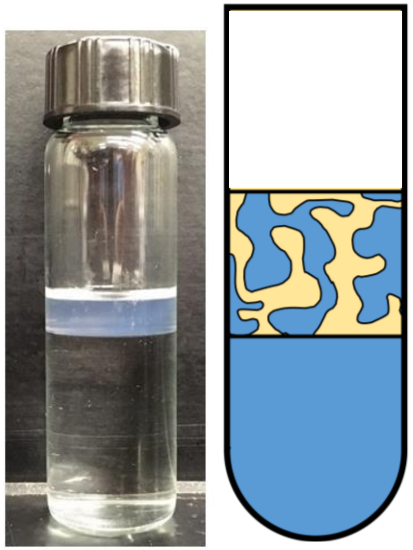
RheoSANS Capabilities

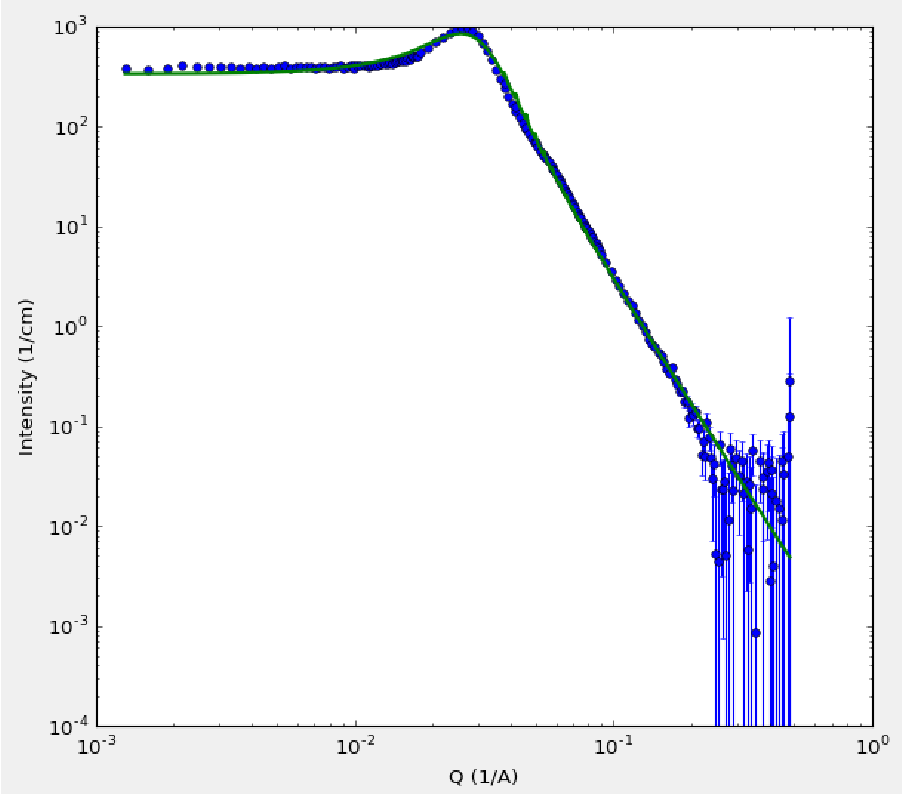
Temperature	**-50°C to 200°C**
Pressure	**Atmospheric**
High Shear Rate + Low Shear Stress	
Shear Rate	**12,000 s^{-1}**
Shear Stress	**900 Pa**
Low Shear Rate + High Shear Stress	
Shear Rate	**3,500 s^{-1}**
Shear Stress	**4,500 Pa**

Shear thickening emulsions



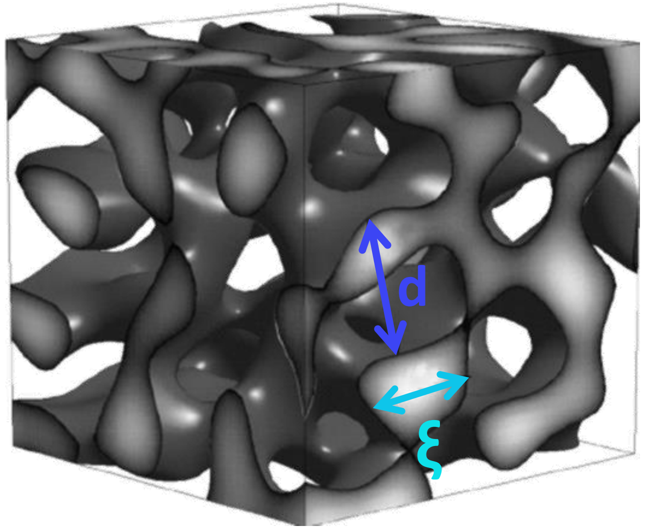
ALFOTERRA 8-41 S





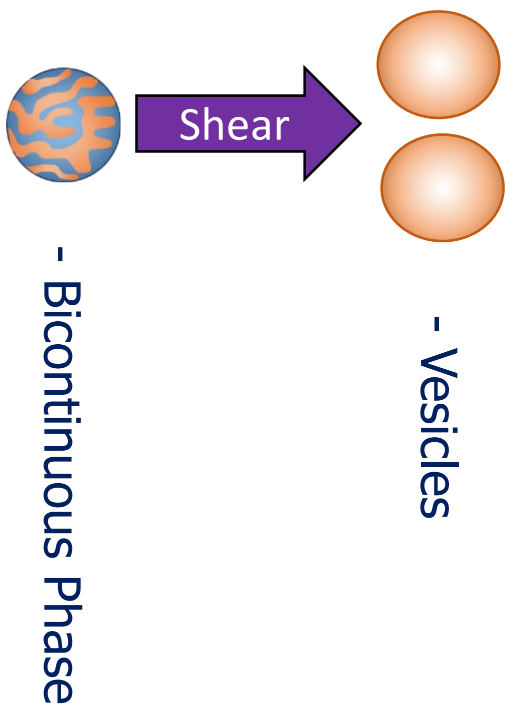
Teubner Strey model uses three parameters along with SLDs of both phases to describe scattering

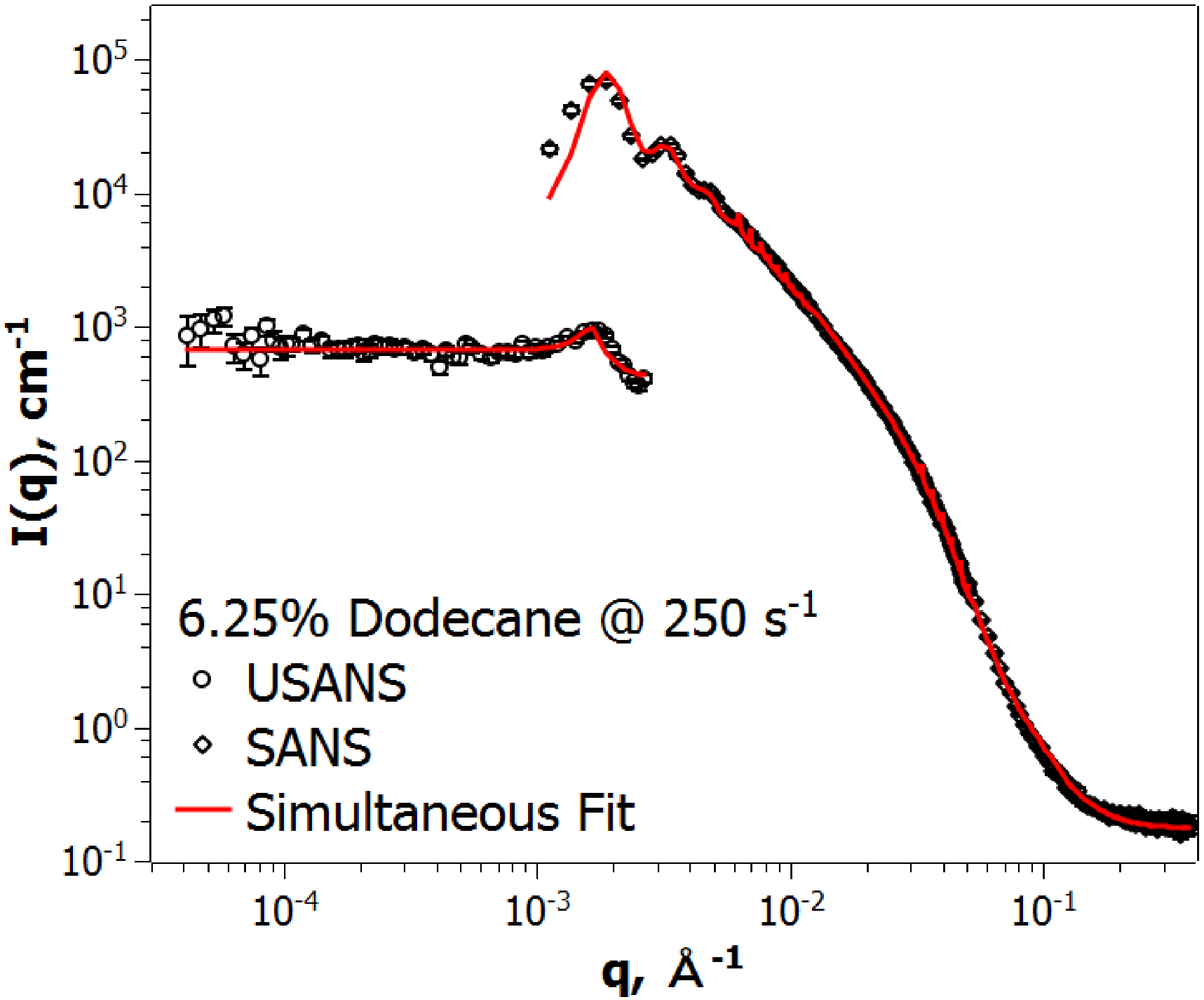
- **Aqueous Volume Fraction –** 0.49
- **Periodicity, d –** 22.6 nm
  - Describes size of oil/water domains
- **Correlation Length, ξ –** 10.5 nm
  - Describes decay of periodic order

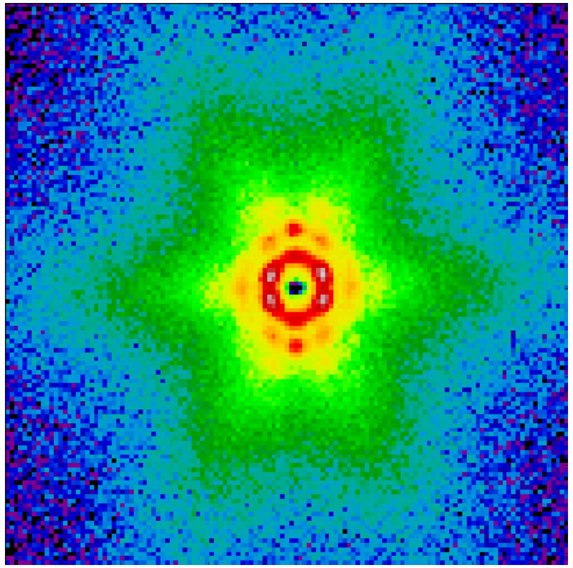


N. F. Berk, Phys. Rev. Lett. 25, 2718 (1987)

Shearing makes vesicles







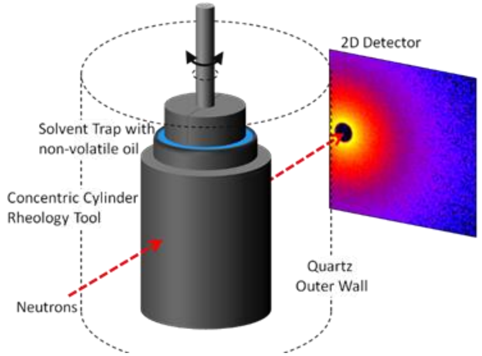
Vesicle Radius – 206 nm

Wall Thickness – 7.4 nm

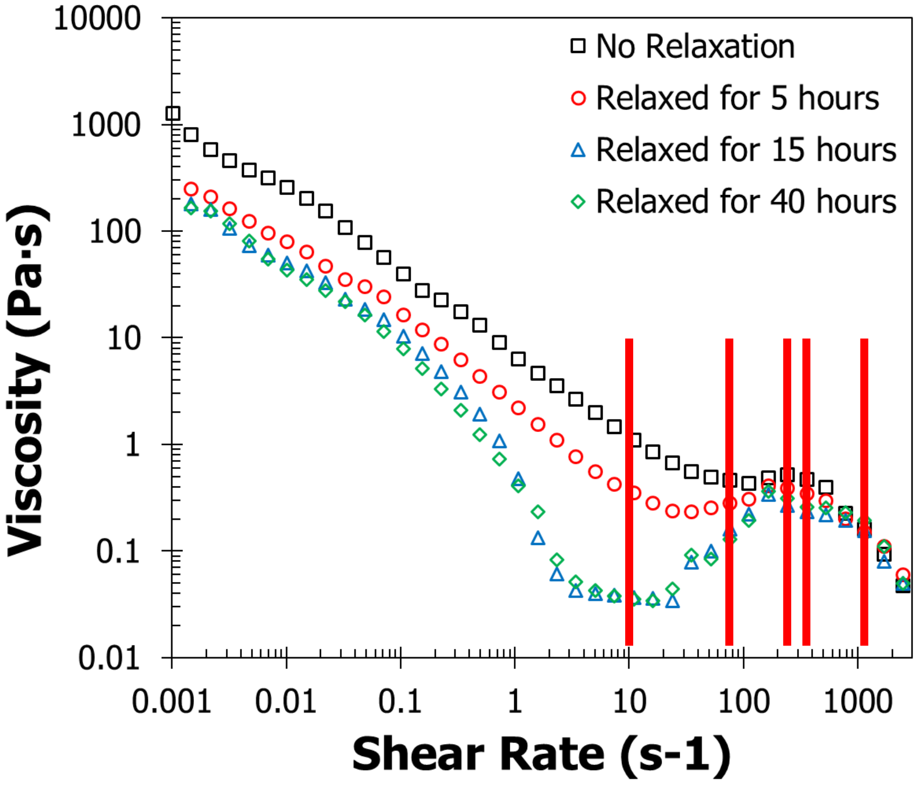
Vol Fraction – 0.52

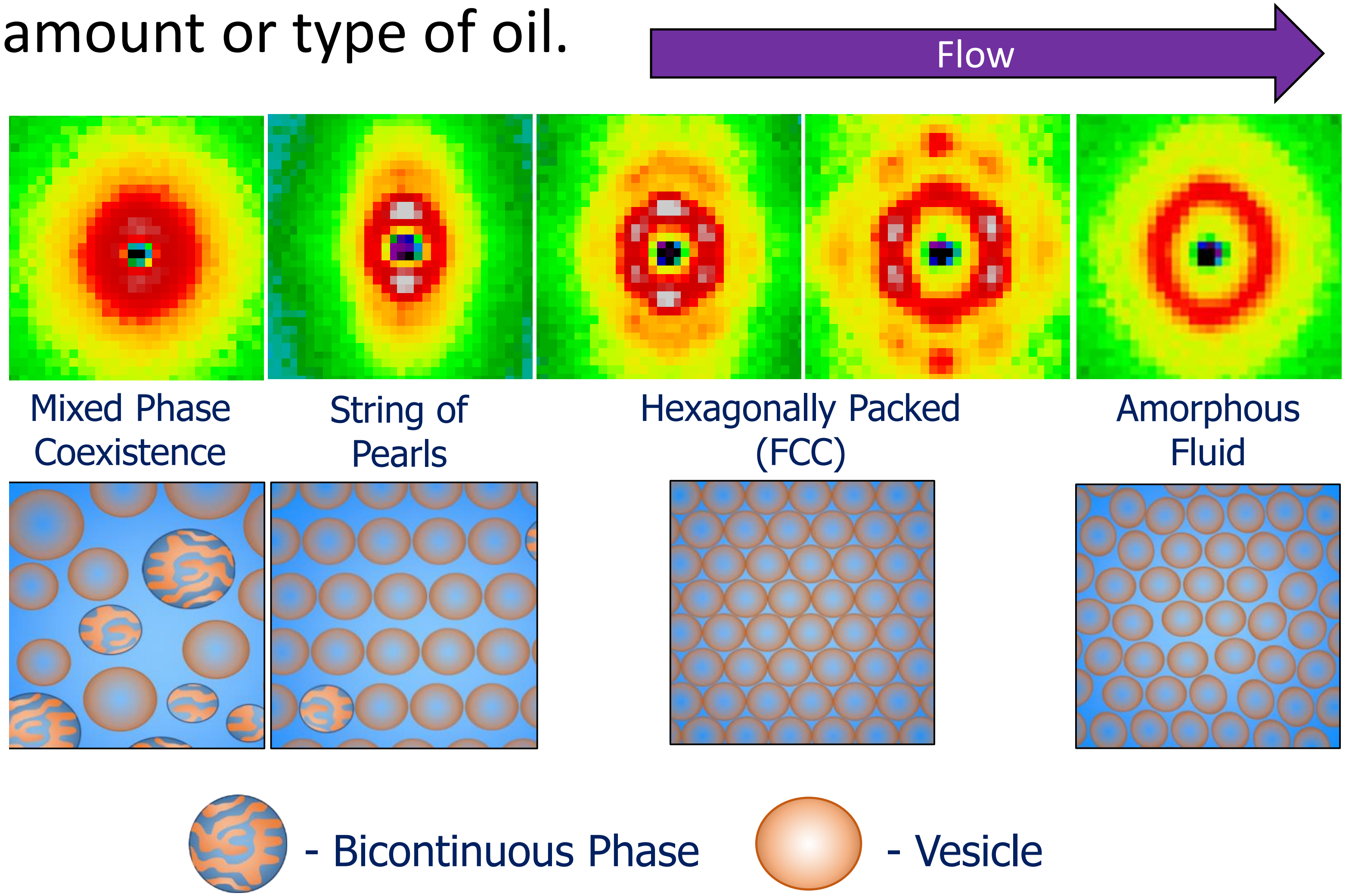
Fit using a vesicle form factor model with a hard sphere structure factor

Shear thickening emulsions



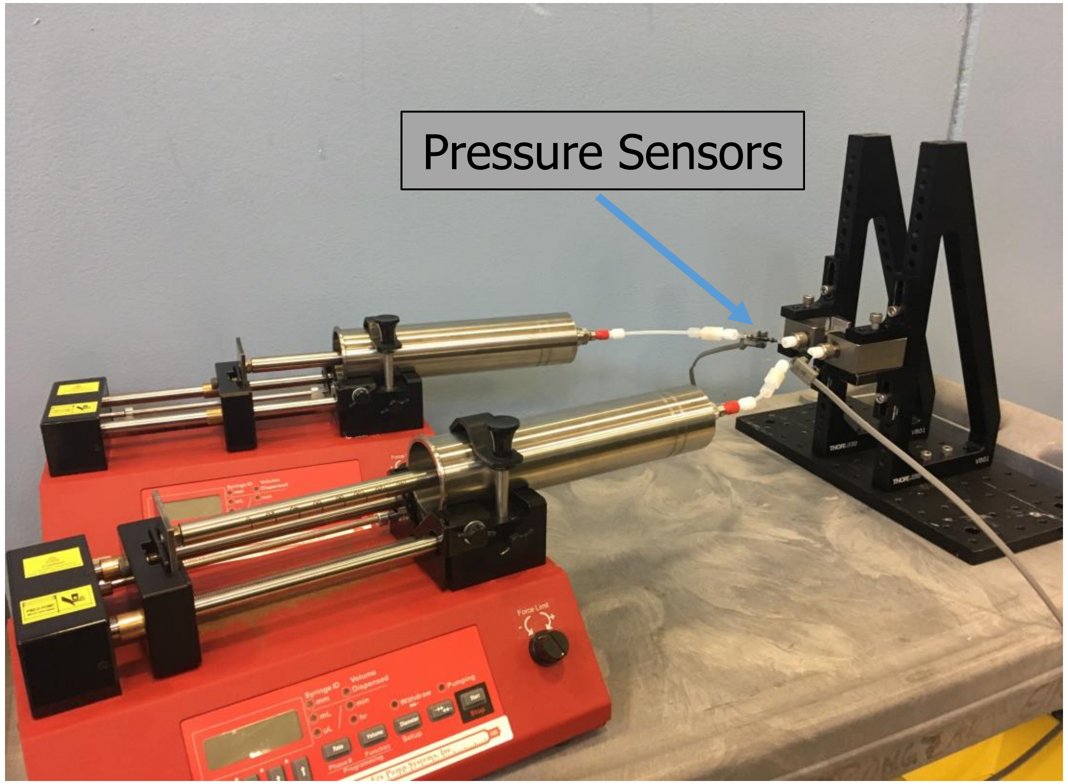
- Vesicle size reduces with shear rate.
- Size in thickened state is set by amount of surfactant, not amount or type of oil.



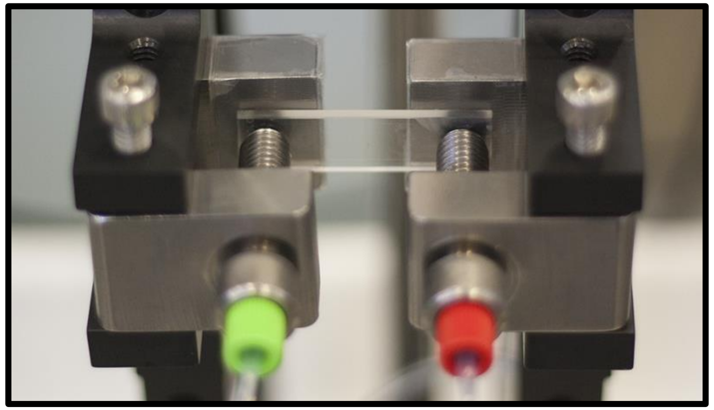


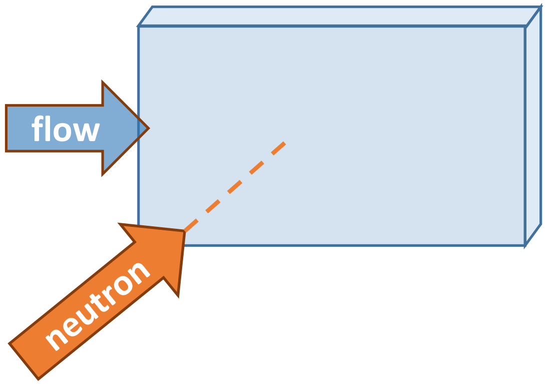
µRheoSANS

- Higher shear rate



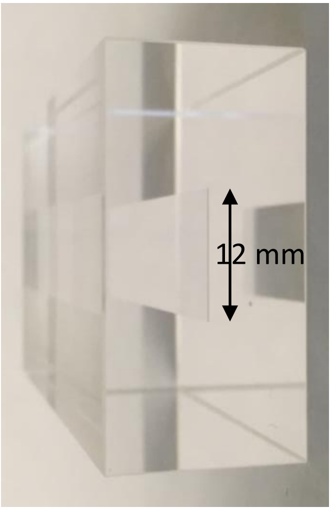
Microfluidic Cell

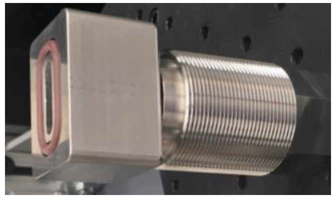




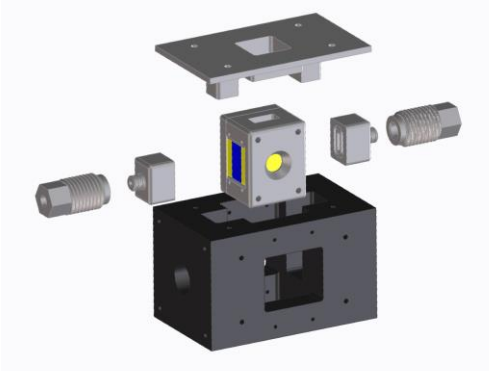
µRheoSANS, high pressure upgrade

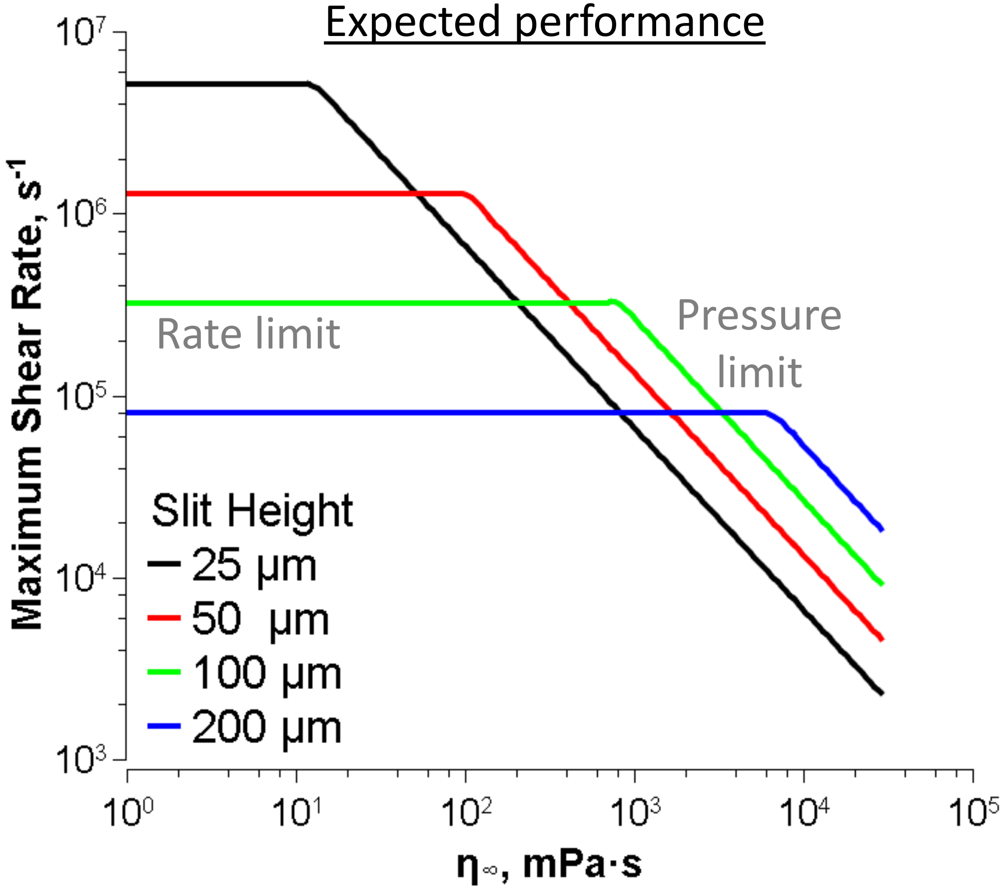
Quartz cell





fittings



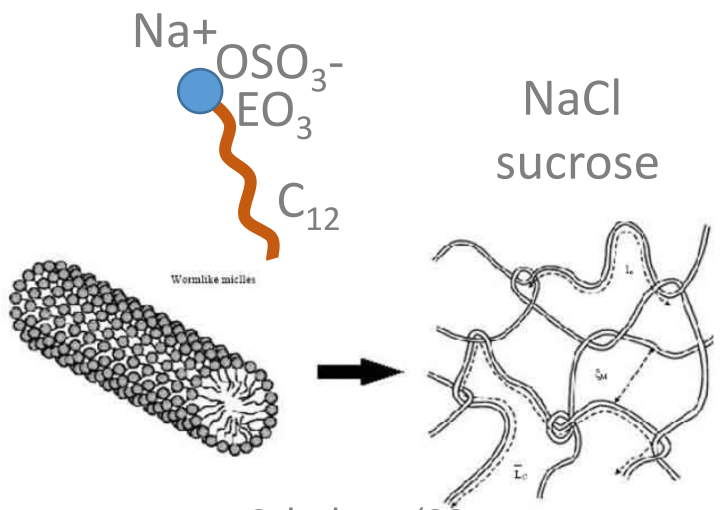


Not yet tested.

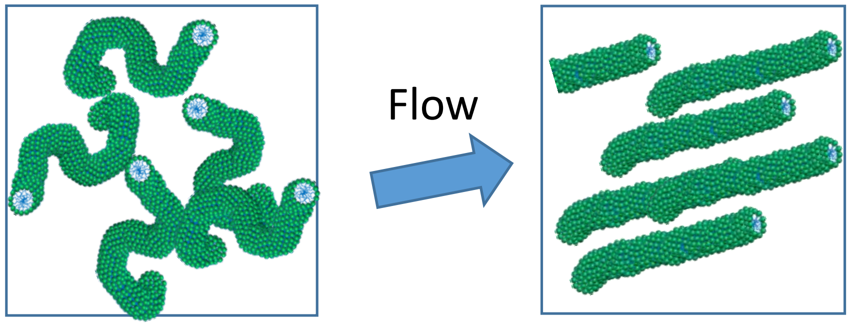
Up to 350 bar, suited for dense suspensions.

How do wormlike micelles respond to shear?

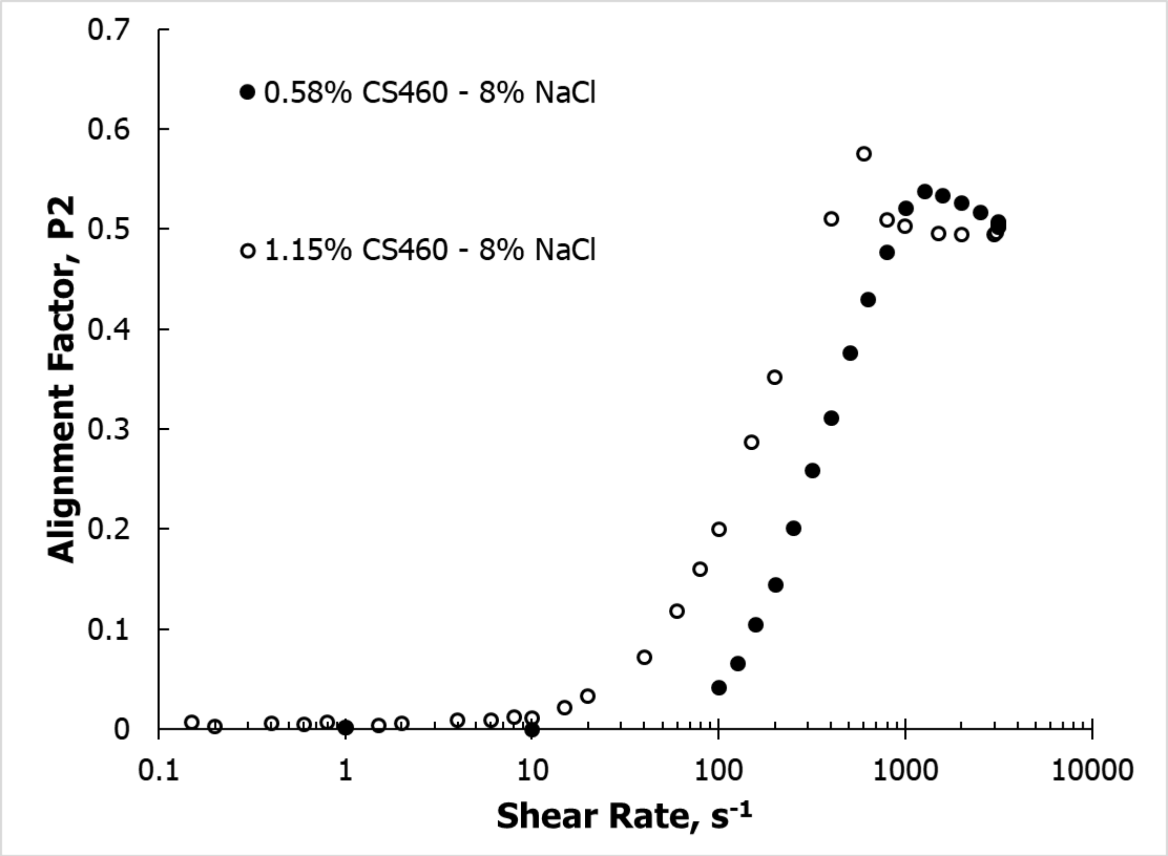
Sodium Laureth Sulfate (Steol CS460) in D_2O bodywash



Schubert '03



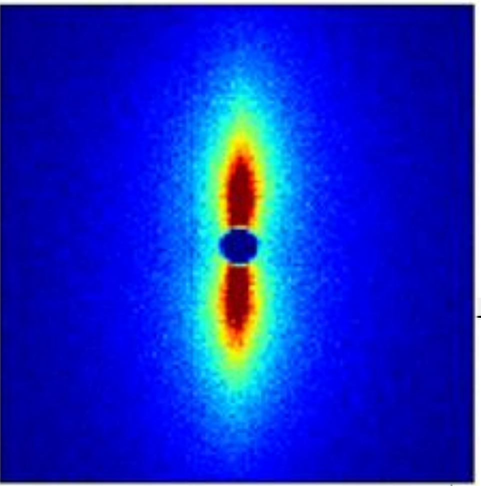
Alignment is the lowest order response, Wi > 1.

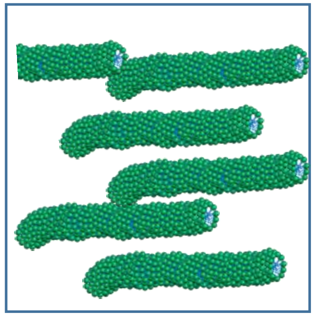


Why does apparent alignment decrease at high shear rate?

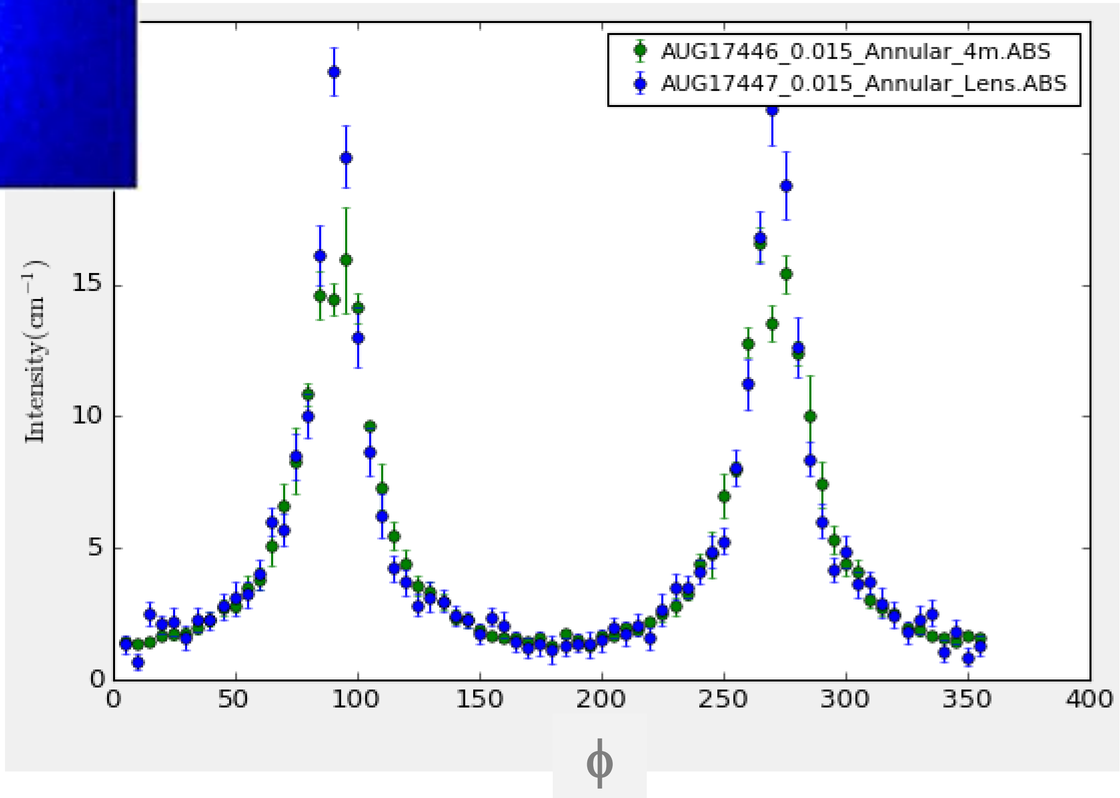
Alignment, P2

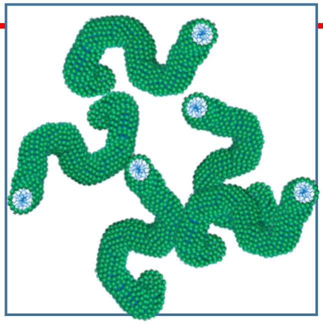
2nd order Legendre fit

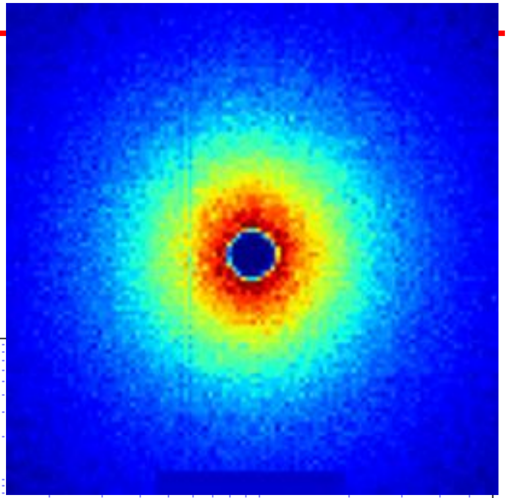


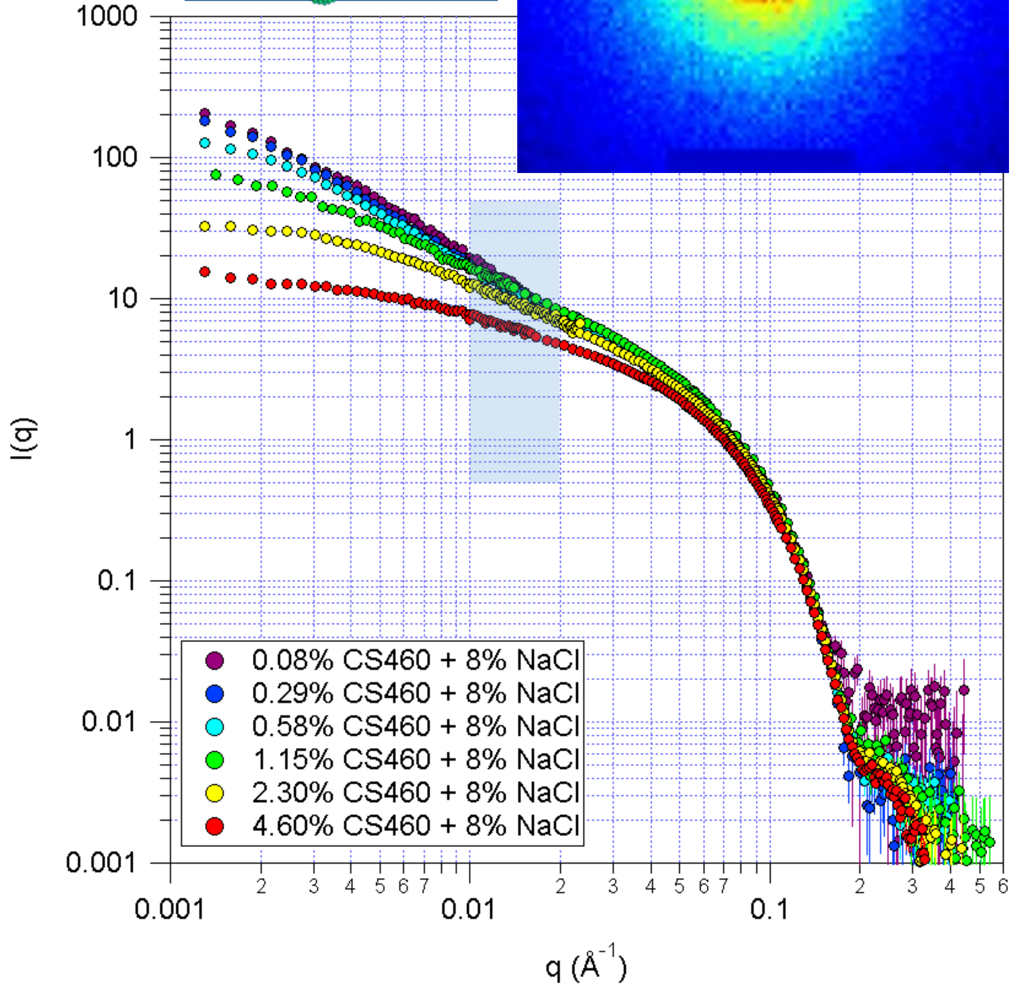


Flow



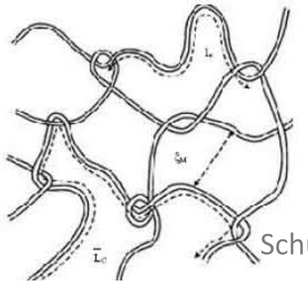




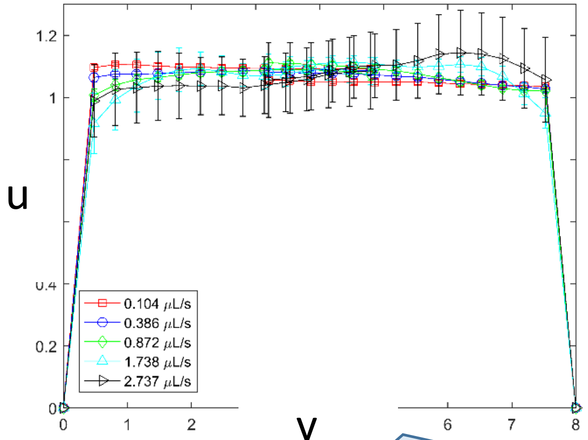


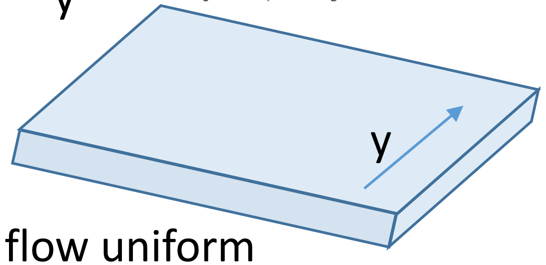
Steady shear rheology of anionic wormlike micelles

1.15% Steol CS460/8% NaCl in D_2O
Sodium Laureth Sulfate

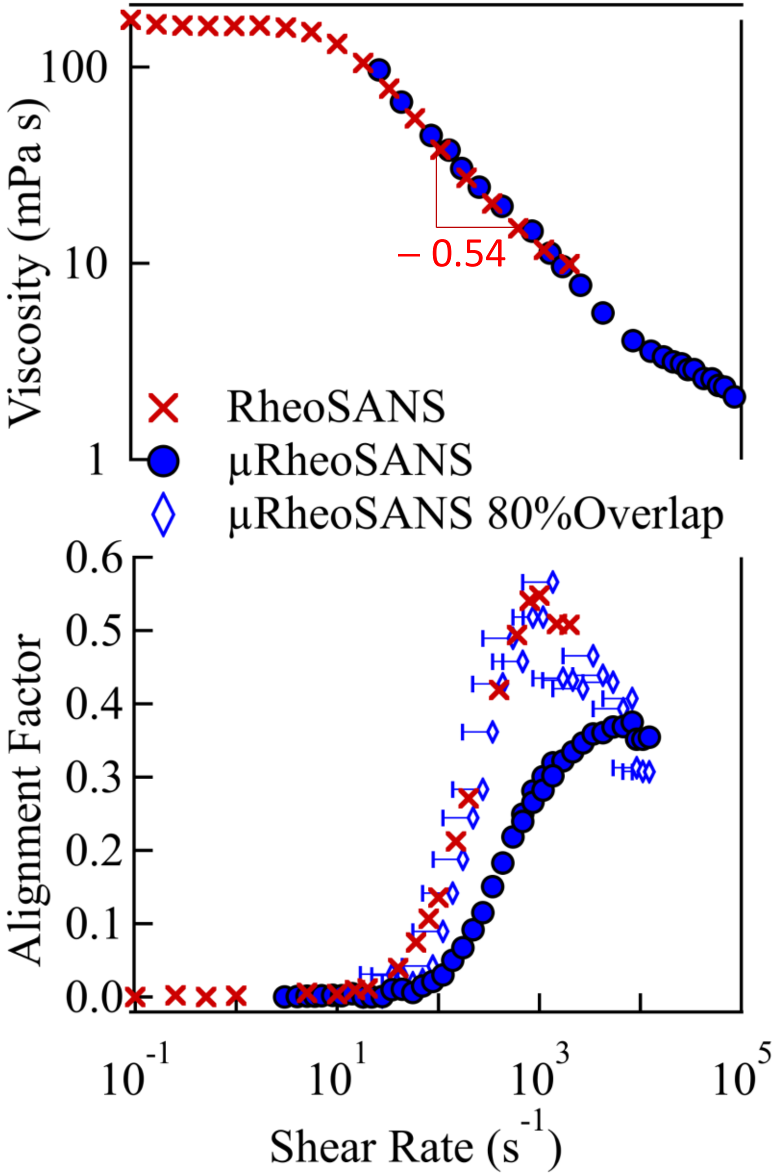


Schubert '03

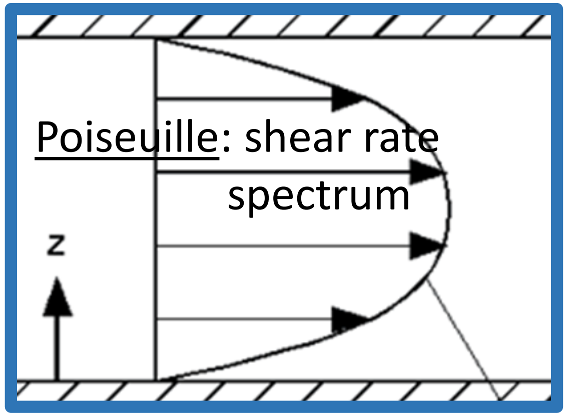


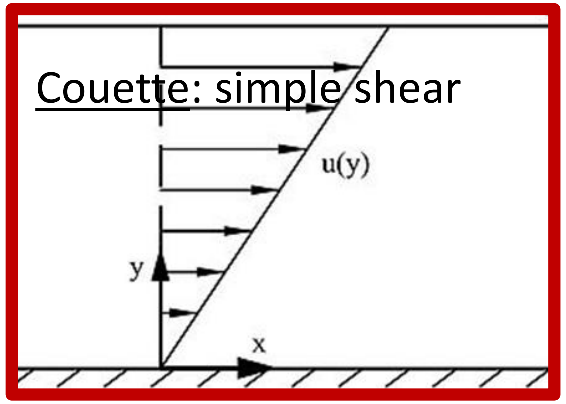


PIV: flow uniform across channel width

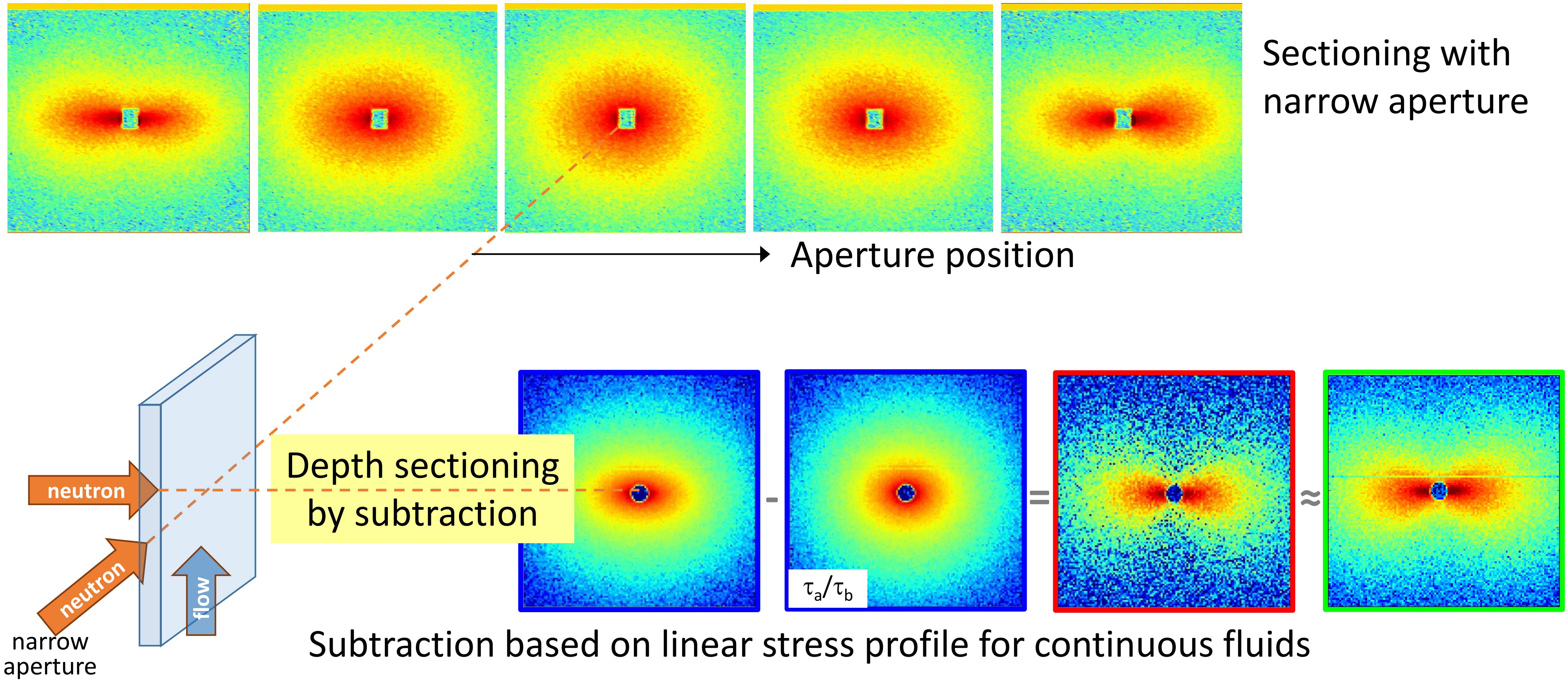


$$\dot{\gamma}_w = \frac{2Q}{w_{eff} h^2}\left[2 + \frac{d\ln(Q)}{d\ln(p)}\right]$$



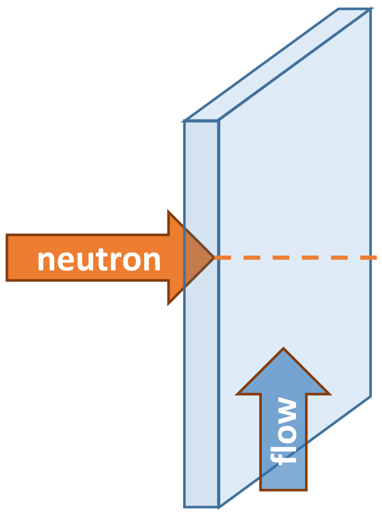


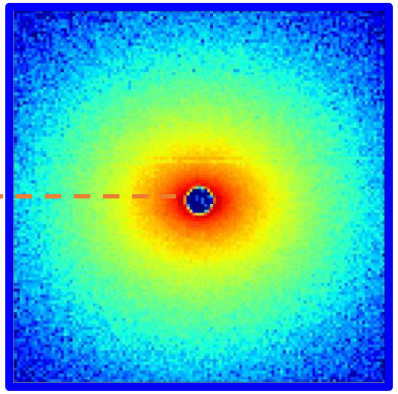
Poiseuille flow: How to section?



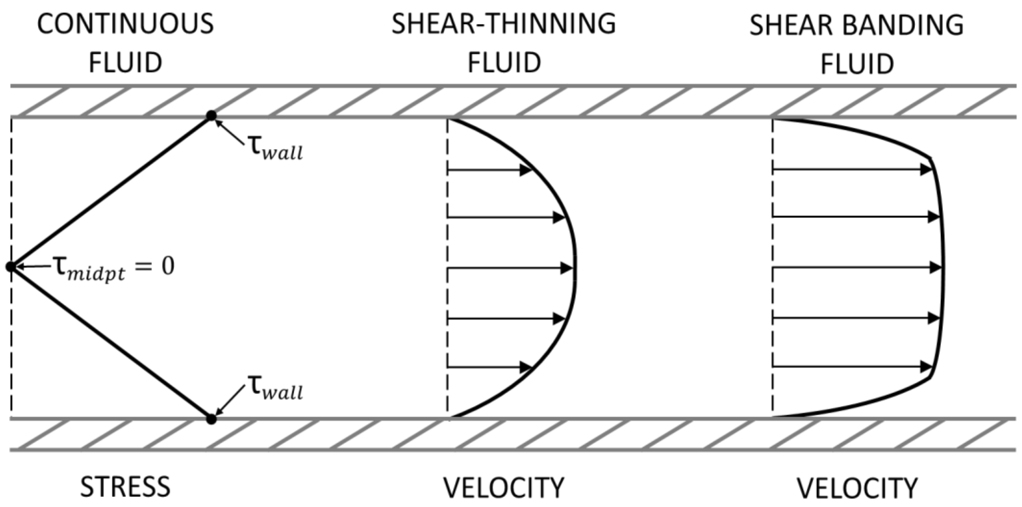
Depth sectioning method

- How to isolate a certain stress, when a whole spectrum is present?
  - demonstrated by Fernandez-Ballester et al., JoR ’09 (WAXS).
  - Linear stress profile from channel wall to center (continuum)
    - Scattering produced from a superposition of these stress states.
  - When the pressure is increased from one state to another, the difference comes only from the highest stress near the channel walls.





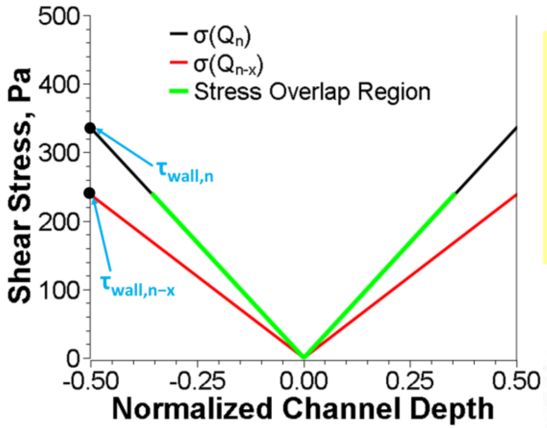
The fluid may be shear thickening or thinning.



Subtraction based on linear stress profile for continuous fluids

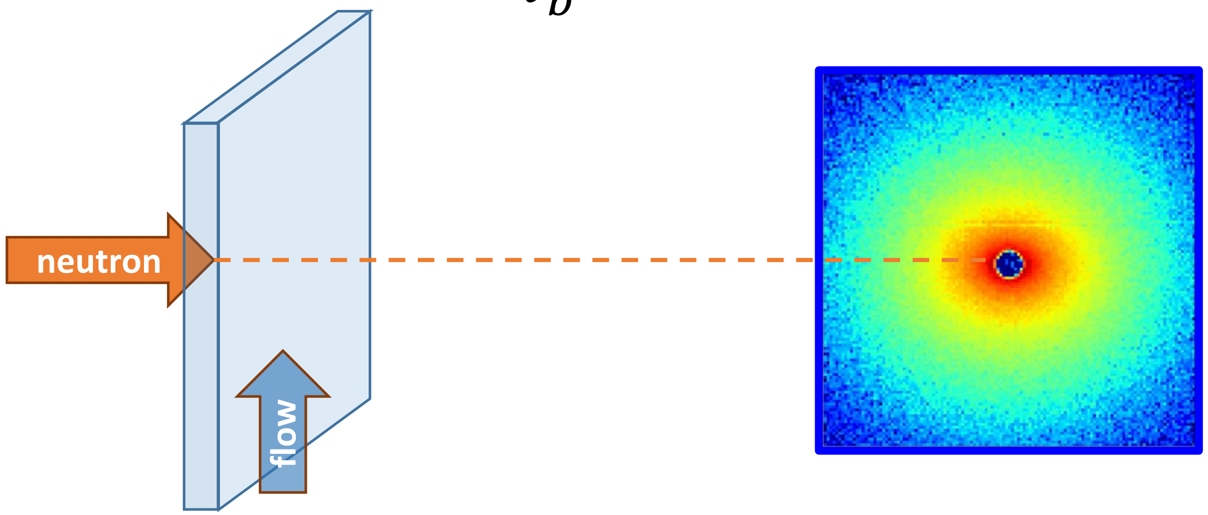
High shear SANS in rectangular channels

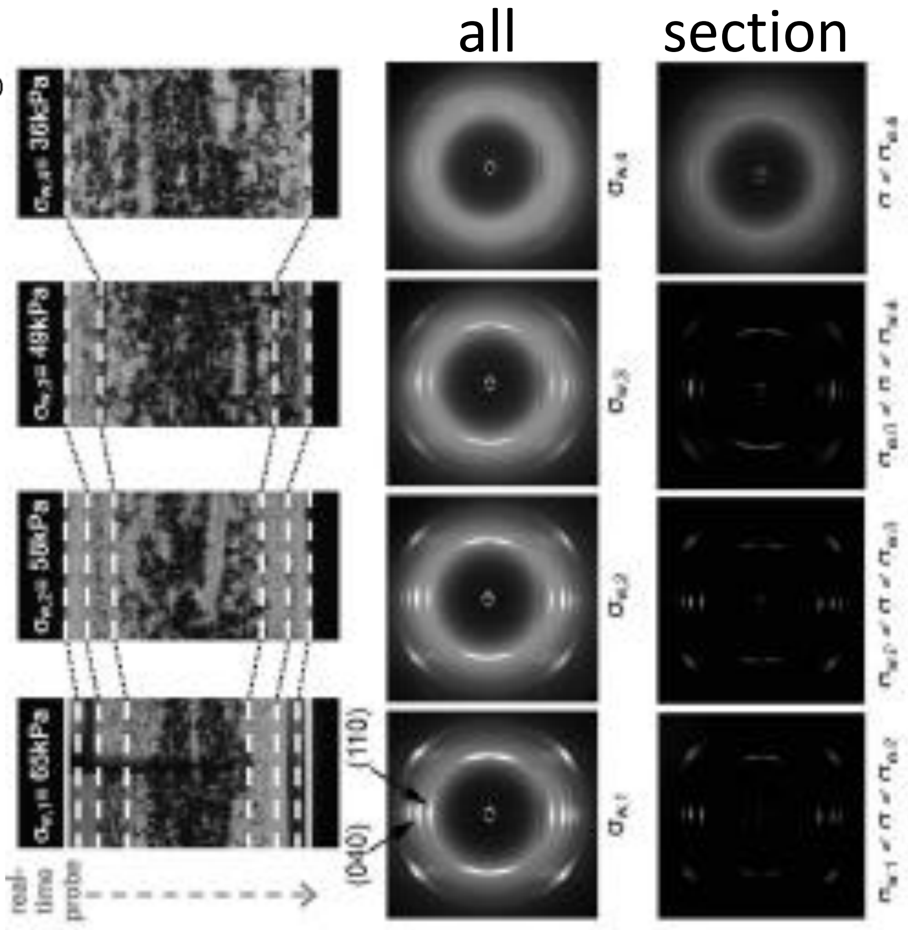
- Depth sectioning method demonstrated by Fernandez-Ballester et al., JoR '09 (WAXS).
  - Isolate high stress region



Subtraction based on linear stress profile for continuous fluids

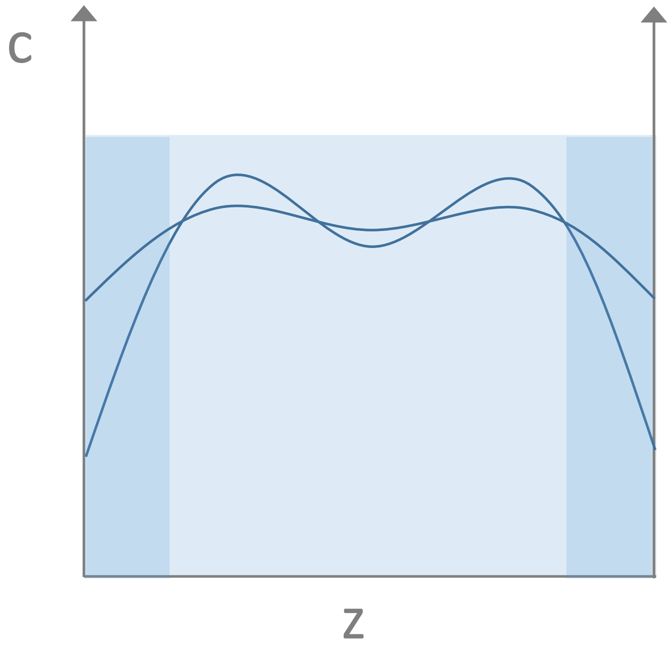
$$I_{q_x,q_y}(wall) = \frac{1}{1-\frac{\tau_a}{\tau_b}}\left[I_{q_x,q_y}(\tau_b) - \frac{\tau_a}{\tau_b} I_{q_x,q_y}(\tau_a)\right]$$





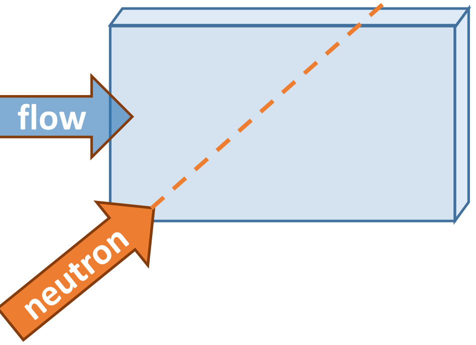
When will this analysis fail?

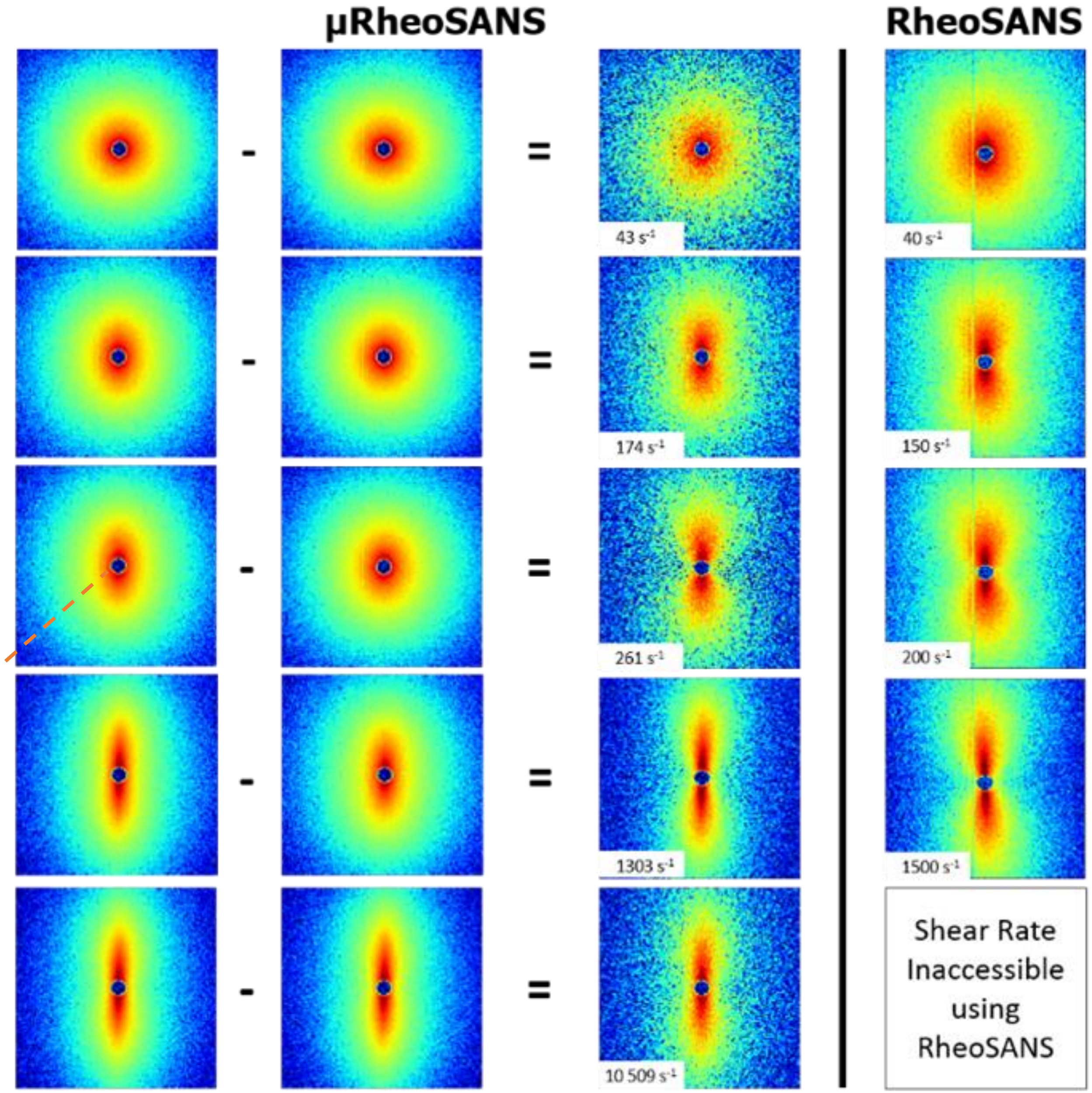
- Whenever the scattering depends on position, **independent of stress**.
  - E.g., concentration gradients. Subtraction is then **NOT** depth sectioning

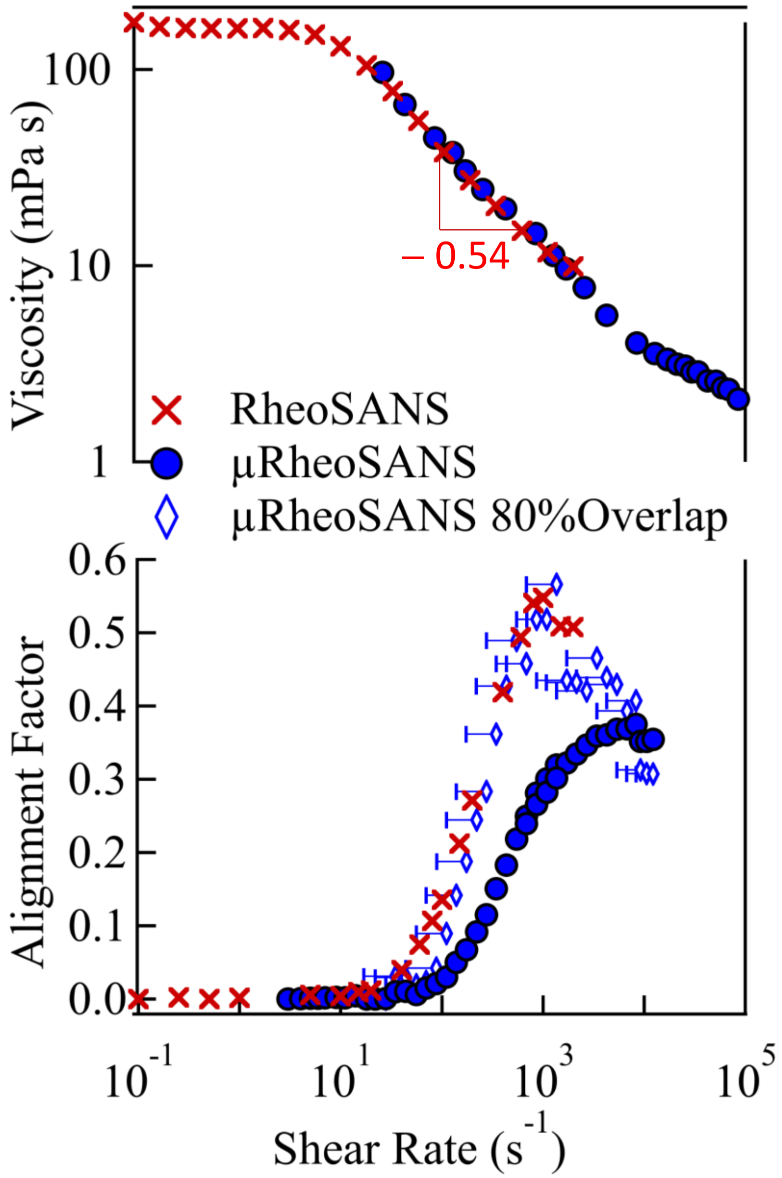


High shear SANS in rectangular channels

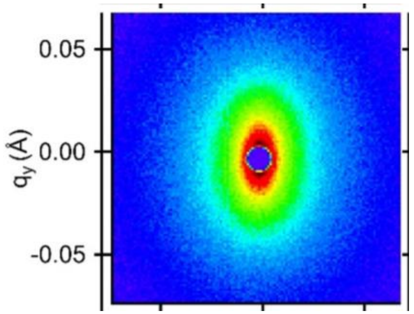
Quantitative comparison in visual form.
(All scattering is background subtracted.)



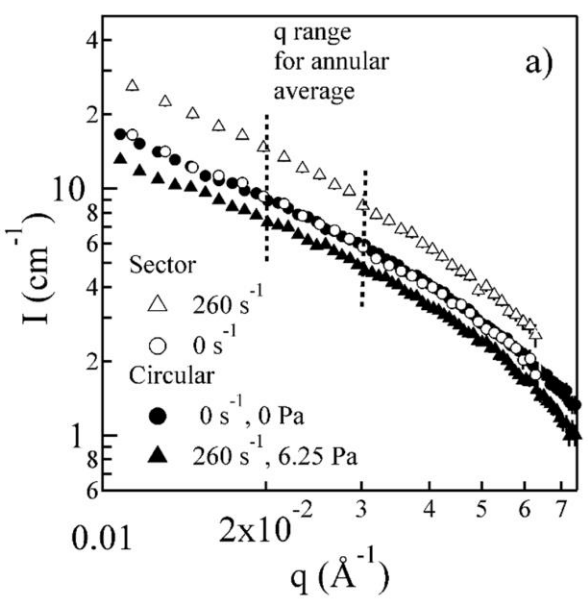




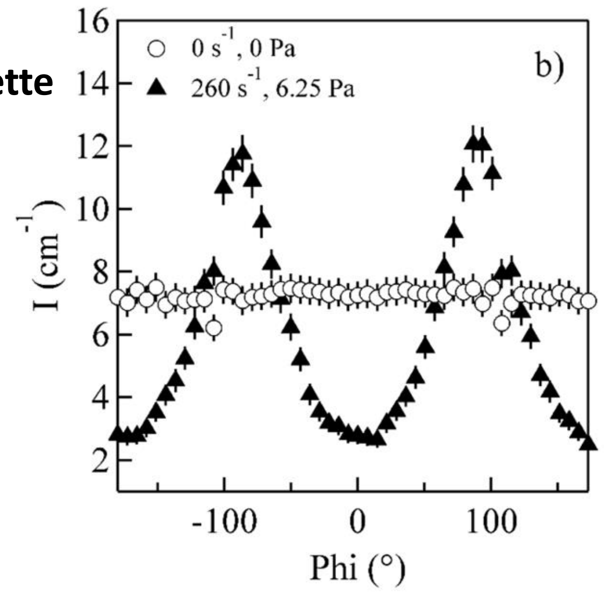
Quantitative comparison in graphical form



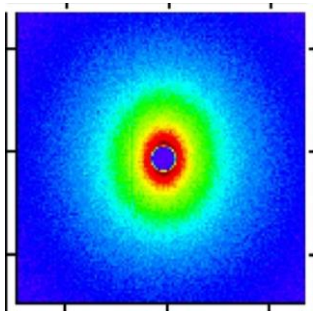
high

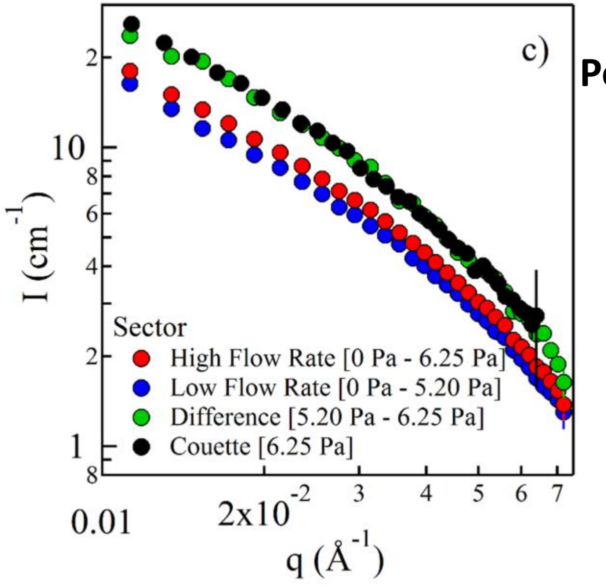


Couette

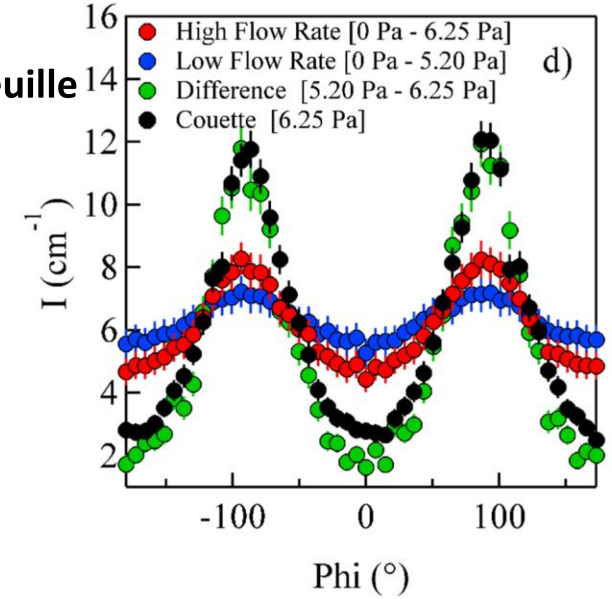


low



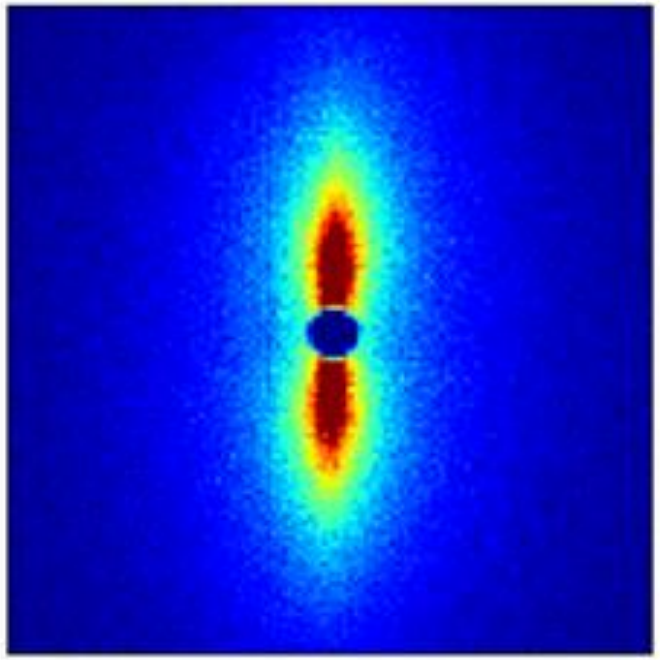


Poiseuille

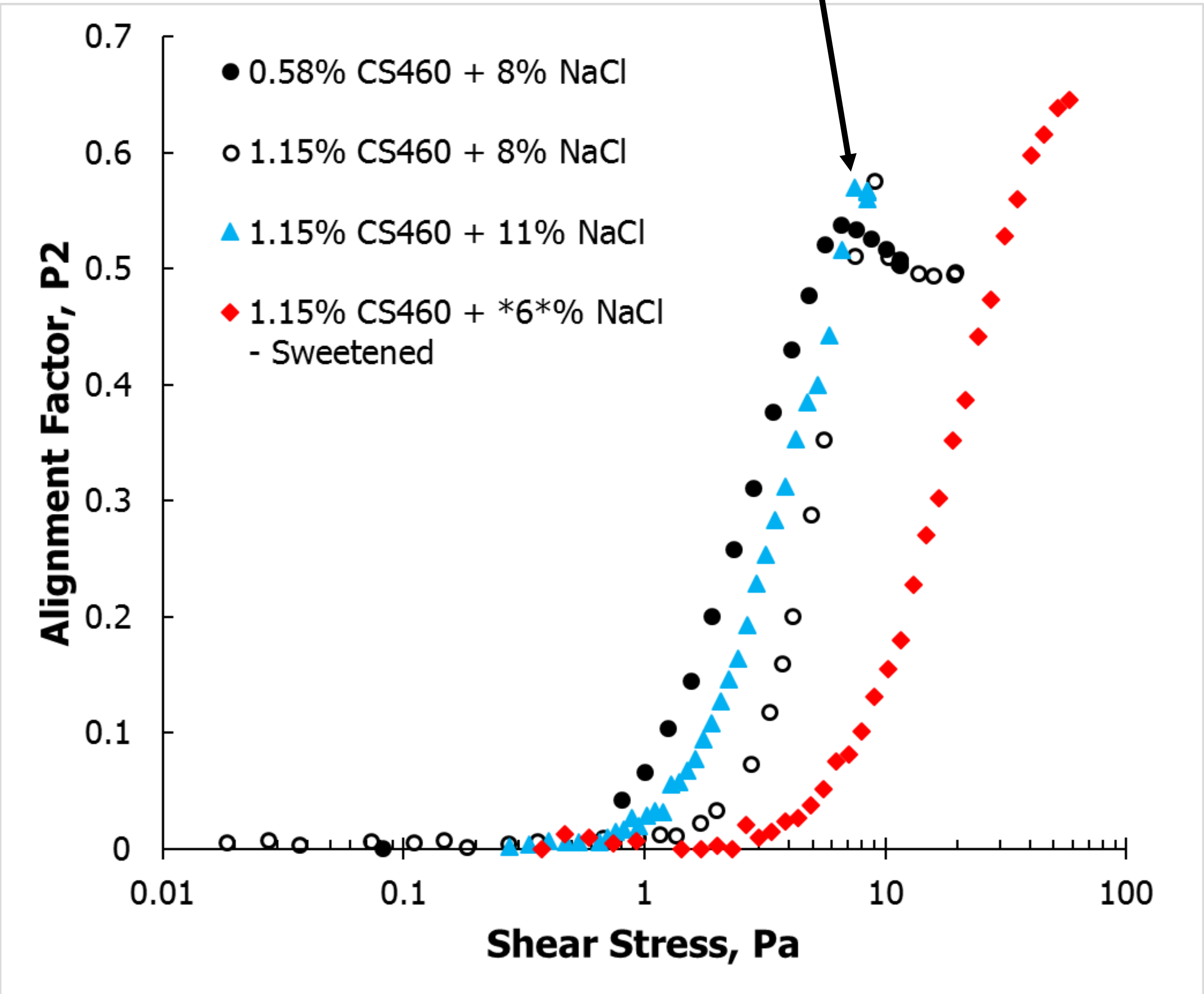


Alignment behavior of various micelles

- The effects of T, salt, conc. and solvent viscosity.
  - Equilibrium properties (by DWS and simulation).
  - Alignment in flow.

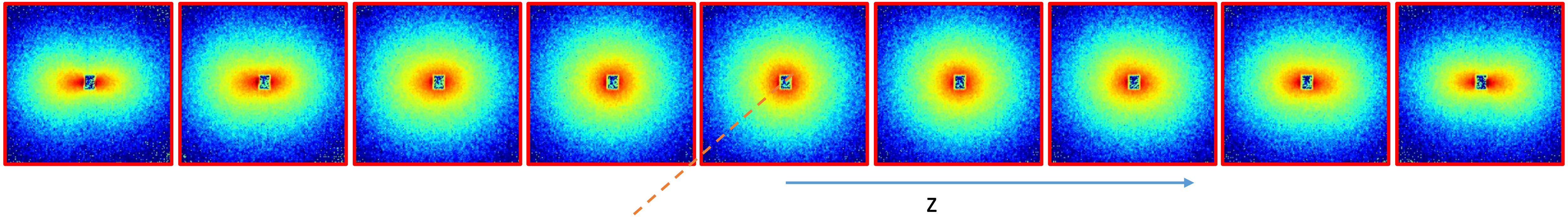


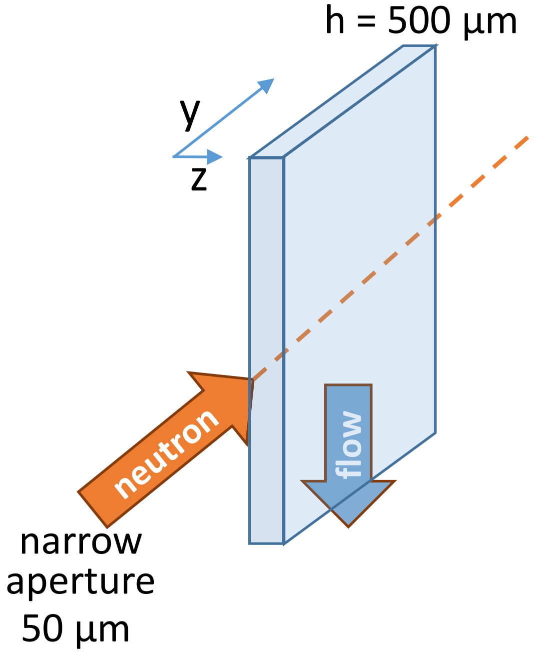
Is the peak in alignment associated with stress-induced micelle breakup?

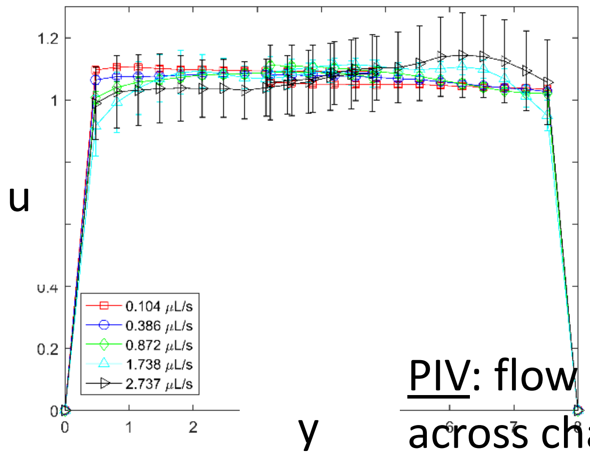


1,2 scattering: section with narrow aperture

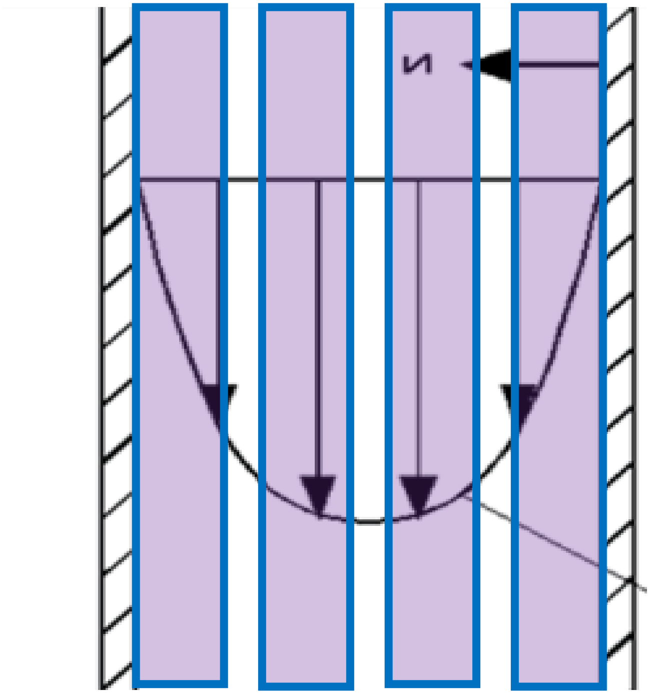
- Alignment tracks local shear rate





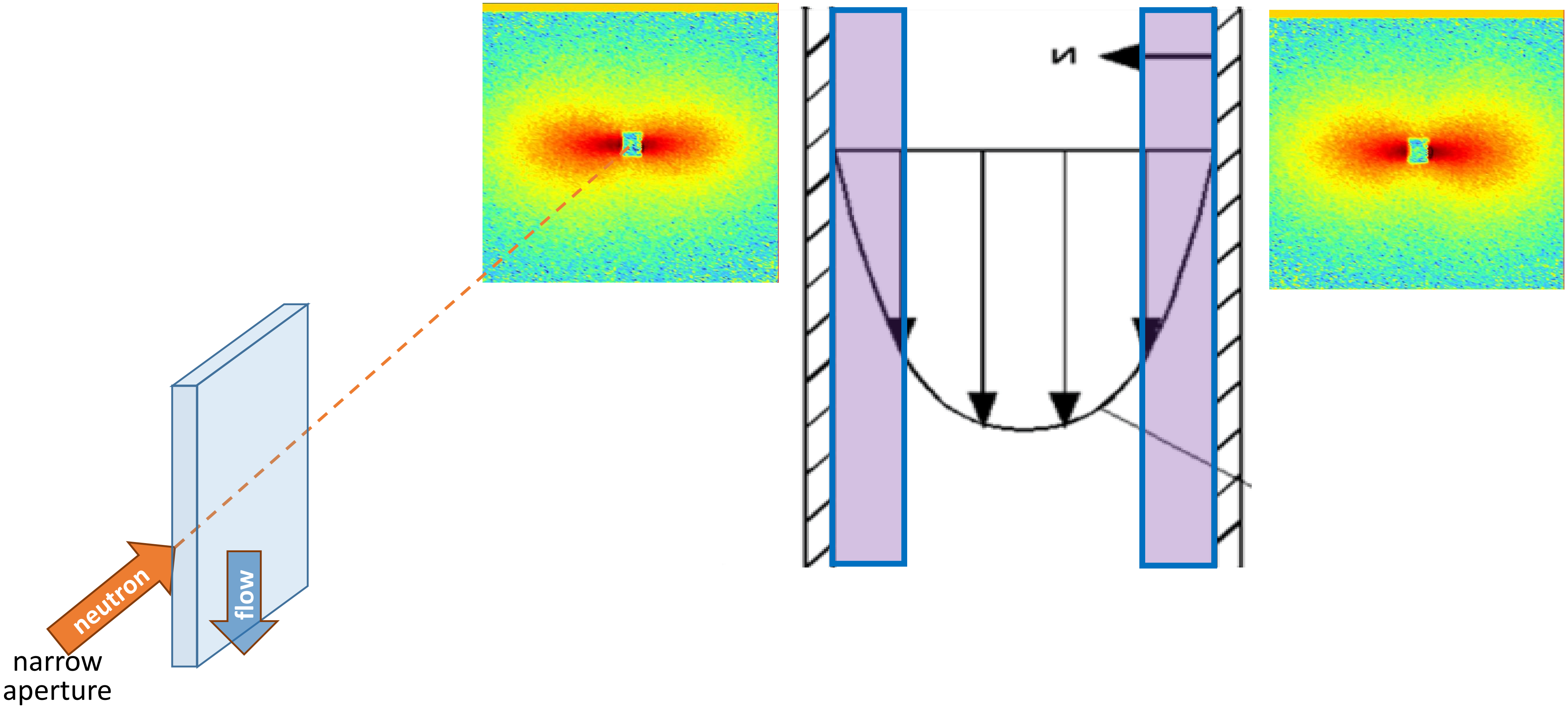


PIV: flow uniform across channel width



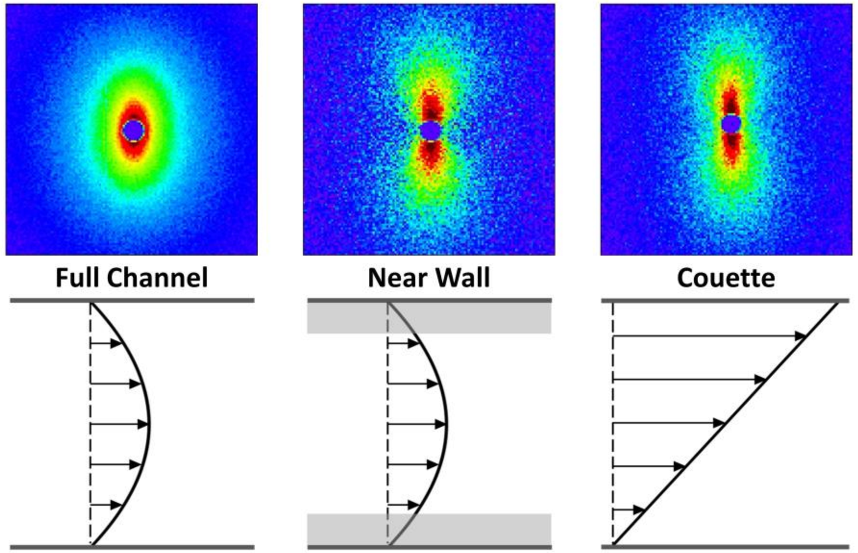
1,2 scattering

- Slight inclination of worms towards velocity gradient.



Summary

- RheoSANS of shear thickening emulsions.
- New μRheoSANS for very high shear rate.
- Results from SLES wormlike micelles match well with measurements with traditional RheoSANS.
  - What is the rheology at highest shear rates?
  - Test other fluids, i.e. suspensions.
- Please contact steven.hudson@nist.gov, kathleen.weigandt@nist.gov



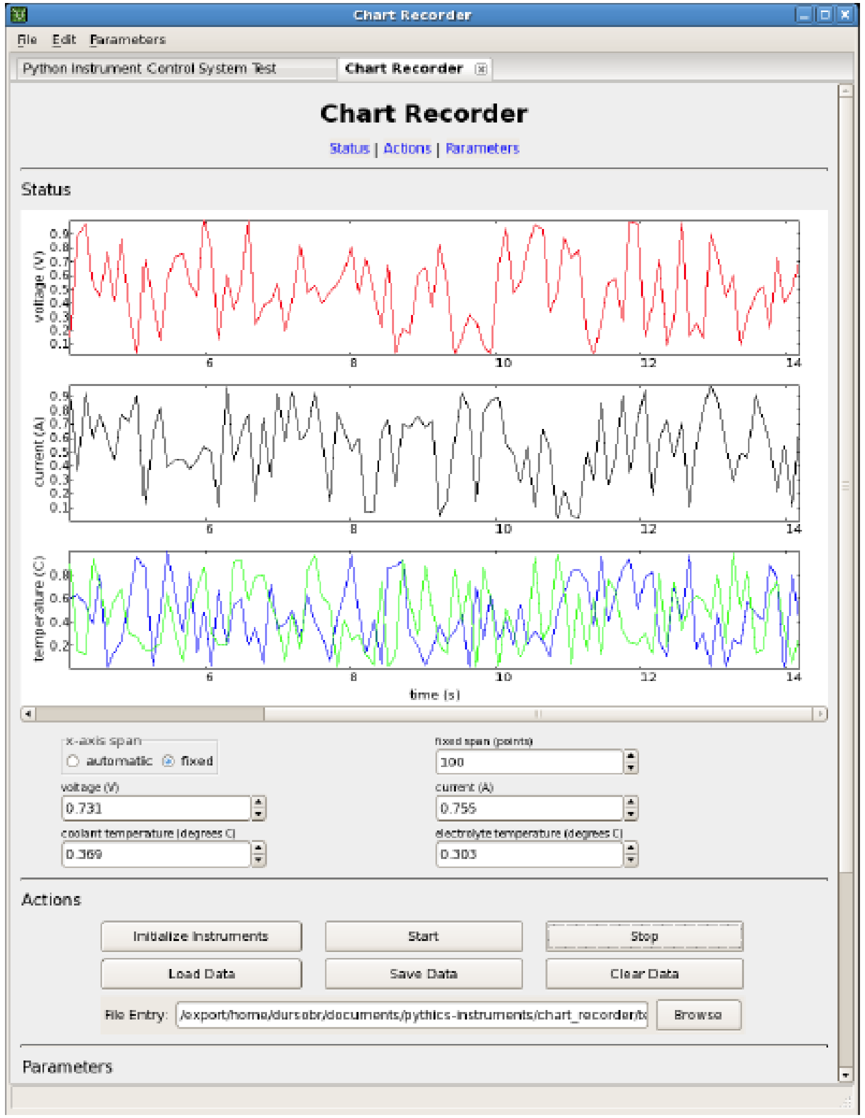
Frustrated with LabVIEW?

- Need a framework for large applications.

- **Try a python framework developed by Brian D’Urso (Montana St)**
  - 3 files to write:
    - xml: defines GUI
    - txt: default GUI values
    - py: code

Solution: Pythics Overview

- Pure Python implementation.
- Organized as a program that manages ‘documents’ – virtual instruments or VI’s.
  - Single GUI process and thread (mandated by GUI toolkits).
  - Each VI gets its own process for executing actions.
- GUI is web browser style:
  - Tabbed interface, one tab per VI.
  - Layout within each tab is html-like.
- User-programmer writes two files:
  - GUI specification: html/xml.
  - Callback functions: pure Python.



Rheology of insulin assemblies

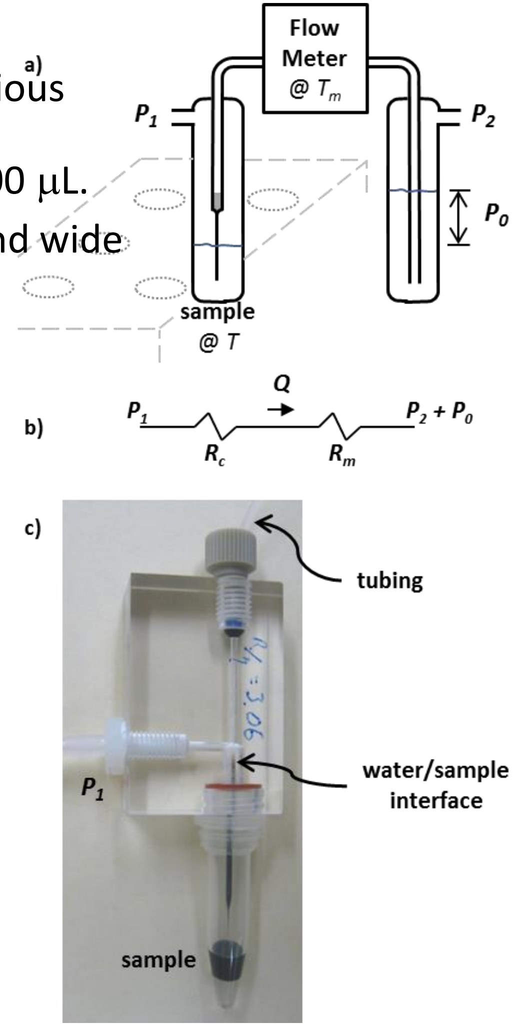
- Grethe Jensen
- Shear thickening

Micro-capillary rheometer

Why a new approach for viscosity of protein drugs?

- **Convenience & cost.** 100’s of conditions (various excipients, buffers, and pH) are screened for properties including viscosity. Target: < 100 μL.
- **Accuracy & breadth.** Target: interface free and wide range of rate.

High shear rates



flow meter

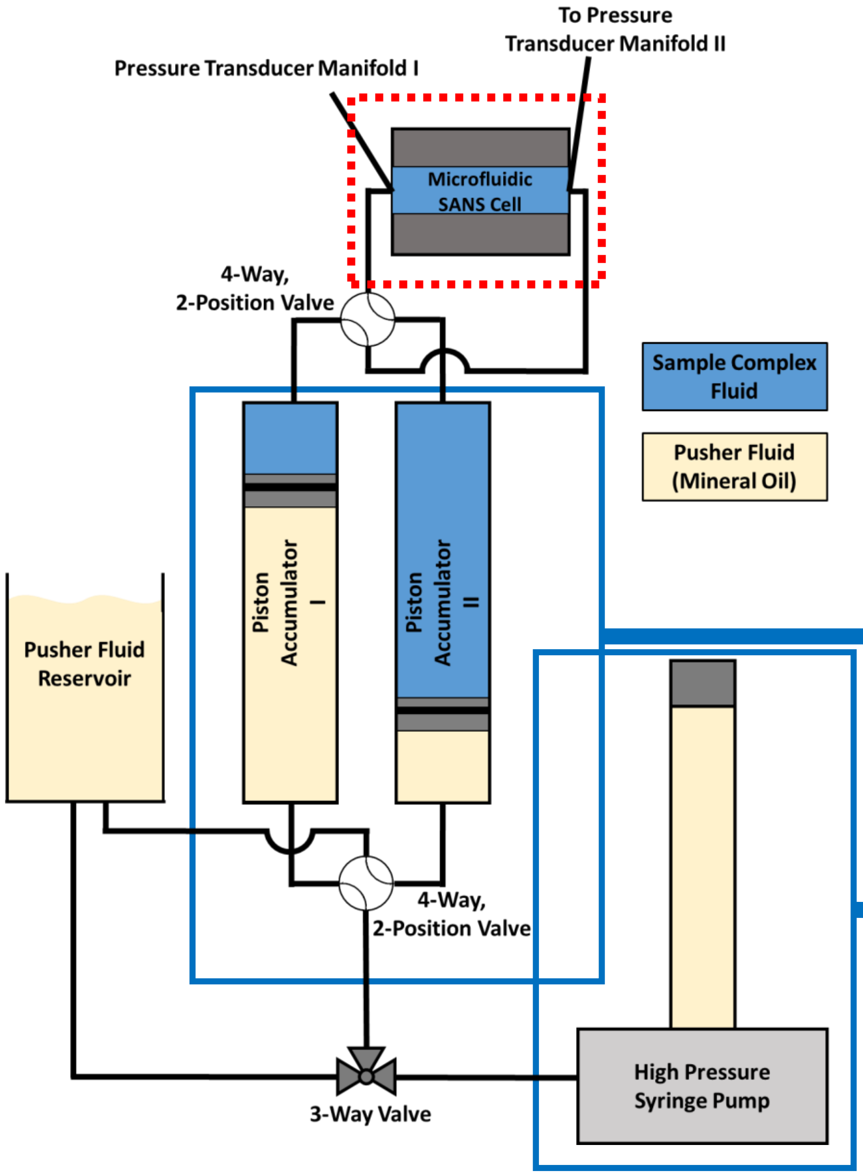
pressure controller

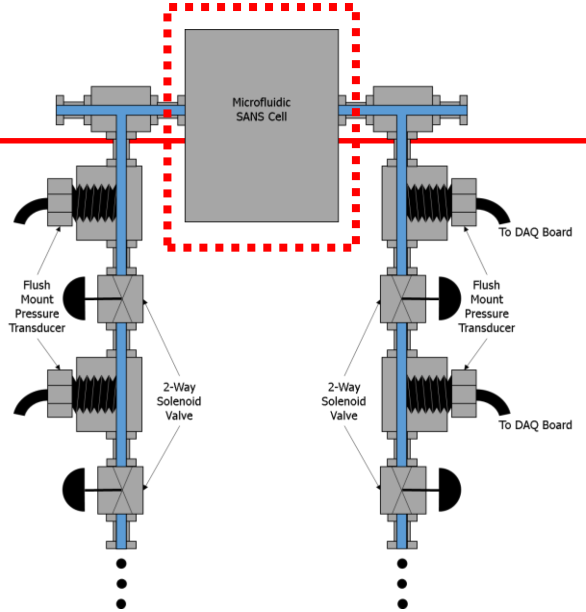
MedImmune

Biomanufacturing

Hudson et al., J Pharm Sci, 2015

Full Apparatus Schematic





HiP Tubular Reactor w/Piston

- 125 mL each
- 10 000 psi – 700 bar
- 304 Stainless Steel
- 0 – 125°C

DCI VPA Syringe Pump

- 400 mL/min
- 5000 psi – 345 bar
- Stainless Steel Cylinder
- 12 nL volume resolution