SAND2009-6812C

Experimental Rheological Measurements at Gas-Liquid Interfaces

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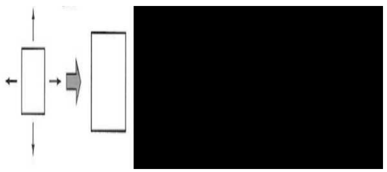
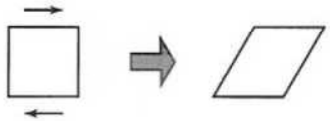
Microscale Science and Technology,
Sandia National Laboratories

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Outline

- Foams and the importance of interfacial rheology
- Review experimental methods
  - Dilatational rheology
    - Surface Dilatational Rheometer (SDR)
  - Shear rheology
    - Interfacial Shear Rheometer (ISR)
    - Micro- Interfacial Rheometer (MIR)
- Materials
- Preliminary results
  - Surface Dilatational Rheometer (SDR)
  - Interfacial Shear Rheometer (ISR)
  - Micro-Interfacial Rheometer (MIR)

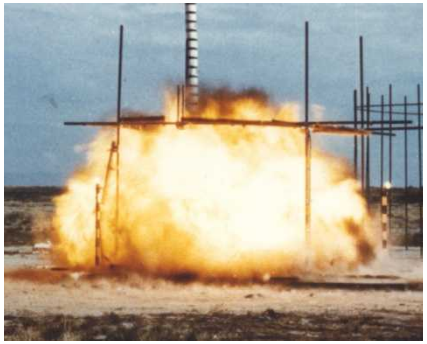


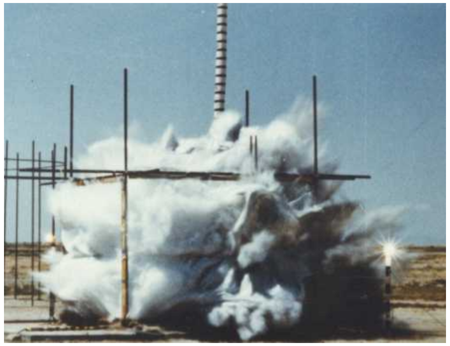


Sandia's Foam Interests

Explosion Suppression

no foam **foam**





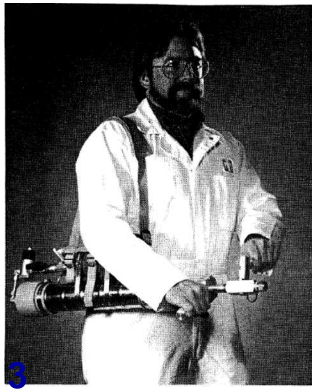
no foam **foam**

Aubert et al. *Scientific American* 254 74 (1986)

Courtesy of P.B. Rand

Encapsulation

Intruders/Unruly Crowds



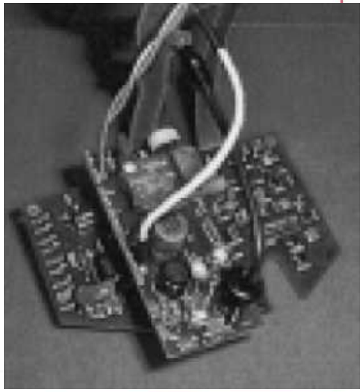
Scott *SAN096-2495C*; Russick *SAND2002-1103P*

Electronics—removable foam

reversible chemistry

→

90°C



McElhanon et al. *J. Appl. Polym. Sci.* 85 1496 (2002)

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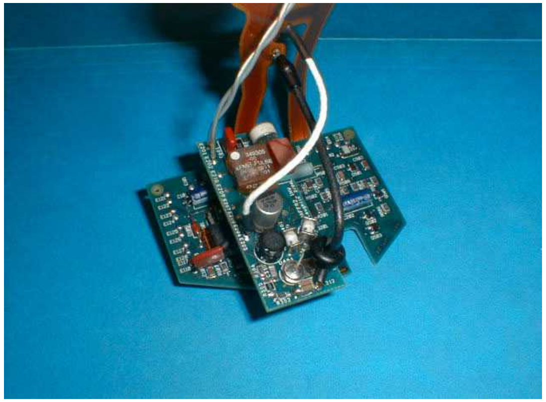
Understanding Foams

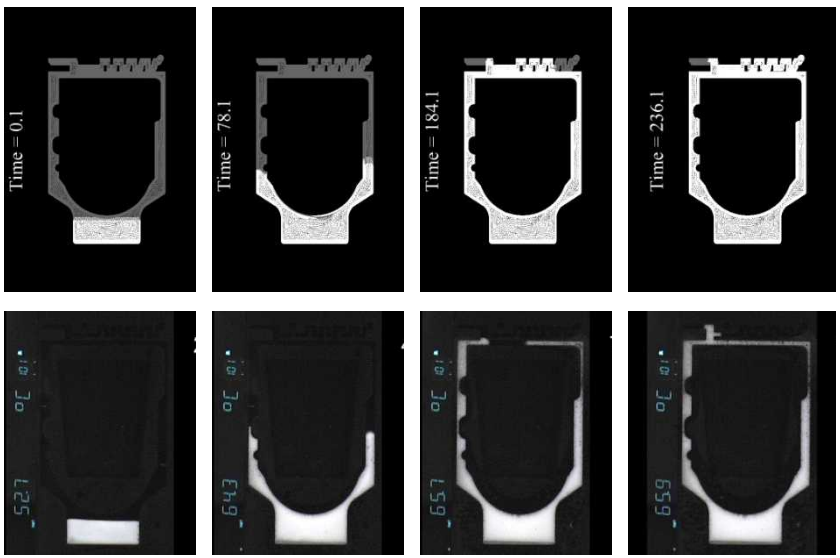
- Foams are frequently used to encapsulate and protect sensitive electronics from shock and environmental disturbance



Flow studies with physically blown epoxy foam channel 6x12mm

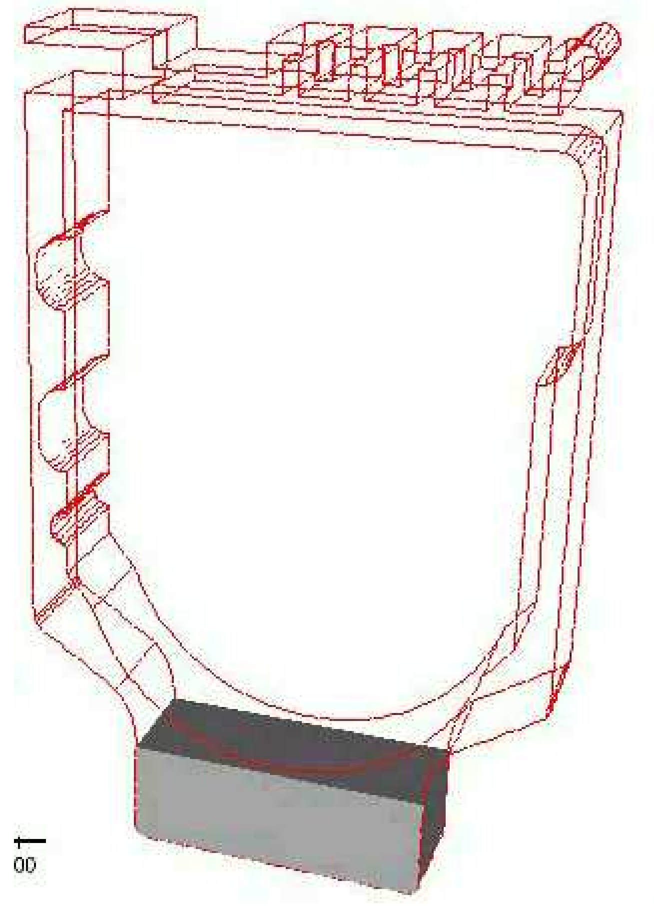
Predictive Computational Models

- Sandia has developed predictive modeling capability to improve encapsulation processes



T=0s T=78.6s T=184.1s T=236.4s

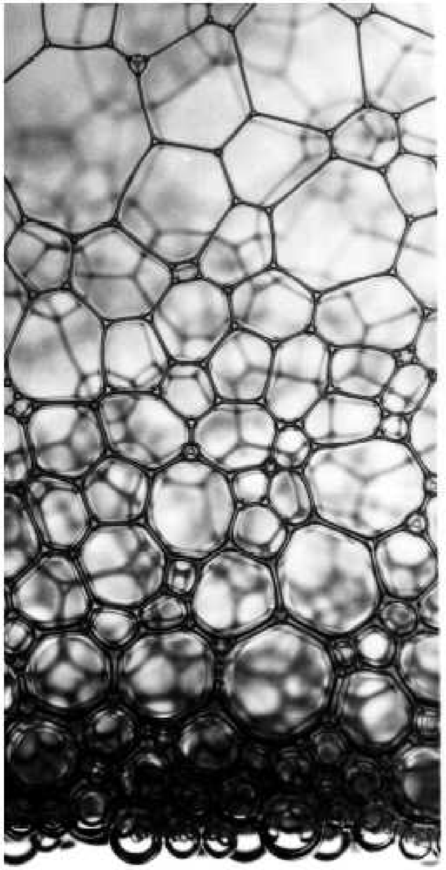
Complex mold filling with physically blown epoxy foam



Rekha Rao

Interfacial Link to Foam Properties

5% SDS in water

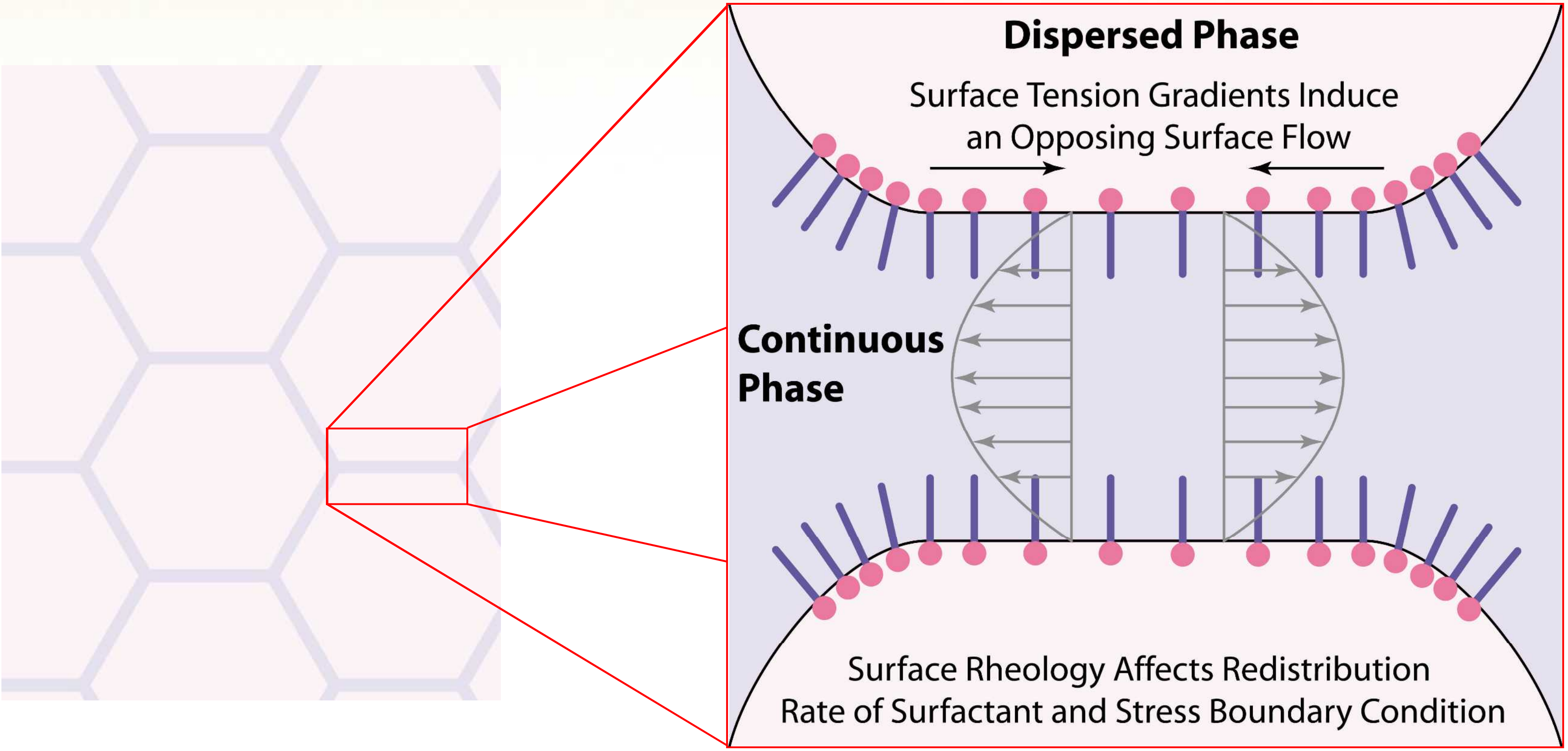


3 mm bubbles

http://www.physics.upenn.edu/liugroup

- Foam stability
  - Ostwald ripening
  - Coalescence
  - Flow effects
- Importance of Surface Rheology
  - Surface dilatational properties
    - High frequency – coalescence
    - Low frequency – ripening
  - Surface shear viscosity – resistance to flow at the interface
  - Fruhner et al. 2000, Stubenrauch & Miller 2004, Georgieva et al. 2008

Role of Surface Rheology in Foam Stability



The rheology of the interface between the phases (air-liquid for foams, liquid-liquid for emulsions) affects the drainage of the continuous phase as the dispersed phase coalesces

Incorporate Interfacial Rheology Effects

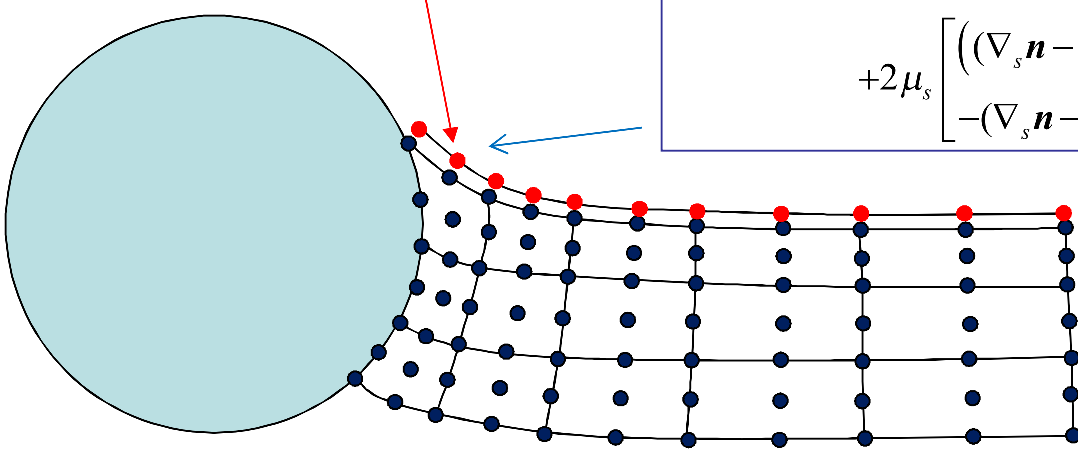
Shell unknowns Γ_i defined on shell elements are used to calculate intermediate quantities at the interface

$$\int_{d\Omega} (\Gamma_1 - \nabla_s \cdot v)\varphi^i dA = 0 \qquad \int_{d\Omega} (\Gamma_3 - (\nabla_s \times v)\cdot n)\varphi^i dA = 0$$

$$\int_{d\Omega} (\Gamma_2 - (\nabla_s v)\cdot n)\varphi^i dA = 0 \qquad \int_{d\Omega} (\Gamma_4 - 2H)\varphi^i dA = 0$$

To eliminate second derivatives in the Boussinesq-Scriven model equations, integral BC's on NS equations are written in terms of the shell unknowns Γ_i defined on shell elements

$$\begin{aligned} \boldsymbol{n}\cdot(\underline{\underline{T}} - \boldsymbol{\tau}_{ext}) = {} & 2H\sigma\boldsymbol{n} + \nabla_s\sigma + \Gamma_4\boldsymbol{n}(\kappa_s + \mu_s)\Gamma_1 \\ & + \Gamma_4(\kappa_s + \mu_s)\nabla_s(\Gamma_1) + \mu_s(\boldsymbol{n}\times\nabla_s\Gamma_3) \\ & + 2\mu_s\left[\begin{array}{l} \left((\nabla_s\boldsymbol{n} - \Gamma_4\mathbf{I}_s):\nabla_s\boldsymbol{v}\right)\boldsymbol{n} \\ -(\nabla_s\boldsymbol{n} - \Gamma_4\mathbf{I}_s)\cdot\underline{\Gamma}_2) \end{array}\right] \end{aligned}$$



Bulk NS finite element residuals specify the stress tensor via a weak formulation, that includes the extra surface rheology terms

$$R_w = \int\left[\rho\left(\frac{dv}{dt} + v\cdot\nabla v\right) - f\right]\varphi^i d\Omega + \int \underline{\underline{T}}\cdot\nabla\varphi^i d\Omega - \int n\cdot\underline{\underline{T}}\varphi^i d\Omega$$

Harry Moffat

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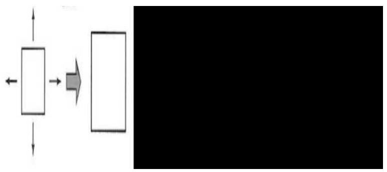
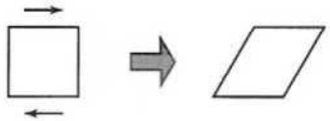
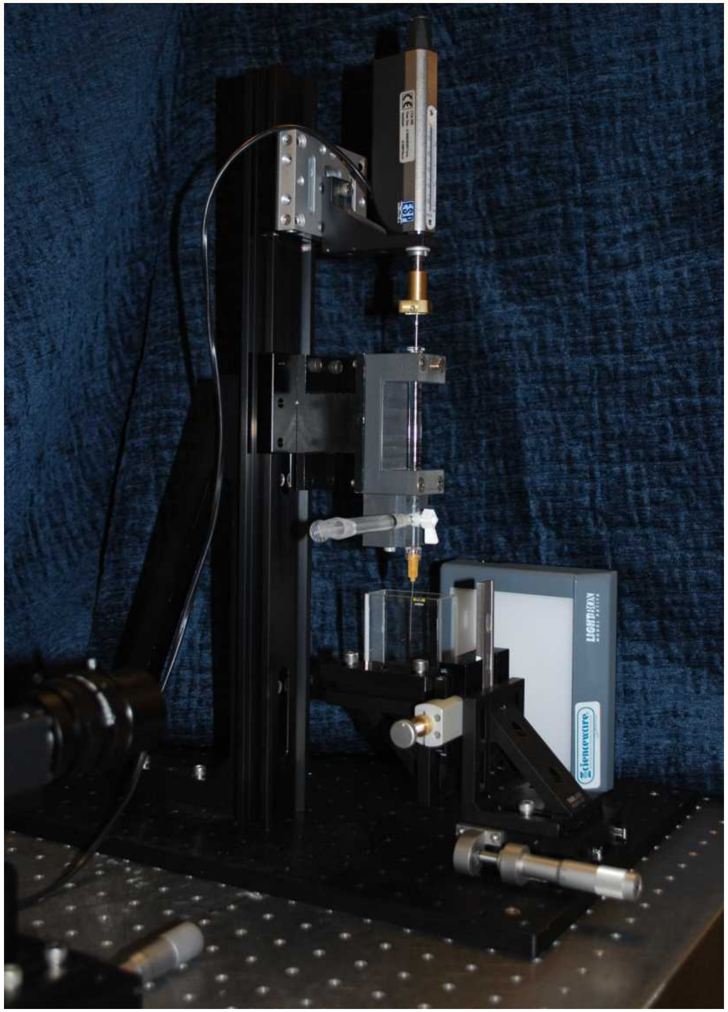
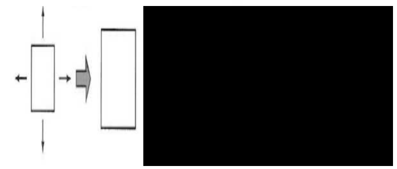




Surface Dilatational Rheometer (SDR)

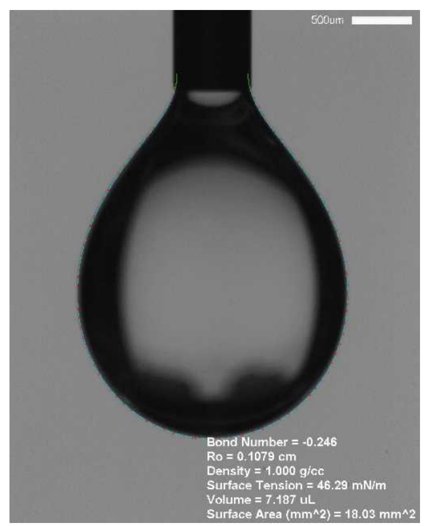


Measure interfacial *dilatational* rheology by oscillating the volume of a pendant drop and measuring changes in surface tension (σ) with surface area (A).



Dilatational deformation of interface probed

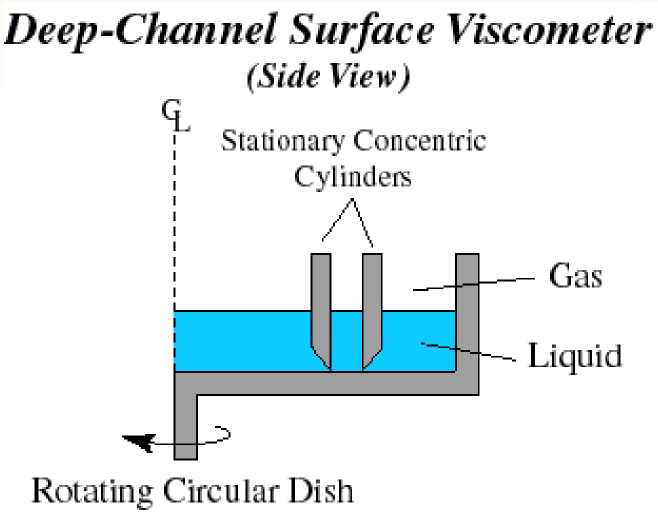
Surface tension is measured by performing a pendant drop analysis (fitting drop shape to a solution of the Laplace-Young equation ±1°C). The surface dilatational modulus (E_s*) is

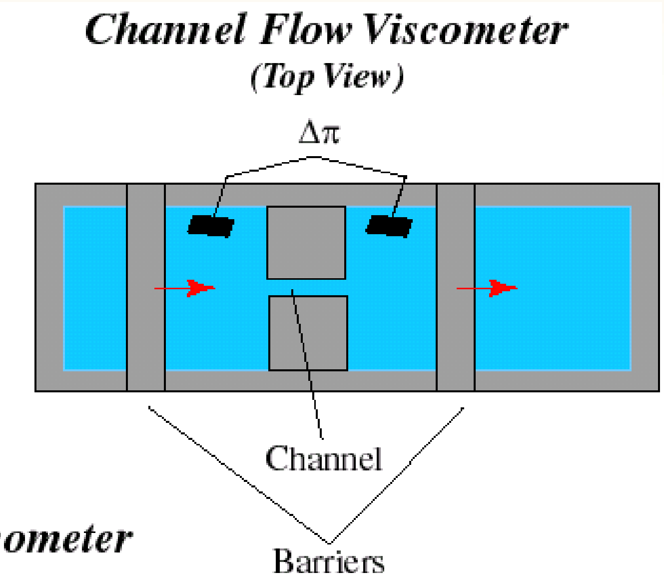


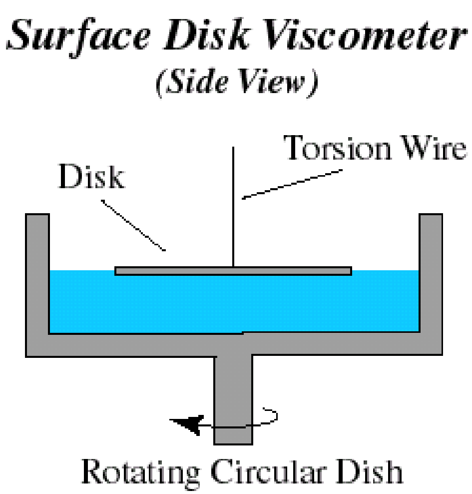
$$A\frac{\partial\sigma}{\partial A} = E_s^* = E_s' + iE_s''$$

Drop oscillating in volume

Methods for Interfacial Shear Viscosity

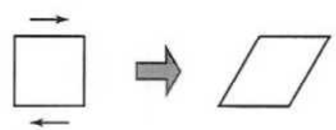






Boussinesq # defines relative contributions from the surface and bulk

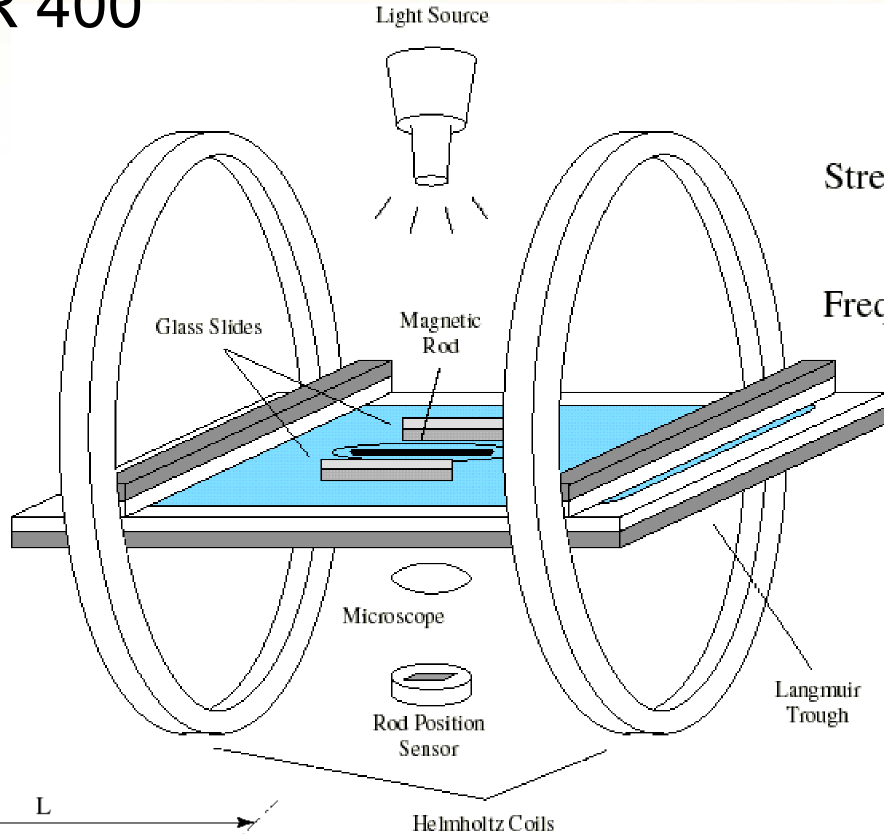
$$Bo_{DISK} = \frac{\text{Surface Drag}}{\text{Subphase Drag}} = \frac{\eta_s P}{\eta_b A} = \frac{2\eta_s}{\eta_b R}$$



To measure surface effects, **large *Bo*** is desired

Interfacial Shear Rheometer

- KVS ISR 400



Specifications

Stress: $10^{-5} < \tau_s < 10^{-1}$ mN/m

Strain: $10^{-4} < \gamma < 0.1$

Frequency: $0.1 < \omega < 10$ rad/s

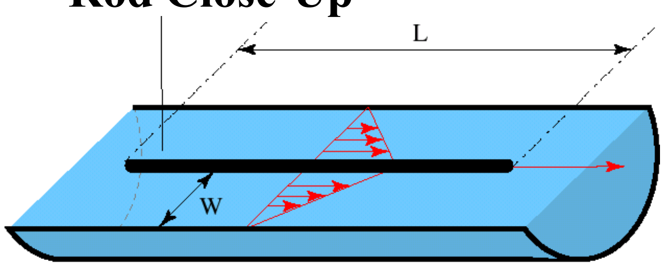
Modulus

$10^{-4} < G_s < 10^{3}$ mN/m

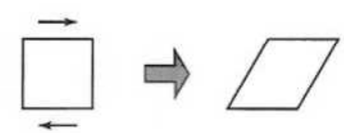
Viscosity

$10^{-5} < \eta_s < 10^{4}$ mN-s/m

Rod Close-Up



$$\mathrm{Bo}_{\mathrm{ISR}} = \frac{\eta_s P}{\eta_b A} = \frac{\eta_s}{\eta_b R(\pi - \theta)}$$



Brooks, Fuller, Frank, Robertson (1999)

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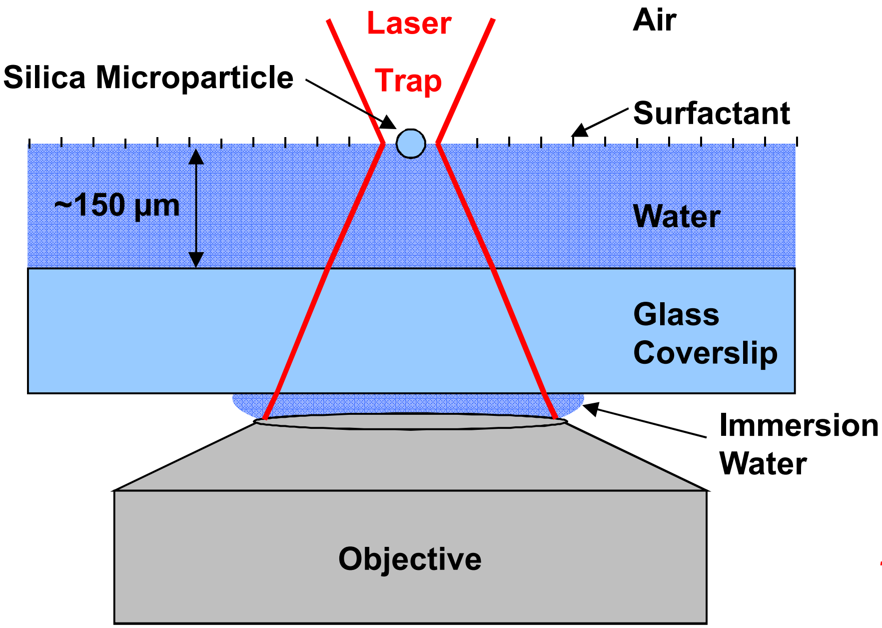
Micro-Interfacial Rheometer

- Use micron-sized particles at the interface to probe interfacial rheology



- Passive μ-rheology

  Observation of particle diffusion to find η_s, G', G"

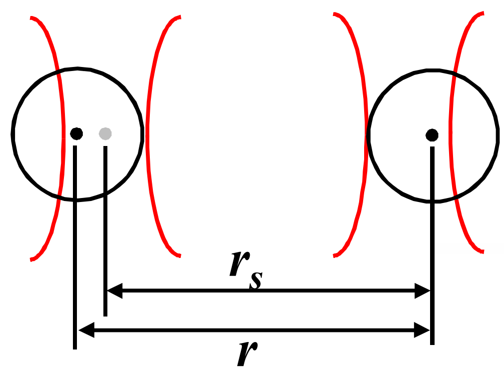
  Prasad, Koehler, Weeks (2006)

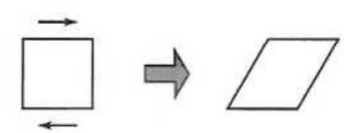
- Active μ-rheology

  Move particle on the interface and measure drag force experienced by the particle

  Park, Furst *et al.* (2008)

$$\mathrm{Bo}_{\mathrm{MIR}} = \frac{\eta_s P}{\eta_b A} = \frac{\eta_s}{\eta_b R}\left(\frac{\sin\theta}{1+\cos\theta}\right)$$



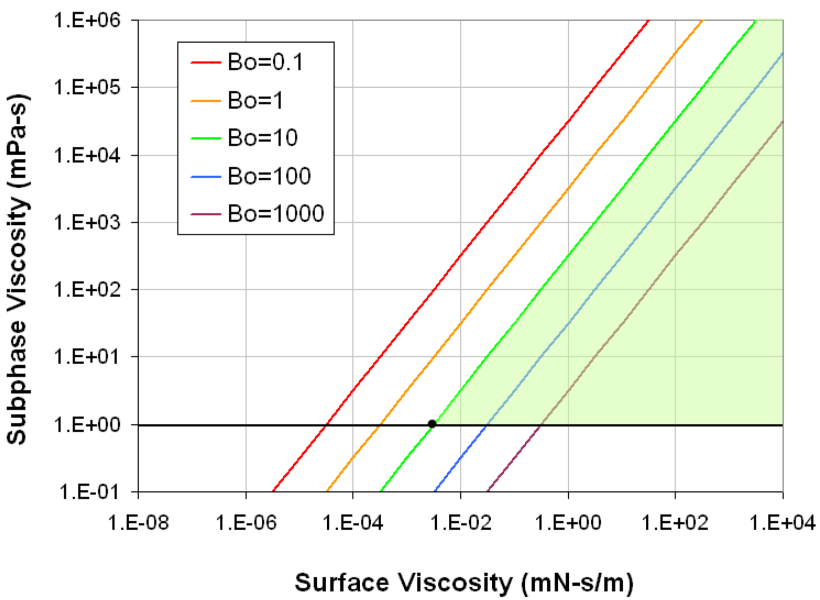


MIR – The Promise

- Enhanced surface sensitivity with small sphere probes

ISR – Magnetic Rod

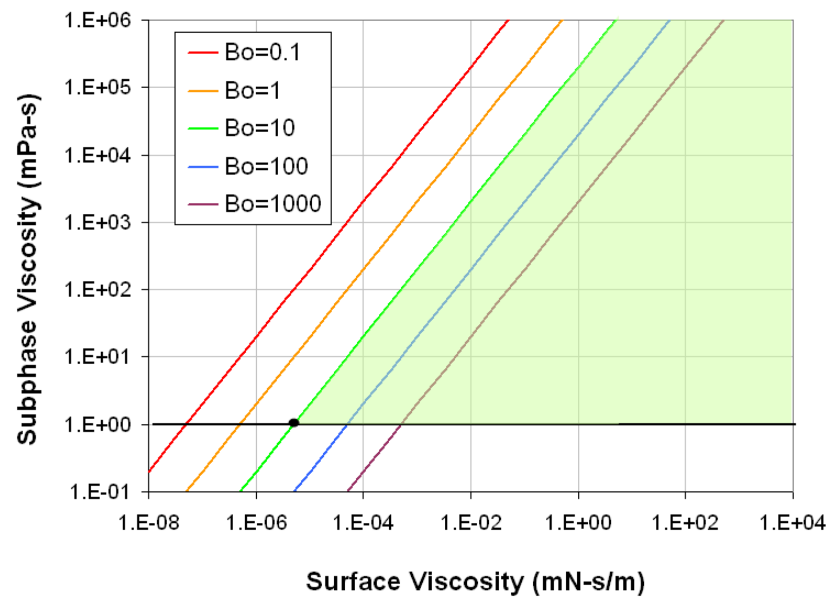
$$\mathrm{Bo}_{\mathrm{ISR}} = \frac{2}{\pi}\frac{\eta_s}{\eta_b R} \qquad 2R = 400\,\mu\mathrm{m} \quad \theta = 90^{\circ}$$



$\eta_s > 3\times10^{-3}$ mN-s/m

MIR – Sphere

$$\mathrm{Bo}_{\mathrm{MIR}} = \frac{\eta_s}{\eta_b R} \qquad 2R = 1\,\mu\mathrm{m} \quad \theta = 90^{\circ}$$



$\eta_s > 5\times10^{-6}$ mN-s/m

Increased sensitivity of MIR can permit examination of surfaces on more viscous subphases

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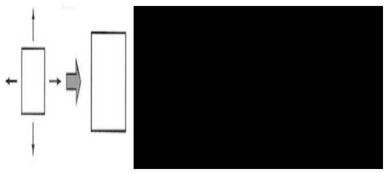
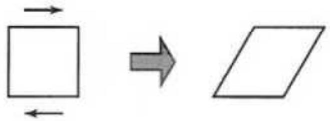
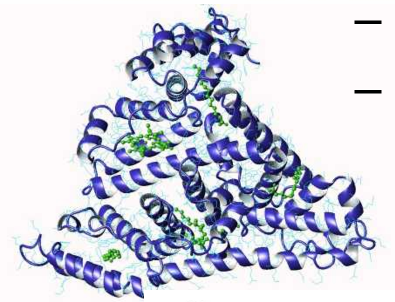


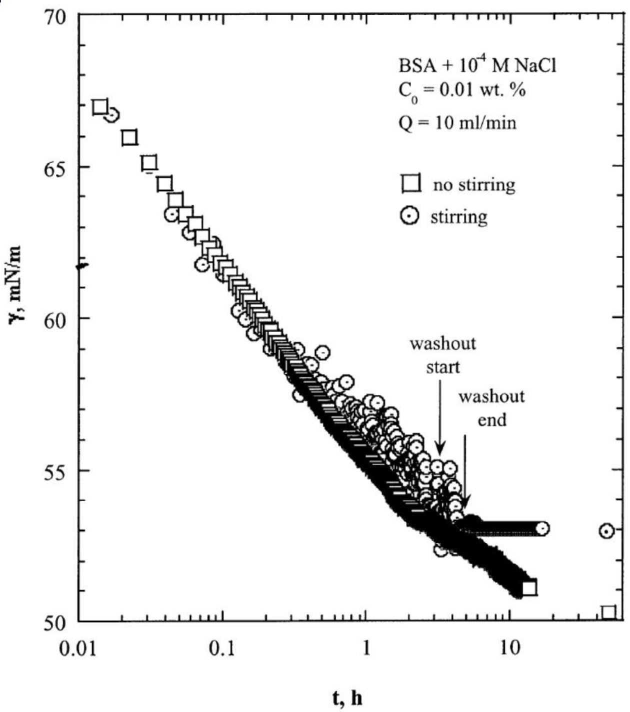


Surface Active Materials

- Bovine serum albumin (BSA)
  - Protein M_w~69,000
  - Irreversibly adsorbs

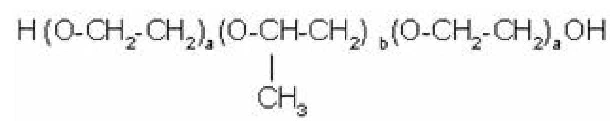


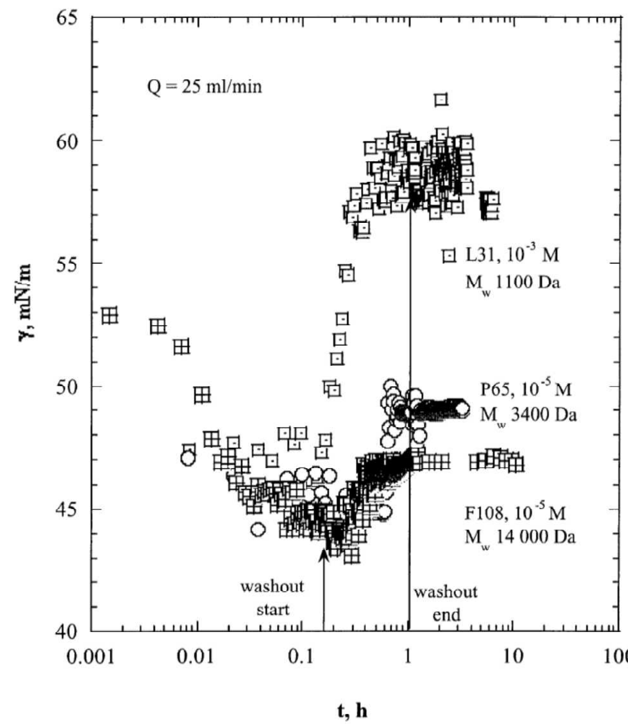
Labrador.eu



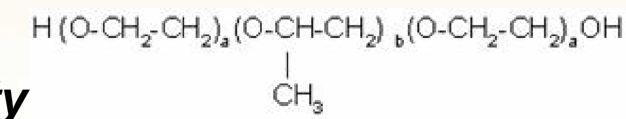
Svitova *et al*. JCIS 261 (2003) 170–179

- Polyoxamer (Pluronic® BASF)
  - Tri-Block copolymer EO-PO-EO
  - Vary weight to tune foam properties

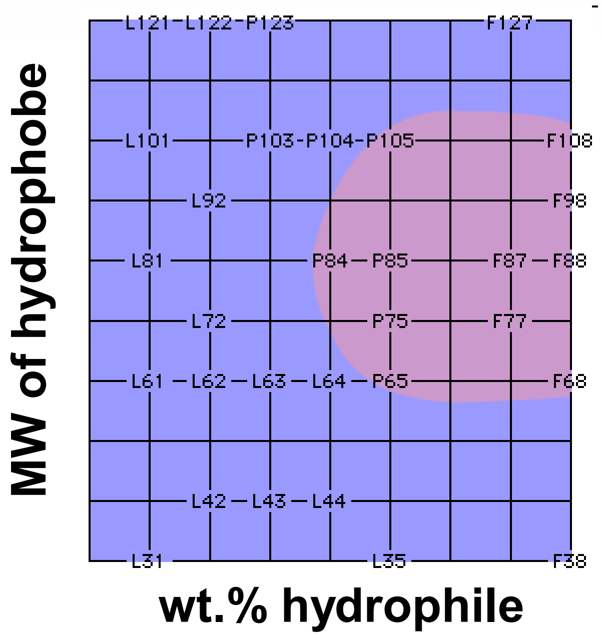




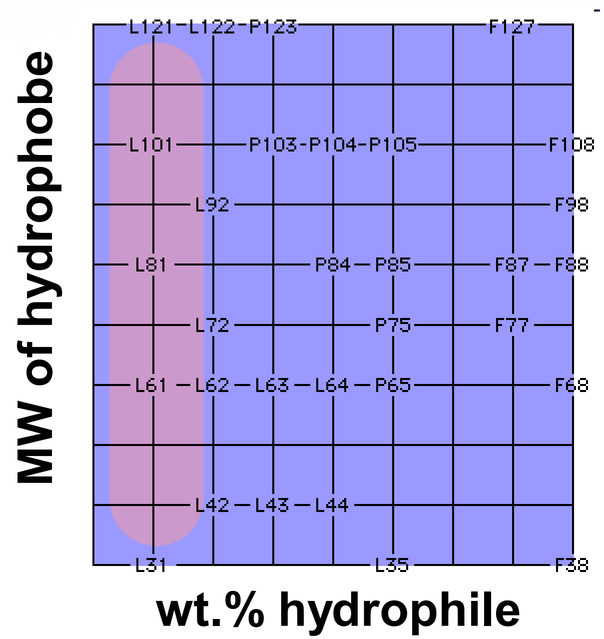
Pluronics®



Foamability



Defoaming



	MW (g/mol)	Surface Tension (mN/m) 0.1% at 25C	HLB
L31	1100	47	1-7
F108	14,600	41	>24

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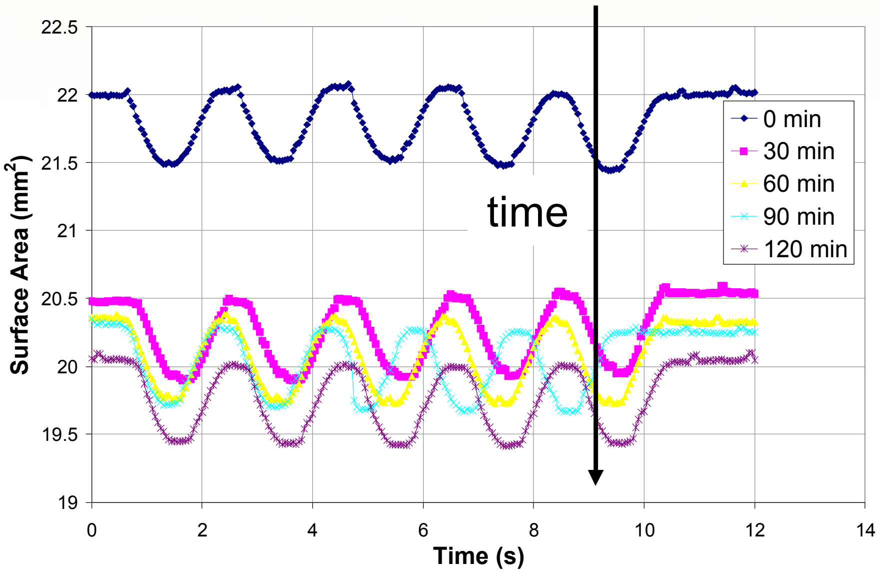
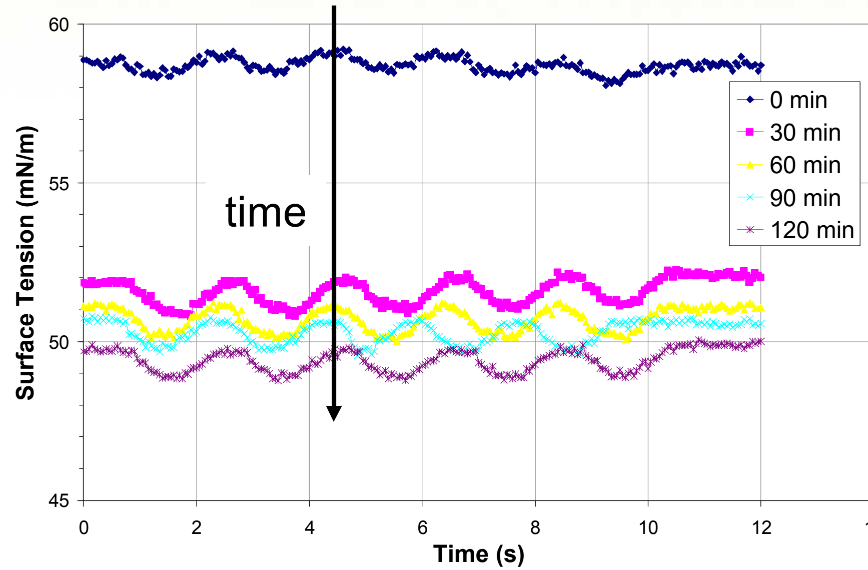
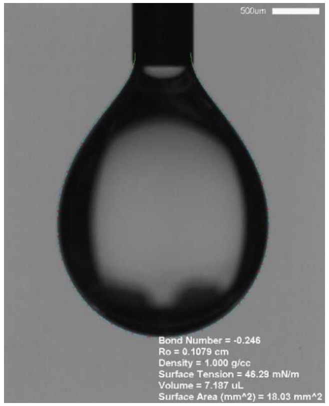
Dilatational Elasticity of BSA

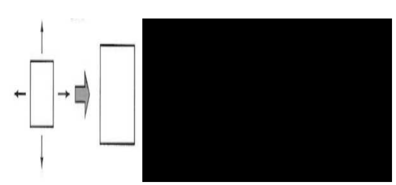
- Bovine Serum Albumin – 0.1 wt% in 1mM NaCl



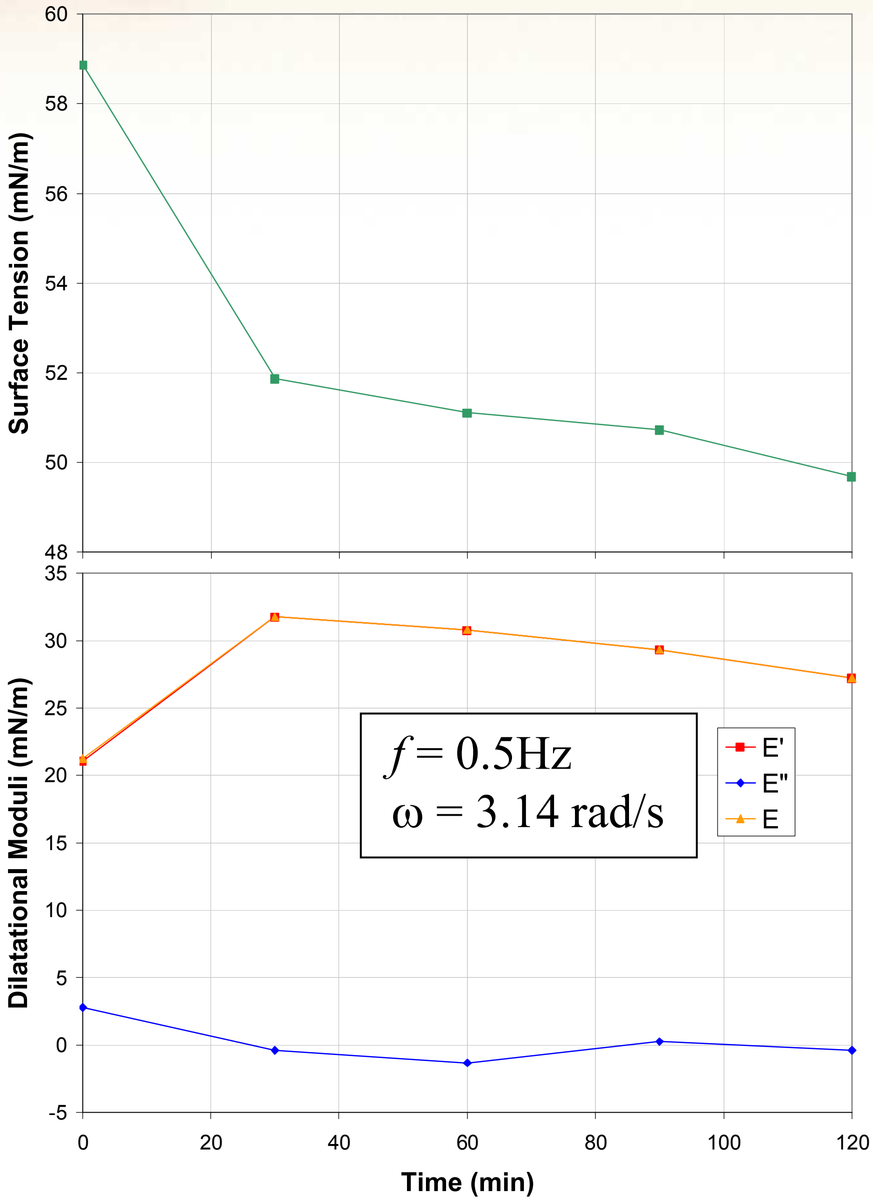


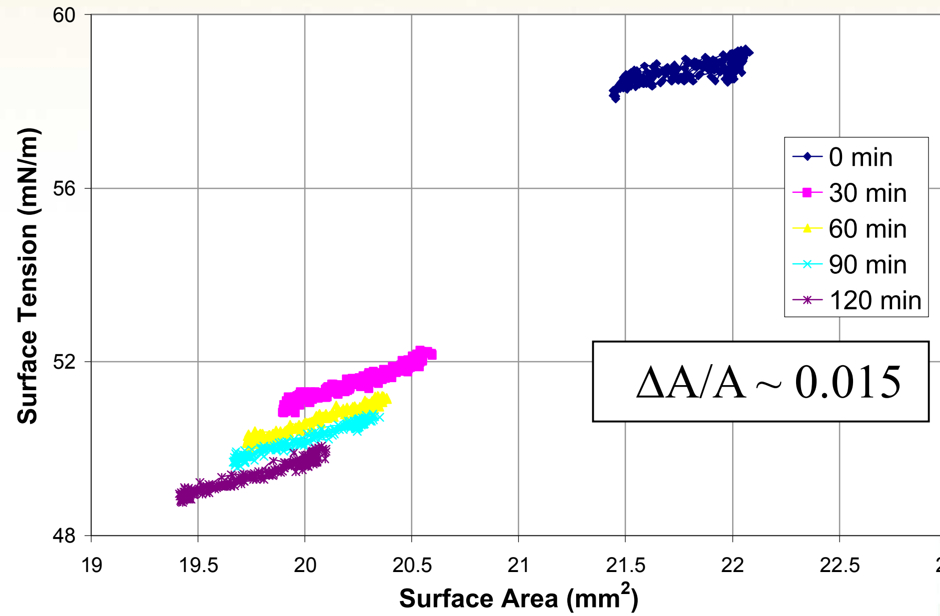


Clear correlation of changes in surface tension with drop surface area



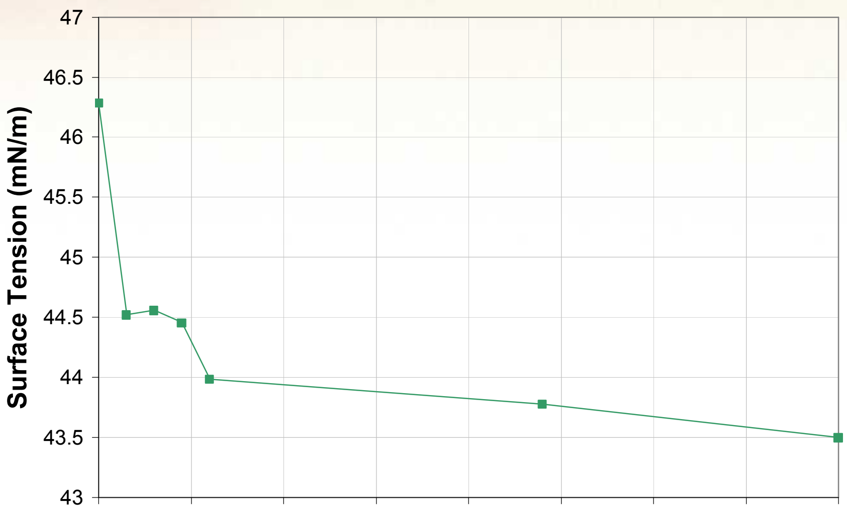
0.1wt.% BSA in 1mM NaCl - Dilatational

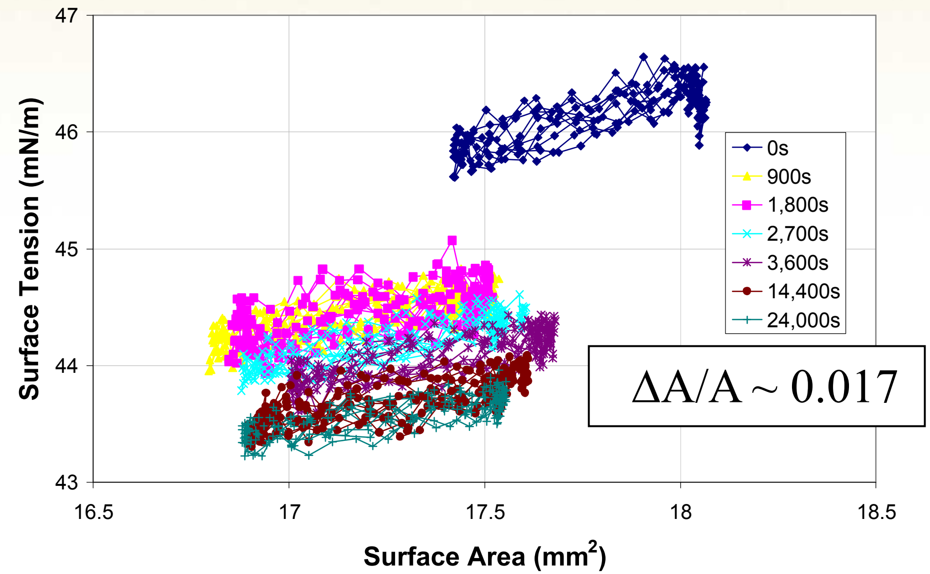


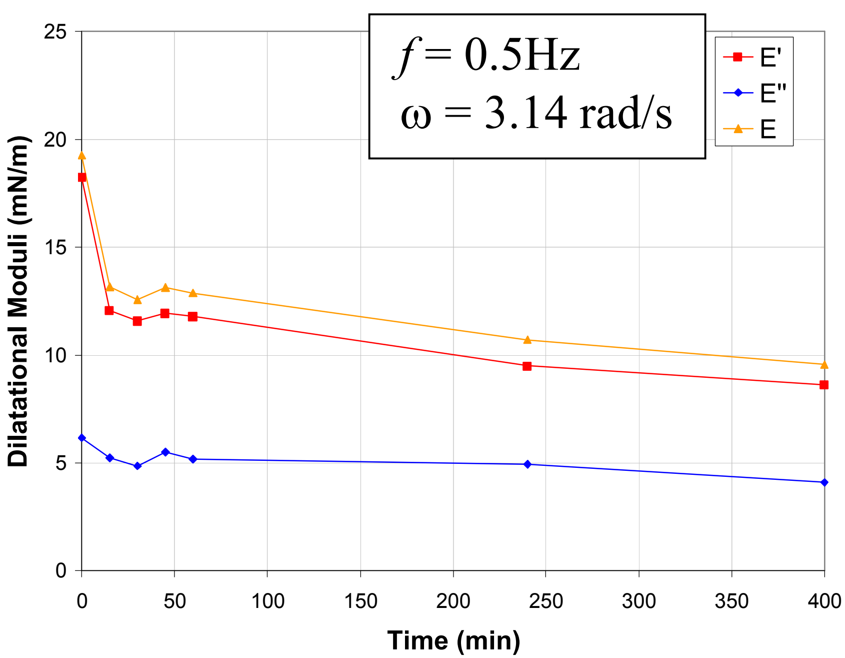


•Change in slope in γ vs. *A* plot shows the rapid increase in elasticity as BSA adsorbs to surface -- after ~30minutes, elasticity is fairly stable

1mM Pluronic F108 - Dilatational

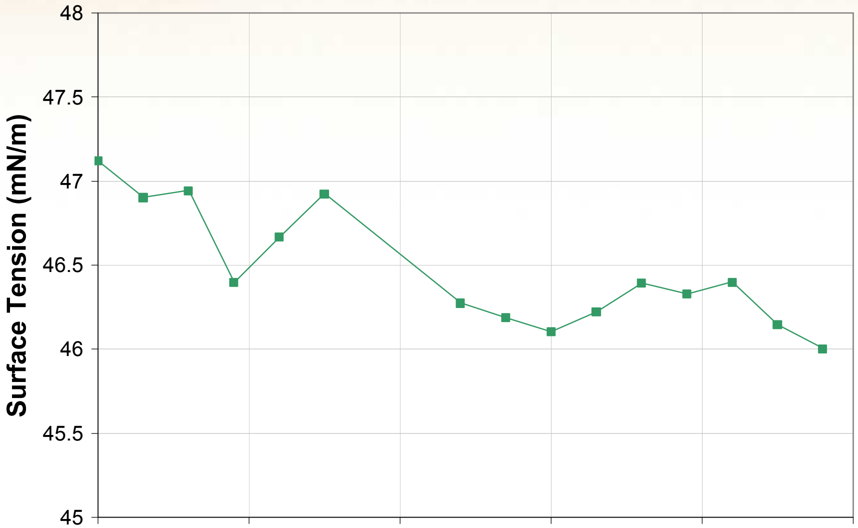


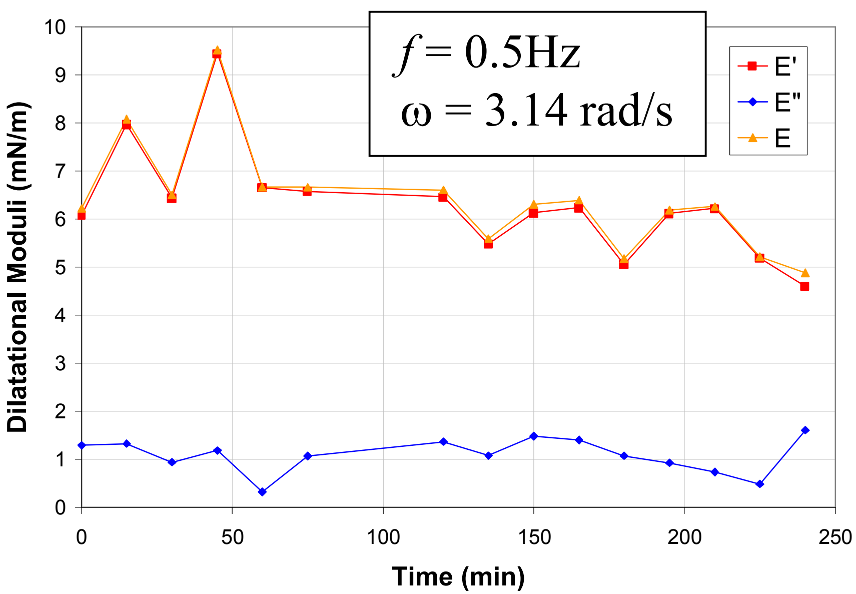


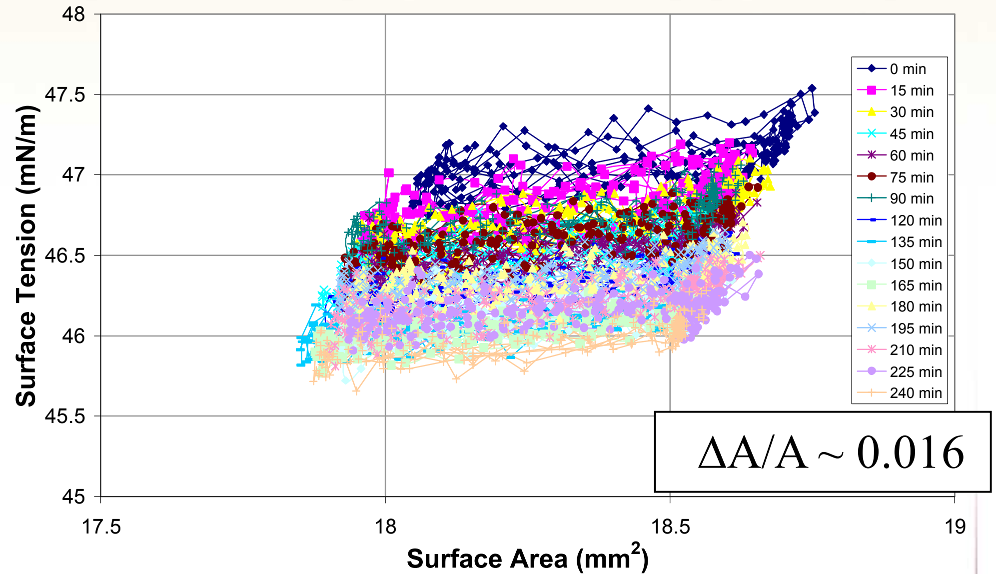


•Upon stabilization, the surface appears viscoelastic, albeit still mostly elastic

1mM Pluronic L31 - Dilatational



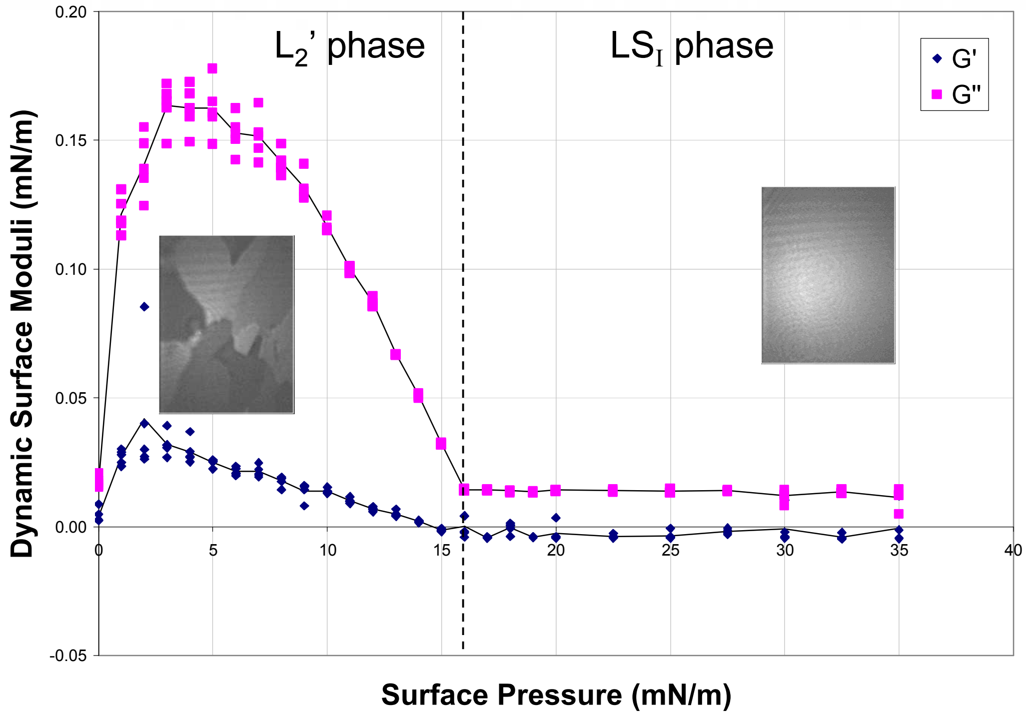




- Surface stabilizes rapidly and is predominantly elastic

ISR Rheology of Eicosanol

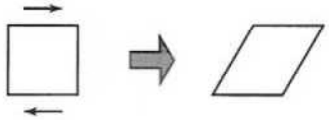
- Validated on well-studied Newtonian surfactant system $C_{20}OH$



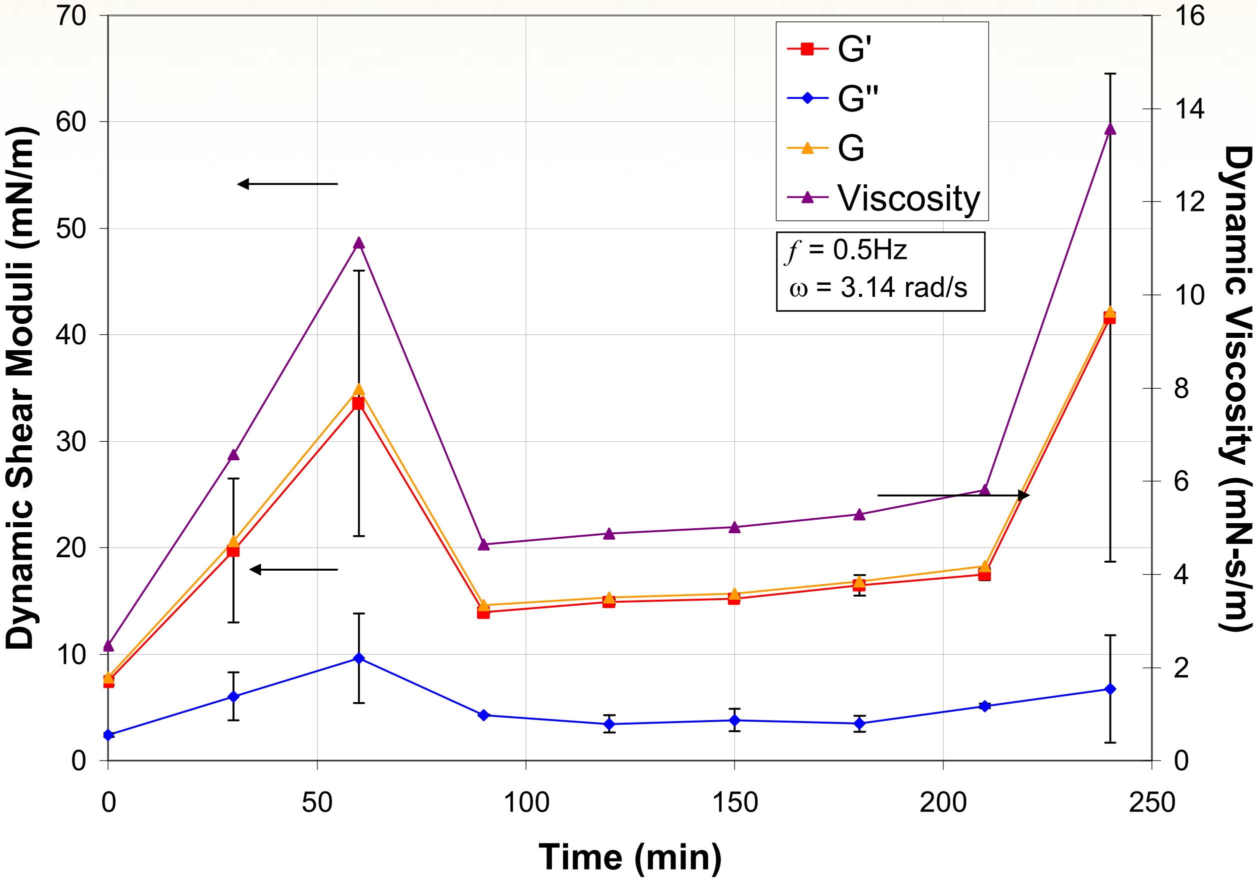
$f = 0.159\text{Hz}$
$\omega = 1$ rad/s

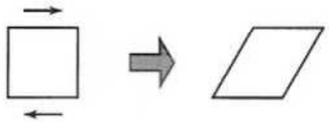
- ISR can detect rheological phase transitions in monolayers

Brooks, Fuller, Frank, Robertson (1999)



Shear Rheology of BSA



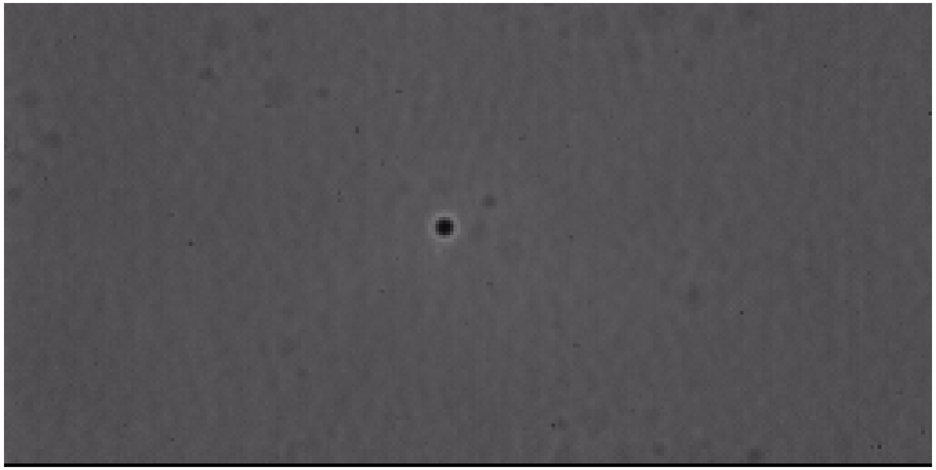


- ISR cannot detect any appreciable rheology (G<0.01 mN/m) for L31 and F108
- Micron-sized spheres with the MIR-passive has potential

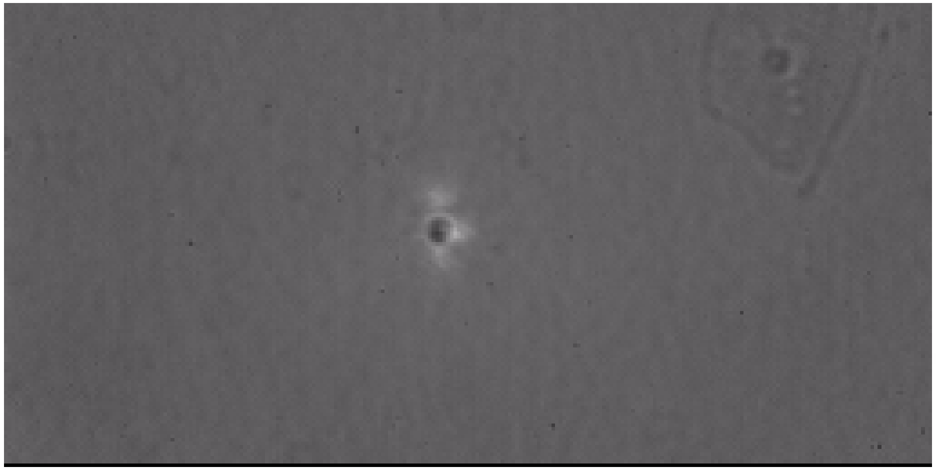
Manipulation of Particles at Interfaces

- Silica particle 1µm, with PDMS grafted brush
- Dragged at the interface using laser tweezers

'clean' water-air interface
Stable trapping at 20µm/s

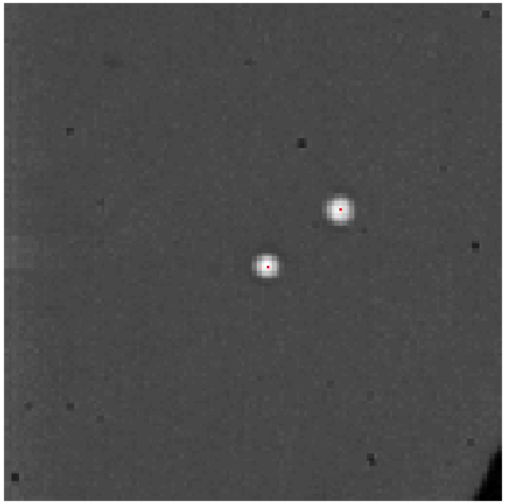


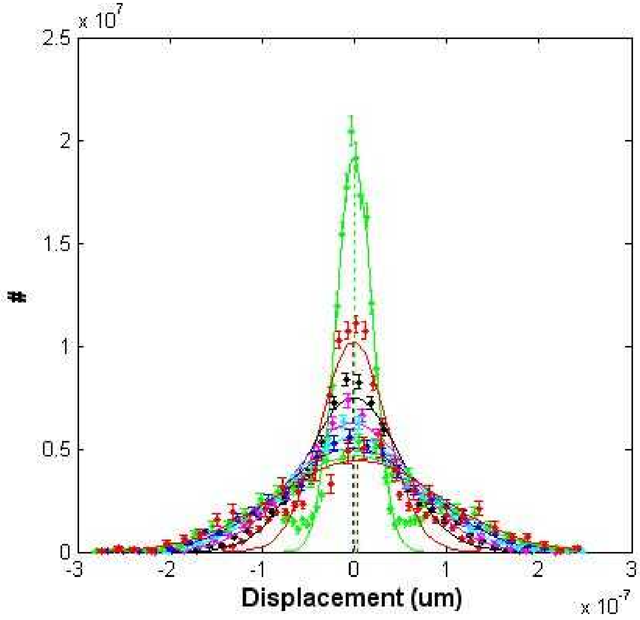
Pluronic F108
c=10 µM
Lose particle at 5µm/s
Increased surface viscosity



MIR - Passive

- Use relative diffusion of two particles to measure interfacial viscosity
- First step – assume uncorrelated motion of the two Brownian particles
- Implemented analysis to measure correlated analysis (Crocker, Weeks, et al.)

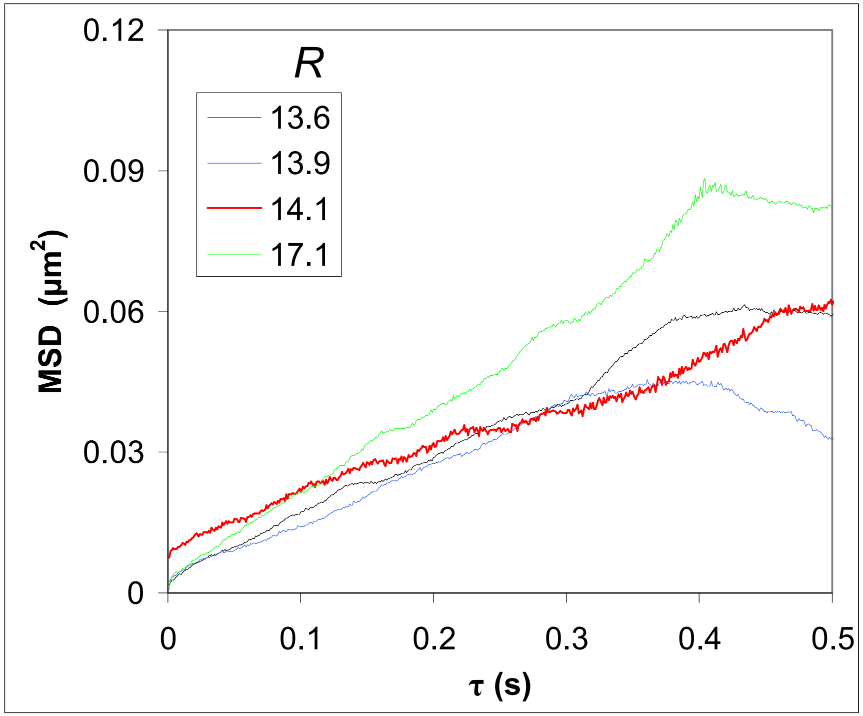




r is the center to center distance between the two particles

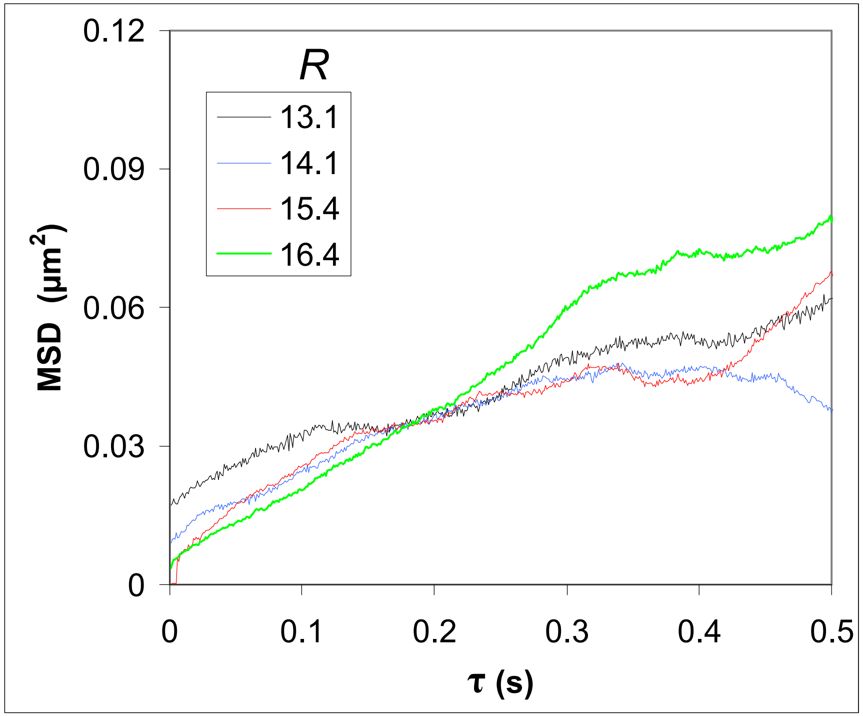
2.5μm SiO_2-OTS on 1mM F108

t = 15 min



η_s = 18 nPa–s-m
= 0.000018 mN-s/m

t = 30 min



η_s = 16 nPa-s-m
= 0.000016 mN-s/m

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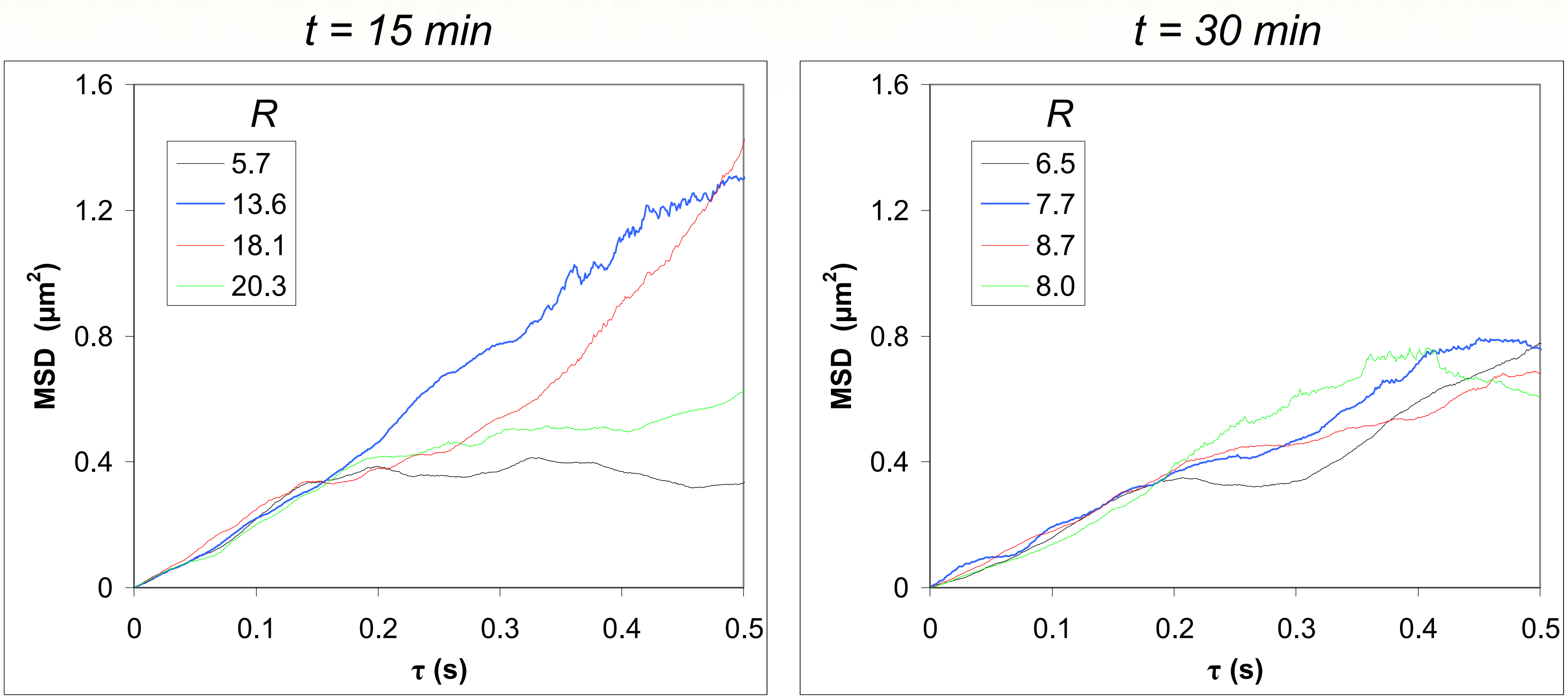
2.5μm SiO_2-APTES on 1mM F108



η_s < Detection limits

η_s < Detection limits

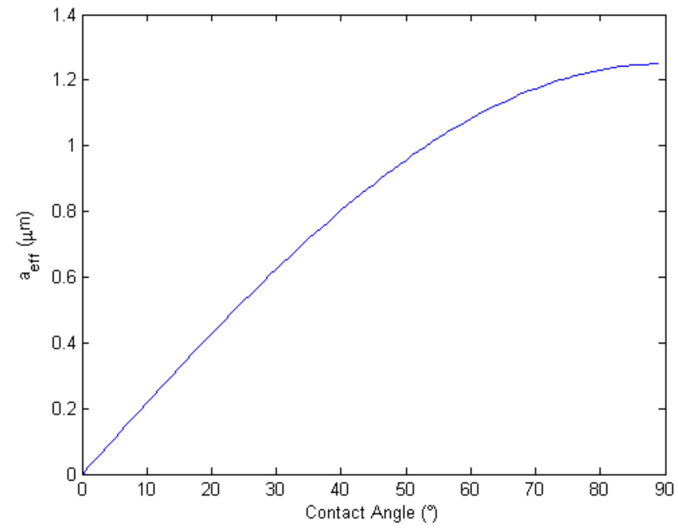
MSD is order of magnitude larger than seen for OTS coated spheres, possibly due to contact angle effects

Contact Angle Effects

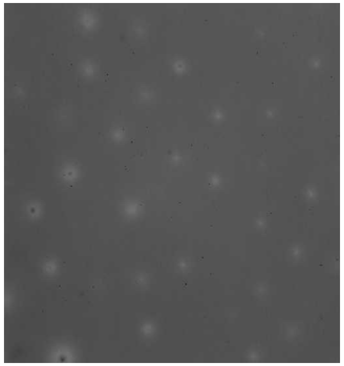
Saffman, Delbrück (1975)
Prasad, Koehler, Weeks (2006)

$$MSD = \langle \Delta r^2 \rangle = 2D'_s\tau$$

$$D'_s = \frac{k_b T}{4\pi\eta_s}\left[\ln\left(\frac{2\eta_s}{\eta_b a_{eff}}\right) - \gamma\right]$$

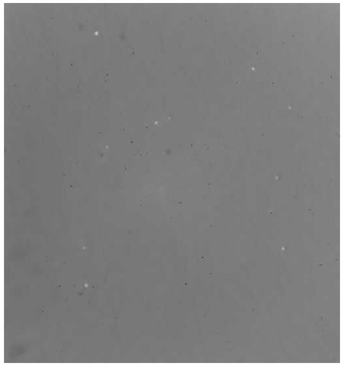


SiO_2-OTS



Water contact angle ~ 90˚

SiO_2-APTES



Water contact angle ~ 40˚

Must account for contact angle effects on a_{eff} when calculating η_s

Summary

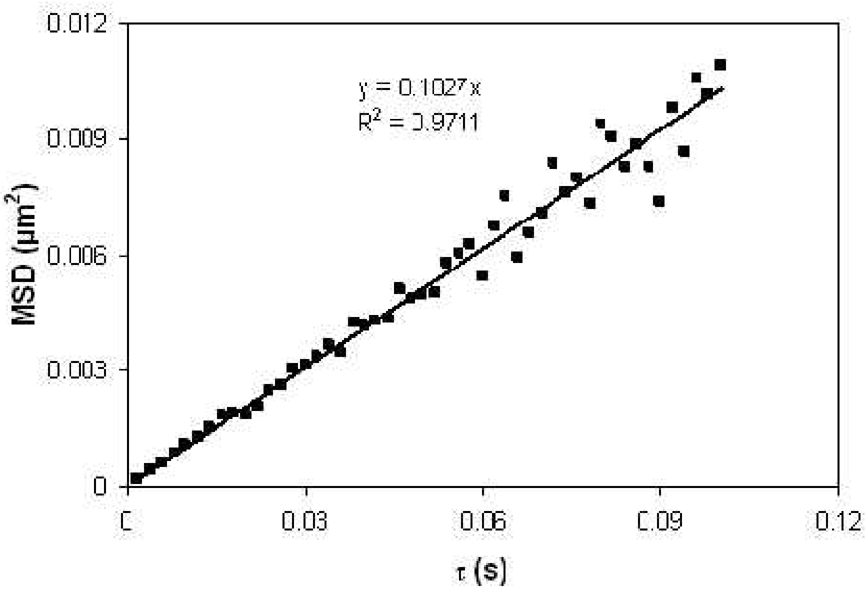
- Variety of techniques will provide a complete picture of interfacial rheology properties
  - –Interfacial Stress Rheometer
  - –Micro-Interfacial Rheometer
  - –Surface Dilatational Rheometer
- Correlate interfacial properties to
  - –Foamability
  - –Foam stability – quiescent and under flow
  - –Effect of additives in foam formulation
- Inform modeling capability with interfacial rheological parameters

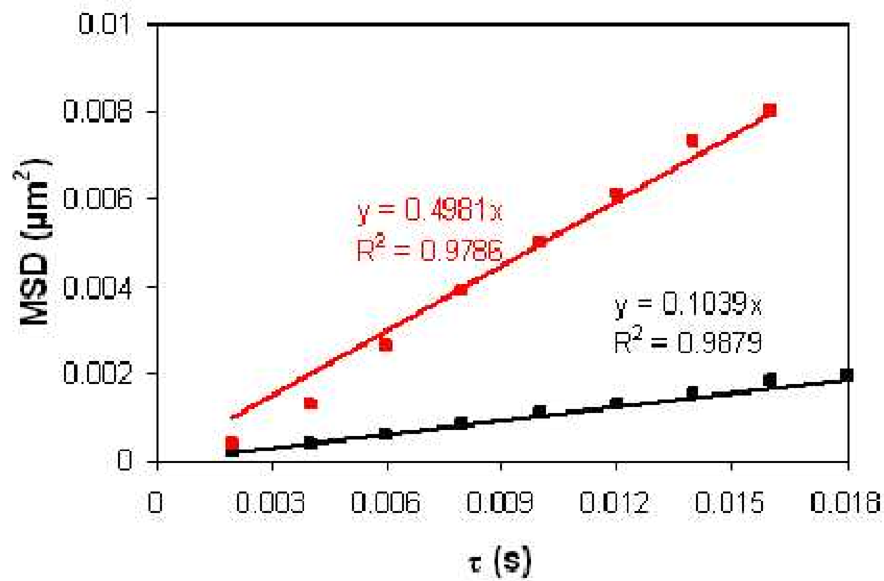
TA Instruments AR-G2 with DWR attachment has potential
(SA5 Mon. 11:25 Franck)

EB19 Wed. 2:45 Kropka – Macro-rheology of foams

Surface Diffusion data

Diffusion related to the surface viscosity





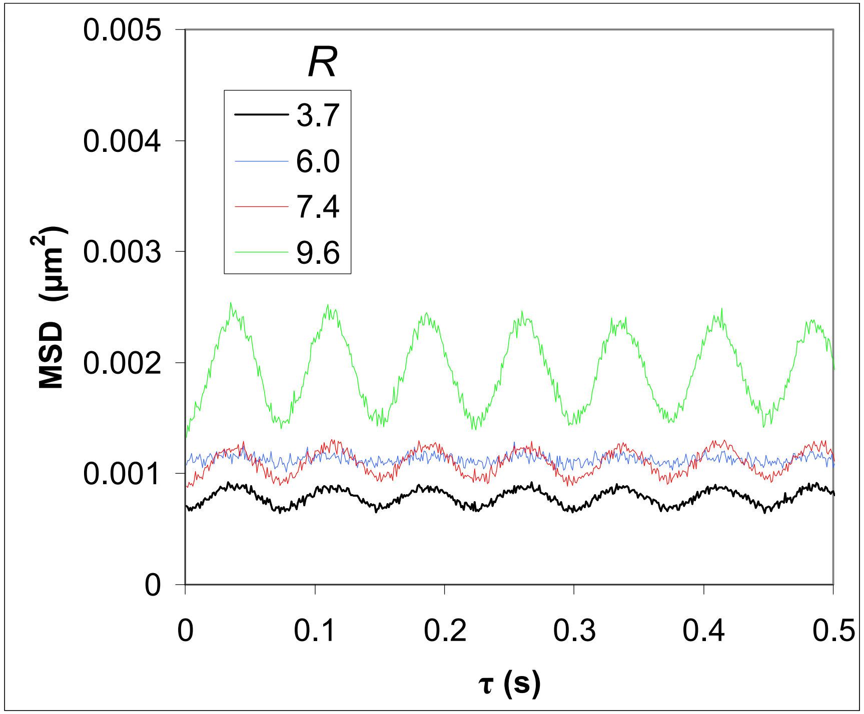
F108 c=10 μM

η_s=140 nPa-s-m

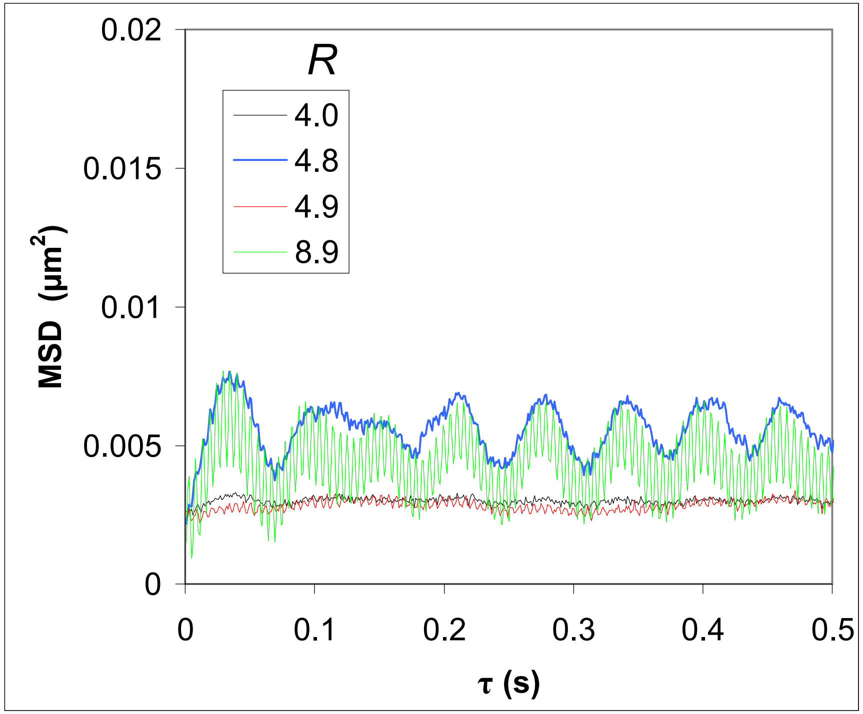
=0.00014 mN-s/m

2.5μm SiO_2-APTES on 0.1% BSA

t = 15 min



t = 30 min



η_s > Detection limit

2.5μm SiO_2-OTS on 0.1% BSA

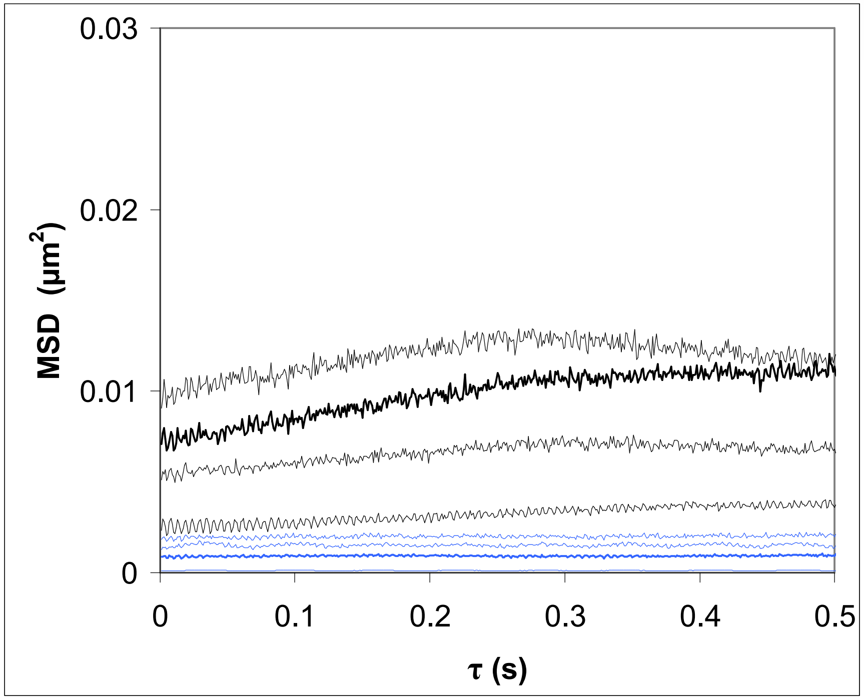
t = 15 min

η_s = 550 nPa s m
= 0.0055 mN s/m

t = 30 min

η_s > Detection limit

Monolayer becomes more rigid over time



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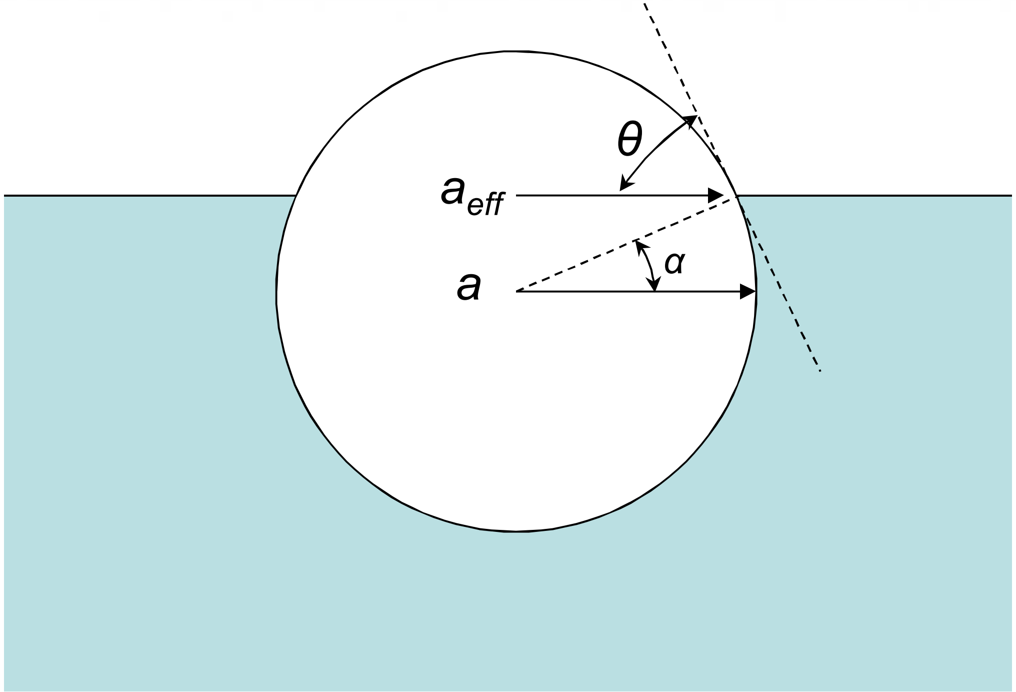
$\theta + \alpha = 90^\circ$

$a_{eff} = a * \cos(\alpha)$

$a_{eff} = a * \cos(90^\circ - \theta) = a * \sin(\theta)$



Computational Model Development

Work is underway in implementing the Newtonian interfacial stress equations in an ALE free surface flow code

This new analysis tool will allow bulk viscosity contributions to be distinguished from surface contributions.

The top line is a standard capillary hydrodynamics implementation.

$$\boldsymbol{n}\cdot(\boldsymbol{\tau}_{in}-\boldsymbol{\tau}_{ext}) = 2H\sigma\boldsymbol{n}+\nabla_s\sigma$$
$$+2H\boldsymbol{n}(\kappa_s+\mu_s)(\nabla_s\cdot\boldsymbol{v})+(\kappa_s+\mu_s)\nabla_s(\nabla_s\cdot\boldsymbol{v})+\mu_s(\boldsymbol{n}\times\nabla_s(\nabla_s\times\boldsymbol{v})\cdot\boldsymbol{n})$$
$$+2\mu_s\left[\left((\boldsymbol{b}-2H\mathbf{I}_s):\nabla_s\boldsymbol{v}\right)\boldsymbol{n}-(\boldsymbol{b}-2H\mathbf{I}_s)\cdot\nabla_s\boldsymbol{v}\cdot\boldsymbol{n}\right]$$

The second line involves second derivatives on the free surface and requires surface degrees of freedom (shell equations) to implement.

The complex form of the Boussinesq-Scriven equations

The third line is zero for spherical and cylindrical geometries and has yet to be implemented.

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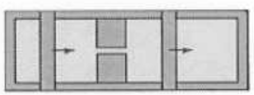
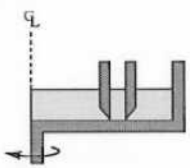
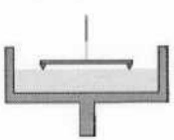
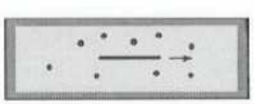
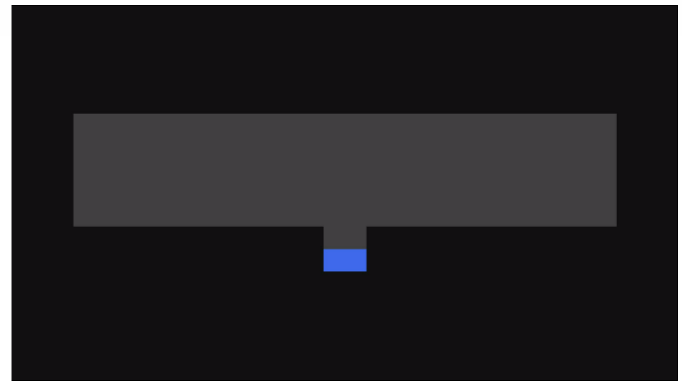
Measuring Interfacial Rheology: Shear

Table 2.1: Comparison of Different Devices to Measure Mechanical Shear Properties of Langmuir Films

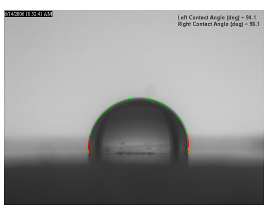
Surface Rheometer	Advantages	Disadvantages	Dynamic Range	Sensitivity mN-s/m	References
Canal Viscometer 	- Easy to implement - Straightforward determination of μ_s - High sensitivity - Can study well-developed flows (high strains)	- Pressure gradients - Assumes Newtonian interface (require velocity profile to apply for nonNewtonian surfaces) - Variation in shear rate across the channel	***Steady Shear*** 0.1 to 1 s^{-1}	$\mu_s > 10^{-4}$	[38-42]
Deep-Channel Viscometer 	- High sensitivity - Can be used on liquid-liquid interfaces	- Requires tracer particles - Cannot change film Π - Complete analysis of flow required for data analysis - Need to assume constitutive relation	***Steady Shear*** 0 to 10 s^{-1} ***Oscillation*** 0.6 to 0.8 rad/s	$\mu_s > 10^{-4}$	[45-48]
Torsional Devices 	- No tracer particles - Directly measure surface stress - High sensitivity to surface stresses over bulk stresses	- Challenging to design trough with circular symmetry ***Steady Shear*** - Complicated flow field ***Oscillations*** - Have to change torsion wire - Probe inertia	***Steady Shear*** 10^{-4} to 10 s^{-1} ***Oscillation*** 0.01 to 3 rad/s	$\mu_s > 10^{-4}$	[49-54]
Rod Viscometer 	- Directly measure surface stress - High sensitivity to surface stresses over bulk stresses - Low inertia (few moving parts)	- Flow must be visualized with tracer particles - Cannot change film Π - Pressure Gradients - Upper limit on Π (rod can sink)	***Steady Shear*** 0.01 to 0.2 $s^{-1\dagger}$	$\mu_s > 10^{-2}$ ***Theoretically Predicted*** $\mu_s > 10^{-5}$	[55]

Validate Using Drop Spreading

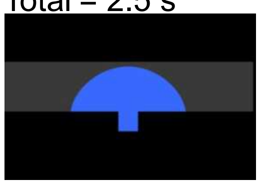
- Dynamic wetting of Sylgard on polycarbonate

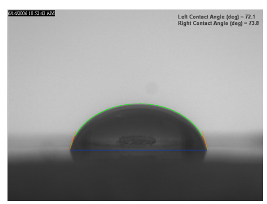


Direct comparison:

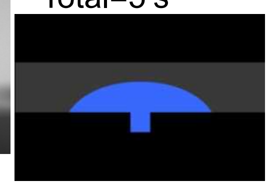


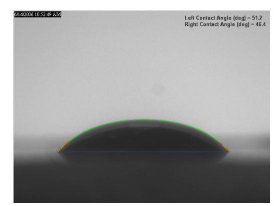
End of injection
Total = 2.5 s





Gravity only, 2 s
Total=5 s





Gravity only, 8 s
Total=11 s

- 1mM F108 multiple particle tracking
- 0.1% BSA particle tracking
  - too stiff for passive (maybe MIR-active will work)

  - 2.5um SiO2–OTS on 1 mM F108
    - Uncorrected
    - Drift corrected
    - Oscillation corrected – notch filter, still see oscillation in MSD
    - Try to remove oscillation from tracking

  - 2.5um SiO2–OTS on 0.1% BSA
  - 2.5um SiO2–APTES on 0.1% BSA