Structure and Rheology of Surfactant Solutions

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Sponsors: Procter and Gamble, NSF

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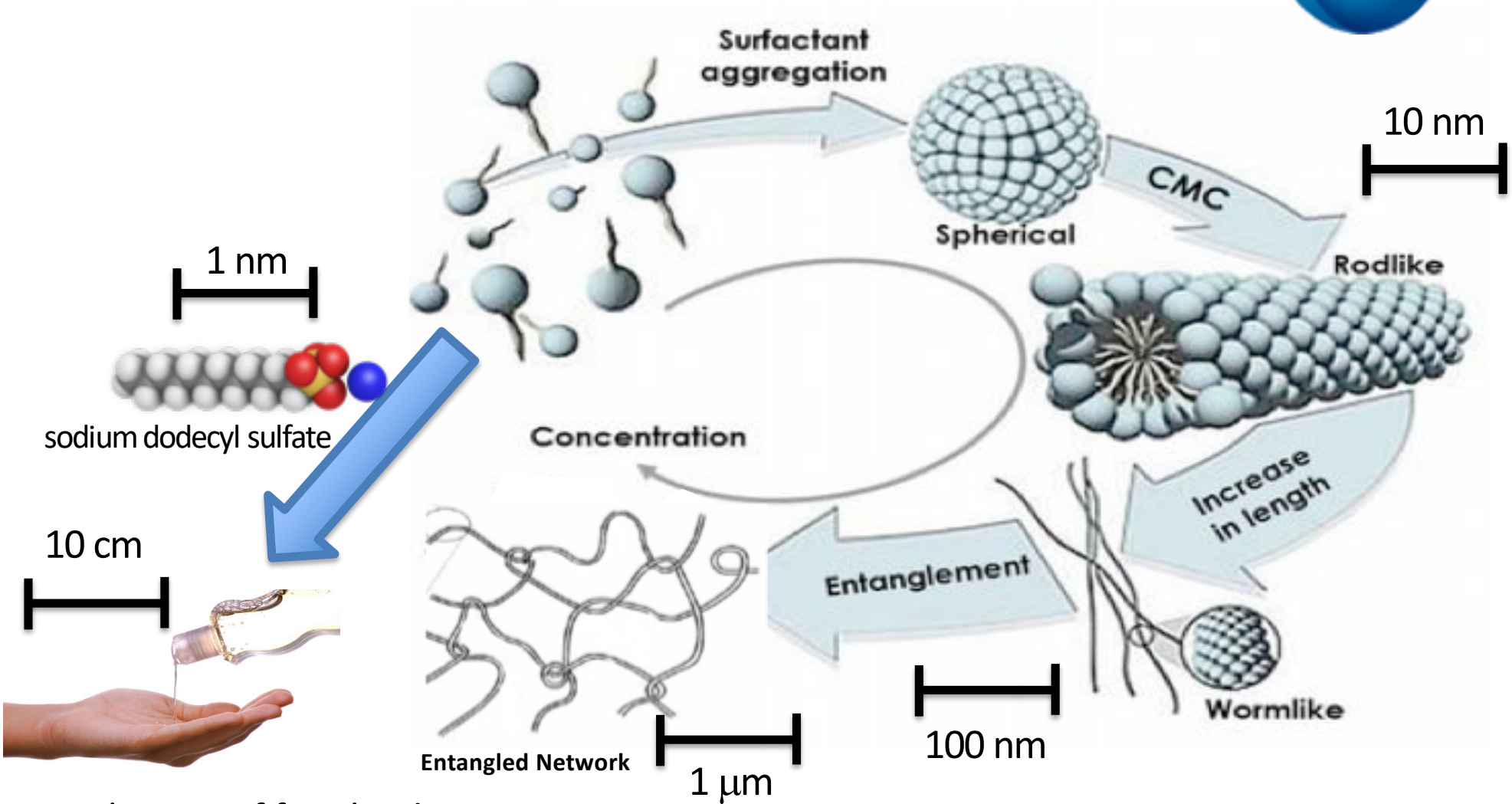
Taraknath Mandal

Peter Koenig

Mike Weaver

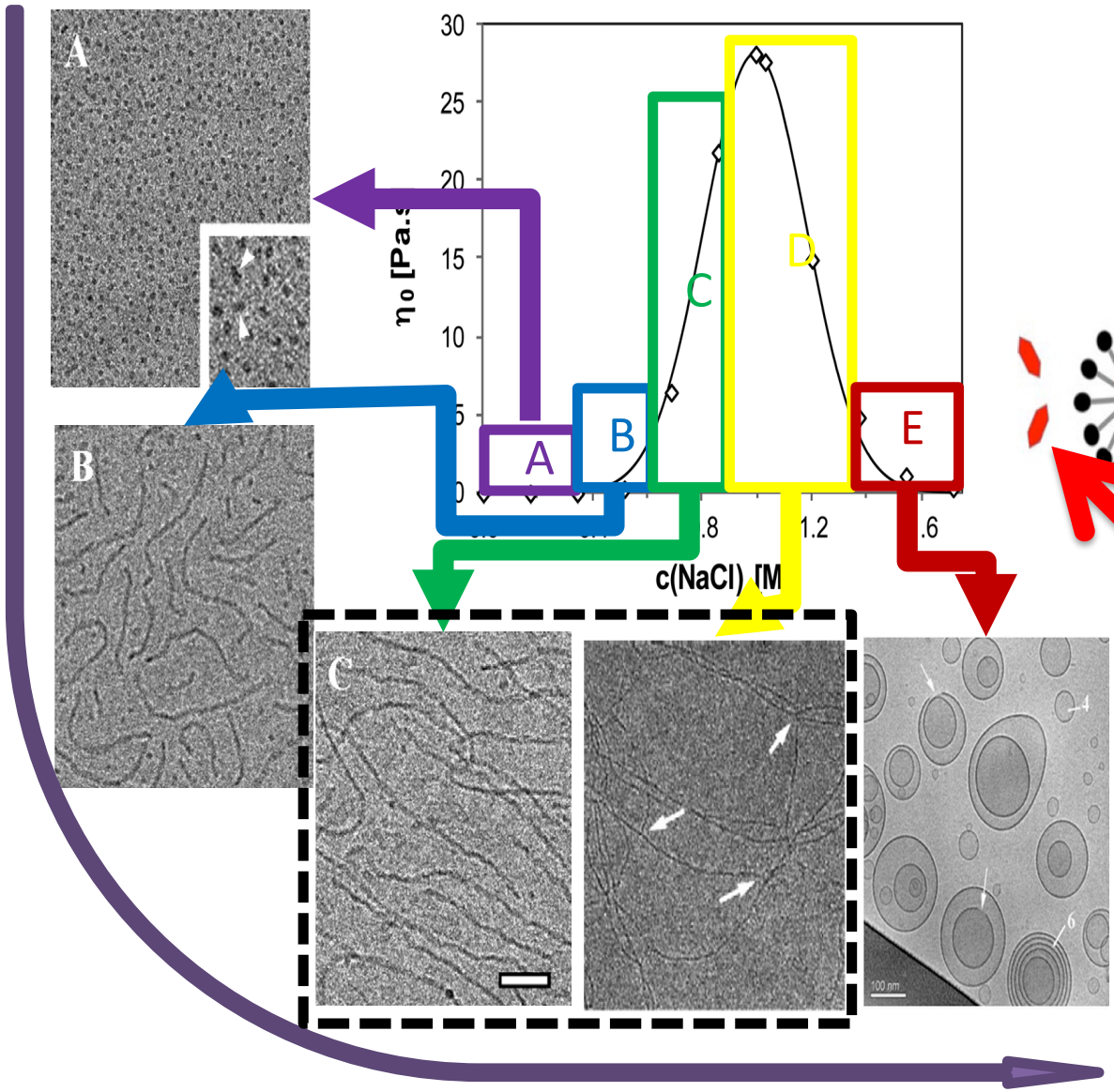
The Challenge of Multiple Length and Time Scales in Surfactant Solutions



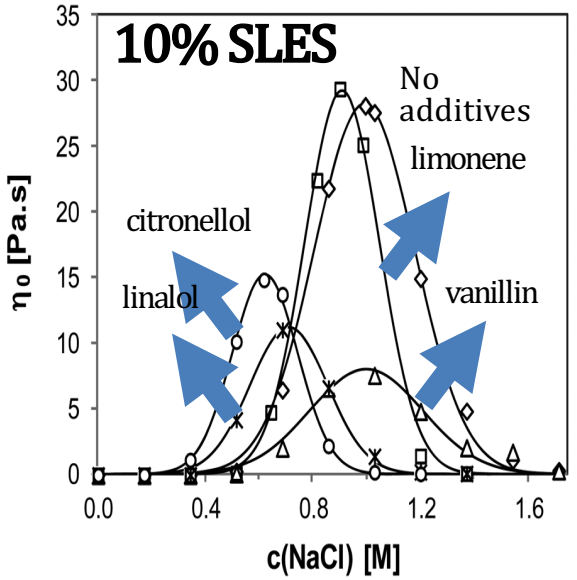
10^{23} degrees of freedom!

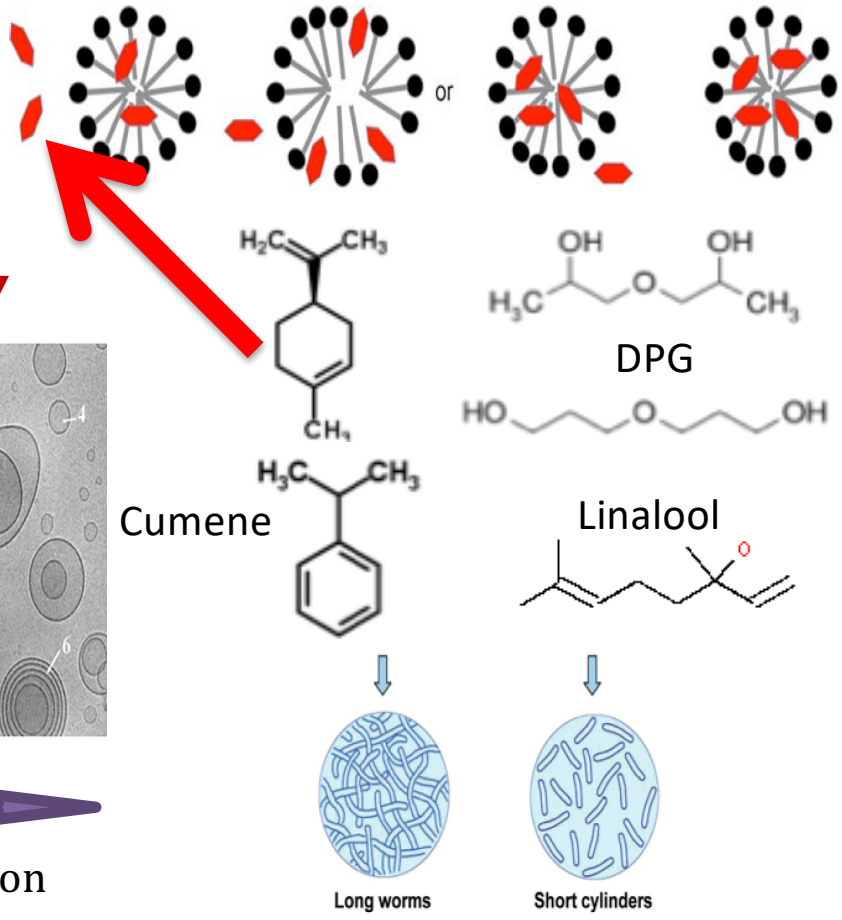
http://www.ifnh.ethz.ch/vt/research/projects/vivianel

Micellar solutions: the salt curve



Increase surfactant/salt concentration

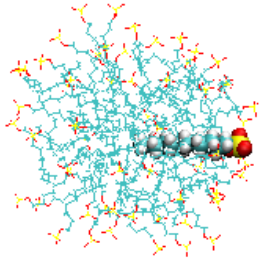


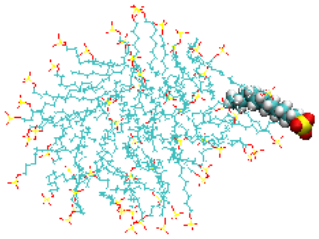


Umbrella Sampling

Weighted Histogram Analysis Method (WHAM)

PMF $w(z)$





z = r, radial coordinate

molecular dynamics (MD) simulations:

$$m_i \frac{d^2 \mathbf{v}_i}{dt^2} = \mathbf{f}_i$$

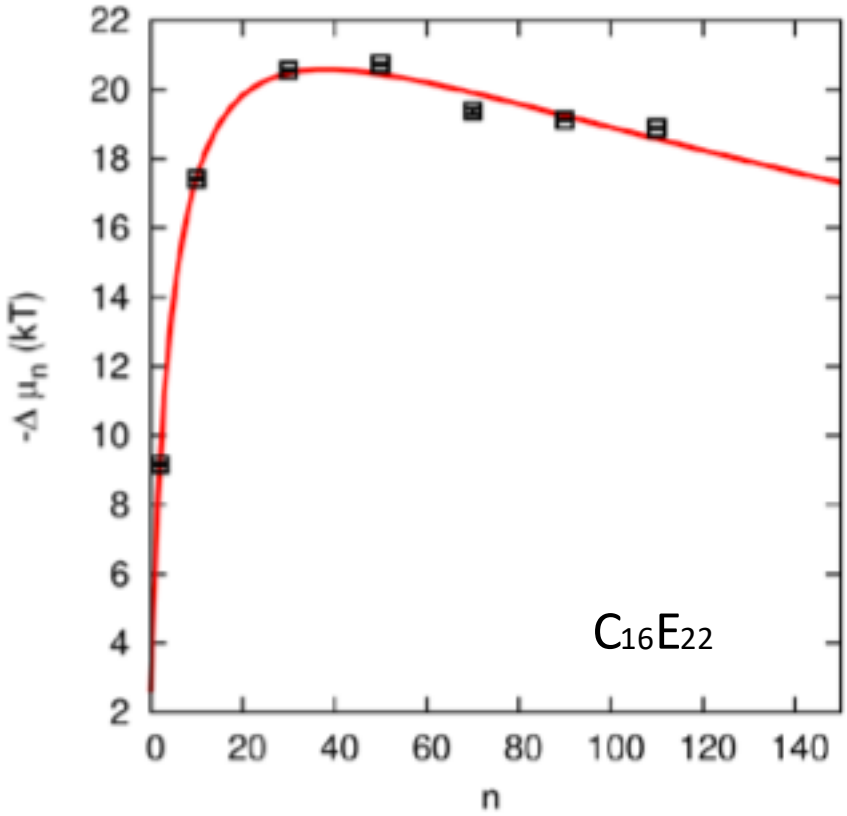
Video from student Kyle Huston

density $\rho(z)$

Micelle Size Distribution

(inferred from potentials of mean force)

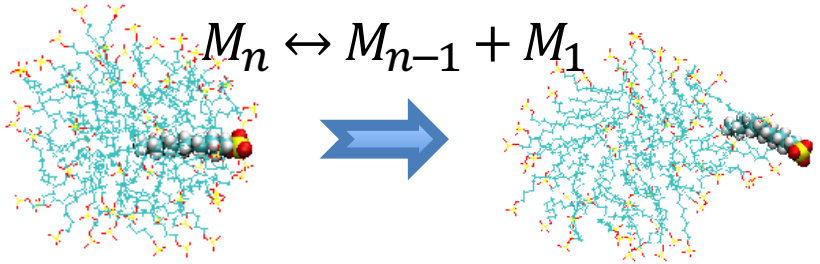
Yuan and Larson, JPC B (2015)



PMF = $\Delta\mu_n^0 = \mu_n^0 - (\mu_{n-1}^0 + \mu_1^0)$

$\mu_n = \mu_n^0 + k_B T \ell n(X_n)$

$M_n \leftrightarrow M_{n-1} + M_1$



n surfactants

n-1 surfactants

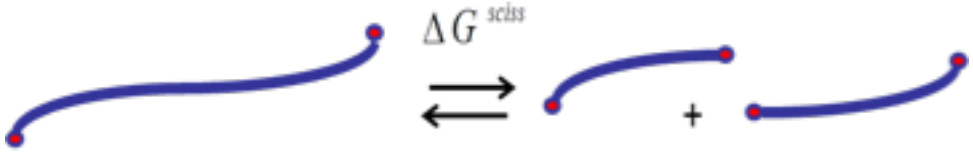
$$X_n = X_1^n \exp\left(-\frac{1}{k_B T}\sum_{j=2}^{n}\Delta\mu_j^0\right)$$

$$X_n = X_{n-1} X_1 exp\left(-\frac{\Delta\mu_n^0}{k_B T}\right)$$

12:07:01

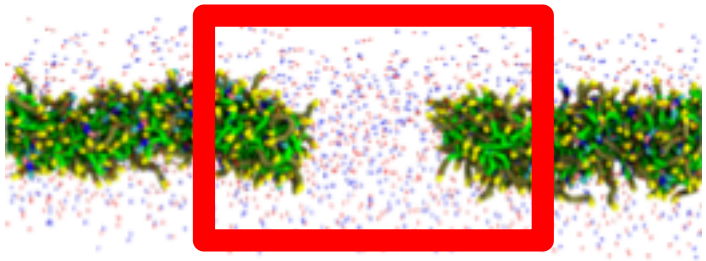
Time

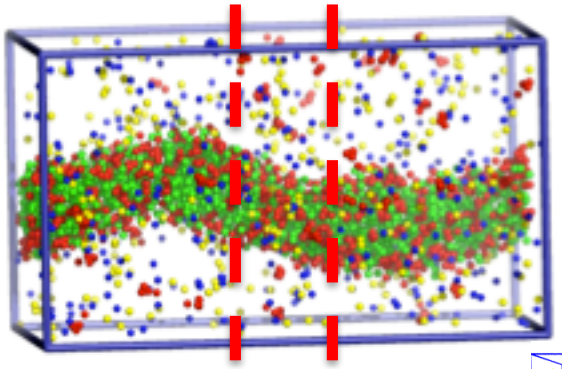
Simulation of scission energy using weighted histograms



Cates, M., & Candau, S., J. Phys.: Condens. Matter (1990), 6869.

$$\bar{L} \propto \exp\left(\Delta G^{sciss} / kT\right) \qquad c(L) \sim \exp(-L/\bar{L})$$





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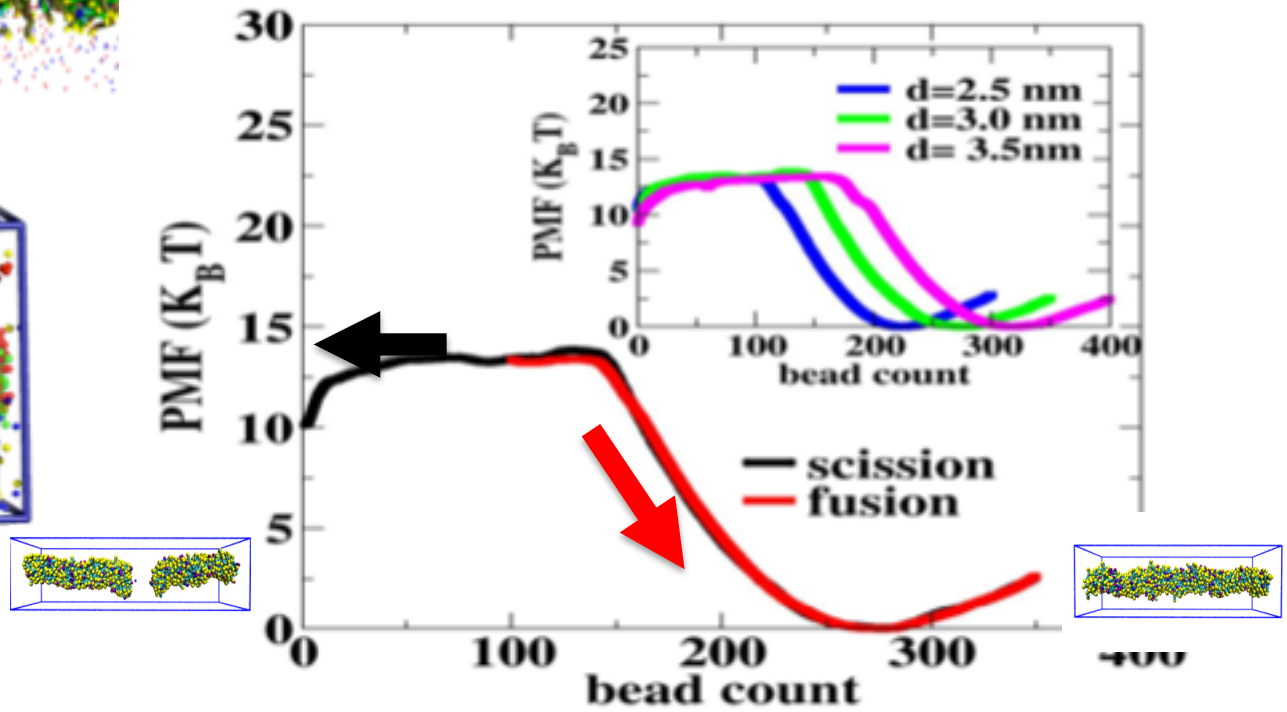
Peter Koenig, P&G

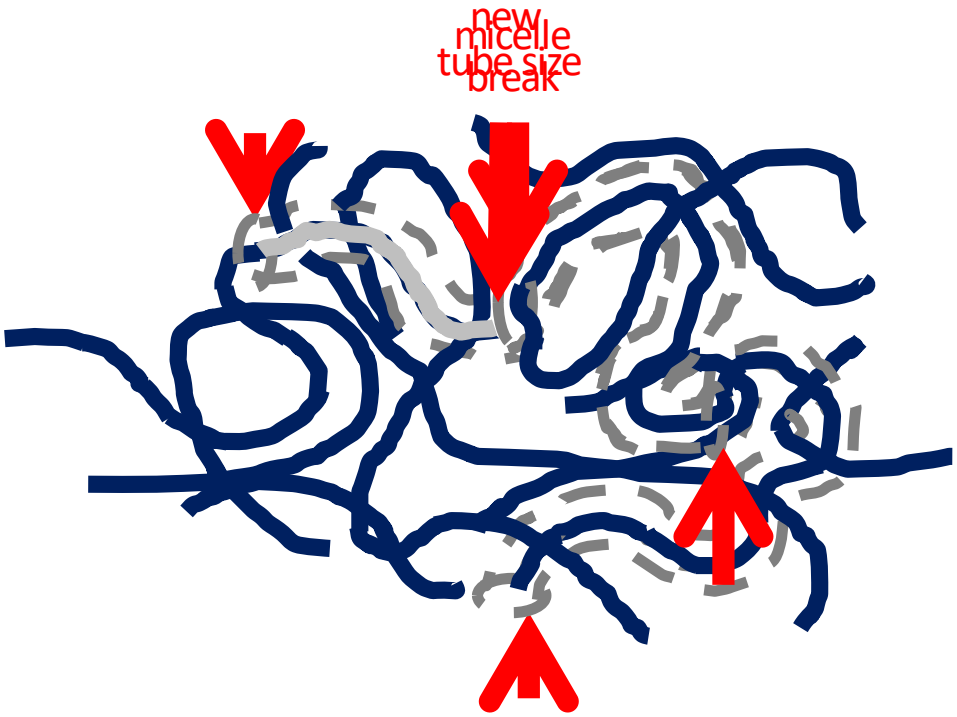
Use bead count in region to bias simulation towards scission/fusion. *PLUMED, Comp. Phys. Comm. 180 (2009), 1961*

Taraknath Mandal

$$V_s = \frac{1}{2} k(N(\{x_i, y_i, z_i\}, v) - N_0)^2$$



Micellar relaxation dynamics

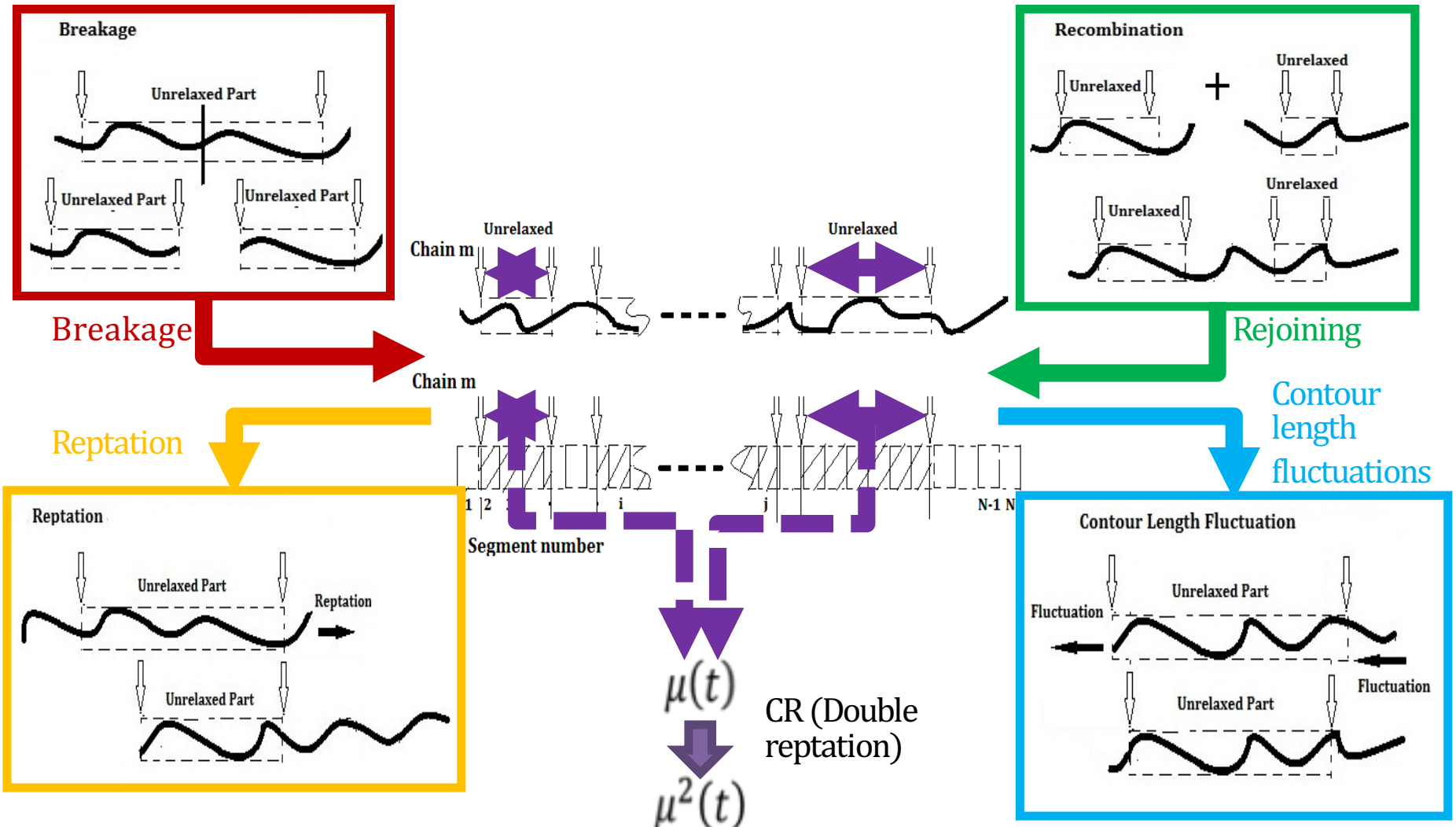


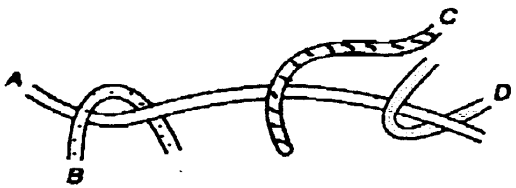
Reptation:
Edwards, De Gennes,
$\tau_{rep} \sim L^3$

Micelle breakage &
Re-joining:
M.E. Cates (1989):
$\tau_{break} \sim 1/L$

Slide from Peter Koenig, P&G

Pointer algorithm: simulation of ensemble of micelles

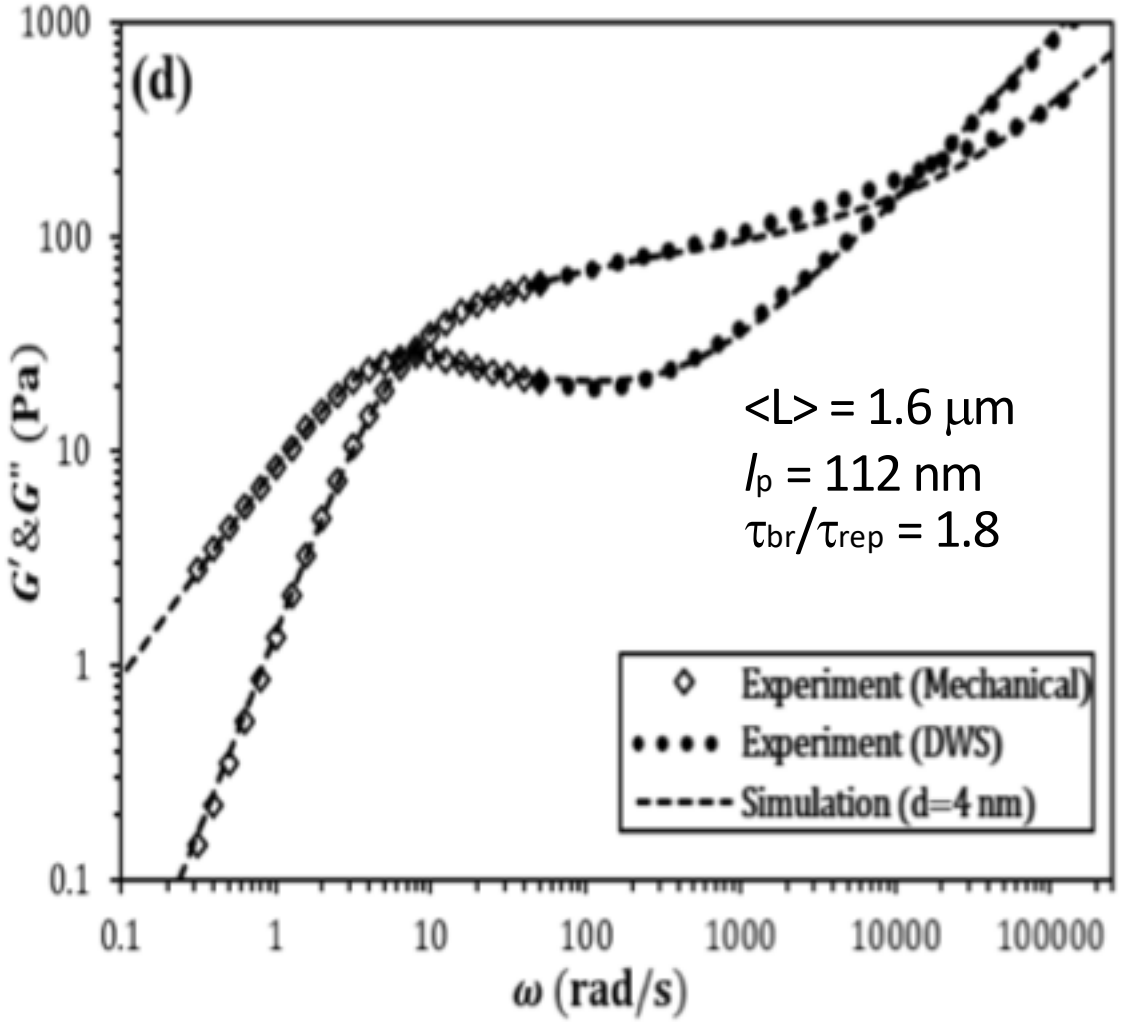




$$G(t) = G_N \mu^2(t) + \text{Rouse} + \text{bending modes}$$

Zou, W. and Larson, R.G. J Rheology 58 (2014) 681-721.

Fitting Data

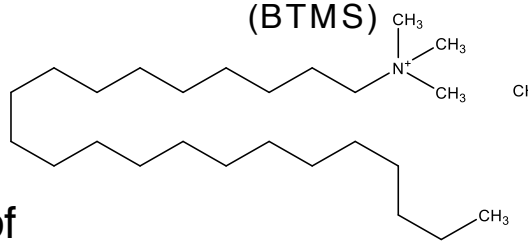


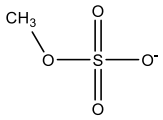
Procter and Gamble is using this predictive method in their research into design of shampoos and body washes

Lamellar Gels for Hair Conditioners

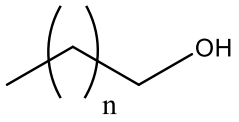
Excess Water (85-95%) + **Cationic Surfactant** + **Fatty Alcohol**

Behentrimonium methosulfate (BTMS)





Cetostearyl Alcohol
(cetyl : stearyl = 1:2.5 by weight)



n = 14-16

Forms a **lamellar gel network** of

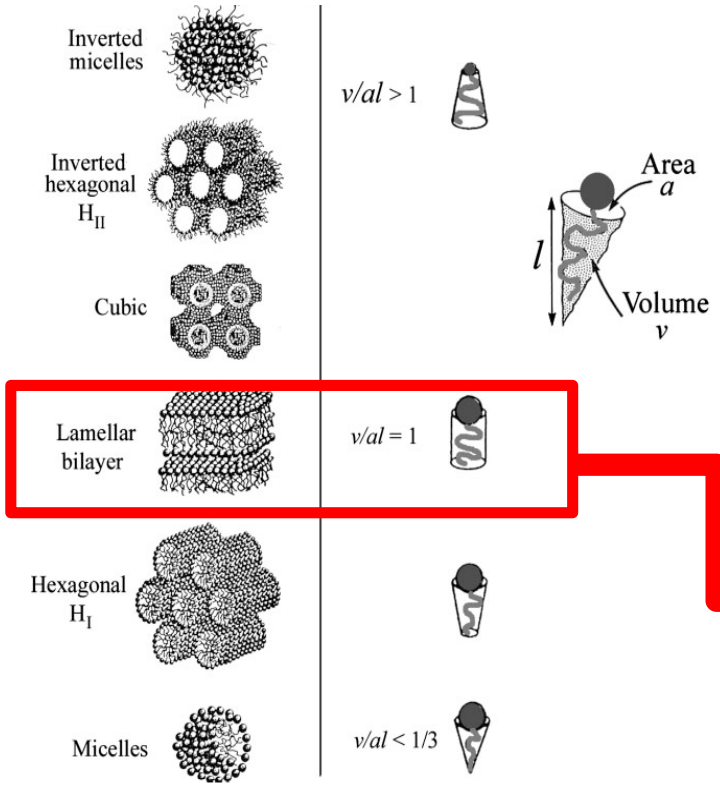
1. regularly spaced bilayers with
2. trapped interlamellar water and bulk water

Additives

- Salts (NaCl/EDTA)
- Perfumes
- Preservatives

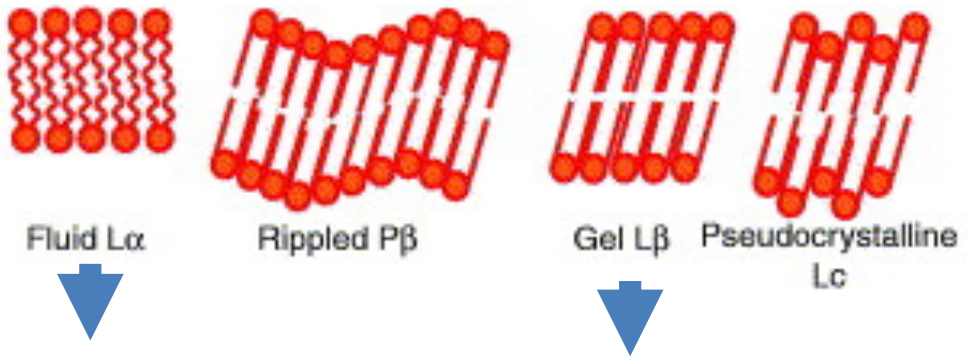
S. Fukushima, M. Takahashi, and M. Yamaguchi, “Effect of cetostearyl alcohol on stabilization of oil-in-water emulsion. I. Difference in the effect by mixing cetyl alcohol with stearyl alcohol,” *J. Colloid Interface Sci.*, vol. 57, no. 2, pp. 201–206, 1976.

Self-assembly of surfactants in water



- In these cosmetic emulsions, critical packing parameter ~ 1
  - Form lamellar bilayers
- Two different phases of lamellar bilayer structures depending on the temperature :
  - Liquid crystalline (L_α) phase – above gel transition temperature
  - Gel phase (L_β) phase – below gel transition temperature

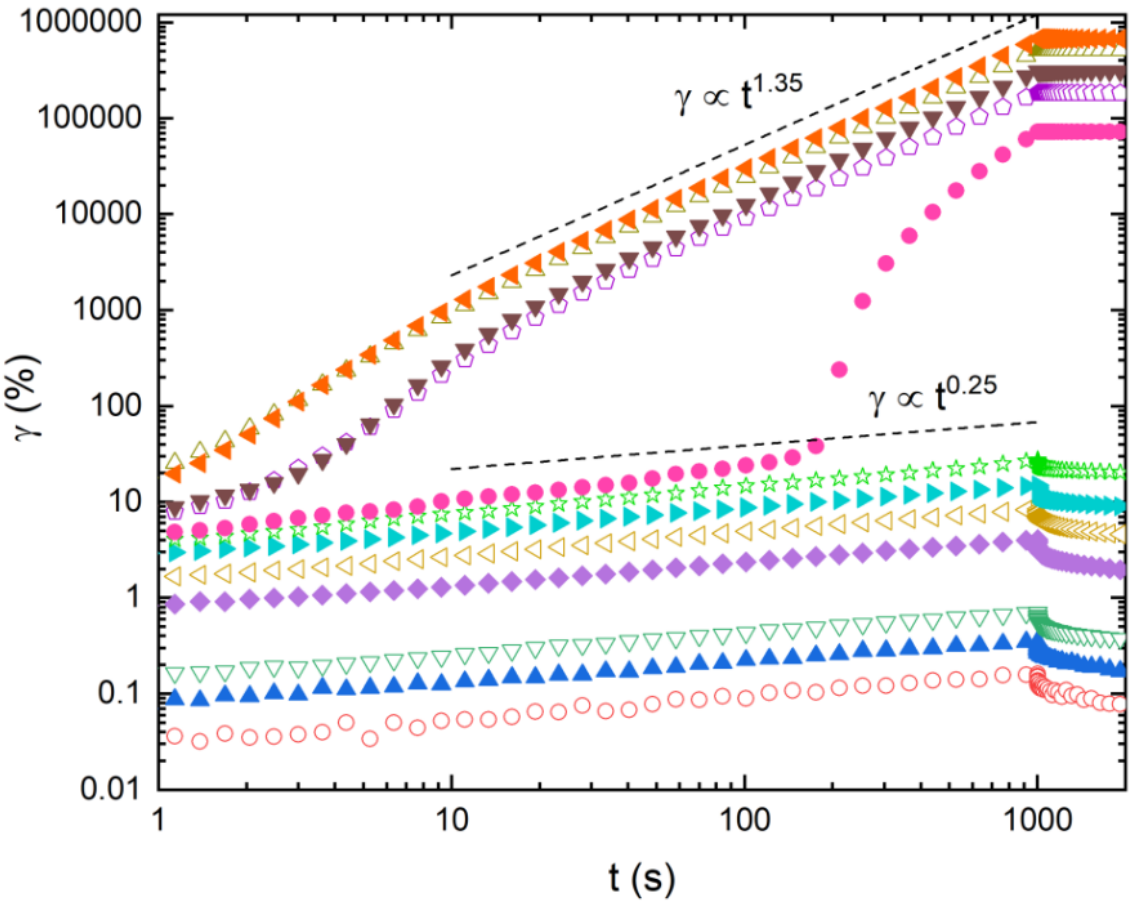
Hydrocarbon chains in the bilayer can exist in a number of physical states:



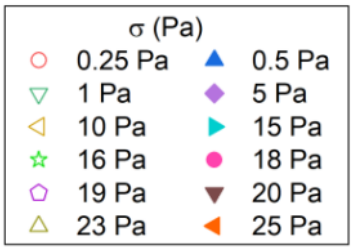
Disordered state

Ordered state: Hexagonally packed

Solid-like Creep Response and “Apparent Yield-Stress”



< 18 Pa	Solid-like creep response, with $\gamma \propto t^{0.25}$	Partial strain recovery
> 18 Pa	Apparent yielding behavior, with $\gamma \propto t^{1.35}$	No strain recovery, flows like a fluid

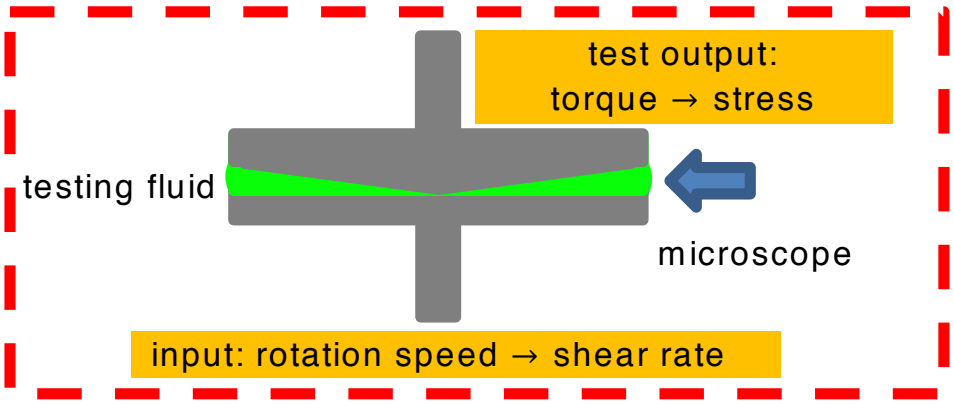


Materials:

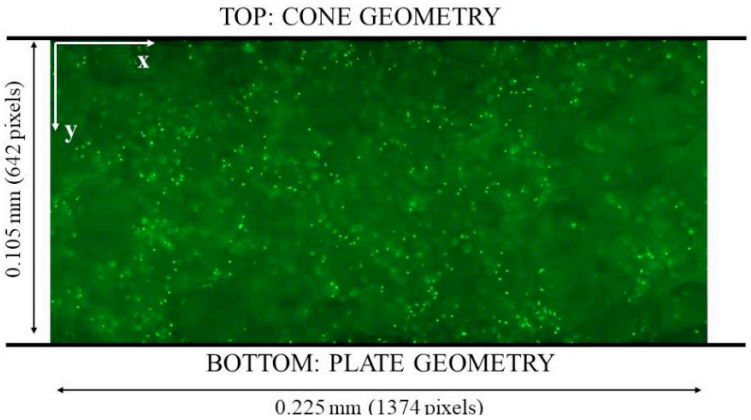
Ternary system lamellar gel network seeded with fluorescent tracer particles (diameter 1.5 um, 0.1 vol%).

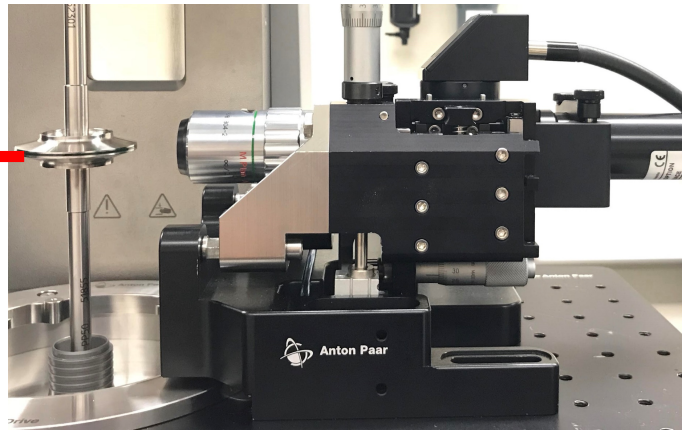
Instruments:

- MCR 702 rheometer
- Cone (2°) and plate geometry
- Fluorescent microscope

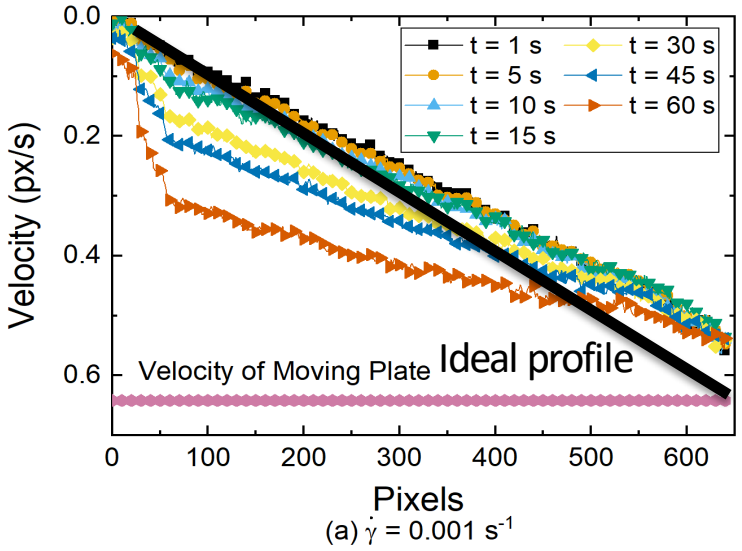


Example of velocimetry raw data

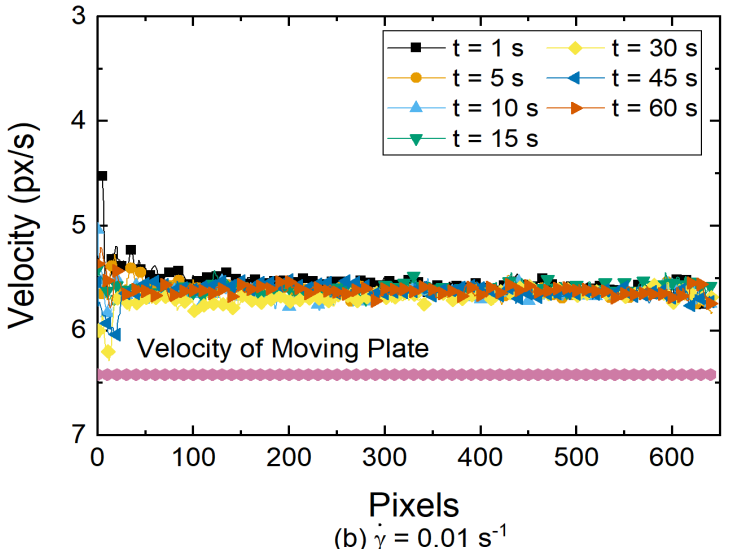




Shear banding



(a) $\dot{\gamma}$ = 0.001 s^{-1}



(b) $\dot{\gamma}$ = 0.01 s^{-1}

Plug flow

END