Modeling of Complex Fluids: Wormlike Micellar Solutions, Polymers and Mucins

SIAM Julian Cole Lectureship

July 11, 2018

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Julian D. Cole 1925-1999

NAE, NAS, AAA&S, SIAM von Karman Prize

(1947 Chuck Yaeger – broke the "sonic barrier")

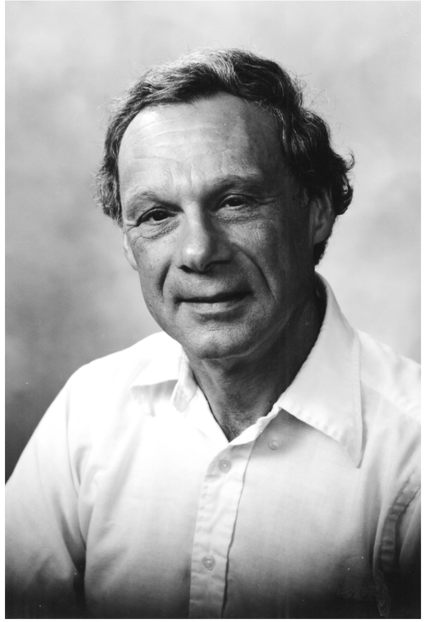
Perturbation methods

$$\epsilon \frac{d^2 u}{dt^2} + \frac{du}{dt} + u = o$$

$$\epsilon << 1$$

$$\epsilon u_{,yy} = u_{.t} + u u_{.y}$$

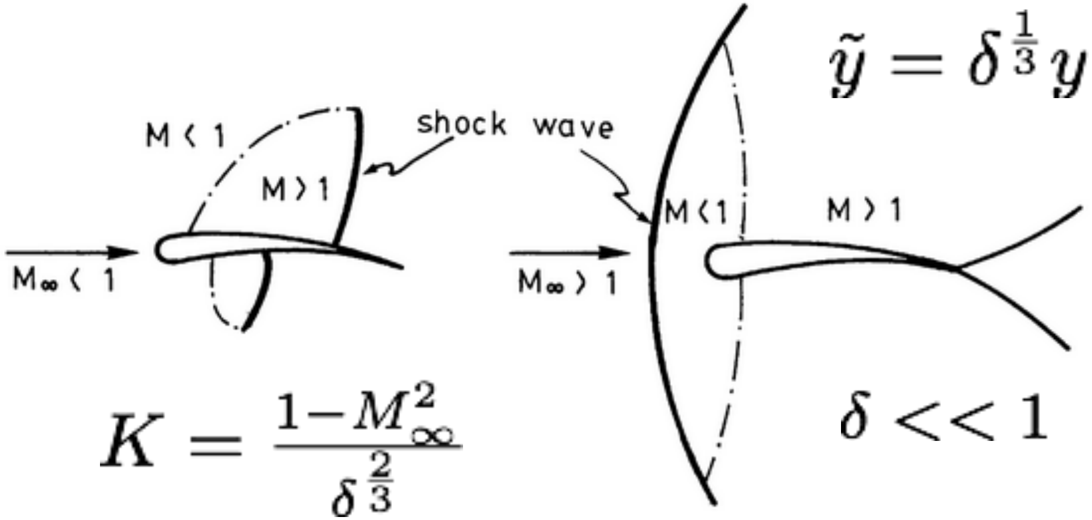
partial derivative



Transonic small disturbance equation

$$(K - (\gamma + 1)\phi_{,x})\phi_{,xx} + \phi_{\tilde{y}\tilde{y}} = 0$$

$$\tilde{y} = \delta^{\frac{1}{3}} y$$



$$K = \frac{1 - M_\infty^2}{\delta^{\frac{2}{3}}}$$

$$\delta << 1$$

Math is for Solving Problems - SIAM, 1996

J.D. Cole books

- *Perturbation Methods in Applied Mathematics* 1968 Ginn-Blaisdell
- *Perturbation Methods in Applied Mathematics* 1981, *Perturbation Methods in Applied Mathematics* 1985, *Multiple Scale and Singular Perturbation Methods* 1996 (with J. Kevorkian) Springer
- *Similarity Methods for Differential Equations* 1974 (with G. Bluman) Springer
- *Transonic Aerodynamics* 1986 (with P. Cook) Elsevier

36 PhD students – Cal Tech, UCLA, and RPI

- 18 **Journals** (newest: Data Science)
- 21 **SIAM Interest Groups** (newest being Applied Mathematics Education, the Mathematics of Planet Earth and this meeting co-located with Materials Science SIAG)
- **Books** (and discounts for members!)
- **Geographic Sections** (7 US, 5 non US: newest; Texas-Louisiana, Pacific Northwest sections.
- **Student sections**, Gene Golub summer school
- Committees - to support SIAMs mission
- **Meetings** (like this one and smaller more topical meetings)
- Science Policy!
- News
- **Prizes**

- To all of you who have volunteered, whether through your student section, as an editor or associate editor of a journal, as a minisymposium organizer, as a speaker, as a committee member, . . . **THANK YOU!**

- To all of you in the audience who aren't members, join up! There are many benefits (Book discounts etc.)

- And to those of you who are members – its great. SIAM looks forward to your engagement, involvement and suggestions!

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Complex Fluids

Polymers, colloidal fluids, wormlike micelles:

- Mucin, bodily fluids (eye tear film, saliva, lung mucous)
- Shampoo/detergent
- Entangled polymers (plastics)
- Foods (ketchup)
- Toys (silly putty, oobleck)

A *polymer* is a long string like molecule made of chemical units (more than several thousands) called monomers. (proteins, rubber)

A *colloid* is a mixture in which small particles are dispersed in a fluid. (milk)

A *wormlike micelle* (surfactants) . . . .

Complex Fluids

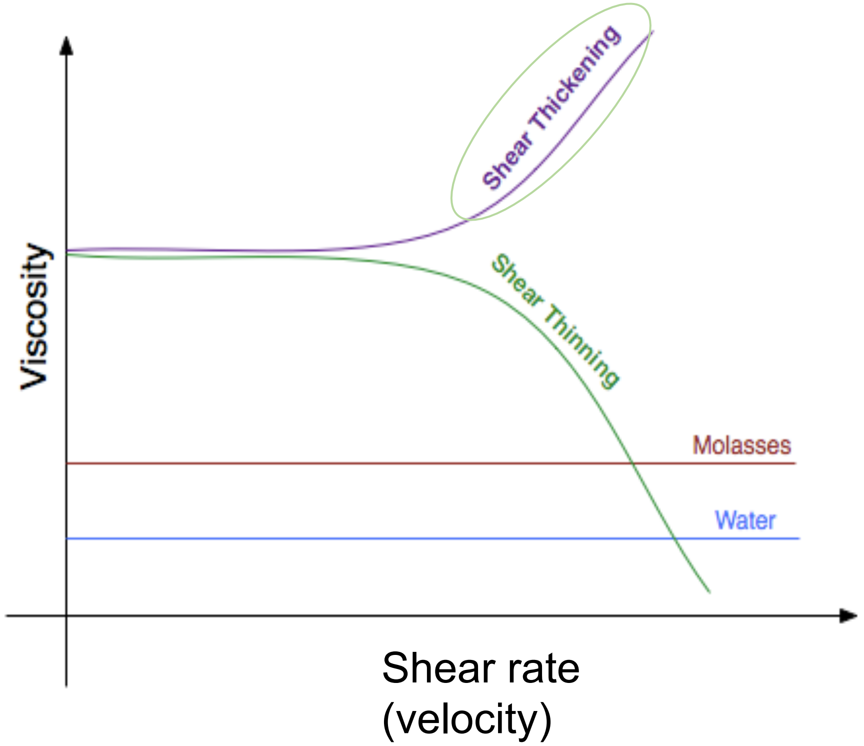
Properties may include:

- High viscosity

- Shear thickening
- Shear thinning

- Elasticity (recoil)
- Extensional fracture

- Self healing (self assembling)



Multiple Scales

- Multiple time scales

silly putty

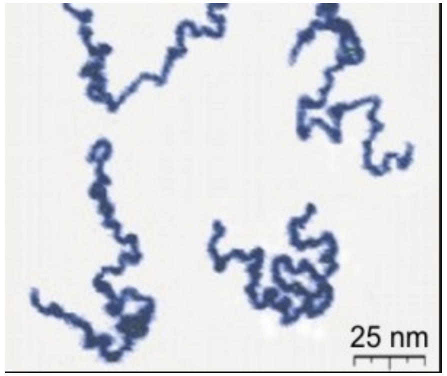
spagetti

- Multiple length scales (micro vs macro)

  - human hair r=25 microns, L=6”
    aspect ratio L/r = 3,000

  - wormlike micelle r=0.001 micron, L=2 microns
    aspect ratio L/r = 2,000

  Floppy, WORMY



polymer chains
https://en.wikipedia.org/wiki/Polymer

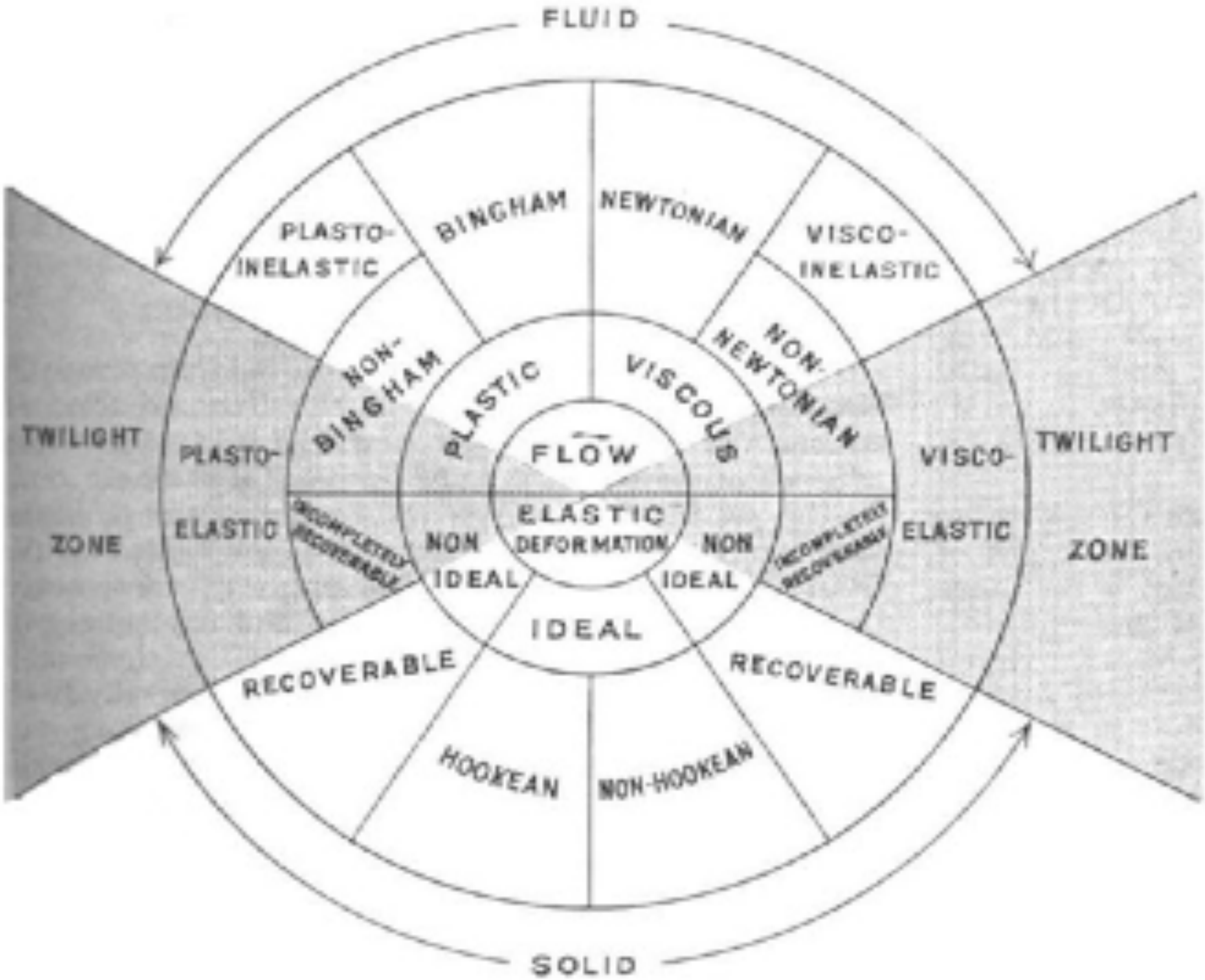
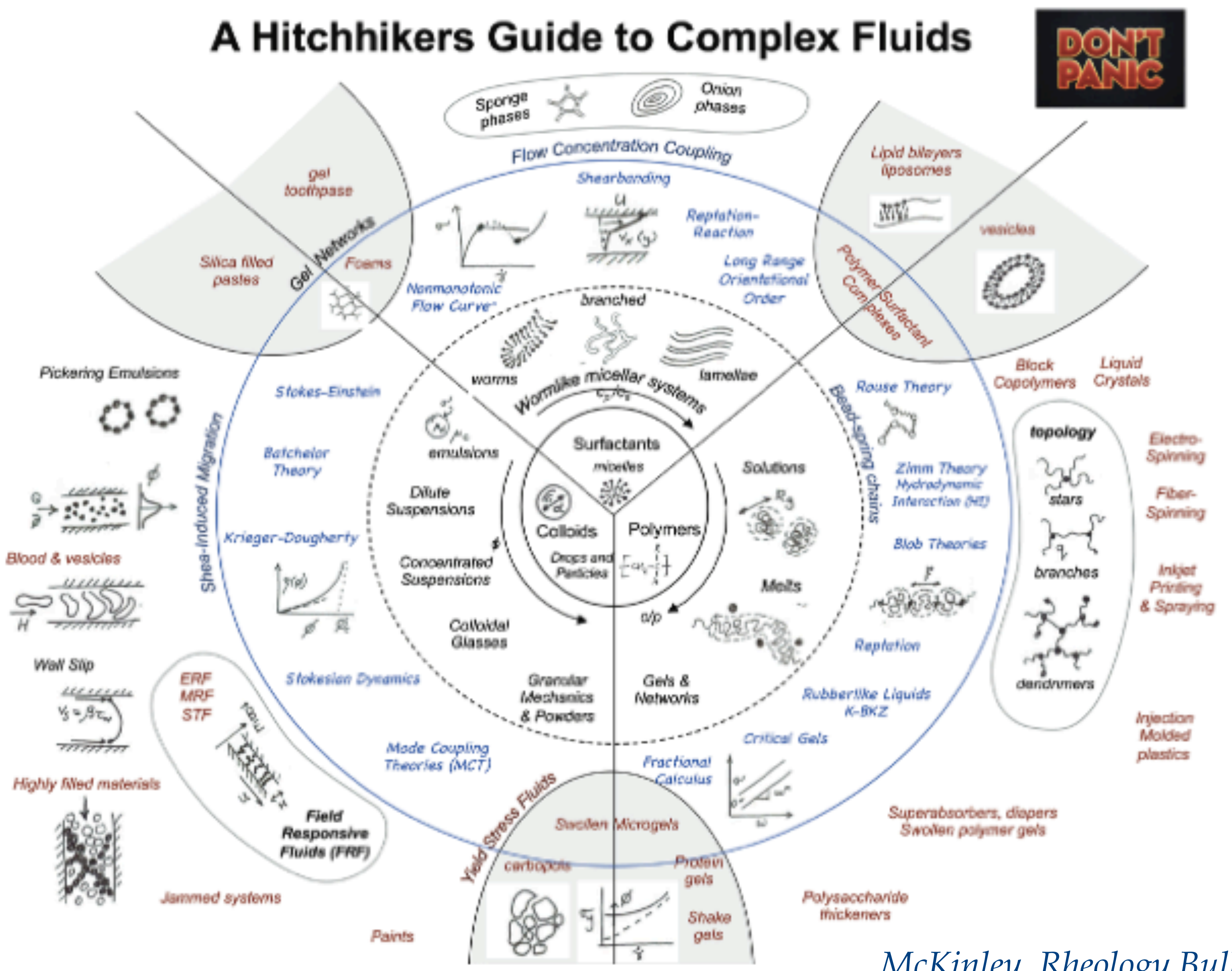


Figure 1: A Rheological Chart that mapped the continuum world of complex fluids and soft solids soon after the birth of rheology (L. Bilmes, 1942).

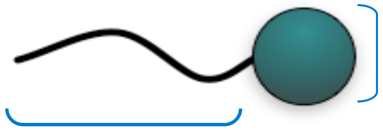
A Hitchhikers Guide to Complex Fluids



McKinley, Rheology Bulletin, 84(1) Jan. 2015

Wormlike Micellar Solutions

Surfactant Molecules

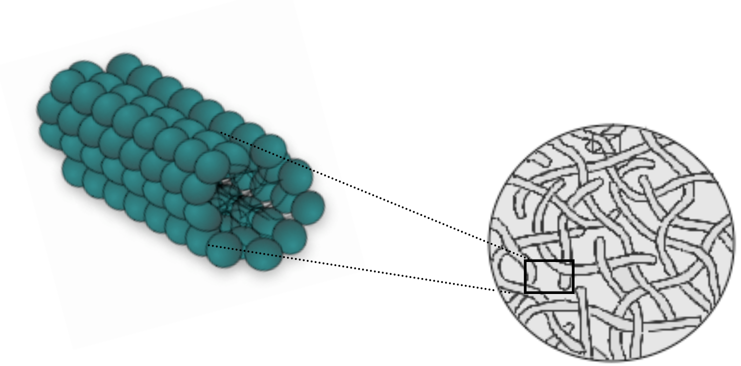


Hydrophilic Head

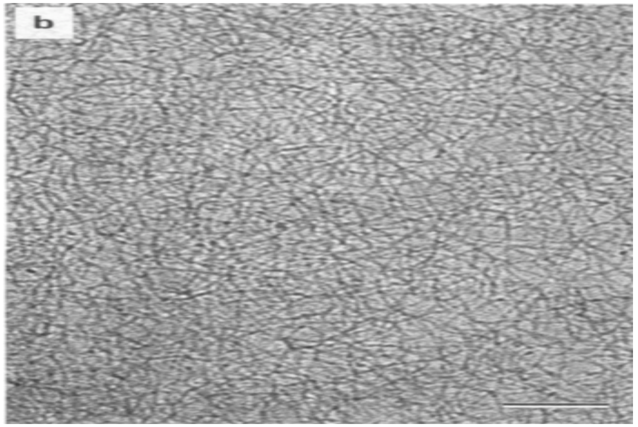
Hydrophobic Tail

Self-assemble

Wormlike Micelles

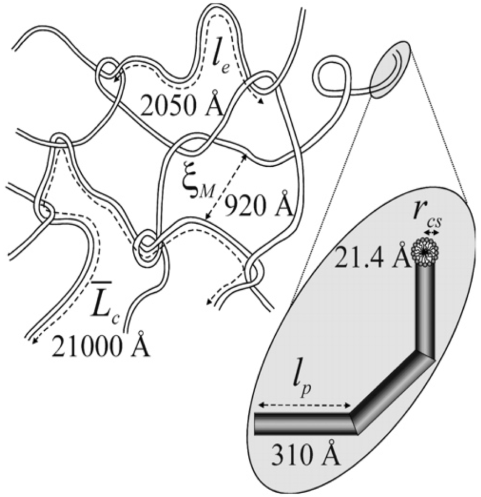


Entangled Systems



Clausen et al. (1992) J. Phys. Chem.

bar = 100nm



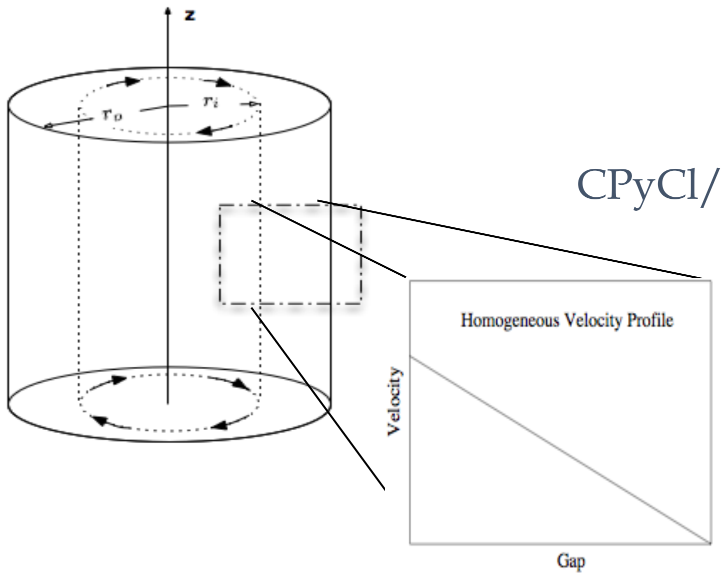
Schubert et al. (2003) Langmuir

"Living polymers" – worms break and reform continuously.

Properties depend on temperature, salt concentration etc.

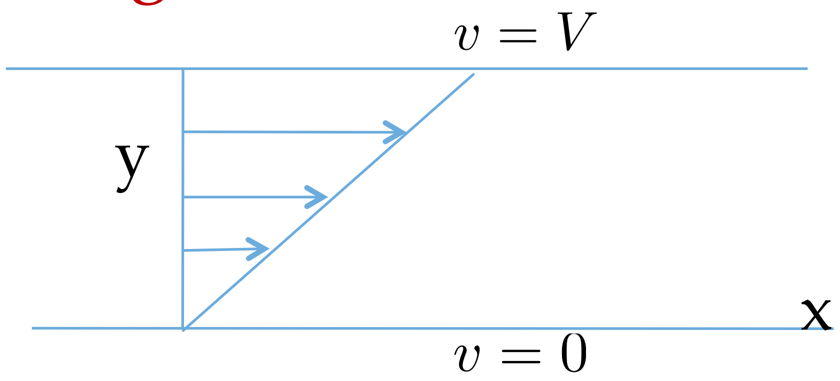
Wormlike Micelles in Shear Flow

Shear rate control:



CPyCl/NaSal

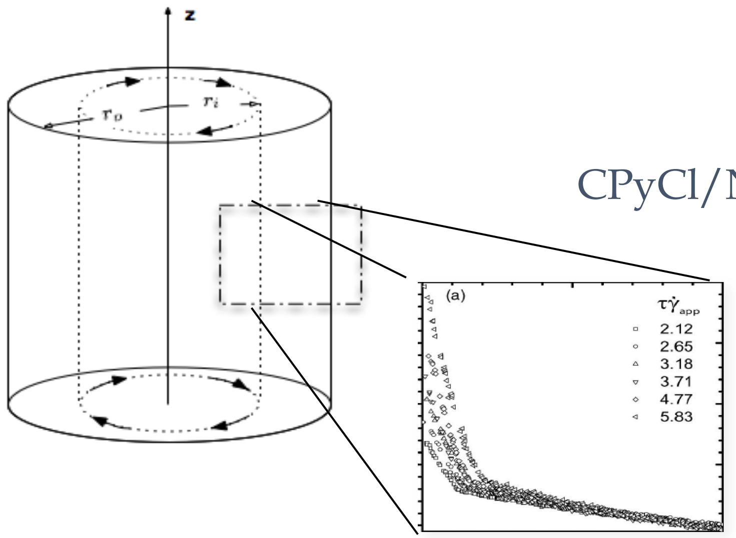
Shearing flow



- Newtonian "linear" velocity response

Wormlike Micelles in Shear Flow

Shear rate control:



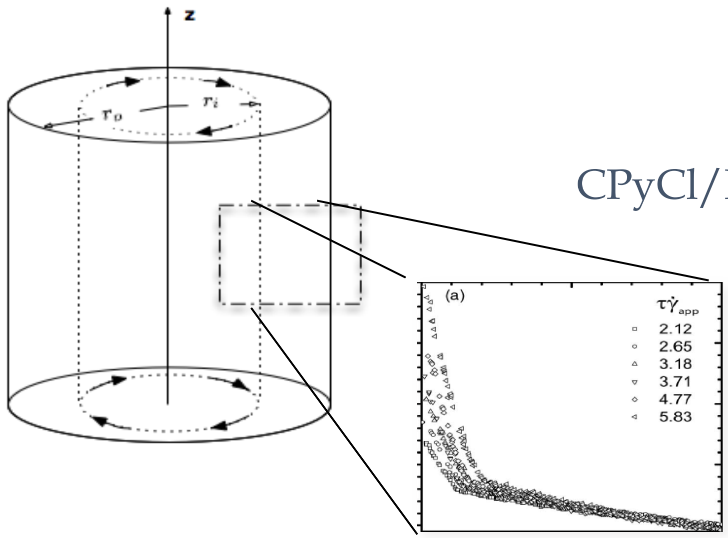
CPyCl/NaSal

At higher velocities shear bands appear ––a high shear rate band near the inner wall and a low shear rate band near the outer wall

Hu and Lips (2005) J. Rheology

Wormlike Micelles in Shear Flow

Shear rate control:

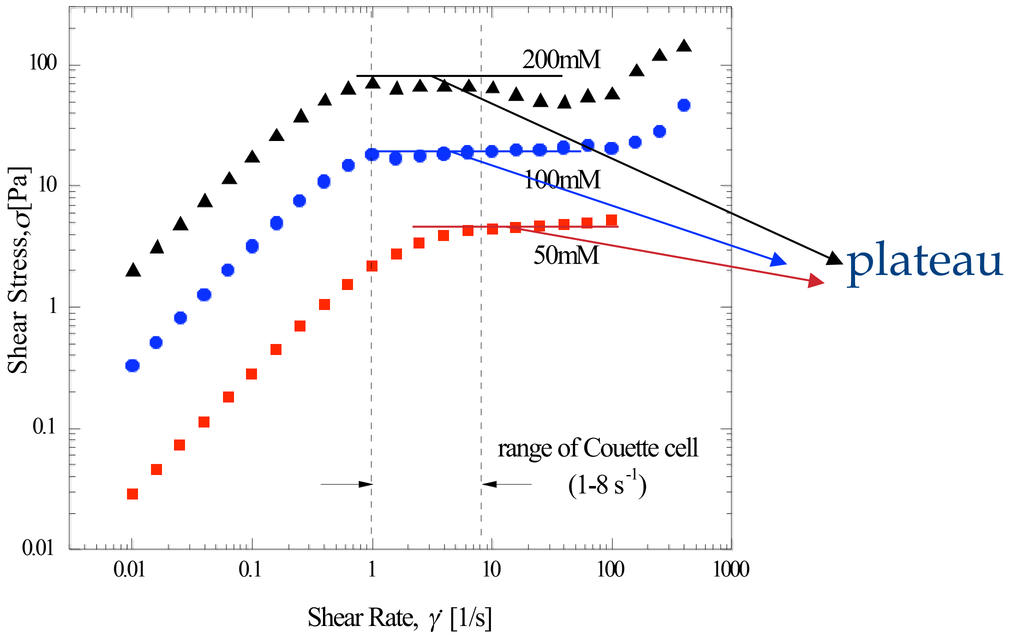


CPyCl/NaSal

At higher velocities shear bands appear ––a high shear rate band near the inner wall and a low shear rate band near the outer wall

Hu and Lips (2005) J. Rheology

Flow curve plateau

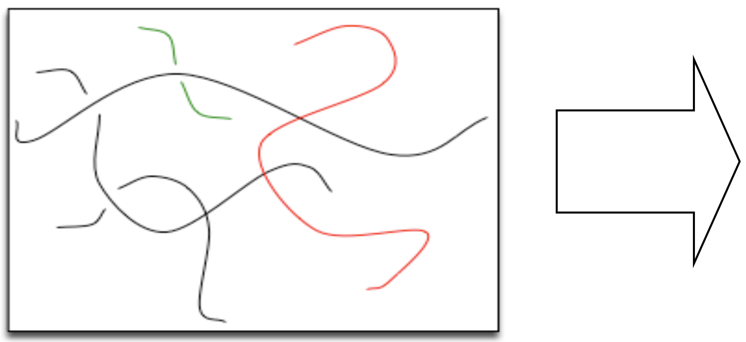


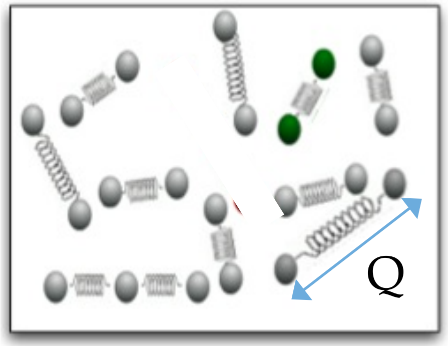
shear stress - stress at the inner wall

apparent hear rate – inner wall velocity/gap

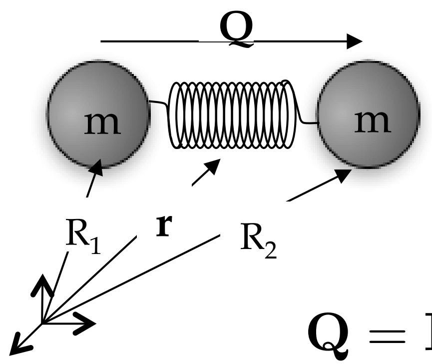
Miller and Rothstein (2007) JNNFM

Elastic Dumbbell Theory





$\psi(\mathbf{r}, \mathbf{Q}, t)$



$\mathbf{Q} = \mathbf{R}_2 - \mathbf{R}_1$

Q - the dumbbell configuration vector - stretch and direction

Configuration distribution function $\psi(\mathbf{r}, \mathbf{Q}, t)$

Polymer stress: $\boldsymbol{\sigma}_p = -\int \mathbf{Q}\mathbf{F}_s(\mathbf{Q})\psi(\mathbf{Q}, t)d\mathbf{Q}$

Bird et al. (1986)

Elastic (Linear) Dumbbell Equations

- Langevin - stochastic differential - equation - mesoscale

$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + [\mathbf{v}_0 + \boldsymbol{\kappa}\cdot\mathbf{r}_i(t) - \frac{H}{\zeta}\mathbf{Q}_{ij}]\delta t + \sqrt{\frac{2kT}{\zeta}}\delta\mathbf{W}$$

$$\boldsymbol{\kappa} = (\boldsymbol{\nabla}\mathbf{v})^t$$

- Fokker-Planck equation – mesoscale

$$\psi_{,t} = -\{\boldsymbol{\nabla}_Q\cdot(\boldsymbol{\kappa}\cdot\mathbf{Q} - \frac{2kT}{\zeta}\boldsymbol{\nabla}_Q \ln\psi - \frac{2H}{\zeta}\mathbf{Q})\psi\}$$

- Upper Convected Maxwell Model (UCM) - macroscale

$$\frac{\zeta}{4H}\boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - nkT\mathbf{I} = 0$$

$$\sigma_p = -H\int \mathbf{Q}\mathbf{Q}\psi(\mathbf{Q},t)d\mathbf{Q}$$

$$(\cdot)_{(1)} = \frac{\partial(\cdot)}{\partial t} + (\mathbf{v}\cdot\nabla)(\cdot) - (\nabla\mathbf{v})^T\cdot(\cdot) - (\cdot)\cdot(\nabla\mathbf{v})$$

Linearized - UCM

$$\lambda \boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - G_0 \mathbf{I} = 0$$

$$\lambda = \frac{\zeta}{4H}$$

$$\boldsymbol{\tau} = -\boldsymbol{\sigma}_p + G_0 \mathbf{I}$$

$$\eta_0 = \lambda G_0$$

$$\lambda \boldsymbol{\tau}_{(1)} + \boldsymbol{\tau} = -\eta_0 \dot{\boldsymbol{\gamma}}$$

Linearization

$$\lambda \frac{d\tau}{dt} + \tau = -\eta_0 \dot{\gamma}$$

$$\tau(t) = -\frac{\eta_0}{\lambda} \int_0^t e^{\frac{t'-t}{\lambda}} \dot{\gamma}(t') dt' + \tau(0)$$

Memory kernel

1. Imposed steady shear flow

$$\dot{\gamma} = \begin{cases} 0, & t < 0 \\ \dot{\gamma}, & t \geq 0 \end{cases}$$

$$\tau \sim G_0 \lambda \dot{\gamma}_0 [1 - e^{-t/\lambda}]$$

Linearized - UCM

$$\lambda \boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - G_0 \mathbf{I} = 0$$

$$\boldsymbol{\tau} = -\boldsymbol{\sigma}_p + G_0 \mathbf{I}$$

$$\lambda \boldsymbol{\tau}_{(1)} + \boldsymbol{\tau} = -\eta_0 \dot{\boldsymbol{\gamma}}$$

Linearization

$$\lambda \frac{d\tau}{dt} + \tau = -\eta_0 \dot{\gamma}$$

$$\tau(t) = -\frac{\eta_0}{\lambda} \int_0^t e^{\frac{t'-t}{\lambda}} \dot{\gamma}(t') dt' + \tau(0)$$

Memory kernel

2. Subsequent stress relaxation

$$\dot{\gamma} = \begin{cases} \dot{\gamma}_0, & t < 0 \\ 0, & t \geq 0 \end{cases}$$

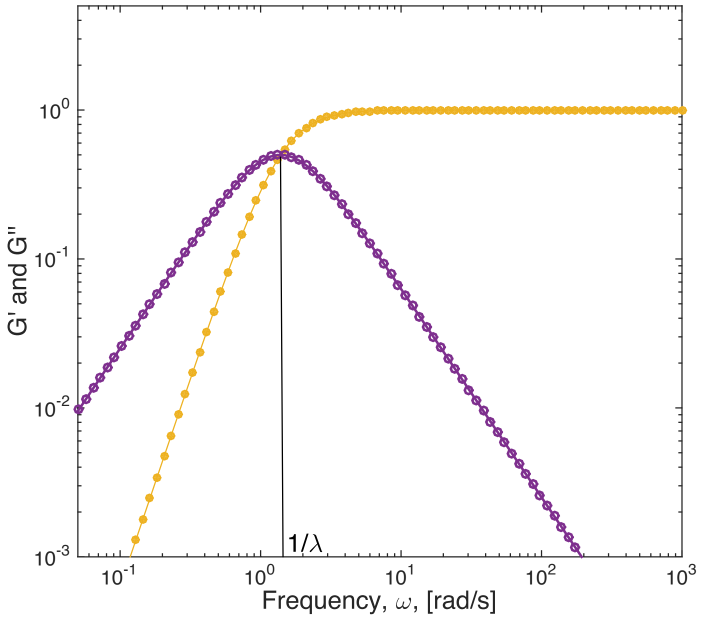
$$\tau = -G_0 \lambda \dot{\gamma}_0 e^{-\frac{t}{\lambda}}$$

Small Amplitude Oscillatory Shear- UCM

$$\lambda \frac{d\tau}{dt} + \tau = -\eta_0 \dot{\gamma}$$

3. SAOS

$$\gamma = \gamma_0 \sin(\omega t)$$



ω_0

crossover frequency

$$\tau = -G'(\omega)\gamma_0 \sin(\omega t) - G''(\omega)\gamma_0 \cos(\omega t)$$

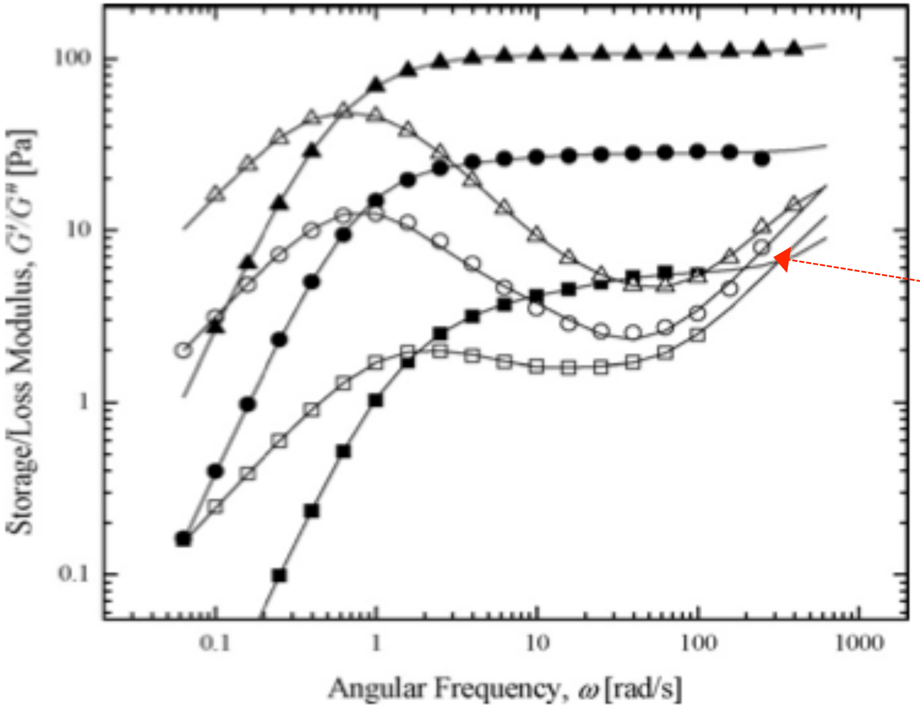
$$G'(\omega) = G_0 \frac{\omega^2 \lambda^2}{1+\omega^2\lambda^2}$$ storage modulus

$$G''(\omega) = G_0 \frac{\omega \lambda}{1+\omega^2\lambda^2}$$ loss modulus

$$G'' = G' = \lambda\omega_0 = 1$$

$\lambda = \frac{1}{\omega_0}$: relaxation time

SAOS – Wormlike Micellar Mixtures



■ 50/25 mM CPyCl/NaSal

● 100/50 mM CPyCl/NaSal

▲ 200/100 mM CPyCl/NaSal

2nd (small time, high frequency) relaxation

$$G' = G_0\left[\frac{(\lambda\omega)^2}{1+(\lambda\omega)^2} + n_2\frac{(\lambda_2\omega)^2}{1+(\lambda_2\omega)^2}\right]$$

$$G'' = G_0\left[\frac{(\lambda\omega)}{1+(\lambda\omega)^2} + n_2\frac{(\lambda_2\omega)}{1+(\lambda_2\omega)^2}\right]$$

$$\lambda_2 \ll \lambda$$

- Appears to be two Maxwell modes well separated in time
- Unusual simplicity, almost single mode despite the polydispersity of the mixture!

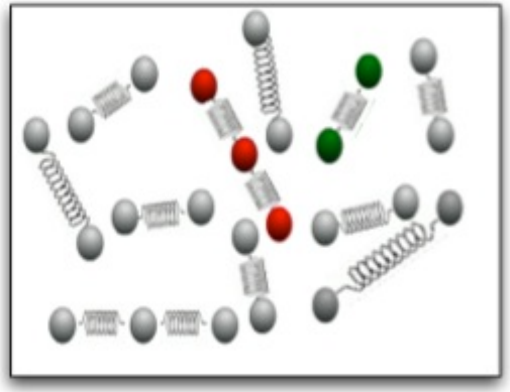
Miller et al. (2007) JNNFM

Wormlike Micelles – VCM Model

Number Densities:

$$n_\alpha(\mathbf{r},t) = \int \Psi_\alpha d\mathbf{Q}$$

$$\alpha = A,B$$



Stress Tensors:

$$\mathbf{A} = \{\mathbf{QQ}\}_A = \int \mathbf{QQ}\Psi_A d\mathbf{Q}$$

$$\mathbf{B} = \{\mathbf{QQ}\}_B = \int \mathbf{QQ}\Psi_B d\mathbf{Q}$$

- VCM Model – Two-species breaking and reforming UCM variant

Extra Stress: $\boldsymbol{\sigma} = \mathbf{A} + 2\mathbf{B}$

Total Stress: $\mathbf{\Pi} = p\mathbf{I} + (n_A + n_B)\mathbf{I} - \mathbf{A} - 2\mathbf{B} - \beta\dot{\boldsymbol{\gamma}}$

Vasquez, Cook and McKinley, *JNNFM* (2007)

Wormlike Micelles – VCM Model

Number Densities:

$$n_\alpha(\mathbf{r},t) = \int \Psi_\alpha d\mathbf{Q}$$

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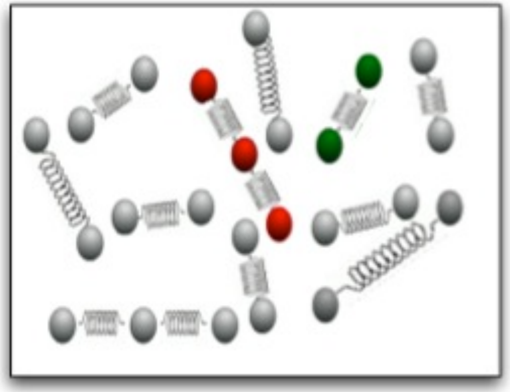


Stress Tensors:

$$\mathbf{A} = \{\mathbf{QQ}\}_A = \int \mathbf{QQ}\Psi_A d\mathbf{Q}$$

$$\mathbf{B} = \{\mathbf{QQ}\}_B = \int \mathbf{QQ}\Psi_B d\mathbf{Q}$$

Constitutive Equations:

$$\mu \frac{Dn_A}{Dt} = \delta_A 2\nabla^2 n_A + \tfrac{1}{2} c_B n_B^2 - c_A n_A$$

$$\mu \frac{Dn_B}{Dt} = \delta_B 2\nabla^2 n_A - c_B n_B^2 + 2 c_A n_A$$

$$\mu \mathbf{A}_{(1)} + \mathbf{A} - n_A \mathbf{I} = \delta_A \boldsymbol{\nabla}^2 \mathbf{A} + c_B n_B \mathbf{B} - c_A \mathbf{A}$$

$$\epsilon \mu \mathbf{B}_{(1)} + \mathbf{B} - \tfrac{n_B}{2} \mathbf{I} = \epsilon \delta_B \boldsymbol{\nabla}^2 \mathbf{B} - 2 c_B n_B \mathbf{B} + 2 c_A \mathbf{A}$$

$$\epsilon, \delta_A, \delta_B << 1$$

Vasquez, Cook and McKinley, *JNNFM* (2007)

Wormlike Micelles – VCM Model

Breaking Rate:

$$c_A = \frac{\xi\mu}{3}\left(\dot{\gamma} : \frac{\mathbf{A}}{n_A}\right) + c_{Aeq}$$

Reforming Rate:

$$c_B = \text{constant} = c_{Beq}$$

Constitutive Equations:

$$\mu \frac{Dn_A}{Dt} = \delta_A 2\nabla^2 n_A + \tfrac{1}{2} c_B n_B^2 - c_A n_A$$
$$\mu \frac{Dn_B}{Dt} = \delta_B 2\nabla^2 n_A - c_B n_B^2 + 2 c_A n_A$$

$$\mu \mathbf{A}_{(1)} + \mathbf{A} - n_A \mathbf{I} = \delta_A \boldsymbol{\nabla}^2 \mathbf{A} + c_B n_B \mathbf{B} - c_A \mathbf{A}$$
$$\epsilon \mu \mathbf{B}_{(1)} + \mathbf{B} - \tfrac{n_B}{2} \mathbf{I} = \epsilon \delta_B \boldsymbol{\nabla}^2 \mathbf{B} - 2 c_B n_B \mathbf{B} + 2 c_A \mathbf{A}$$

$$\epsilon, \delta_A, \delta_B << 1$$

Vasquez, Cook and McKinley, *JNNFM* (2007)

Wormlike Micelles – VCM Model

Conservation of mass: $$\nabla \cdot \mathbf{v} = 0$$

Conservation of momentum: $$E^{-1}\frac{D\mathbf{v}}{Dt} = -\boldsymbol{\nabla} \cdot \Pi$$

Constitutive Equations:

$$\mu\frac{Dn_A}{Dt} = \delta_A 2\nabla^2 n_A + \frac{1}{2}c_B n_B^2 - c_A n_A$$
$$\mu\frac{Dn_B}{Dt} = \delta_B 2\nabla^2 n_A - c_B n_B^2 + 2c_A n_A$$

$$\mu\mathbf{A}_{(1)} + \mathbf{A} - n_A\mathbf{I} = \delta_A\boldsymbol{\nabla}^2\mathbf{A} + c_B n_B\mathbf{B} - c_A\mathbf{A}$$
$$\epsilon\mu\mathbf{B}_{(1)} + \mathbf{B} - \frac{n_B}{2}\mathbf{I} = \epsilon\delta_B\boldsymbol{\nabla}^2\mathbf{B} - 2c_B n_B\mathbf{B} + 2c_A\mathbf{A}$$

$$\epsilon, \delta_A, \delta_B << 1$$

Vasquez, Cook and McKinley, *JNNFM* (2007)

VCM Model

- 18 coupled nonlinear partial differential equations in 18 unknowns

- In shear flow $\mathbf{v}(x, y, z, t) = (u(y, t), 0.0)$
  9 coupled nonlinear partial differential equations in 9 unknowns

- *Initial conditions* –equilibrium or . . .

- *Boundary conditions*
  - velocity at the inner wall: $\mathrm{De}\ \tanh(at)$
  - velocity at the outer wall given: 0
  - no flux of number density or stress at the walls

Vasquez, Cook and McKinley, *JNNFM* (2007)

VCM Model

- Nondimensionalization

$$l = \frac{l'}{h}$$

$$t = \frac{t'}{\lambda_{eff}}$$

$$De = \frac{\lambda_{eff} V'}{h}$$

Parameters

$$\mu = \frac{\lambda_A}{\lambda_{eff}} = O(1)$$

$$\beta = \frac{\eta_s}{\eta_0} = O(10^{-5})$$

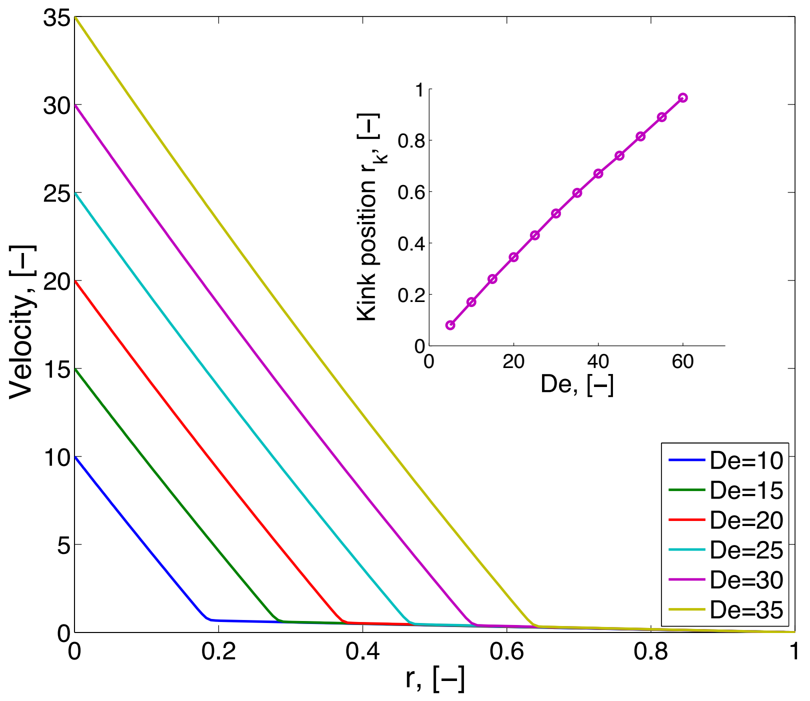
$$\epsilon = \frac{\lambda_B}{\lambda_A} = O(10^{-3})$$

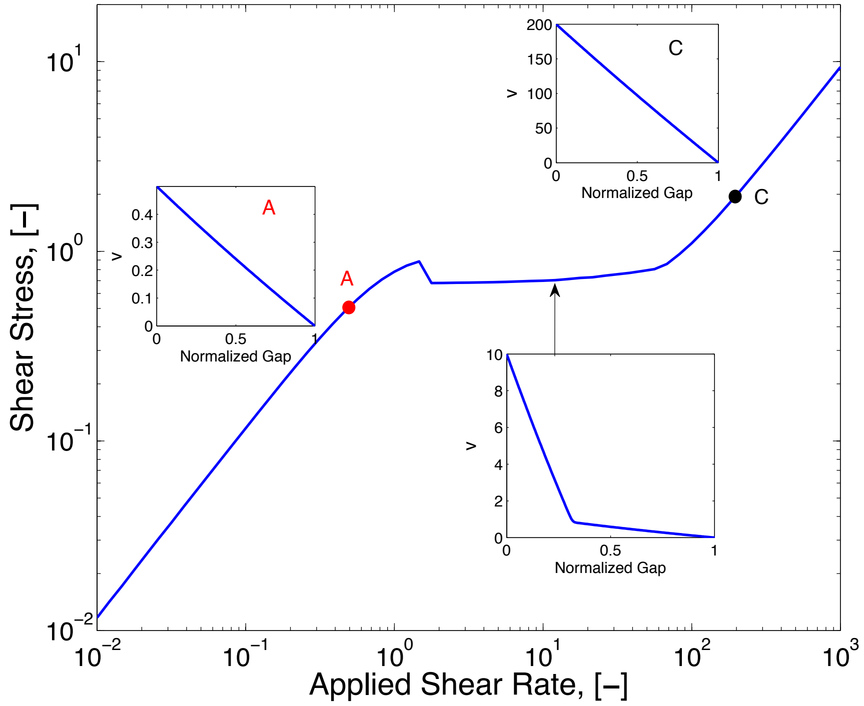
$$E^{-1} = \frac{\rho h^2}{\lambda_{eff} \eta_0} << 1$$

$$\delta_\alpha = \frac{D_\alpha \lambda_\alpha}{h^2} << 1$$

Vasquez, Cook and McKinley, *JNNFM* (2007)

Predictions in Simple Shear (VCM)





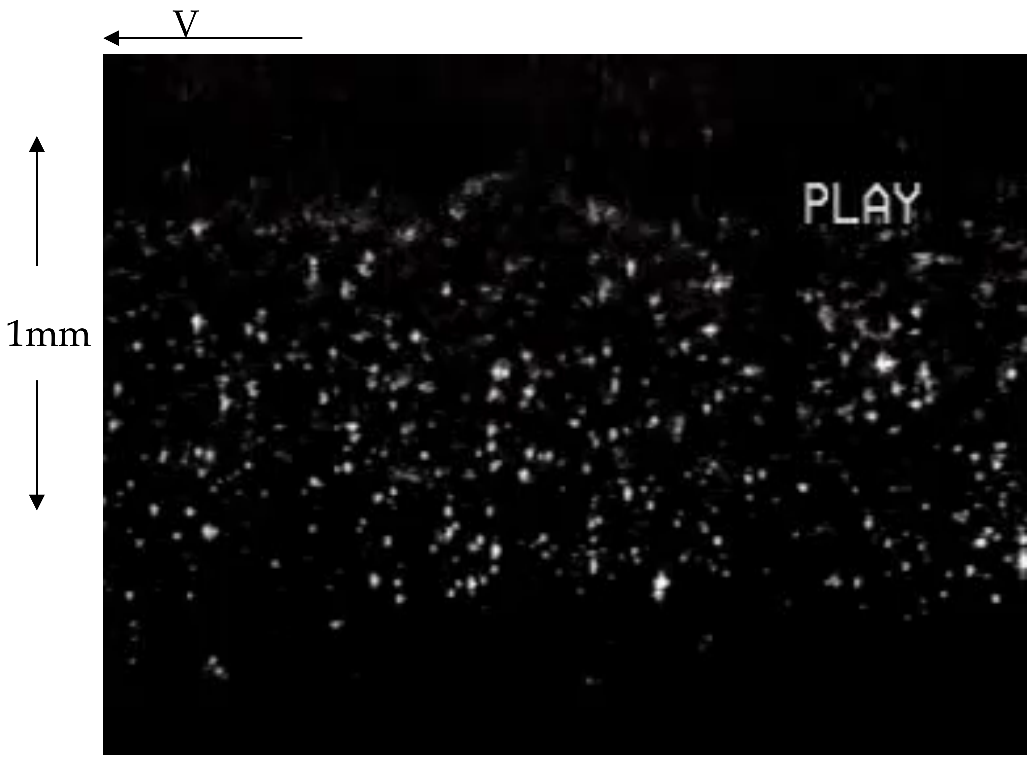
- Shear bands: high shear rate near the inner (moving)wall
- High shear rate band spatial extent increases linearly with velocity across the gap

- Stress plateau in the steady flow curve

Zhou et al (2014) JNNFM

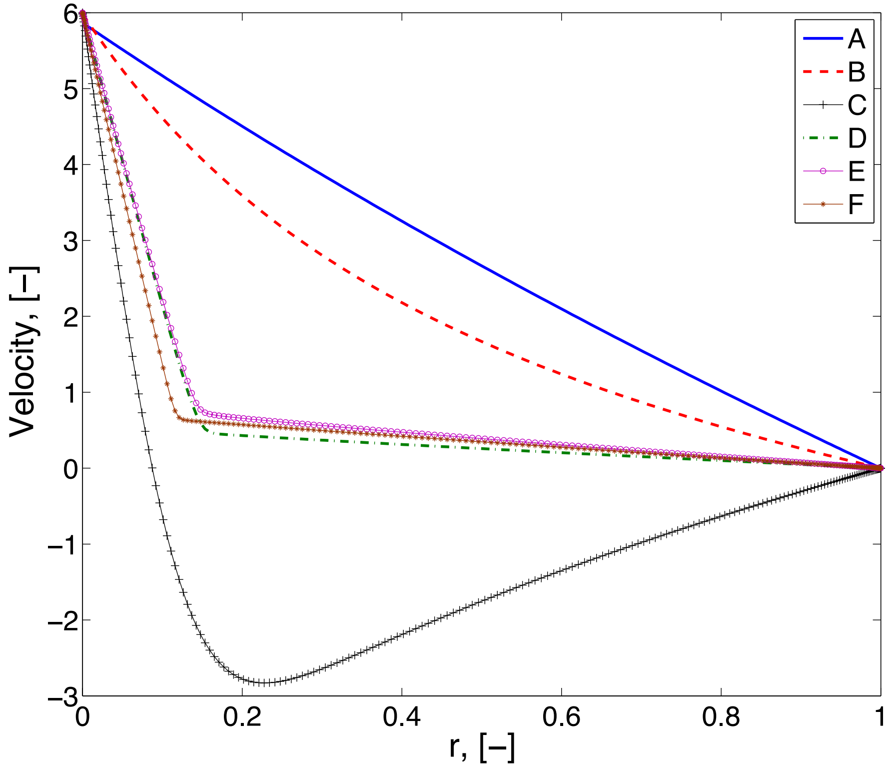
Elastic Recoil in Shear Flow(VCM)

- Reverse flow is observed



Wang et al. (2006a) PRL

1.24X10^6 PBd /10^3 g/mol oligomeric butadiene



Zhou et al (2014) JNNFM

http://www3.uakron.edu/rheology/a-startup-shear.htm

Other Predictions of the VCM Model

- Inclusion of inertia allows for multiple banding (depending on the size of the elastic parameter and the rate of the ramp-up initial condition)

Zhou et. al, SIAM J. Appl. Math 2012

- On a long time scale diffusive effects dominate, on a short time scale elasticity/elastic waves dominate

Miller, Rothstein J. Non-Newt. Fluid Mech. 2007

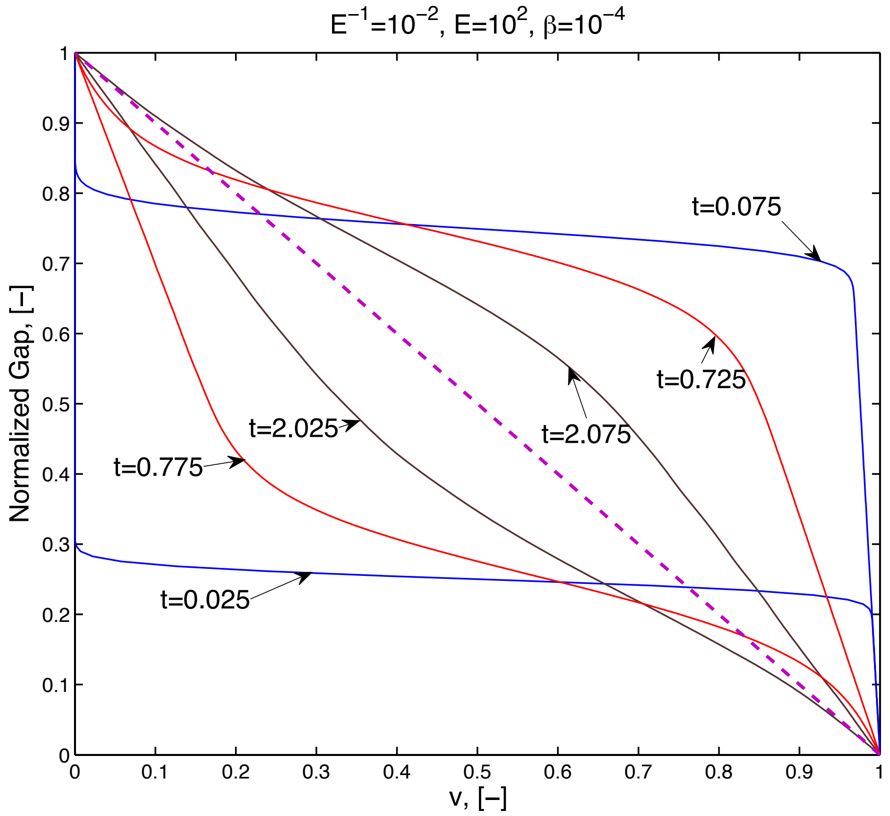
Zhou et al. J. Non-Newt. Fluid Mech. 2014

Inertial Waves UCM

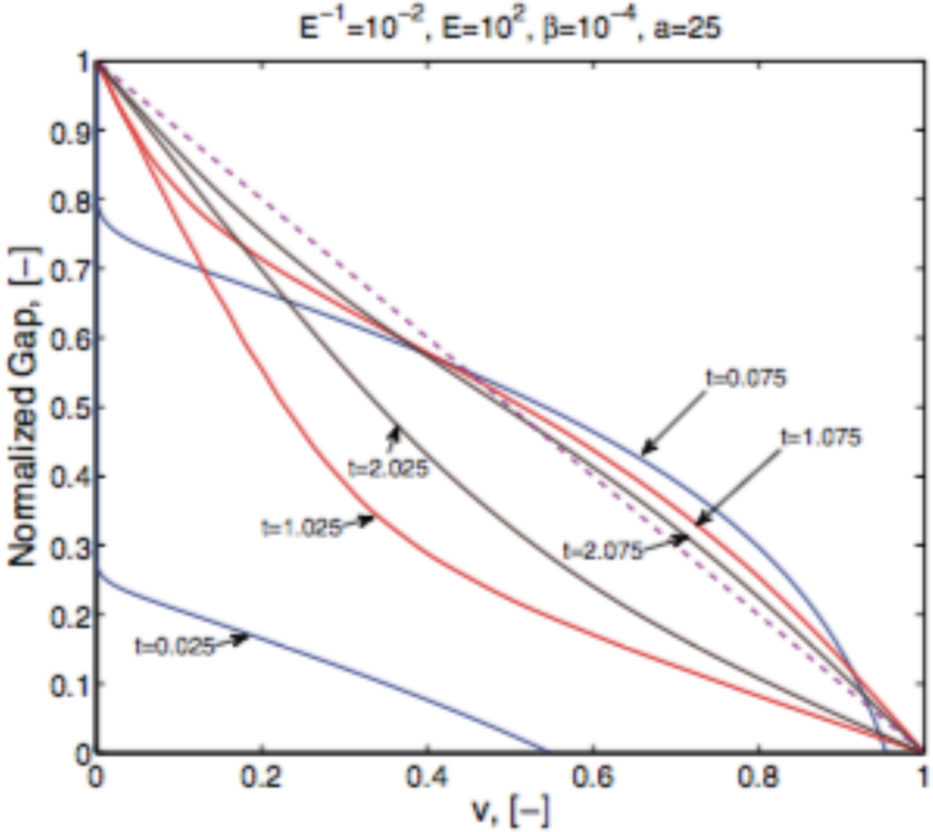
Inertial Waves: $v(y,t)$ with $v(0,t) = \mathrm{De}\tanh(at)$

$$E = 10^2, \quad \beta = 10^{-4}$$

$a = \infty$



$a = 25$

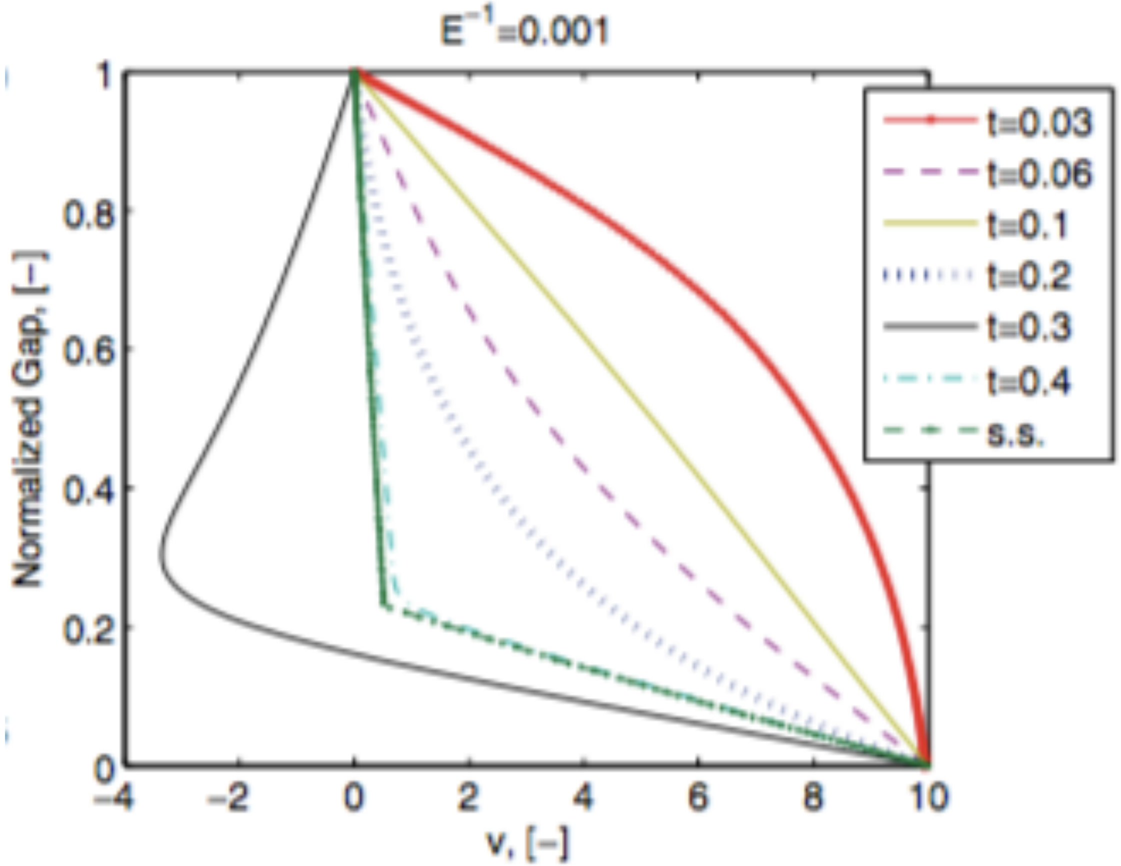


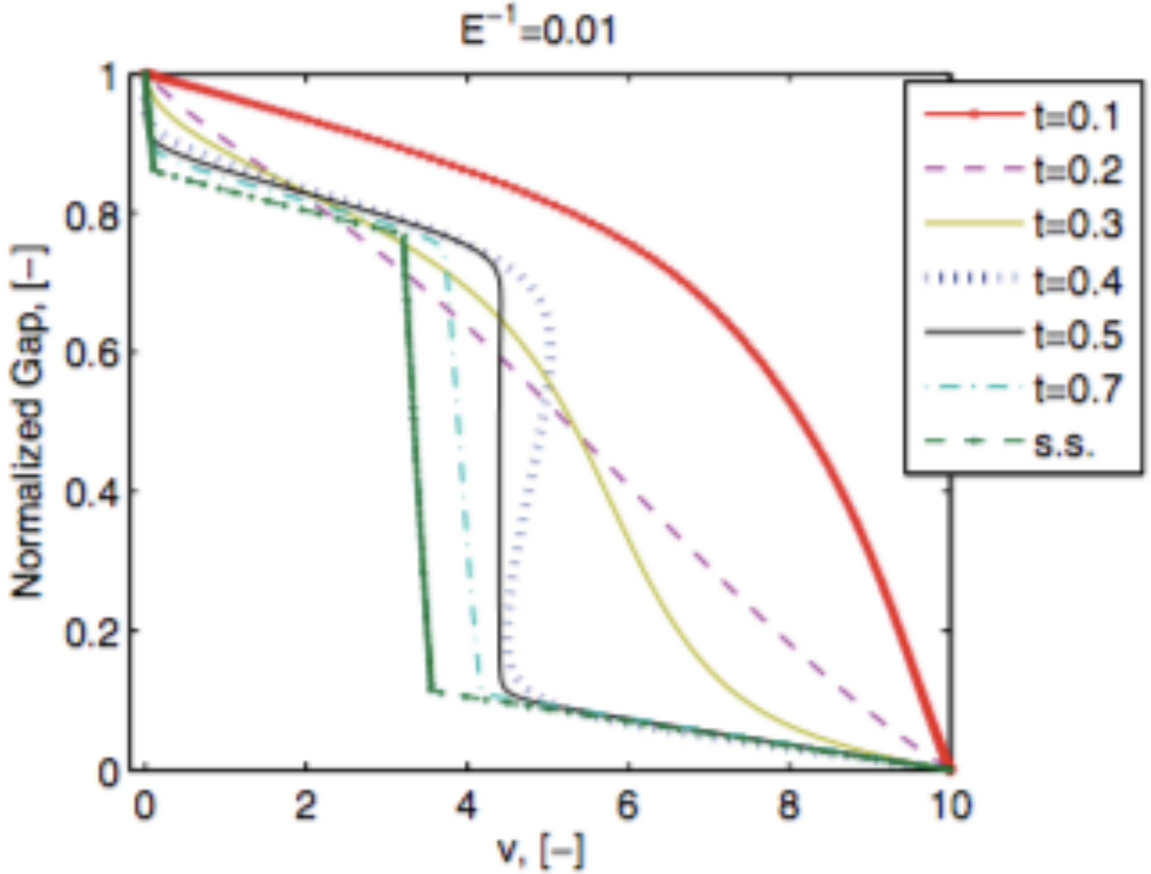
$$v_{,tt} + v_{,t} = E\beta v_{,yyt} + E v_{,yy}$$

Inertial Waves VCM

Inertial Waves: $v(y,t)$ with $v(0,t) = \mathrm{De}\tanh(at)$

$a = 100$





Zhou et. al, SIAM J. Appl. Math 2012

Multiple (4) shear bands

Other Predictions of the VCM Model

- In channel flow – spurt (formation of high shear rate band at the walls)

  Cromer et. al J. Non-Newt. Fluid Mech 2011

- In extension – fracture is a function of the extension rate. Elastic recoil and sudden fracture. (needs two species model).

  Cromer et al. Chemical Engineering Science 2009

  Bhardwaj, Miller, Rothstein J. Rheol. 2007

Breaking/Reforming Rates

- VCM model

$$c_B = \text{constant} = c_{Beq}$$

$$c_A = \frac{\xi\mu}{3}\left(\dot{\gamma} : \frac{\mathbf{A}}{n_A}\right) + c_{Aeq}$$

??

- Germann, Beris, Cook (GBC) (nonequilibrium thermodynamically consistent formulation)

$$c_B = f(\mathbf{B}, n_B)$$

$$c_A = f(\mathbf{A}, n_A)$$

??

Germann et al, J. non-Newt. Fluid Mech. 2013

Limitation of the VCM Model

- Linear springs – if nonlinear springs need an *ad hoc* closure
- Breakage/reforming – were *ad hoc* at the macroscale – no direct connection to attractive energy of beads
- Lack of definition of local (parameter) effects – concentration\salt effects on attractive energy of the bead, lack of definition of network topology
- Exponential relaxation where as, as concentration changes relaxation is stretched exponential (not exponential) $\tau(t) \sim G_0 \text{exp}[-(t/\lambda)^{\alpha}]$

BACK TO THE MESOSCALE

Elastic (Nonlinear) Dumbbell Chains

Langevin – stochastic differential -equation - mesoscale

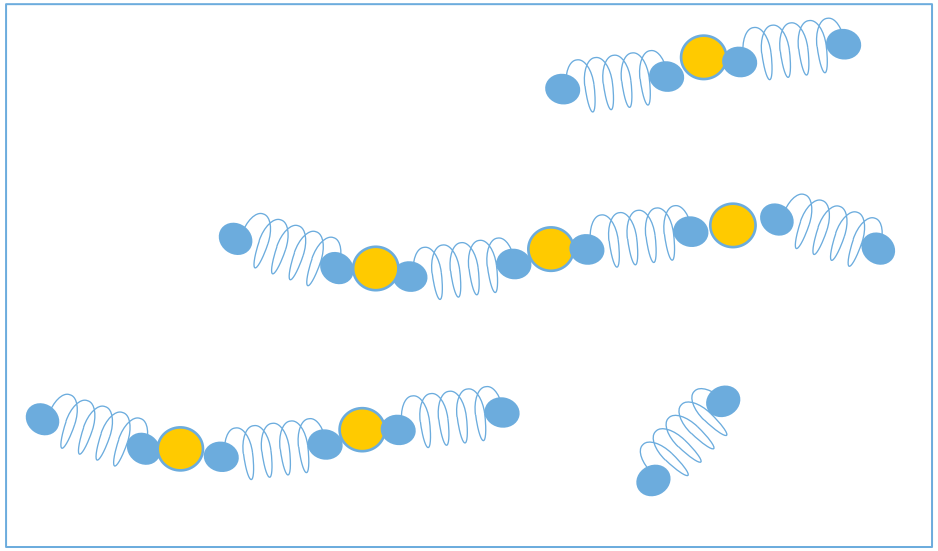
$$\mathbf{r}_i(t+\delta t) = \mathbf{r}_i(t) + [\mathbf{v}_0 + \boldsymbol{\kappa}\cdot\mathbf{r}_i(t) - \tfrac{1}{\zeta}\mathbf{F}_s(\mathbf{Q}_{ij})]\delta t + \sqrt{\frac{2kT}{\zeta}}\delta\mathbf{W}$$

&

coupled chain links

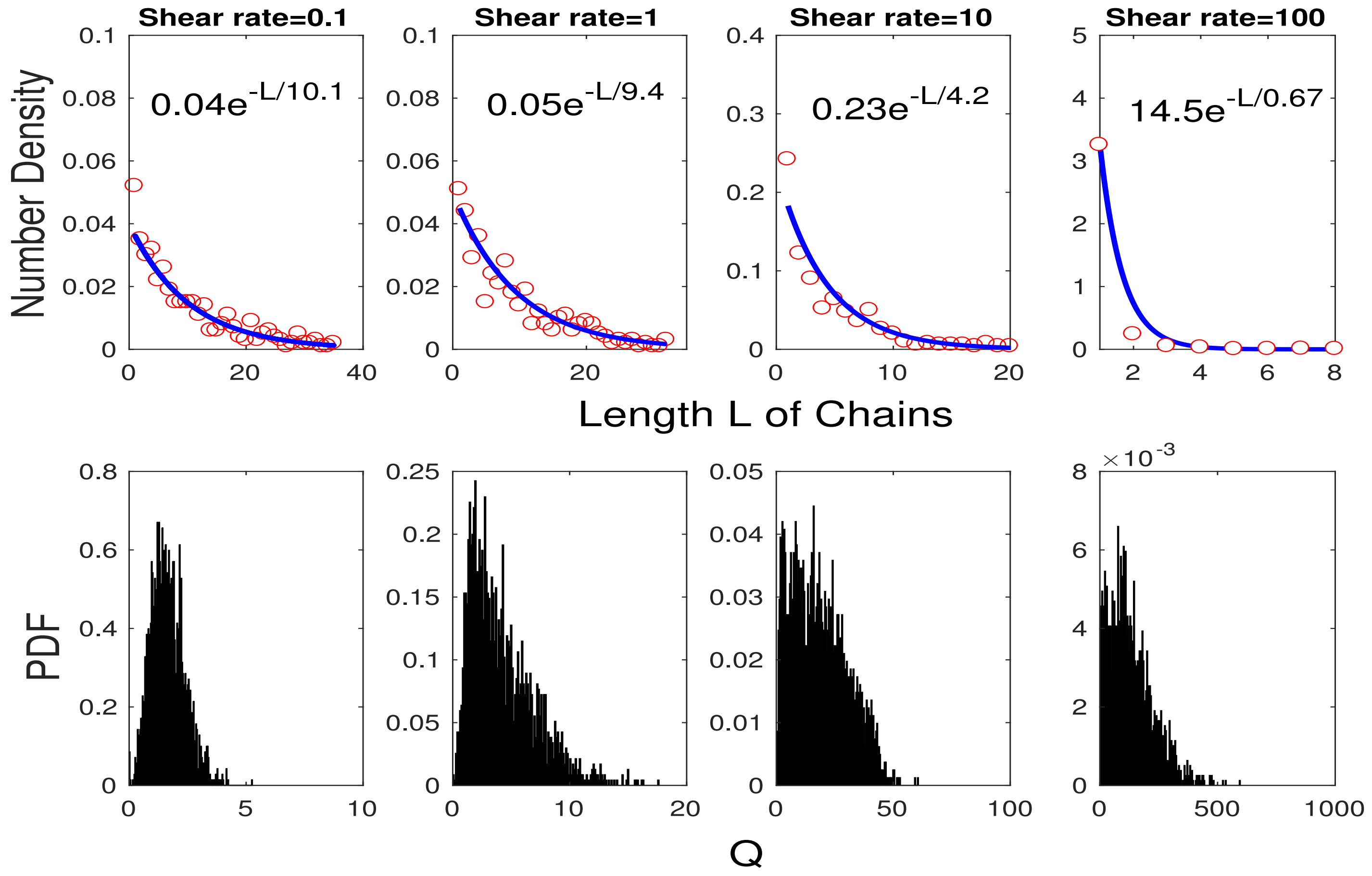
&

breakage reforming criteria (energy)



Chain Length vs. Q distribution (Hookean)

- Steady state distributions under a stretch dependent breakage



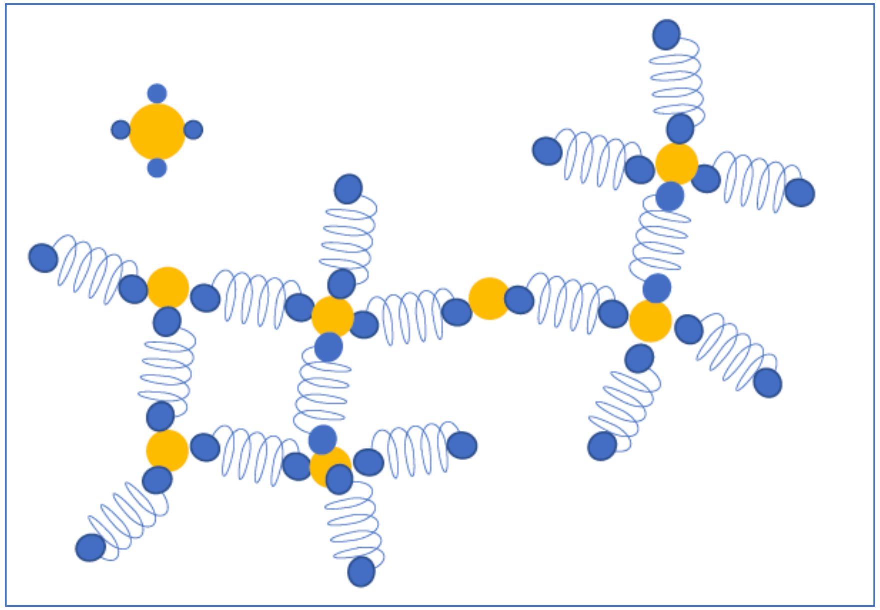
Density of chains with L linked dumbbells

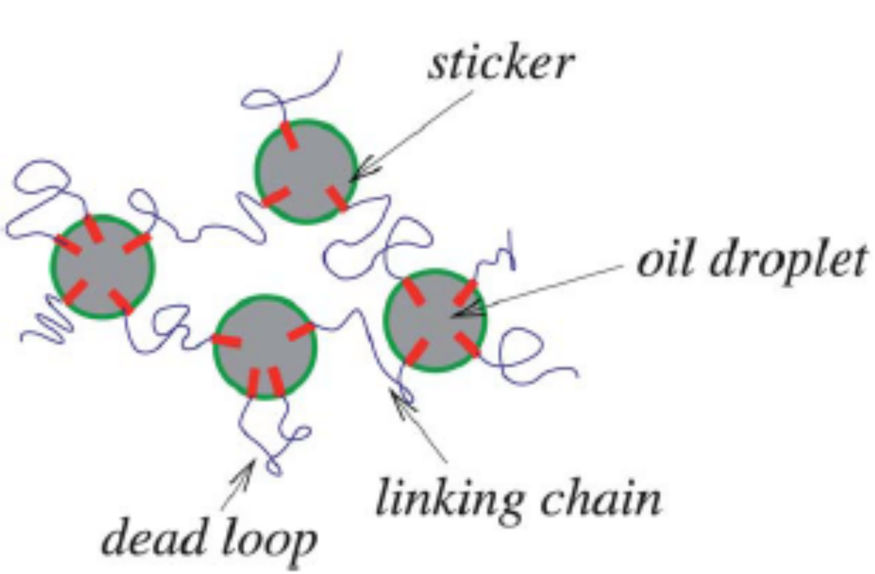
$\psi(\mathbf{Q})$

Density of configurations

Increasing shear rate

Transiently Networked Fluids



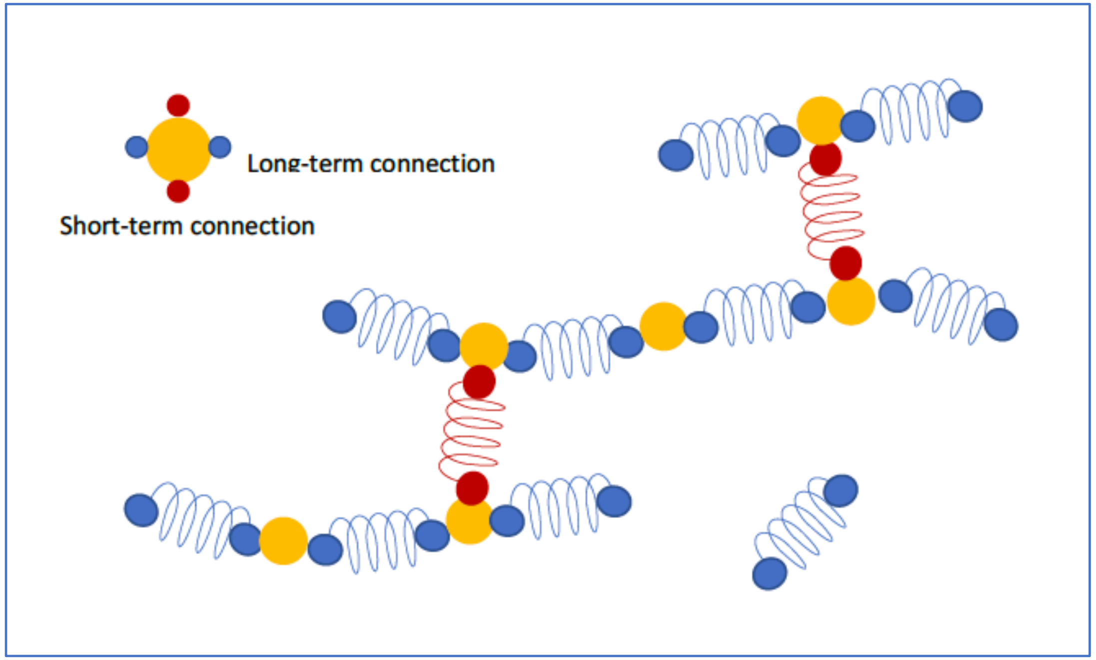


bead-spring network with transient connections, nodes of up to m beads

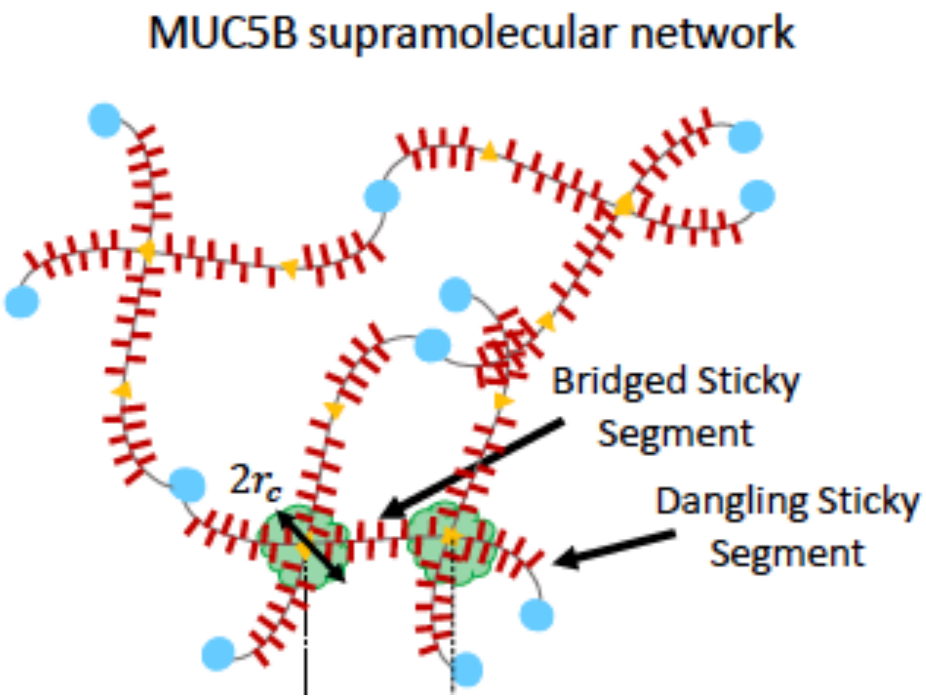
schematic of telechelic polymers (polymer with hydrophobic ends) -spheres represent oil droplets in the water solvent, collection nodes for the hydrophobic polymer ends

Mora, Soft Matter, 2011

Transient Network Model



bead-spring network
long chains crosslinked by transiently connected shorter chains



schematic of cross-linked saliva mucin chains *Wagner & McKinley, JOR, 2017*

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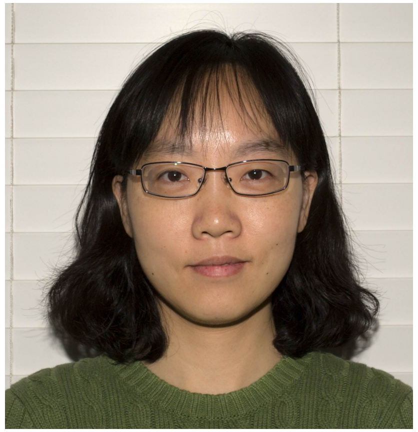

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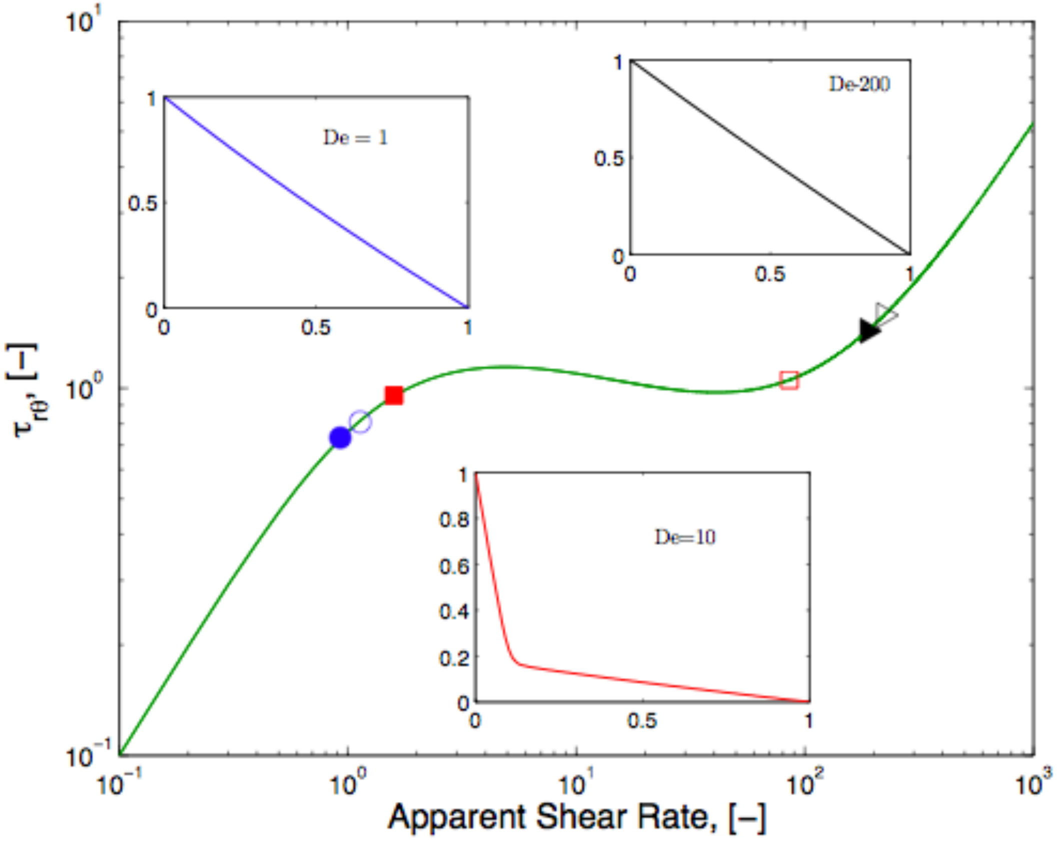
Collaborators

Thank you

VCM Underlying Non-monotone Constitutive Curve



The homogeneous constitutive curve is multi-valued.

For shear rate controlled flow:

- In a positively sloped (stable) region the shear rate at the inner cylinder is higher than at the outer cylinder due to curvature.
- In the negatively sloped (unstable) region the (already biased) flow splits further to a high shear rate (near the inner cylinder) & a low shear rate (near the outer cylinder).
- For an appropriate range of times (ramp, inertial, diffusive, imposed flow and relaxation) the inertial wave interferes with the the ramped relaxation creating multiple bands.

Four Scenarios in Steady Shearing Flow

- Case I: Constant mean node life time τ and capture radius d *(CMBR)*.
- Case II: Mean node life time τ is governed by the force balance between the attractive node and the connected bead-springs, while the capture radius d remains constant.

Cifre et al. (2003,2007) JNNFM

- Case III: Both the mean node life time τ and the capture radius d depend on the attached chain stretch through the force balance.

- Case IV: Both the mean node life time τ and the capture radius d depend on the attached chain stretch through the energy balance.

(Tripathi et al. (2006) Macromoleculus)

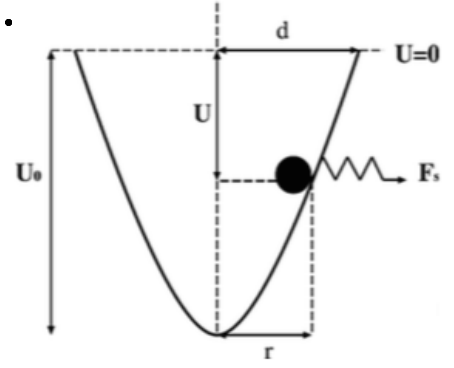
Stretch Dependent Breakage and Reforming

- Case III: Balance the maximum force, the force at the edge of an attractive node potential, with the spring force.

Cifre et al. (2003,2007) JNNFM

Detachment: $$\tau = \tau_0 \exp\left(-d^2 Q^2 / 4U_0\right)$$

Attachment: $$r < \min\left(d, 2U_0/Q\right)$$



Parabolic potential well

- Case IV: Balance the node attractive energy with the spring stretch energy.

Tripathi et al. (2006) Macromoleculus

Detachment: $$\tau = \tau_f\, e^{E + \int_Q^{Q-d} Q\,dQ} = \tau_0\, e^{-Qd + d^2/2}$$

Attachment: $$E = \int_Q^{Q+d} Q\,dQ \xrightarrow{\text{yields}} r < \min\left(d, -Q + \sqrt{Q^2 + 2E}\right)$$

Mesoscale – topology tracking - equations

Governing equations:

$$\mathbf{r}(t+\delta t) = \mathbf{r}(t) + \Sigma \mathbf{F}^s(t)/f\zeta + \delta \mathbf{w}$$

$\delta\mathbf{w}$ Wiener process

Mean
variance

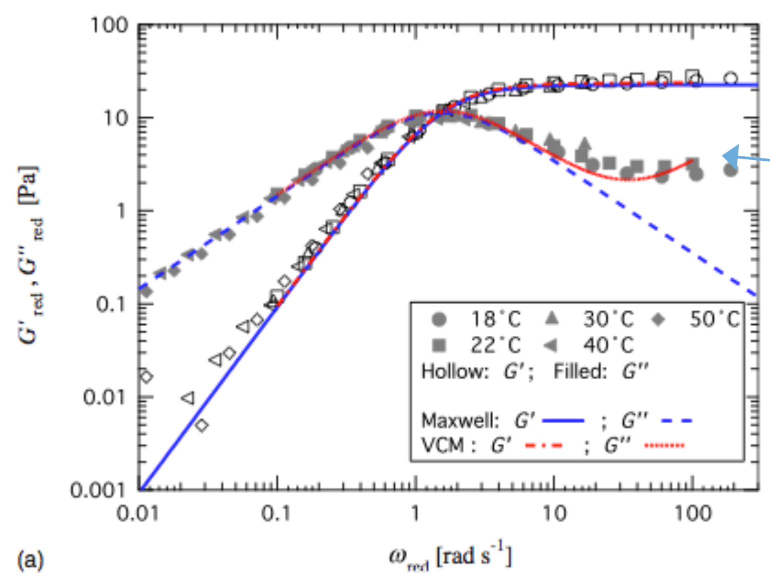
$\mathbf{F}^S = H\mathbf{Q}$ Hookean spring

$F^S = \frac{H\mathbf{Q}}{1-(\frac{\mathbf{Q}}{Q_0})^2}$ FENE spring

Attachment/detachment rules:

- Detachment of beads from a node:
  Assuming that the mean life time of a sticky node is τ , then the probability of detachment or breakage in each time step Δt is given by
- Attachment of a bead to a node:
  If a bead is within a *capture radius d* of an available node it attaches to that node

SAOS – Wormlike Micellar Mixtures



100/50 mM CPyCl/NaSal

Relaxation time: $\lambda = 0.63$ s

Plateau modulus: $G_0 = \dfrac{\eta_0}{\lambda} = 22.6$ Pa

2nd (small time, high frequency) relaxation

$$G' = G_0\left[\frac{(\lambda\omega)^2}{1+(\lambda\omega)^2} + n_2\frac{(\lambda_2\omega)^2}{1+(\lambda_2\omega)^2}\right]$$

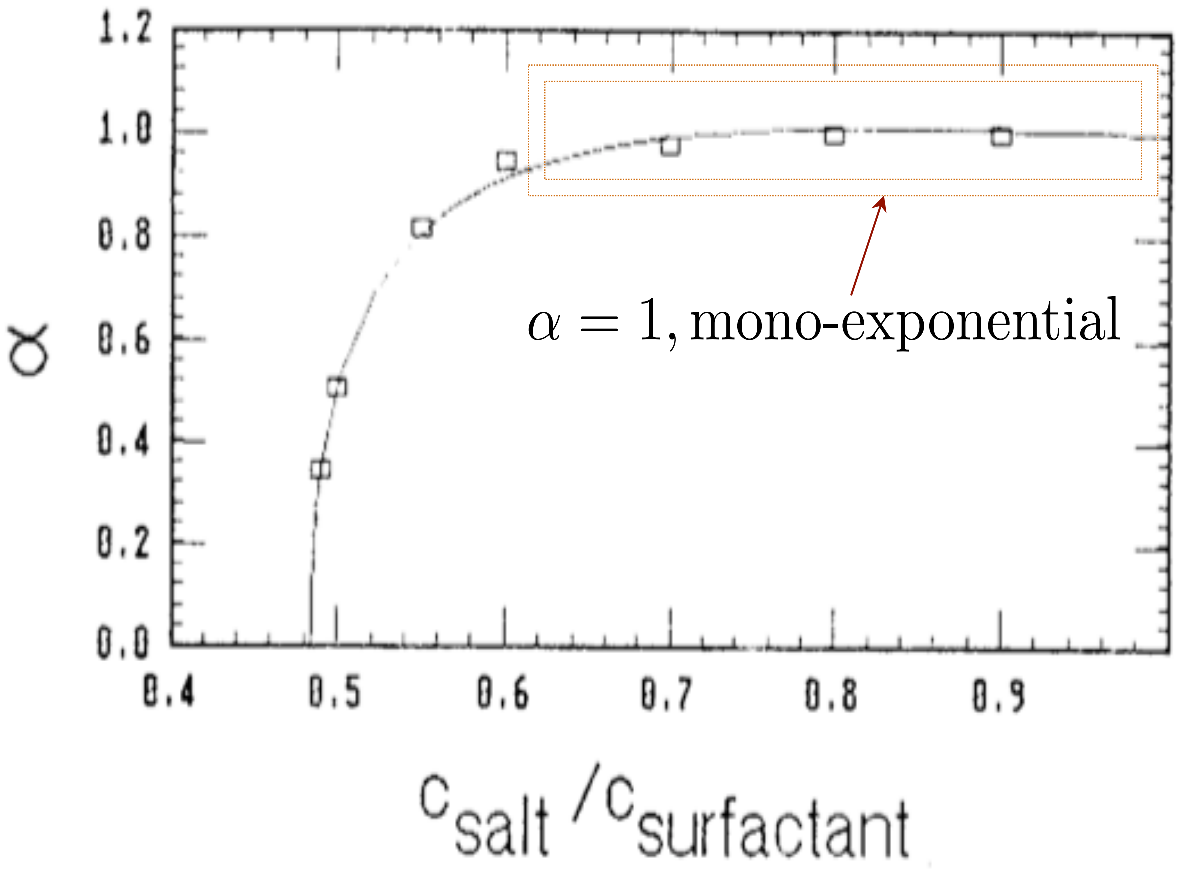
$$G'' = G_0\left[\frac{(\lambda\omega)}{1+(\lambda\omega)^2} + n_2\frac{(\lambda_2\omega)}{1+(\lambda_2\omega)^2}\right]$$

$$\lambda_2 \ll \lambda$$

- Appears to be two Maxwell modes well separated in time
- Unusual simplicity, almost single mode despite the polydispersity of the mixture!

Reference here

Wormlike Micellar Solutions



Rehage & Hoffmann (1991) Mol. Phys.

Properties depend on type of surfactant and on temperature and on salt concentration!!

CPyCl/NaSal

$$\tau(t) \sim G_0 \exp[-(t/\lambda)^{\alpha}]$$

stretched exponential relaxation after step strain

Upper Convected Maxwell Model (UCM)

$$\lambda = \frac{\zeta}{4H}, G_0 = nkT$$

$$\frac{\zeta}{4H}\boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - nkT\mathbf{I} = 0 \longrightarrow \lambda\boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - G_0\mathbf{I} = 0$$

$$(\cdot)_{(1)} = \frac{\partial(\cdot)}{\partial t} + (\mathbf{v}\cdot\nabla)(\cdot) - (\nabla\mathbf{v})^T\cdot(\cdot) - (\cdot)\cdot(\nabla\mathbf{v})$$

Quasi-linear

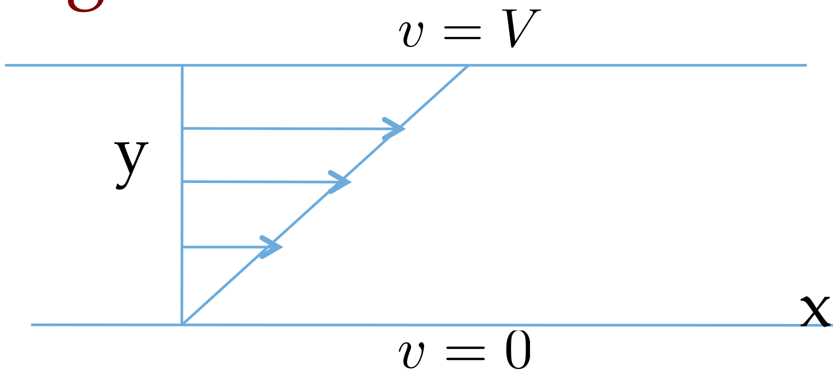
- Total Stress: $\boldsymbol{\tau} = -\boldsymbol{\sigma}_p + G_0\mathbf{I}$

$v = 0$

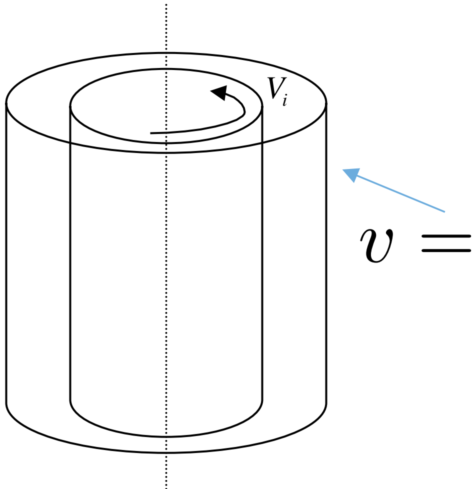
$$\lambda\boldsymbol{\sigma}_{p,(1)} + \boldsymbol{\sigma}_p - G_0\mathbf{I} = 0 \longrightarrow \lambda\boldsymbol{\tau}_{(1)} + \boldsymbol{\tau} = -\eta_0\dot{\boldsymbol{\gamma}}$$

$$\eta_0 = \lambda G_0$$

Shearing flow

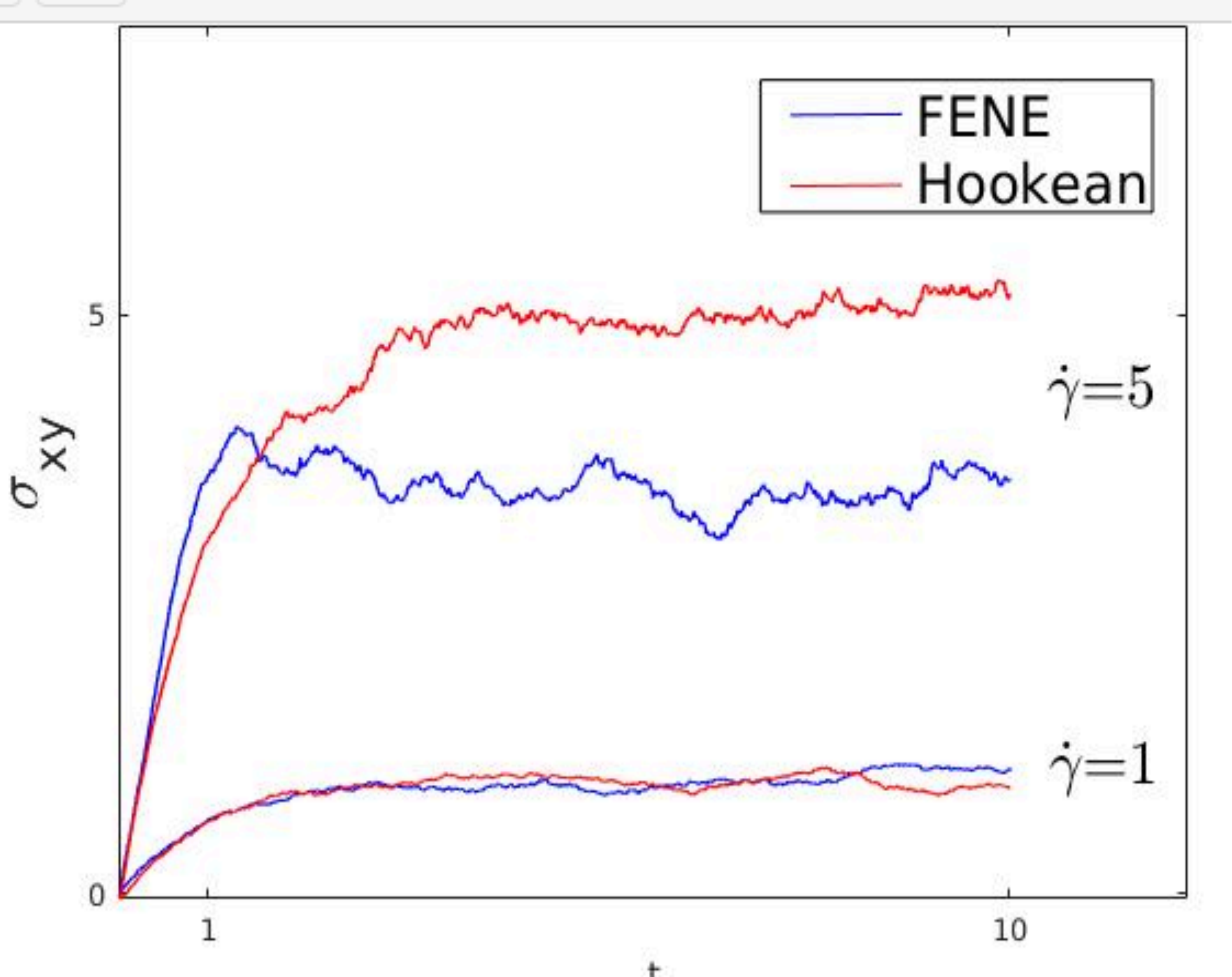


$\longrightarrow$



$v = 0$

Linear vs. Nonlinear Spring (Single Dumbbell)



Hookean (Linear Spring)

$$\mathbf{F}_s(\mathbf{Q}) = -\mathbf{Q}$$

FENE (Finitely Extensible Nonlinear Elastic Spring)

$$\mathbf{F}_s(\mathbf{Q}) = -\frac{\mathbf{Q}}{1-\frac{Q^2}{Q_0^2}}$$