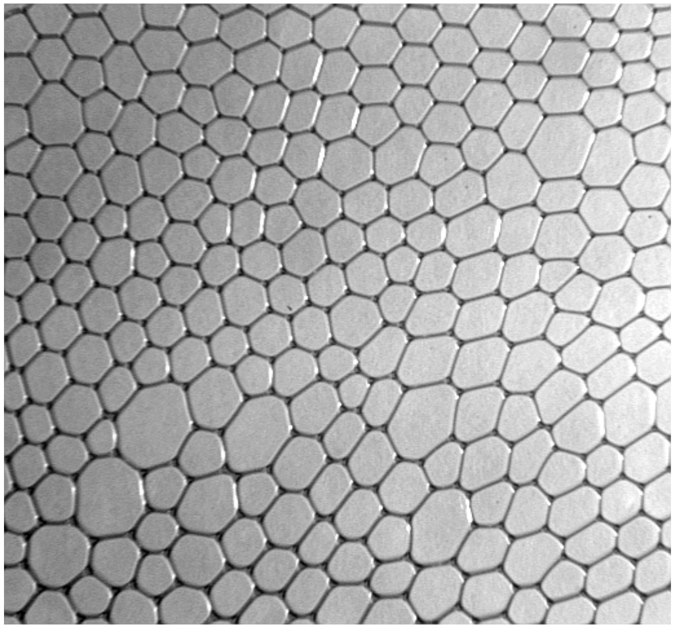
# Les Houches School of Foam: Rheology of Complex Fluids



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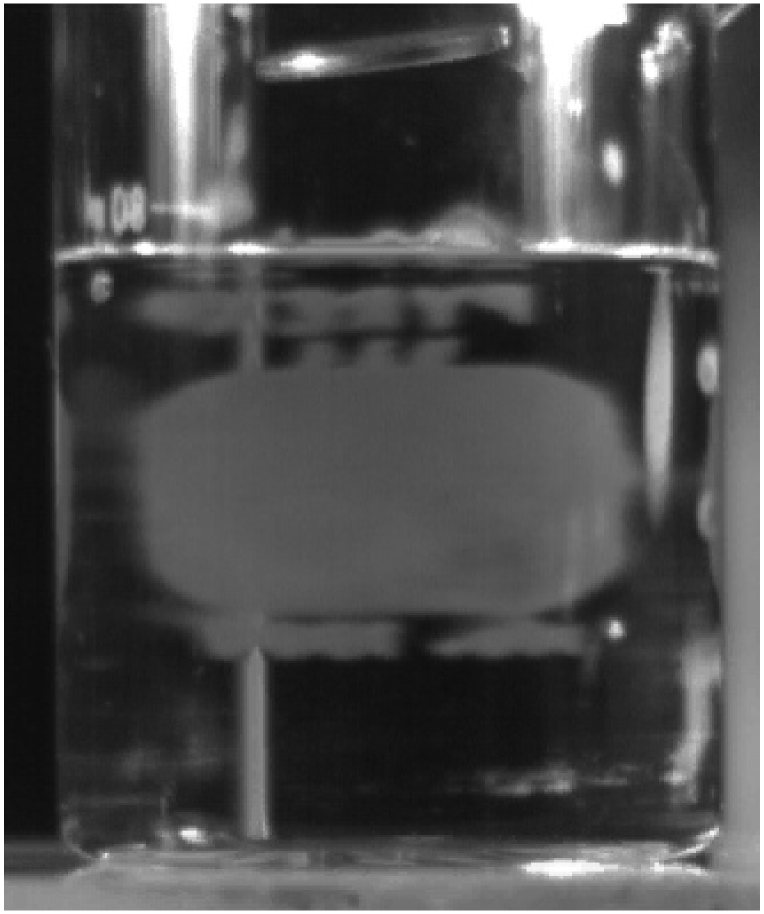
# Fluid Dynamics

(tossing a coin)



# The Variety of Fluid Behavior

So how can we measure the properties of a fluid in a controlled way when it can swirl and splash?

Somehow separate the study of:

* what velocity fields occur in a fluid flow

* what are the material properties of the fluid

This is what rheology is meant to do!

Viscometric flows vs Non-viscometric flows
($\rightarrow$ control the velocity field through confined geometry)

# Overall Plan for Two Lectures

Today (Complex Fluids I):

- Tools to study the rheology of complex fluids
- Constitutive equations, stress tensor
- What is seen in rheology of polymers and other fluids

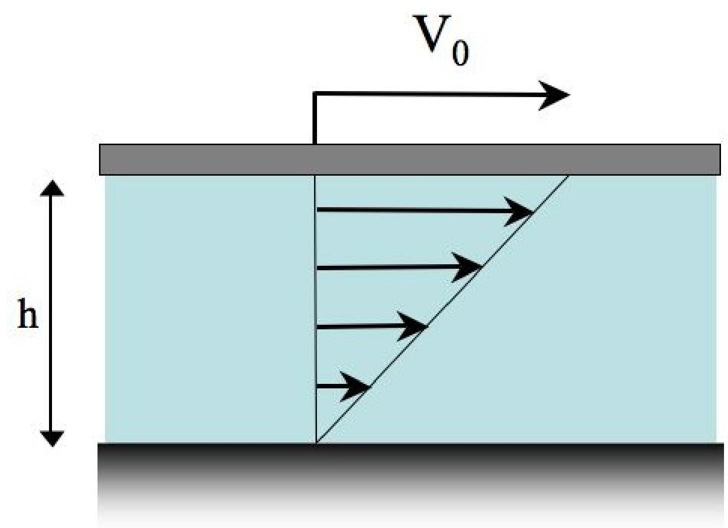
Connections to foamy issues: talks of Francois (today) and Sylvie (Monday?)

Monday (Complex Fluids II - Le Retour):

- Possible rheology continuation
- Hydrodynamic flows - compare Newtonian, polymeric, other
- Flows of other non-foam systems (brief)

# Steady shear rheology

Consider a fluid between two plates, where the top plate moves at a speed $V_0$, and a steady state has been reached:




In this simple geometry the velocity field with be linearly dependent on the distance $y$ from the stationary plate:

$$V(y) = \frac{V_0}{h} y$$

It is important that $h$ be small enough for this to occur

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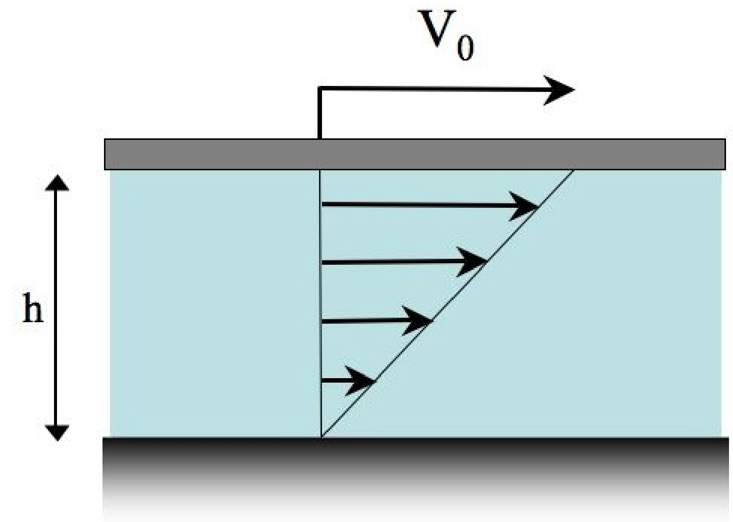


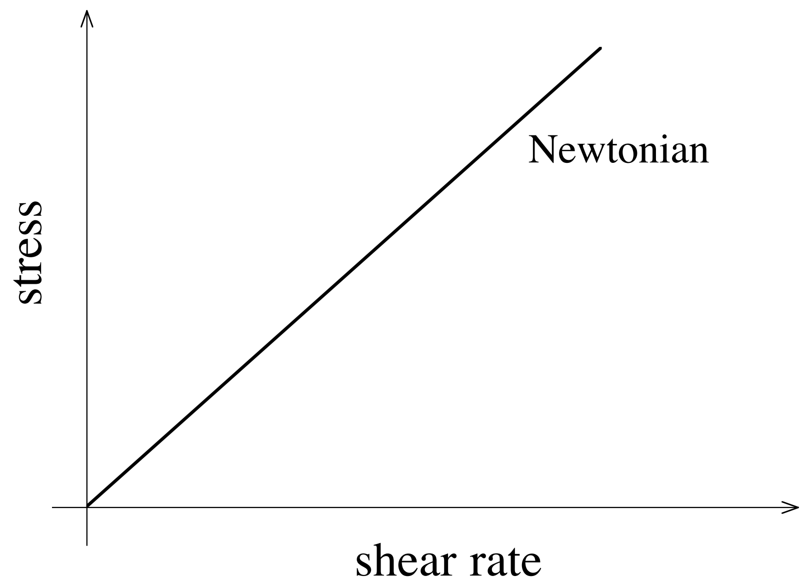

For certain materials the force per unit area $\sigma$ on the moving plate will be proportional to $V_0$, and inversely proportional to $h$:

$$\sigma = \eta \frac{V_0}{h} \qquad \left( = \eta \frac{dV}{dy} = \eta \dot{\gamma} \right)$$

where $\eta$ is the viscosity. These fluids are called Newtonian.

# What is a Newtonian Fluid?

Most fluids with simple structure at the microscale (point-like atoms or molecules) are Newtonian - though we are not yet to the point of predicting this *a priori*... It's better to measure first (shear stress $\sigma$ vs shear rate $\dot{\gamma}$):




Newtonian case is linear, slope is the viscosity $\eta$

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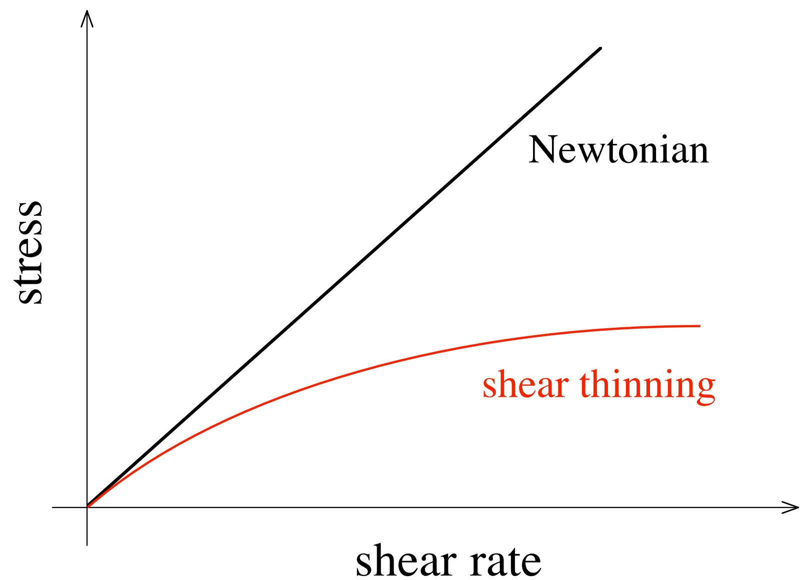


More complex, structured fluids can be nonlinear in shear.

Most polymer fluids are shear-thinning,

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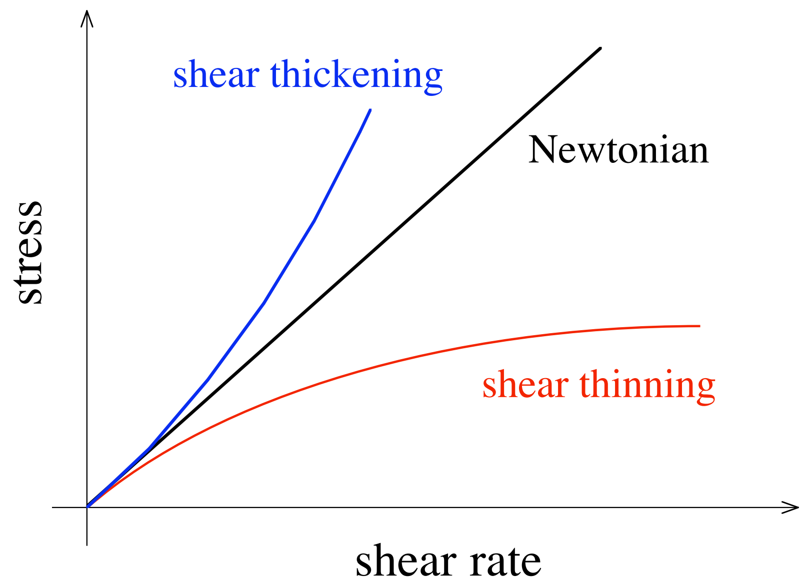


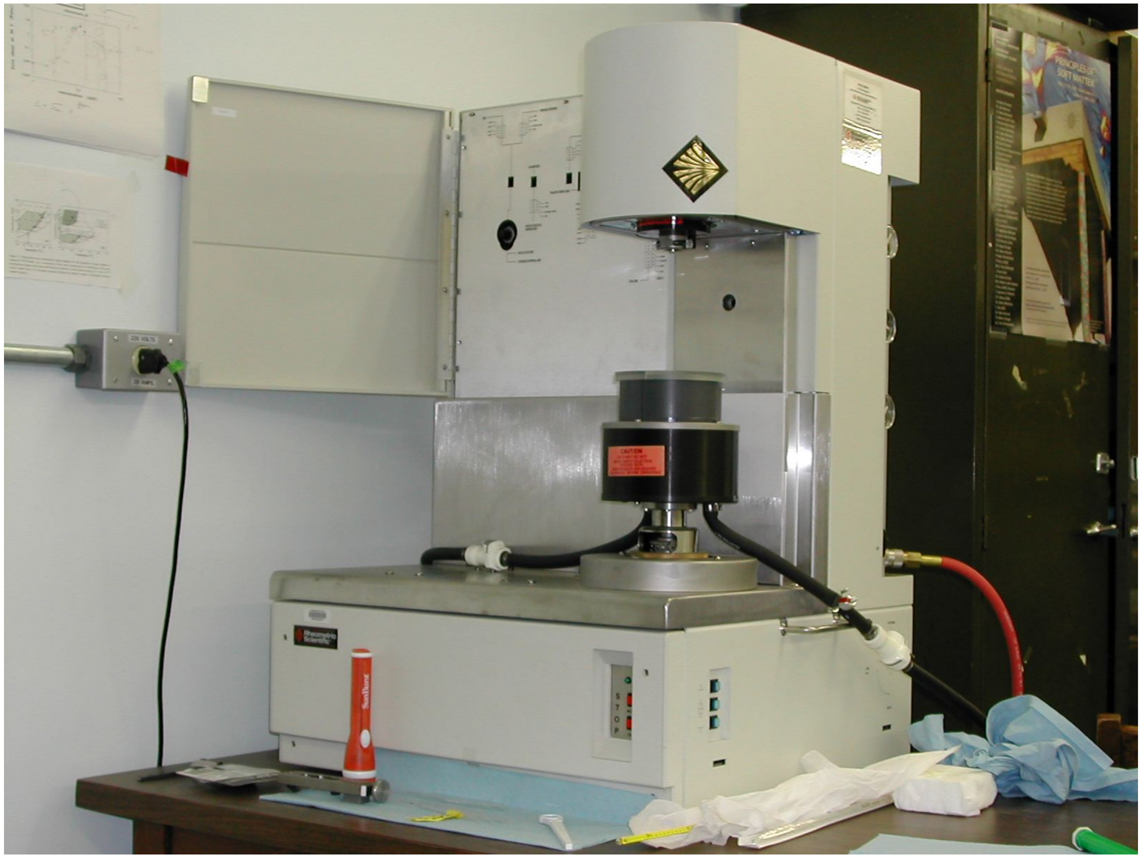

though shear-thickening is also possible.

As we will see later, there are several other ways to be non-Newtonian...

# How to Measure this in Practice?

A closed fluid volume is preferable, which usually implies rotational flow.

Commercial rheometer - fits on a (strong) table, includes fluid cell attachments (usually temperature controlled), motors and transducers:



Rheometrics (TA Inst) RFS-III controlled rate of strain rheometer

# Rheological cell: Cone-and-Plate geometry

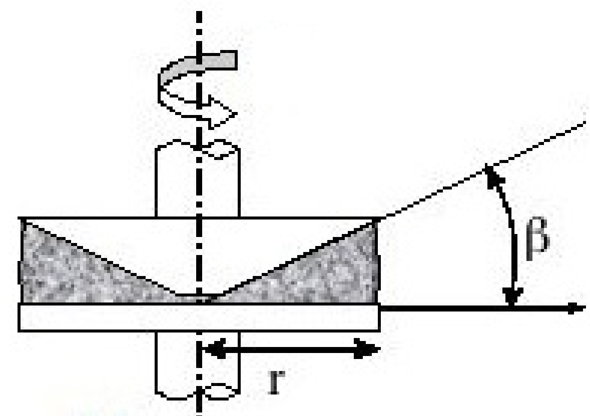
The problem with rotation is that the outer fluid moves the fastest, whereas near the center it hardly moves at all. A Cone-and-Plate geometry compensates for this, with the cone surface leading to a homogenous shear rate (see Blackboard)

· usually bottom rotates, torque measured at top

· angle $\beta$ must be small for viscometric flow

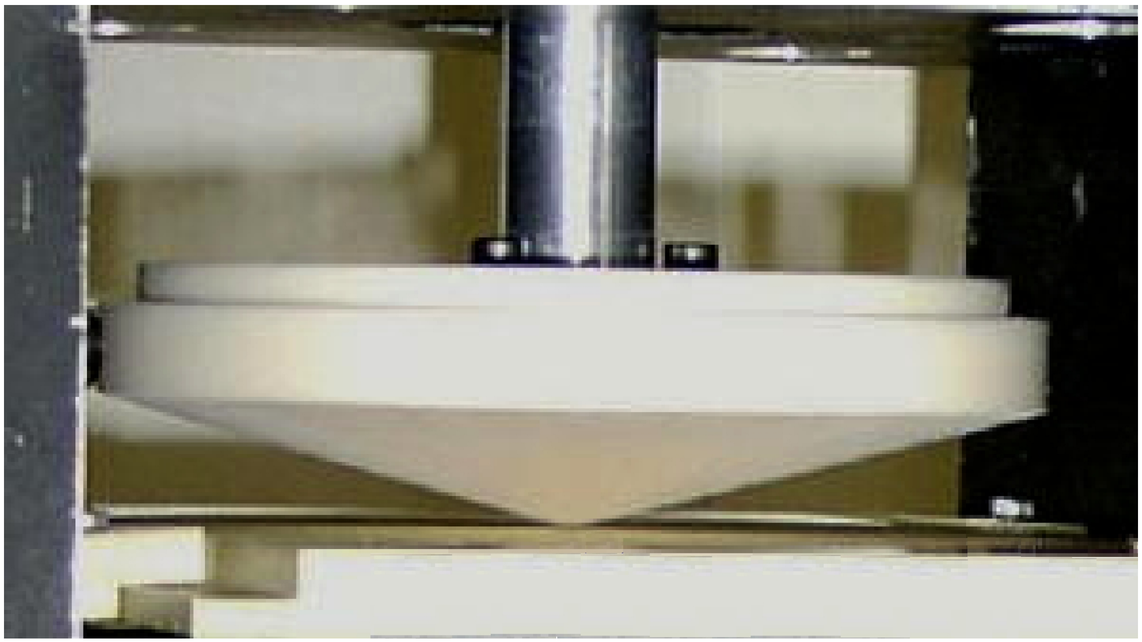
· note open edge - requires viscous material; fast enough rotation spins out fluid

· normal forces can also be measured (pushing up on cone)
$\rightarrow$ Sylvie's talk



# Rheological cell: Cone-and-Plate geometry

Cone-and-Plate rheometer for foams (Sylvie's talk):



# Rheological cell: Couette geometry

The Couette or concentric cylinder geometry is more convenient for less viscous fluids (they cannot flow out), and can also have a greater surface area. Moreover laminar Couette flow is an exact solution to the Navier-Stokes equations.

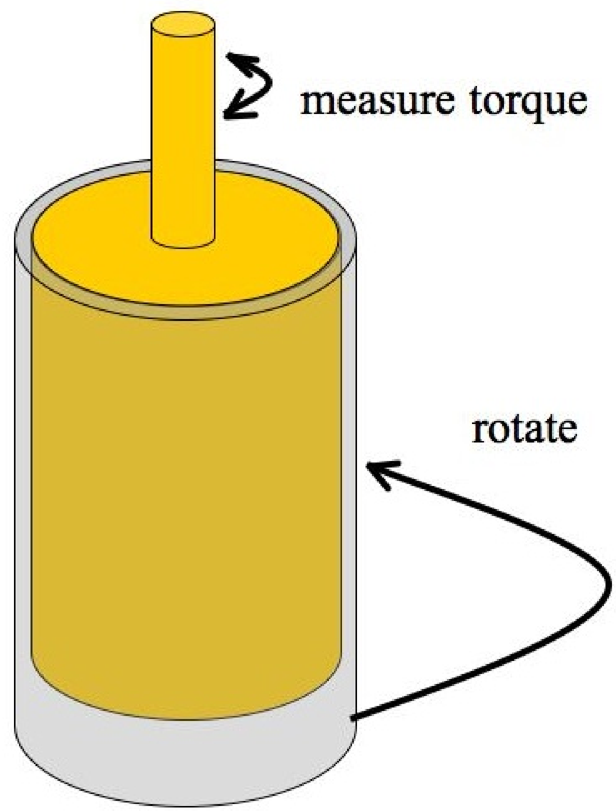
However...

· inhomogeneous shear rate, but approx. constant for $h/R << 1$

· typically $h \sim 1$ mm, $R \sim 30$ mm

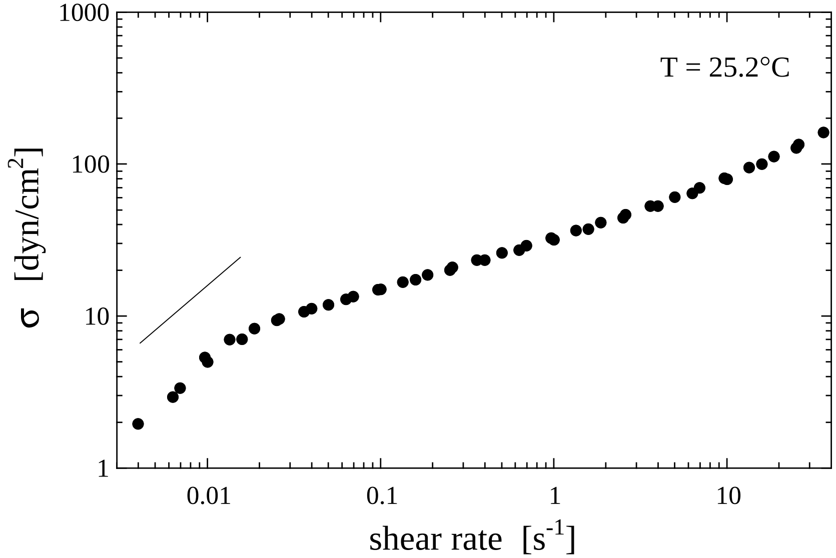
· rod climbing instability can draw fluid up out of cylinder

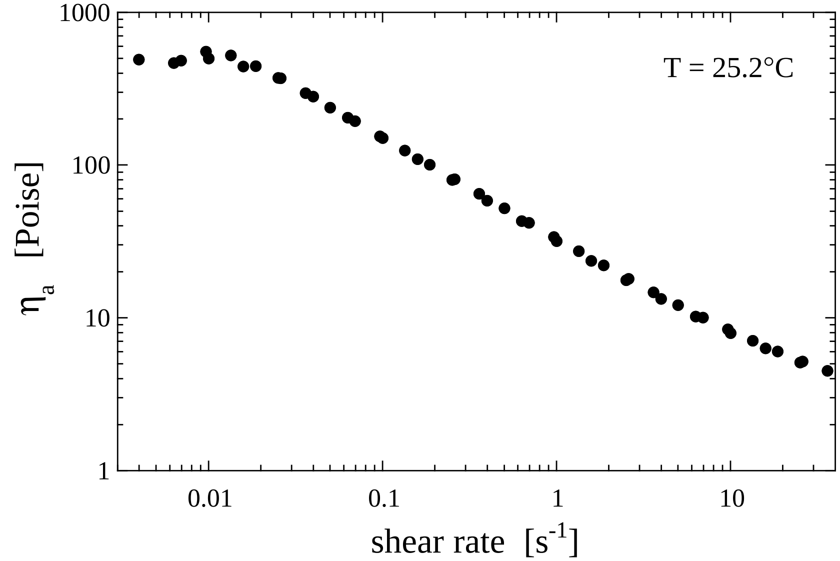
· cannot measure normal forces



# Survey of Steady Shear Rheology in Complex Fluids

Shear thinning polymer solution:




(*0.2% xanthan gum in 80:20 glycerol/water*)

The 'zero shear viscosity' $\eta_0 \simeq$ 500 Poise.

Estimated relaxation time $\lambda \simeq 40$ s.

This is a 'power law fluid', with $\eta_a \sim \dot{\gamma}^{\beta}$, and $\beta = -0.63$

# Survey of Steady Shear Rheology in Complex Fluids

Experimentally obtained rheological quantities:

1. Apparent or effective viscosity $\eta_a$ - simply defined as

$$\eta_a = \frac{\sigma}{\dot{\gamma}}$$

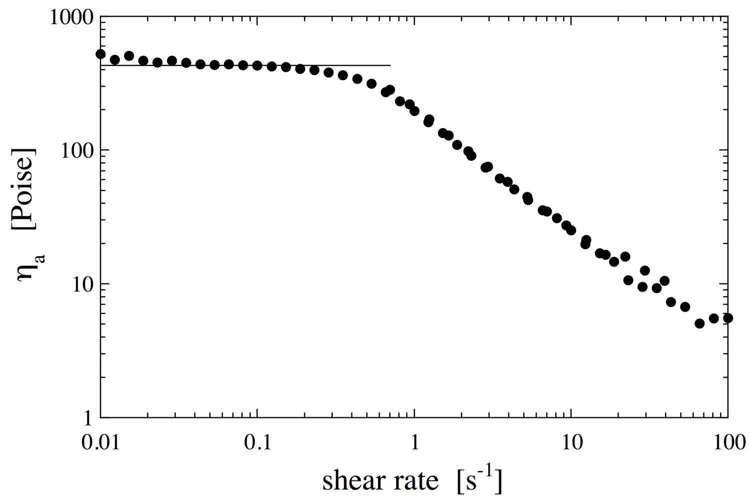
2. Zero shear viscosity $\eta_0$ - for small enough $\dot{\gamma}$, it seems that every fluid is Newtonian. This is the low shear rate plateau of $\eta_a$.

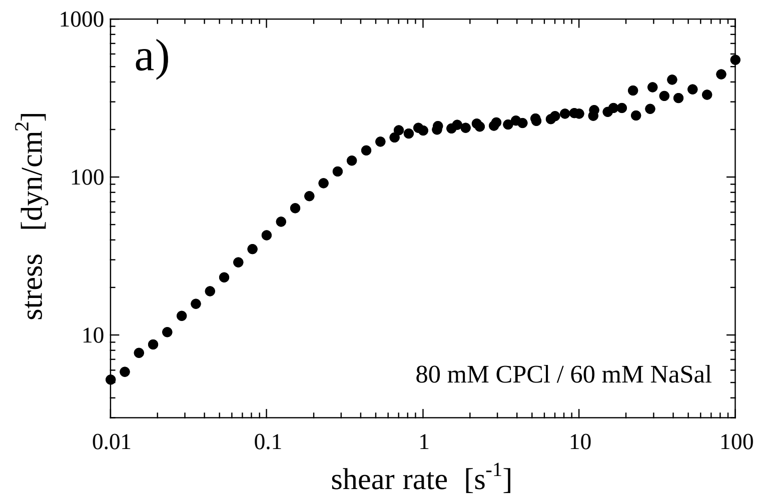
3. (Longest) relaxation time $\lambda$ - estimated in steady shear rheology using the shear rate $\dot{\gamma}_c$ at the edge of the plateau in effective viscosity:

$$\lambda = \frac{1}{\dot{\gamma}_c}$$

# Survey of Steady Shear Rheology in Complex Fluids

Shear thinning Wormlike Micellar Fluid*



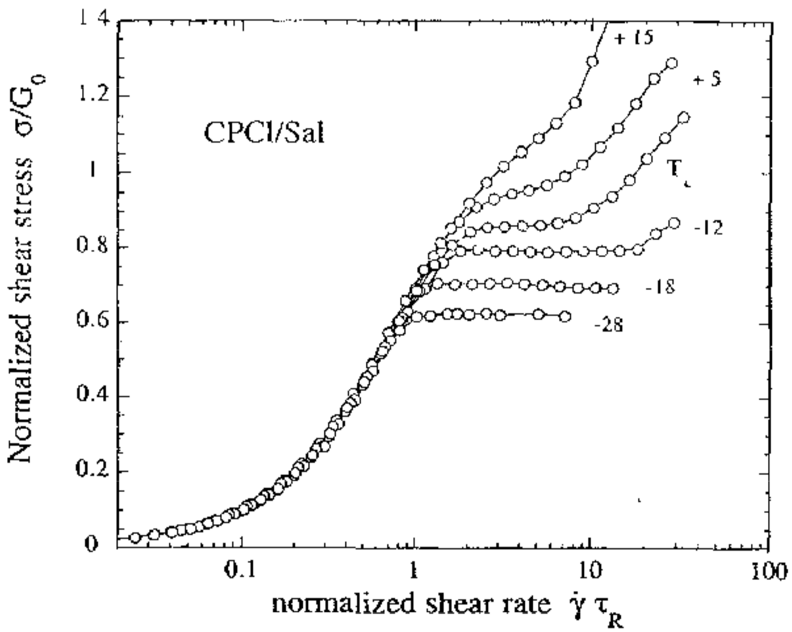

From this data we obtain

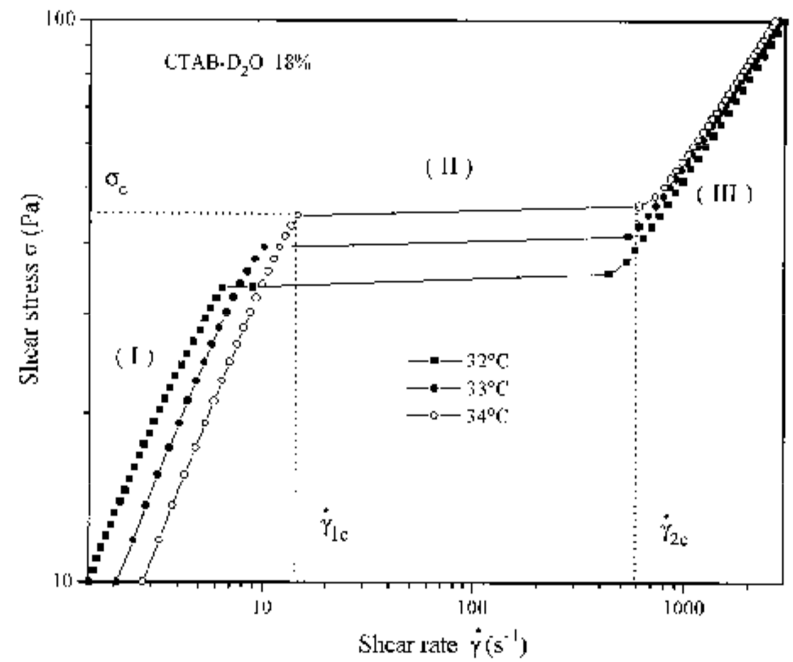
- relaxation time $\lambda \simeq 2$ s
- zero shear viscosity $\eta_0 \simeq 430$ Poise.

*briefly defined at the blackboard

# Survey of Steady Shear Rheology in Complex Fluids

Certain fluids have a stress plateau in steady shear, or a shear rate gap (can be rheometer dependent - discuss stress or shear rate controlled):




Porte, Berret, & Harden, *J. Physique II* 7 (1997), 459.

Cappelaere, Berret, Decruppe, Cressely, & Lindner, *Phys. Rev. E* 56 (1997), 1869.

The plateau region corresponds to a nonhomogeneous state: the coexistence of two or more *shear bands*:

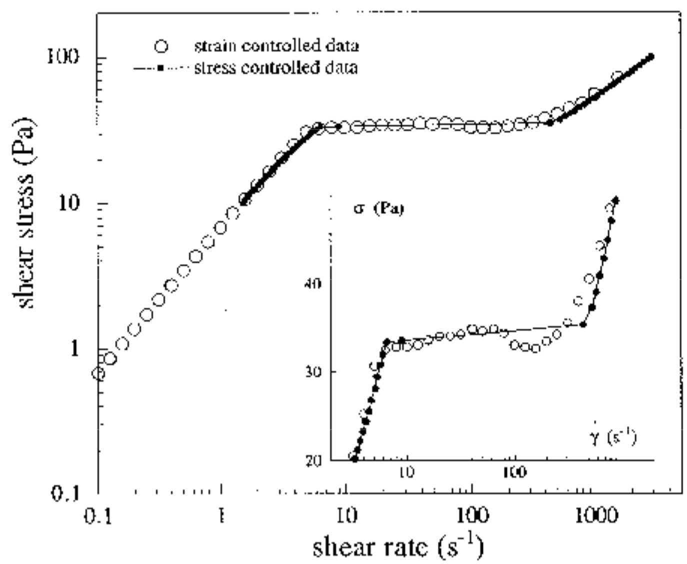
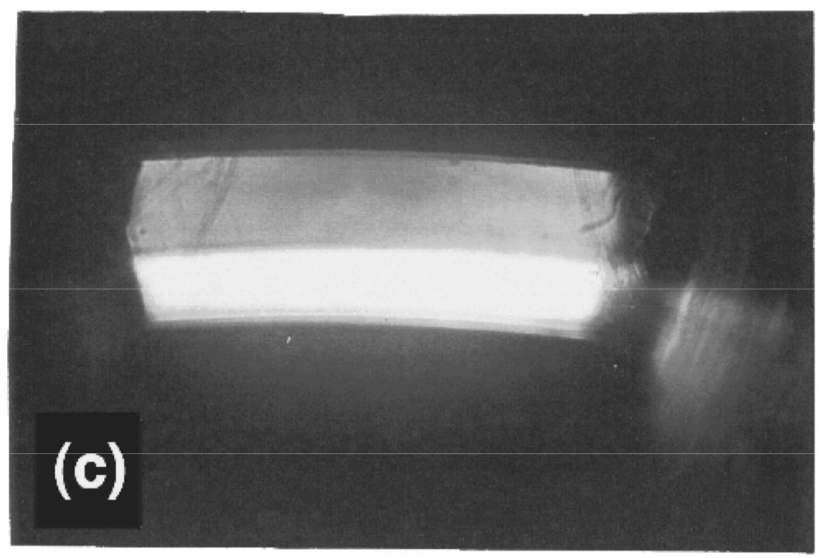



FIG. 4. Comparison between the $\sigma(\dot{\gamma})$ values in a log-log representation obtained with a controlled shear rate (open symbols) and a controlled shear stress (closed symbols) rheometer for the CTAB-$D_2O$ without salt system at $T = 32$ °C. Shown in the inset is the variation of the shear stress versus shear rate in a semilogarithmic representation.



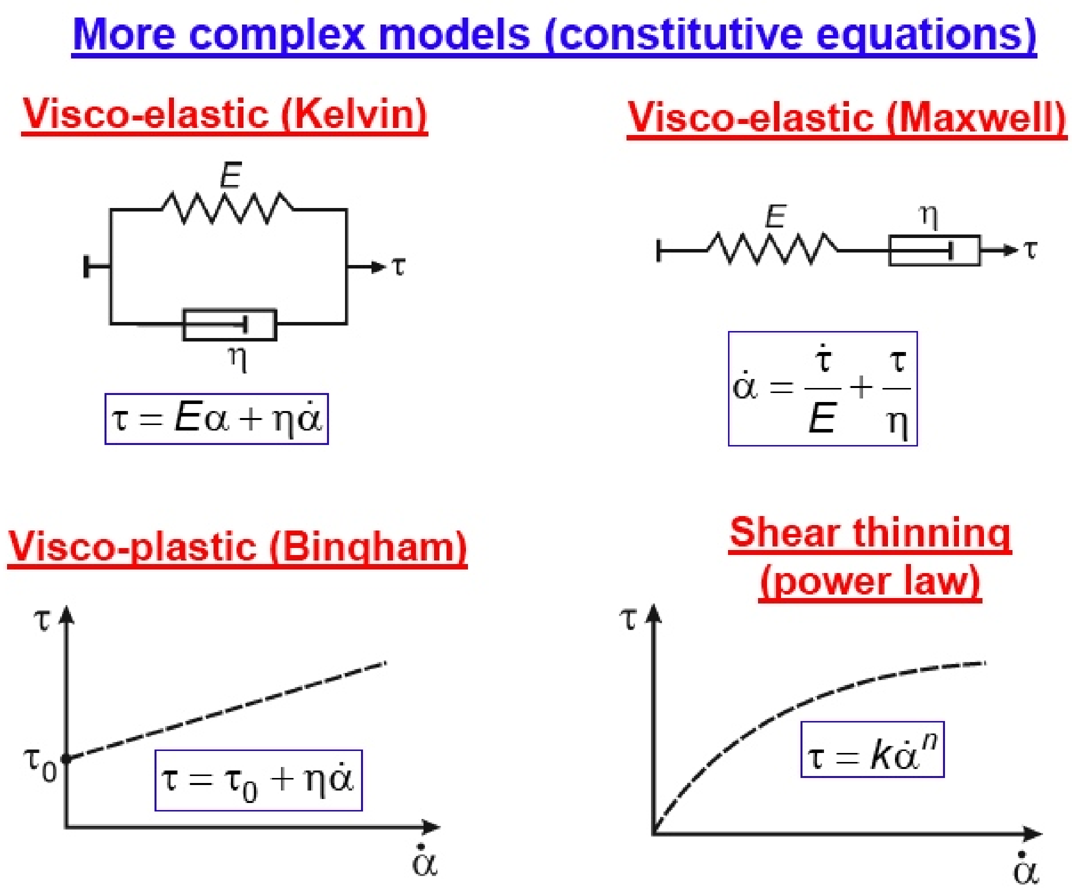

Cappelaere, Berret, Decruppe, Cressely, & Lindner, *Phys. Rev. E* 56 (1997), 1869.

Shear bands also seen in foams (→ Sylvie's talk)

# What Equation to Use for Complex Fluids?

A difficult question, still open in general; in many ways we were lucky to be surrounded with Newtonian fluids...

Recall Nikolai's slide:



# What Equation to Use for Complex Fluids?

The question of the Constitutive Equation for a given fluid is a problem in Material Science.

Here we will discuss in a little detail:

- what we can expect
- some of what has been done
- an example of where these equations can come from

# The Flow of a Fluid in General

Your beloved Navier-Stokes equation (momentum equation)

$$\rho\,(\partial_t \vec{u} + (\vec{u}\cdot\nabla)\vec{u}) = -\nabla p + \eta\nabla^2\vec{u}$$

is actually *two* equations!

Momentum (Cauchy) equation:

$$\rho\,(\partial_t \vec{u} + (\vec{u}\cdot\nabla)\vec{u}) = -\nabla p + \nabla\cdot\mathbf{T}$$

where $\mathbf{T}$ is the extra stress tensor, and

Constitutive equation:

$$\mathbf{T} = 2\eta\mathbf{D},$$

where

$$\mathbf{D} = \frac{1}{2}(\nabla\mathbf{u} + \nabla\mathbf{u}^T)$$

is the deformation rate tensor....

# The Flow of a Fluid in General

Before we talk about this tensor $\mathbf{T}$, note that:

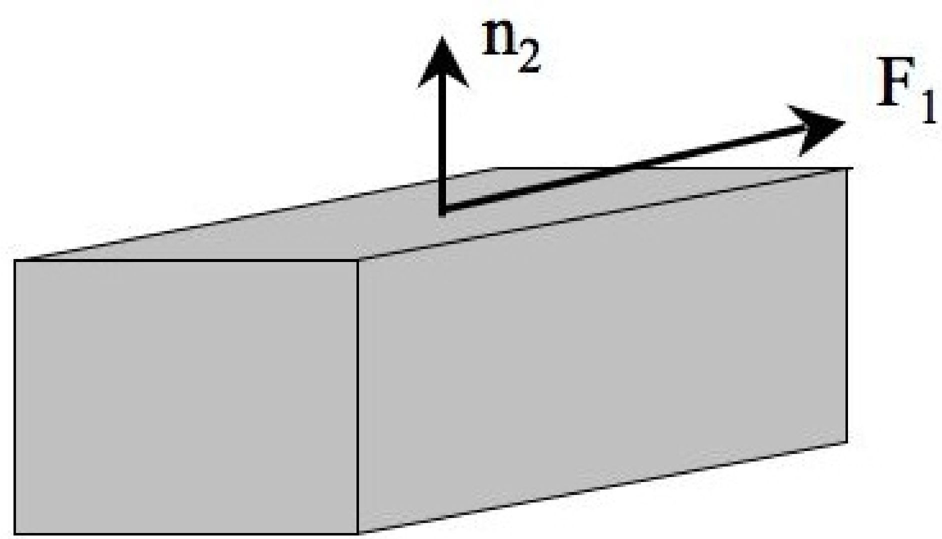
Any other constitutive equation is non-Newtonian...

Besides shear thinning / thickening, what can happen?

- memory / relaxation effects
- elastic effects (related)
- nonlinearities in deformation
- tensor product 'mixing' (e.g. normal stresses)

# Physical Reasons Why Stress Must Be a Tensor

Consider an internal region of a flowing fluid (below). As this material moves past a particular face (say with normal $\mathbf{n}_2$), it may exert a force $F_1$ in the 1 direction:



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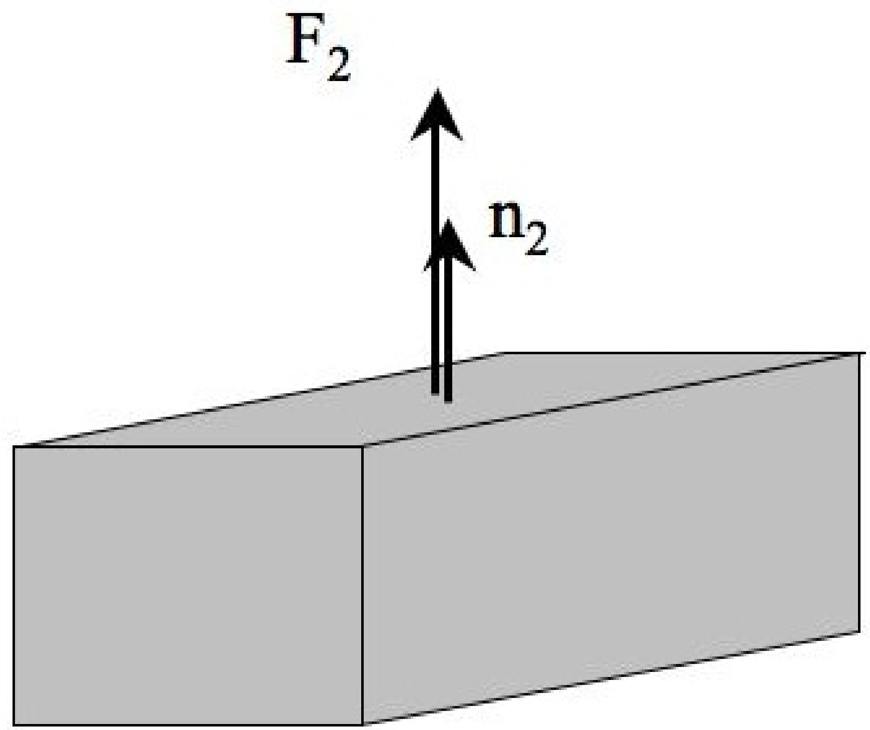


- and additionally a force $F_2$ in the 2 direction

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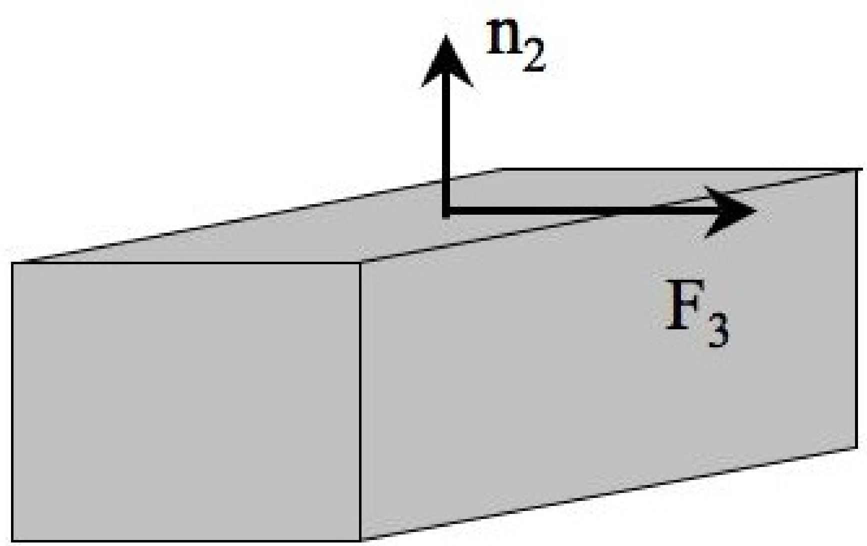


- and additionally a force $F_3$ in the 3 direction

# Physical Reasons Why Stress Must Be a Tensor

All of these forces act on the face with normal $\mathbf{n}_2$. But then there are the other faces...

We would like a quantity to describe the forces that flowing fluid can exert, which we can dot product with $\mathbf{n}_2$ to get a vector force:

$$\vec{F} = \mathbf{n}_2 \cdot \mathbf{T}$$

this is a tensor (2-tensor: 2 directions, discuss?)

Similarly we will use not just the shear rate velocity gradient $\dot{\gamma}$, but the symmetric tensor of all velocity gradients, which represents the deformation:

$$D_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right)$$

# Physical Reasons Why Stress Must Be a Tensor

Thus whatever constitutive equation we derive, propose, or find should be in terms of these tensors.

We will briefly look at some of the most well-known in the non-Newtonian fluids community.

## Maxwell model

The first non-Newtonian constitutive equation is due to J. C. Maxwell (gas theory, 1867):

$$\lambda \frac{\partial \mathbf{T}}{\partial t} + \mathbf{T} = 2\eta \mathbf{D}$$

In addition to the viscosity, this gives one more material property, the relaxation time $\lambda$.

Solve this using the integrating factor $e^{t/\lambda}$:

$$\mathbf{T}(x,t) = \mathbf{T}(x,0)e^{-t/\lambda} + \int_0^t 2\eta \mathbf{D}(s) \left( \frac{e^{-(t-s)/\lambda}}{\lambda} \right) ds$$

*(fading memory)* *(memory kernel)*

# Two Material Properties → Two Nondimensional Parameters

- viscous fluids: viscosity → Reynolds number

$$\frac{\text{diffusion time}}{\text{advection time}} \sim \frac{L^2/\nu}{L/U} = \frac{UL}{\nu} = Re$$

- viscoELASTIC fluids: stress relaxation time → Deborah number

$$\frac{\text{relaxation time}}{\text{advection time}} \sim \frac{\lambda}{L/U} = \frac{\lambda U}{L} = De$$

*Note:* in the limit $De \to 0$, one gets Navier-Stokes.

# Normal Stress Effects

The Rod Climbing or Weissenberg effect is driven by extra stresses which are exerted radially *inward*:

(*Gareth McKinley's lab - MIT, USA*)

→ will be discussed later for foams (Sylvie)

# Constitutive List: of Increasing Mathematical Horrors

$$\mathbf{T} = 0$$

(Euler 1748)

$$\mathbf{T} = 2\eta\mathbf{D}$$

(Newton / Navier-Stokes 1660 - 1845)

$$\lambda\frac{\partial\mathbf{T}}{\partial t} + \mathbf{T} = 2\eta\mathbf{D}$$

(Maxwell 1867)

$$\lambda\left(\frac{\partial\mathbf{T}}{\partial t} + (\vec{u}\cdot\nabla)\mathbf{T}\right) + \mathbf{T} = 2\eta\mathbf{D}$$

(convected + Maxwell)

$$\lambda\left(\frac{\partial\mathbf{T}}{\partial t} + (\vec{u}\cdot\nabla)\mathbf{T} - \nabla\mathbf{u}^T\cdot\mathbf{T} - \mathbf{T}\cdot\nabla\mathbf{u}\right) + \mathbf{T} = 2\eta\mathbf{D}$$

(Oldroyd 1950)

# Pause - Back to Experiments for Inspiration

(we stopped here, continue in Complex Fluids II)

# Summary

Today: viscometric flows of Newtonian and non-Newtonian fluids

1. Steady rheology

2. Rheometers: cone-and-plate, couette

3. Rheology of complex fluids: shear thinning, shear banding,

   normal stresses (more to come)

4. Constitutive equations