Viscoelasticity

- Basic Notions & Examples
- Formalism for Linear Viscoelasticity
- Simple Models & Mechanical Analogies
- Non-linear behavior

Viscoelastic Behavior

- Generic Viscoelasticity: exhibition of both viscous and elastic properties, depending on the time scale over which an external stress is applied

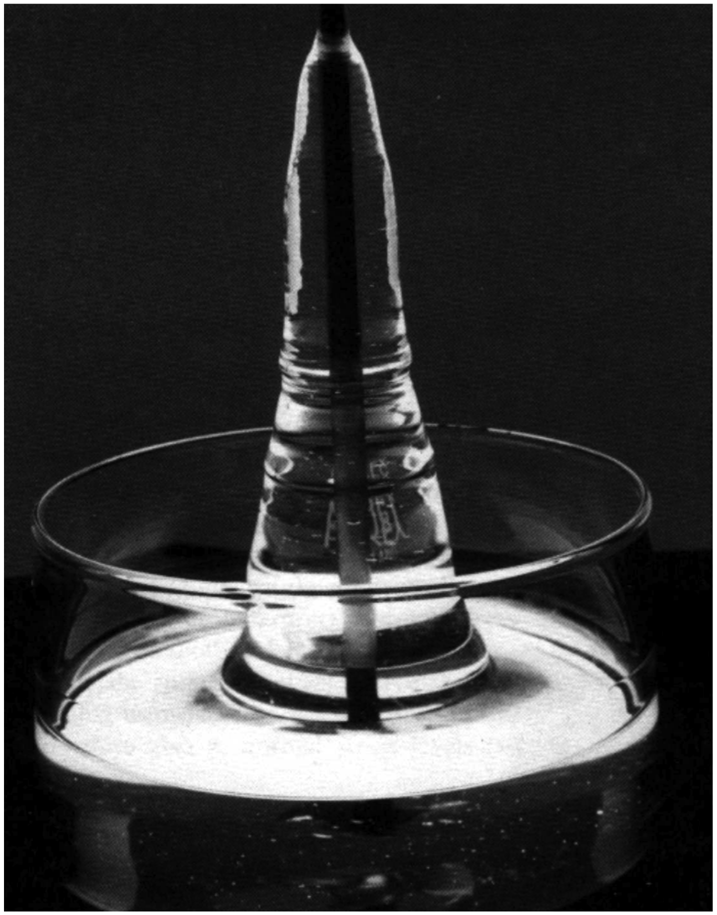
Specific Effects:

- *Dilatancy:* viscosity increases with the rate of shear ("shear-thickening")
- *Pseudo-plasticity:* viscosity decreases with the rate of shear ("shear-thinning")
- *Thixotropy:* viscosity decreases with duration of stress
- *Rheopecticity:* viscosity increases with duration of stress

Bouncing Drops

Viscoelastic Flows

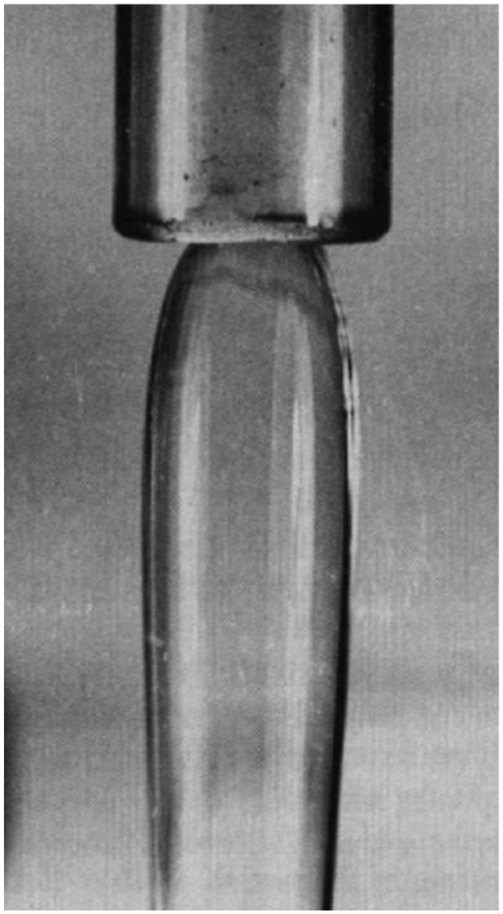
- Climbing a Rotating Rod:



Example of a Weissenberg instability

Viscoelastic Flows

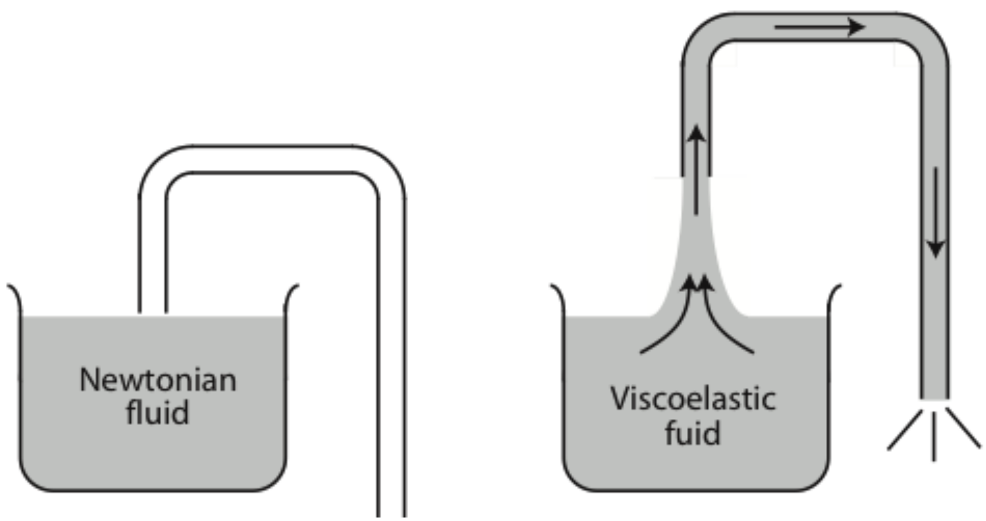
- Die Swell:



Another Weissenberg instability

Viscoelastic Flows

- <u>Tubeless Siphon:</u>



Due to extensional elastic stress

Viscoelastic Flow Movies

Momentum Balance

- Integrate Newton's Second Law over a volume element

$$\int_{V_m} \rho \frac{d\vec{v}}{dt}\, dV = \int_{S_m} \sigma \cdot \hat{n}\, dS + \int_{V_m} \vec{f}\, dV$$

- Gives a generalized equation of motion for a complex fluid:

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla)\vec{v} = \nabla \cdot \sigma + \vec{f}$$

- For a simple viscous fluid, $\sigma_{ij} = -P\delta_{ij} + \eta \left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right)$, we obtain the Navier-Stokes Eq:

$$\rho \frac{\partial \vec{v}}{\partial t} + \rho(\vec{v} \cdot \nabla)\vec{v} = -\nabla P + \eta \nabla^2 \vec{v} + \vec{f}$$

Creeping Flow Limit

- Dissipative terms dominate over inertial terms:

$$\nabla \cdot \sigma + \vec{f} = 0$$

$$\sigma_{ij}(t) = \mathcal{F}[\epsilon_{ij}(t' \leq t), \dot{\epsilon}_{ij}(t' \leq t)]$$

$$\dot{\epsilon}_{ij} = \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \qquad \epsilon_{ij} = \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}$$

generalized Stokes flow for a complex fluid

- c.f.: Stokes flow for a simple viscous fluid:

$$\eta \nabla^2 \vec{v} + \vec{f} = \nabla P$$

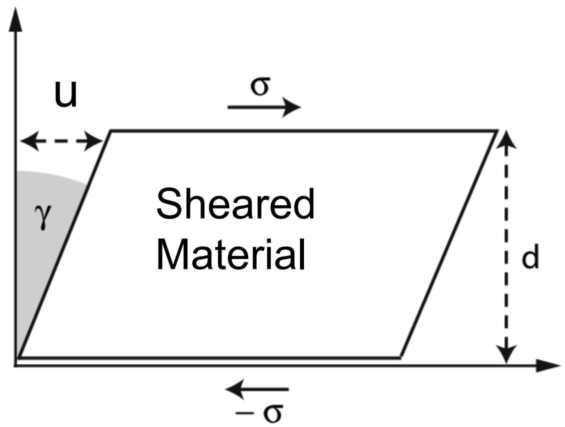
Rheological Measurements

- Apply a controlled strain; measure the stress response
  - Relaxation after step strain
  - Response to steady strain rate
  - Dynamic response to oscillatory strain
- Apply a controlled stress; measure the strain response
  - Creep after step stress
  - Dynamic response to oscillatory stress

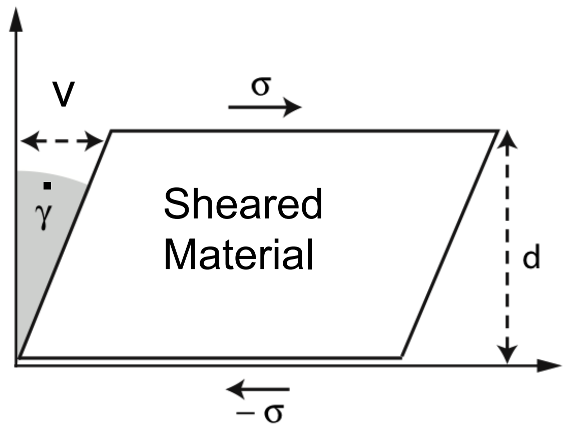
generalized Stokes flow for a complex fluid

Simple Shear

- Consider unidirectional shear deformation between parallel plates



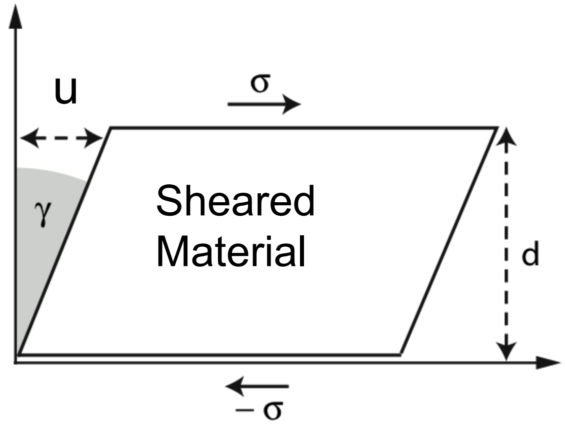
Solid-Like



Liquid-Like

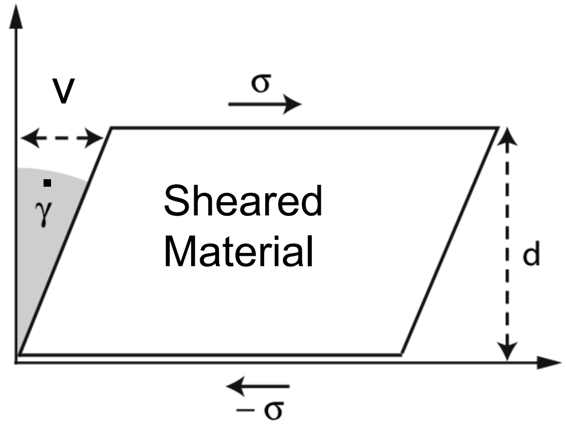
- Scalar parameters: $\sigma, \gamma, \dot{\gamma}$

Linear Solid and Liquid



$$\sigma = G\gamma$$

Hookian Solid



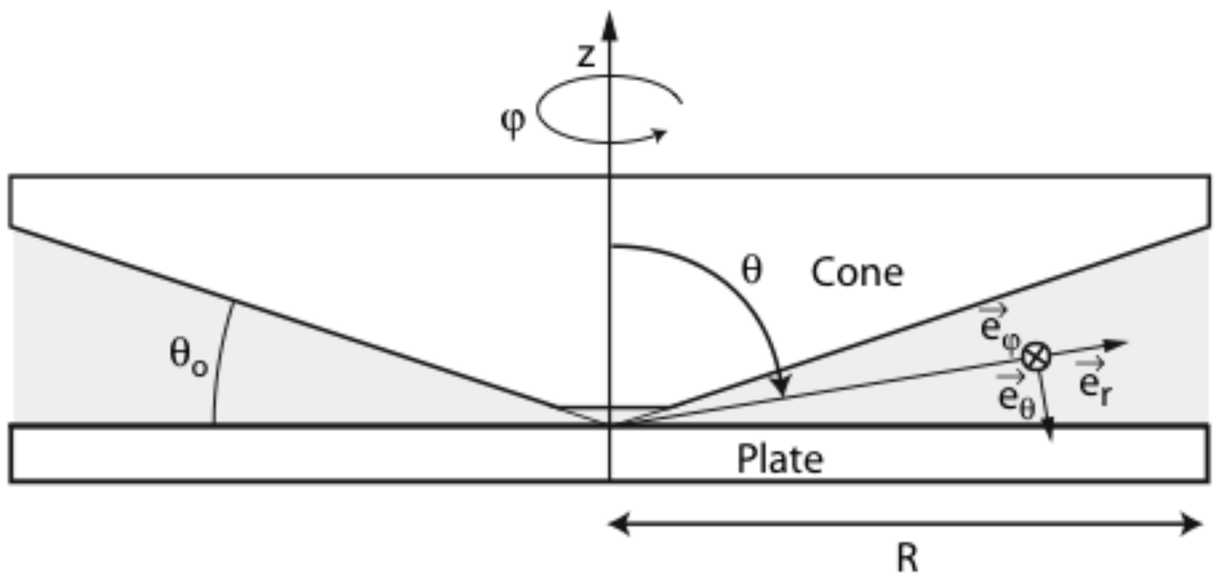
$$\sigma = \eta\dot{\gamma}$$

Newtonian Liquid

- Typical VE material shares features of each

Rheometer

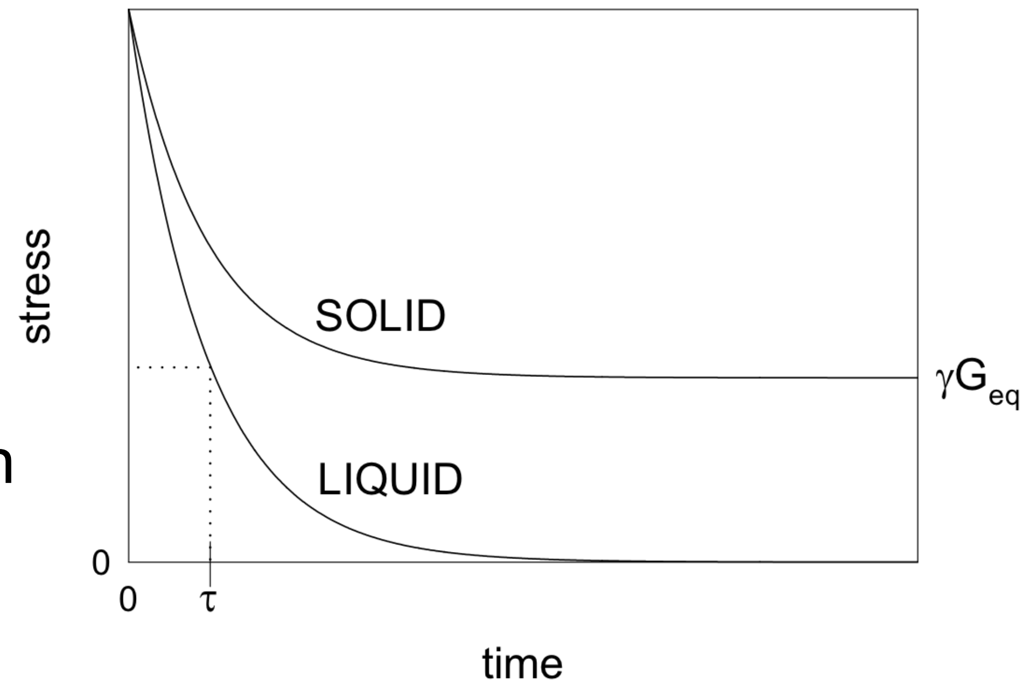
Cone-Plate Rheometry



Uniform strain rate: $$\dot{\gamma} = \frac{\dot{\Omega}}{\theta_0}$$

Stress Relaxation

- Consider applying a small fixed "step strain" γ_0 and measuring the resulting stress (linear response)
- For all but perfect elastic solids, stress will decrease with time:



- Define the linear relaxation shear modulus:

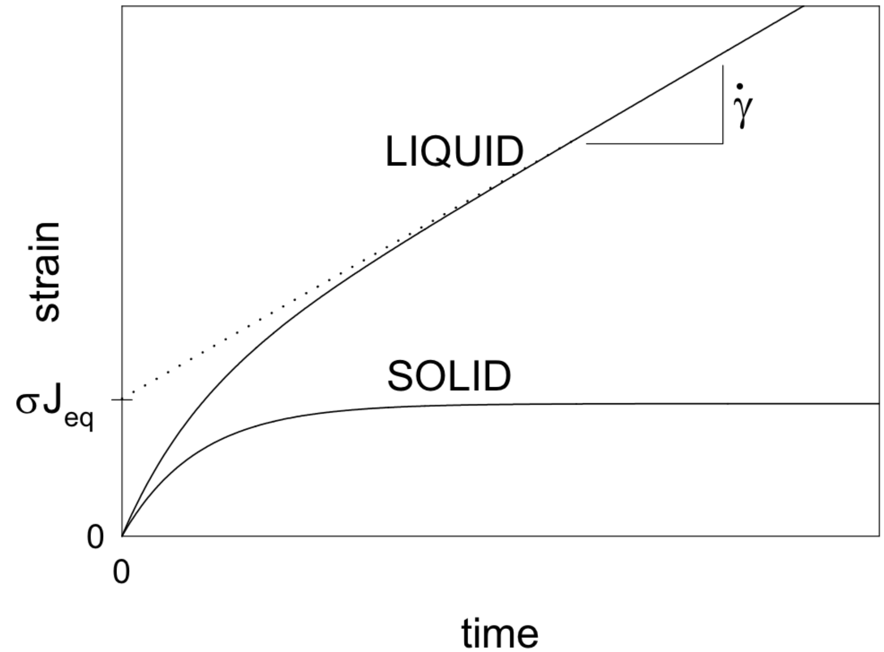
$$G(t) = \sigma(t)/\gamma_0$$

- Equilibrium shear modulus (residual elasticity):

$$G_{eq} = \lim_{t \to \infty} G(t)$$

Creep

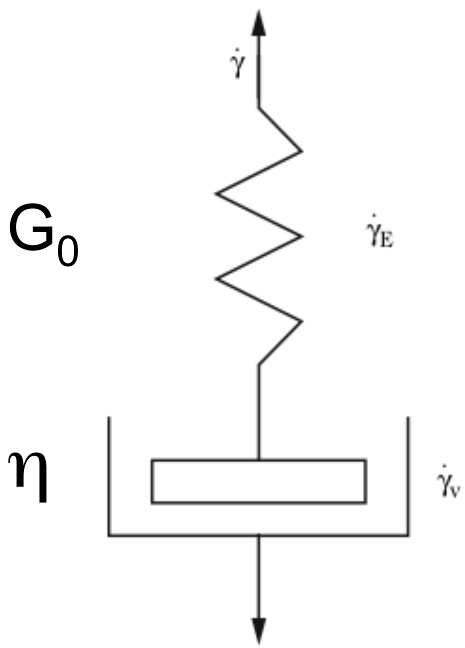
- Under a weak, constant shear stress σ_0, most viscoelastic materials slowly deform (creep):



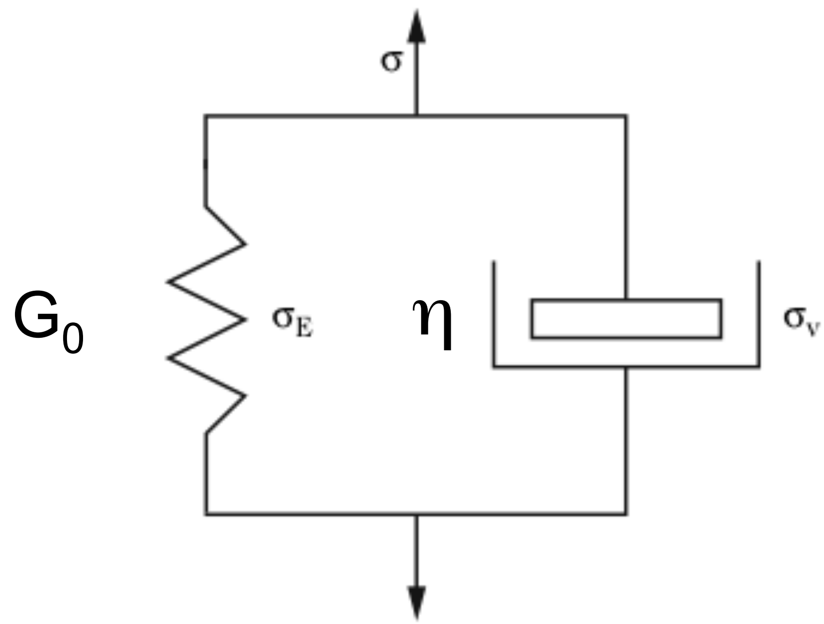
- Defines the linear creep compliance:

$$J(t) = \gamma(t)/\sigma_0$$

Prototype VE Solid and Liquid



Maxwell VE Liquid



Voigt VE Solid

Maxwell Fluid

- Strain is additive:

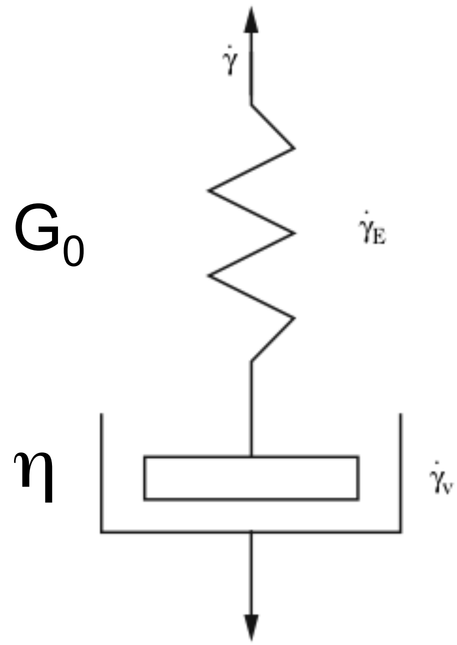
$$\gamma = \gamma_E + \gamma_v$$

- Stress is uniform:

$$\sigma_E = \sigma_v = \sigma$$

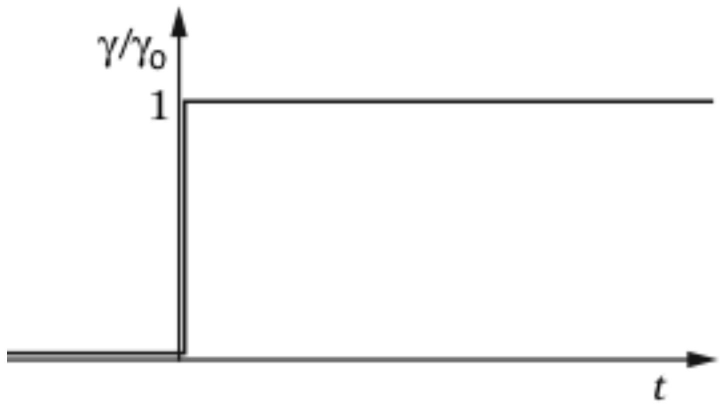
- Gives:

$$\boxed{\tau\dot{\sigma}(t) + \sigma(t) = \eta\dot{\gamma}(t)}$$

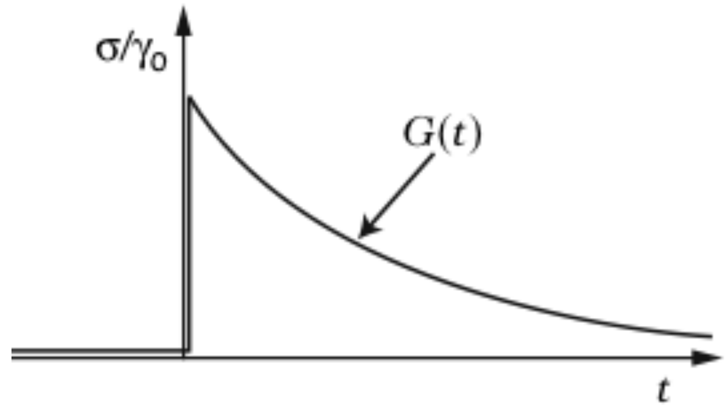


$$\tau = \eta / G_0$$

Response to a Step Shear Strain: Maxwell Fluid



Step Strain :



Stress Relaxation

γ_0 is the step shear strain

$$G(t) = G_0 \exp(-t/\tau)$$

General Stress Relaxation

- Apply a series of infinitessimal fixed "step strains" $\delta\gamma_i$ at time t_i
- The resulting stress $\sigma(t)$ is a linear superposition of responses:

$$\sigma(t) = \sum_i G(t - t_i)\delta\gamma_i = \sum_i G(t - t_i)\dot{\gamma}_i \delta t_i$$

- Go to the continuum limit of infinitessimal step durations:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')dt'$$

General Linear Viscoelastic Fluid

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\,\dot{\gamma}(t')\,dt'$$

Can do the same for a series of step stresses:

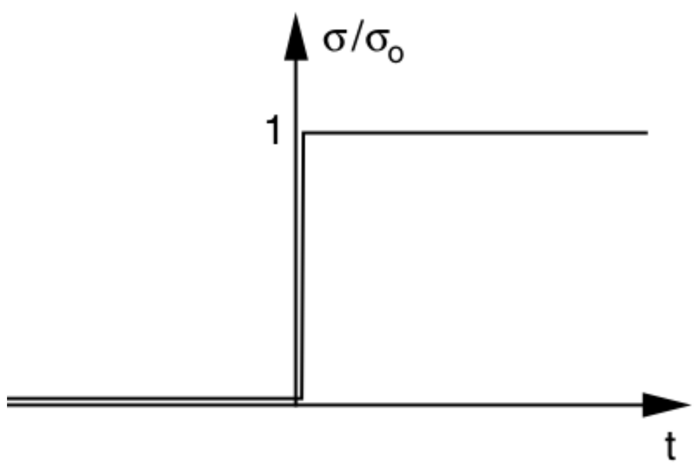
$$\gamma(t) = \int_{-\infty}^{t} J(t-t')\,\dot{\sigma}(t')\,dt'$$

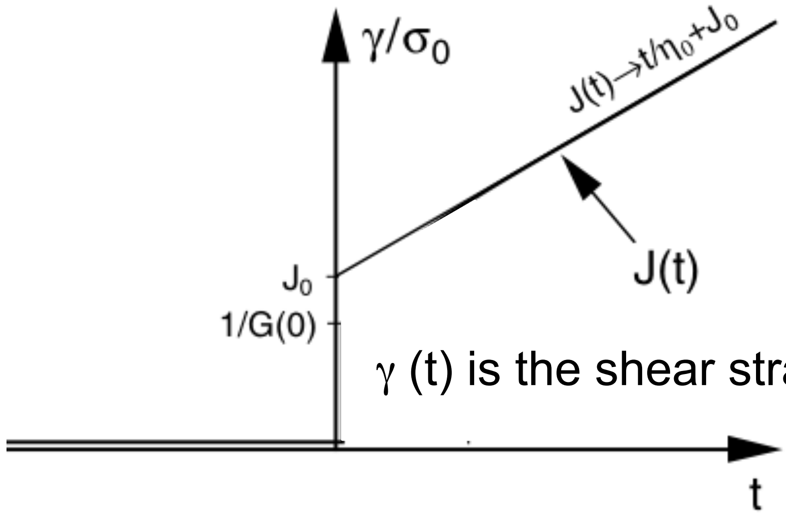
Constraint: $G(t)J(t) \leq 1$

Response to a Step Shear Stress: Maxwell Fluid

Step Stress : σ_0

Creep: $J(t) = \gamma(t)/\sigma_0$





γ (t) is the shear strain

$$J(t) = J_0 + \frac{t}{\eta} \quad \text{where} \quad J_0 = 1/G_0$$

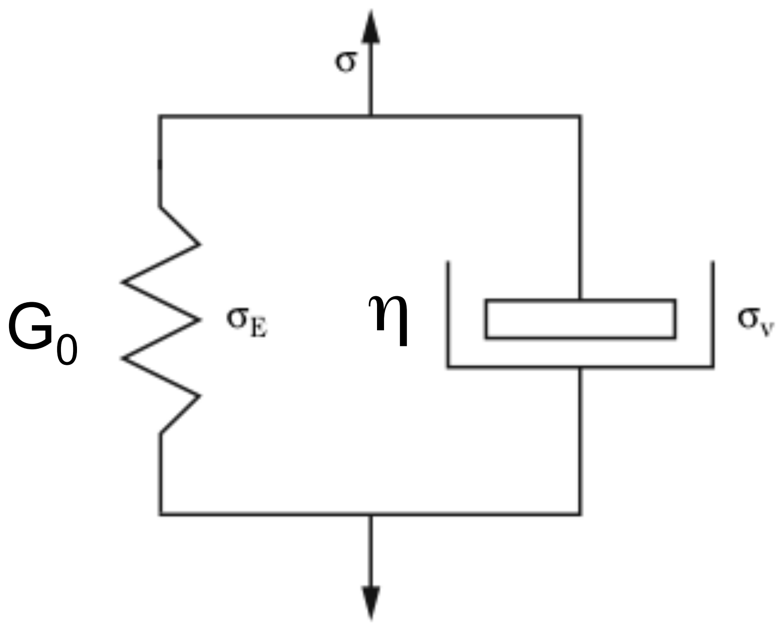
Voigt Fluid

- Stress is additive:

$$\sigma = \sigma_E + \sigma_v$$

- Strain is uniform:

$$\gamma_E = \gamma_v = \gamma$$

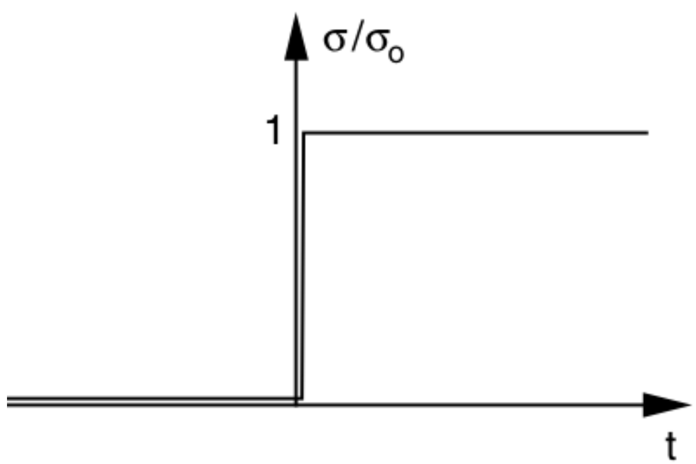


- Gives:

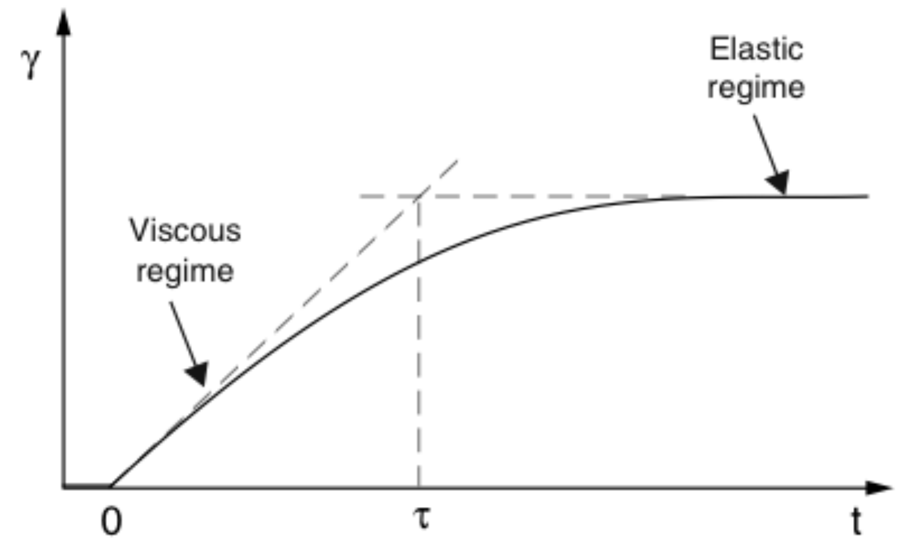
$$G_0\,\gamma(t) + \eta\,\dot{\gamma}(t) = \sigma(t)$$

Response to a Step Shear Stress: Voigt Solid

Step Stress : σ_0



Creep: $J(t) = \gamma(t)/\sigma_0$



$$J(t) = \frac{1}{G_0}\left[1 - \exp(-t/\tau)\right]$$ where $\tau = \eta/\mathrm{G}_0$

Steady Shear

- For a constant applied rate of shear strain:

$$\sigma(t) = \int_{-\infty}^{t} G(t-t')\dot{\gamma}(t')dt' = \dot{\gamma}\int_{-\infty}^{t} G(t-t')dt'$$

- Defines the viscosity:

$$\eta = \int_0^\infty G(t)dt$$

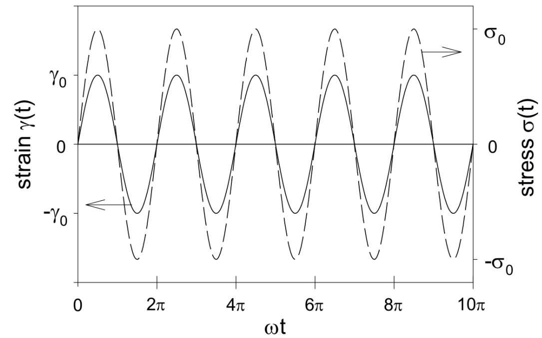
- Maxwell model:

$$\eta = G_0 \int_0^\infty \exp(-t/\tau)\, dt \;=\; G_0\,\tau$$

Oscillatory Shear

- Apply a simple harmonic shear strain: $\gamma(t) = \gamma_0 \sin(\omega t)$
- Shear stress response is simple harmonic with a phase shift:

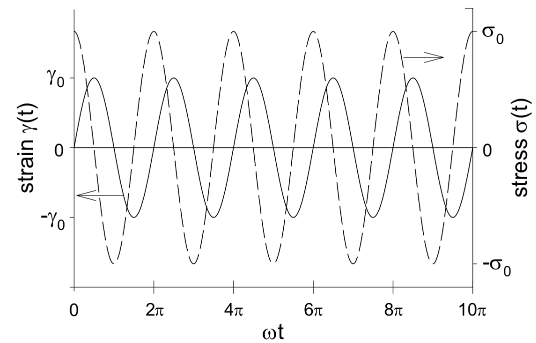
$$\sigma(t) = \sigma_0 \sin(\omega t + \delta)$$



- In-phase response is elastic: $(\delta=0)$

$$\sigma(t) = \gamma_0 G'(\omega) \sin(\omega t)$$

- Out-of-phase response is viscous: $(\delta=\pi/2)$



$$\sigma(t) = \gamma_0 G''(\omega) \cos(\omega t)$$

- General response is a sum of of these two:

$$\sigma(t) = \gamma_0 \left[G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)\right]$$

Complex Modulus

- Complex modulus contains the storage and loss components:

$$G^*(\omega) \equiv G'(\omega) + iG''(\omega) \qquad \eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}$$

- Given by the Fourier transform of the relaxation modulus G(t):

$$G^*(\omega) = i\omega \int_0^\infty G(t)\exp(-i\omega t)dt$$

Applied Oscillatory Stress

$$\sigma(t) = \sigma_0 \exp(i\omega t)$$ gives:

$$\gamma(t) = J^*(\omega)\sigma(t)$$

$$J^*(\omega) = i\omega \int_0^\infty J(t) \exp(-i\omega t) dt$$

$$J^*(\omega) = J'(\omega) + iJ''(\omega)$$

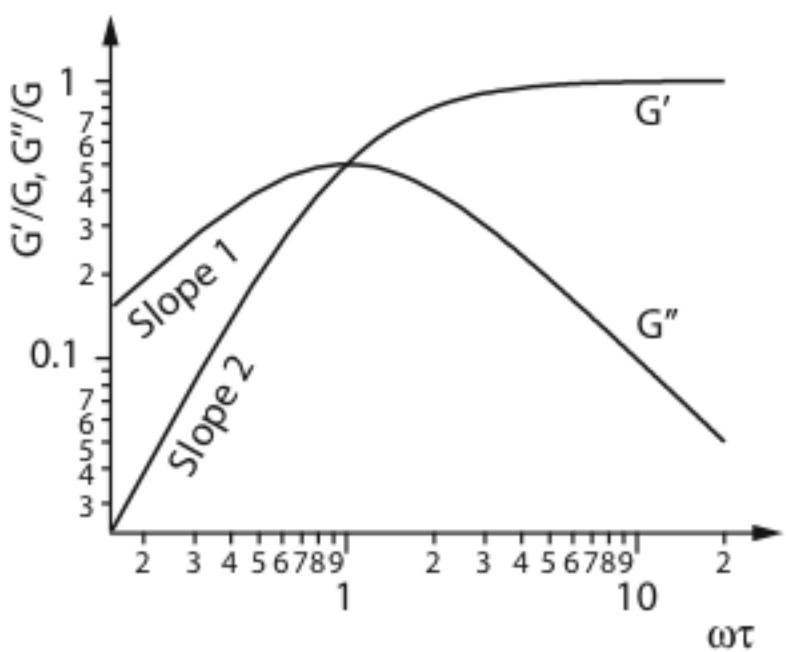
Dynamic Creep Compliance

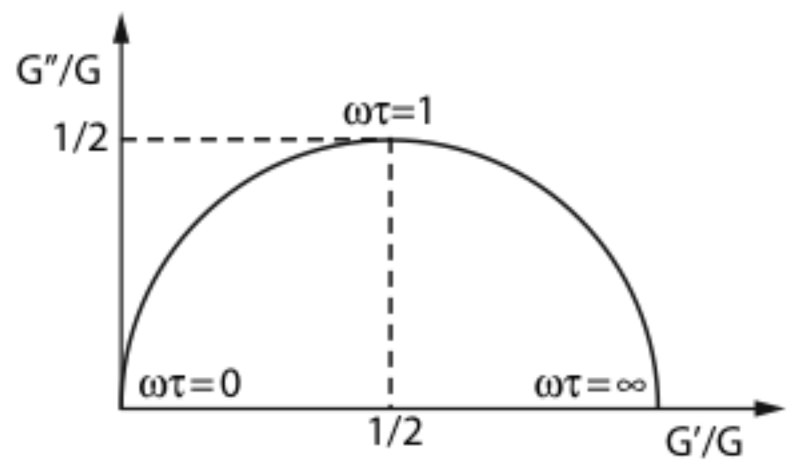
$$J^*(\omega)G^*(\omega) = 1$$

Oscillatory Maxwell Fluid

Can show:

$$G'(\omega) = \frac{G_0 \tau^2 \omega^2}{(1 + \tau^2 \omega^2)} \qquad G''(\omega) = \frac{G_0 \tau \omega}{(1 + \tau^2 \omega^2)}$$

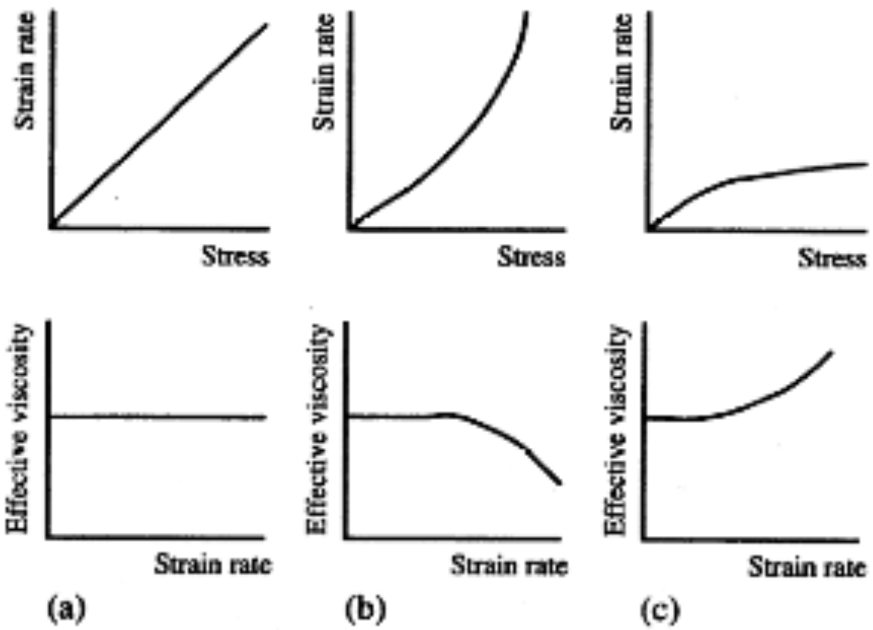




Cole-Cole Plot

Flow of Complex Fluids

- Complex fluids exhibit non-Newtonian behavior in steady state flow conditions (non-linear response):



Newtonian Thinning Thickening

- Thickening/Thinning behavior is due to microstructural changes
- Numerous phenomenological constitutive relations

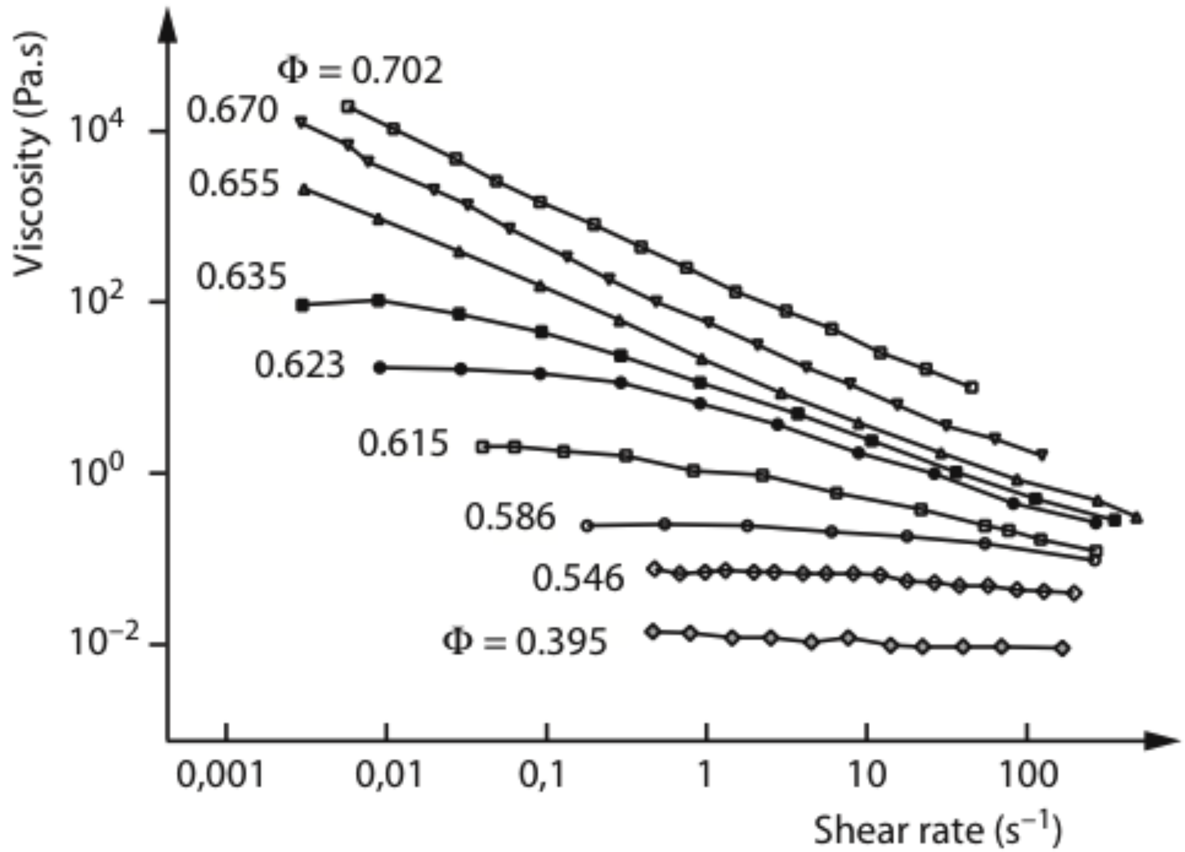
e.g. "power-law" fluids: $\sigma = \eta(\dot{\gamma})\dot{\gamma} = \kappa\,\dot{\gamma}^n$

Shear Thinning Fluids

- Strong deformation leads (eventually) to micro-structural rearrangements that lower resistance to further deformation
- Typical flow-induced changes:
  - break-up of clusters
  - flow alignment of domains
  - disentanglement of polymers
- Reversible vs permanent thinning

Shear Thinning Fluids

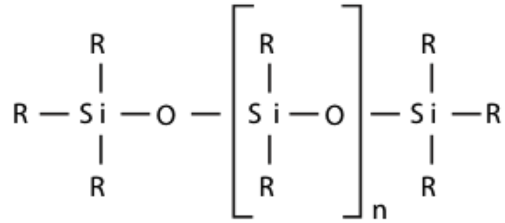
- Dense colloidal suspensions:



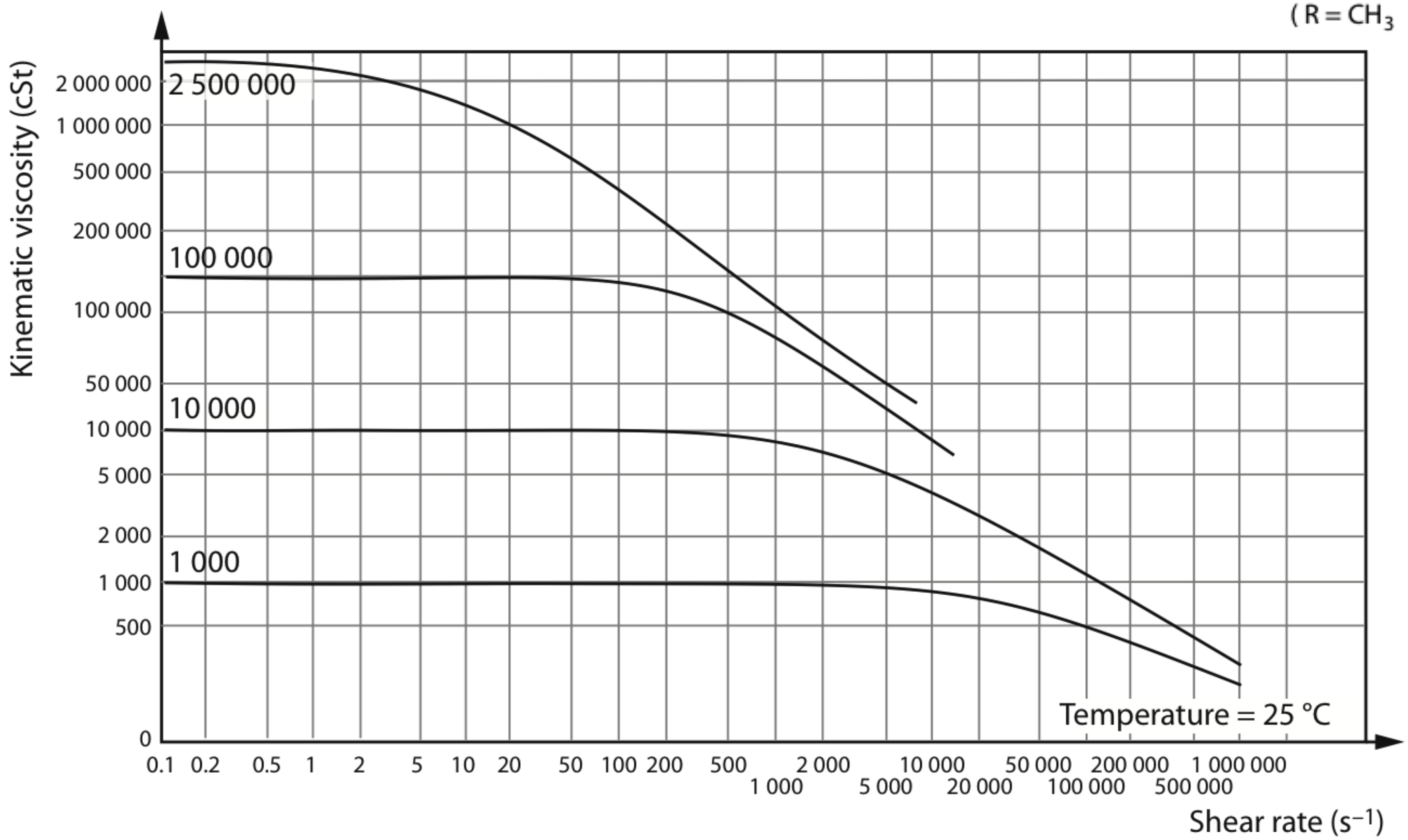
- Reversible thinning behavior for high enough concentrations

Shear Thinning Fluids

- Concentrated polymer fluids: PDMS



(R = CH_3 or C_5H_6)



- Almost always reversible thinning behavior

Shear Thickening Fluids

- Strong deformation leads (eventually) to micro-structural rearrangements that increases resistance to further deformation

- Typical flow-induced changes:

  - transient cluster formation (jamming)
  - order-to-disorder transitions
  - formation and resistance of topological entanglements

- Reversible vs permanent thickening

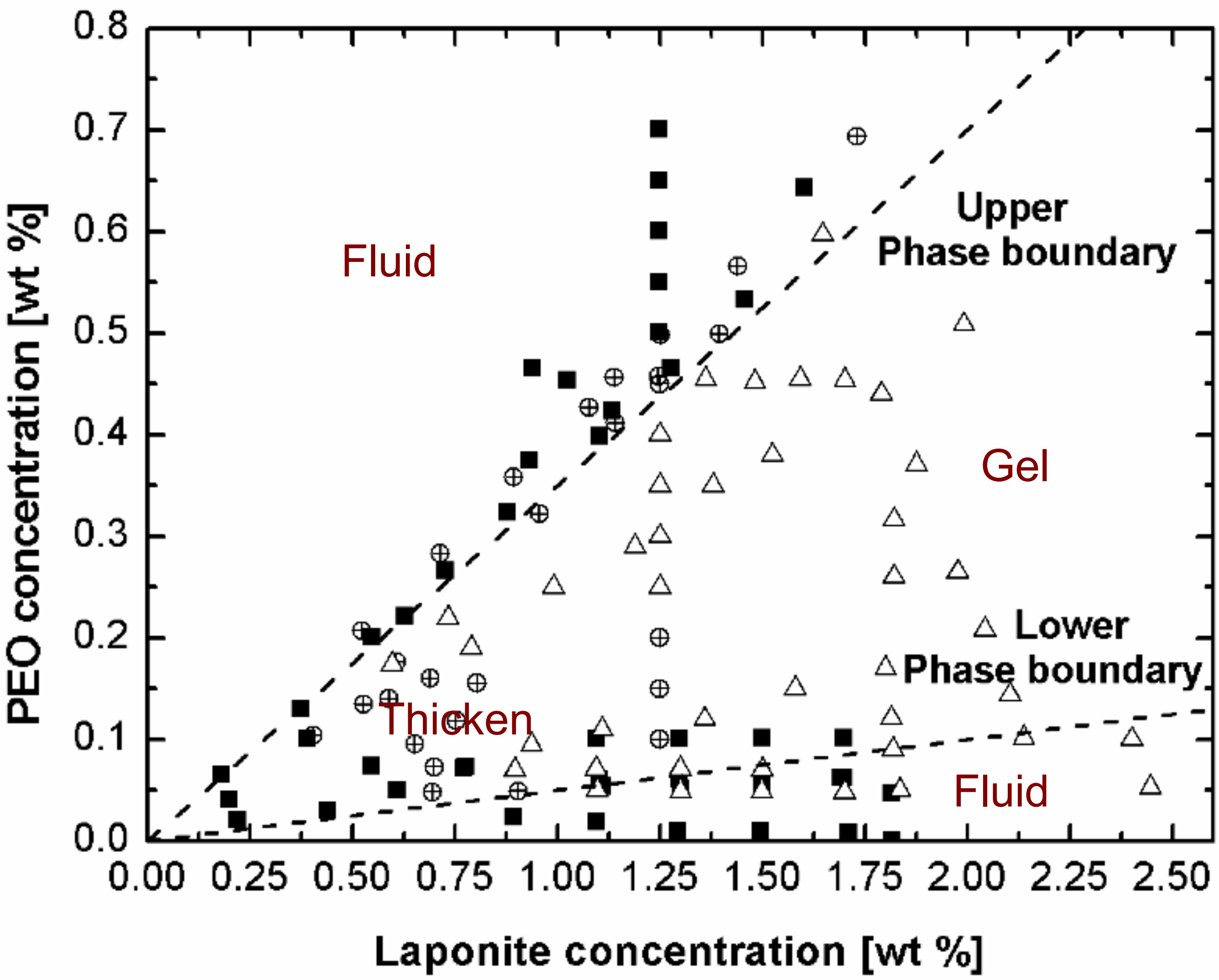
Shear Thickening-Example 1

Polymer-Colloid Shake Gels

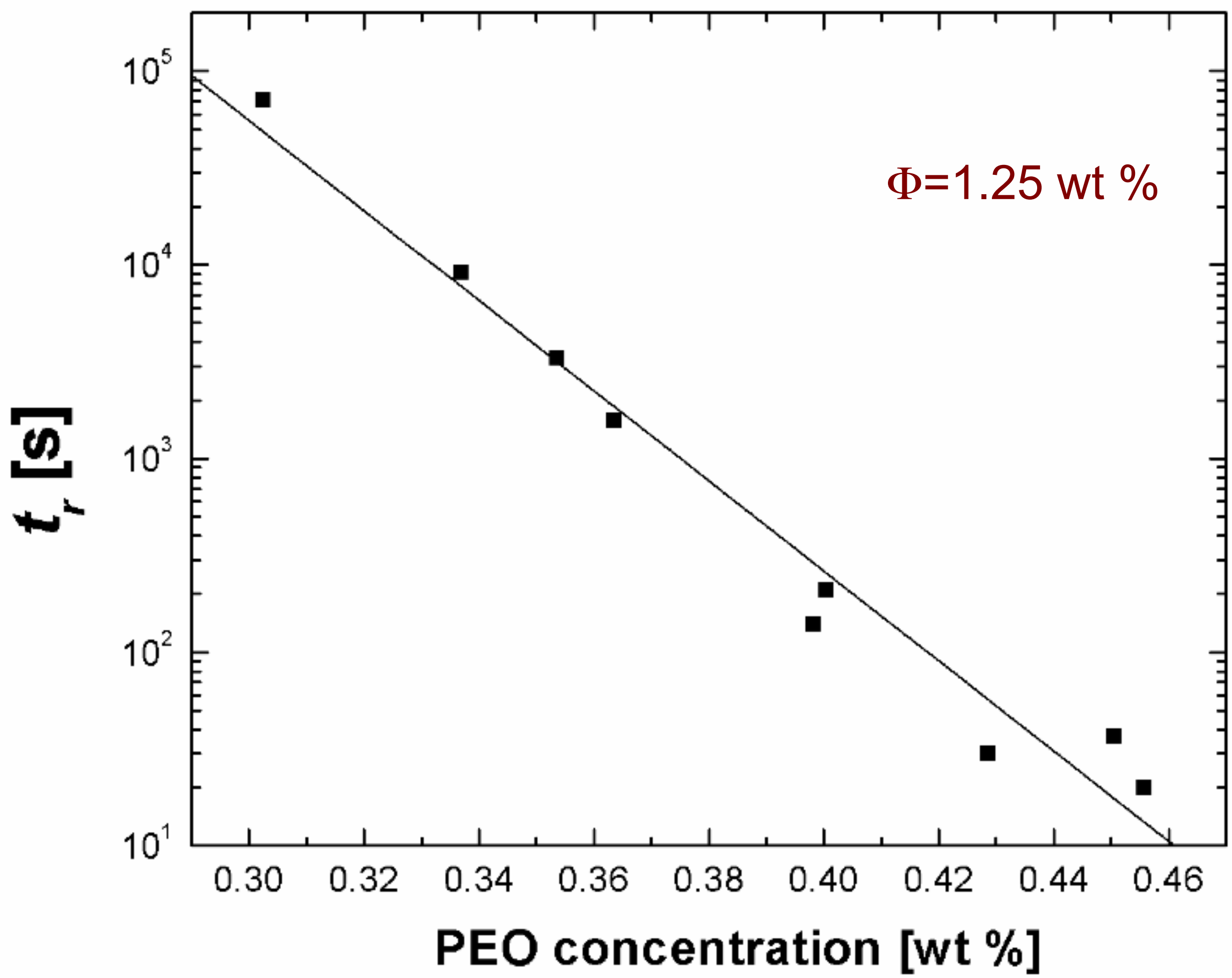
- Strong deformation leads to transient extension of polymers
- Extended polymers form bridges between colloids
- Transient network is formed
- Example: Laponite-PEO mixture

J. Zebrowski, et al., Coll. Surf Sci. A,(2006)

Shake Gel Phase Diagram



Shake Gel Relaxation



Relaxation time is a decreasing function of PEO concentration!

Shear Thickening-Example 2

Concentrated starch suspensions

- Strong deformation leads to transient jamming of starch grains
- Transient stress pillars are formed that resist deformation
- Suspension flows if not strongly perturbed

Shear Thickening Instability

Driven concentrated starch suspensions:

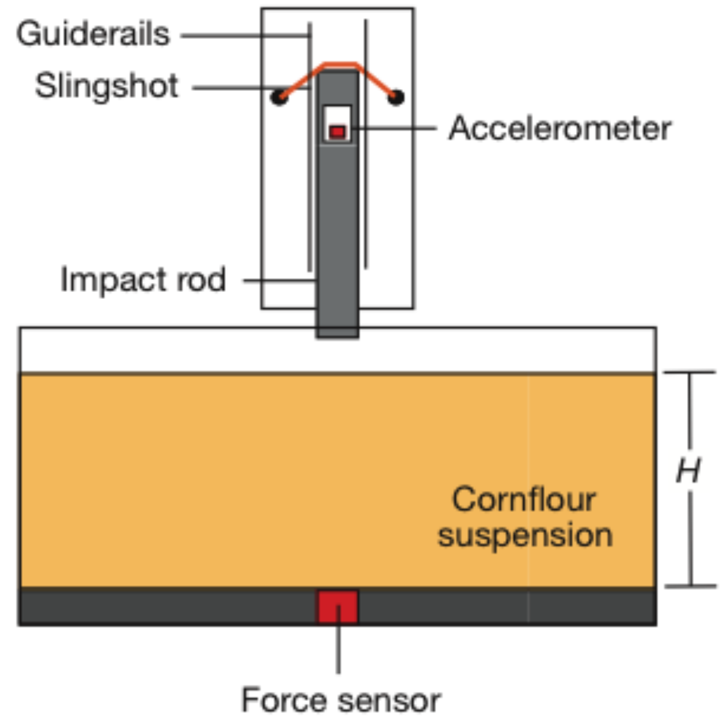
Transient Solid-Like Behavior

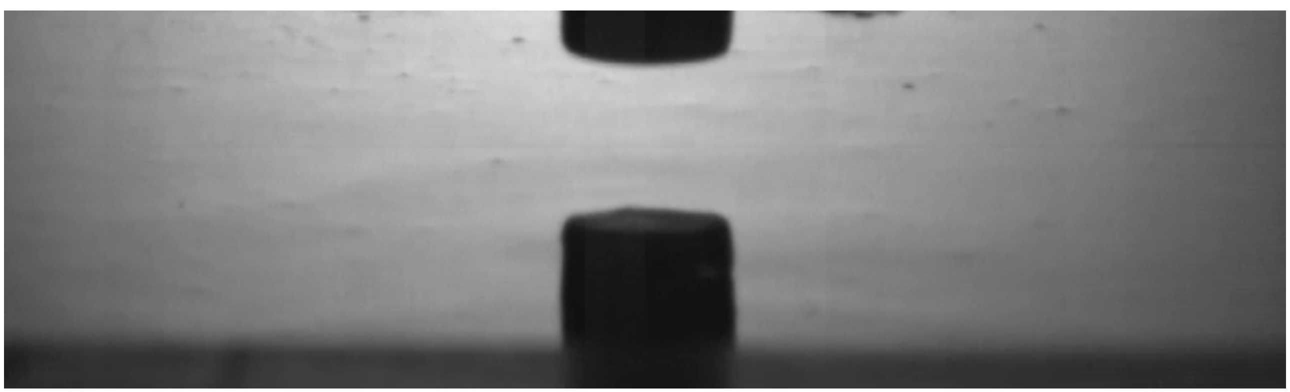
Walking on corn starch solutions:

- Rapid steps: solid response
- Slow steps: fluid response

Chicago Experiments

Impact experiments:

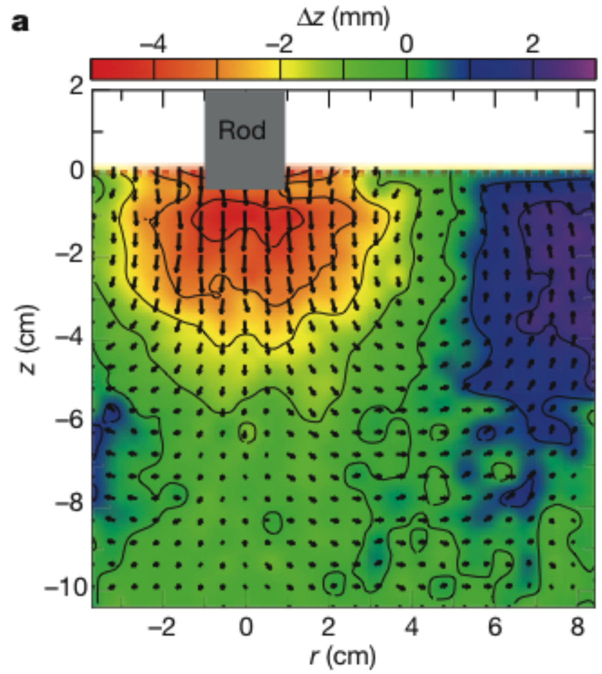


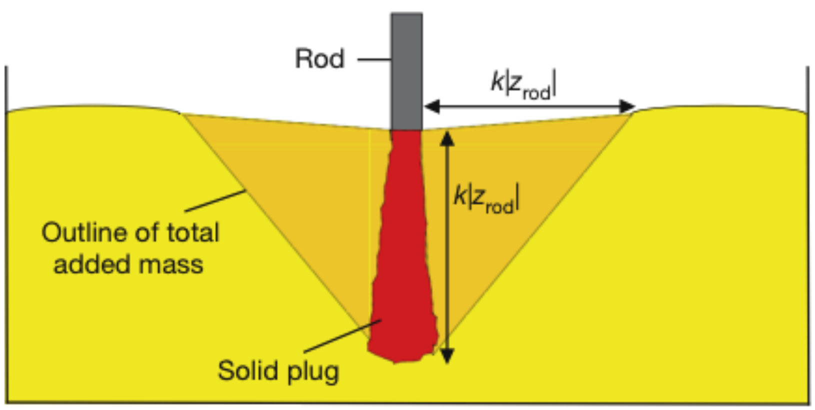


SR Waitukaitis & HM Jaeger, Nature **487**, 205-209 (2012)

Chicago Experiments

Displacement field near rod:





Interpretation:

formation of transient, localized solid support pillar

SR Waitukaitis & HM Jaeger, Nature **487**, 205-209 (2012)

Non-Newtonian Pipe Flow

- Pressure-driven flow of a power-law fluid in a cylinder (radius R and length L; long axis in the z direction)

- Creeping flow limit without body forces: $\nabla \cdot \sigma = 0$

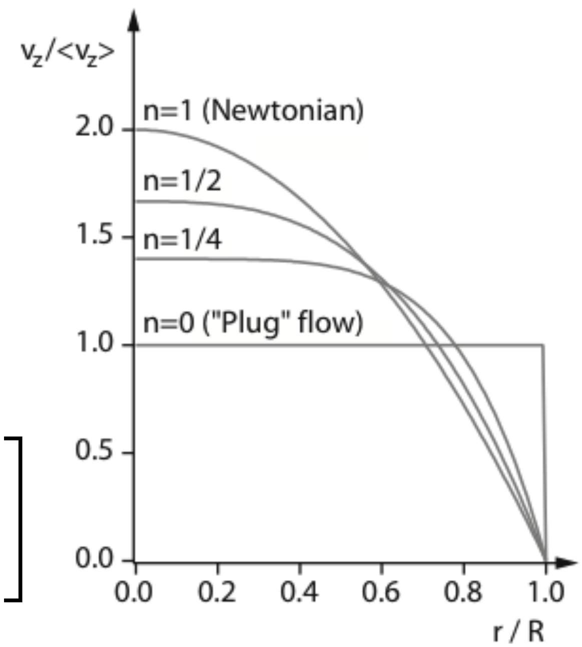
$$\frac{1}{r}\frac{d}{dr}(r\sigma_{rz}) = \frac{dP}{dz} = -\frac{\Delta P}{L} \implies \sigma_{rz}(r) = -\frac{\Delta P r}{2L}$$

- Constitutive equation:

$$\sigma_{rz}(r) = \kappa\,\dot{\gamma}(r)^n = \kappa\left(-\frac{dv_z}{dr}\right)^n$$

- Flow solutions:

$$v_z(r) = \left(\frac{\Delta P R}{2L}\right)^{1/n}\frac{R}{1+1/n}\left[1-\left(\frac{r}{R}\right)^{1+1/n}\right]$$



Yield Stress Fluids

- Fluids that are apparently solid-like below a critical stress σ_c
- The solid-like state is usually a very slowly creeping fluid
- Models:

Bingham Fluid: $\sigma = \sigma_c + \eta_p \dot{\gamma} \quad \text{for} \quad \sigma > \sigma_c$

(Newtonian at high shear rates)

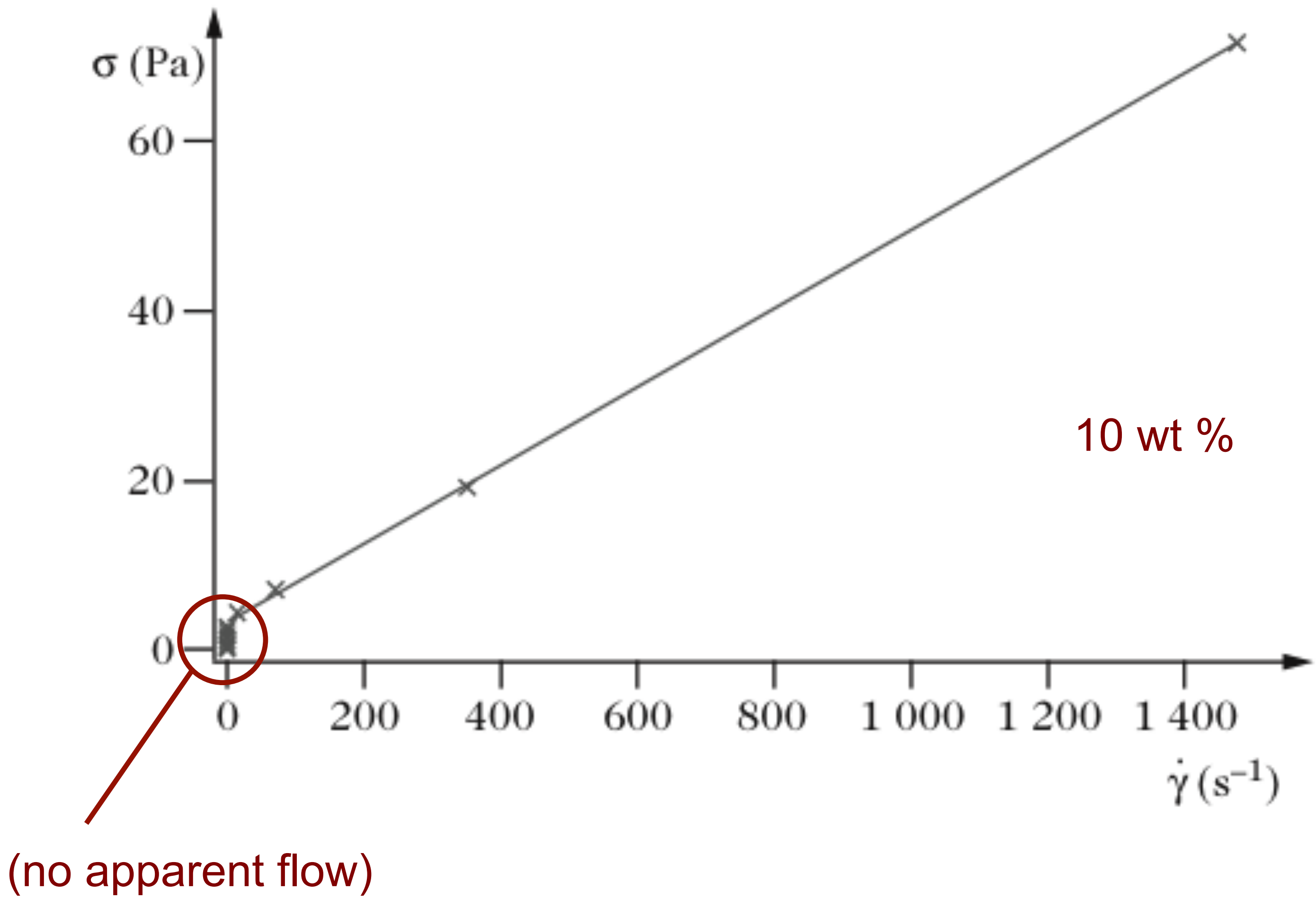
Hershel-Buckley Fluid: $\sigma = \sigma_c + \kappa \dot{\gamma}^n \quad \text{for} \quad \sigma > \sigma_c$

$0 < n < 1$

(non-Newtonian at high shear rates)

Yield Stress Fluids

- Model Bingham fluid: Bentonite clay particles in water:



Bingham Fluid in Pipe Flow

- Low stress region near center is below σ_c and thus not sheared (plug flow)
- All shear occurs near the higher stress regions near the wall
- Flow solution is a combination of the two regimes: