Soft Matter

Lecture 6

Today's lecture (6): Mechanical properties of soft matter

- Deformation: elongation and shear
- Strain, strain rate and stress
- Elastic solids and viscous liquids and viscoelasticity
  - Viscosity, Maxwell model, Kelvin-Voigt model
- Rheology: instrumentation and measurement types
- Strange fluids: some soft matter examples
  - Shear thinning, yield stress, shear thickening, thixotropy

Deforming soft matter in daily life

painting

mixing

squirting

squeezing

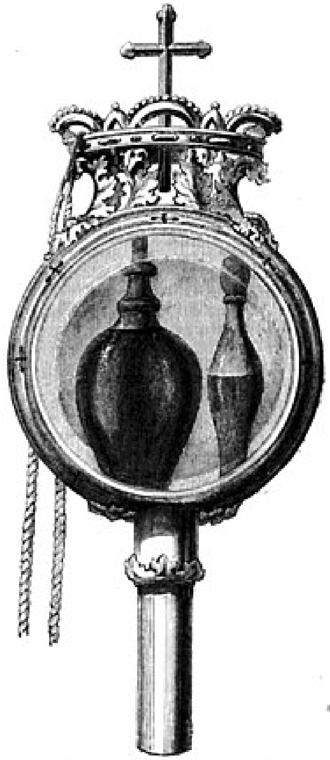
The blood miracle of Saint Gennaro (Januarius)

- Annual liquefaction of blood kept in sealed glass ampoule, Naples

2005

2013

2019



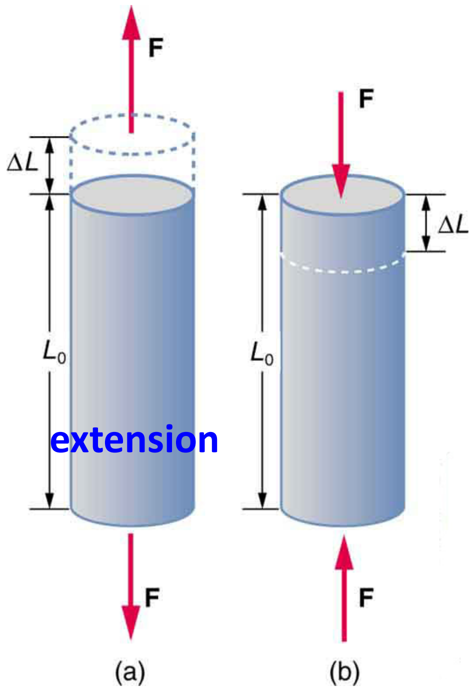
Das Blut des heiligen Januarius.
Nach der Natur gezeichnet von C. Grob.
(Hälfte der natürlichen Größe.)

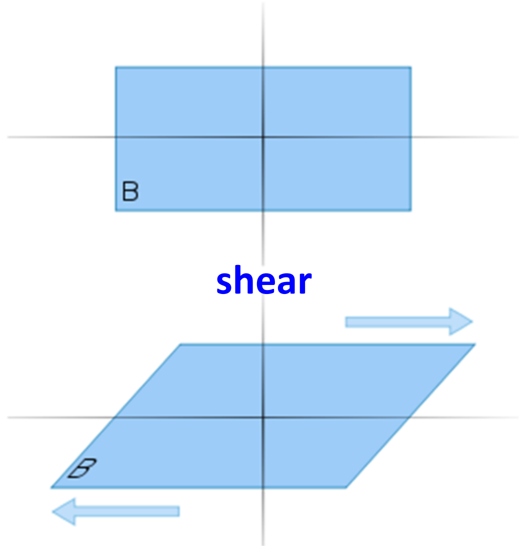
https://www.youtube.com/watch?v=Z7kkiNf1hLA

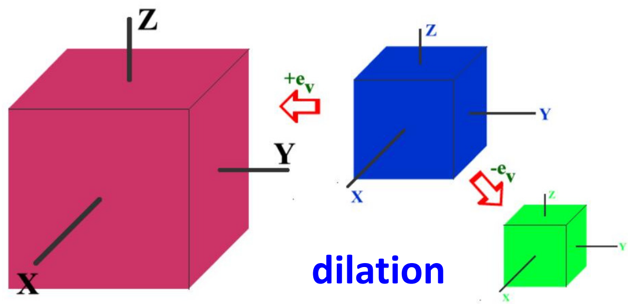
Deformation

- Change in the metric properties of a continuous body (e.g., a material)
- Useful to elucidate material behavior
  - Linear/extension
  - Plane
  - Volume

  - Uniform extension
  - Simple shear
  - Pure dilation/compression (overall shape remains the same)







Strain and stress

- **Strain**: deformation per unit length (dimensionless)

$$\gamma = \Delta x / y$$

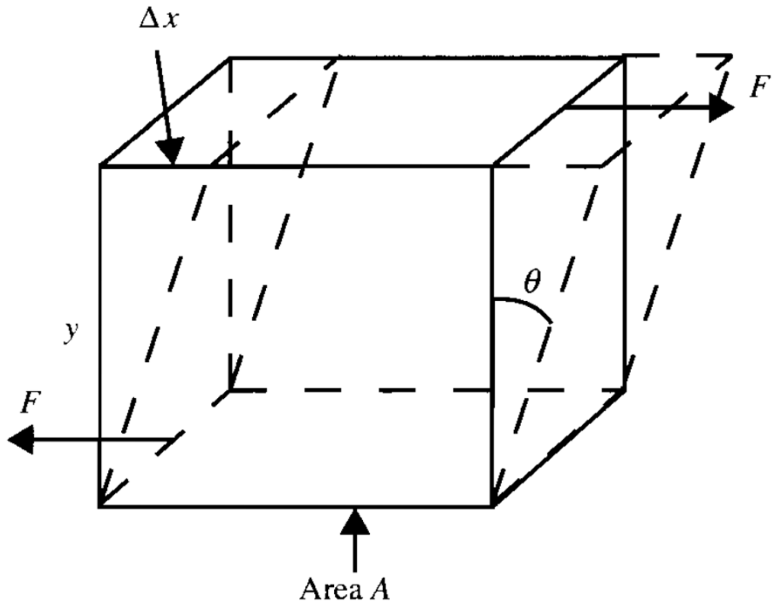
- Time derivative of strain = **strain rate** (s^{-1})

$$\dot{\gamma} = d\gamma / dt = v_x / y$$

- **Stress**: force per unit area (N/m^2 = Pa)

$$\sigma = F / A$$

- Depending on direction, one can have:
  - Elongational strain / elongational stress
  - Shear strain / shear stress
  - Shear (strain) rate

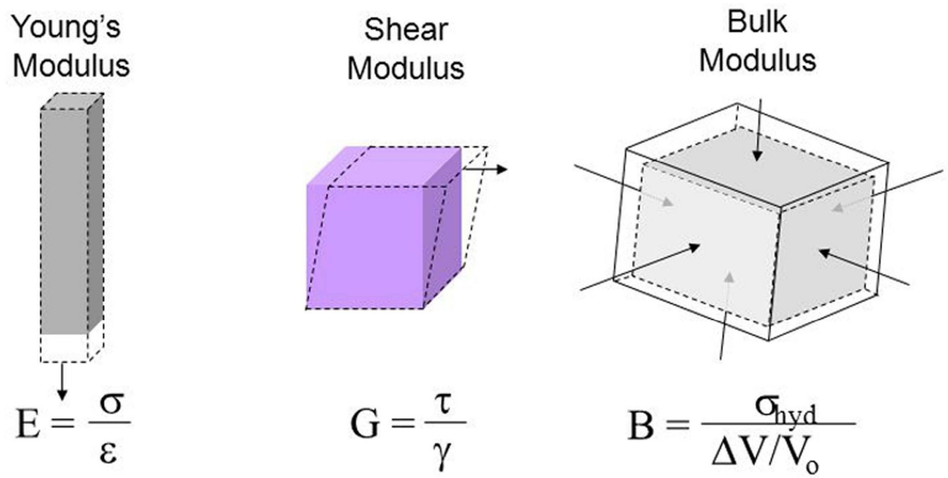


Simple materials

- Hookean solids: elastic deformation

$$\sigma = G\,\gamma$$

  - Modulus *G* (Pa)



- Newtonian liquids: plastic deformation (viscous)

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

  - Viscosity *η* (Pa·s)

Soft matter is really "soft"

- Hookean solids: elastic deformation

$$\sigma = G\,\gamma$$

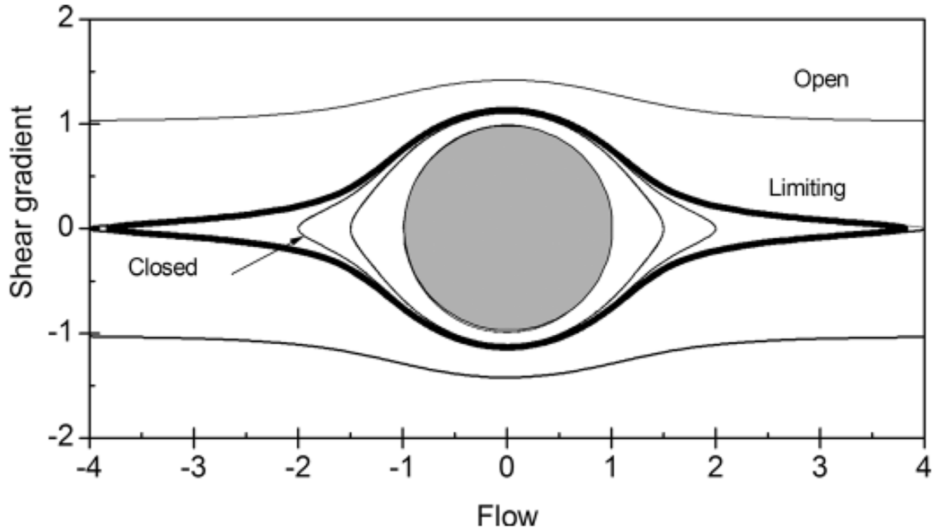
  - Modulus G (Pa) = energy per unit volume (N m^{-2} = N · m · m^{-3} = J m^{-3})
  - Crystal E = 1 eV (96 kJ/mol), l = 0.1 nm, G = 100 GPa
  - Soft matter E = 1 $k_B T$ (2.4 kJ/mol), l = 100 nm, G = 10 Pa

10^{-10}

Viscosity and soft matter characteristics

- Newtonian liquids: plastic deformation (viscous)

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



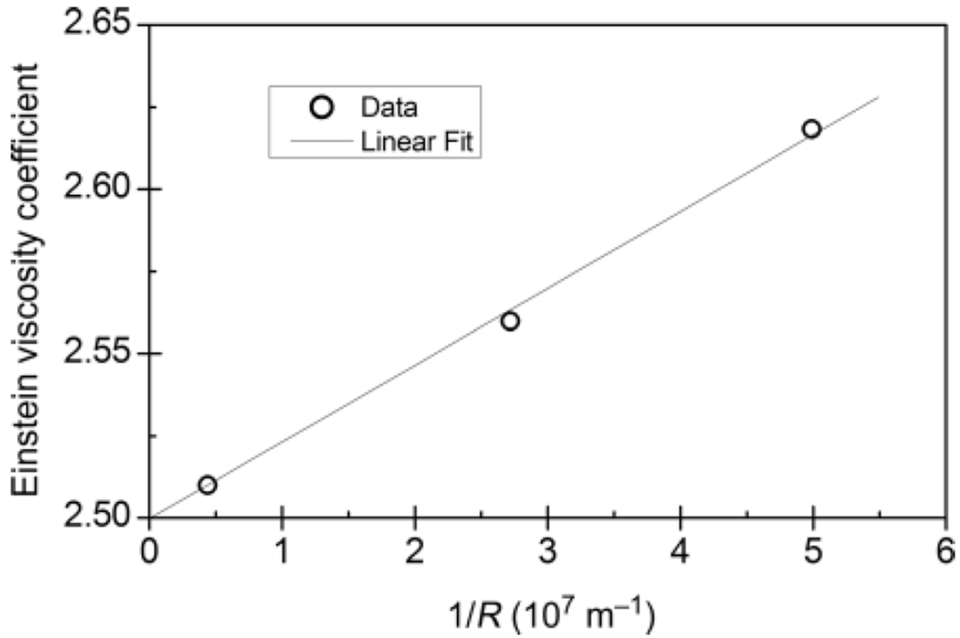
  - Dispersed particles increase the viscosity
  - Hydrodynamic effect
  - Einstein's equation for suspension rheology:

$$\eta = \eta_0 (1 + 2.5 \, \phi)$$

Viscosity and soft matter characteristics

- Einstein's equation for suspension rheology

$$\eta = \eta_0(1 + 2.5\phi)$$



Brodnyan 1968

Viscosity of semidilute suspensions

- Einstein's equation for suspension rheology

$$\eta = \eta_0(1 + 2.5\phi)$$

- are the first two term from a Taylor series for the suspension viscosity:

$$\eta = \eta_0(1 + 2.5\phi + c_2\phi^2 + c_3\phi^3 + ..)$$

- Batchelor and Green (1972) showed that for hard spheres, three terms is accurate up to crystallization:

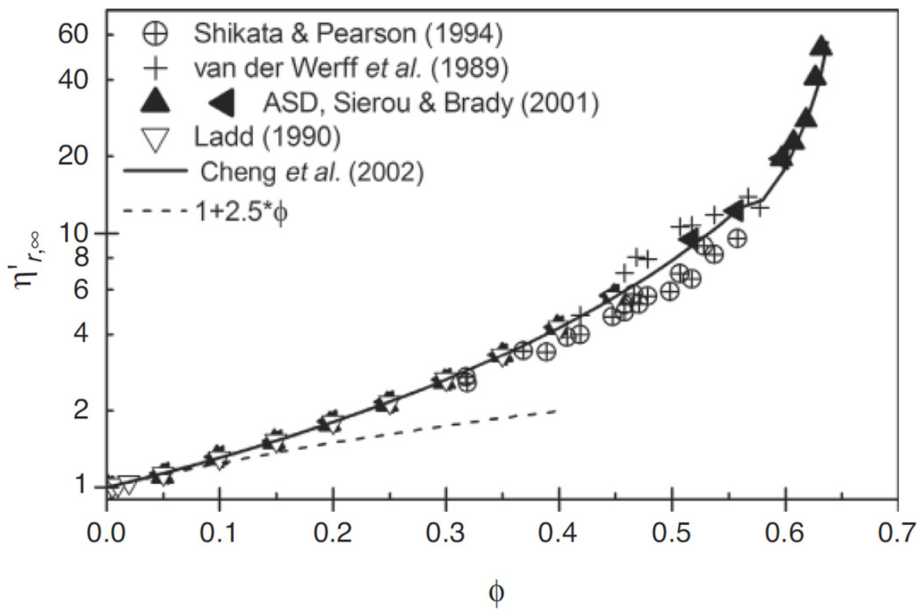
$$\eta = \eta_0(1 + 2.5\phi + 7.6\phi^2)$$

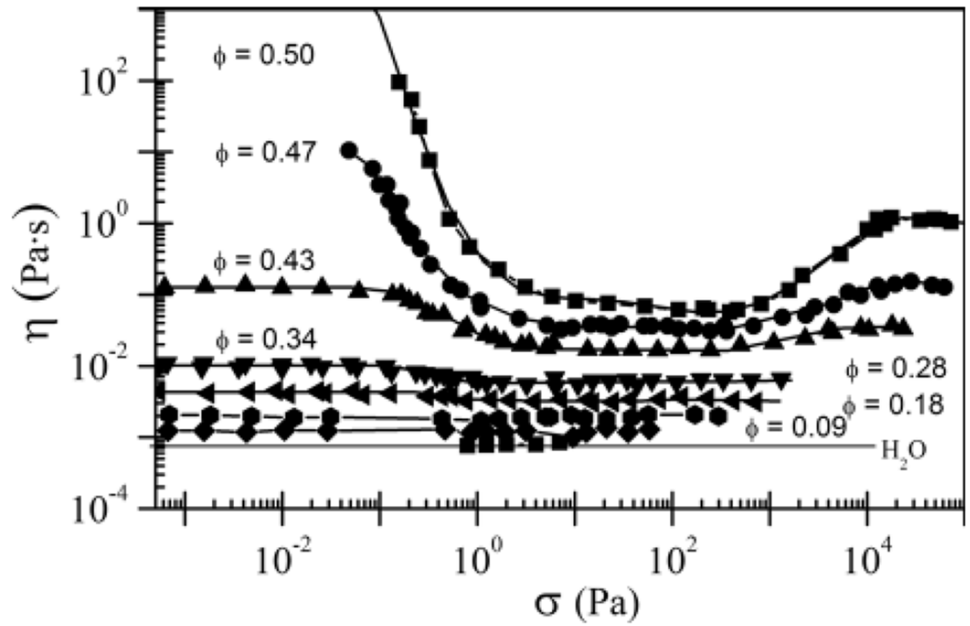
Viscosity of concentrated suspensions

- Increasingly difficult to flow

$$\eta'_{r,\infty} = \frac{1 + \frac{3}{2}\phi\left[1 + \phi\left(1 + \phi - 2.3\phi^2\right)\right]}{1 - \phi\left[1 + \phi\left(1 + \phi - 2.3\phi^2\right)\right]}, \qquad 0 \le \phi \le 0.56,$$

$$= 15.78 \ln\left(\frac{1}{1 - 1.160\phi^{1/3}}\right) - 42.47, \quad 0.60 \le \phi \le 0.64.$$





On viscosity

• Viscosity	η_s	$\eta_0(1 + 2.5\phi)$
• Relative viscosity	$\eta_r = \eta_s/\eta_0$	$1 + 2.5\phi$
• Specific viscosity	$\eta_{\text{sp}} = \eta_r - 1 = \dfrac{\eta_s - \eta_0}{\eta_0}$	2.5ϕ
• Reduced viscosity	$\eta_{\text{red}} = \dfrac{\eta_{\text{sp}}}{C}$	$2.5/\rho$
• Intrinsic viscosity	$[\eta] = \lim_{C\to 0} \dfrac{\eta_{\text{sp}}}{C}$	

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Viscosity of dilute polymer solutions

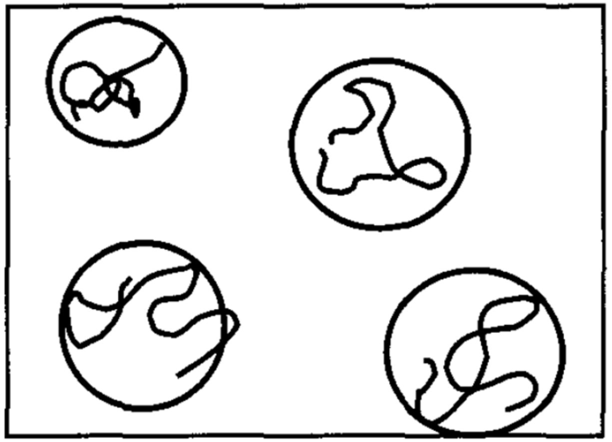
- Viscosity $$\eta_s = \eta_0(1 + 2.5\phi)$$

- Hydrodynamic size of polymer coil:

$$\eta_{sp} = 2.5\phi = 2.5\left(\frac{n_p}{V}\right)V_h$$

$$\eta_{sp} = 2.5\left(\frac{4\pi N_A C}{3M_w}\right)R_h^3 \sim R_h^3$$

$$[\eta] = \frac{2.5N_A V_h}{M_w}$$



Dilute ($\phi < \phi^*$)

ϕ = volume fraction of particles/polymers
n_p = number of particles/polymer coils
V = volume
V_h = hydrodynamic volume of a particle/polymer coil
R_h = hydrodynamic radius
C = mass concentration (kg/m^3)
N_A = Avogadro's number

Viscosity of dilute polymer solutions

- Hydrodynamic size of polymer coil:

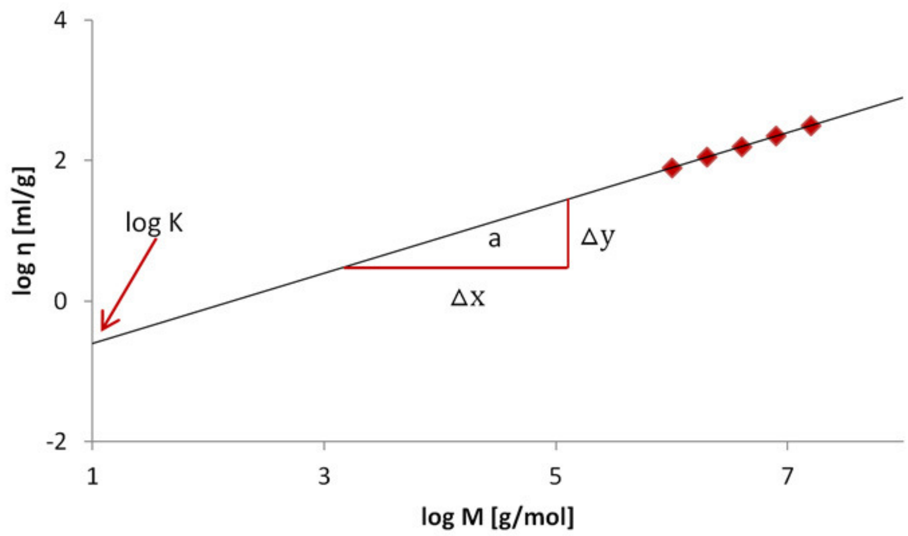
$$[\eta] = \frac{2.5 N_A V_h}{M_w}$$

- Combine with polymer size scaling:

$$R \sim N^{\nu} \sim (M_w)^{\nu}$$

- Mark-Houwink-Sakurada relationship:

$$[\eta] = K_M (M_w)^a$$



Ideal chain: $a = 0.5$

Real chain in a good solvent $a = 0.76$

Flory approximation: $a = 0.8$

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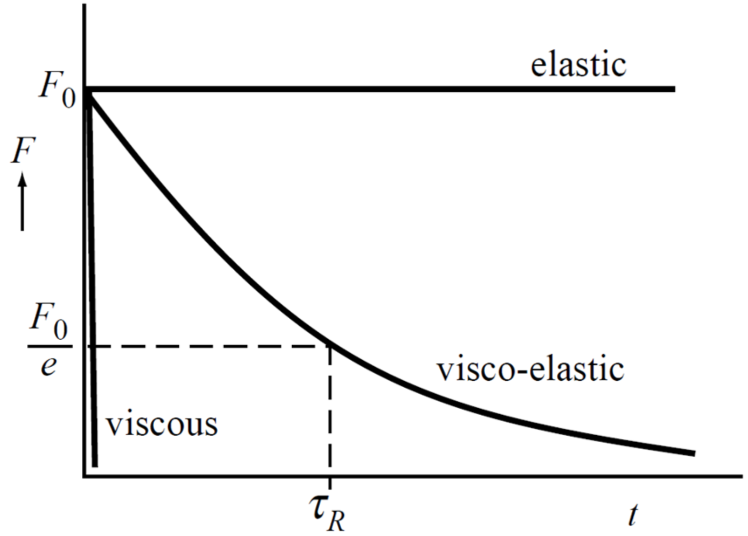
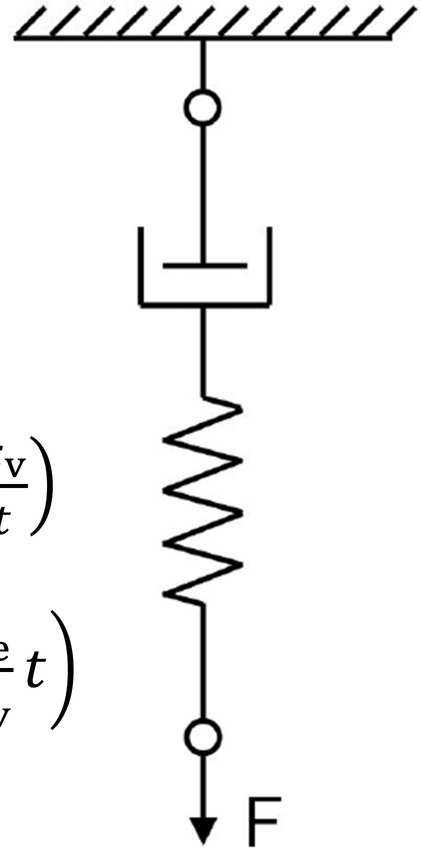
Viscoelasticity

- Response to an applied stress or strain in a time-dependent manner
- Combination of viscous and elastic response
- Typically: elastic at short timescales, viscous at long timescales, relaxation time τ defines crossover
- Panta rhei: everything flows



Viscoelasticity



- Maxwell model: a viscoelastic liquid
  - Spring and dashpot in series

$$F = k_e x_e = k_v \left(\frac{dx_v}{dt}\right)$$

$$x_v = 0 \text{ (at } t = 0)$$

$$x_t = x_e + x_v$$

$$k_e(x_t - x_v) = k_v \left(\frac{dx_v}{dt}\right)$$

$$\frac{x_t - x_v}{x_t} = \exp\left(-\frac{k_e}{k_v}t\right)$$

$$F(t) = k_e x_t \exp\left(-\frac{k_e}{k_v}t\right)$$

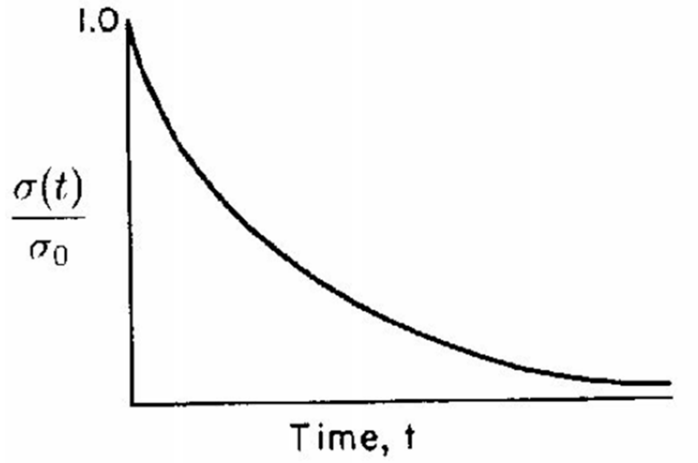
Converting to stress and strain gives:

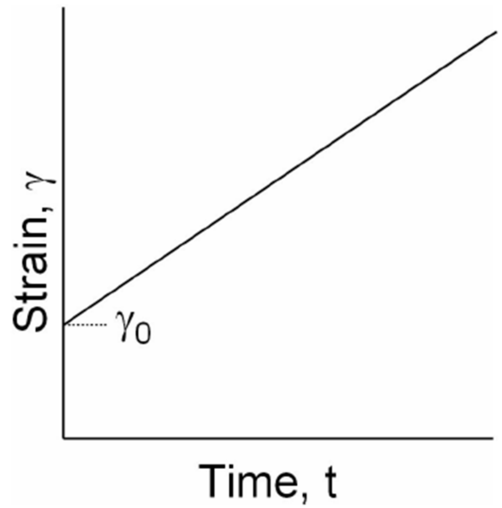
$$\sigma(t) = G_0 \gamma \exp(-t/\tau)$$

with: $\eta_0 = G_0 \tau$

Viscoelasticity

- Maxwell model: a viscoelastic liquid
  - Spring and dashpot in series
  - Stress relaxation: $\sigma(t) = G_0 \gamma \exp(-t/\tau)$
  - Creep: $\gamma(t) = \gamma_0 (1 + t/\tau)$





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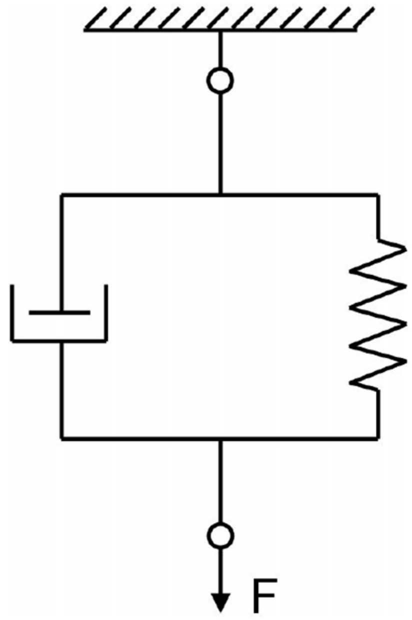
Viscoelasticity

- Kelvin-Voigt model: a viscoelastic solid
  - Spring and a dashpot in parallel

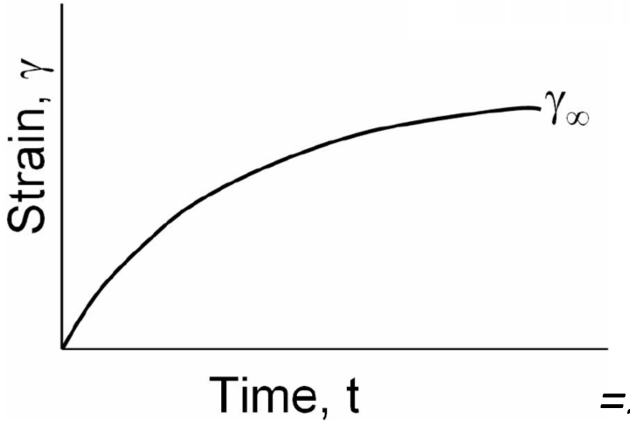
$$F = k_e x + k_v \left(\frac{dx}{dt}\right) \qquad x = 0 \text{ (at } t = 0)$$



$$\frac{k_e}{k_v}\, dt = \frac{1}{F/k_e - x}\, dx$$

$$x(t) = \left(\frac{F}{k_e}\right)\left(1 - \exp\left(-\frac{k_e}{k_v}\, t\right)\right)$$

$$\gamma(t) = \gamma_\infty(1 - \exp(-t/\tau))$$



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Fantastic materials and where to find them

- Many soft materials are viscoelastic, and show non-linear response

- Response depends on stress, rate of deformation, time, and the history of previous deformations….

- A recipe for "strange" behaviors

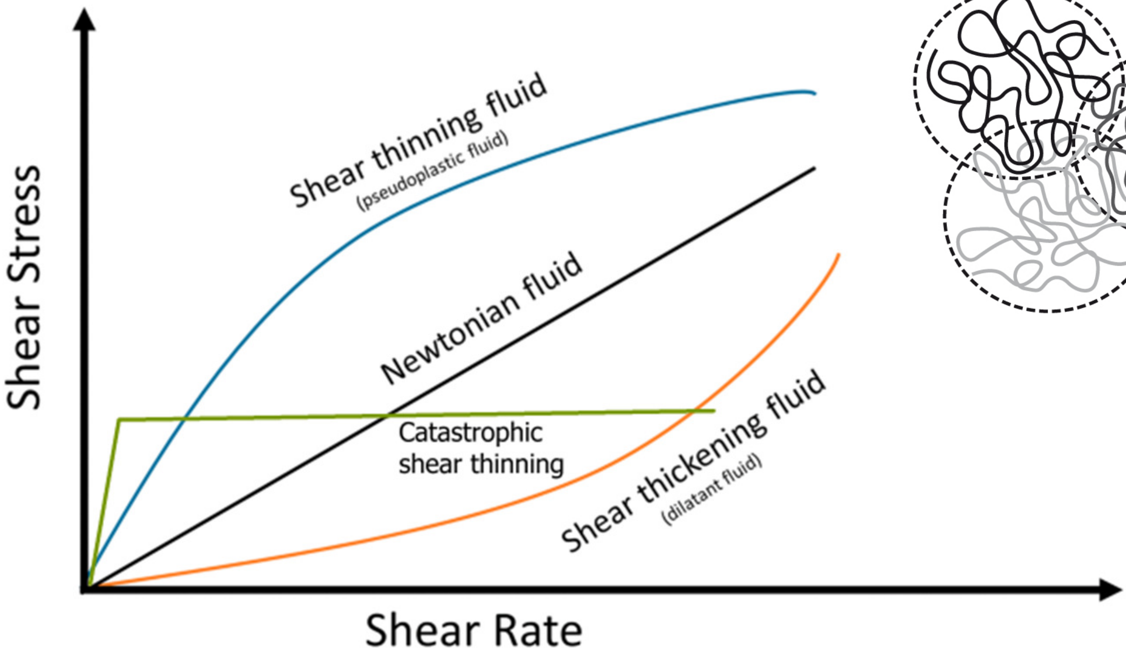
Fantastic materials and where to find them

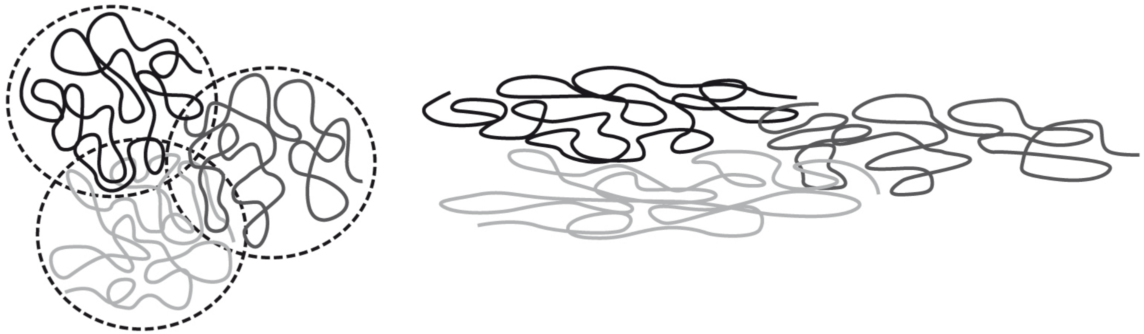
- Shear thinning (plasticity)
- Shear thickening (dilatancy)
- Strain stiffening
- Yield stress (Bingham fluid)
  - No deformation below a threshold stress

- Thixotropy: time-dependent decrease in viscosity
  - Fluidize when shaken
- Rheopexy: time-dependent increase in viscosity
  - Solidify when shaken

Shear thinning

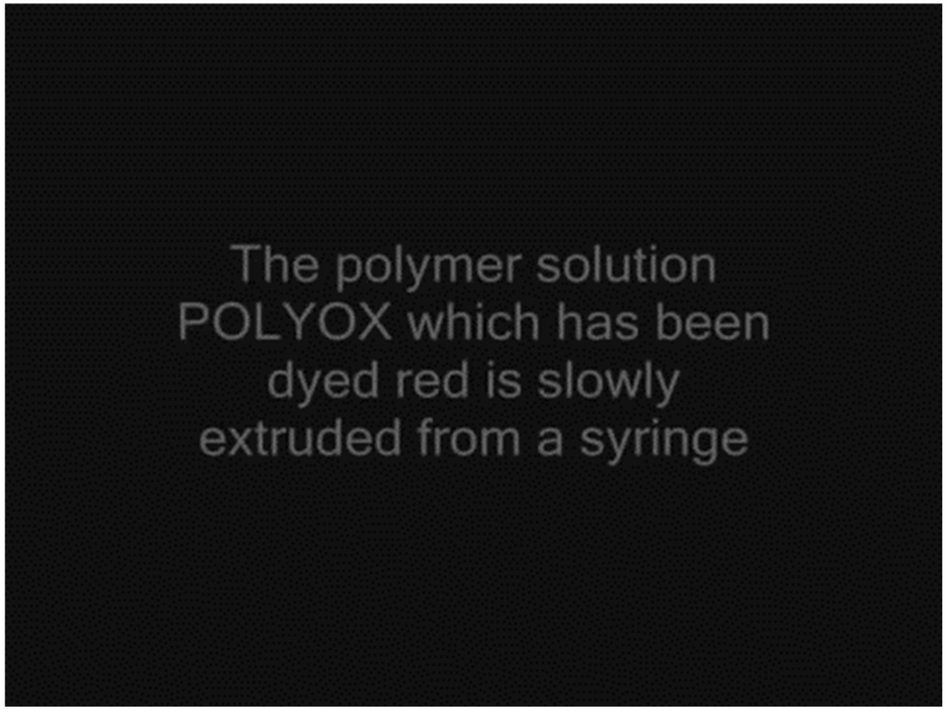
- Common property of polymer solutions

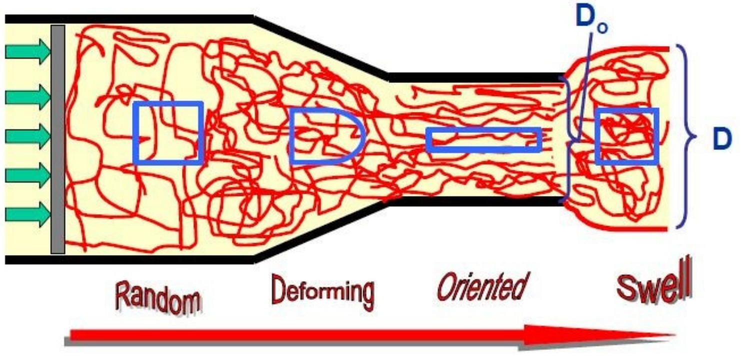




Shear thinning: Barus effect

- Barus effect (die swelling) of compressed polymer solution

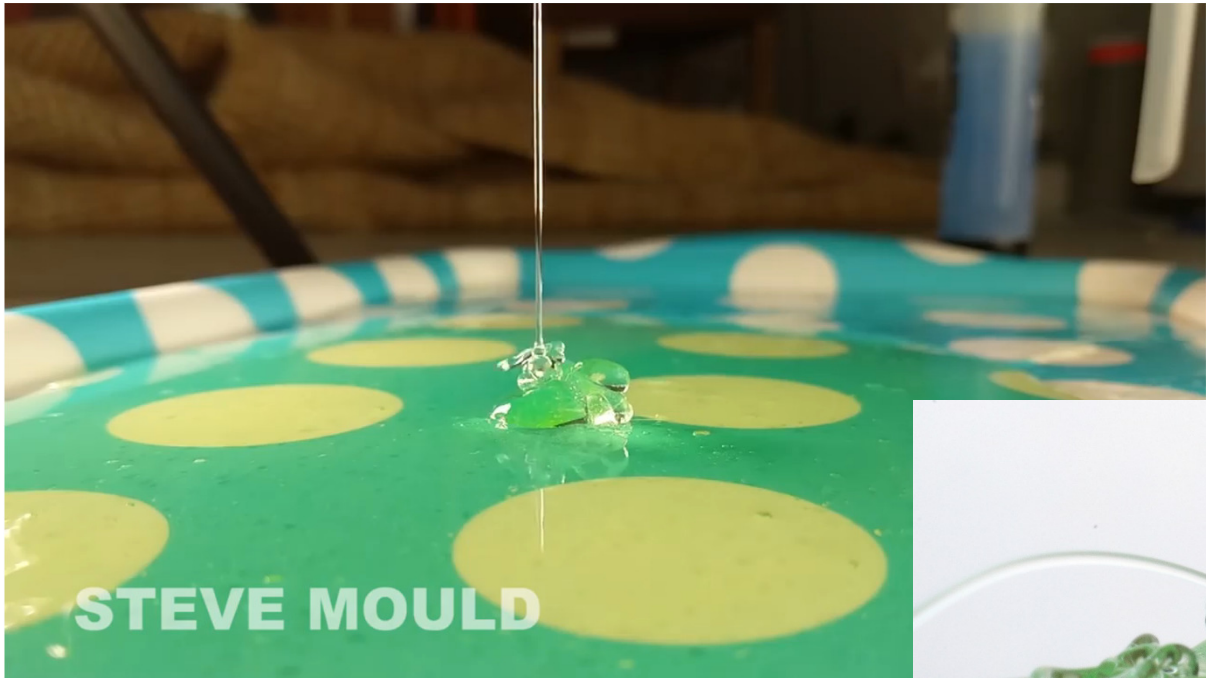


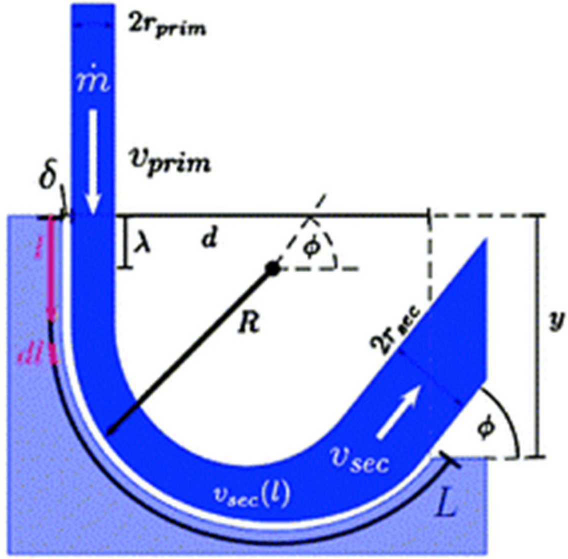


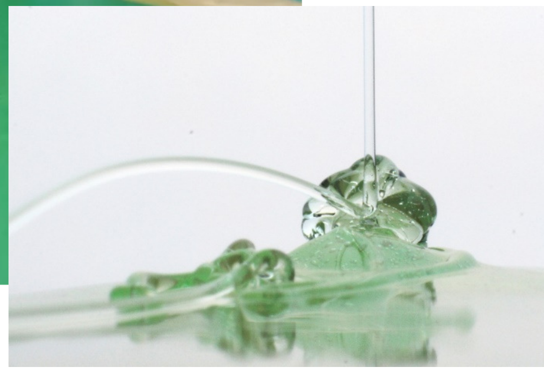
https://www.youtube.com/watch?v=KcNWLIpv8gc

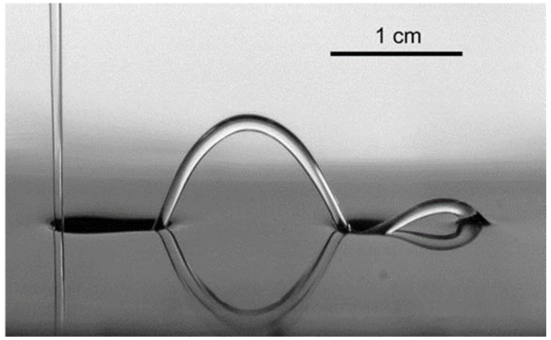
Shear thinning: Kaye effect

- Shear thinning on a tilted surface





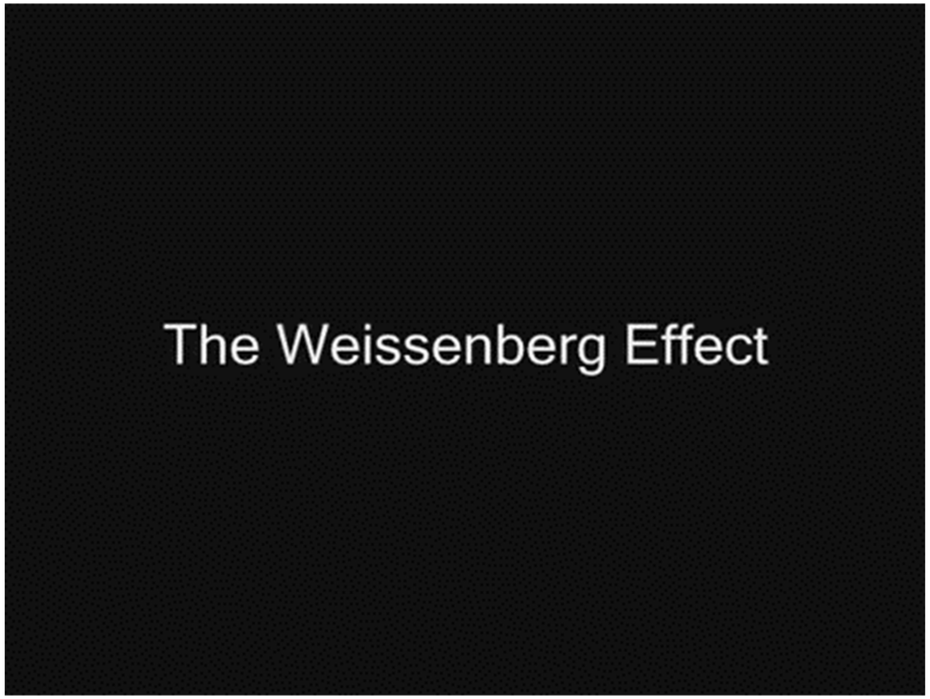


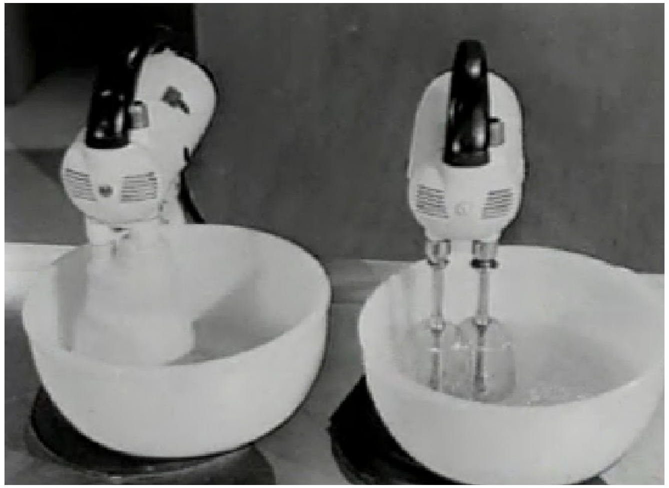


https://www.youtube.com/watch?v=wmUx-1o3Lzs
https://www.youtube.com/watch?v=WC6tjcDOShU

Shear thinning: Weissenberg effect

- Normal forces due to shear





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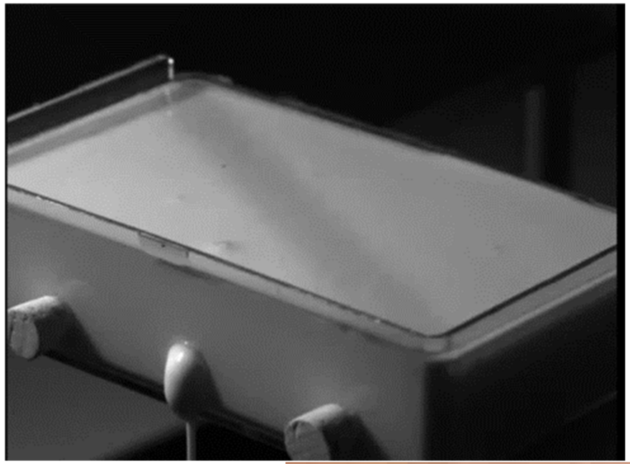
Shear thickening

- Can be observed in suspensions of particles (spherical or nonspherical)

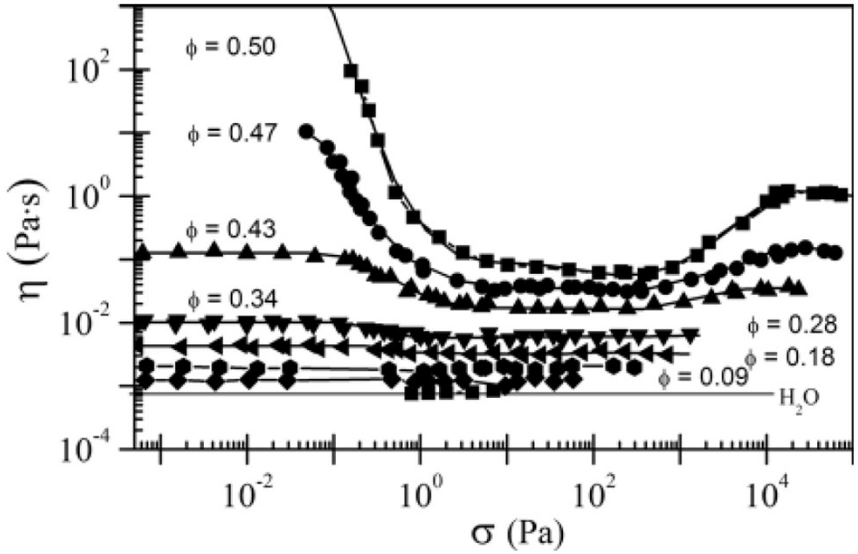


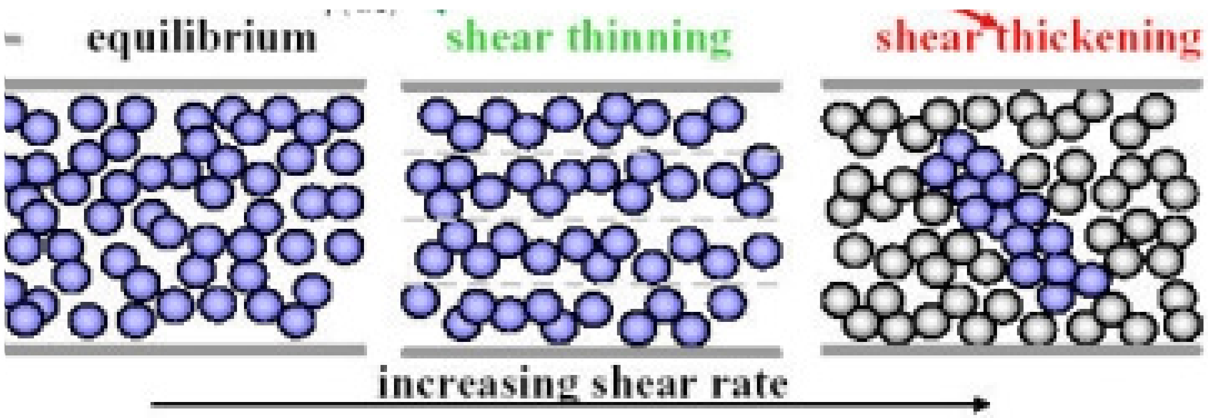
https://www.youtube.com/watch?v=f2XQ97XHjVw

https://www.youtube.com/watch?v=hP88C-_LgnE

Shear thickening

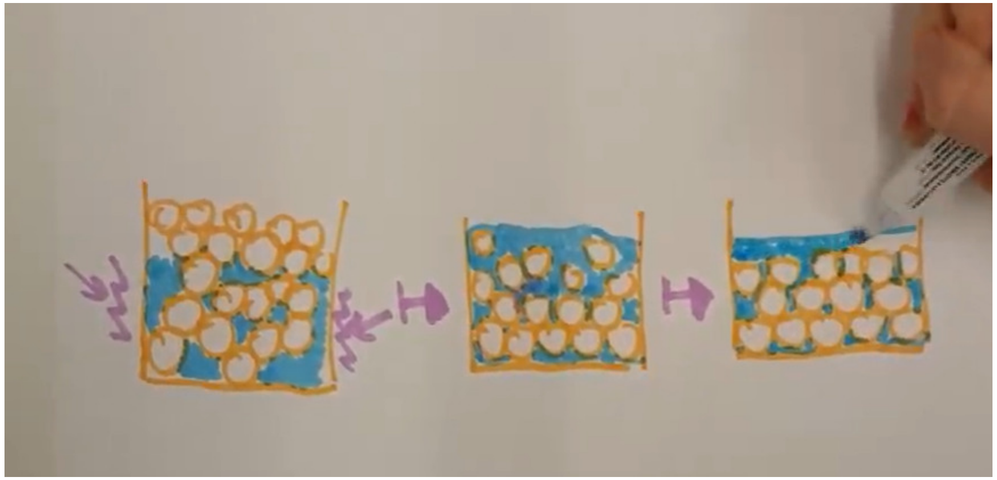
- Can be observed in suspensions of particles (spherical or nonspherical)
  - Slow deformation: alignment of particles in flow direction (thinning)
  - Fast deformation: jamming and solidification (thickening)





Reynolds dilation

- If the equilibrium state of particle suspension is already solid…
  … and you start to shake gently



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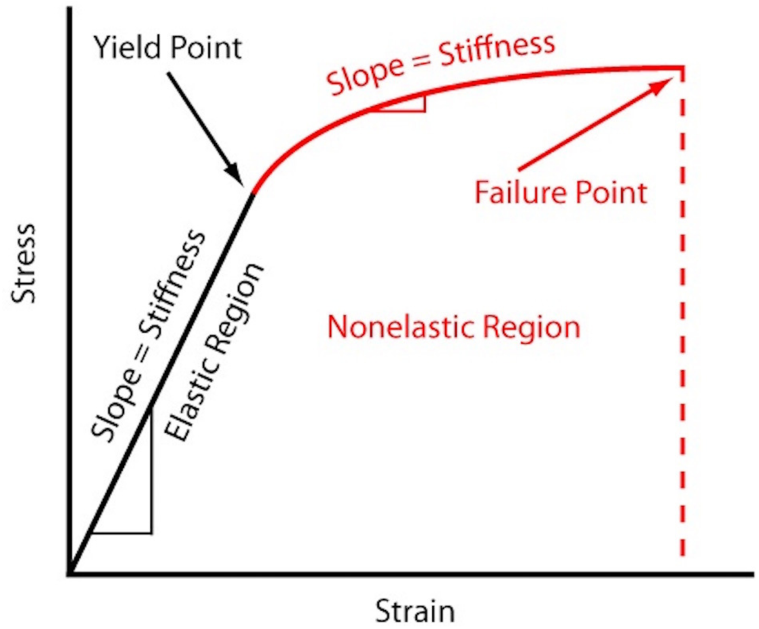
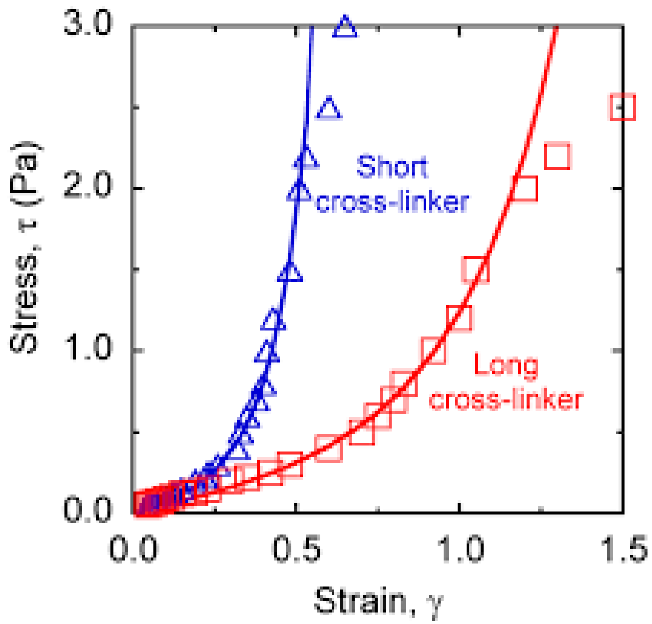
Strain stiffening

- Can be observed in crosslinked networks of rigid polymers



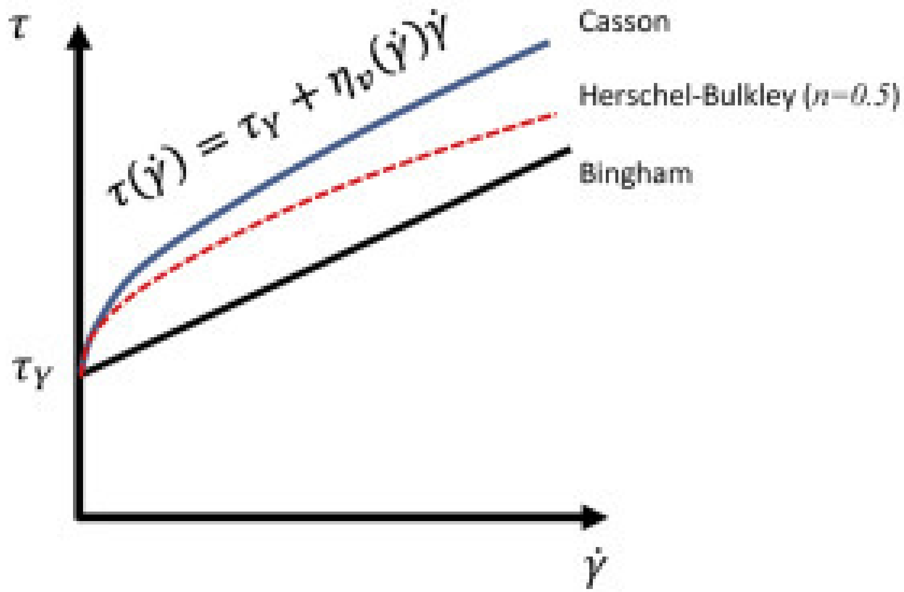
Normal, "yielding" network



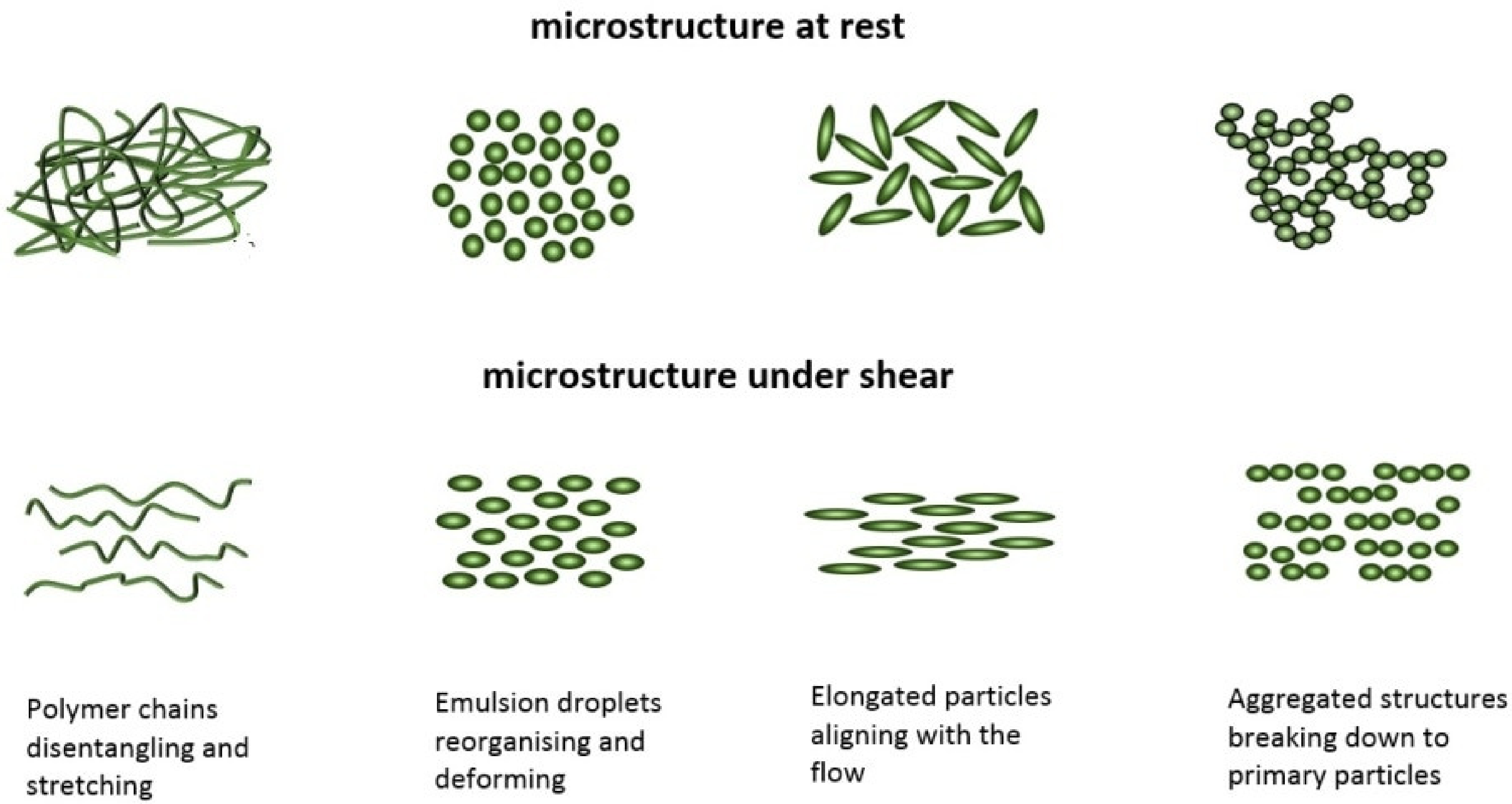
Strain stiffening network

Yield stress

- Common in many microstructured soft materials



Yield stress

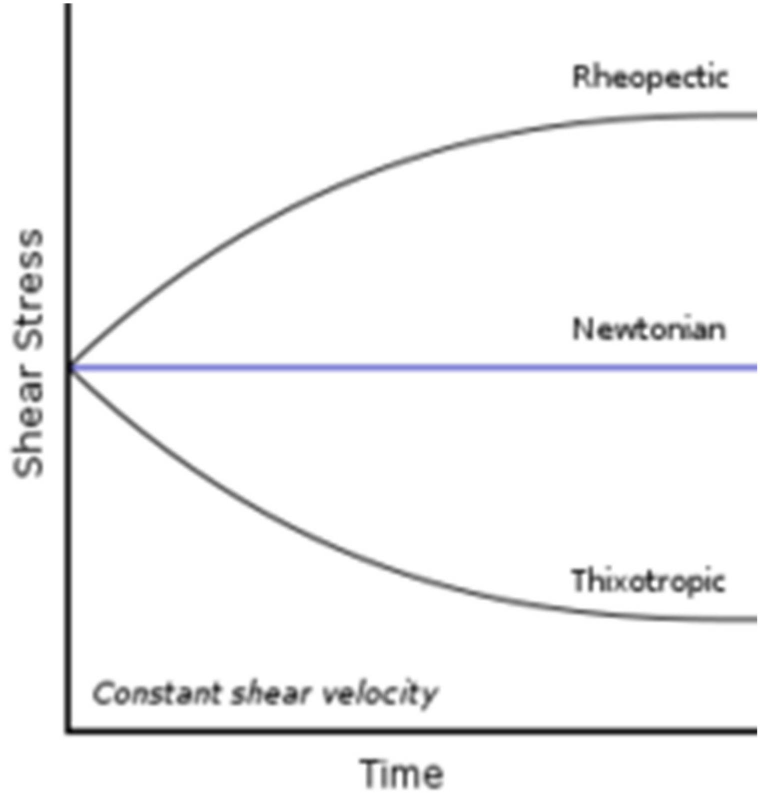
- 

Thixotropy and rheopexy

- Time-dependence and hysteresis effects

Ketchup is a good example of a thixotropic substance. It does not flow even when the bottle is held upside down

However, when the bottle is struck (vibrated), the ketchup temporarily liquefies and flows.



Thixotropy and rheopexy

- Time-dependence and hysteresis effects