Introduction to dispersion rheology

Contents

Introduction to dispersion rheology

States of matter

- **Solids**

  - **keep their shape**
  - **do not flow**

- **Liquids**

  - **flow**
  - **take the shap of the (solid) container**

? butter, yoghourt, ketchup…

liquids ? or solids ?

- **Solids → elastic deformation**
  returns to its original shape

- **Liquids flow if forces are applied**
  on it → viscous flow

- **Question of time scale and magnitude of exerted forces**

  - **water : small forces during very short times**
    → elastic deformation

  - **mountains : large forces during very long times**
    → flow

? Intermediate times and forces ?

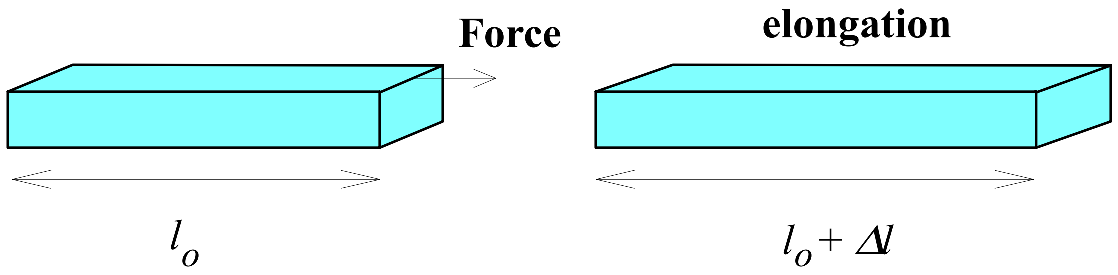
→ Viscoelasticity

Dispersions

In general viscoelastic "liquid like" behaviour

→ flows on time scales short compared to human lifetime

Elastic deformation



Strain $$\frac{\Delta l}{l_o} = \varepsilon$$

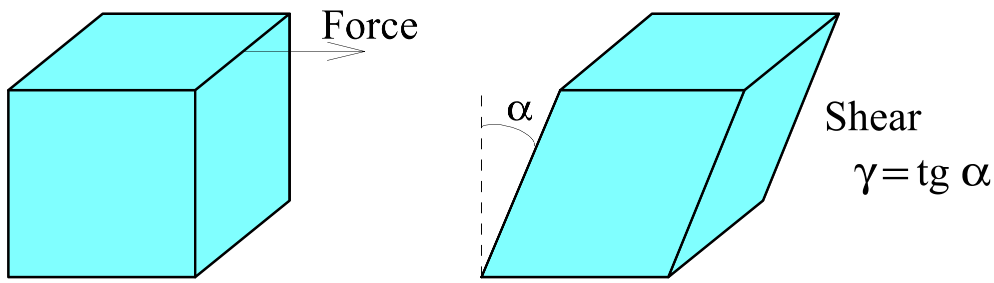
Stress T = Force / unit area

→ linear relation stress / strain (Hooke's law)

$$T = E\varepsilon$$

Young's modulus

Shear deformation



Shear deformation with constant speed on liquid → flow

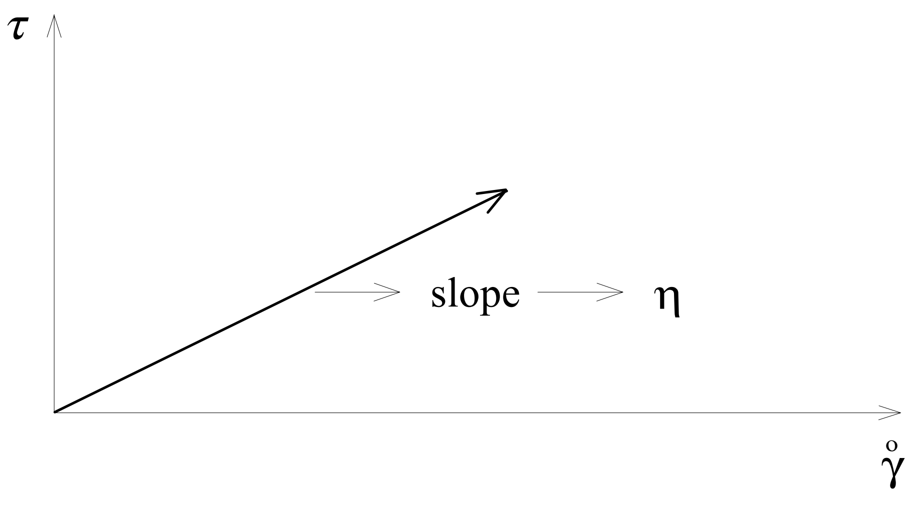
→ **Shear rate $\dot{\gamma}$**

Shear stress τ = force / unit area

→ **Linear relation shear stress / shear rate (Newtonian viscosity)**

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

(Newtonian) viscosity



Non-Newtonian behaviour

- **Most dispersions (also blood)**

  η dependent on the shear rate

  → viscosity is a material function

  $$\eta = \eta(\dot{\gamma})$$

  Reason : complexity of the micro structure of the system

  Structural changes due to exerted forces
  → changes in viscosity

  ⇒ rheology can be used to learn about the microstructure of dispersions

- **More general**

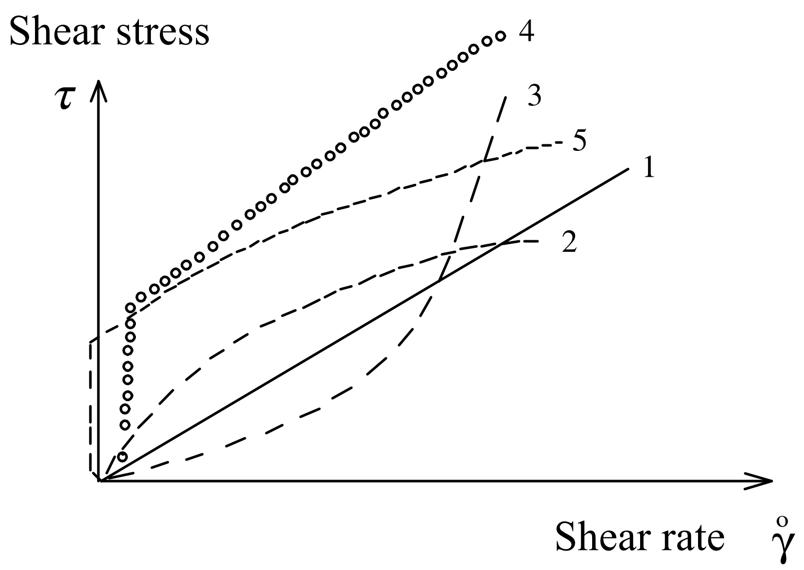
  $$\eta = \eta(\dot{\gamma}, \boldsymbol{time})$$

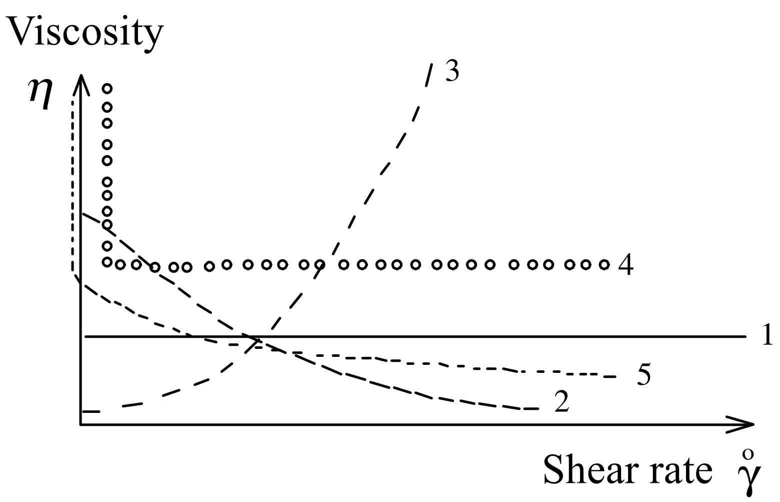
  → structural changes

  require in general some time

  → η is not a material function

Shear dependent behaviour



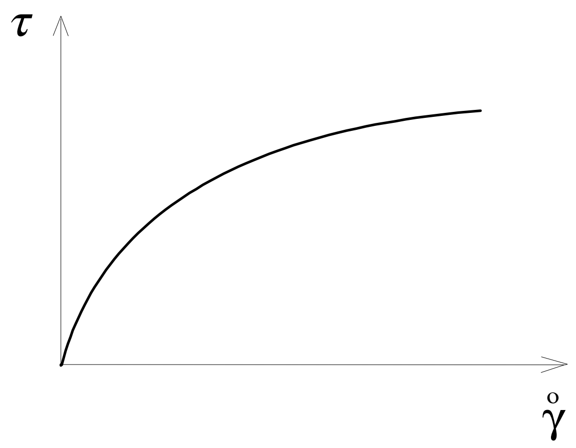


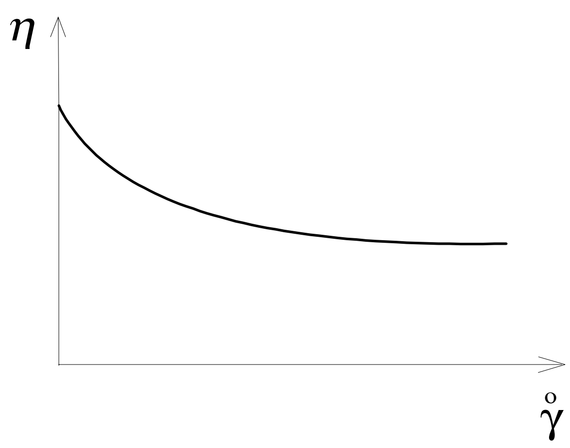
How to define viscosity

a) slope viscosity $\eta(\dot{\gamma}) = d\tau / d\dot{\gamma}$

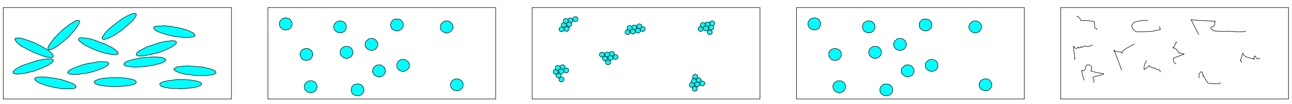
b) apparent viscosity $\eta_a(\dot{\gamma}) = \tau / \dot{\gamma}$

Shear thinning behaviour

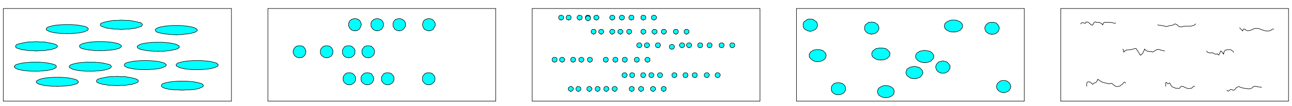




Systems at rest



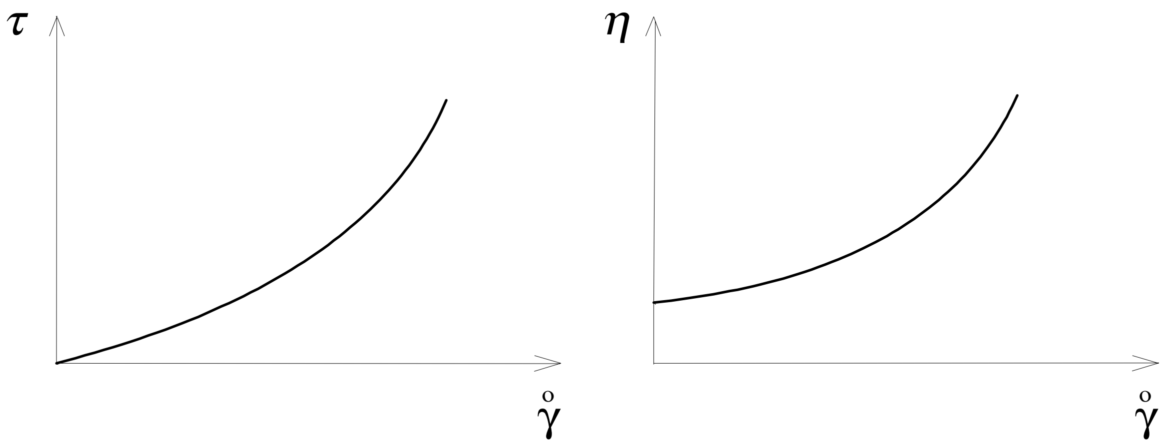
Flowing systems



orientation ordering desaggregation deformation elongation

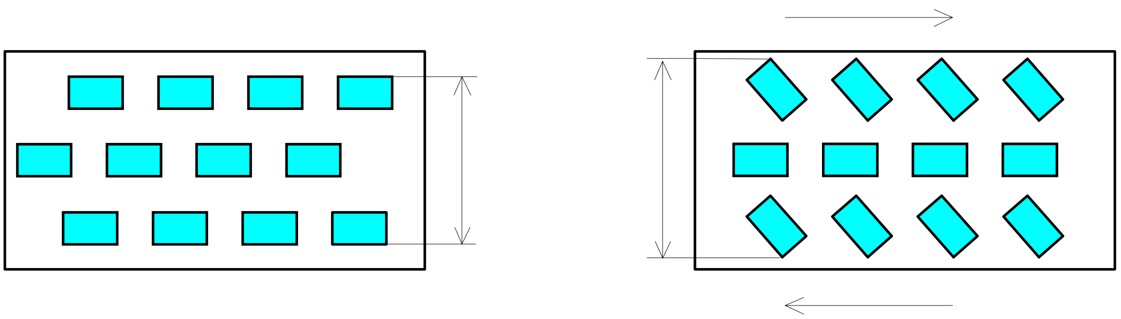
Empirical equations $\tau = k\dot{\gamma}^n$ $n < 1$

Shear thickening



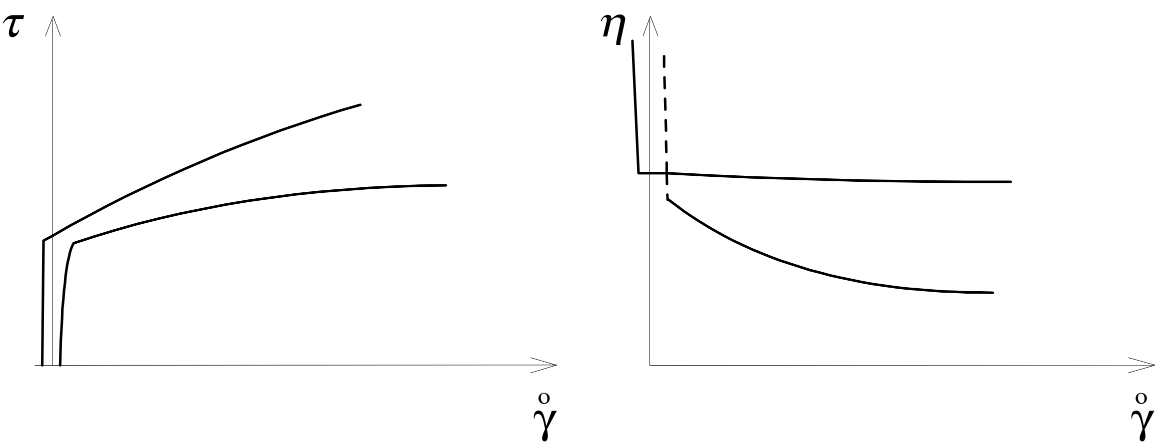
System at rest

System in motion



Empirical law $\tau = k\dot{\gamma}^n$ $n > 1$

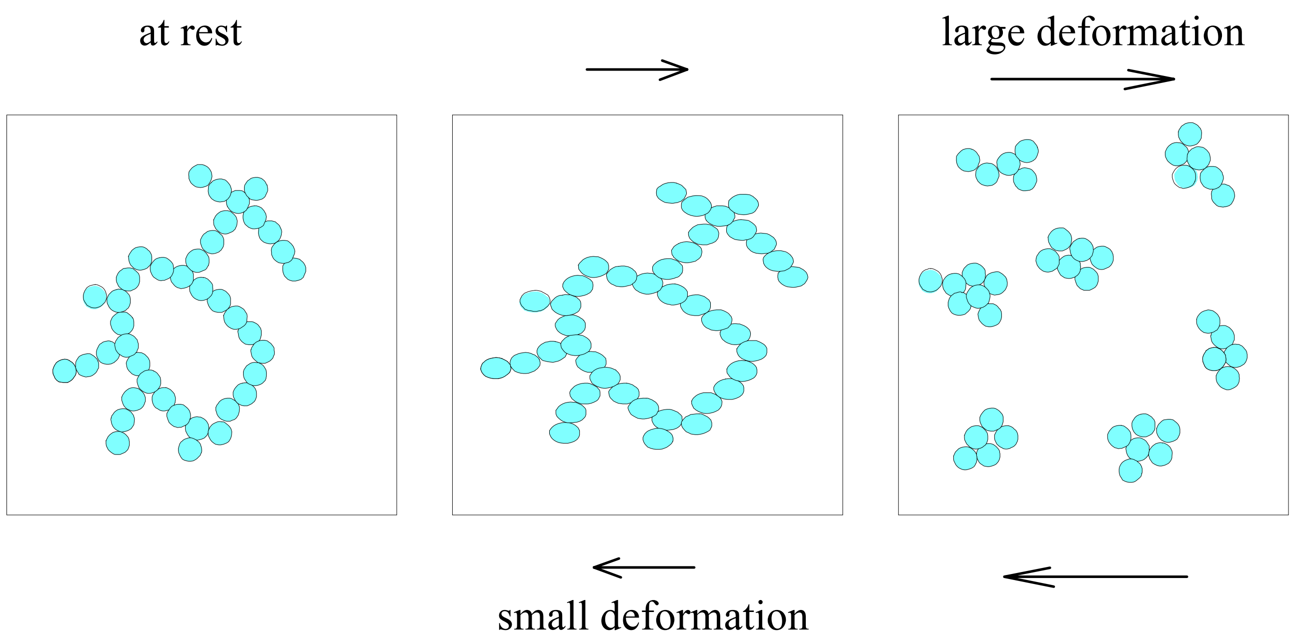
Materials with yield value



1 Bingham flow $\tau = \tau_0 + k\dot{\gamma}$

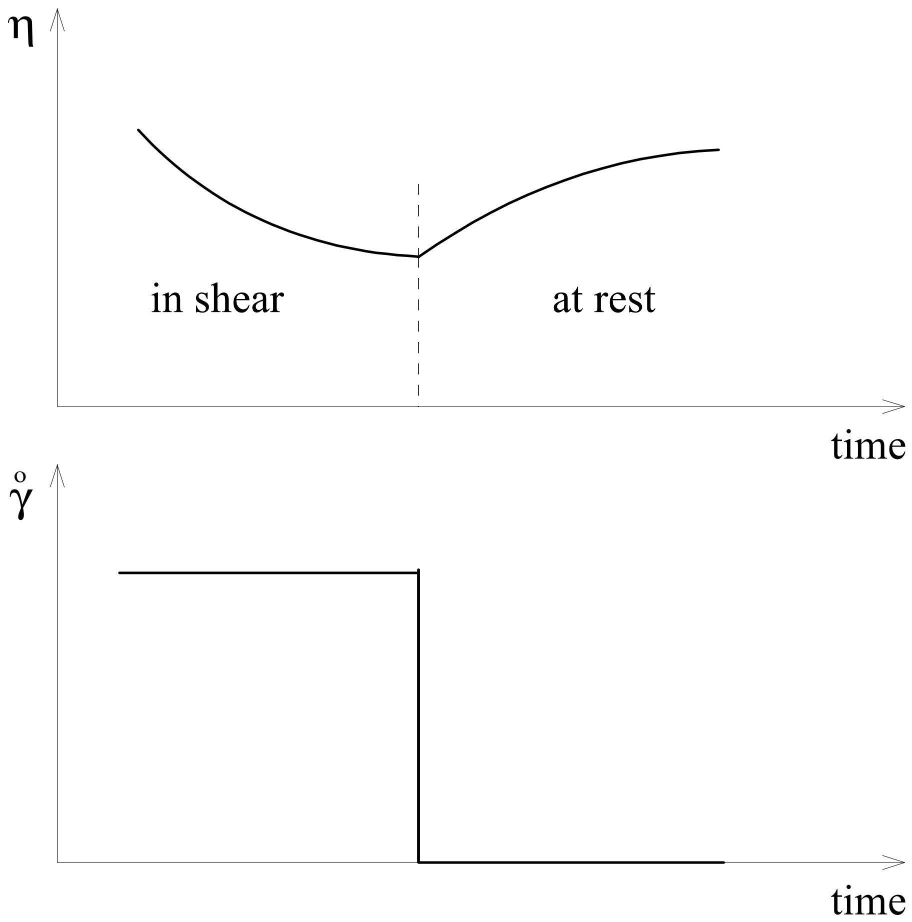
yield value

2 Hershel-Bulkly $\tau = \tau_0 + k\dot{\gamma}^n$

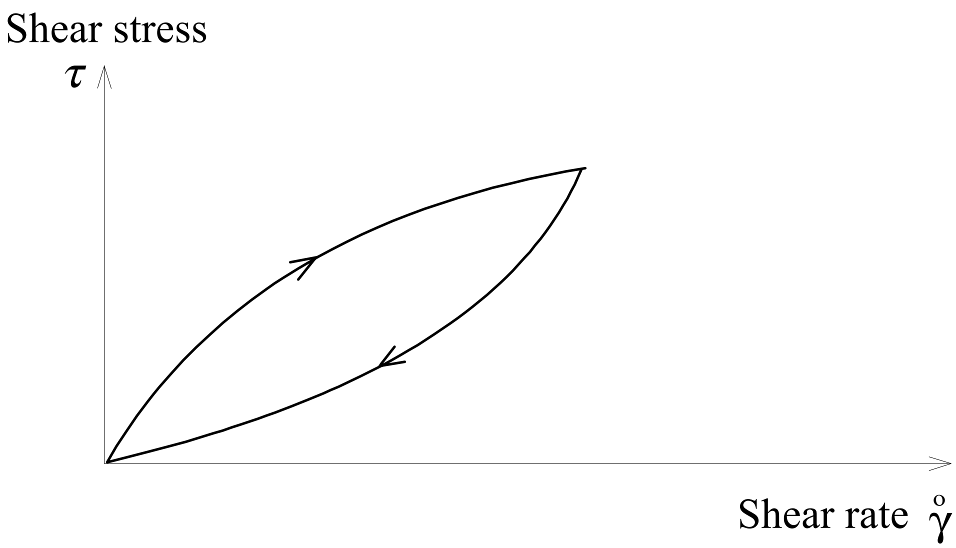


Time dependent behaviour

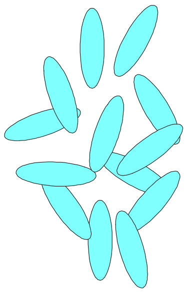
Thixotropy ("memory effects")



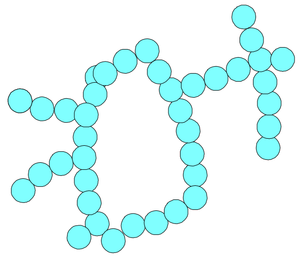
Thixotropic hysteresis



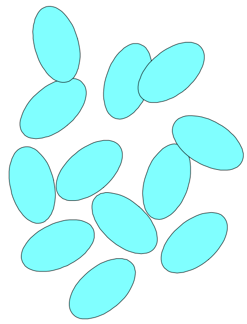
Reason → mesh-work structure



bars

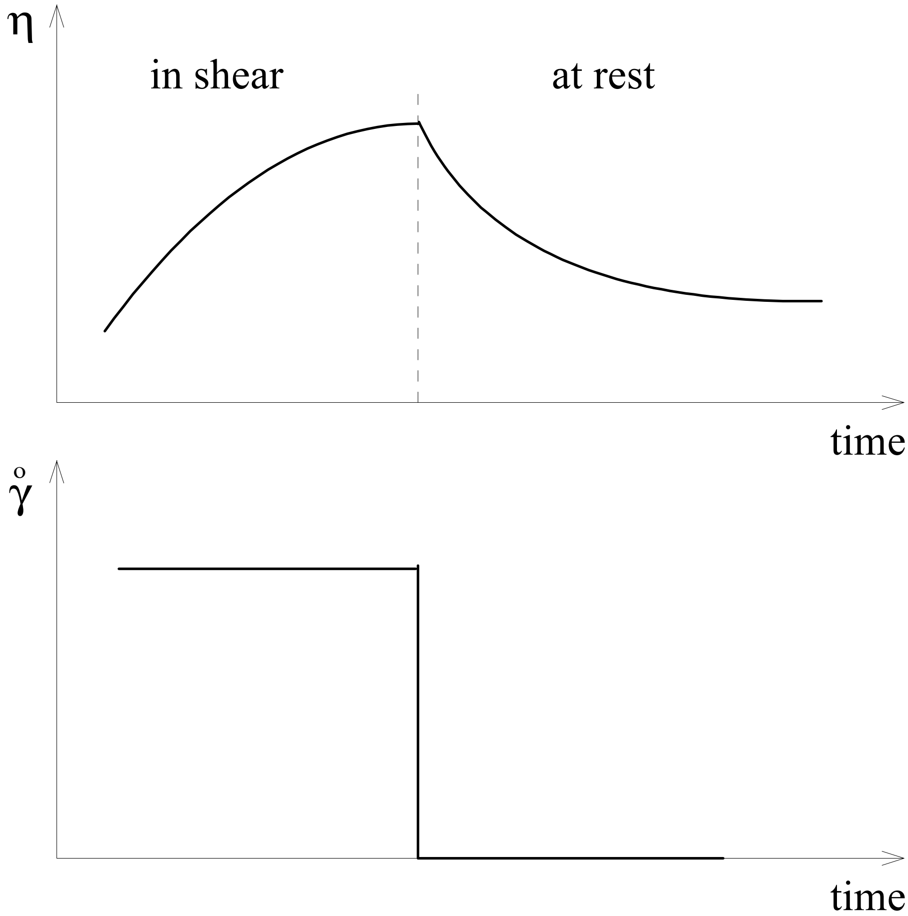


balls



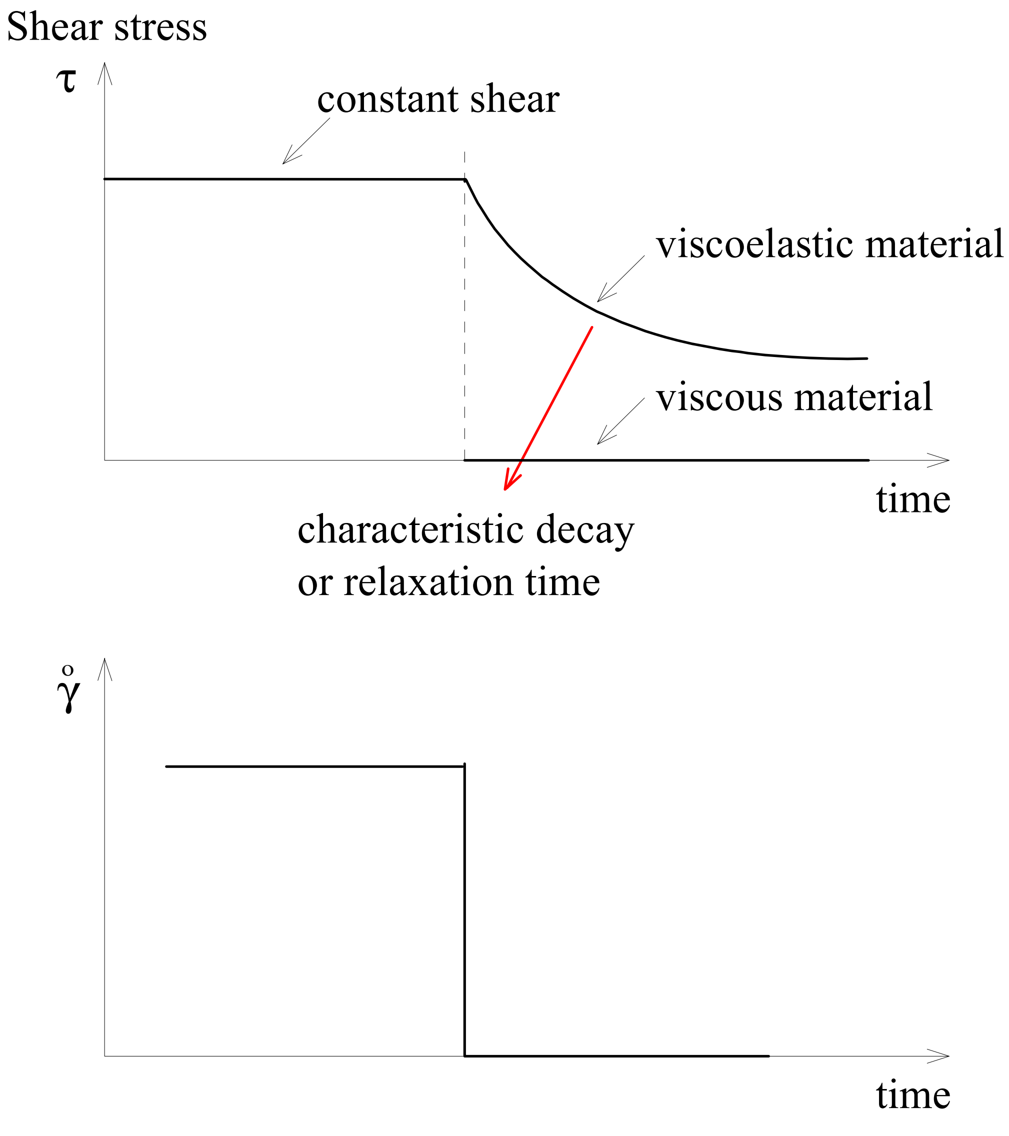
plates

Rheopecty

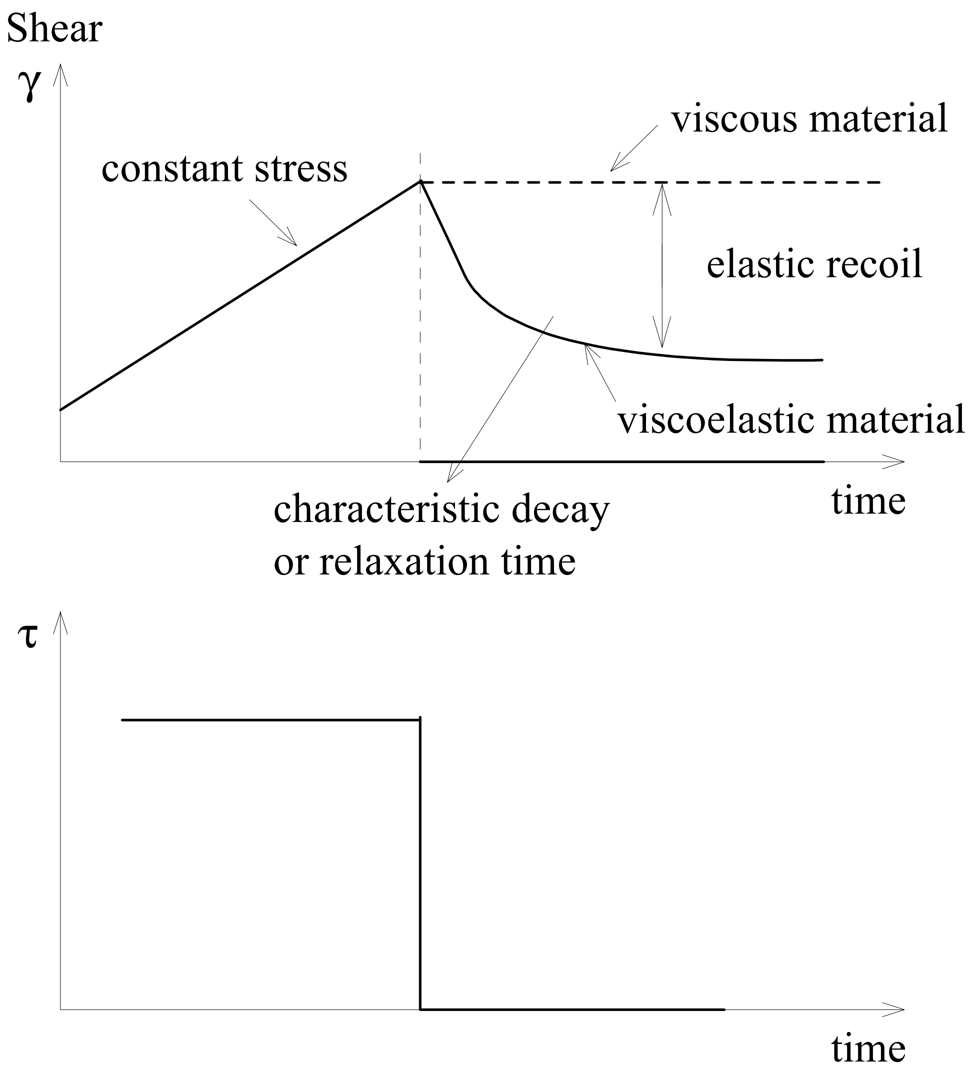


Viscoelastic materials

Stress relaxation



Elastic recoil



Deborah number

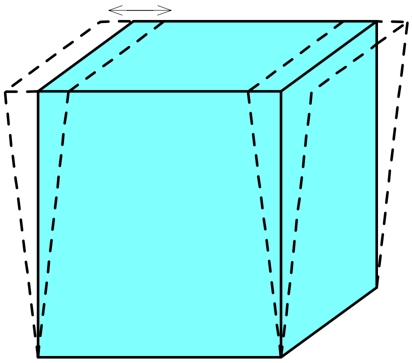
$$Deborah = \frac{relaxation\ time}{observation\ time}$$

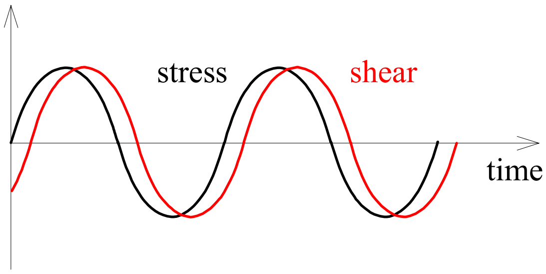
Deborah « 1 → viscous liquid

Deborah » 1 → elastic solid

Viscoelasticity → Deborah ~ 1

Dynamic viscosity measurements





Shear

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

Stress

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

elastic term	viscous term
in phase	90° out of phase
G' storage modulus	G" loss modulus

- **Elastic material** → **G" = 0**
- **Viscous material** → **G' = 0**

$$\tau(t) = \tau_0 \sin(\omega t + \delta)$$

→ **loss angle**

$$G' = \frac{\tau_0}{\gamma_0} \cos\delta \qquad G'' = \frac{\tau_0}{\gamma_0} \sin\delta$$

$$\frac{G''}{G'} = tg\,\delta$$

δ = 0 → **elastic**

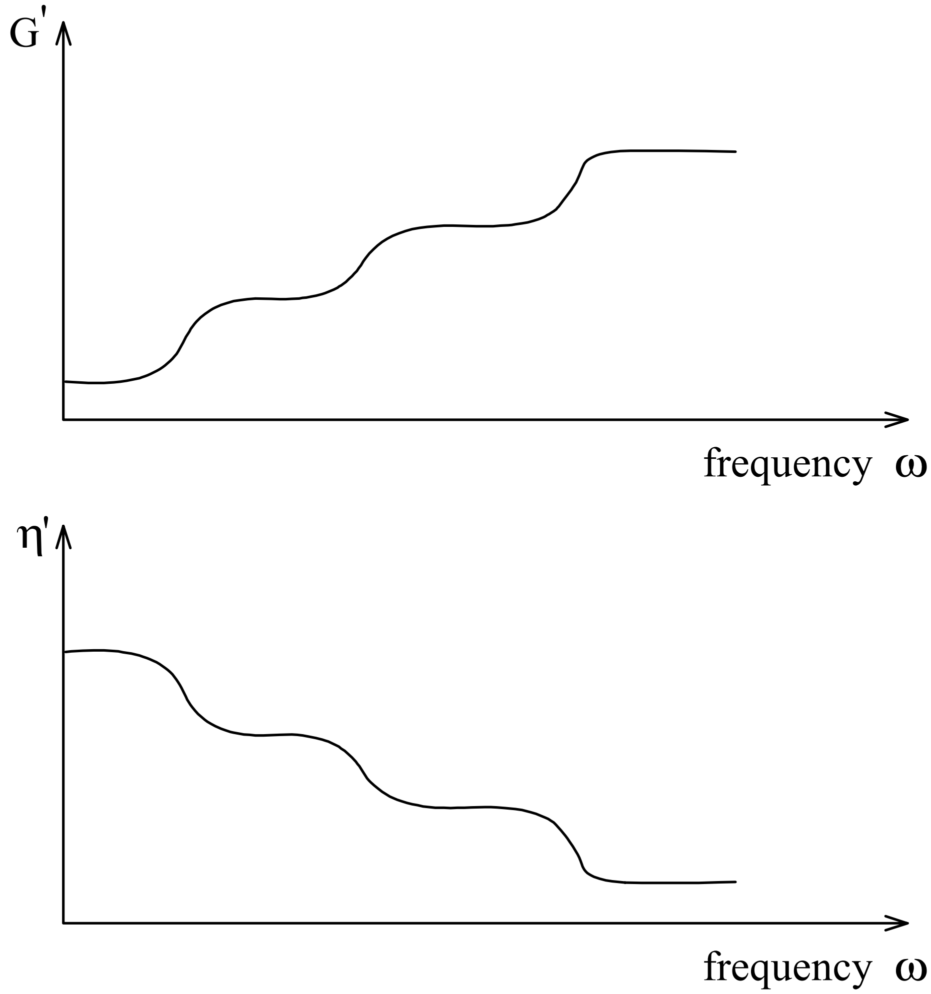
δ = 90° → **viscous**

δ ~ 45° → **viscoelastic**

Dynamic or complex viscosity η^*

$$\eta^* = \eta' + i\,\eta'' \qquad (i^2 = -1)$$

$$\eta' = G''/\omega \qquad \eta'' = G'/\omega$$


G'
frequency ω
η'
frequency ω

Viscosity of dispersions of spherical particles

- **Newtonian behaviour for volume fractions $\phi \leq 0.1$**
- **$0.1 \leq \phi \leq 0.5$ shear thinning**
- **$\phi \geq 0.5$ shear thickening**
- **Low ϕ (≤ 0.1) → Einstein equation**

$$\eta_r = \frac{\eta_s}{\eta_0} = 1 + \frac{5}{2}\phi$$

relative viscosity (η_r) **viscosity of medium** (η_0)

- **Slightly higher ϕ (≤ 0.15)**

$$\eta_r = 1 + k_1\phi + k_2\phi$$

k_1 → **2.5** k_2 → **6.2 – 5.2**

- **High ϕ ($\leq$ 0.15)**

  → **empirical equations**

- **Krieger-Dougherty equation**

$$\eta_r = \left[1 + k_p \phi\right]^{-2.5/k_p}$$

$1/k_p = \phi_\infty$ → **closest packing volume fraction**

- **Mooney equation**

$$\eta_r = \left[\exp 2.5\phi / (1 + k_p \phi)\right]$$