Thixotropy- a review
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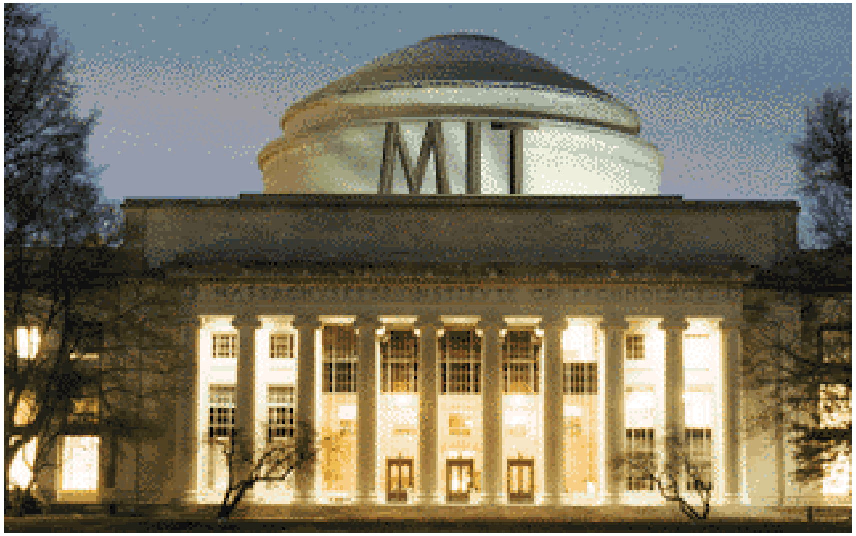


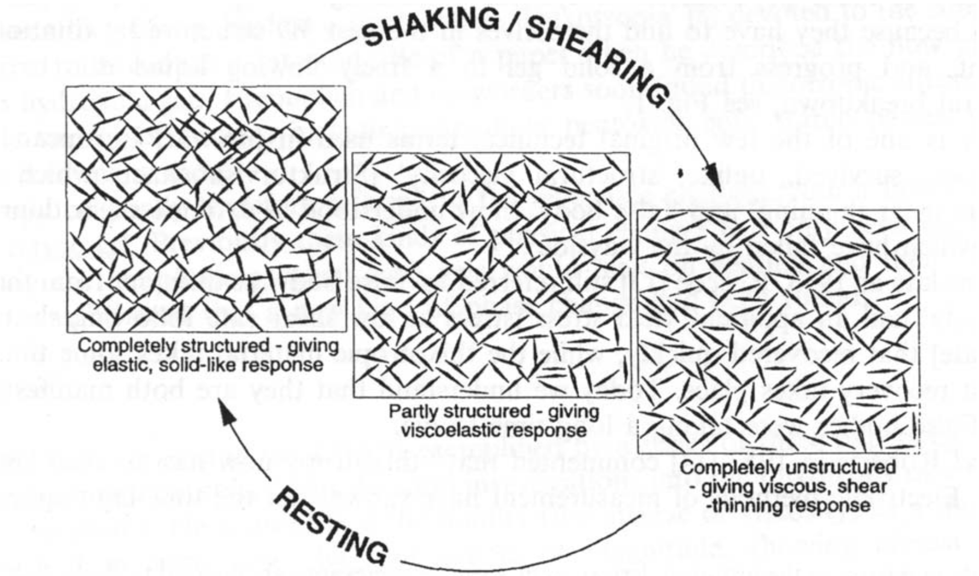
http://web.mit.edu/nnf

Introduction

- Thixotropy is seen in many fluids:
  - ❑ Paints
  - ❑ Resins
  - ❑ Clays
  - ❑ Personal products
  - ❑ Chemical products
  - ❑ Home cleaning supplies: detergents

History of Thixotropy

- The term Thixotropy was first used by Peterfi in 1927 from the Greek work **thixis** (stirring or shaking) and **trepo** (turning or changing)
- Thixotropy was originally referred to reversible changes from fluid to solid-like elastic gel.
- ‘explanation of thixotropy as being due to the secondary minimum so that particles can form a loose association which is easily destroyed by shaking but re-established itself on standing’
- Shear-thinning (‘structural viscosity’) vs. Thixotropy: ‘structural viscosity is seen as a material with nearly zero time of recovery’



Thixotropy: Description of the phenomena

'All liquids with microstructure can show thixotropy'

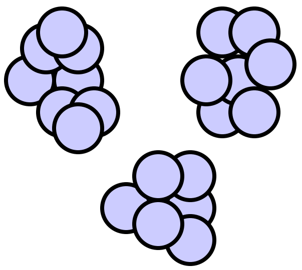
Competition between:

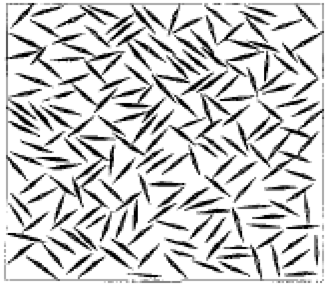
Break-down v.s **Build up**

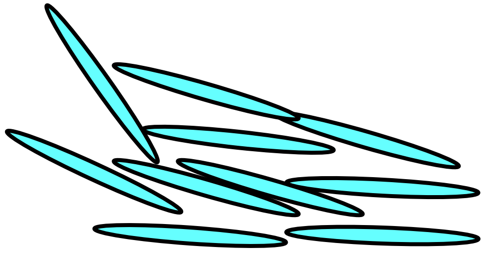
due to flow stresses — due to in-flow collisions and Brownian motion

The magnitude of the viscosity of thixotropic fluids is dependent on the microstructure, in particular:

- Size of the floc (for suspension)
- Mean alignment of fibers
- Favorable spatial distribution of particles
- Entanglement density
- Molecular association (in polymer solution)

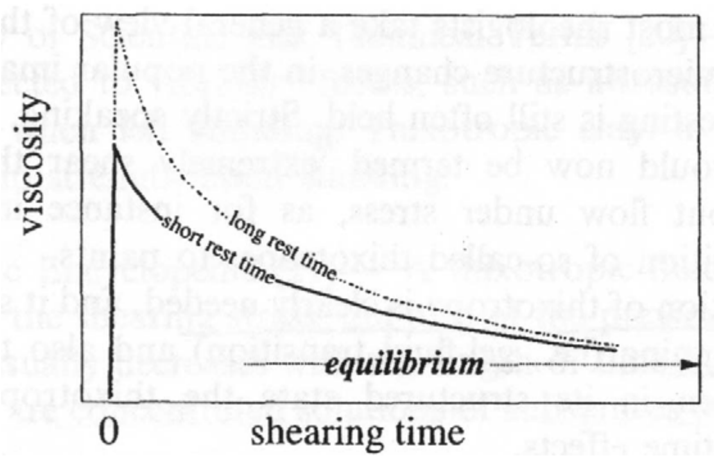






Thixotropic Behavior

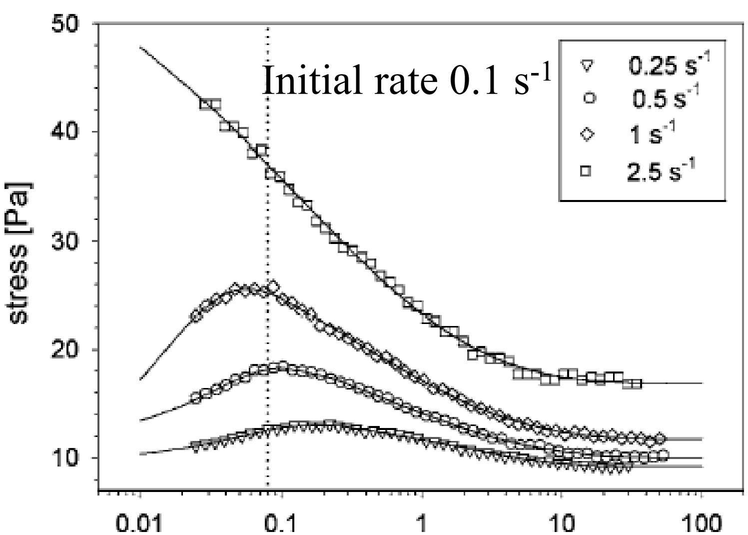
- The 'transient' viscosity of the fluid depends on its shearing history



Stretched exponential model

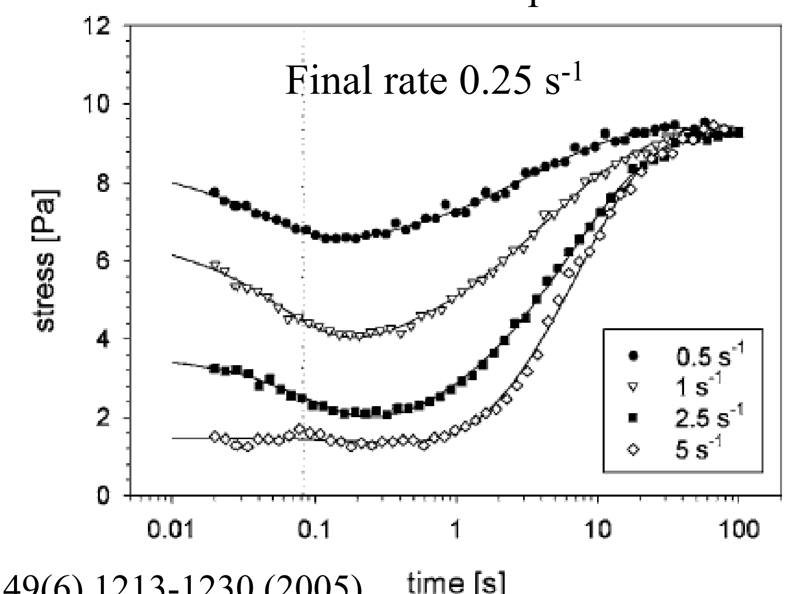
$$\eta = \eta_{e,\infty} + (\eta_{e,\infty} - \eta_{e,0})\left(1 - e^{-(t/\tau)^{r}}\right)$$

Structure break-down



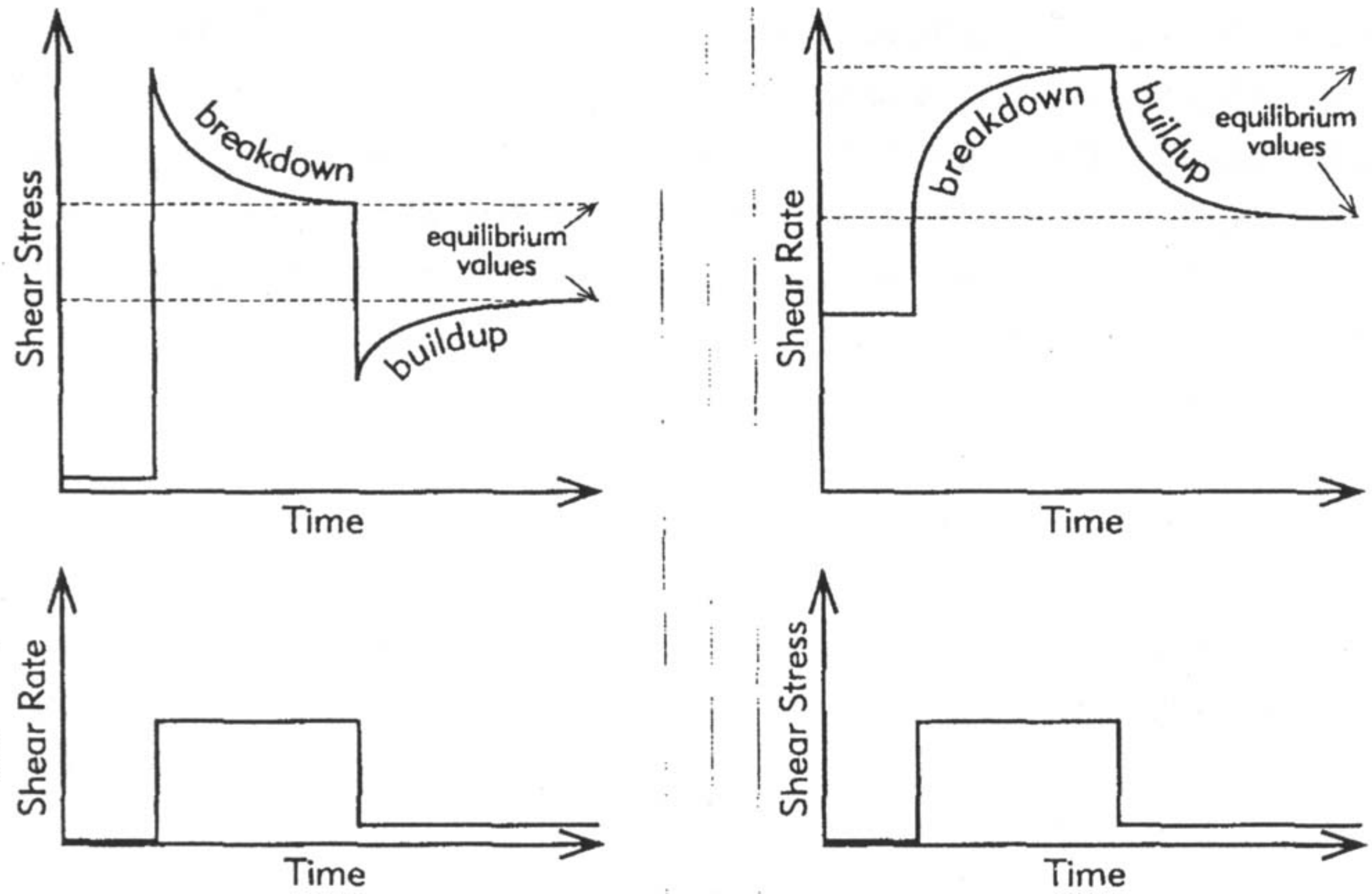
time [s]

Structure build-up



Dullaert K, Mewis J, JoR 49(6) 1213-1230 (2005)

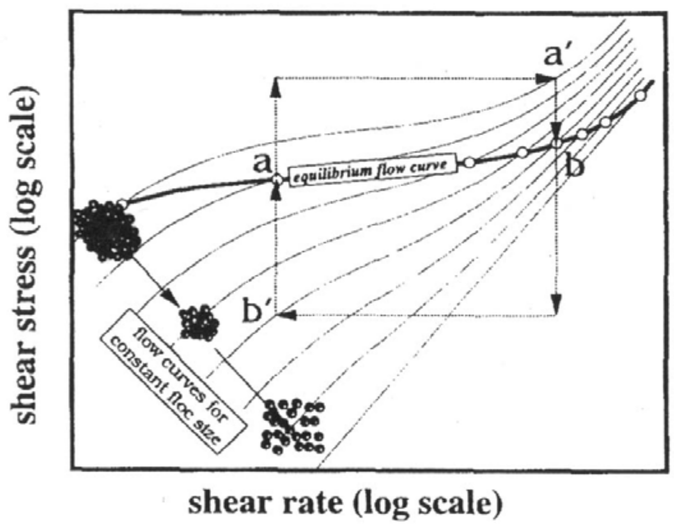
Step Experiments



Extreme Shear Thinning & Antithixotropy

Double shear-thinning effect:

- Shear thinning of floc
- Reduction in floc size with shear rates



Antithixotropy

- Give the right particles attraction, shearing can promote aggregation
- Certain flocs can became looser and more open under shear

Viscoelasticity & Thixotropy

- Linear viscoelasticity: the microstructure responds to flow but it remains unchanged
- Thixotropy: the microstructure responds to flow & it is broken down by deformation.

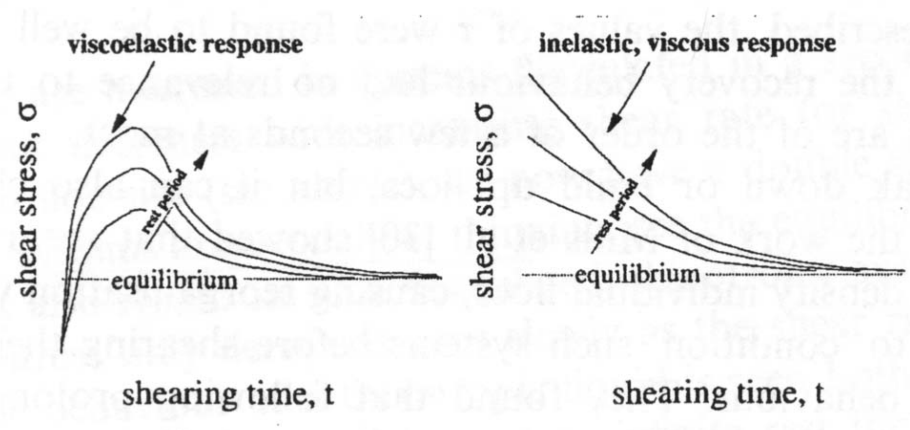
Shear Thinning mechanism:

- Alignment of rod-like particles in flow direction
- Loss of junctions in polymer solutions
- Rearrangement of microstructure in suspension and emulsion
- Breakdown of flocs

Thixotropy is always expected from shear-thinning mechanism

BUT

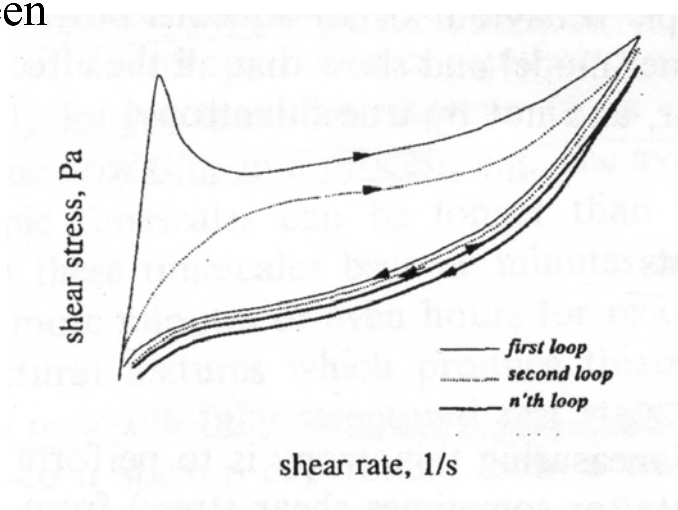
becomes significant only if time-scale is longer than instrument response time



Thixotropy Loops & Start-up experiments

Hysteresis loops

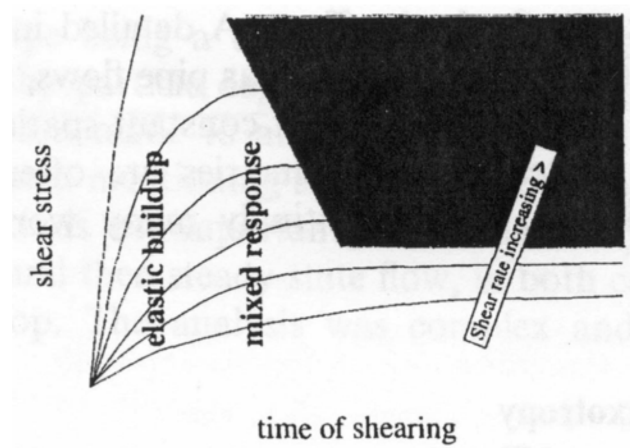
Hysteresis loops are repeated again and again until a constant loop behavior is seen



Hysteresis loops:

- Often carried out too quickly
- Both shear rate & time changes simultaneously
- On startup the behavior is elastic but as strains increase it becomes non-linear elastic response

Start-up experiments



Artifacts:

- Instrument inertia causes delayed instruments response often mistaken for thixotropy
- Slip at wall (wall depletion)

Mathematical theories

- Viscous theories
  - **Indirect microstructural theories**
  - Direct structure theories
  - Simple viscosity theories

Scalar measure of structure λ

$\lambda = 1,$ build structure

$\lambda = 0,$ broken-up structure

Build-up term

$$\frac{d\lambda}{dt} = g(\dot{\gamma},\lambda) = a(1-\lambda)^b - c\lambda\dot{\gamma}^d$$

Breakdown term

$g(\dot{\gamma},\lambda) > 0,$ system is building up

$g(\dot{\gamma},\lambda) < 0,$ system is breaking down

Relate λ to stress and viscosity

$$\eta(\sigma,t) = \eta(\lambda) = \frac{\eta_\infty}{(1-K\lambda)^2}, \quad K = 1 - \left(\frac{\eta_\infty}{\eta_0}\right)^{1/2}$$

$$\lambda = \left(1 - \left(\frac{\eta_\infty}{\eta}\right)^{1/2}\right) / K$$

Direct Structure theories

- Viscous theories
  - Indirect microstructural theories
  - **Direct structure theories**
  - Simple viscosity theories

$$-\frac{d\left(unbroken\right)}{dt} = k_1\left(unbroken\right)^n - k_2\left(broken\right)^m$$

Assume viscosity is proportional to unbroken structure

Example: Cross Model

$$\frac{dN}{dt} = k_2 P - \left(k_0 + k_1\dot{\gamma}^m\right)N$$

N number of link per chain
k_2 rate constant associated with Brownian collisions
k_0 k_1 rate constants for brownian and shear contribution to breakup
P particles per unit volume

$$N_e = \frac{k_2 P}{k_0\left(1+\frac{k_1}{k_0}\dot{\gamma}^m\right)}$$

$$\frac{\eta_e - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1+\frac{k_1}{k_0}\dot{\gamma}^m}$$

Simple viscosity theories

- Viscous theories
  - Indirect microstructural theories
  - Direct structure theories
  - **Simple viscosity theories**

Examples:

$$\frac{d\Theta}{dt} = k_1 \dot{\gamma}^2 \left[\frac{\Theta_\infty - \Theta}{\Theta} \right] - k_2 \left[\Theta - \Theta_0 \right] \qquad \Theta = \frac{1}{\eta}$$

$$\frac{d\eta}{dt} = K \left(\eta_s \left(\dot{\gamma} \right) - \eta \right)^n$$

$$\left(\eta - \eta_\infty \right)^{1-m} = \left[\left(m-1 \right) kt + 1 \right] \left(\eta_0 - \eta_\infty \right)^{1-m}$$

Viscoelastic Theories

- Generalized Maxwell model can be modified to account for thixotropy

$$\sigma = \sum_i \sigma_i \qquad \frac{\sigma_i}{G_i} + \theta_i \frac{d}{dt}\left(\frac{\sigma_i}{G_i}\right) = \theta_i \dot{\gamma}$$

Introduce thixotropy by letting G and θ be a function of λ, the structure parameter

$$G_i = G_{0i}\lambda_i \qquad \theta_i = \theta_{0i}\lambda_i$$

$$\frac{d\lambda_i}{dt} = \frac{1-\lambda_i}{\theta_i} - \frac{a\lambda_i}{\theta_i}\left(\frac{E_i}{G_i}\right)^{1/2}$$

Break-up and Build-up of flocs

- Two mechanism: floc erosion and Brownian collision
- Rate translational diffusion $D_{tran} \propto \frac{1}{a}$
- Rotational diffusion $D_{rot} \propto \frac{1}{a^3}$
- Rebuild starts relatively fast but then floc grow in size and the process gets slower and slower

In Shear Flow

Size of the floc $d_f = C\dot{\gamma}^g$

Surface shear stress experience by the floc $\tau = d_f d\eta\dot{\gamma}$

Conclusion

- Thixotropy happens because of the finite time required for flow-induced changes in the microstructure.
- When flow stops Brownian motion slowly allows microstructure to return to initial configuration
- The process is completely reversible