Thixotropy- a review
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http://web.mit.edu/nnf
• Thixotropy is seen in many fluids:
  - Paints
  - Resins
  - Clays
  - Personal products
  - Chemical products
  - Home cleaning supplies: detergents
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:

<table>
<thead>
<tr>
<th>Break-down</th>
<th>v.s</th>
<th>Build up</th>
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<tbody>
<tr>
<td>due to flow stresses</td>
<td></td>
<td>due to in-flow collisions and Brownian motion</td>
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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

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

Dullaert K, Mewis J, JoR 49(6) 1213-1230 (2005)
Step Experiments
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 become 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.

![Graph of hysteresis loops](image)

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**

![Graph of start-up experiments](image)

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 \( \lambda \)
- \( \lambda = 1 \), 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 \( \lambda \) to stress and viscosity

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

\[
\lambda = \left(1 - \left(\frac{\eta_\infty}{\eta}\right)^{1/2}\right) / K
\]
Direct Structure theories

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

\[-\frac{d(unbroken)}{dt} = k_1(unbroken)^n - k_2(broken)^m\]

Assume viscosity is proportional to unbroken structure

Example: Cross Model

\[\frac{dN}{dt} = k_2P - (k_0 + k_1\dot{\gamma}^m)N\]

- \(N\) 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

\[N_e = \frac{k_2P}{k_0\left(1 + \frac{k_1}{k_0}\dot{\gamma}^m\right)}\]

\[\frac{\eta_e - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \frac{k_1}{k_0}\dot{\gamma}^m}\]
Simple viscosity theories

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

Examples:

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

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

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

- Generalized Maxwell model can be modified to account for thixotropy

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

Introduce thixotropy by letting \( G \) and \( \theta \) be a function of \( \lambda \), the structure parameter

\[
G_i = G_{0i} \lambda_i \quad \theta_i = \theta_{0i} \lambda_i
\]

\[
\frac{d \lambda_i}{dt} = \frac{1 - \lambda_i}{\theta_i} - a \lambda_i \left( \frac{E_i}{G_i} \right)^{1/2}
\]
Break-up and Build-up of flocs

- Two mechanisms: floc erosion and Brownian collision

- Rate translational diffusion: \( D_{\text{tran}} \propto \frac{1}{a} \)

- Rotational diffusion: \( D_{\text{rot}} \propto \frac{1}{a^3} \)

- 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 experienced 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