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

The splash/bounce of a viscoelastic drop

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Gallery of Fluid Motion
DFD-APS 2008
Viscoelastic Flows

- Climbing a Rotating Rod:

Example of a Weissenberg instability
Viscoelastic Flows

- Die Swell:

Another Weissenberg instability
Viscoelastic Flows

- **Tubeless Siphon:**

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:

\[ \nabla \cdot \sigma + \vec{f} = 0 \]

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

\[ \dot{\epsilon}_{ij} = \frac{\partial \epsilon_{ij}}{\partial x_j} + \frac{\partial \alpha_{ij}}{\partial x_i} \quad \epsilon_{ij} = \frac{\partial u_{ij}}{\partial x_j} + \frac{\partial u_{ij}}{\partial x_i} \]

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

\[ \frac{\dot{\gamma}}{\dot{\gamma}} \]

- 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” $\gamma_0$ 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 $\sigma_0$, most viscoelastic materials slowly deform (creep):

- Defines the linear creep compliance:

\[ J(t) = \frac{\gamma(t)}{\sigma_0} \]
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:
  \[ \tau \dot{\sigma}(t) + \sigma(t) = \eta \dot{\gamma}(t) \]

\[ \tau = \eta / G_0 \]
Response to a Step Shear Strain: Maxwell Fluid

Step Strain:

\( \gamma_0 \) is the step shear strain

Stress Relaxation

\[ G(t) = G_0 \exp\left(-\frac{t}{\tau}\right) \]
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:** \( \sigma_0 \)

**Creep:** \[ J(t) = \frac{\gamma(t)}{\sigma_0} \]

\[ J(t) = J_0 + \frac{t}{\eta} \]

where \( J_0 = \frac{1}{G_0} \)

\( \gamma(t) \) is the shear strain
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: \( \sigma_0 \)

Creep: \( J(t) = \frac{\gamma(t)}{\sigma_0} \)

\[
J(t) = \frac{1}{G_0} \left[ 1 - \exp\left( -\frac{t}{\tau} \right) \right] \quad \text{where} \quad \tau = \frac{\eta}{G_0}
\]
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:
  \[
  \eta = G_0 \int_{0}^{\infty} \exp\left(-t/\tau\right) dt = G_0 \tau
  \]
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 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:

\[ G^*(\omega) \equiv G'(\omega) + iG''(\omega) \quad \eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \]

- 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:

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

\[ G''(\omega) = \frac{G_0 \tau \omega}{(1 + \tau^2 \omega^2)} \]
Flow of Complex Fluids

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

- Thickening/Thinning behavior is due to microstructural changes
- Numerous phenomenological constitutive relations
  
  \[ \sigma = \eta(\dot{\gamma})\dot{\gamma} = \kappa \dot{\gamma}^n \]

  - e.g. “power-law” fluids:
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

- 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
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

Shake Gel Phase Diagram

- **Gel**
- **Fluid**
- **Thicken**

**Graph Details:**
- **Y-axis:** PEO concentration [wt %]
- **X-axis:** Laponite concentration [wt %]

**Legend:**
- Upper Phase boundary
- Lower Phase boundary
Shake Gel Relaxation

Relaxation time is a decreasing function of PEO concentration!

$\Phi = 1.25 \text{ wt } \%$
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:

Displacement field near rod:

Interpretation:
formation of transient, localized solid support pillar

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: \( \nabla \cdot \sigma = 0 \)

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

- Constitutive equation:

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

- Flow solutions:

\[
v_z(r) = \left( \frac{\Delta PR}{2L} \right)^{1/n} R \frac{R}{1 + 1/n} \left[ 1 - \left( \frac{r}{R} \right)^{1+1/n} \right]
\]
Yield Stress Fluids

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

  Bingham Fluid: \[ \sigma = \sigma_c + \eta_p \dot{\gamma} \] for $\sigma > \sigma_c$
  
  (Newtonian at high shear rates)

  Herschel-Buckley Fluid: \[ \sigma = \sigma_c + \kappa \dot{\gamma}^n \] for $\sigma > \sigma_c$
  \[ 0 < n < 1 \]
  
  (non-Newtonian at high shear rates)
Yield Stress Fluids

- Model Bingham fluid: Bentonite clay particles in water:

![Graph showing stress (σ) vs. shear rate (γ) for 10 wt% bentonite clay particles in water. The graph shows a linear relationship and a point indicating no apparent flow.]
Bingham Fluid in Pipe Flow

- Low stress region near center is below $\sigma_c$ 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:

![Diagram showing Bingham Fluid in Pipe Flow](image-url)