Lecture 7. Complex Fluids

We have now discussed in depth the differences between fluids and solids

Fluid

- * Resist compression i.e has a bulk modulus
- * If shear is applied the material will flow
- * Work is not stored but dissipated by viscosity. (When you stop applying shear stress fluid will stop flowing but never spontaneously flow back to its original position
- * stress-strain rate relation

$$\sigma_{ij} = \eta \, \dot{\gamma}_{ij}$$

viscous stress for incompressible fluids

Solid

- * Resists both compression and shear deformation
- * Elastic energy can be stored in deformations
- * stress - strain relation

$$\sigma_{ij} = \frac{1}{2} K \gamma_{kk} \delta_{ij} + G\left(\gamma_{ij} - \frac{1}{3}\gamma_{kk}\delta_{ij}\right)$$

Hooke's law for isotropic materials

Materials classified as a solid or fluid can undergo phase transitions from one to the other as a function of thermodynamic variables like temperature or pressure.

There is also the "in between", mostly soft materials exhibit properties of fluids and solids] Rheology: study of how materials flow & deform under applied F's. i.e. stress-strain relations for viscoelastic materials.

e.g. tooth paste, shaving cream, honey and batter
- push gently → materials spring back
- push harder → materials start to flow
- stir them → adapt "weird" configurations that don't resemble the parabolic surface of water in a rotating system

Viscoelastic materials

Materials that exhibit properties of fluids and solids. To understand the response of this materials to an applied stress, first we'll start with thinking about the strain.

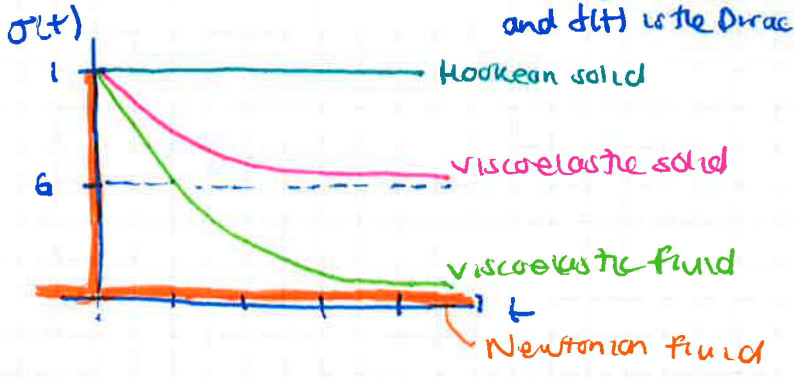
Let's assume that at $t=0$ we apply a 'step strain', i.e. we deform the material by a small amount γ_0:

$$\gamma(t) = \gamma_0 \, \Theta(t) = \begin{cases} 0 & t<0 \\ \gamma_0 & t>0 \end{cases}$$ where $\Theta(t)$ is the heaviside function

What is the associated stress for this step strain?

For a solid $\longrightarrow \sigma \propto \gamma G$ strain × shear modulus ≡ Hookean solid

For a fluid $\longrightarrow \sigma \propto \dot{\gamma}$ stress is almost always zero except at $t=0$ where $\sigma(t) = \eta \gamma_0 \delta(t)$ where η is the fluid viscosity and $\delta(t)$ is the Dirac delta ≡ Newtonian fluid



For a viscoelastic solid or viscoelastic fluid stress due to the step strain decreases over time, with a characteristic timescale (rather than the zero time for the Newtonian fluid or the ∞ time for the Hookean solid). The difference between them is what happens at long timescales.

viscoelastic solid	Viscoelastic fluid
Some of the energy put into the deformation is stored and the stress relaxes to a finite value.	All of the energy put into the deformation is eventually dissipated and the stress relaxes to zero.

We can generalize the stress-strain relationship for elastic solids $\sigma = G\gamma$ to viscoelastic materials by making the shear modulus a function of time:

$$\sigma(t) = \gamma_0 G(t)$$

, G(t) is also know as the "relaxation modulus", ~~[illegible] depends on~~ because it describes how a material relaxes over time.

From this eq we can see that for a viscoelastic material, the stress at any point in time depends on the history. The strains applied to it in the past all affect the strain in the present.

To find the stress at time t we need to know and account for the strain $\gamma(t)$ from $t = -\infty$ to the present time. As long as the stresses are not too large, we can also add up the stresses due to multiple step strains:

$$\gamma(t) = \sum_i \Delta\gamma_i \Theta(t - t_i)$$

then the stress becomes:

$$\sigma(t) = \sum_i G(t - t_i)\Delta\gamma_i$$

We can approximate any continuous function $\gamma(t)$ by steps by dividing up the time intervals Δt and writing $\Delta\gamma_i \simeq \dot{\gamma}(t)\Delta t$, and taking the limit $t \to 0$:

$$\sigma(t) = \lim_{\Delta t \to 0} \sum_i G(t - t_i)\dot{\gamma}(t)\Delta t = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')dt' \quad \circledast$$

In rheological experiments the most commonly applied strain is not a step strain or continuous shear, but an oscillatory one:

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

For this strain, equation $\circledast$ turns into a fourier transform:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')(-\gamma_0\omega)\sin(\omega t')dt'$$

, if we ~~define~~ change variables $u = t - t'$

$$= (-\gamma_0\omega)\int_0^{\infty} G(u)\sin(\omega(t - u))du$$

$$= \gamma_0\left[G'(\omega)\cos(\omega t) - G''(\omega)\sin(\omega t)\right]$$

where we have defined the two moduli for a viscoelastic material:

$$G'(\omega) \equiv \omega\int_0^{\infty} G(t)\sin(\omega t)dt$$ storage modulus

$$G''(\omega) \equiv \omega\int_0^{\infty} G(t)\cos(\omega t)dt$$ loss modulus

We can also write an oscillatory strain as $\gamma(t) = \gamma_0 e^{i\omega t}$, in which case we get a single complex modulus:

$$G^*(\omega) = i\omega \int_0^\infty G(t)\, e^{-i\omega t} dt = G'(\omega) + iG''(\omega)$$

As we'll see later, the simplest models for viscoelastic materials have a relaxation function given by:

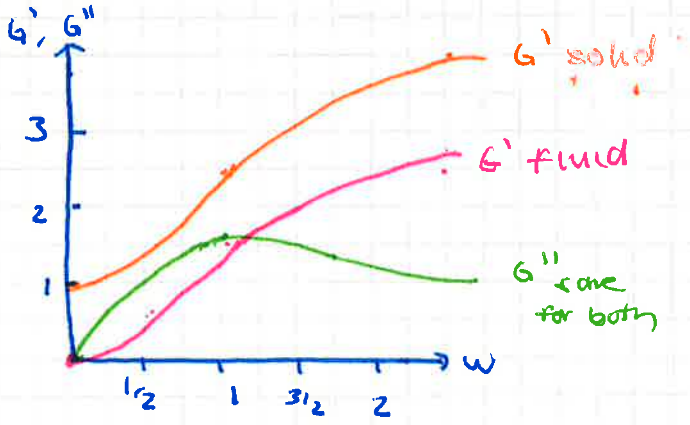
$$G(t) = G_e + G_0 e^{-t/\tau} \quad \text{where } G_e,\ G_0 \text{ and } \tau \text{ are constants}$$

from our earlier plot we can see that $G_e = 0$ for a viscoelastic fluid
$G_e \neq 0$ for a viscoelastic solid

The storage and loss moduli are simply the Fourier sine and Fourier cosine transform of this function, they are given by:

storage modulus $$G'(\omega) = G_e + G_0 \frac{(\omega\tau)^2}{1+(\omega\tau)^2}$$

loss modulus $$G''(\omega) = G_0 \frac{(\omega\tau)}{1+(\omega\tau)^2}$$



For $G_0 = 3$, $\tau = 1$ and $G_e = 0$ or 1

taking the limit $\omega \to 0$

$$\lim_{\omega \to 0} G'(\omega) = G_e$$

$$\lim_{\omega \to 0} G''(\omega) = \omega G_0 \tau \equiv \omega \eta_0$$

where $\eta_0 \equiv G_0 \tau = \int_0^\infty G(t)dt$ is the steady state viscosity.

Two simple models for viscoelastic materials

We can derive the constitutive equations for viscoelastic materials by representing the viscous and elastic part of a material with "elements" in the same way as we combine elements to build a circuit:

spring

elastic part
$\sigma = G_e \gamma$
characterized by its modulus G_e

Dashpot

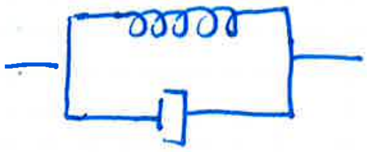
viscous part
$\sigma = \eta \dot{\gamma}$
characterized by its viscosity

As in electronics, there are 2 ways to combine these elements

In series:

Maxwell fluid

In parallel:



Kelvin-Voigt solid

Maxwell fluid

In this case we consider that the spring and the dashpot are connected together in series.

If we apply a stress to this material (imagine we pull)
→ both components feel the same force
→ each component will deform differently

This means that for a Maxwell fluid:

$$\sigma = \sigma_{el} = \sigma_{visc} \quad \text{same stress}$$

$$\gamma = \gamma_{el} + \gamma_{visc} \quad \text{strain of two components adds up}$$

Now, σ_{el} = spring and σ_{visc} = dashpot, which are given by:

$$\sigma_{el} = G_e \gamma_{el} \quad \text{and} \quad \sigma_{visc} = \eta \dot{\gamma}_{visc} \quad (**)$$

$$\Rightarrow \dot{\sigma}_{el} = G_e \dot{\gamma}_{el}$$

$$\Rightarrow \frac{\dot{\sigma}_{el}\eta}{G_e} = \eta \dot{\gamma}_{el} \quad (*)$$

Summing (*) and (**) and noting that $\sigma_{el} = \sigma_{visc} = \sigma$

$$\sigma + \frac{\dot{\sigma}\eta}{G_e} = \eta\left(\dot{\gamma}_{el} + \dot{\gamma}_{visc}\right) \underset{\uparrow}{=} \eta\dot{\gamma}$$

considering strain of two components adds up

Note that this equation carries an intrinsic timescale $\tau = \frac{\eta}{G_e}$ which will be the characteristic timescale of relaxation of the material!

For $t \ll \tau$ material behaves like a solid
$t \gg \tau$ material behaves like a fluid

Given an applied strain we can solve for σ. Considering the step strain $\gamma(t) = \gamma_0\, \Theta(t) = \begin{cases} 0 ; t<0 \\ \gamma_0 ; t>0 \end{cases}$

For $t>0$, $\dot{\gamma} = 0$ so we have:

$$\dot{\sigma} = -\sigma\left(\frac{G_e}{\eta}\right) \Rightarrow \sigma(t) = G_0\, e^{-t/\tau} \quad \text{where } G_0 \text{ is an integration constant}$$

For $t=0$, both $\dot{\sigma}$ and $\dot{\gamma}$ diverge while the stress itself is finite so we have:

$$\overset{0}{\cancel{\frac{\sigma}{\eta}}} + \frac{\dot{\sigma}}{G_e} = \dot{\gamma} \Rightarrow \sigma(t=0) = G_e\gamma_0, \quad \text{with this we find } G_0 = G_e\gamma_0$$

So the response of a Maxwell fluid to a step strain of magnitude γ_0 at $t=0$ is given by:

$$\sigma(t) = G_e\gamma_0\, e^{-t/\tau}$$

(viscoelastic fluid curve we had drawn at the beginning of class)

Kelvin-Voigt solid

In this case we consider a spring and a dashpot in parallel

If we apply a stress to this material
→ both components deform together
→ each component resists the deformation differently

This means that for a Kelvin-Voigt solid

$$\dot{\gamma} = \dot{\gamma}_{el} = \dot{\gamma}_{visc} \quad \text{same strain / strain rate}$$

$$\sigma = \sigma_{el} + \sigma_{visc} \quad \text{stress adds up}$$

Now σ_{el} = spring σ_{visc} = dashpot

$$\sigma_{el} = G_e \gamma_{el} \quad \text{and} \quad \sigma_{visc} = \eta \dot{\gamma}_{visc} \qquad \text{considering } \gamma_{el} = \gamma_{visc} = \gamma$$

$$\Rightarrow \sigma = G_e \gamma + \eta \dot{\gamma}$$

Considering a step strain $\gamma(t) = \gamma_0 \Theta(t)$ we find:

$$\sigma(t) = \gamma_0 \Big[\underbrace{G_e \Theta(t)}_{\text{step stress}} + \underbrace{\eta \delta(t)}_{} \Big]$$

term that spikes as the strain is applied since the derivative of the step function is the Dirac delta function.

Characterizing viscoelastic fluids

For an ordinary viscous fluid, the stress is linear in the strain rate, with the viscosity being the proportionality constant:

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

stress increases proportional to the rate of deformation

⇒ fluid's resistance to flow is independent on how fast you strain it.

For viscoelastic flows this relation breaks down in general, the stress may depend on the magnitude of the strain rate, the history of deformation or both. BUT we can still define a viscosity function:

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

For any strain rate we can measure the corresponding stress and define an effective viscosity

η is no longer constant, it can change with the strain rate.

↳ shear thinning → η decreases with $\dot{\gamma}$ e.g. paints → spread smoothly under a brush, but don't drip when left still

↳ shear thickening → η increases with $\dot{\gamma}$ e.g. corn-starch + water ↳ runny if you move slowly, you can walk on it if you're fast.

The viscosity we use in the dashpot element corresponds to the low-strain-rate limit:

$$\eta = \lim_{\dot{\gamma} \to 0} \eta(\dot{\gamma})$$

Fluid's viscosity when it's deformed very slowly

In addition to shearing you can make a viscoelastic fluid flow by applying a normal stress difference, i.e. a difference in the diagonal components of the applied stress. Since there are 3 diagonal components, there are 2 independent normal stress differences which conventionally are taken to be:

$$N_1(\dot{\gamma}) = \sigma_{xy} - \sigma_{yy}$$

$$N_2(\dot{\gamma}) = \sigma_{yy} - \sigma_{xx}$$

To see how this would work let's consider a shear flow in the $\hat{x}$ direction, which sets a ~~gr~~ velocity gradient in the $\hat{y}$ direction.

The normal stresses in this case are:

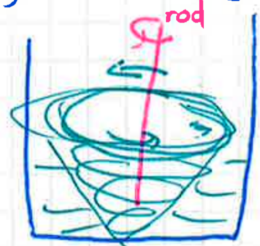
σ_{xx} normal stress in flow direction
σ_{yy} normal stress in velocity gradient direction.
σ_{zz} normal stress out of plane

For an ordinary viscous fluid $\sigma_{xx} = \sigma_{yy} = \sigma_{zz} \Rightarrow N_1 = 0$
But for a viscoelastic fluid $N_1 > 0$

If we imagine a polymeric fluid (fluid made of material w/ long 'strands')
As we shear the fluid the long polymer chains will stretch and align with the direction of the flow. The stretching stores elastic energy in that direction. As a result the stress along the flow direction σ_{xx} becomes larger than σ_{yy} → fluid pulls inward towards regions of high shear & push outward along the flow direction.

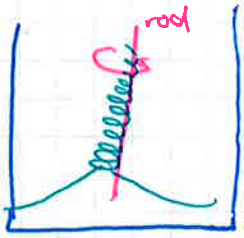
$N_1 > 0$ gives rise to what is known as the Weissenberg effect.
This, is also known as the rod climbing effect.

Ordinary viscous fluid (e.g. water)



water moves outward centrifugally if rotated by a rod

Viscoelastic polymeric fluid



fluid will "climb up" the rod

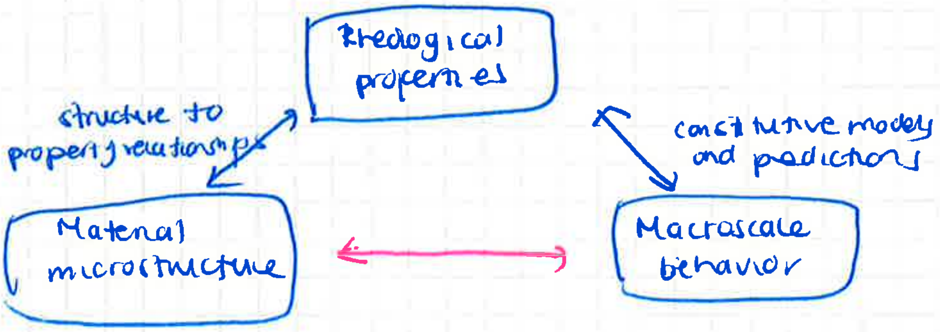
because $N_1 > 0$ there is a tensile stress along the circular flow direction. The fluid is under more tension along the streamlines which generates an inward elastic force pulling the liquid up the spinning rod.

Measuring viscoelastic behavior: Rheology

Rheology is the study of the deformation and flow of complex materials
- e.g. viscoelastic materials
- e.g. Non-newtonian fluids

As we discussed during this lecture, what this means is to understand ~~how~~ the stress-strain relation for the material. We know that this relationship will depend on both history (time) and magnitude of stress or strain.

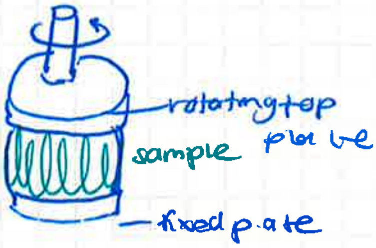
The big picture of rheology



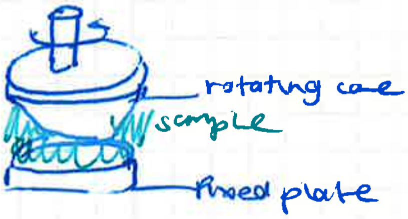
Connecting the microstructure with macroscopic behavior of a material can be considered the overall goal of rheology (measuring rheological properties is the bridge)

Rheological properties are usually tested with a rheometer, which is an instrument that measures → how a material flows and deforms in response to an applied force → stress controlled measurement
↳ the resulting stress from a known applied deformation or strain → strain controlled measurement

parallel plates



cone and plate



*stress controlled measurement: → Apply $\sigma(t)$, measure $\gamma(t)$ or $\dot{\gamma}(t)$, creep compliance $J(t) = \frac{\gamma(t)}{\sigma_0}$
how materials "hold up" under long term load.
↳ good for yield stress measurements or weakly structured materials
↳ natural choice for creep or stress relaxation measurements.

*strain controlled measurement → Apply $\dot{\gamma}(t)$ or $\gamma(t)$ and measure σ.
↳ oscillate upper plate at amplitude $\gamma_0 \cos \omega t$ and measure the stress response.
↳ Measures the storage and loss modulus
$\sigma(t) = \gamma_0 [G'(\omega)\cos(\omega t) - G''(\omega)\sin(\omega t))]$
↳ good for sensitive gels, polymers (better control at small strains).