Lecture 7: Rheology and milli-microfluidic

Introduction

In this chapter, we come back to the notion of viscosity, introduced in its simplest form in the chapter 2. We saw that the deformation of a Newtonian fluid under a shear stress is proportional to this stress, the proportionality coefficient being the viscosity. In reality, many fluids have a more complex response to stress which can be a function of temperature, shear rate, time and can involve elastic components…The first section of this chapter introduces the notion of rheology which is the study of the relation between fluid deformation and stress.

Why is rheology important for fluid mechanics at milli and micro-meter scales? First, most of the fluids used in this field are non-Newtonian fluids. To cite a few: emulsions, suspensions, polymers solutions/melts and most of the biological fluids. Second, due to the velocities and dimensions at stake, a wide range of shear rates may be reached. Neglecting the variations of viscosity with shear rate is not possible anymore; the response time of the fluid has to be adequately taken into account. The second part of this chapter focuses on polymers rheology (melts). Various response time scales are introduced and their consequences on rheological behaviours are discussed.

We close this chapter showing how milli and micro fluid mechanics can be used via the design of a capillary and elongational rheometers to shine some light on non-Newtonian rheological behaviors.

1) Rheology

1)1) Qualitative definitions

Rheology is the science that studies how a body (and especially a fluid) deforms under stress.

It adopts a macroscopic point of view and assumes hypothesis of continuum mechanics are valid (homogeneous media, studied length scale>>molecular sizes and intermolecular distances).
Practically, for gases, the limit is reached for low pressures when the mean free path becomes comparable to typical flow length scale (Knudsen number). For liquids, the apparition of slip condition is often seen as the limit of continuum mechanics.

Viscosity corresponds to the resistance a fluid opposes to any flow.

Typically, Newtonian liquids are viscous and are irreversibly displaced by a flow. The energy supplied to the liquid via shear is dissipated (heat) by viscosity. To maintain a flow, energy must be continuously supplied to the liquid.

Elasticity describes how a solid returns to its initial shape after a small deformation.

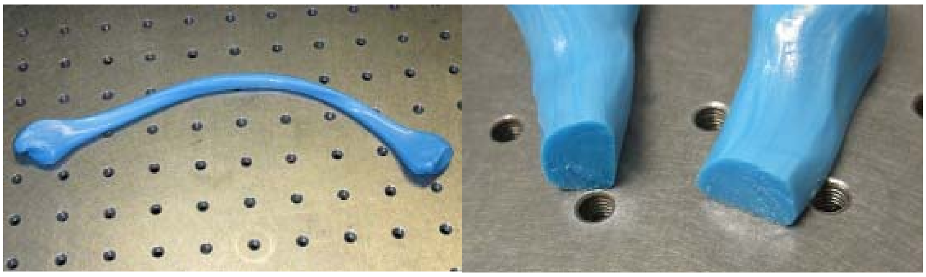
Ideally, a solid subjected to a small deformation will "store" the supplied energy in a mechanical form which will be restituted (no loss) after the deformation stopped. It acts like a spring. The strain is proportional to the stress and the proportionality coefficient is called elastic modulus or Young modulus (in Pa).

Visco-elasticity describes any rheological behaviors which comprises both a viscous term (loss of energy, viscosity, liquid like behavior) and an elastic term (storage of energy, elastic modulus, solid like behavior).

In other words, the response of the material to a strain depends on the time scales (rate of strain). At short time scale, a solid like behavior is observed (purely elastic for small deformation); the energy is stored in strain and fully restituted. The stress is proportional to strain (and not strain rate), the proportionality coefficient is a shear modulus (equivalent to Young modulus for tensile stress) G [Pa]. At long time scale, the fluid adopts a liquid like behavior (purely viscous), the energy is dissipated via viscosity (heat).

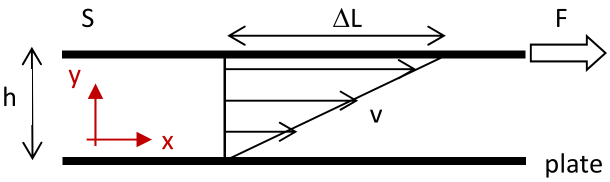
Example Silly Putty:

A sculpted Silly Putty flows very slowly under gravity.



When stretched slowly, the Silly Putty flows while it breaks like a solid if pulled too quickly.

1)2) Viscosity – Newtonian fluids - shear



Deformation (shear strain) $\gamma = x/y = \Delta L/h$,

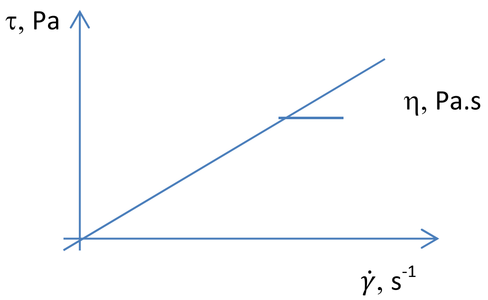
Shear (strain) rate $\dot{\gamma} = \frac{dv}{dy}$

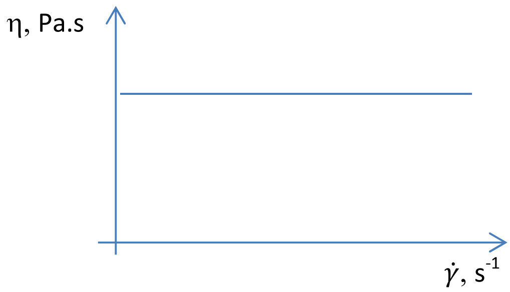
Shear stress: $\tau = F/S$

For the Newtonian fluids, the stress τ is proportional to the shear rate $\dot{\gamma}$ and the ratio between stress and shear rate is the dynamic viscosity.

$\tau = \eta\,\dot{\gamma}$ or $\eta = \tau / \dot{\gamma}$ with η the dynamic viscosity [Pa.s].

Data are typically presented in terms of flow curve (left) and viscosity curve (right).



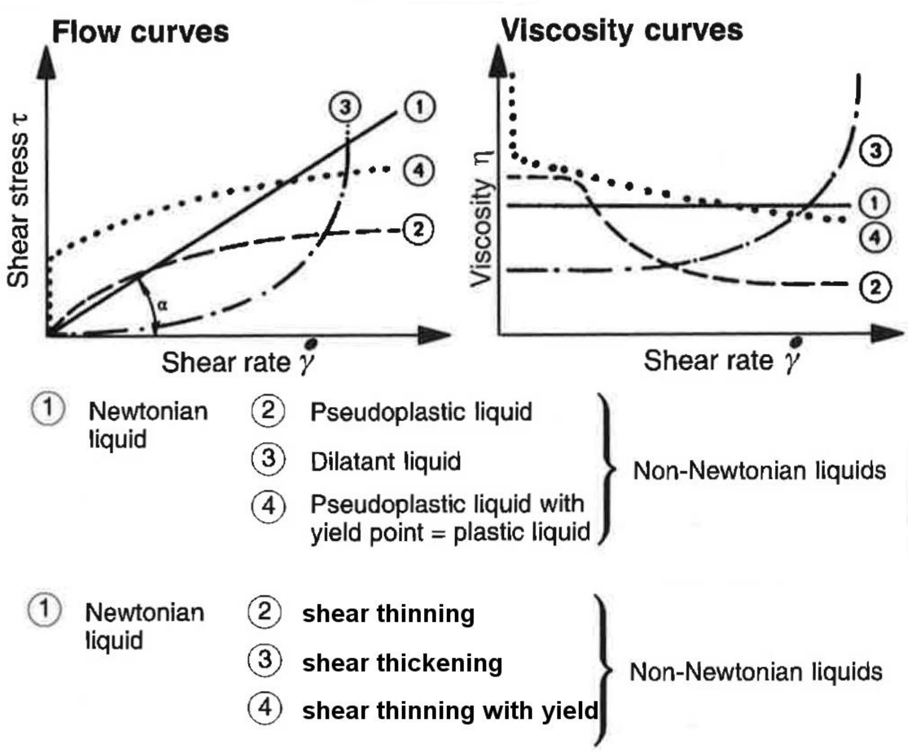


1)3) Viscosity – non Newtonian fluids

Existence of Shear thinning/thickening behaviours and yield. Type of deformation (here shear) may also play a role (for example elongation versus shear)

Corresponding flow and viscosity curves are illustrating these behaviours, see figure below for a shear.

Viscosity corresponds to the local slope of the flow curves; in other words:
$\eta = d\tau / d\dot{\gamma}$

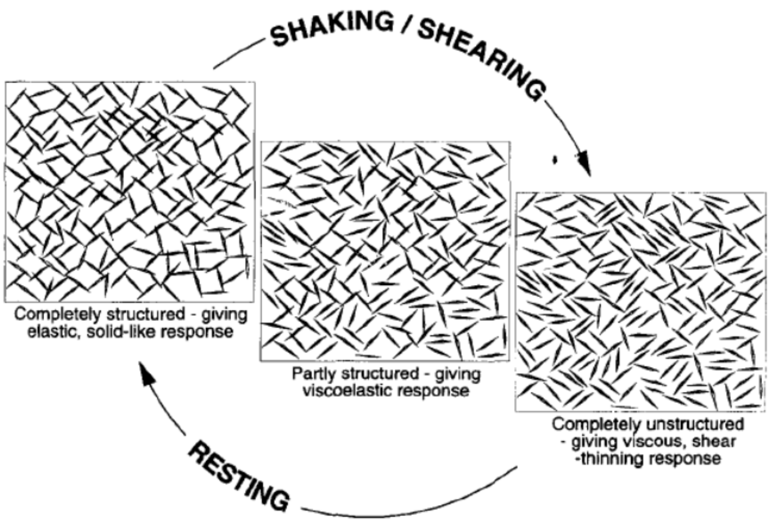


From "A practical approach to rheology and rheometry"

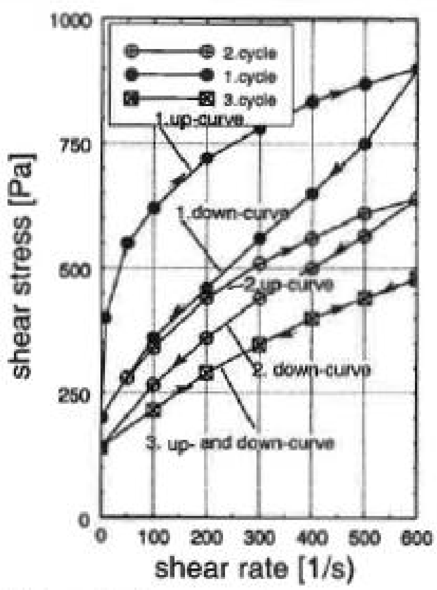
Shear thinning: tooth paste, ketchup
Shear thickening: starch, “maizena”
Bingham plastic: mayonnaise, mustard (can be associated to strong shear thinning, no consensus)

Notion of thixotropy → response is time dependent

The viscosity is a function of time (sample history). Mainly observed for gels, suspensions,polymers… when a micro network between molecules/particles can form.



Barnes, 1997



left: multiple up– + down ramps

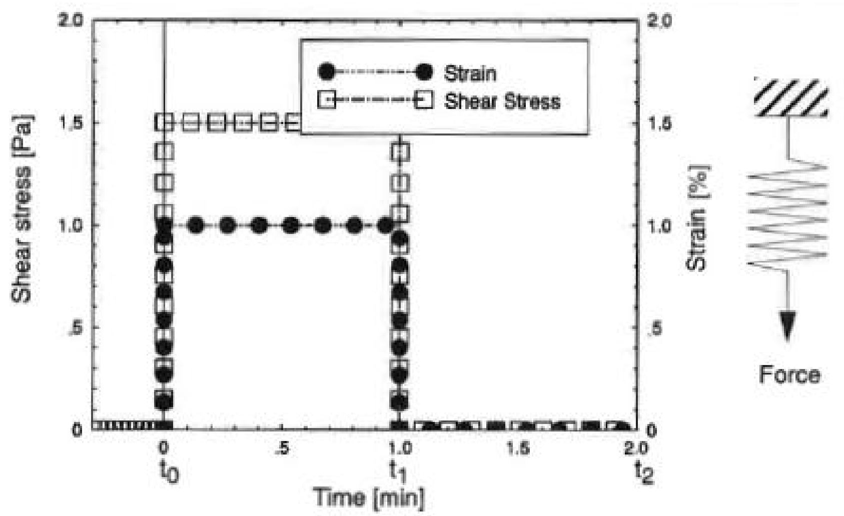
Common test for thixotropy:
cycles ramps up/down shear rate measuring stress. The existence of an hysteresis demonstrates that the flow impacts on the microstructure of the fluids (network broken, fibers aligned, droplets distorted,…) with further impacts on its rheological behavior.
It is a very challenging aspect in rheology as measurements will reflects the “history” of the samples.

1) 4) Visco-elasticity

Weissenberg effect, tubeless syphon → normal stresses difference

Mixture of solid like behavior (left) and liquid like behavior. Time scales are crucial!

Creep and recovery times

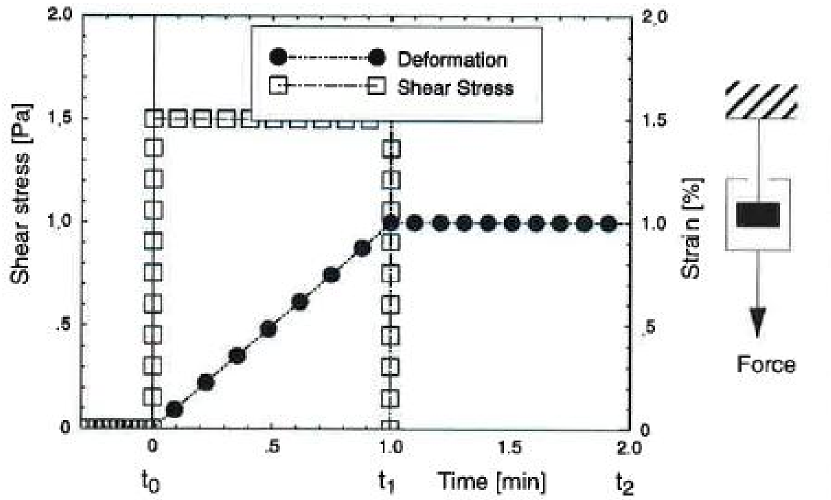


Solid

$\tau = G\gamma$

G: shear modulus in Pa

Stress and strain are non-time dependent

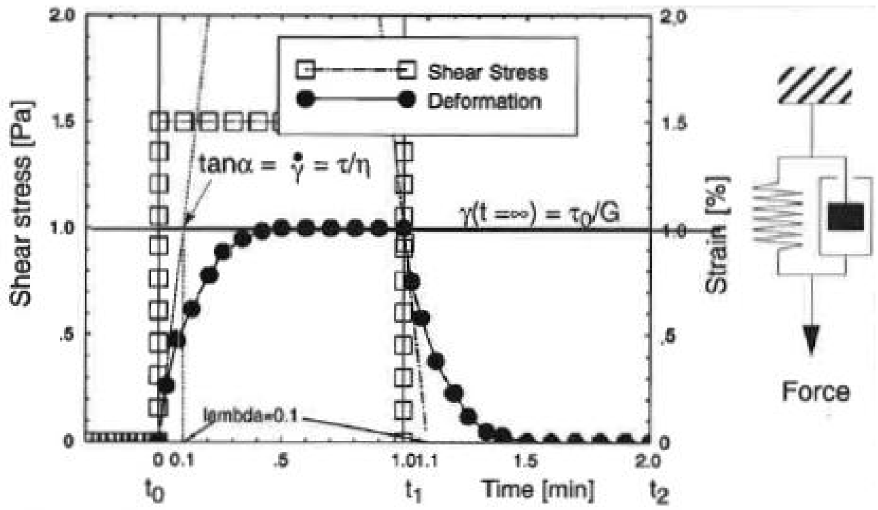


Liquid

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

η: viscosity in Pa.s

Strain increases linearly with time for a constant stress



Visco-elastic fluid

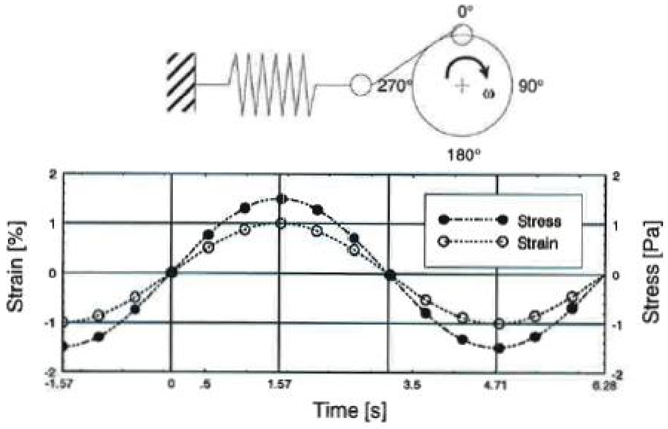
$\tau = G\gamma + \eta\dot{\gamma}$

$\gamma(t) = \frac{\tau_0}{G}(1 - e^{-t/\lambda})$

$\lambda = \tau_0/G$ is a relaxation time (in s)

Oscillatory measurements → applying $\gamma(t)$ and measuring $\tau(t)$

Typically $\gamma(t)=\gamma_0 \sin(wt)$ and w can be screen to probe short and long time scale

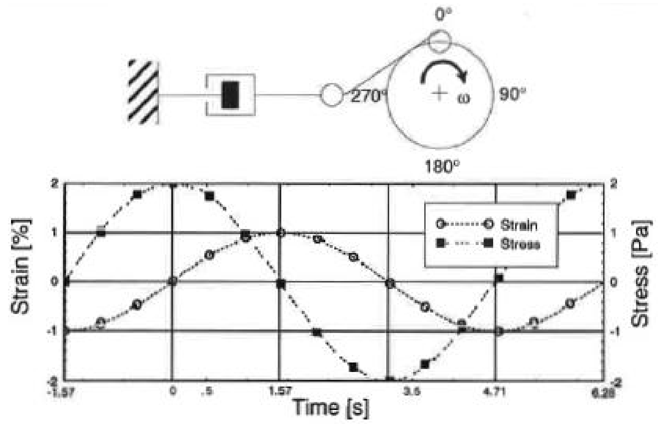


Solid

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

$$\tau(t) = G\, \gamma_0 \sin(\mathrm{wt})$$

Strain and stress are in phase



Liquid

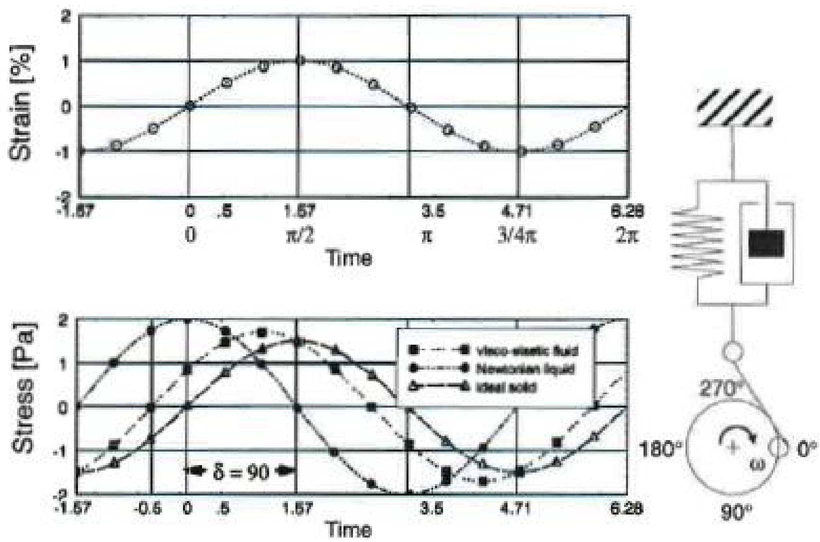
$\gamma(t)=\gamma_0 \sin(wt)$

$$\tau(t) = \eta\, \frac{d\gamma}{dt}$$

$$\tau(t) = \eta\, \gamma_0 \mathrm{w} \cos(\mathrm{wt})$$

$$\tau(t) = \eta\, \gamma_0 \mathrm{w} \sin(\mathrm{wt} + \pi/2)$$

Strain and stress are in opposition of phase



Visco-elastic fluid

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

$$\tau(t) = G\gamma_0 \sin(\mathrm{wt}) + \eta\gamma_0 \mathrm{w} \cos(\mathrm{wt})$$

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

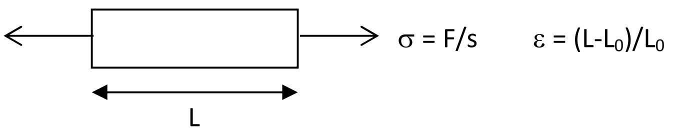
Stored energy (G') — Dissipated energy (G'')

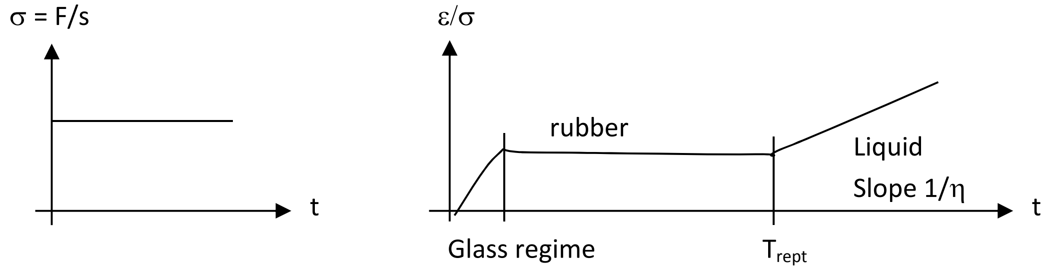
G´and G´´ are function of w → time scales!

2) Focus on polymer melts

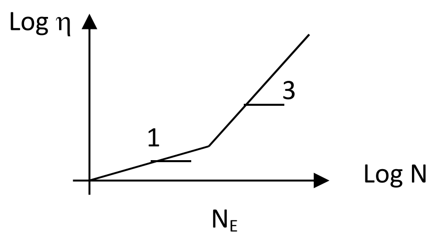
$t \ll T_{ref}$: Young modulus as for a solid

$t \gg T_{ref}$: viscous liquid





Concept of reptation (T_{rept} or N_E entanglements)



For $N<N_E$: → Rouse, $D_{Rouse} \sim D_{mono}/N$; time required to diffuse of R is $T_{Rouse} \sim T_{mono}\ N^2$ and $\eta \sim \eta_{mono} N$

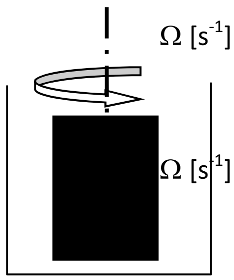
For $N>N_E$: Reptation in a tube due to topological constrains (spaghetti). $T_{rept} = L_{tube}^2/D_{Rouse}$ and $L_{tube} \sim N/N_E\ d = N/N_E\ N_E^{1/2}\ a$. It has also be shown that $\eta \sim \eta_{mono}\ N^3/N_E$

Remark: semi dilute solutions can be treated similarly to melt but using SAW instead of ideal chain. The concentration c plays more or less the role of N_E in a melt.*

3) Overview of rheometers – applications to Milli-microfluidics

Purely viscous fluids

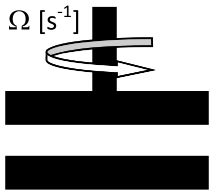
- Couette rheometer:



$\Omega = \dot{\gamma}\,\frac{r_{ext}-r_{in}}{r_{in}}$ (for narrow gap)

$M = 2\pi h r^2 \tau(r)$

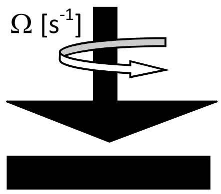
- Cone-plate or plate-plate rheometer



$\dot{\gamma} = \frac{\Omega r}{h}$

(shear rate non constant)

$M = \int_0^R 2\pi r^2 \tau(r)\, dr$

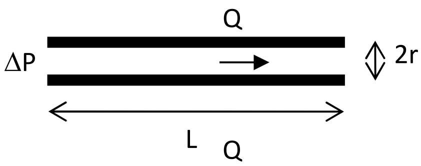


$\dot{\gamma} = \Omega\Theta$

(shear rate constant)

$M = \int_0^R 2\pi r^2 cos^2\Theta\, \tau(r)\, dr$

- Capillary rheometer



Money Rabinowitsch

$\tau_w = \frac{\Delta P}{L}\frac{r}{2}$, Q is measured → $\delta Q/\delta\tau_w$

$\dot{\gamma_w} = \frac{1}{\pi\, r^3}\left(3Q + \tau_w \frac{\delta Q}{\delta \tau_w}\right)$ and $\eta = \frac{\tau_w}{\dot{\gamma_w}}$

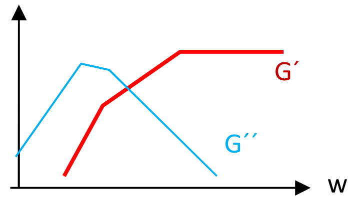
Visco-elastic fluids

- Stress relaxation modulus G_r → applying a step strain γ_0 and measuring the stress $\tau(t)$ over time → $G_r(t)=\tau(t)/\gamma_0$

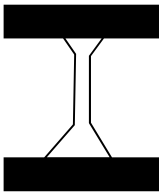
- Oscillation approach : applying oscillating strain $\gamma(t)=\gamma_0$ sin(wt) → $\dot{\gamma}$ (t)=γ_0 w cos(wt) and $\tau(t)=\tau_0(w)\sin(wt+\delta(w))= \gamma_0\,(G'(w)\sin(wt) + G''(w)\cos(wt))$

$\underbrace{G'(w)\sin(wt)}_{\text{Storage (elastic)}} \quad \underbrace{G''(w)\cos(wt)}_{\text{loss (viscous)}}$

Classically performed with cone plate, typical results:



- Elongational rheometer



Drainage of the ligament under surface tension →exponential decay → relaxation time