Rheophysics

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Chapitre 1
Introduction:
Motivations and objectives

Rheology

Science of the deformation and flow of materials

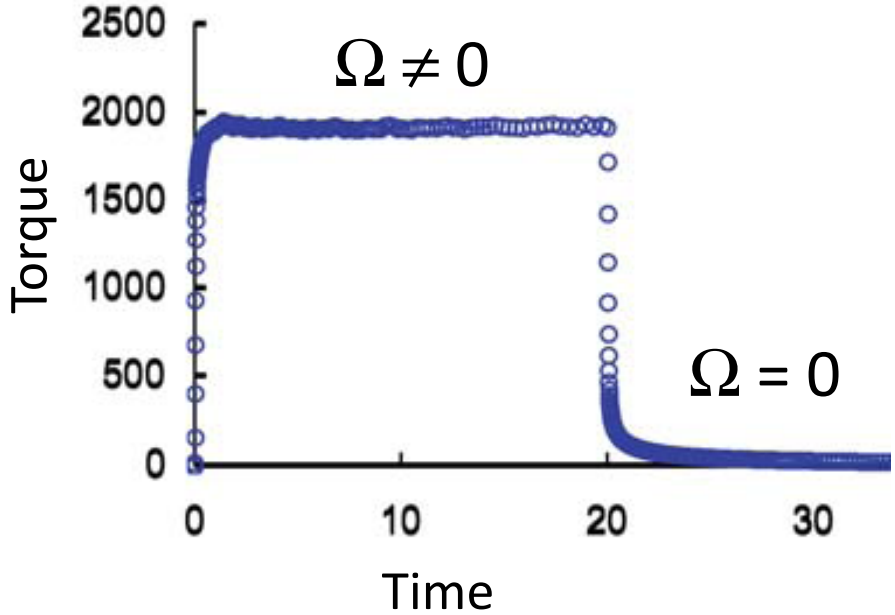
Material properties can be classified according to two parameters: the amplitude of the applied force and the time of observation

Class I: materials that are solid at short times but flow at long times. They are called viscoelastic materials (*polymer melts and solutions*)

Class II: materials that resist to small forces but flow when they ar elarge enough. They are called viscoplastic materials (*colloidal and granular materials: concentrated suspensions, pastes, glasses*)

1.1 Class I: Viscoelastic materials

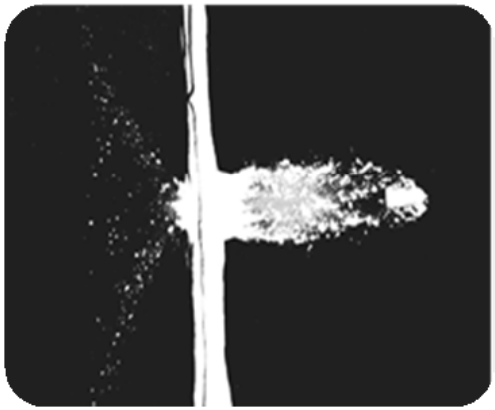
Polymer melts

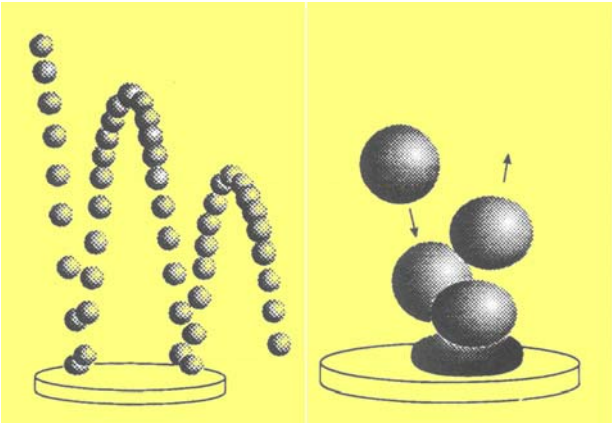


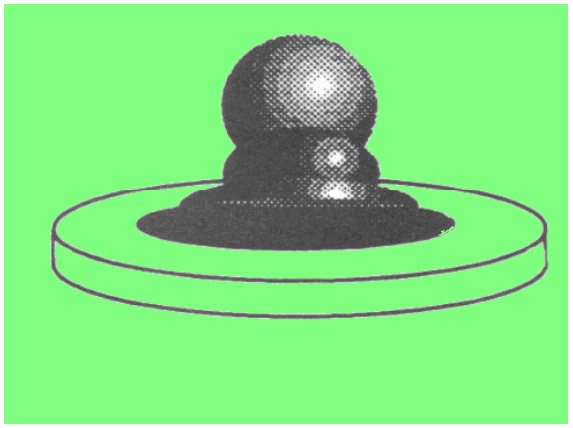
Upon flow inception and/or flow cessation, steady-state conformation is reached after a period of time that characterizes molecular motions

Macroscopic behavior

time







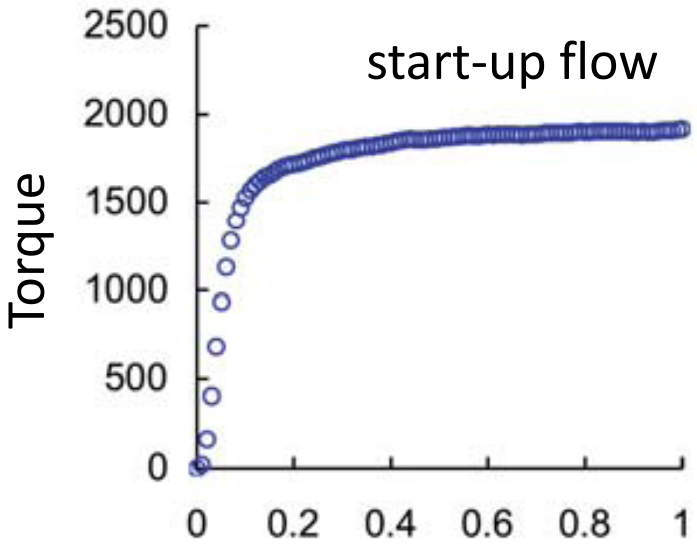
Courtesy:
MIT Edgerton Strobe laboratory

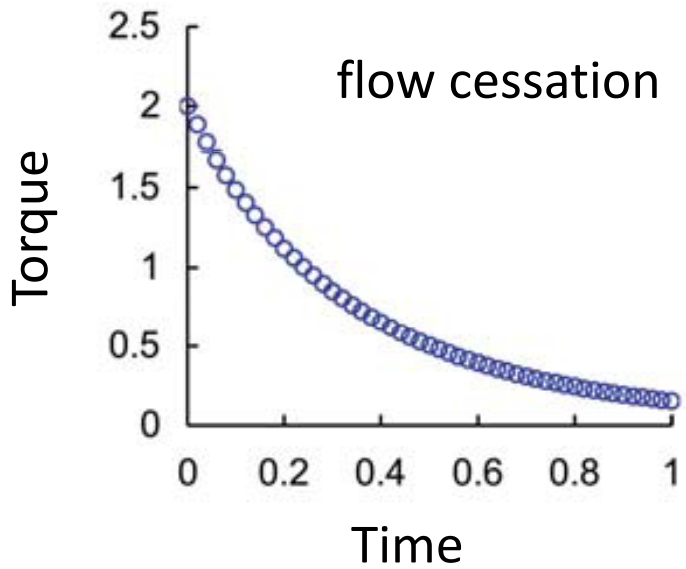
Fracture

Elastic rebound

Creep

Micro-macro relationship



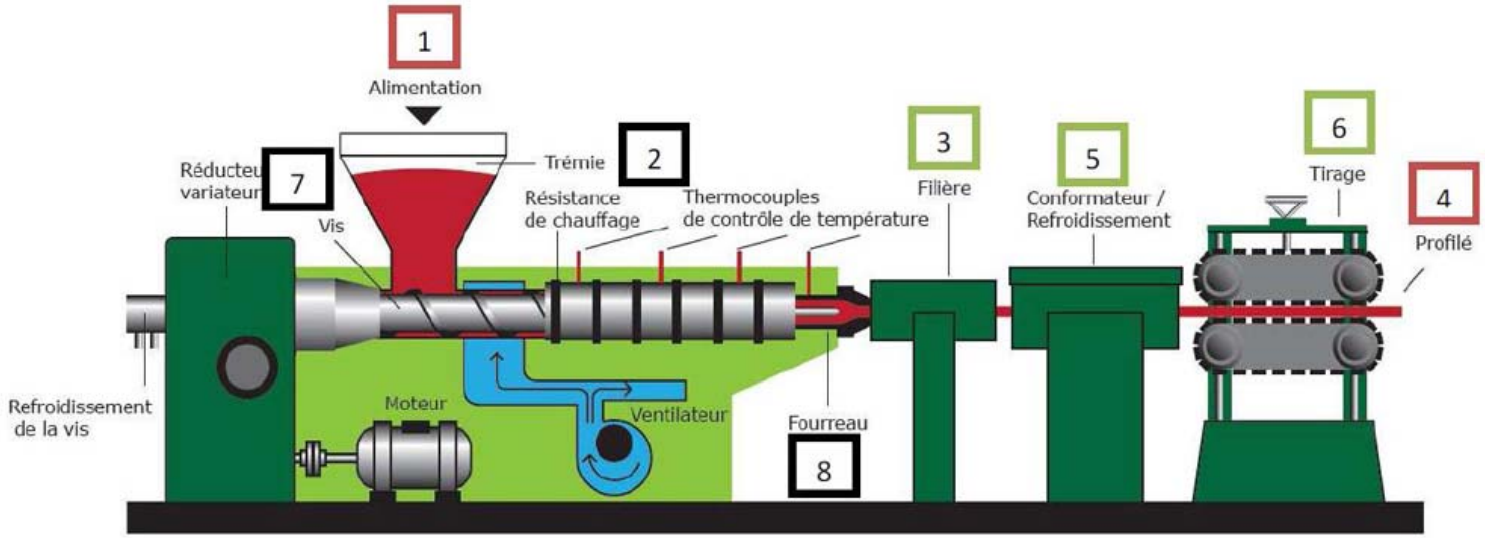


The time necessary to reach steady state is related to the characteristic time associated with local motions

Deborah number: $De = t/\tau_{mol}$

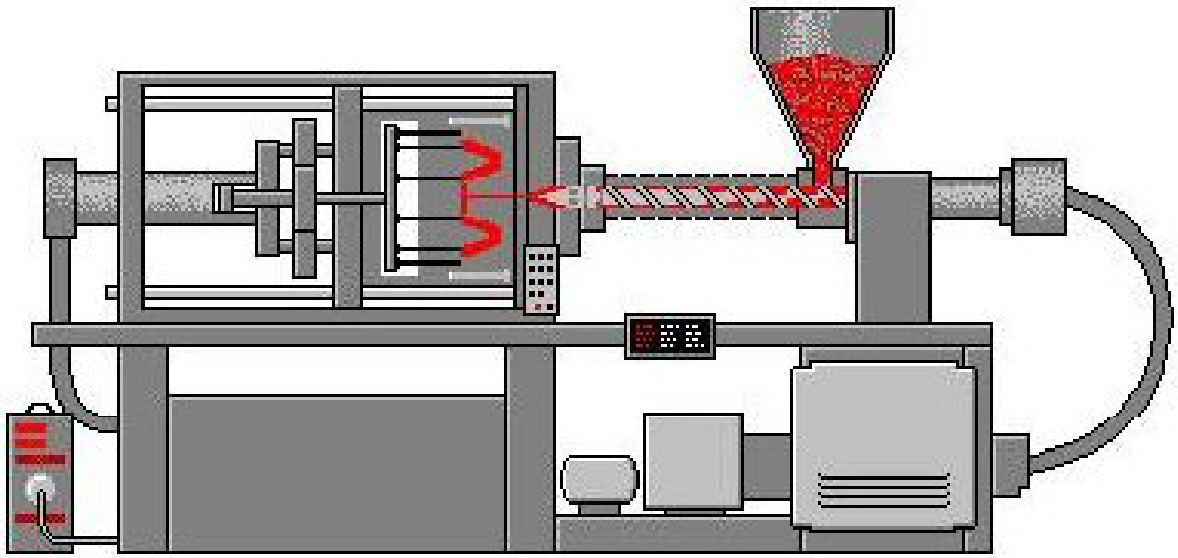
Motivation 1:
Rheological measurements probe the local dynamics of macromolecules at the local scale

Extrusion



Materials are heated, mixed, and transported by screws towards a die at the exit.

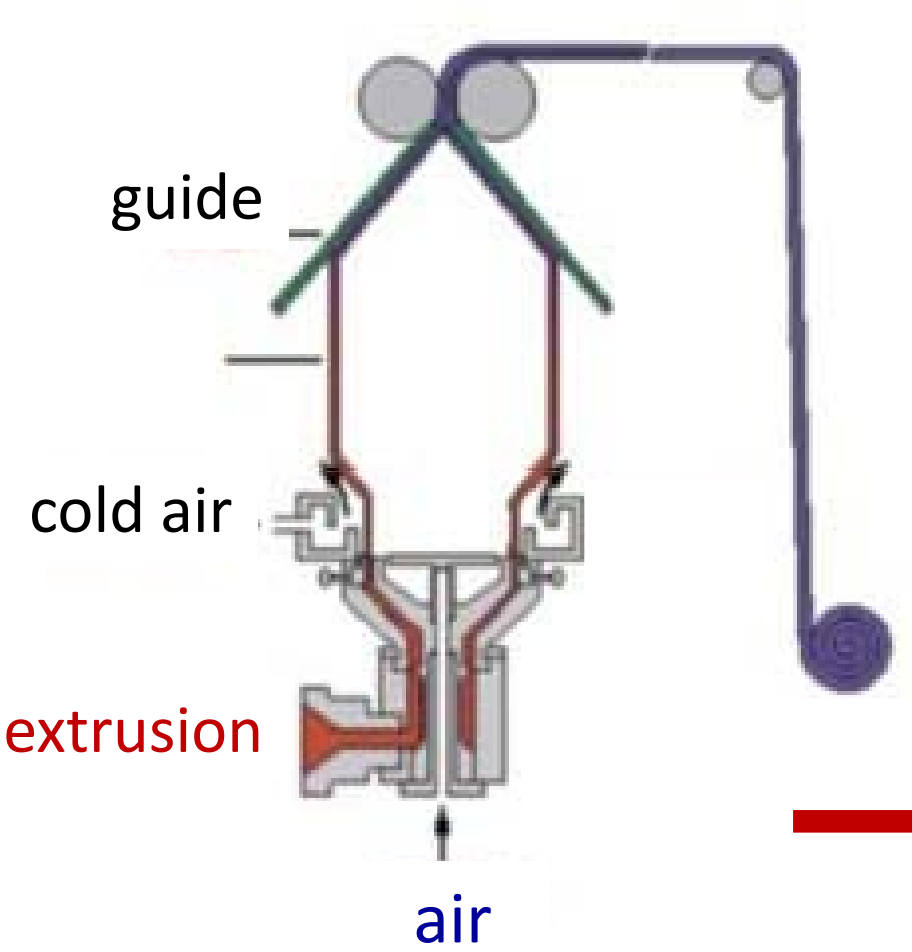
Injection-molding

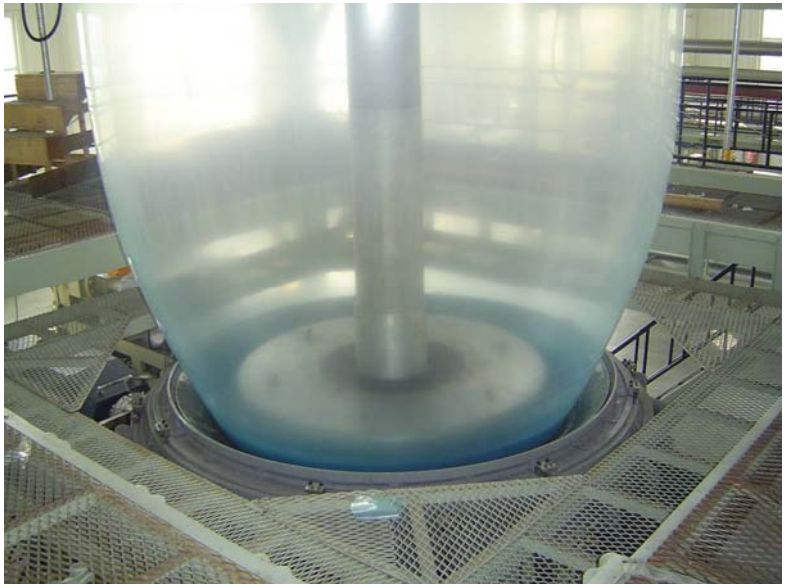


As in extrusion: (i) the materials properties (viscosity, relaxation times, normal stresses) have to be adapted to (ii) the processing conditions (cycle, flow rate, cooling rate)

Motivation 2:
The molecular design of the polymer is the key-to-success: molar mass distributions, linear or branched architecture

Extrusion-blowing of polyethylene





During blowing the film becomes thin and can break

It is possible to increase the resistance of the film to stretching by specifically designing the polymer

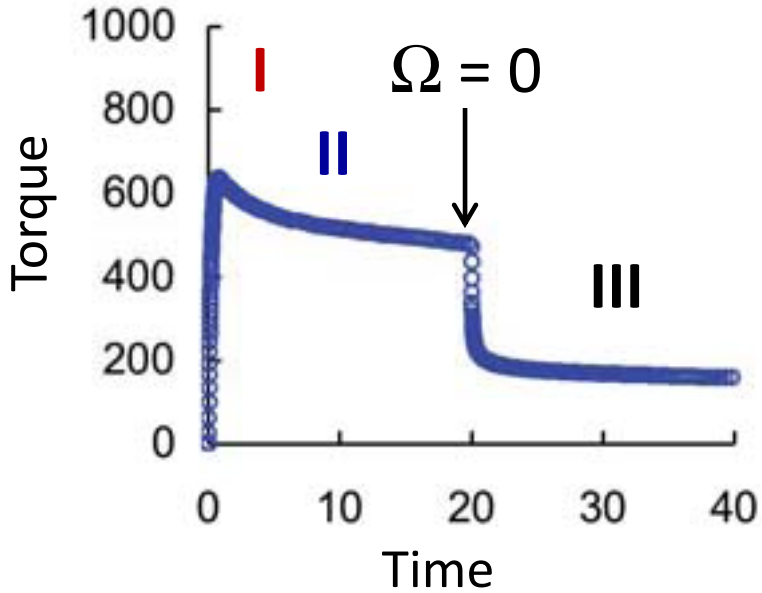
Branching

Mixtures of small and long chains

1.2 Class II: Viscoplastic dispersions

Viscoplasticity of dispersions

Toothpaste



I : weak force – no flow

II: the structure breaks

III: build-up of a new structure but a residual stress persists

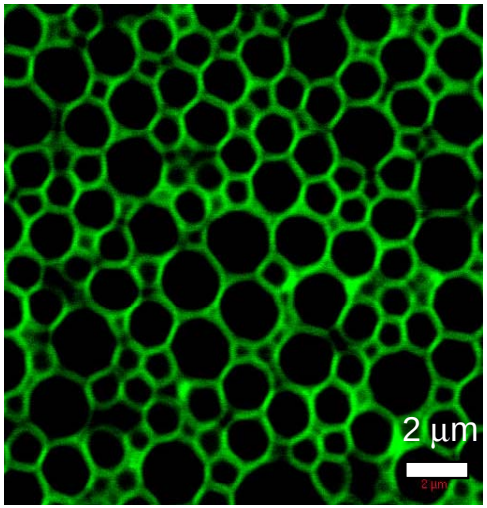
Micro-macro relationship

Colloidal glasses
Deformable particles in the jamming regime (repulsive interactions)

($\Phi > \Phi_C \sim 0.64$)

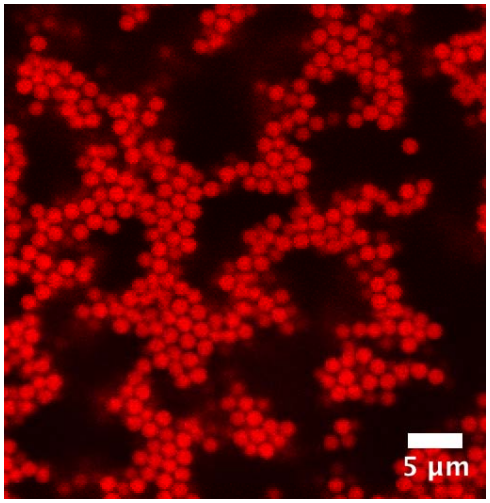
Colloidal gels
Weak attractive interactions

Confocal microscopy



Concentrated oil in water emulsion

Polystyrene spheres aggregated by depletion forces

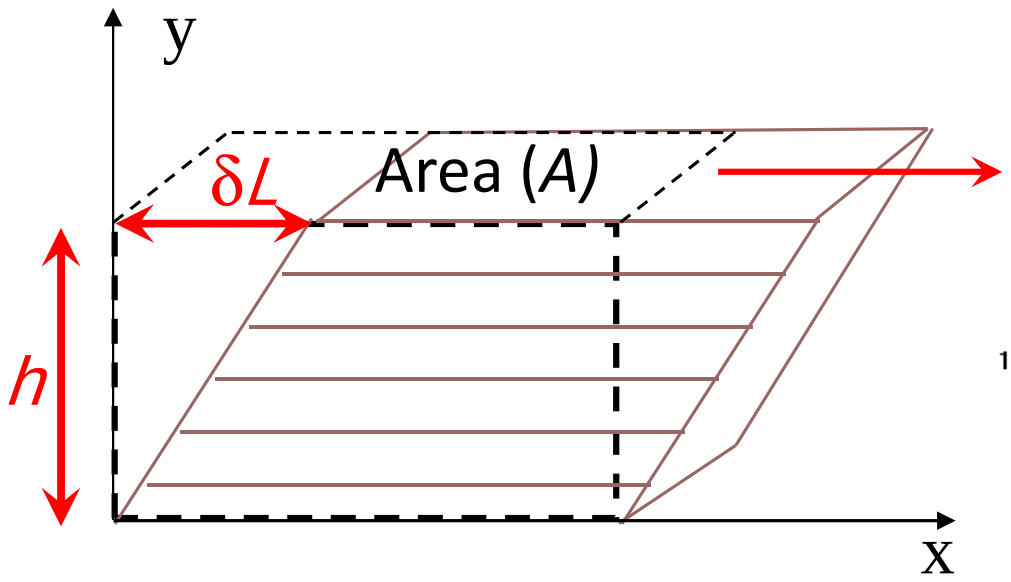


Displacements of particules beyond the yield strain

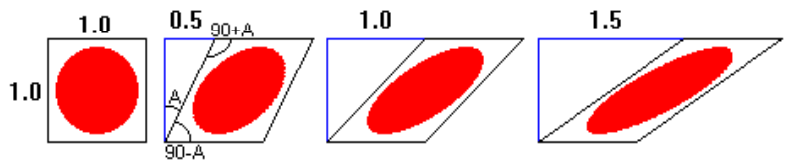
Break up of interparticles bonds

1.3 Stress and strain

Deformation in simple shear



Force (*F*), velocity (*v*)



Stress (N/m^2 = Pa) $\sigma = \frac{F}{A}$

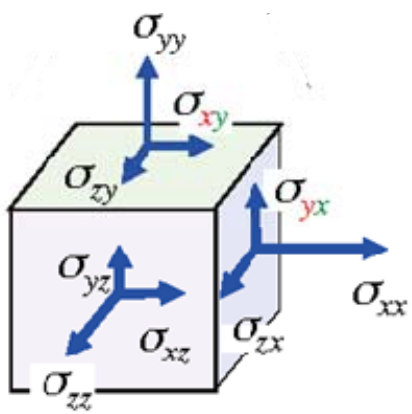
Strain $\gamma = \frac{\delta L}{h}$

Strain rate(s^{-1})
(=rate of deformation) $\dot{\gamma} = \frac{dv}{dy}$ $\dot{\gamma} = \frac{d\gamma}{dt}$

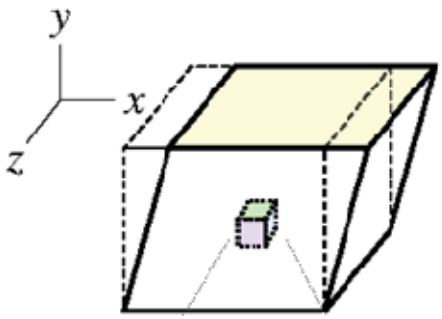
$1/\dot{\gamma}$: characteristic time imposed by the flow

Shear viscosity $\eta = \frac{\sigma}{\dot{\gamma}}$

Stress tensor



Stress tensor components



$$\underline{\sigma} = \begin{pmatrix} \sigma_{xx} & \sigma_{xy} & 0 \\ \sigma_{xy} & \sigma_{yy} & 0 \\ 0 & 0 & \sigma_{zz} \end{pmatrix}$$

Normal stress differences

$$N_1 = \sigma_{xx} - \sigma_{yy}$$

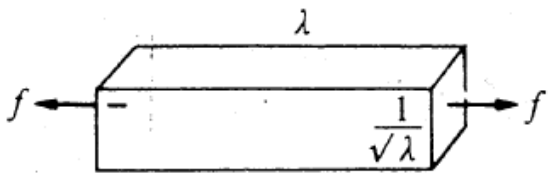
$$N_2 = \sigma_{yy} - \sigma_{zz}$$

$$\eta(\dot{\gamma}) = \frac{\sigma_{xy}}{\dot{\gamma}}$$ **viscosity**

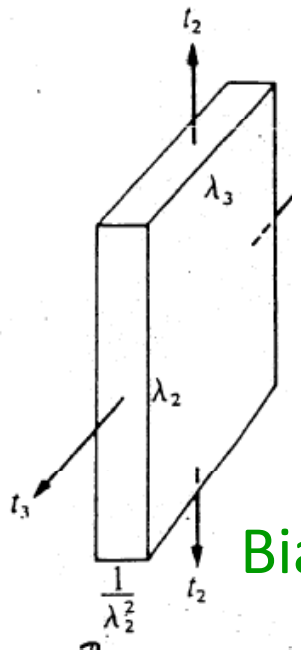
$$\Psi_1(\dot{\gamma}) = \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\gamma}^2} = \frac{N_1}{\dot{\gamma}^2} > 0$$

$$\Psi_2(\dot{\gamma}) = \frac{\sigma_{yy} - \sigma_{zz}}{\dot{\gamma}^2} = \frac{N_2}{\dot{\gamma}^2} < 0$$

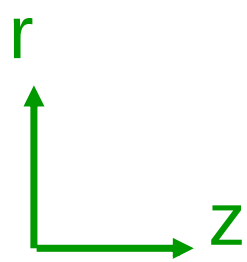
Extensional deformation



Uniaxiale



Biaxiale



Length of a liquid thread:

$\dot{\varepsilon} = dV/dz$

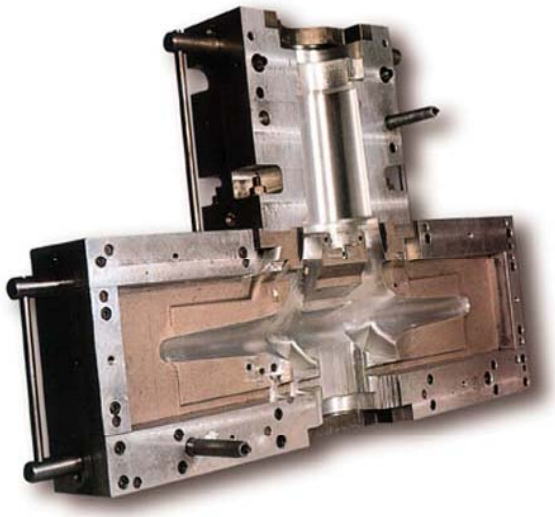
$L(t)/L(0) = \exp(\dot{\varepsilon}t)$

Very efficient!

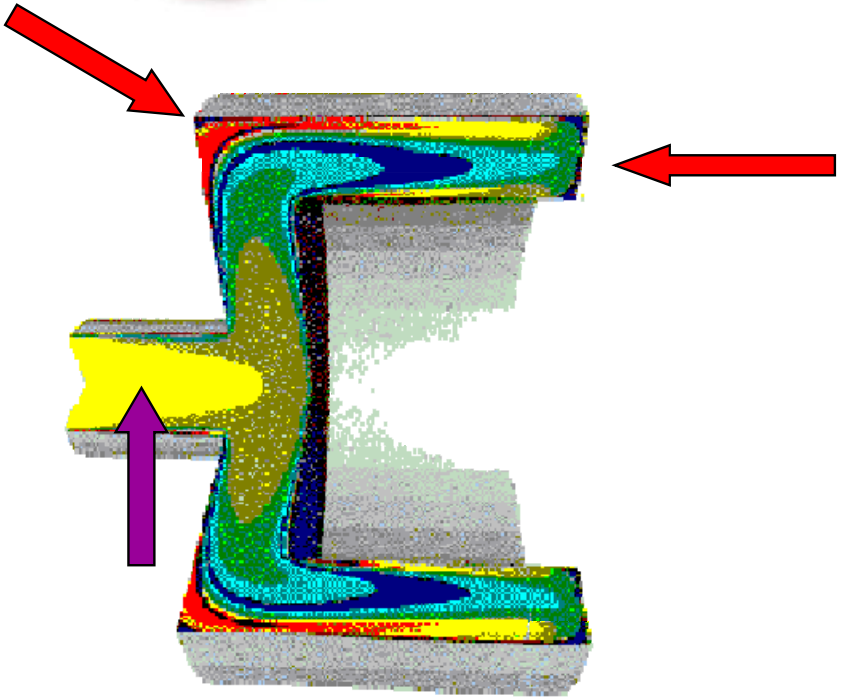
Elongational "viscosity"

$$\eta_e = \frac{\sigma_{rr} - \sigma_{zz}}{\dot{\varepsilon}}$$

Injection - molding



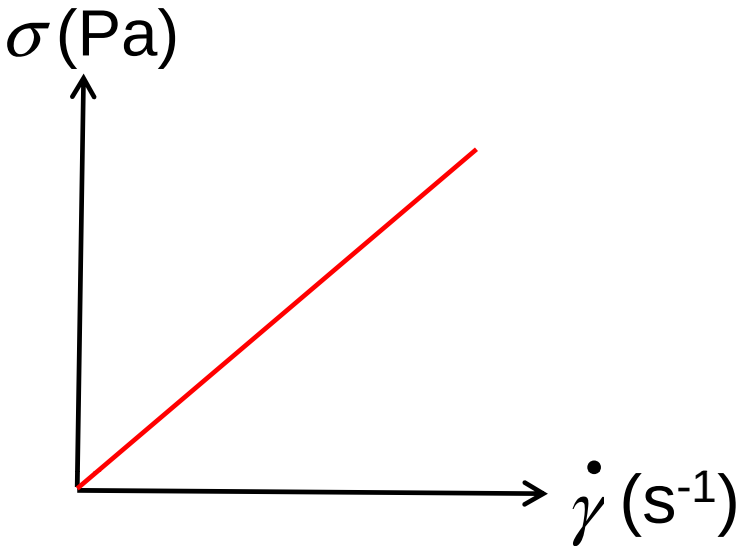
Injection consists in pushing a materials in the fluid state in a cold mold.
After solidification, the workpiece is ejected

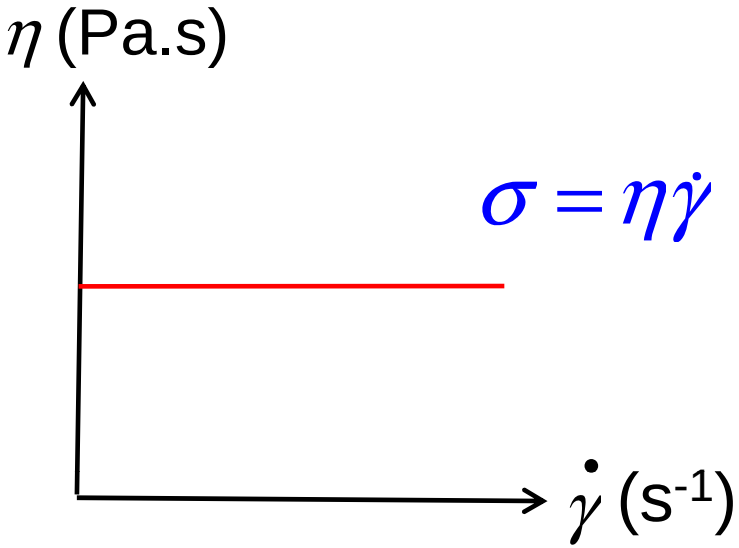


Complex flow situation involving elongation, compression, and shearing deformation

1.4 Some rheological behaviours

Newtonian liquids





Simple liquids: water, milk, oil, solutions of small molecules in solvents…

Solutions of low molar mass polymers, colloidal suspensions of small particles ….

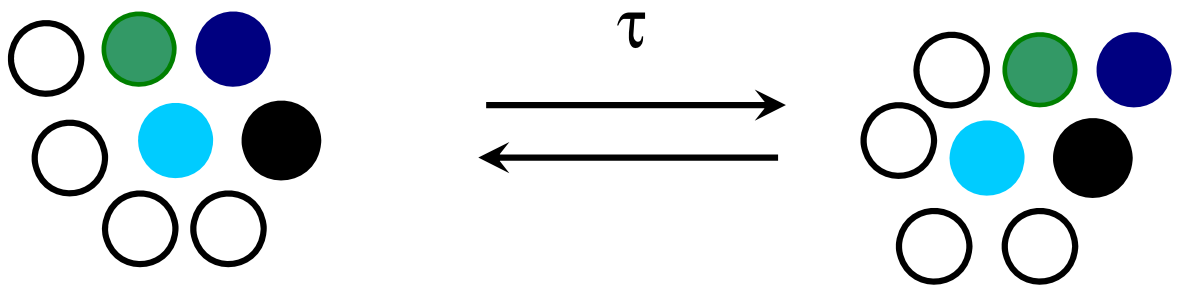
The equilibrium structure is not affected by the flow:

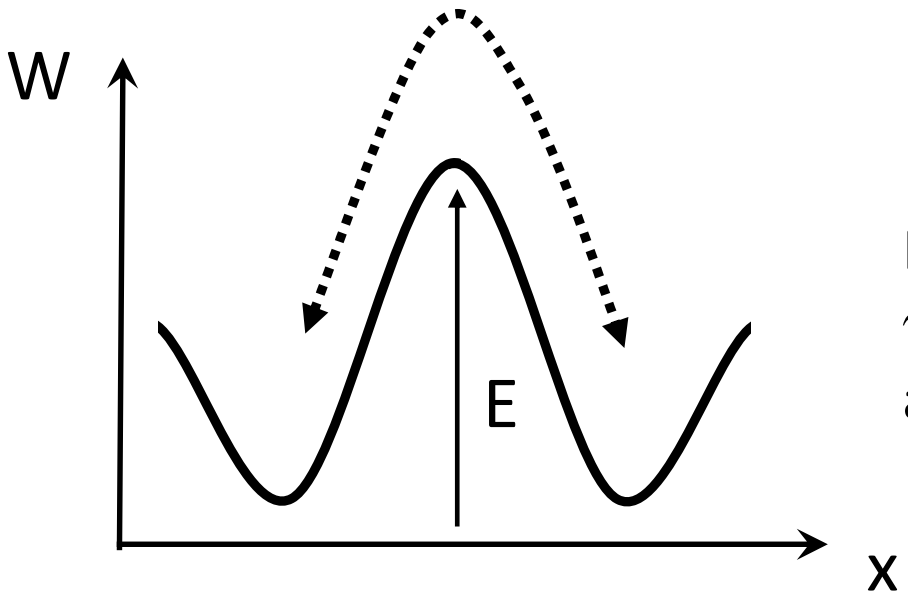
$$\mathrm{Pe} = \frac{R^2 / D_0}{1/\dot{\gamma}} = \frac{\dot{\gamma} R^2}{D_0} = \frac{6\pi\eta_S \dot{\gamma} R^3}{kT} << 1$$

Orders of magnitude

	Pa·s
Bitumen.....	10^5
Polymer melts....	10^3
Liquid honey.....	10
Glycerol...	1
Vegetable oil.....	10^{-1}
Water	10^{-3}
Acetic acid.....	10^{-4}

Activated hopping motion





Energy landscape

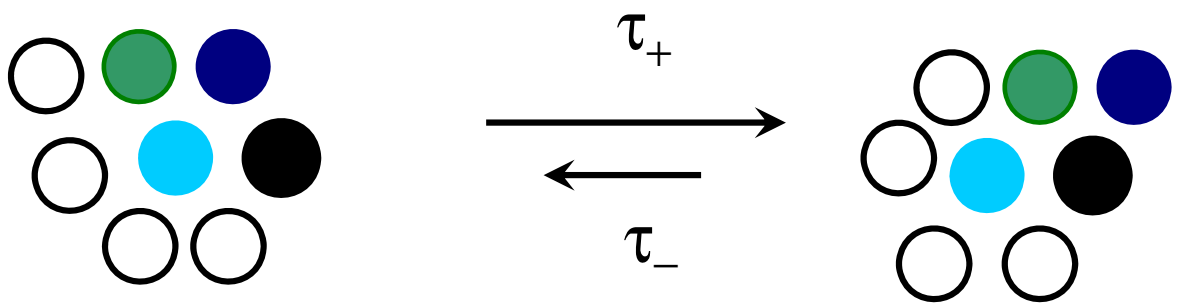
Molecules undergo thermally activated hopping motion

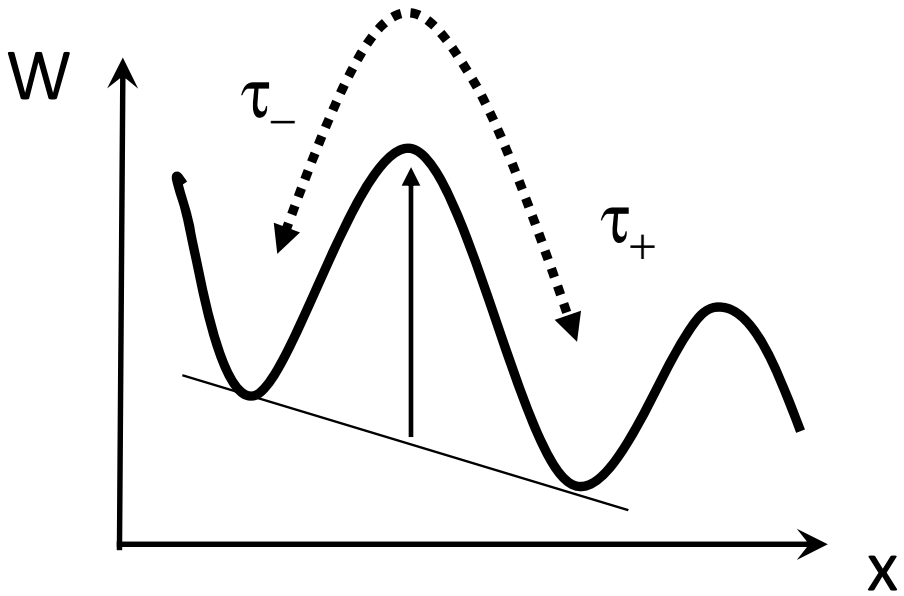
E: energy barrier for a hopping event
τ: characteristic time scale associated to a hopping event

$$\tau = \tau_0 e^{E/kT}$$

Eyring model

A stress σ is applied





Energy landscape

Energy contribution due to the mechanical stress σ: σV

(V : activation volume ≅ volume of molecules)

$$\tau_+ = \tau_0 e^{(E-\sigma V)/kT}$$

$$\tau_- = \tau_0 e^{(E+\sigma V)/kT}$$

Viscosity in the Eyring model

$$\dot{\gamma} = \frac{1}{\tau_+} - \frac{1}{\tau_-} = \frac{1}{\tau_0} e^{-E/kT}\left(e^{\sigma V/kT} - e^{-\sigma V/kT}\right)$$

$$\dot{\gamma} = \frac{1}{\tau_0} e^{-E/kT} \sinh(\sigma V/kT)$$

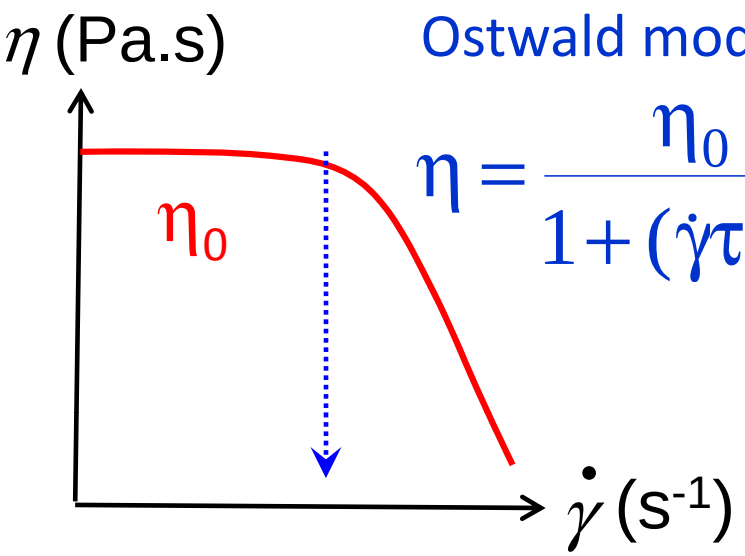
Near equilibrium: $\sigma V/kT << 1$

$$\dot{\gamma} = \frac{1}{\tau_0} e^{-E/kT} \frac{V}{kT} \sigma = \frac{\sigma}{\eta}$$

$$\eta = \left(\tau_0 e^{E/kT}\right) \frac{kT}{V} = G_0 \tau$$

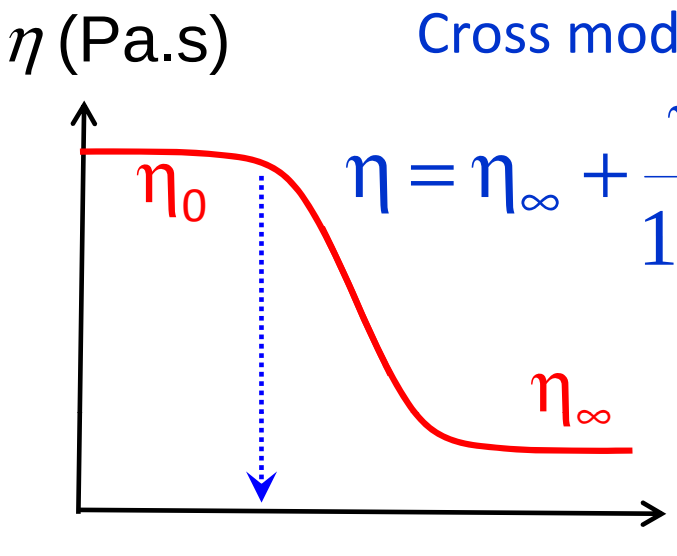
G_0=kT/V : elastic modulus; τ : relaxation time

Shear thinning behaviour



Ostwald model

$$\eta = \frac{\eta_0}{1+(\dot{\gamma}\tau_r)^n}$$



Cross model

$$\eta = \eta_\infty + \frac{\eta_0 - \eta_\infty}{1+(\dot{\gamma}\tau_r)^n}$$

$$\mathrm{Pe} = \dot{\gamma}_c \tau_r \cong 1$$

Polymer solutions and melts.

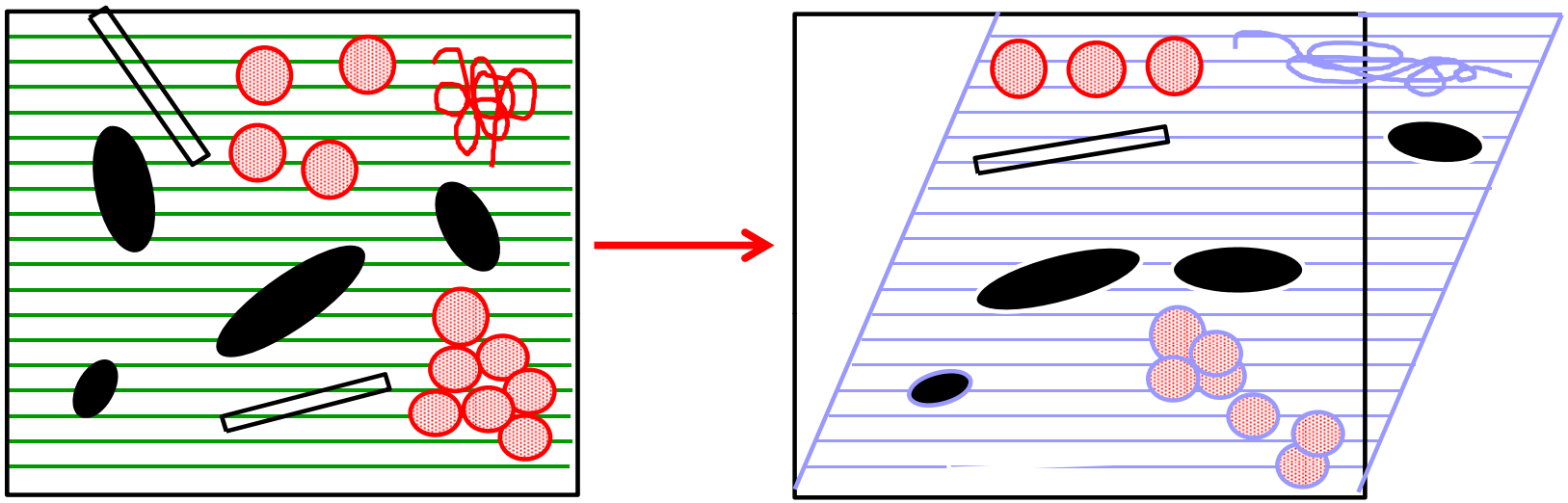
Surfactant solutions…

The equilibrium structure is distorted by the flow: non-linearities in the large deformation regime

Microscopic origin of shear-thinning

At rest

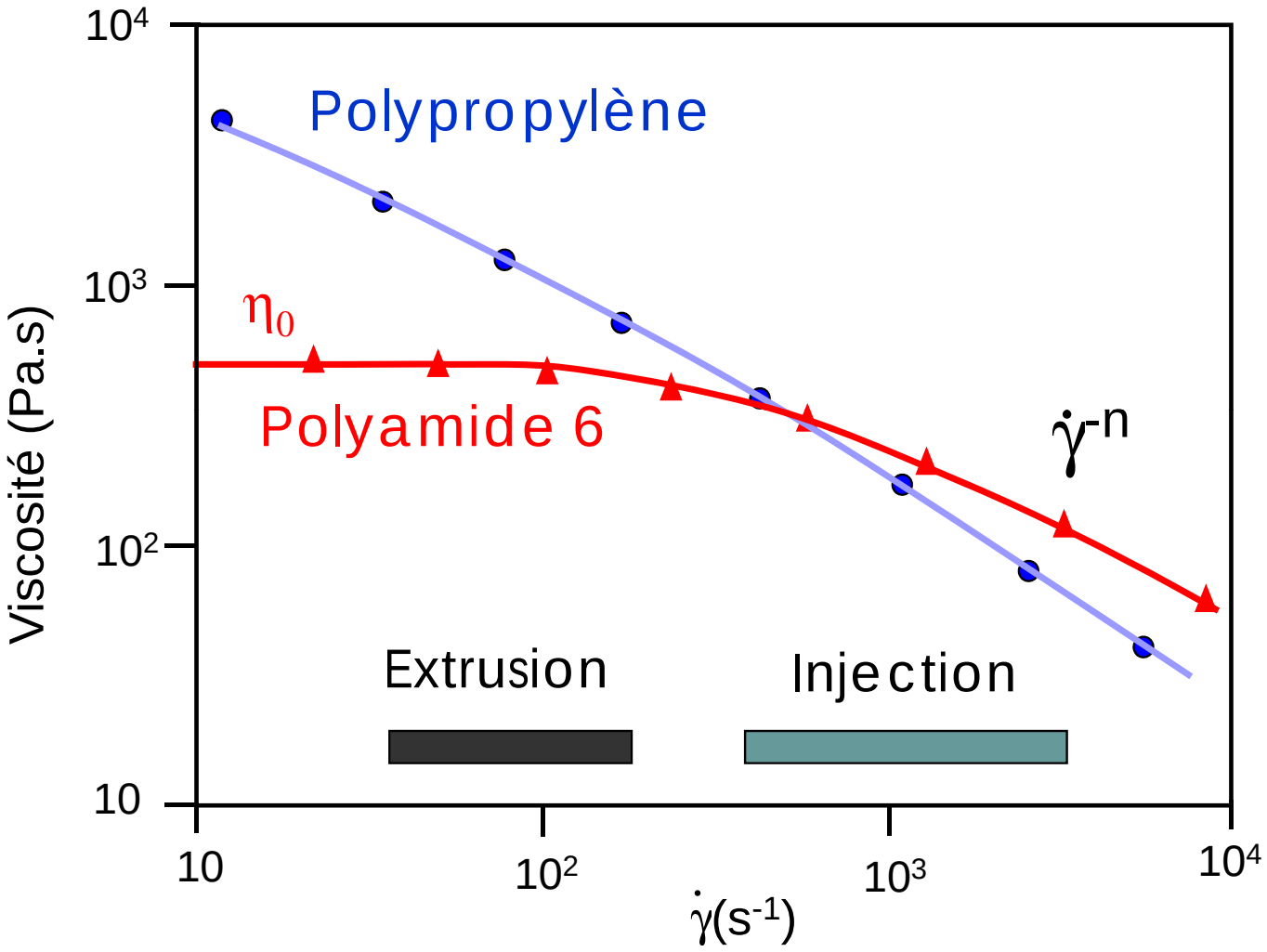
Under flow



Statistical coils (polymers):	Stretching and orientation
Agreggated suspensions:	Fracture
Colloidal particles:	Formation of chains
Anisotropic particles	Orientation

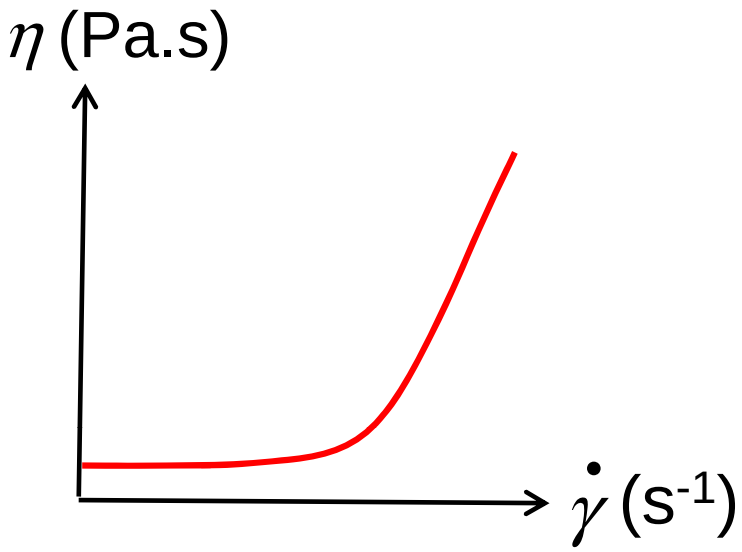
Nonlinear effect induced by a change of structure

Relevance for processing



Rheological properties have to be adapted to processing requirements

Shear-thickening

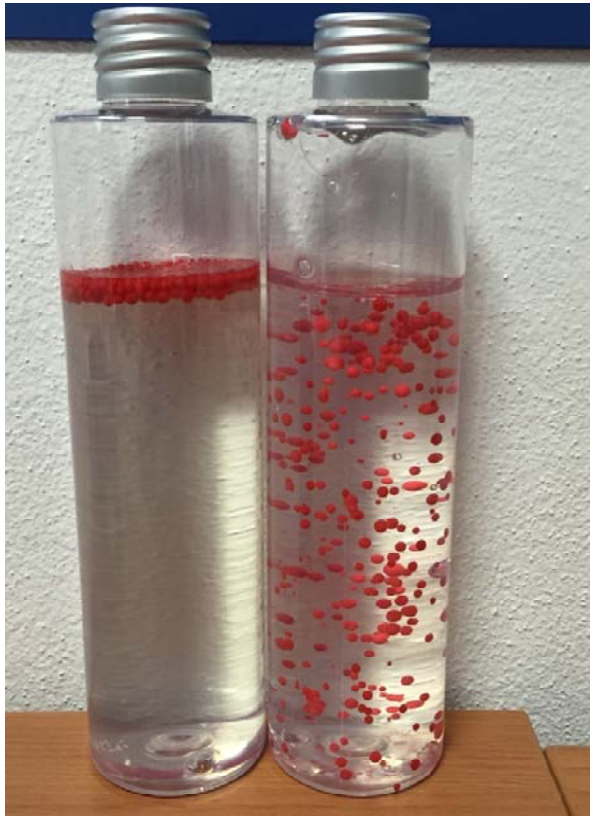


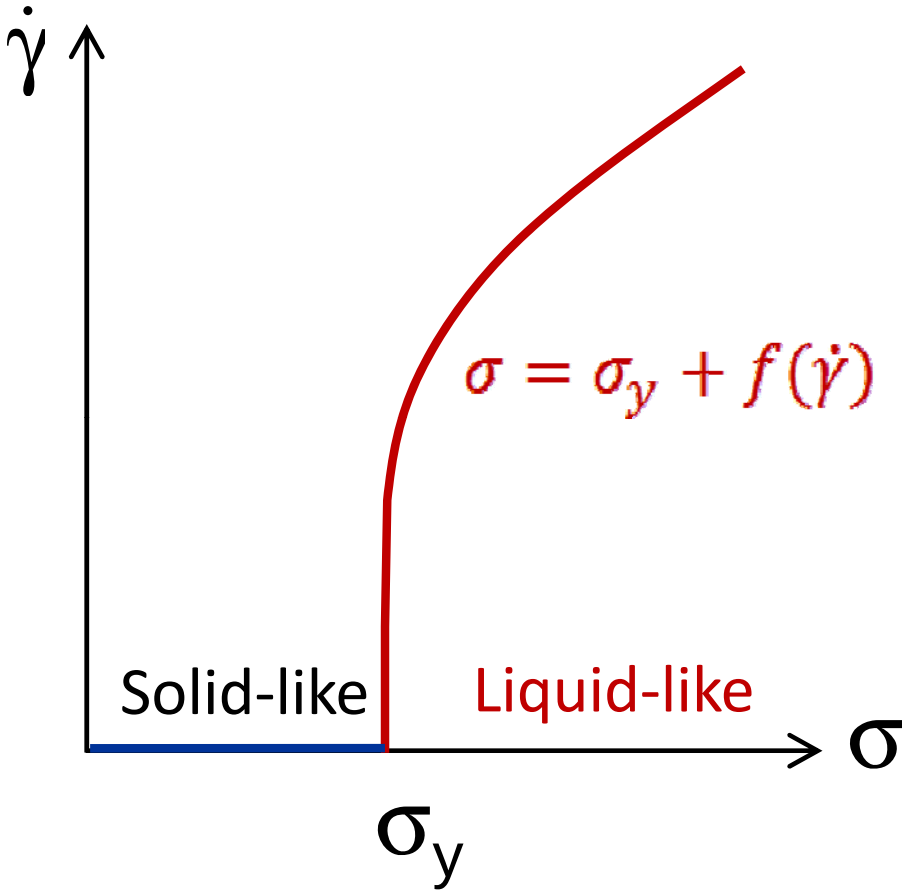
Surfactant solutions, associative polymer solutions, concentrated colloidal and granular suspensions, various food materials (starch, melted chocolate).

Various microscopic origins; poorly understood

Flow induces a connected structure which is permanent or transient

Yield stress fluids



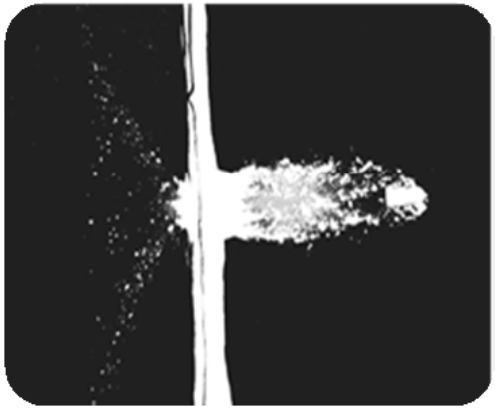


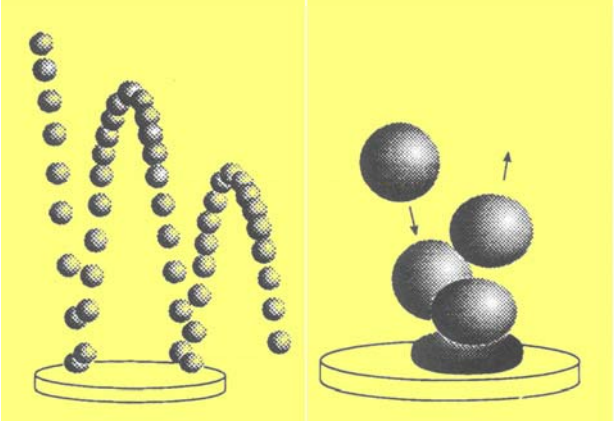
Relevant in many technologies:
Additive manufacturing
Solid inks
.....

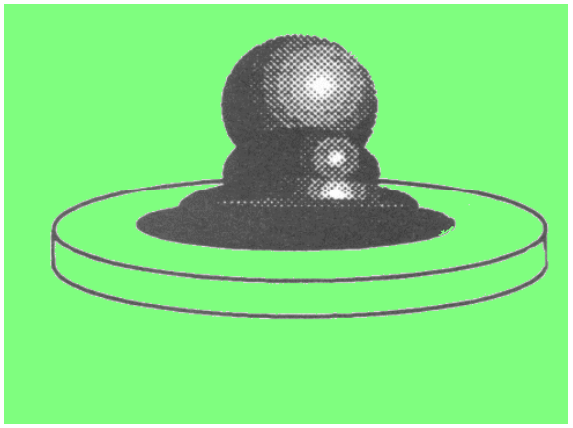
1.5 Linear viscoelasticity

Comportement macroscopique

temps







Courtesy:
MIT Edgerton Strobe laboratory

Fracture

Rebond élastique

Ecoulement

Small deformations – linear response

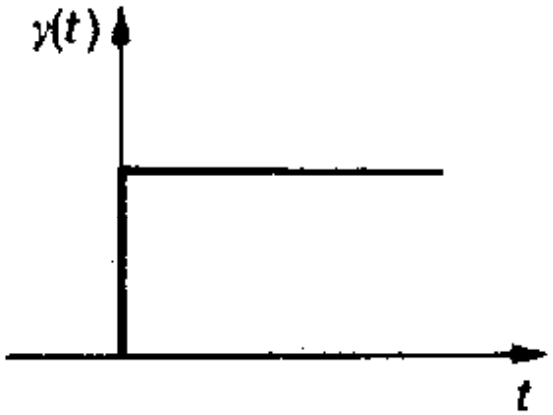
The relaxation of a material is the return to equilibrium after a solicitation. It is characterized by one or several relaxation times, which are associated to one or several structural mechanisms. Very often only the longest time is considered

The response is linear if : $\lambda\dot{\gamma} << 1$ (limit of small deformations)
This condition expresses that the structure is not affected by the solicitation

Properties of the linear response:
- Additivity of the responses due to a series of solicitations
- Scaling: the amplitude of the response is proportional to the amplitude of the excitation
- Reciprocity : excitation and response can be exchanged (controlled stress and controlled strain measurements are equivalent)

Relaxation modulus

$\gamma(t) = \gamma_0 H(t)$

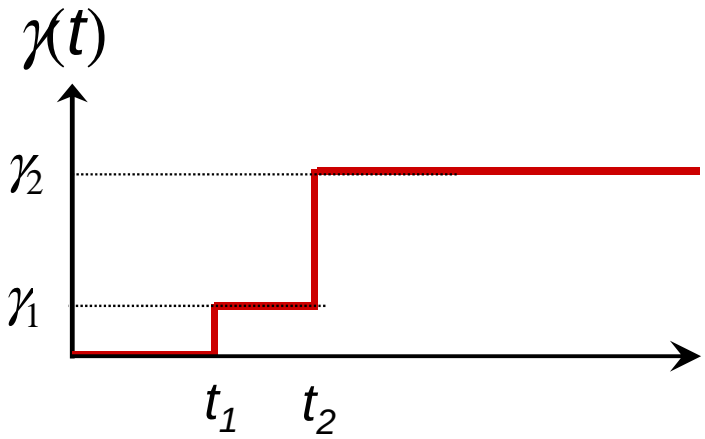


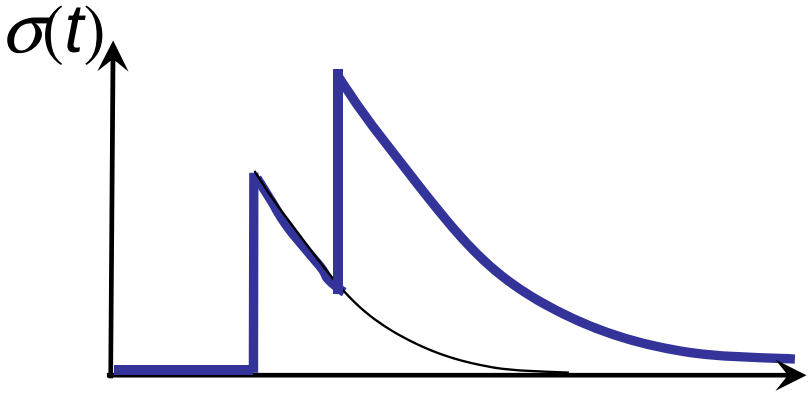
$\sigma = G(t)\gamma_0$

$G(t)$ contains the information of microscopic origin which is relative to the linear viscoelasticity

The relaxation modulus can be linear (γ_0<<1, equilibrium structure) or non linear (dynamical structure induced by large deformations)

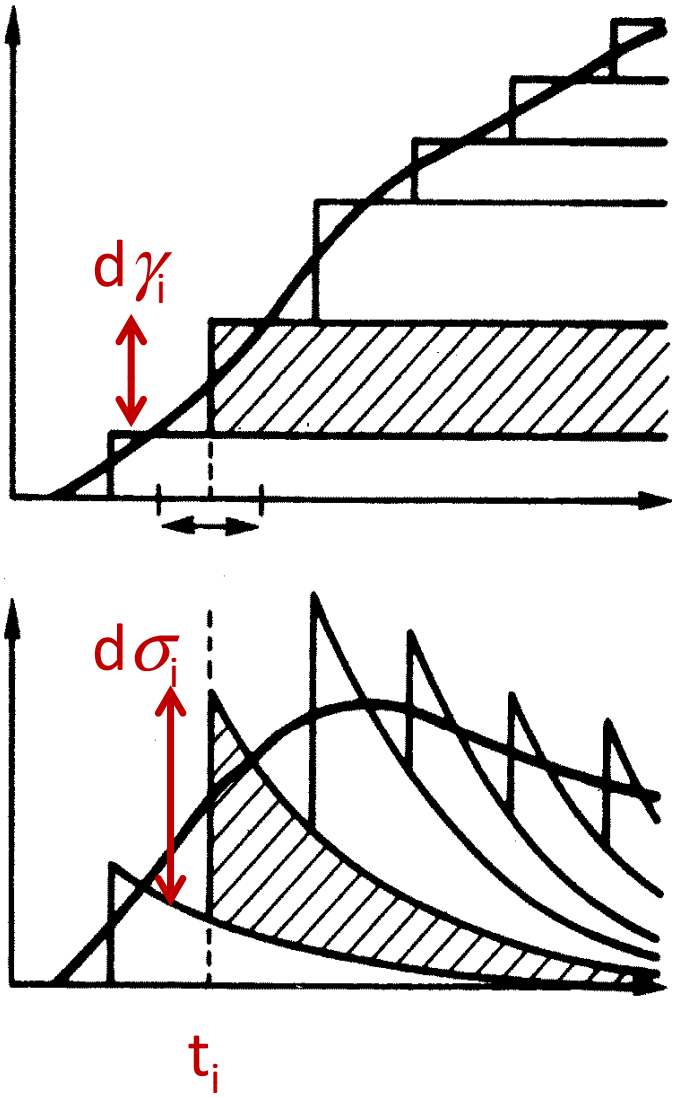
Additivity of response





$$\sigma(t) = \gamma_1 G(t-t_1)$$
$$\sigma(t) = \gamma_1 G(t-t_1) + (\gamma_2-\gamma_1) G(t-t_2)$$

Boltzmann superposition principe



$$d\sigma_i = G(t - t_i)d\gamma_i$$

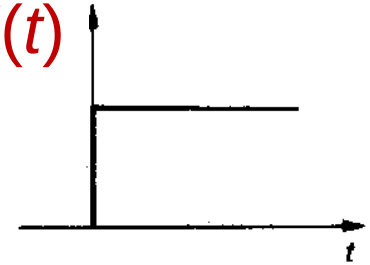
$$\sigma = \sum_{t_i<t} d\sigma_i = \sum_{t_i<t} G(t - t_i)d\gamma_i$$

$$\sigma = \int_{-\infty}^{t} G(t - t')d\gamma(t') = \int_{-\infty}^{t} G(t - t')\dot{\gamma}(t')dt'$$

Using this relation it is possible to calculate all the viscoelastic properties in the linear response regime

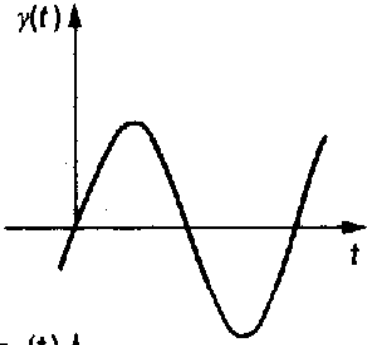
2- Time-frequency duality

$\gamma(t) = H(t)$

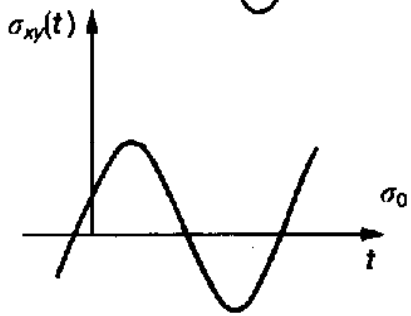


$\sigma = G(t)\gamma_0$

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



$\sigma(t)$



$\sigma = \gamma_0[G'(\omega)\cos(\omega t) + G''(\omega)\sin(\omega t)]$

$G(t)$
Relaxation function

$\longrightarrow$

G' : storage modulus
G'' : loss modulus

$$G'(\omega) \sim \omega \int_0^\infty \sin(\omega t) G(t) dt$$

Fourier transform

$$G''(\omega) \sim \omega \int_0^\infty \cos(\omega t) G(t) dt$$

Kramers – Kronig relations

$$G'(\omega) \sim \omega \int_0^\infty \sin(\omega t) G(t) dt$$

$$G''(\omega) \sim \omega \int_0^\infty \cos(\omega t) G(t) dt$$

Inverse Fourier transform:

$$G(t) \sim \frac{2}{\pi} \int_0^\infty G'(\omega) \frac{\sin(\omega t)}{\omega} d\omega$$

$$G(t) \sim \frac{2}{\pi} \int_0^\infty G''(\omega) \frac{\cos(\omega t)}{\omega} d\omega$$

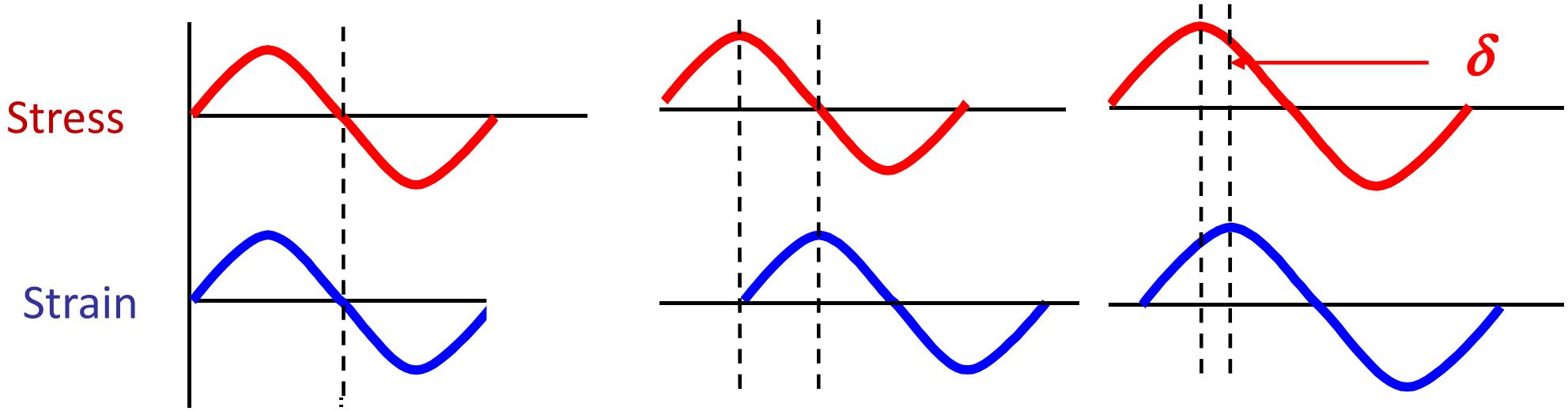
G’(ω) and G’’(ω) are related

(see electromagnetism textbooks)

Causality principle

Viscoelastic response

Elastic | Viscous | Viscoelastic



$\delta = 0°$

$\delta = 90°$

$0° < \delta < 90°$

$$G'(\omega) = \frac{\sigma_o \cos\delta}{\gamma_0}$$

$$G''(\omega) = \frac{\sigma_o \sin\delta}{\gamma_0}$$

Storage modulus
G'

Loss modulus
G''

Complex notation

The complex modulus

Characterizes the total resistance of a material to deformation

$$G^* = G' + iG''$$

$$|G^*| = (G'^2 + G''^2)^{1/2}$$

Complex viscosity

$$\eta^* = \eta' - i\eta''$$

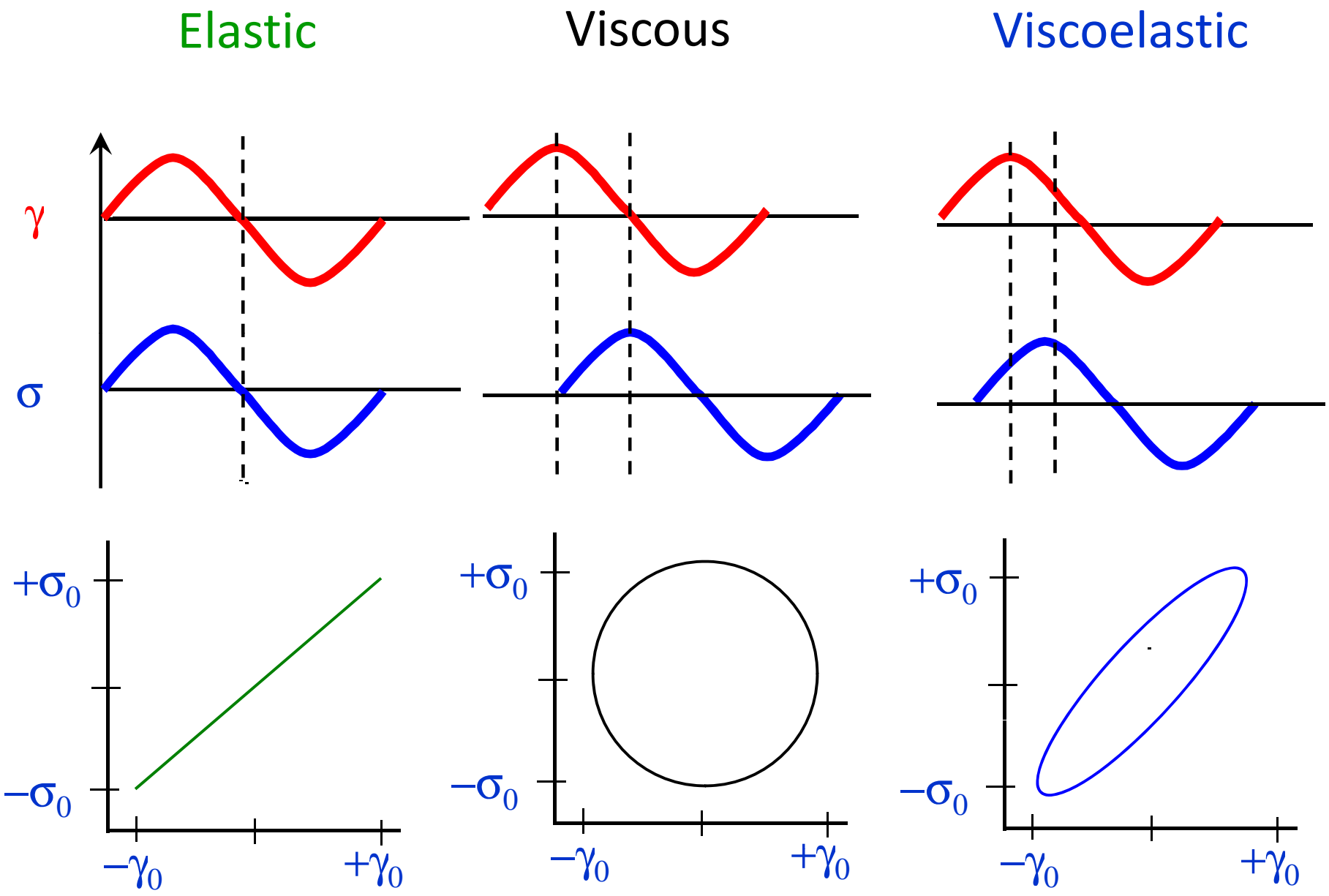
or

$$\eta^* = G^*/\omega$$

$$\left|\eta^*(\omega)\right| = \frac{(G'^2 + G''^2)^{1/2}}{\omega}$$

$\eta(\dot{\gamma})$ et $\left|\eta^*(\omega)\right|$ Are sometimes equal (Cox-Merz empirical principle)

Lissajous–Bowditch representation



The Maxwell model

This phenomenological model incorporates several important notions: *relaxation time, elastic and dissipative components*…
It provides a simple model for the final relaxation of many materials and is obeyed by some real systems

Elastic material: $\sigma(t) = G_0 \gamma(t)$

Newtonian liquid (constant viscosity) $\sigma(t) = \eta_0 \dot{\gamma}(t)$

Maxwell equation (1867):

$$\sigma(t) + \frac{\eta_0}{G_0}\frac{d\sigma(t)}{dt} = \eta_0 \dot{\gamma}(t)$$

$\lambda = \eta_0/G_0$ is the unique relaxation time

For $t > \lambda$: Newtonian liquid
For $t < \lambda$: elastic solid (Hooke)

Maxwell relaxation modulus

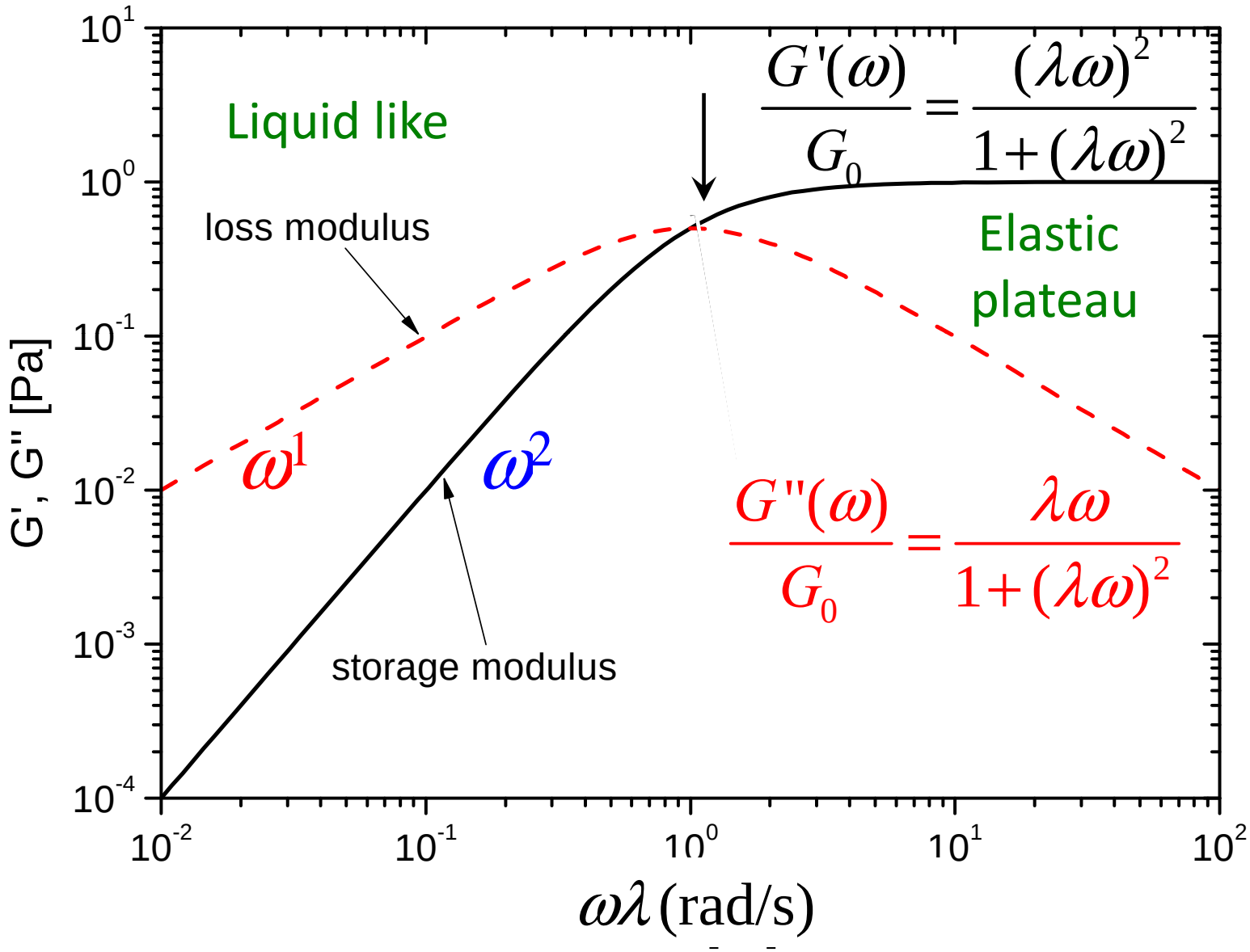
$$\sigma(t) = \int_{-\infty}^{t} \underbrace{\frac{\eta_0}{\lambda} \exp\left[-\frac{(t-t')}{\lambda}\right]}_{G(t\text{-}t')} \dot{\gamma}(t')dt'$$

The relaxation modulus in the Maxwell model is an exponential with a single relaxation time

Generalized Maxwell model: $$G(t) = \sum_{k=1}^{N} g_k \exp\left(\frac{-t}{\lambda_k}\right)$$

Physical interpretation of the relaxation time?

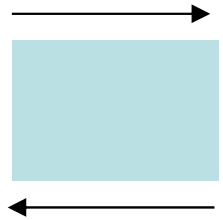
Loss and storage moduli



1.6 Other sollications (in the linear regime)

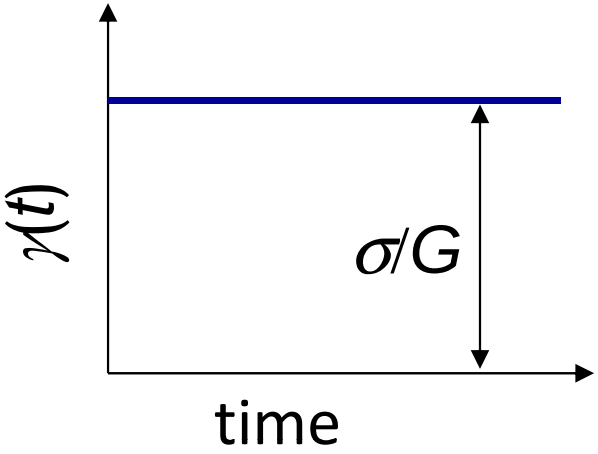
3-Creep

A stress σ is applied at $t = 0$:
What is the time response?

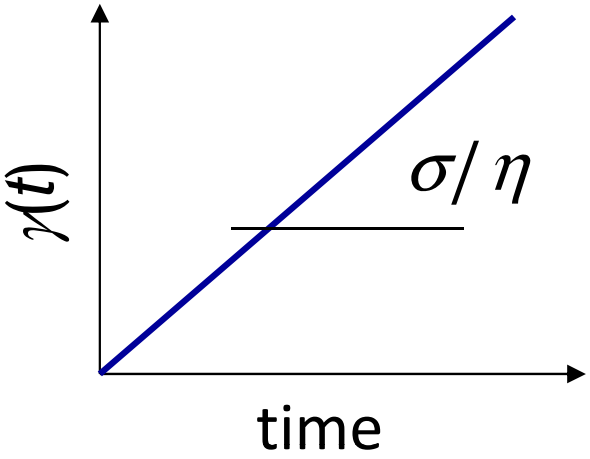


Creep measurements at controlled stress

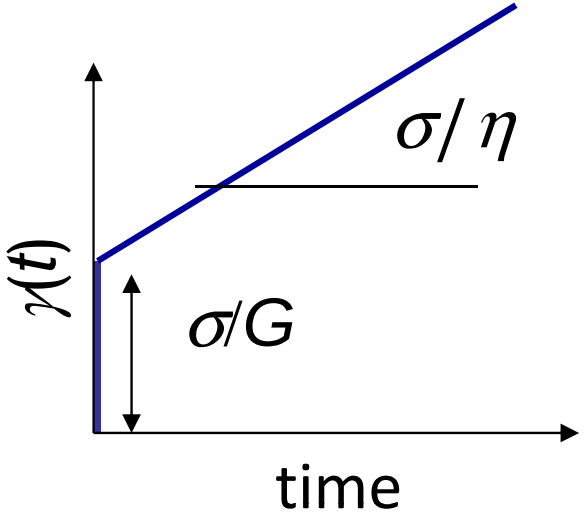
Elastic solid



Viscous liquid



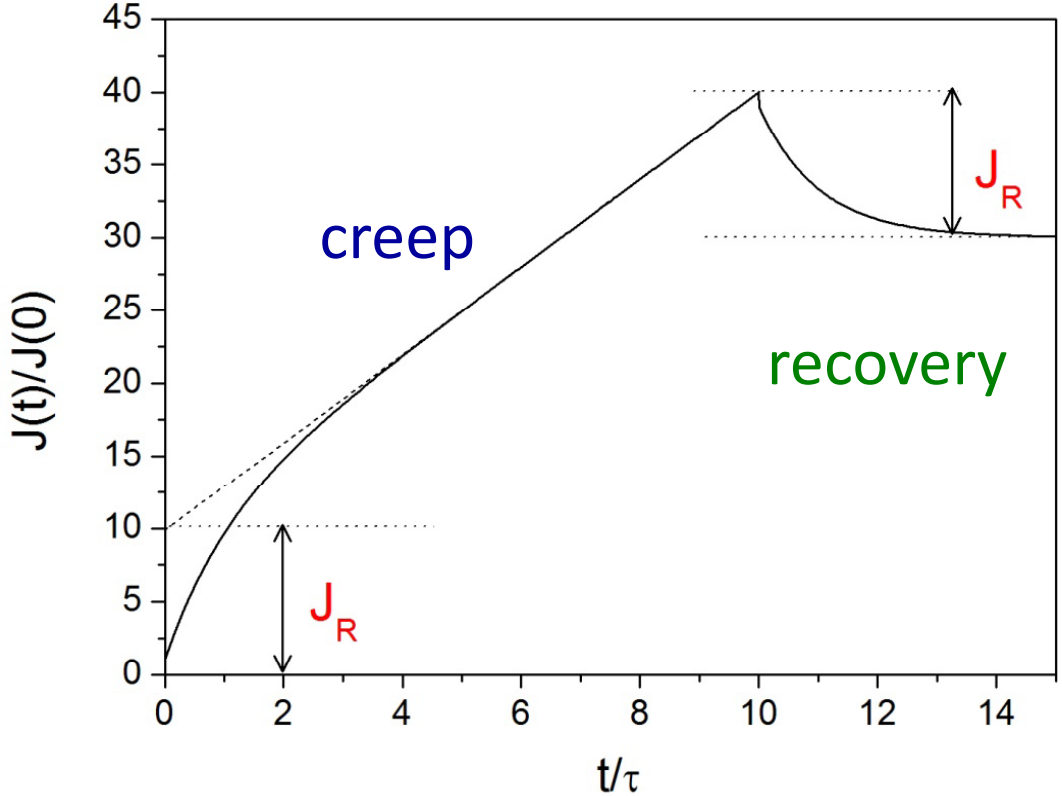
Viscoelastic material



Creep - recovery

$J(t) = \gamma(t)/\sigma$:
Creep compliance

J_R : recoverable compliance
$J(0)$: instantaneous compliance
$J(0) \propto 1/G_\infty$ where:
G_∞ : high frequency modulus

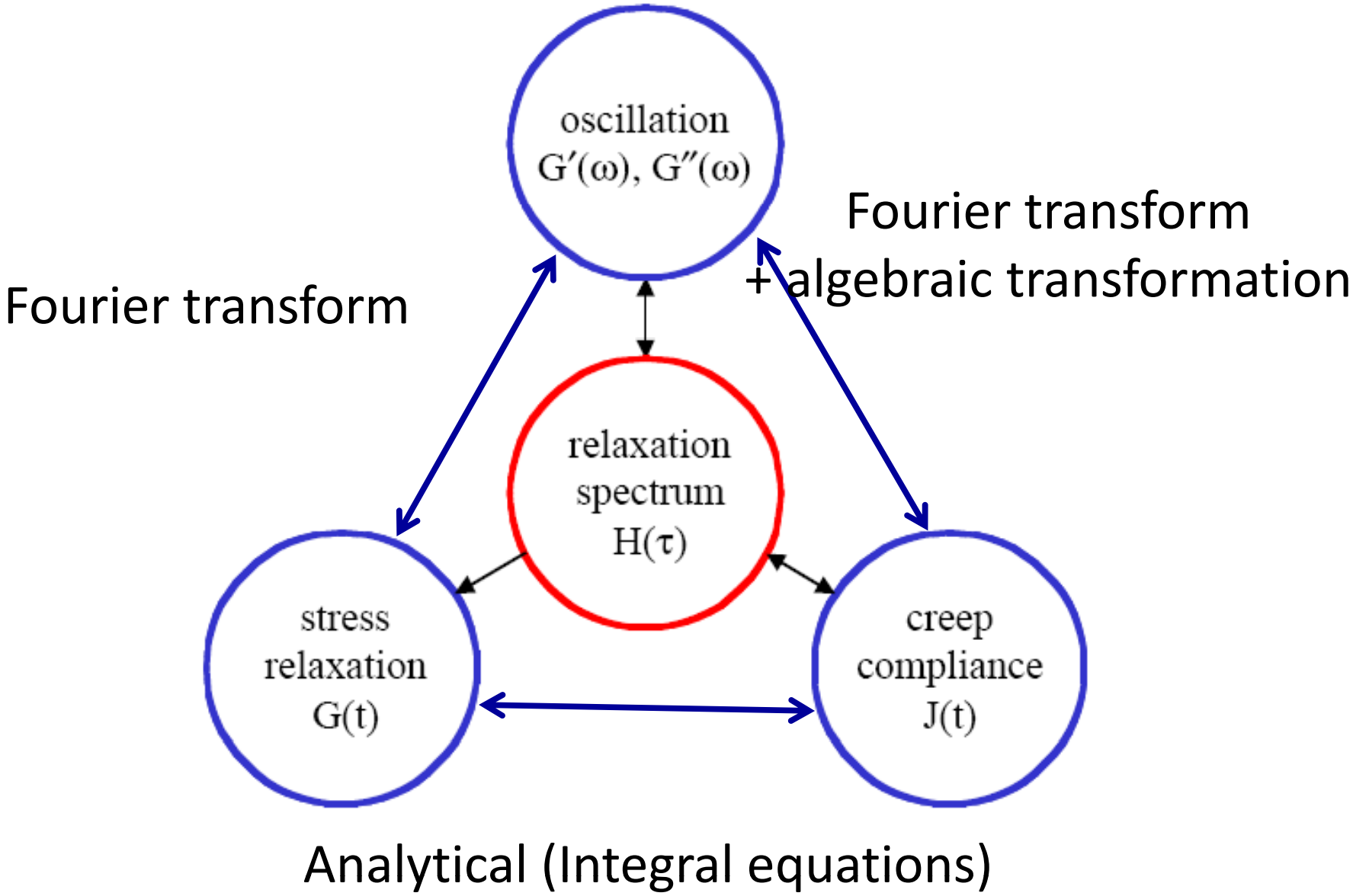


J(*t*) contains the microscopic information relative to the linear viscoelasticity

Single relaxation time model:

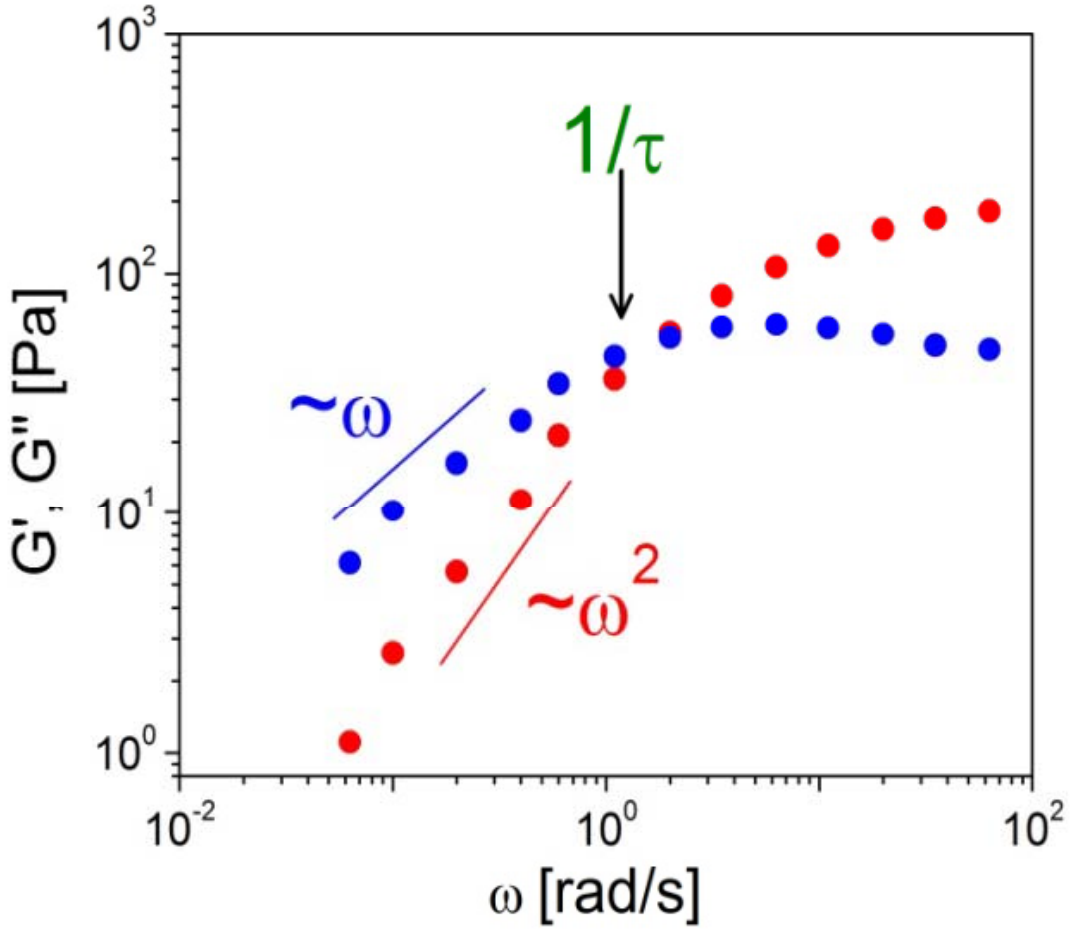
$$J(t) = J(0) + (J_R - J(0))\exp\left(-\frac{t}{\tau}\right) + \frac{t}{\eta}$$

Relations (linear regime)



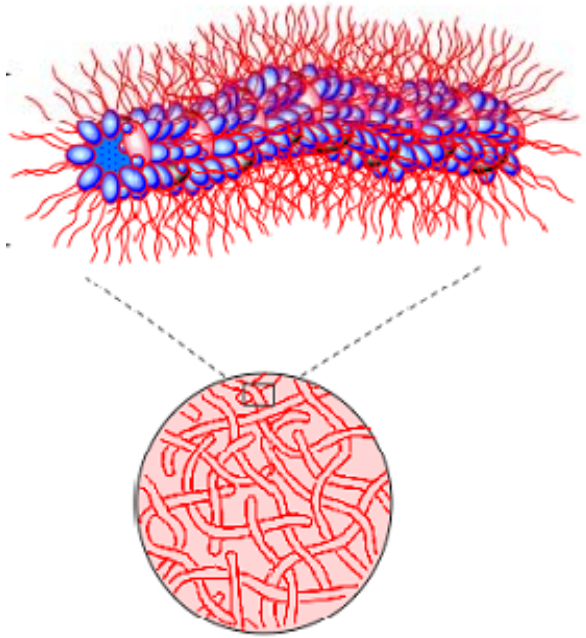
1.7 Examples of viscoelastic materials

Entangled polymer solutions



Wormlike micelles

$\overline{L} \sim 1\mu m$, $d \sim 20$ Å



Entangled wormlike micelles

<u>Recombination:</u>
Reduction of the energy associated with the extremities

<u>Break up</u>
Entropy increases

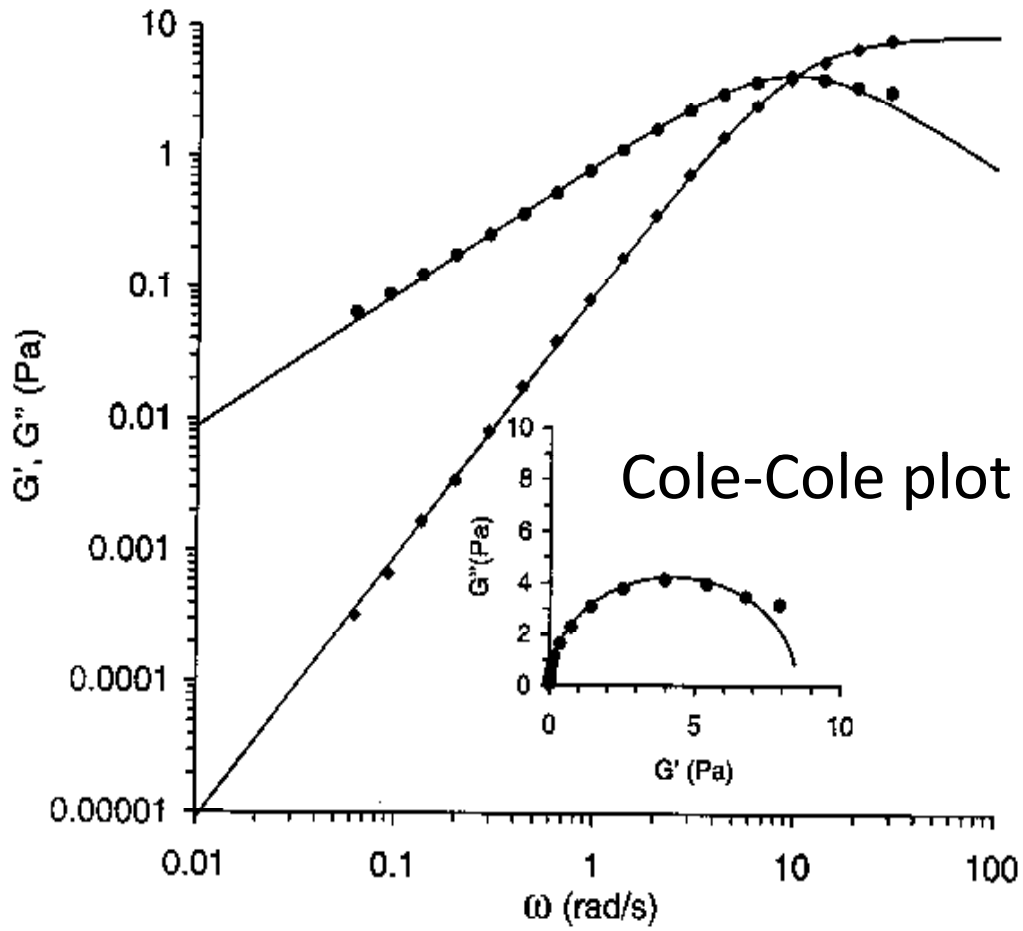
Living polymers
Very broad distribution of lengths

Wormlike micelles: a Maxwell fluid

Reptation: τ_e
Break up - recombination: τ_b

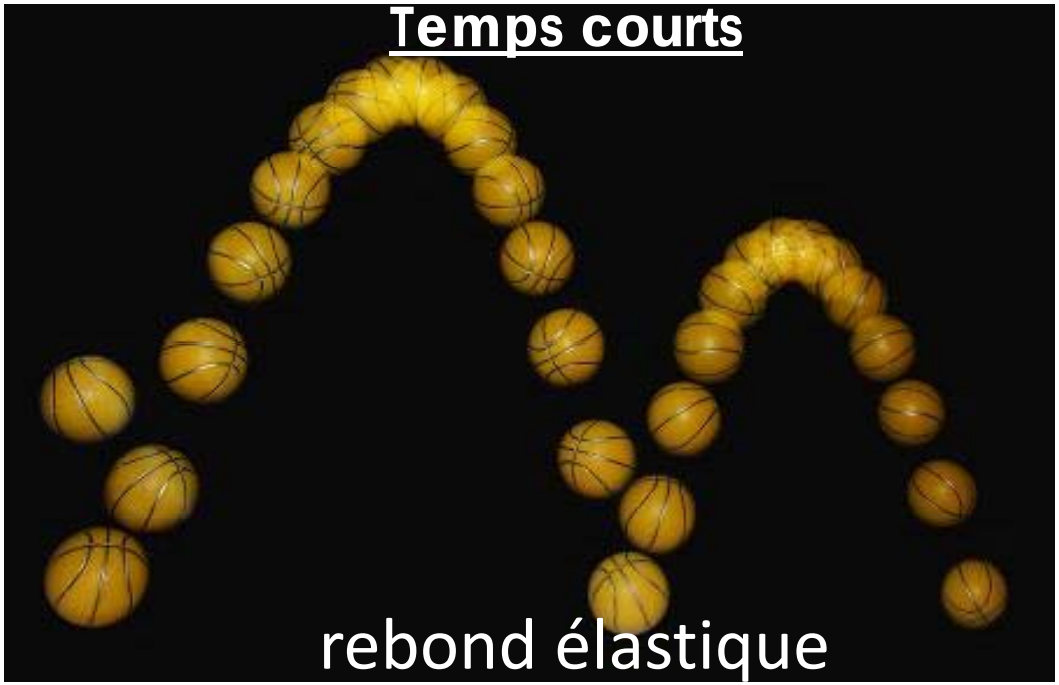
A single characteristic time

$$\tau_0 = \sqrt{\tau_r \tau_b}$$



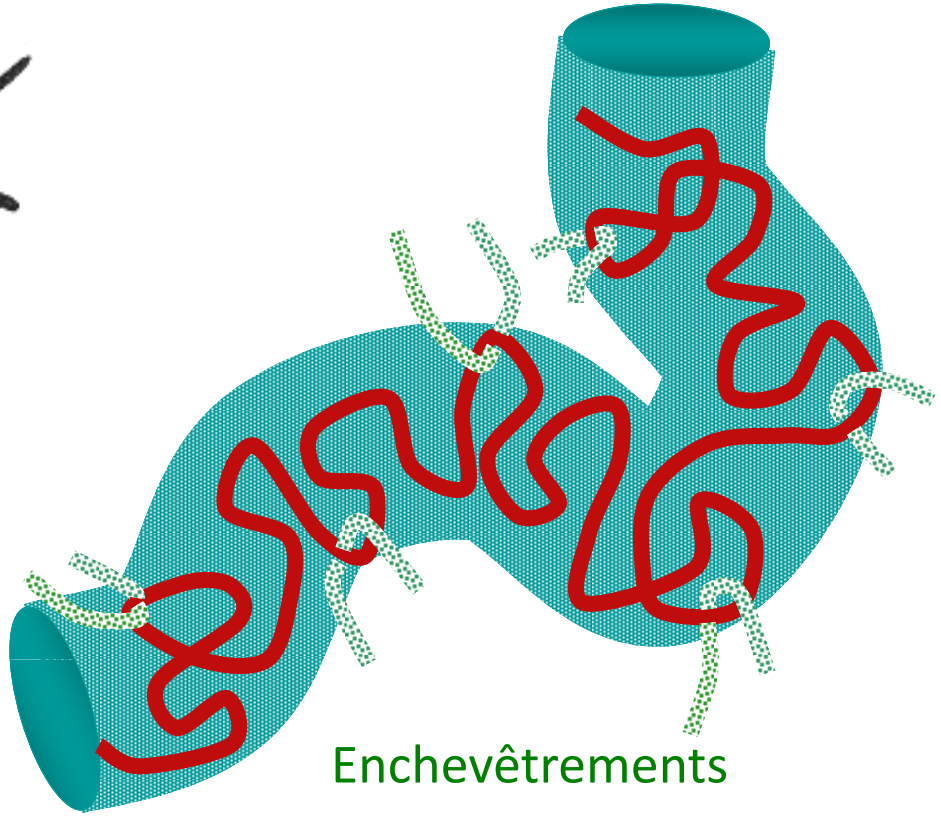
Elastic and gel-like solution that flows
Maxwell fluid
Applications : shampoo

Behaviour of polymer melts



Entangled polymer melts

M_e, (N_e): molar mass (number of statistical units) between two entanglements



τ_0: relaxation of statistical units

τ_e: relaxation of segments between entanglements

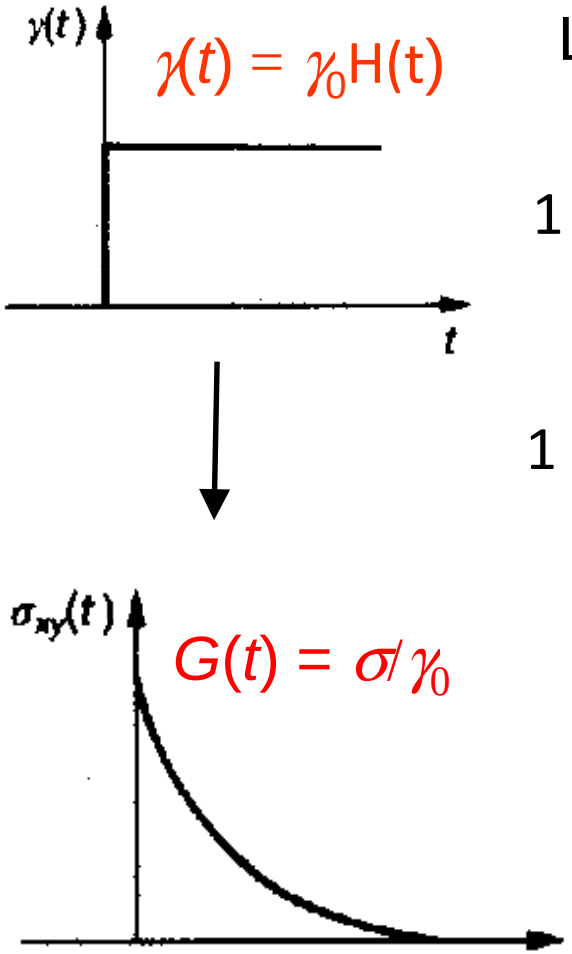
τ_d: relaxation of chains through reptation

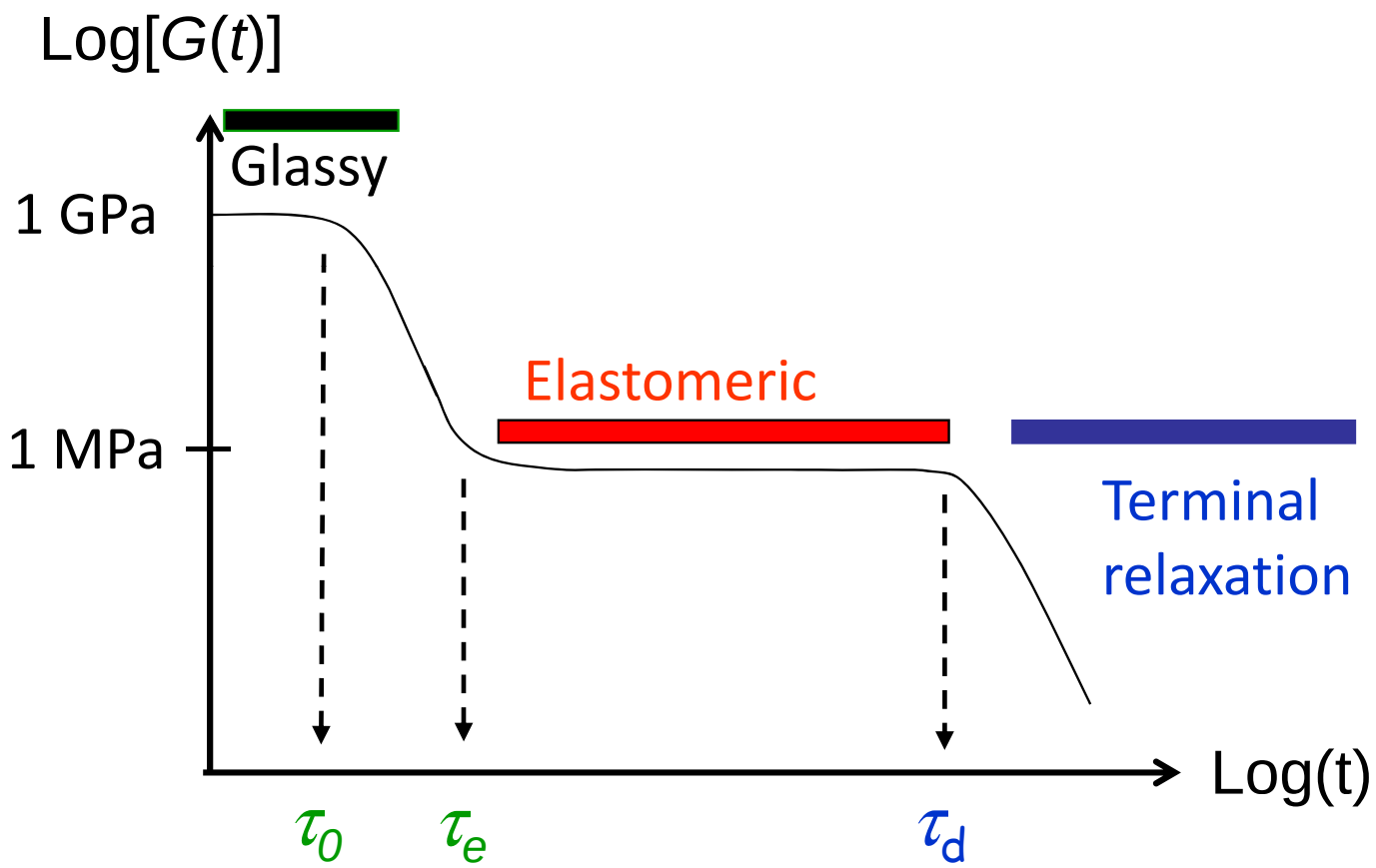
$\tau_0 \cong 10^{-10}$ s; $\tau_e \cong 0.01$ s; $\tau_d \cong 1\text{-}10$ s;

Doi & Edwards (1967), de Gennes (1971)

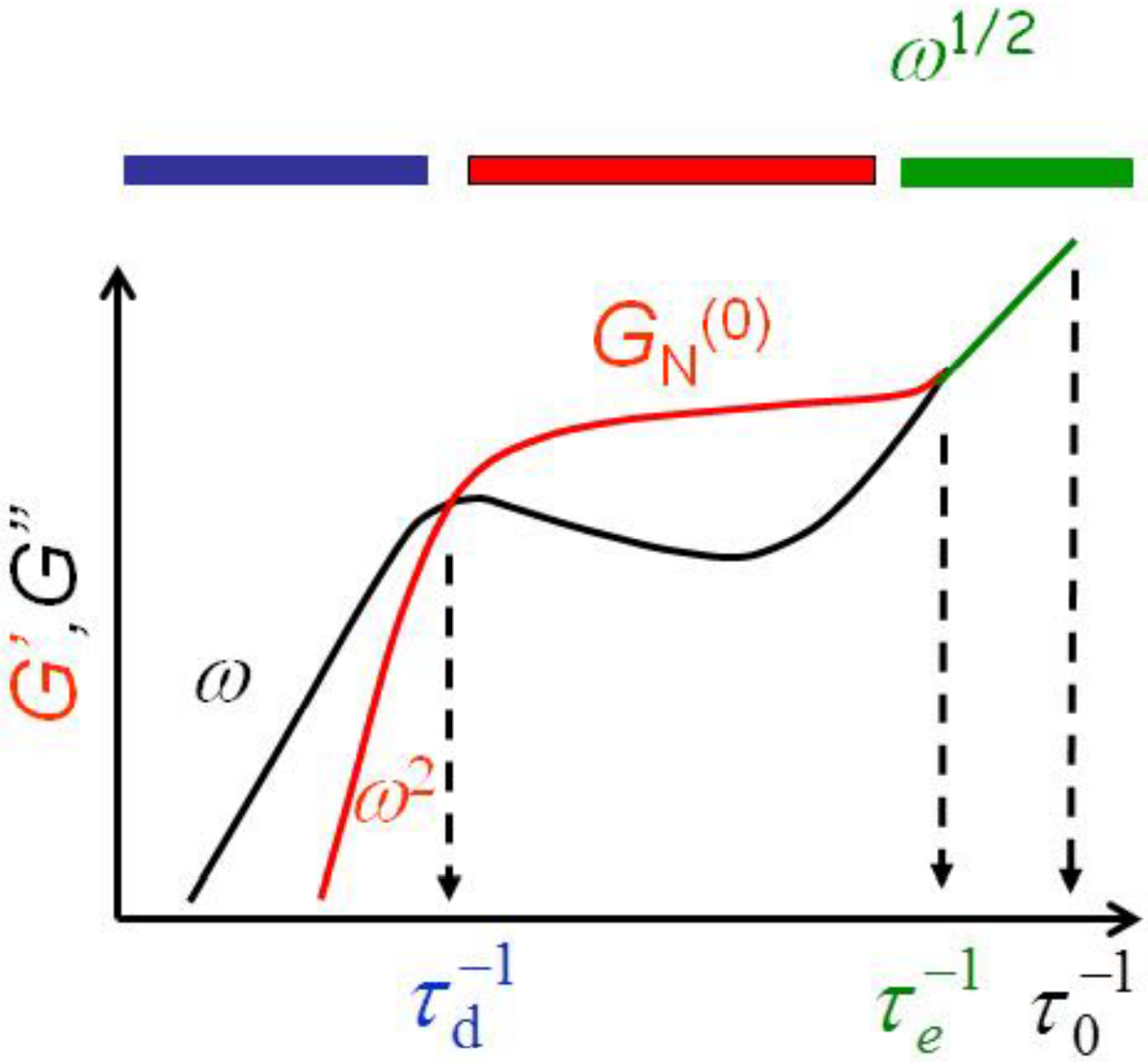
Viscoelasticity probed by stress relaxation

Stress relaxation

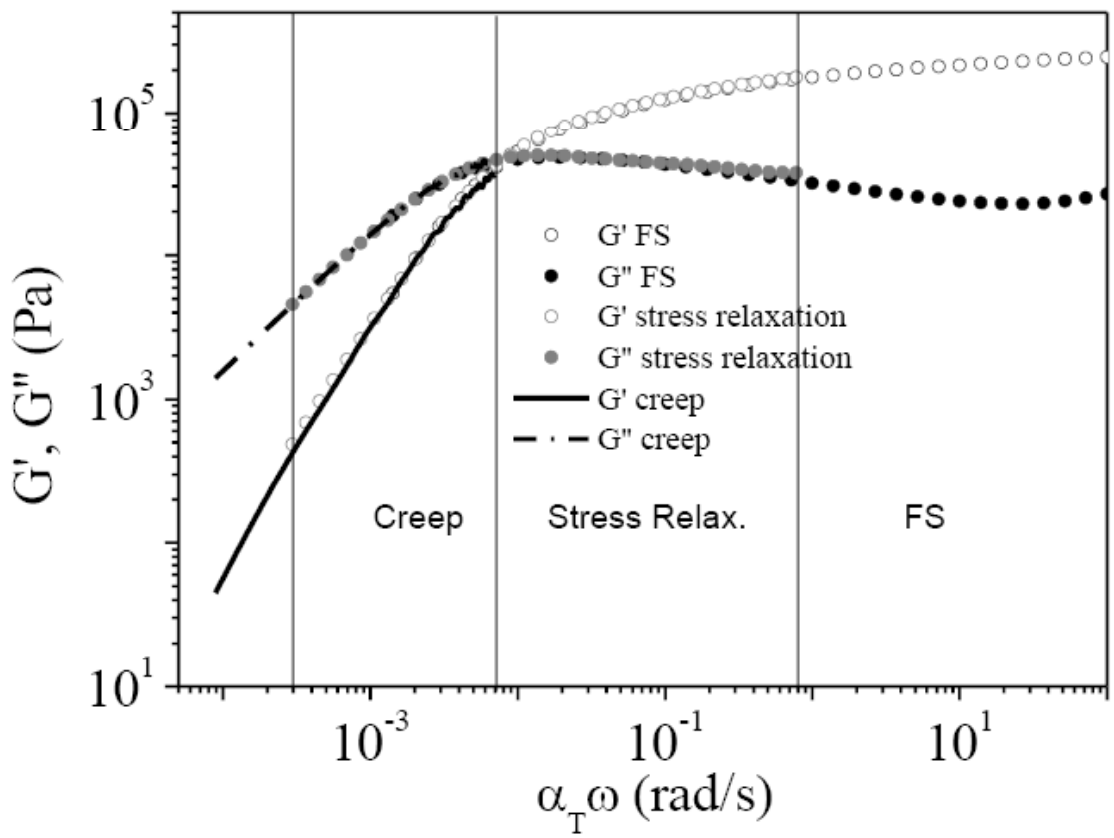




Viscoelasticity probed by frequency sweeps



Combined implementation of rheological tests



Viscoelastic spectrum of a polystyrene melt measured using oscillatory measurements (FS), stress relaxation and creep

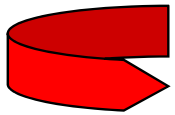
(H Lentzakis, thèse Université de Crète, 2014)

The combination of different rheological tests makes possible to widen the frequency window which is accessible

1.8 Large deformations

Large deformations

σ (stress)



γ (strain)

Small deformation
Linear response
Equilibrium structure

$$\dot{\gamma}\tau << 1$$

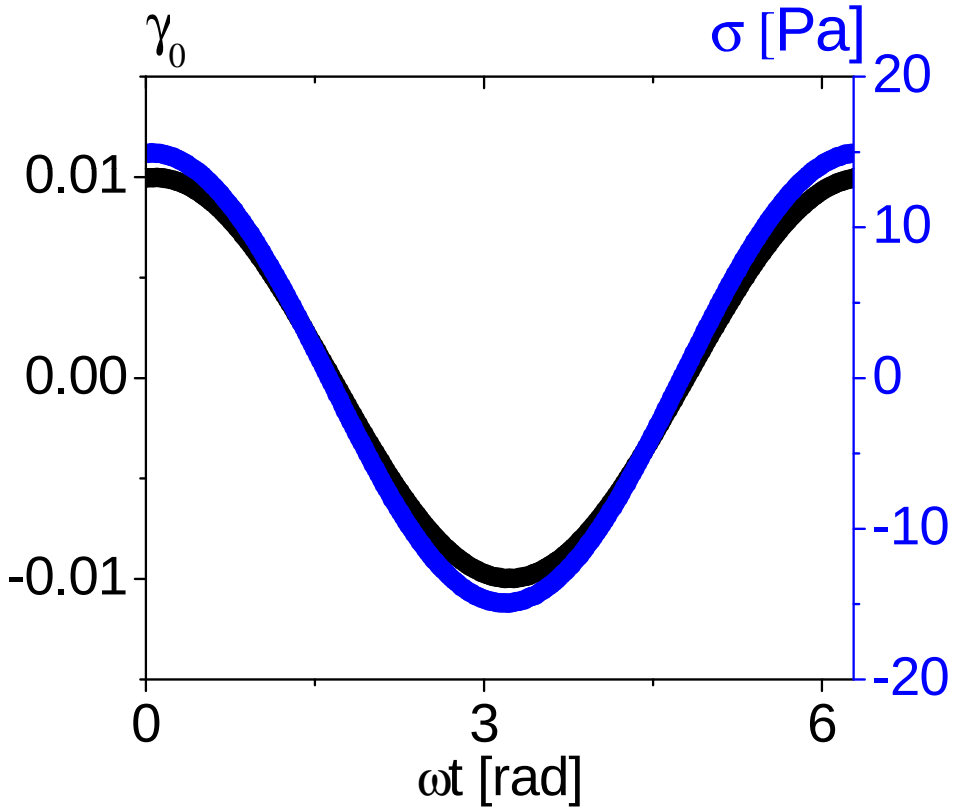
Large deformation
Non linear response
Out of equilibrium structure

$$\dot{\gamma}\tau >> 1$$

Large amplitude oscillatory shear (LAOS)

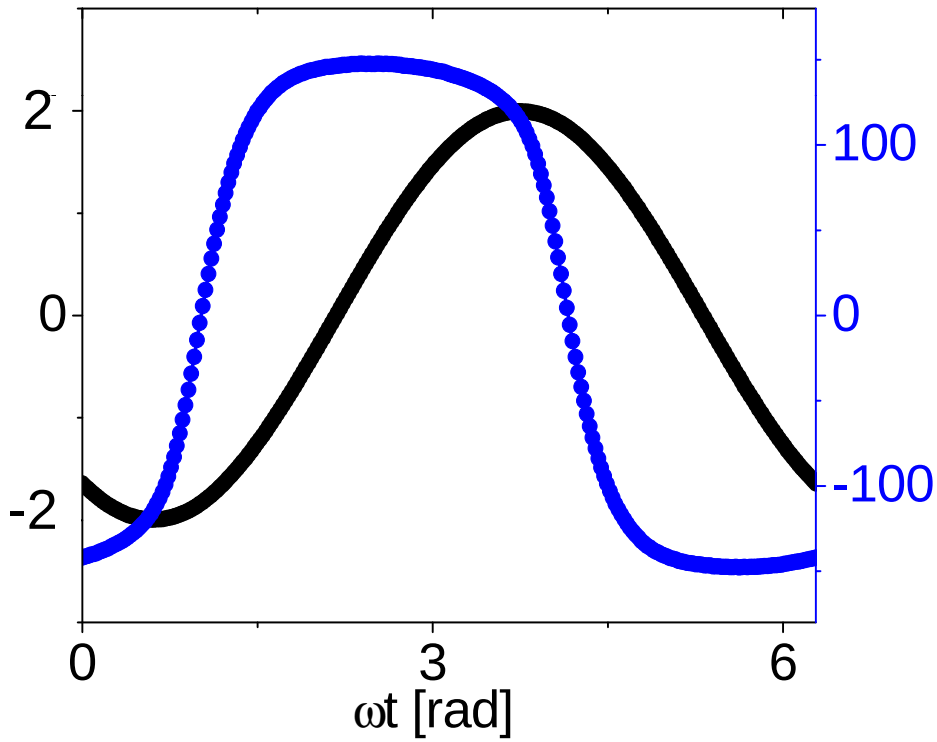
Linear response

$\gamma_0 = 0.01$



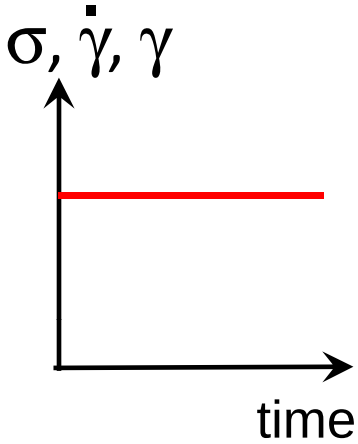
Non linear response

$\gamma_0 = 2$

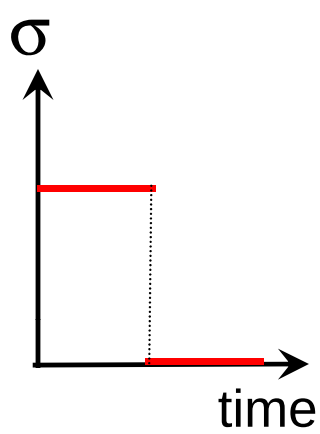


Non-linear rheology

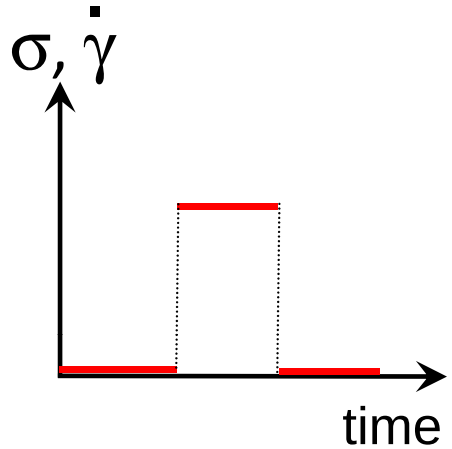
Many experimental tests can be implemented



Creep (σ)
Steady shear ($\dot{\gamma}$)
Stress relaxation (γ)



Creep - recovery

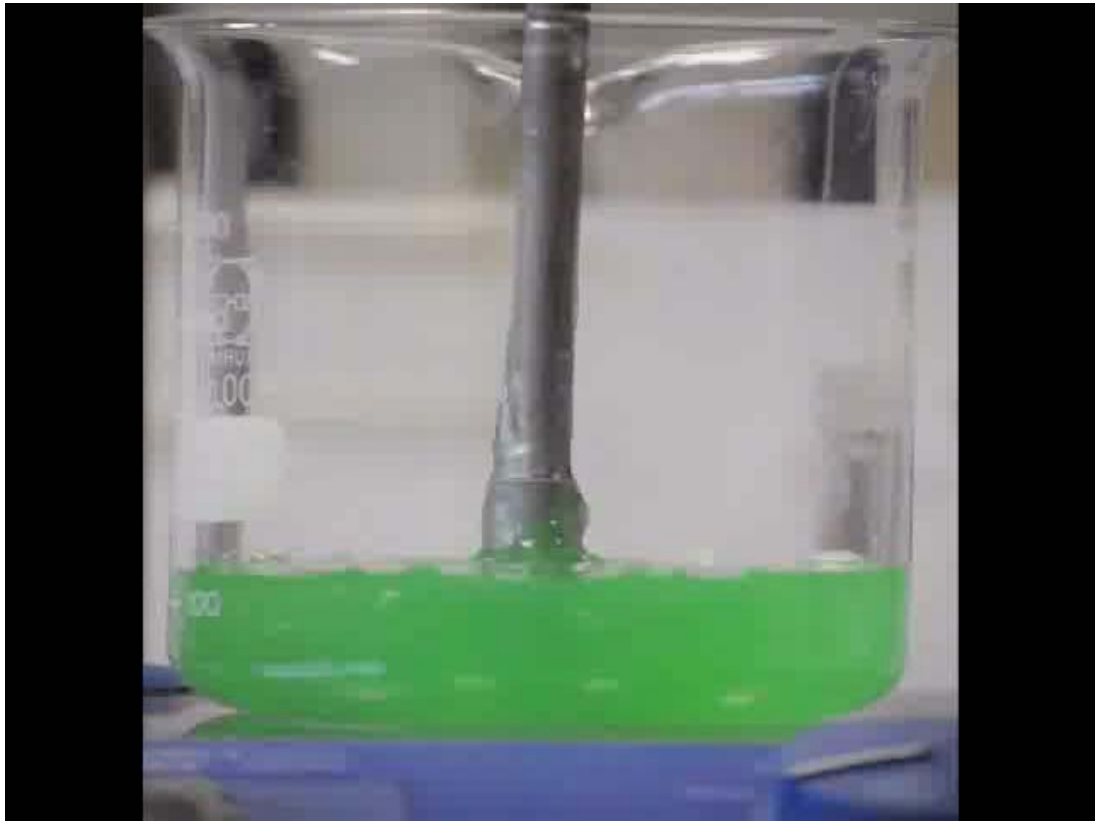


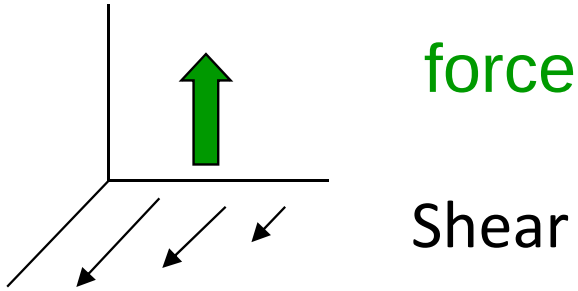
Start-up flow
Flow cessation

The response is associated with a non-equilibrium structure
The microscopic interpretation/modelling is difficult
It is generally necessary to determine the dynamic structure
Flow heterogeneities are frequent

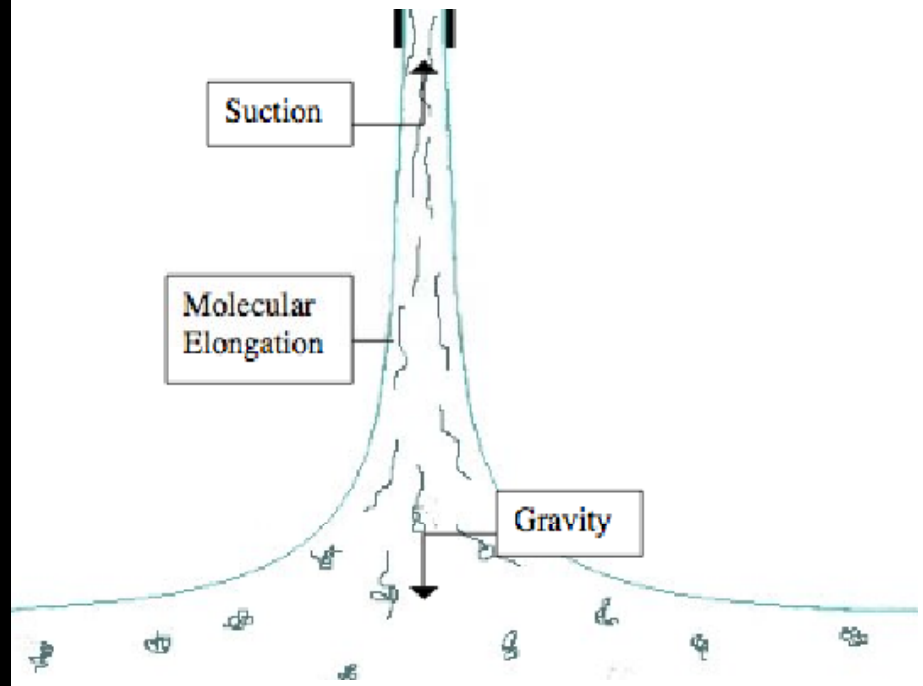
Normal stresses

Weissenberg effect





Tubeless siphon (polymer threads)

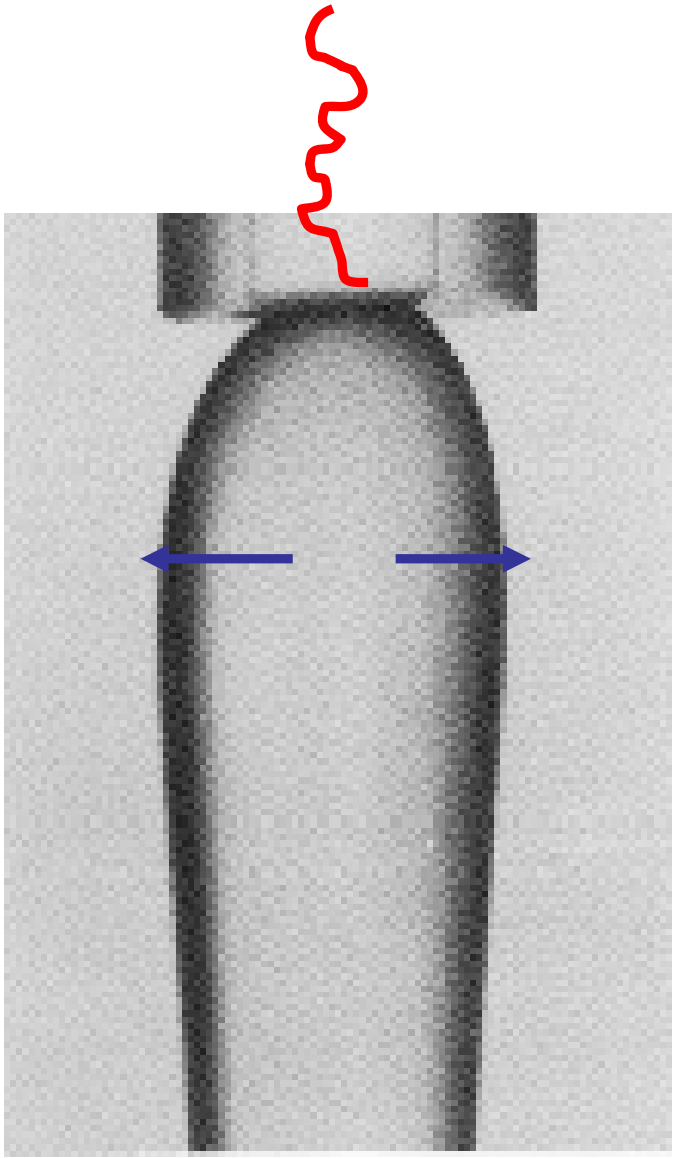


http://web.mit.edu/nnf/

The weight of the column of liquid is balanced by the viscoelastic stress associated with the elongation of the macromolecules

Condition : $\dot{\varepsilon}\tau_R >> 1$

Die-swell



http://web.mit.edu/nnf/