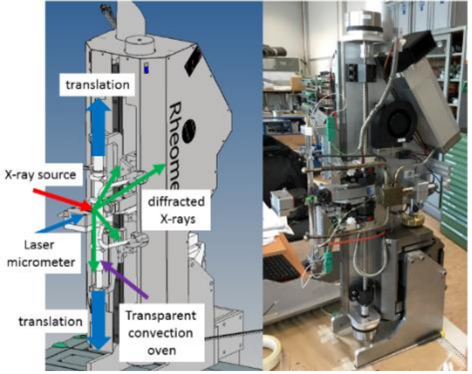
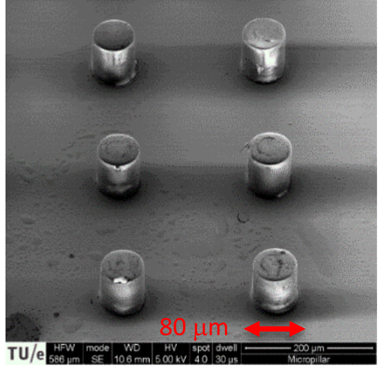
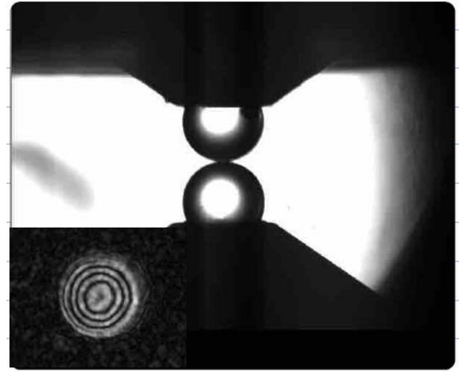
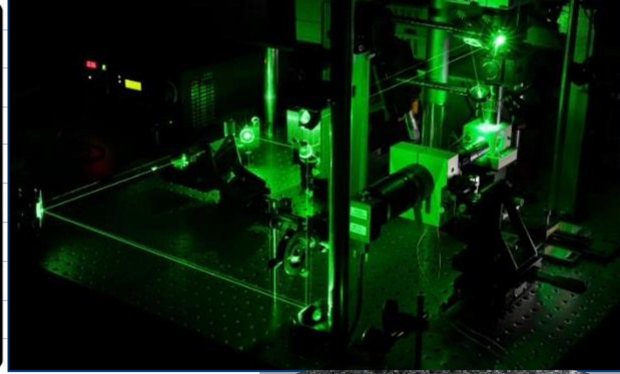
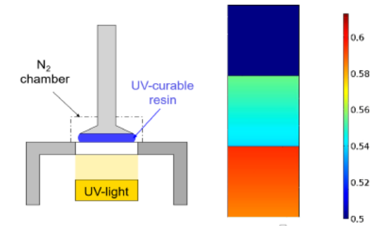
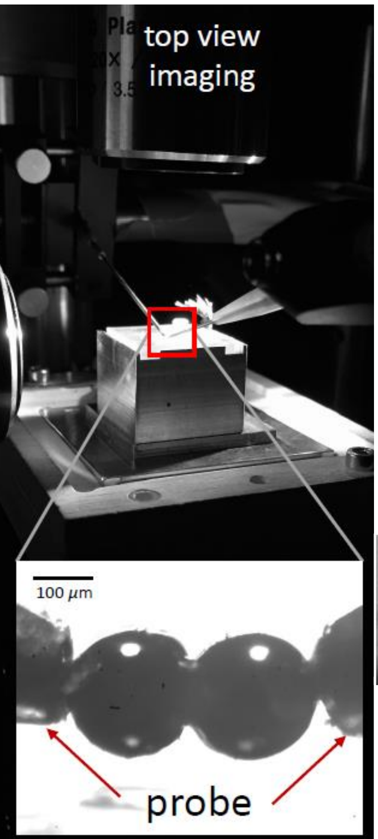


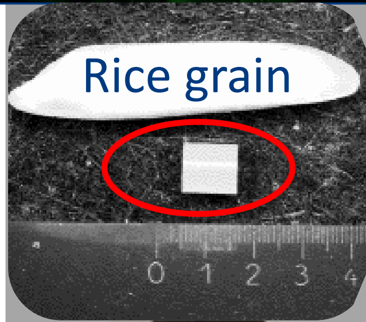






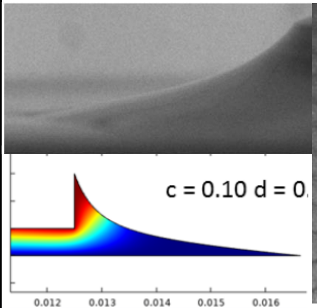


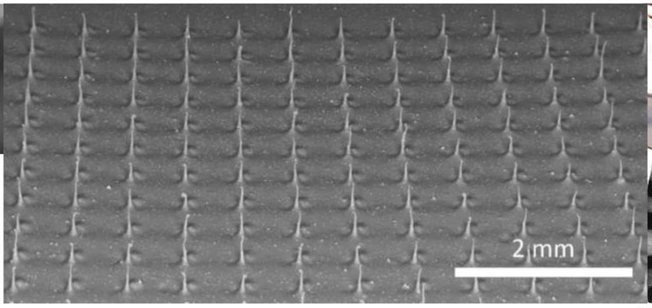


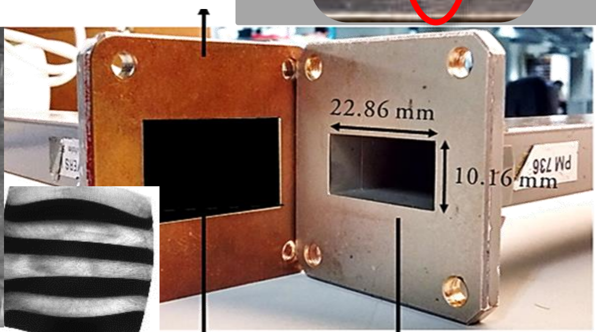


Rheology Part 2

Ruth Cardinaels
Associate Professor
Soft Matter Rheology and Technology
KU Leuven, Belgium
&
Polymer Technology
TU Eindhoven, The Netherlands







0. Lecture overview

1. What is rheology?

2. Rotational rheometry

3. Linear viscoelasticity

4. Application examples

Viscoelastic fluids/solids based on the memory view

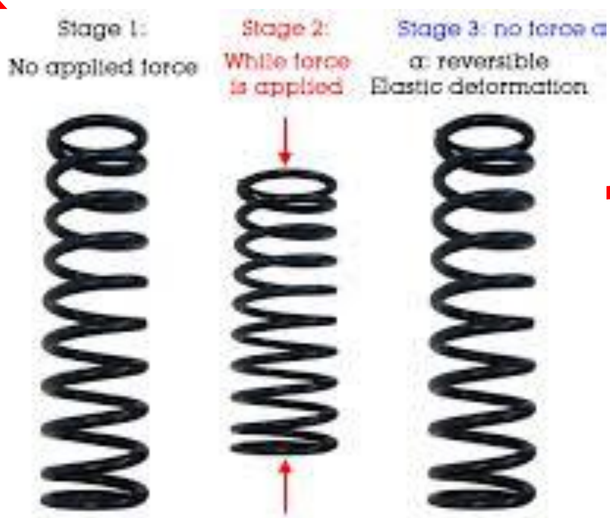
Perfect elastic solid

Infinite memory

Real fluid/solid

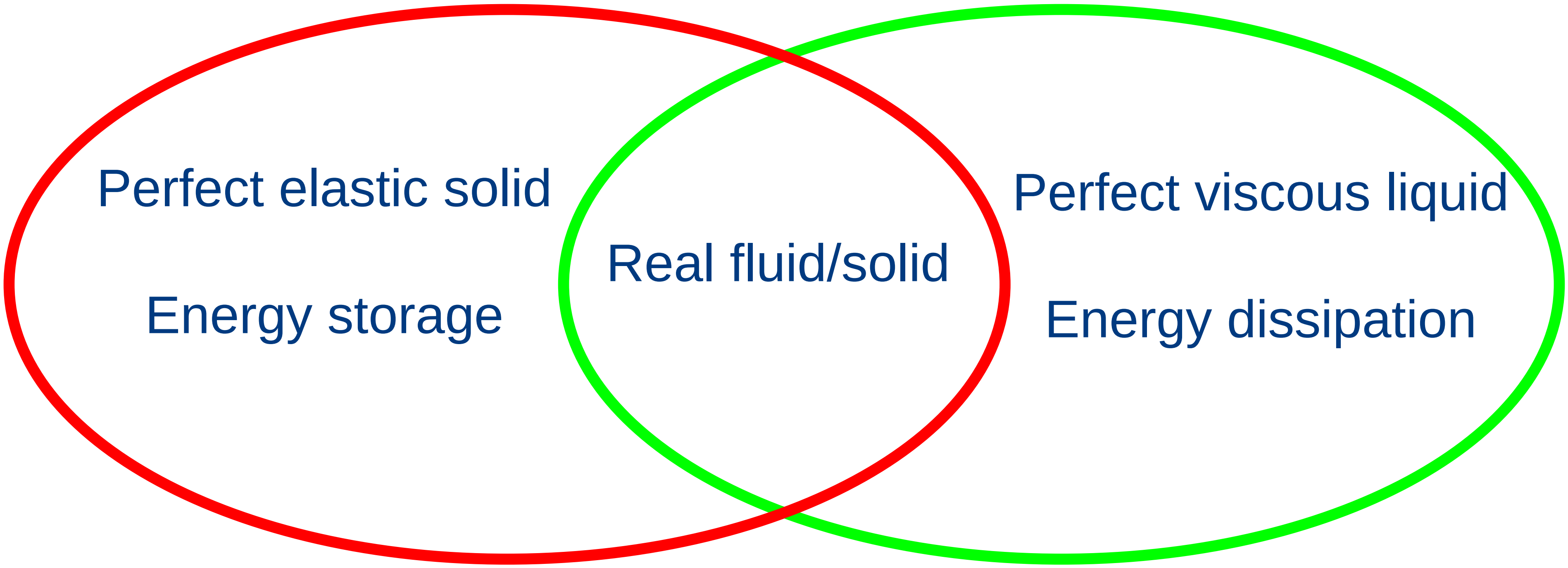
Perfect viscous liquid

No memory



http://nhminsci.blogspot.be/p/glossary.html

Viscoelastic fluids/solids based on the energy view



$$E = \int_0^\infty \tau_{12} \, d\gamma_{12}$$

$$D = \int_0^\infty \tau_{12} \, \dot{\gamma}_{12} \, dt$$

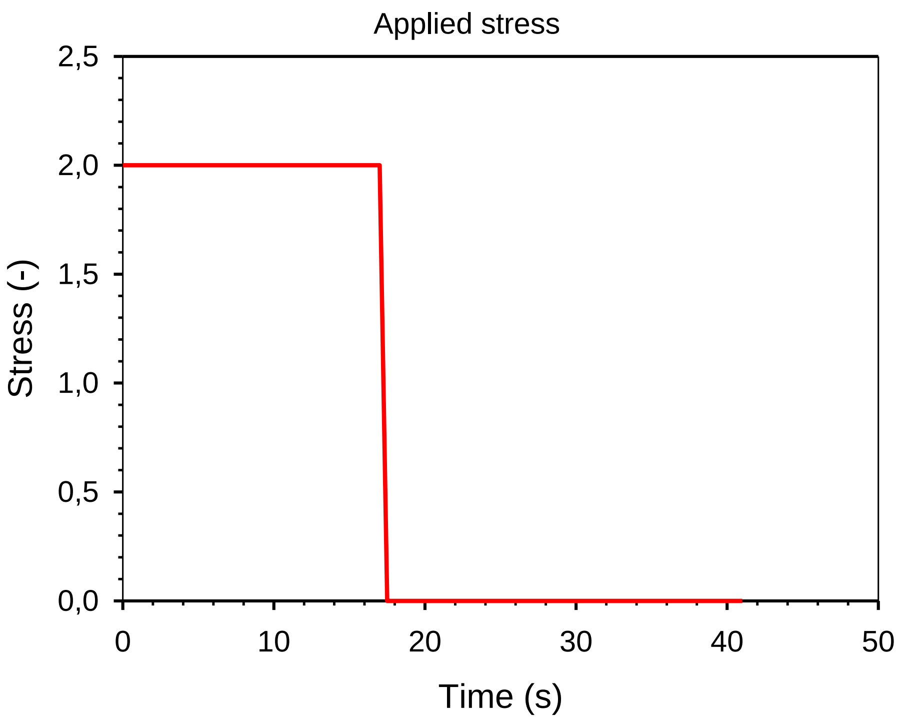
Definition of linear viscoelasticity

- Linear viscoelasticity indicates a **linear relation** between the **stress** and the **strain** history
- This linear relation only occurs at **small deformation** strains

Use of linear viscoelasticity

- Allows to describe **time effects** due to intermediate behaviour between viscous and elastic behaviour
- Is the limiting behaviour for **all materials** at small strains
- Linear viscoelastic behaviour provides insight in the **material structure**

Shear creep

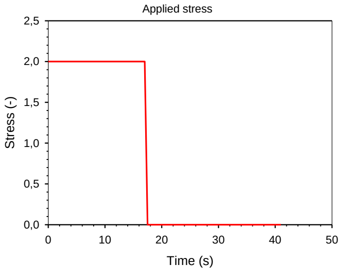


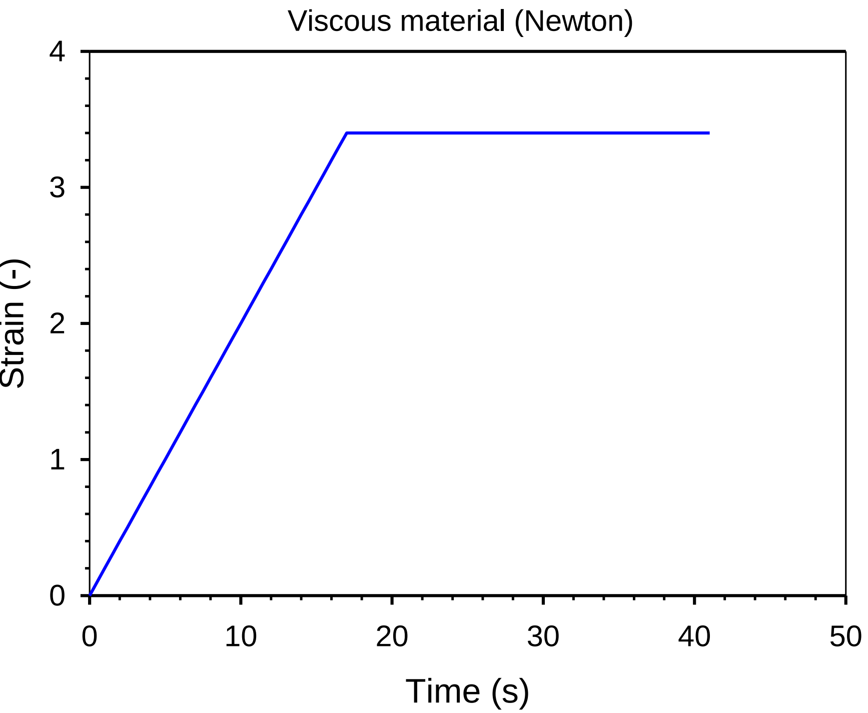
Prescribed stress function for creep

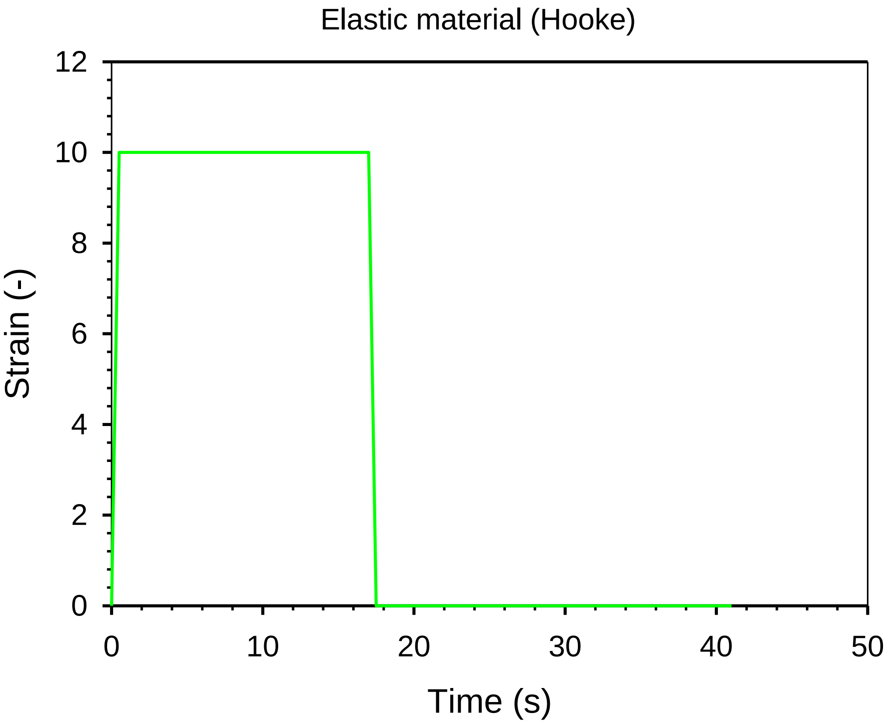
$$\tau_{21}(t) = \begin{cases} 0 & t < 0 \\ \tau_0 = \text{constant} & t \geq 0 \end{cases}$$

In a creep experiment, a constant stress is applied while the strain is measured.

Shear creep

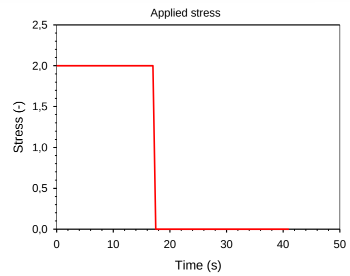






Viscous material: shear with constant shear rate, no recovery
Elastic material: constant strain, full recovery

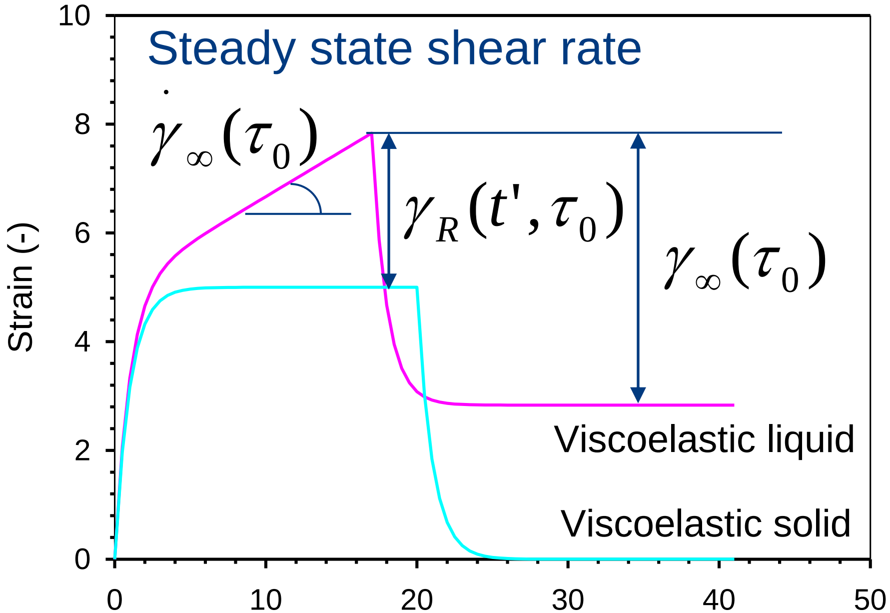
Shear creep

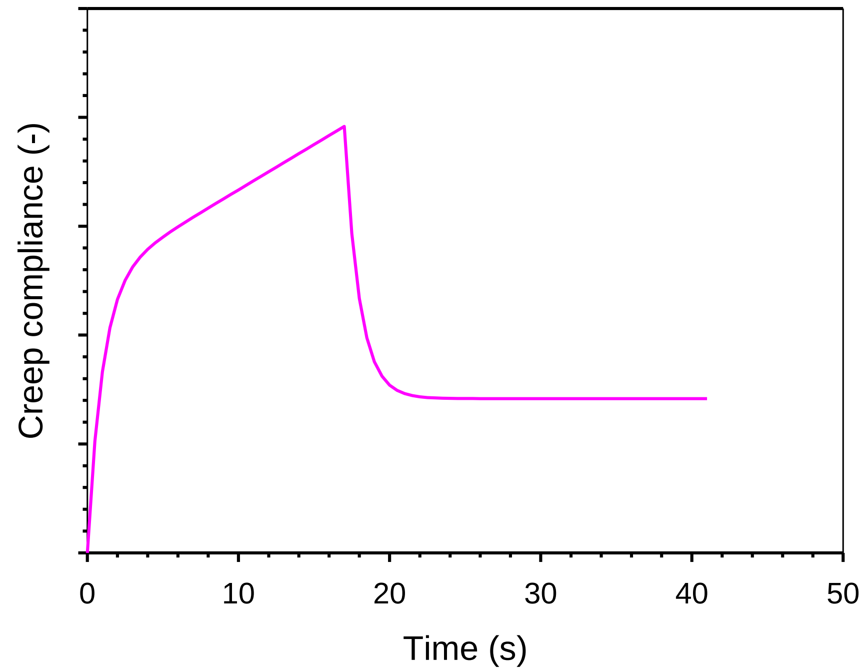


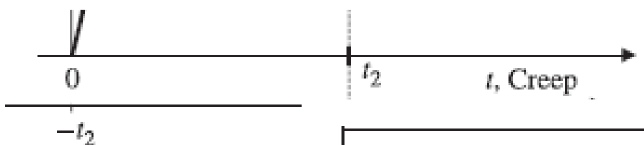
Shear creep compliance

$$J(t, \tau_0) \equiv \frac{\gamma_{21}(0, t)}{\tau_0}$$

Viscoelastic liquid and solid





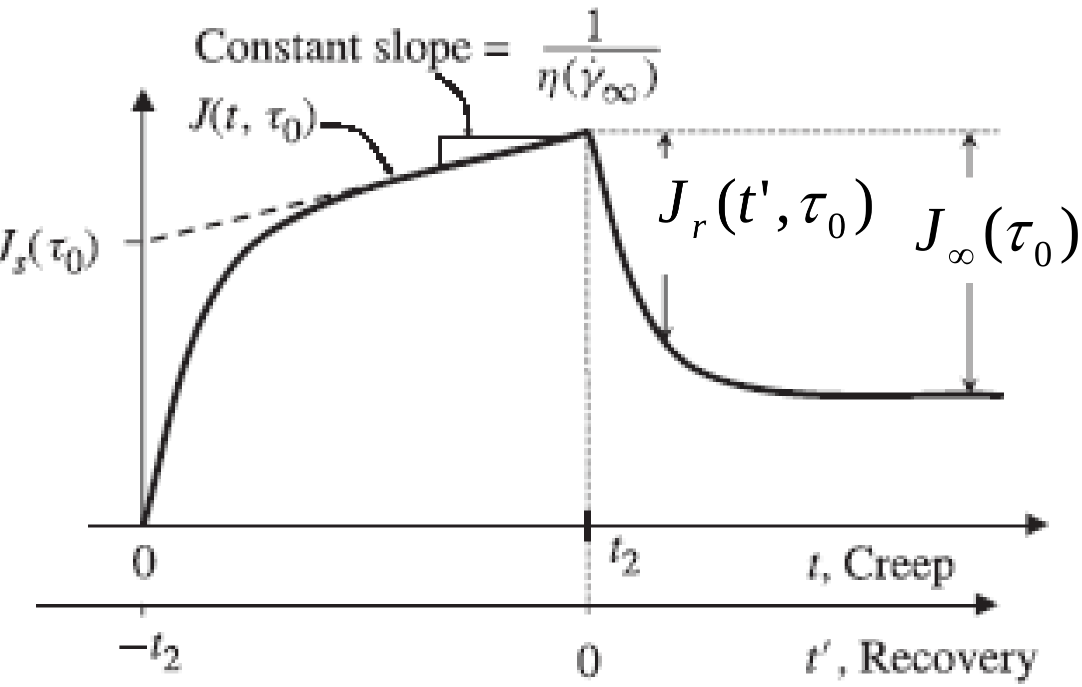


$$\gamma_\infty \equiv \lim_{t' \to \infty} \gamma_r(t')$$

$\gamma_R(t', \tau_0)$ Recoverable shear strain

$\gamma_\infty(\tau_0)$ (Ultimate) recoverable shear (strain)

Shear creep



Steady-state compliance $J_s(\tau_0)$

$$J_s(\tau_0) \equiv J(t, \tau_0)|_{\text{steady state}} - \frac{t}{\eta(\dot{\gamma}_\infty)}$$

Recoverable creep compliance

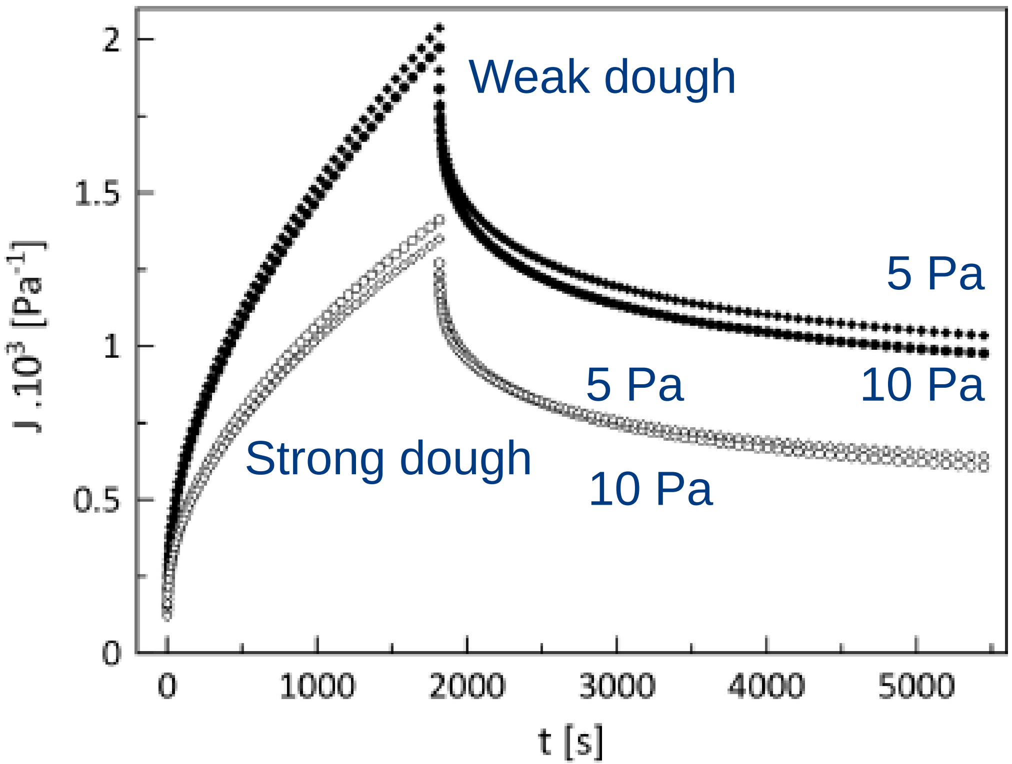
$$J_r(t', \tau_0) \equiv \frac{\gamma_r(t')}{\tau_0}$$

Ultimate recoverable Creep compliance

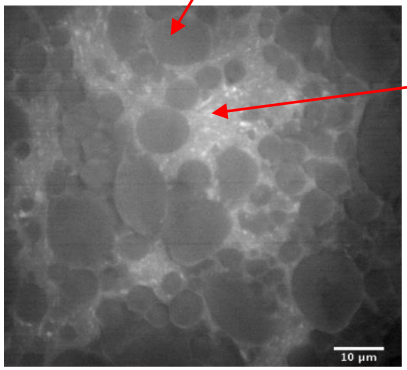
$$J_\infty(\tau_0) = \frac{\gamma_\infty}{\tau_0}$$

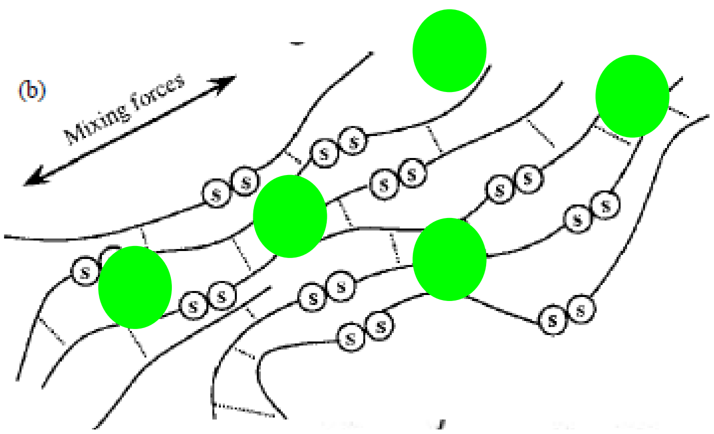
In case of linear viscoelasticity: $J(t) = J_r(t) + \frac{t}{\eta_0}$ and $J_s = J_\infty$

Creep curves of bread dough



Data Courtesy M. Meerts, KU Leuven





Zaidel, Chin, Yusof, J. Appl. Sci. 2010

Creep curves of bread dough

	5 Pa		10 Pa	
	Weak Bilux	Strong Bison	Weak Bilux	Strong Bison
J_c^{max} [10^{-3} Pa^{-1}]	1.98	1.42	1.99	1.35
J_r^{max} [10^{-3} Pa^{-1}]	1.00	0.80	1.00	0.80
recovery [%]	50.6	56.4	50.3	59.4
η [10^6 Pa s]	1.59	2.45	1.48	2.48

The dough with a larger gluten content shows a larger viscosity, which results in less viscous creep. Hence, a larger part of the deformation is recovered.

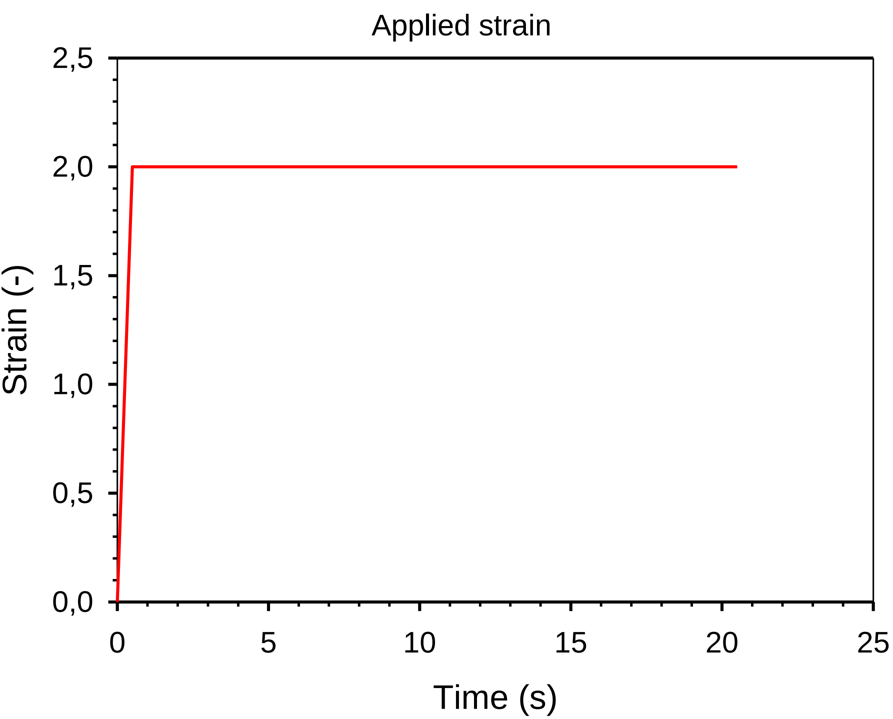
Step shear strain

$$\gamma_{21}(-\infty, t) = \begin{cases} 0 & t < 0 \\ \gamma_0 & t \geq 0 \end{cases}$$

$$= \gamma_0 H(t)$$

Heaviside step function

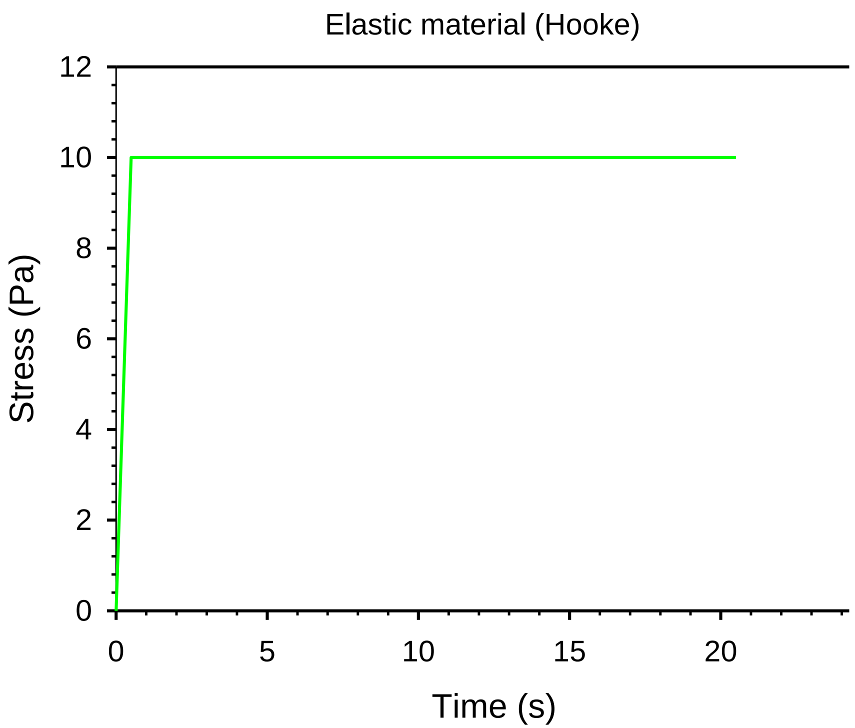
$$H(t) \equiv \begin{cases} 0 & t < 0 \\ 1 & t \geq 0 \end{cases}$$

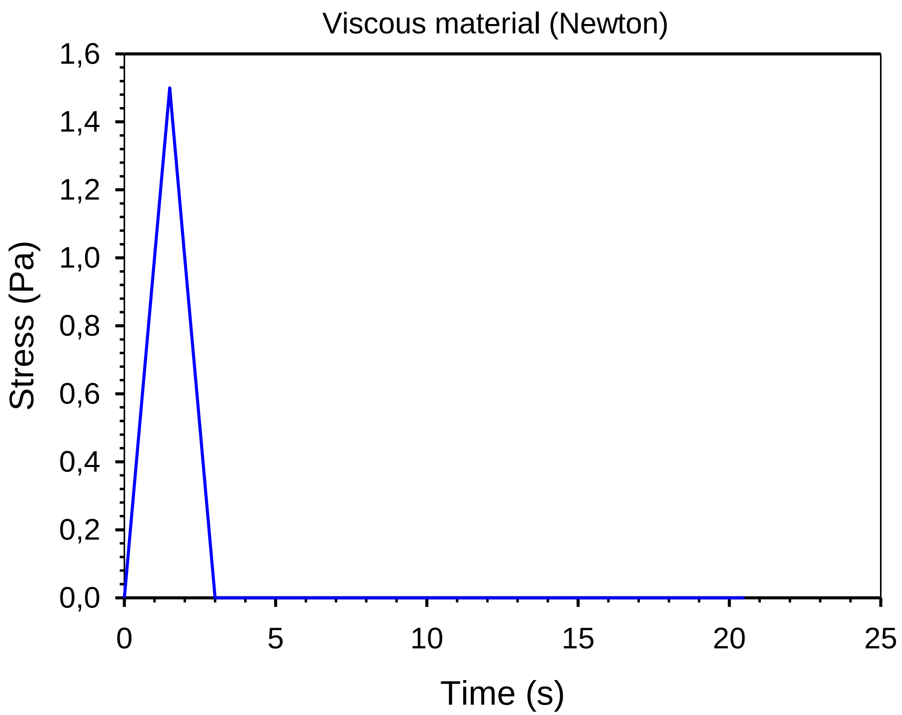


$$\dot{\gamma}_{21}(t) = \lim_{\varepsilon \longrightarrow 0} \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & 0 \leq t < \varepsilon \\ 0 & t \geq \varepsilon \end{cases}$$

$$\dot{\gamma}_0 \varepsilon = \text{constant} = \gamma_0$$

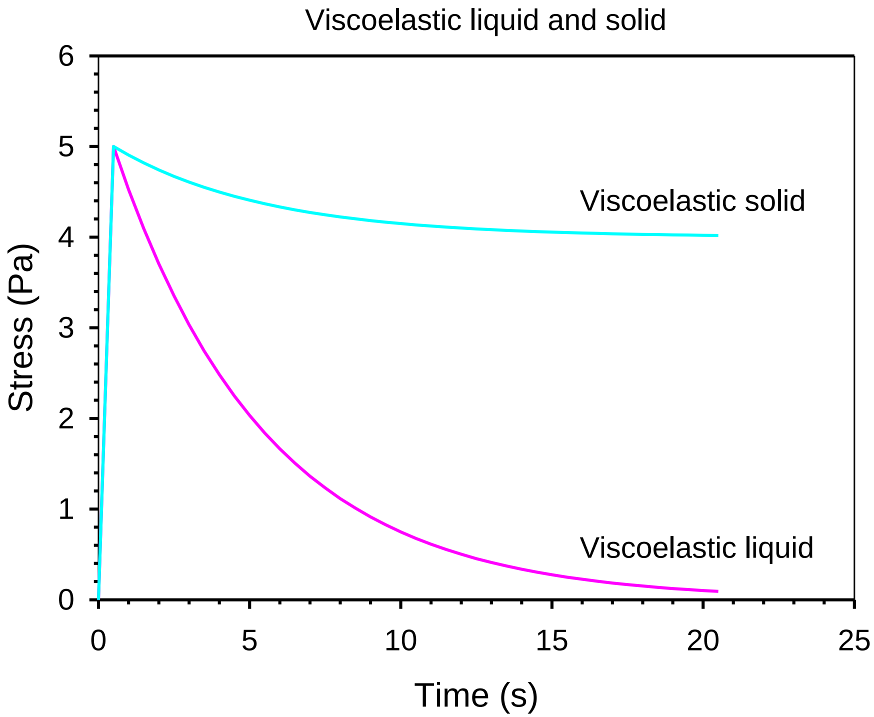
Step shear strain





In a viscous liquid, there will only be an instantaneous stress peak whereas in the elastic solid, the stress will remain constant.

Step shear strain



Relaxation modulus

$$G(t,\gamma_0) \equiv \frac{\tau_{21}(t,\gamma_0)}{\gamma_0}$$

First normal stress step shear relaxation modulus

$$G_{\Psi_1}(t,\gamma_0) \equiv \frac{(\tau_{11}-\tau_{22})}{\gamma_0^2}$$

In case of linear viscoelasticity: G(t) and $G_{\Psi 1}$ are independent of strain

Small amplitude oscillatory shear: Modulus formalism

Applied signal:

$$\gamma_{21} = \gamma_0 \sin(\omega t)$$

$$\dot{\gamma}_{21} = \gamma_0 \omega \cos(\omega t)$$

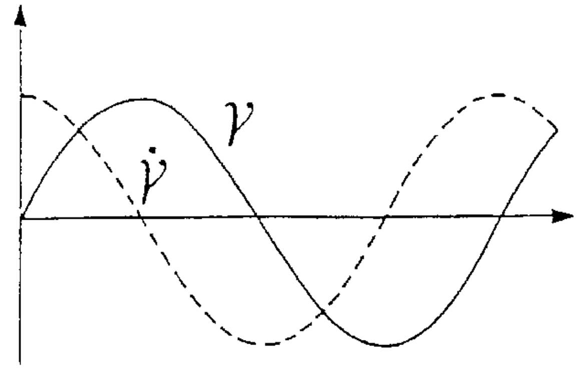
Material response:

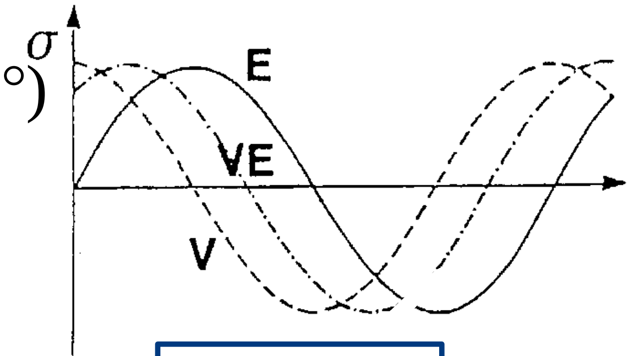
(Elastic)

$$\tau = G \cdot \gamma_{21} = G \cdot \gamma_0 \sin(\omega t)$$

(Viscous)

$$\tau = \eta \cdot \dot{\gamma}_{21} = \eta \gamma_0 \omega \sin(\omega \cdot t + 90°)$$





(Viscoelastic)

$$\tau = \tau_0 \sin(\omega t + \delta)$$

$$\tau_{21} = \tau_0 \left[\sin(\omega t)\cos(\delta) + \cos(\omega t)\sin(\delta)\right]$$

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

$$\tan\delta = \frac{G''}{G'}$$

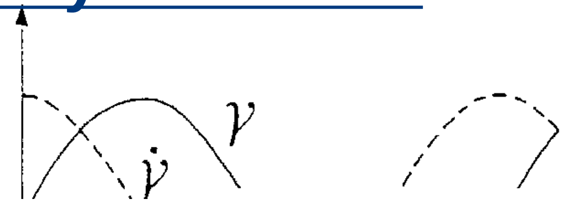
G': elastic modulus or storage modulus

G": viscous modulus or loss modulus

$$G'(\omega) = \frac{\tau_0}{\gamma_0}\cos\delta \quad ; \quad G''(\omega) = \frac{\tau_0}{\gamma_0}\sin\delta$$

Small amplitude oscillatory shear: Viscosity formalism

Applied signal: Material response:



(Elastic)

$$\gamma_{21} = \gamma_0 \sin(\omega t)$$

$$\dot{\gamma}_{21} = \gamma_0 \omega \cos(\omega t)$$

$$\tau = G \cdot \gamma_{21} = G \cdot \gamma_0 \sin(\omega t)$$

$$G^*(\omega) = G' + iG''$$

(Viscous)

$$\tau = \eta \cdot \dot{\gamma}_{21} = \eta \gamma_0 \omega \sin(\omega \cdot t + 90°)$$

(Viscoelastic)

$$\eta^*(\omega) = \frac{G^*}{i\omega} = \eta' - i\eta''$$

$$\tau = \tau_0 \sin(\omega t + \delta)$$

$$\tau_{21} = \tau_0 \left[\sin(\omega t)\cos(\delta) + \cos(\omega t)\sin(\delta)\right]$$

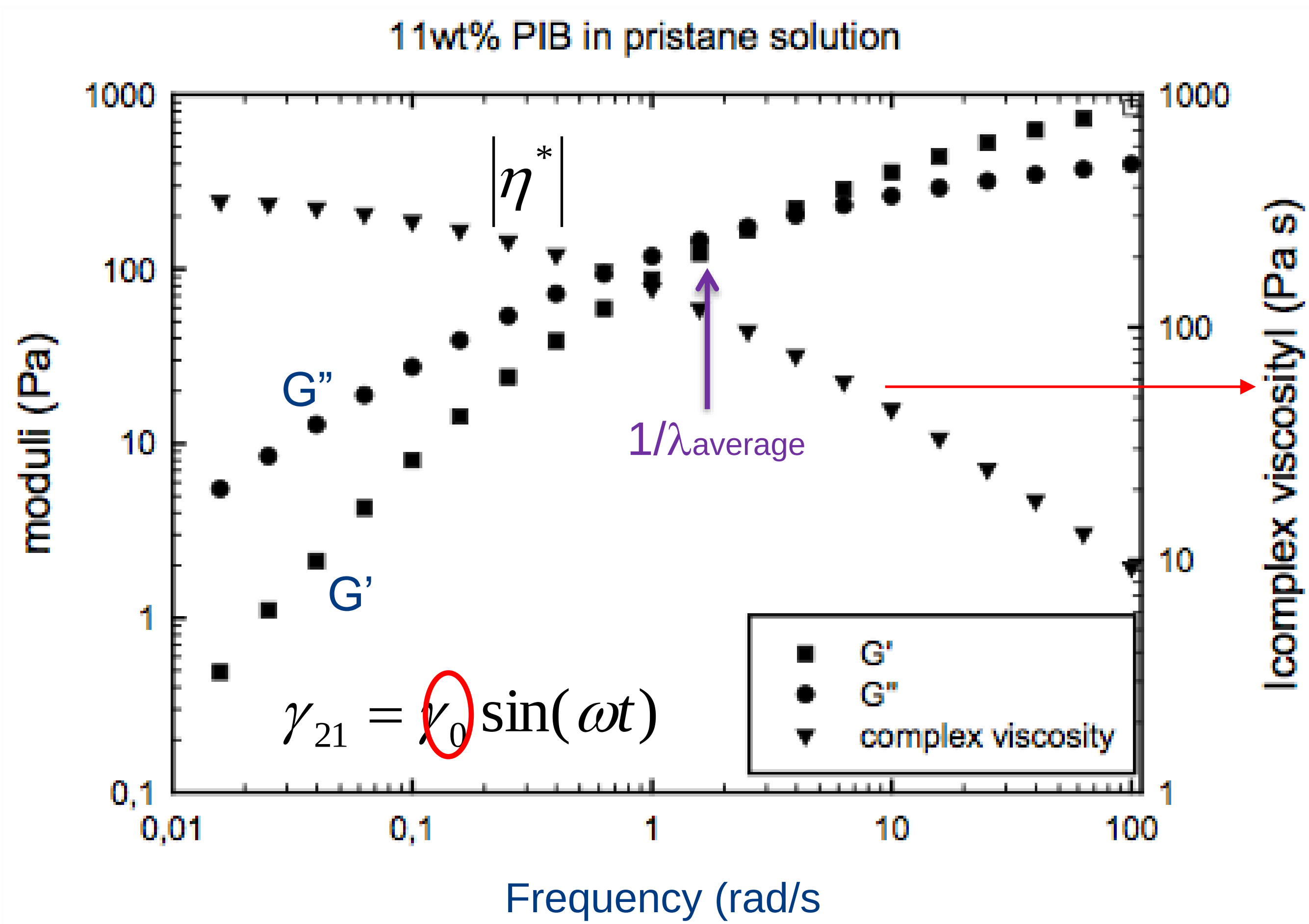
$$= \gamma_0 \cdot \omega \left[\eta'' \sin(\omega t) + \eta' \cos(\omega t)\right] \qquad = \gamma_0 \cdot [$$

$$|\eta^*| = \sqrt{\eta'^2 + \eta''^2}$$

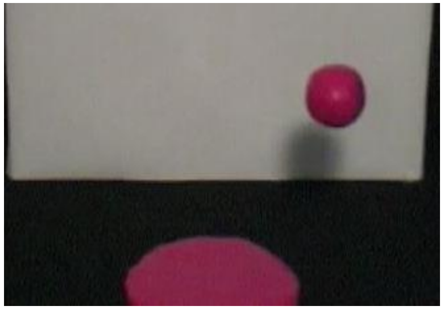
η': dynamic viscosity
η'': elastic part of the complex viscosity

$$\eta' = \frac{G''}{\omega} \qquad \eta'' = \frac{G'}{\omega}$$

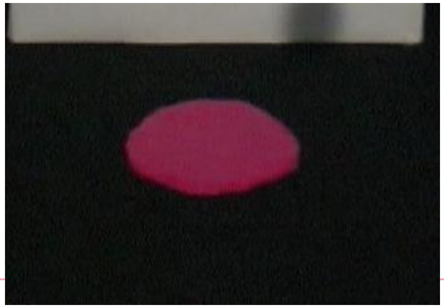
Small amplitude oscillatory shear: Frequency sweep



High frequency

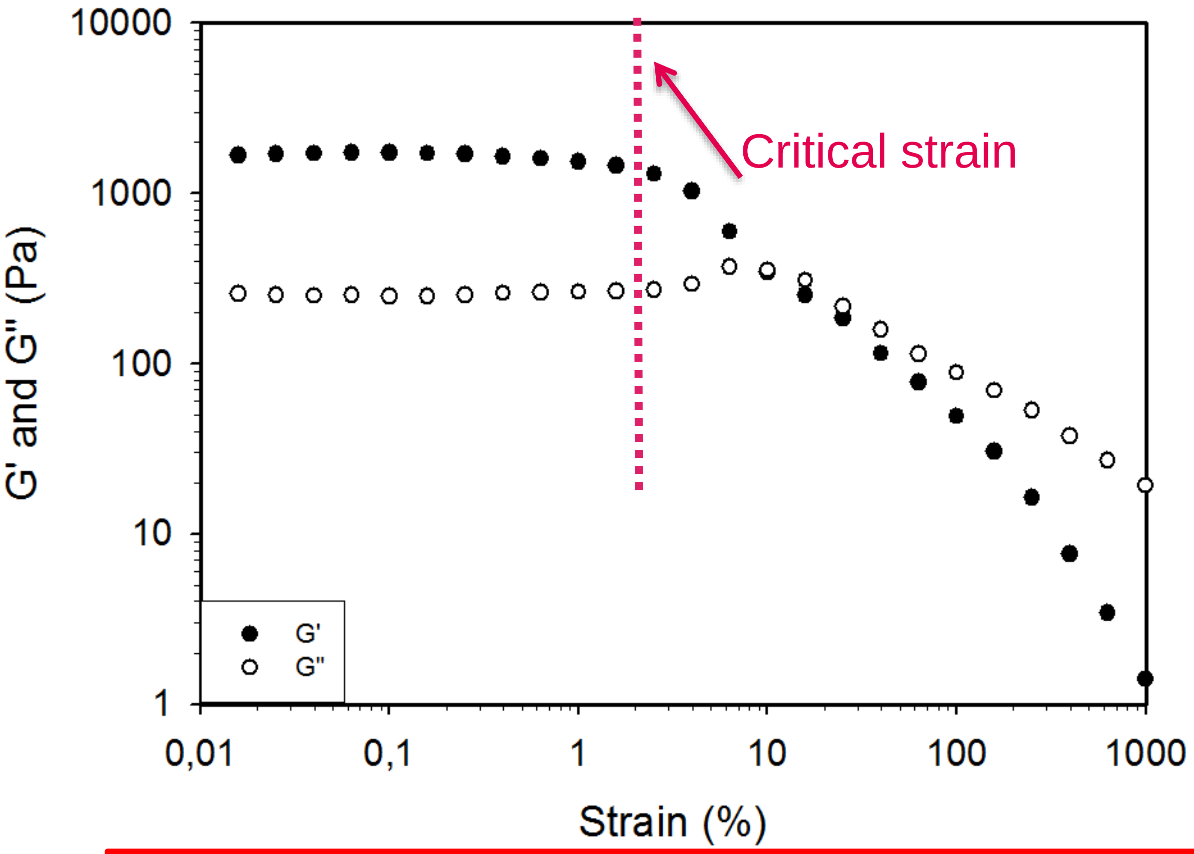


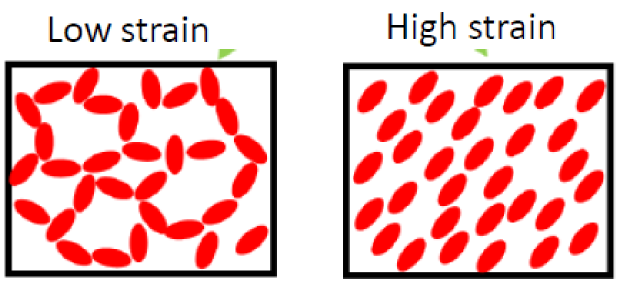
Low frequency



Small amplitude oscillatory shear: Strain sweep

Polydimethylsiloxane polymer containing 3,2wt% clay platelets



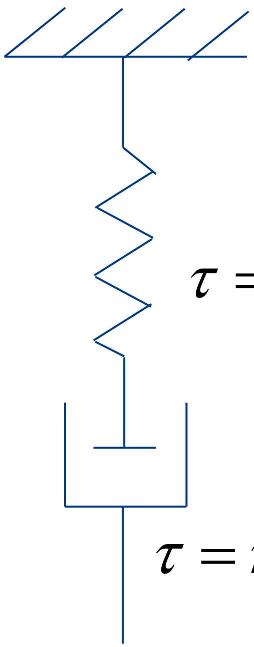


$$\omega = 10 rad/s$$

$$\gamma_{21} = \gamma_0 \sin(\omega t)$$

A strain sweep allows to determine the linear viscoelastic region

Maxwell constitutive equation



$$\tau = G\gamma_1$$

$$\tau = \eta\dot{\gamma}_2$$

$$\gamma = \gamma_1 + \gamma_2$$

$$\dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2$$

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

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

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

Scalar version

λ = relaxation time

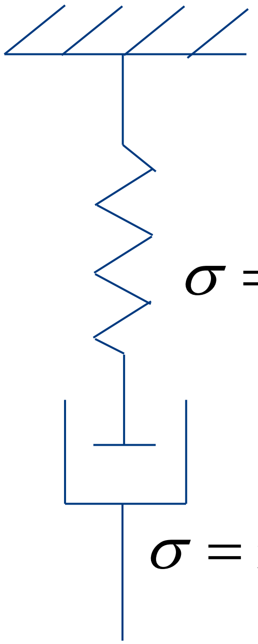
Rate of deformation tensor:

$$\underline{\underline{\dot{\gamma}}}$$

$$\underline{\underline{\tau}} + \lambda\frac{\partial \underline{\underline{\tau}}}{\partial t} = \eta_0\underline{\underline{\dot{\gamma}}}$$

Tensor version

Maxwell constitutive equation: Relaxation modulus



$$\sigma = G\gamma_1$$

$$\sigma = \eta\dot{\gamma}_2$$

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

Response to a stepstrain:

$$\gamma = \gamma_0$$

For t ≥ 0

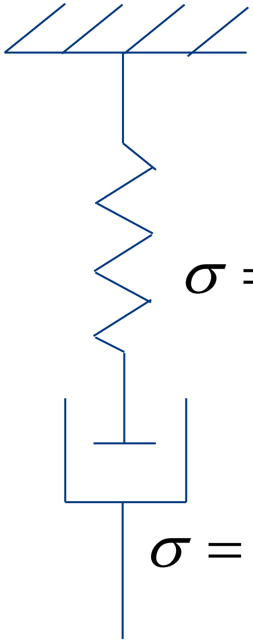
$$\tau + \lambda\dot{\tau} = 0$$

$$\frac{d\tau}{dt} = -\frac{\tau}{\lambda}$$

$$\tau(t) = \tau_0 \exp(-t/\lambda)$$

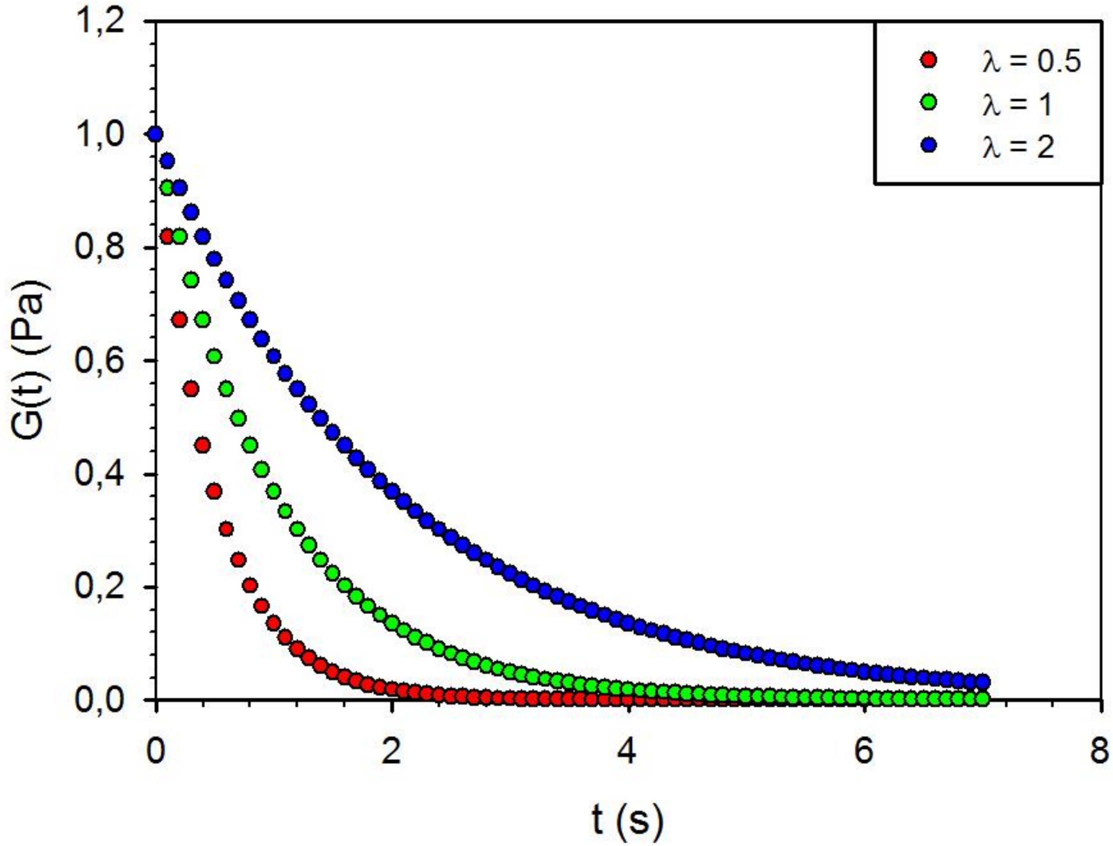
$$G(t) = \frac{\tau(t)}{\gamma_0} = G_0 \exp(-t/\lambda)$$

Maxwell constitutive equation: Relaxation modulus



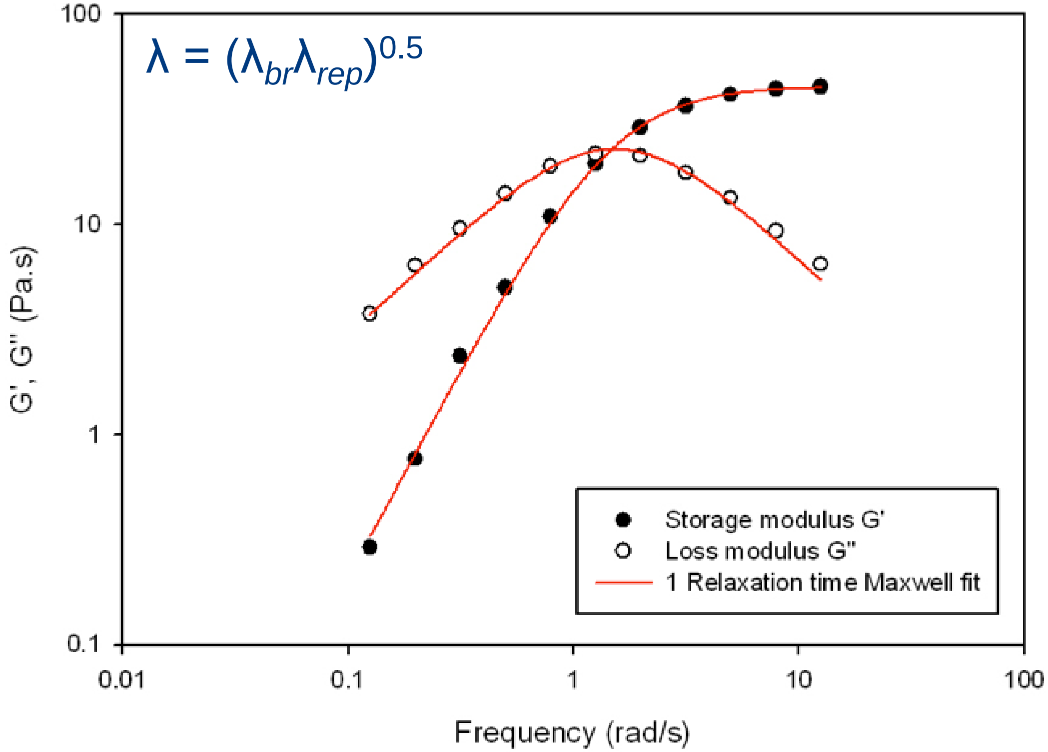
$$\sigma = G\gamma_1$$

$$\sigma = \eta\dot{\gamma}_2$$



$$G(t) = \frac{\tau(t)}{\gamma_0} = G_0 \exp(-t/\lambda)$$

Maxwell constitutive equation in SAOS



Wormlike micellar surfactant solution

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

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

$\eta_0 = 29.9 Pa.s$ and $\lambda = 0.67s$.

Data Courtesy S. Van Loon KU Leuven

Maxwell constitutive equation: Relaxation modulus

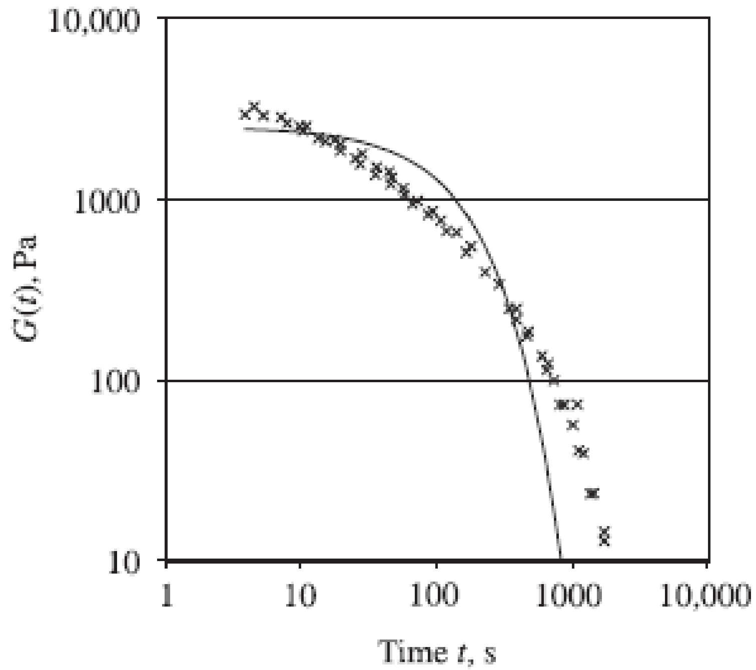


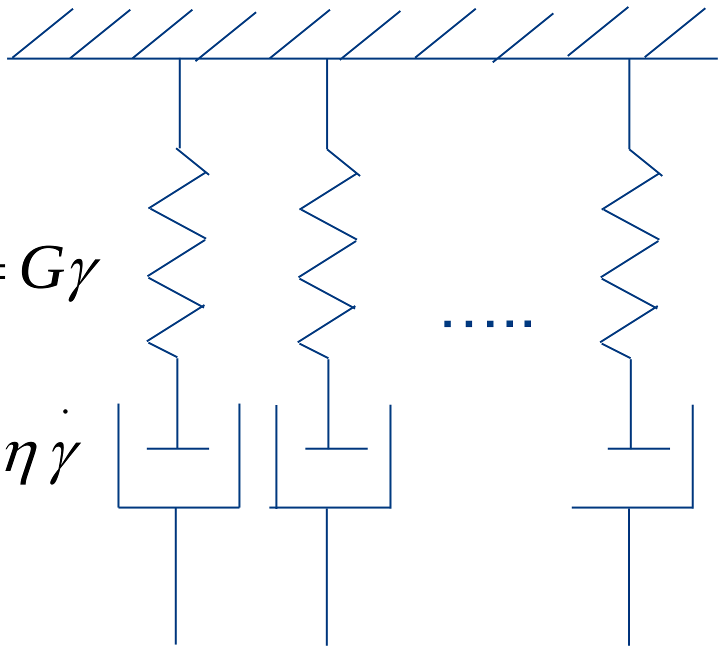
Figure 8.4 Relaxation-modulus data at 33.5°C for a polystyrene of narrow molecular-weight distribution, $M_w = 1.8 \times 10^6$, 20% solution in chlorinated diphenyl; from Einaga et al. [72]. The data are for small strains ($\gamma_0 = 0.41, 1.87$) and are independent of strain. Also shown is a predicted $G(t)$ using the Maxwell model with $\lambda = 150$ s and $g = \eta_0/\lambda = 2500$ Pa.

Maxwell model predicts the correct trend of a gradual decay of the stress. However, a single relaxation time is not sufficient to quantitatively describe the material behavior.

Generalized Maxwell model

$$\sigma = G\gamma$$

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



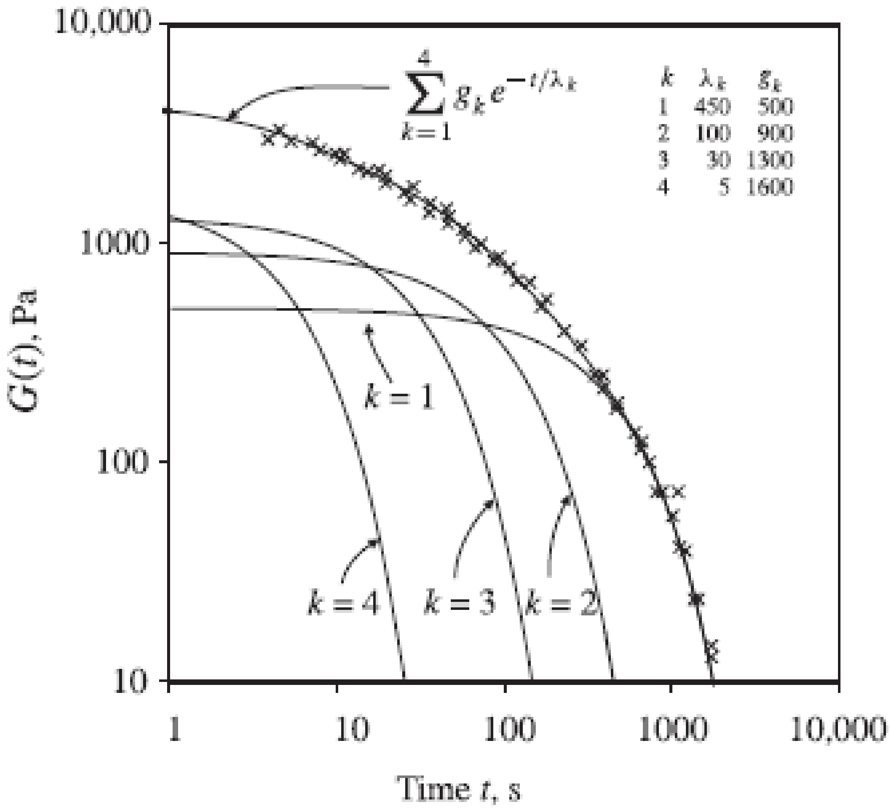
$$\underline{\underline{\tau}}_{(k)} + \lambda_k \frac{\partial \underline{\underline{\tau}}_{(k)}}{\partial t} = -\eta_k \underline{\underline{\dot{\gamma}}}$$

$$\underline{\underline{\tau}} = \sum_{k=1}^{N} \underline{\underline{\tau}}_{(k)}$$

Relaxation modulus for the generalized Maxwell model

$$G(t) = \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{\frac{-t}{\lambda_k}}$$

Generalized Maxwell model



$$G(t) = \sum_{k=1}^{N} \frac{\eta_k}{\lambda_k} e^{\frac{-t}{\lambda_k}}$$

Figure 8.5 Relaxation-modulus data from Figure 8.4 fit to the sum of four $G(t)$ contributions calculated using the Maxwell model with parameters λ_k and $g_k = \eta_k/\lambda_k$ as indicated. The fit can be made arbitrarily good by choosing to use more λ_k and g_k.

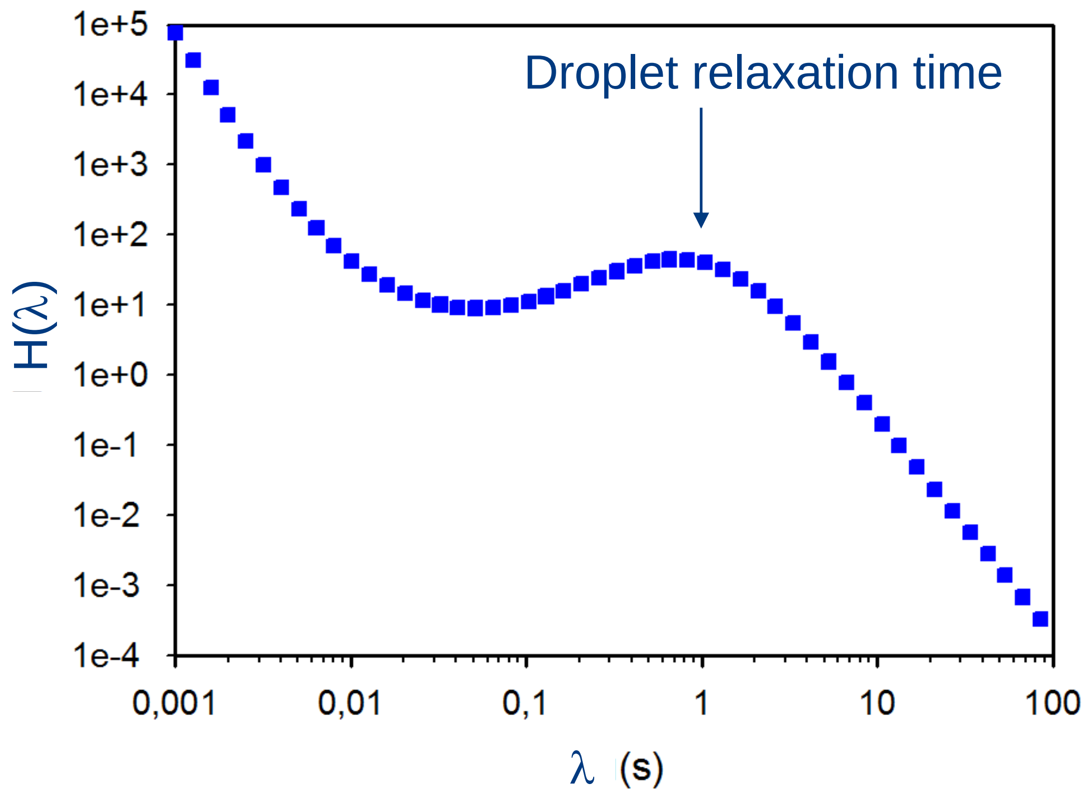
From discrete to continuous spectrum of relaxation times

$$G(t) = \sum_{k=1}^{n} G_k \exp(-t/\lambda_k)$$

$$G(t) = \int_0^{\infty} F(\lambda) \exp(-t/\lambda) d\lambda$$

$$G(t) = \int_0^{\infty} H(\lambda) \exp(-t/\lambda) d \ln \lambda$$

Polymer blend



The relaxation spectrum H(λ) is uniquely defined for a material

Boltzmann superposition principle

- The stress in a material is determined by the entire loading history
- Each additional deformation makes an indepedendent and additive contribution to the total stress

$$d\underline{\underline{\tau}} = G\, d\underline{\underline{\gamma}}$$

$$d\underline{\underline{\tau}} = G \frac{d\underline{\underline{\gamma}}}{dt} dt = G\, \dot{\underline{\underline{\gamma}}}\, dt$$

$$\underline{\underline{\tau}}(t) = \int_{-\infty}^{t} G(t-t')\, \dot{\underline{\underline{\gamma}}}(t')\, dt'$$

Once we know the relaxation modulus, we can determine the stress response to any arbitrary flow history.

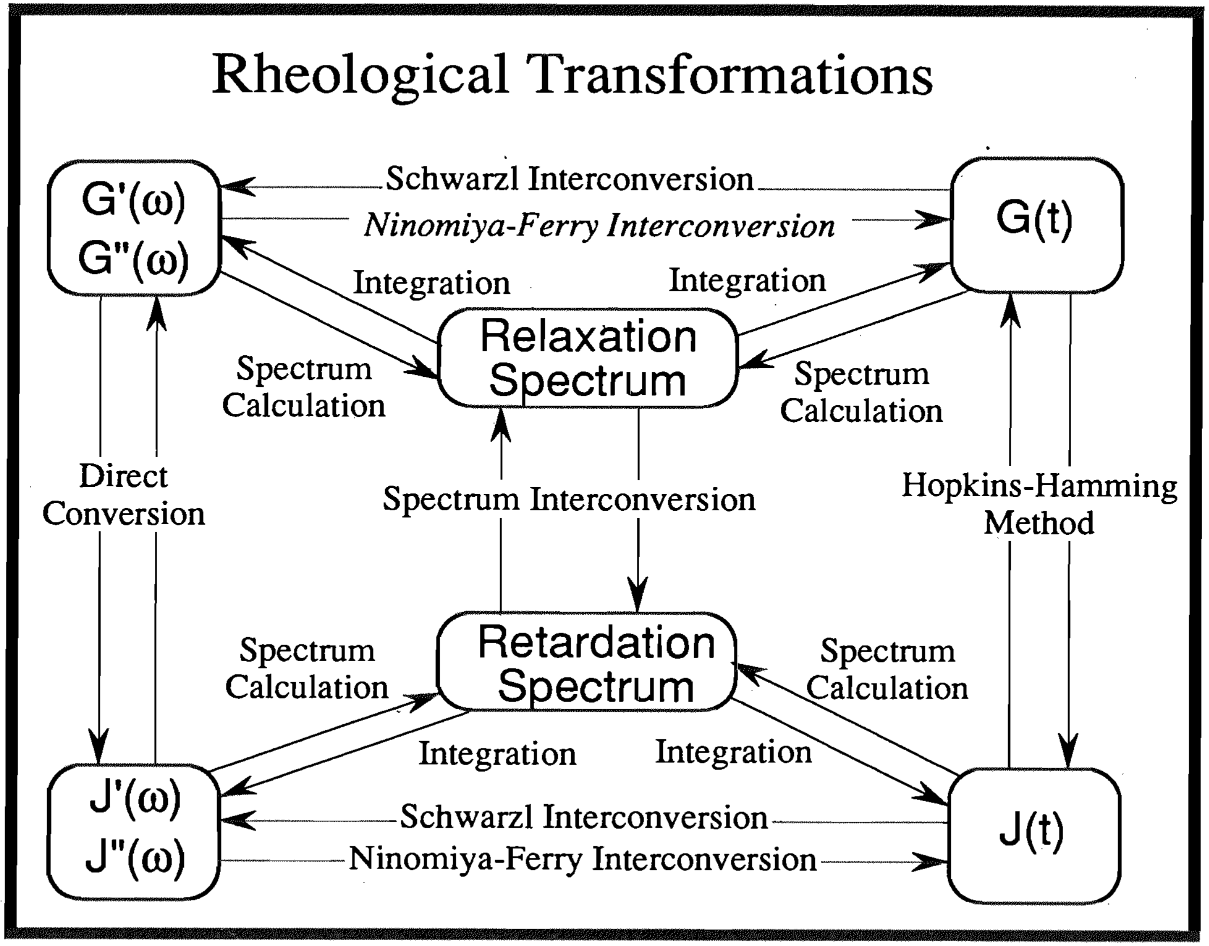
Generalized linear viscoelastic model

$$\underline{\underline{\tau}}(t) = -\int_{-\infty}^{t} G(t-t^{'})\,\underline{\underline{\dot{\gamma}}}(t')\,dt^{'}$$

If: $$G(t) = \frac{\tau(t)}{\gamma_0} = G_0 \exp(-t/\lambda)$$ Maxwell model

The Maxwell model is one example of a class of linear viscoelastic models.

3. Linear viscoelasticity

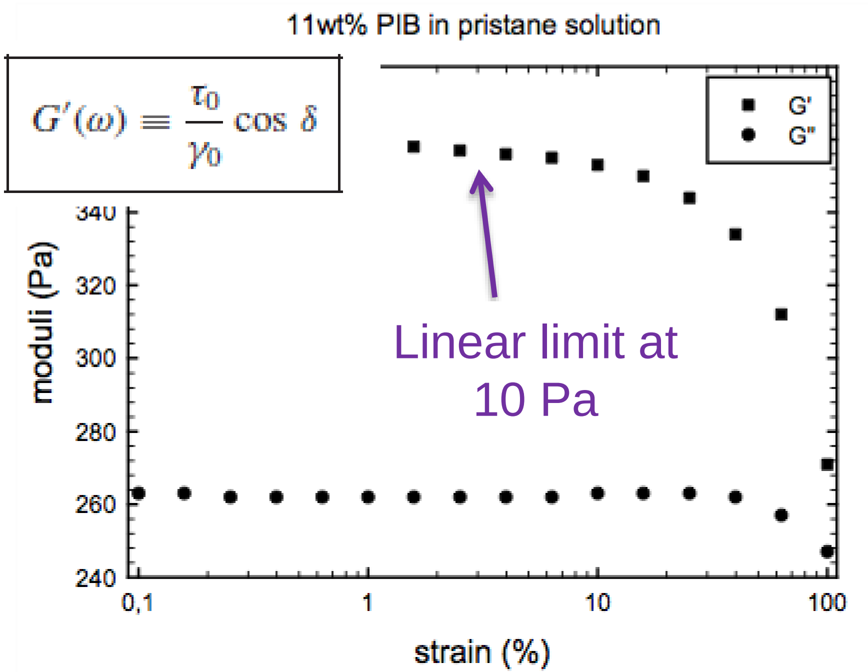


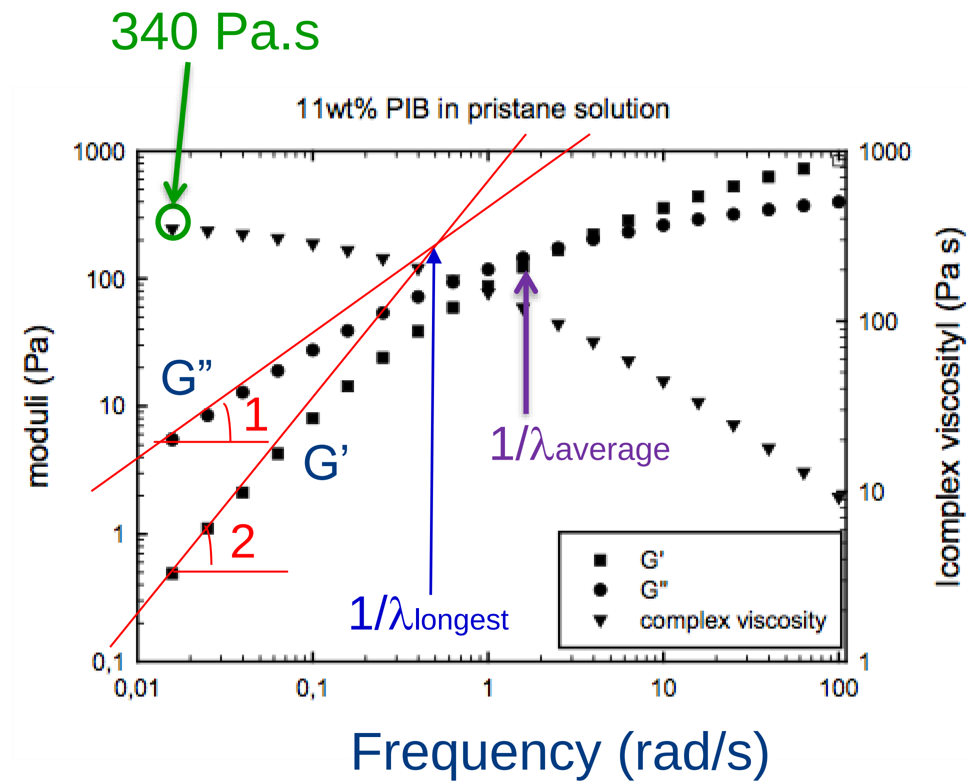
Morrison, Understanding Rheology, 2001

Ferry, Viscoelastic properties of polymers, 1970

3. Linear viscoelasticity

Oscillatory shear rheology





Slopes at low frequencies:

$$G^{'}(\omega) = \frac{G_0 \lambda^2 \omega^2}{1+\lambda^2 \omega^2} \qquad G^{''}(\omega) = \frac{G_0 \lambda \omega}{1+\lambda^2 \omega^2}$$

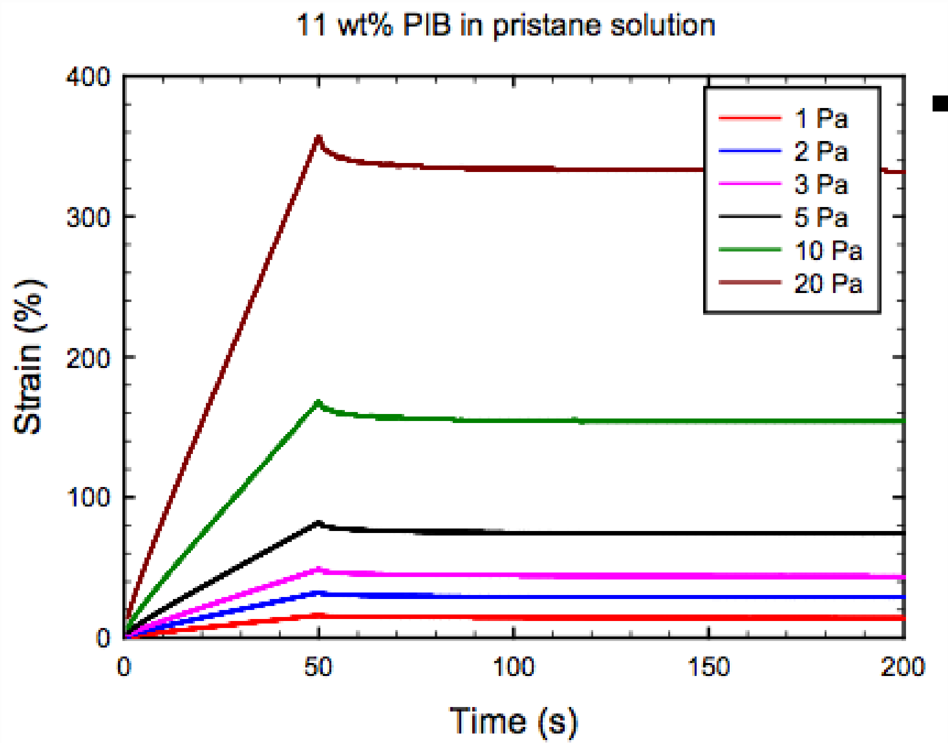
$\lambda_{average}$ = 0,5 s

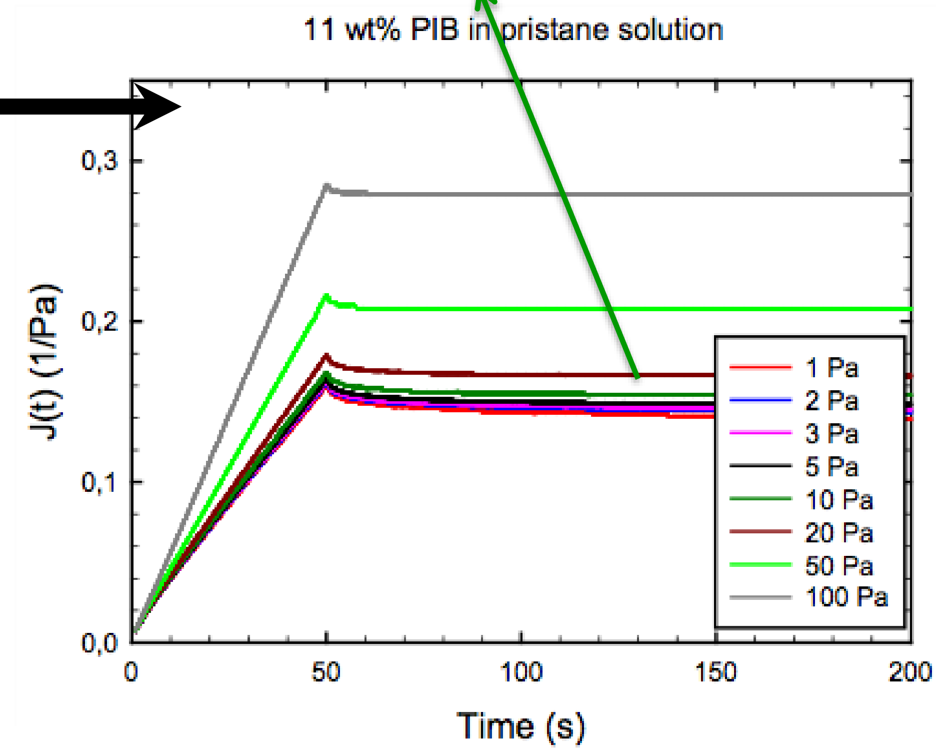
$\lambda_{longest}$ = 2 s

Both the average and the longest relaxation time can be estimated from the small amplitude oscillatory data.

Creep-recovery

Linear behavior limit between 10 and 20 Pa



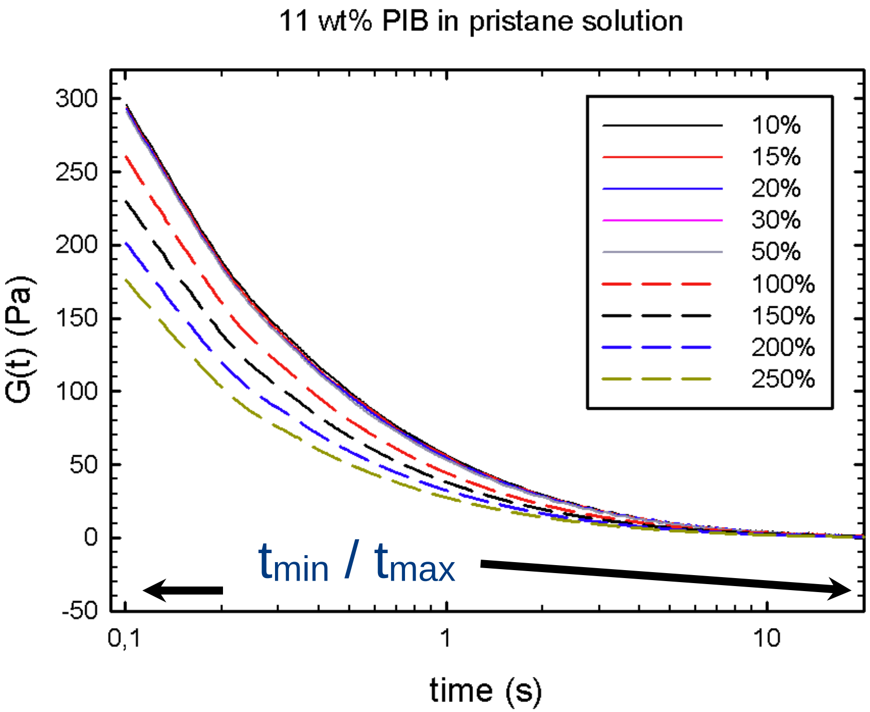


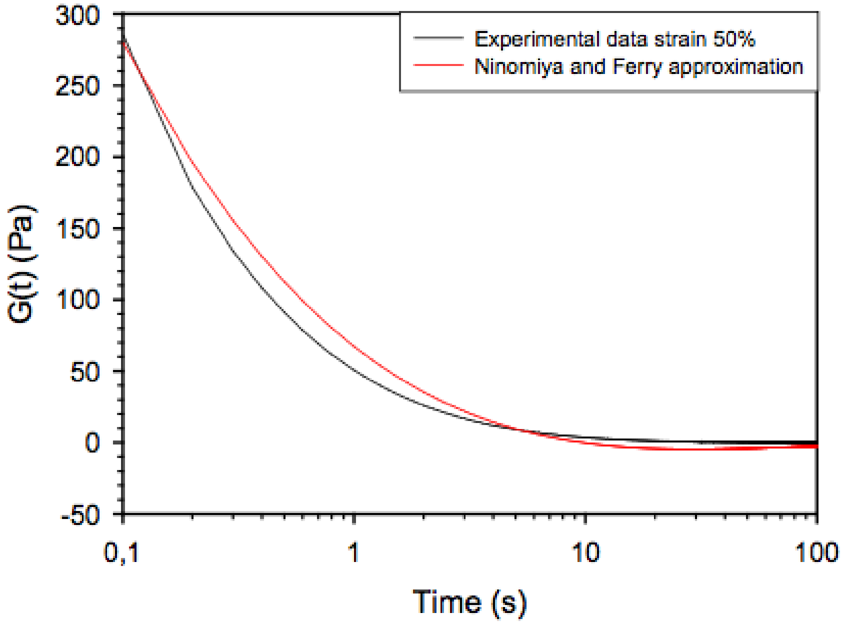
$$J(t) = J_r(t) + \frac{t}{\eta_0}$$

$$\eta_0 = 333 Pa.s$$

Creep-recovery allows to determine the longest relaxation time and the zero-shear viscosity.

Stress relaxation





$$G(t) = G'(\omega) - 0.4G''(0.4\omega) + 0.014G''(10\omega)|_{\omega=1/t}$$

Ninomiya and Ferry approximation

Oscillatory data can be converted into a stress relaxation modulus.

Relaxation spectrum

$$G'(\omega) = \int_{-\infty}^{\infty} \frac{H(\lambda)\omega^2\lambda^2}{1+\omega^2\lambda^2} d\ln\lambda$$

$$G''(\omega) = \int_{-\infty}^{\infty} \frac{H(\lambda)\omega\lambda}{1+\omega^2\lambda^2} d\ln\lambda$$

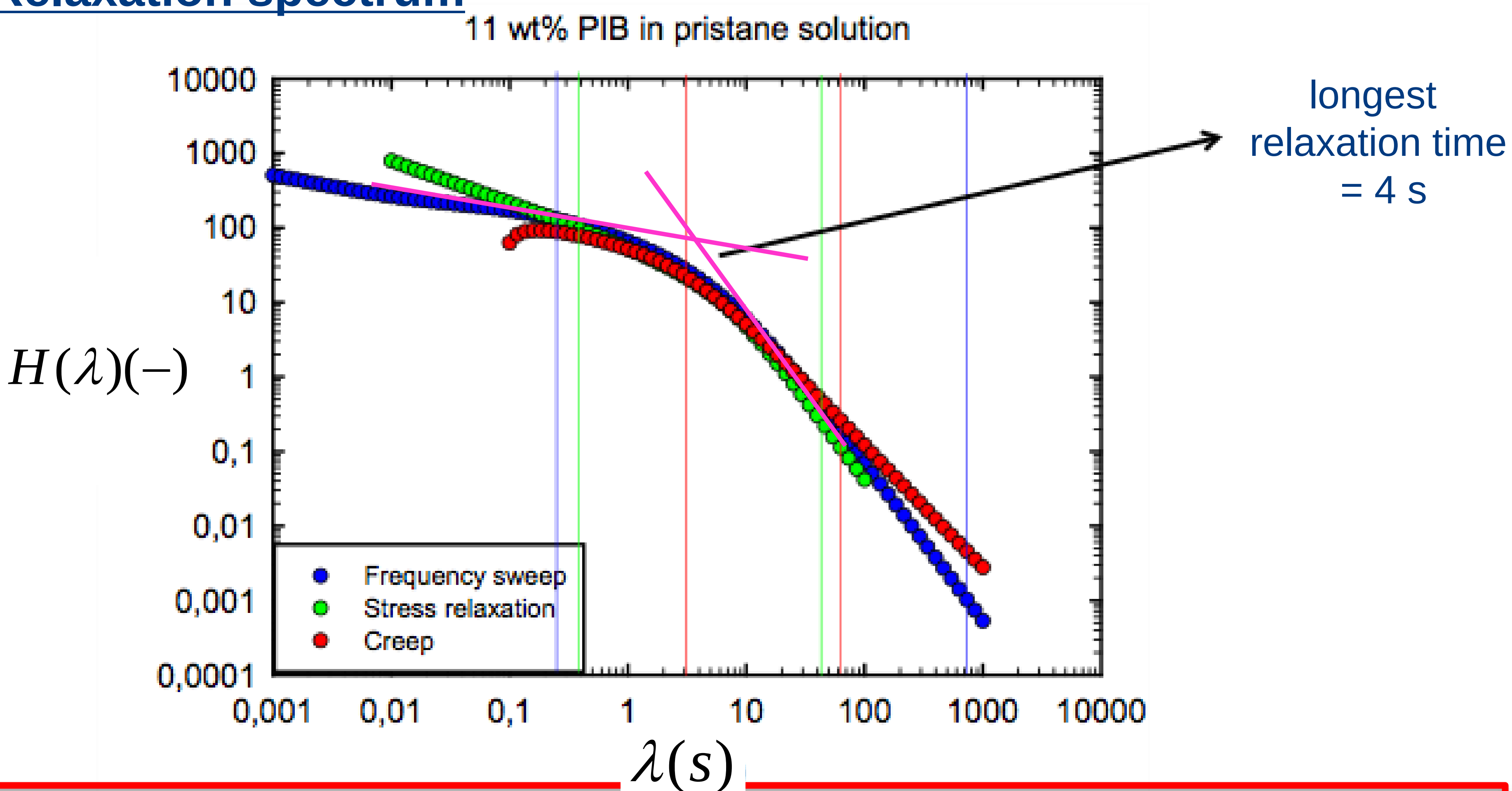
$$G(t) = \int_{-\infty}^{\infty} H(\lambda)\exp(-t/\lambda) d\ln\lambda$$

$$t = \int_{0}^{t} G(t-t')J(t')dt'$$

Ferry, Viscoelastic properties of polymers, 1970

A whole set of interconversion formula's is available.

Relaxation spectrum



The different linear viscoelastic tests contain similar information, but for a different time range.

0. Lecture overview

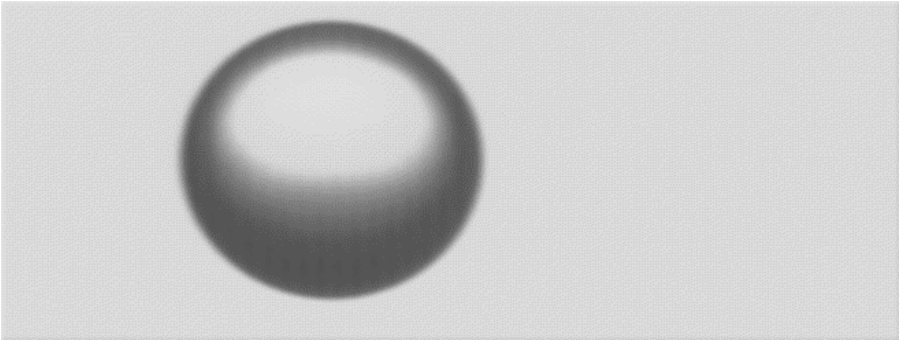
1. What is rheology?

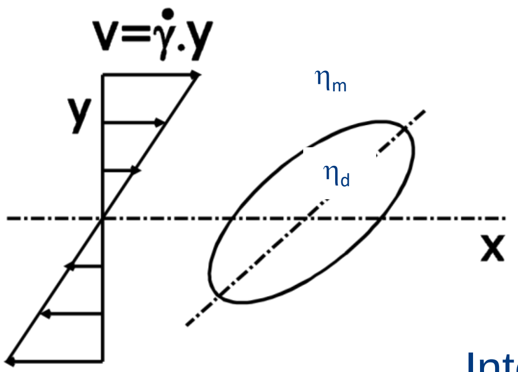
2. Rotational rheometry

3. Linear viscoelasticity

4. Application examples

Relevant parameters





$$p = \frac{\eta_d}{\eta_m}$$

Hydrodynamic stress

$$\eta_m \cdot \dot{\gamma}$$

Interfacial stress

$$\gamma_S / R$$

$$Ca = \frac{\eta_m \cdot \dot{\gamma} \cdot R}{\gamma_S}$$

Droplets deform at high capillary number

η_d: *droplet viscosity*

η_m: *matrix viscosity*

$\dot{\gamma}$: *shear rate*

R: droplet radius

γ_S: *interfacial tension*

For η_m~0.01 Pas, γ_s~10 mN/m, R~1 μm → τ~10^{-7} s

For η_m~100 Pas, γ_s~10 mN/m, R~10 μm → τ~10^{-2} s

4. Application examples

Relevant parameters

Hydrodynamic stress

$\eta_m \cdot \dot{\gamma}$

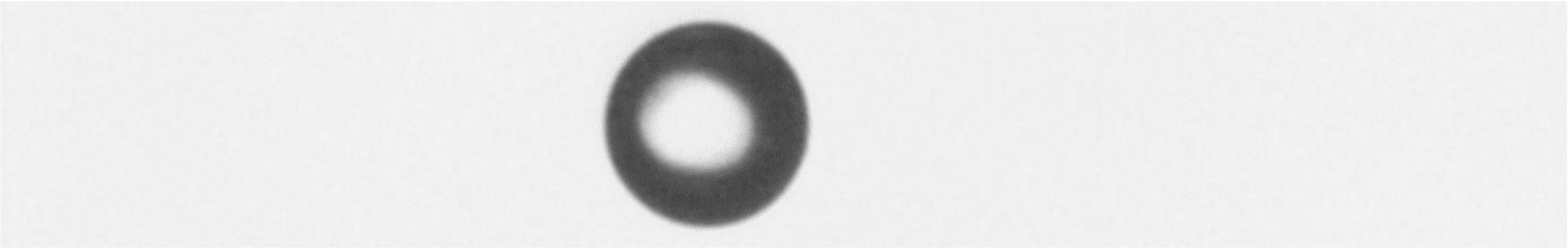
Interfacial stress

γ_s / R

$$Ca = \frac{\eta_m \cdot \dot{\gamma} \cdot R}{\gamma_s}$$

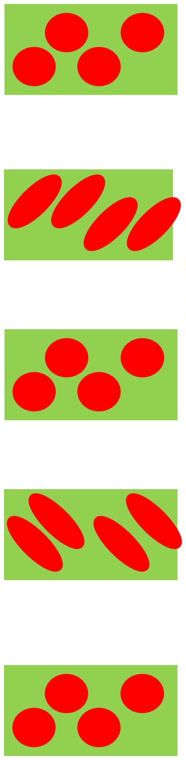
Droplet retraction time, λ

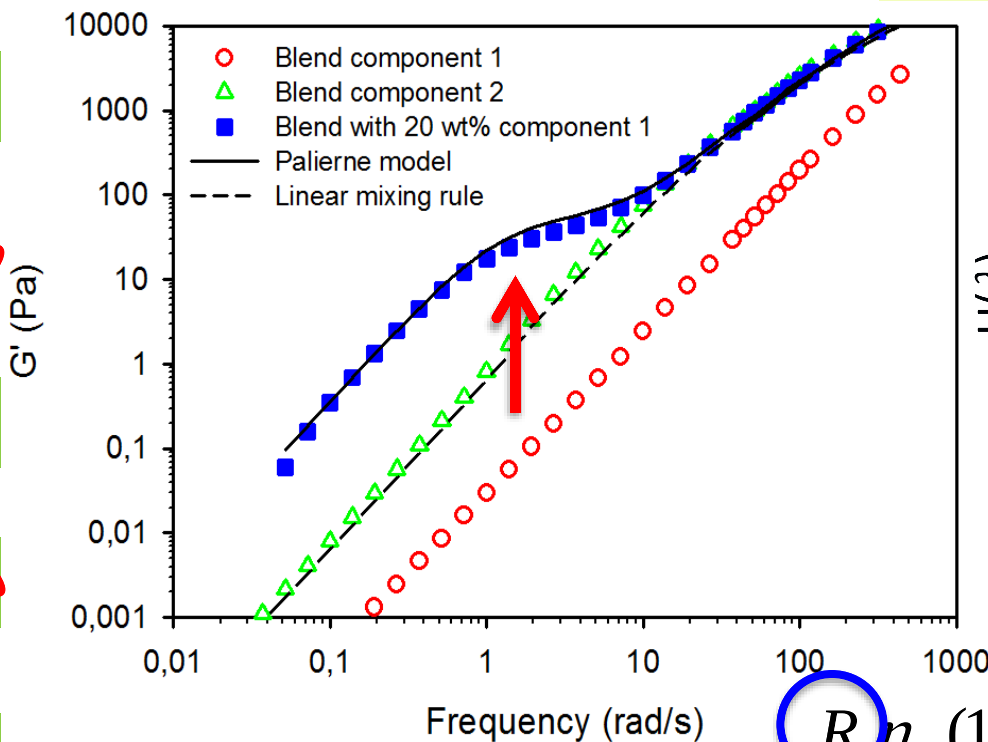
$$\lambda = \frac{R\eta_m}{\gamma_s}$$

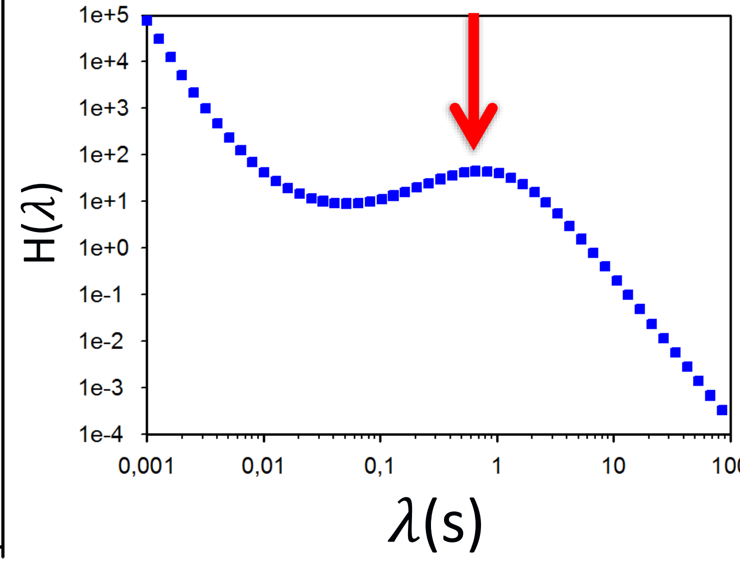


Extra elasticity due to the interface

20% PIB in PDMS
Cone-Plate







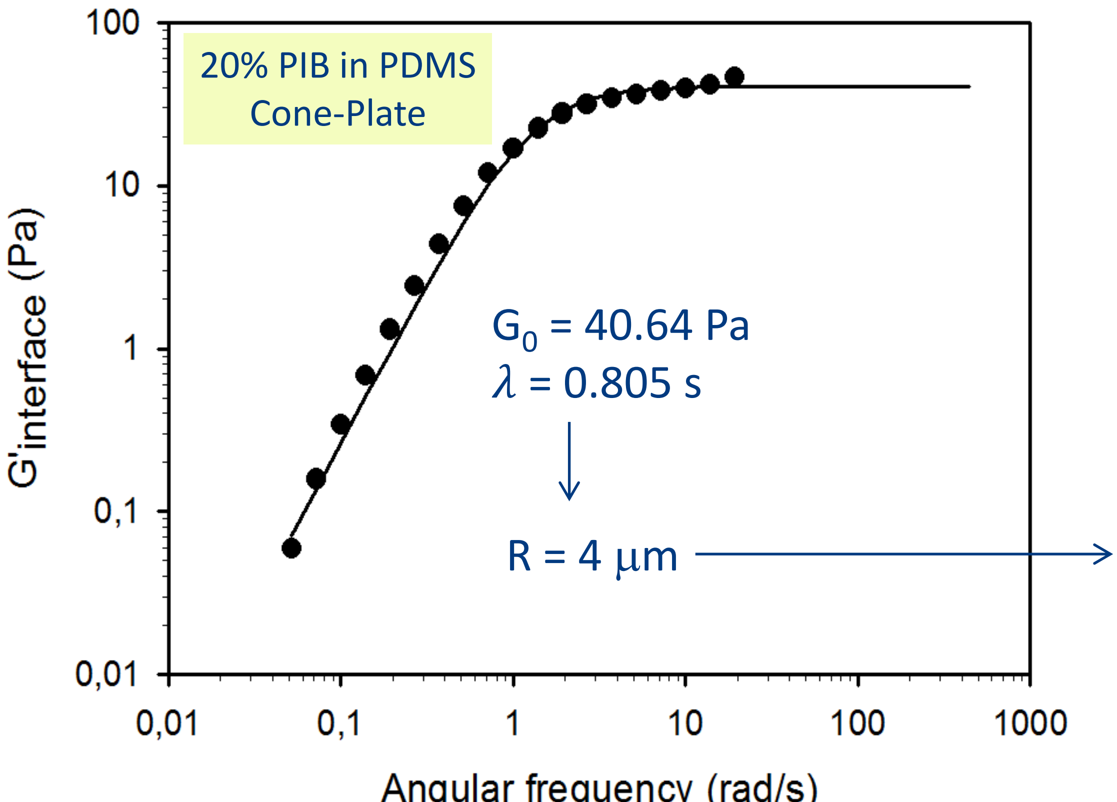
$$\lambda = \frac{R}{\gamma_s}\frac{\eta_m(19p+16)(2p+3-2\phi(p-1))}{10(p+1)-2\phi(5p+2)}$$

The droplet size can be determined from the characteristic relaxation time of the blend.

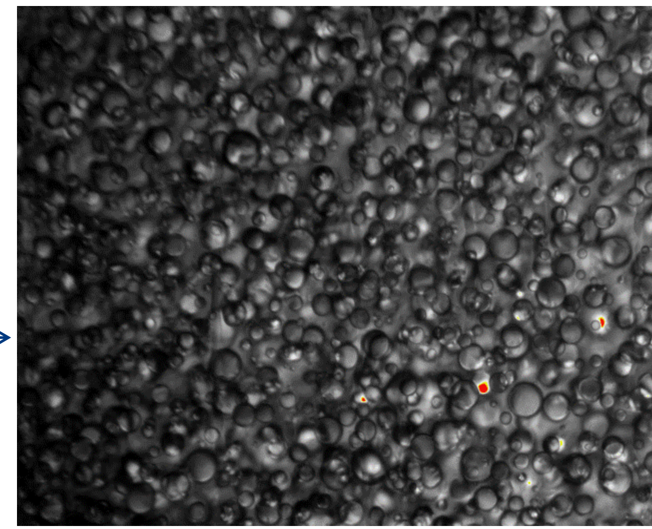
Cardinaels and Moldenaers, Encyclopedia of Polymeric Nanomaterials, 2015

Describing the extra elasticity with the Maxwell model

$$G'_{blend} = (1-\phi)G'_{matrix} + \phi G'_{droplet} + G'_{interface}$$



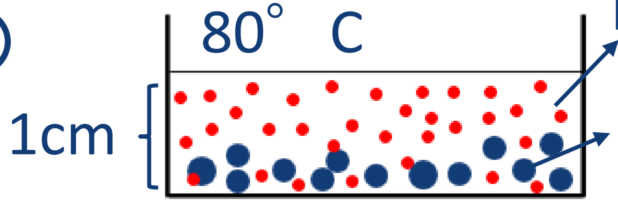
$$G'_{interface} = \frac{G_0\lambda^2\omega^2}{1+\lambda^2\omega^2}$$



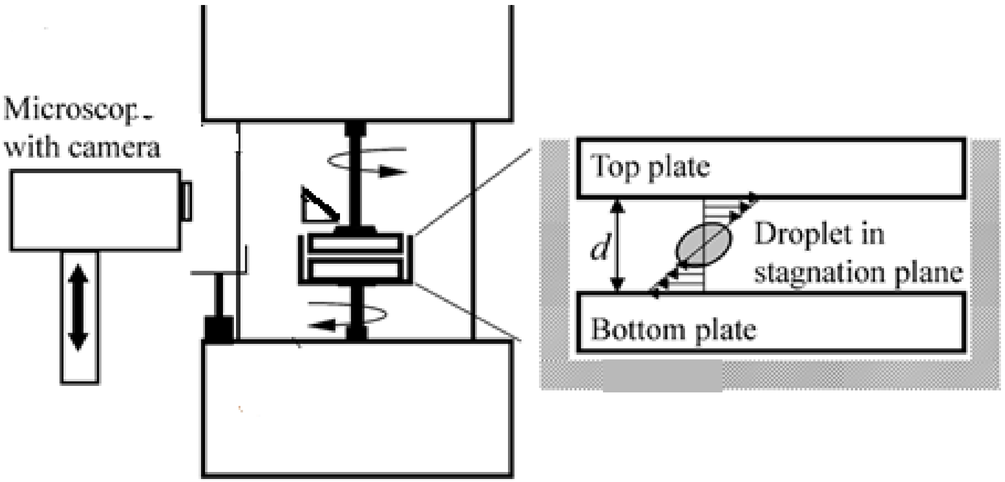
The interfacial contribution to the elasticity can be well-described by a one-mode Maxwell model.

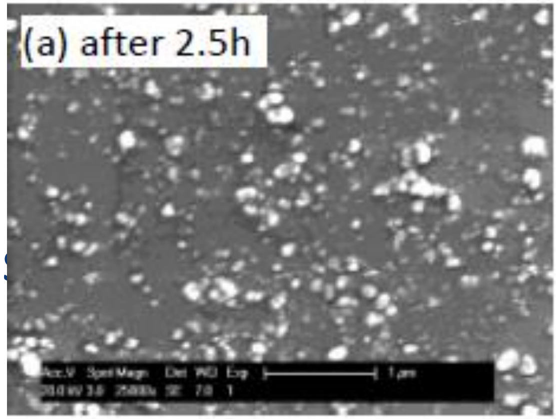
Droplet deformation and breakup

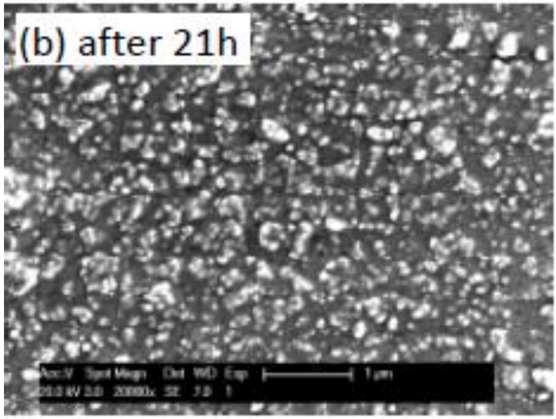
①

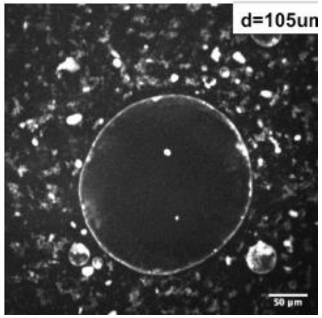


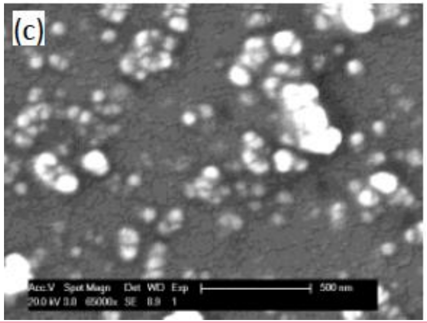
PIB suspension of 1wt% …



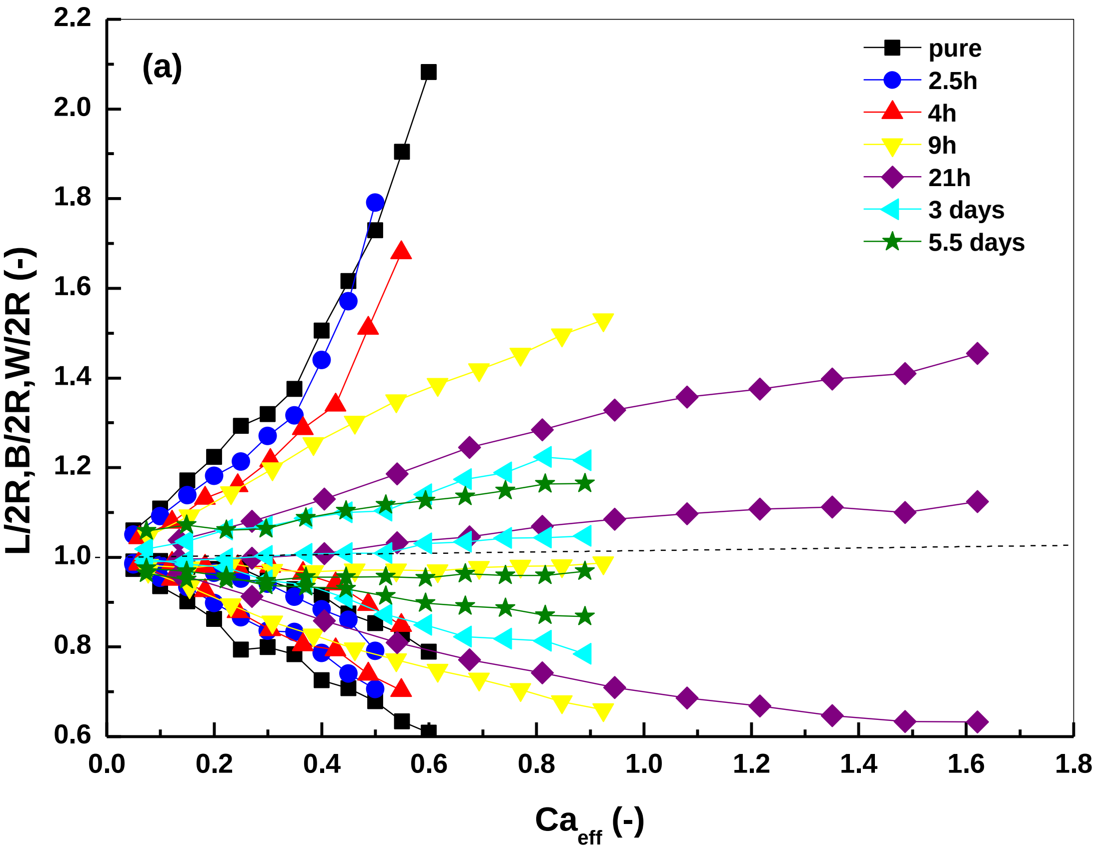


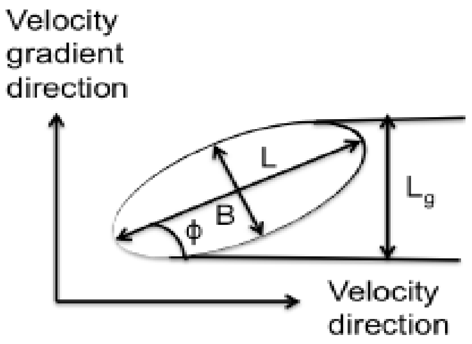


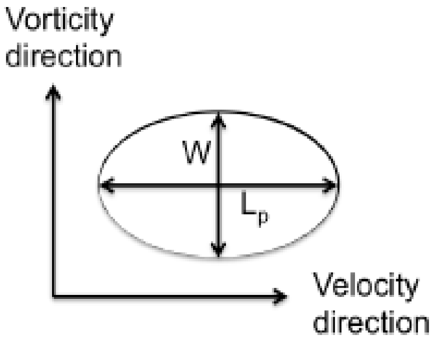




Droplet deformation and breakup

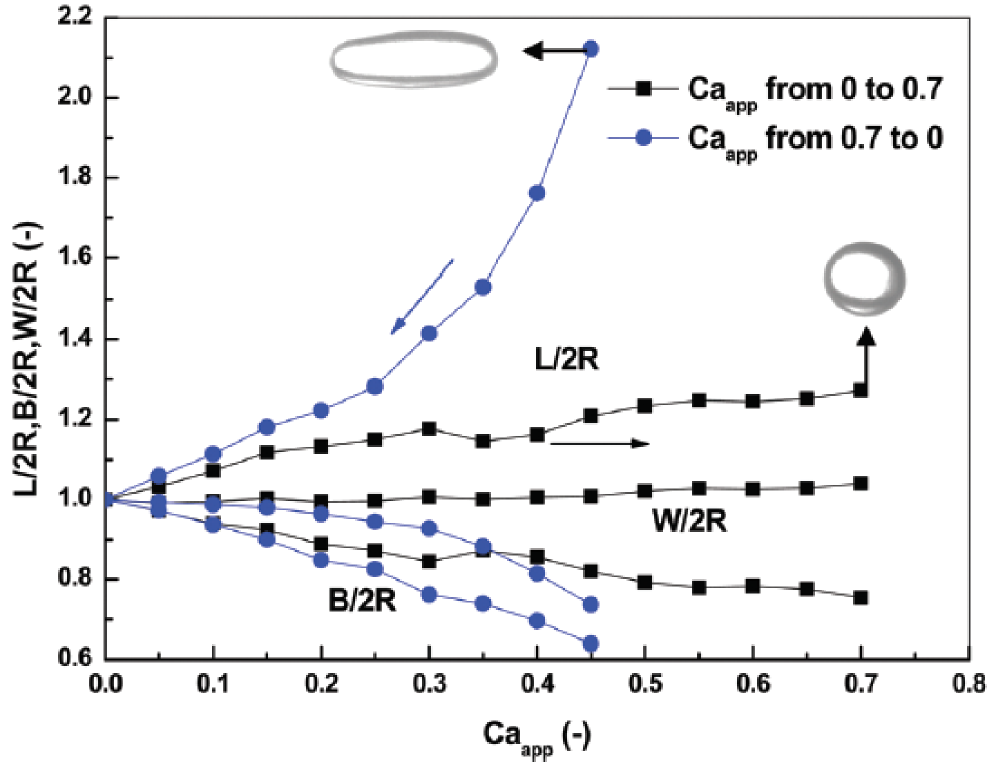


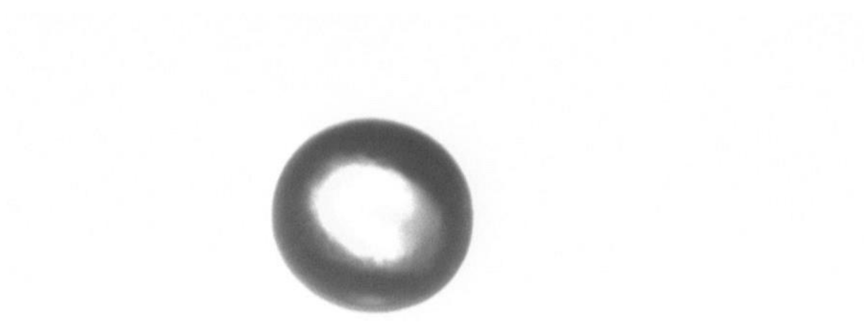


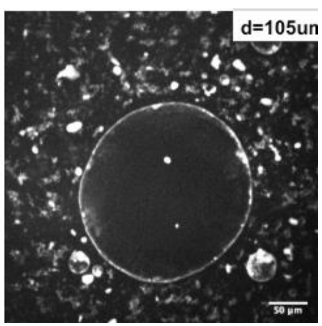


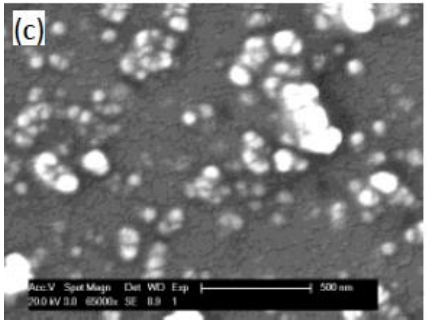
$$Ca = \frac{\eta_m \dot{\gamma} R}{\alpha}$$

Droplet deformation and breakup









$$Ca = \frac{\eta_m \dot{\gamma} R}{\alpha}$$

Link with interfacial rheology