Linear Viscoelasticity

(its all a matter of time)

NORDIC RHEOLOGY SOCIETY

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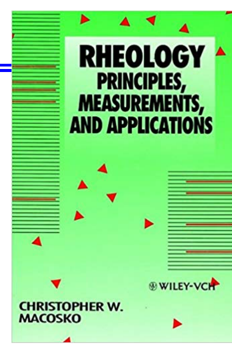
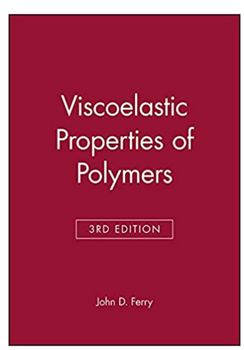
Introduction to Viscoelasticity | Göteborg, Sweden | Aug. 21 2019

Key References

- Rheology: Principles, Measurements and Applications
  - C.W. Macosko (Wiley, 1994)
- Viscoelastic Properties of Polymers
  - J.D. Ferry (3rd Edition, 1980)

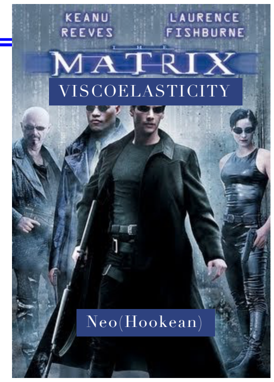




LVE-2

The Goal of Today…
(in honor of 20th anniversary)

- *"I'm going to learn ~~Jiu-Jitsu~~ VISCOELASTICITY?*



How to Learn Viscoelasticity

Before…

After… *want some more*???

LVE-3

So What is a Complex Fluid?

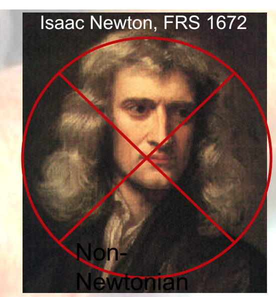
- Complex fluids possess an underlying microstructure that can be affected by (and in turn then affect) a flow field
  - Gives rise to *Visco-Elasticity*
- Examples include:
  - Polymer solutions, polymer melts, liquid crystals
  - Foams, gels, bubbly-liquids,
  - Suspensions, emulsions, slurries, mud..
  - Food stuffs, paints, adhesives and other consumer products
- Basically everything except air, oil, water!
- These fluids violate Newton's law of viscosity :

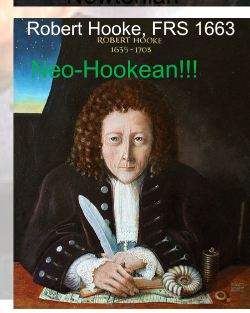
$$\tau_{yx} = \mu \frac{\partial v_x}{\partial y} \qquad \boldsymbol{\tau} = \mu \left\{ \nabla \boldsymbol{v} + \nabla \boldsymbol{v}^t \right\}$$

•**Rheology**: study of the material properties of complex fluids in specified/known flow fields

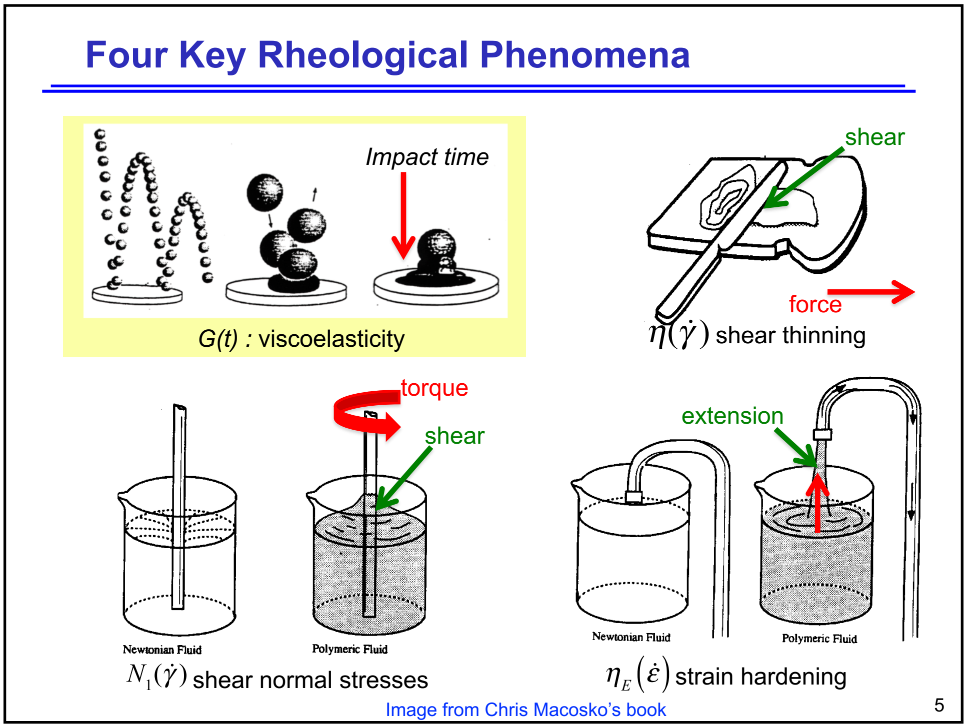
•**Non-Newtonian Fluid Dynamics**: self-consistent solutions of conservation of mass, momentum PLUS a *constitutive model* (rheological equation of state)

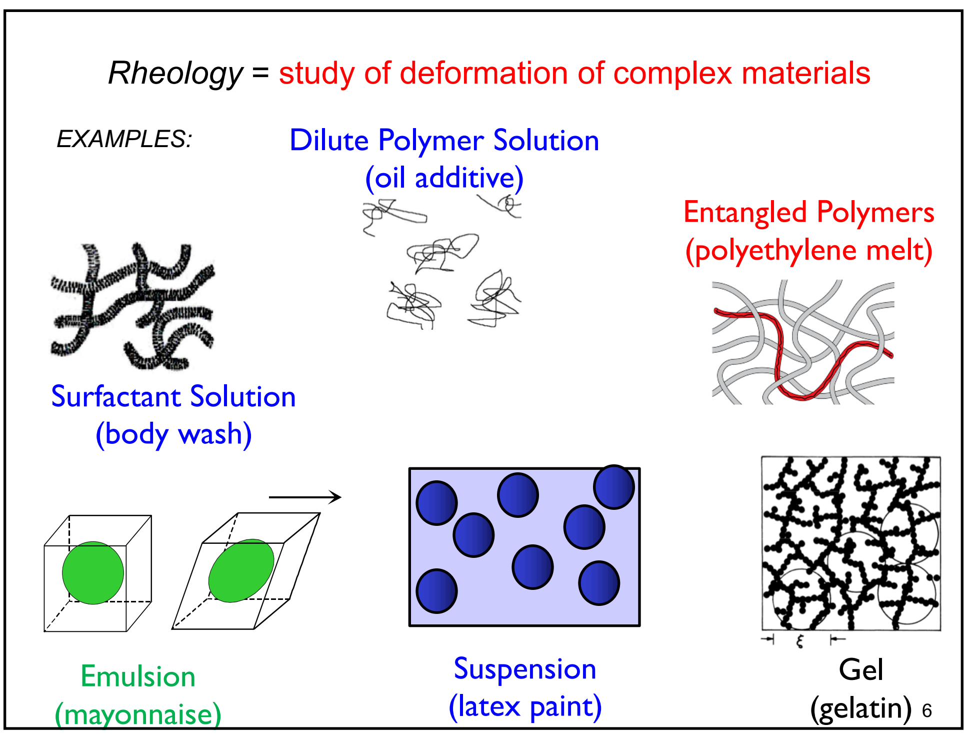
For example: "Neo-Hookean Dumbbell Model"





*Posthumous Portrait by Rita Greer (Wikipedia)

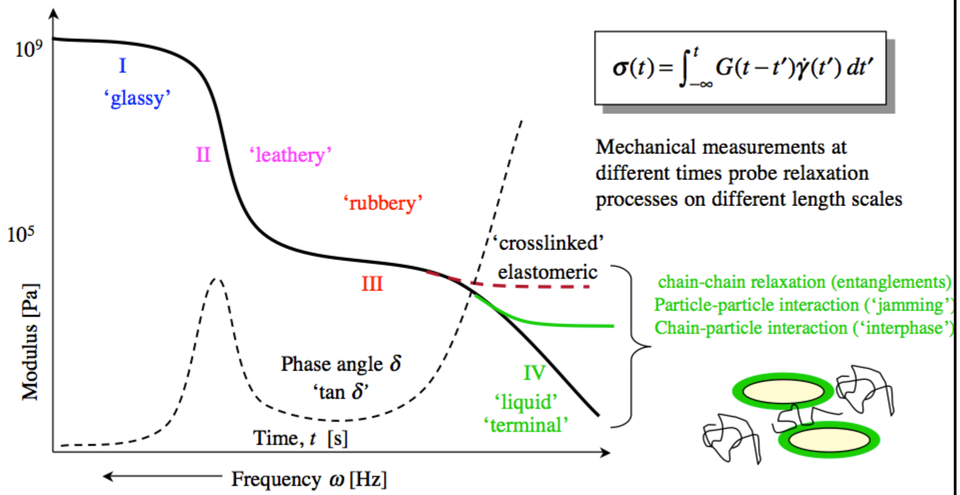

Four Key Rheological Phenomena
Impact time
G(t) : viscoelasticity
shear
force
$\eta(\dot{\gamma})$ shear thinning
torque
shear
Newtonian Fluid
Polymeric Fluid
$N_1(\dot{\gamma})$ shear normal stresses
extension
Newtonian Fluid
Polymeric Fluid
$\eta_E(\dot{\varepsilon})$ strain hardening
Image from Chris Macosko's book
5


Rheology = study of deformation of complex materials
EXAMPLES:
Dilute Polymer Solution
(oil additive)
Entangled Polymers
(polyethylene melt)
Surfactant Solution
(body wash)
Emulsion
(mayonnaise)
Suspension
(latex paint)
ξ
Gel
(gelatin)
6

Probing the Viscoelastic Response of Polymeric Materials

- Viscoelastic materials are characterized by a relaxation modulus *G(t)* and a fading memory of previous deformations
- They typically show four clearly identifiable zones of mechanical behavior:

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



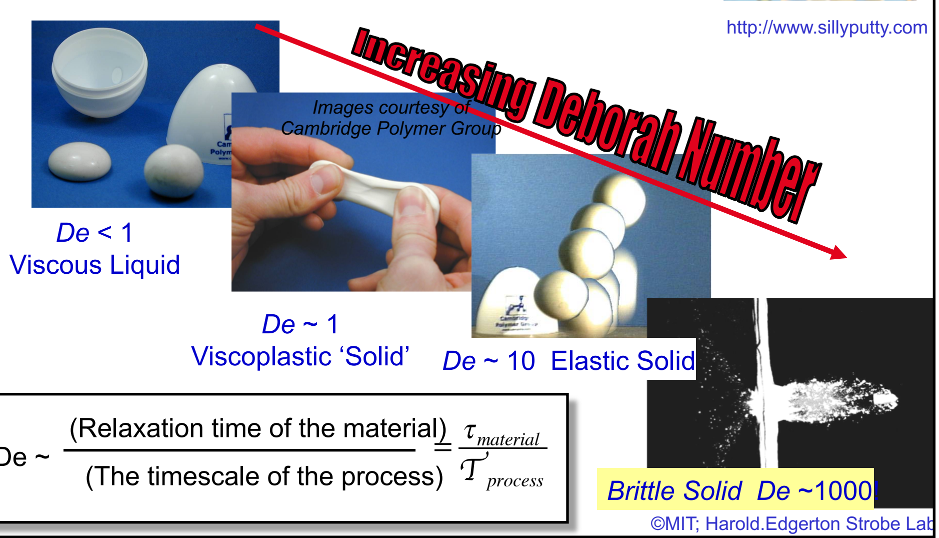
Mechanical measurements at different times probe relaxation processes on different length scales

- Frequency and time are Fourier transforms of each other $G^*(\omega) \Rightarrow |G(\omega)|, \tan\delta$

Natural Time Scale of Complex Fluids

http://www.sillyputty.com

- Natural time scale $\lambda \equiv \tau_{material} \approx 10$ sec.
- The **Deborah number** is a dimensionless measure compared with the time scale of the deformation...

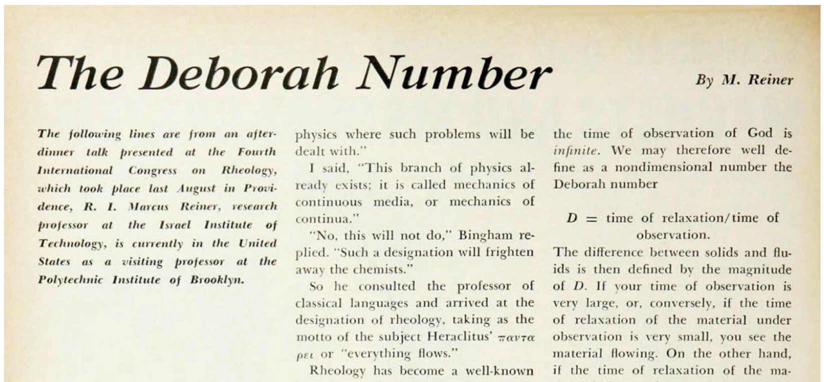


$$De \sim \frac{\text{(Relaxation time of the material)}}{\text{(The timescale of the process)}} = \frac{\tau_{material}}{\mathcal{T}_{process}}$$

Origin of the Deborah number

see M. Reiner, Physics Today, January 1964, p. 62

Judges 5:5 famous song after the victory over the Philistines, she sang, "The mountains flowed before the Lord."



The Deborah Number

By M. Reiner

The following lines are from an after-dinner talk presented at the Fourth International Congress on Rheology, which took place last August in Providence, R. I. Marcus Reiner, research professor at the Israel Institute of Technology, is currently in the United States as a visiting professor at the Polytechnic Institute of Brooklyn.

physics where such problems will be dealt with."

I said, "This branch of physics already exists; it is called mechanics of continuous media, or mechanics of continua."

"No, this will not do," Bingham replied. "Such a designation will frighten away the chemists."

So he consulted the professor of classical languages and arrived at the designation of rheology, taking as the motto of the subject Heraclitus' *παντα ρει* or "everything flows."

Rheology has become a well-known

the time of observation of God is *infinite*. We may therefore well define as a nondimensional number the Deborah number

D = time of relaxation/time of observation.

The difference between solids and fluids is then defined by the magnitude of D. If your time of observation is very large, or, conversely, if the time of relaxation of the material under observation is very small, you see the material flowing. On the other hand, if the time of relaxation of the ma-

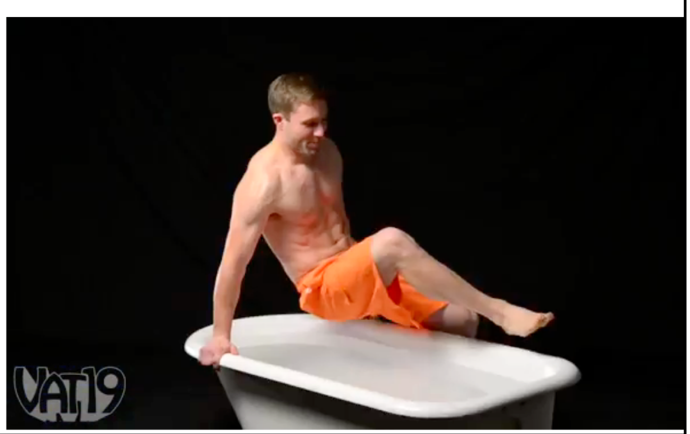
9

A creep test:

A creep test (constant load) on silly putty

Another creep test (silicone gum!!)

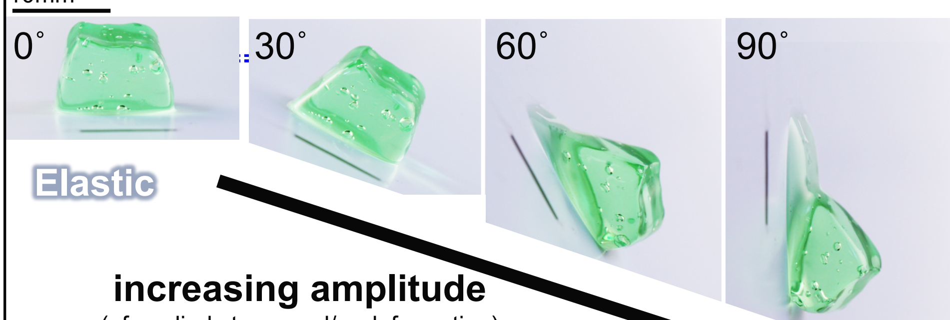
From Youtube:



USGS Image Library "Byrd Glacier Flow". Photo: Dr Bill Servais
(http://www.rosssea.info/glaciers.html)

11

10mm



Elastic

increasing amplitude
(of applied stress and/or deformation)

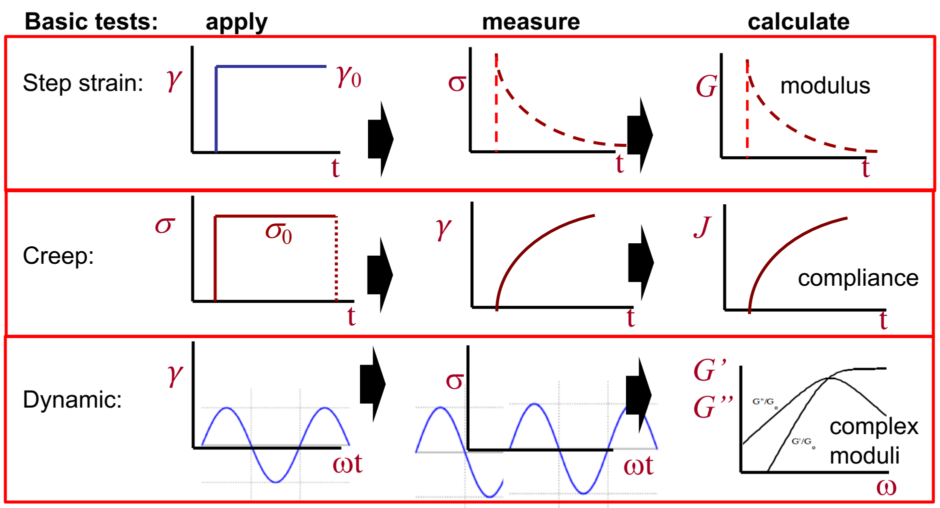
Viscous

"**Linear viscoelasticity**" is the limit of small loading amplitude (does not disrupt microstructure)

ideal elastic : $\sigma = G\gamma$ $\leftarrow$ viscoelastic $\rightarrow$ ideal viscous : $\sigma = \eta \frac{d\gamma}{dt} = \eta\dot{\gamma}$

ideal elastic : $\sigma = G\gamma$ ← **viscoelastic** → ideal viscous : $\sigma = \eta \dfrac{d\gamma}{dt} = \eta\dot{\gamma}$

stress *strain* (old literature: *elastico-viscous*) *strain-rate* *"shear rate"*



Stress Relaxation Modulus, *G*(*t*)

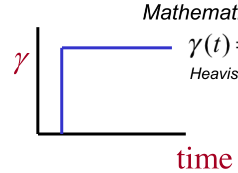
Impose: step strain $\gamma_0 = \text{constant}$

(How? Use a rheometer)

Mathematically:

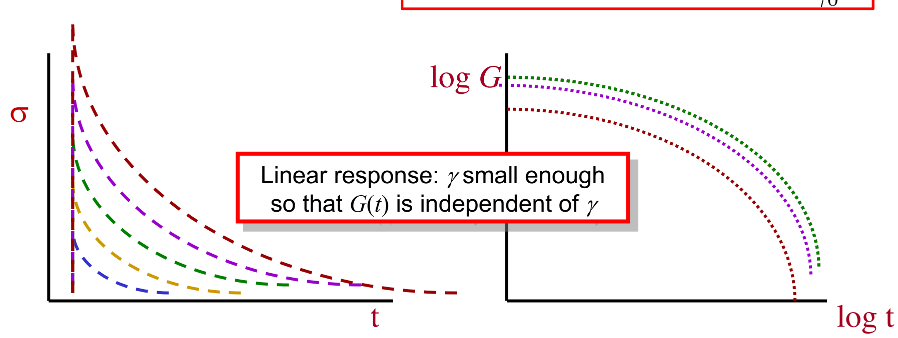
$\gamma(t) = \gamma_0 H(t)$

Heaviside Step Function

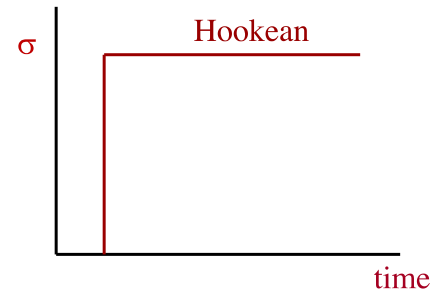


Observe : stress $\sigma(t, \gamma_0)$

Material function : $G(t, \gamma_0) = \dfrac{\sigma(t, \gamma_0)}{\gamma_0}$

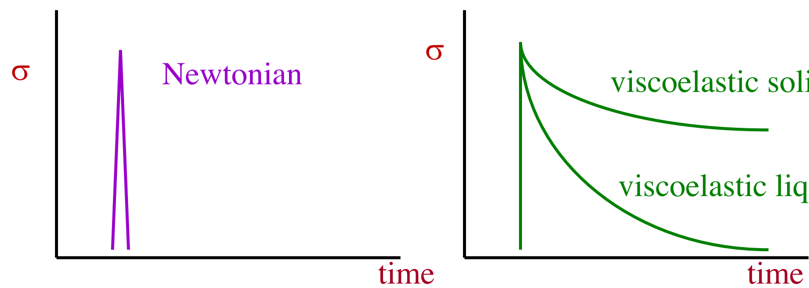


Stress Relaxation Modulus, *G*(*t*), Limiting Cases



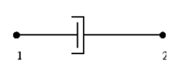
$$G(t,\gamma_0) = \frac{\sigma(t,\gamma_0)}{\gamma_0}$$

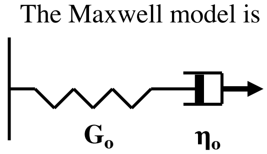
Experimental difficulty:
True "step" displacement impossible
(instrument inertia at short times)



LVE-15

Maxwell Viscoelastic Model

- Let's motivate these linear tests using a simple model
- Elastic solid: $\sigma_e = G\gamma$  spring
- Viscous liquid: $\sigma_v = \eta\dot{\gamma}$  dashpot
- The Maxwell model is a *superposition* of these two:



total strain : $\gamma = \gamma_e + \gamma_v$

stress is equal : $\sigma = \sigma_e = \sigma_v$

$$\sigma + \frac{\eta_0}{G_0}\frac{d\sigma}{dt} = \eta_0\frac{d\gamma}{dt} \rightarrow \sigma + \lambda\frac{d\sigma}{dt} = \eta_0\frac{d\gamma}{dt}$$

$\lambda = \eta_0/G_0$: relaxation time

16

Example: Maxwell Model in Step Strain

- In a step-strain experiment, the material is subjected to an instantaneous strain of magnitude γ_o
- Following the step, the strain is held fixed at this constant value and the stress is monitored in time.
- The initial stress is then $G_0\gamma_o$
- Solving the Maxwell model, we have

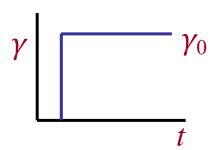
$$\sigma + \lambda \frac{d\sigma}{dt} = \eta_0 \frac{d\gamma}{dt} \quad (\frac{d\gamma}{dt} \to 0)$$

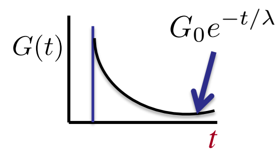
$$\sigma = \sigma(t=0)e^{-t/\lambda} = G_0\gamma_0 e^{-t/\lambda}$$

- Dividing the stress by the strain, we get the “relaxation modulus”

$$G(t) = G_0 e^{-t/\lambda}$$

- *No strain dependence*
- *Single relaxation time*

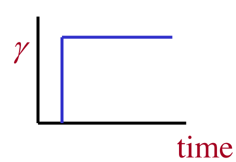




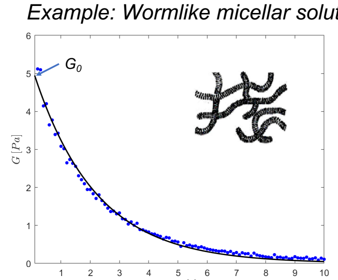
17

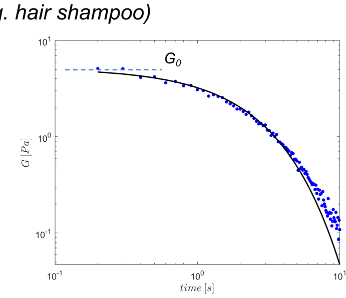
Comparing with Measurements of *G*(*t*)

1. Impose: step strain γ_0 = constant
2. Observe : stress $\sigma(t, \gamma_0)$
3. Material function : $G(t, \gamma_0) = \dfrac{\sigma(t, \gamma_0)}{\gamma_0}$
4. Choose a model and fit to data; e.g. Maxwell $G(t) = G_0 e^{-t/\lambda}$



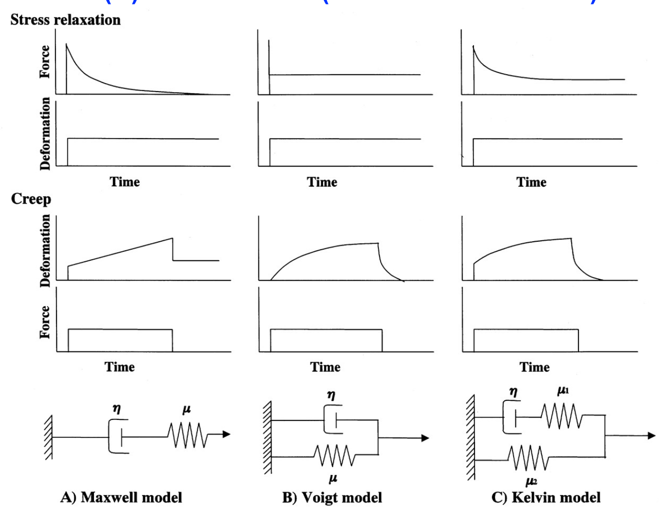
Example: Wormlike micellar solution (e.g. hair shampoo)





There are many other possible models…

Relaxation and creep function of (A) Maxwell, (B) Voigt, and (C) Kelvin model (standard linear solid).



Eiji Tanaka, and Theo van Eijden CROBM 2003;14:138-150

Critical Reviews in Oral Biology & Medicine

Generalized Maxwell Model

$$G(t) = \sum_k G_k \exp(-t/\lambda_k)$$

A spectrum of relaxation times $\{\lambda_k\}$ "Prony Series"

Extract spectrum by inversion (tricky) or
Fit to model e.g. for polymers, Rouse, Zimm, reptation…

$G(t)$ usually follows a kind of "equipartition":

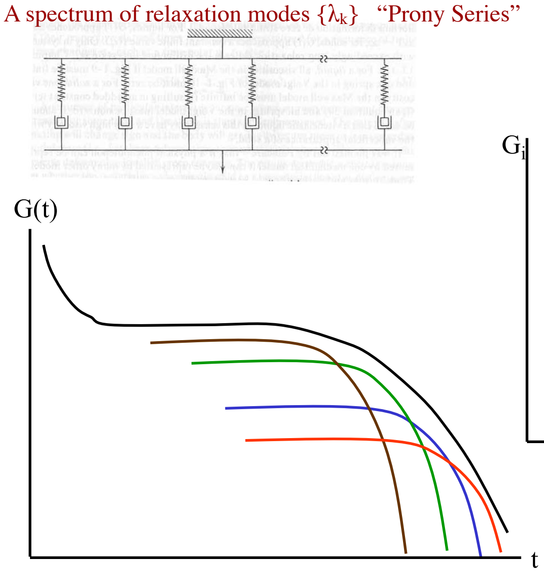
$$G(t) = \frac{\rho N_{av}}{M} k_B T \sum_k \exp(-t/\lambda_k)$$

other models: $G(t) = At^{-n}$ power-law spectra, near gel point

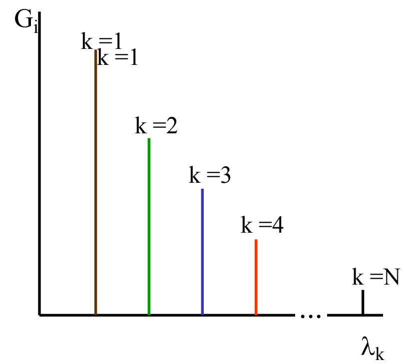
LVE-20

Fitting to a sum of exponentials

A spectrum of relaxation modes $\{\lambda_k\}$ "Prony Series"



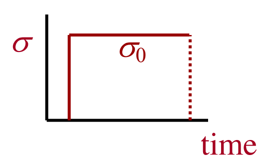
"Mechanical Spectroscopy"



LVE-21

Creep Compliance, $J(t)$

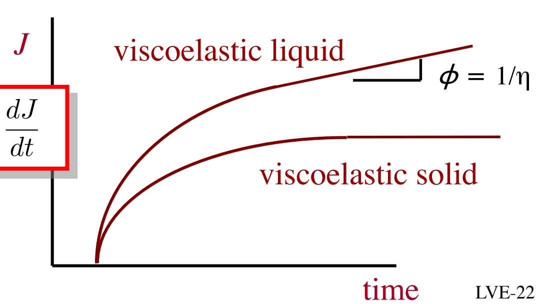
$$\text{Impose: step stress } \sigma_0 = \text{constant}$$



$$\text{Observe: strain } \gamma(t, \sigma_0)$$

$$\text{Material function}: J(t, \sigma_0) = \frac{\gamma(t, \sigma_0)}{\sigma_0}$$

$$\text{Fluidity}: \phi(t, \sigma_0) = \frac{\dot{\gamma}(t, \sigma_0)}{\sigma_0} = \frac{dJ}{dt}$$



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