Rheology

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Rheology

Rheology = the study of flow and deformation of matter.

Water, tar, syrup, shampoo, shaving foam, cream, paint, wet sand, toothpaste, ketchup, yoghurt, mayonnaise display different responses to deformation.

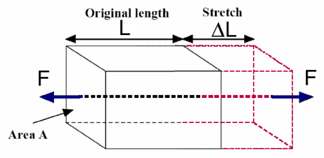
Rheology measures liquid structure and its dynamics.

Concepts: Force - Extension

Relation between force and extension - Hooks law

$$F(\Delta L) = k\Delta L$$

Concepts: Stress - Strain



Strain (dimensionless)

$$\epsilon = \frac{\text{stretch}}{\text{original length}} = \frac{\Delta L}{L}$$

Stress (dimension pressure)

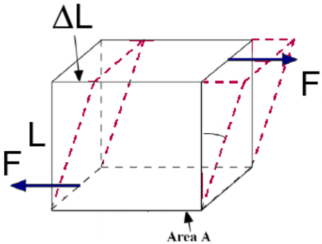
$$\sigma = \frac{\text{force}}{\text{current area}} = \frac{F}{A}$$

Hookian solid

$$\sigma = Y\epsilon$$

Y is the (Young) modulus, and corresponds to the spring constant in Hooks law.

Shearing Solid



Strain

$$\epsilon = \frac{\text{stretch}}{\text{original length}} = \frac{\Delta L}{L}$$

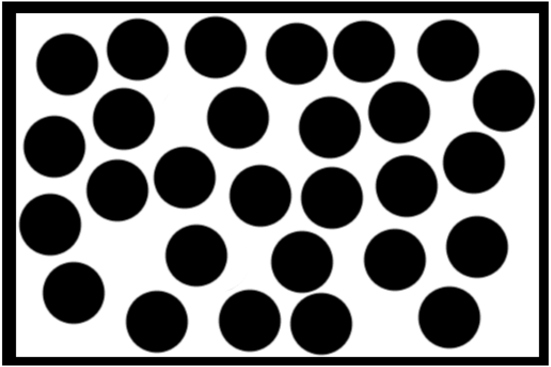
Hookian solid

$$\sigma(\epsilon) = G\epsilon$$

Stress depends on instantaneous deformation. G is the shear modulus.

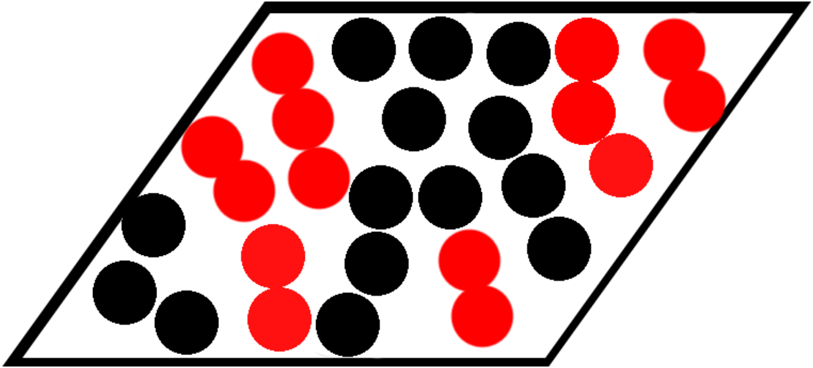
Molecular explanation of elasticity

Structure of solid



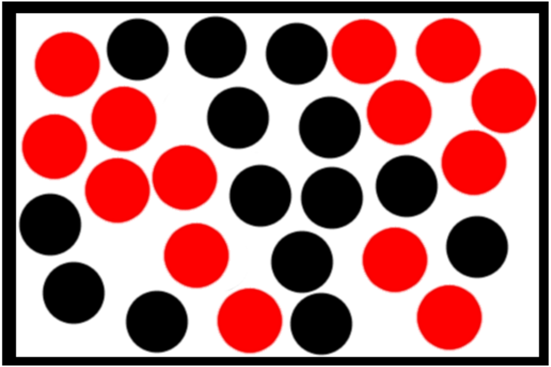
Molecular explanation of elasticity

Structure after shear, high deformation energy stored in configuration

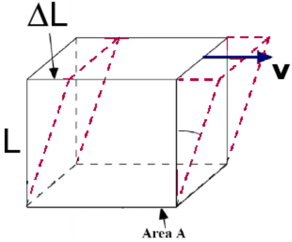


Molecular explanation of elasticity

Deformation energy released by returning to original structure.



Shearing Liquid



Strain ($\Delta L = vt$)

$$\epsilon(t) = \frac{\Delta L}{L} = \frac{vt}{L}$$

Strain rate

$$\dot{\epsilon} = \frac{\partial \epsilon}{\partial t} = \frac{v}{L}$$

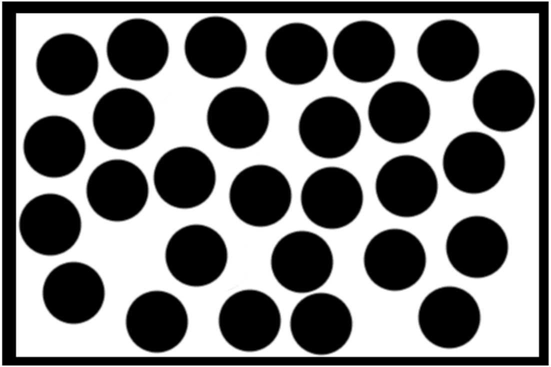
Newtonian liquid

$$\sigma(\dot{\epsilon}) = \eta \dot{\epsilon}$$

Stress depends on instantaneous rate of deformation. η is the shear-viscosity.

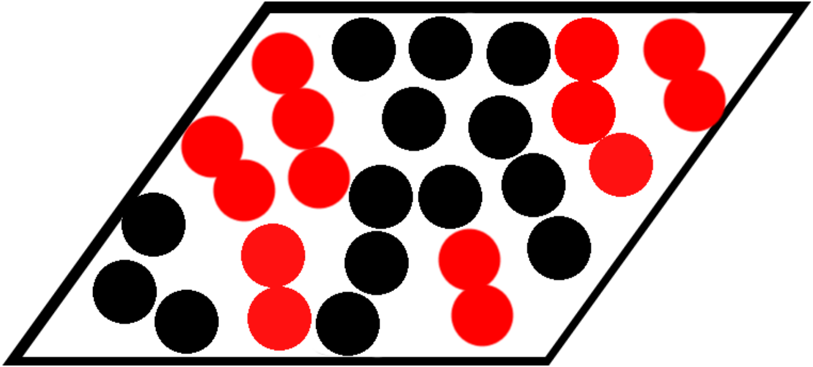
Molecular explanation of viscosity

Structure of liquid



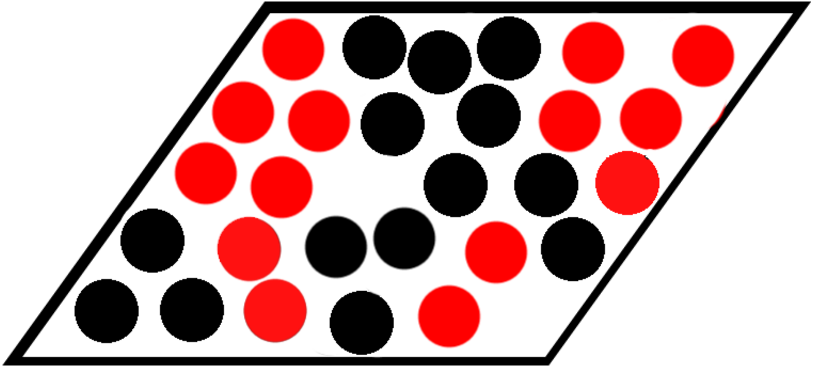
Molecular explanation of viscosity

Structure of liquid just after shear, high energy



Molecular explanation of viscosity

Structure of liquid after equilibration = as before, energy dissipated



Liquid/Soft Matter/Solid

Solids are elastic. Stores deformation energy. Returns to initial state when deformation stops.

$$\sigma(\epsilon) = G\epsilon$$

Liquids are viscous. Resists rate of deformation, dissipates energy, and stops flowing when deformation stops.

$$\sigma(\dot{\epsilon}) = \eta\dot{\epsilon}$$

Liquid/Soft Matter/Solid

Solids are elastic. Stores deformation energy. Returns to initial state when deformation stops.

$$\sigma(\epsilon) = G\epsilon$$

Soft-matter is viscoelastic. Stores part of the deformation energy the rest is lost to dissipation. Complex dependence on deformation and structure.

$$\sigma[\epsilon(t)] = \cdots$$

Liquids are viscous. Resists rate of deformation, dissipates energy, and stops flowing when deformation stops.

$$\sigma(\dot{\epsilon}) = \eta\dot{\epsilon}$$

Apparent viscosity

$$\eta(\dot{\epsilon}) = \sigma(\dot{\epsilon})/\dot{\epsilon}$$

If η is constant. Newtonian liquid.

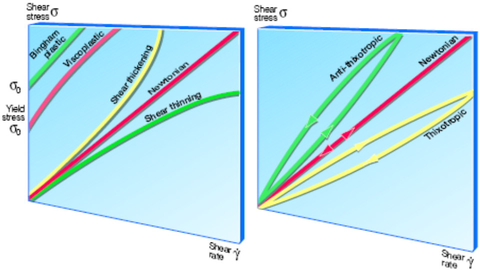
$\eta \uparrow$ when $\dot{\epsilon} \uparrow$ Shear thickening.

$\eta \downarrow$ when $\dot{\epsilon} \uparrow$ Shear thinning.

$\eta \uparrow$ with duration of shear. Rheopectic.

$\eta \downarrow$ with duration of shear. Thixotropic.

Rheological behaviour of soft-matter[1]



Shear thinning: Shampoo, cream, paint. Thickening: wet sand, concentrated suspensions. Viscoplastic: toothpaste, ketchup. Bingham: Salat dressing. Thixotropic: yoghurt, mayonnaise, some clay, paint. Rheopectic: Gypsum paste, whipped cream.

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[1] ref: http://www.afns.ualberta.ca/Courses/Nufs403/PDFs/chapter3.pdf

Peclet Number

Time scale of shear

$$\tau_{perturb} = \dot{\epsilon}^{-1}$$

Time scale of structural relaxation

$$\tau_{struct} \sim D/a^2$$

τ_{struct}: $10^{-12} - 10^{-10}s$ in simple liquids, but $10^{-3} - 10^{0}s$ in polymer melts, and ∞ for glasses!
Peclet number

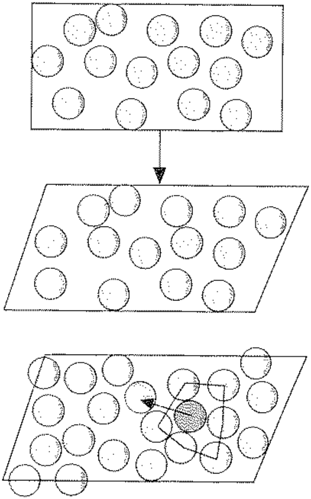
$$Pe = \tau_{struct}/\tau_{perturb} = D\dot{\epsilon}/a^2\tau_{struct}$$

If $Pe \ll 1$ liquid structure can always relax faster than perturbation, if $Pe \gg 1$ structure is strongly perturbed.

Typical Numbers

Shear rates	sedimentation	$10^{-6} - 10^{-4}$ s^{-1}
	chewing	$10^{1} - 10^{2}$ s^{-1}
	stirring	$10^{1} - 10^{3}$ s^{-1}
	pumping	$10^{2} - 10^{3}$ s^{-1}
	spraying	$10^{3} - 10^{4}$ s^{-1}
	rubbing	$10^{4} - 10^{5}$ s^{-1}
Viscosities	air	10^{-5} Pas
	water	10^{-3} Pas
	olive oil	10^{-1} Pas
	glycerol	10^{0} Pas
	syrup	10^{2} Pas
	molten polymers	10^{3} Pas
	molten glass	10^{12} Pas
	glass	10^{40} Pas

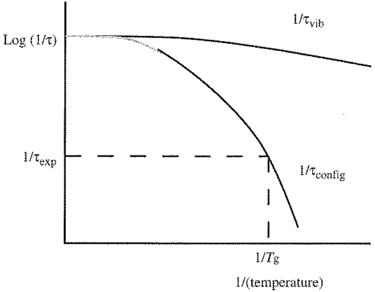
Simple liquid



Relaxation time related to life time of particle in cage.
$\tau^{-1} \sim \nu \exp(-A/k_B T)$

Viscosity (Arrhenius behaviour)
$\eta \sim G_0 \tau = \frac{G_0}{\nu} \exp(A/k_B T)$.

Glass



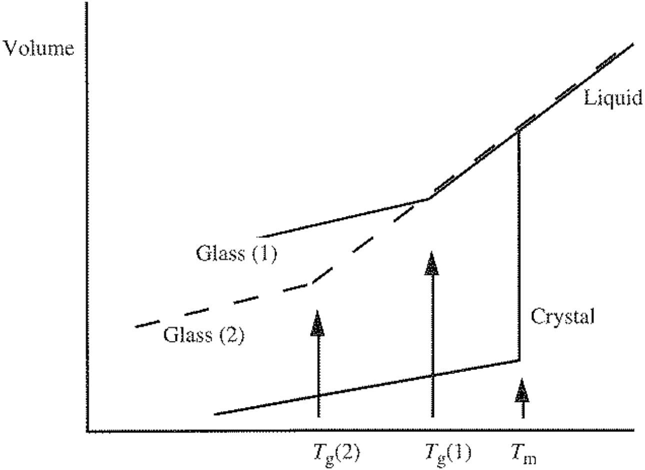
Separation between vibrational and configurational time scales.

Glass (Vogel-Fulcher) $\eta \sim \eta_0 \exp(B/(T - T_0))$.

At $T = T_0$ $\tau_{config} = \infty$.

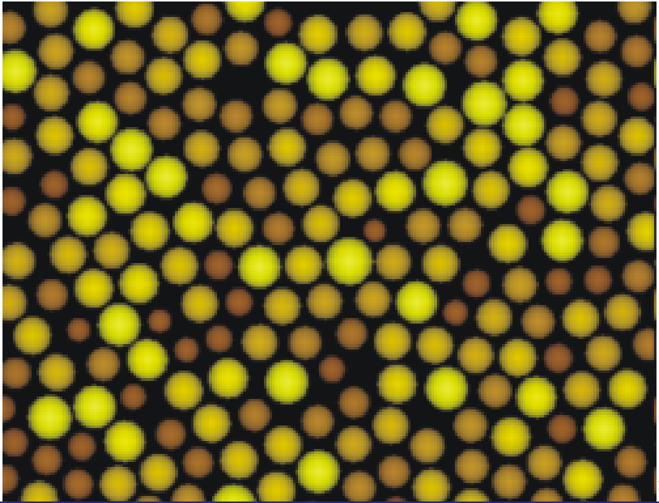
Different glass transition temperatures

Faster cooling rate, higher glass transition temperature.

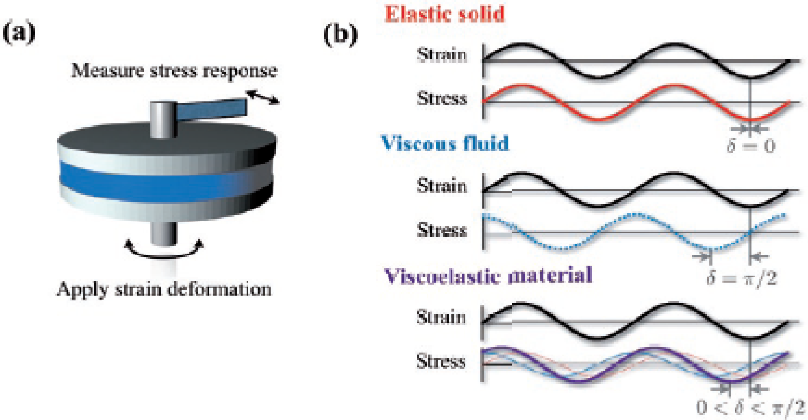


Glass state

Polydisperse spheres. No long range order, but local liquid order.



Oscillatory rheology



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[2] ref: http://people.seas.harvard.edu/h̃wyss/files/Wyss_GIT_Lab_J_2007.pdf

Analysis

Impose strain

$$\epsilon(t) = \epsilon_0 \sin \omega t$$

Measure at small deformations (linear response)

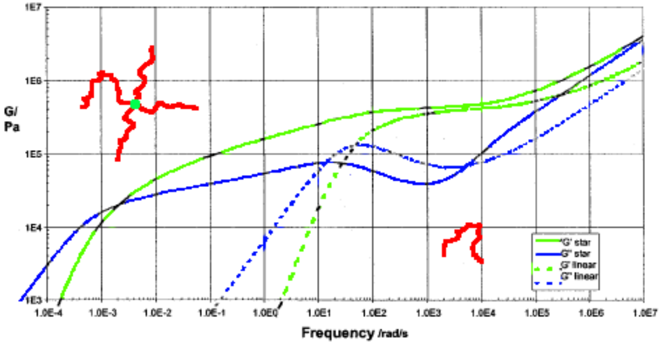
$$\sigma(t) = \sigma'(\omega) \sin \omega t + \sigma''(\omega) \cos \omega t = G'\epsilon + \frac{G''}{\omega}\dot{\epsilon}$$

Compare:

$$\sigma(t) = G\epsilon \qquad \sigma(t) = \eta\dot{\epsilon}$$

Storage modulus $G'(\omega) = \sigma'/\epsilon_0$ measures elasticity. Loss modulus $G''(\omega) = \sigma''/\epsilon_0$ and $\eta(\omega) = G''/\omega$ measures viscosity.

Influence of molecular architecture[3]



Monodisperse linear (broken lines) and star (continuous lines) polyisoprene melts.

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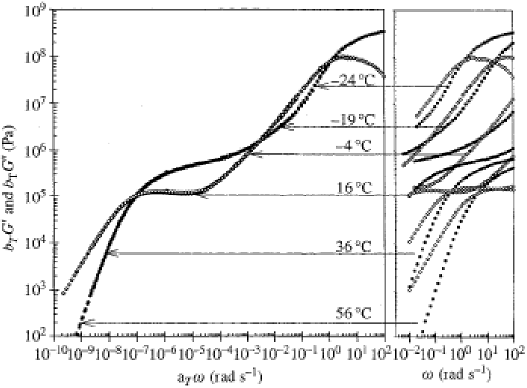
[3] ref: TCB McLiesh. Advances in physics 51, 1379 (2002).

Time temperature superposition

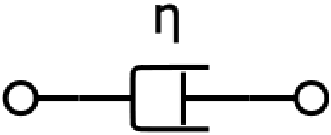


Demonstration of the time–temperature superposition principle, using oscillatory shear data (G', filled circles and G'', open diamonds) on a PVME melt with $M_w = 124\,000$ g mol^{-1}. The right-hand plot shows the data that were acquired at the six temperatures indicated, with $T_g = -24$ °C chosen as the reference temperature. All data were shifted empirically on the modulus and frequency scales to superimpose, constructing master curves for G' and G'' in the left-hand plot. Data and plot courtesy of J. A. Pathak.

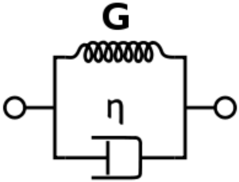
Mechanical analogy

Hookian elastic $\sigma = G\epsilon$

Newtonian liquid $\sigma = \eta\dot{\epsilon}$



Kelvin-Voigt solid



Simplest possible viscoelastic solid

$$\sigma(t) = \sigma_1(t) + \sigma_2(t) = G\epsilon + \eta\dot{\epsilon}$$

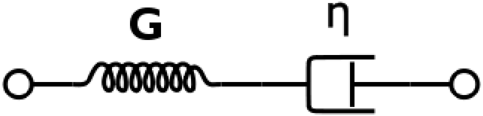
Compare

$$\sigma(t) = G'\epsilon(t) + \frac{G''}{\omega}\dot{\epsilon}(t)$$

Solution

$$G' = G \quad G''(\omega) = \eta\omega$$

Maxwell liquid



Simplest possible viscoelastic liquid

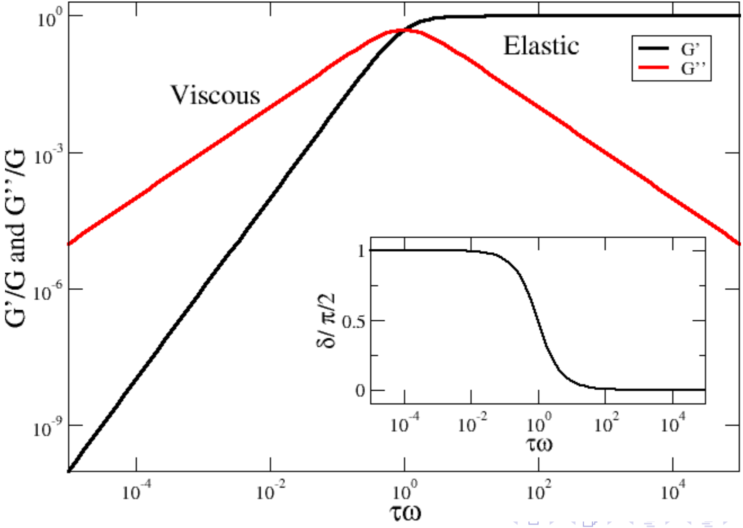
$$\epsilon(t) = \epsilon_1(t) + \epsilon_2(t) \quad \text{so} \quad \dot{\epsilon}(t) = \dot{\epsilon}_1(t) + \dot{\epsilon}_2(t)$$

Dash-pot $\dot{\epsilon}_2(t) = \sigma(t)/\eta$. For the spring $\epsilon_1(t) = \sigma(t)/G$ so $\dot{\epsilon}_1(t) = \dot{\sigma}(t)/G$. Result ($\tau = \eta/G$):

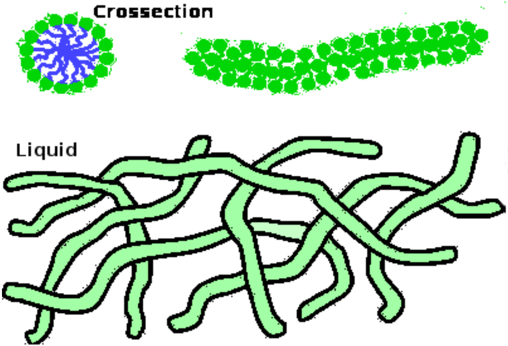
$$\dot{\epsilon}(t) = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta}$$

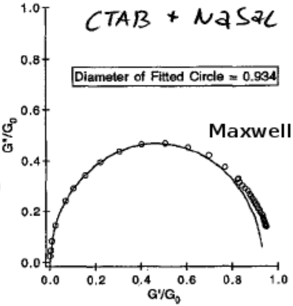
$$G'(\omega) = G\frac{\tau^2\omega^2}{1+\tau^2\omega^2} \quad G''(\omega) = G\frac{\tau\omega}{1+\tau^2\omega^2}$$

Maxwell liquid



Worm-like surfactant micelles[4]





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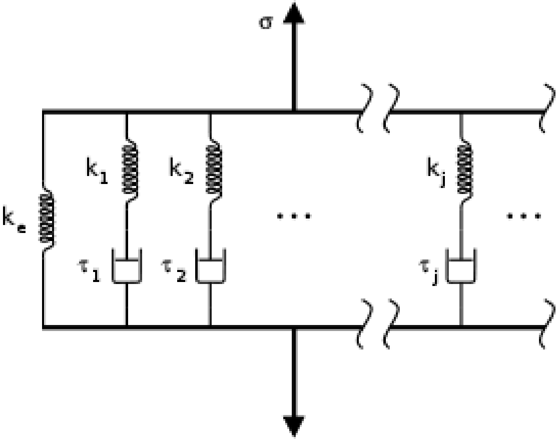
[4] ref: E.K. Weeler et al. Rheol. Acta 35, 139 (1996).

Maxwell-Weichert model

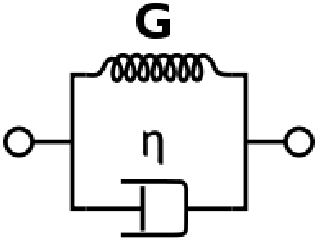
Maxwell model generalised to a distribution of relaxation time scales.



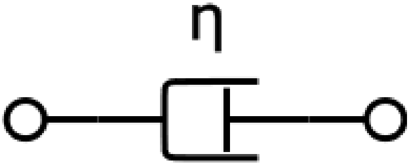
Summary

Hookian elastic $\sigma = G\epsilon$

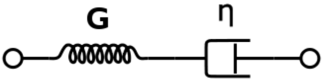
Kelvin-Vogt solid $\sigma = G\epsilon + \eta\dot{\epsilon}$



Newtonian liquid $\sigma = \eta\dot{\epsilon}$



Maxwell liquid $\dot{\epsilon} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\eta}$



Summary - Rheology

- Very sensitive to molecular structure and dynamics
- Viscoelasticity! Typical soft-matter behaviour is viscoelastic.
- Time-scales matter! Soft-matter has slow structural relaxation times that can be comparable to experimental time scales.
- Maxwell model is the simplest model of a viscoelastic material (characterised by just one relaxation time).
- Glasses have liquid structure, but relaxation times much longer than the experimental time scales.