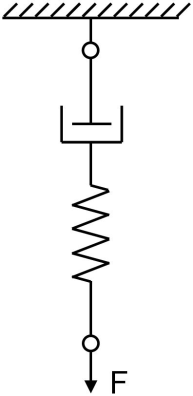
Oversimplified Viscoelasticity

THE MAXWELL MODEL



At time $t = 0$, suddenly deform to constant displacement X_o.

The force F is the same in the spring and the dashpot.

$$F = K_e X_e = K_v (dX_v/dt) \tag{1-20}$$

X_e is the displacement of the spring
X_v is the displacement of the dashpot
K_e is the linear spring constant (ratio of force and displacement, units N/m)
K_v is the linear dashpot constant (ratio of force and velocity, units Ns/m)

The total displacement X_o is the sum of the two displacements (X_o is independent of time)

$$X_o = X_e + X_v \tag{1-21}$$

Oversimplified Viscoelasticity

THE MAXWELL MODEL (p. 2)

Thus:

$$K_e(X_o - X_v) = K_v(dX_v/dt) \text{ with B. C. } X_v = 0 \text{ at } t = 0 \tag{1-22}$$

$$(K_e/K_v)dt = dX_v/(X_o - X_v)$$

Integrate:

$$(K_e/K_v)t = -\ln(X_o - X_v) + C$$

Apply B. C.: $X_v = 0$ at $t = 0$ means $C = \ln(X_o)$

$$-(K_e/K_v)t = \ln[(X_o - X_v)/X_o]$$

$$(X_o - X_v)/X_o = \exp(-K_e t/K_v)$$

Thus:

$$F(t) = K_e X_o \exp(-K_e t/K_v) \tag{1-23}$$

The force from our constant stretch experiment decays exponentially with time in the Maxwell Model. The **relaxation time** is

$$\lambda \equiv K_v/K_e \text{ (units s)}$$

The force drops to $1/e$ of its initial value at the relaxation time λ.
Initially the force is $F(0) = K_e X_o$, the force in the spring,
but eventually the force decays to zero $F(\infty) = 0$.

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THE MAXWELL MODEL (p. 3)

Constant Area A means stress $\sigma(t) = F(t)/A$
$\sigma(0) \equiv \sigma_0 = K_e X_o / A$
Maxwell Model **Stress Relaxation**:

$$\sigma(t) = \sigma_0 \exp(-t/\lambda)$$

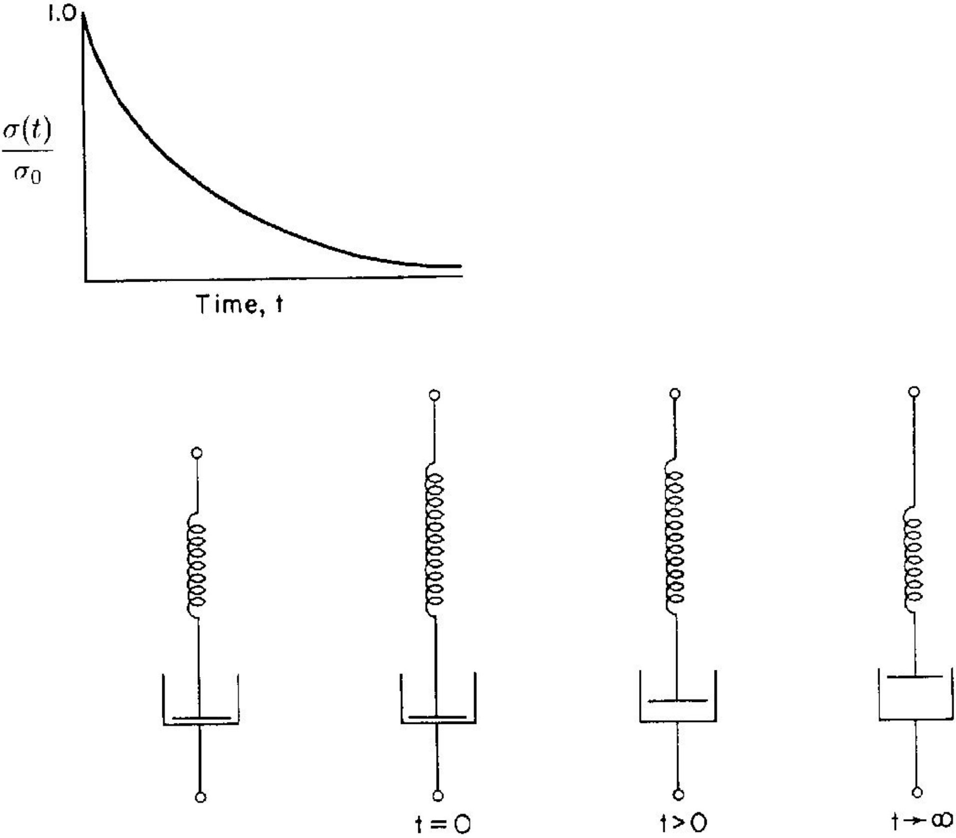

Figure 1: Stress Relaxation of a Maxwell Element

Oversimplified Viscoelasticity

THE MAXWELL MODEL (p. 4)

A creep experiment applies constant force F (or constant stress).

$$F = K_e X_e = K_v (dX_v/dt) \tag{1-20}$$

Thus:

$X_e = F/K_e$ and $dX_v/dt = F/K_v$ with B. C. $X_v = 0$ at $t = 0$

Integrate:

$$X_v = Ft/K_v$$

The total displacement is $X_o = X_e + X_v = F(1/K_e + t/K_v)$
Strain $\gamma \equiv X_o/L_0$

$$\gamma = (1 + K_e t/K_v) F/(K_e L_0)$$

The instantaneous strain in the spring is $\gamma_0 \equiv F/(K_e L_0)$ and the relaxation time is again $\lambda \equiv K_v/K_e$.

Maxwell Model **Creep:**

$$\gamma(t) = \gamma_0 (1 + t/\lambda)$$

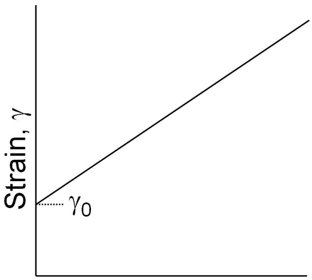

Figure 2: Creep of a Maxwell Element

Oversimplified Viscoelasticity

THE VOIGT MODEL

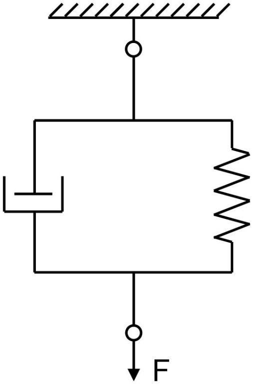

Figure 3: Voigt Element: A Spring and a Dashpot in Parallel

At time $t = 0$, apply a constant force F.
The displacement X is the same in the spring and the dashpot.
The force F is the sum of forces in the spring and the dashpot.

$$F = K_e X + K_v (dX/dt) \text{ with B. C. } X = 0 \text{ at } t = 0 \qquad \text{(1-18)}$$

$$(K_e/K_v)dt = dX/[(F/K_e) - X]$$

Integrate:

$$(K_e/K_v)t = -\ln[(F/K_e) - X] + C$$

Apply B. C.: $X = 0$ at $t = 0$ means $C = \ln(F/K_e)$

$$-(K_e/K_v)t = \ln[1 - XK_e/F]$$

$$1 - XK_e/F = \exp(-K_e t/K_v)$$

Thus:

$$X(t) = (F/K_e)[1 - \exp(-K_e t/K_v)] \qquad \text{(1-19)}$$

Oversimplified Viscoelasticity

THE VOIGT MODEL (p. 2)

$$X(t) = (F/K_e)[1 - \exp(-K_e t/K_v)] \tag{1-19}$$

We again have strain $\gamma(t) \equiv X(t)/L_0$, and relaxation time $\lambda \equiv K_v/K_e$.
We define $\gamma_\infty \equiv F/(K_e L_0)$ as the long time limit of the strain.
Voigt Model **Creep**:

$$\gamma(t) = \gamma_\infty[1 - \exp(-t/\lambda)]$$

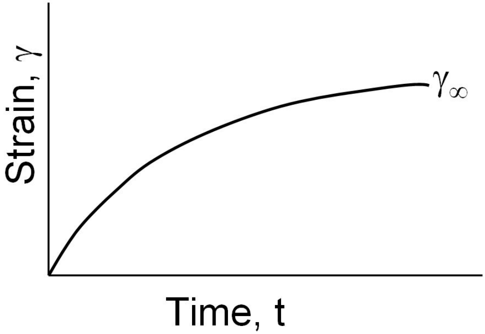

Figure 4: Creep of a Voigt Element

The Voigt Model captures the essential physics of creep for a **viscoelastic solid**.

Oversimplified Viscoelasticity

MAXWELL AND VOIGT MODELS IN SERIES

Strains of elements combined in series always add in creep.

$$\gamma(t) = \gamma_{Maxwell}(t) + \gamma_{Voigt}(t)$$

$$\gamma(t) = \gamma_0(1 + t/\lambda) + \gamma_\infty[1 - \exp(-t/\lambda)]$$

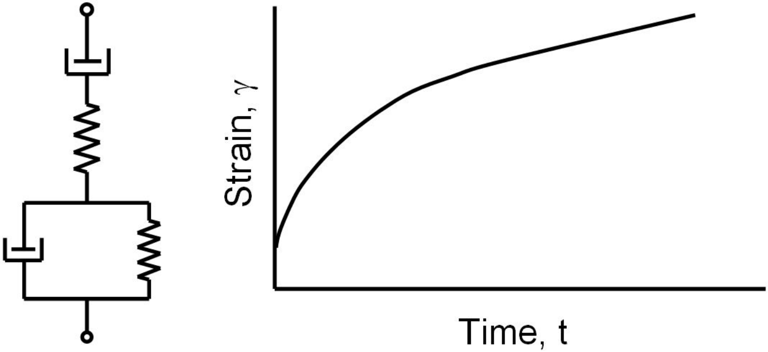

Figure 5: Maxwell and Voigt Elements in Series and their Strain in Creep

Maxwell and Voigt Elements in Series capture the essential physics of creep for a **viscoelastic liquid**.

Rheological Terminology

THE JARGON OF STRANGE FLUIDS

Dilatancy *n.* Increase in apparent viscosity with shear rate (also **shear-thickening)**. Rare, but seen in some solutions of associating polymers.

Rheopexy *n.* Apparent viscosity increases with time at a given rate (also **anti-thixotropy** or **structure-building**). Rare, but seen in some suspensions.

Thixotropy *n.* Apparent viscosity decreases with time at a given rate (also **structure-breaking**). Common for concentrated suspensions.

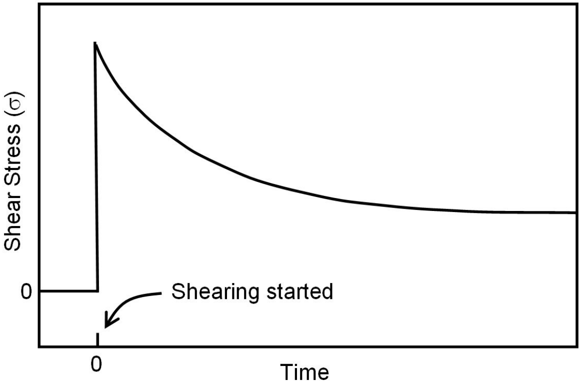

Figure 6: Thixotropic behavior of a structured fluid.

Shear-thinning *n.* Decrease in apparent viscosity with shear rate. Very important for nearly all polymers and suspensions.

Yield Stress *n.* The stress required for a structured fluid to flow (also **Bingham stress**). Common for concentrated suspensions and liquid crystals.

Yield Stress
THE BINGHAM MODEL

Structured fluids, such as concentrated suspensions and liquid crystals show solid rheological response at low stress levels. The simplest model for this class of flow is the Bingham Model.

$$\sigma = \begin{cases} G\gamma & \sigma < \sigma_0 \\ \sigma_0 + \eta_p\dot{\gamma} & \sigma > \sigma_0 \end{cases} \tag{1-24}$$

σ_0 is the yield stress, below which there is no flow, and above which flow occurs with σ_0 of the stress being used to maintain the liquid response, and the remainder ($\eta_p\dot{\gamma}$) causing simple Newtonian flow.

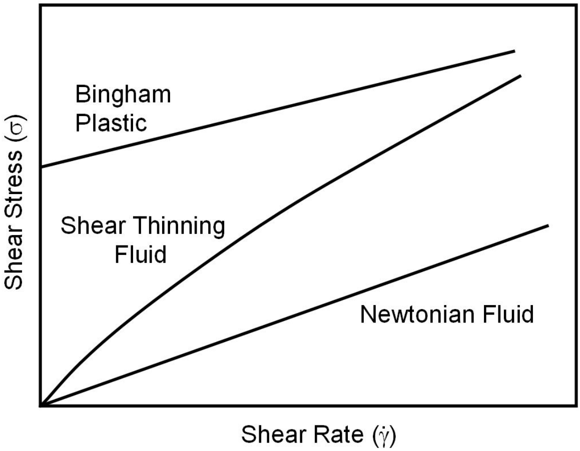

Figure 7: Flow Curve of a Bingham Plastic compared to Newtonian and shear-thinning fluids.

Flexible polymer melts and solutions are either Newtonian ($\sigma = \eta\dot{\gamma}$) or shear-thinning (meaning that the apparent viscosity decreases with shear rate) but do NOT have a yield stress.

Origins of Elasticity in Polymer Liquids

The configuration of a polymer chain in a melt is a random walk because it **maximizes configurational entropy**.

Flow Field $\Longrightarrow$ Stretch Chain $\Longrightarrow$ Lower Entropy Configuration

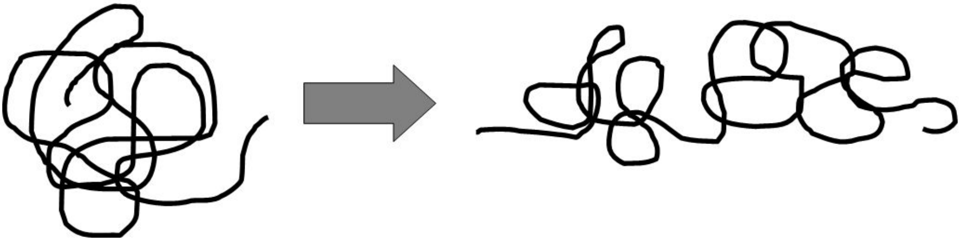

Figure 8: By stretching the chain, the number of configurations is reduced, which decreases the entropy (and requires work).

Using Statistical Mechanics, it is easy to show that the chain actually behaves like a linear spring. The (entropic) free energy G is quadratic in the end-to-end distance R.

$$G = \frac{3kTR^2}{2Nb^2}$$

k is Boltzmann's constant
T is absolute temperature
N is the number of monomers in the chain
b is the monomer size

In the upstretched state $R^2 = Nb^2$, and the configurational free energy is $3kT/2$.

The force required to stretch the chain is

$$F = \frac{\partial G}{\partial R} = \frac{3kTR}{Nb^2}$$

This is precisely why a rubber band behaves like a linear spring.