

Viscoelasticity

Books

Most polymer texts cover this reasonably well in outline.

More specialist texts for reference:

JJ Aklonis and WJ Macknight Introduction to Polymer Viscoelasticity, Wiley 1983

IM Ward Mechanical Properties of Solid Polymers Wiley

Introduction

A viscoelastic material is, as the name suggests, one which shows a combination of viscous and elastic effects.

The viscous term leads to energy dissipation.

The elastic term to energy storage.

Rate effects are very important for these materials

For a viscous liquid with viscosity η , the constitutive equation relating stress σ to strain ϵ is

$$\sigma = \eta \frac{d\epsilon}{dt}$$

There is **dissipation of energy** – and irreversible shape changes – associated with the flow.

The viscosity can be related to the diffusion equation.

If an external force \underline{f} on a particle/atom gives rise to a velocity \underline{u} then

$$\underline{u} = \mu \underline{f} \quad \text{where } \mu \text{ is the mobility}$$

Einstein relation gives

$$\mu = D/kT \quad \text{where } D \text{ is the diffusion coefficient}$$

Stokes Law says for a particle of radius a

$$\underline{f} = 6\pi\eta a \underline{u}$$

$$\Rightarrow \eta = \frac{kT}{6\pi a D}$$

In general then **η and D are inversely related**, and as D increases with temperature viscosity decreases.

In contrast most solids exhibit pure elasticity

Ideal elastic material

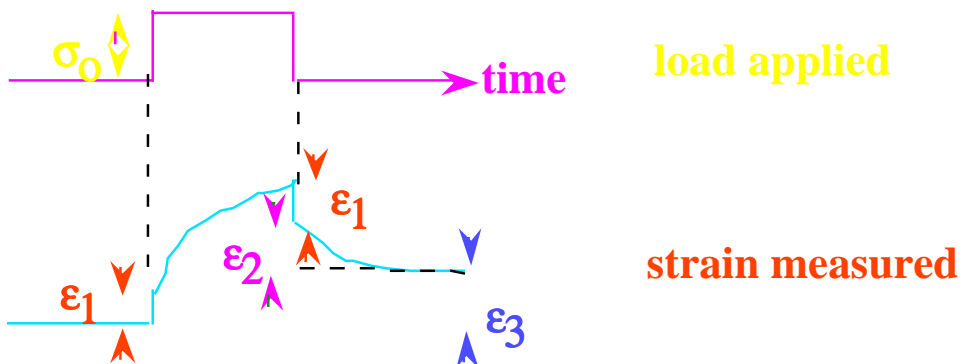
$$\sigma = E\varepsilon \quad E \text{ is Young's modulus}$$

Energy is **stored** as elastic energy.

Material **returns to original shape** once stress removed.

Polymeric liquids, and various solids, have attributes of both and these are known as viscoelastic materials.

Creep



A constant load is applied and the resulting strain is measured.

ϵ_1 = immediate elastic deformation

ϵ_2 = delayed elastic deformation

ϵ_3 = Newtonian flow (i.e. permanent deformation)

Define creep compliance

$$J(t) = \frac{\epsilon(t)}{\sigma_0}$$

so there are 3 components of the creep compliance J_1 in general associated with the 3 components of strain.

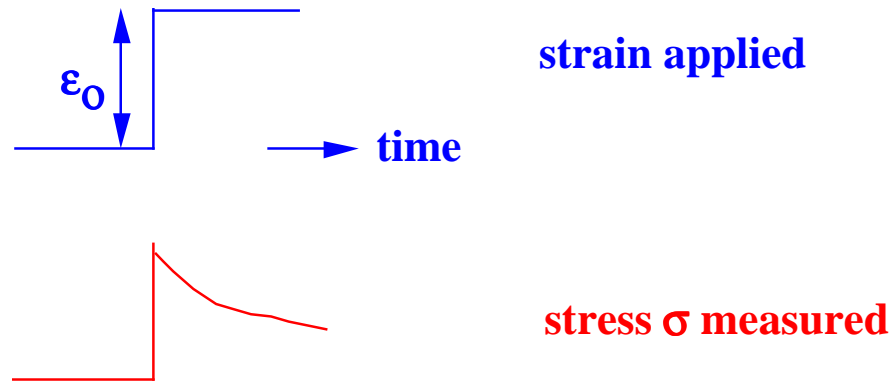
One exception to this is a crosslinked rubber: its memory effect means that there is no permanent shape change so that $\epsilon_3 = 0$ and so J_3 also is zero.

Division into J_1 and J_2 (or equivalently ϵ_1 and ϵ_2) fairly arbitrary.

J_1 and J_2 sometimes known as unrelaxed and relaxed responses.

Stress Relaxation

A fixed extension (strain) is applied



Define stress relaxation modulus

$$G(t) = \frac{\sigma(t)}{\epsilon_0}$$

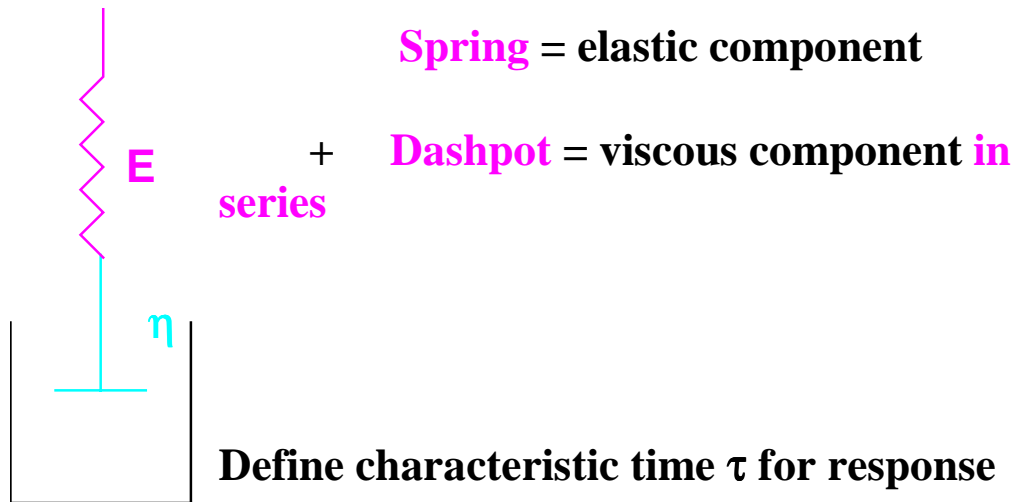
If no viscous flow occurs, stress drops to finite value at infinite times → **relaxed modulus**.

If there is viscous flow, **stress can drop to zero**.

Models for Viscoelastic Response

1. Maxwell Model

Spring and Dashpot model



$$\tau = \eta/E$$

Equation of motion

$$\frac{d\varepsilon}{dt} = \frac{1}{E} \frac{d\sigma}{dt} + \frac{\sigma}{\eta}$$

↑ ↑ ↑

total **spring** **dashpot**
strain rate

Stress relaxation experiment

$d\varepsilon/dt = 0$ in equation of motion

$$\therefore 0 = \frac{1}{E} \frac{d\sigma}{dt} + \frac{1}{\eta} \sigma(t)$$

$$\Rightarrow \frac{d\sigma}{\sigma} = -\frac{E}{\eta} dt = \frac{dt}{\tau}$$

$$\ln \sigma(t) = \ln \sigma_o - t / \tau$$

$$\frac{\sigma(t)}{\varepsilon_o} = \frac{\sigma_o}{\varepsilon_o} \exp - t / \tau$$

$$E(t) = E_o \exp - t / \tau$$

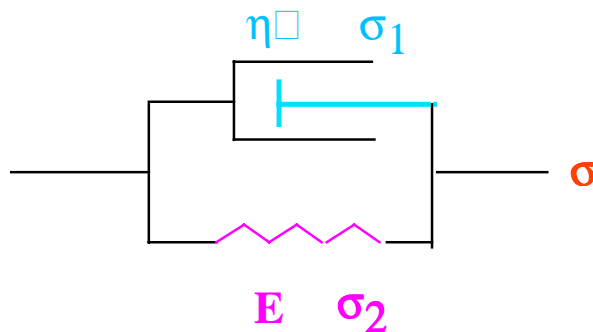
At very short times, the Maxwell model behaves as a simple spring.

Takes longer for the viscous component to respond.

For $t \gg \tau$ stress drops to zero as only the response of the dashpot remains.

2. Kelvin or Voigt Model

Spring and dashpot in parallel



Total stress $\sigma = E\varepsilon + \eta \frac{d\varepsilon}{dt}$

In a **creep experiment**, σ is a constant σ_0 so, dividing by η

$$\frac{\sigma_0}{\eta} = \frac{\varepsilon}{\tau} + \frac{d\varepsilon}{dt}$$

Can solve for ε with integrating factor $\exp t/\tau$

$$\varepsilon(t) = \sigma_0/E (1-\exp-t/\tau)$$

This model cannot be used for stress relaxation experiments, since it would require infinite force to strain viscous elements instantaneously.

Both these models are **too simple**.

Next step is to combine them to produce a '**standard linear solid**'.

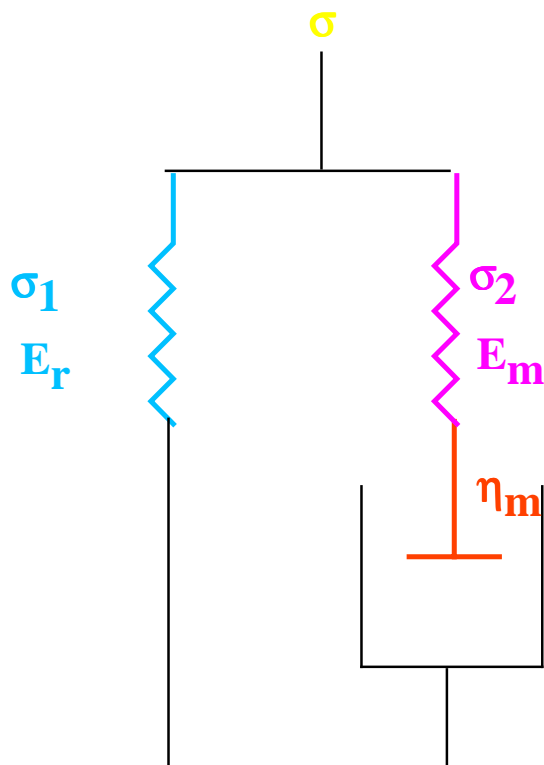
This is an improvement, but there is still only one characteristic time associated with the model.

In general there will be a whole spectrum of these – for instance in a polydisperse polymer melt, different chain lengths respond differently.

Fast chains respond faster than long chains.

So to model a polymer melt properly we might imagine we need a **whole system of standard linear solids each with its own τ** .

Standard Linear Solid (due to Zener)



$$\sigma_2 = \eta_m \frac{d\varepsilon}{dt} - \frac{\eta_m}{E_m} \frac{d\sigma_2}{dt}$$

$$\sigma = E_r \varepsilon + \eta_m \frac{d\varepsilon}{dt} - \frac{\eta_m}{E_m} \frac{d\sigma_2}{dt}$$

Add $\frac{\eta_m}{E_m} \frac{d\sigma}{dt}$ to each

$$\sigma + \frac{\eta_m}{E_m} \frac{d\sigma}{dt} = E_r \varepsilon + \eta_m \frac{d\varepsilon}{dt} + \frac{\eta_m}{E_m} \frac{d\sigma}{dt}$$

$$E_r \frac{d\varepsilon}{dt}$$

$$\sigma + \tau \frac{d\sigma}{dt} = E_r \varepsilon + \tau \frac{d\varepsilon}{dt} (E_m + E_r)$$

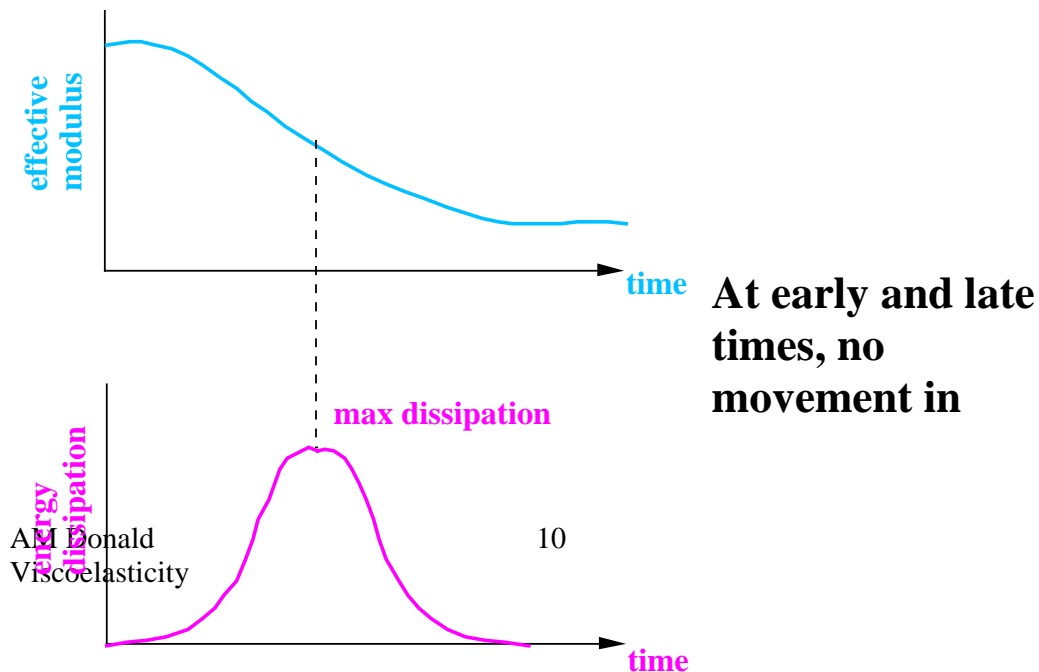
Instantaneous response ($\varepsilon=0$), finite $d\varepsilon/dt$) – no response from dashpot

\therefore **modulus = $E_r + E_m$**

Long time response, dashpot takes all the strain and E_m does not contribute

\therefore **modulus = E_r relaxed modulus**

Energy dissipated (in dashpot) a maximum at some intermediate time.



dashpot and hence no dissipation.

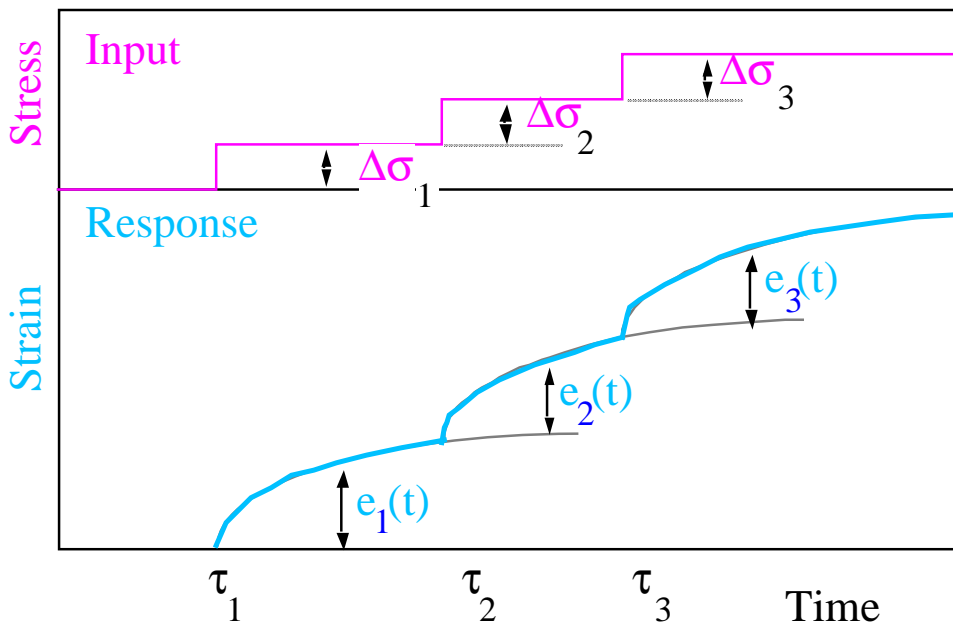
Boltzmann Superposition Principle

To describe the general response of a system, must allow for details of loading history.

This can be done using the Boltzmann superposition theory.

Boltzmann proposed:

- Creep is a function of the whole sample loading history.
- Each loading step makes independent contribution to total loading history.
- Total final deformation is the sum of each contribution.



In general, for a **creep experiment**, increments of stress $d\sigma$ at times t_n

$$\varepsilon(t) = \int_{-\infty}^t J(t-u) \frac{d\sigma(u)}{du} du$$

For **stress relaxation**, incremental additions of strain $d\varepsilon$ at times t_n

$$\sigma(t) = \int_{-\infty}^t G(t-u) \frac{d\varepsilon(u)}{du} du$$

For a steady state shear rate, this can be rewritten as

$$\sigma(t) = \eta_o d\varepsilon/dt$$

viscosity

Newton's law of

$$\text{where } \eta_o = \int_0^{\infty} G(t-u) du$$

(by change of variable)

Note that this theory only works for small deformations – this is **linear viscoelastic theory**.

Complex Modulus and Dynamic Experiments

Two types of processes occurring – storage and dissipation of energy.

Looking at the analogous situation of LCR circuits, where V and I are out of phase for oscillating signals, can anticipate that for viscoelastic materials, **stress**

and strain will be out of phase in dynamic experiments.

Furthermore the modulus must be described by a complex modulus.

If an alternation stress/strain is applied to a viscoelastic solid, stress and strain are out of phase.

Complex modulus $G = G_1 + G_2$

storage modulus = real part G_1
 loss modulus = imaginary part G_2

This is a general description for all viscoelastic materials.

Let phase angle be δ , apply sinusoidal strain

$$\begin{aligned} \epsilon &= \epsilon_0 \exp(i\omega t) & \sigma &= \sigma_0 \exp(i(\omega t + \delta)) \\ \frac{\sigma}{\epsilon} &= G = \frac{\sigma_0}{\epsilon_0} \exp(i\delta) \end{aligned}$$

In general $|G_2| \ll |G_1|$

G_1 represents stress in phase with strain – i.e. energy stored during deformation

G_2 is a measure of energy dissipated/cycle.

Consider energy loss/cycle

$$\Delta E = \text{Re} \int \sigma d\epsilon = \text{Re} \int_0^{2\pi/\omega} \sigma \frac{d\epsilon}{dt} dt$$

or rate of loss/cycle = $\frac{1}{2} \text{Re}[\sigma \frac{d\varepsilon^*}{dt}]$

$\therefore \Delta E = \pi \varepsilon_0^2 G_2$

Phase angle δ related to G_1 and G_2 by

$\tan \delta = G_2/G_1$

Measurement of Complex Modulus

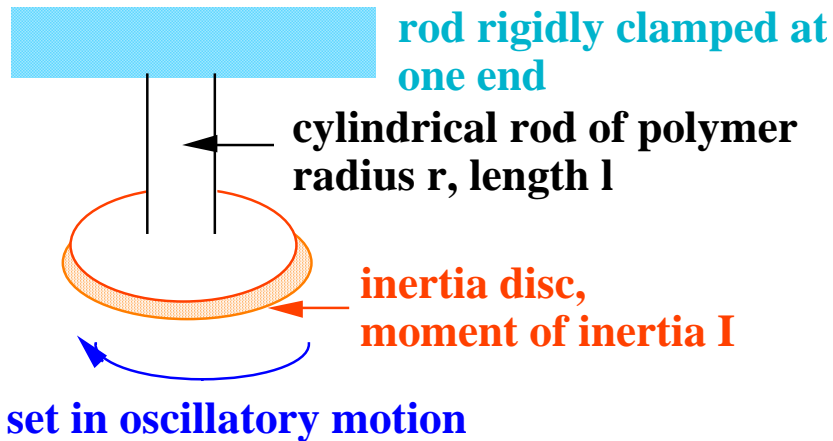
Measuring the in phase and out of phase components of the response of strain to an imposed stress (or vice versa) at different frequencies provides the two components of G to be determined.

The modulus may vary greatly with frequency/time scale of the experiment.

Different techniques are used for different frequencies (see Ward).

Example – torsion pendulum

Motion is damped SHO



For thin walled tube, angular strain = $r (\theta/l)$
Restoring force for rotation $\theta = Gr(\theta/l) \times \text{area}$
Torque = $r Gr (\theta/l) 2\pi r dr$

$$\text{Total torque} = \int \frac{G2\pi\theta r^3}{l} dr = \frac{G\pi r^4 \theta}{2l}$$

Equation of motion becomes

$$I\ddot{\theta} + \frac{\pi r^4}{2l} (G_1 + iG_2)\theta = 0$$

This is the equation for damped SHM with the $\dot{\theta}$ term being $i\omega\theta$

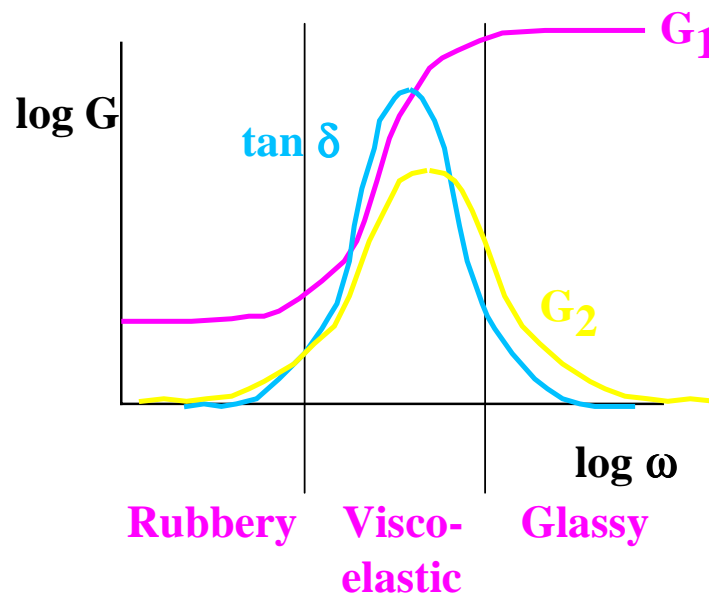
With $\omega^2 = \frac{\pi r^4}{2l} \frac{G_1}{I}$ and $\tan \delta = \frac{G_2}{G_1} = \frac{\Lambda}{\pi}$

Λ is the logarithmic decrement.

As expected frequency is determined by G_1 and damping by G_2

This apparatus works over frequency range 0.01-50Hz. At higher frequencies wavelength of the stress waves becomes comparable with the dimensions of the specimen.

Results of Measurements



These terms apply to polymer melts, but the phenomena are much more general.

$\tan \delta$ and G_2 are both large at intermediate frequencies in the viscoelastic regime.

This behaviour is the same for solids with any damping mechanism.

In the case of metals etc this is sometimes known as **internal friction.**

Example – Snoek damping

In bcc metals, the damping occurs due to movement of interstitials e.g. C or N in α iron.

Interstitials sit at the centres of the cube edges, and slightly distort the lattice.

When an external stress applied, the energy associated with the different interstitial sites is no longer degenerate.

Under oscillatory stress the interstitials will try to move to accommodate this.

At high frequencies this is impossible.

At low frequencies it will occur to completion.

In both these cases stress and strain will be in phase.

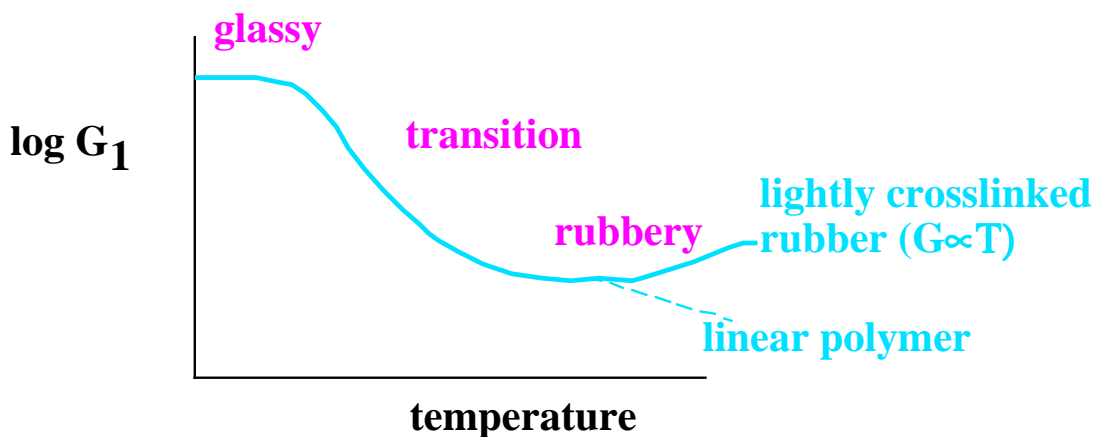
However at intermediate frequencies, around the natural frequency of interstitial jumping, there is significant damping and G_1 and G_2 will be out of phase.

Jumping will be thermally activated and so the frequency at which **damping is maximum will be temperature dependent.**

This is generally true.

Time-Temperature Superposition

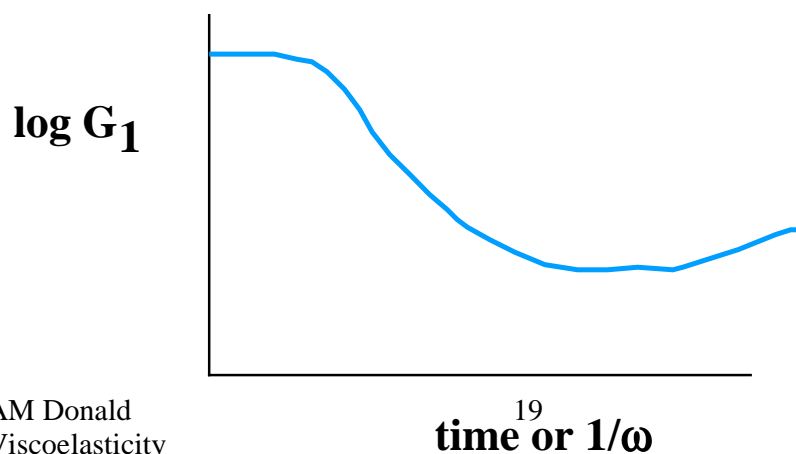
Using polymer analogy again.



This represents the behaviour over the whole temperature range at a given ω (or time t).

Alternatively can study at fixed temperature and range of frequencies ω .

Similar shaped curve is found.



Experimentally observed that there is a **correspondence between time and temperature**.

Can shift curves for viscoelastic properties at different temperatures onto a single curve at a single temperature to create a **master curve**.

Then $G(T_1, t) = G(T_2, t/a_T)$

where a_T is the **shift factor** and given by

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)}$$

WLF equation

(Williams-Landel-Ferry)

and T_0 is the reference temperature.

C_1 and C_2 are approximately universal constants

$$C_1 = 17.4 \text{ and } C_2 = 51.6K$$

Note that a_T is not a function of time, only temperature.

This same equation can be used for any of the viscoelastic constants including viscosity.

In which case it recovers the Vogel-Fulcher Law.

$$\begin{aligned} \eta(T) &= \int_0^{\infty} E(T, t) dt = \int_0^{\infty} E(T_g, t_{ref}) dt \\ &= \int_0^{\infty} E(T_g, t_{ref}) a_T dt_{ref} = a_T \eta(T_g) \end{aligned}$$

$$\Rightarrow \log\left(\frac{\eta(T)}{\eta(T_g)}\right) = \log a_T$$

$$\therefore \eta(T) = A \exp\frac{-B}{T - T_g}$$

as we saw before

Experimentally the WLF equation is very important because it enables the response of a system under a wide range of conditions to be described from limited experimental data.

Theoretically it implies that all the timescales in the problem scale in the same way with T.

Implies there is a single basis parameter which for polymers turns out to be the segment mobility.

Dynamics of Polymer Chains

The flow of polymers is dominated by long range motions.

However because of the complexity of chains, there are many internal motions possible.

These show up in the loss modulus (below T_g).

In the glassy state, local segmental motions not sufficient to relax the strains imposed by external stress, and G_1 is high.

Situation more complicated for crystalline polymers, where also have to pass through T_m before bulk flow occurs.

However remember that polymer chains are **entangled – so how do they move at all?**

These entanglements will affect viscosity, diffusion.....

At first it was thought that this was too difficult to deal with at all, but much progress has now been made.

De Gennes conceived of the idea of **reptation – moving like a snake (1971).**

Ideas developed further here by Doi and Edwards.

See the book by M Doi and SF Edwards **Theory of Polymer Dynamics 1986, OUP.**

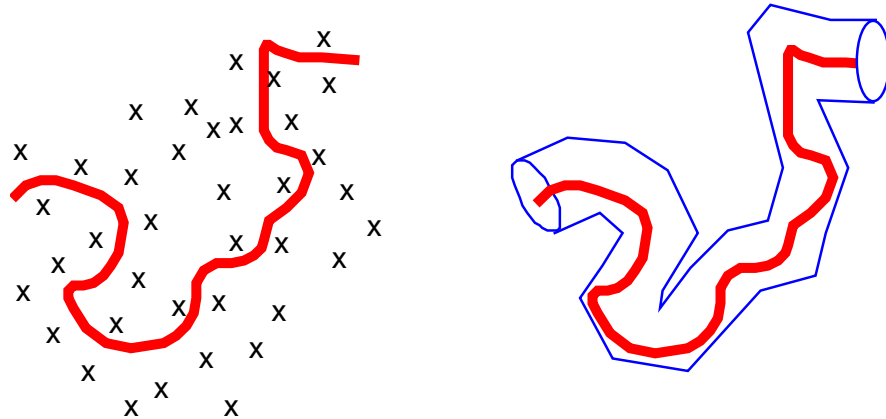
Think of the motion of snakes in a nest – constrained laterally but can move along their length.

Where one chain interacts strongly with another chain (naively as a simple knot), identify an entanglement.

All the surrounding chains provide constraints for the movement of a test chain.

These surrounding chains can be averaged to provide a tube of diameter equal to the entanglement separation.

Consider a chain confined in such a tube.



The chain can slowly escape this tube as it undergoes Brownian motion, thereby creating a new tube.

Mobility μ of whole chain = monomeric mobility μ_1/N

where N is the number of monomers in the chain.

Einstein relation $D=\mu kT$ implies

$$D_{tube} = \frac{\mu_1 kT}{N}$$

If τ is tube relaxation time, ie time length L of old tube takes to be lost and new length L to be created, then by random walk

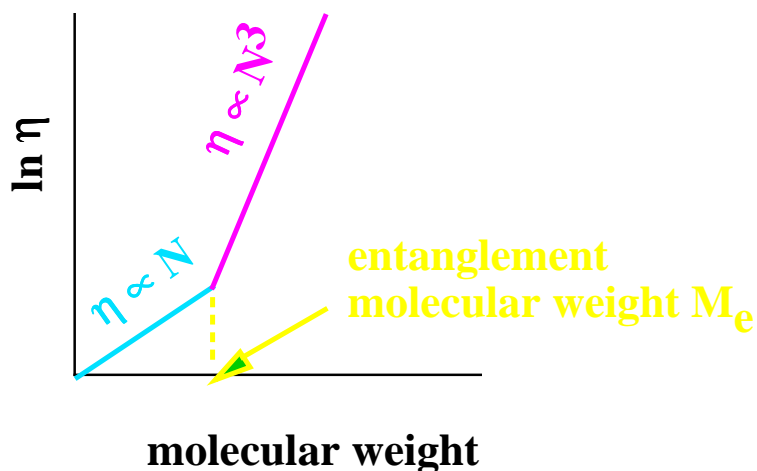
$$\tau \sim \frac{L^2}{D} = \frac{NL^2}{\mu_1 kT}$$

Now L is curvilinear length of tube/chain $\therefore L \propto N$

And $\tau \propto N^3$ (or equivalently M^3)

And since $\eta \propto \tau$, reptation model implies $\eta \propto N^3$
 This result is in contrast to small molecules (ie ones for which entanglements and the tube concept do not apply) for which

$$\tau \propto N$$



Schematically one might expect

Experimentally the dependence in the entangled regime is found to be

$$\eta \propto N^{3.4}$$

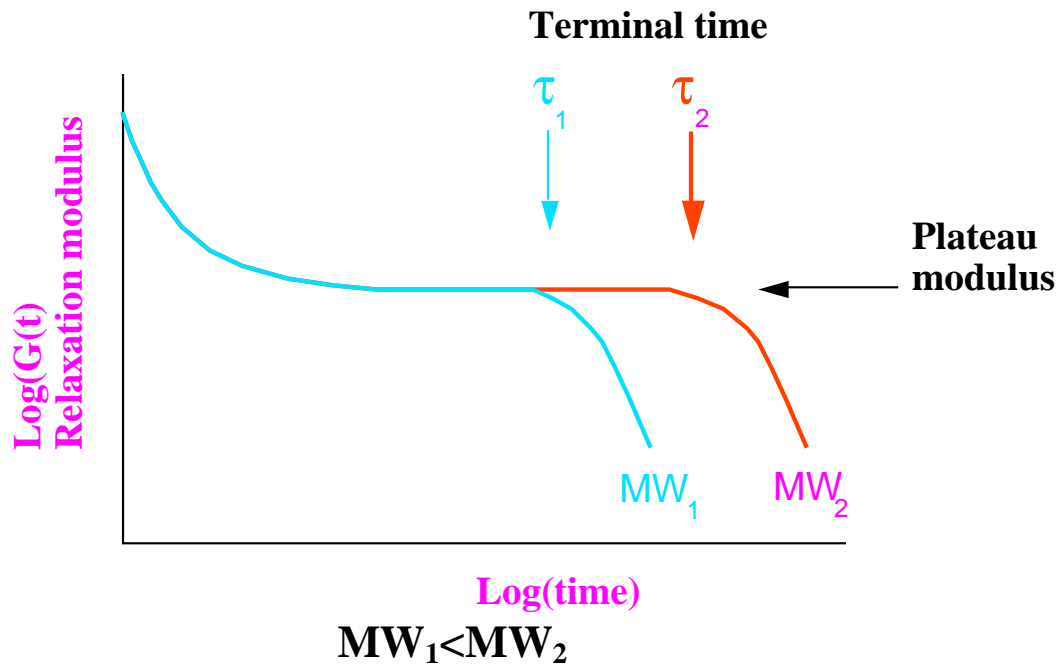
Origin of discrepancy with simple theory is thought to lie in fluctuations.

If we apply a deformation to a polymer melt, the constraints are deformed.

The chain can gradually escape from its tube, to form a new undeformed tube.

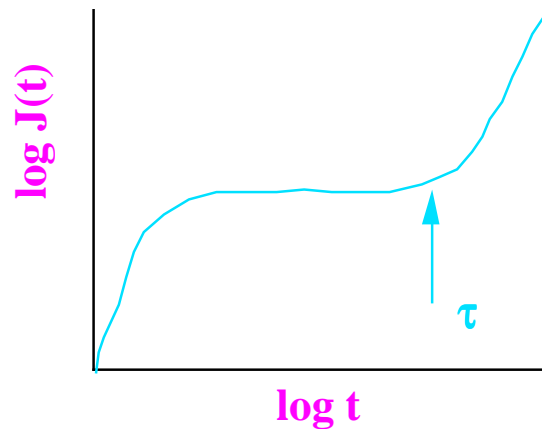
The relaxation time can therefore be found from experiment – often known as the terminal time.

$\tau \propto N^3$ in simple reptation theory



Once the chain has completely escaped no further resistance to deformation, and hence G drops.

Alternatively can find the terminal time from the creep compliance curves.



As with rubbers, for which we identified a plateau modulus inversely related to M_x (the MW between crosslinks), for entangled polymers we can find an equivalent quantity – M_e , the MW between entanglements – from the value of the plateau modulus.

By analogy with the theory of rubber elasticity, the value of G at the plateau:

$$G = \frac{\rho N_A k T}{M_e}$$