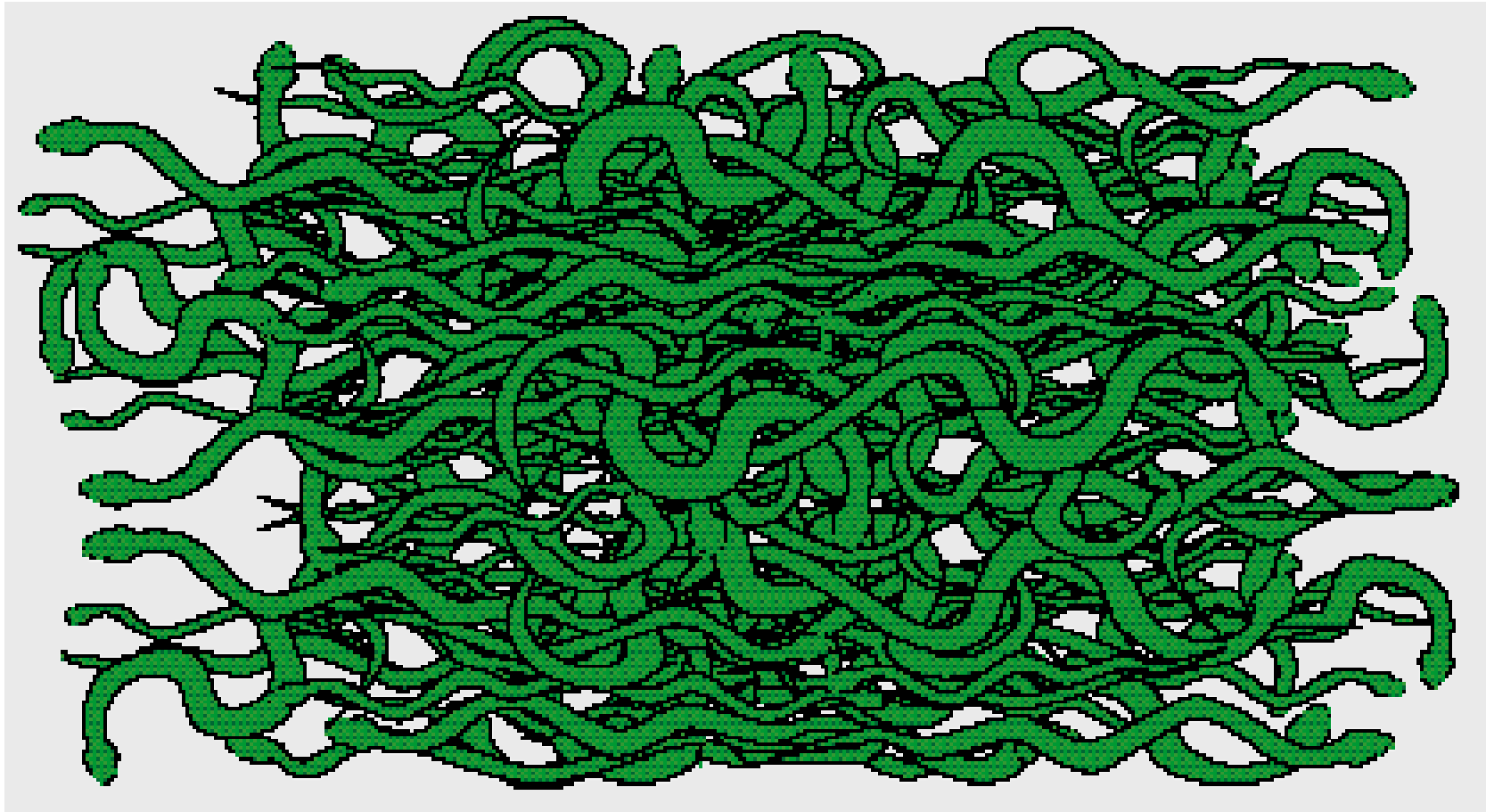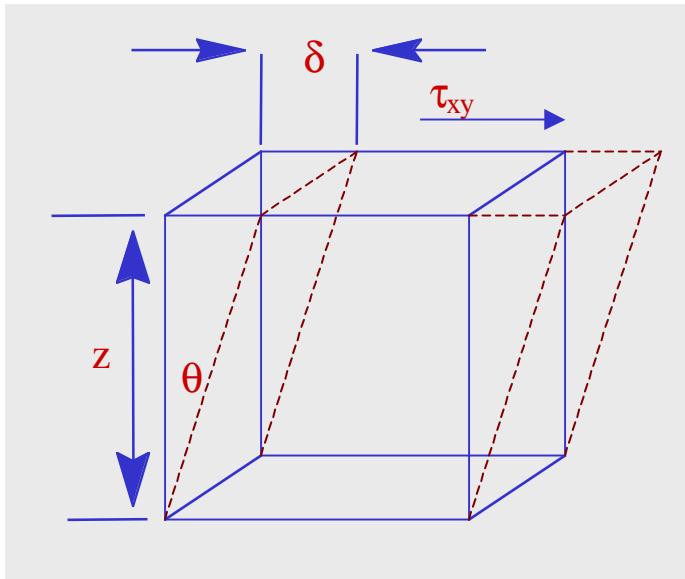# Topics to be Covered

- *Polymer Melt Rheology*

- *Introduction to Viscoelastic Behavior*

- *Time-Temperature Equivalence*

Chapter 11 in CD (Polymer Science and Engineering)

Polymer Melt Rheology

Newton's Law

The most convenient way to describe deformation under shear is in terms of the angle θ through which the material is deformed;

$$\tan \theta = \frac{\delta}{z} = \gamma_{xy}$$
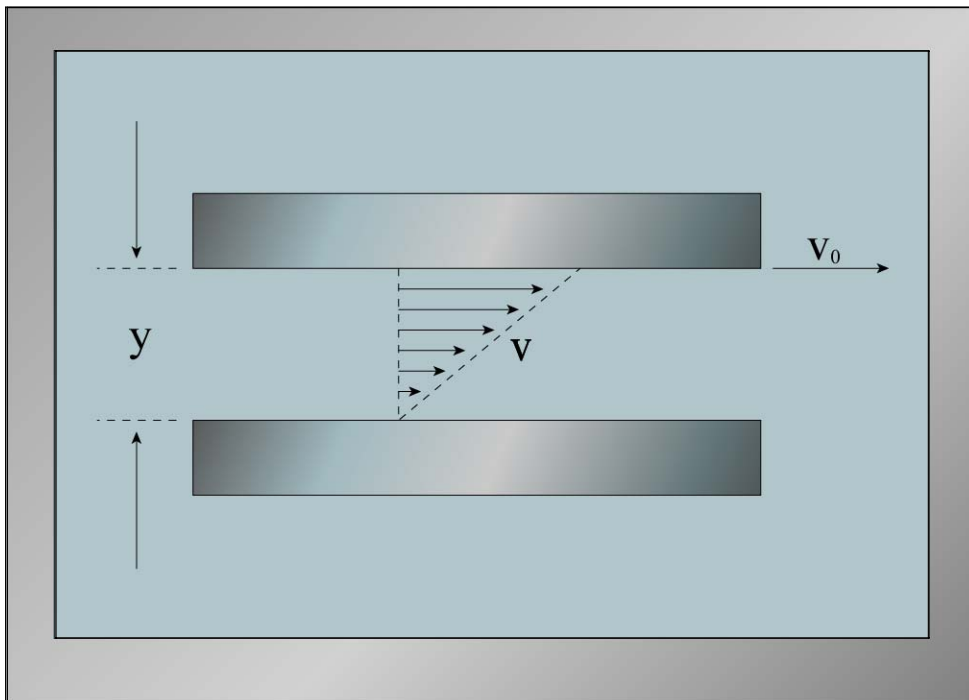
Then if you shear a fluid at a constant rate

$$\dot{\gamma}_{xy} = \frac{\dot{\delta}}{z} = \frac{v_0}{z}$$

$$\dot{\gamma}_{xy} = \frac{dv}{dz} = \frac{d}{dt}\left[\frac{dx}{dz}\right]$$
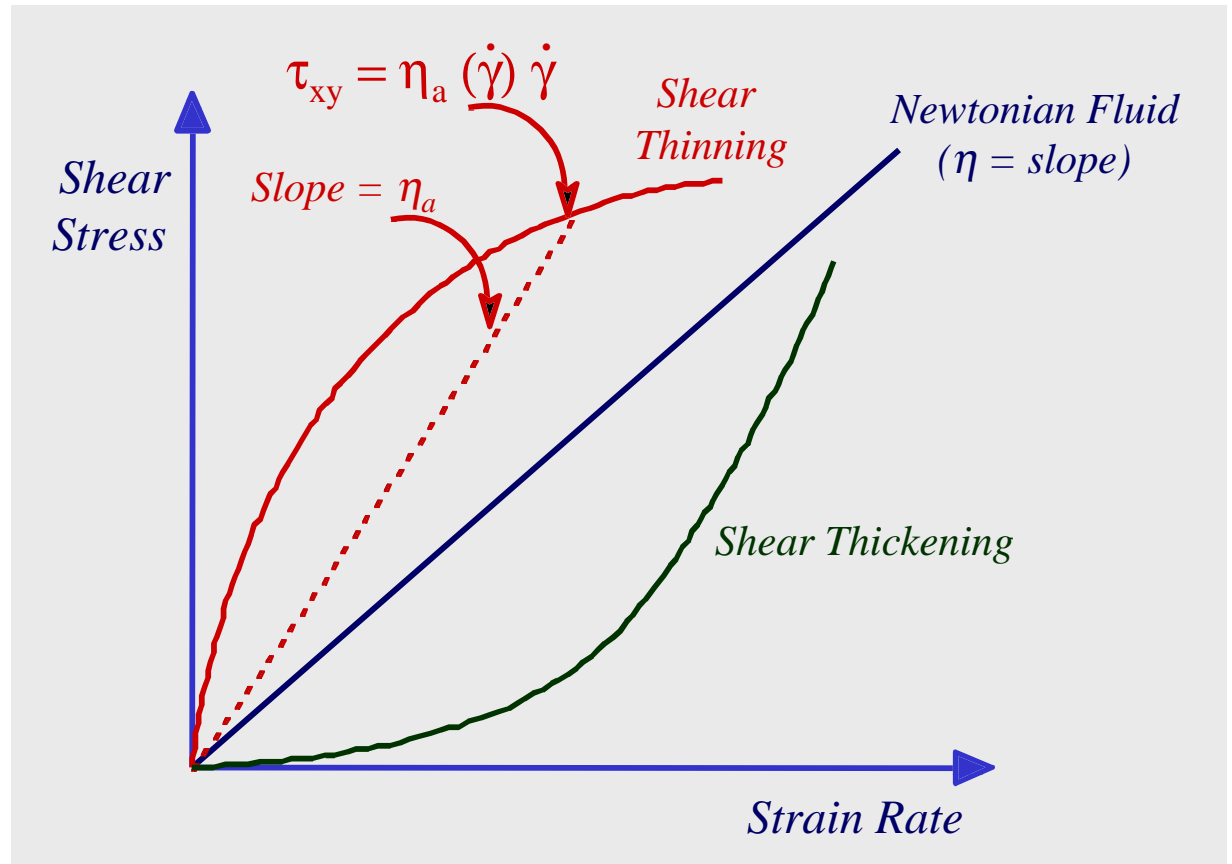
Just as stress is proportional to strain in Hooke's law for a solid, the shear stress is proportional to the rate of strain for a fluid

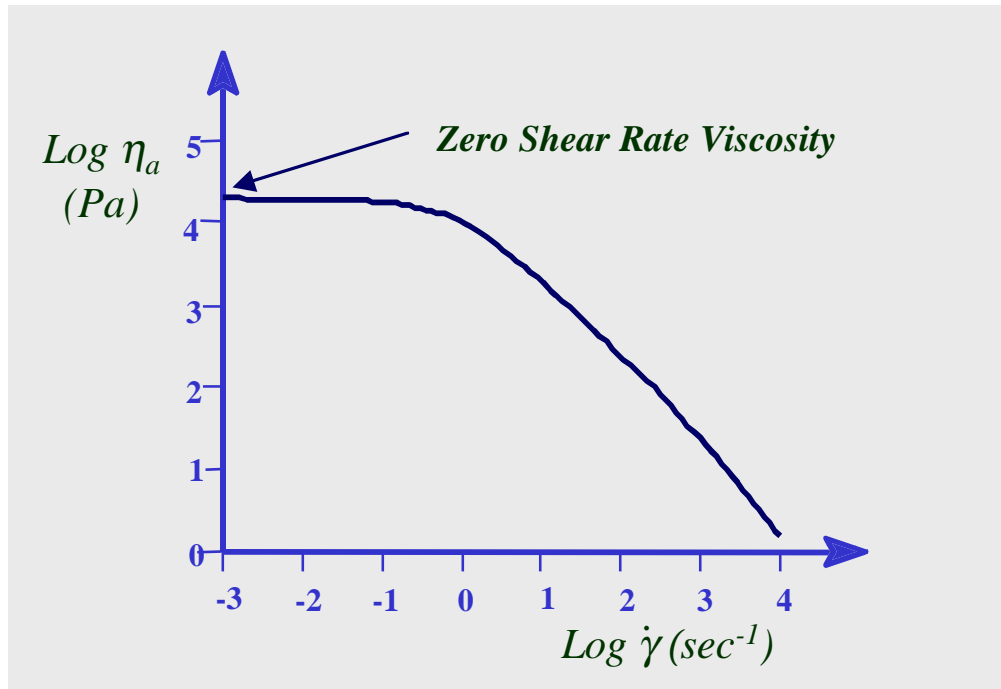$$\tau_{xy} \propto \dot{\gamma}_{xy}$$

$$\tau_{xy} = \eta\dot{\gamma}_{xy}$$

Newtonian and Non - Newtonian Fluids

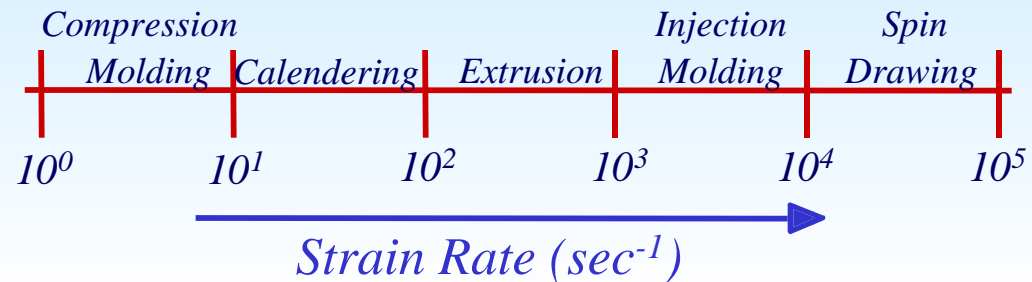When the chips are down, what do you use?

$$\tau_{xy} = \eta_a \, (\dot{\gamma}) \, \dot{\gamma}$$

Slope = η_a

Shear Thinning

Newtonian Fluid (η = slope)

Shear Stress

Shear Thickening

Strain Rate

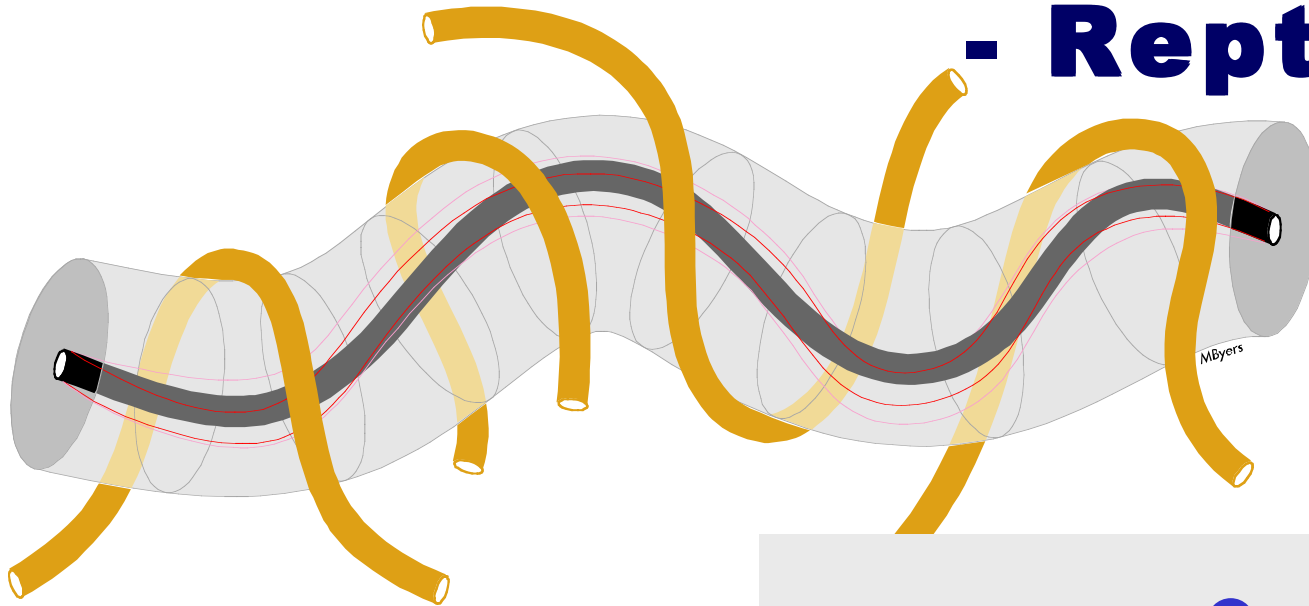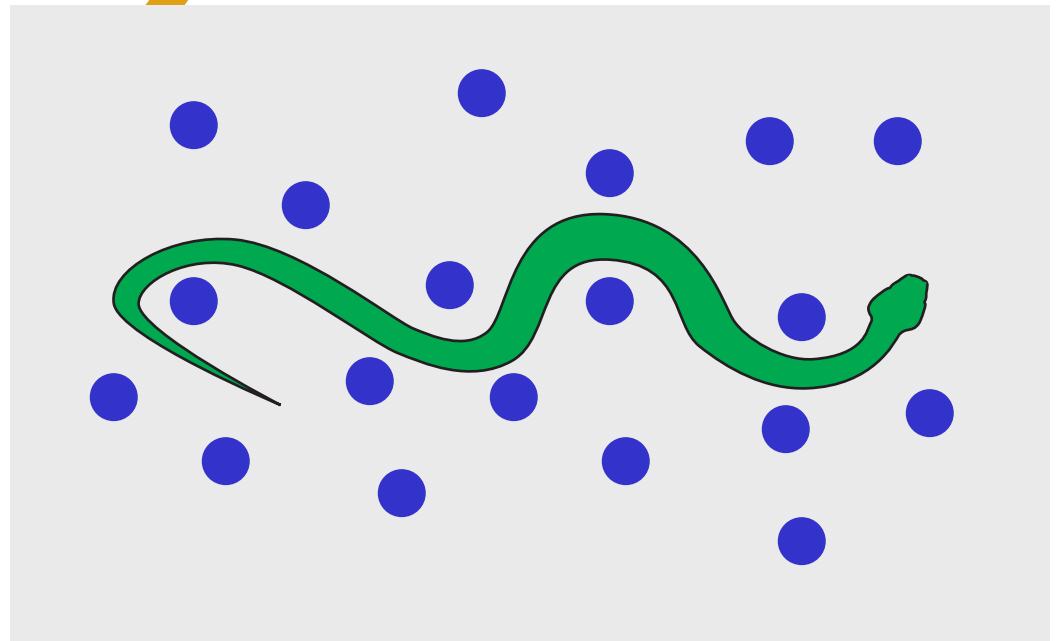# Variation of Melt Viscosity with Strain Rate

How Do Chains Move - Reptation

$$D \sim 1/M^2$$

$$\eta_0 \sim M^3$$

Variation of Melt Viscosity with Molecular Weight
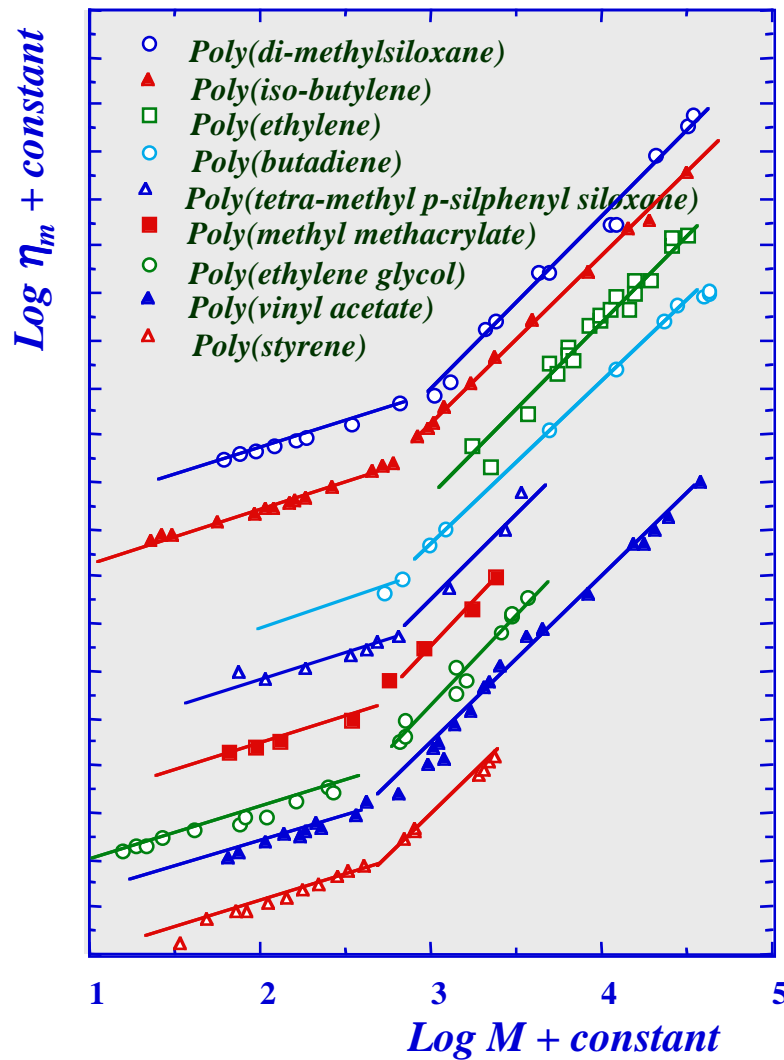
Legend:
- ○ Poly(di-methylsiloxane)
- ▲ Poly(iso-butylene)
- ☐ Poly(ethylene)
- ○ Poly(butadiene)
- △ Poly(tetra-methyl p-silphenyl siloxane)
- ■ Poly(methyl methacrylate)
- ○ Poly(ethylene glycol)
- ▲ Poly(vinyl acetate)
- △ Poly(styrene)

Y-axis: Log η_m + constant

X-axis: Log M + constant

$$\eta_m = K_L(DP)^{1.0}$$

$$\eta_m = K_H(DP)^{3.4}$$

Entanglements

Short chains don't entangle but long ones do - think of the difference between a nice linguini and spaghettios, the little round things you can get out of a tin (we have some value judgements concerning the relative merits of these two forms of pasta, but on the advice of our lawyers we shall refrain from comment).
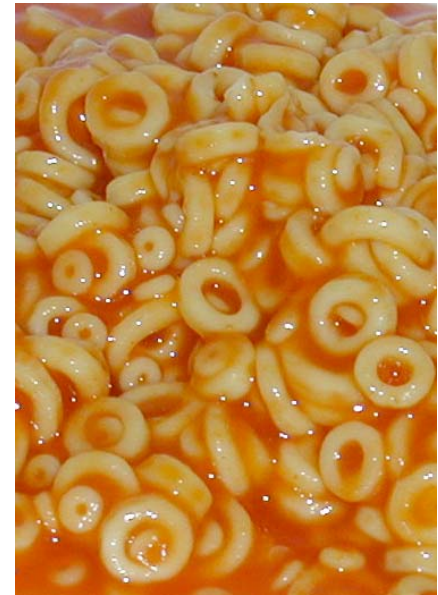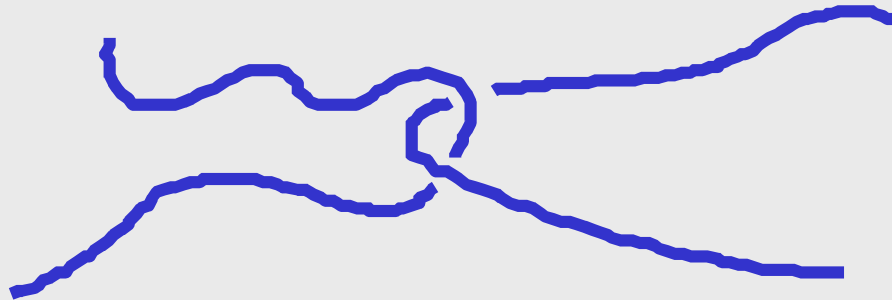
Entanglements

Viscosity - a measure of the frictional forces acting on a molecule

$$\eta_m = K_L(DP)^{1.0}$$

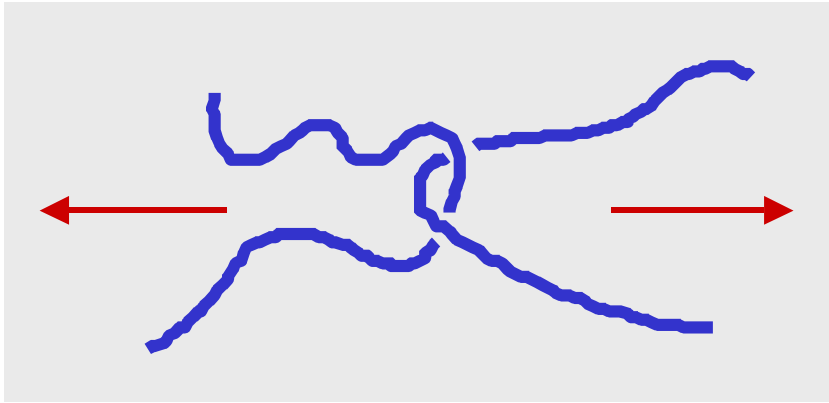Small molecules - the viscosity varies directly with size

At a critical chain length chains start to become tangled up with one another, however
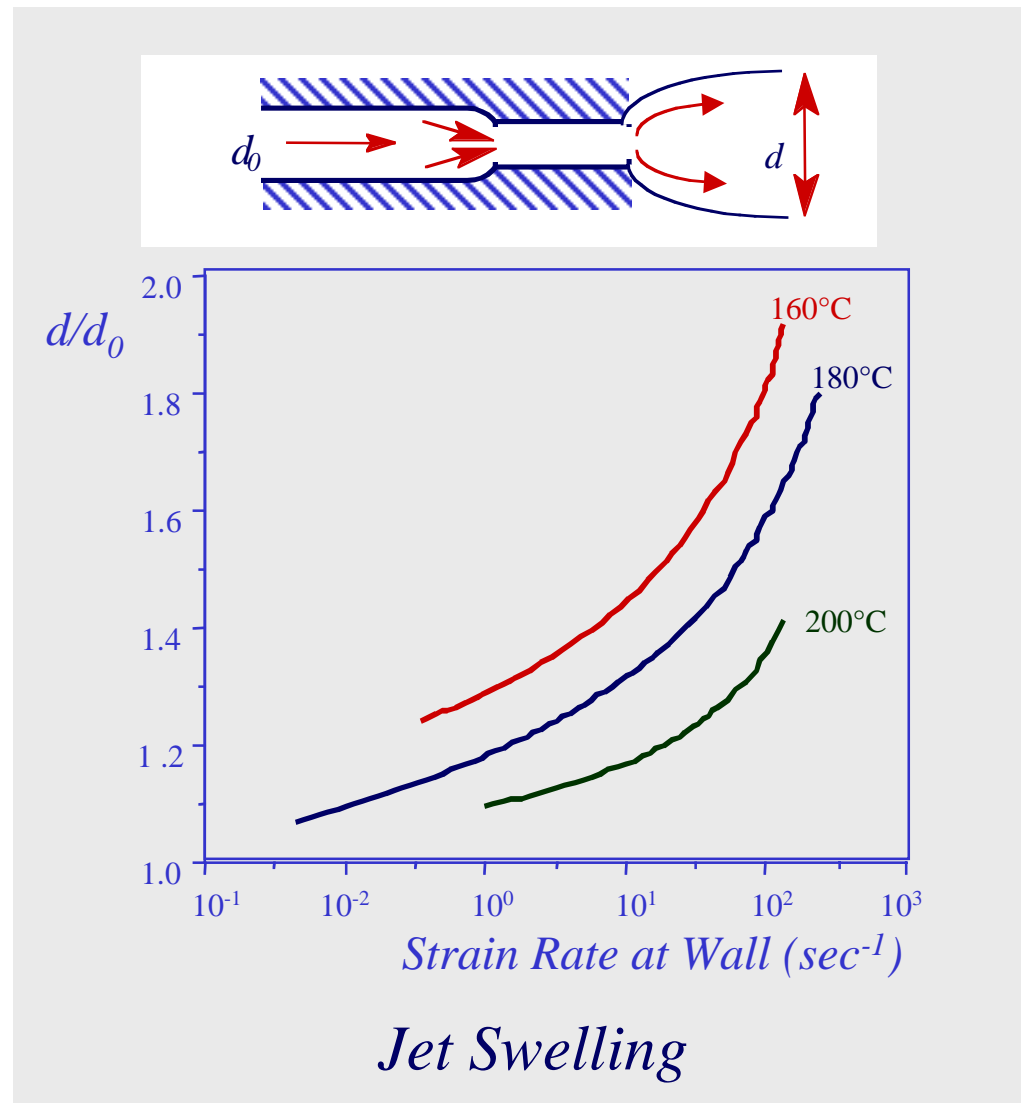

Then

$$\eta_m = K_H(DP)^{3.4}$$

Entanglements and the Elastic Properties of Polymer Melts
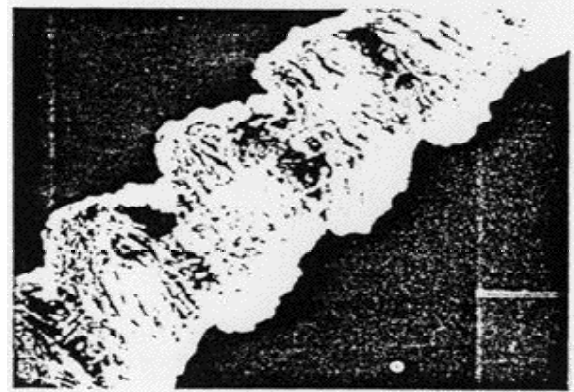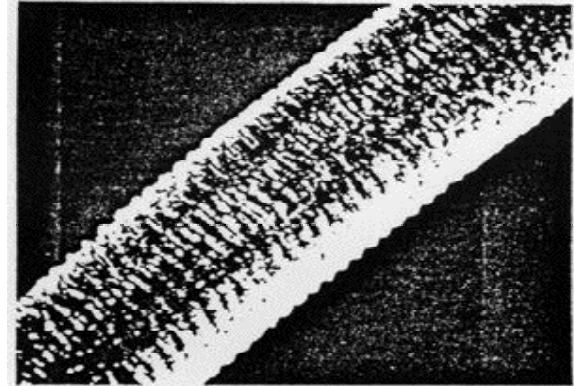
Depending upon the rate at which chains disentangle relative to the rate at which they stretch out, there is an elastic component to the behavior of polymer melts. There are various consequences as a result of this.
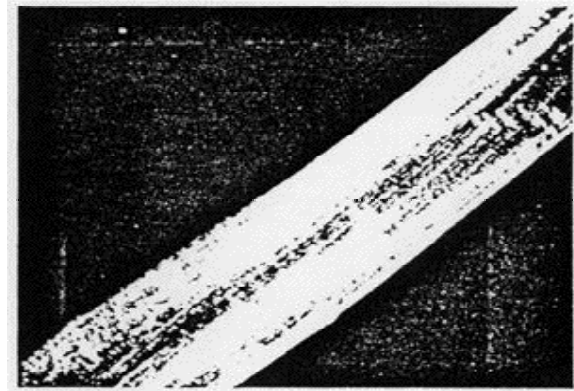
d/d_0

160°C

180°C

200°C

10^{-1} 10^{-2} 10^0 10^1 10^2 10^3

Strain Rate at Wall (sec^{-1})

Jet Swelling

Melt Fracture

Viscoelasticity

If we stretch a crystalline solid,
The energy is stored in the
Chemical bonds

If we apply a shear stress to
A fluid,energy is dissipated
In flow

VISCOELASTIC

*Ideally elastic
behaviour*

*Ideally viscous
behaviour*

Viscoelasticity
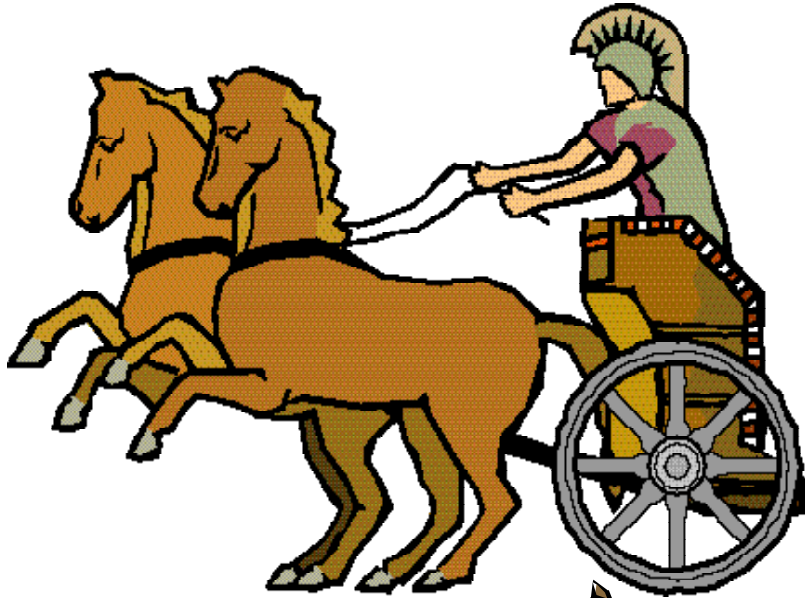
Homer knew that the first thing To do on getting your chariot out in the morning was to put the wheels back in.
(Telemachus, in *The Odyssey*, would tip his chariot against a wall)
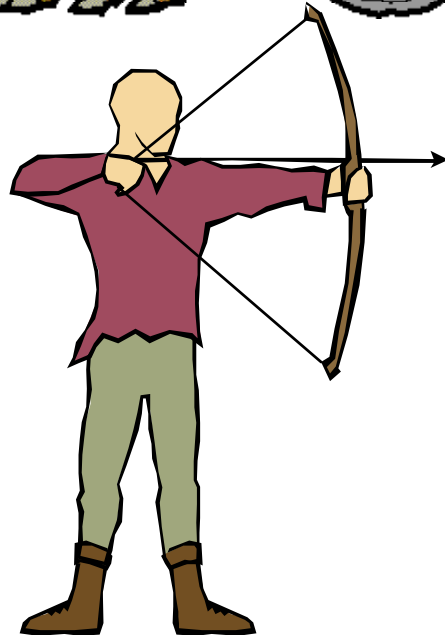
Robin hood knew never to leave his bow strung

Experimental Observations

- *Creep*

- *Stress Relaxation*

- *Dynamic Mechanical Analysis*

Creep and Stress Relaxation

Creep - deformation under a constant load as a function of time

5lb
5lb
5lb
5lb

TIME

Stress Relaxation - constant deformation experiment

5lb **4lb** **3lb** **2lb**
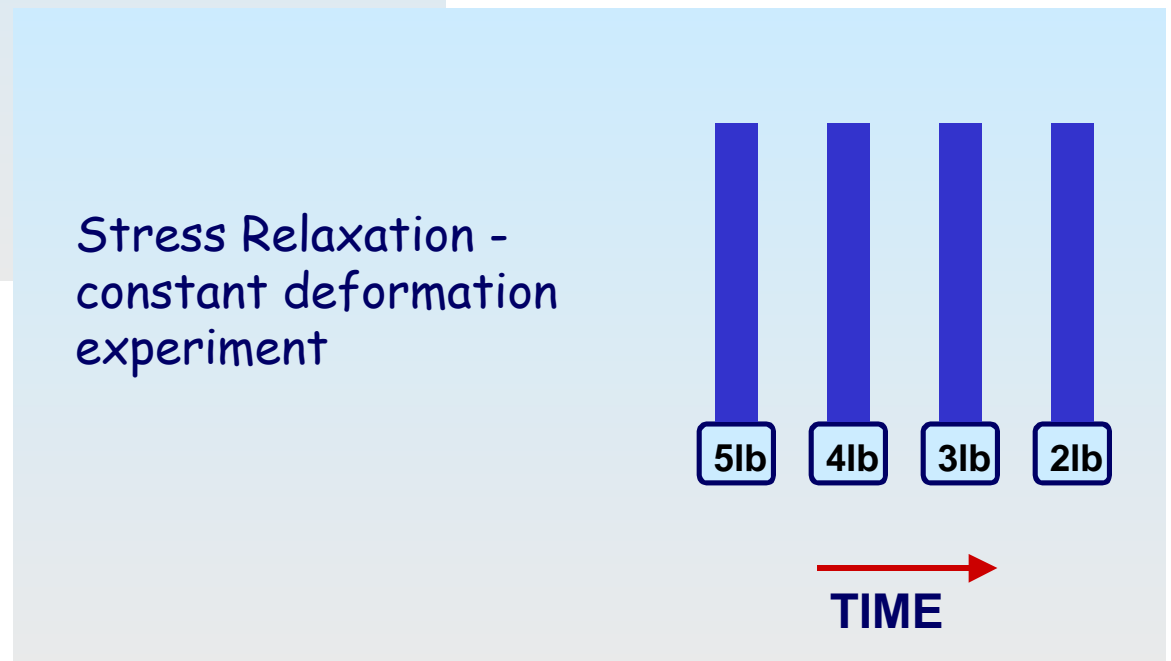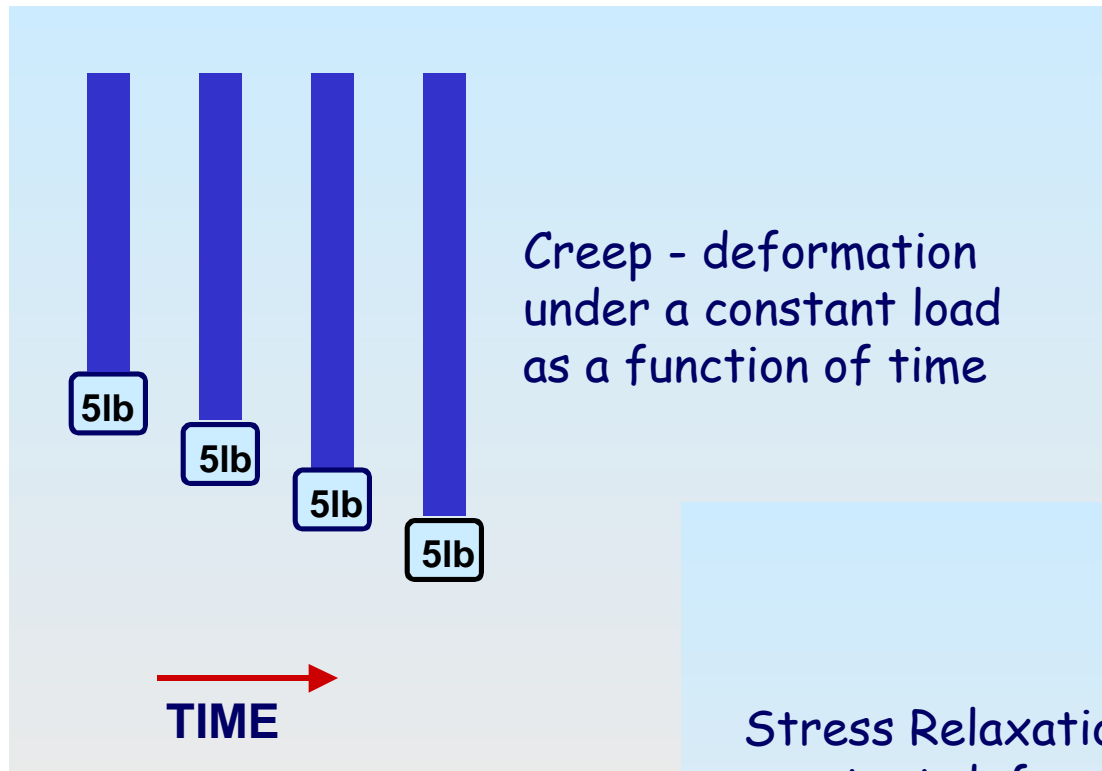
TIME

Redrawn from the data of W. N. Findley, Modern Plastics, 19, 71 (August 1942)

Creep and Recovery

(c) VISCOELASTIC RESPONSE
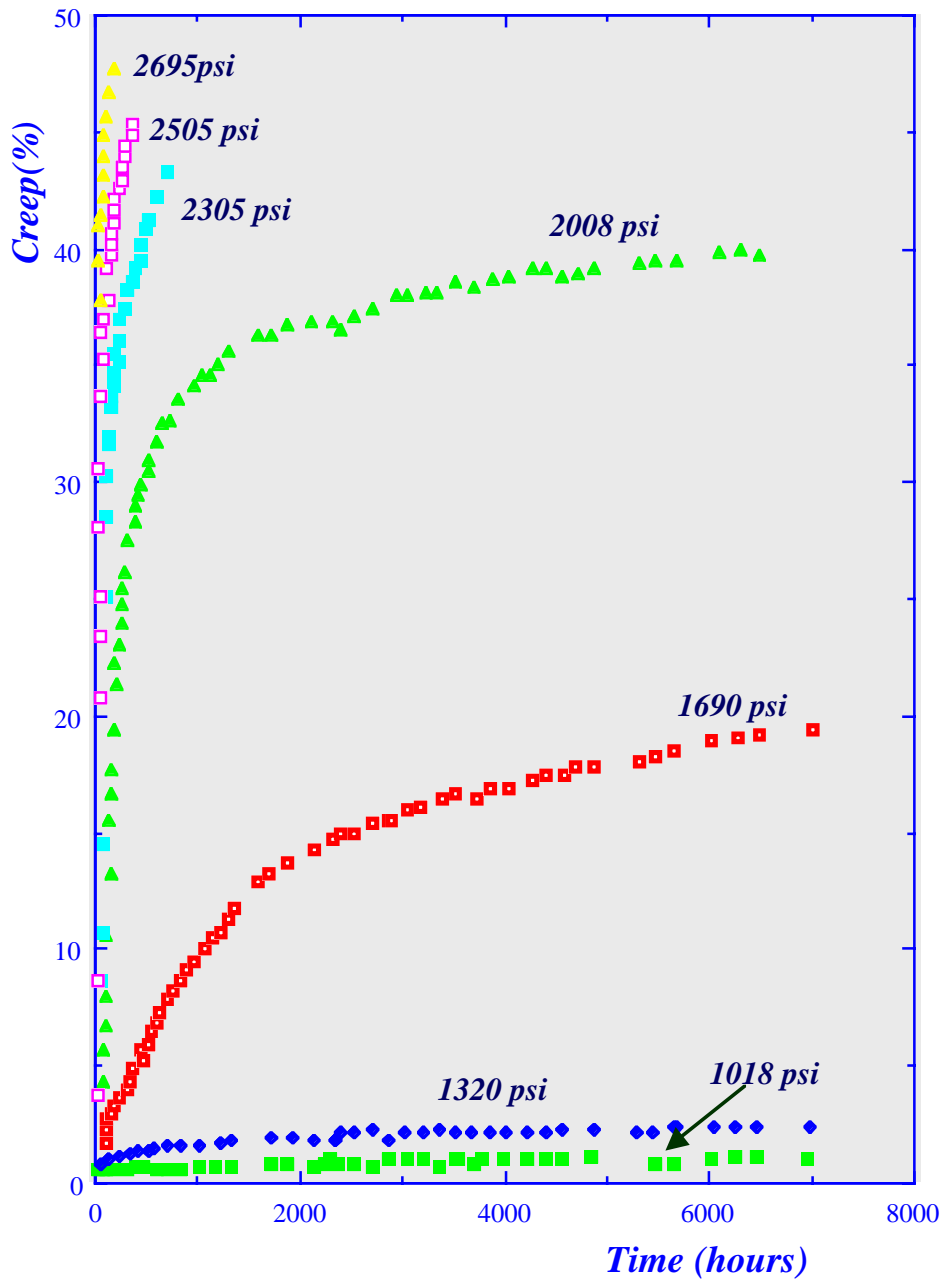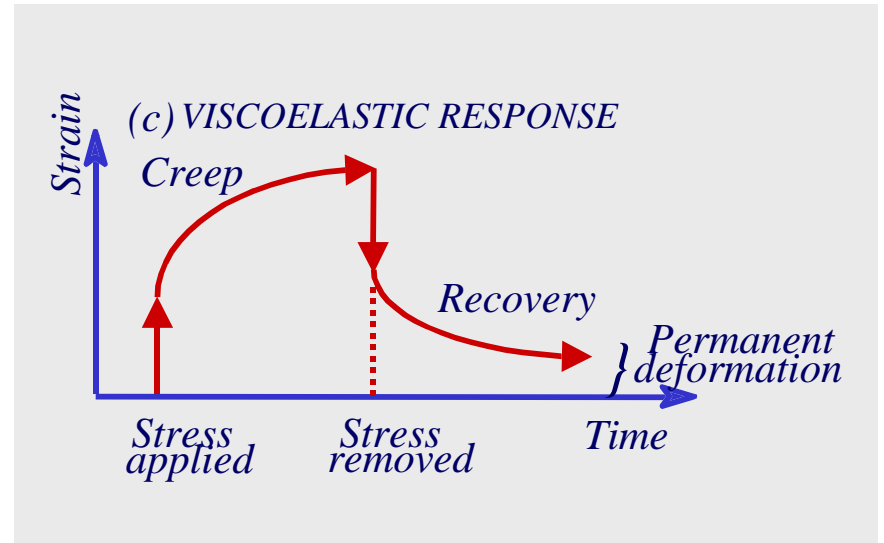
Strain vs. Time Plots - Creep

(a) *PURELY ELASTIC RESPONSE*

Strain

Stress applied   Stress removed   Time

(b) *PURELY VISCOUS RESPONSE*

Strain

Permanent Deformation

Shear Stress applied   Shear Stress removed   Time

(c) *VISCOELASTIC RESPONSE*

Strain   *Creep*

Recovery

} *Permanent deformation*

Stress applied   Stress removed   Time
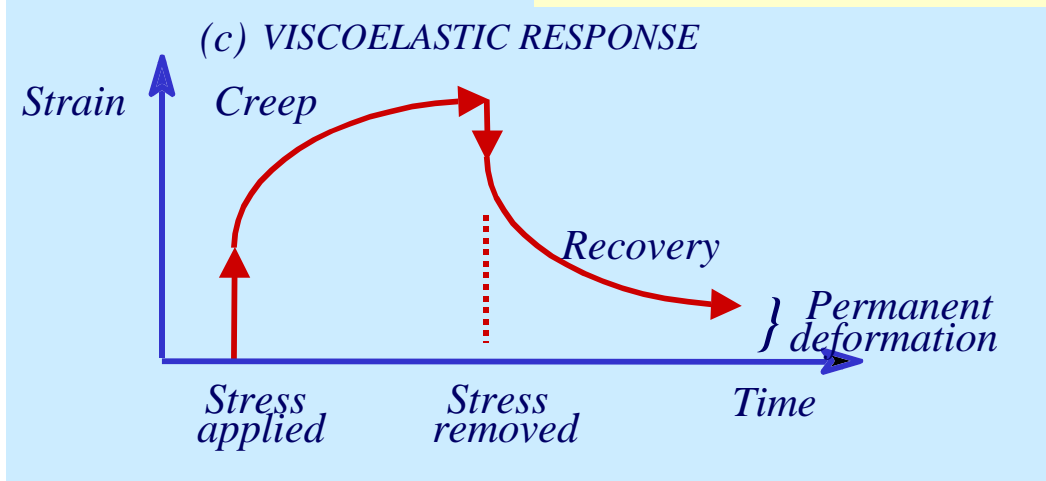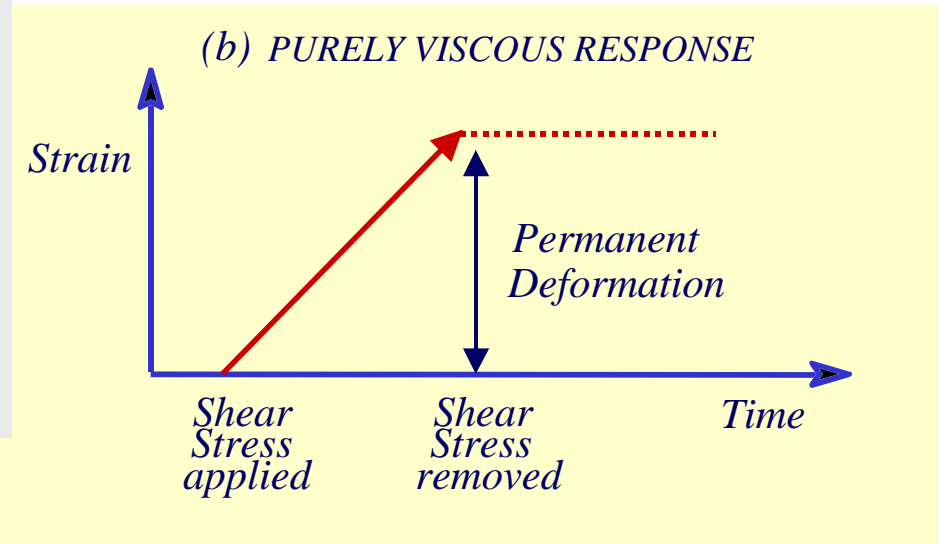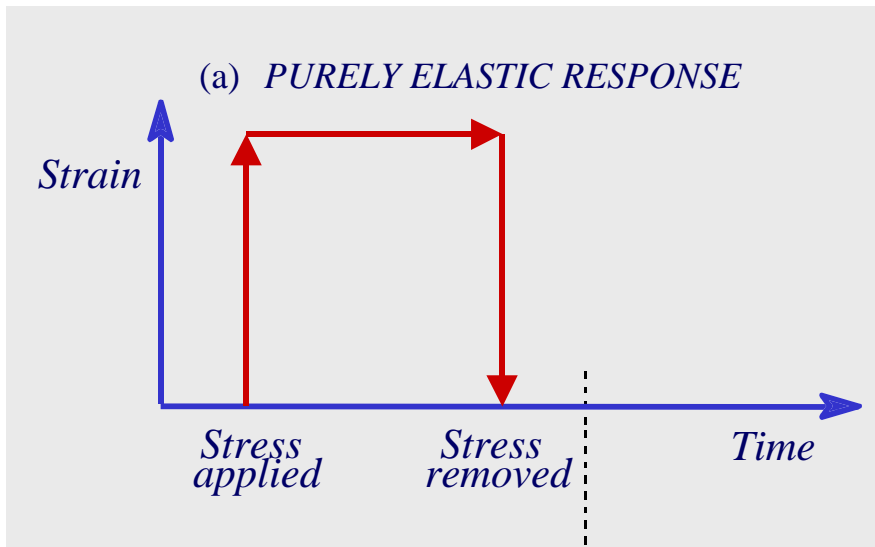
Stress Relaxation

The data are not usually reported as a stress/time plot, but as a modulus/time plot. This time dependent modulus, called the *relaxation modulus*, is simply the time dependent stress divided by the (constant) strain

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}$$

Log E(t), (dynes/cm²)

Time (hours)

Stress relaxation of PMMA

40⁰C
60⁰C
92⁰C
80⁰C
100⁰C
110⁰C
112⁰C
120⁰C
115⁰C
125⁰C
135⁰C

10

9

8

7

0.001   0.01   0.1   1   10   100   1000
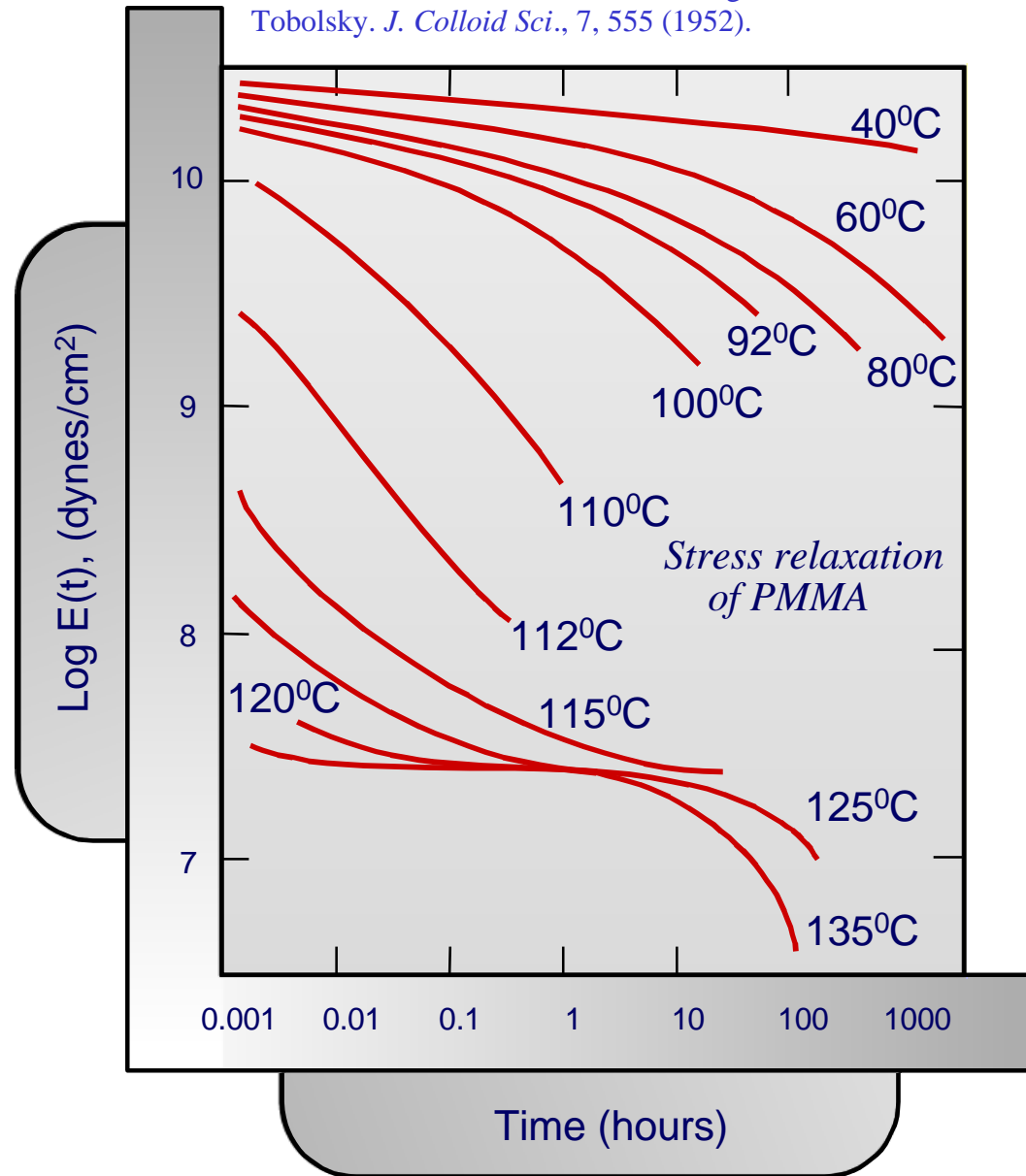
Amorphous Polymers - Range of Viscoelastic Behaviour

Viscoelastic Properties 0f Amorphous Polymers

Measured over
Some arbitrary
Time period - say
10 secs

Viscoelastic Properties Of Amorphous Polymers

Stretch sample an arbitrary amount, measure the stress required to maintain this strain.
Then $E(t) = \sigma(t)/\varepsilon$

Glassy Region

Glass Transition

Rubbery Plateau

$Log\ E(t)\ (dynes/cm^2)$

Low Molecular Weight

High Molecular Weight

Log Time (Sec)
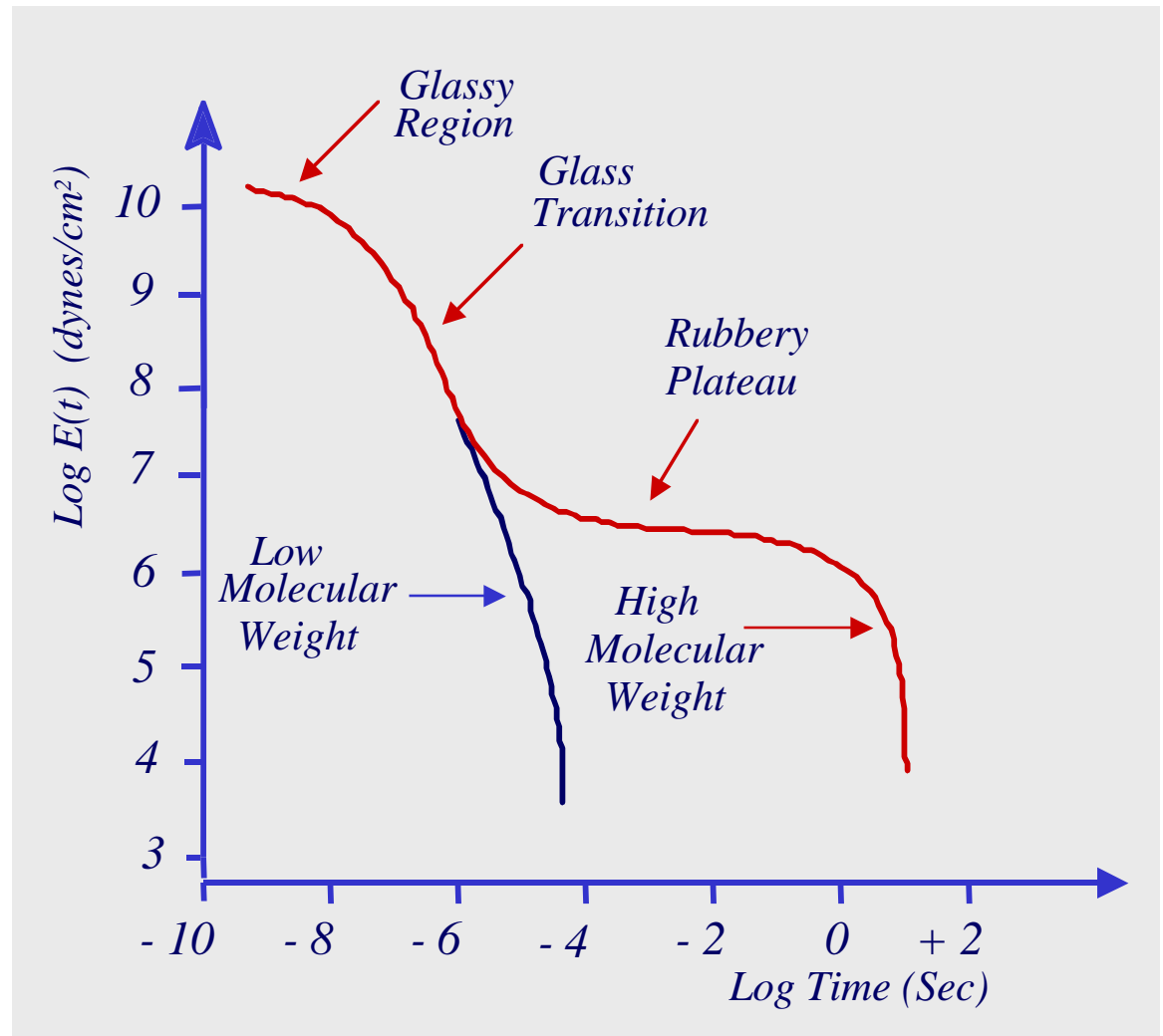
Time Temperature Equivalence
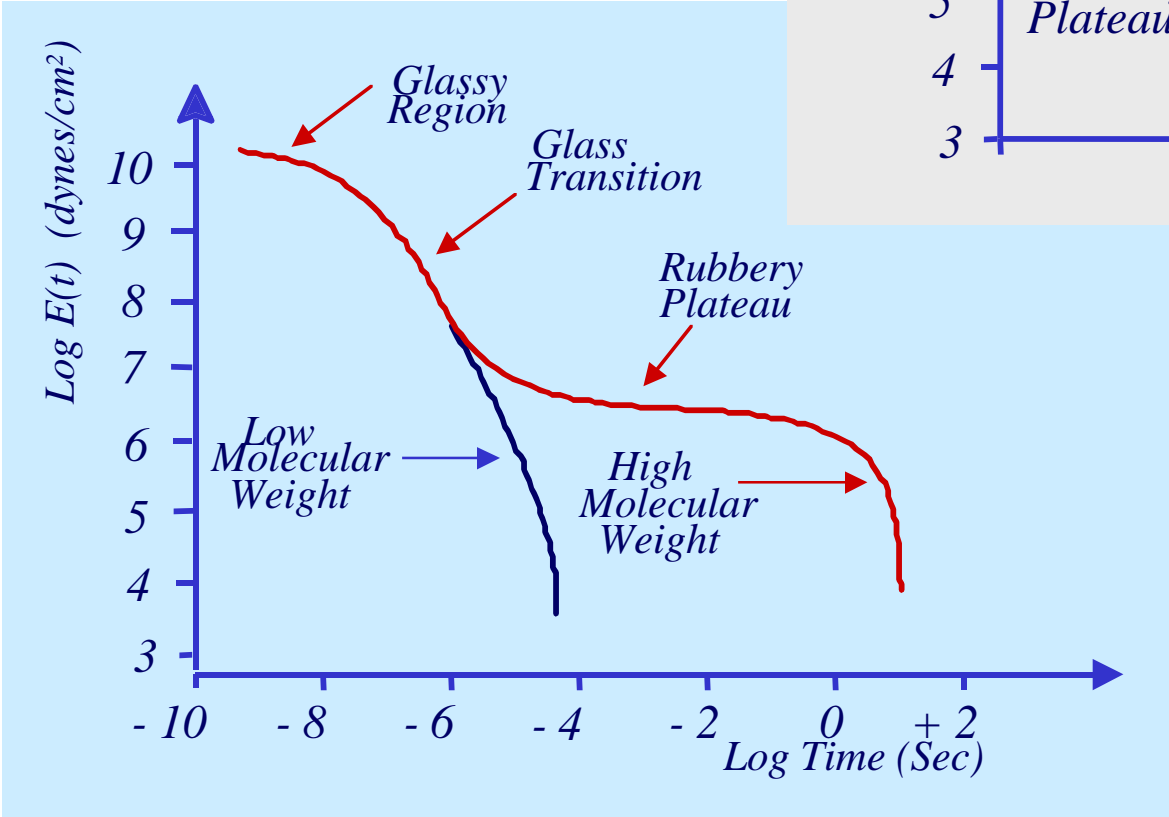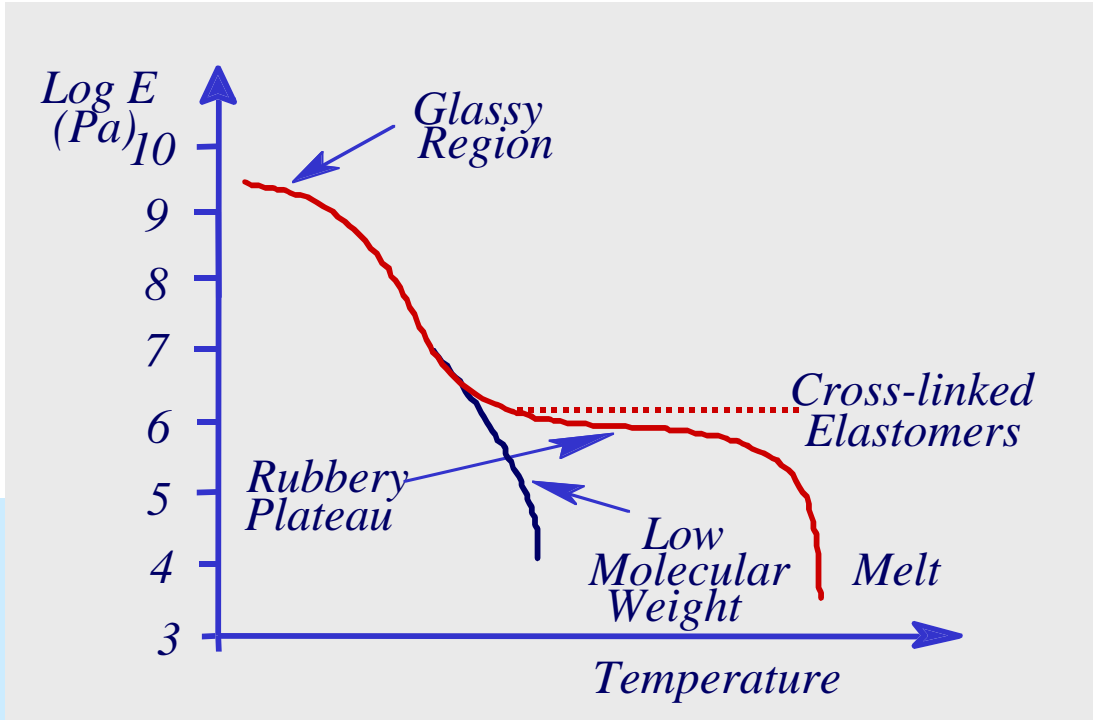
Relaxation in Polymers

First consider a hypothetical isolated chain in space, then imagine stretching this chain instantaneously so that there is a new end - to - end distance. The distribution of bond angles (trans, gauche, etc) changes to accommodate the conformations that are allowed by the new constraints on the ends. Because it takes time for bond rotations to occur, particularly when we also add in the viscous forces due to neighbors, we say the chain *RELAXES* to the new state and the relaxation is described by a characteristic time τ.

How quickly can I do these things?
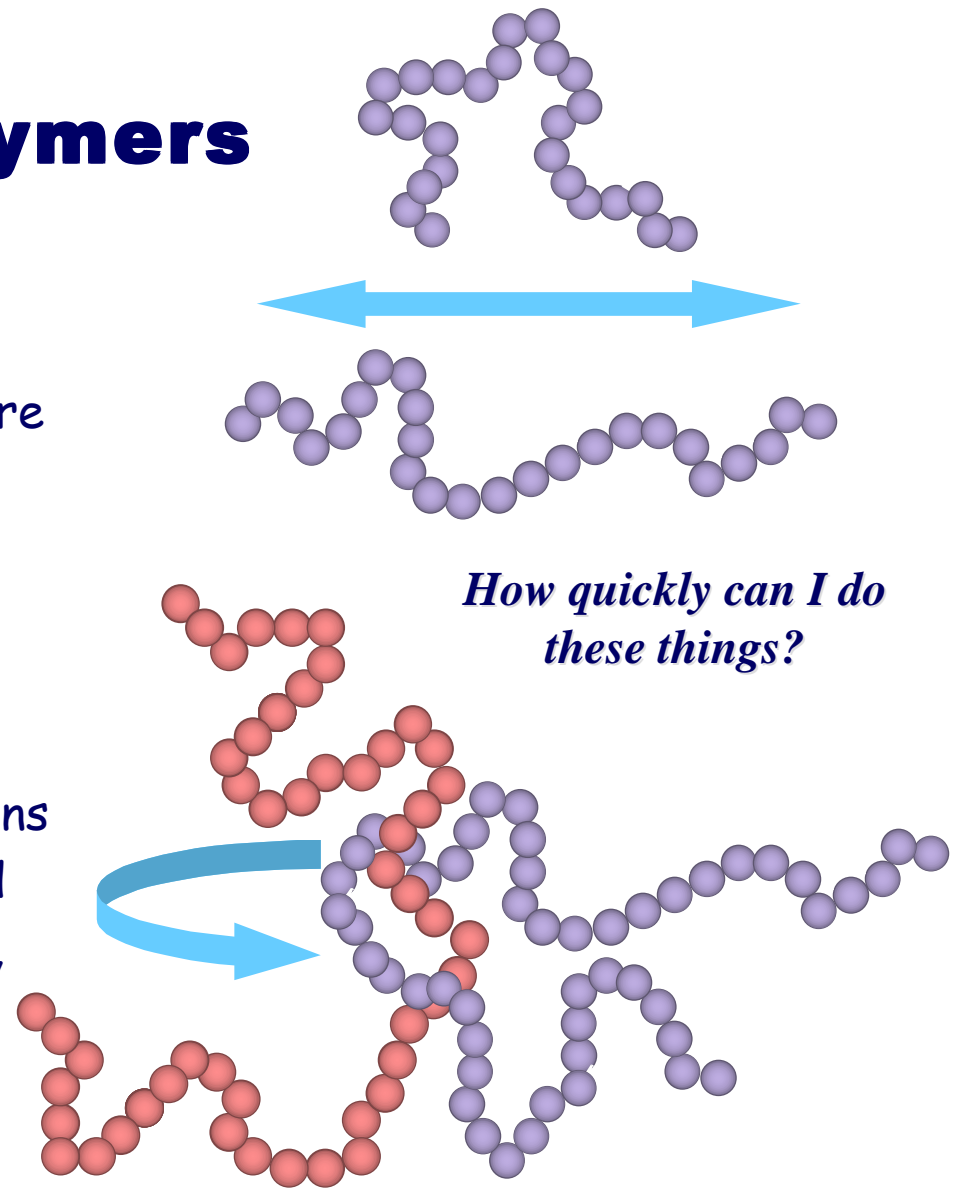
Amorphous Polymers - the Four Regions of Viscoelastic Behavior

GLASSY STATE - conformational changes severely inhibited.

Tg REGION - cooperative motions of segments now occur, but the motions are sluggish (a maximum in tan δ curves are observed in DMA experiments)

RUBBERY PLATEAU - τ_t becomes shorter, but still longer than the time scale for disentanglement
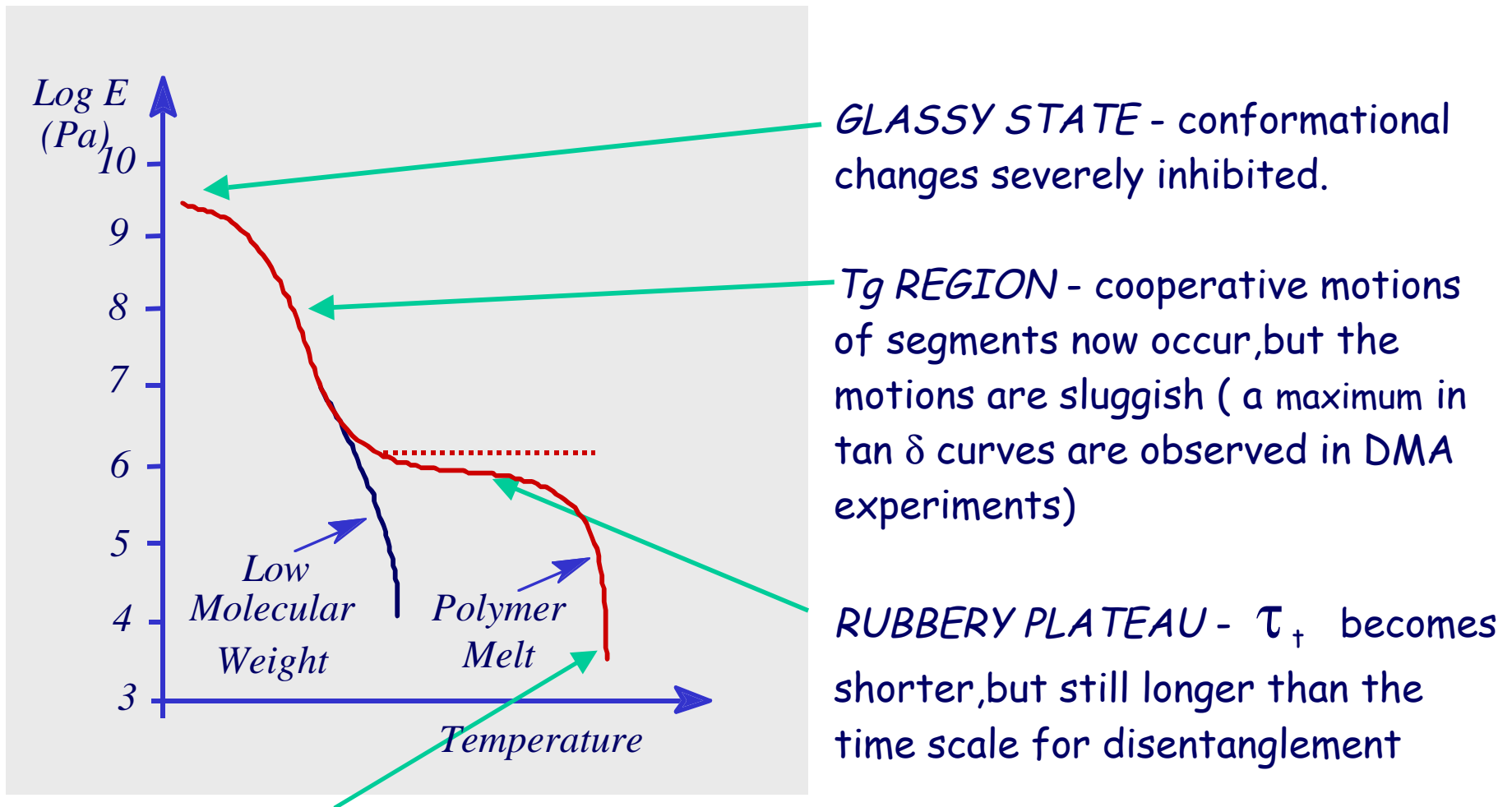
TERMINAL FLOW - the time scale for disentanglement becomes shorter and the melt becomes more fluid like in its behavior

Semicrystalline Polymers
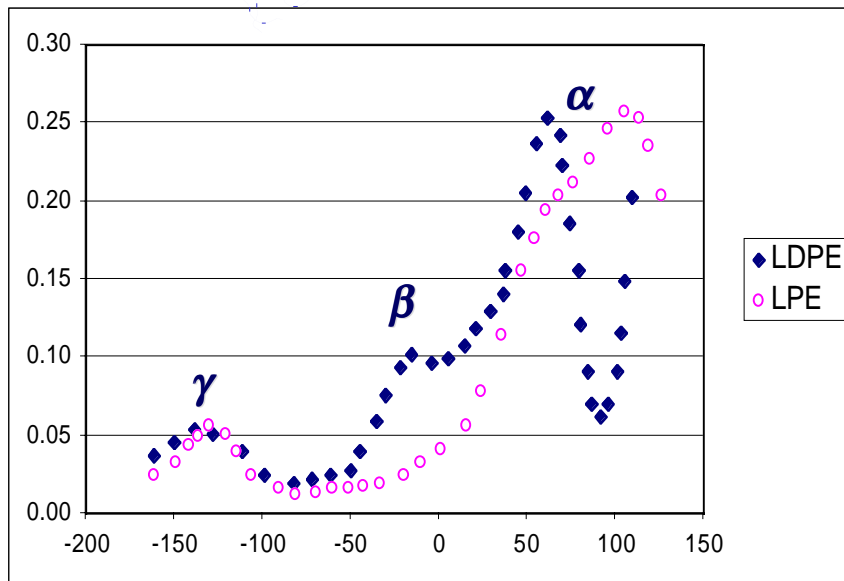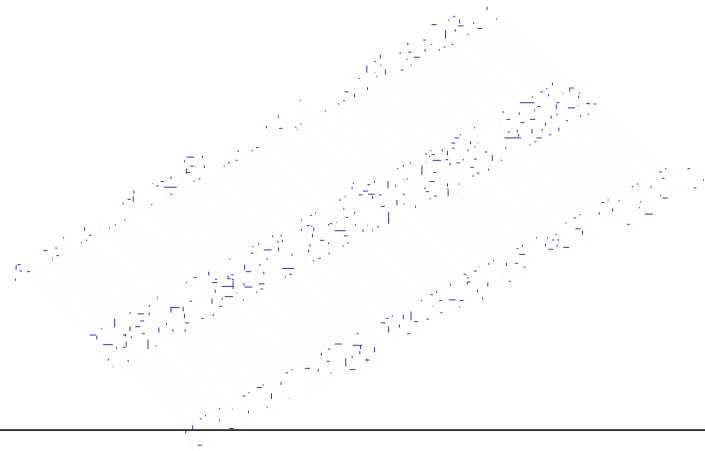
Redrawn from the data of H. A. Flocke,
Kolloid–Z. Z. Polym., **180**, *188 (1962).*

- Motion in the amorphous domains constrained by crystallites

- Motions above Tg are often more complex, often involving coupled processes in the crystalline and amorphous domains

- Less easy to generalize - polymers often have to be considered individually - see DMA data opposite

Topics to be Covered

- *Simple models of Viscoelastic Behavior*

- *Time-Temperature Superposition Principle*

Chapter 11 in CD (Polymer Science and Engineering)

Mechanical and Theoretical Models of Viscoelastic Behavior

GOAL - relate G(t) and J(t) to relaxation behavior.
We will only consider *LINEAR MODELS*. (i.e. if we double G(t) [or $\sigma(t)$], then $\gamma(t)$ [or $\varepsilon(t)$] also increases by a factor of 2 (small loads and strains)).

TENSILE EXPERIMENT	SHEAR EXPERIMENT

Stress Relaxation

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \qquad G(t) = \frac{\tau(t)}{\gamma_0}$$

Creep

$$D(t) = \frac{\varepsilon(t)}{\sigma_0} \qquad J(t) = \frac{\gamma(t)}{\tau_0}$$

Linear Time Independent Behavior

$$E = \frac{1}{D} \qquad G = \frac{1}{J}$$
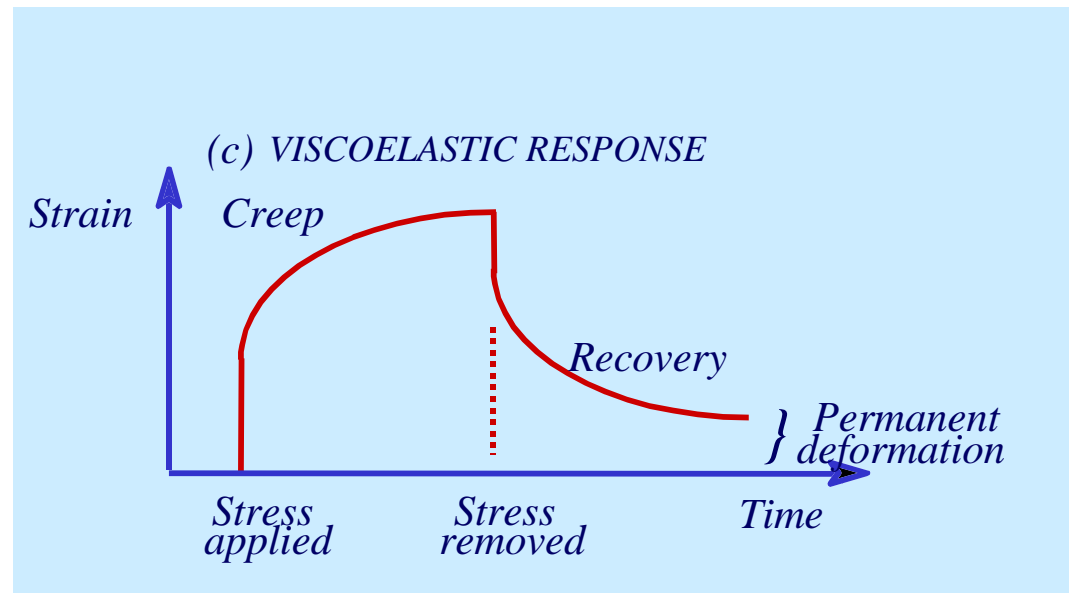
Time Dependent Behavior

$$E(t) \neq \frac{1}{D(t)} \qquad G(t) \neq \frac{1}{J(t)}$$

Simple Models of the Viscoelastic Behavior of Amorphous Polymers

Keep in mind that simple creep and recovery data for viscoelastic materials looks something like this

Simple Models of the Viscoelastic Behavior of Amorphous Polymers

While stress relaxation data look something like this;
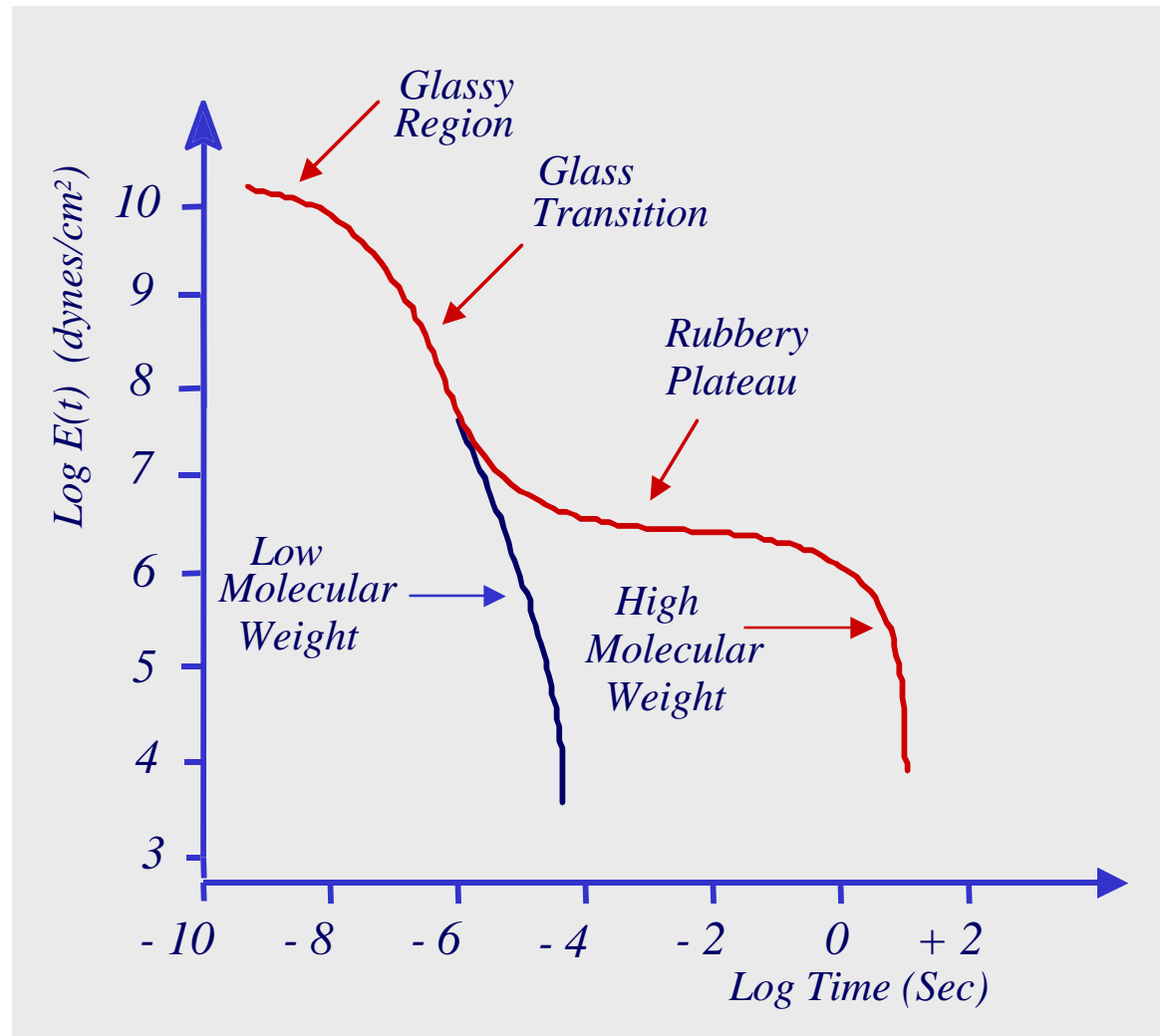
Simple Models of the Viscoelastic Behavior of Amorphous Polymers

Extension

l_0

Δl

σ

Hooke's law

$$\sigma = E\varepsilon$$

I represent linear elastic behavior

$$\sigma = E\varepsilon$$
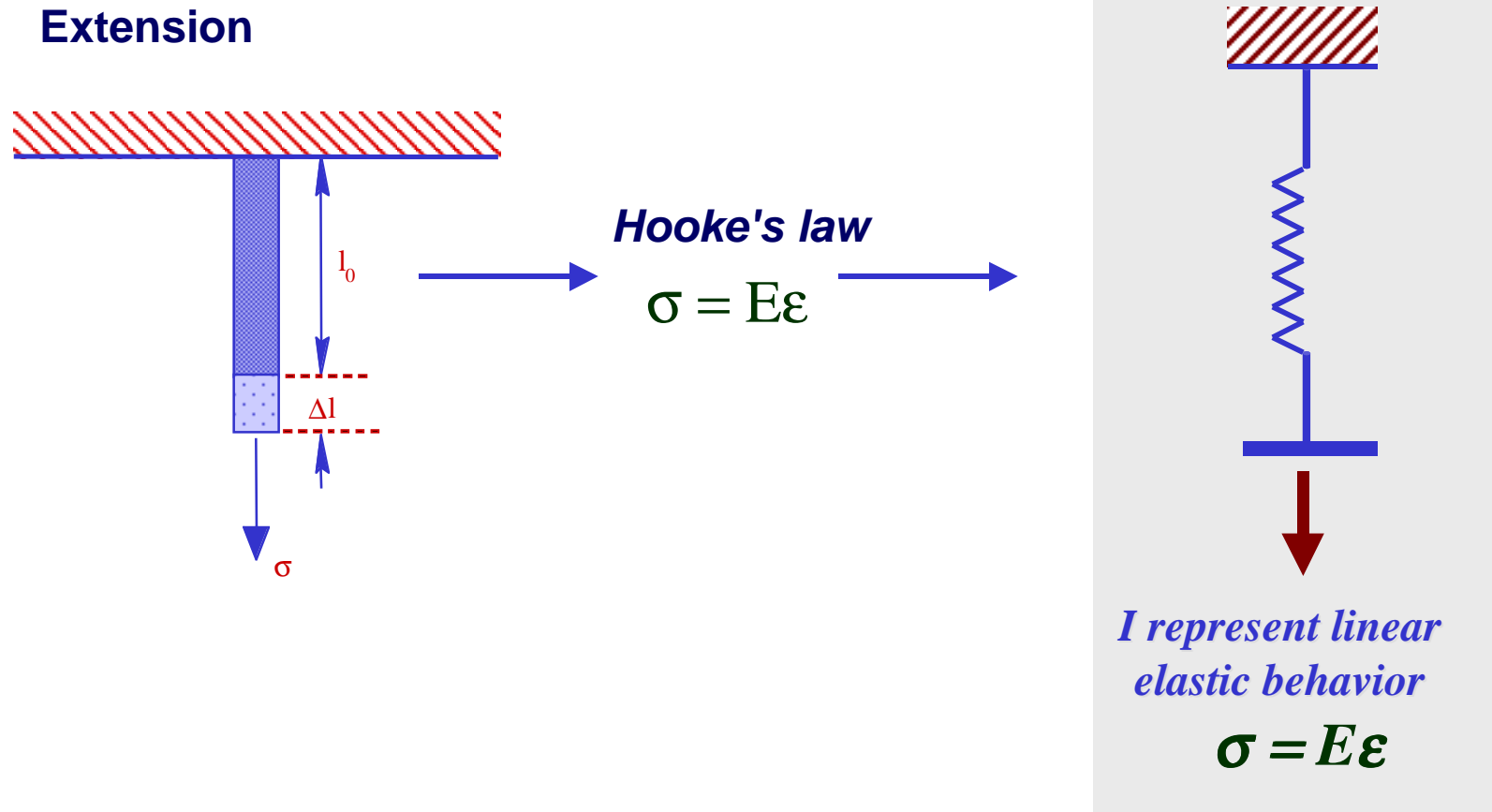
Simple Models of the Viscoelastic Behavior of Amorphous Polymers

Viscous flow

v_0

y

v
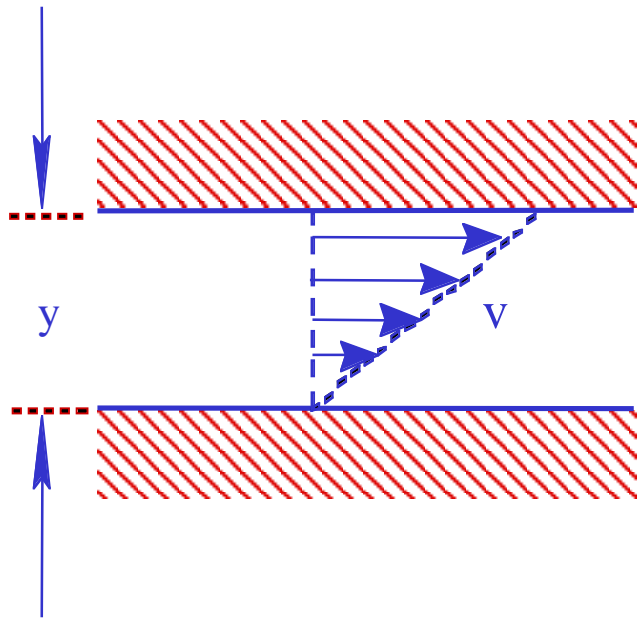
Newtonian fluid

$$\tau_{xy} = \eta\dot{\gamma}$$

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

Strain vs. Time for Simple Models

PURELY ELASTIC RESPONSE

$$\sigma = E\varepsilon$$

Strain

Time

Stress applied

Stress removed

PURELY VISCOUS RESPONSE

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

Strain

Permanent Deformation

Shear Stress applied

Shear Stress removed
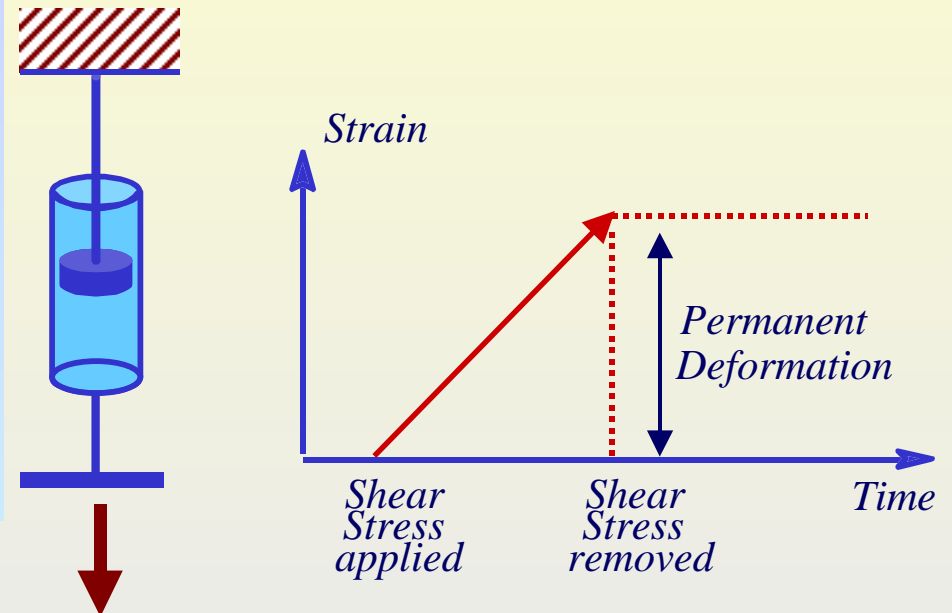
Time

Maxwell Model

Maxwell was interested in creep and stress relaxation and developed a differential equation to describe these properties
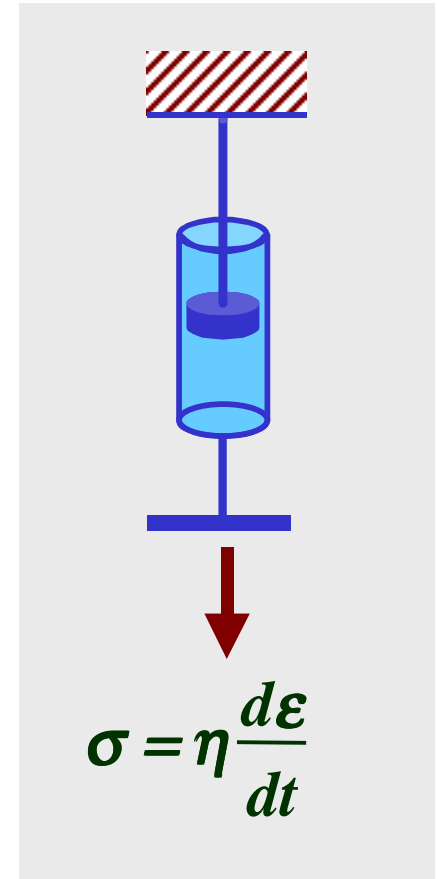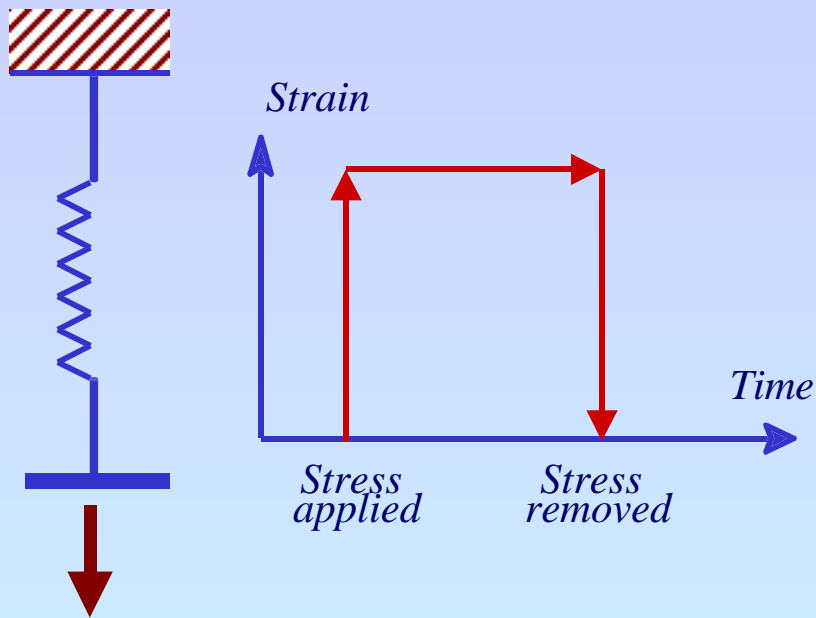
Maxwell started with Hooke's law

$$\sigma = E\varepsilon$$

Then allowed σ to vary with time

$$\frac{d\sigma}{dt} = E\frac{d\varepsilon}{dt}$$

Writing for a Newtonian fluid

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

Then assuming that the rate of strain is simply a sum of these two contributions

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

MAXWELL MODEL - *Creep and Recovery*
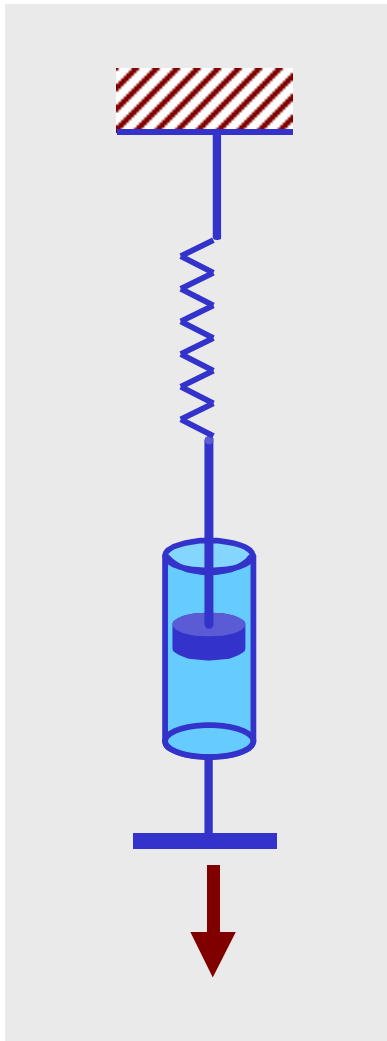
A picture representation of Maxwell's equation

Creep and recovery

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

Strain

0   t   Time
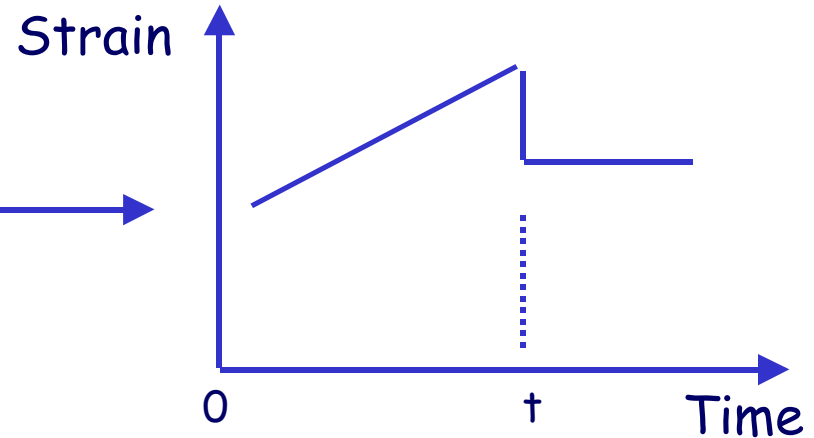
Recall that real viscoelastic behaviour looks something like this

Strain

0   t   Time
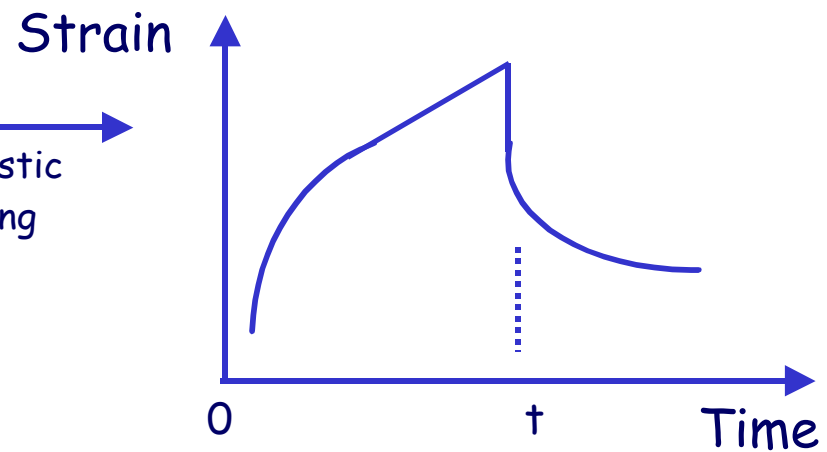
Maxwell Model -*Stress Relaxation*

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

In a stress relaxation experiment

$$\frac{d\varepsilon}{dt} = 0$$

Hence $\quad \dfrac{d\sigma}{\sigma} = \dfrac{\sigma}{\eta}\,dt$

$$\sigma = \sigma_0 \exp[-t/\tau_t]$$

Where

$$\tau_t = \frac{\eta}{E}$$

Relaxation time

Maxwell Model -*Stress Relaxation*

Log E(t) *(Pa)*

Real data looks like this

The Maxwell model gives curves like this, OR like this

Time

MAXWELL MODEL

$$E(t) = \frac{\sigma(t)}{\varepsilon_0} = \frac{\sigma_0}{\varepsilon_0} exp\left[-\frac{t}{\tau_t}\right]$$
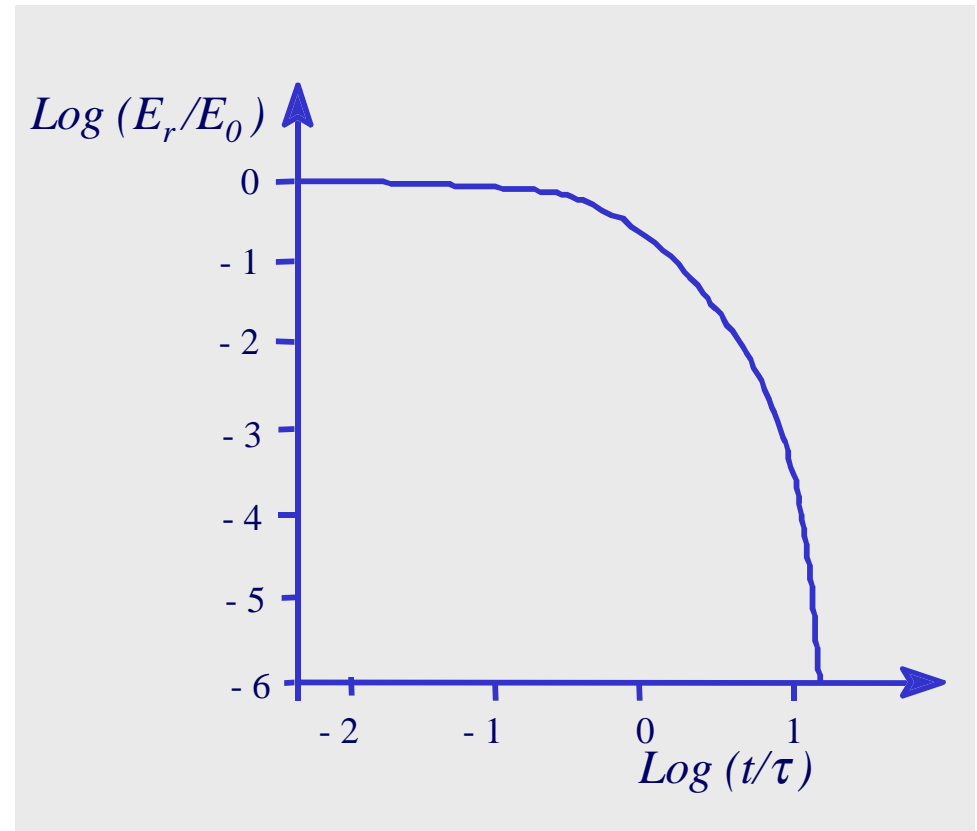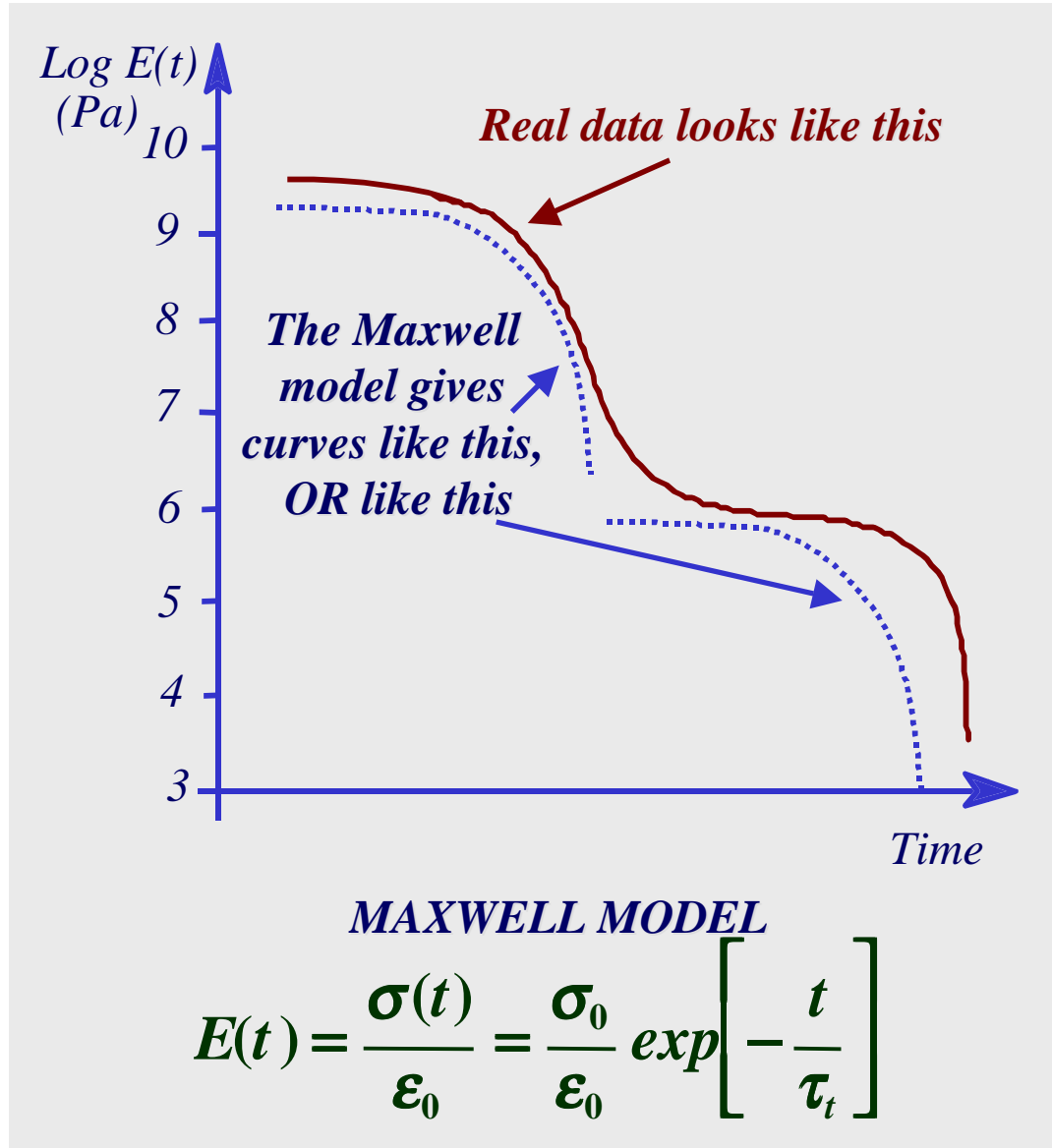
Voigt Model

Maxwell model essentially assumes a uniform distribution
Of stress.Now assume uniform distribution of strain -
VOIGT MODEL

Picture representation $\longrightarrow$

Equation

$$\sigma(t) = E\varepsilon(t) + \eta \, \frac{d\varepsilon(t)}{dt}$$

(Strain in both elements of the
model is the same and the total
stress is the sum of the two
contributions)

σ_1 σ_2

$$\sigma = \sigma_1 + \sigma_2$$

Voigt Model - *Creep and Stress Relaxation*

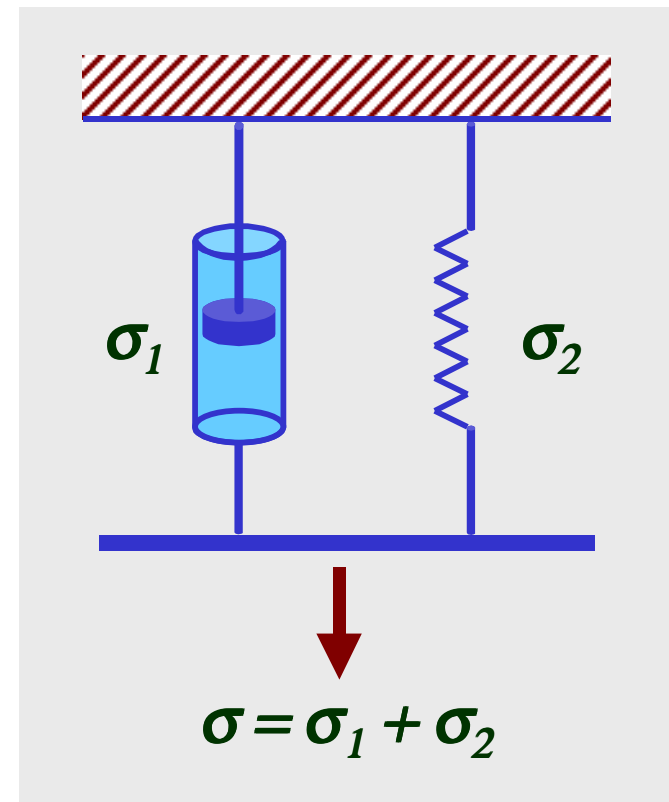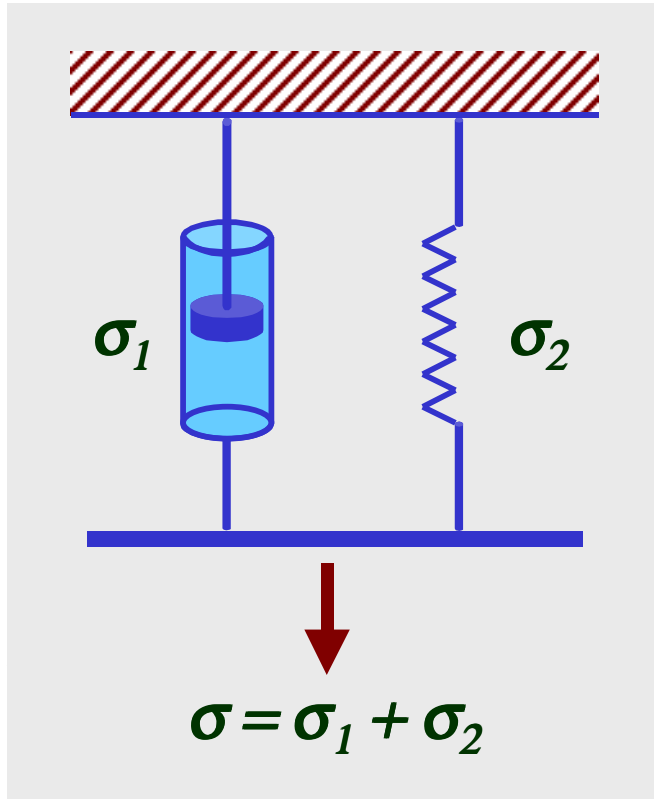Gives a retarded elastic response but does not allow for "ideal" stress relaxation, in that the model cannot be "instantaneously" deformed to a given strain.

But in *CREEP* σ = constant, σ_0

$$\sigma(t) = \sigma_0 = E\varepsilon(t) + \eta \frac{d\varepsilon(t)}{dt}$$

$$\frac{d\varepsilon(t)}{dt} + \frac{\varepsilon(t)}{\tau_t'} = \frac{\sigma_0}{\eta}$$

σ_1 σ_2

$$\sigma = \sigma_1 + \sigma_2$$

$$\varepsilon(t) = \frac{\sigma_0}{E}[1 - \exp(-t/\tau_t')]$$

τ_t' – retardation time (η/E)

RETARDED ELASTIC RESPONSE

Strain

Time

t_1 t_2
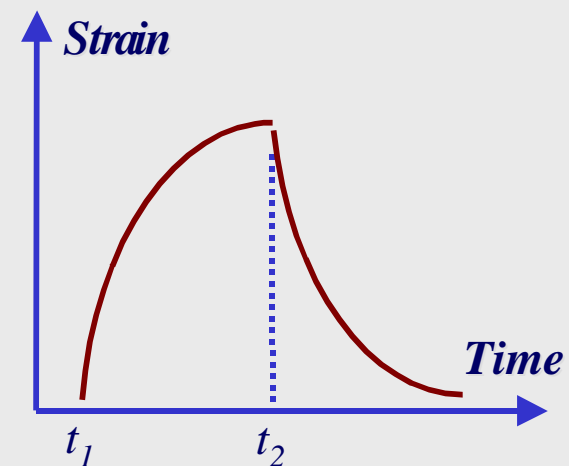
Summary
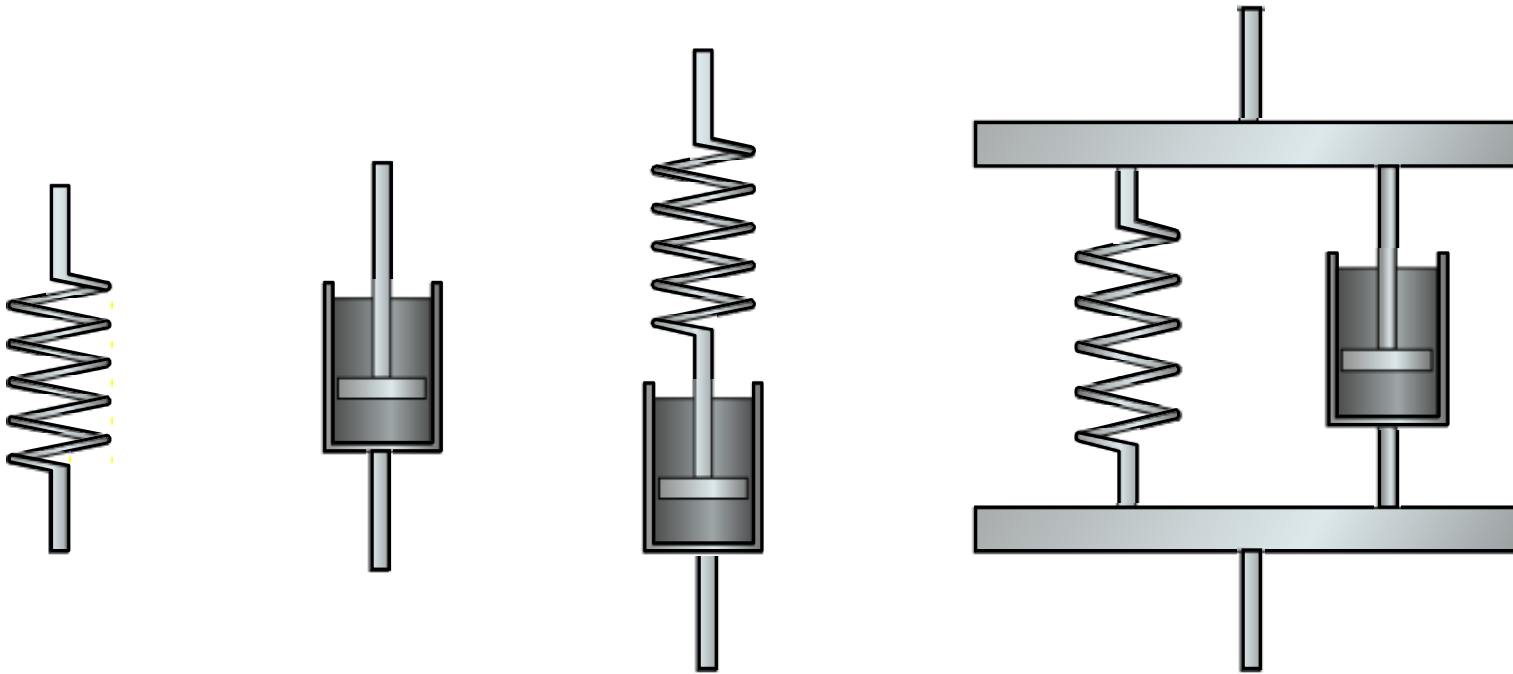
What do the strain/time plots look like?

Problems with Simple Models

I can't do creep

And I can't do stress relaxation
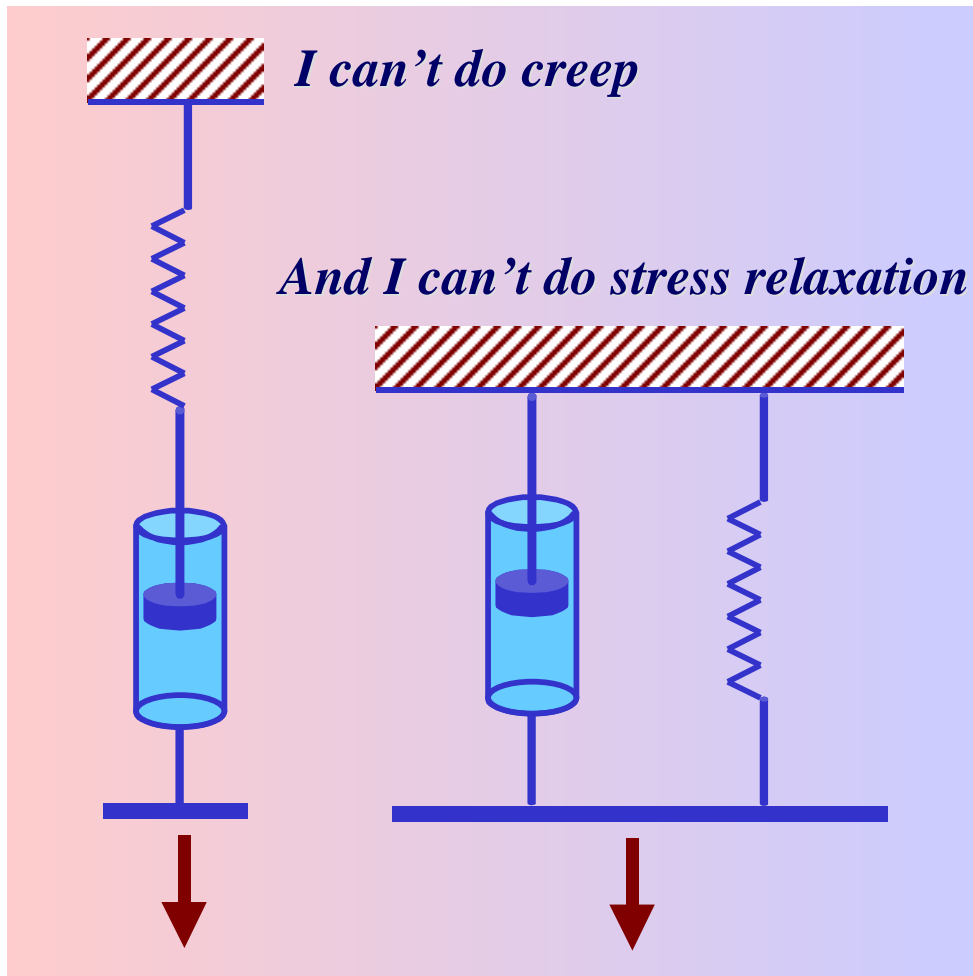
• The maxwell model cannot account for a retarded elastic response

• The voigt model does not describe stress relaxation

• Both models are characterized by single relaxation times - a spectrum of relaxation times would provide a better description

NEXT - CONSIDER THE FIRST TWO PROBLEMS
THEN -THE PROBLEM OF A SPECTRUM OF RELAXATION TIMES

Four - Parameter Model

Elastic + viscous flow + retarded elastic

Eg CREEP

$$\varepsilon = \frac{\sigma_0}{E_M} + \frac{\sigma_0 t}{\eta_M} + \frac{\sigma_0}{E_M}[1 - exp(-t/\tau_t)]$$

Strain

Retarded or Anelastic Response

Elastic Response

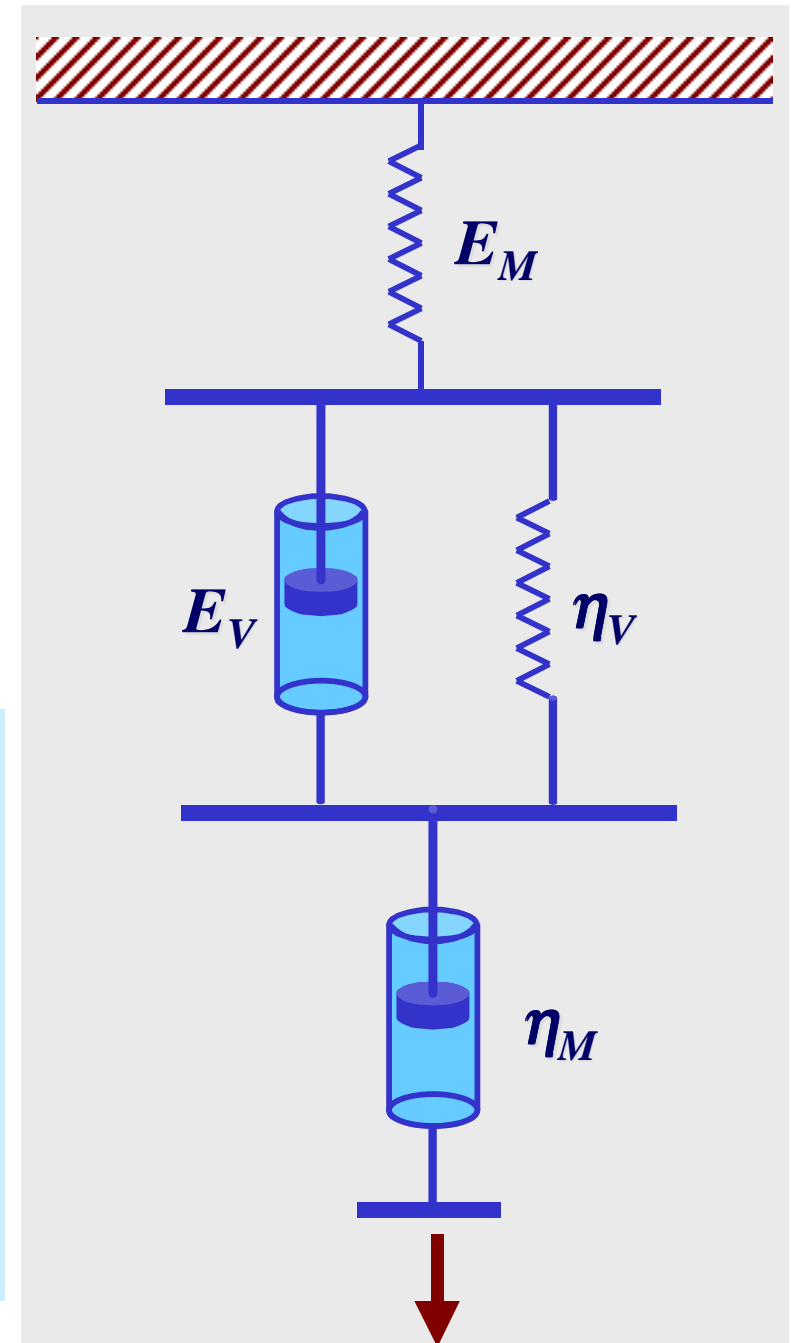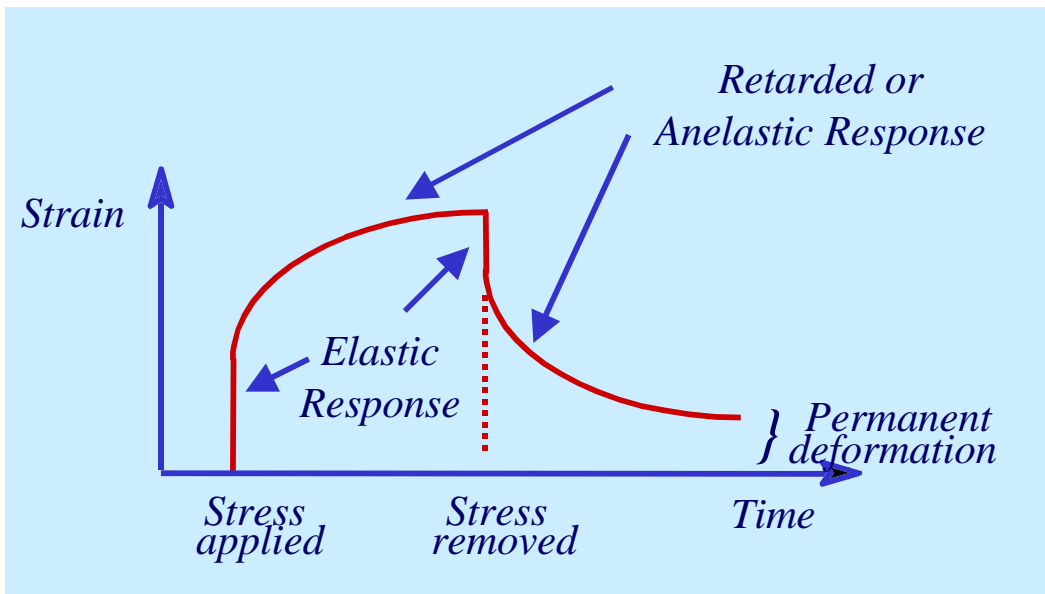*Permanent deformation*

Stress applied

Stress removed

Time

E_M

E_V

η_V

η_M

Distributions of Relaxation and Retardation Times

We have mentioned that although the Maxwell and Voigt models are seriously flawed, the equations have the right form.

What we mean by that is shown opposite, where equations describing the Maxwell model for stress relaxation and the Voigt model for creep are compared to equations that account for a continuous range of relaxation times.

Stress Relaxation

$$E(t) = E_0 \, exp\,(-t/\tau_t)$$

$$E(t) = \int_0^\infty E(\tau_t)\,exp(-t/\tau_t)\,d\tau_t$$

Creep

$$D(t) = D_0[1 - exp(-t/\tau_t')]$$

$$D(t) = \int_0^\infty D(\tau_t')[1 - exp(-t/\tau_t')]\,d\tau_t'$$

These equations can be obtained by assuming that relaxation occurs at a rate that is linearly proportional to the distance from equilibrium and use of the Boltzmann superposition principle. We will show how the same equations are obtained from models.

The Maxwell - Wiechert Model

$$\frac{d\varepsilon}{dt} = \frac{\sigma_1}{\eta_1} + \frac{1}{E_1}\frac{d\sigma_1}{dt}$$

$$= \frac{\sigma_2}{\eta_2} + \frac{1}{E_2}\frac{d\sigma_2}{dt}$$

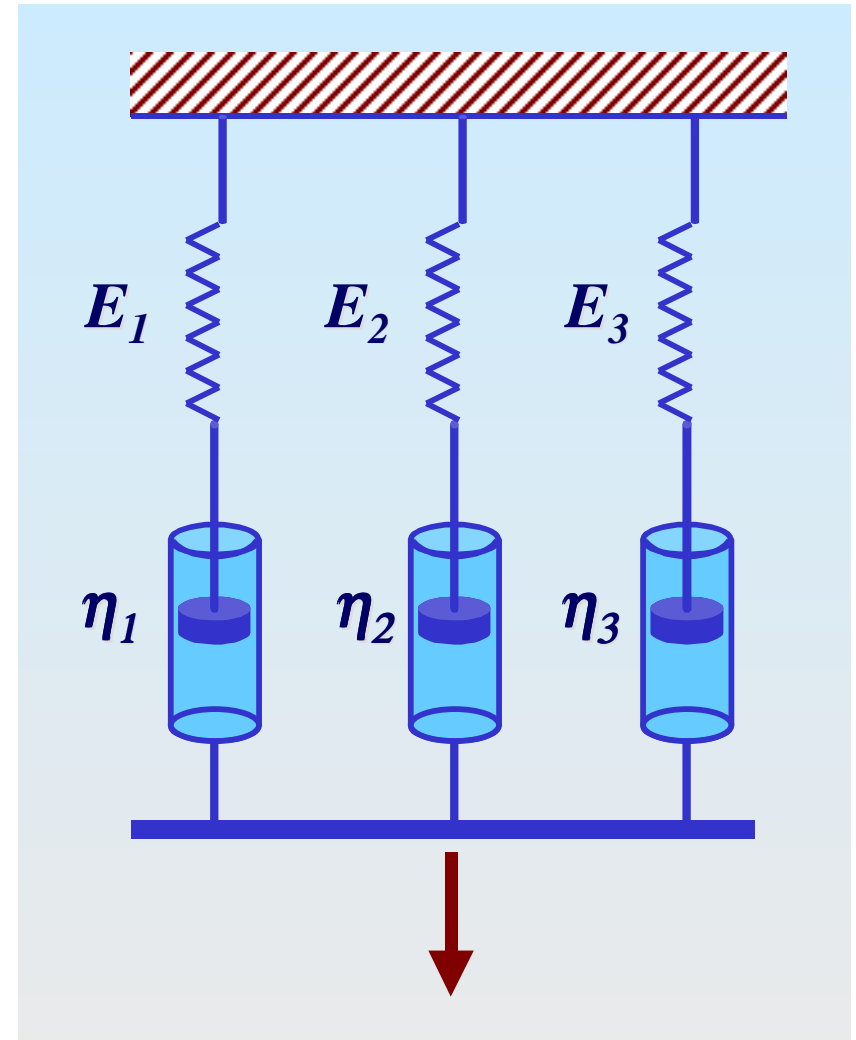$$= \frac{\sigma_3}{\eta_3} + \frac{1}{E_3}\frac{d\sigma_3}{dt}$$

Consider stress relaxation

$$\frac{d\varepsilon}{dt} = 0$$

$$\sigma_1 = \sigma_0\, exp[-t/\tau_{t1}]$$

$$\sigma_2 = \sigma_0\, exp[-t/\tau_{t2}]$$

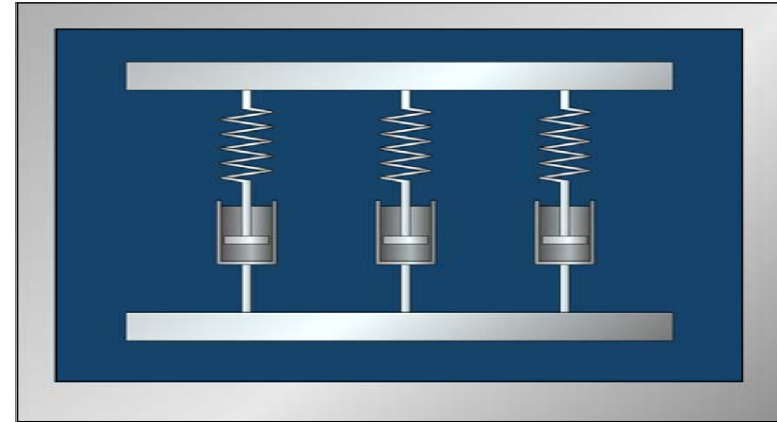$$\sigma_3 = \sigma_0\, exp[-t/\tau_{t3}]$$

Distributions of Relaxation and Retardation Times

Stress relaxation modulus

$$E(t) = \sigma(t)/\varepsilon_0$$

$$\sigma(t) = \sigma_1 + \sigma_2 + \sigma_3$$

$$E(t) = \frac{\sigma_{01}}{\varepsilon_0}\exp(-t/\tau_{01}) + \frac{\sigma_{02}}{\varepsilon_0}\exp(-t/\tau_{02}) + \frac{\sigma_{03}}{\varepsilon_0}\exp(-t/\tau_{03})$$

Or, in general

$$E(t) = \sum E_n \exp(-t/\tau_{tn}) \quad \text{where} \quad E_n = \frac{\sigma_{0n}}{\varepsilon_0}$$
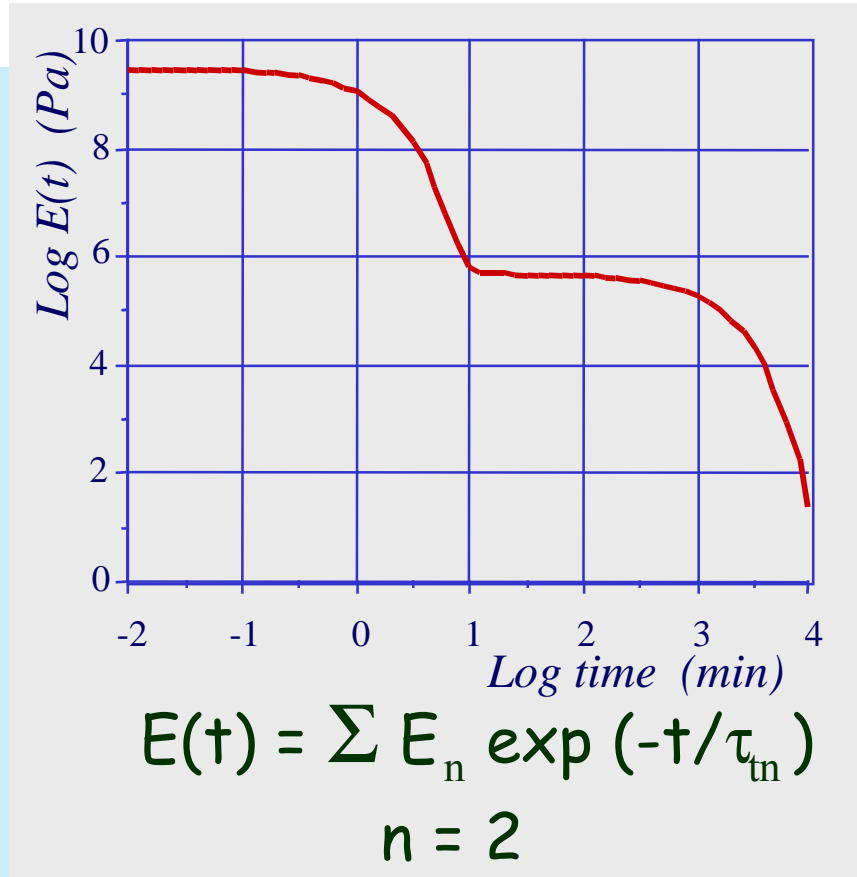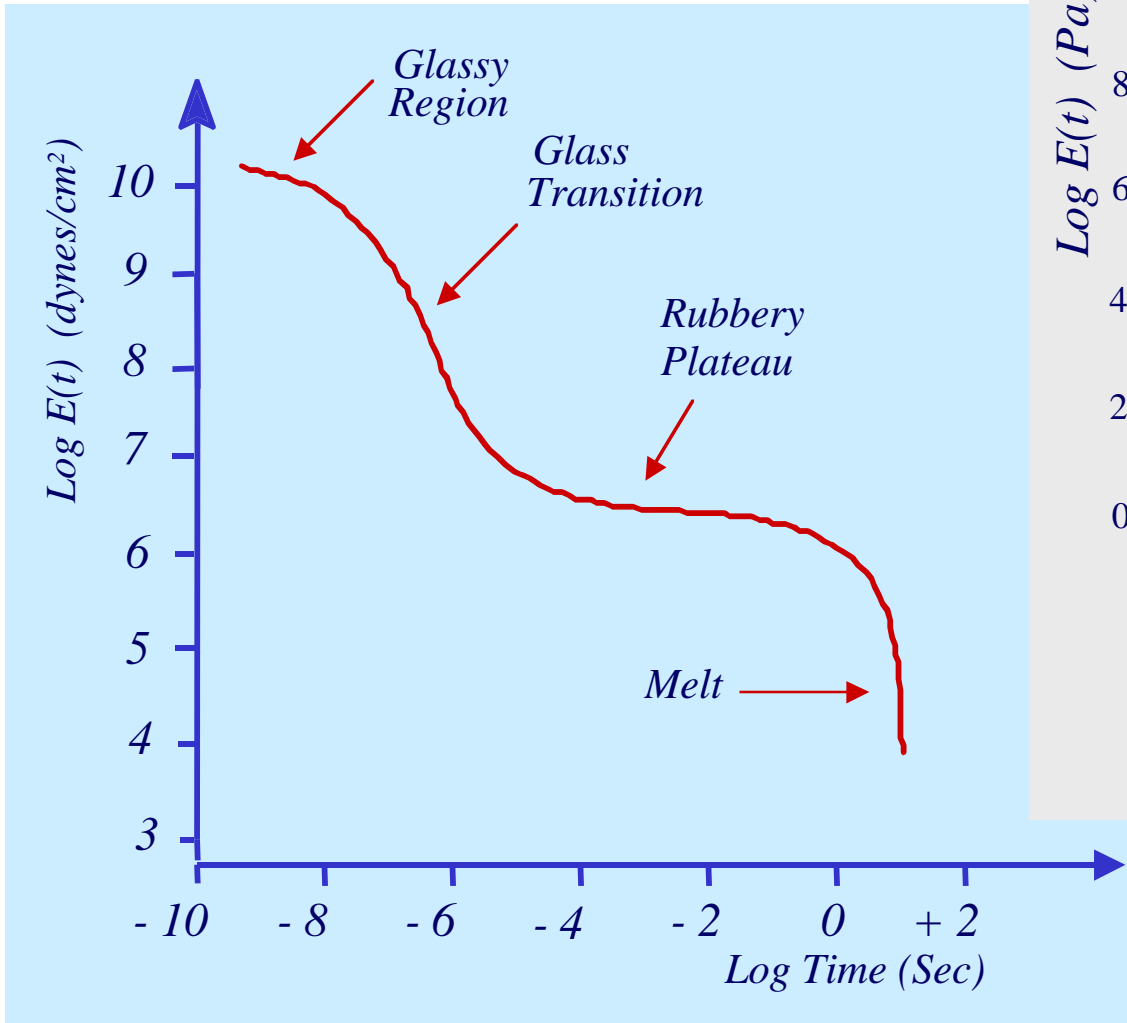
Similarly, for creep compliance combine voigt elements to obtain

$$D(t) = \sum D_n [1 - \exp(-t/\tau_{tn}')]$$

Distributions of Relaxation and Retardation Times
Example - the Maxwell - Wiechert Model With
n = 2
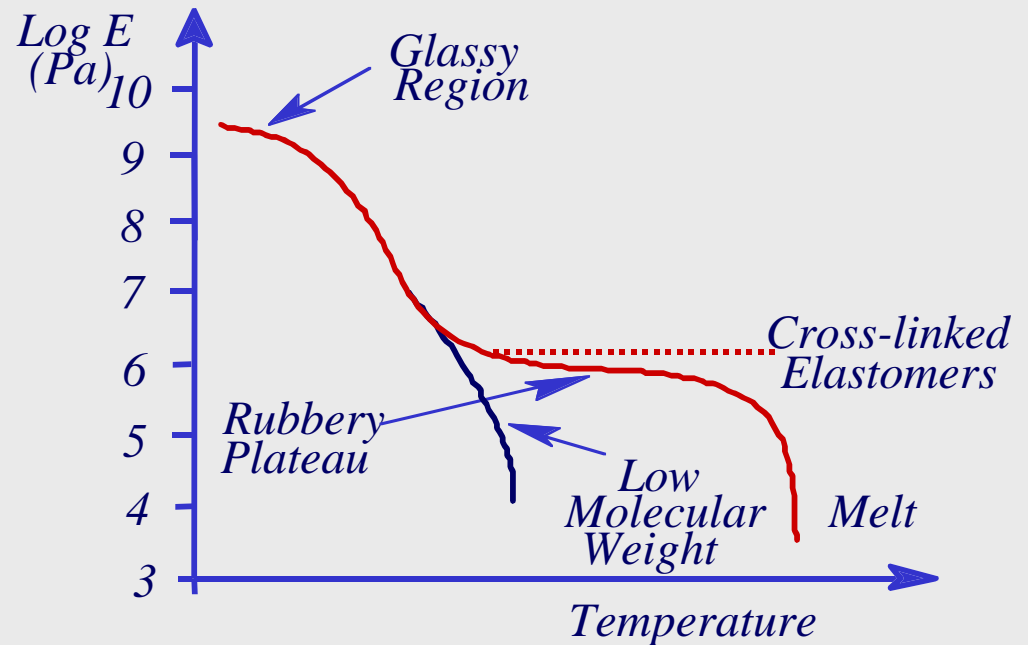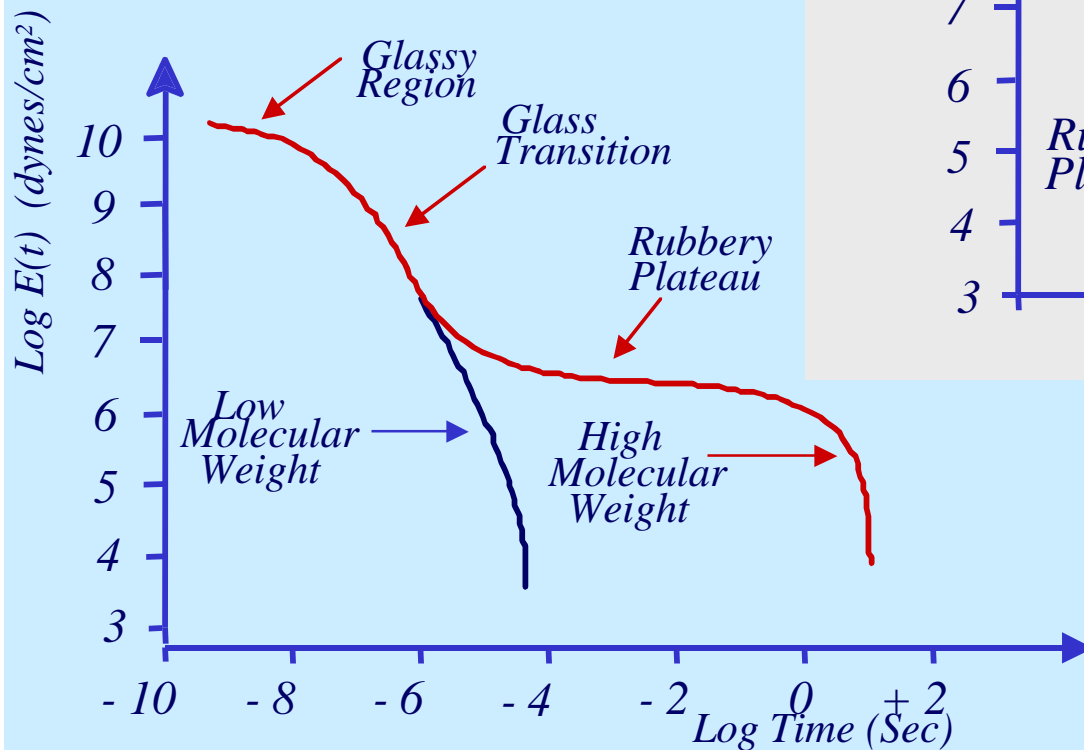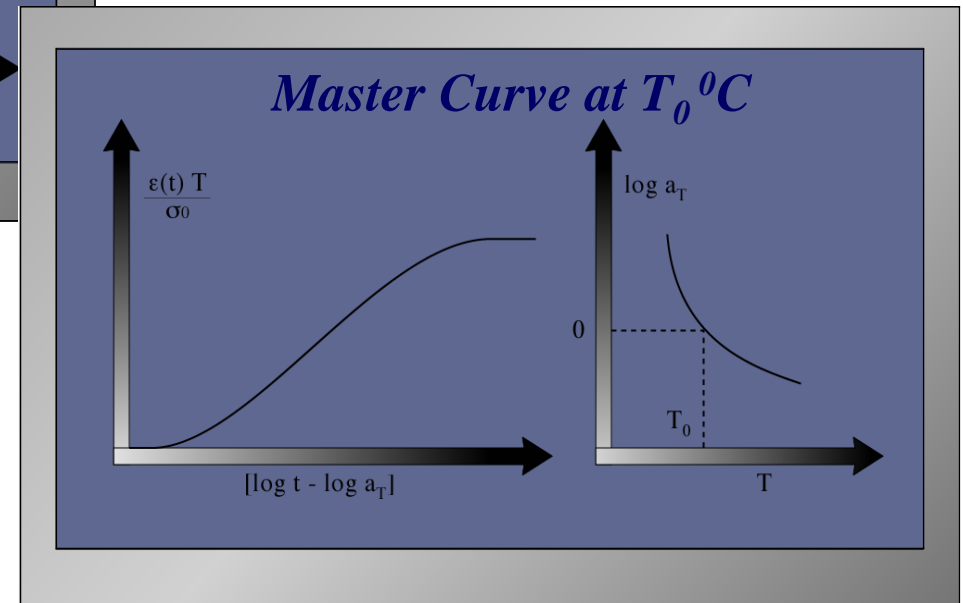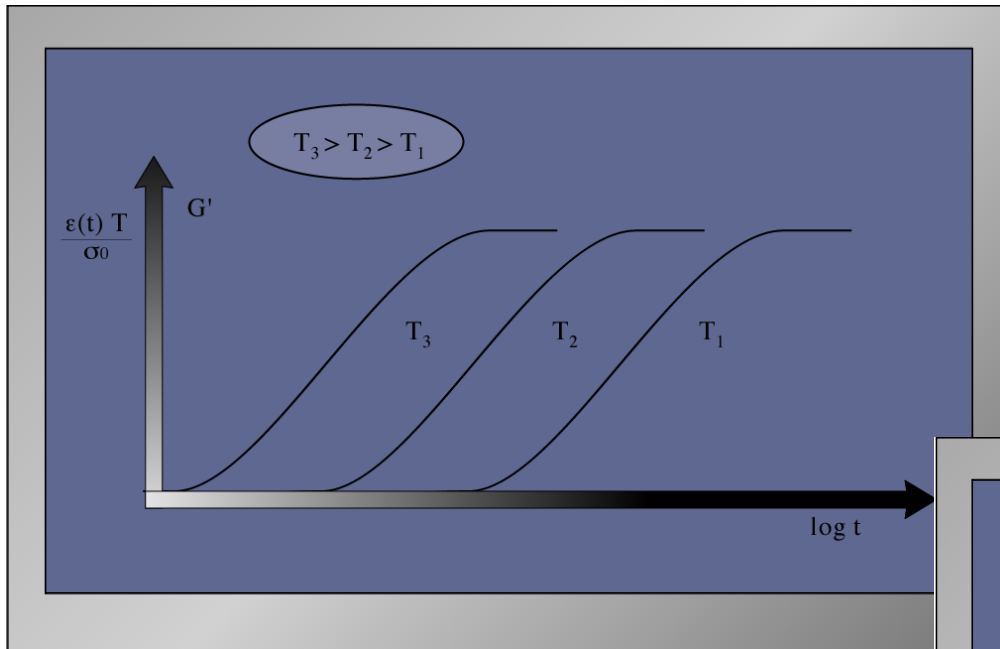

$$E(t) = \sum E_n \exp(-t/\tau_{tn})$$
$$n = 2$$

Time - Temperature Superposition Principle

Recall that we have seen that there is a time - temperature equivalence in behavior

This can be expressed formally in terms of a superposition principle

Time Temperature Superposition Principle - *Creep*

Time Temperature Superposition Principle - *Stress Relaxation*

Log Shift Factor

+8

+4

0

-4

SHIFT FACTOR vs TEMPERATURE

-80   -40   0   40   80

Temperature ^0C

Stress Relaxation Modulus *dynes/cm²*

10^{11}

10^{10}

10^9

10^8

10^7

10^6

10^5

Stress Relaxation Data

-80.8°C

-76.7°C

-74.1°C

-70.6°C

-65.4°C

-58.8°C

-49.6°C

-40.1°C

-0.0°C

+25°C

+50°C

Master Curve at 25⁰C

-80°   -60°   -40° -20° -10° 0°   25°

10^{-2} 10^0 10^2

10^{-14} 10^{-12} 10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2} 10^{-0} 10^{+2}

Time (hours)
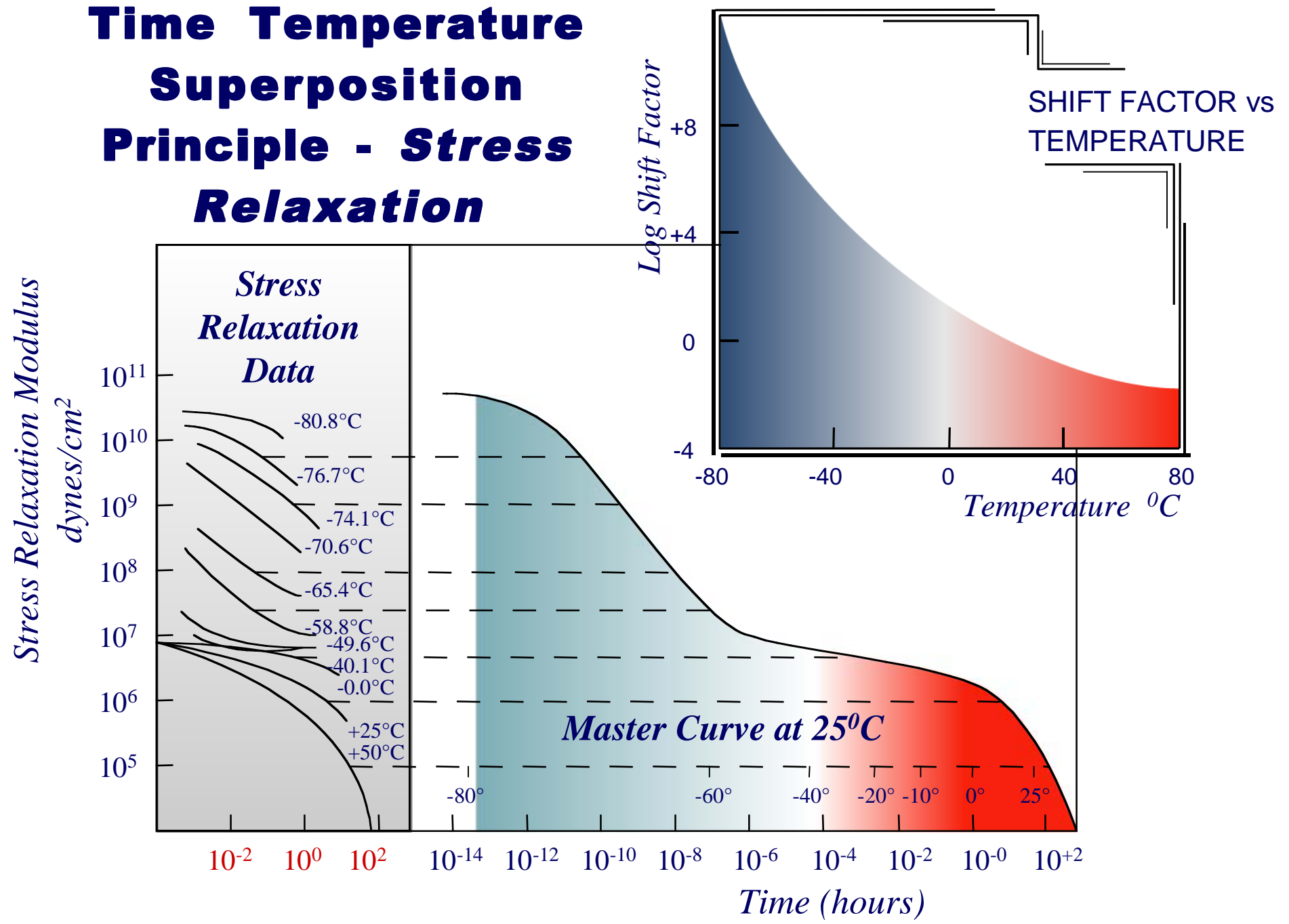
Relaxation Processes above Tg - the WLF Equation

From empirical observation

$$\text{Log } a_T = \frac{-C_1 (T - T_s)}{C_2 + (T - T_s)} \qquad \text{For } Tg > T < \sim(Tg + 100^0C)$$

Originally thought that C_1 and C_2 were universal constants, = 17.44 and 51.6, respectively, when T_s = Tg. Now known that these vary from polymer to polymer.

Homework problem - show how the WLF equation can be obtained from the relationship of viscosity to free volume as expressed in the Doolittle equation

Semi - Crystalline Polymers

NON - LINEAR RESPONSE TO STRESS.SIMPLE
MODELS AND THE TIME - TEMPERATURE
SUPERPOSITION PRINCIPLE DO NOT APPLY

Temperature

T_m

Amorphous melt

Rigid crystalline domains
Rubbery amorphous domains

T_g

Rigid crystalline domains
Glassy amorphous domains