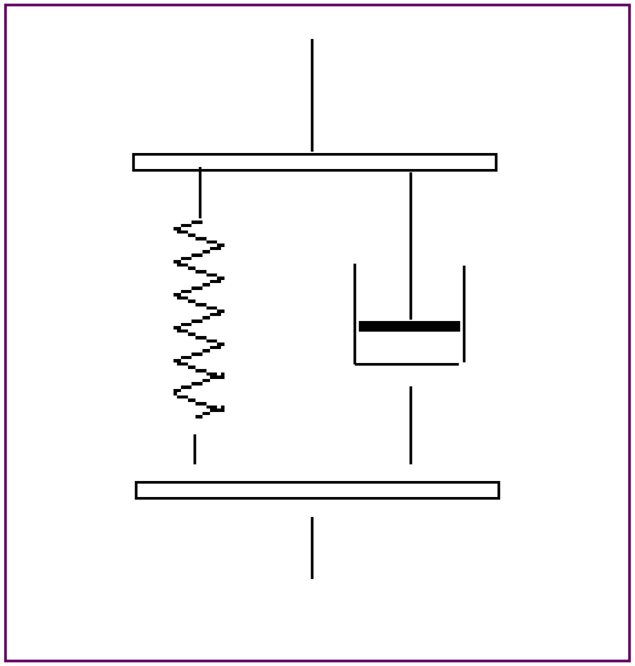
VOIGT MODEL

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

Picture representation →

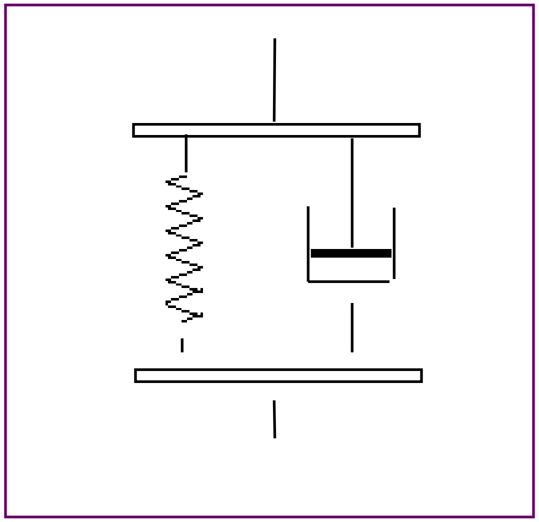


Equation

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

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

VOIGT MODEL - creep and stress relaxatio



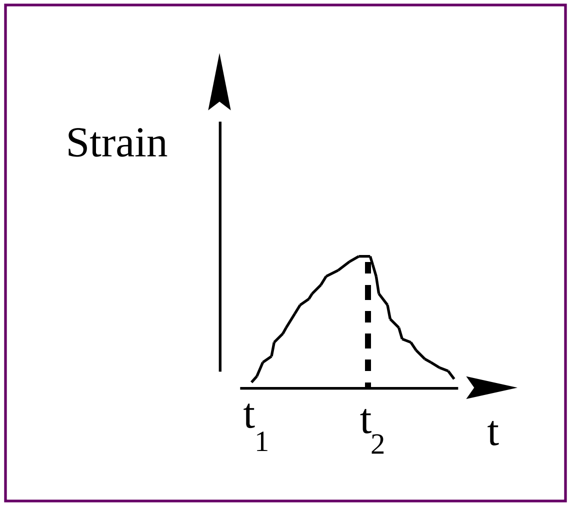
Gives a retarded elastic response but does not allow for "ideal" stress relaxation, in that the model cannot be "instantaneously" deformed to a given strain.

But in CREEP σ ***= constant,*** σ_0

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

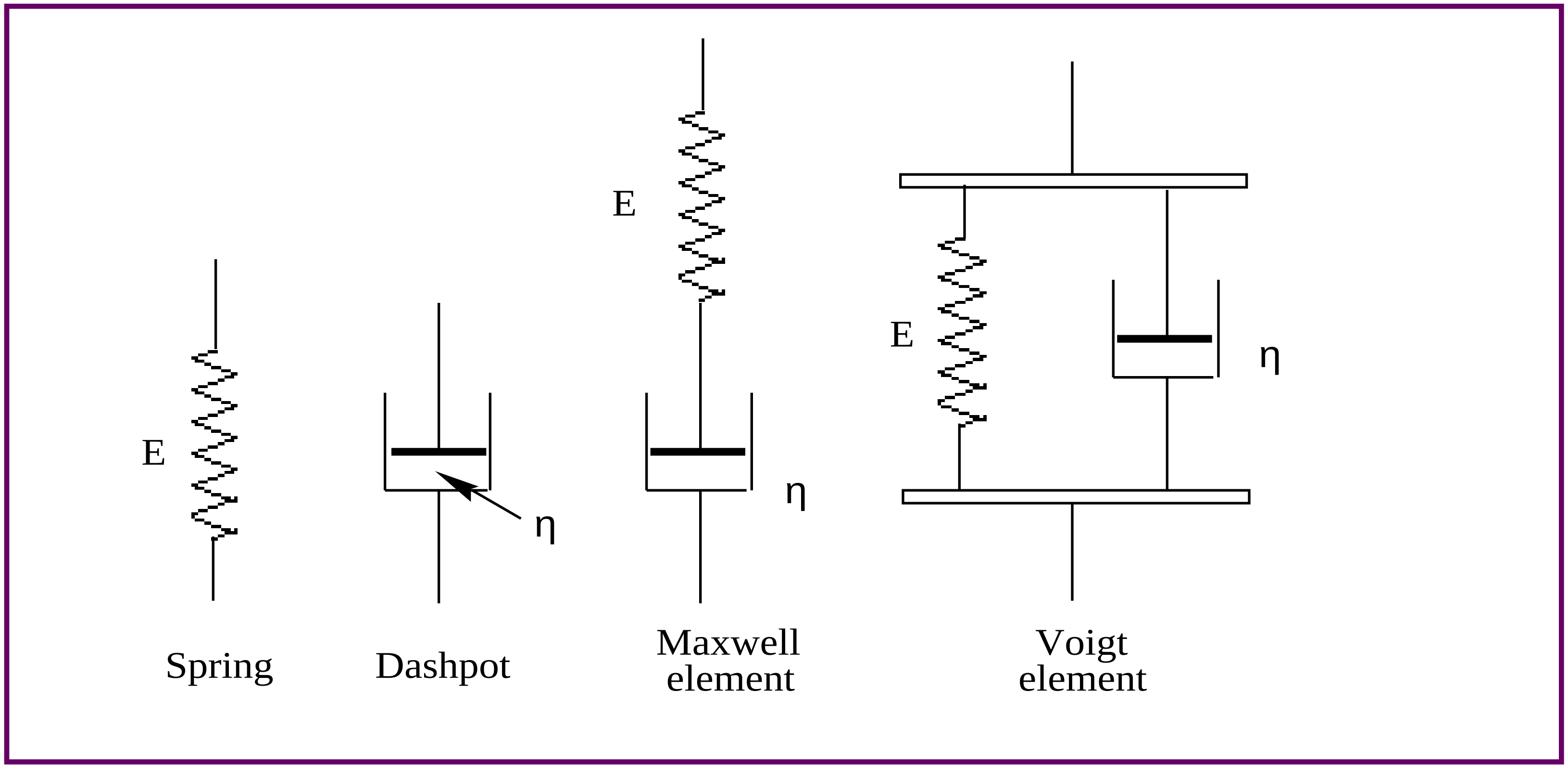
$$\frac{d\varepsilon(t)}{dt} + \frac{\varepsilon(t)}{\tau_t'} = \frac{\sigma_0}{\eta}$$

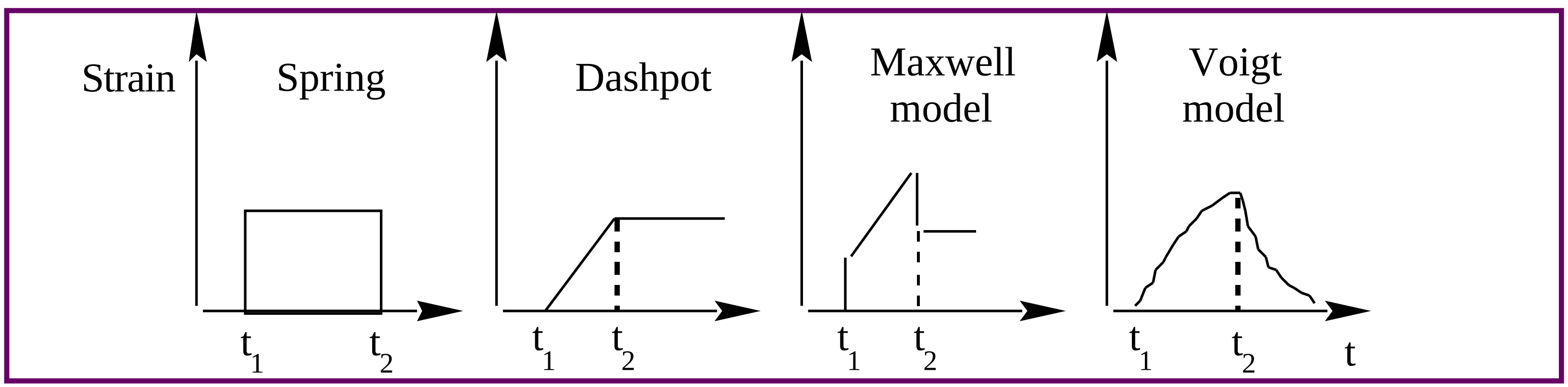
$$\varepsilon(t) = \frac{\sigma_0}{E}[1 - \exp(-t/\tau_t')]$$



τ_t' - *retardation time* (η/E)

SUMMARY


E
Spring
η
Dashpot
E
η
Maxwell
element
E
η
Voigt
element


Strain
Spring
t1
t2
Dashpot
t1
t2
Maxwell
model
t1
t2
Voigt
model
t1
t2
t

PROBLEMS WITH SIMPLE MODELS

- *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*

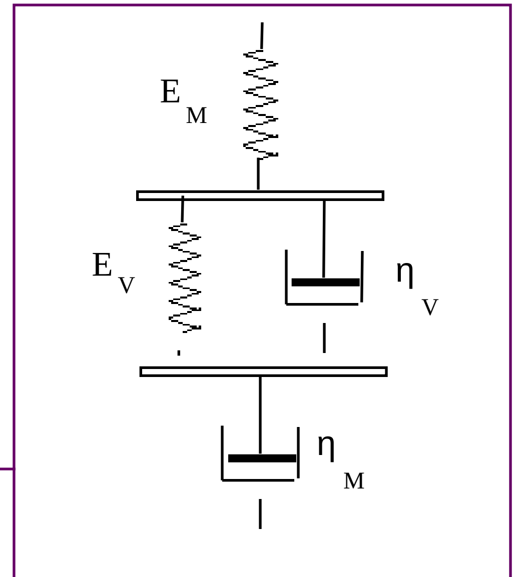
NEXT - CONSIDER THE FIRST TWO PROBLEMS
THEN -THE PROBLEM OF A SPECTRUM OF RELAXATION TIMES

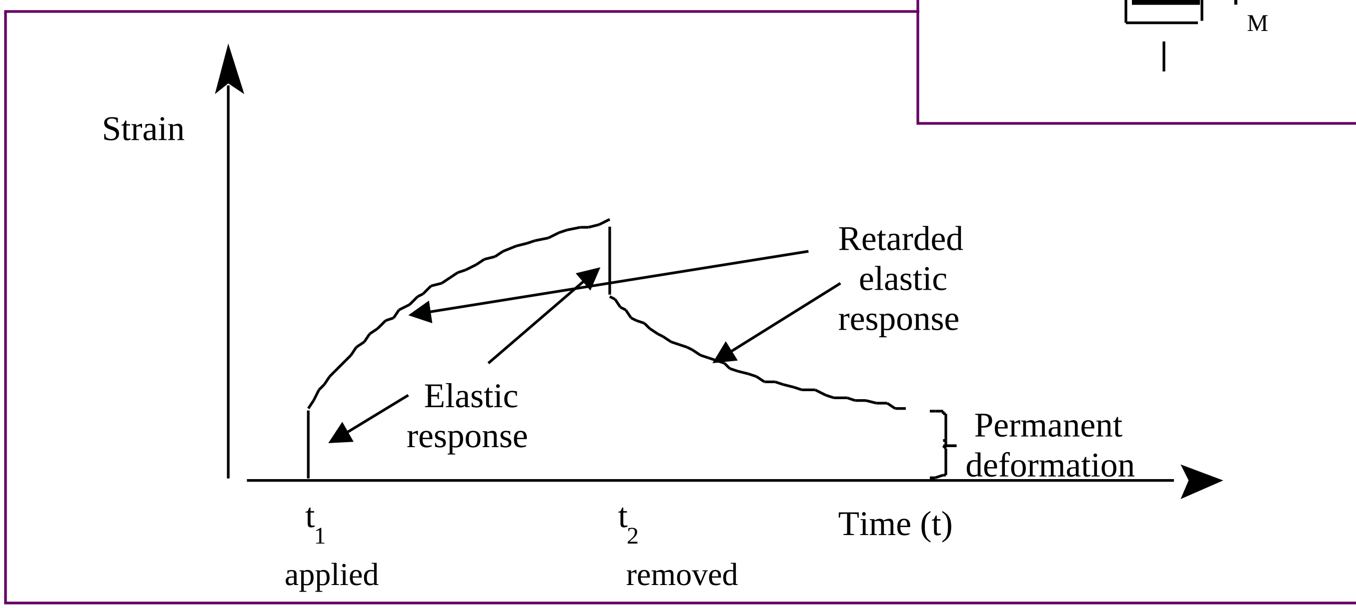
FOUR - PARAMETER MODEL

ELASTIC + VISCOUS FLOW + RETARDED ELASTIC

eg CREEP

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





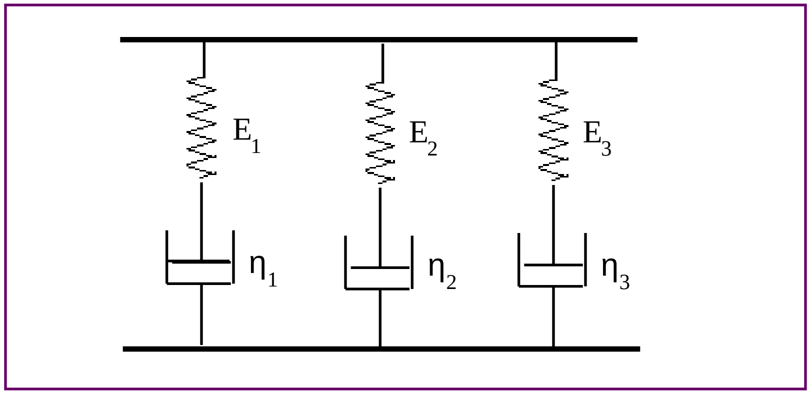
DISTRIBUTIONS OF RELAXATION AND RETARDATION TIMES

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

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

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

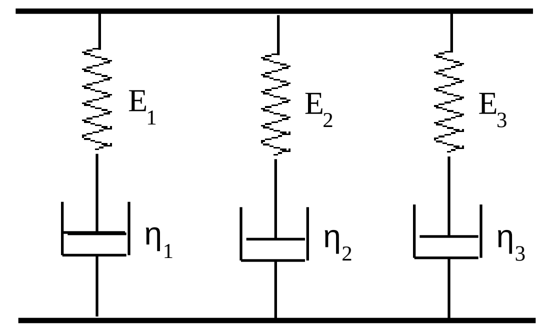
$$\sigma_3 = \sigma_0 \exp[-t/\tau_{t3}]$$

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

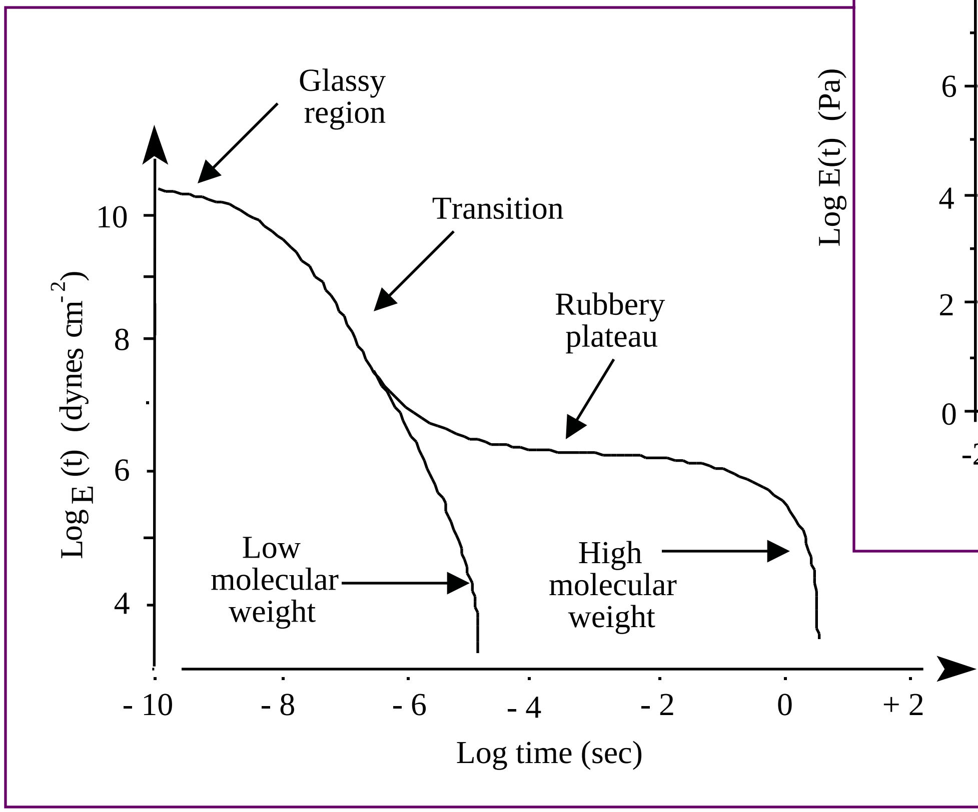
$$D(t) = \sum D_n [1 - \exp(-t/\tau_{tn})]$$

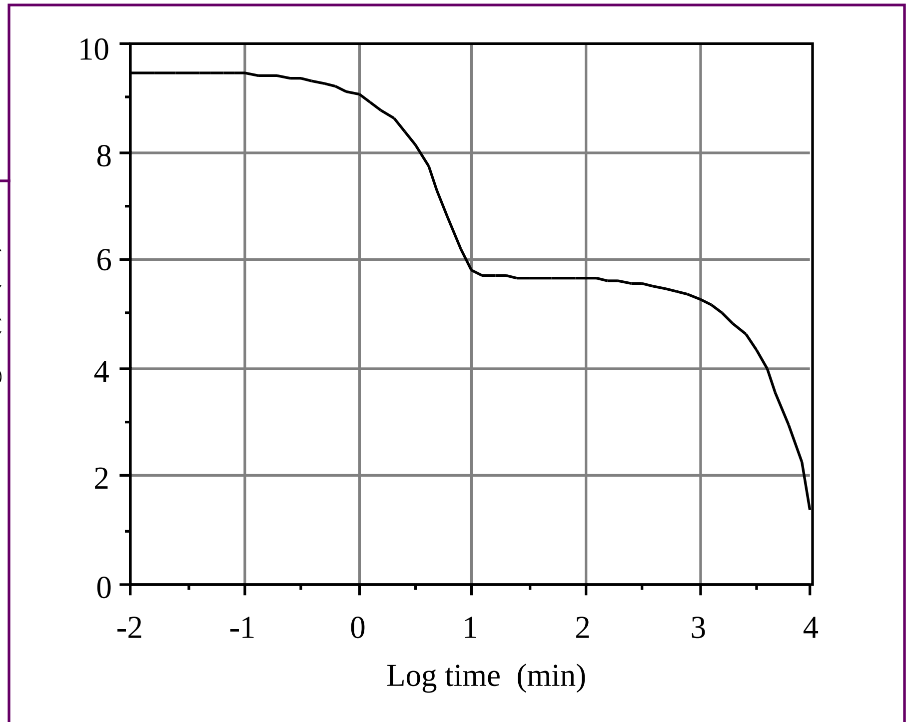
DISTRIBUTIONS OF RELAXATION AND RETARDATION TIMES

Example - The Maxwell - Wiechert Model with

$$E(t) = \sum E_n \exp\left(-t/t_{tn}\right)$$

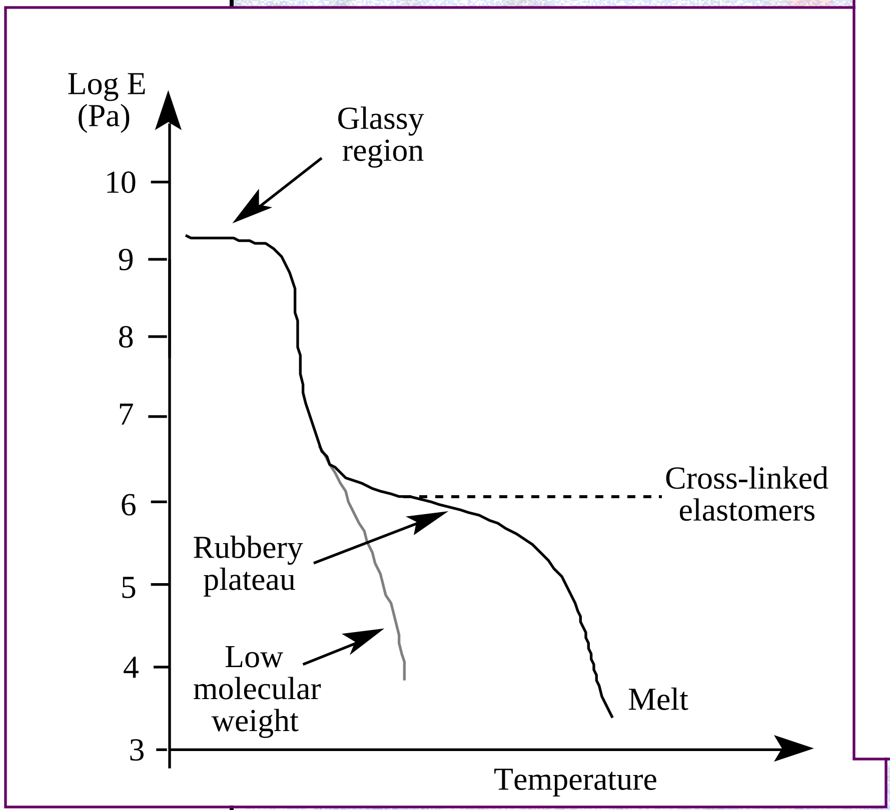
$n = 2$

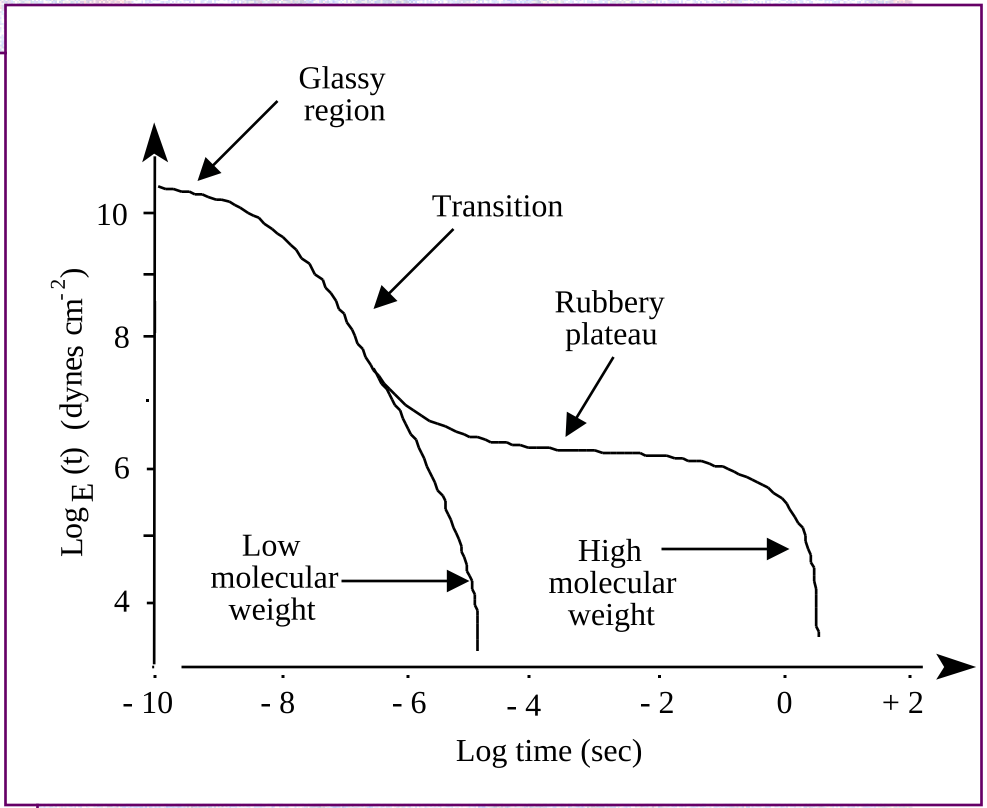




TIME - TEMPERATURE SUPERPOSITION PRINCIPLE

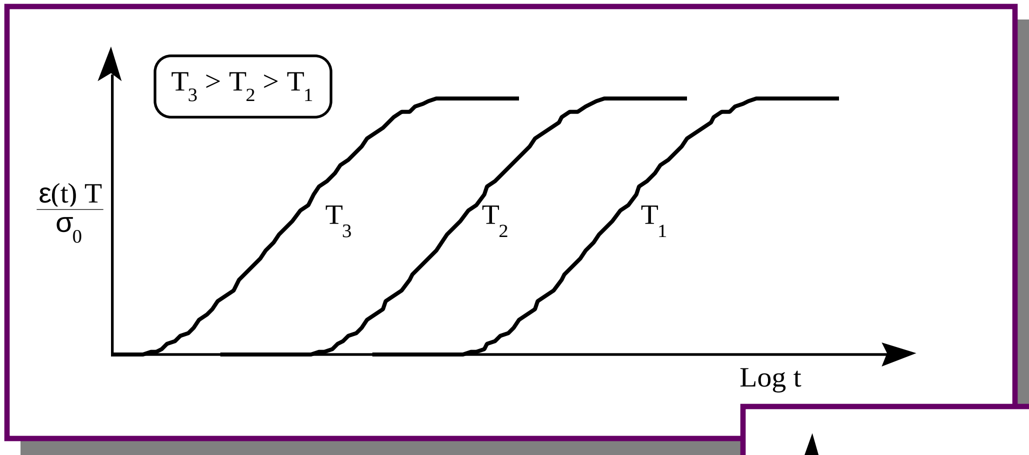
Recall that we have seen that there is a time - temperature equivalence in behaviour

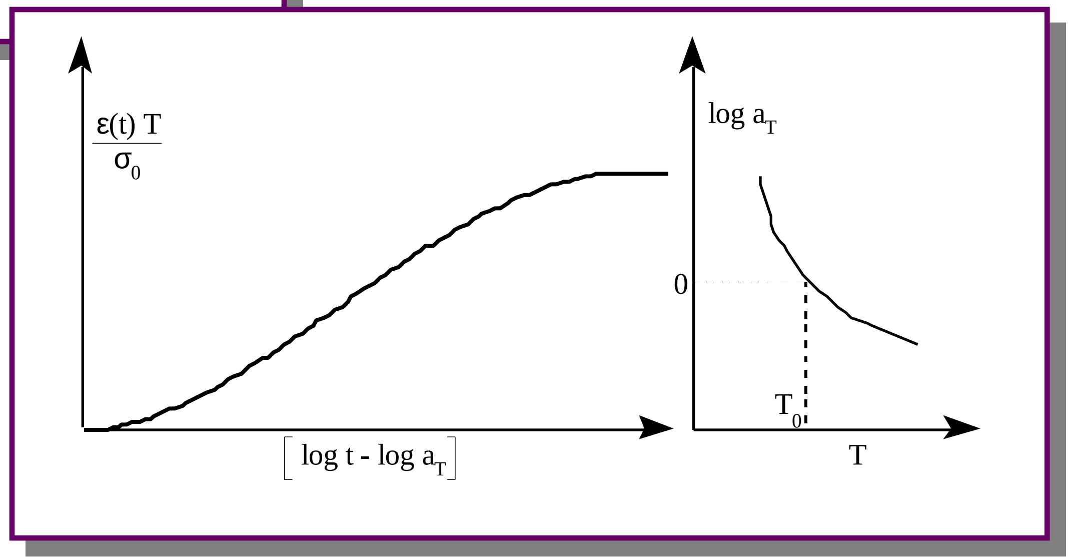




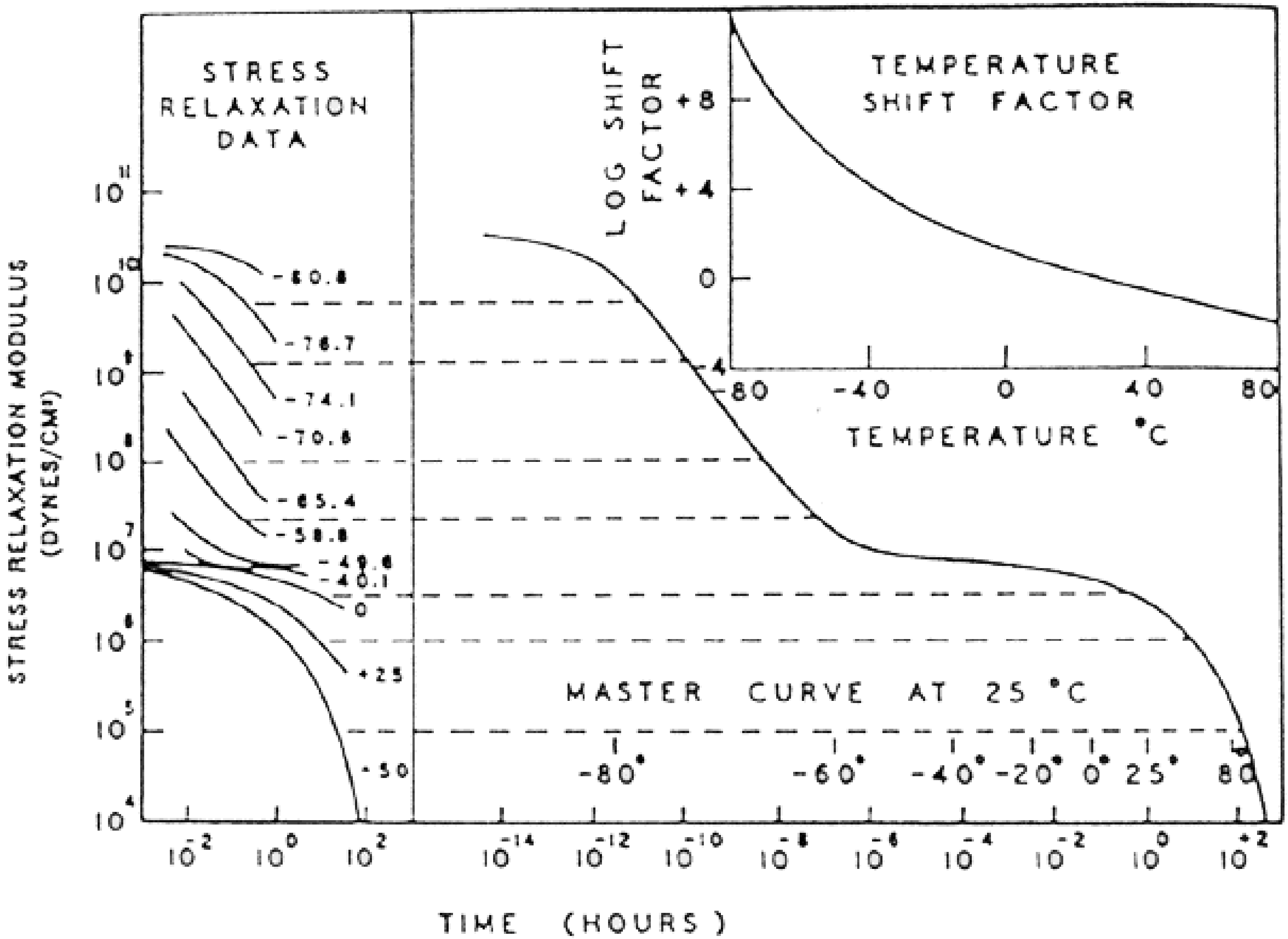
This can be expressed formally in terms of a suprposition principle

TIME TEMPERATURE SUPERPOSITION PRINCIPLE - creep





TIME TEMPERATURE SUPERPOSITION PRINCIPLE - stress relaxation



SIGNIFICANCE OF SHIFT FACTOR

What is the significance of the log scale for a_T, and what does this tell us about the temperature dependence of relaxation behaviour in amorphous polymers ?

Consider stress relaxation:

$$E(t) = \sum E_n \exp(-t/\tau_{t_n})$$

Let a particular mode of relaxation have a characteristic time τ_{t0} at T_0, and a characteristic time τ_{t1} at T_1. Then DEFINE

$a_T = \dfrac{\tau_{t1}}{\tau_{t0}}$	*So that the exponential term can be written* $\dfrac{t}{\tau_{t1}} = \dfrac{t}{a_T \tau_{t0}}$

Hence, taking logs

$$\log(t/\tau_{t1}) = \log(t/\tau_{t0}) + \log a_T$$

SIGNIFICANCE OF SHIFT FACTOR

$$\log (t/\tau_{t1}) = \log (t/\tau_{t0}) + \log a_T$$

- *ie relaxation behaviour at one temperature can be superimposed on that at another by shifting an amount a_T along a log scale.*

- *BUT ,real behaviour is characterized by a distribution of relaxation times and relaxation mechanisms vary and have different length scales as a function of temperature*

- *This implies that all the relaxation processes involved have (more or less) the same temperature dependence*

RELAXATION PROCESSES ABOVE Tg
- THE WLF EQUATION

From empirical observation

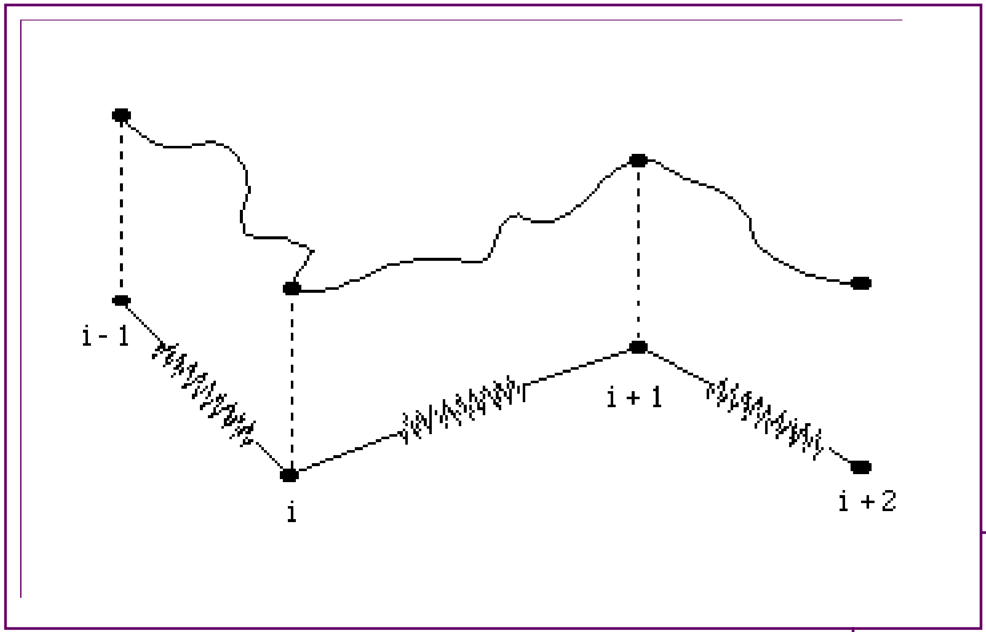
$$\log a_T = \frac{-C_1 \, (T - T_s)}{C_2 + (T - T_s)} \quad \text{For } T_g > T < \sim T_g + 100\,^0C$$

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

DYNAMICS OF POLYMER CHAINS

An advanced topic that we will not discuss in detail



Rouse - Bouche model
A chain as a string of
Beads linked by springs

Reptation, scaling concepts
And other advanced theories