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

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

(Strain in both elements of the model is the same and the total stress is the sum of the two contributions)
VOI GT 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 $\sigma = \text{constant}, \sigma_0$

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

\[
\frac{d\varepsilon(t)}{dt} + \frac{\varepsilon(t)}{\tau_t} = \frac{\sigma_0}{\eta}
\]

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

$\tau_t'$ - retardation time ($\eta/E$)
SUMMARY

Spring  Dashpot  Maxwell element  Voigt element
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

e.g. CREEP

\[ \varepsilon = \frac{\sigma^0}{E_M} + \frac{\sigma^0}{\eta_M} + \frac{\sigma^0}{E_M} \left[ 1 - \exp \left( -\frac{t}{\tau} \right) \right] \]
DI S T R IB U T I O N S O F R E L A X A T I O N A N D R E T A R D A T I O N T I M E S
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

\[ E(t) = \sigma(t)/\varepsilon_0 \]

\[ \sigma(t) = \sigma_1 + \sigma_2 + \sigma_3 \]

\[ E(t) = \frac{\sigma_{01}}{\varepsilon_0} \exp\left(-\frac{t}{\tau_{01}}\right) + \frac{\sigma_{02}}{\varepsilon_0} \exp\left(-\frac{t}{\tau_{02}}\right) + \frac{\sigma_{03}}{\varepsilon_0} \exp\left(-\frac{t}{\tau_{03}}\right) \]

Or, in general

\[ E(t) = \sum E_n \exp\left(-\frac{t}{\tau_{tn}}\right) \text{ where } E_n = \frac{\sigma_{0n}}{\varepsilon_0} \]

SIMILARLY, FOR CREEP COMPLIANCE COMBINE VOIGT ELEMENTS TO OBTAIN

\[ D(t) = \sum D_n \left[1 - \exp\left(-\frac{t}{\tau_{tn}}\right)\right] \]
DISTRIBUTIONS OF RELAXATION AND RETARDATION TIMES

Example - The Maxwell-Wiechert Model with $n = 2$

$$E(t) = \sum E_n \exp\left(-\frac{t}{\tau_n}\right)$$

$n = 2$
Recall that we have seen that there is a time - temperature equivalence in behaviour. This can be expressed formally in terms of a superposition 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:

$$E(t) = \sum E_n \exp (-t/\tau_t)$$

Let a particular mode of relaxation have a characteristic time $\tau_{t0}$ at $T_0$, and a characteristic time $\tau_{t1}$ at $T_1$. The shift factor

$$a_T = \frac{\tau_{t1}}{\tau_{t0}}$$

So that the exponential term can be written

$$\frac{t}{\tau_{t1}} = \frac{t}{a_T \tau_{t0}}$$

Hence, taking logs

$$\log (t/\tau_{t1}) = \log (t/\tau_{t0}) + \log a$$
SIGNIFICANCE OF SHIFT FACTOR

\[
\log \left( \frac{t}{\tau_{t_1}} \right) = \log \left( \frac{t}{\tau_{t_0}} \right) + \log a
\]

• i.e. relaxation behaviour at one temperature can be superimposed on that at another by shifting an amount \(a\) 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

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

Originally thought that \(C_1\) and \(C_2\) were universal constants, \(= 17.44\) and \(51.6\), respectively, when \(T = T_g\). 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