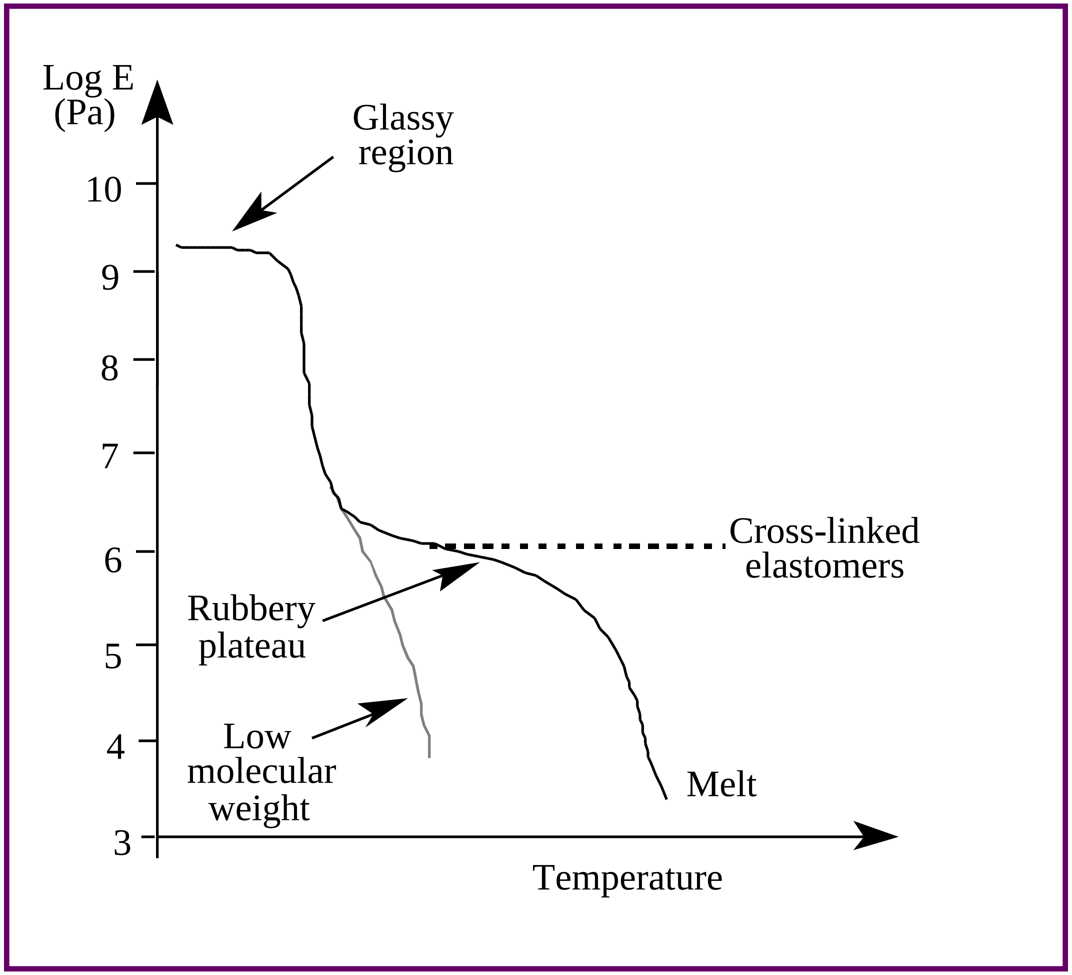
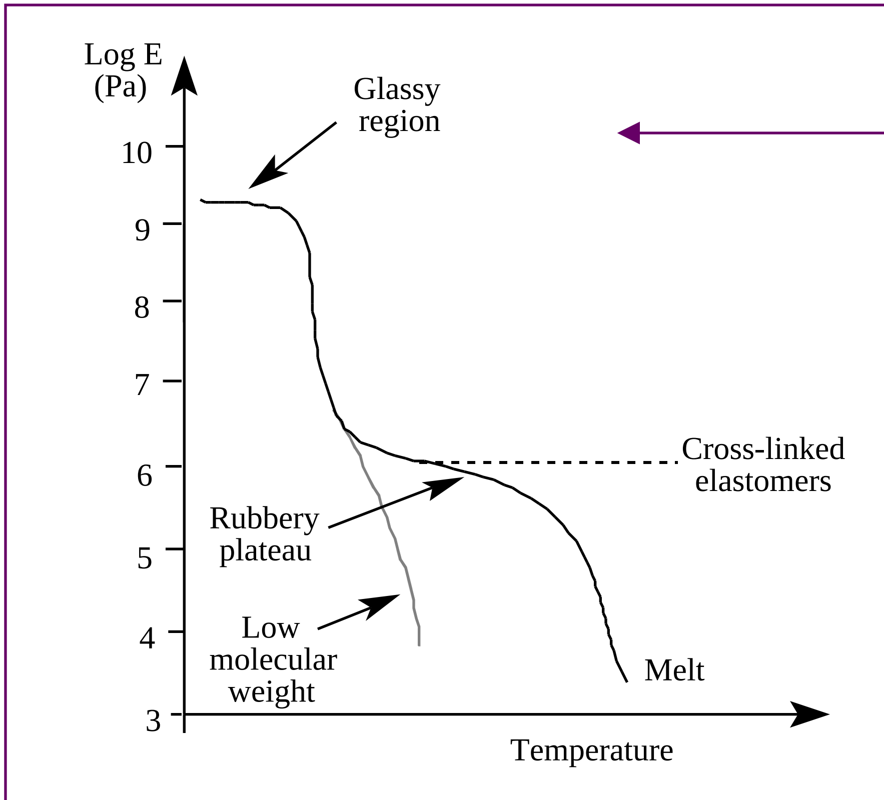
# VISCOELASTIC PROPERTIES OF AMORPHOUS POLYMERS

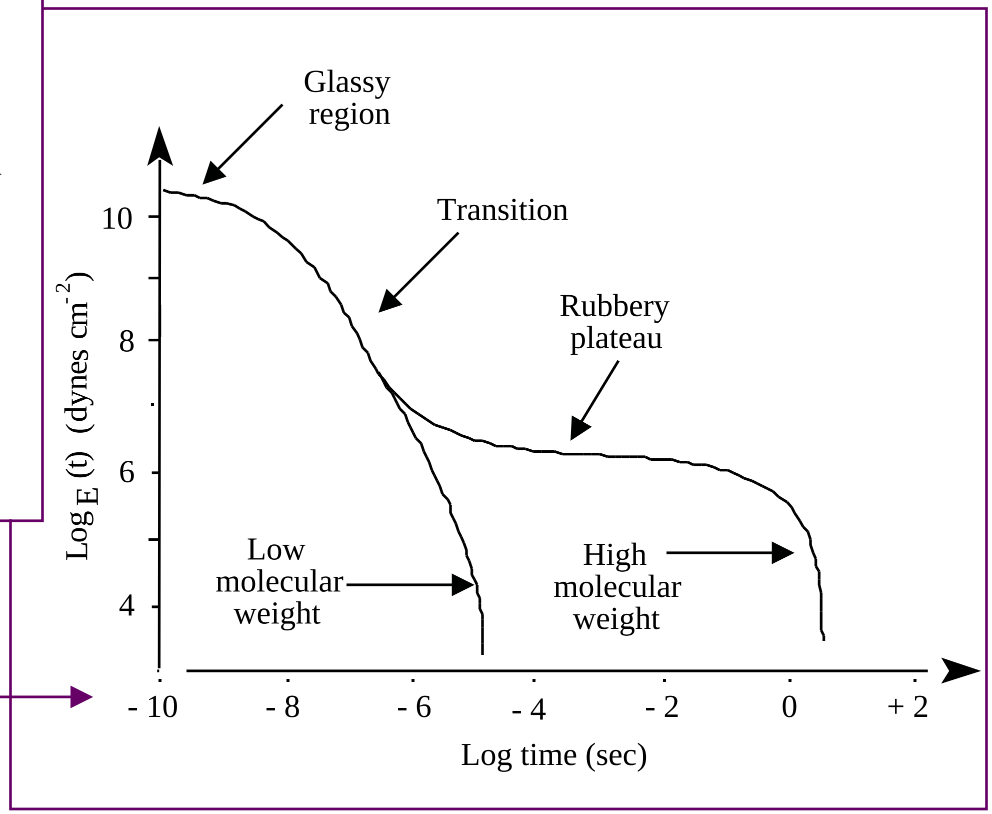



***Measured over Some arbitrary Time period - say 10 secs***

# TIME TEMPERATURE EQUIVALENCE

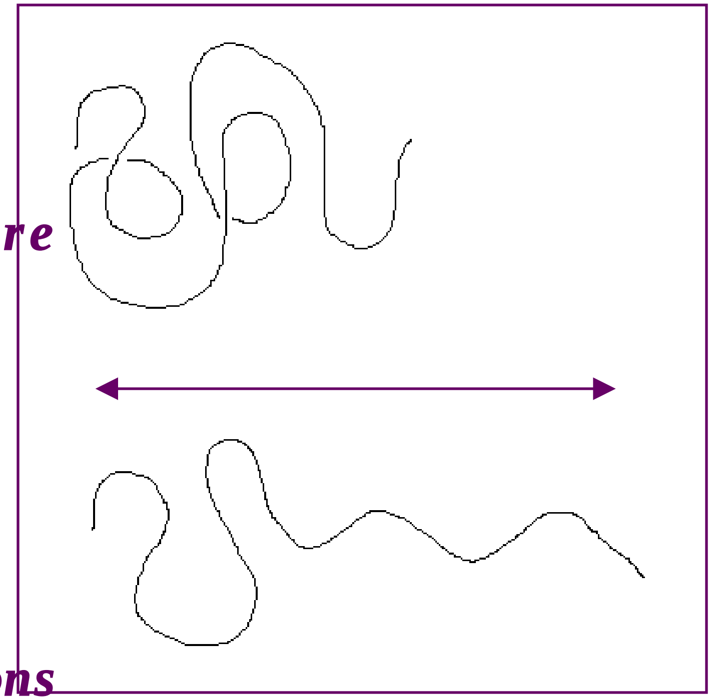



***10 sec modulus***



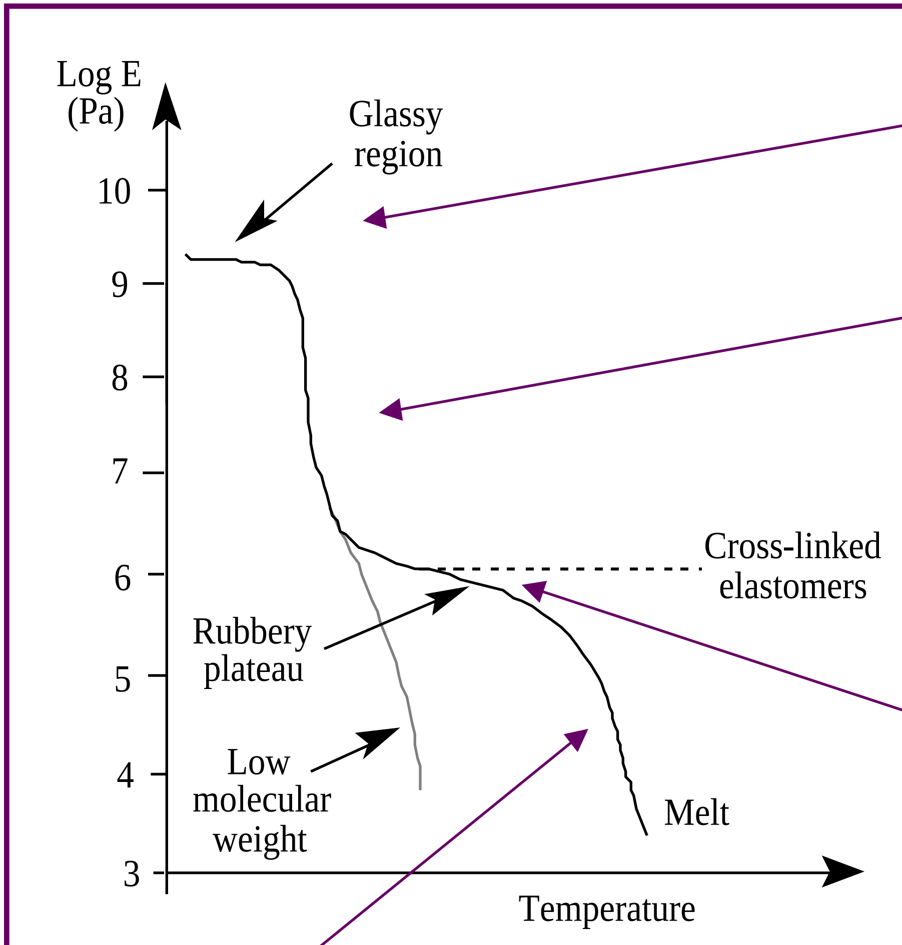

***Stretch sample an arbitrary Amount, then measure the Stress required to maintain This strain .Then $E(t) = \sigma(t)/\varepsilon_0$***

# 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 accomodate the conformations that are allowed by the new constraints on the ends. Because it takes time for bond rotations to occur, particularlywhen we also add in the viscous forces due to neighbours, we say the chain RELAXES to the new state and the relaxation is described by a characteristic time $\tau_t$*

# AMORPHOUS POLYMERS - THE FOUR REGIONS OF VISCOELASTIC BEHAVIOUR



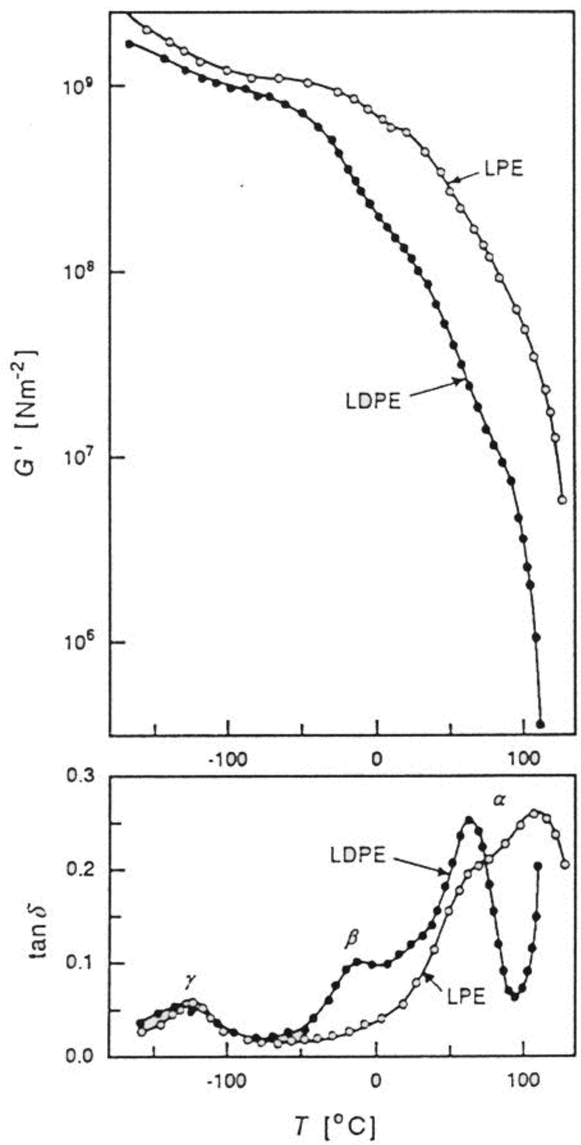

***GLASSY STATE - conformational changes severely inhibited.***

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

***RUBBERY PLATEAU -*** $\tau_t$ ***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 behaviour***

# SEMI - CRYSTALLINE POLYMERS




- *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*

*Reproduced with permission from H. A. Flocke,* Kolloid–Z. Z. Polym., **180**, *188 (1962).*

# MECHANICAL AND THEORETICAL MODELS OF VISCOELASTIC BEHAVIOUR

## *DEFINITIONS*

*Relaxation modulus* $$G(t) = \frac{\tau(t)}{\gamma_0}$$

*Creep compliance* $$J(t) = \frac{\gamma(t)}{\tau_0}$$

$$\boxed{G(t) \neq \frac{1}{J(t)}}$$

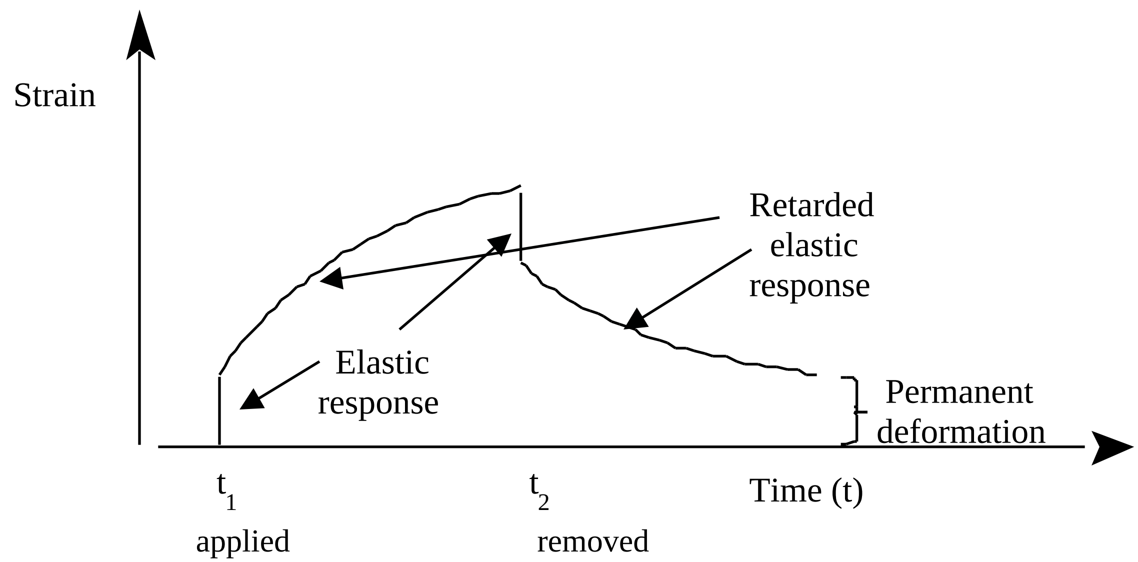
***GOAL - relate G(t) and J(t) to relaxation behaviour.***

***We will only consider LINEAR MODELS***

***ie if we double G(t) [or $\sigma(t)$], then $\gamma(t)$ [or $\varepsilon(t)$] also increses by a factor of 2 (small loads and strains).***

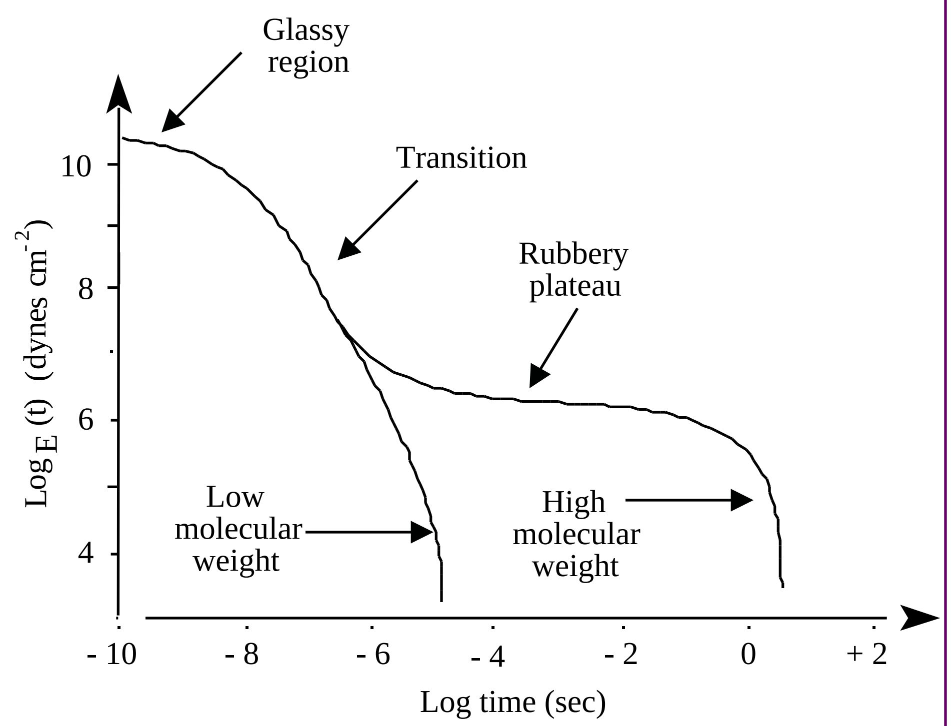
# SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

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



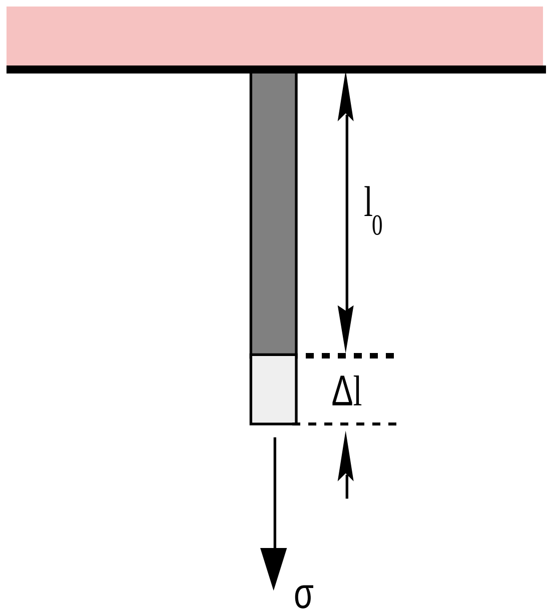
# SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

***While stress relaxation data look something like this***



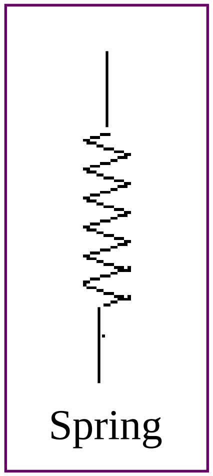
# SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

**Extension**




***Hooke's law***

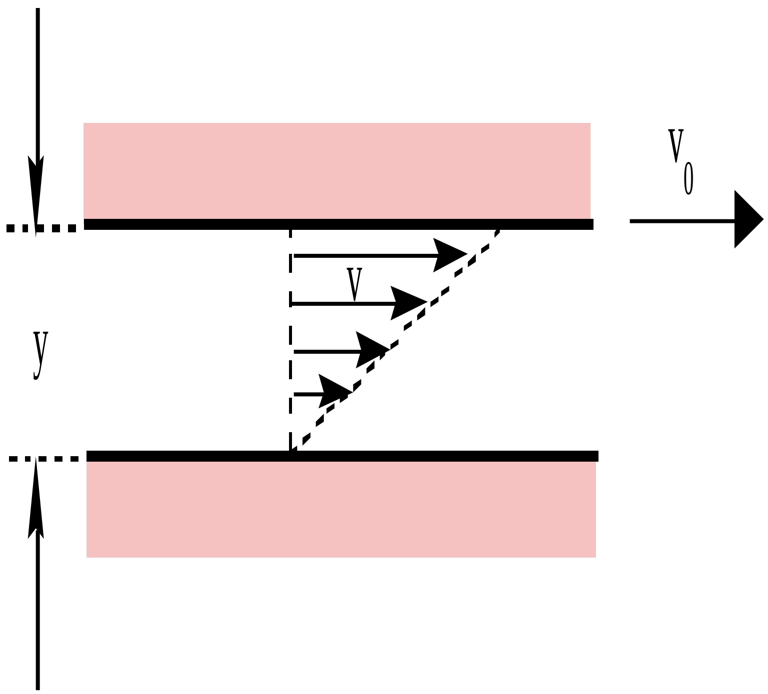
$$\sigma = E\varepsilon$$




**Model**

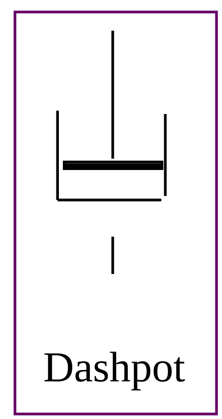
# SIMPLE MODELS OF THE VISCOELASTIC BEHAVIOUR OF AMORPHOUS POLYMERS

**Viscous flow**



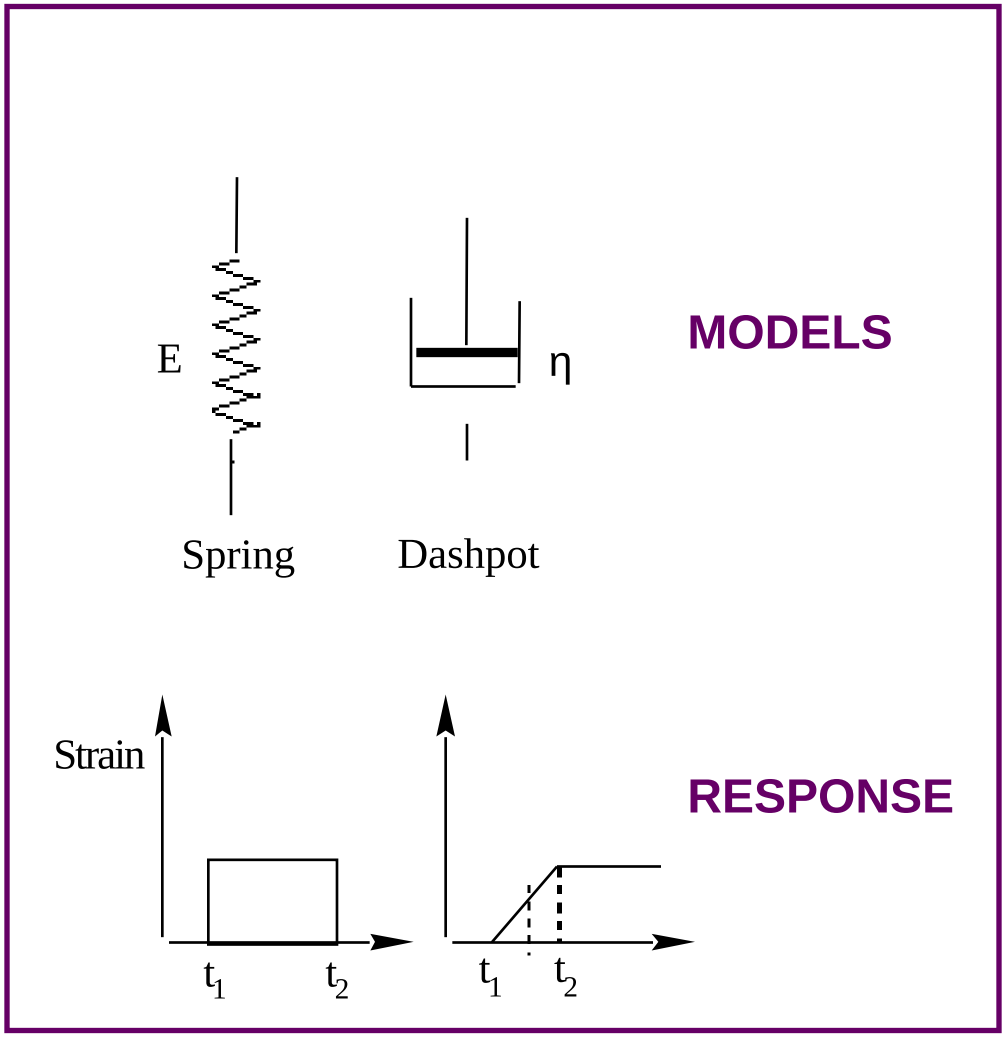

**Newtonian fluid**

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




**Model**

# STRAIN VS. TIME FOR SIMPLE MODELS



# 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* $\sigma = E\varepsilon$

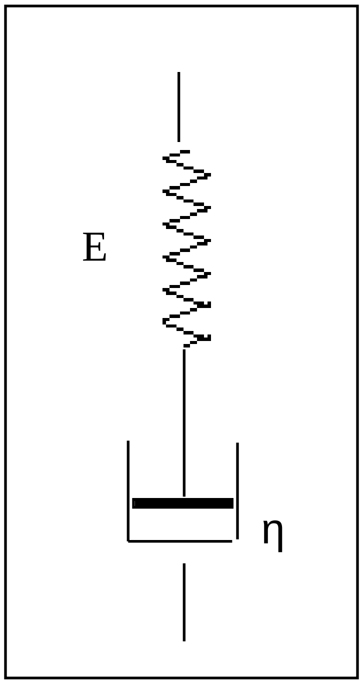
*Then allowed* $\sigma$ *to vary with time* $\frac{d\sigma}{dt} = E\frac{d\varepsilon}{dt}$

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

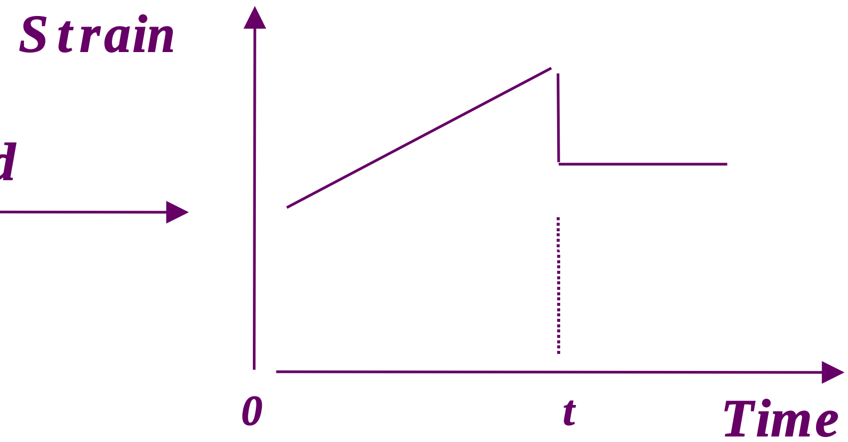
# MAXWELL MODEL - creep and recovery

*A picture representation of Maxwell's equation*

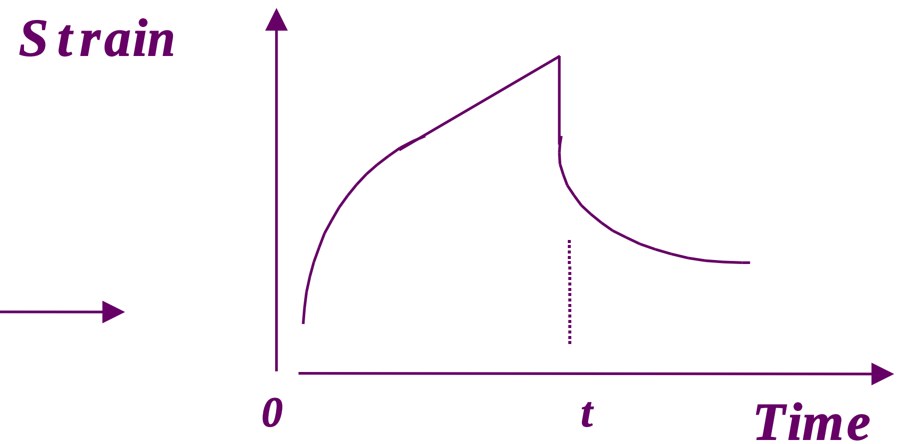



*Creep and recovery*

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




*Recall that real viscoelastic behaviour looks something like this*



# MAXWELL MODEL - stress relaxation

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

*In a stress relaxation experiment*

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

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

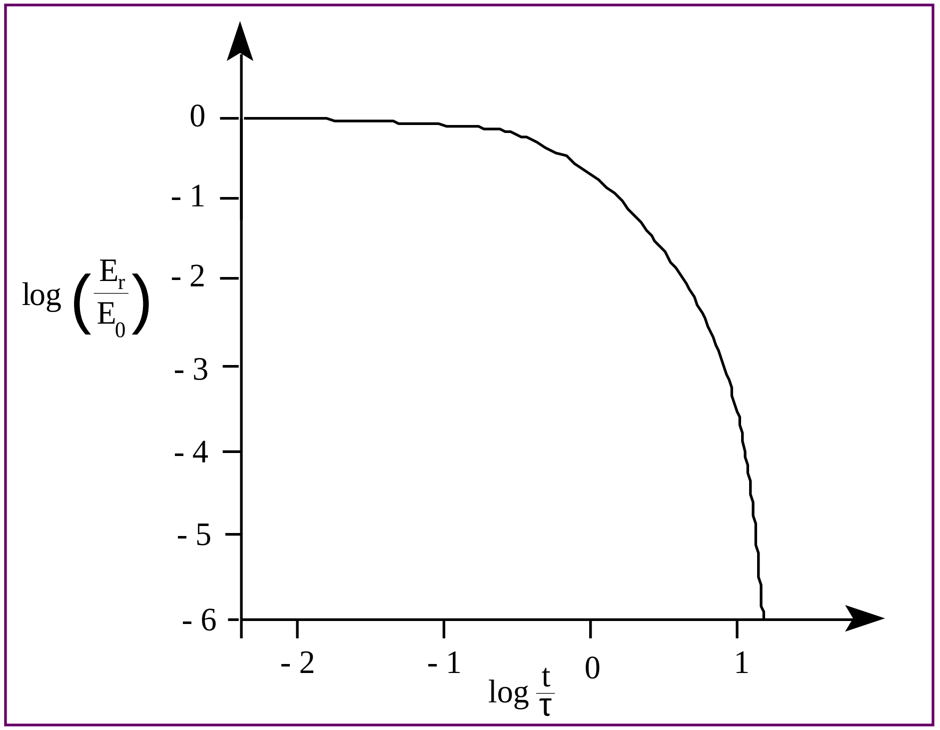
***Hence***

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

***Where***

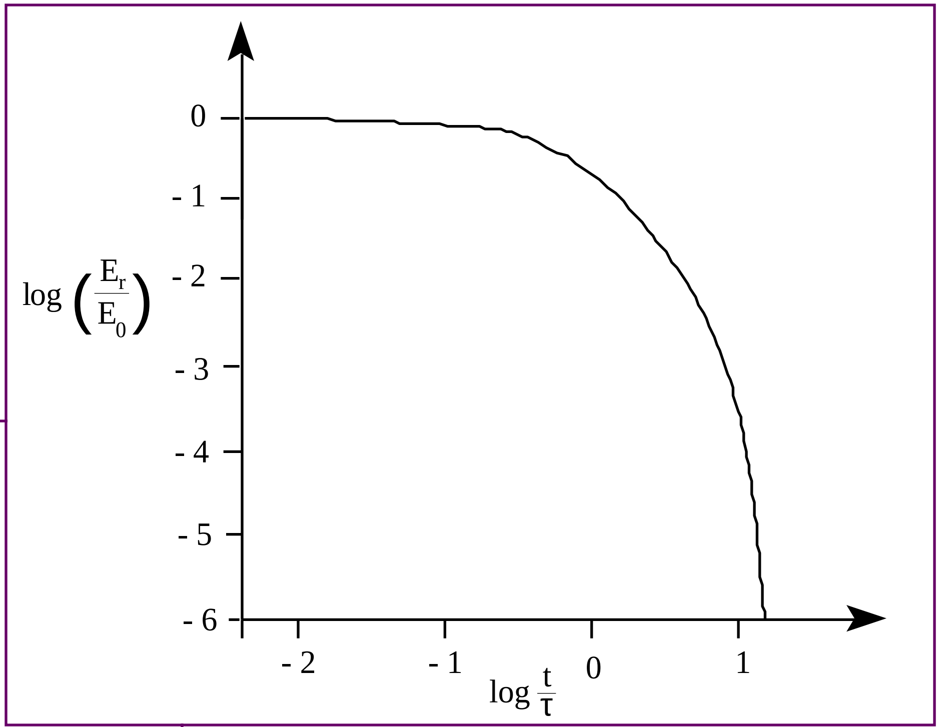
$$\tau_t = \frac{\eta}{E}$$

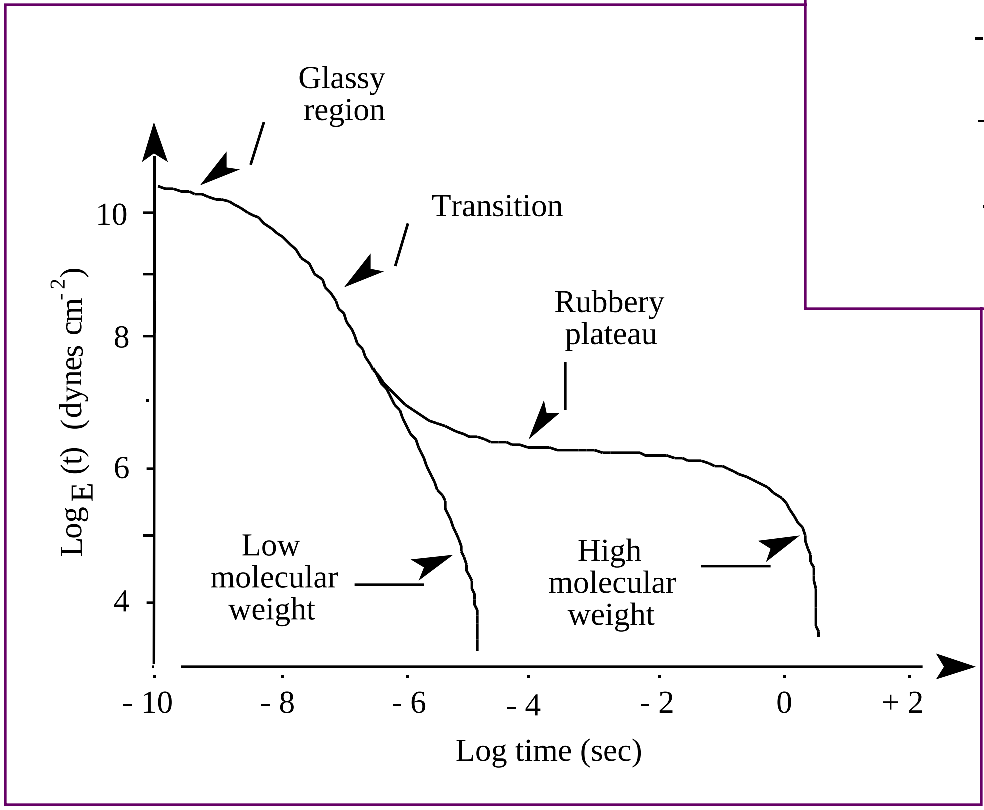
***Relaxation time***



# MAXWELL MODEL -stress relaxation

***Maxwell model***




***Real data looks something like this***