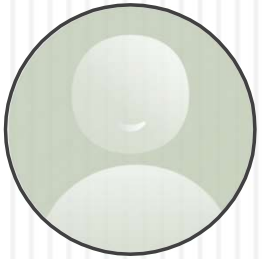
VISCOELASTICITY IN GLASS, RUBBER AND MELT PHASE

Contents



WEBCAM

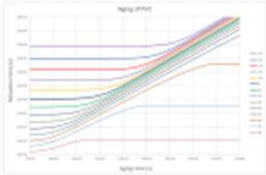
WHAT CAUSES VISCOELASTICITY?

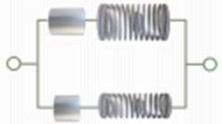
DEFORMATION OF POLYMER MOLECULES

GLASS, RUBBER AND MELT PHASE

INFLUENCE OF STRESS ON RELAXATION TIME

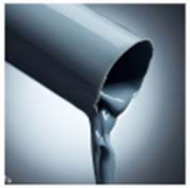
STRESS RELAXATION


PHYSICAL AGING

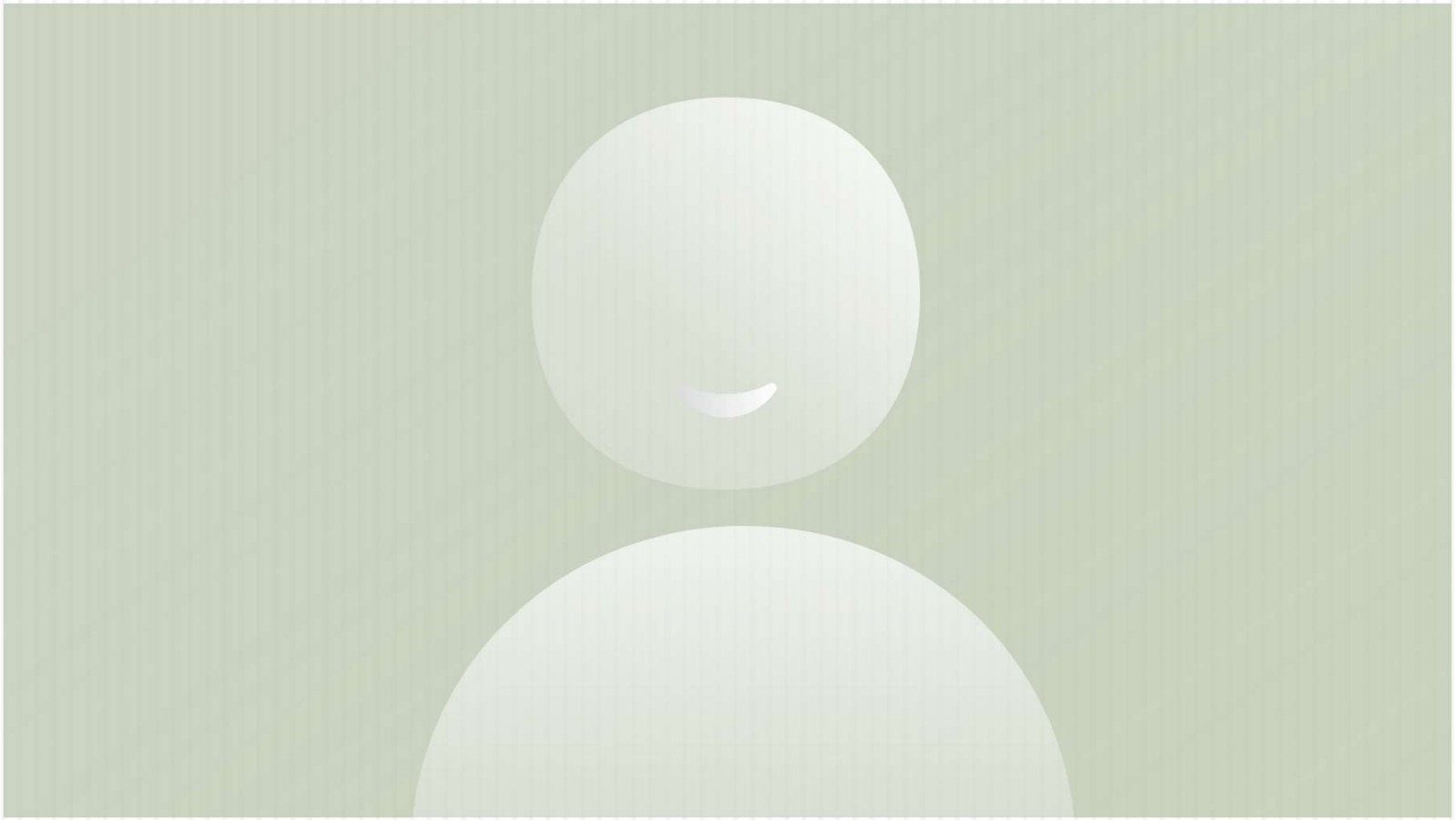

MECHANICAL ANALOGUE FOR STRESS IN POLYMERS

YIELD STRESS

BEHAVIOR UNDER CONSTANT LOAD


VISCOSITY

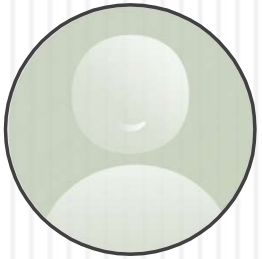
DIE SWELL



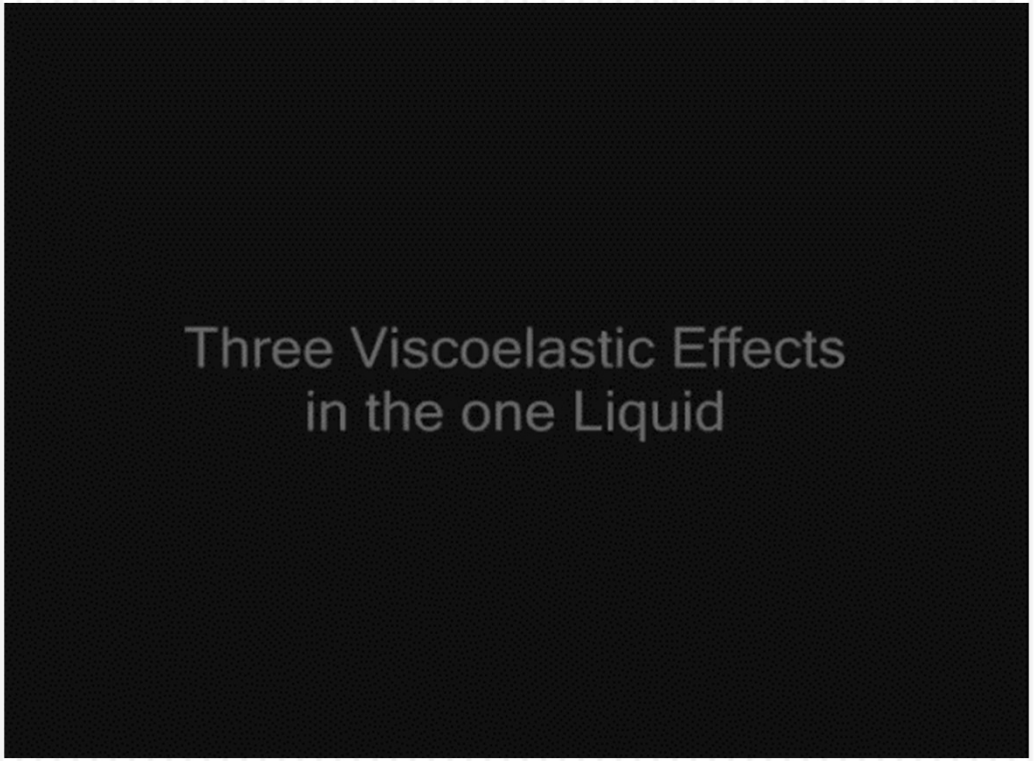
WEBCAM

WHAT CAUSES VISCOELASTICITY?

Elastic and viscous



- A viscoelastic material has at the same time both elastic and viscous properties.

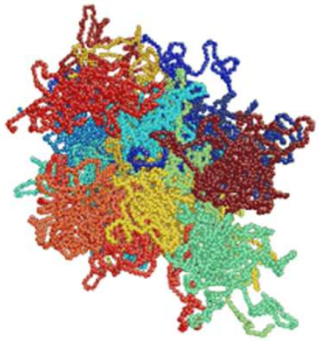


Cause of viscoelasticity

- Viscoelasticity is caused by entanglement of long particles.
- Any material that consists of long flexible fibre-like particles is in nature viscoelastic.
  - Polymers are always viscoelastic.

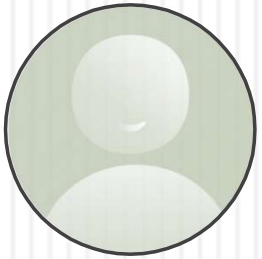
Glass phase

Rubber phase



Melt phase

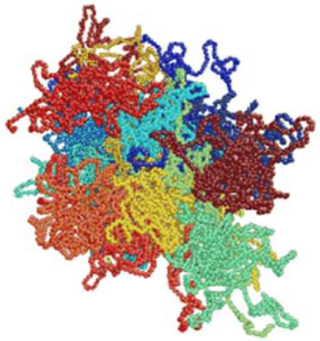
Some viscoelastic materials



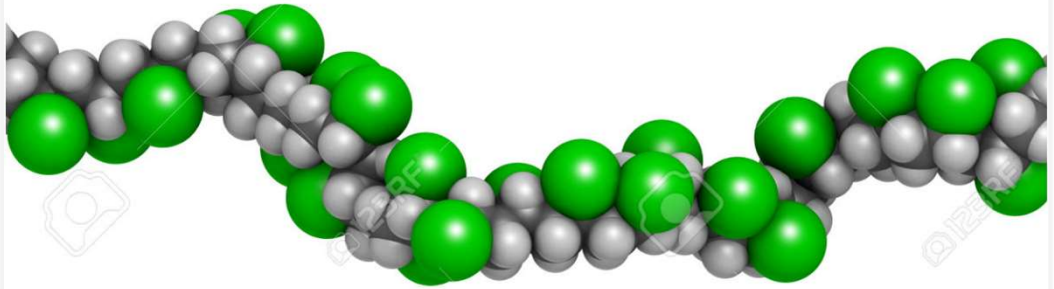
- A pile of snakes.
- Spaghetti.
- Tobacco.
- All fibre-like particles.

Glass phase

Rubber phase



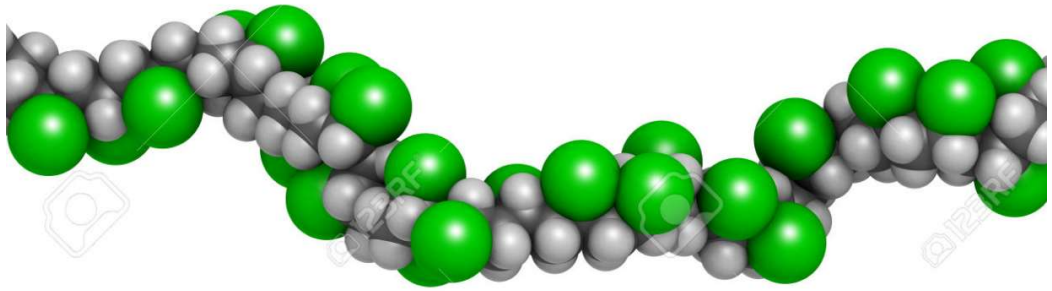
Melt phase



ABOUT POLYMER MOLECULES

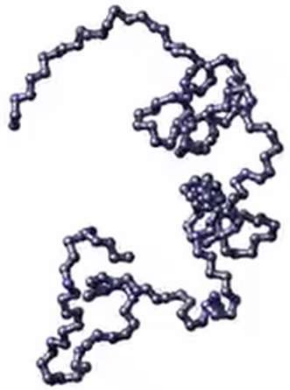
Repeat unit (1)

- Polymer molecules are long Kuhns built from many small identical repeat units (or monomers).
  - Polyvinylchloride (PVC) consists of many vinyl chloride (-CH2-CHCl-) repeat units.
  - Polyethylene (PE) consists of many ethylene (-CH2-CH2-) repeat units.
- The number of repeat units in a macromolecule can be very large: up to 10000 or more.



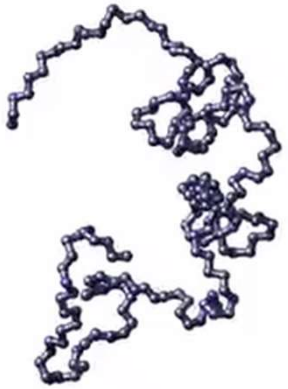
Repeat unit (2)

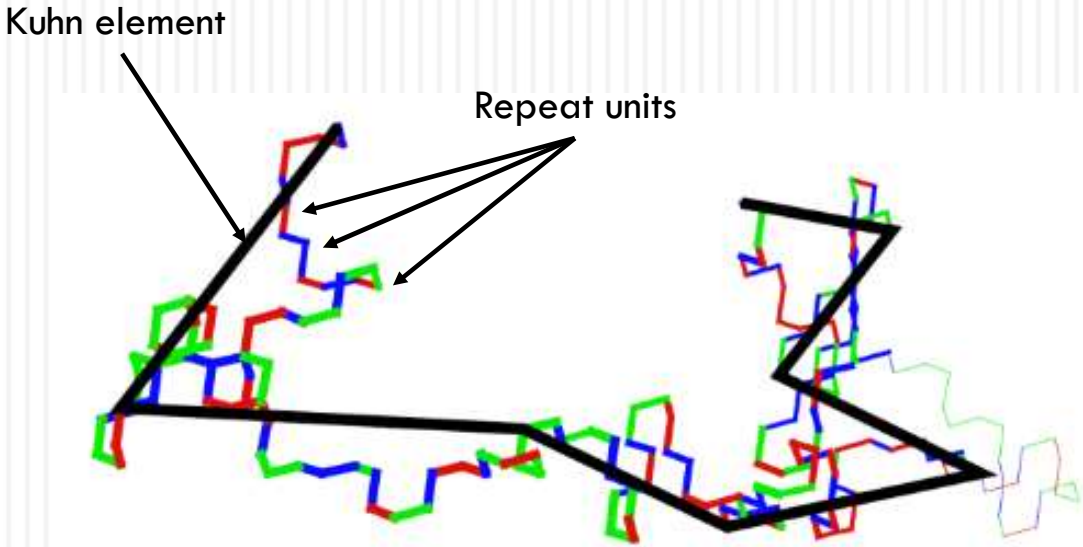
- The mutual direction between two neighbouring repeat units is not fixed but can change due to thermal movements.
- Each repeat unit is hindered in its freedom by neighbouring repeat units. Their possibility to change their direction is limited.



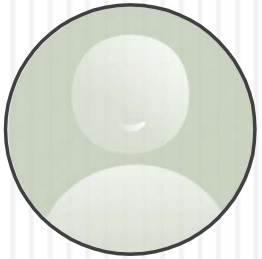
Kuhn segment (1)

- It takes several repeat units in a row in order to be able to randomly take any direction.
- Such a group of repeat units is called a Kuhn segment.





Kuhn segment (2)



- The number of repeat units in a Kuhn segment is a fixed number for each polymer.
  - It is called the characteristic ratio C_∞.
  - Examples:

Characteristic ratio and Kuhn length for several polymers.							
	PB	PP	PE	PVC	PMMA	PS	PC
C_∞	5.5	6.0	8.3	6.8	8.2	9.5	1.3
l_K (Å)	10	11	15	26	15	18	2.9

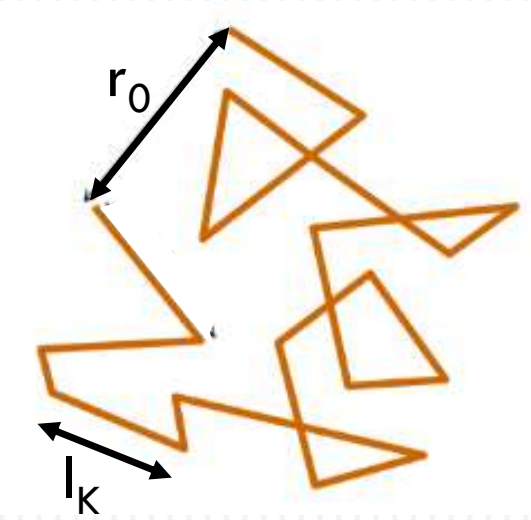
  - Number of Kuhn segments (N_K) in a molecule with N repeat units:

$$N_K = \frac{N}{C_\infty}$$

Size of the macromolecule

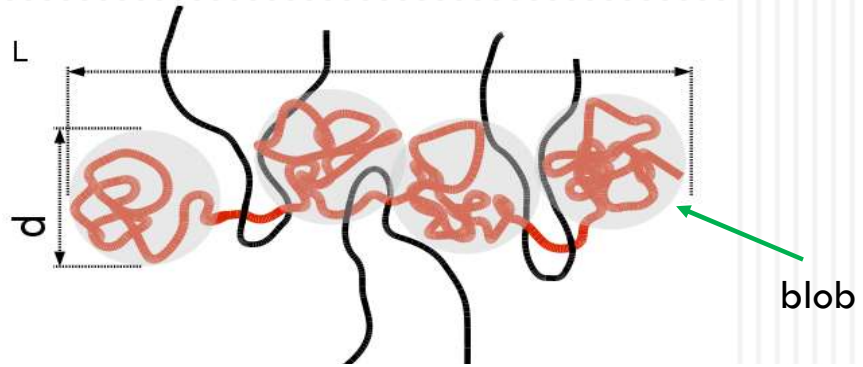
- Each Kuhn segment can randomly take any direction in space.
- The shape of the macromolecule in space therefor follows a random path.
- Average size (r_0) macromolecule:

$$r_0 = l_K \sqrt{N_K}$$

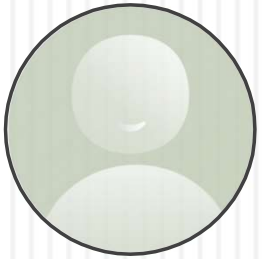


Entanglements and blobs (1)

- Each macromolecule will be entangled with several other macromolecules.
- At each entanglement the possible movements of the Kuhn segments will be seriously limited.
- In between two entanglements the Kuhn segments will follow a random path. This part of the macromolecule is called a blob.



Entanglements and blobs (2)

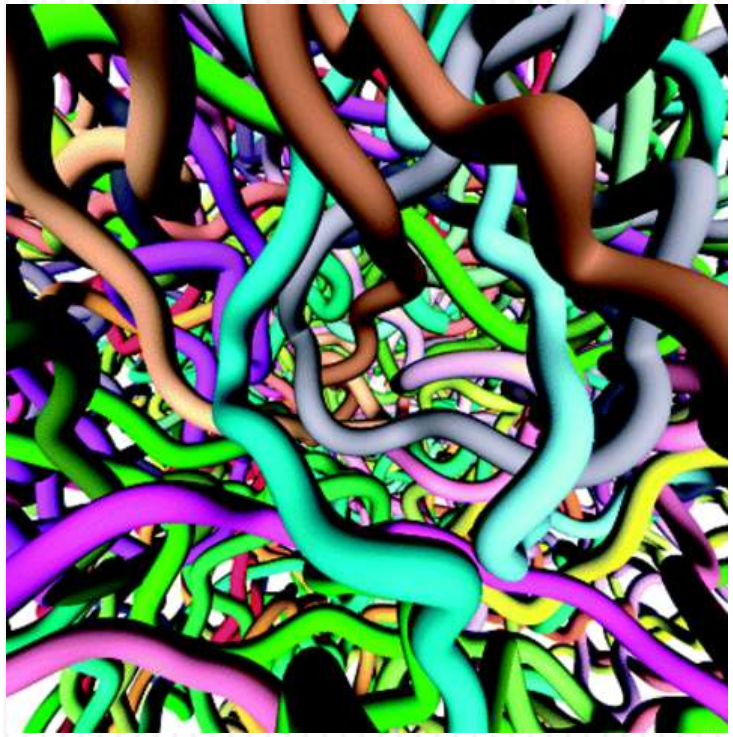


- If there are on average N_e Kuhn segments in a blob then the average radius of the blobs r_{blob} will be:

$$r_{blob} = l_K \sqrt{N_e}$$

- A macromolecule contains N_K/N_e blobs. The blobs follow a random path in space.
- The start to end distance L of the macromolecule will be:

$$r_0 = r_{blob} \sqrt{\frac{N_K}{N_e}} = l_K \sqrt{N_K}$$

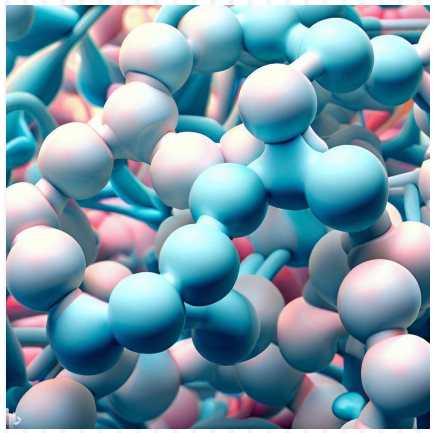


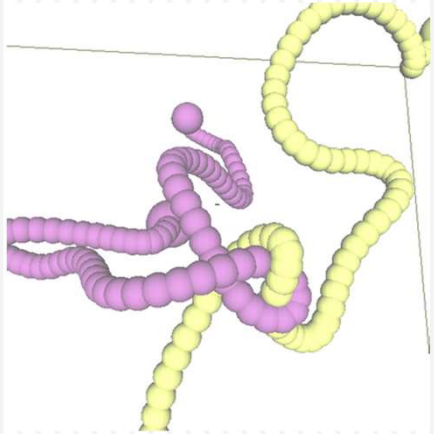
POLYMER STRUCTURE

Network density (1)

- The polymer molecules form a disordered structure.
- The molecules are entangled with many neighbouring molecules. They form a network.
- The network density ν_c is the number of entanglements per volume:

$$\nu_c = \frac{\rho}{m_K N_e}$$

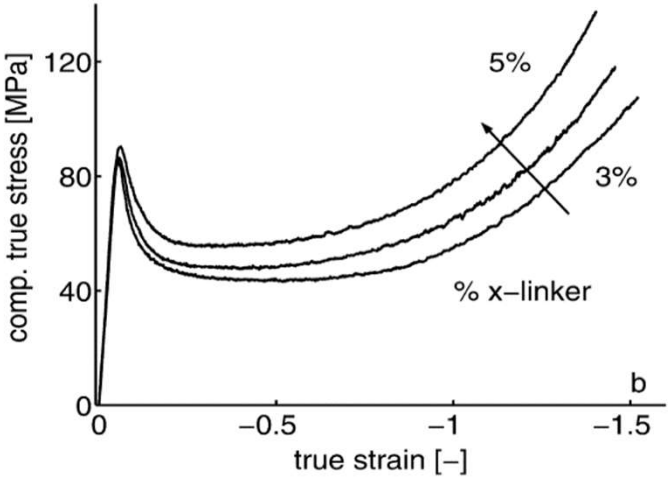


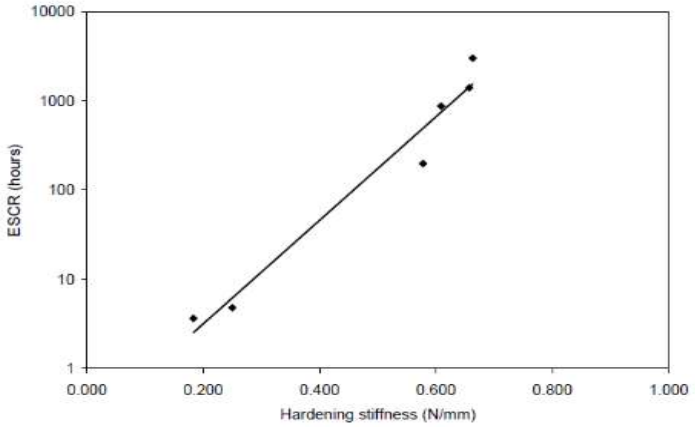


Network density (2)

The network density influences:

- Strain hardening modulus (glass phase).
- Rubber modulus (rubber and melt phase): $G_{rub} = \nu_c kT$
- Stress crack resistance.

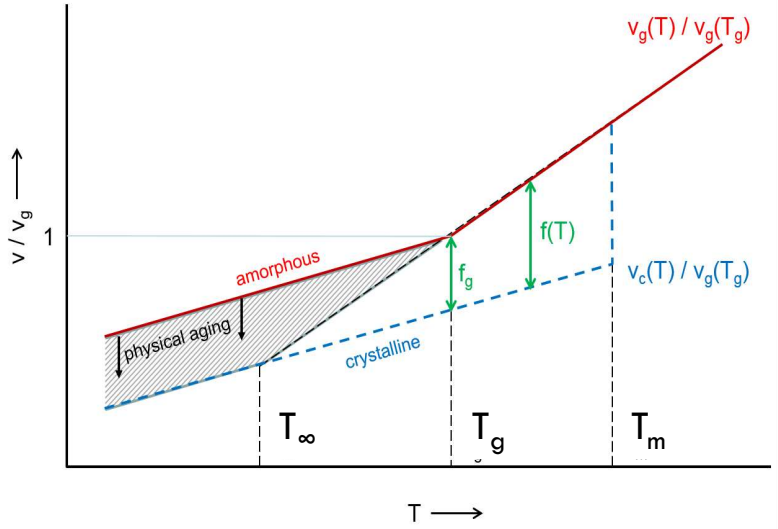




Free volume

- In between the molecules free volume is present.
- The free volume is small. The molecules hinder each other strongly in their movements.
- The free volume fraction ψ_{free} is the relative difference between the amorphous and the crystalline volume:

$$\psi_{free} = \frac{v_a - v_c}{v_a} \approx (\alpha_a - \alpha_c)(T - T_\infty)$$



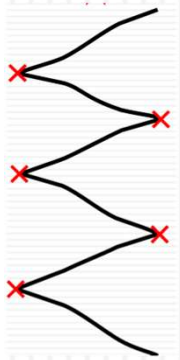
DEFORMATION OF POLYMER MOLECULES

Deformation options of polymer molecules

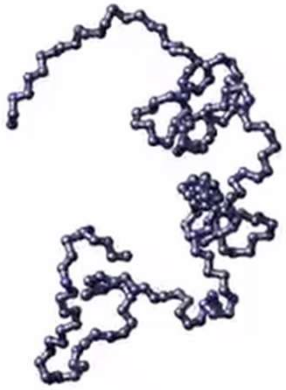
Polymer molecules have three ways to deform:

- Bending of chain segments = small deformation
- Rotation of chain segments = large deformation
- Reptation of the macromolecule = large deformation + displacement

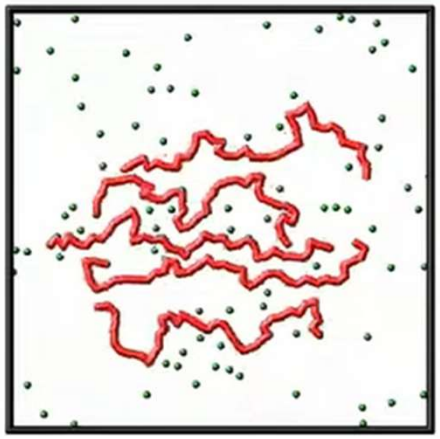
Segment bending



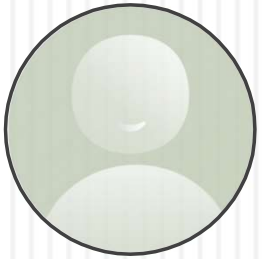
Segment rotation



Reptation



Deformation options of polymer molecules



Polymer molecules have three ways to deform:

- Bending of chain segments = small deformation
- Rotation of chain segments = large deformation
- Reptation of the macromolecule = large deformation + displacement

Segment bending

- Chain segments bend; the molecule itself is not displaced
- Bending is important for the glass phase properties:
  - Glass elasticity modulus

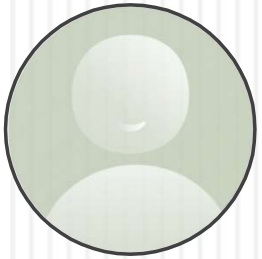
Segment rotation

- Chain segments rotate; the molecule itself is not displaced
- The rotation time θ_{rot} is strongly dependent on temperature.
- Rotation is important for the glass phase properties:
  - Rubber elasticity modulus
  - Glass – rubber transition temperature
  - Glass stress relaxation
  - Yield stress

Reptation

- The molecule moves into another position.
- The reptation time is proportional to the rotation time ($\theta_{rep} = \alpha\ \theta_{rot}$) with $\alpha = 10^4 – 10^8$.
- Reptation is important for the fluid properties:
  - Rubber – melt transition temperature
  - Viscosity
  - Elasticity
  - Rubber stress relaxation

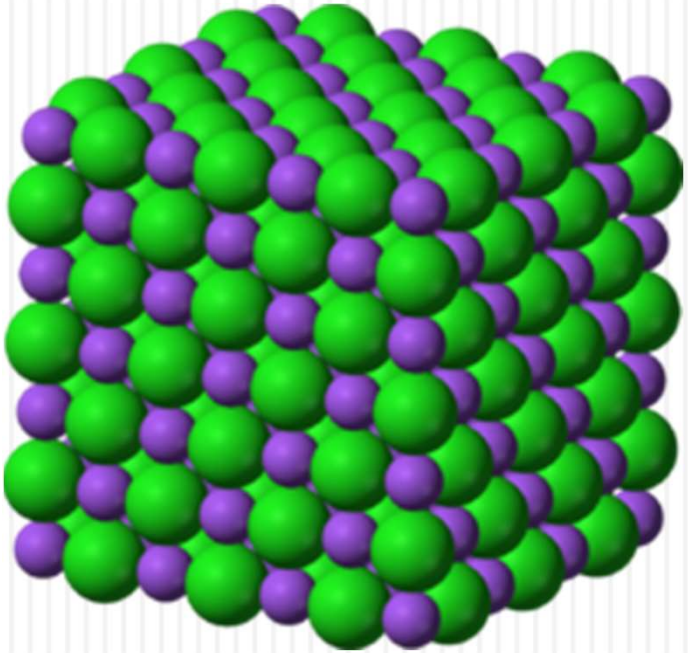
Chain segment rotation



- The glass transition temperature T_g is the temperature at which the rotation time of the chain segments is 1 second.
- The polymer feels stiff when the rotation time is much more than the observation time (usually 1 second).
- The polymer feels flexible when the rotation time is much shorter than the observation time (usually 1 second).

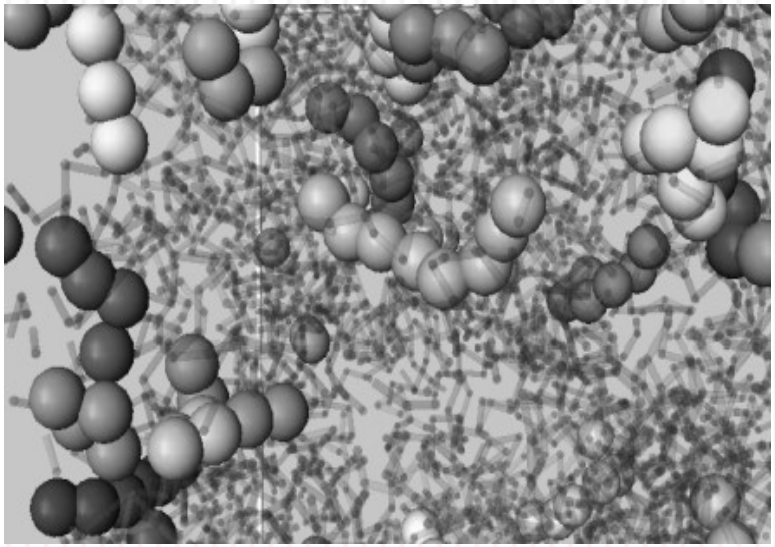
Chain segment rotation

- All molecules attract each other.
  - Below the melting temperature they form a regular crystalline structure.



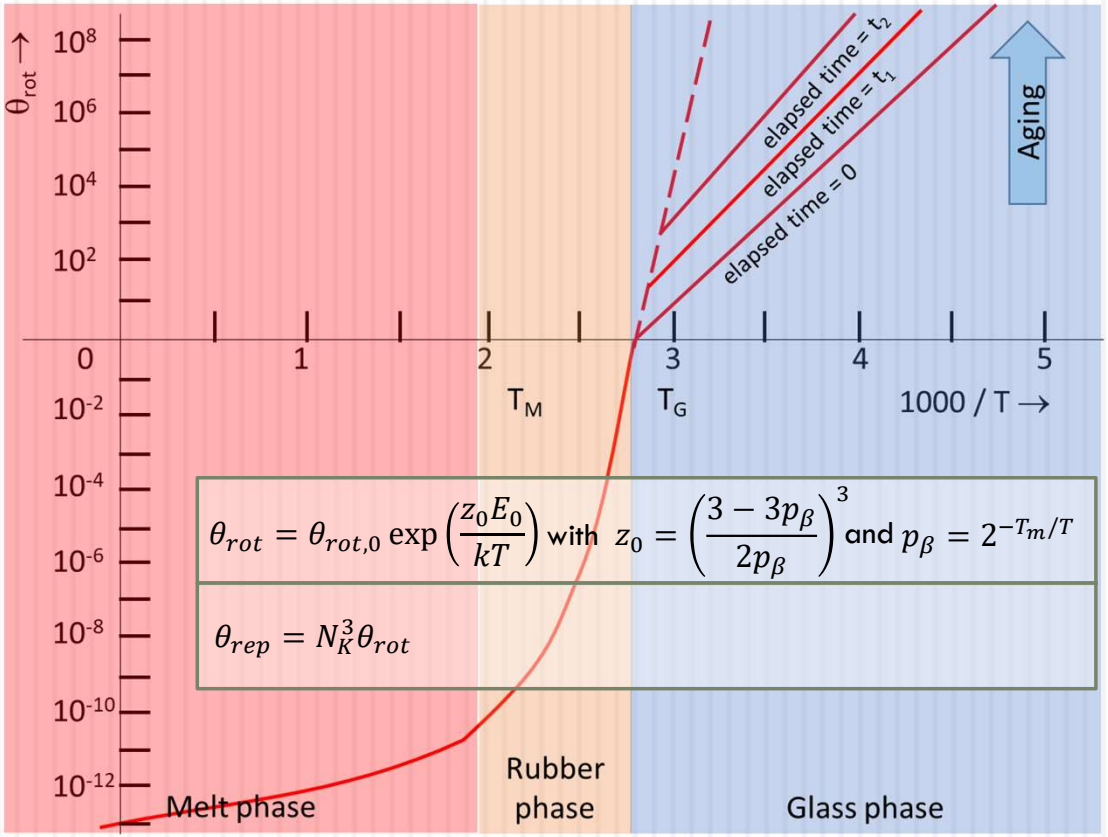
Chain segment rotation

- The repeat units in a polymer also attract each other.
  - Below the melting temperature the formation of a crystalline structure is difficult due to the limited mobility of the repeat units.
  - They cluster together in cooperatively rearranging regions (CRR's).
  - This seriously hinders the rotation of the Kuhn segments.

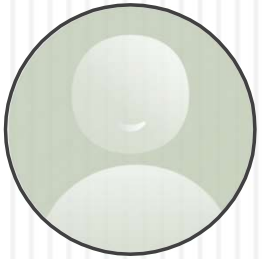


Chain segment rotation

- The rotation time θ_{rot} of the chain segments increases strongly with reducing temperature.



Chain segment rotation



- Above and below the glass transition temperature T_g cooperative rotation of the Kuhn segments:

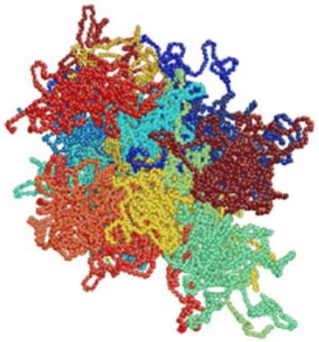
$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{z_0 E_0}{kT}\right) \qquad z_0 = \left(\frac{3-3p_\beta}{2p_\beta}\right)^3 \qquad p_\beta = 2^{-T_m/T}$$

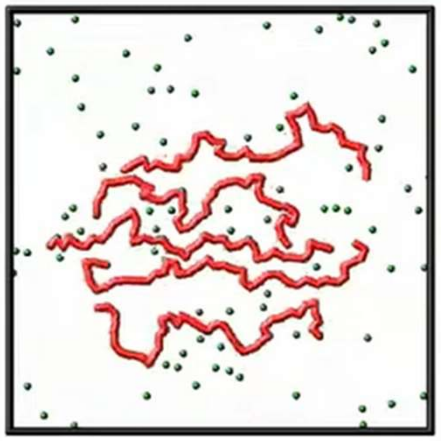
  - The level of cooperativity z_0 is only a function of temperature.
- Above the glass transition temperature a dynamic equilibrium is always reached.
- Below glass transition temperature T_g the Kuhn rotation time is very long (>> 1 s).
  - Reaching equilibrium takes time.
  - The properties of the polymer change with time.
  - This is called aging.

Reptation of the macromolecule

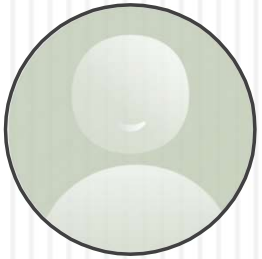
- At times longer than the reptation time the polymer behaves like a fluid.
- At times shorter than the reptation time the polymer behaves like a rubber.

rubber





Reptation of the macromolecule

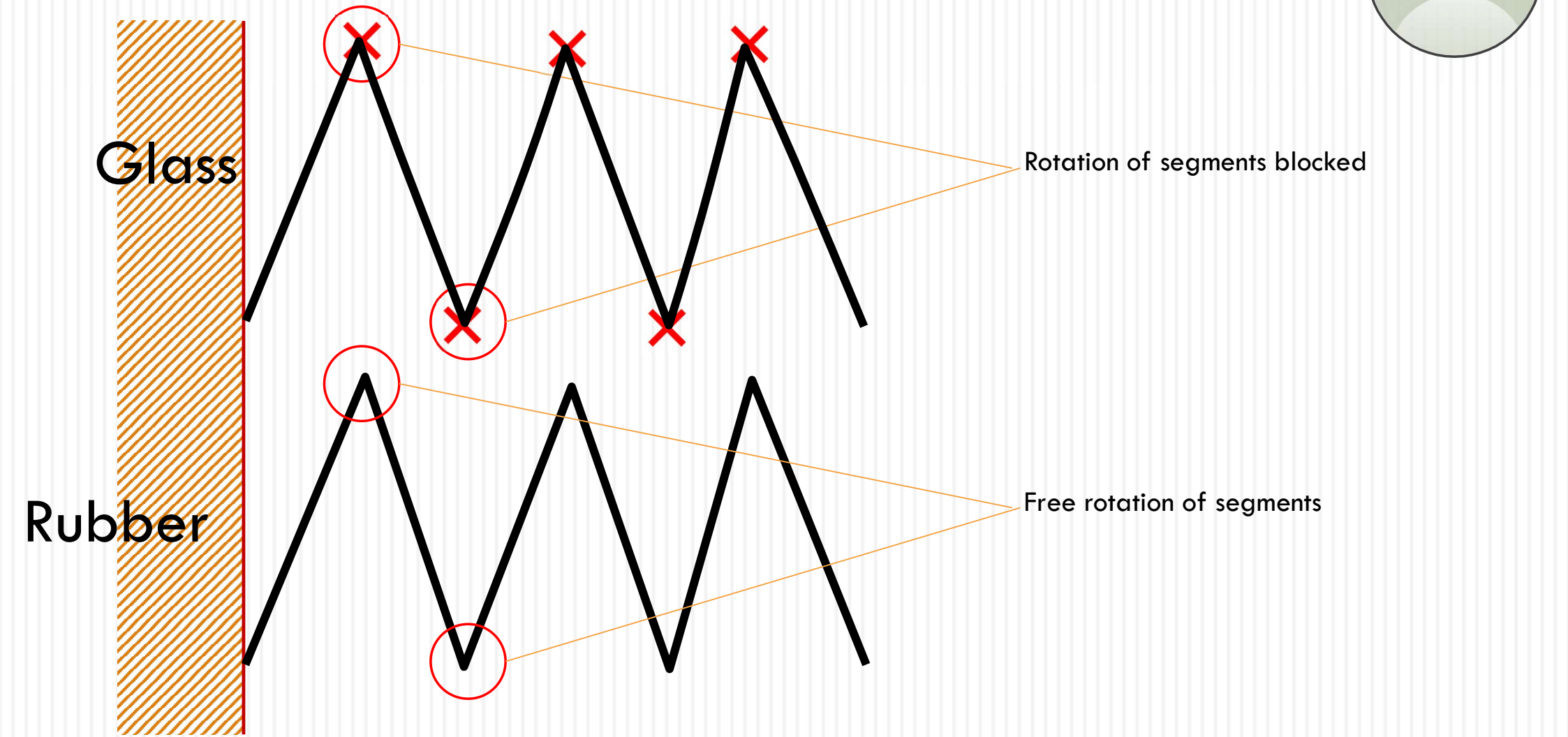


- The reptation time is proportional to the rotation time.
- The proportionality strongly depends on the number of Kuhn segments N_K in the macromolecule:
  - 1 Kuhn segment: + or - give step $-l_K$ or $+l_K$ during θrot.
  - 2 Kuhn segments: ++ or -- give step step $-l_K$ or $+l_K$
    +- and -+ give no displacement
    $\rightarrow$ Step $-l_K$ or $+l_K$ takes $2\theta_{rot}$.
  - N_K Kuhn segments: Step $-l_K$ or $+l_K$ takes $N_K\theta_{rot}$.
  - Reptation over N_K Kuhn segments takes N_K^2 steps:

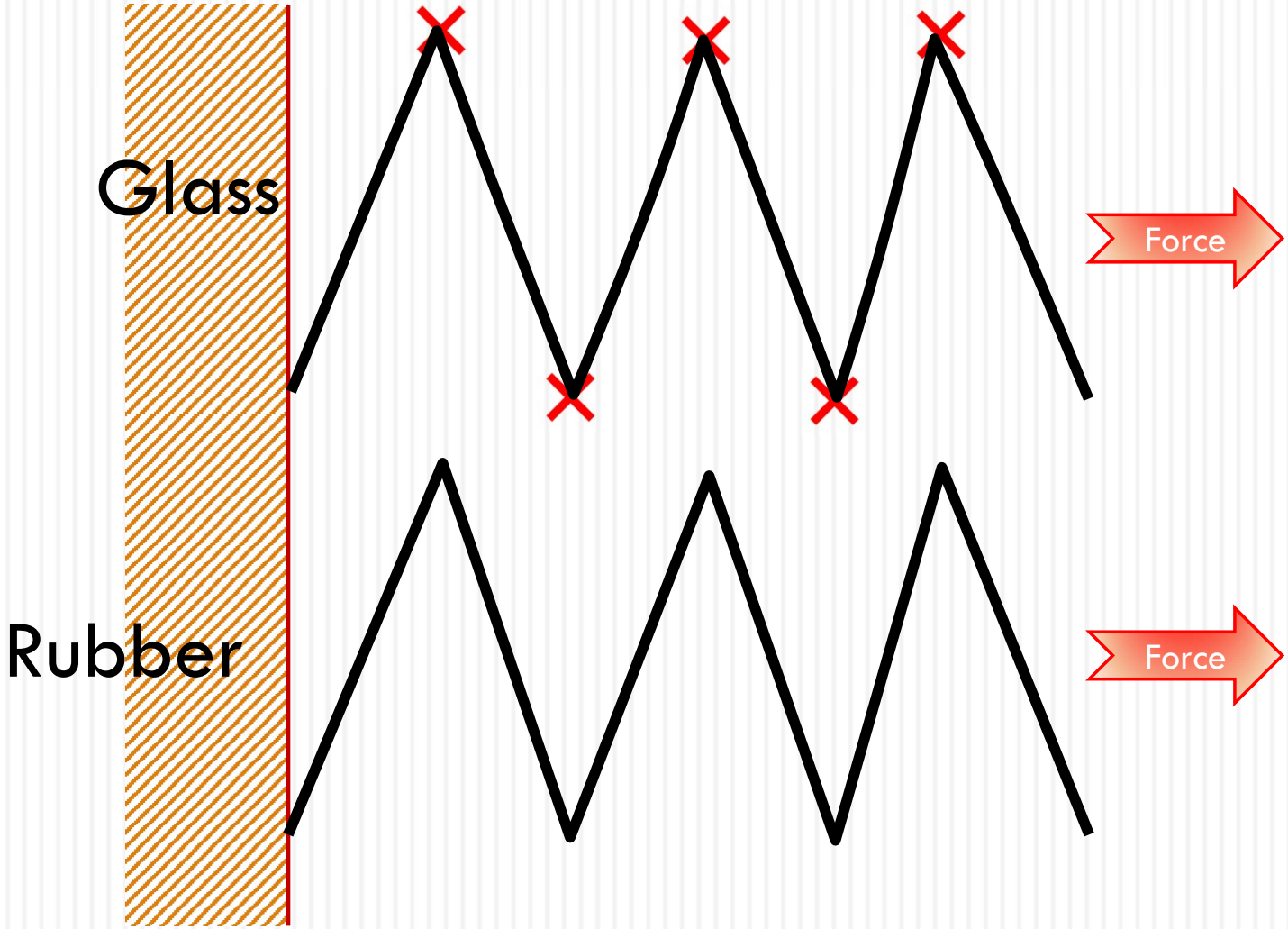
    $\theta_{rep} = N_K^2 N_K \theta_{rot} = N_K^3 \theta_{rot}$

GLASS, RUBBER AND MELT PHASE

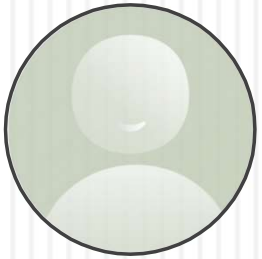
Glass and rubber phase

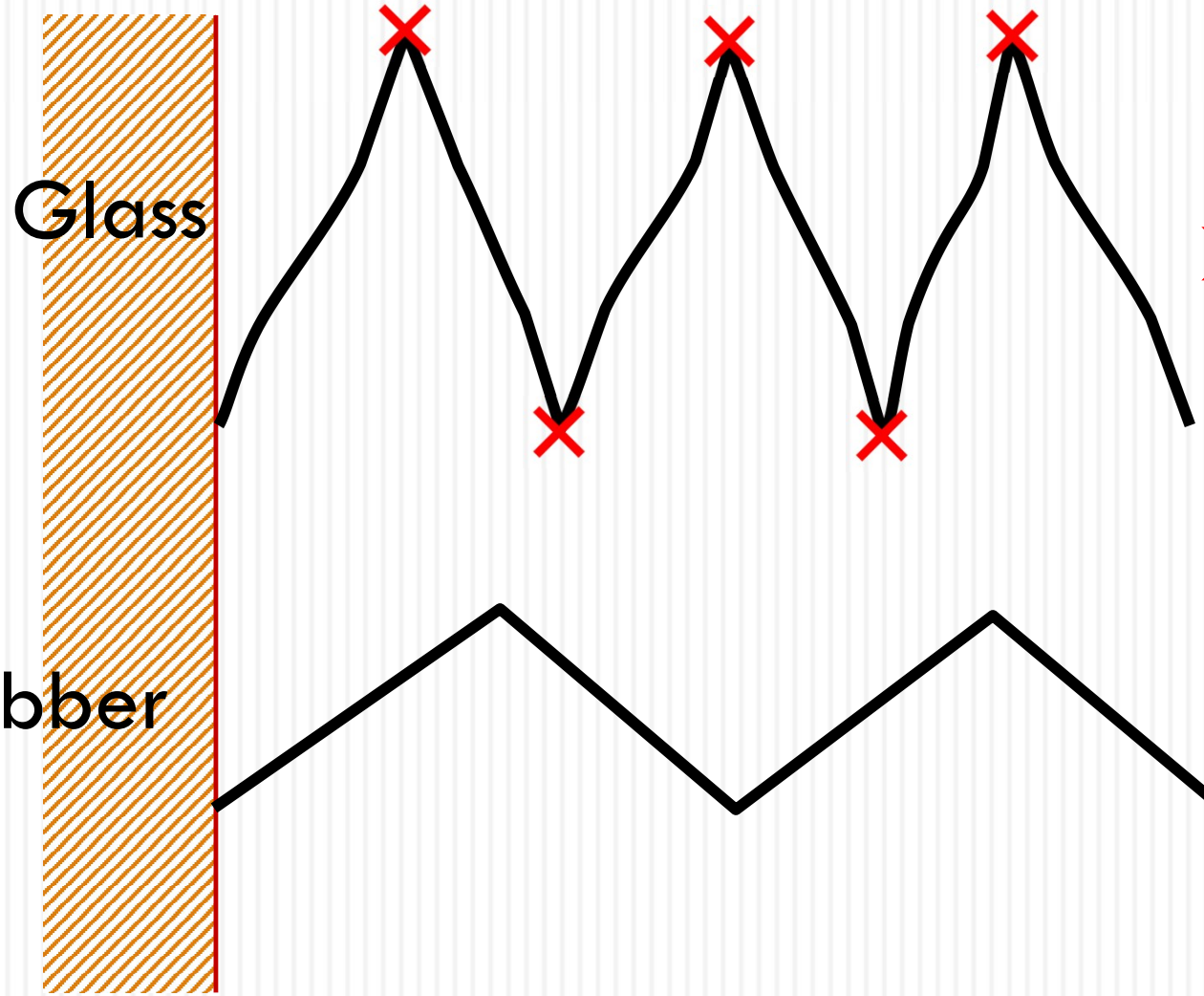


Glass and rubber phase



Glass and rubber phase

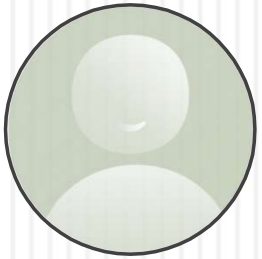




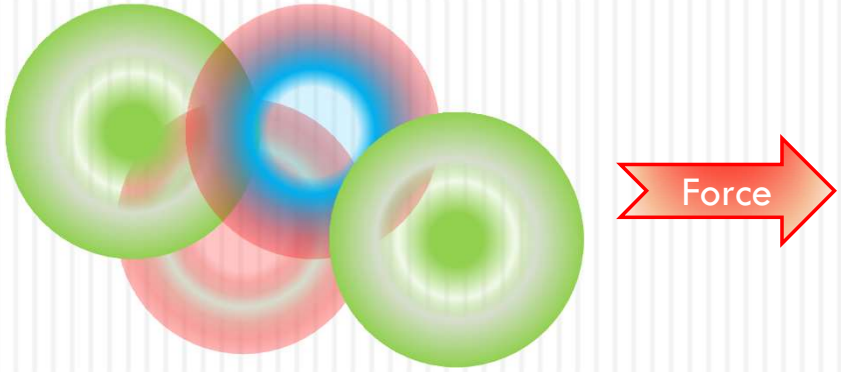
- Deformation by segment bending
- High stiffness
- Rotation time >> 1 s

- Deformation by segment rotation
- Low stiffness
- Rotation time << 1 s

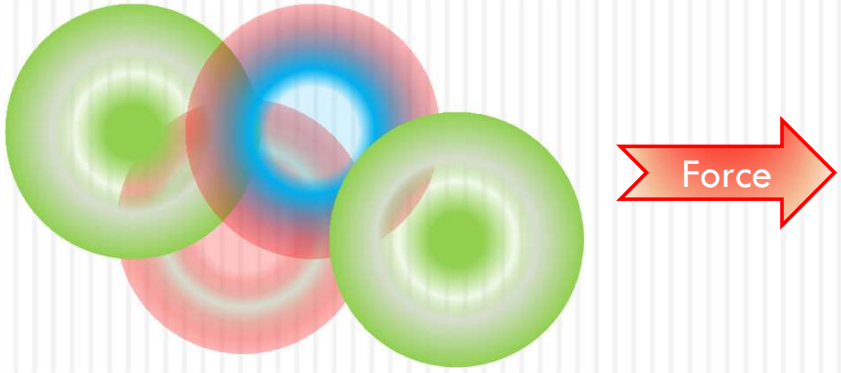
Glass and rubber phase



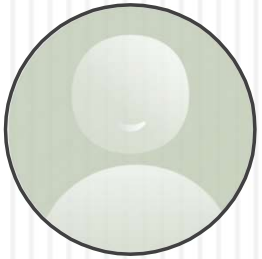
Glass



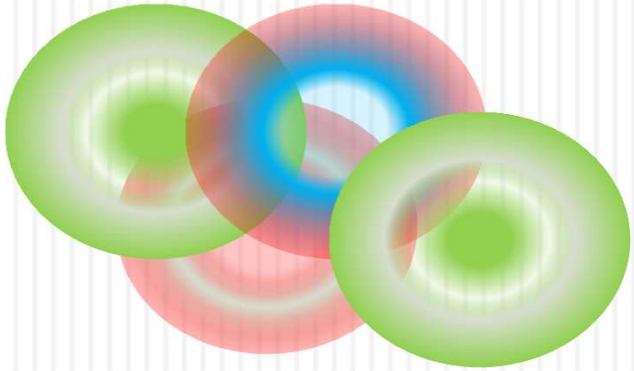
Rubber



Glass and rubber phase



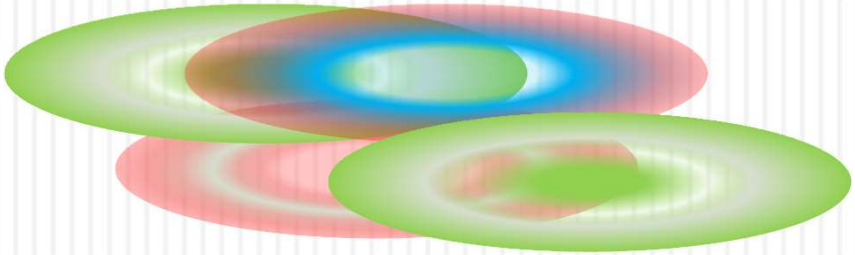
Glass



Force

- Deformation by segment bending
- High stiffness
- Rotation time >> 1 s

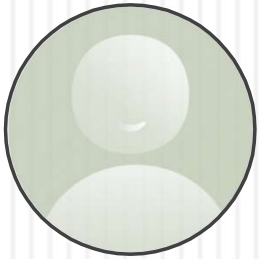
Rubber



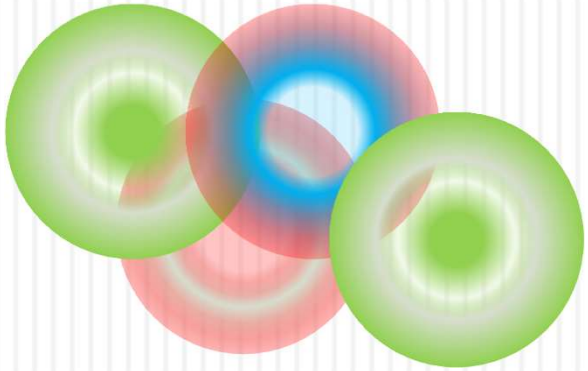
Force

- Deformation by segment rotation
- Low stiffness
- Rotation time << 1 s

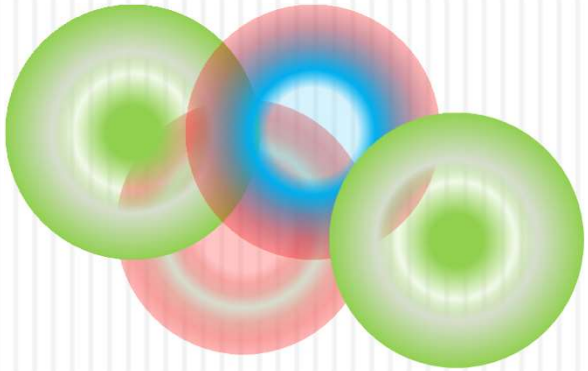
Rubber and melt phase



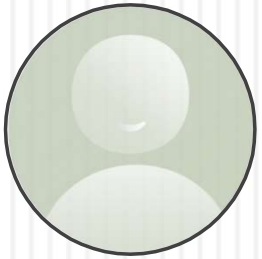
Rubber



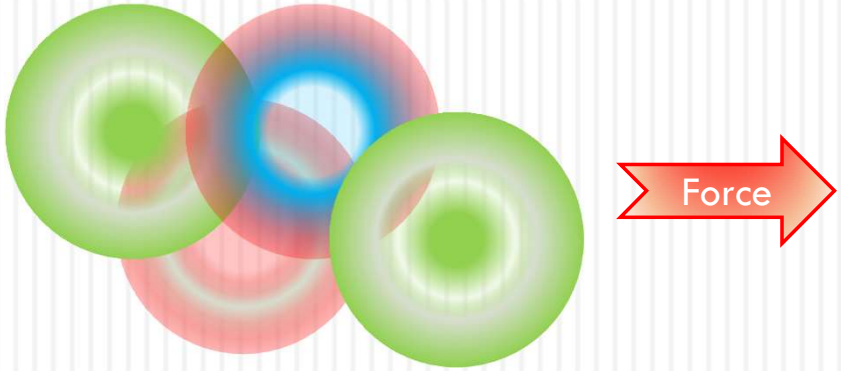
Melt



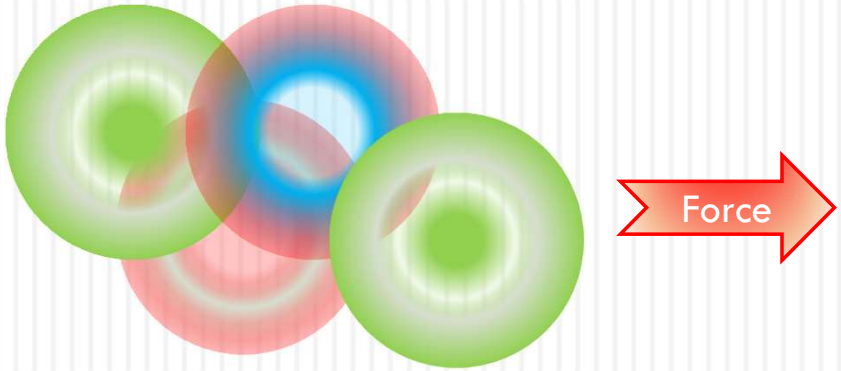
Rubber and melt phase



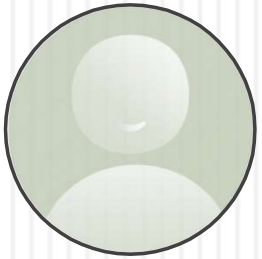
Rubber



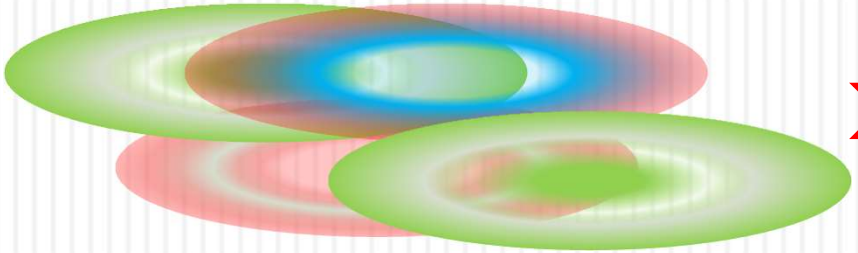
Melt



Rubber and melt phase



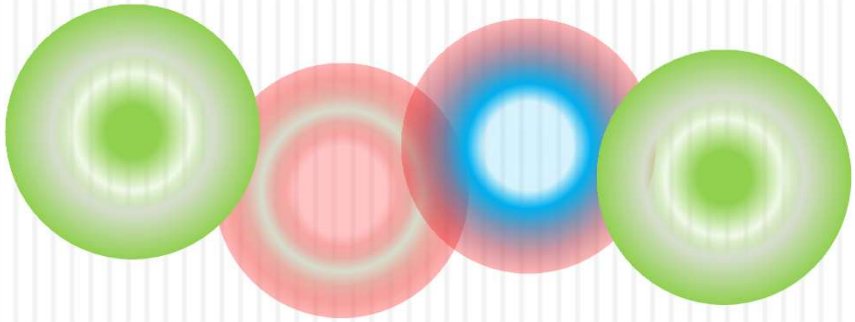
Rubber



Force

- Low stiffness
- Molecules in fixed position
- Reptation time >> 1 s

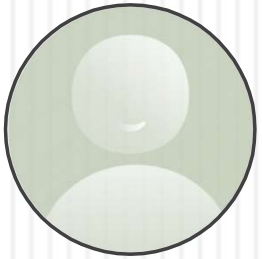
Melt



Force

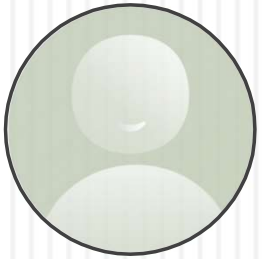
- Very low stiffness
- Molecules change position
- Reptation time << 1 s

Glass phase (short term)



- Kuhn segments have a rotation time of (much) more than 1 second.
  - The plastic is rigid on a human time scale (observation time is a few seconds).
- The polymer is difficult to deform:
  - Kuhn segments can only bend a little bit. The macromolecules are rigid.
  - An applied force will only result in a small deformation of the plastic.

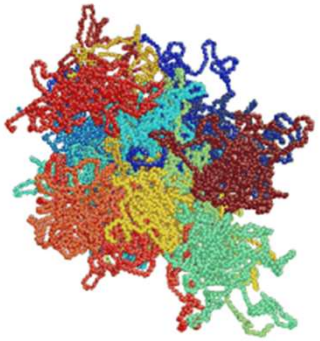
Glass phase (long term)



- Kuhn segments have a rotation time of (much) more than 1 second.
  - The plastic is rigid on a human time scale (observation time is a few seconds).
- A force applied for a long time is still able to deform the polymer in the glass phase.
  - The time should be longer than the time that the Kuhn segments need to rotate.
  - This slow deformation is called creep.
  - The polymer now behaves like a rubber.

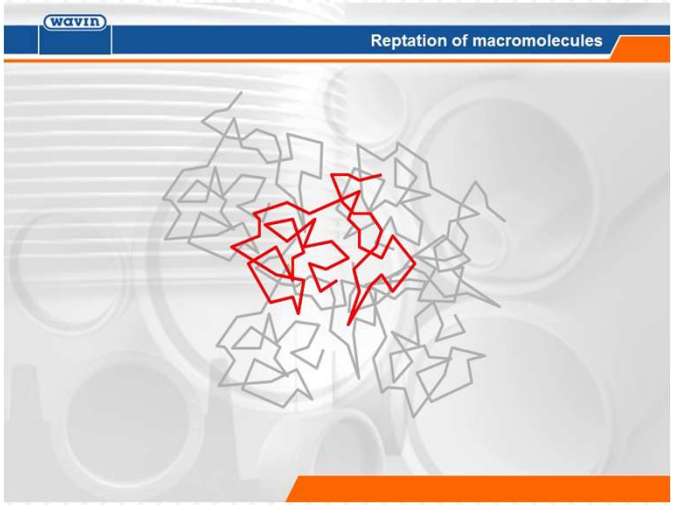
Rubber phase

- In the rubber phase the Kuhn segments rotate in a time less than 1 second.
  - The plastic is flexible.
- The reptation time of the macromolecules is much higher than 1 s.
  - The relative position of the macromolecules will not change.

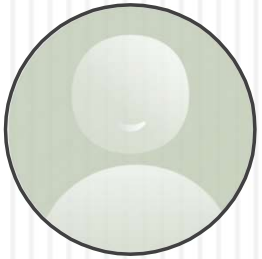


Melt phase

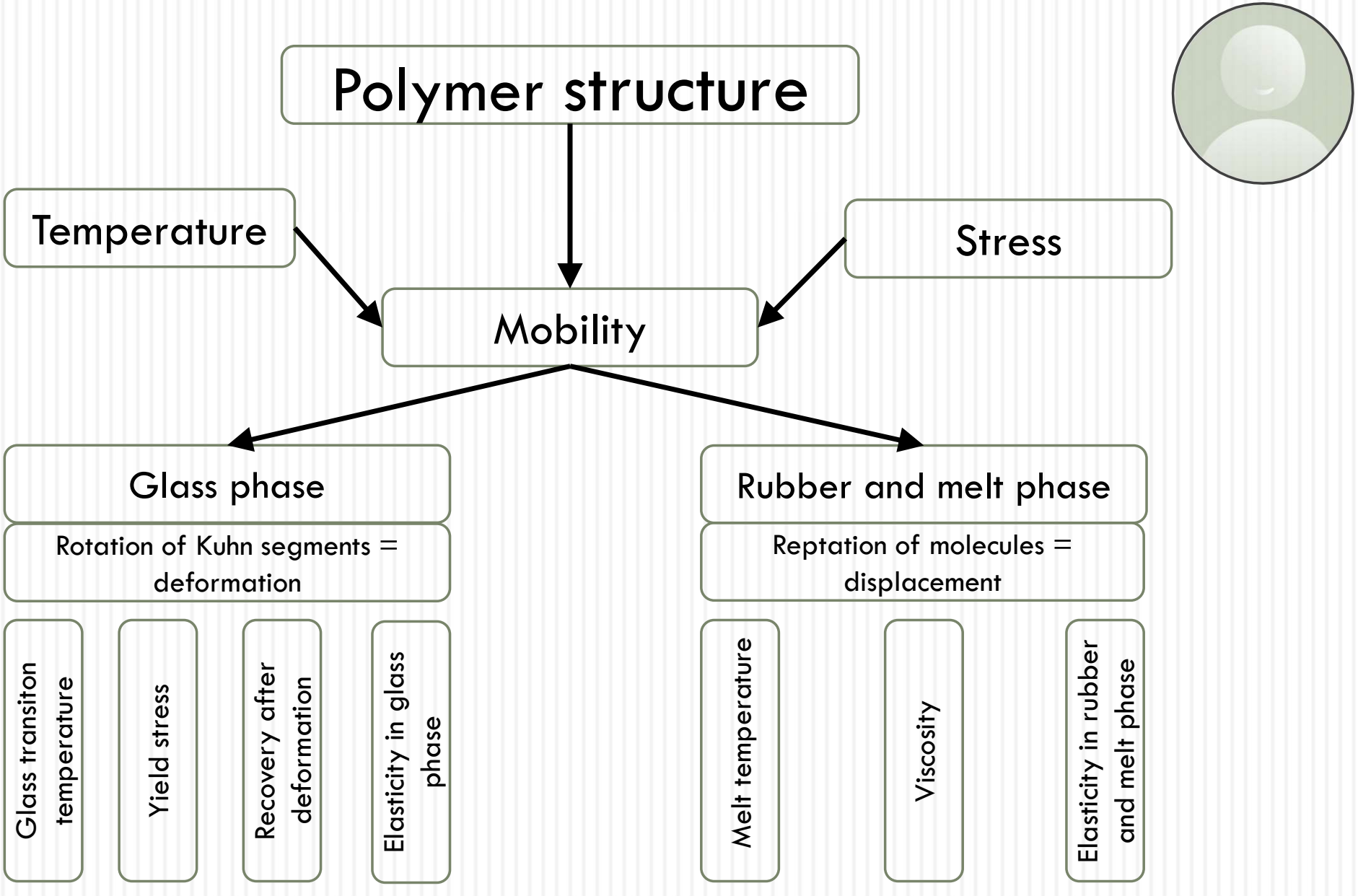
- In the melt phase the reptation time of the macromolecules is less than 1 second.
  - The macromolecules can change their relative position.
- In this condition the plastic can be shaped into products by means of extrusion, injection moulding or blow moulding.



Glass, rubber and melt phase

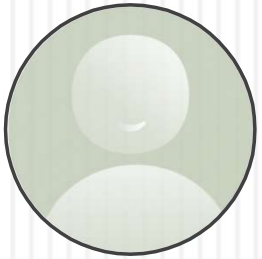


	Rotation time	Reptation time
Glass phase	> 1 s	>> 1 s
Glass – rubber transition temperature	1 s	
Rubber phase	< 1 s	> 1 s
Rubber – melt transition temperature		1 s
Melt phase	<< 1 s	< 1 s


Polymer structure
Temperature
Stress
Mobility
Glass phase
Rotation of Kuhn segments = deformation
Glass transiton temperature
Yield stress
Recovery after deformation
Elasticity in glass phase
Rubber and melt phase
Reptation of molecules = displacement
Melt temperature
Viscosity
Elasticity in rubber and melt phase

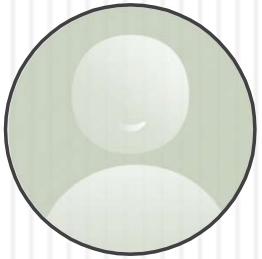
INFLUENCE OF STRESS ON RELAXATION TIME

Stress and relaxation time



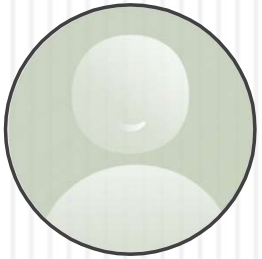
- The stress relaxation time is the characteristic time that the stress needs to reduce.
- The stress relaxation time is strongly influenced by:
  - Temperature
  - Stress

Stress and relaxation time

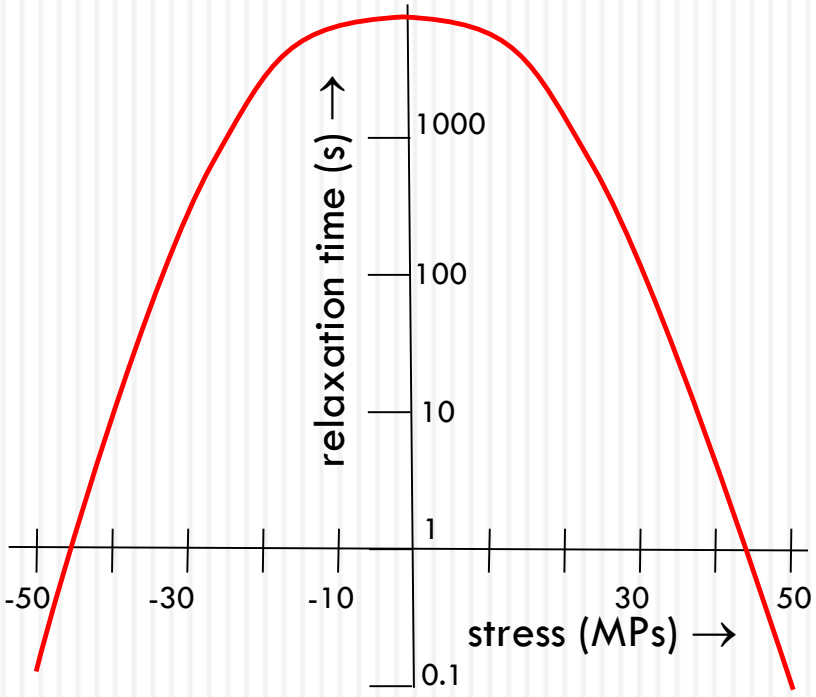


- Stresses in the glass phase are caused by bending of chain segments.
  - Relaxation of stresses in the glass phase is caused by rotation of the chain segments.
- Stresses in the rubber and melt phase are caused by rotation of the chain segments.
  - Relaxation of stresses in the rubber and melt phase is caused by reptation of the macromolecules.

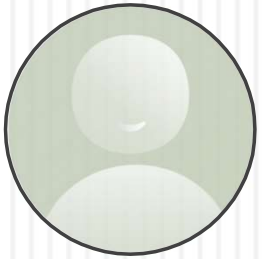
Stress and relaxation time



Nett result: The relaxation time decreases exponentially with the applied stress.



Stress and relaxation time



- Relaxation of stresses in the glass phase is caused by rotation of the Kuhn segments.
- Rotations that reduce the stress will speed up.

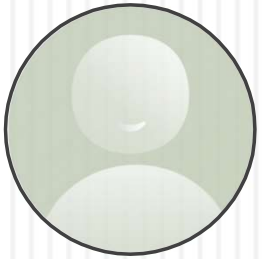
$$\theta_{rot}(T,\sigma_{rot}) = \theta_{rot,0}\exp\left(\frac{E_{rot} - V_{rot}\sigma_{gla}}{kT}\right)$$

- Rotations that increase the stress will slow down.

$$\theta_{rot}(T,\sigma_{rot}) = \theta_{rot,0}\exp\left(\frac{E_{rot} + V_{rot}\sigma_{gla}}{kT}\right)$$

- On average any stress will reduce the rotation time.

Stress and relaxation time

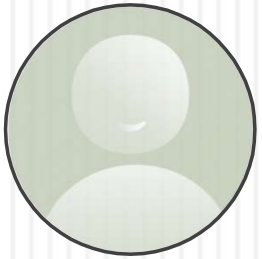


- V_{rot} is the activation volume.
- $V_{rot}\sigma_{gla}$ is the energy that is consumed during rotation of a Kuhn segment in a blob.
- If the deformation of the blob during Kuhn segment rotation is $\Delta\varepsilon$ and the stress σ_{gla} is approximately constant then:

$$V_{rot}\sigma_{gla} = \frac{1}{\nu_c}\int_0^{\Delta\varepsilon}\sigma_{gla}\,d\varepsilon \approx \frac{\Delta\varepsilon}{\nu_c}\sigma_{gla}$$

- ν_c is the network density.

Stress and relaxation time

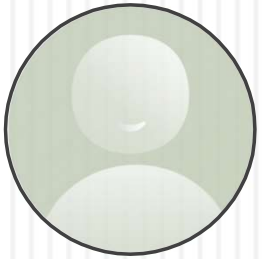


- The average number of rotations will increase.
- The average rotation time will decrease.
- Since rotations can occur in any direction the average must be determined by integration over all stresses from $-\sigma_{gla}$ to $+\sigma_{gla}$:

$$\theta_{rot} = \left[\frac{1}{\theta_{av}}\right]^{-1} = \left[\frac{1}{2V_{rot}\sigma_{gla}}\int_{-\sigma_{gla}}^{\sigma_{gla}}\frac{d\sigma}{\theta_{rot}(\sigma)}\right]^{-1} = \theta_{rot,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rot}\sigma_{gla}}{kT}\Big/\sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

- Net result: The glass stress relaxation time will strongly decrease with increasing stress.

Stress and relaxation time



- The rotation time decreases with stress:

$$\theta_{rot} = \theta_{rot,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rot}\sigma_{gla}}{kT} \Big/ \sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

- The reptation time is proportional to the rotation time:

$$\theta_{rep} = N_K^3 \theta_{rot}$$

- Therefor the reptation time also decreases with stress:

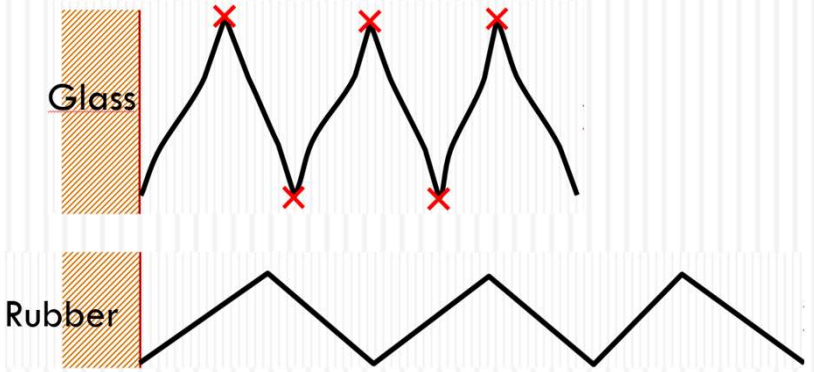
$$\theta_{rep} = \theta_{rep,0} \exp\left(\frac{E_{rot}}{kT}\right) \frac{V_{rep}\sigma_{rub}}{kT} \Big/ \sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)$$

- Net result: The rubber stress relaxation time will strongly decrease with increasing stress.

STRESS RELAXATION

Stress relaxation

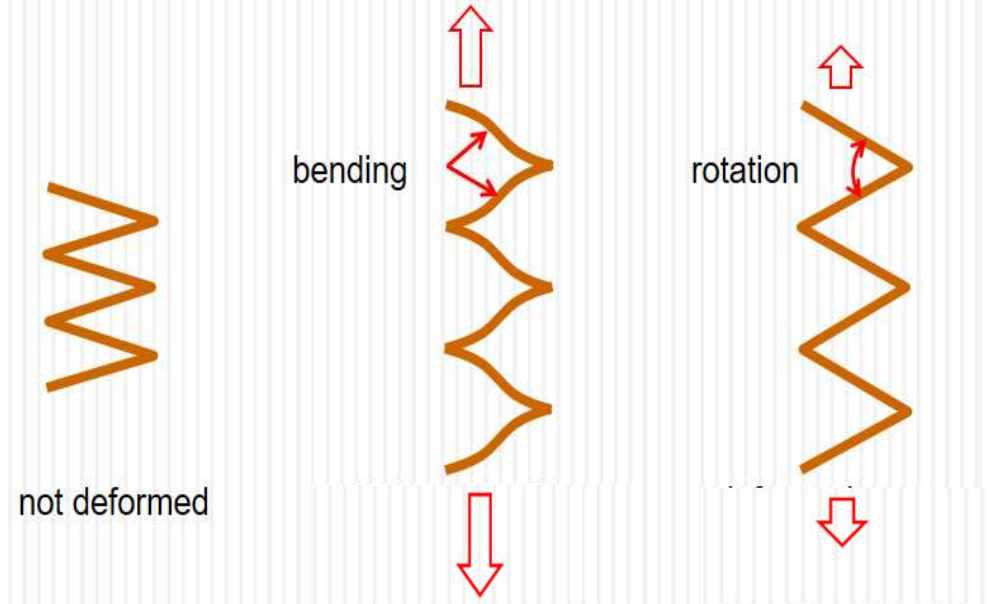
- The stress in a polymer is composed from two components:
  - Glass stress from deformation by segment bending.
  - Rubber stress from deformation by segment rotation.

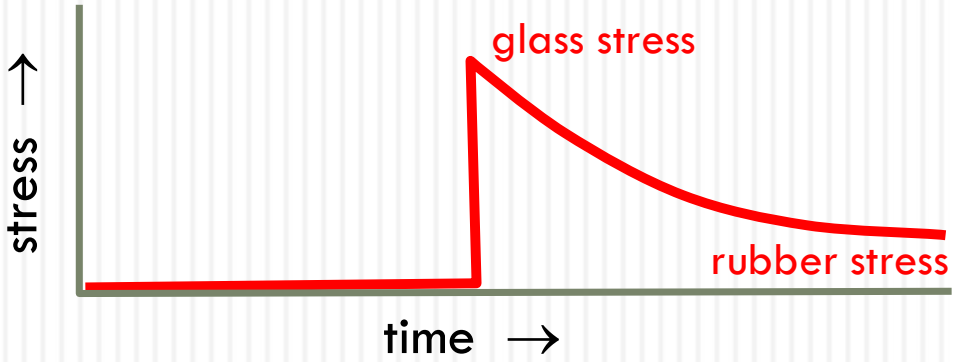


- Relaxation of stress is caused by rotation of chain segments and reptation of macromolecules.
  - Glass phase: relaxation by rotation is dominant.
  - Rubber and melt phase: relaxation by reptation is dominant.

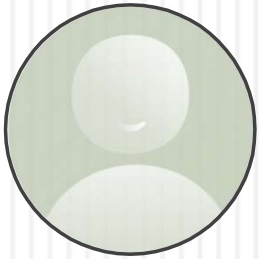
Glass stress relaxation

- Deformation of the polymer causes bending of the chain segments.
  - Rigid material; high glass stress.
- Rotation of the chain segments reduces the bending.
  - Glass stress reduces
  - Rubber stress increases (~ 1/1000 of glass stress)





Glass stress relaxation



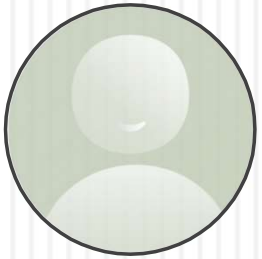
- Deformation of the polymer causes bending of the Kuhn segments.
  - Rigid material; high glass stress.
- Rotation of the Kuhn segments reduces the bending.
  - Deformation by bending is converted into deformation by rotation:

$$\varepsilon_{ben} + \varepsilon_{rot} = \text{constant} \rightarrow \mathrm{d}\varepsilon_{\mathrm{rot}} = -d\varepsilon_{ben}$$

  - Glass stress changes with change in deformation by bending.
  - Rubber stress is 1000 x lower than glass stress.
- The typical relaxation time is the Kuhn segment rotation time:

$$\theta_{gla} = \theta_{rot}$$

Glass stress relaxation



- Differential equation for relaxation below the glass transition temperature:

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

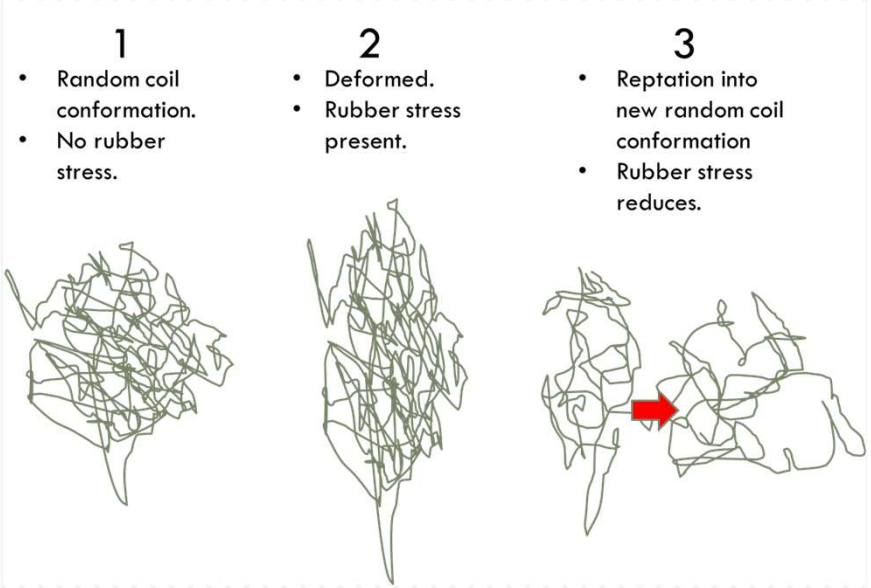
with

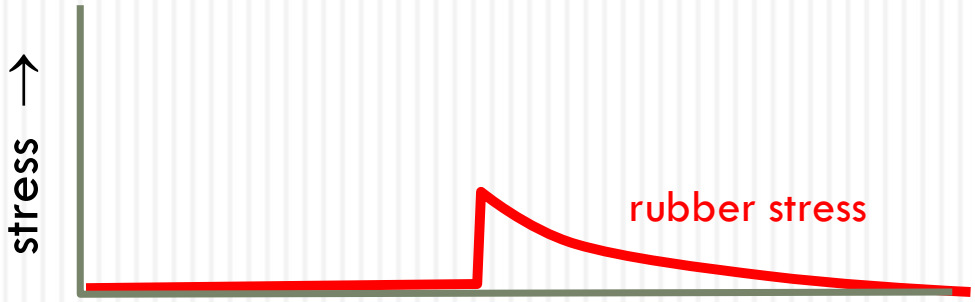
$$G_{gla} = \frac{d\sigma_{gla}}{d\varepsilon_{ben}}$$

$$\theta_{rot} = \theta_{rot,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rot}\sigma_{gla}}{kT}\Big/\sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

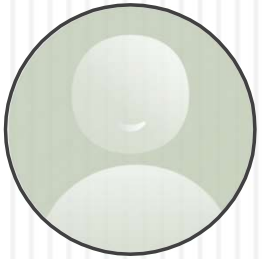
Rubber stress relaxation

- Deformation of the polymer causes rotation of the chain segments.
  - Macromolecules deformed; rubber stress.
- Reptation of the macromolecules into new positions reduces deformation.
  - Rubber stress reduces to zero





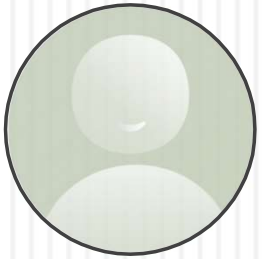
Rubber stress relaxation



- Deformation of the polymer causes rotation of the Kuhn segments.
  - Macromolecules deformed; rubber stress.
- Reptation of the macromolecules into new positions reduces deformation.
  - Elastic energy from deformation by rotation is converted into heat.
  - Rubber stress reduces to zero.
- The typical relaxation time is the reptation time:

$$\theta_{melt} = \theta_{rep}$$

Rubber stress relaxation



- Differential equation for relaxation above the glass transition temperature:

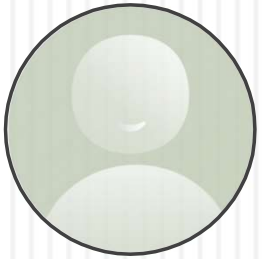
$$\frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

with

$$G_{rub} = \frac{d\sigma_{rub}}{d\varepsilon_{rot}}$$

$$\theta_{rep} = \frac{\theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\sigma_{rub}}{kT}}{\sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)}$$

Glass and rubber stress relaxation



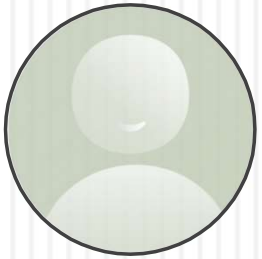
- Deformation of the polymer causes bending of the Kuhn segments → glass stress.
- Rotation of the Kuhn segments reduces the bending.
  - Deformation by bending is converted into deformation by rotation.
  - Glass stress reduces to rubber stress.
- Differential equation for relaxation of the glass stress:

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

Glass modulus

Deformation by bending is converted into deformation by rotation

Glass and rubber stress relaxation



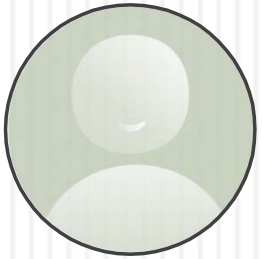
- Reptation of the macromolecules into new positions reduce deformation by rotation to zero.
  - Elastic energy from deformation by rotation is converted into heat.
  - Rubber stress reduces to zero.
- Differential equation for relaxation of the rubber stress:

$$\frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

Rubber modulus

Deformation by rotation disappears due to reptation

Glass and rubber stress relaxation



- Two relaxation times: θ_{rot} and θ_{rep}

$$\theta_{rep} = N_K^3 \theta_{rot}$$

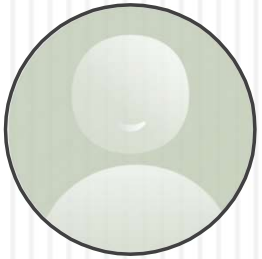
- Two coupled differential equations:

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

$$\frac{d\sigma_{rub}}{dt} = \frac{G_{rub}}{G_{gla}}\frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

Glass and rubber stress relaxation



- Two relaxation times: θ_{rot} and θ_{rep}

$$\theta_{rep} = N_K^3 \theta_{rot}$$

- Two coupled differential equations:

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

~~$$\frac{d\sigma_{rub}}{dt} = \frac{G_{rub}}{G_{gla}}\frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}}$$~~

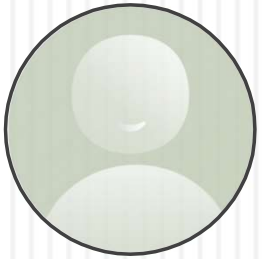
$\theta_{rep} = \infty \; and \; G_{rub} \ll G_{gla}$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

$\sigma_{rub} << \sigma_{gla}$

Glass phase

Glass and rubber stress relaxation



- Two relaxation times: θ_{rot} and θ_{rep}

$$\theta_{rep} = N_K^3 \theta_{rot}$$

- Two coupled differential equations:

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}} \quad = 0 \rightarrow \quad \frac{\sigma_{gla}}{\theta_{rot}} = G_{gla}\frac{d\varepsilon}{dt}$$

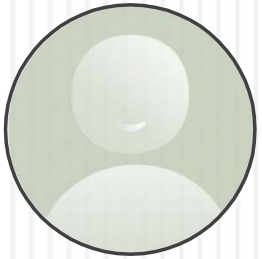
$$\frac{d\sigma_{rub}}{dt} = \frac{G_{rub}}{G_{gla}}\frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

Melt phase

Stress relaxation small deformations

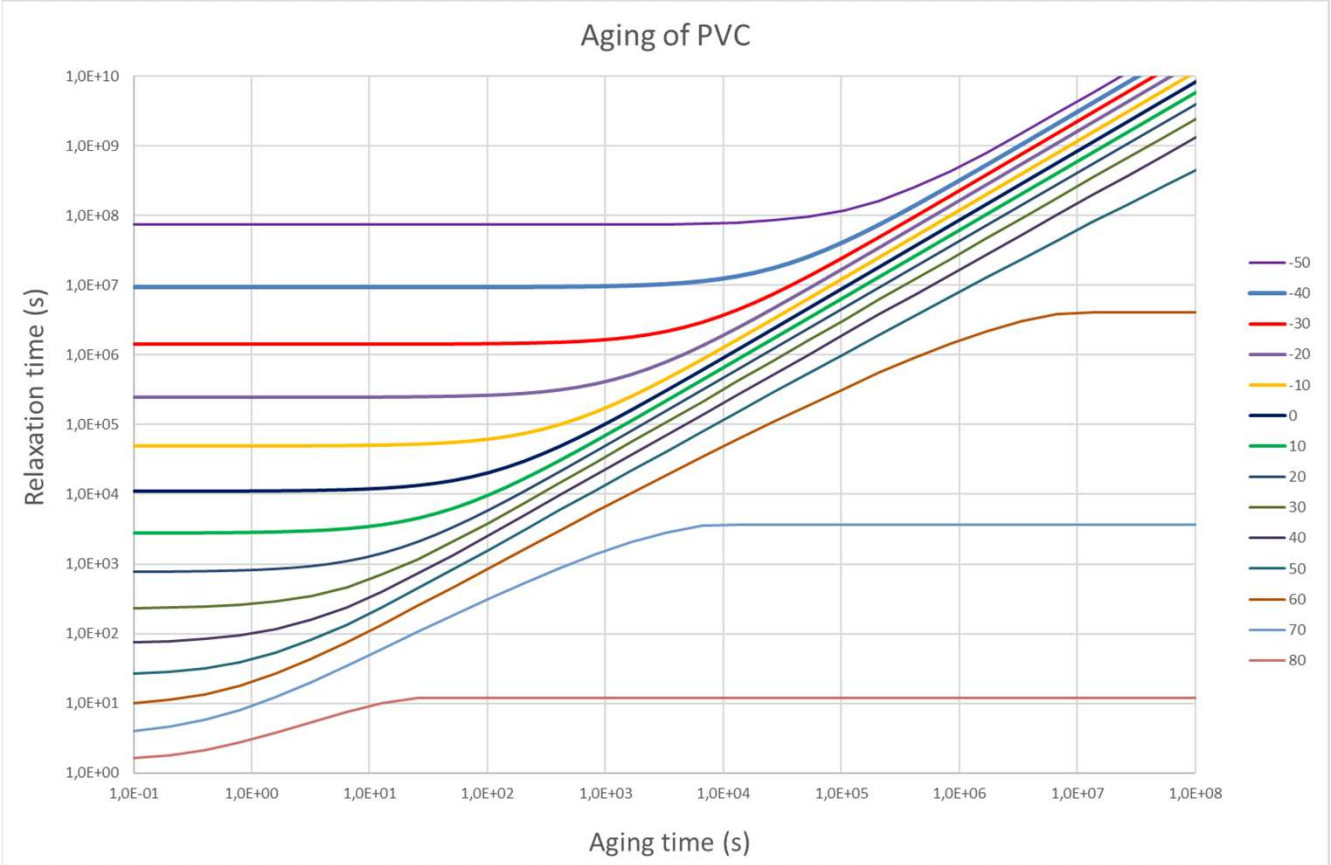


- In case of small deformations the moduli $d\sigma_{gla}/d\varepsilon_{ben}$ and $d\sigma_{rub}/d\varepsilon_{rot}$ are independent of strain.
- The differential equations then reduce to:

$$\frac{d\varepsilon_{ben}}{dt} = \frac{d\varepsilon}{dt} - \frac{\varepsilon_{ben}}{\theta_{rot}}$$

$$\frac{d\varepsilon_{rot}}{dt} = \frac{\varepsilon_{ben}}{\theta_{rot}} - \frac{\varepsilon_{rot}}{\theta_{rep}}$$

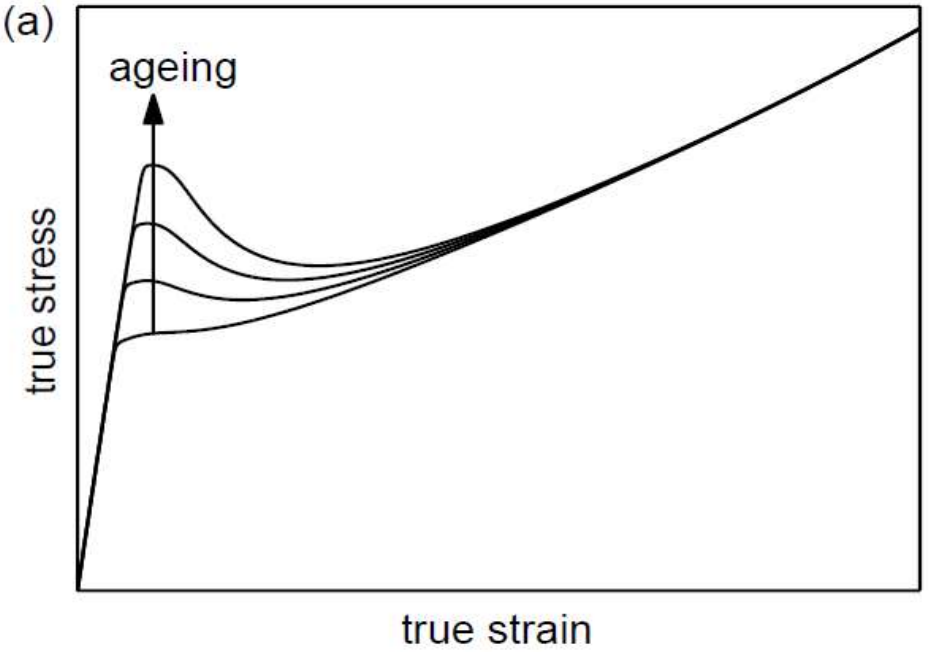
Deformation by bending is converted into deformation by rotation.



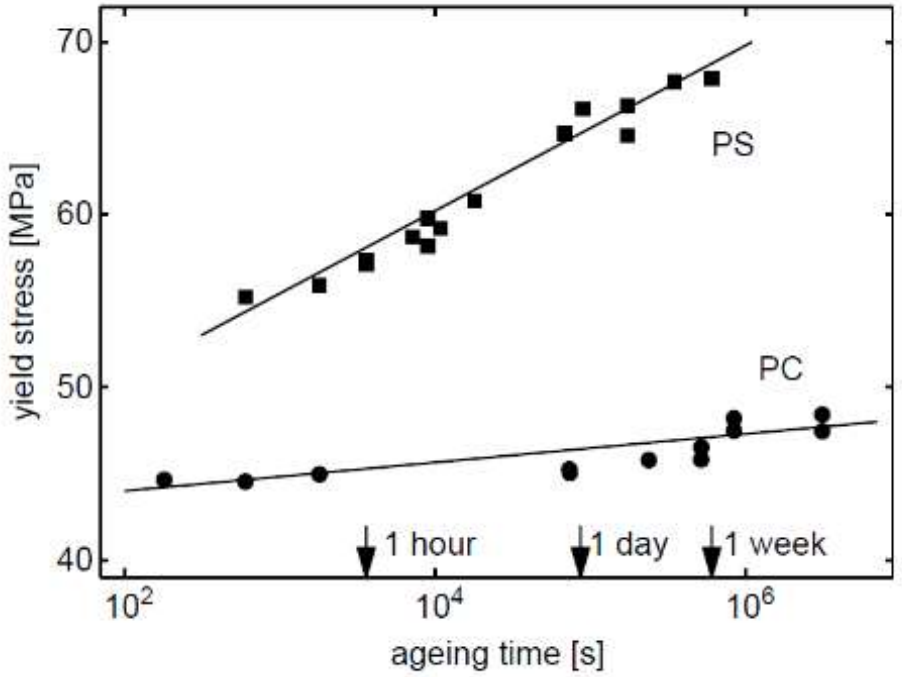
PHYSICAL AGING

Tensile strength and aging

Stress – strain diagram changes with time

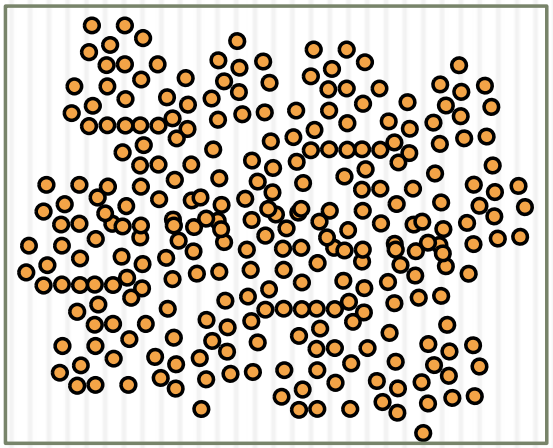


Yield strength changes with time



Mechanism of physical aging

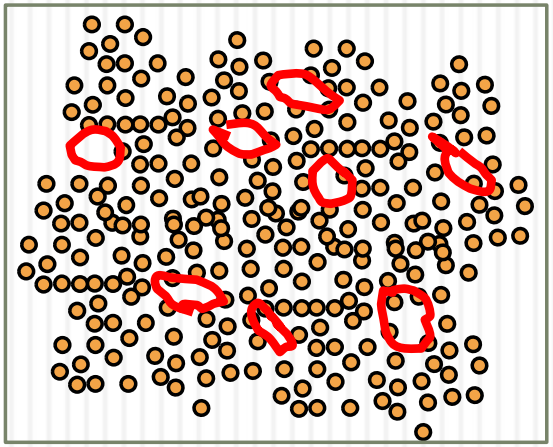
- After processing the polymer is cooled down to below the glass transition temperature.
- The mobility of the polymer molecules is now very low.
- The physical structure of the polymer corresponds to that of a polymer at a higher temperature.



Mechanism of physical aging

Result:

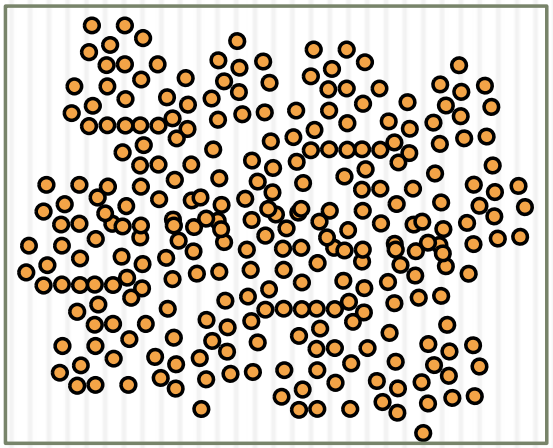
- Lots of free volume in between the molecules.



Mechanism of physical aging

Result:

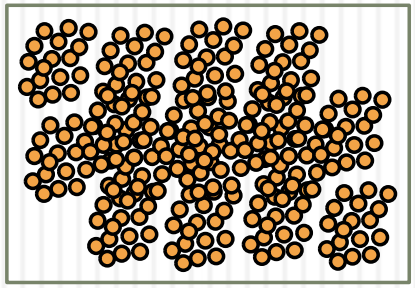
- Lots of free volume in between the molecules.
- Segments of the macromolecules will slowly cluster together.
- The cooperatively rearranging regions will grow.
- The free volume reduces with time.



Mechanism of physical aging

Result:

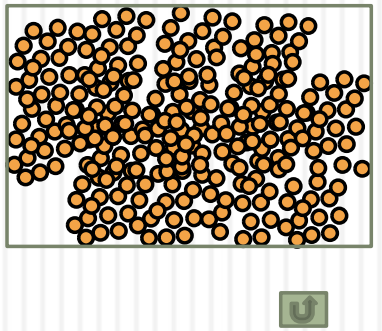
- Lots of free volume in between the molecules.
- Segments of the macromolecules will slowly cluster together.
- The cooperatively rearranging regions will grow.
- The free volume reduces with time.



Mechanism of physical aging

Result:

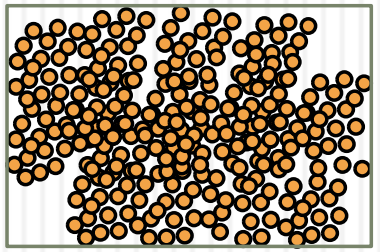
- Lots of free volume in between the molecules.
- Segments of the macromolecules will slowly cluster together.
- The cooperatively rearranging regions will grow.
- The free volume reduces with time.

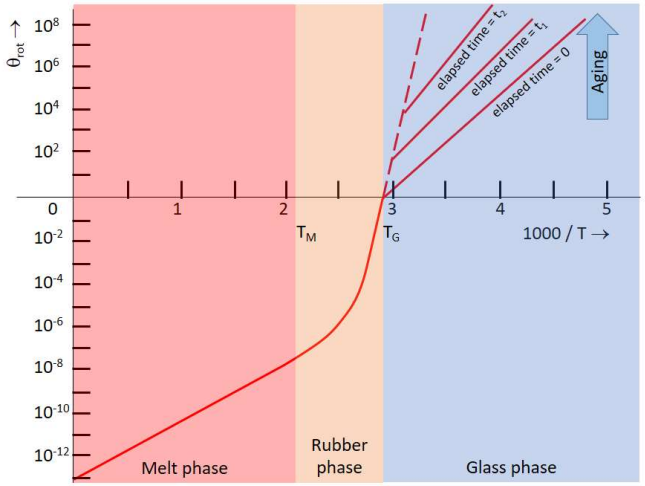


Mechanism of physical aging

Result:

- The molecular mobility reduces.
- The segmental rotation time (θ_{rot}) increases with time.
- The continuous reduction of the molecular mobility causes aging to become a self-retarding process.





Mechanism of physical aging

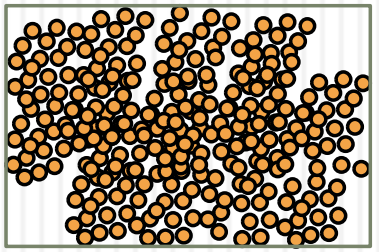
Result:

- Aging stops when the size of the clusters has grown to the equilibrium value that corresponds to the current temperature.

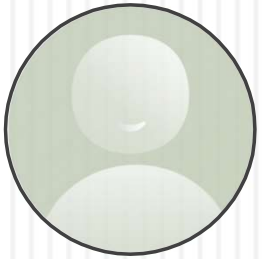
Mechanism of physical aging

Result:

- Polymer properties will change during aging on the same time scale.
  - Density increases.
  - Tensile strength increases.
  - Stiffness increases.
  - Brittleness increases.



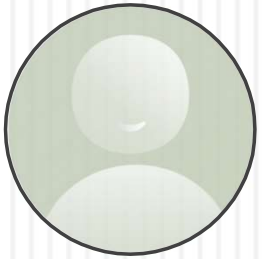
Mathematical description 1



Physical aging occurs when a polymer is quickly cooled from the melt to a temperature below the glass transition temperature.

- In the glass phase, the segmental rotation time immediately increases to very high levels ($\theta_{rot} >> 1$ s).
- During aging the segmental rotation time increases due to the growing clusters (CRR's).
- Aging progresses with the same speed as the segmental rotation time. Therefore $\theta_{aging} = \theta_{rot}$.

Mathematical description 2



- During aging the cooperatively rearranging regions will slowly grow until equilibrium has been reached:

$$\frac{dz}{dt} = \frac{z_\infty - z}{\theta_{rot}} \text{ with } \theta_{rot} = \theta_0 exp\left(\frac{E_0 z}{kT}\right)$$

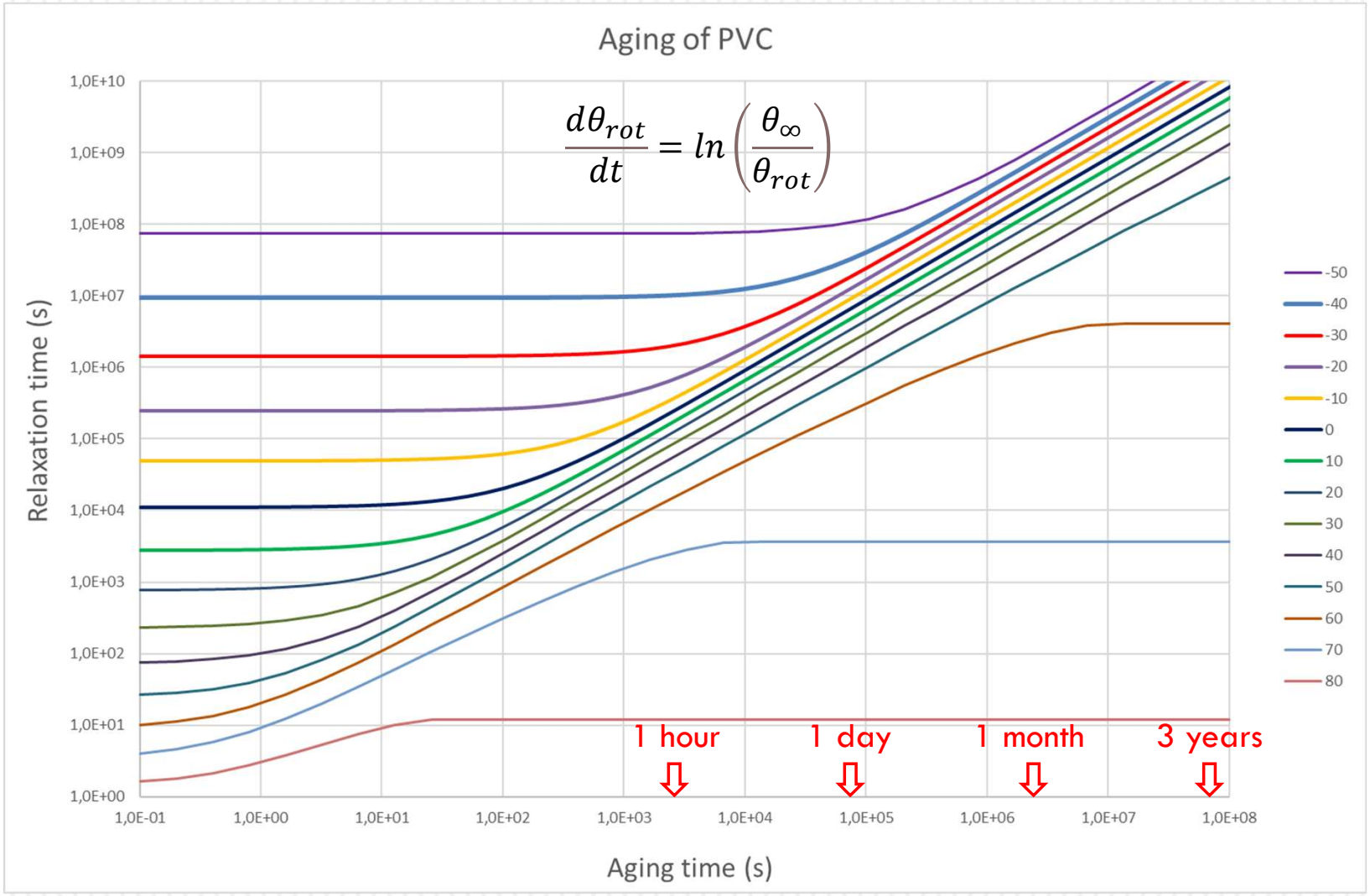
- The relaxation time will change according to:

$$\frac{d\theta_{rot}}{dt} = \frac{d\theta_{rot}}{dE_{rot}} \frac{dE_{rot}}{dz} \frac{dz}{dt} = \frac{E_0}{kT}(z_\infty - z)$$

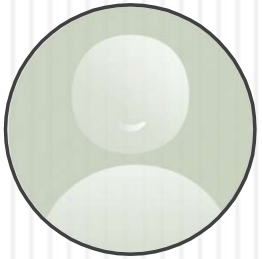
- Which leads to:

$$\frac{d\theta_{rot}}{dt} = ln\left(\frac{\theta_\infty}{\theta_{rot}}\right)$$

Time scale of physical aging

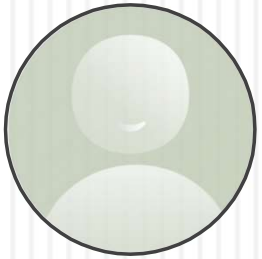


Time scale of physical aging

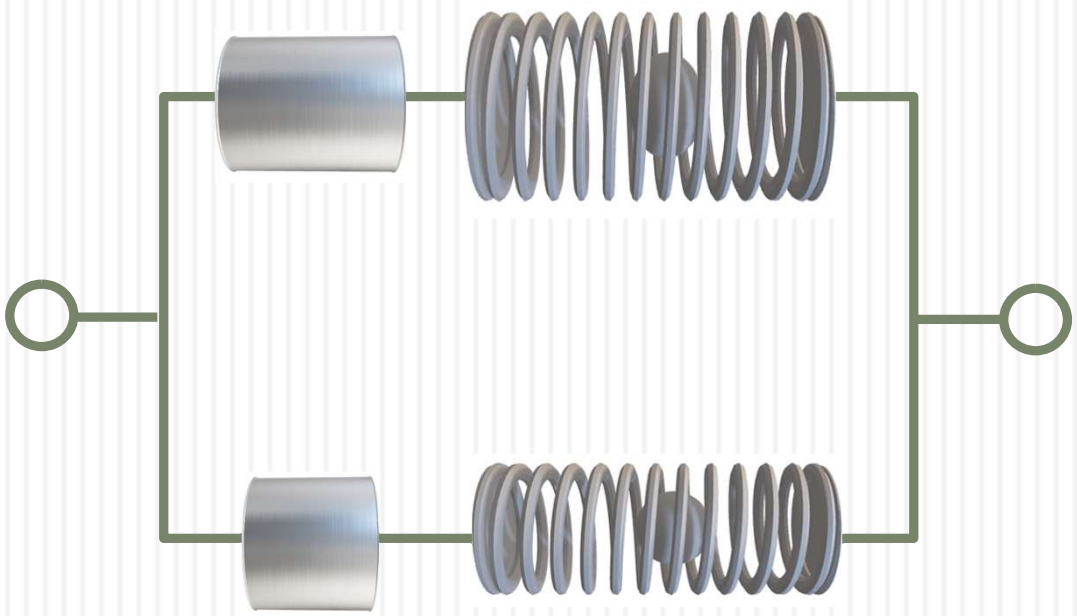


- During physical aging the segmental rotation time increases linearly with time during many decades.
- At temperatures of 30 K or more below the glass transition temperature reaching equilibrium takes a very long time.
- Physical aging is negligeable close to and above the glass transition temperature.

Physical aging - summary

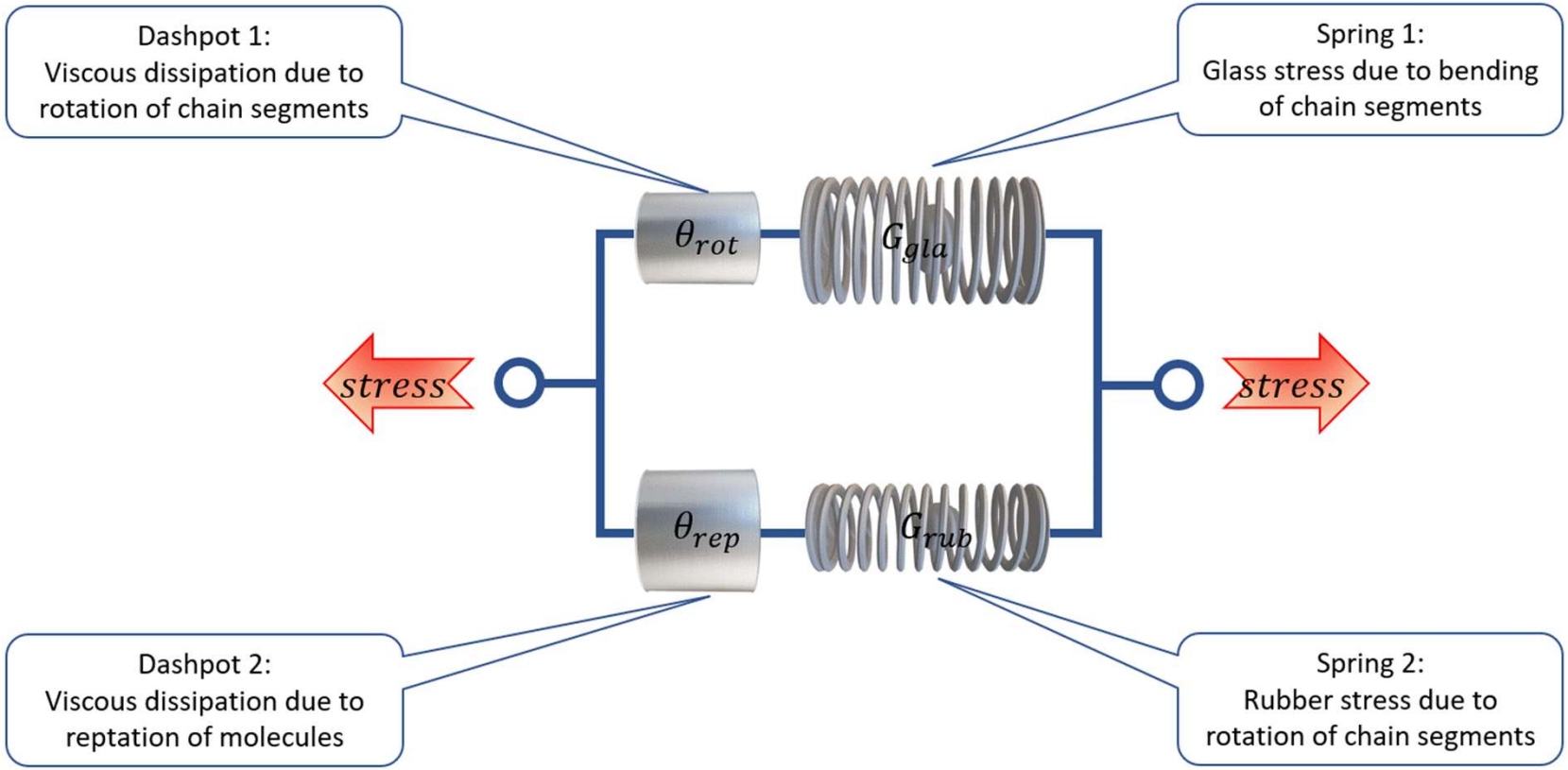


- Physical aging is the process of the polymer molecules slowly adapting their conformation to a new temperature below the glass transition temperature.
- During aging the volume of the polymer reduces, which slows-down the mobility of the polymer molecules. Therefore, aging is a self-retarding process.
- Aging influences important product properties. The tensile strength, the stiffness and the brittleness increase with time, the impact strength reduces with time

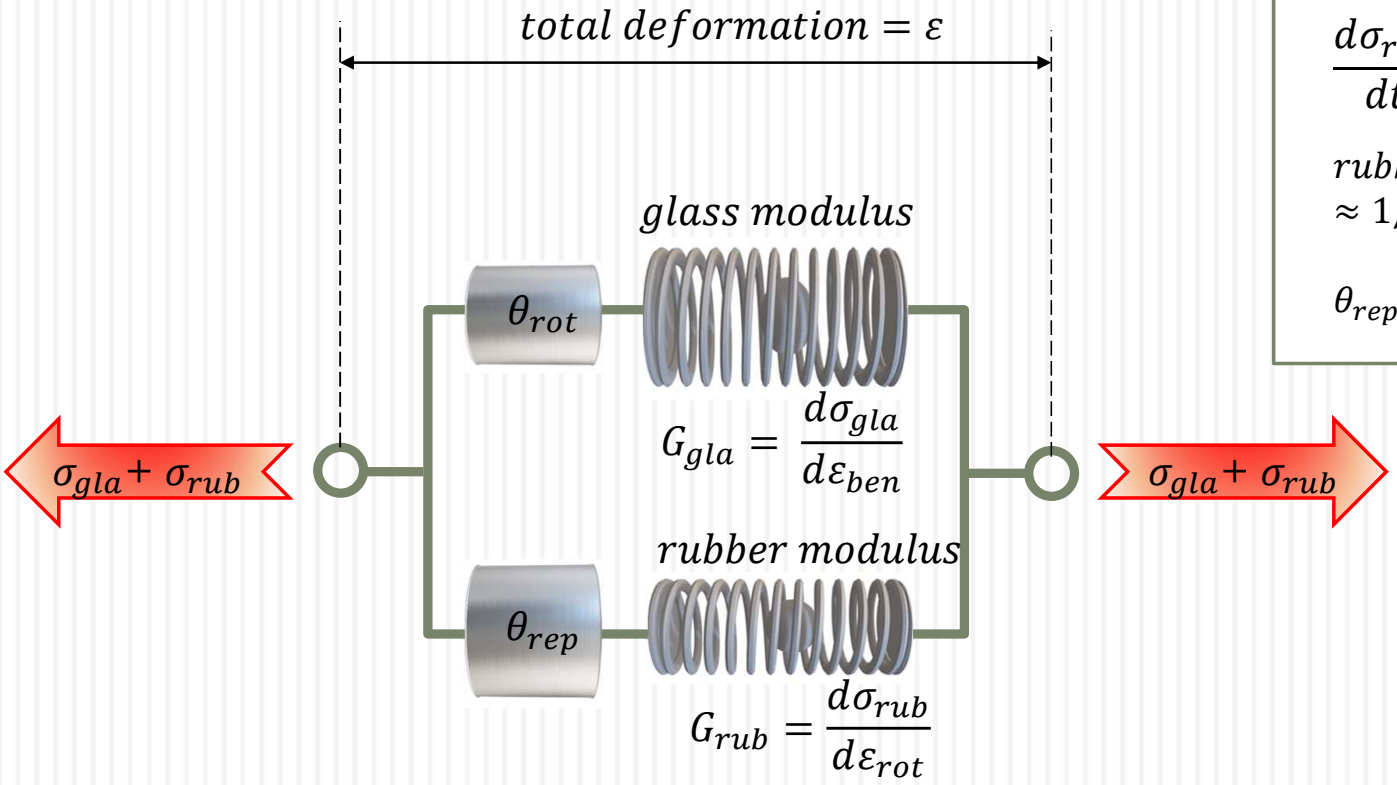


MECHANICAL ANALOGUE FOR STRESS IN POLYMERS

Mechanical analogue for stress in polymers



Mechanical analogue for stress in polymers



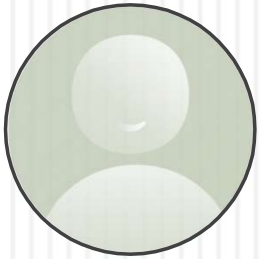
$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

$$\frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

rubber modulus $\approx 1/1000$ *glass modulus*

$\theta_{rep} \approx 10^6 \theta_{rot}$

Mechanical analogue for stress in polymers



- Effects of temperature, stress and aging follow from the chain segment rotation time and the molecular reptation time.
- The model with dashpots and springs provides no molecular basis for the viscoelastic response.
  - Only useful for investigating the macroscopic behavior of the polymer.

Mechanical analogue for stress in polymers

Molecular model

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

$$\frac{d\sigma_{rub}}{dt} = \frac{G_{rub}}{G_{gla}}\frac{\sigma_{gla}}{\theta_{rot}} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

$rubber\ modulus \approx 1/1000\ glass\ modulus$

$$\theta_{rep} \approx 10^6 \theta_{rot}$$

Mechanical analogue

$$\frac{d\sigma_{gla}}{dt} = G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

$$\frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\sigma = \sigma_{gla} + \sigma_{rub}$$

$rubber\ modulus \approx 1/1000\ glass\ modulus$

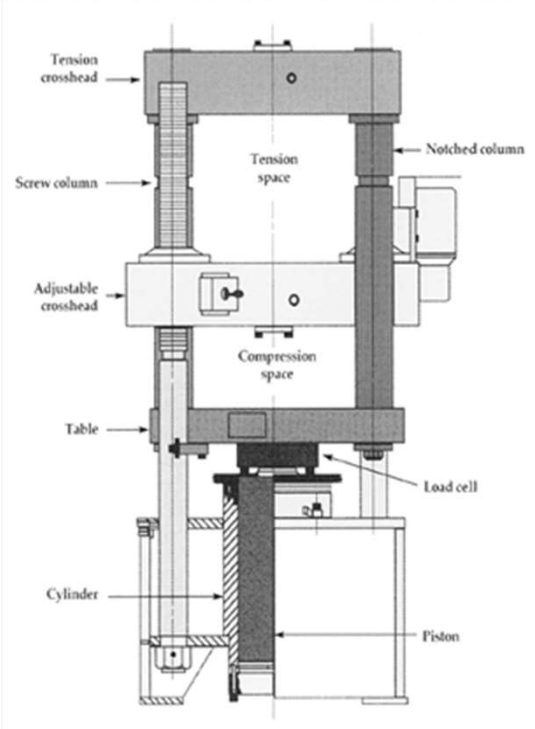
$$\theta_{rep} \approx 10^6 \theta_{rot}$$

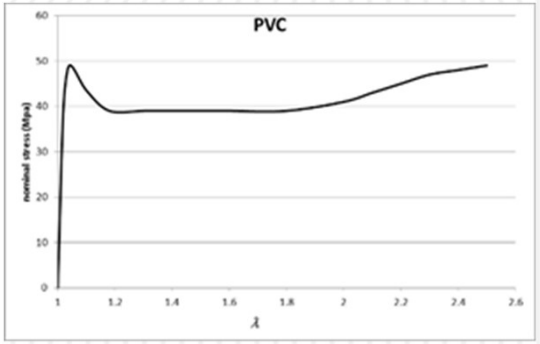
The result is almost the same!

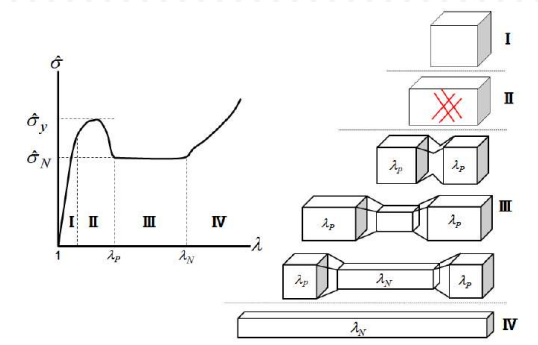
Error ~ 0.1 %

YIELD STRESS

Yield stress

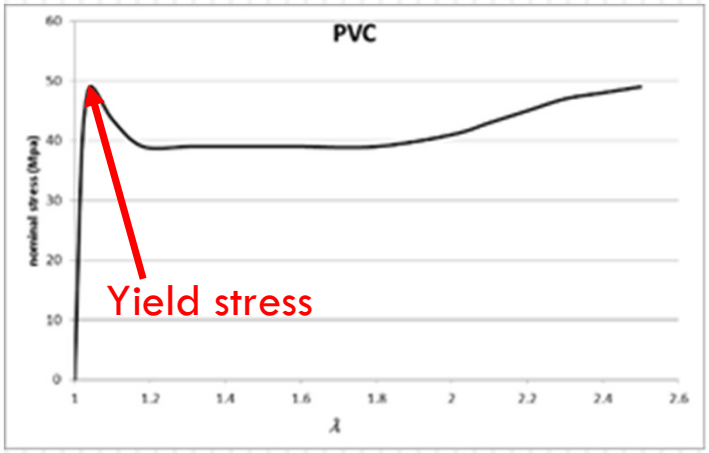


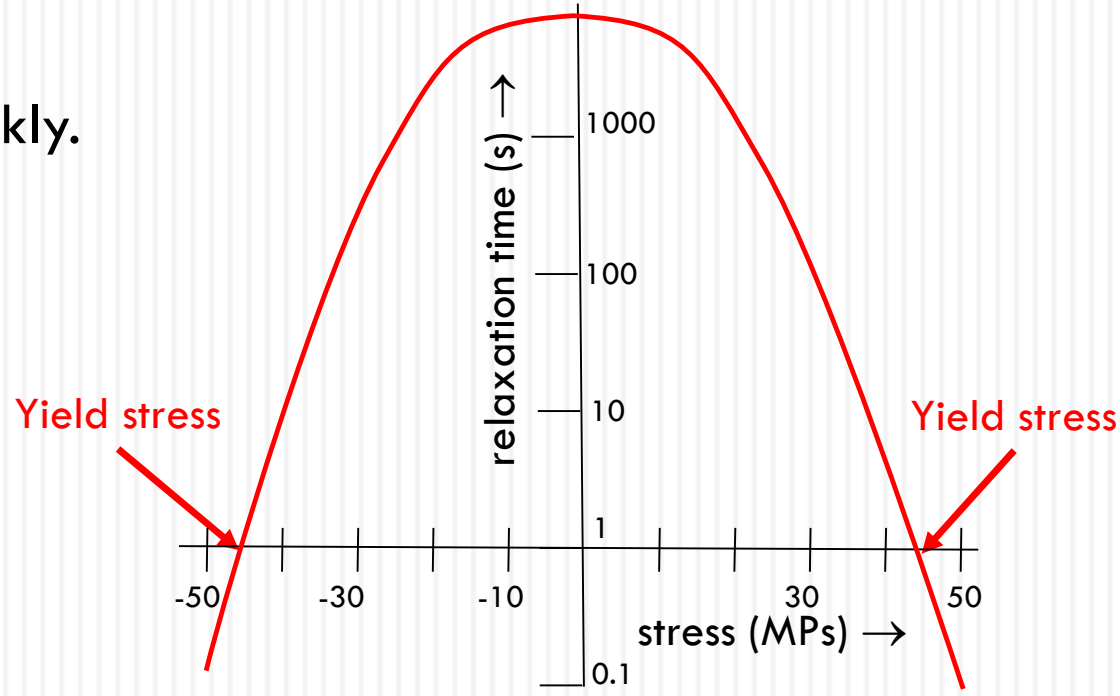




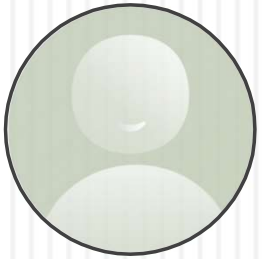
Yield stress

- In the glass phase the rotation time of the chain segments is very long.
- The rotation time strongly reduces with stress.
- At a certain stress the rotation time has reduced to1second.
  - The yield stress has been reached
  - The polymer starts to deform quickly.





Yield stress



- The yield stress is determined in the glass phase.
- Equations to use:

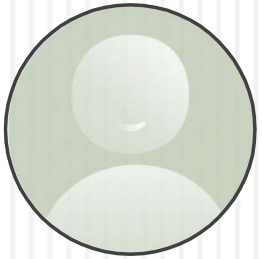
$$\frac{d\sigma_{gla}}{dt} = \frac{d\sigma_{gla}}{d\varepsilon_{ben}}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

$$\theta_{rot} = \theta_{rot,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rot}\sigma_{gla}}{kT}\Big/\sinh\left(\frac{V_{rot}\sigma_{gla}}{kT}\right)$$

- Uniaxial elongation:

$$\frac{d\sigma_{gla}}{d\varepsilon_{ben}} = 3G_{gla} \Longrightarrow \frac{d\sigma_{gla}}{dt} = 3G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_{gla}}{\theta_{rot}}$$

Yield stress



- At yield the stress is constant ($\sigma_{gla} = \sigma_y$):

$$\frac{d\sigma_y}{dt} = 0 = 3G_{gla}\frac{d\varepsilon}{dt} - \frac{\sigma_y}{\theta_{rot}} \quad \Longrightarrow \quad \sigma_y = 3G_{gla}\theta_{rot}\frac{d\varepsilon}{dt}$$

$$\theta_{rot} = \theta_{rot,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rot}\sigma_y}{kT}\Big/\sinh\left(\frac{V_{rot}\sigma_y}{kT}\right) \quad \Longrightarrow$$

- Resulting yield stress:

$$\sigma_y = \frac{kT}{V_{rot}}\sinh^{-1}\left(\frac{3G_{gla}V_{rot}}{kT}\exp\left(\frac{E_{rot}}{kT}\right)\theta_{rot,0}\frac{d\varepsilon}{dt}\right)$$

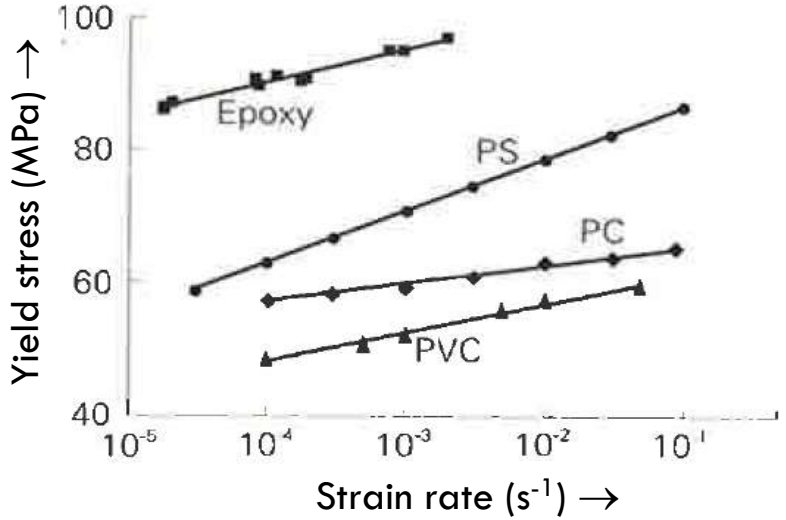
$$\sigma_y \approx \frac{E_{rot}}{V_{rot}} + \frac{kT}{V_{rot}}\ln\left(\frac{6G_{gla}V_{rot}}{kT}\right) + \frac{kT}{V_{rot}}\ln\left(\theta_{rot,0}\frac{d\varepsilon}{dt}\right)$$

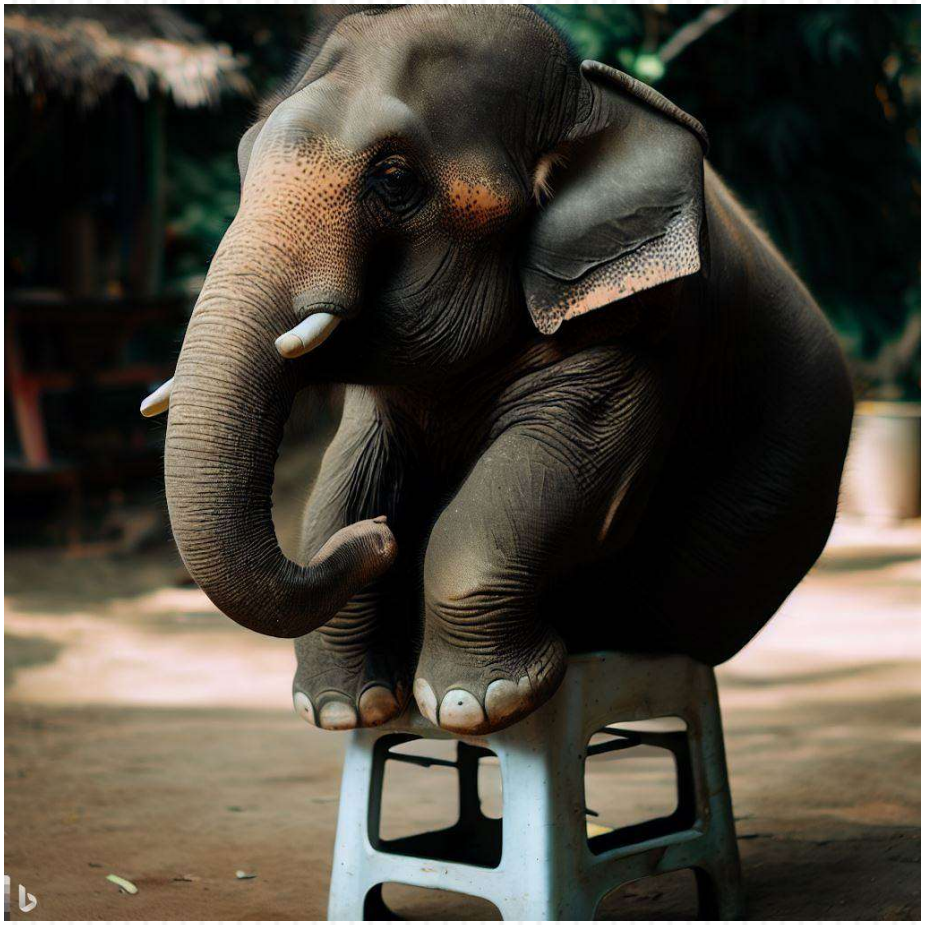
Yield stress

- Resulting yield stress:

$$\sigma_y = \frac{kT}{V_{rot}} \sinh^{-1}\left(\frac{3G_{gla}V_{rot}}{kT} \exp\left(\frac{E_{rot}}{kT} \right) \theta_{rot,0} \frac{d\varepsilon}{dt} \right)$$

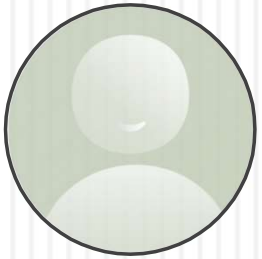
$$\sigma_y \approx \frac{E_{rot}}{V_{rot}} + \frac{kT}{V_{rot}} \ln\left(\frac{6G_{gla}V_{rot}}{kT} \right) + \frac{kT}{V_{rot}} \ln\left(\theta_{rot,0} \frac{d\varepsilon}{dt} \right)$$



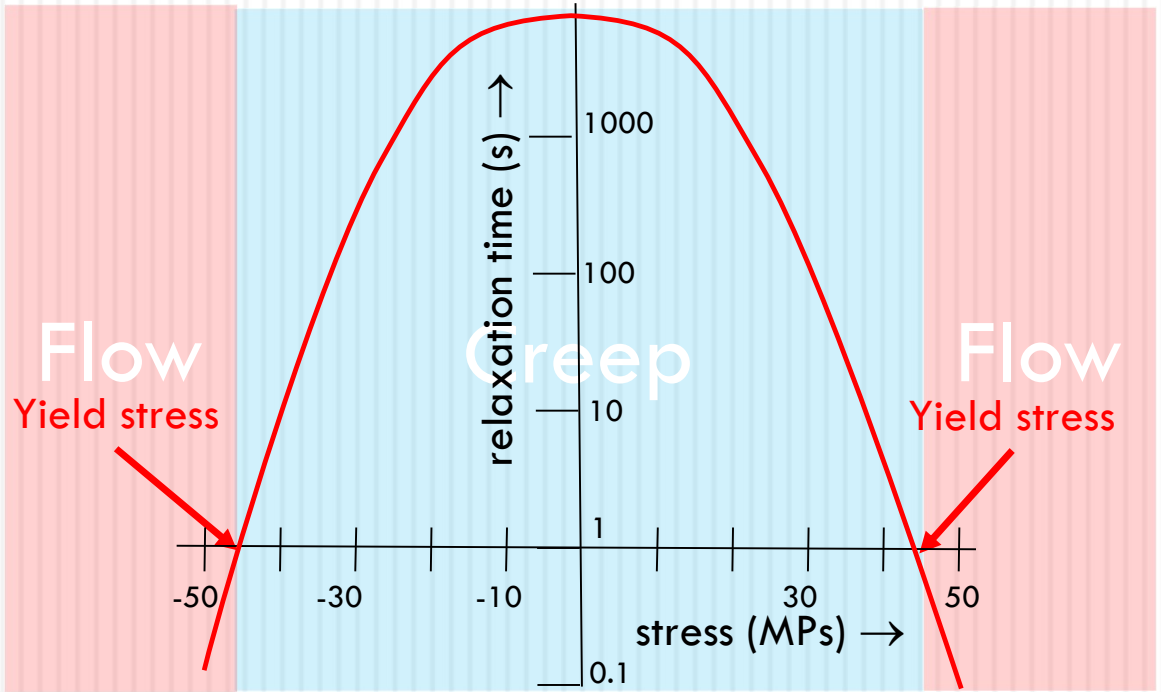


BEHAVIOR UNDER CONSTANT LOAD

Creep or flow

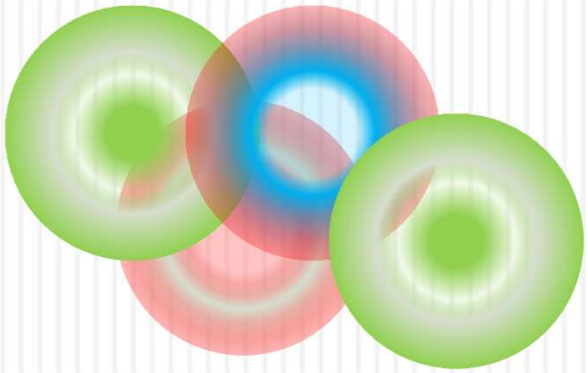


- High stress → relaxation time << 1 second → quick deformation = flow
- Low stress → relaxation time >> 1 second → slow deformation = creep



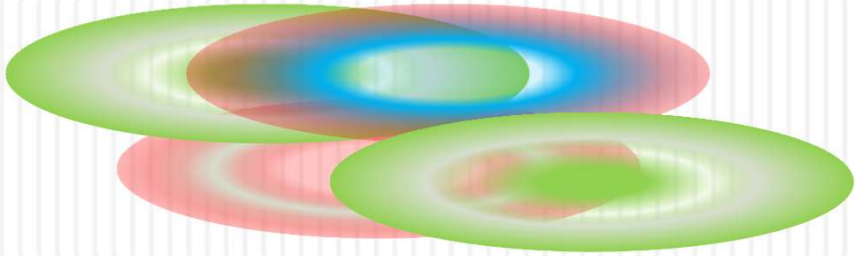
Creep and recovery

- Creep is a common feature of many materials. Examples are basalt, ice, window glass, metals and plastics.
- The deformation of a polymer body during creep or flow is mainly caused by deformation of the polymer molecules due to chain segment rotation.
- No flow!



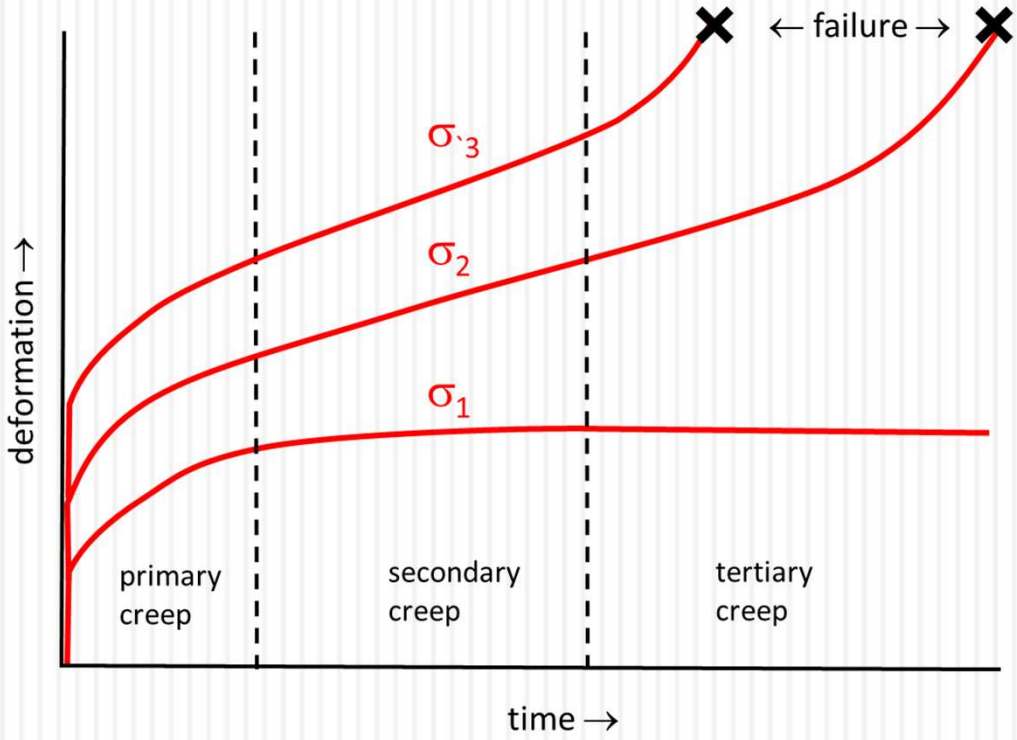
Creep and recovery

- Creep is a common feature of many materials. Examples are basalt, ice, window glass, metals and plastics.
- The deformation of a polymer body during creep or flow is mainly caused by deformation of the polymer molecules due to chain segment rotation.
- No flow!



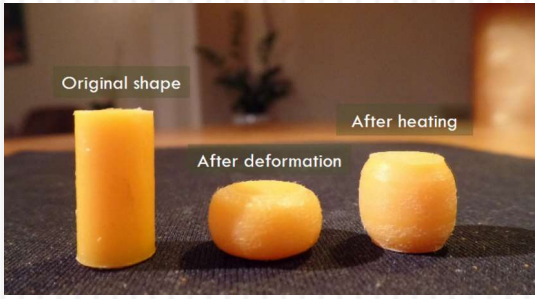
Creep and recovery

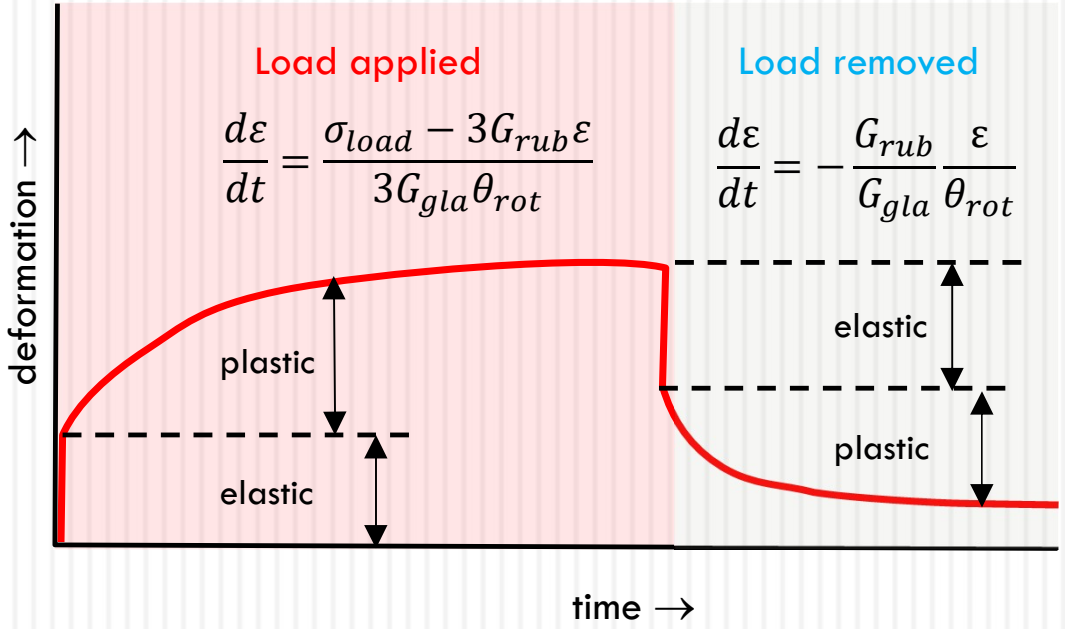
- The speed of deformation during creep strongly increases with the temperature and the level of the load.
- Failure due to creep occurs as soon as the plastic deformation exceeds the elongation at yield.



Creep and recovery

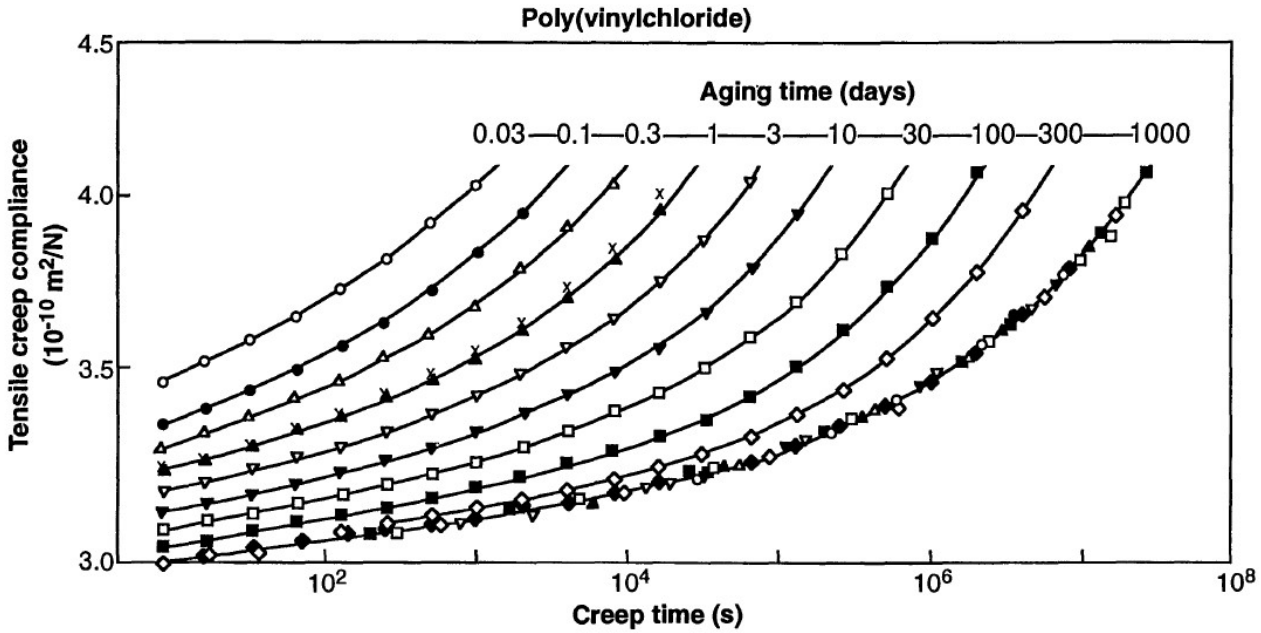
- After removing the load, the dimensions of the plastic body are not fully recovered.
  - The rubber stress is the driving force for recovery.
  - Full recovery will take a very long time due to the low rubber stress.



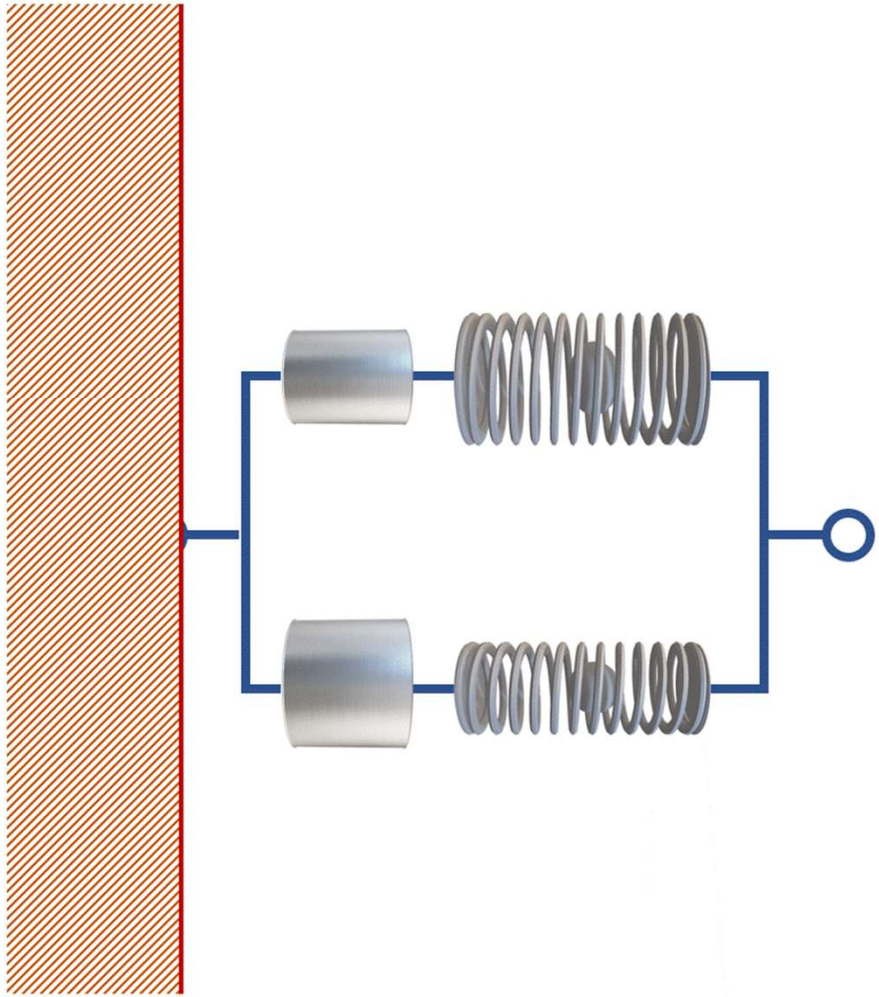


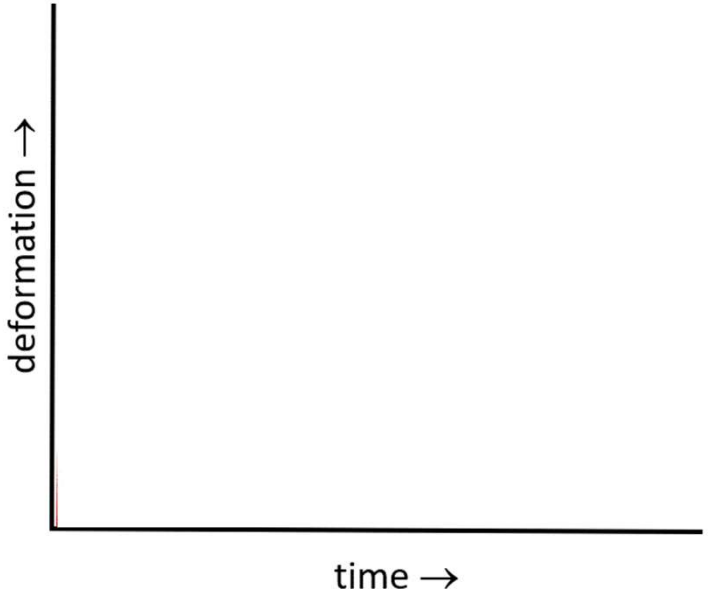
Creep and physical aging

- Creep is a slow process; it will be influenced by physical aging.
- Due to aging the speed of creep reduces inversely proportional with the elapsed time.
  1. The speed of creep is inversely proportional with the segmental rotation time.
  2. Aging causes the segmental rotation time to increase linearly with the elapsed time.



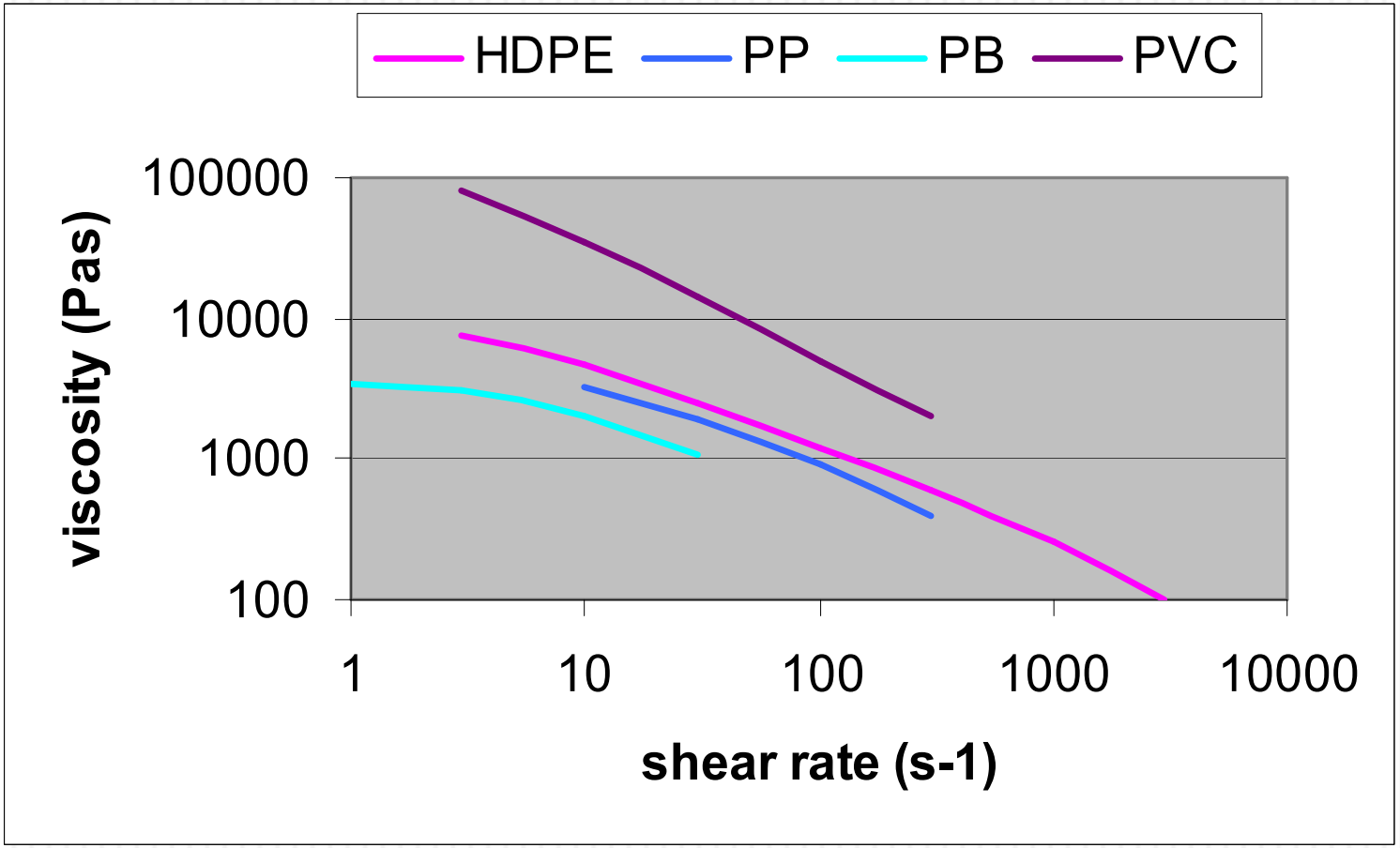
Creep



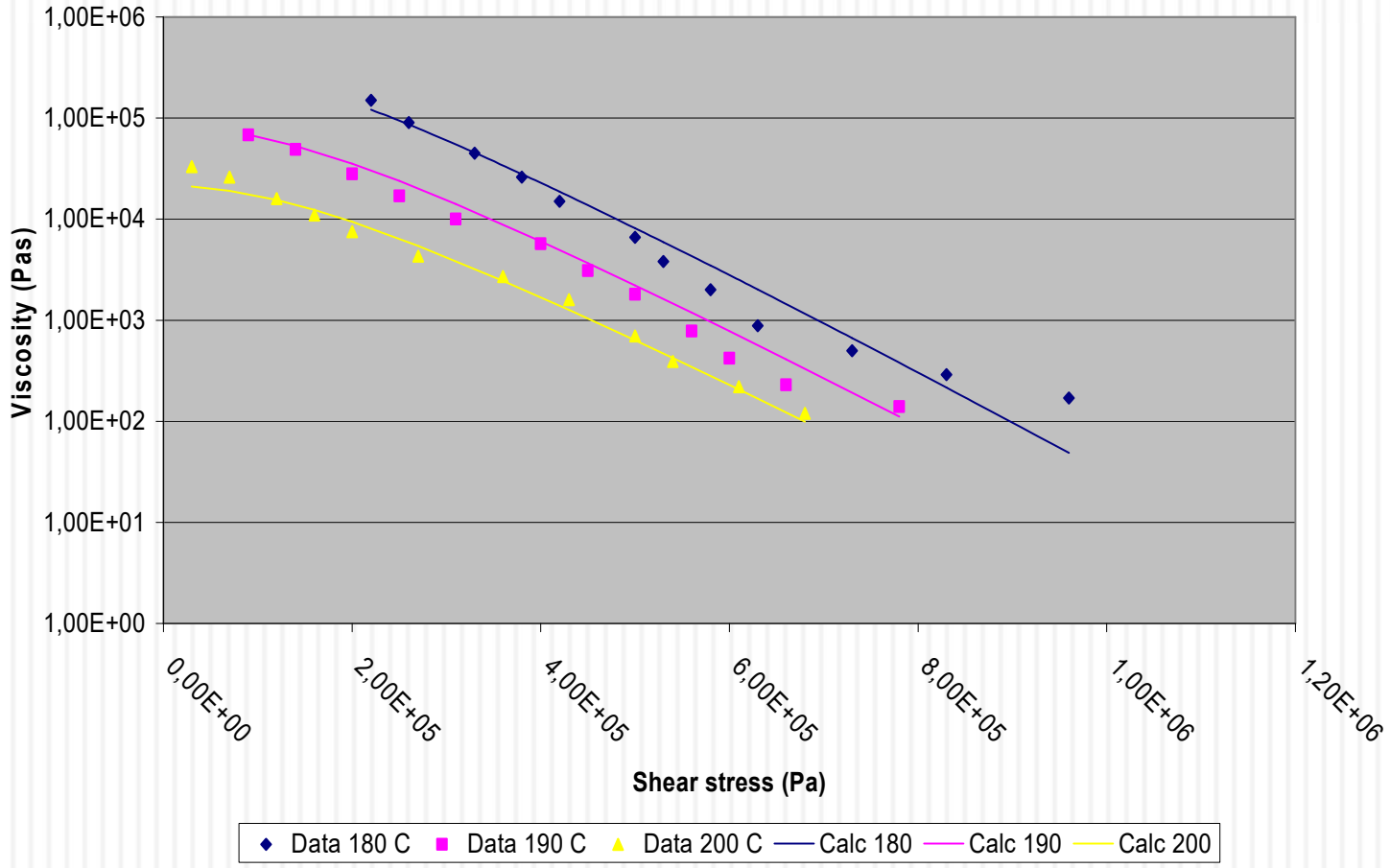


VISCOSITY

Viscosity of several polymers

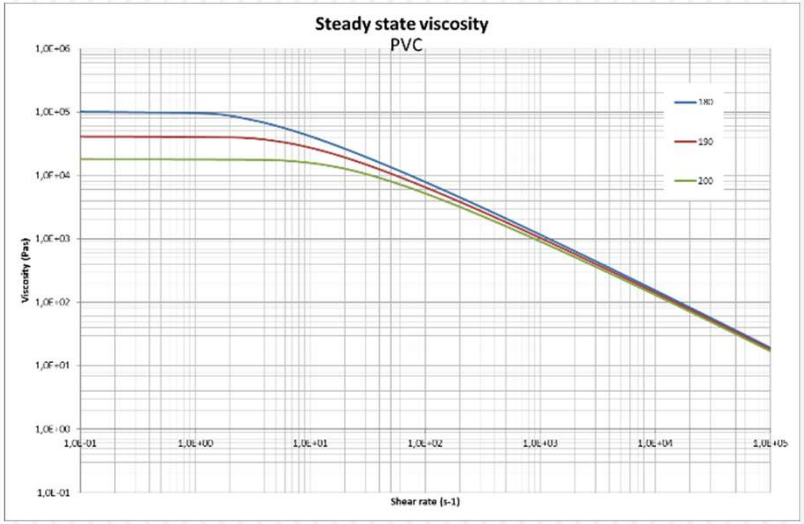


Viscosity of PVC

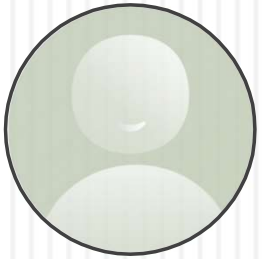


Reduction of viscosity

- With increasing stress the reptation time of the polymer molecules reduces.
- The viscosity is the product of rubber shear modulus and reptation time: $\eta = G_{rub}\theta_{rep}$
- The viscosity will reduce with stress because the reptation time reduces with stress.
- High stress = high shear rate:
- The viscosity will reduce with shear rate.



Viscosity



- The viscosity is determined in the melt phase.
- Equations to use:

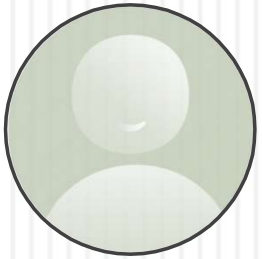
$$\frac{d\sigma_{rub}}{dt} = \frac{d\sigma_{rub}}{d\varepsilon_{rot}}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

$$\theta_{rep} = \theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\sigma_{rub}}{kT}\Big/\sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right)$$

- Shear deformation:

$$\frac{d\sigma_{rub}}{d\varepsilon_{rot}} = G_{rub} \quad \Longrightarrow \quad \frac{d\sigma_{rub}}{dt} = G_{rub}\frac{d\varepsilon}{dt} - \frac{\sigma_{rub}}{\theta_{rep}}$$

Viscosity



- During shear rate $d\gamma/dt$ stress is constant ($\sigma_{rub} = \tau$):

$$\frac{d\tau}{dt} = 0 = G_{rub}\frac{d\gamma}{dt} - \frac{\tau}{\theta_{rep}} \quad \Longrightarrow \quad \tau = G_{rub}\theta_{rep}\frac{d\gamma}{dt}$$

$$\theta_{rep} = \theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\sigma_{rub}}{kT}\Big/\sinh\left(\frac{V_{rep}\sigma_{rub}}{kT}\right) \quad \Longrightarrow$$

- Resulting viscosity:

$$\eta = G_{rub}\theta_{rep}$$

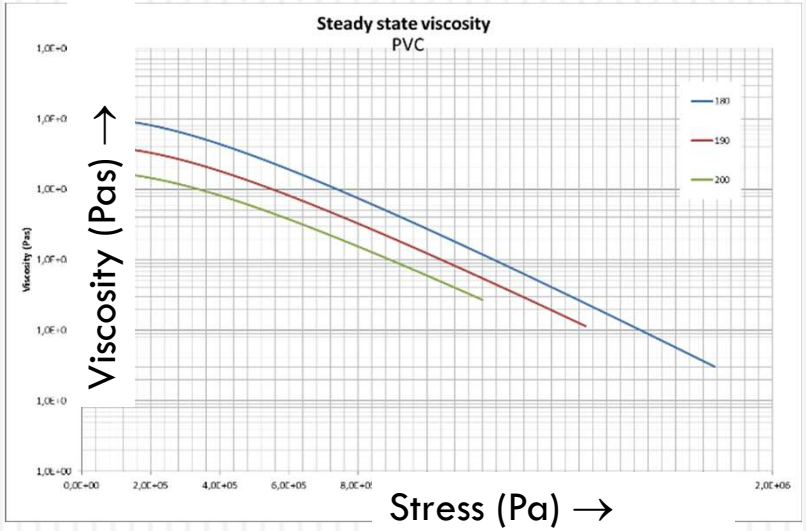
$$\eta = G_{rub}\theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\tau}{kT}\Big/\sinh\left(\frac{V_{rep}\tau}{kT}\right)$$

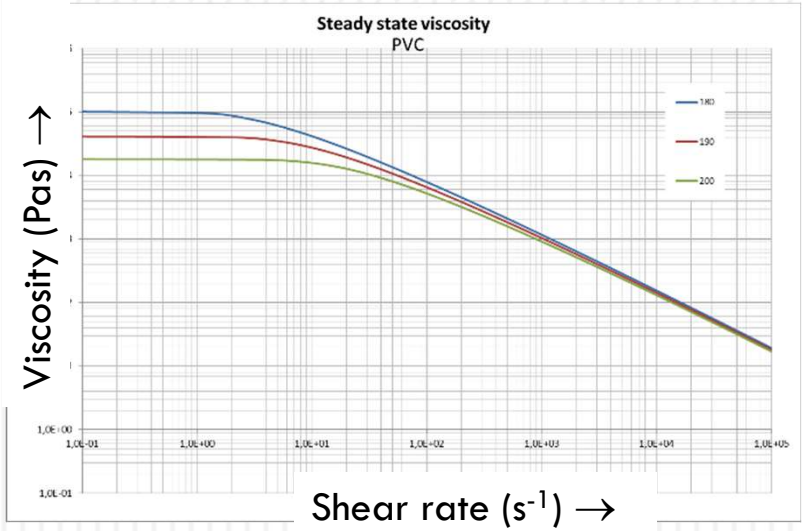
Viscosity

- Resulting viscosity:

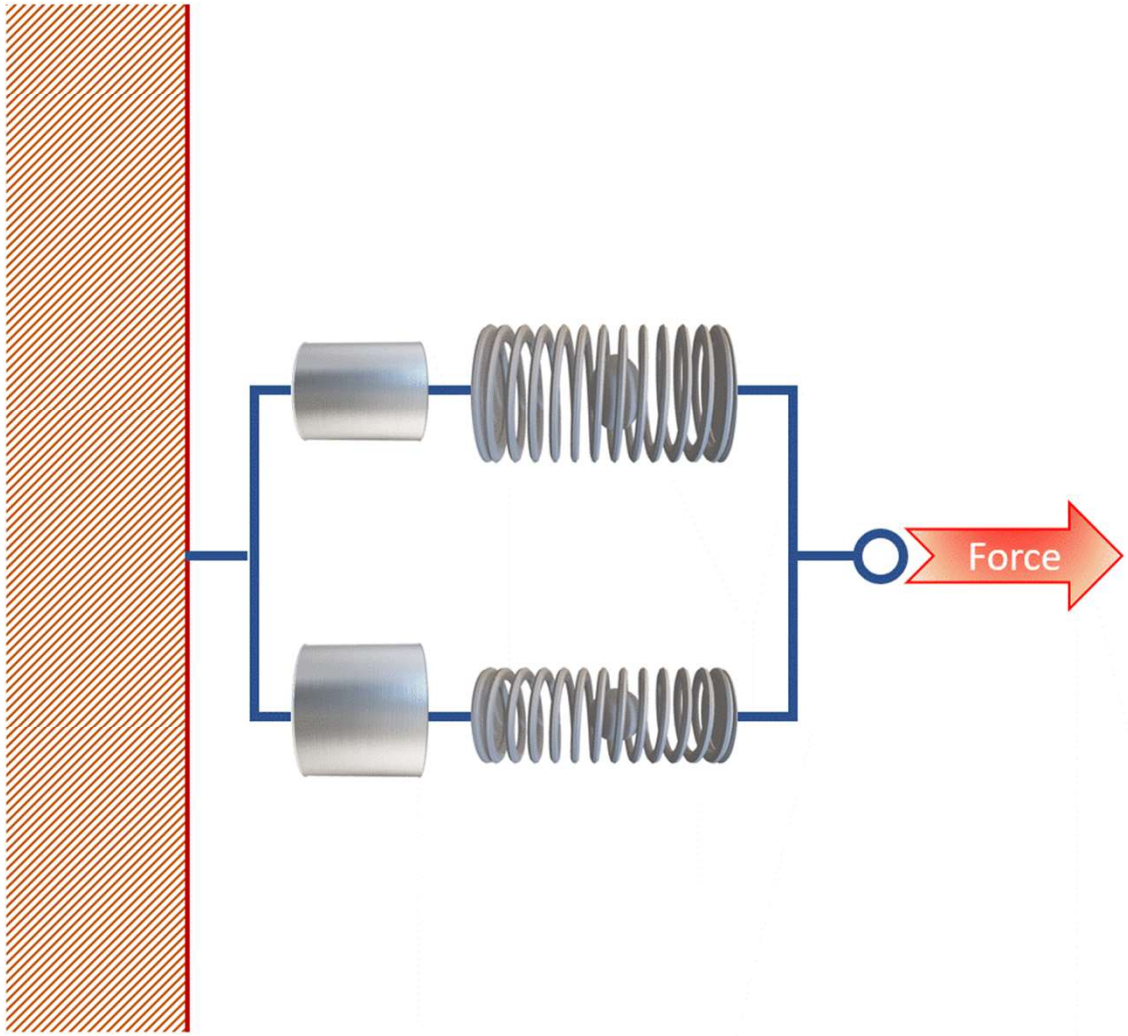
$$\eta = G_{rub}\theta_{rep}$$

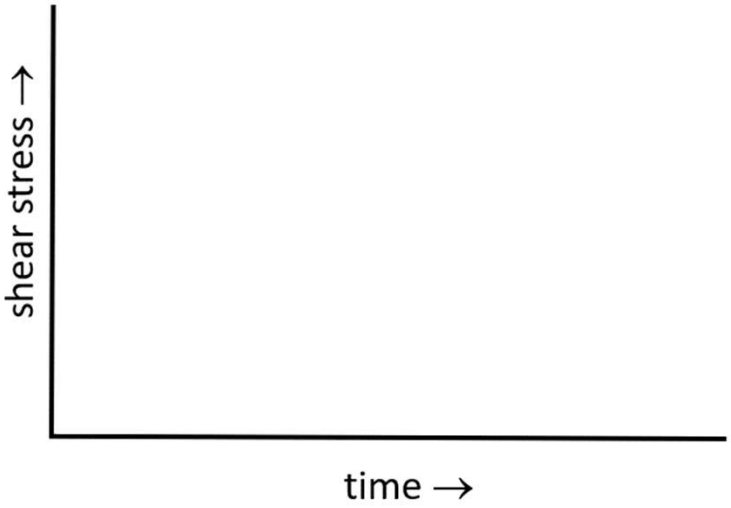
$$\eta = G_{rub}\theta_{rep,0}\exp\left(\frac{E_{rot}}{kT}\right)\frac{V_{rep}\tau}{kT}\Big/\sinh\left(\frac{V_{rep}\tau}{kT}\right)$$





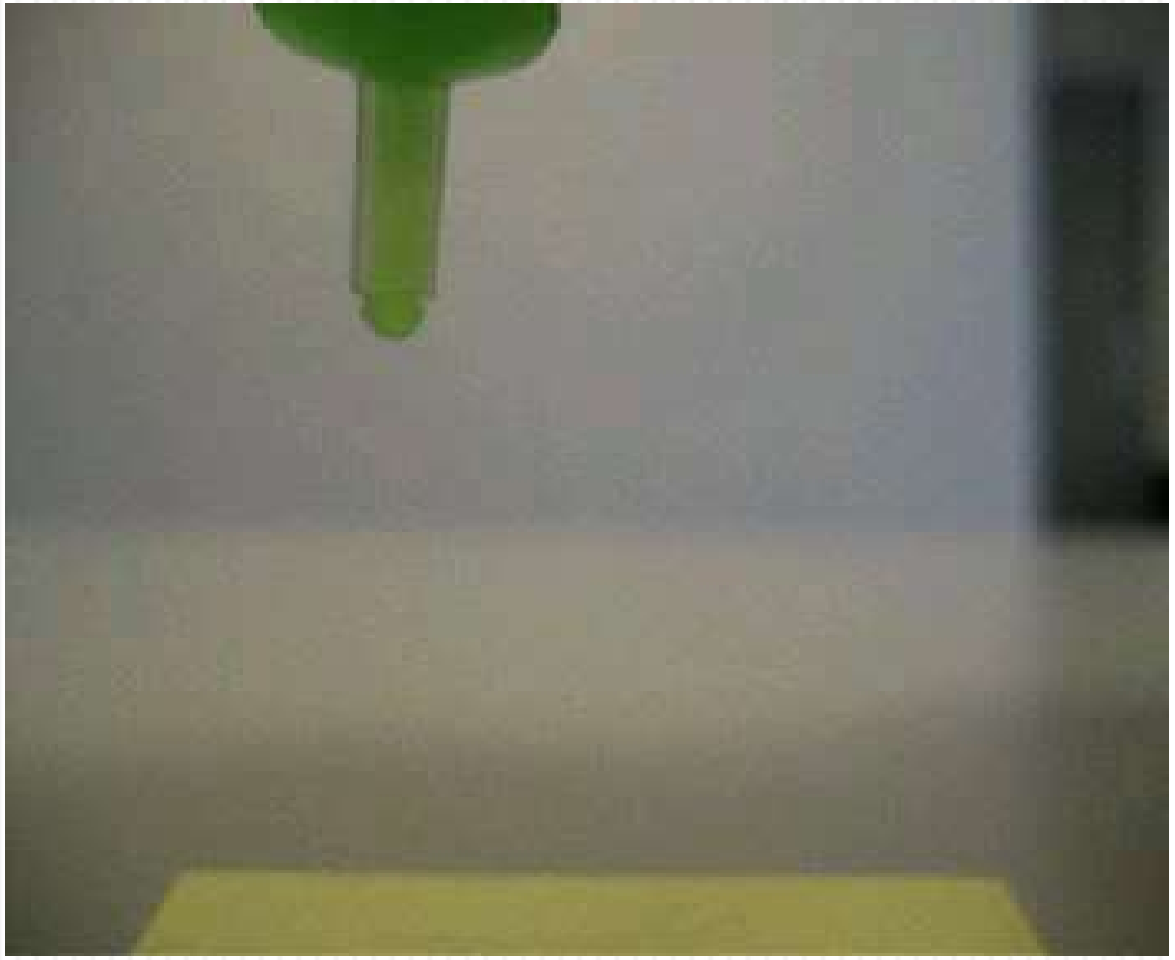
Viscosity





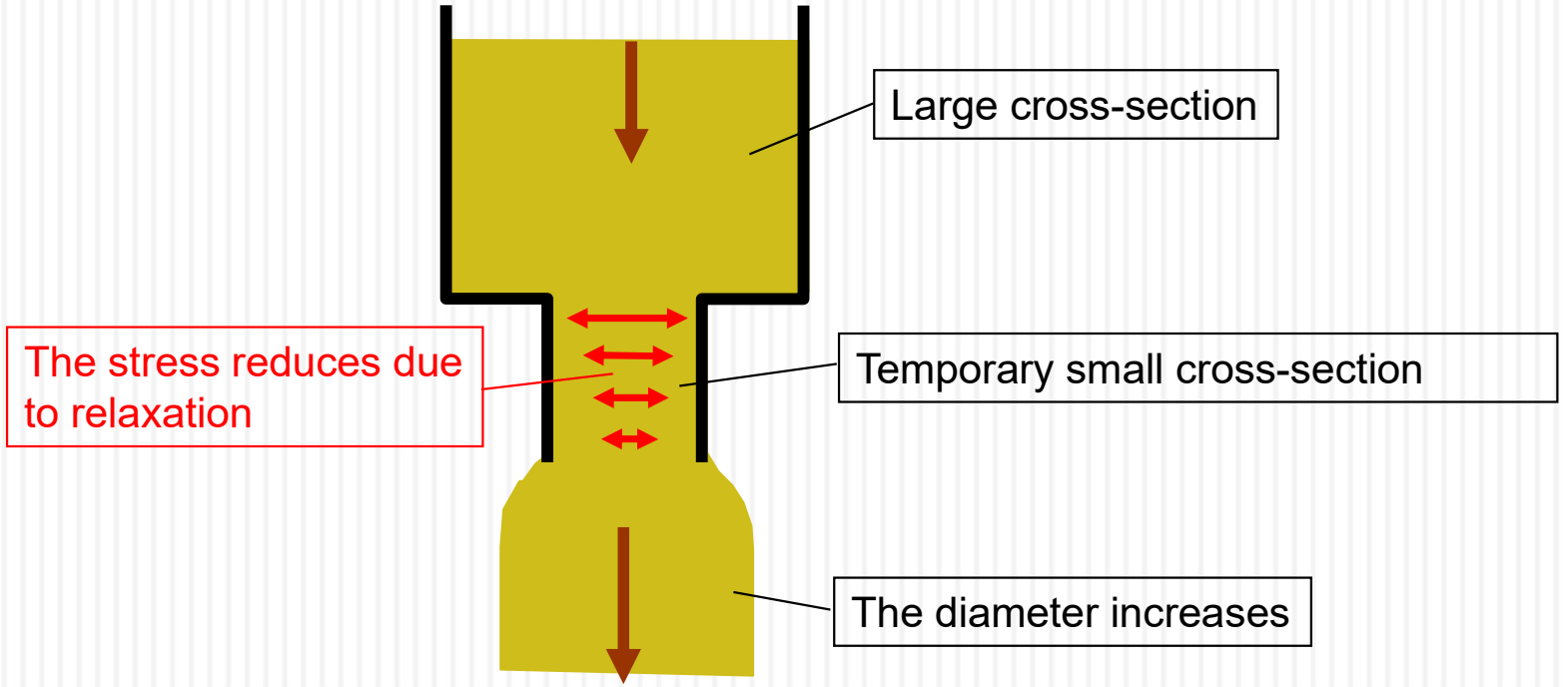
DIE SWELL

Die swell



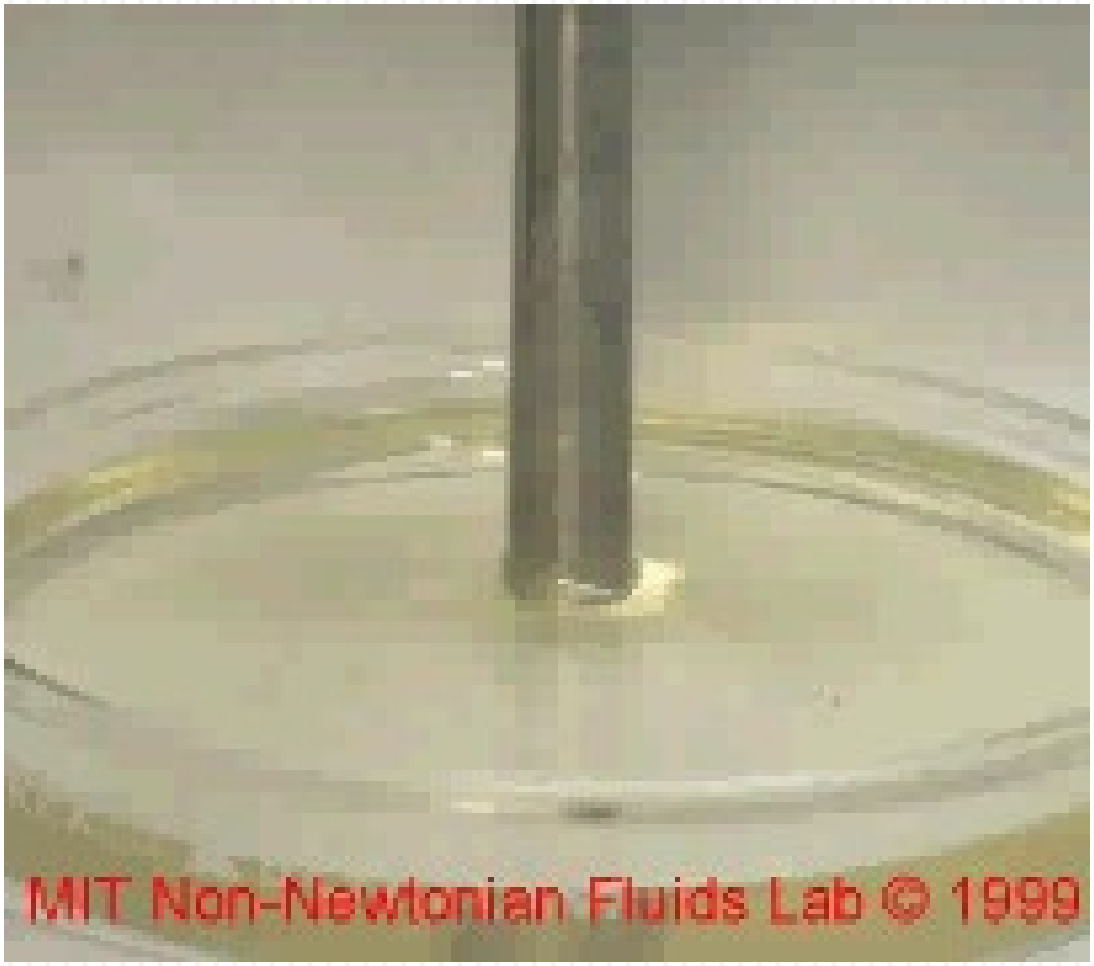
Die swell

- The reduction of the cross-section creates a stress in the polymer.
- At the exit the stress is released; the thickness increases.



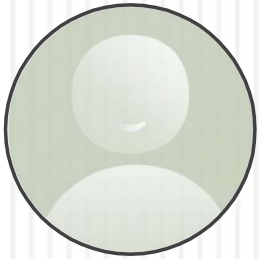
ROD CLIMBING EFFECT

Rod climbing effect



Rod climbing effect

Rod climbing effect



- The rotating rod pulls at the entangled molecules.
- The molecules move towards the rod.
- The molecules near the rod are pushed upwards.