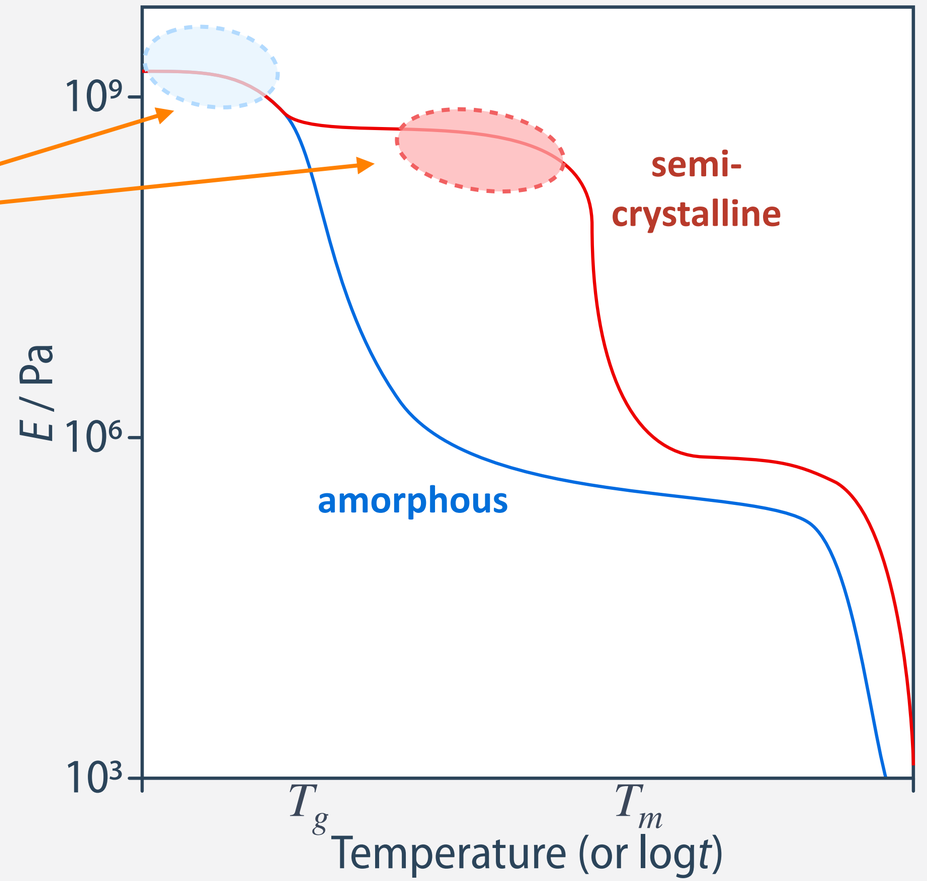
4.3
Yield and Crazing

Small Deformations in the Solid State

- in the “rigid” solid state ($T < T_g$, $T < T_m$), conformational changes are strongly restricted
- at small strains, elasticity is dominated by intermolecular forces (van der Waals, dipolar interactions)

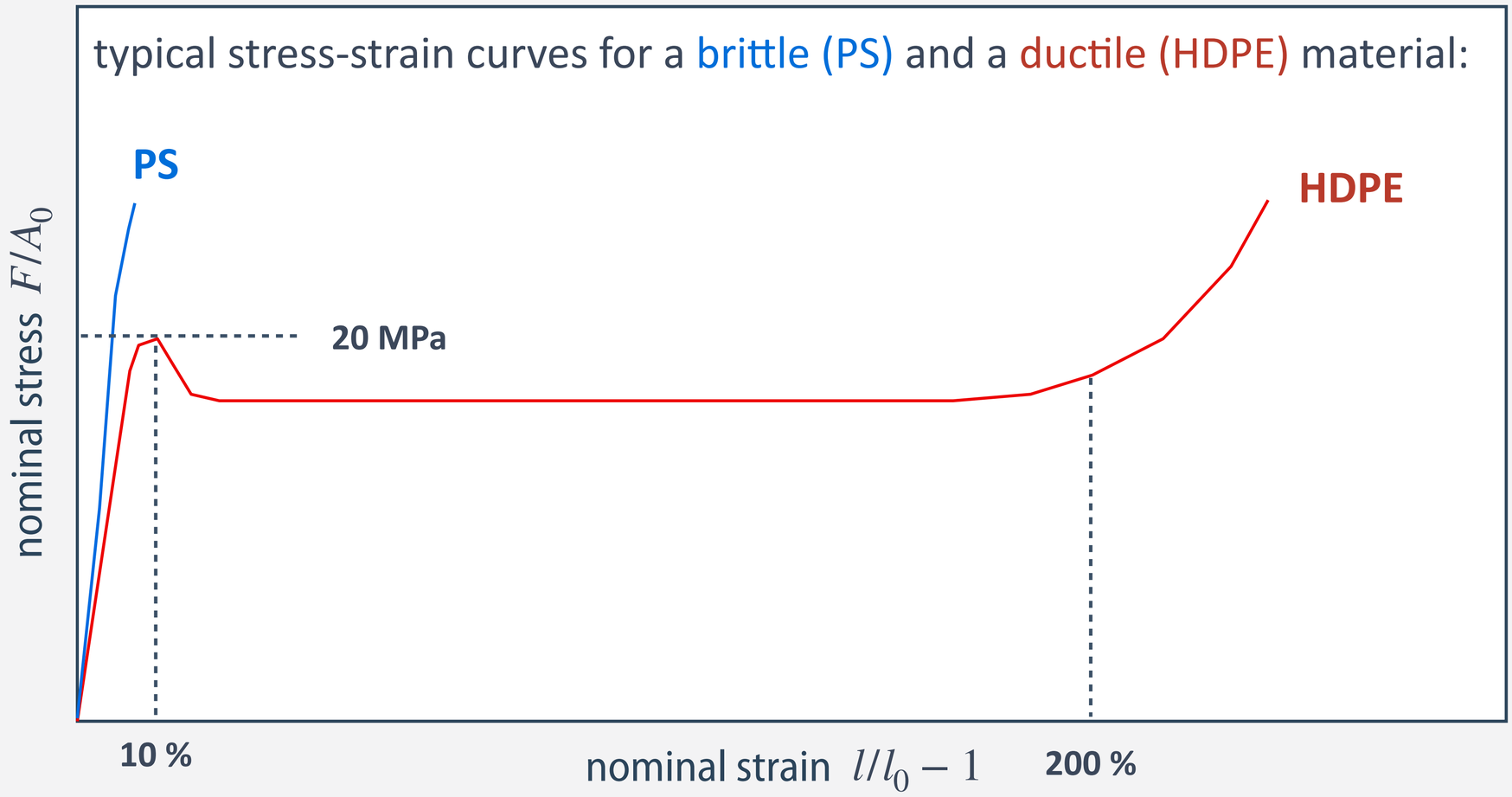
what is happening here,
if we pull very strongly?



- at large deformations, the assumption of linear elasticity breaks down

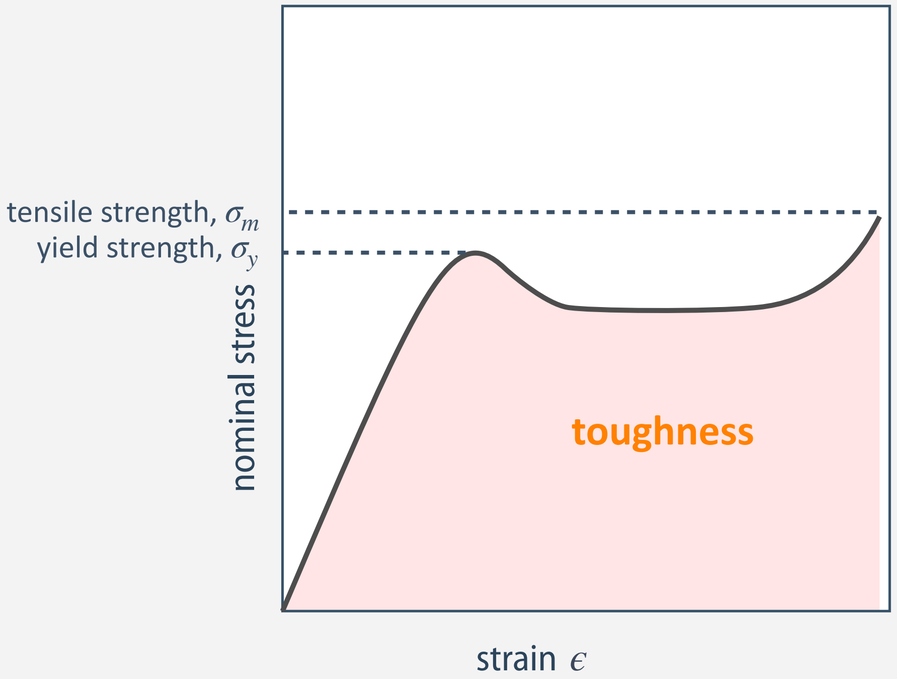
Brittle vs. Ductile Behavior

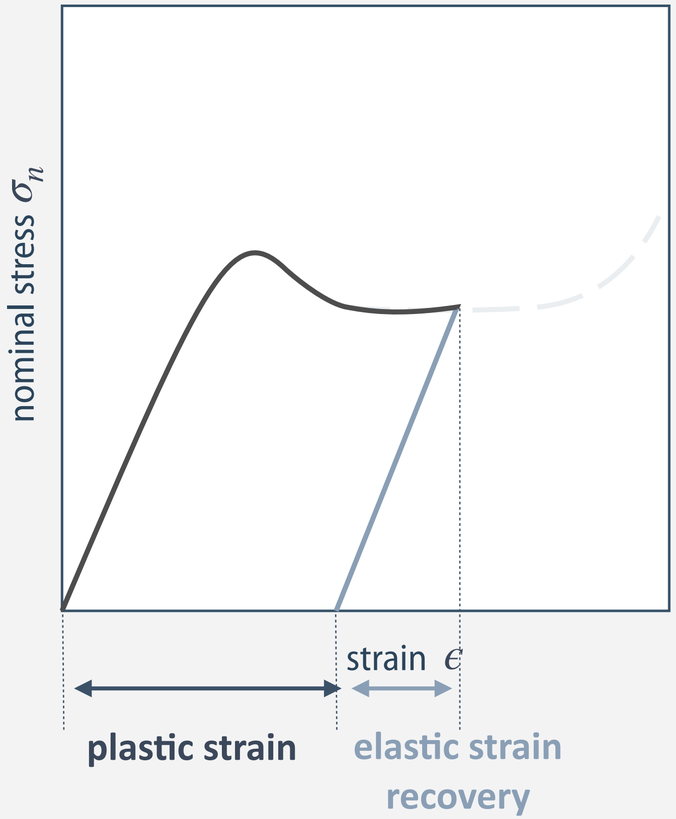
- polymers are generally considered as “plastic”: large“irreversible” strains are possible in the solid state
- degree of ductility varies strongly between glassy and semicrystalline polymers



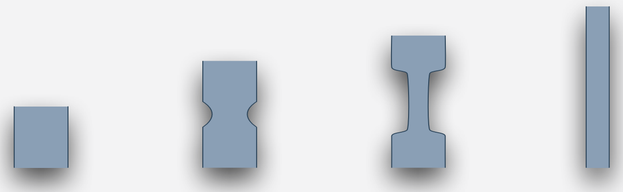
Characterisation of Plasticity

- large-strain behavior characterised by yield strength, tensile strength, and toughness





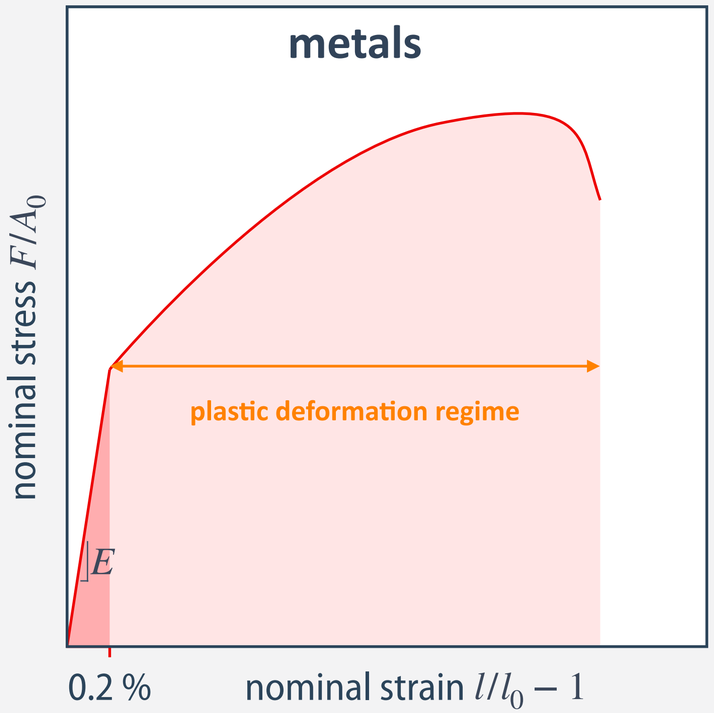
typical strain-dependent specimen shape:

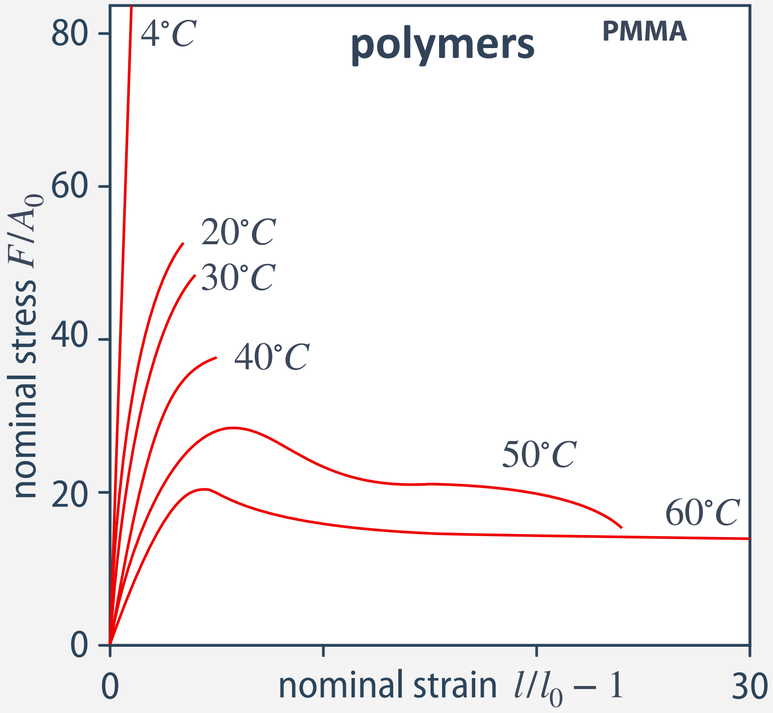


- "onset" of macroscopic plastic deformation often indicated by necking
- upon unloading, specimens usually do not return into their original shape

Metals vs. Polymers

- metals are also capable of plastic deformation, but with important differences





- clear separation between elastic (reversible) and plastic (irreversible) regimes.
- mechanical response only weakly dependent on T and strain rate at typical operating conditions $\mathrm{d}\epsilon/\mathrm{d}t$.
- often diffuse and ill-defined necking

- even very large deformations (up to 100 %) can be recovered by heating above T_g (strain recovery)
- strong sensitivity to T and $\mathrm{d}\epsilon/\mathrm{d}t$; strong heat dissipation
- necking is often sharp and well-defined at a given strain rate

Phenomenology of Polymer Plasticity

Importance of Plasticity

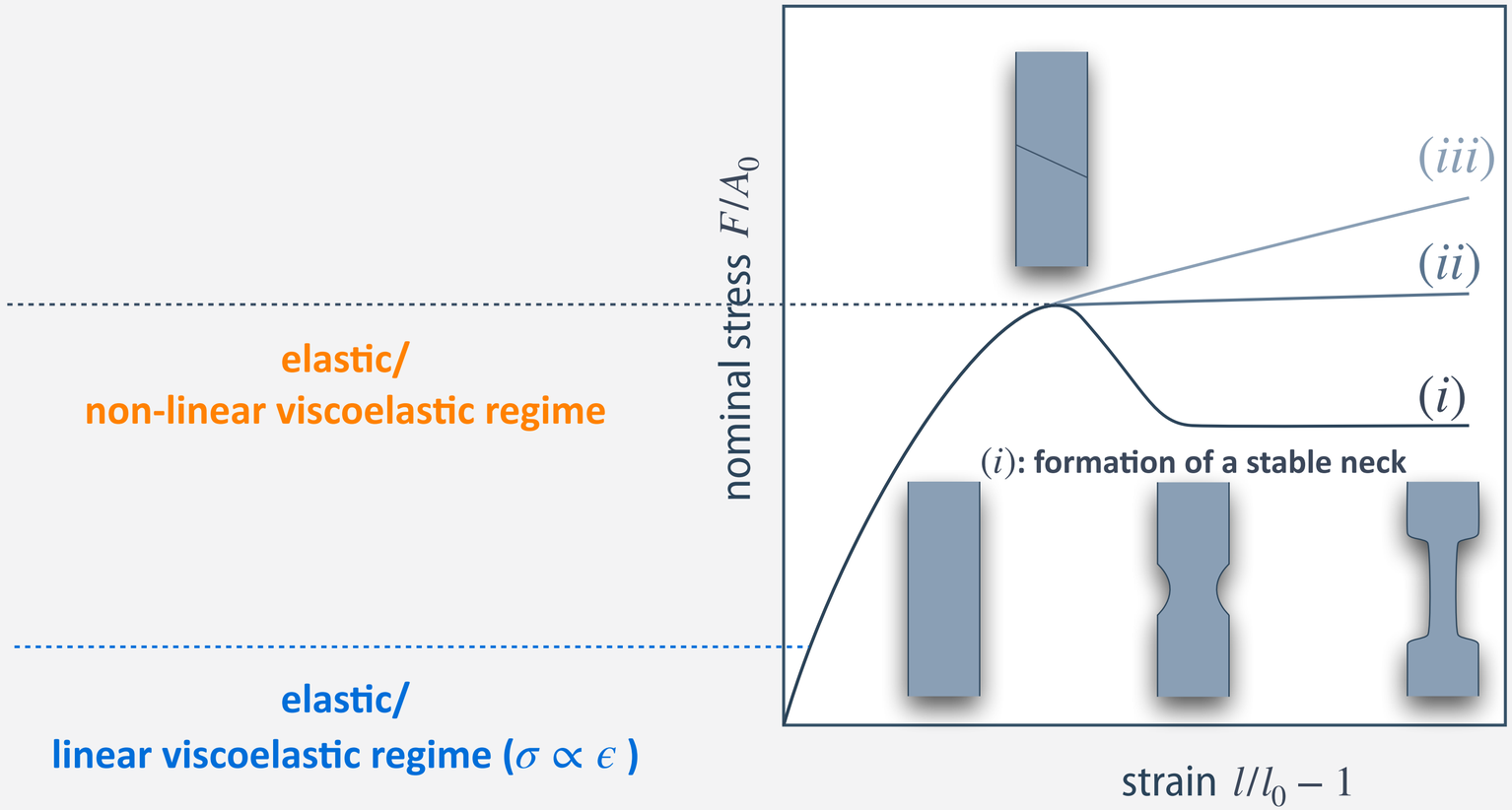
- plastic deformation is a highly dissipative process

dissipated energy: $W = \int \sigma(\epsilon) d\epsilon$

- high toughness of ductile polymers: crack growth requires large amounts of energy

Yield Strength

- one way of describing plastic deformation is via the maximum in stress before necking, σ_y



- at a constant strain rate, the yield point (cases (i) and (ii)) can be defined as: $\left.\frac{\mathrm{d}\sigma}{\mathrm{d}\epsilon}\right|_{\sigma_y} = \left.\frac{\mathrm{d}\sigma}{\mathrm{d}\lambda}\right|_{\sigma_y} = 0$

Geometric Considerations of Necking

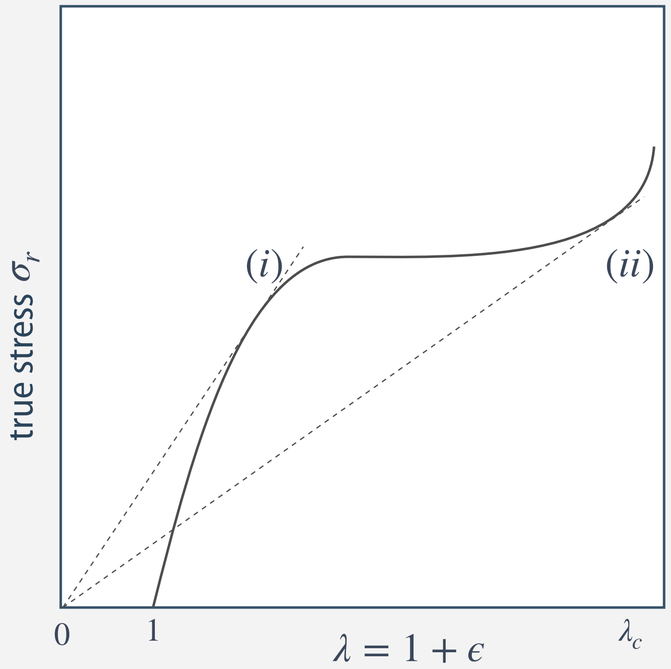
- **Considère construction: plot of true stress versus nominal strain**

true stress: $\sigma_r = \dfrac{f}{A}$ **nominal stress:** $\sigma_n = \dfrac{f}{A_0} = \dfrac{\sigma_r}{1+\epsilon}$

at iso-volumetric conditions: $Al = A_0 l_0 \quad \Rightarrow \quad A = A_0 \dfrac{l_0}{l} = \dfrac{A_0}{\lambda}$

$$\sigma_r = \frac{f}{A} = \frac{A_0 \sigma_n}{A_0 \lambda^{-1}} = \lambda \sigma_n \quad \Rightarrow \quad \frac{\mathrm{d}\sigma_n}{\mathrm{d}\lambda} = \frac{\mathrm{d}}{\mathrm{d}\lambda}\left(\frac{\sigma_r}{\lambda}\right) = \frac{1}{\lambda}\frac{\mathrm{d}\sigma_r}{\mathrm{d}\lambda} - \frac{\sigma_r}{\lambda^2}$$

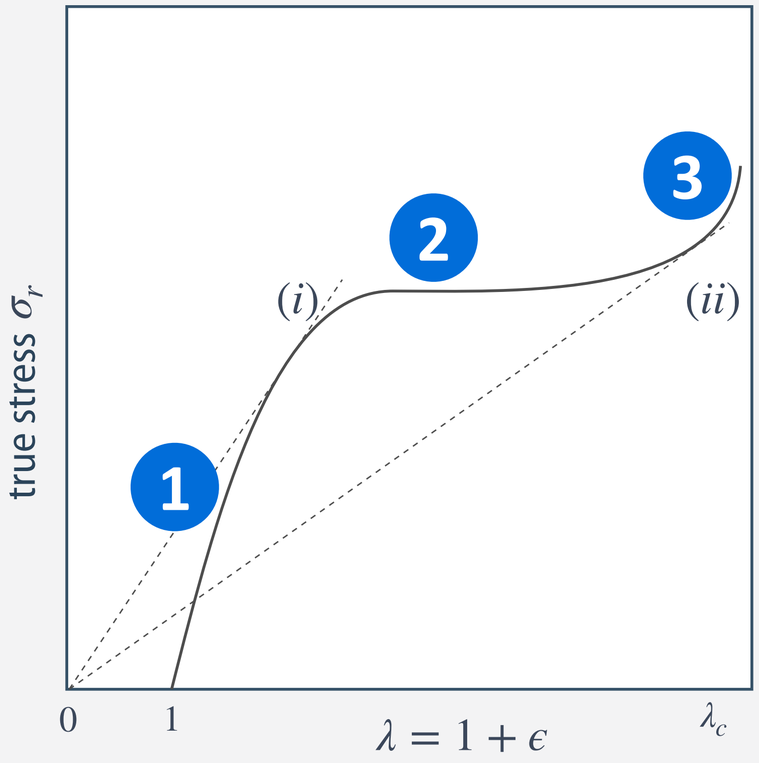
thus, for the yield point: $\dfrac{\mathrm{d}\sigma_n}{\mathrm{d}\lambda} = 0 \quad \Rightarrow \quad \dfrac{\mathrm{d}\sigma_r}{\mathrm{d}\lambda} = \dfrac{\sigma_r}{\lambda}$



- **the slope of the true stress-strain curve decreases monotonically with λ, and σ_r becomes constant**
- **therefore, σ_n decreases: a purely geometric instability ($\mathrm{d}\sigma_n/\mathrm{d}\lambda < 0$) compensated for by necking**

Stable Necking and Cold Drawing

- necking occurs in amorphous thermoplastics as chains orient
- the oriented neck becomes stronger than the surrounding material.



1 undeformed dogbone

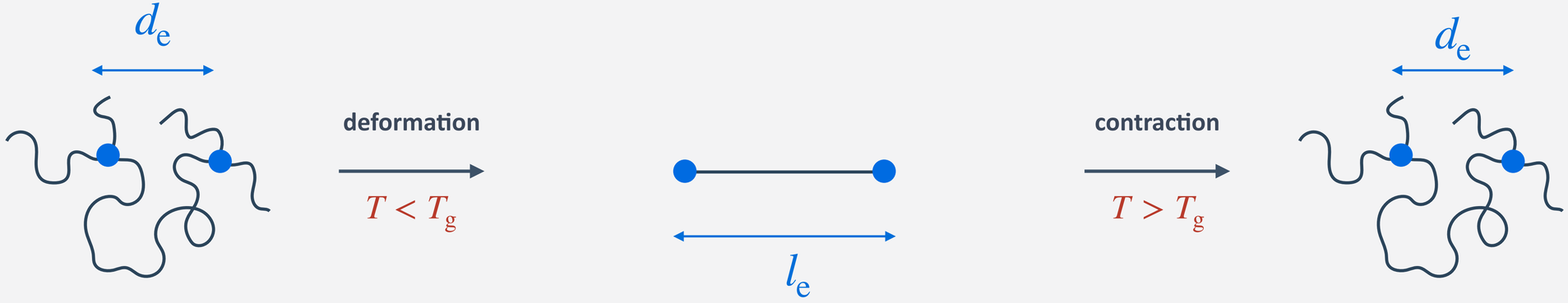
2 necking and chain orientation

3 drawn region: fully developed neck

- load increasingly carried by aligned covalent bonds: stable neck propagation (“cold drawing”)

Role of Entanglements for λ_c

- excellent correlation between **critical draw ratio λ_c** & **maximum extension of an entangled network λ_{max}**



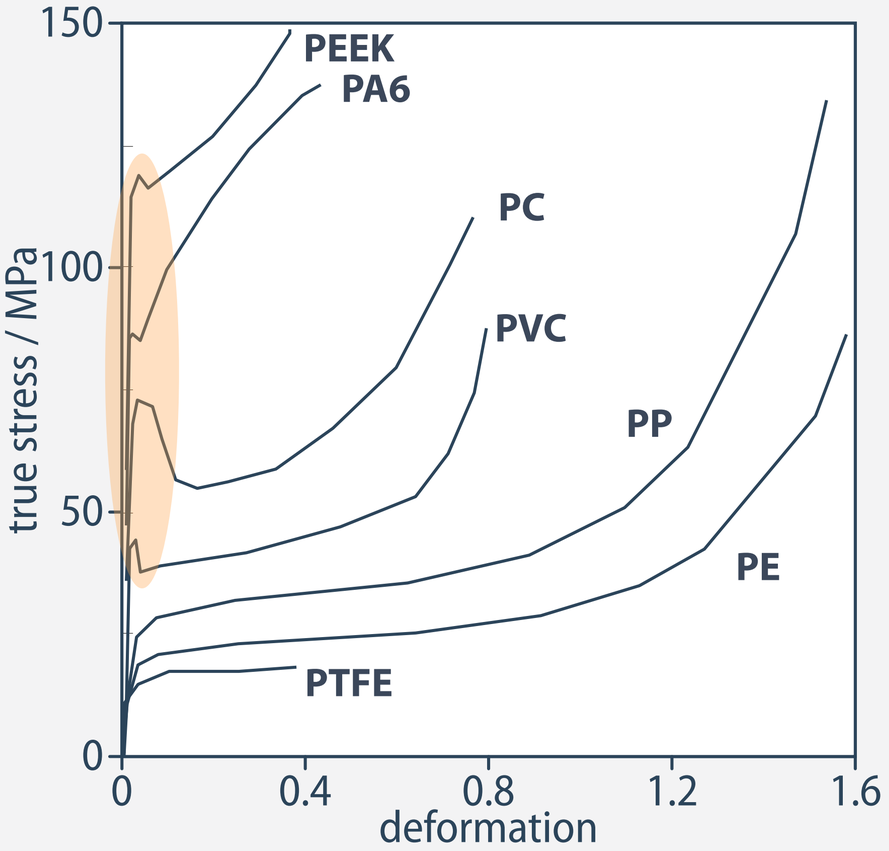
$$l_e \sim \frac{M_e}{M_b} a = n_e a \qquad < d_e >^2 = C_\infty \frac{M_e}{M_b} a^2 \qquad \lambda_{max} = \frac{l_e}{d_e} \sim \sqrt{\frac{M_e}{M_b C_\infty}} = \sqrt{\frac{n_e}{C_\infty}}$$

M_b: molar mass per constitutive repeating unit a: bond length

- **entanglements stabilise plastic deformation in glassy polymers**
- **in the rubbery state ($T > T_g$), large deformations become reversible** (as long as chains do not disentangle)
- **for $M < 2M_e$: insufficient entanglements, plastic deformation is no longer stabilised (→ brittle behavior)**

Physical Aging as Intrinsic Origin of Yield Drop

- **the true stress-strain curves of ductile, glassy polymers show a characteristic “yield drop”**

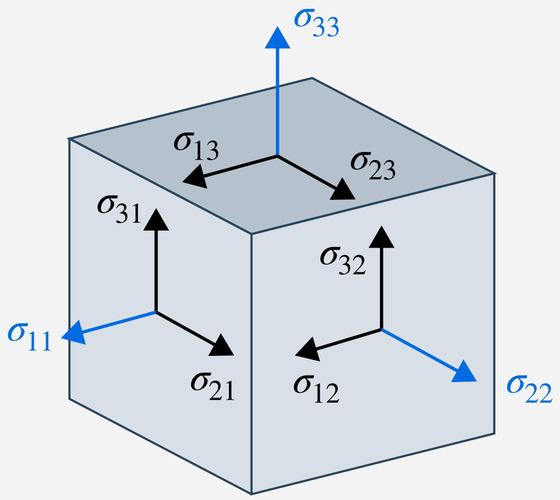


common ductile polymers at
25 °C tested under tension

- **origin: physical ageing (densification and reduced free volume)**
- **this effect becomes intensified by annealing slightly below T_g**

Von Mises Yield Criterion

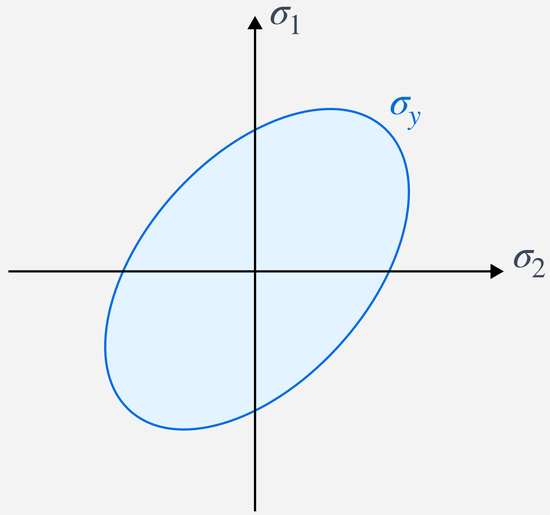
- **assumption: yielding is dominated by shear deformation characterised by normal stresses σ_1 , σ_2 , σ_3**



stress tensor

$$\sigma_{ij} = \begin{pmatrix} \sigma_{11} & \sigma_{21} & \sigma_{31} \\ \sigma_{12} & \sigma_{22} & \sigma_{32} \\ \sigma_{13} & \sigma_{23} & \sigma_{33} \end{pmatrix} \equiv \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

biaxial stretching



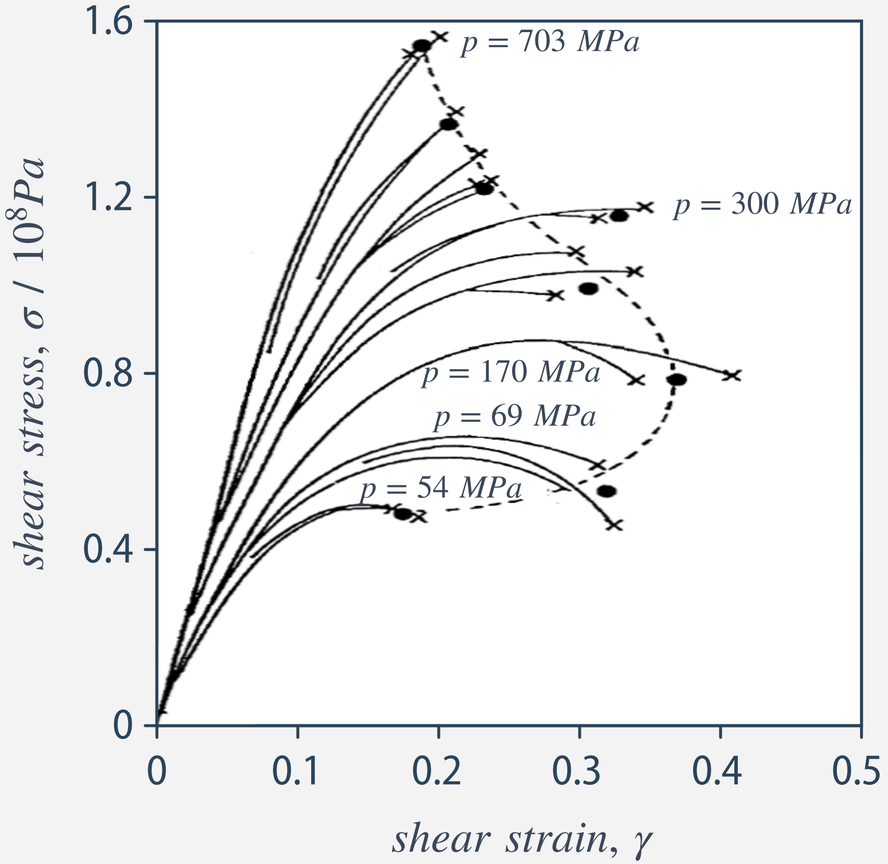
Von Mises criterion: $(\sigma_{11} - \sigma_{22})^2 + (\sigma_{22} - \sigma_{33})^2 + (\sigma_{33} - \sigma_{11})^2 + 6(\sigma_{12}^2 + \sigma_{13}^2 + \sigma_{23}^2) \geq 2\sigma_y^2$

for uniaxial stretching: $2\sigma_{11}^2 \geq 2\sigma_y^2$

- **metals follow von Mises criterion well: σ_y is approximately constant**
- **polymers show pressure dependence of yield strength σ_y which requires a modified criterion**

Influence of Pressure on Yield Strength

- tensile curves of PMMA under various hydrostatic pressures:



hydrostatic pressure:

$$p = -\frac{1}{3}(\sigma_1 + \sigma_2 + \sigma_3)$$

assumption: yield stress increases approximately linearly:

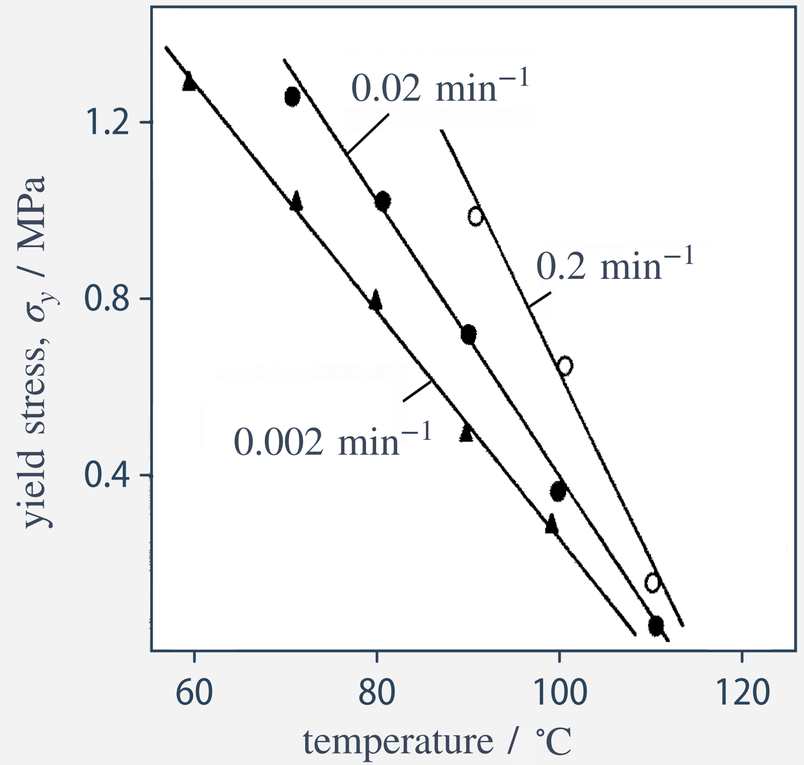
$$\sigma_y = \sigma_{y0} + \mu p$$

- **polymers show large volume changes under pressure (due to their comparably small bulk modulus *K*)**

Models

Effect of Temperature and Strain Rate

- plastic deformation of polymers is a thermally activated processes



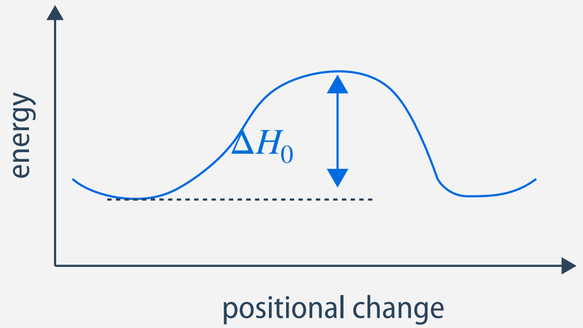
PMMA

- strong dependence on strain rate (like viscoelasticity)
- σ_y becomes approximately zero as the glass transition temperature is approached from below

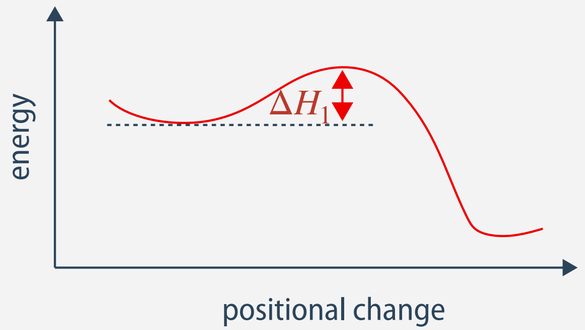
Eyring Model

- **polymer flow described by an activation barrier ΔH lowered for segments moving in stress direction**

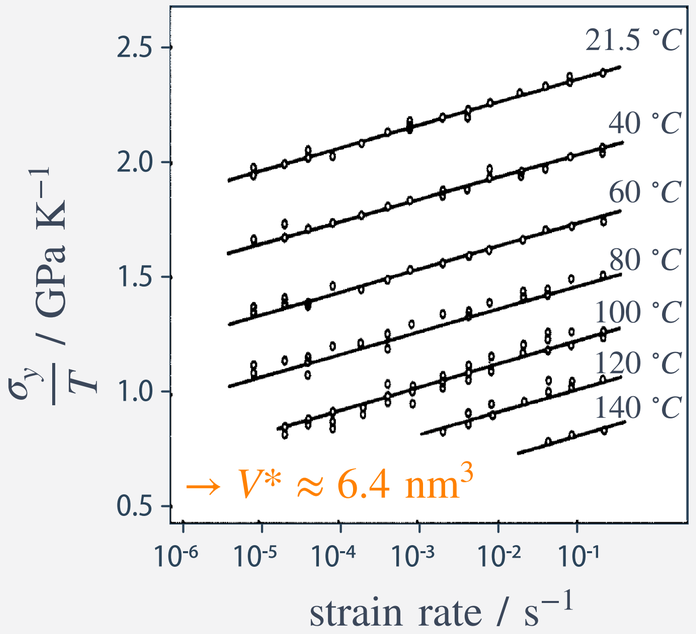
undeformed



deformed



example: PC



$$\dot{\epsilon} = \dot{\epsilon}_0 \exp\left(-\frac{\Delta H - \sigma V^*}{kT} \right)$$

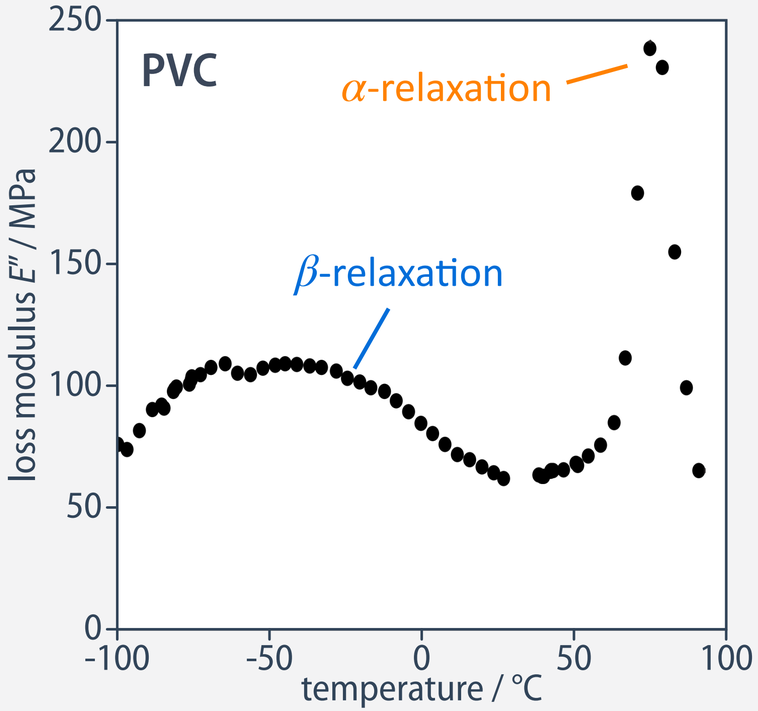
$$\frac{\sigma_y}{T} = \frac{\Delta H}{TV^*} + \frac{\mathrm{k}}{V^*} \ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0}$$

- typical activation volume for glassy polymers: $V^* \sim 5 - 10$ nm^3
- **plastic deformation involves cooperative movement of several monomers (typically between 2 and 10)**

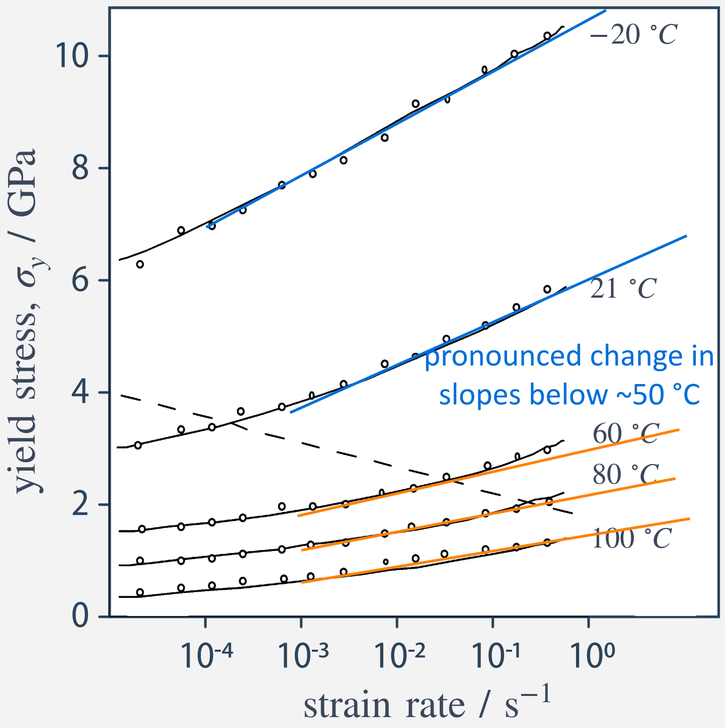
Influence of Secondary Transitions in Poly(vinyl chloride)

- **conformational relaxation involving a limited number of bonds can subsist below T_g**

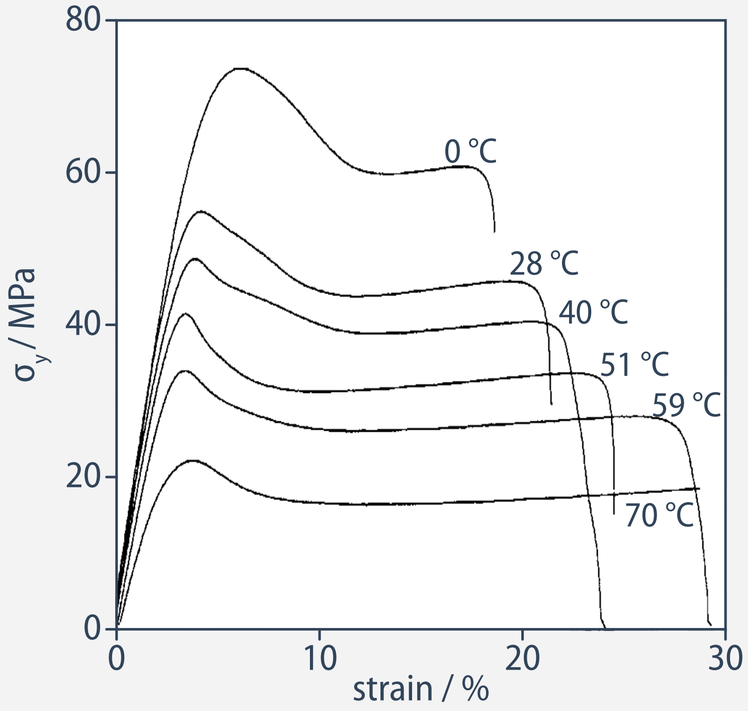
pronounced β-relaxation



Eyring plots



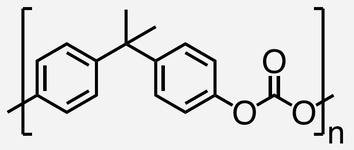
tensile curves



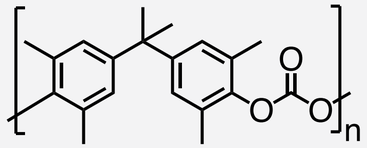
- **PVC displays a strong β-relaxation at around 50 °C with strong influence on yield strength and ductility**

Influence of Secondary Transitions in Polycarbonate

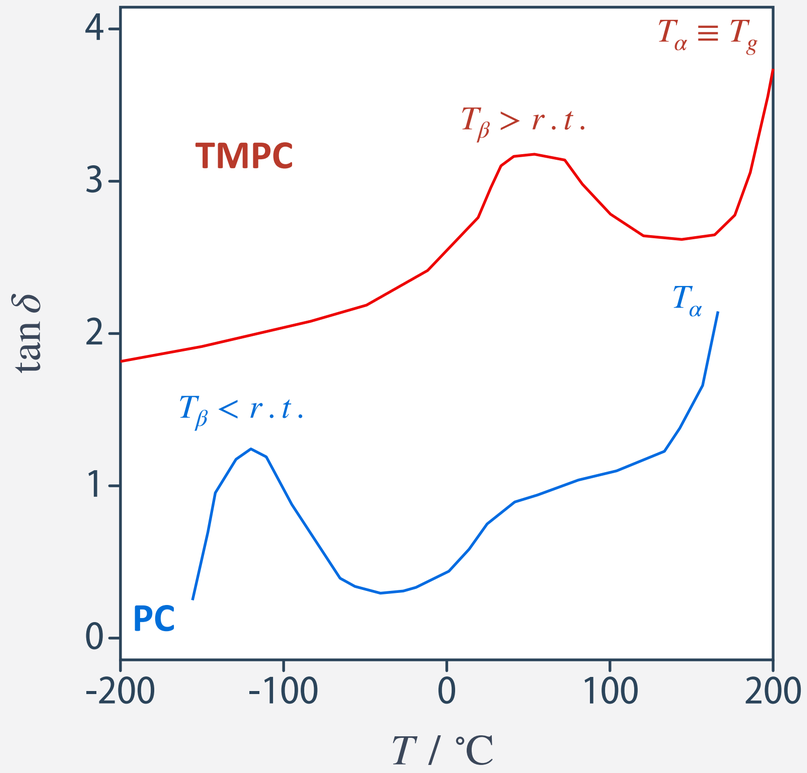
- in PC, there is no major secondary relaxation between 20 °C and T_g

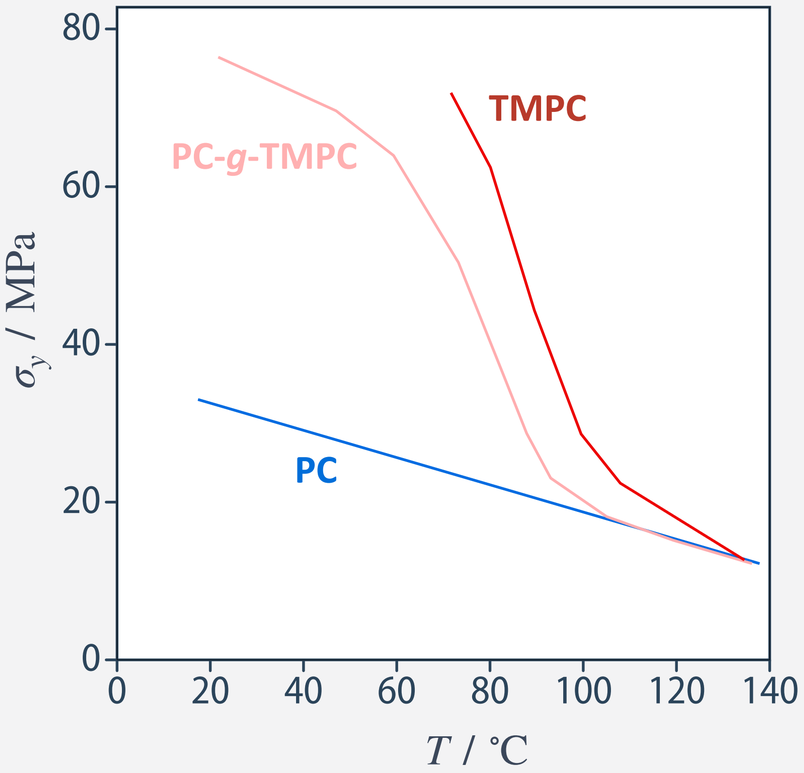


PC



TMPC
(Tetramethyl-PC)

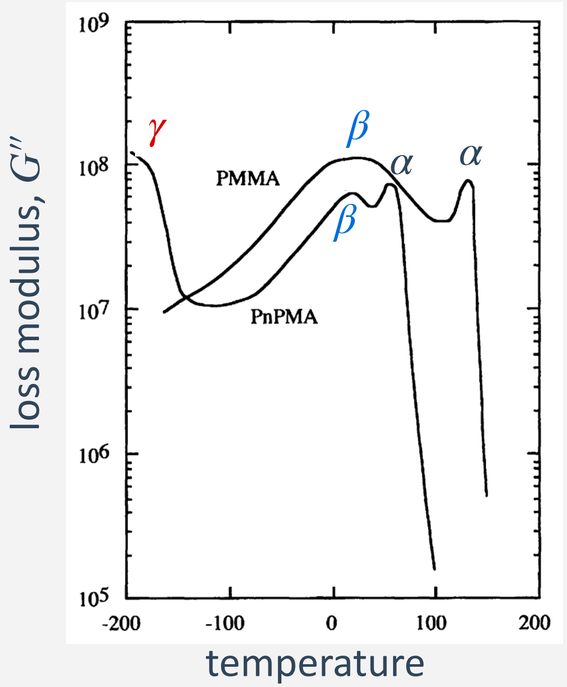


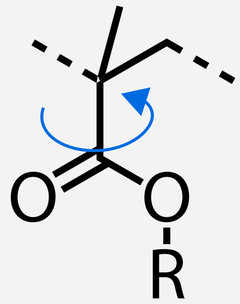


- these motions “lubricate” deformation leading to increased ductility

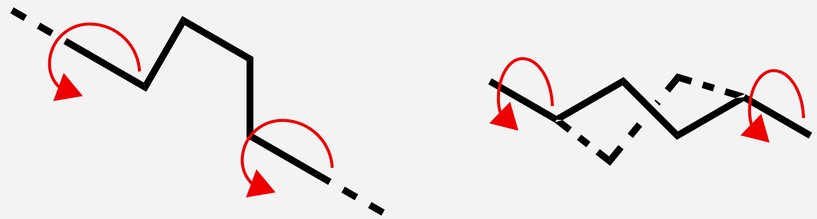
Relaxation Processes in the Glassy State

- at T_g: sudden change in physical properties (E', E'', tan δ, heat capacity)
- below T_g: small mobile subunits still contribute to mechanical dissipation





rotation

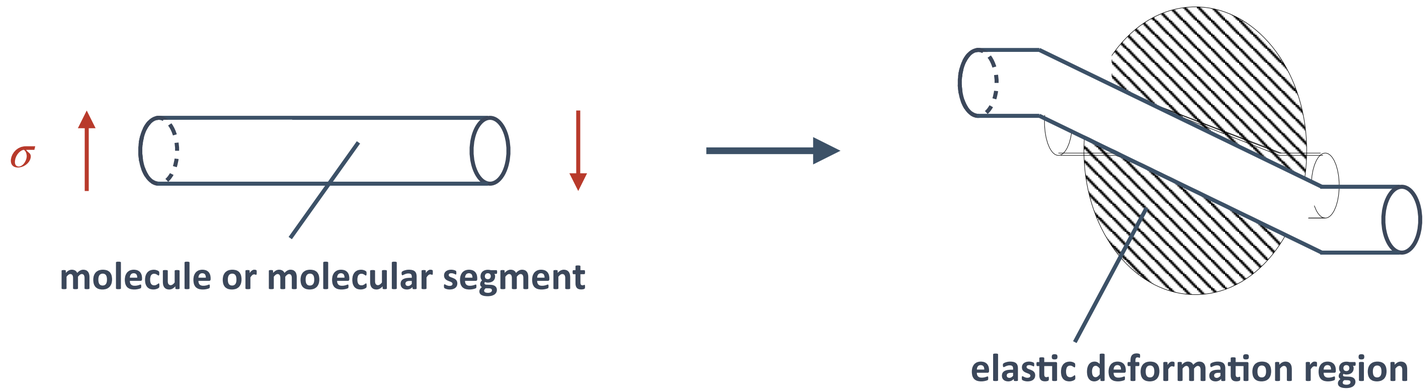


crankshaft motion

- polymer glasses are tougher than inorganic glasses or ceramics because they can dissipate energy via these unique local relaxations

Argon Model

- formally similar to the Eyring model: **intermolecular interpretation of yield via local shear transformation**
- predicts yield behavior well for $T \ll T_g$

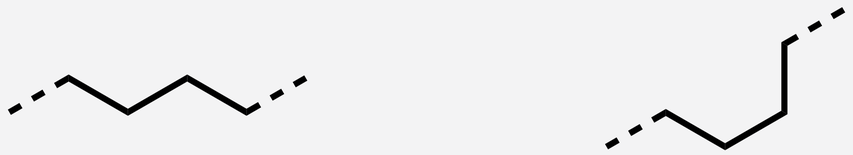


$$\sigma_y = \sigma_0 \left[1 + \frac{16(a-v)}{3\pi G \beta^2 \alpha^3} \mathrm{k}T \ln\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right) \right]^{6/5}$$

- **shear modulus G of the surrounding "matrix" determined the energy barrier height**
- **"elastic energy" is required to accommodate that deformation in the matrix**

Robertson Model

- intramolecular barriers for transition between "*trans*" (low energy) and "*cis*" (high energy) states



trans cis

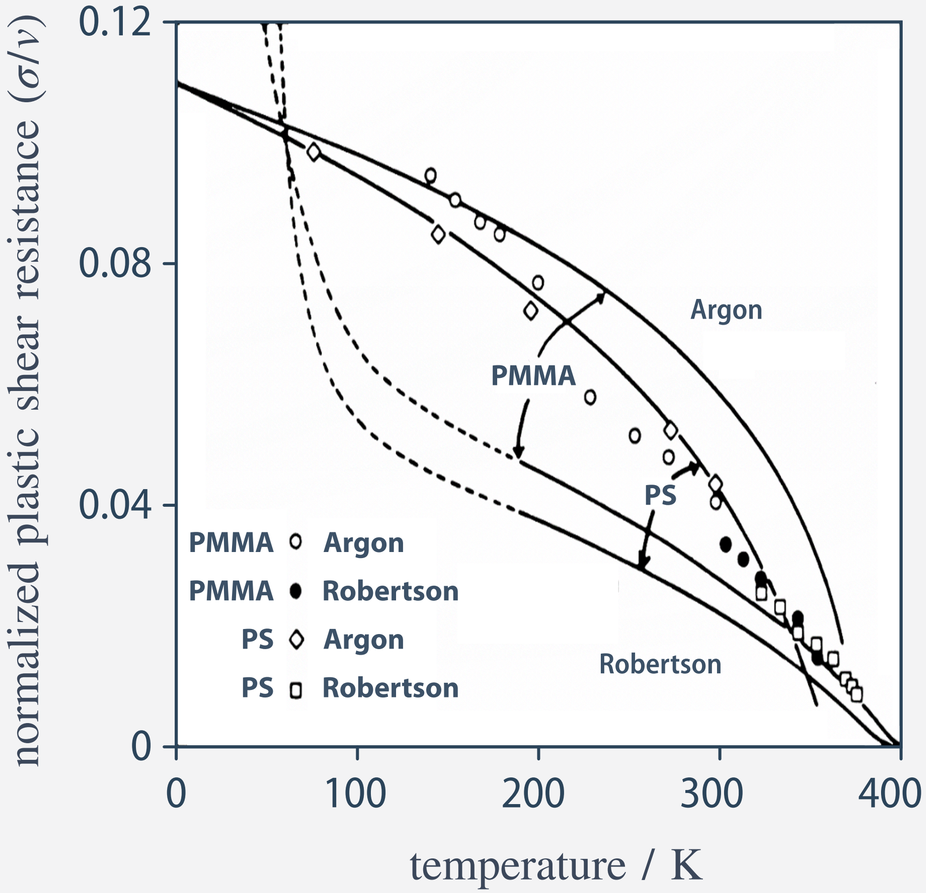
- without stress, the proportion χ of *cis* states depends on the temperature
- stress changes equilibrium between *cis* and *trans* states
- links yield behavior (below T_g) and viscosity (above T_g) via the same mechanism:

$$\sigma = \eta\dot{\epsilon}$$

- viscosity can be predicted using WLF factors

Comparing Argon & Robertson with Experimental Data

- **both models do not work over the full temperature range:**
  Argon: good at low temperatures**, Robertson:** better near T_g



- **both limited because they ignore secondary relaxation**

Molecular Dynamics

- there are many other phenomenological and theoretical models, which more or less account for the data (often depending on the number of adjustable parameters!)
- MD simulations provide microscopic insight into the glassy state
- Limited by box size (few nm) and timescales (ps – ns)
- Still valuable for identifying local deformation mechanisms

Semicrystalline Polymers

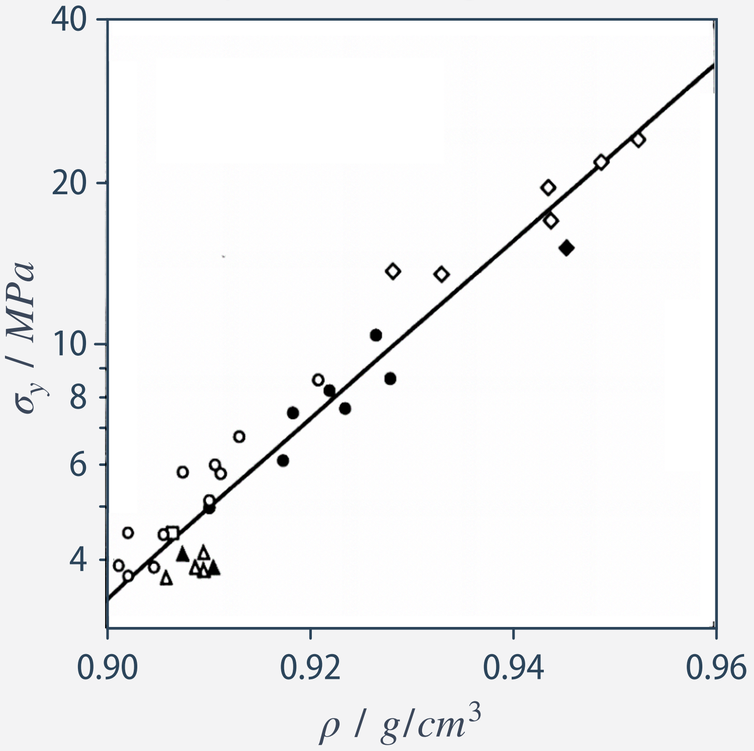
Yield Strength in Semicrystalline Polymers

- similar macroscopic behavior to glassy polymer, but differences are particularly observed at temperatures above the glass transition temperature.

yield stress σ_y increases with:

- **lamellar thickness l**
- **degree of crystallinity**
- **density**

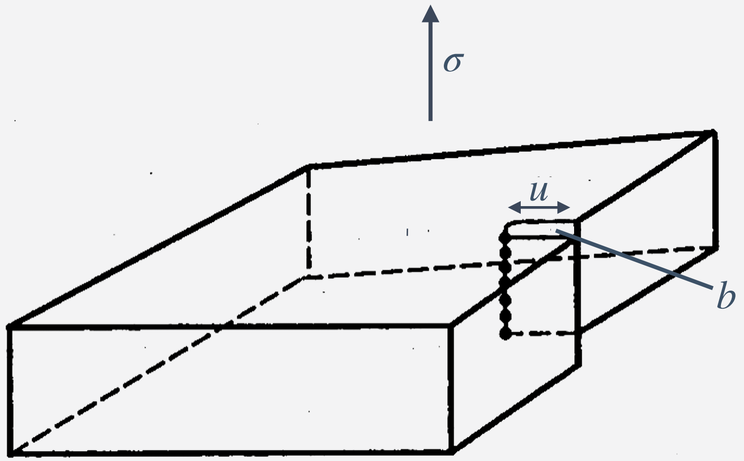
example: diverse grades of PE



- **morphology is crucial:** lamellar thickness, degree of crystallinity, crystalline network amorphous tie-chains

Young's Model Based on Dislocations

- a relation between yield stress and lamellar thickness is given by Young's model
- **Yielding via nucleation and glide of dislocations.**



activation energy for screw dislocations:

$$\Delta U^* = \frac{Gb^2 l}{2\pi}\left(\ln\frac{u^*}{r_0} - 1\right)$$

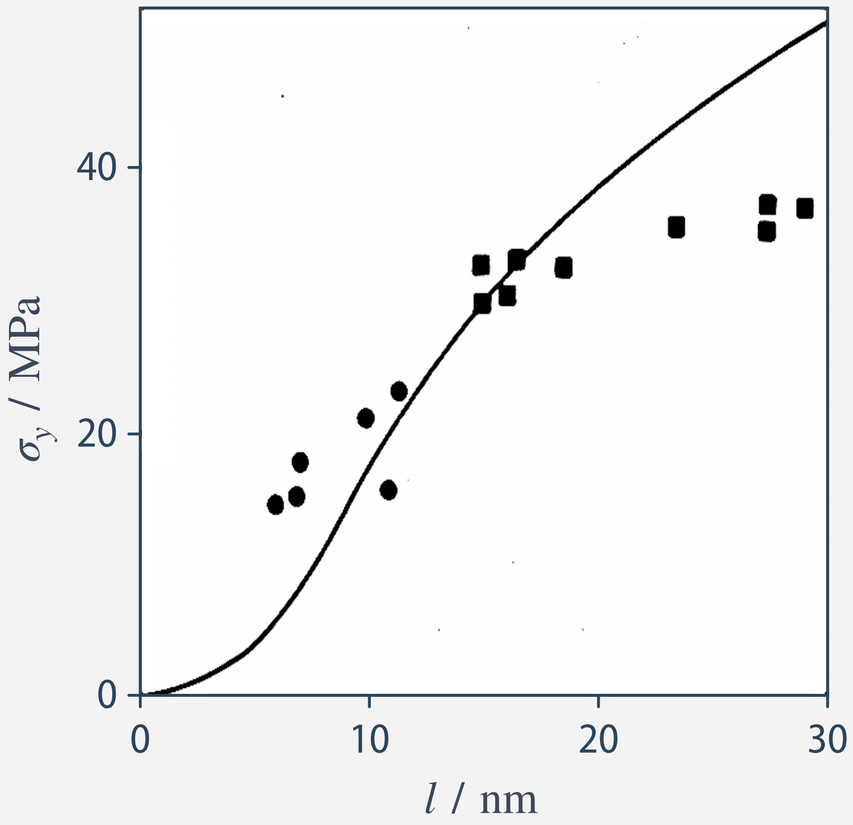
critical width:

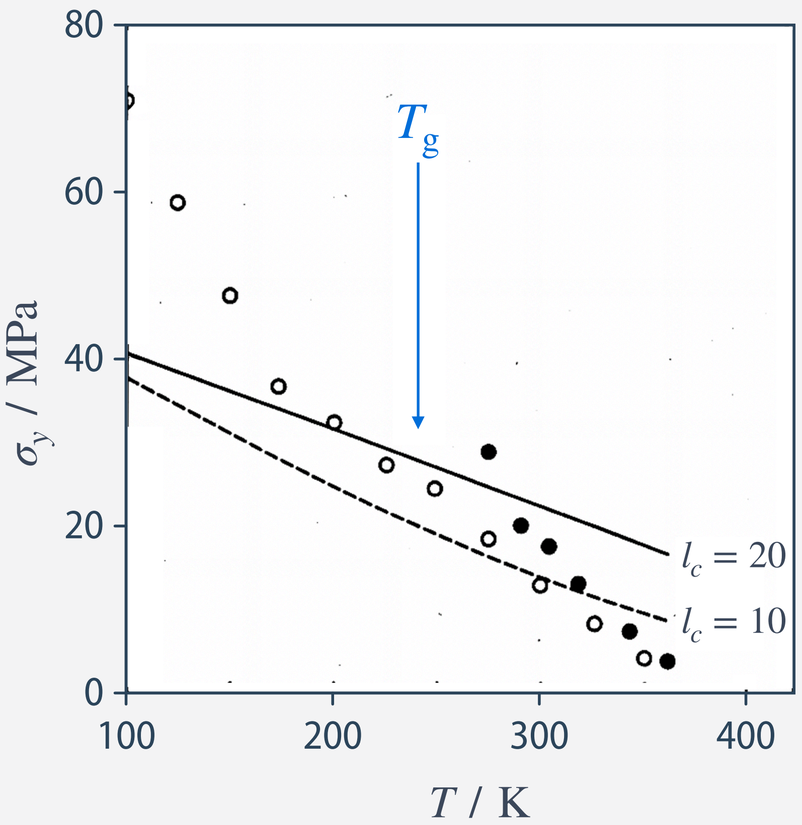
$$u^* = \frac{Gb}{2\pi\sigma}$$

- **for HDPE:** $\Delta U^* \sim 50 - 60\ \mathrm{k}T$ **to nucleate a dislocation**

Young's Model: Limitations

- qualitatively good correlations, captures correct order of magnitude, but not full behavior:

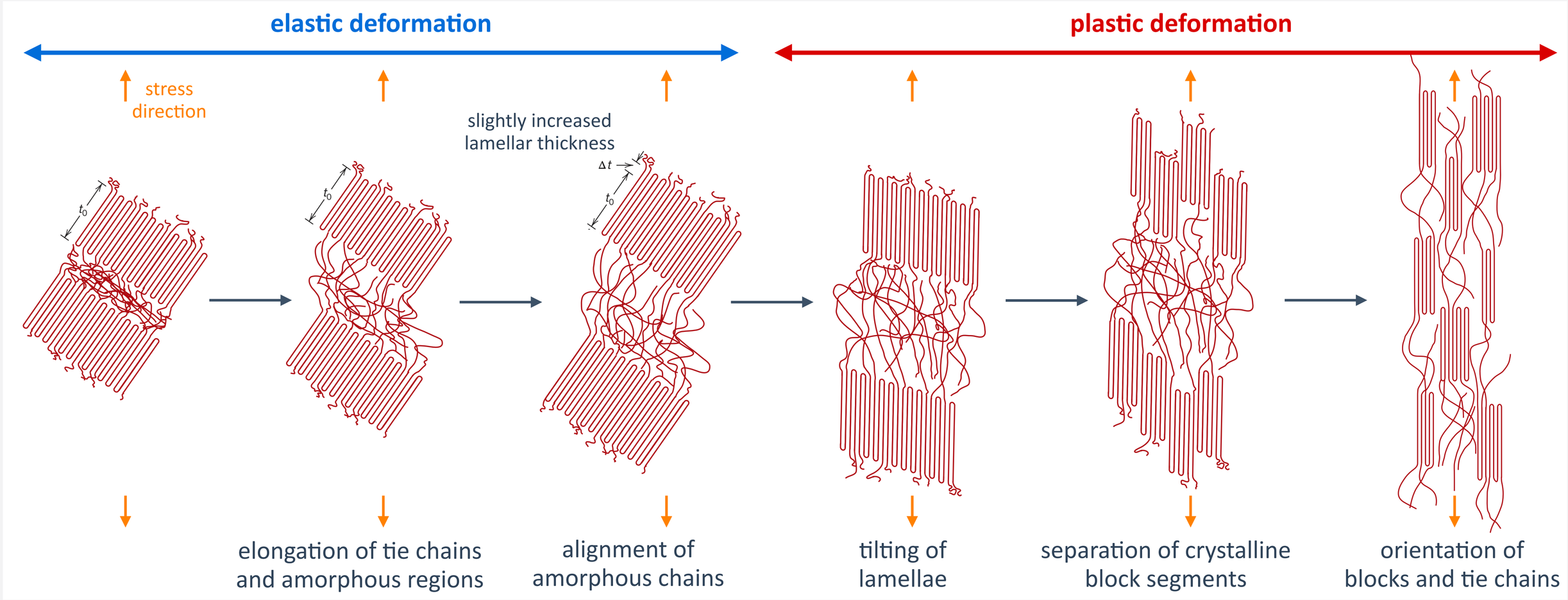




- **ignores role of amorphous regions, therefore unrealistic for $T < T_g$**

Self-Consistent Models

- include interactions between crystalline and amorphous phases and account for evolving crystallographic texture and morphology during plastic deformation

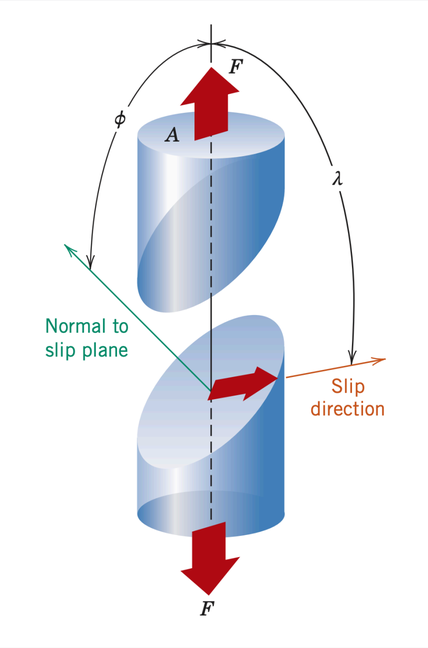


- **complexity arises from: multi-stage deformation, polycrystallinity, multiple slip systems**

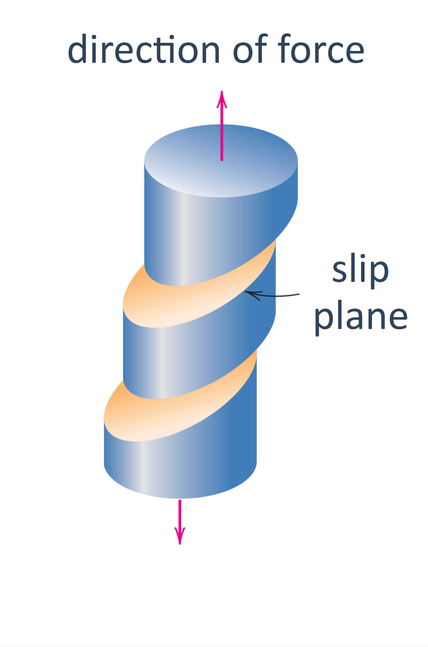
Large Deformations

- significant morphological evolution: lamellae break, crystals rotate
- shear stress τ on the slip plane parallel to the slip direction

geometric relationships

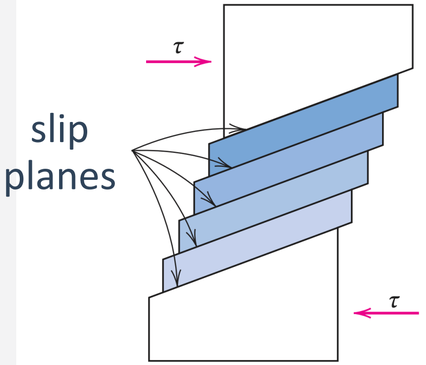


macroscopic slip



shear stress

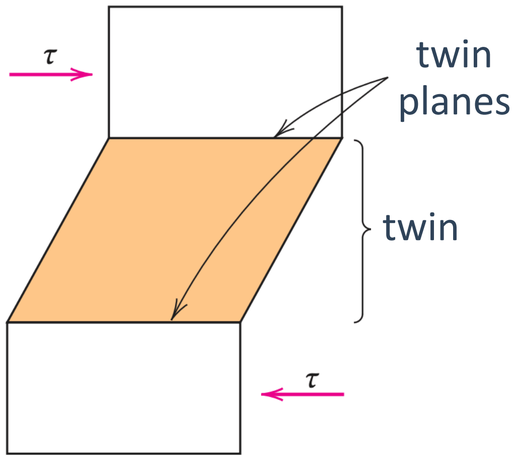
$$\tau = \sigma_y \cos(\phi)\cos(\lambda)$$

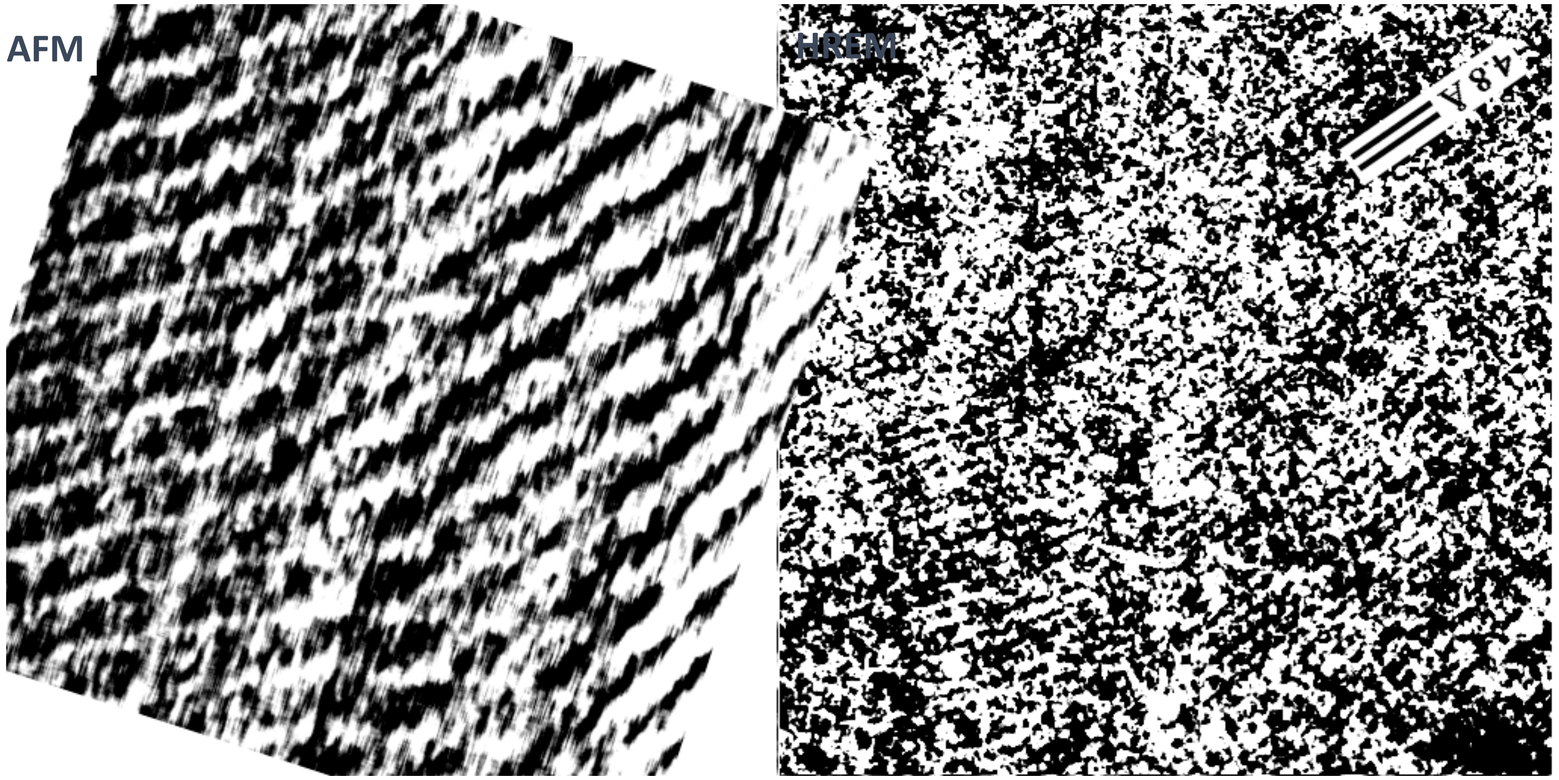


- leads to self-reinforcement: strain hardening partly due to crystallographic realignment & chain stretching

Oriented Polymers

- at very large deformations, nearly parallel chain alignment
- very high tensile strength, high toughness in fibers





- oriented polymers can show significant plasticity in compression (i.e. by twinning)
- explains superior impact resistance of polymer fibers compared to glass or carbon fibers

Learning Outcome

- yielding usually defined as the point where the slope of the stress-strain curve becomes zero during the deformation of glassy or semicrystalline polymers. This often results in the formation of a stable neck at a given draw ratio which is a materials parameter, characteristic of the entanglement network.

- the yield strength decreases roughly linearly with T and decreasing deformation rate under certain conditions, in accordance with the simple Eyring rate theory. However, the yield behavior is also strongly influenced by the presence of sub-T_g relaxations, in some cases providing a link between yielding and molecular structure.

- semicrystalline polymers modelled in terms of crystallographic slip for $T > T_g$. For a constant degree of crystallinity, σ_y increases with lamellar thickness l. Thus, in general, polymers crystallised at higher temperatures have higher yield stresses.