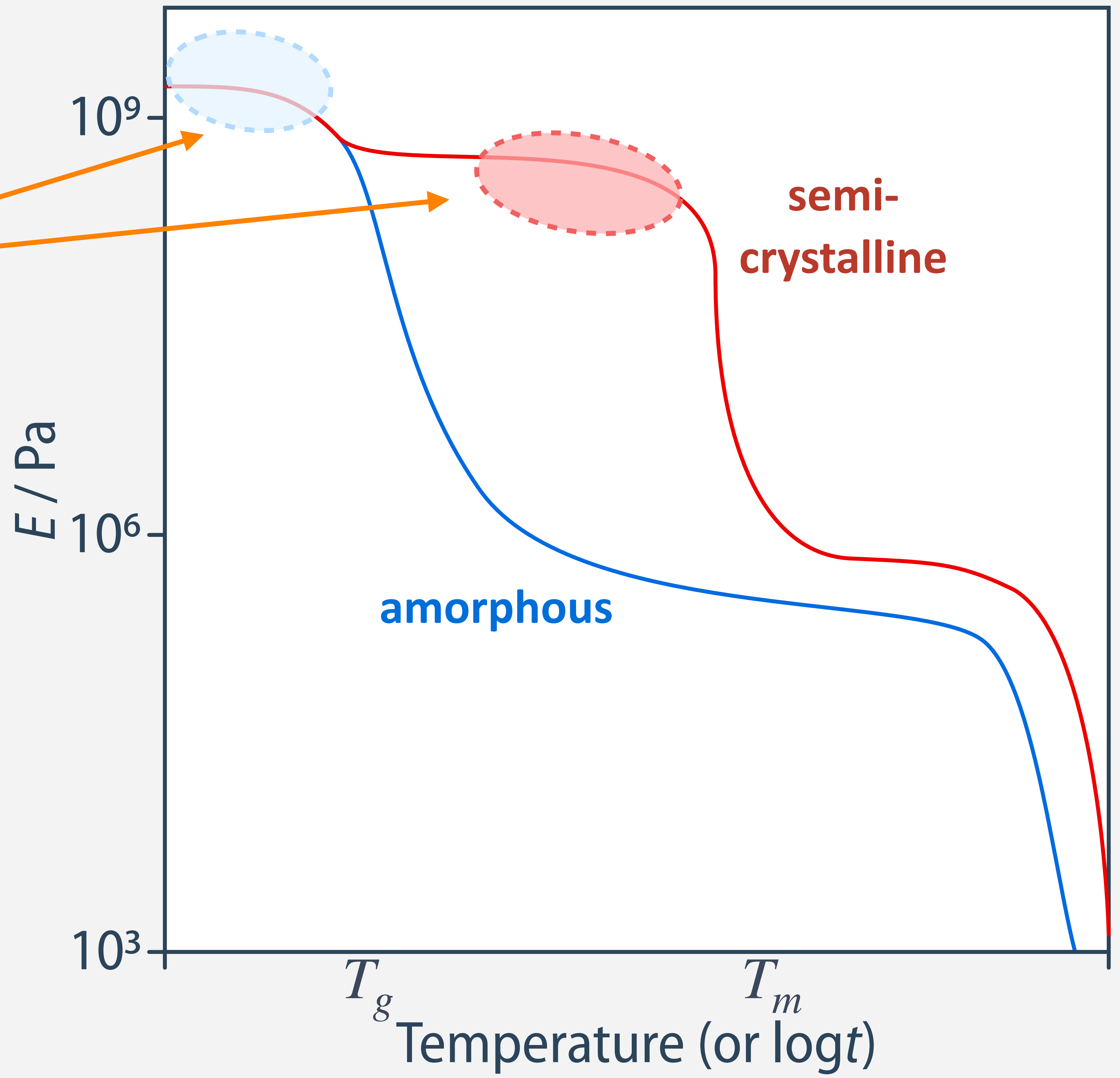
5.3
Yield and Crazing

Small Deformations in the Solid State

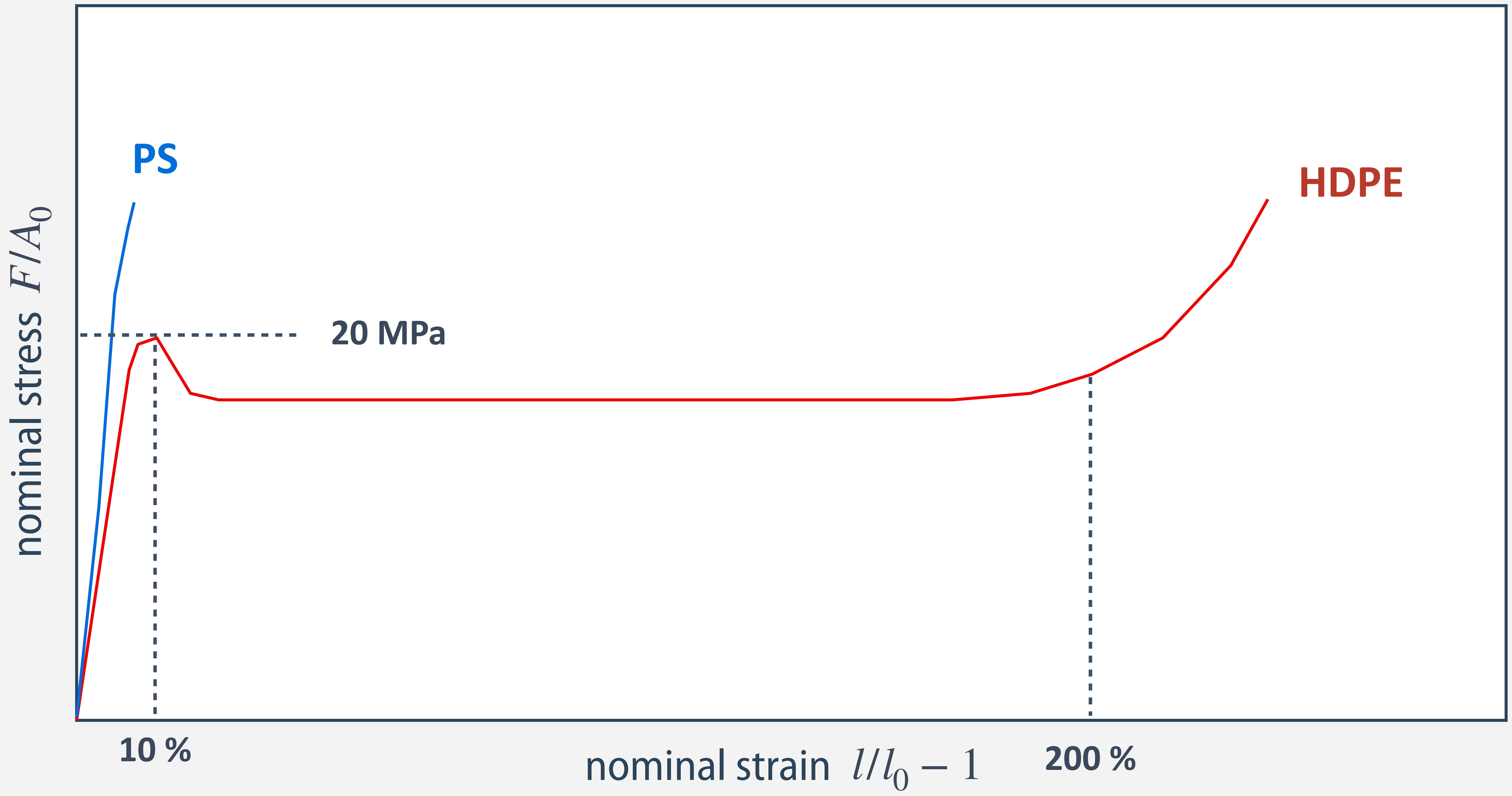
- **in the "rigid" solid state ($T < T_g$, $T < T_m$), conformational changes are restricted**
- **for small deformations, elasticity is dominated by intermolecular forces**
  (for large deformations (or stresses), this is not valid anymore)

what is happening here, if we pull very strongly?



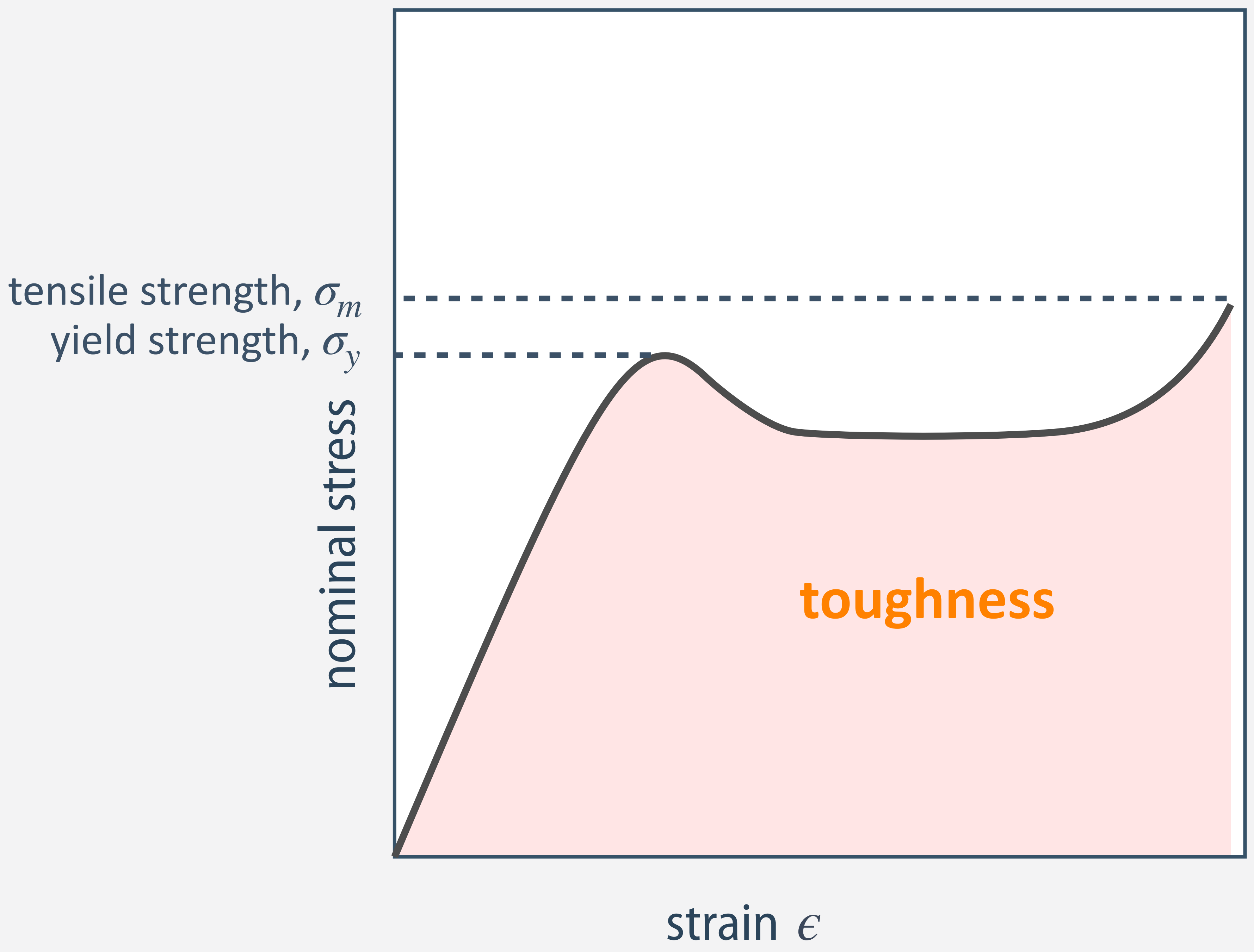
Brittle vs. Ductile Behavior

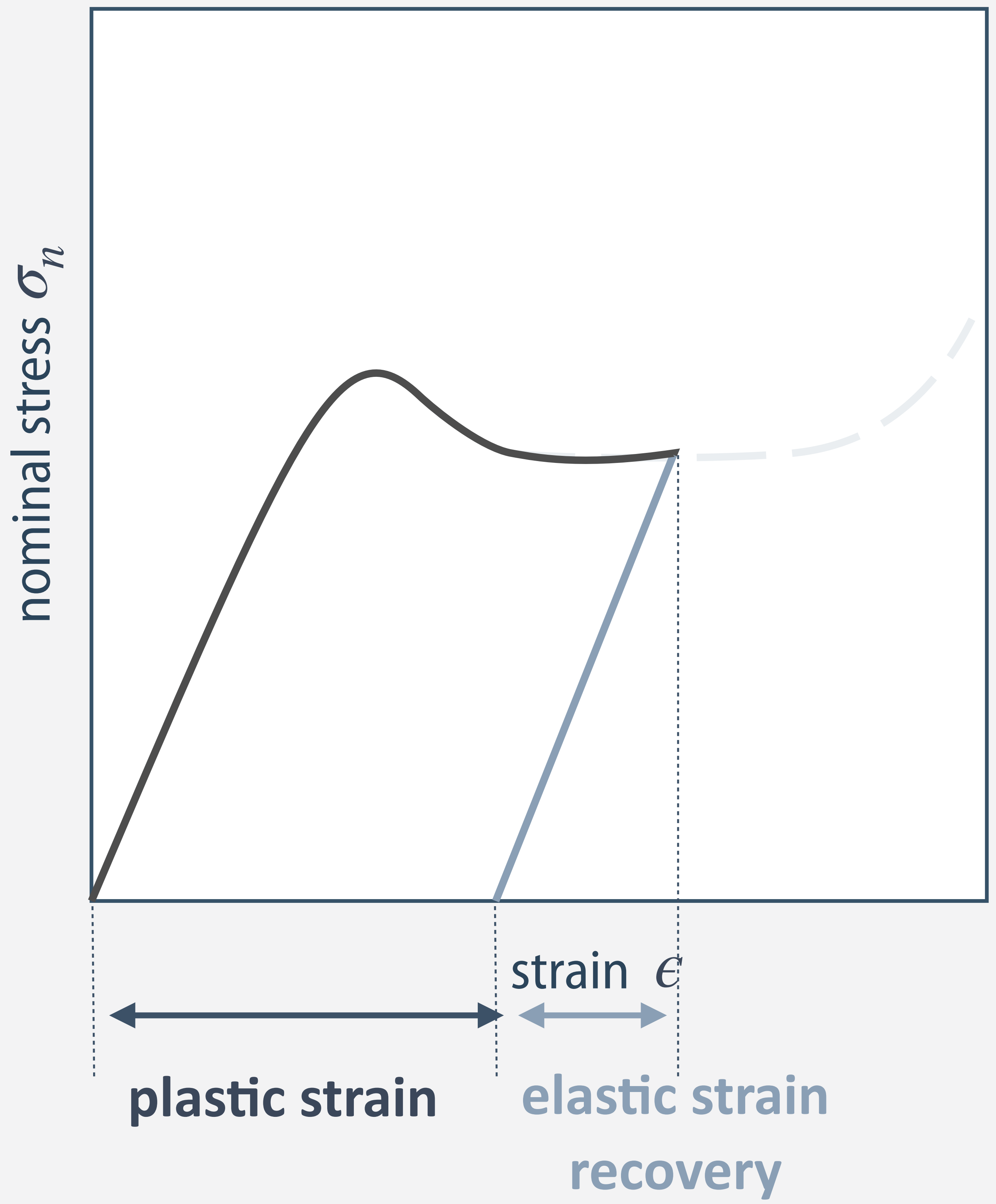
- **polymers are generally considered as "plastic", i.e. capable to undergo large "irreversible" deformations in the solid state (glassy or semicrystalline)**; for some that is more true, but for others to lesser extent…
- typical tensile curves of a brittle (PS) and a ductile (HDPE) material



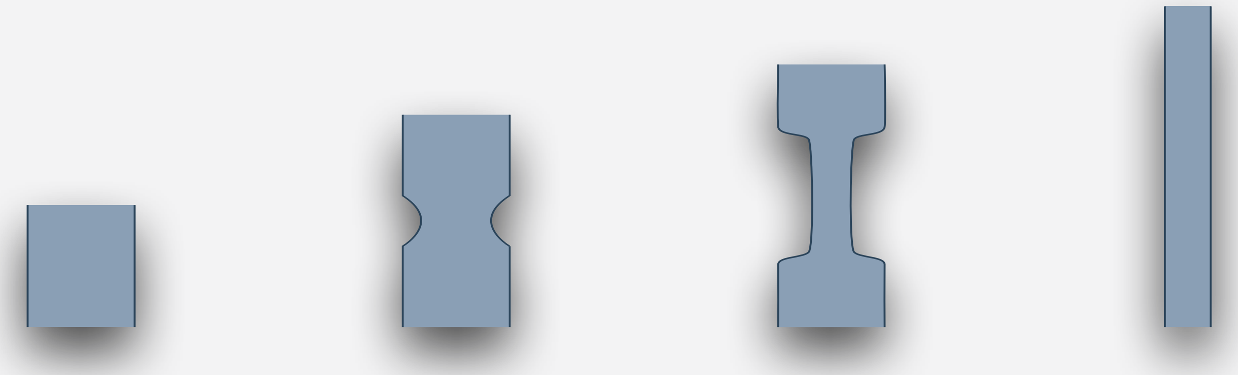
Characterisation of Plasticity

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





typical strain-dependent specimen shape:

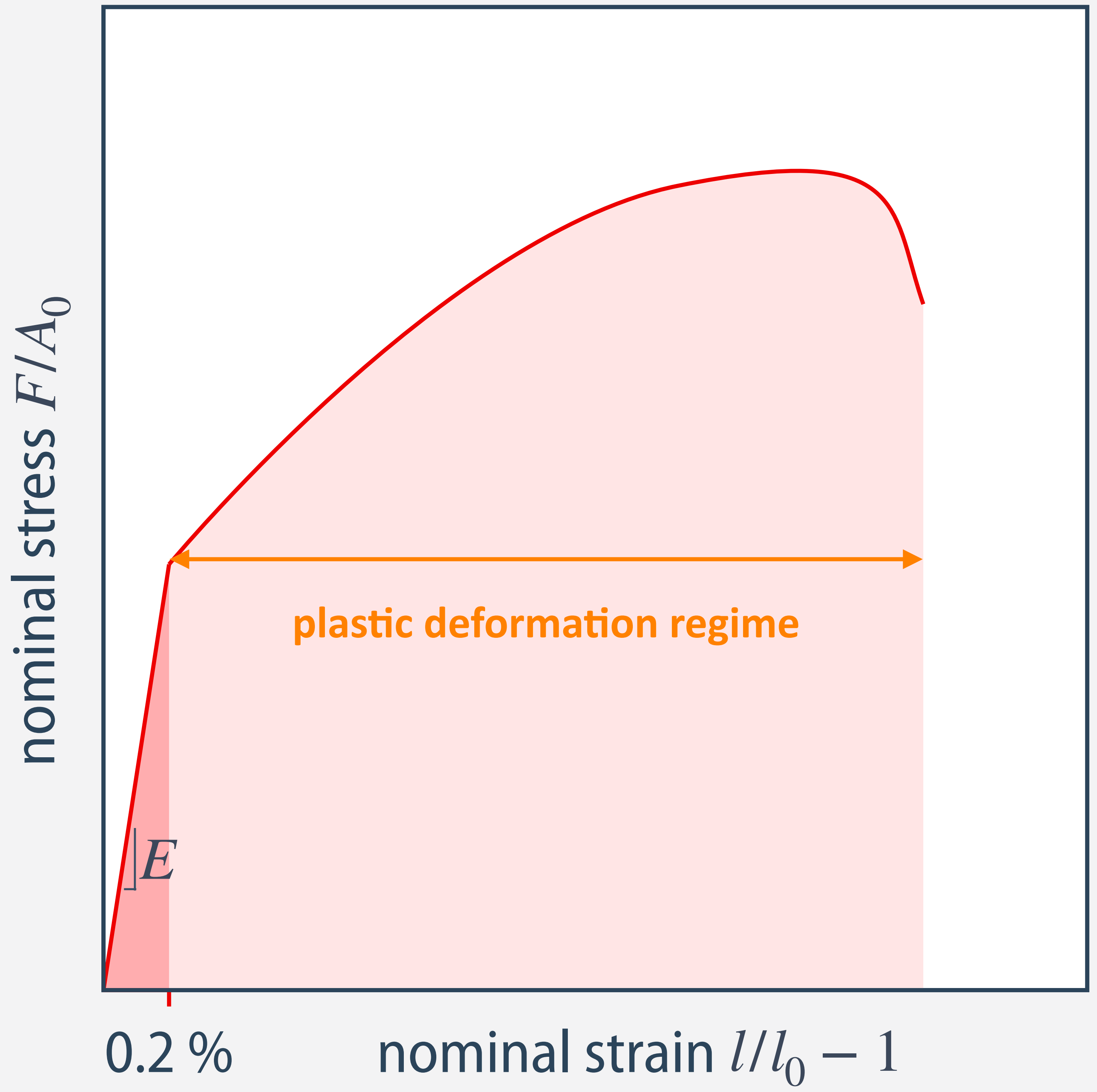


- **for sufficiently ductile materials, “onset” of plastic deformation is indicated by necking**
- **stress release often does not return the specimen into it’s original shape**

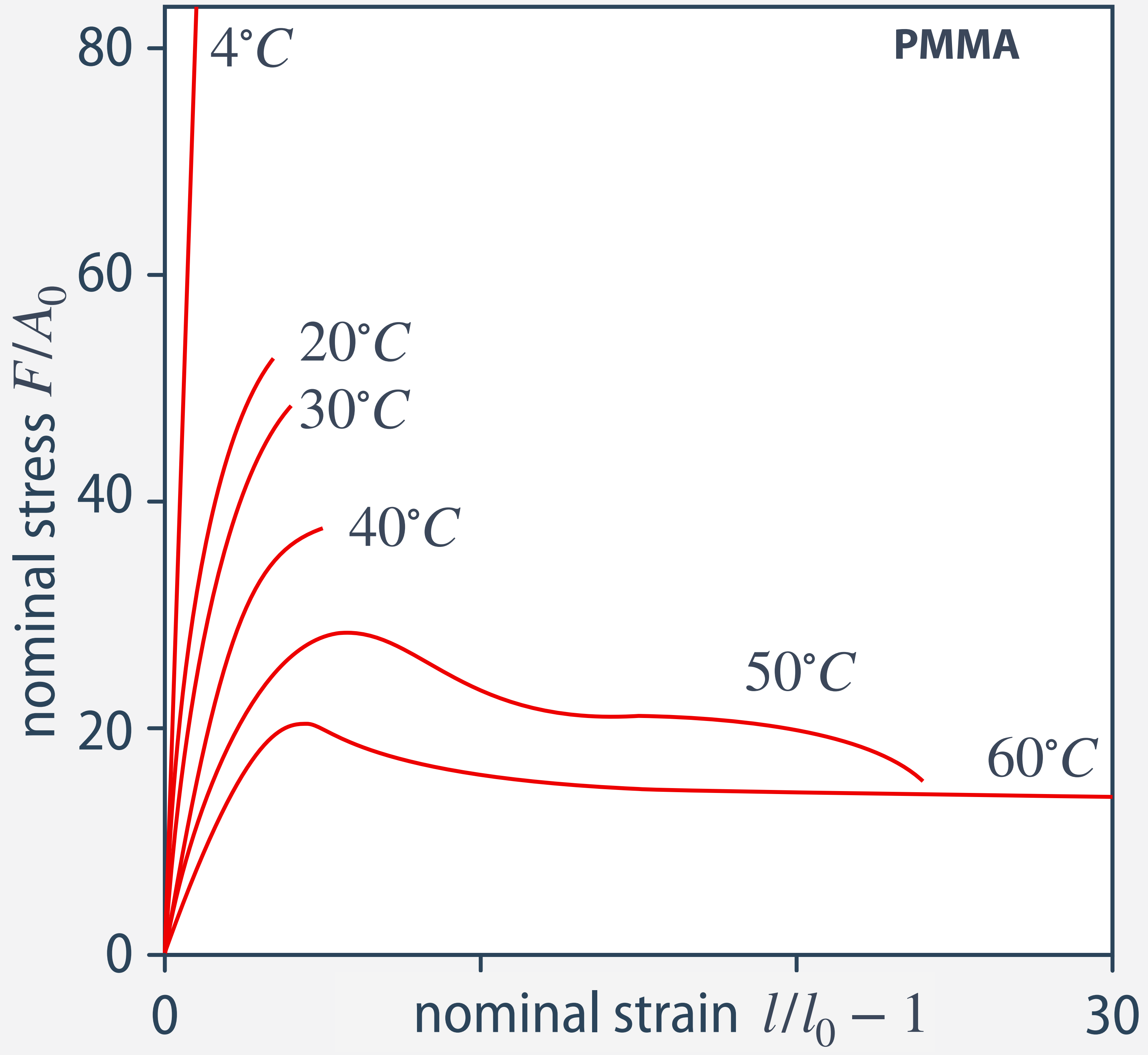
Metals vs. Polymers

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

metals



polymers



- clear distinction between elastic (reversible) and plastic (irreversible) deformation
- at operating temperature: little influence of T and $d\epsilon/dt$; little heat dissipation
- often ill-defined necking

- even very large deformations (up to 100 %) can be recovered, e.g. by heat treatment above T_g
- at operating temperature: strong influence of T and $d\epsilon/dt$; strong heat dissipation
- often well-defined necking at a given strain rate

Phenomenology of Polymer Plasticity

Importance of Plasticity

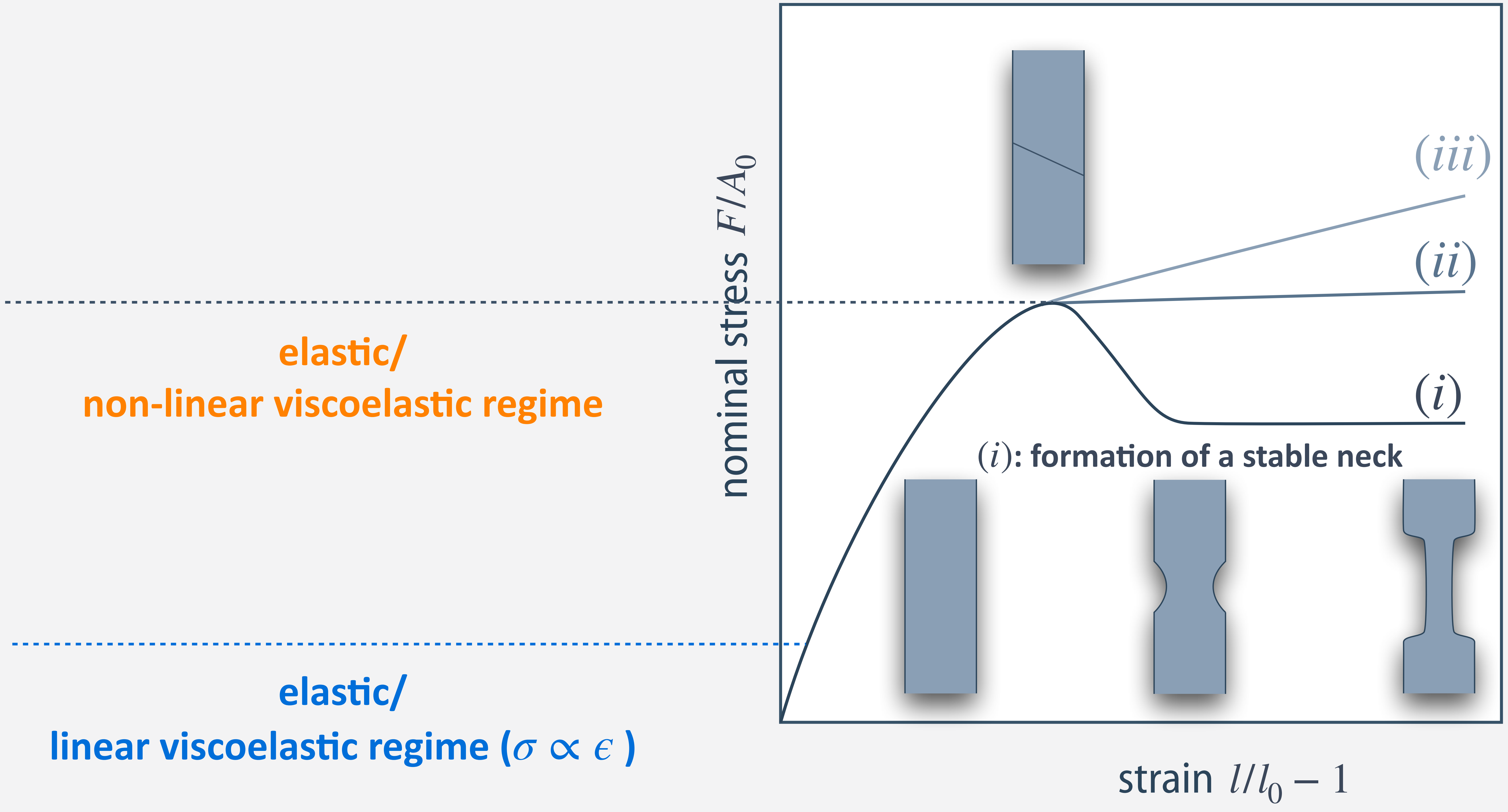
- plastic deformation is a highly dissipative process

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

- good crack resistance of ductile materials (it takes a lot of energy to advance a crack)

Yield Strength

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



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

Geometric Considerations of Necking

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

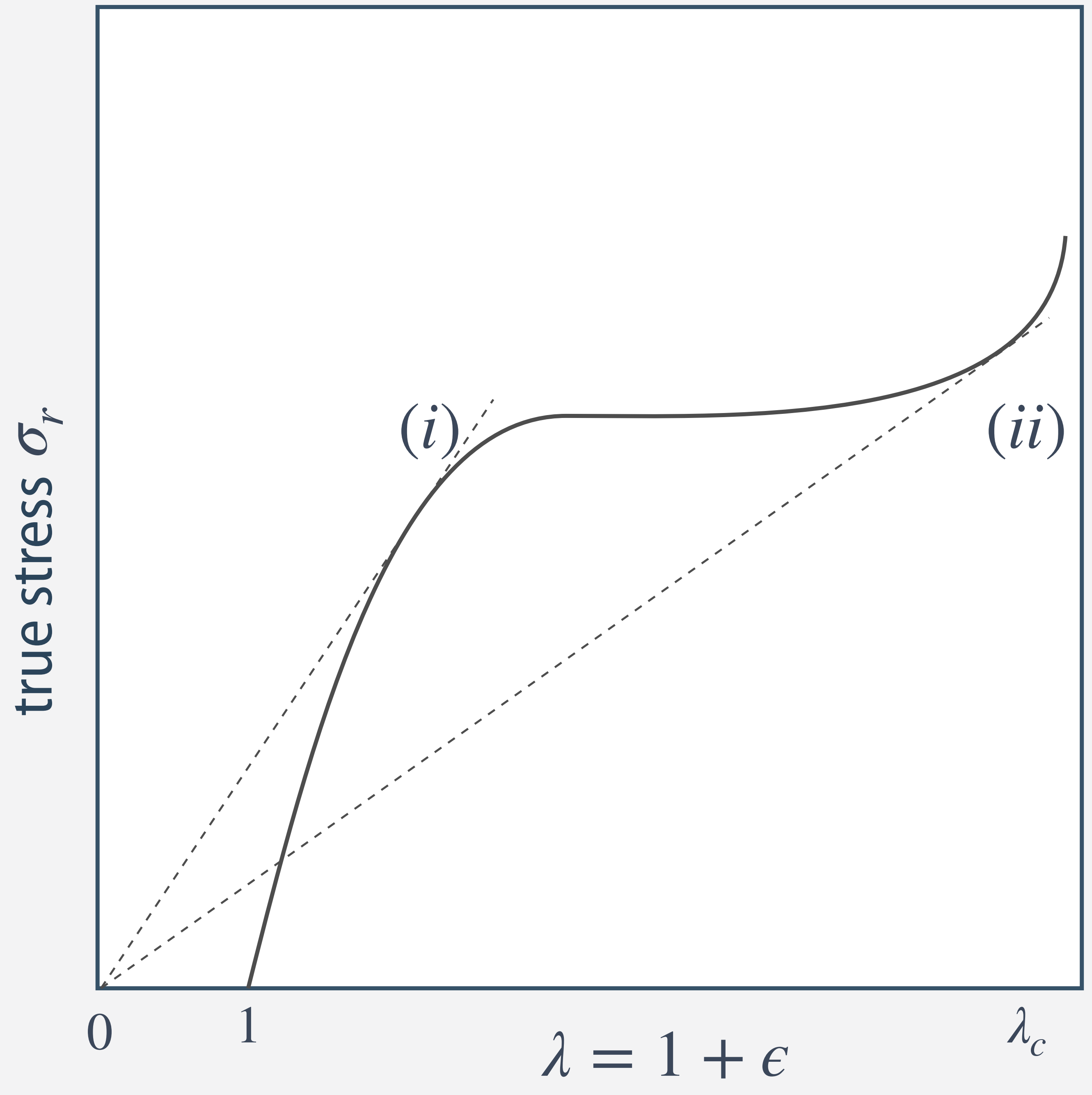
true stress: $\sigma_r = \dfrac{f}{A}$

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

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

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

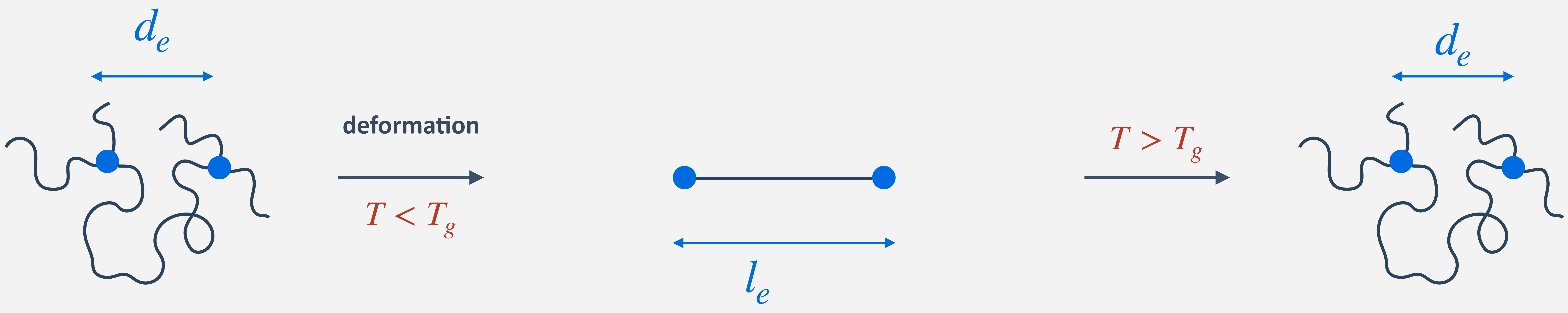
thus, for the yield point: $\dfrac{d\sigma_n}{d\lambda} = 0 \quad \Rightarrow \quad \dfrac{d\sigma_r}{d\lambda} = \dfrac{\sigma_r}{\lambda}$



- **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 ($d\sigma_n/d\lambda < 0$) compensated for by necking**

Role of Entanglements for λ_c

- **excellent correlation between λ_c and the maximum extension, λ_{max}, of an entangled network**



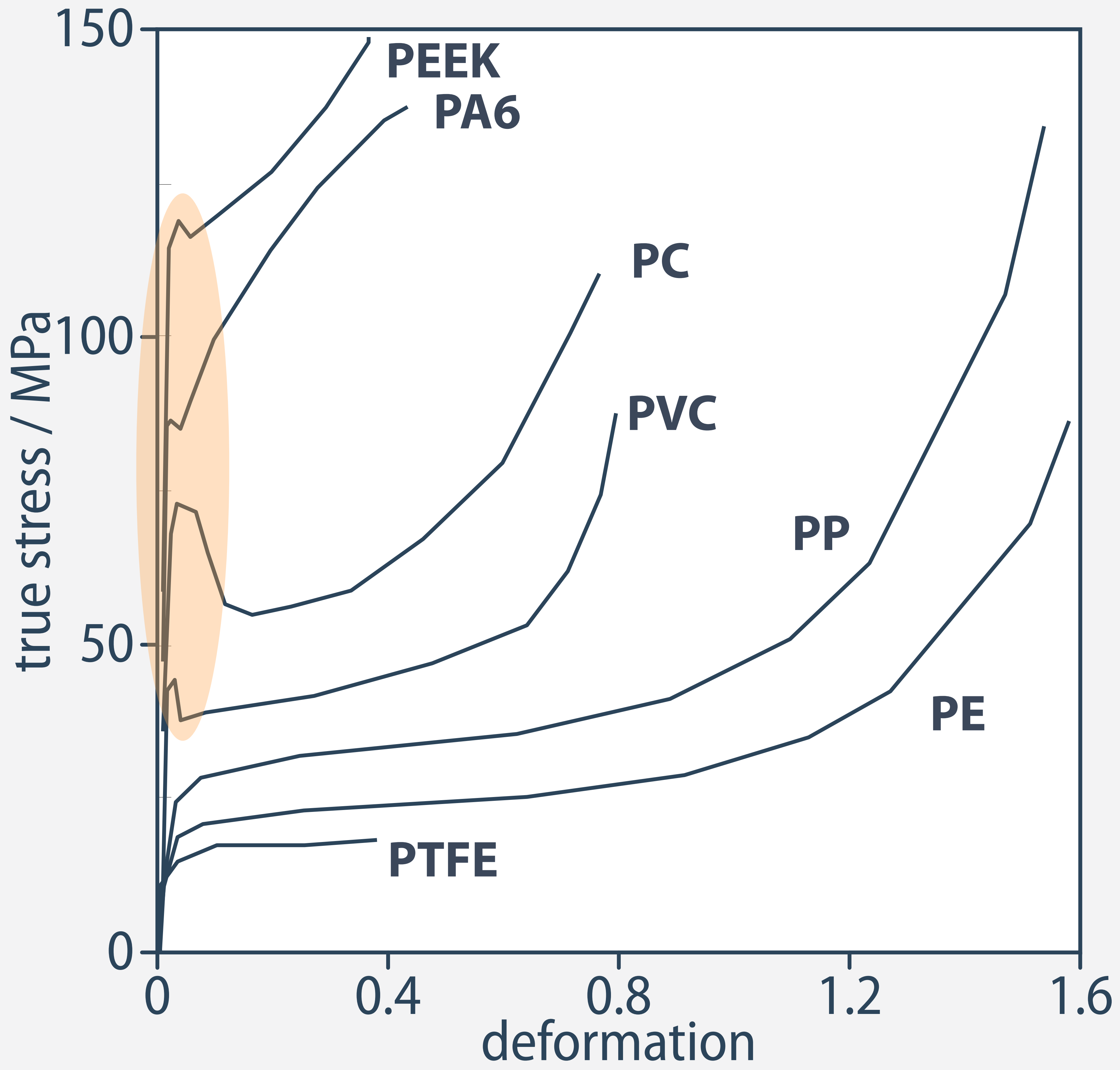
$$l_e \sim \frac{M_e}{M_b} l \qquad < d_e >^2 = C_\infty \frac{M_e}{M_b} l^2 \qquad \lambda_{max} = \frac{l_e}{d_e} \sim \sqrt{\frac{M_e}{M_b C_\infty}} = \sqrt{\frac{N_e}{C_\infty}}$$

M_b: molar mass per constitutive repeating unit $\quad$ l: bond length

- **the plastic deformation is therefore stabilised by entanglement, particularly for glassy polymers.**
- **in the rubbery state (above T_g), even large deformations are reversible as long as no disentanglement takes place.**
- **for $M < 2M_e$, plastic deformation is no longer stabilised ($\Rightarrow$ brittle behavior)**

Physical Aging as Origin of Yield Drop

- **true stress-strain curves of common ductile polymers at 25 °C tested under tension:**

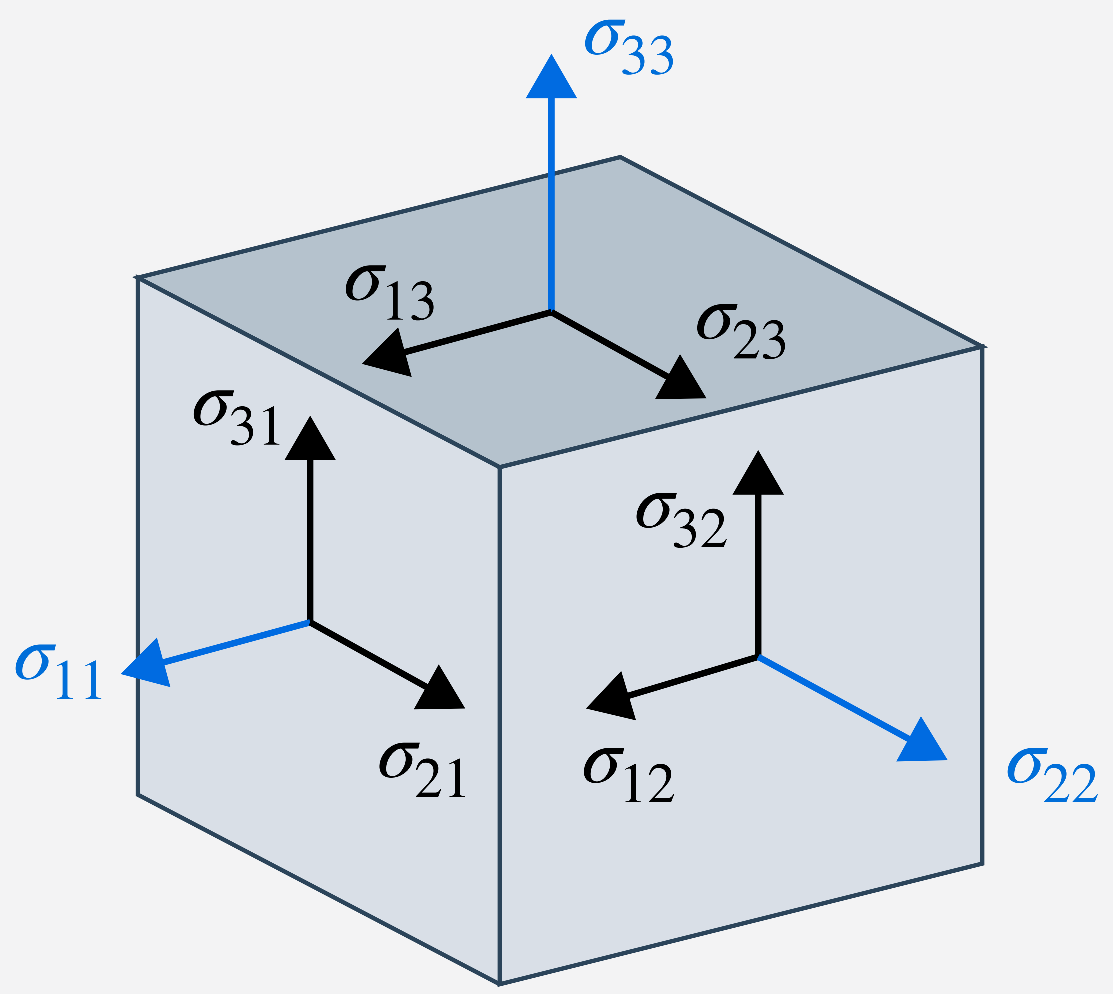


- **the intrinsic yield drop observed for glassy polymers is due to physical ageing**

  (more pronounced after heat treatment at a few K below T_g)

Von Mises Yield Criterion

- **assumption: deformation via shear characterised by normal stresses σ_1 , σ_2 , σ_3**

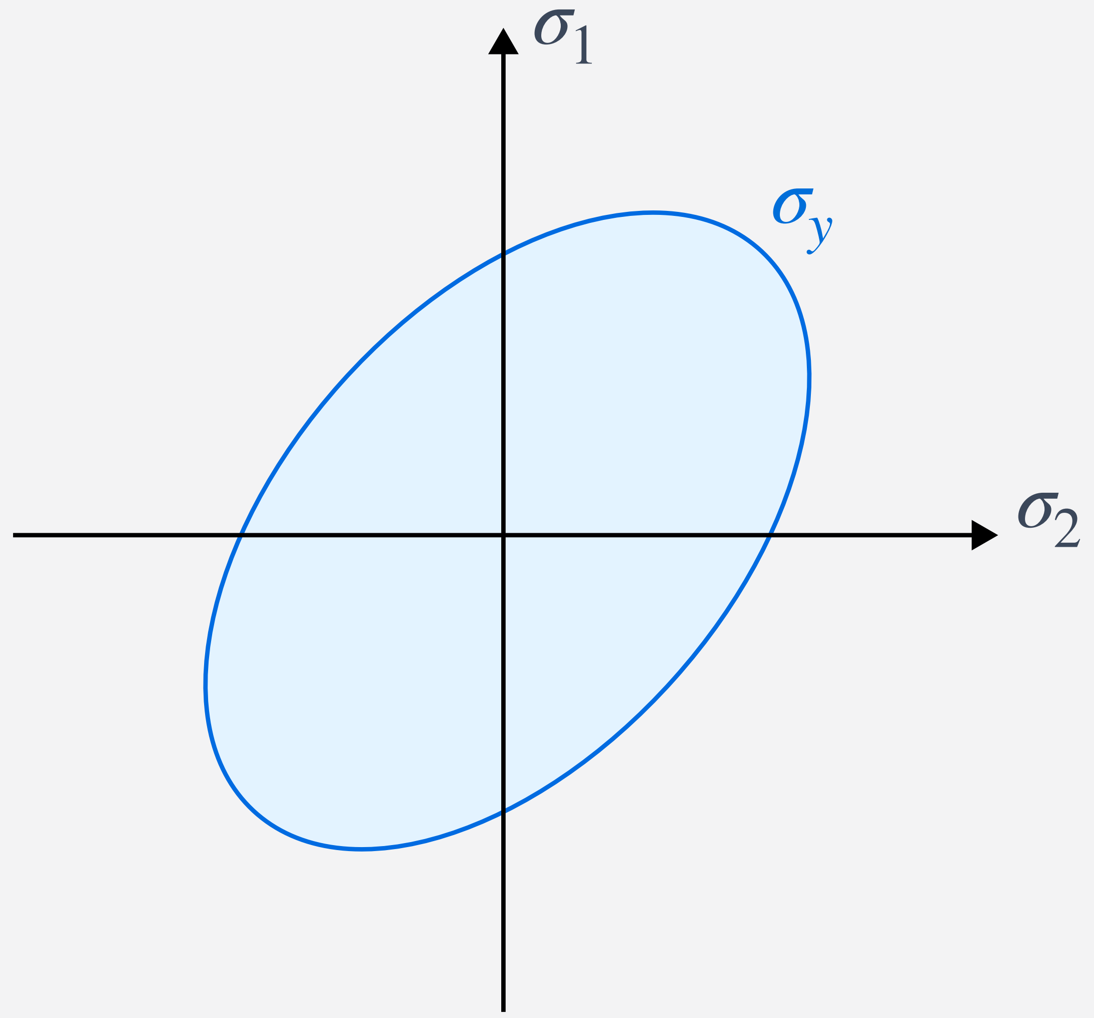


stress tensor

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

$$\equiv \begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

biaxial stretching

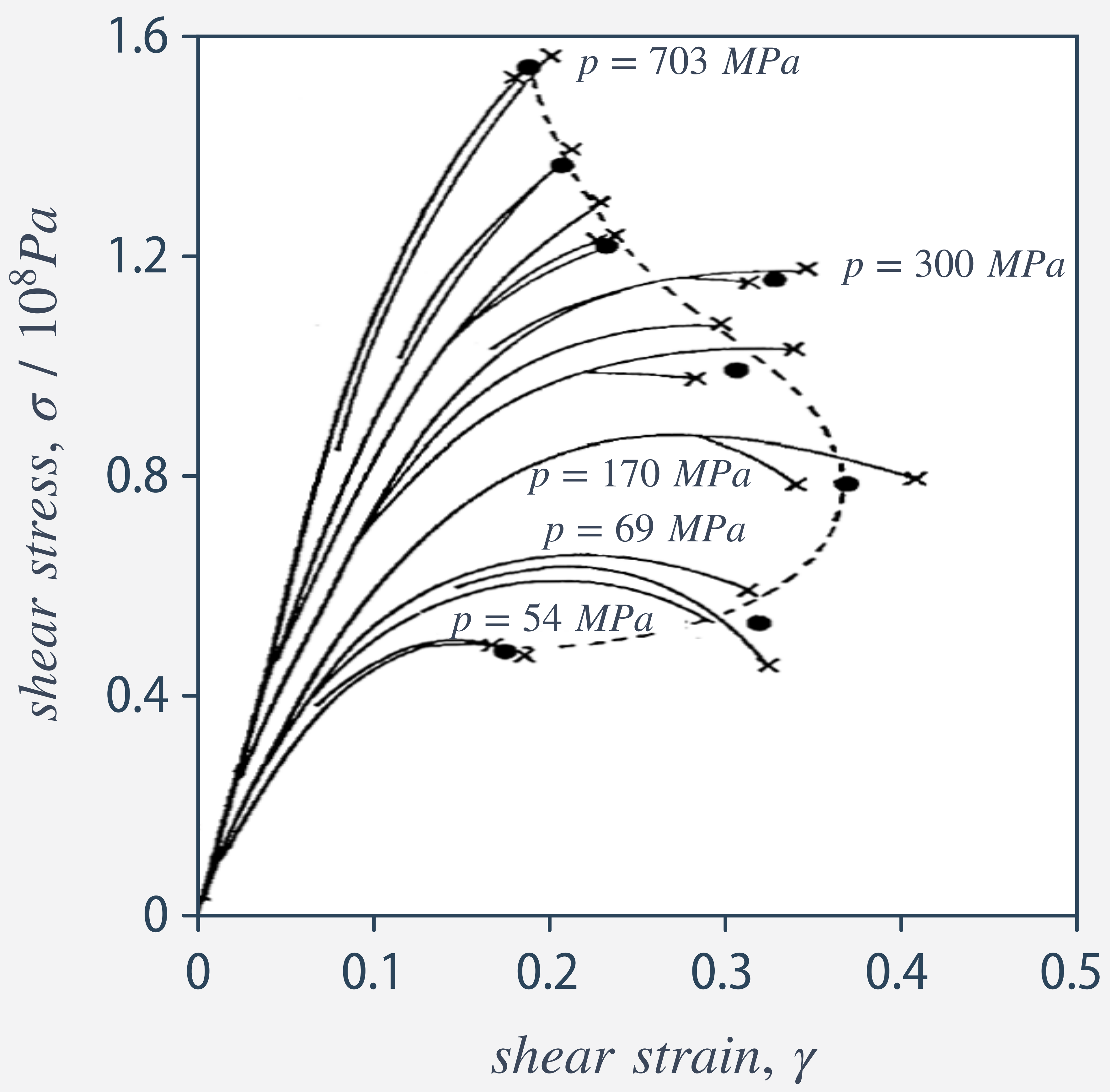


Von Mises criterion: $(\sigma_{11}-\sigma_{22})^2+(\sigma_{22}-\sigma_{33})^2+(\sigma_{33}-\sigma_{11})^2+6(\sigma_{12}^2+\sigma_{13}^2+\sigma_{23}^2) \geq 2\sigma_y^2$

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

- **in metals, σ_y is approximately constant and the von Mises criterion applies**
- **in polymers, σ_y varies with hydrostatic pressure (at constant T and $d\epsilon/dt$)**

- pressure effect on tensile curves of PMMA:



hydrostatic pressure:

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

assumption of a linear dependence:

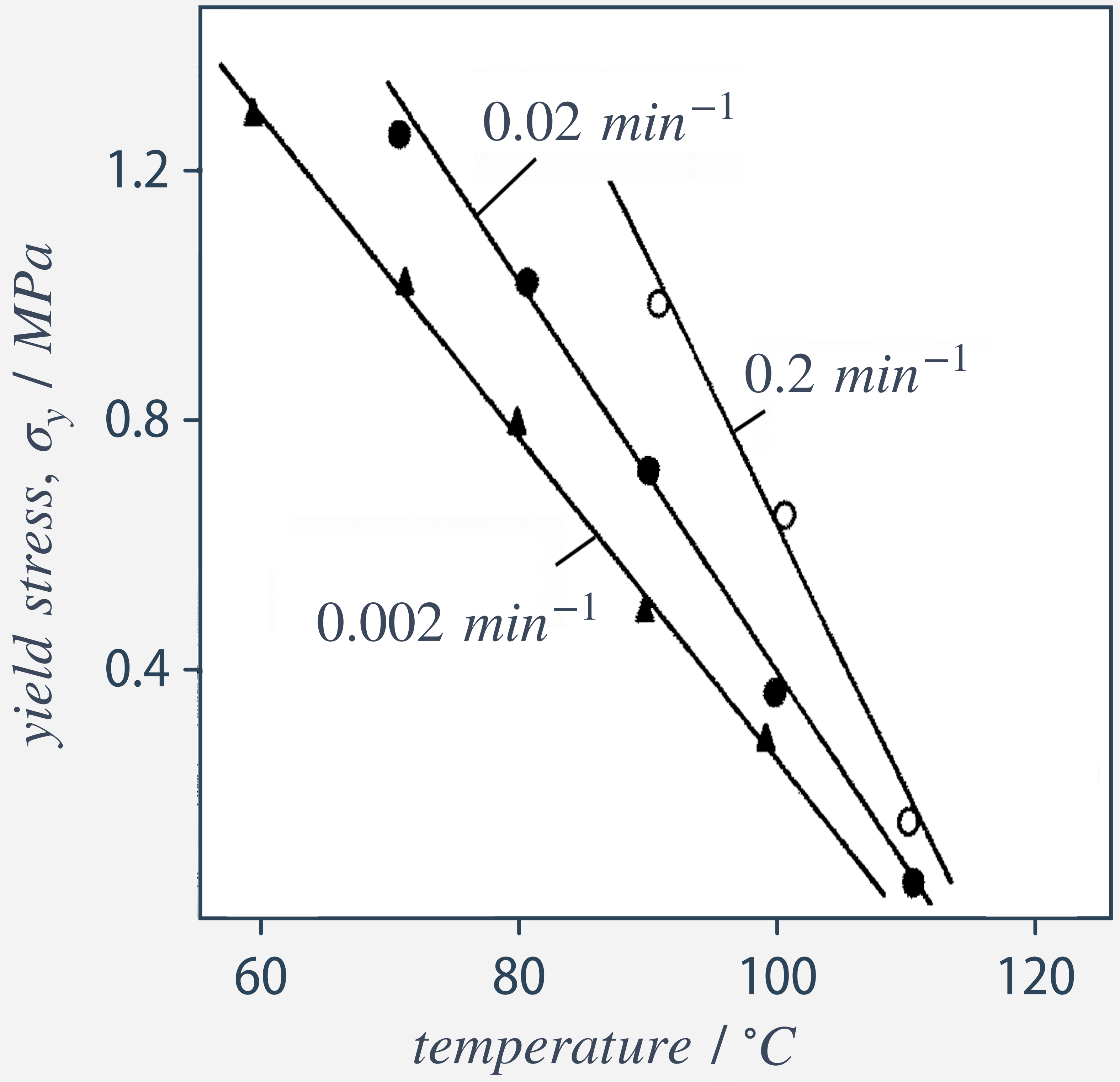
$$\sigma_y = \sigma_{y0} + \mu p$$

- significant volume changes upon pressurisation (much lower K than for metals)

Models

Effect of Temperature and Strain Rate

- plasticity can be thermally activated
- σ_y becomes approximately zero as the glass transition temperature is approached



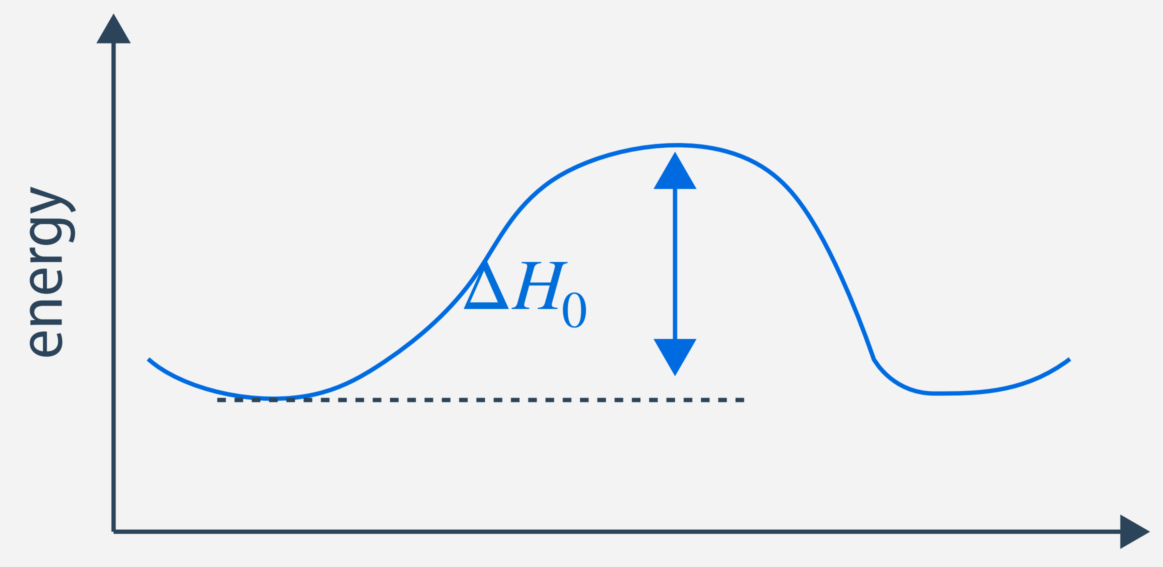
PMMA

- like viscoelasticity, plasticity is strongly influenced by temperature and strain rate

Eyring Model

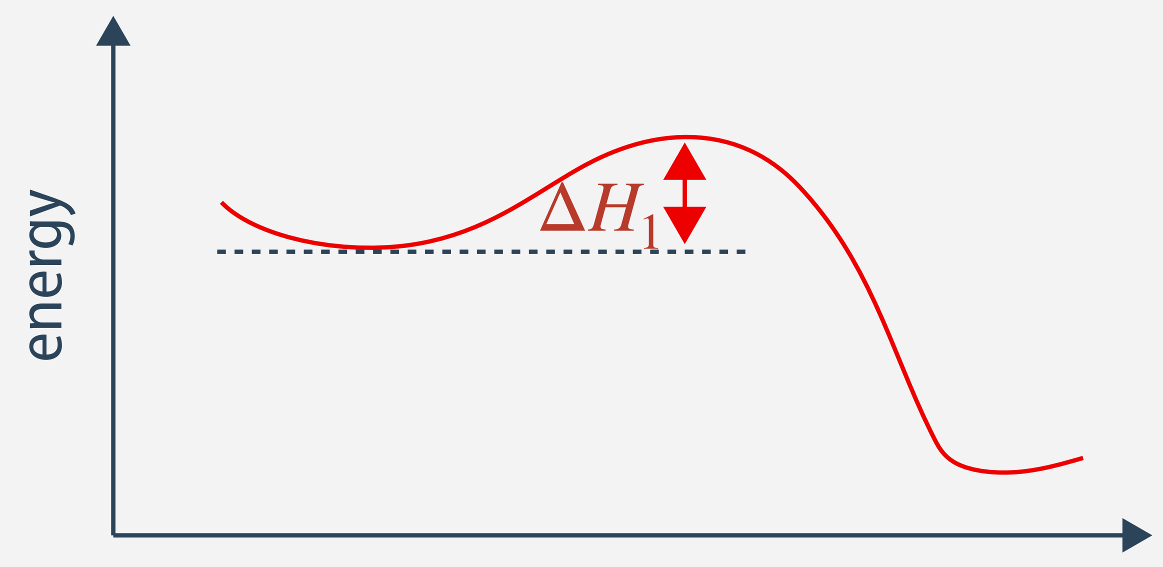
- description of translational movement by an activation barrier ΔH, that is reduced for segments moving into the direction of an applied stress

undeformed



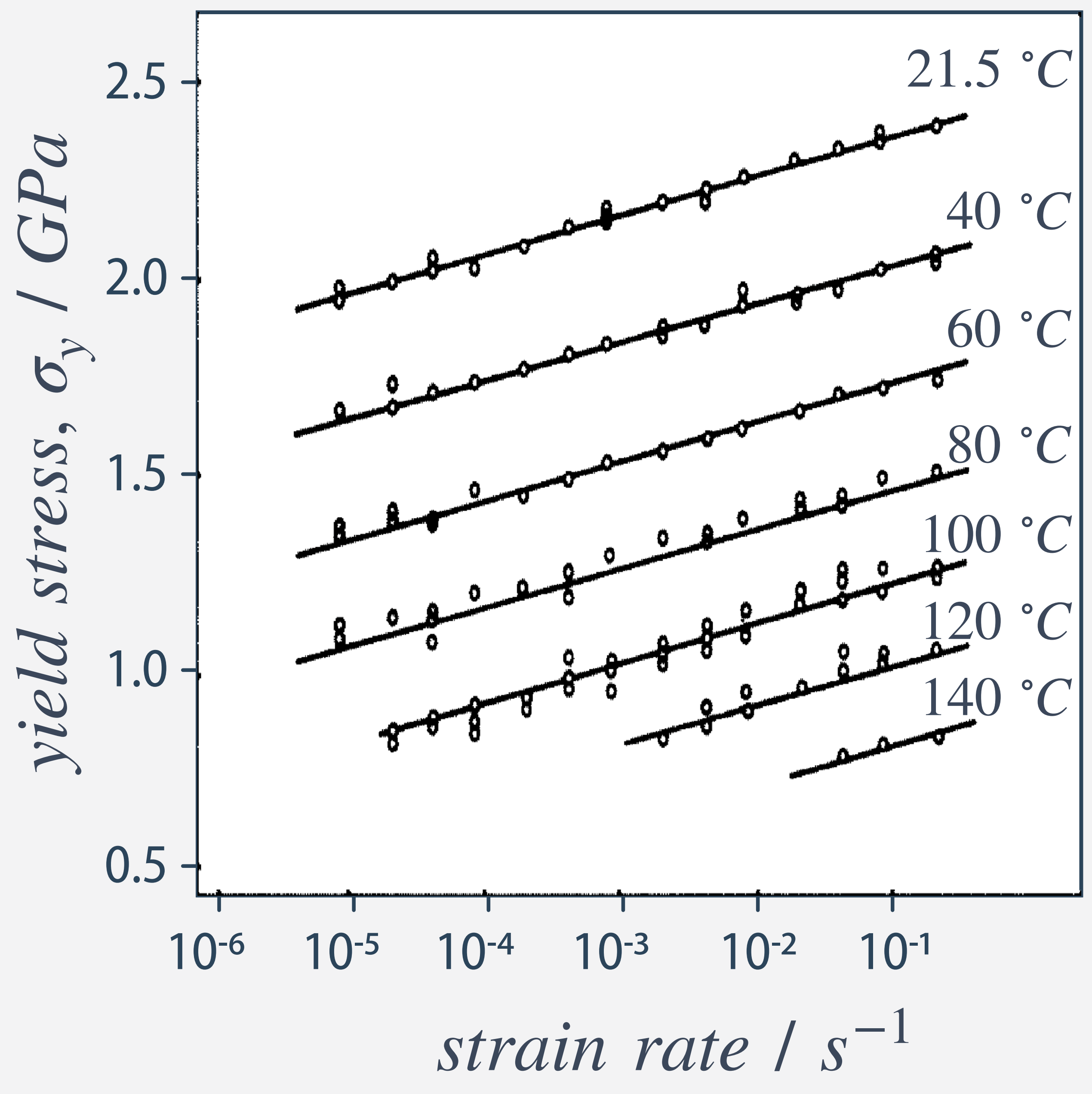
$$\dot{\epsilon} = \dot{\epsilon}_0 e^{-\frac{\Delta H - \sigma V^*}{kT}}$$

deformed



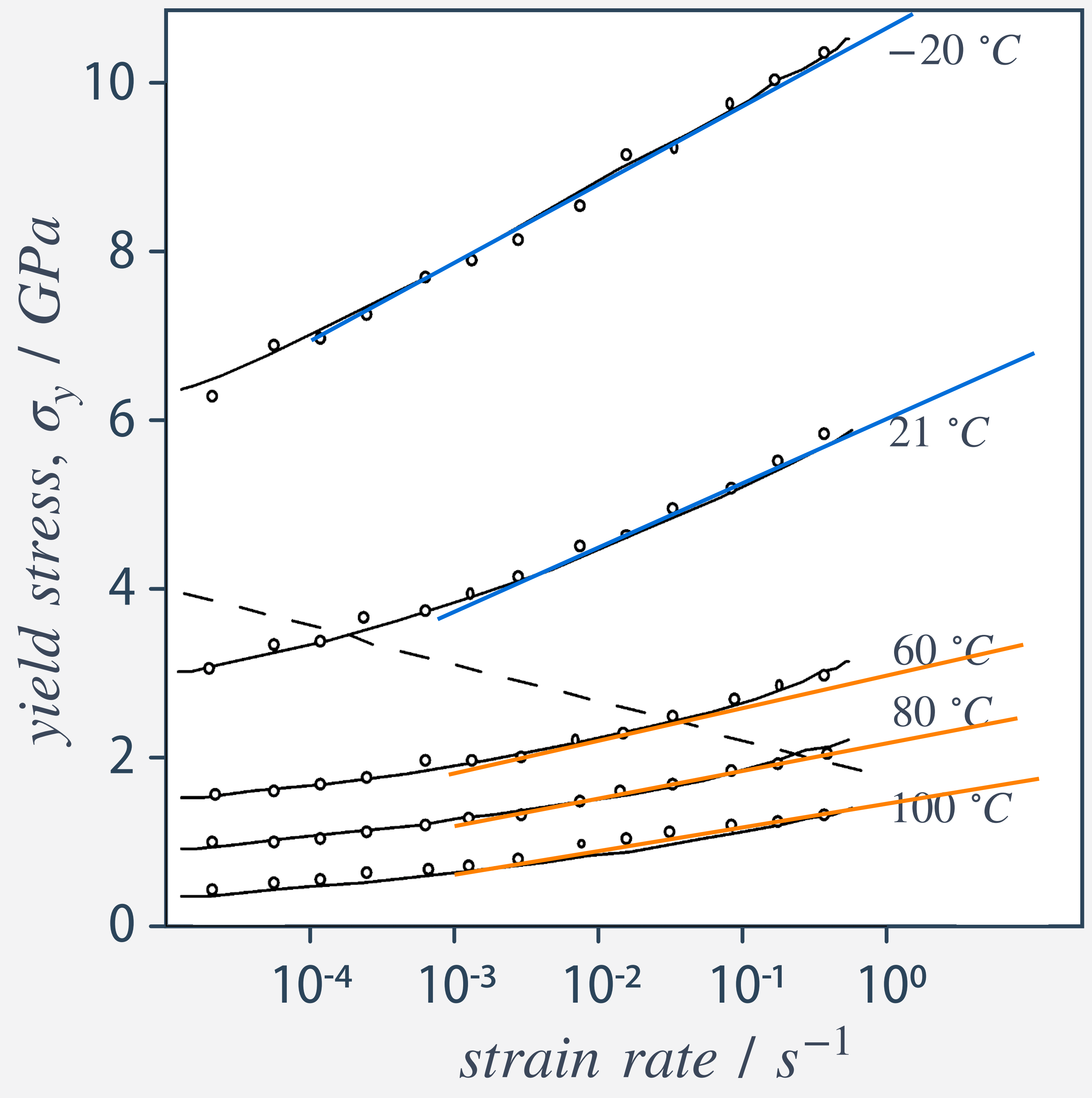
$$\sigma_y = \frac{\Delta H}{V*} + \frac{kT}{V*} ln \frac{\dot{\epsilon}}{\dot{\epsilon}_0}$$

example: PC



- segments from multiple monomers (typically between 2 and 10 for most glassy polymers) are involved in plastic deformation ($V^* \approx 6.4\ nm^3$ for PC)

- in PC, there is no major secondary relaxation between 20 °C and T_g
- in contrast, PVC displays a strong β-relaxation at around 50 °C



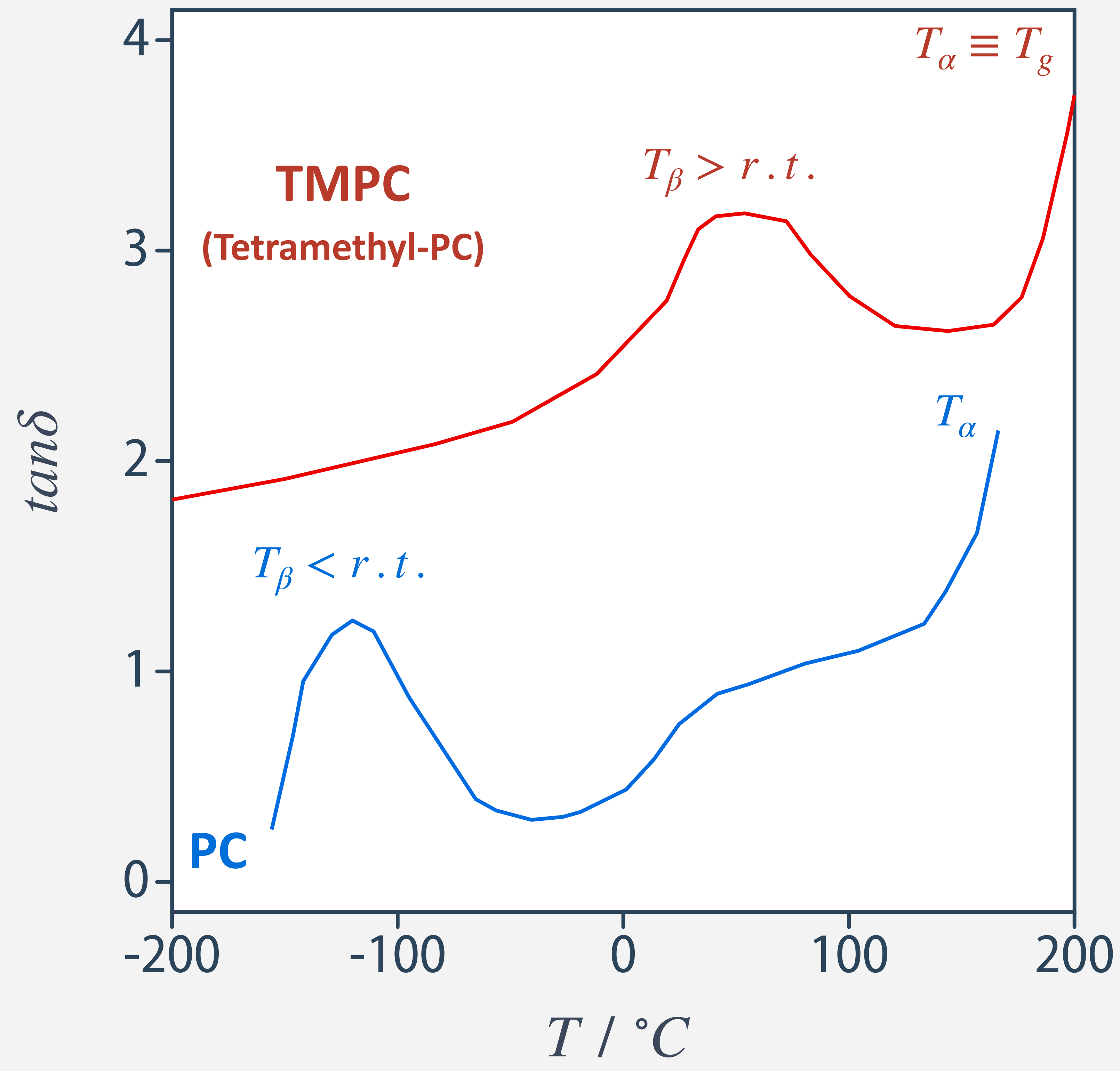
example: PVC

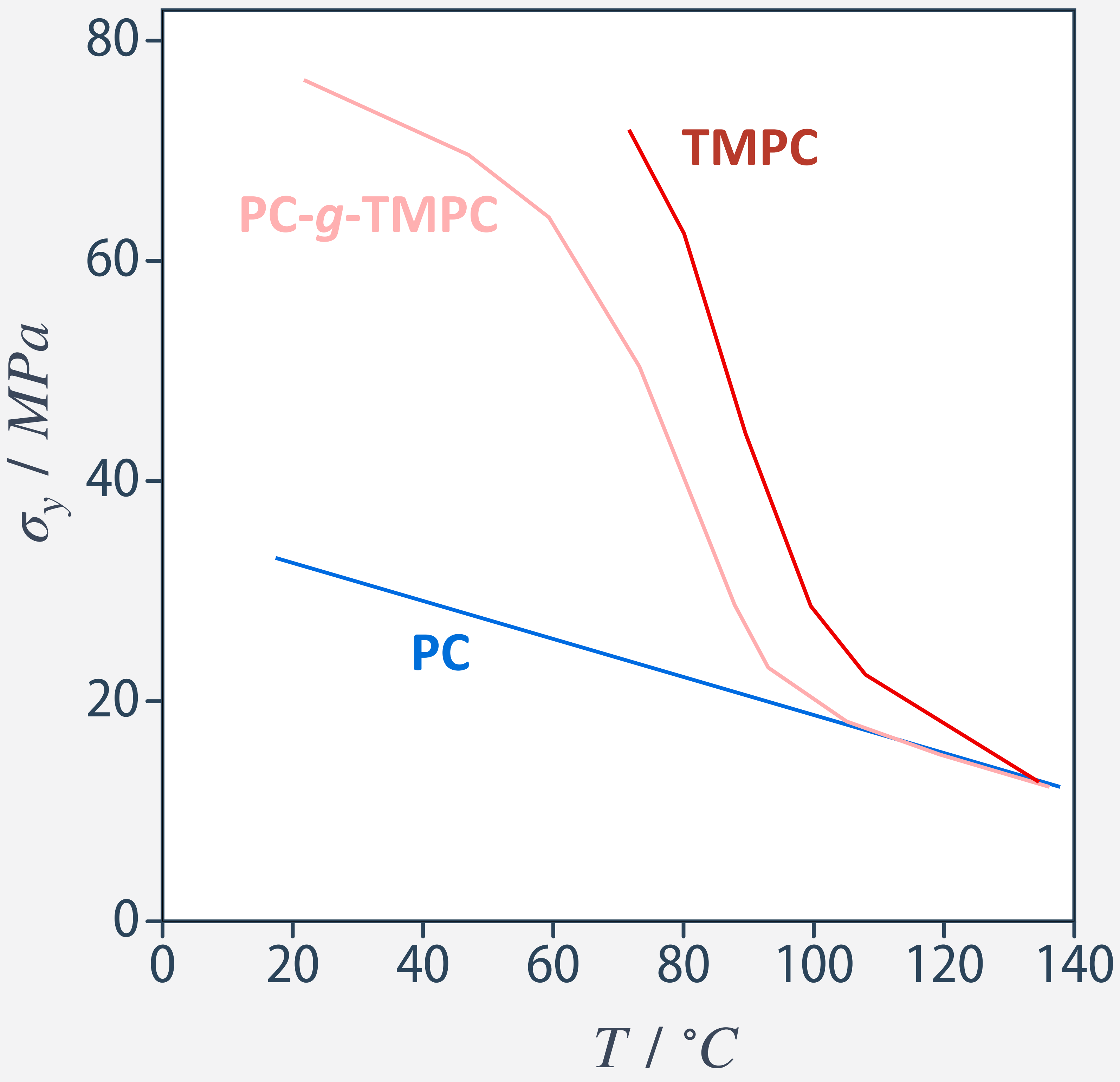
pronounced change in slopes at around 50 °C.

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

Influence of Secondary Transitions

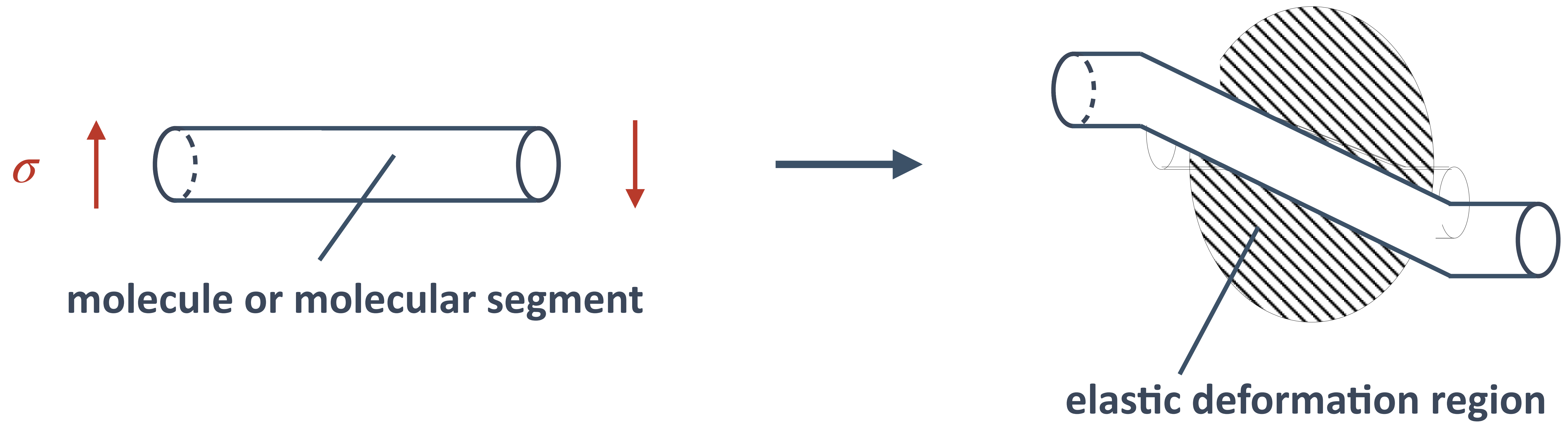
- polymer conformations are not entirely frozen below T_g, but can occur on a highly local level, thus accounting for ductile behavior as compared to inorganic glasses





- the activation of movements corresponding to secondary transitions facilitates plastic deformation ("lubricating" effect)

- **formally similar to the Eyring model - an intermolecular interpretation of the energy barrier:**



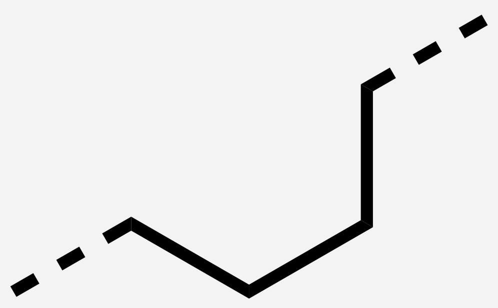
$$\sigma_y = \sigma_0 \left[1 + \frac{16(a - v)}{3\pi G \beta^2 \alpha^3} kTln\left(\frac{\dot{\gamma}}{\dot{\gamma}_0}\right) \right]^{6/5}$$

- **G is the shear modulus of the "matrix" which surrounds the deformed "molecule".**
- **"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

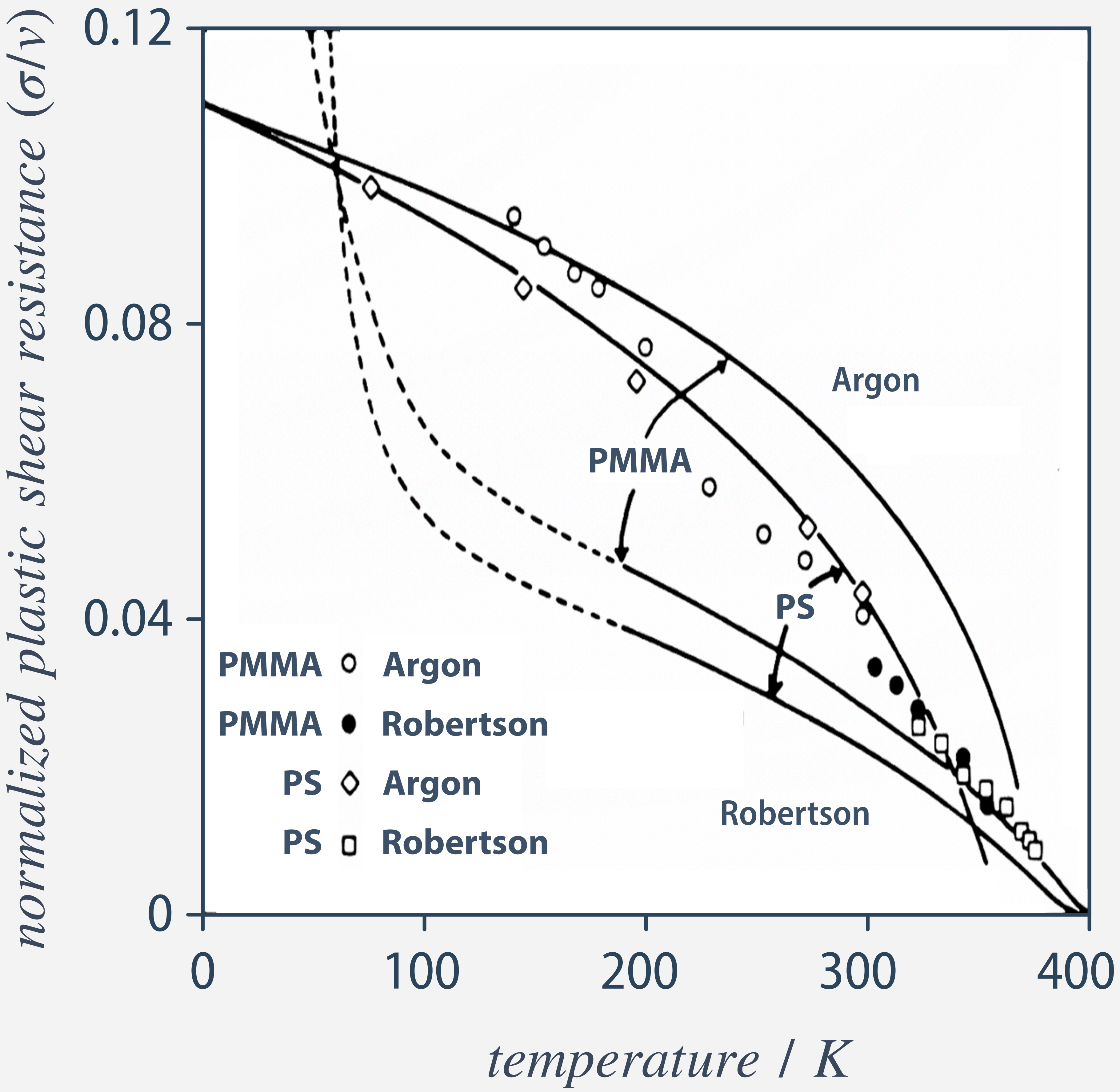
- without stress, the proportion χ of *cis* states depends on the temperature
- at sufficiently high stress, the proportion of *cis* states is comparable to that in the liquid state and allows us to put stress ($T < T_g$) and viscosity ($T > T_g$) into relation:

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

- the viscosity can be determined by the WLF approach

Comparison of Argon and Robertson with Experimental Data

- **both models do not work over the full temperature range:**
  Argon better describes low temperature behavior ($T \ll T_g$), Robertson the behavior close to T_g



- **limitations: Secondary relaxation is not taken into account.**

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!)

- another class of models is based on numerical simulations of molecular dynamics (in particular by Suter and collaborators at ETHZ - see: vitreous state model)

- limited by the IT resources available, i.e. to low volumes (small number of segments) and short times (picoseconds). Promising nonetheless…

Semicrystalline Polymers

Yield Strength in Semicrystalline Polymers

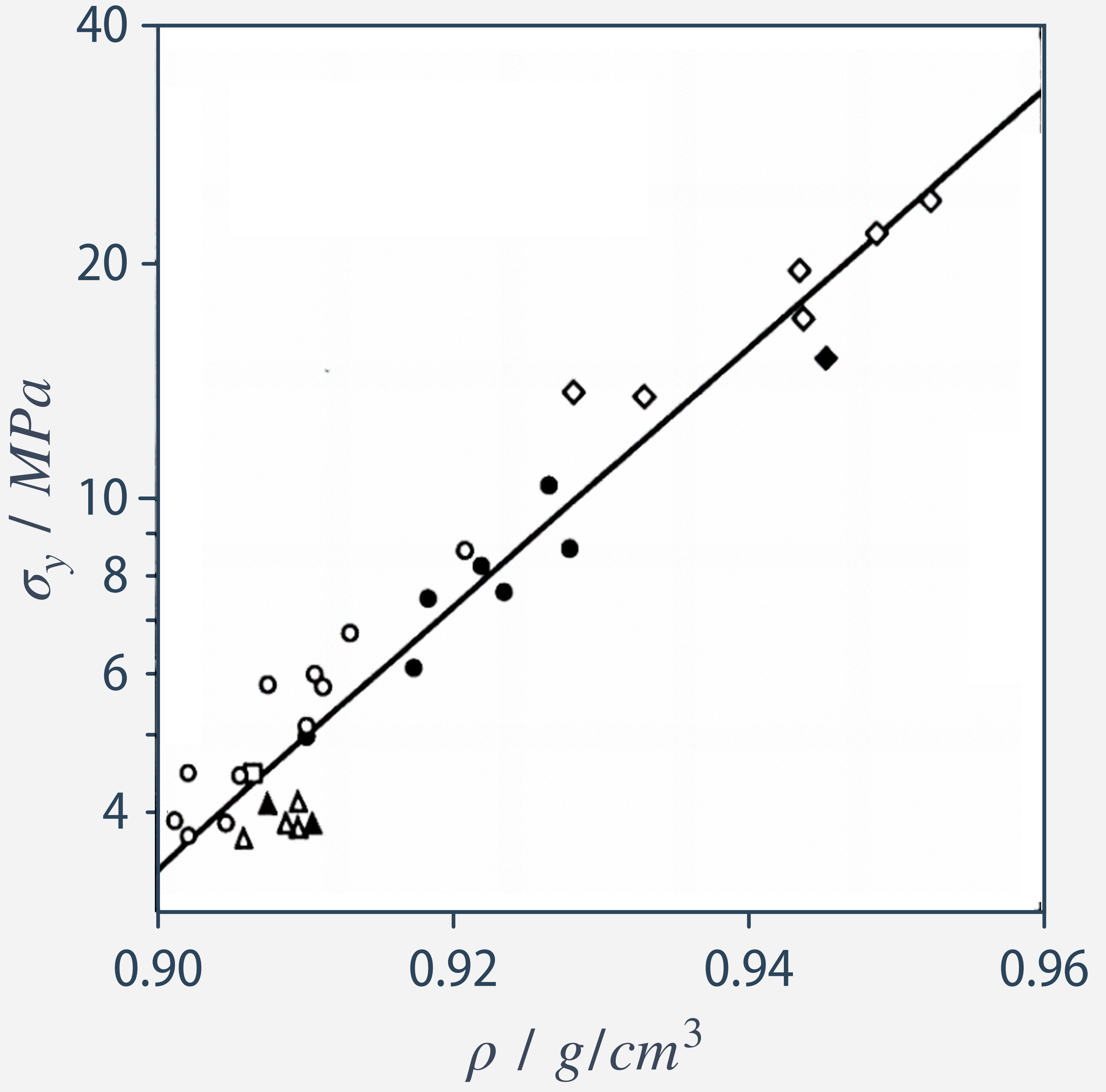
- **macroscopic behavior similar to glassy polymer, but differences are particularly observed at temperatures above the glass transition temperature.**

  - σ_y **increases with lamellar thickness** l **.**

  - σ_y **increases with degree of crystallinity.**

  - σ_y **increases, hence, with density.**

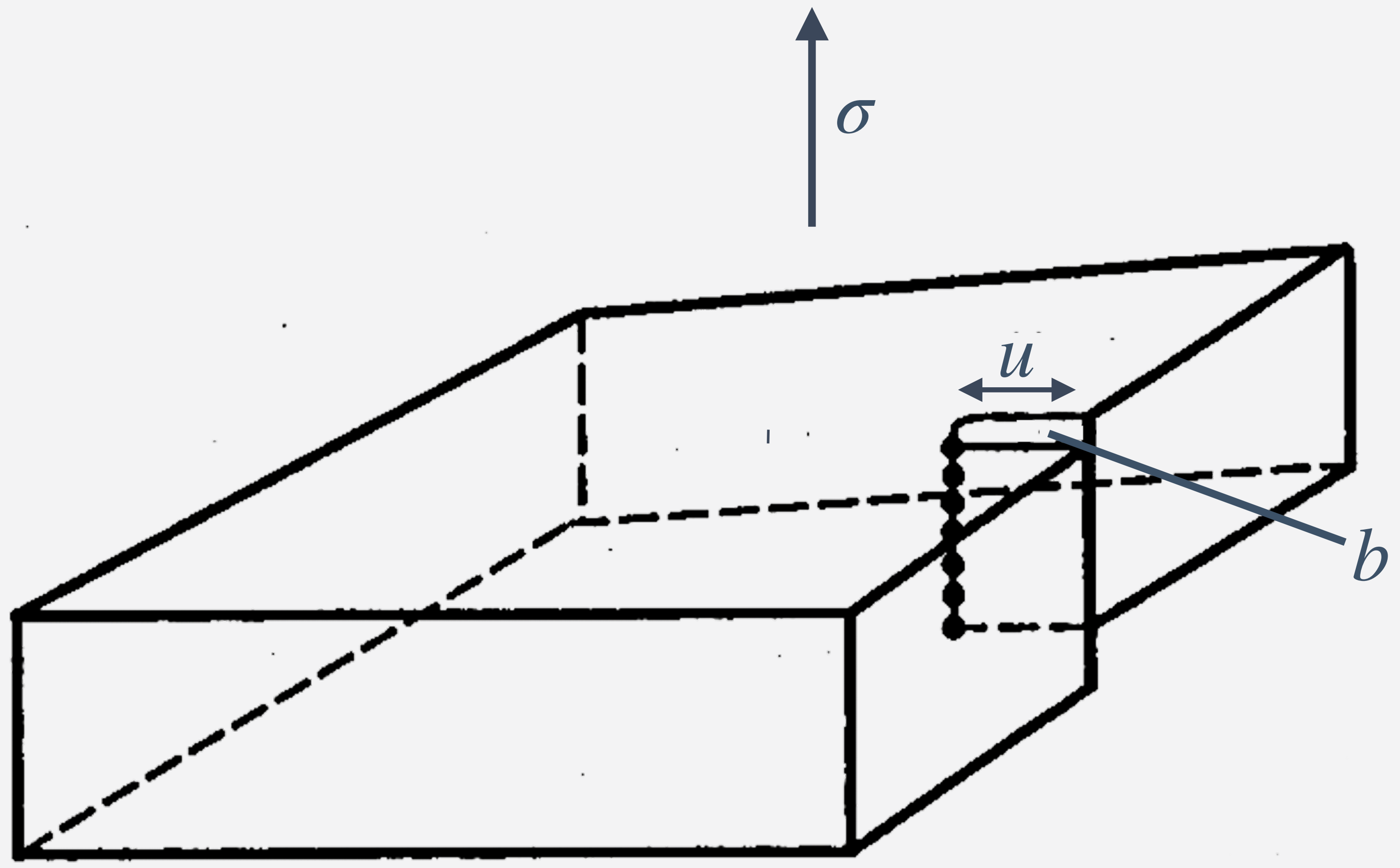
example: diverse grades of PE



- **yield strength depends on morphological features (lamellar thickness and degree of crystallinity)**

Young's Model Based on Dislocations

- a relation between yield stress and lamellar thickness is given by Young's model.
- nucleation of dislocations and crystallographic slip as origin of plasticity.



activation energy for screw dislocations:

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

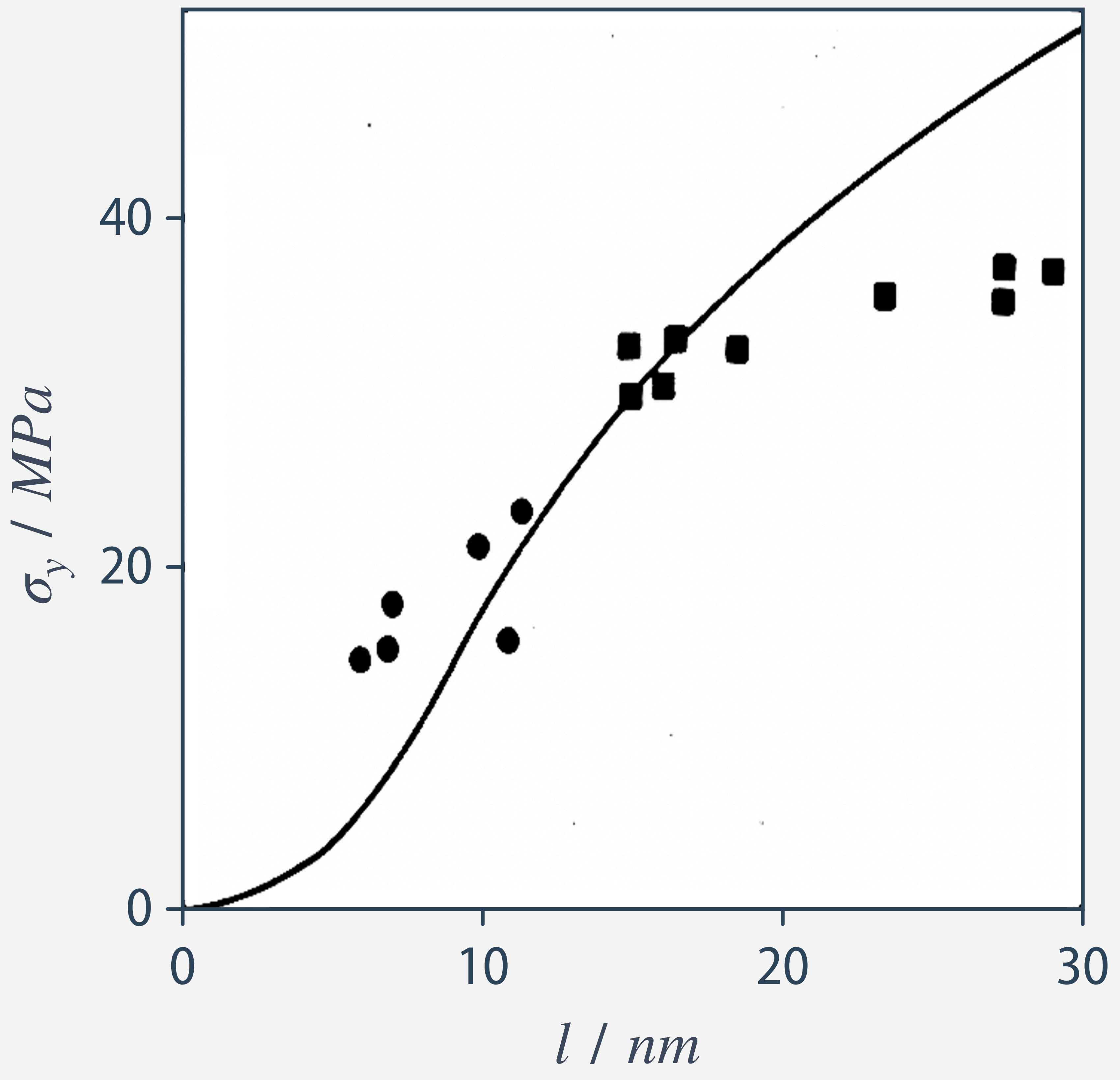
critical width:

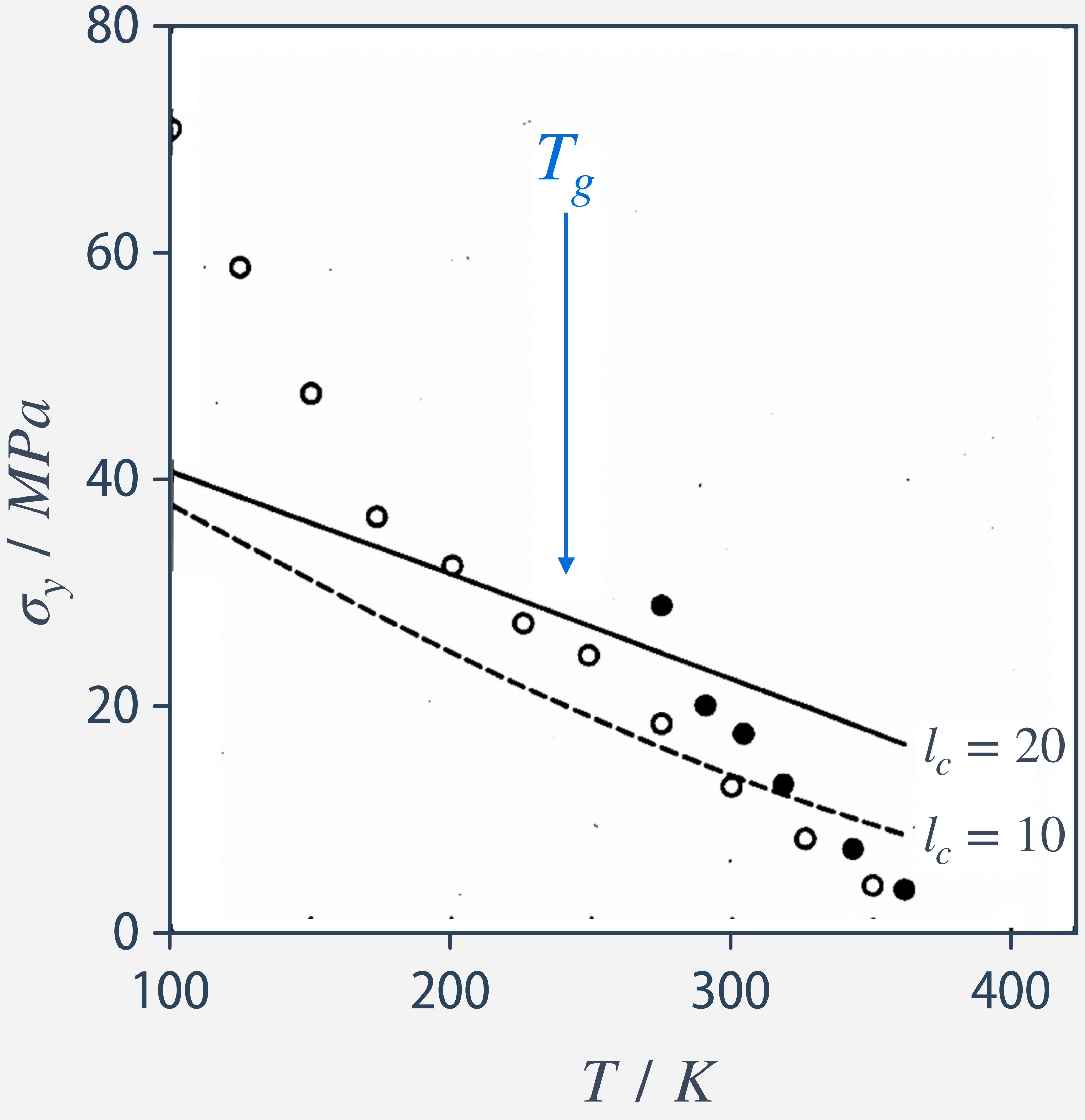
$$u^* = \frac{Gb}{2\pi\sigma}$$

- for HDPE: $\Delta U^* \sim 50 - 60\ kT$ required to nucleate a dislocation

Young's Model and Experiments

- qualitatively good correlations, correct order of magnitude, but severe limitations:

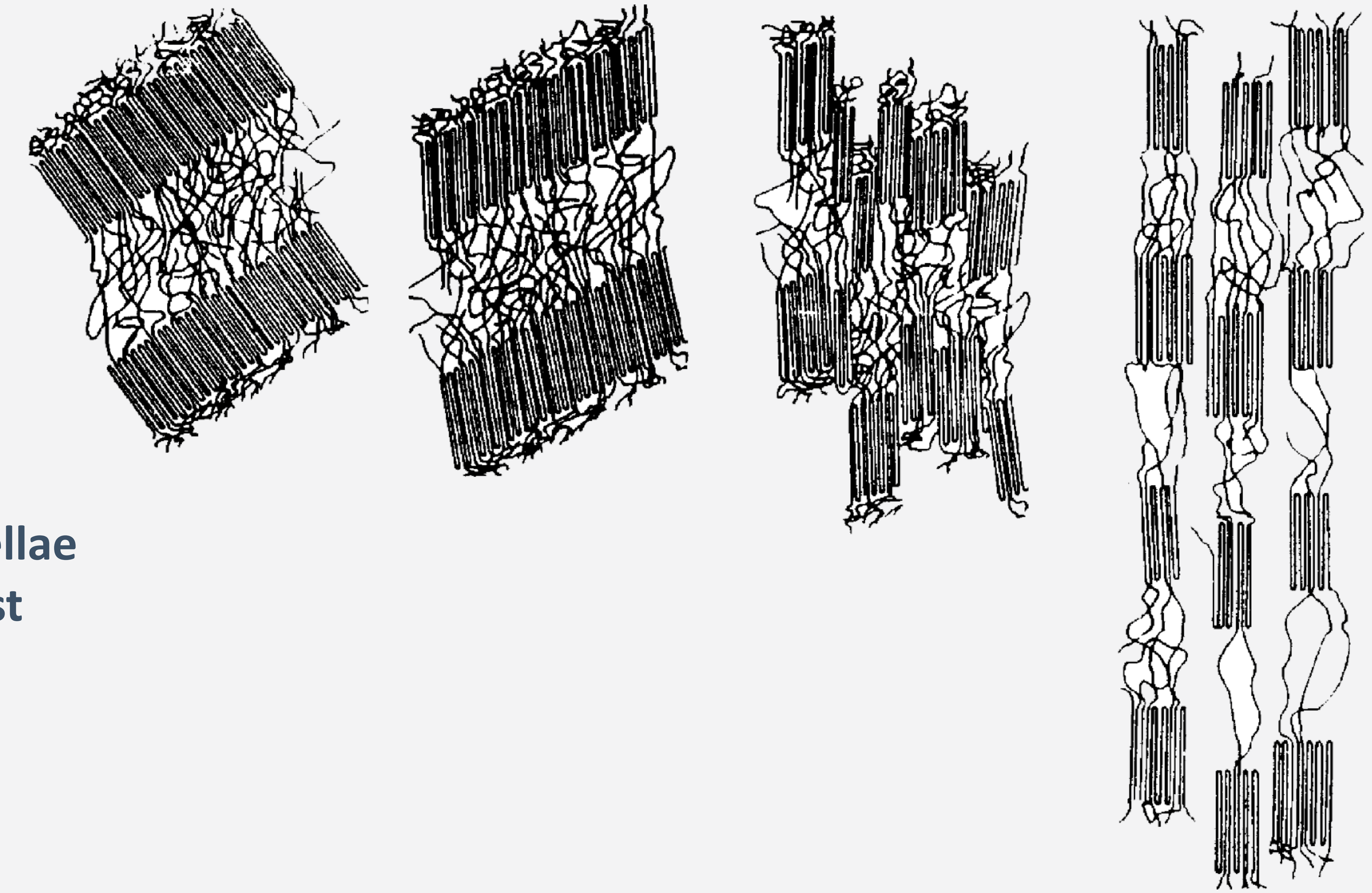




- role of amorphous regions ignored, which is particularly unrealistic for $T < T_g$

Self-Consistent Models

- marked changes in crystallographic texture and morphology upon plastic deformation
- self-consistent models follow the evolution of the crystallographic texture of the material beyond the yield point.

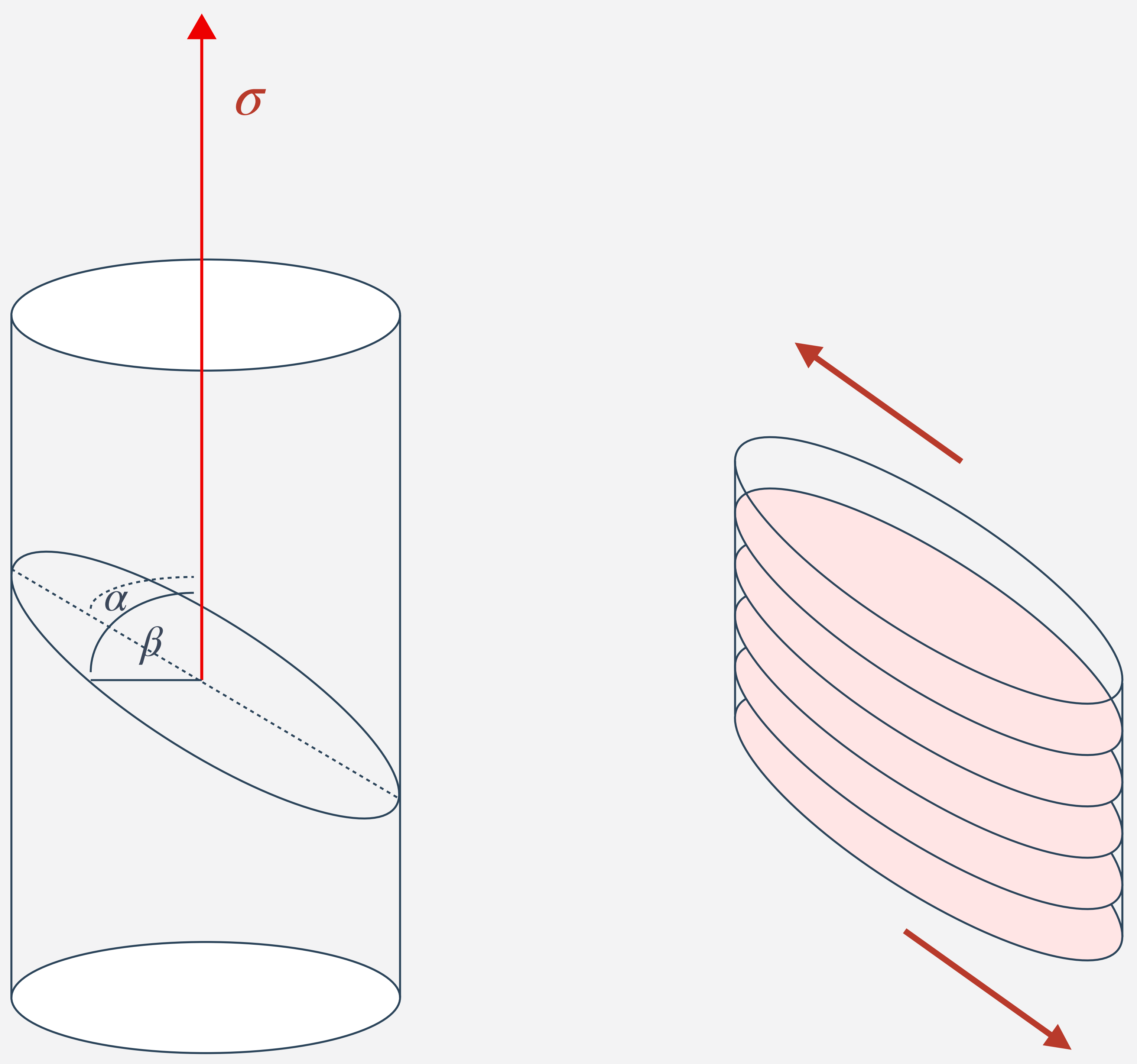


morphology change during lamellae stack deformation in a tensile test

- complexity arises from: multi-stage processes involving both amorphous and crystalline regions, polycrystallinity, possibility of several sliding systems, …

Large Deformations

- at large deformations, major rearrangement of the crystal structure.
- self-reinforcement: chain axes oriented parallel to the pulling direction.



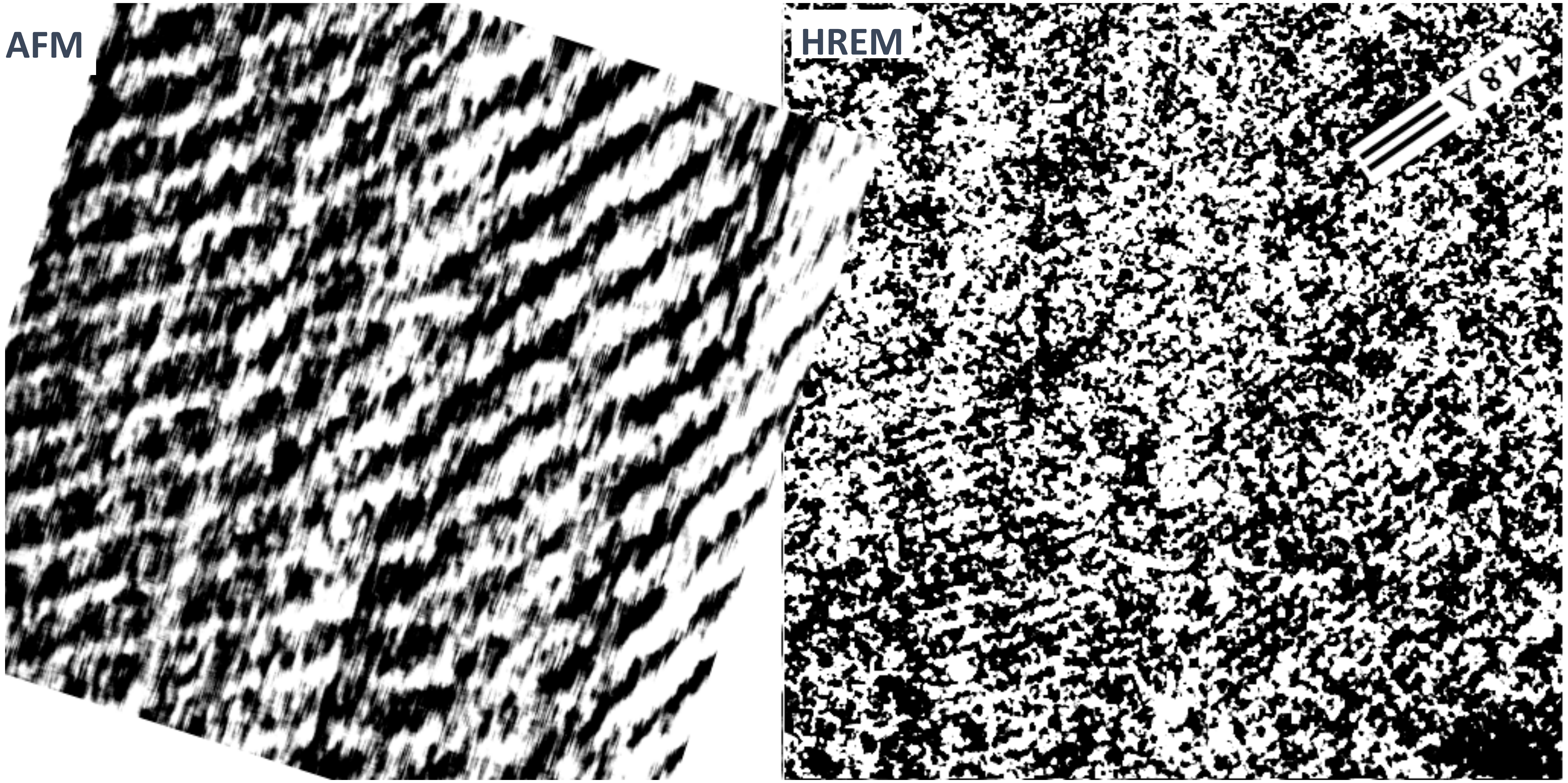
shear stress on the slip plane
parallel to the slip direction:

$$\tau = \sigma_y cos(\beta) cos(\alpha)$$

- in addition to entanglement effects, strain hardening of crystallographic origin

Oriented Polymers

- at very large deformations, total rearrangement of the crystal structure
- parallel oriented chains, little or no active sliding



- oriented polymers can show significant plasticity in compression (i.e. by twinning).
- thus, higher 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.