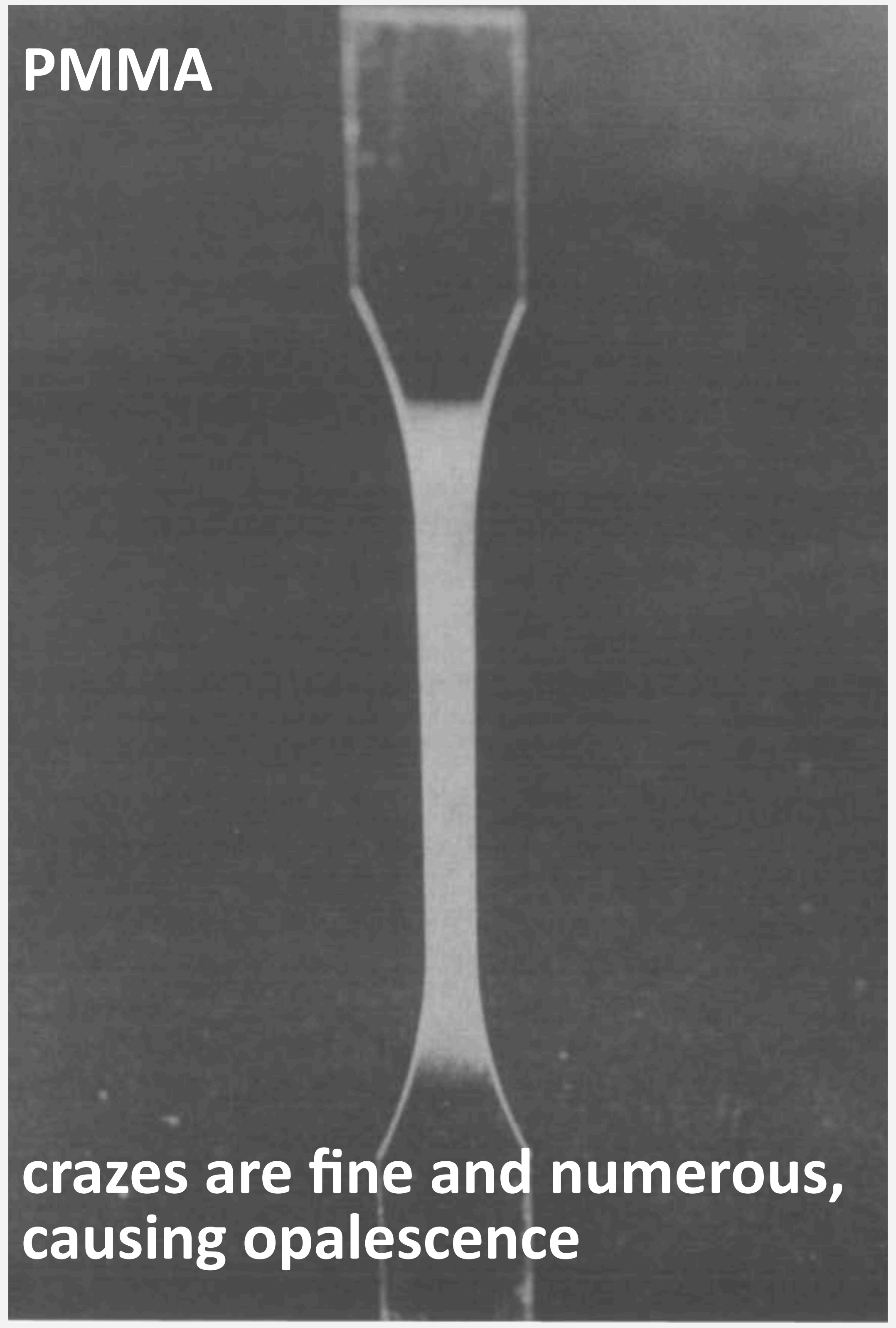
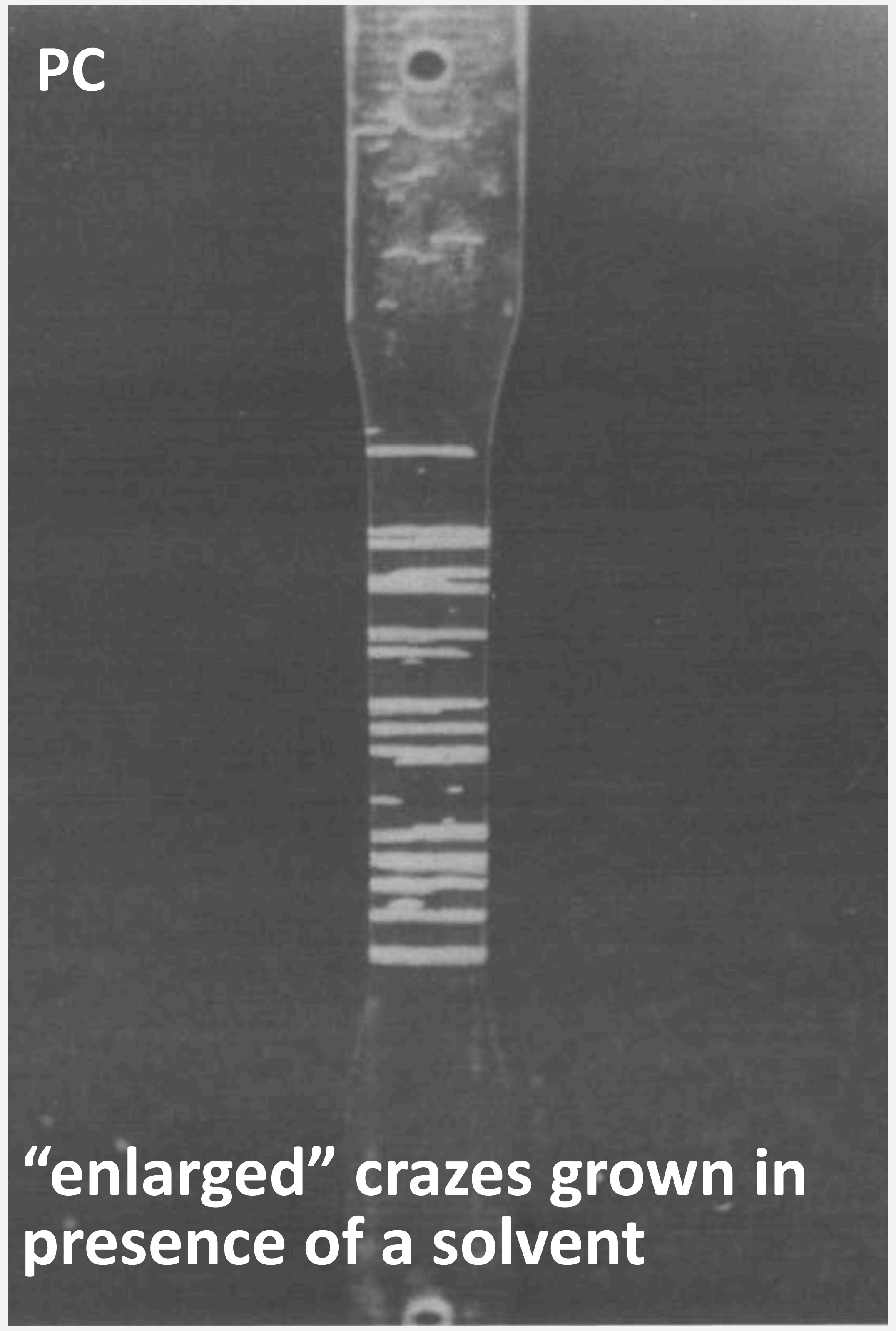
Crazing

What are Crazes?

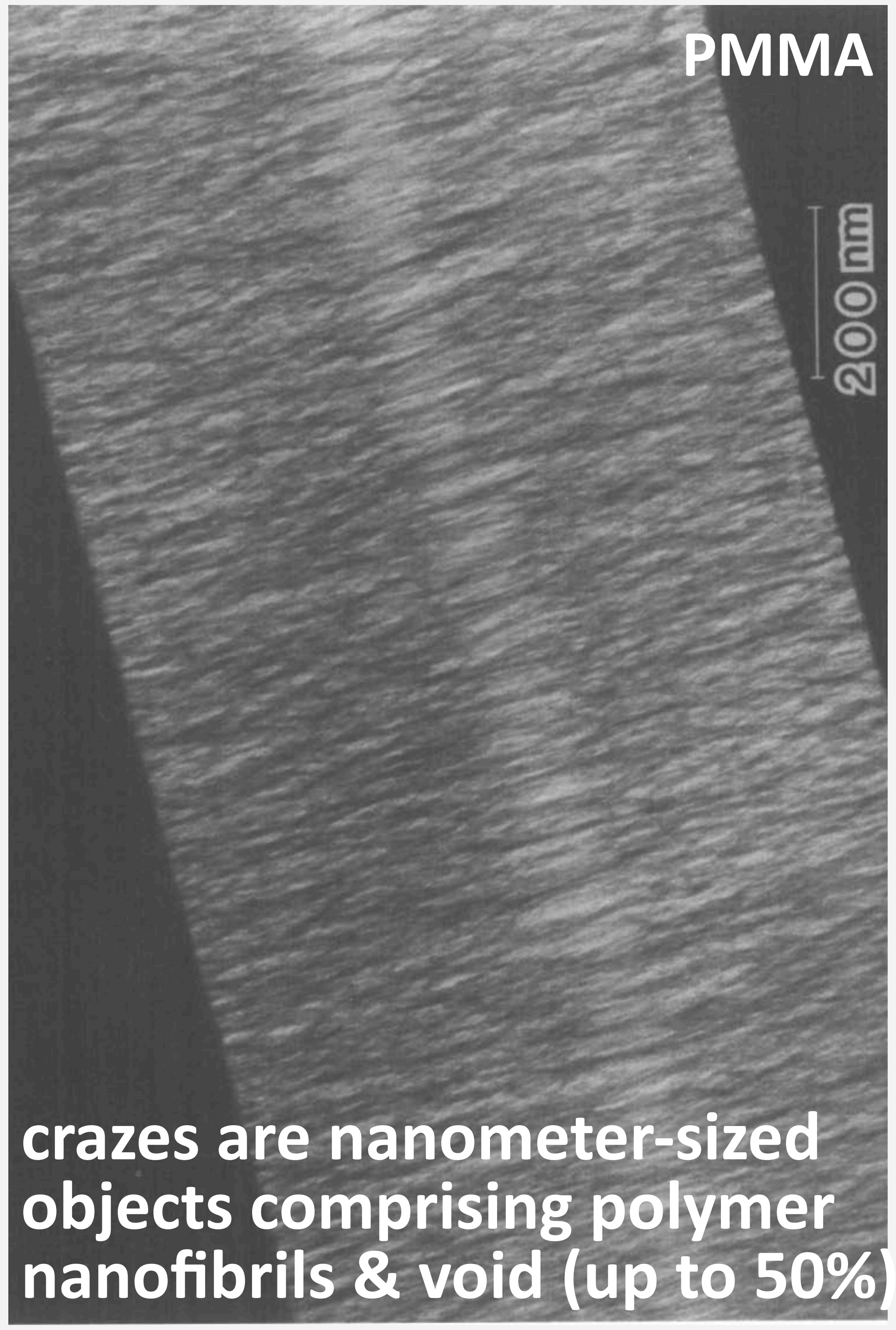
- crazes are fine crack-like striations whose long axis is perpendicular to the tensile direction



crazes are fine and numerous, causing opalescence



“enlarged” crazes grown in presence of a solvent

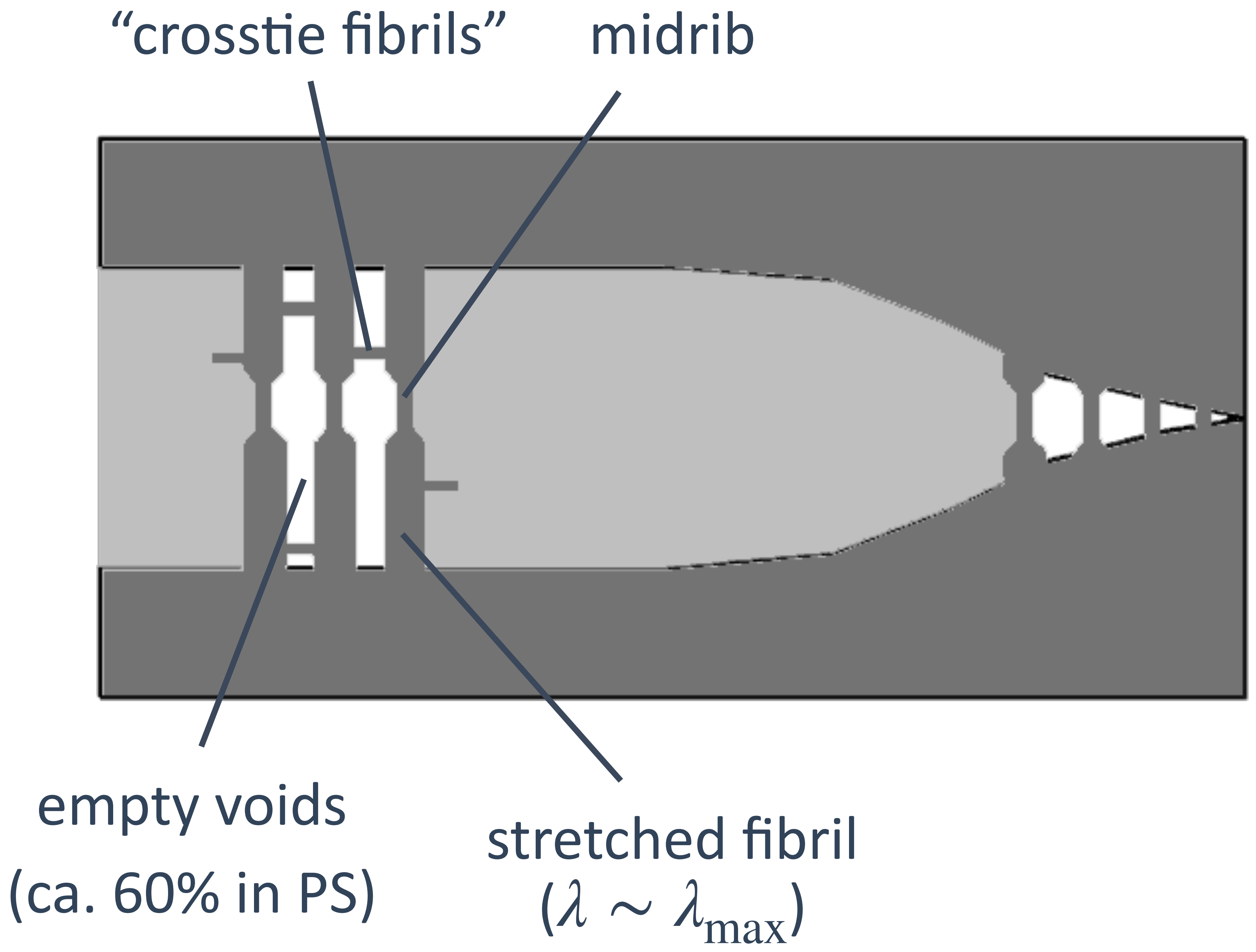


crazes are nanometer-sized objects comprising polymer nanofibrils & void (up to 50%)

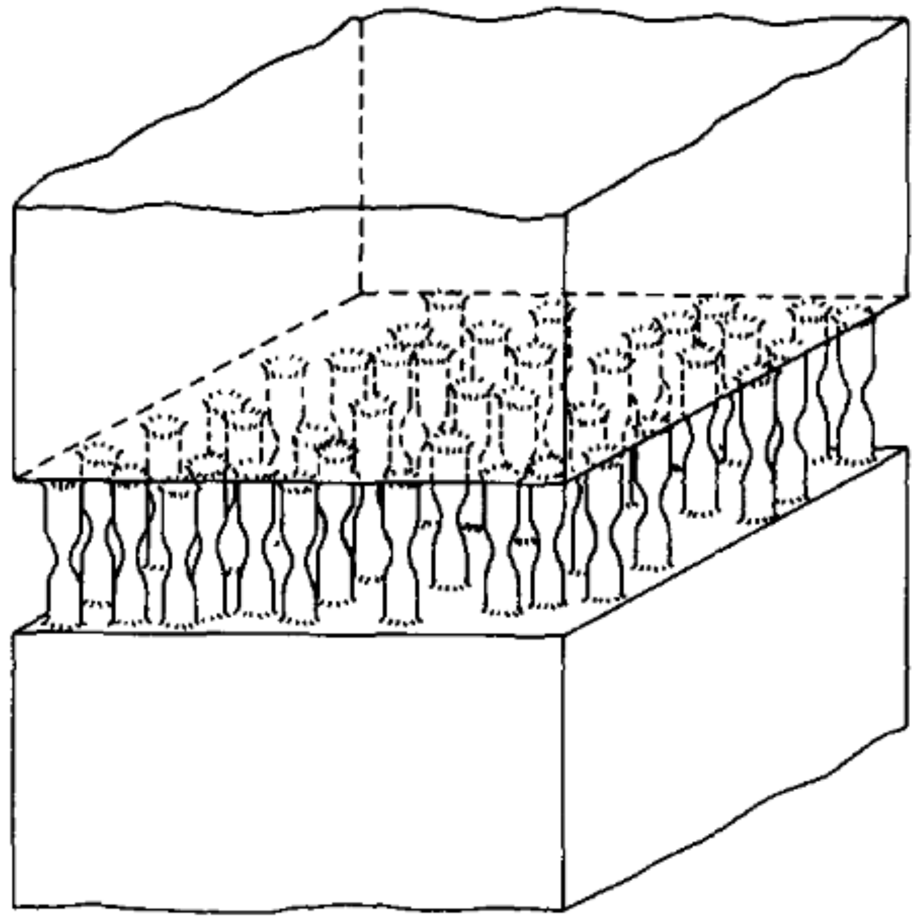
- crazes are only observed in tension and can withstand a significant stress load
- crazes are precursors to failure in many glassy amorphous polymers, but to be distinguished from cracks!

Microstructure of Crazes

- **crazes are observed only in tension, which supports void formation**



craze fibrillar structure



craze criterion:

$$\epsilon_c = A - \frac{B}{p}$$

with

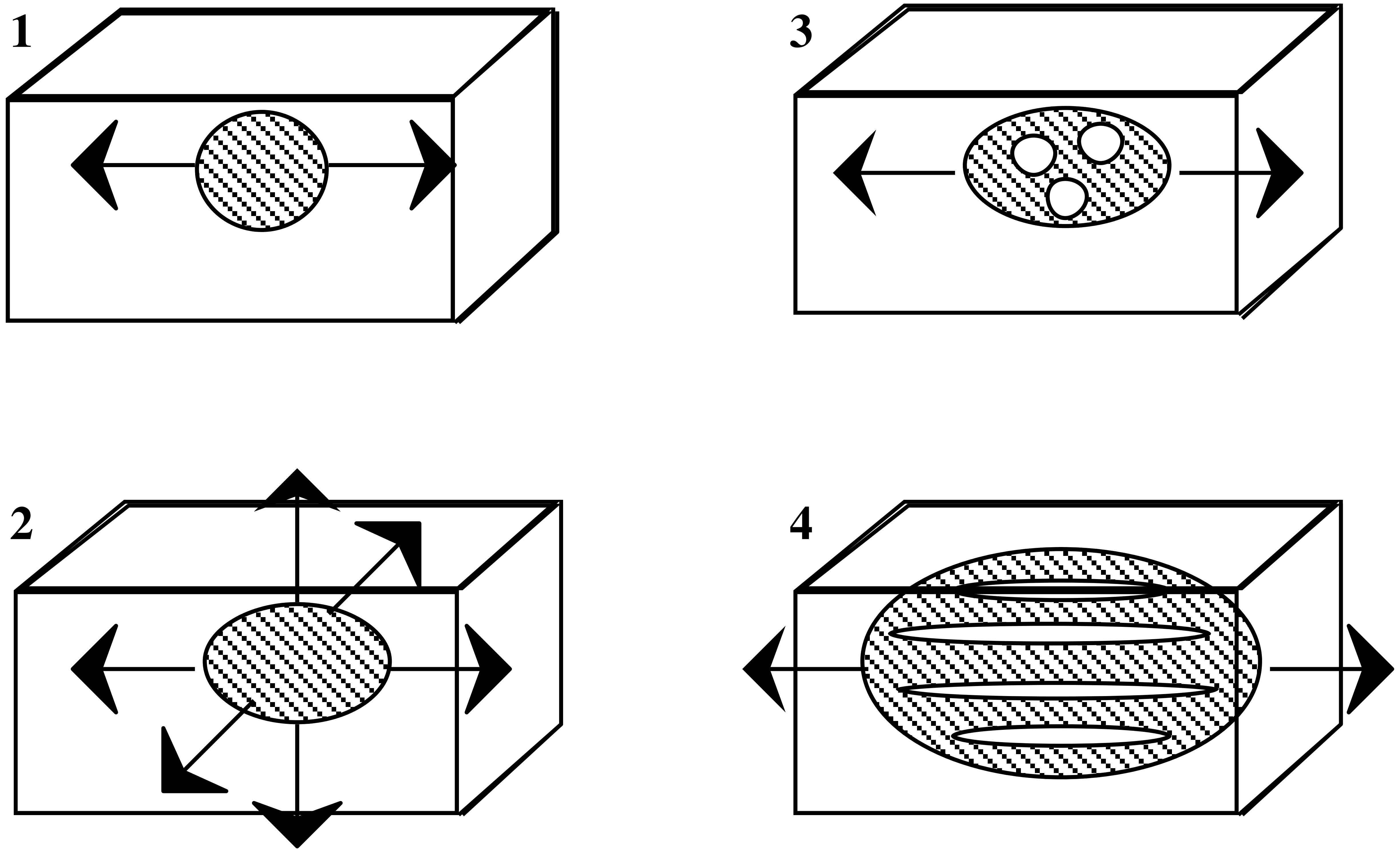
$$\sigma_1 - \mu\sigma_2 - \mu\sigma_3 = C - \frac{D}{\sigma_1 + \sigma_2 + \sigma_3}$$

(cf. $\sigma_y = \sigma_{y0} + \mu p$)

- **the fibrils of a craze are "micronecks" caused by localised plasticity**
- **the formation of a craze requires locallized ductility in the fibrillar region**

Nucleation of Crazing

- **very localised mode of deformation (as compared to the formation of a plastic neck)**



local stress concentration
(due to a hole, dust, etc.)
exceeding the yield stress

deformation and increase
in hydrostatic stress

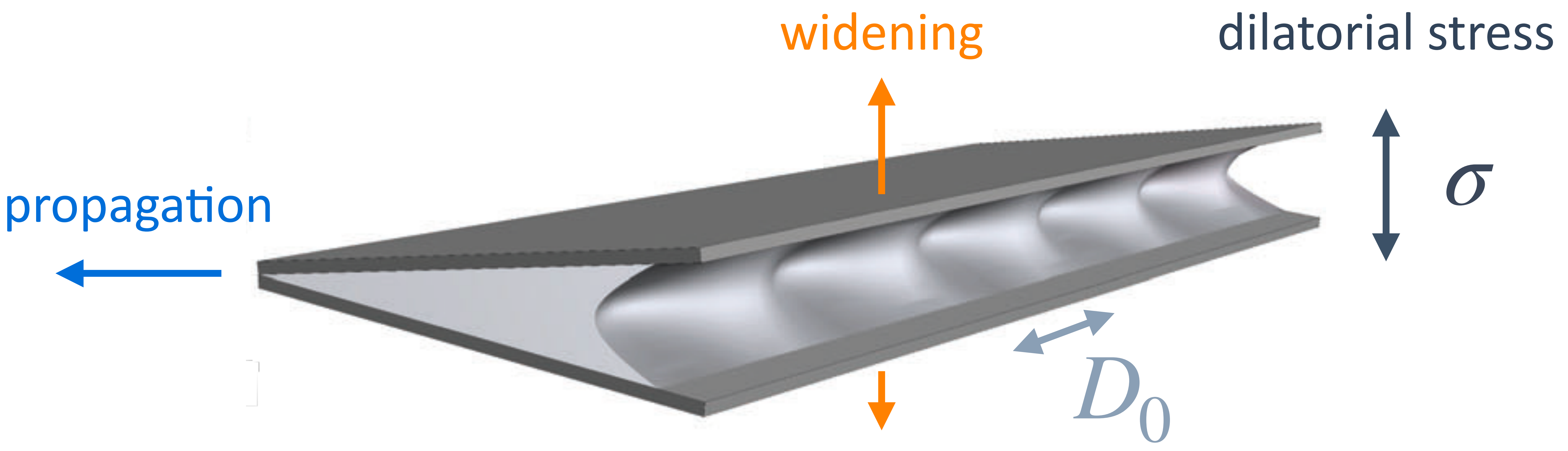
microcaviation

formation of fibrils

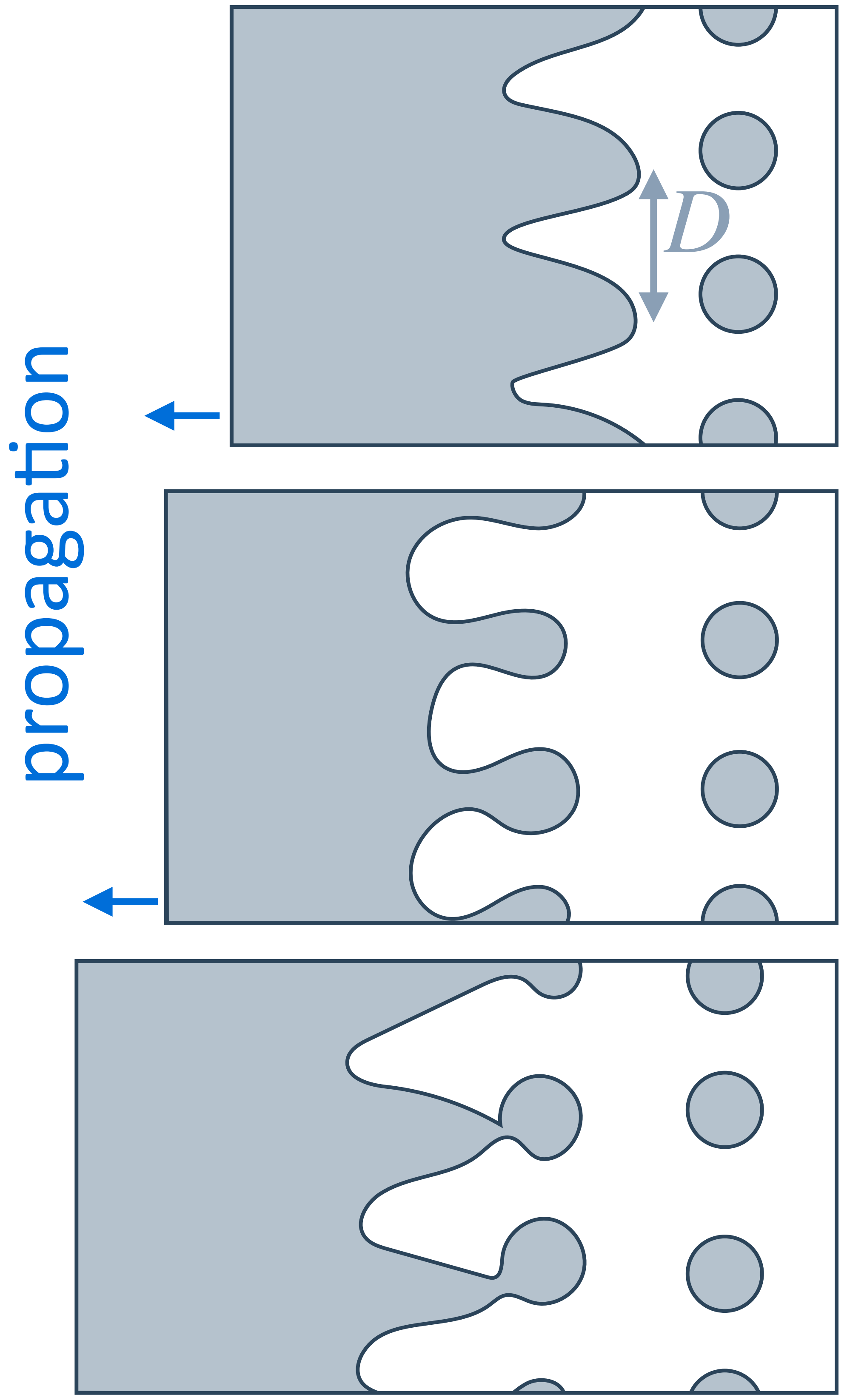
- **crazes serve as nuclei for the formation of (real) cracks, provide little resistance to crack propagation**

Propagation of Crazes

- controversial theories about the propagation mechanism of crazes
- **meniscus instability according to Taylor:** interface between “dry” craze and uncrazed polymer is considered as a sinusoidal perturbation with wavelength D_0



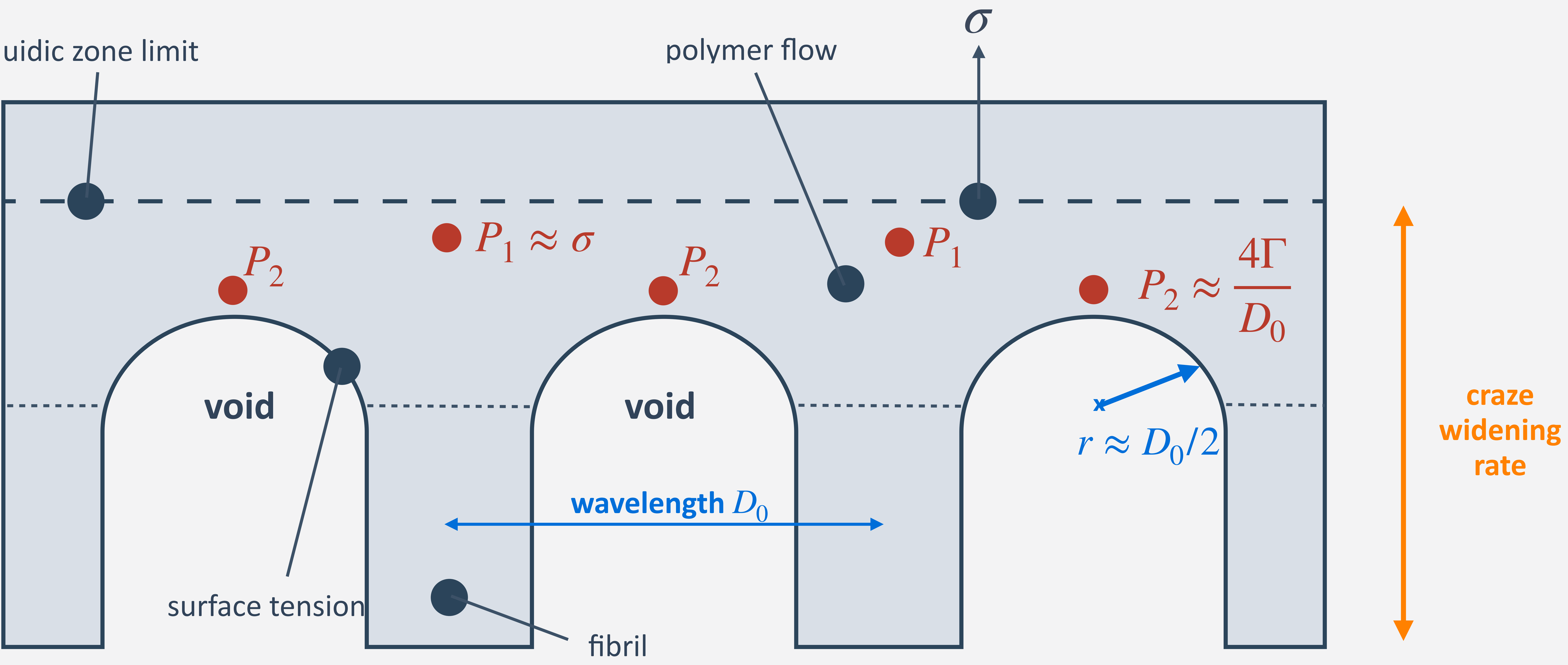
Taylor meniscus instability



- **crazes grow with a constant velocity largely determined by the principal stress**

Craze Widening

- **stress at the craze tip depending on width in the widening zone: surface drawing model** (well understood)



- **continued drawing of more material from the relatively undeformed substrate is the dominant mechanism of craze widening**

Craze Propagation Speed

- **rate of craze widening, v :** $$v^{1/n} \propto \nabla P \propto \frac{P_1 - P_2}{D_0} \approx \frac{\sigma - \frac{4\Gamma}{D_0}}{D_0}$$

$n > 1$: an empirical constant

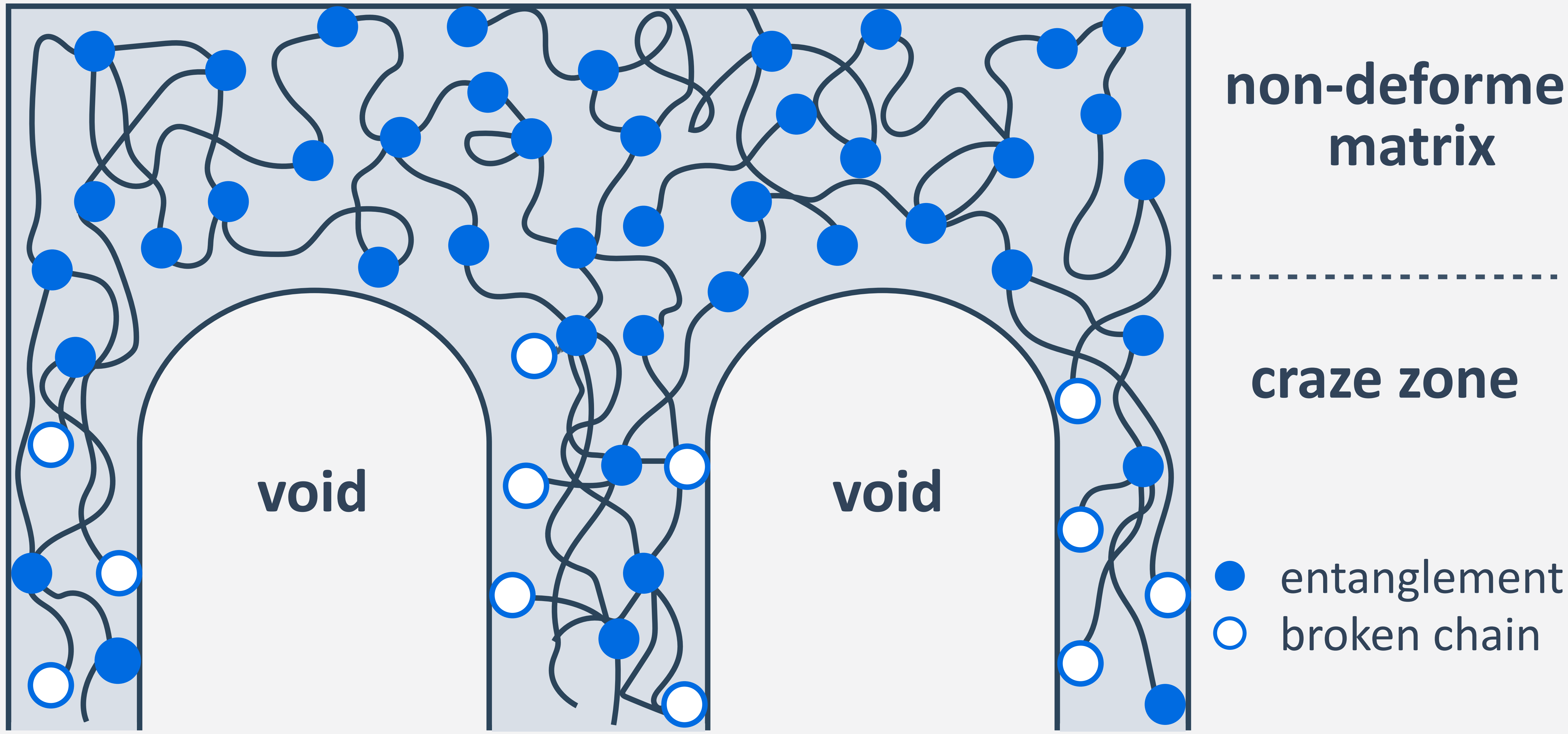
Γ : surface energy of the voids

- **fastest craze widening:** $$\frac{\mathrm{d}\nabla P}{\mathrm{d}D_0} \approx -\frac{\sigma - \frac{4\Gamma}{D_0}}{D_0^2} + \frac{4\Gamma}{D_0^3} = 0 \quad \Rightarrow \quad \sigma D_0^* = 8\Gamma$$
- **the spacing of fibrils (or separation rate) is inversely proportional to the local surface stress**
- **likewise, the speed of expansion is proportional to the applied stress** $$v^{1/n} \propto \nabla P \propto \frac{\sigma^2}{\Gamma}$$
- **the critical stress required to propagate a craze:** $$\sigma_c \propto \sqrt{\Gamma}\sqrt{v^{1/n}}$$
- **the greater the surface energy, the greater the stress required to form a craze (at a given strain rate)**

Crazing and Entanglement

Crazes and Entanglements

- **the extensibility of fibrils is on the order of maximum extensibility of an entangled network**
  (stable crazes are not observed if $M < 2M_\mathrm{e}$)
- **for an intact entanglement network, surface creation during fibrillation involves breaking of chains**



$$\sigma_c \propto \sqrt{\Gamma}\sqrt{v^{1/n}}$$

$$\Gamma = \boxed{\gamma} + \boxed{\frac{d_\mathrm{e} N_\mathrm{e} U}{4}}$$

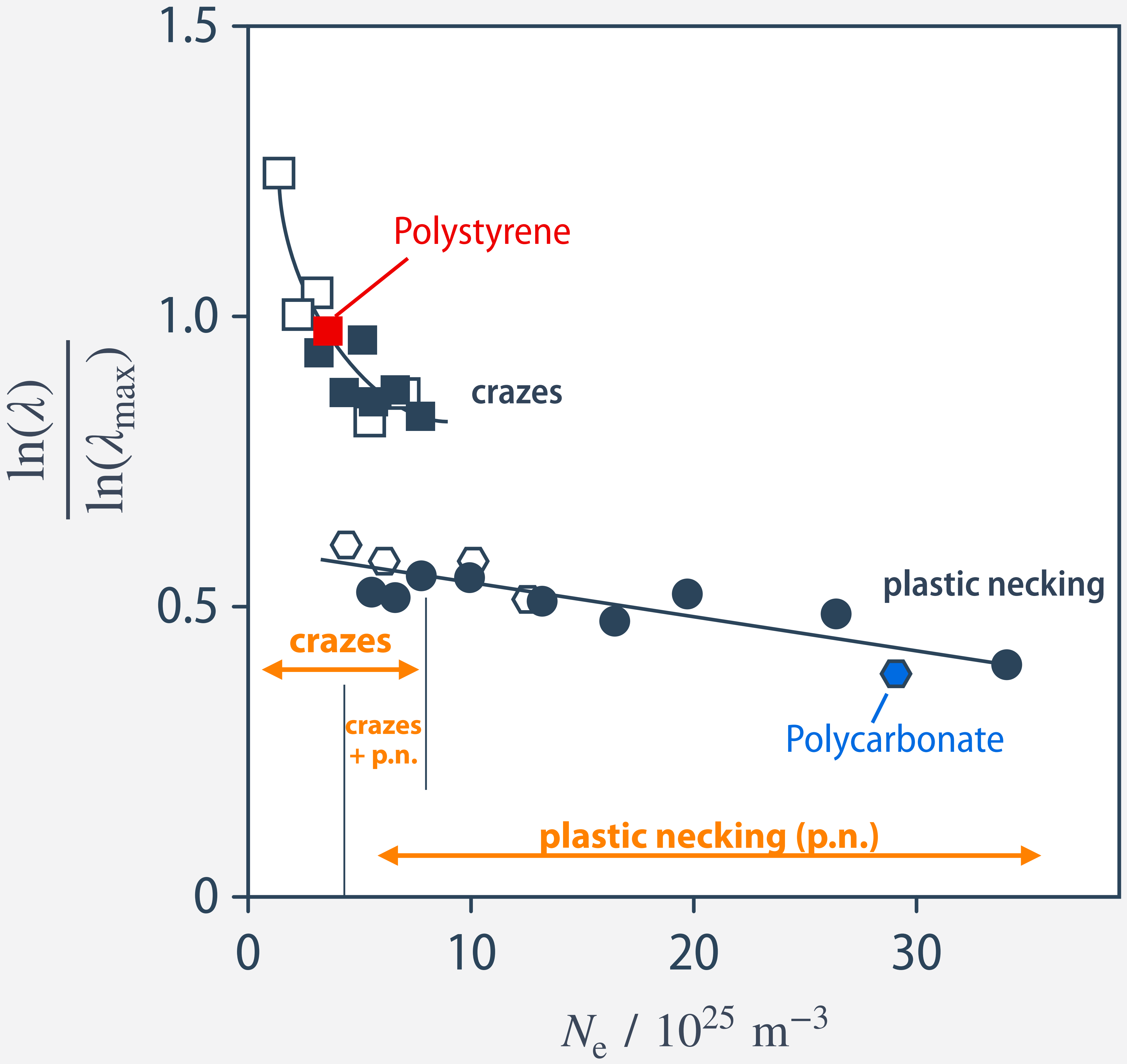
γ: van der Waals surface tension

U: breaking energy of a chain

- **stress required for craze opening increases with the density of entanglements**
  (e.g. easier craze formation in PS ($N_\mathrm{e} \sim 4 \cdot 10^{25}\ \mathrm{m}^{-3}$) than in PC ($N_\mathrm{e} \sim 30 \cdot 10^{25}\ \mathrm{m}^{-3}$))
- **craze formation by chain breakage strongly degrades M in the fibrils**
  (compared to the undeformed material)

Competition Between Crazing and Necking

- observations of crazes and plastic necking in thin films of different polymers (filled symbols: cross-linked PS)



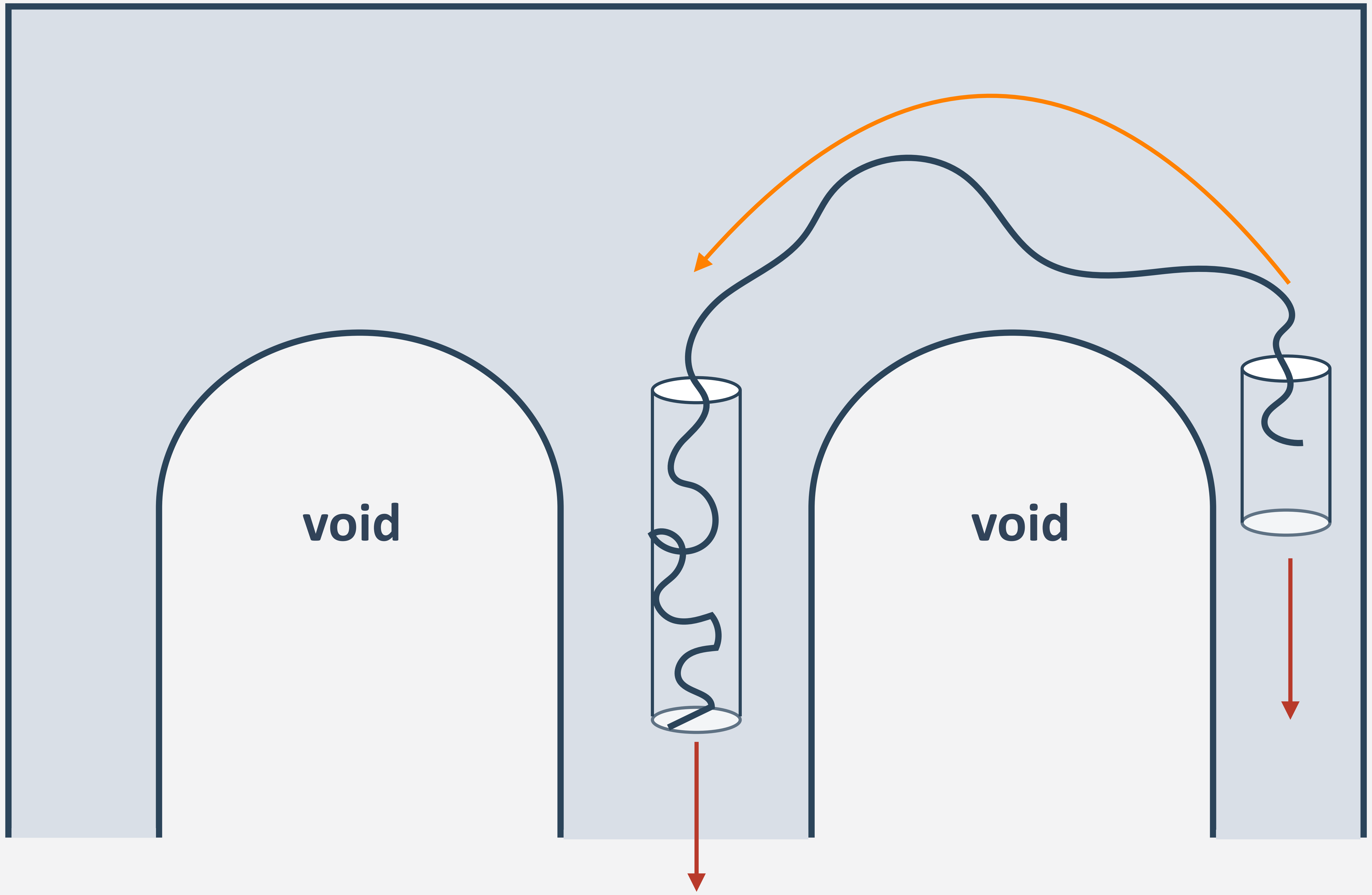
$$\lambda_{\text{craze}} \approx 0.8\ \lambda_{\max}$$

$$\lambda_{\text{necking}} \approx 0.6\ \lambda_{\max}$$

- **dominant craze formation when N_e is small, dominant plasticity when N_e is large**

Crazes and Disentanglement

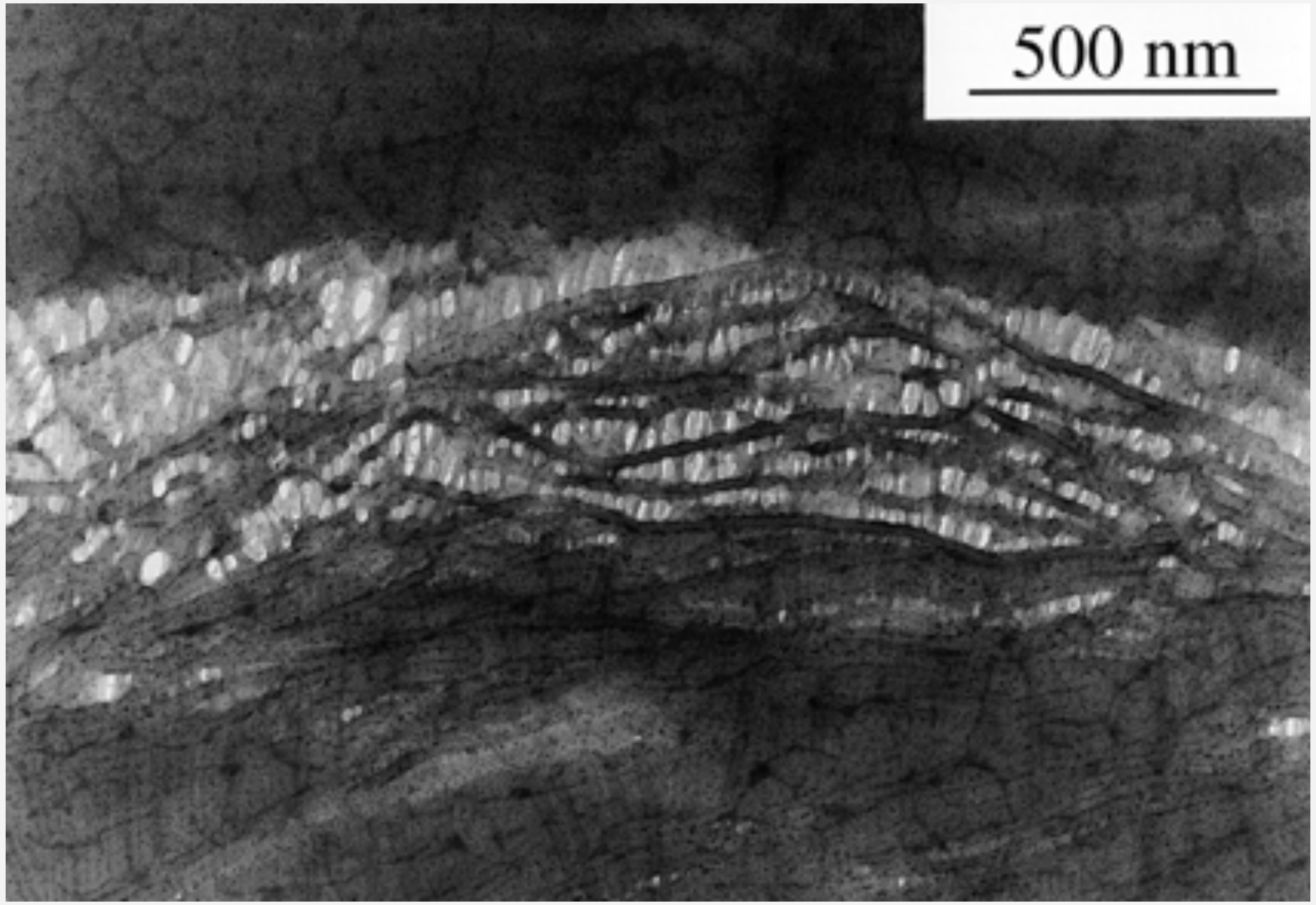
- **at temperatures just below T_g, the mobility may be sufficiently high for disentanglement to occur** (rather than chain breaking)



- **this craze formation mechanism is also favoured by low strain rates and low molar mass.**

Semicrystalline Polymers

- $T < T_g$: **similar behavior like glassy polymers (i.e. craze formation favoured by low entanglement density, low temperature, high strain rate) but no disentanglement!**



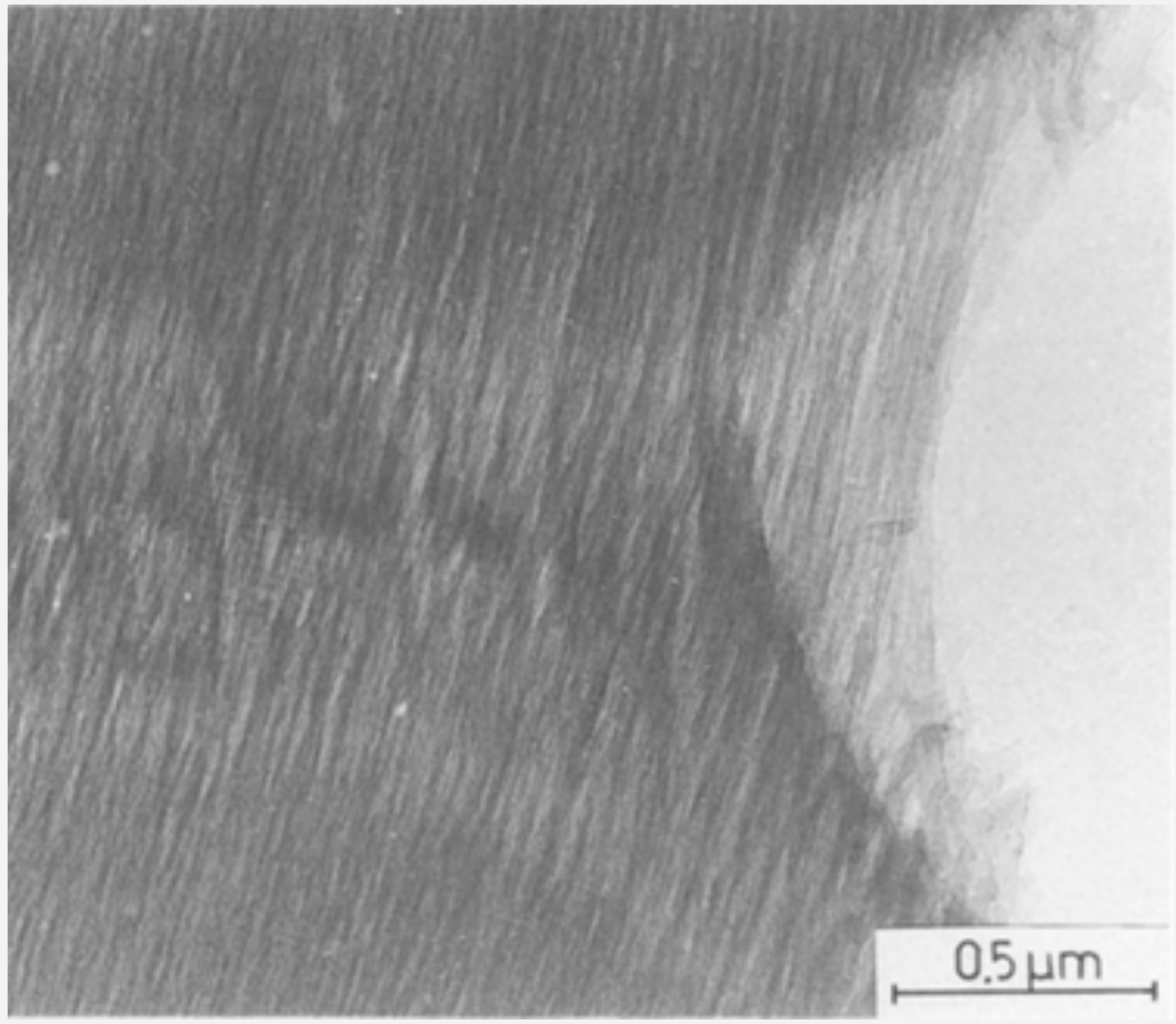
interlamellar cavitation observed in a thin film of PP, deformed under tension

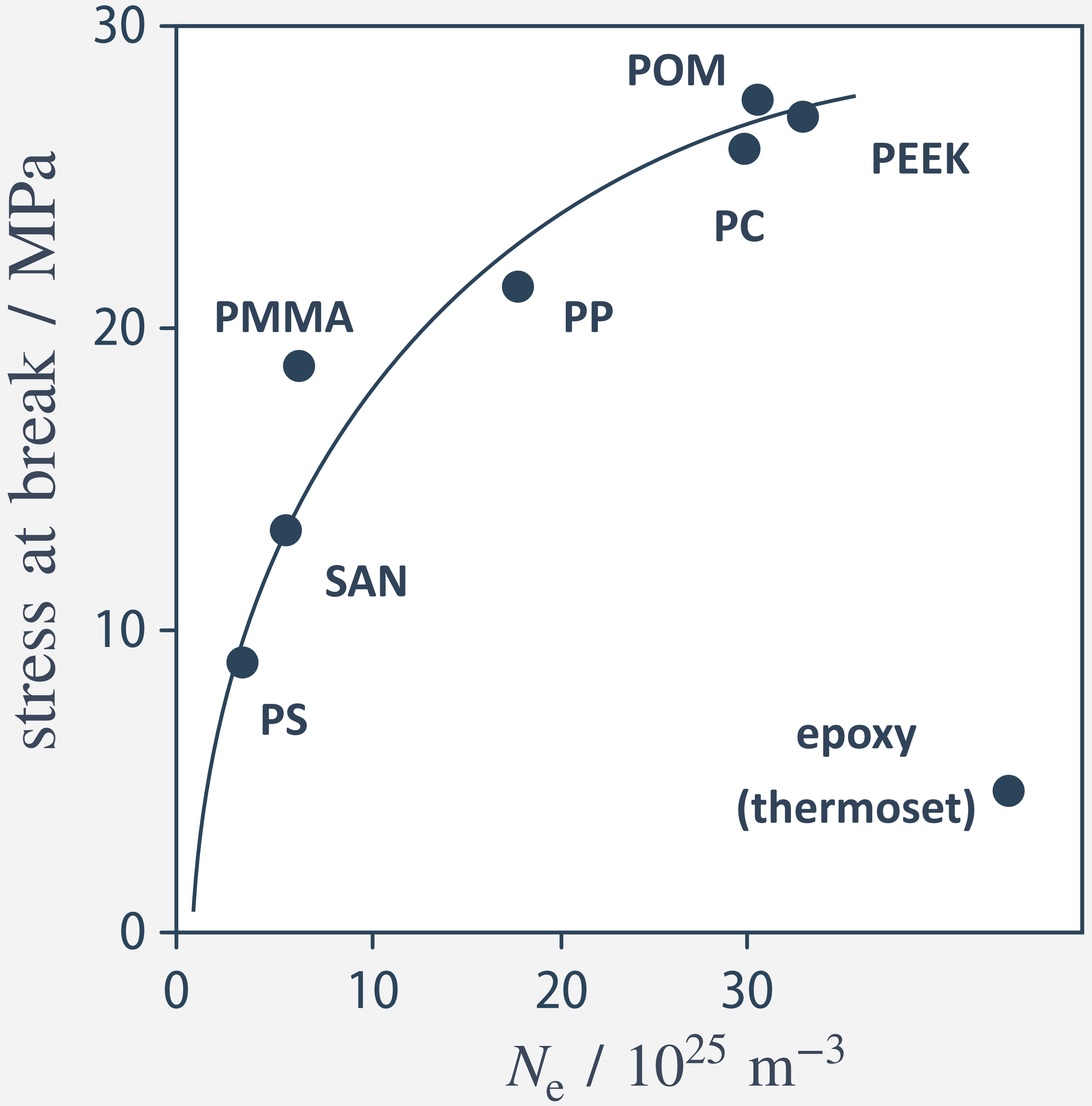
- $T > T_g$ **of the amorphous phase, crazing can still occur when interlameallar cavitation dominates** (mechanism is less clear though)

Crazing and Fracture

Crazing and Fracture

- fracture is due to crack propagation
- in a material that crazes, the fracture resistance depends on the stability of crazes
- for a single craze at the crack tip: $K_{\mathrm{IC}} \propto N_{\mathrm{e}} d_{\mathrm{e}} f_s \sqrt{2\pi D_0}$



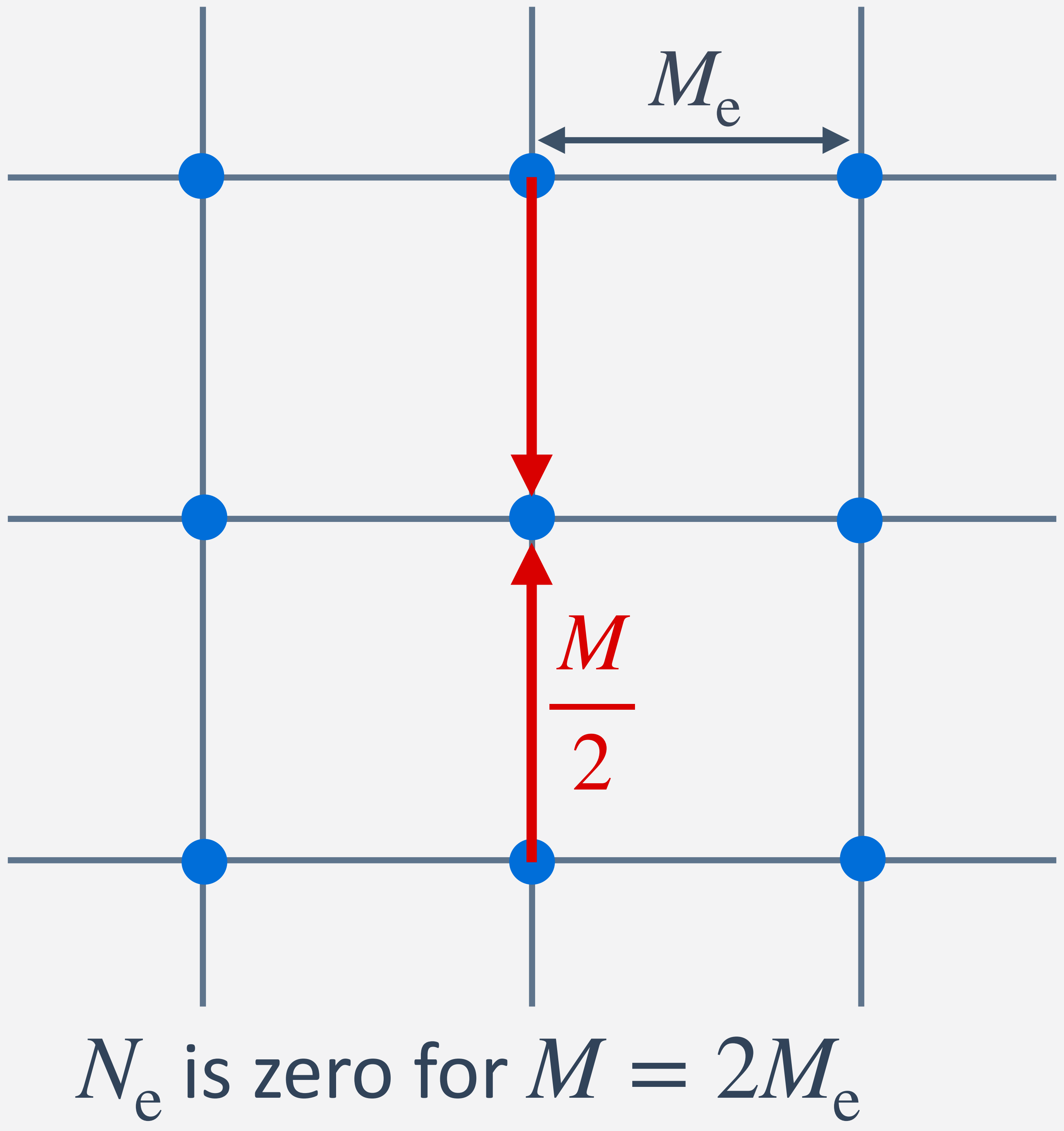


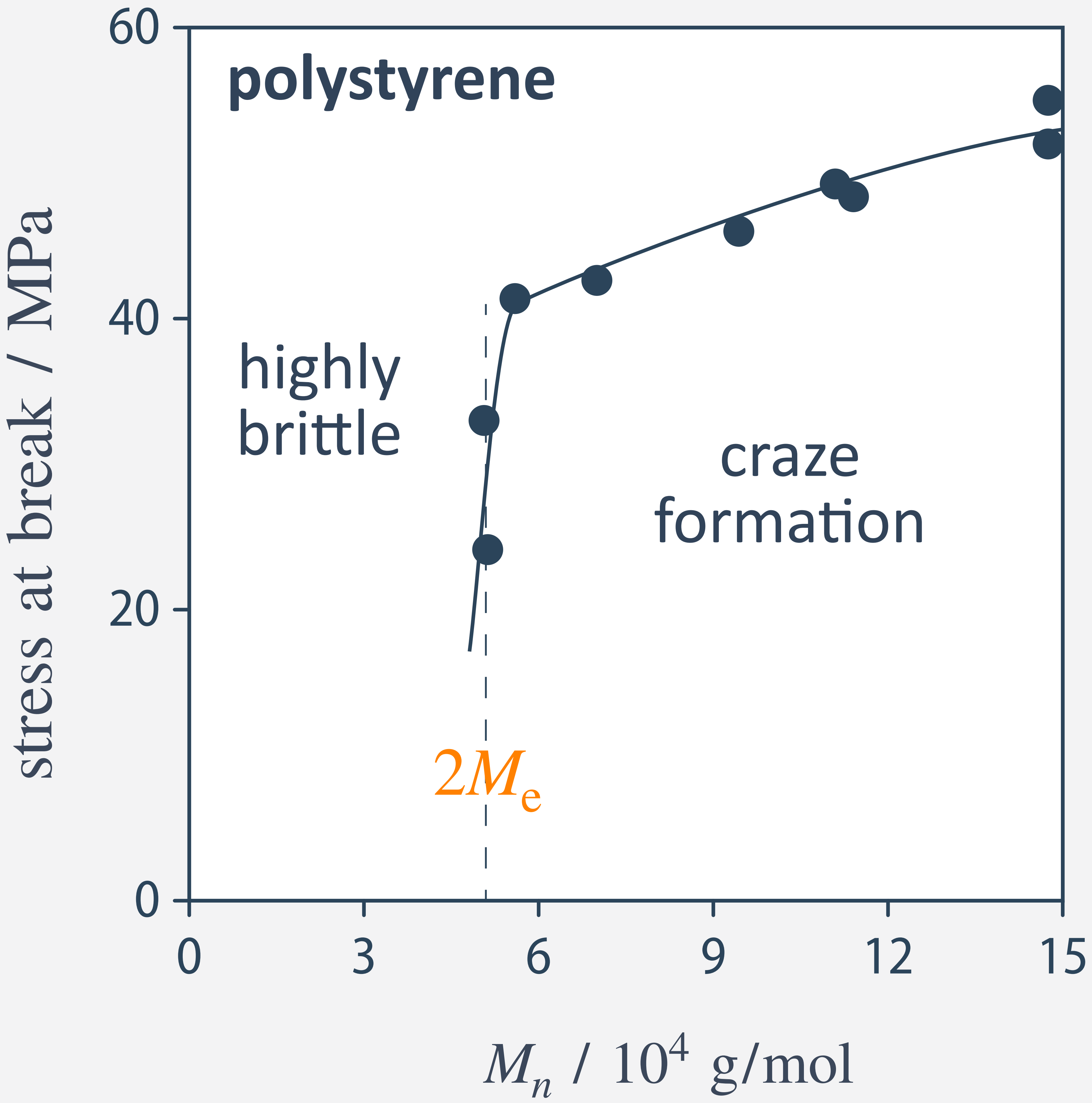
tests at -180 °C (to neglect ductility)

- polymers with high entanglement density should therefore be most resistant
- however, for too high N_{e} (thermosets), no crazing or plastic deformation ⇒ brittle!

Effect of the Molecular Weight

- **polymer chain ends dilute entanglements: a chain with M_e does not participate in network formation**

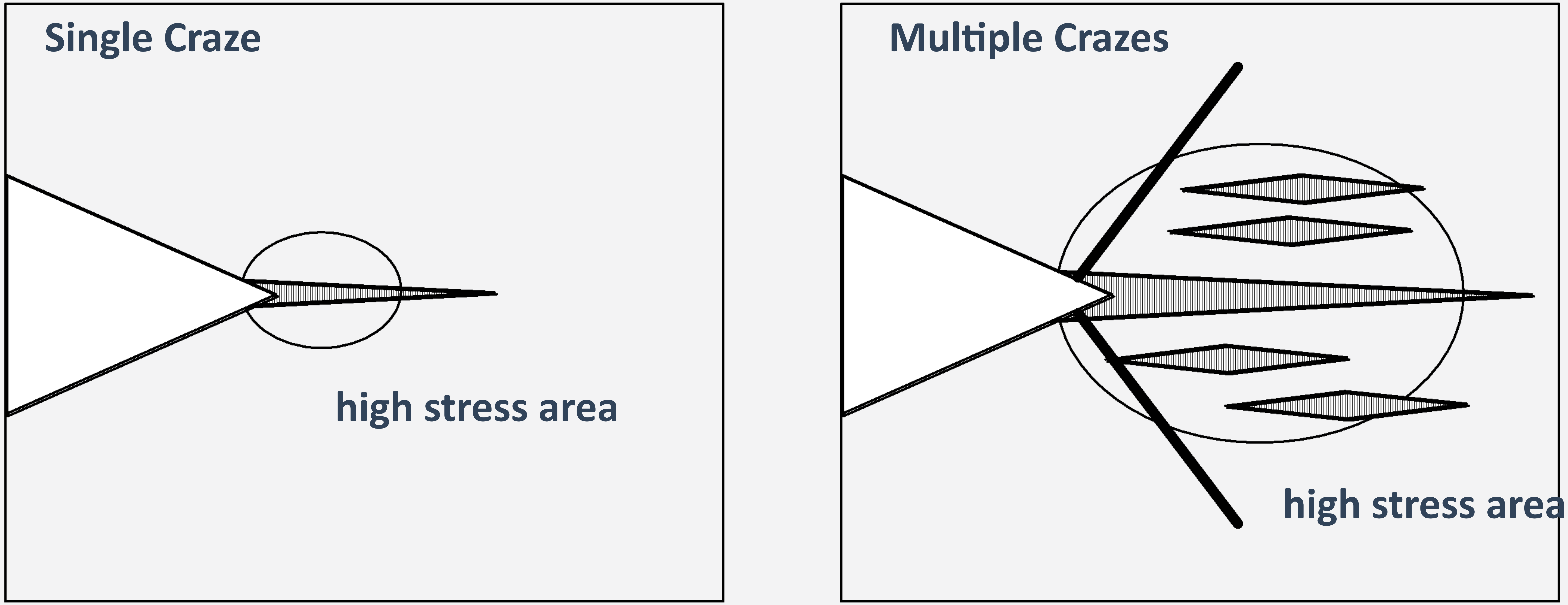




- **mechanical resilience and tensile strength are only observed for two times M_e**

Multiple Crazes

- isolated crazes: little dissipative because of highly localised plasticity
- multiple crazes: little dissipative $\cdot$ large amount $=$ very dissipative!

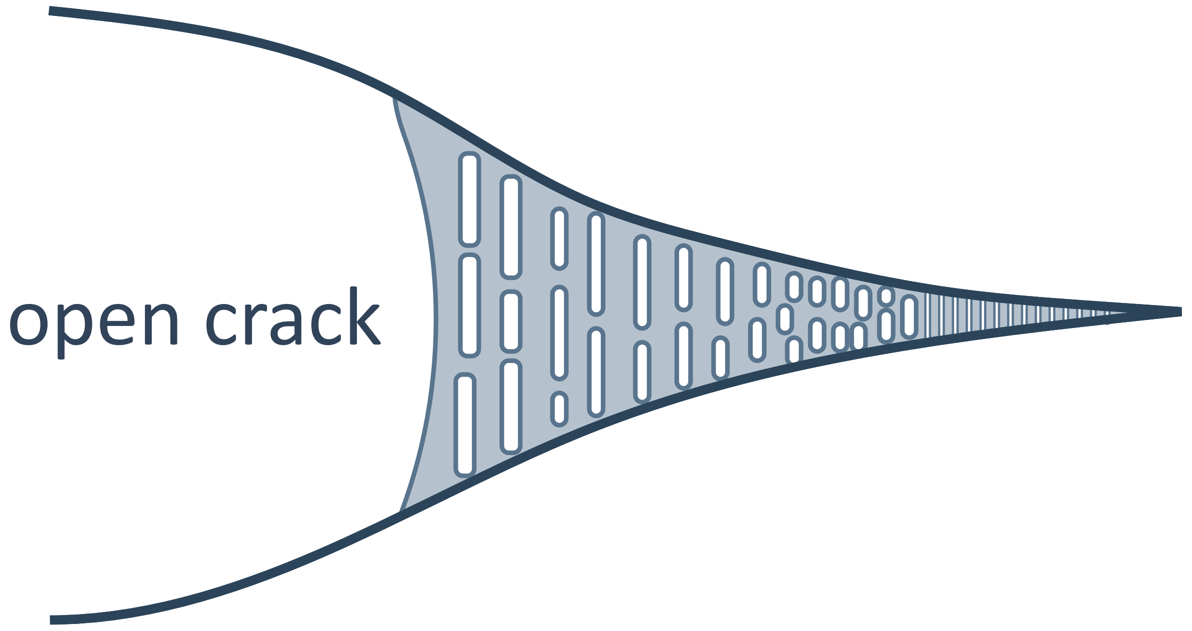


- multiple crazes or combinations of crazes and plasticity are favoured at the crack tip, when the craze resistance is high.

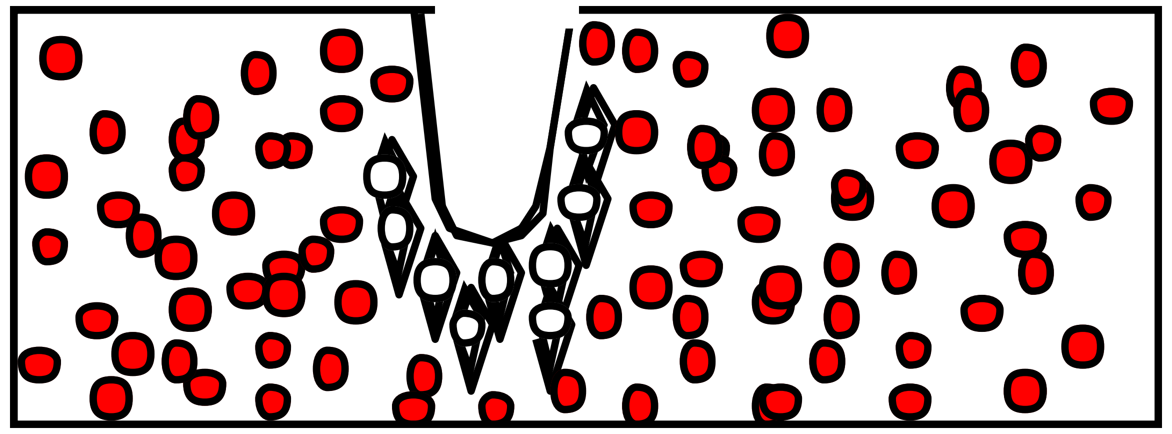
Reducing Fragile Behavior

- **despite load bearing capability, crazing is associated with brittle behavior.**
- **an isolated craze dissipates little energy**

craze-crack transition

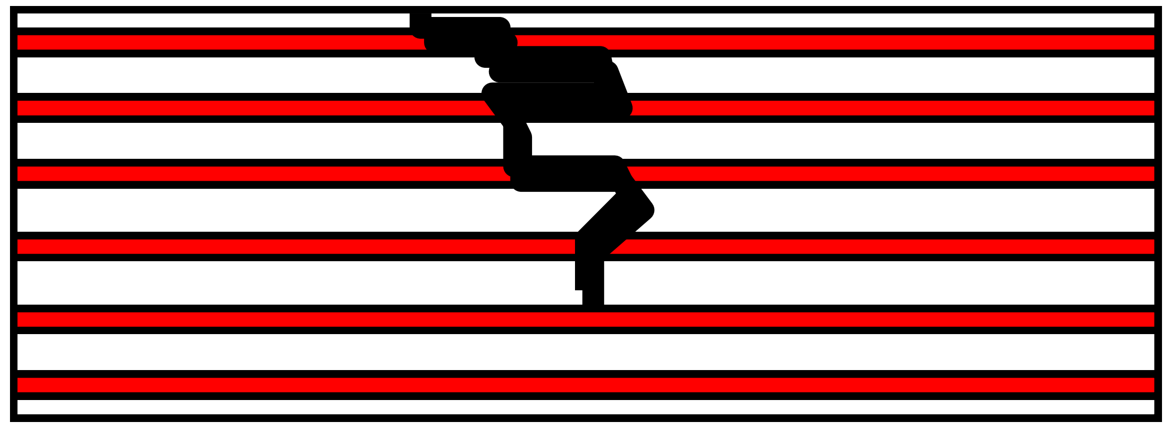


rubber toughening



avoidance of unstable cracking by delocalisation of plastic deformation

fiber reinforcement

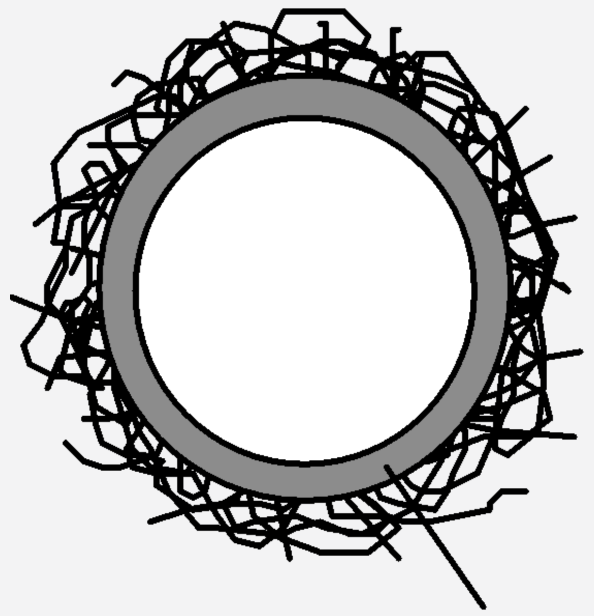


improved resistance to unstable cracking (inorganic composites, Kevlar, etc…)

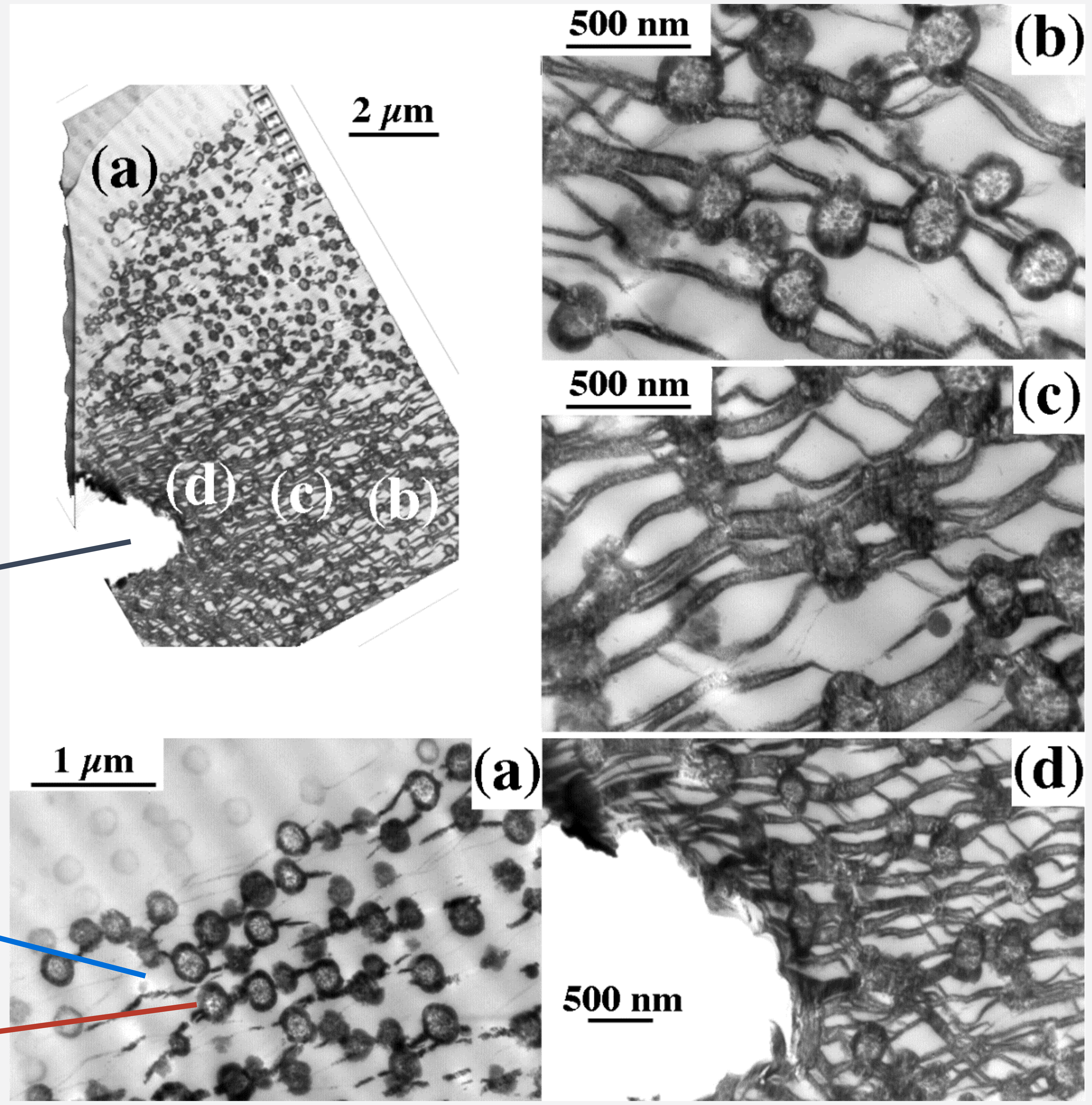
- **toughening strategies to improve the resistance to breakage**

Rubber Toughening

- aim: reducing the effective local stress for craze initiation to produce a high number of crazes
- in brittle materials (PS, PMMA, …) this significantly improves resistance to failure



elastomer



crack tip

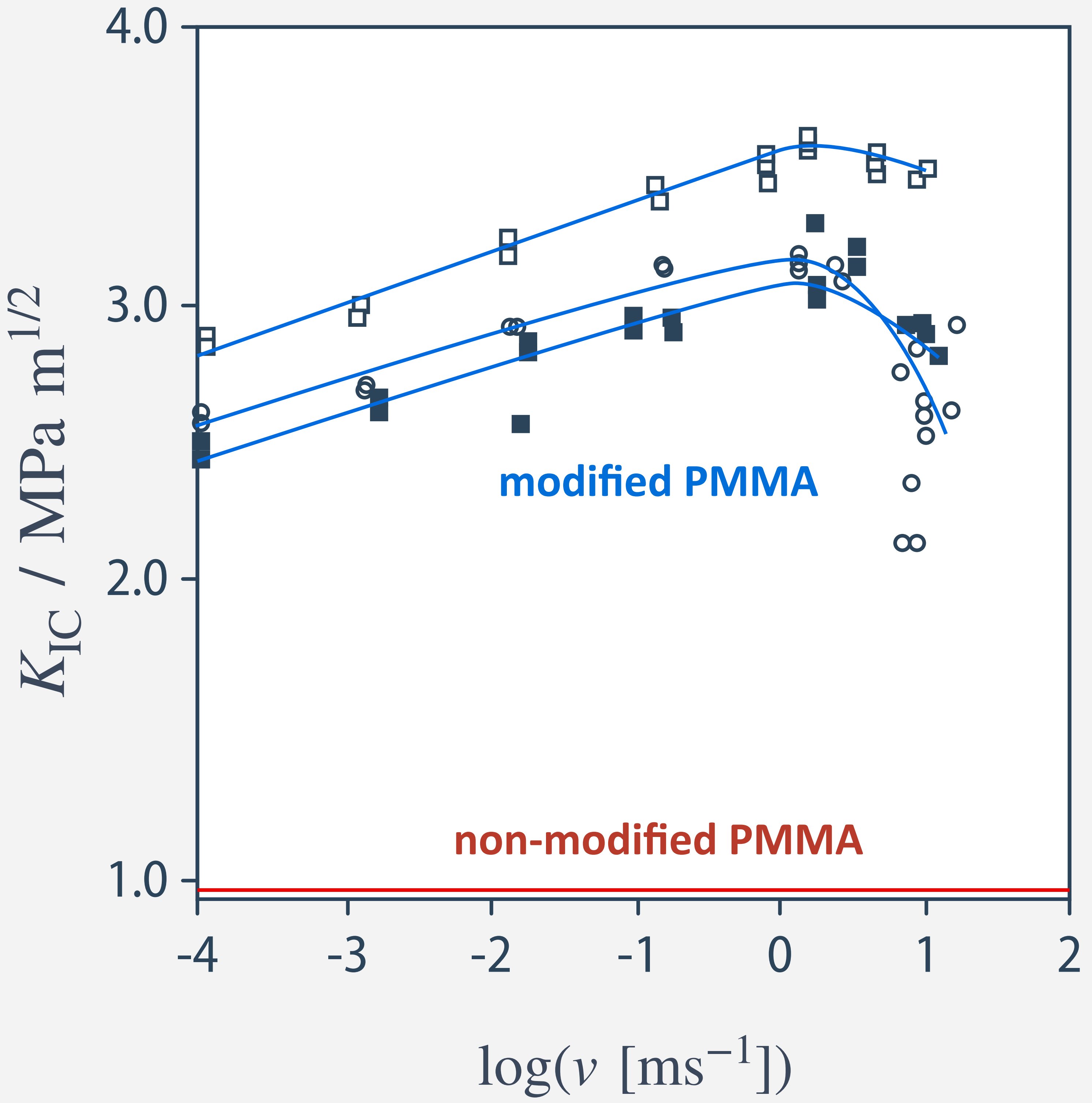
crazes

elastomer particles

- introduction of elastomer particles into the matrix: they cause local stress concentrations and therefore nucleate crazes at reduced overall stress.

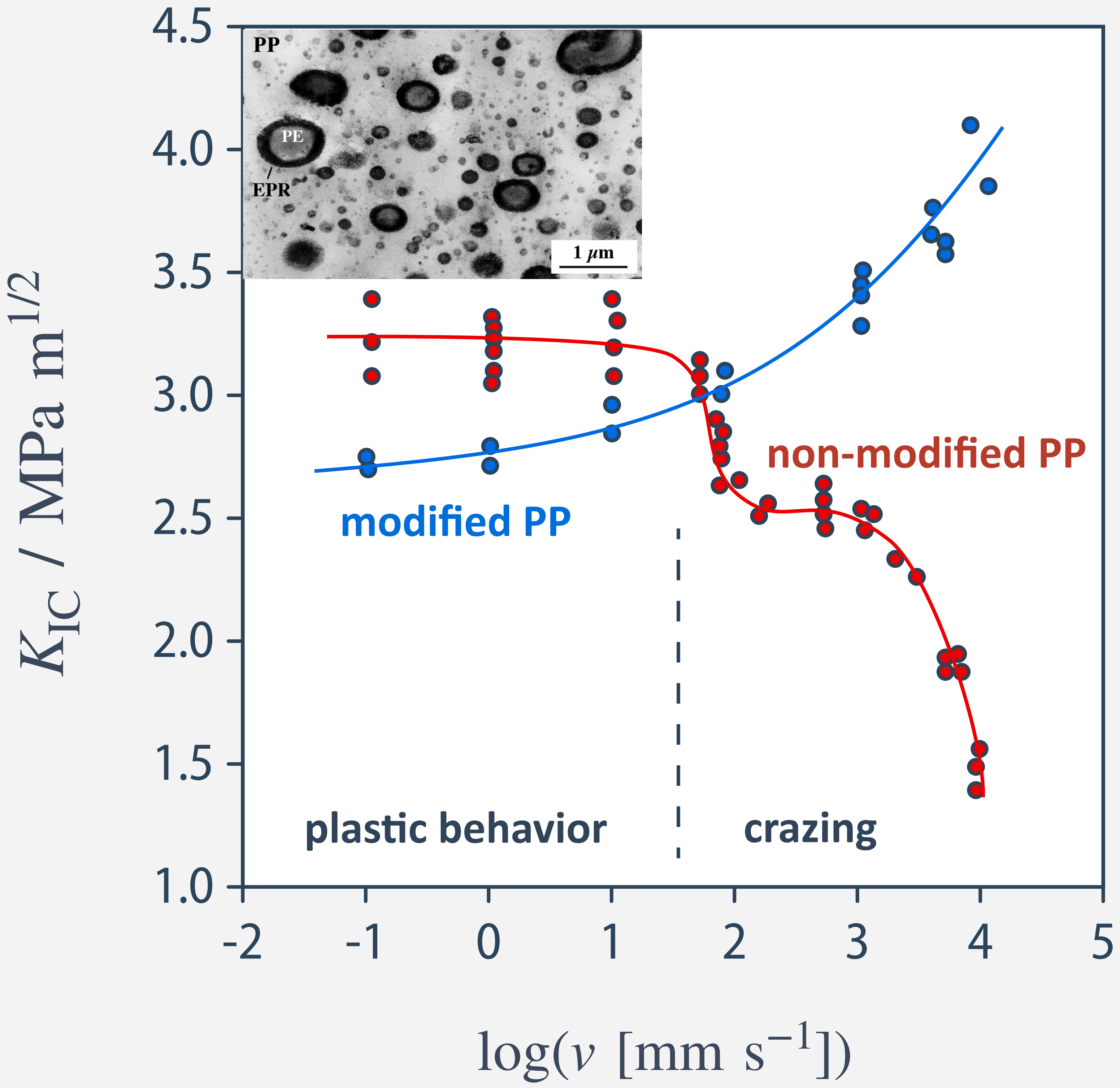
KIC Values in Glassy and Semicrystalline Polymers

fracture resistance in PMMA



the unmodified PMMA shows a single craze at the head of the crack over the entire speed range studied here

fracture resistance in PP



the PP used in this study (high molar mass) is brittle at high deformation rates. Modification is therefore ineffective at low speed, because PP deforms by plastic flow (necking) rather than crazing)

- **high dispersion of the elastomer phase and low contents are required**

Learning Outcome

- crazes are crack-like defects which appear when certain polymers are tested in tension. The craze surfaces are spanned by highly drawn craze fibrils, which are load bearing. Crazing is nevertheless associated with brittle behavior.

- crazes form most readily in *low entanglement density polymers*. The formation of the craze fibrils requires loss of entanglements: the fewer entanglements there are, the less energy per fibril is consumed during fibrillation and the lower the crazing stress.

- the strength of a craze fibril and hence of the craze depends directly on the entanglement density. *Low entanglement density polymers* show little resistance to crack propagation and are fragile. However, although the energy dissipation due to one craze is small, and hence the toughness, it can be increased greatly by increasing the number of crazes at the crack tip. This is the basis of rubber toughening in PS and in PMMA.