

Lecture 29

Stress-strain curves for Polymers



Ludwig Boltzmann

Prof. Divya Nayar
Department of Materials Science and Engineering
divyanayar@mse.iitd.ac.in

Recap...

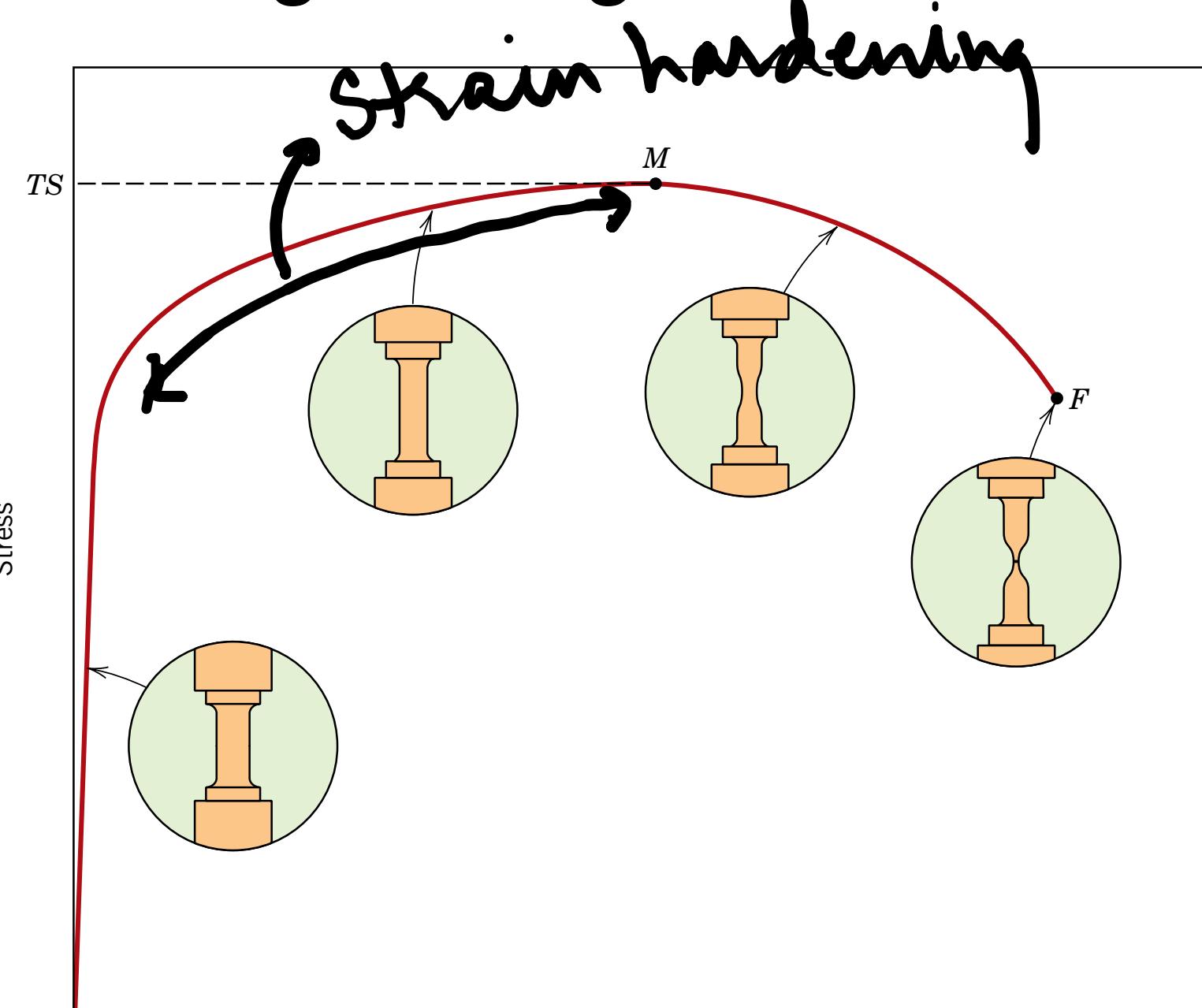
1. Elastic properties of materials
2. True stress-strain
3. Relationship between Engineering stress-strain

Precap

1. True stress-strain curve
2. Stress-strain curves for Polymers
3. A new definition of entropy explaining elastic deformation

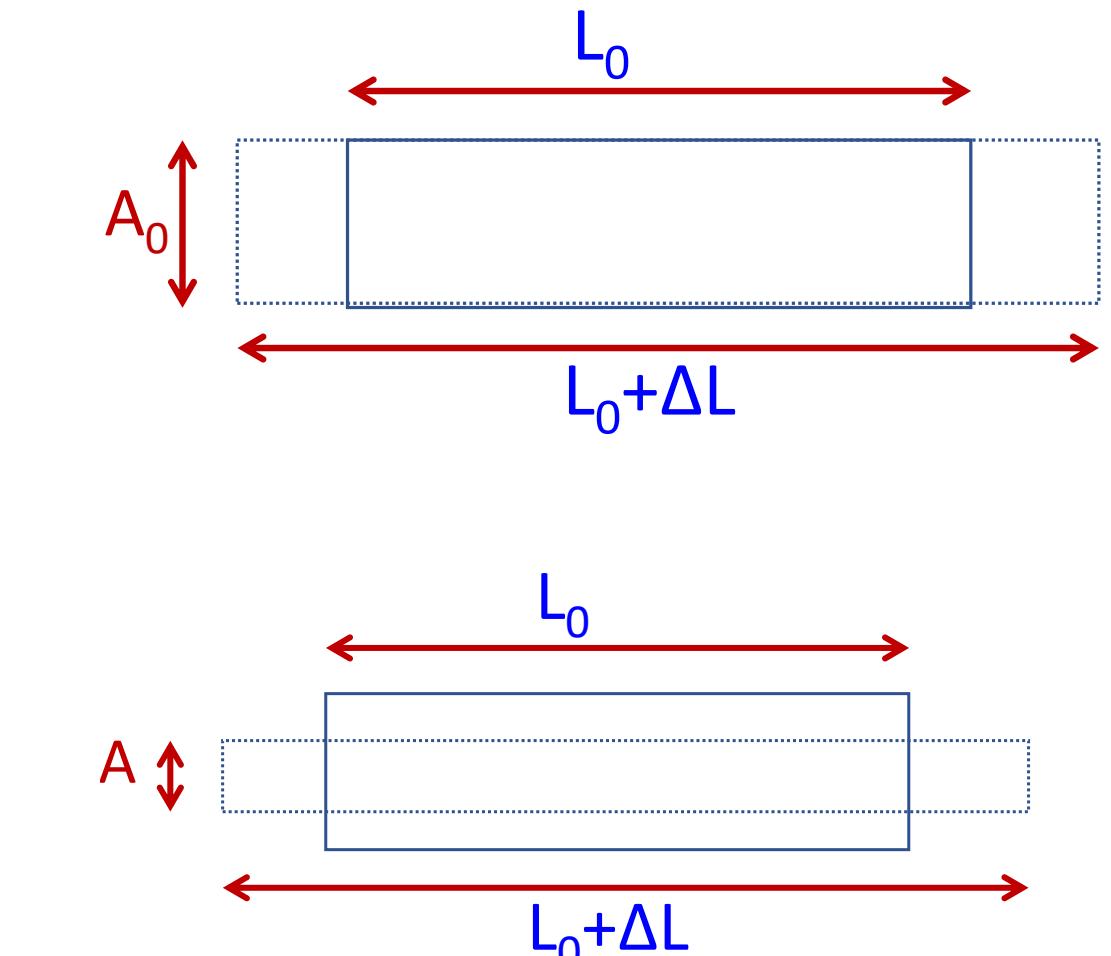
True stress

Engineering stress does not consider the instantaneous change in the cross-section area

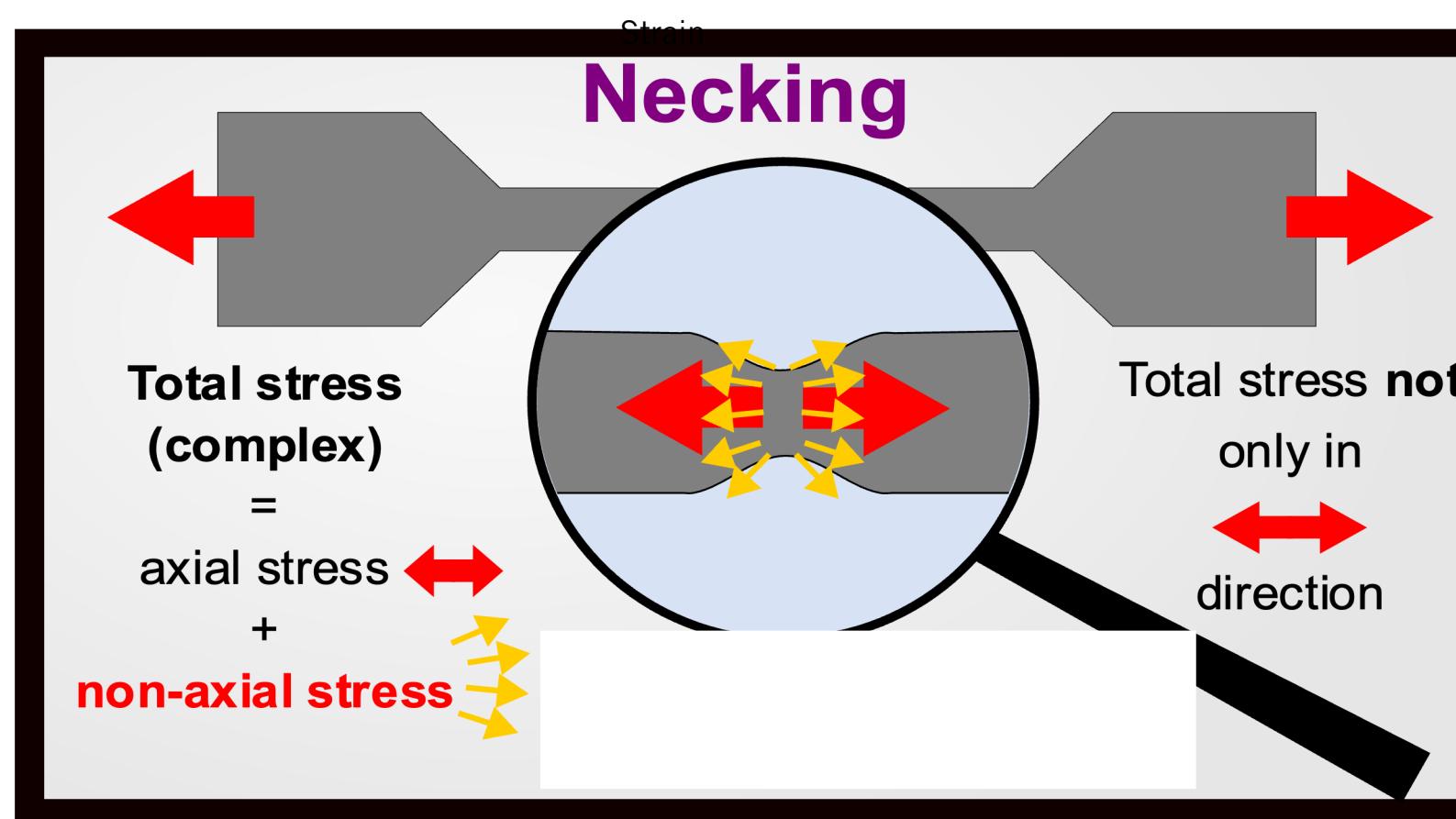


$$\text{Engineering stress, } \sigma_E = \frac{F}{A_0}$$

$$\text{True stress, } \sigma_T = \frac{F}{A}$$



Instantaneous area



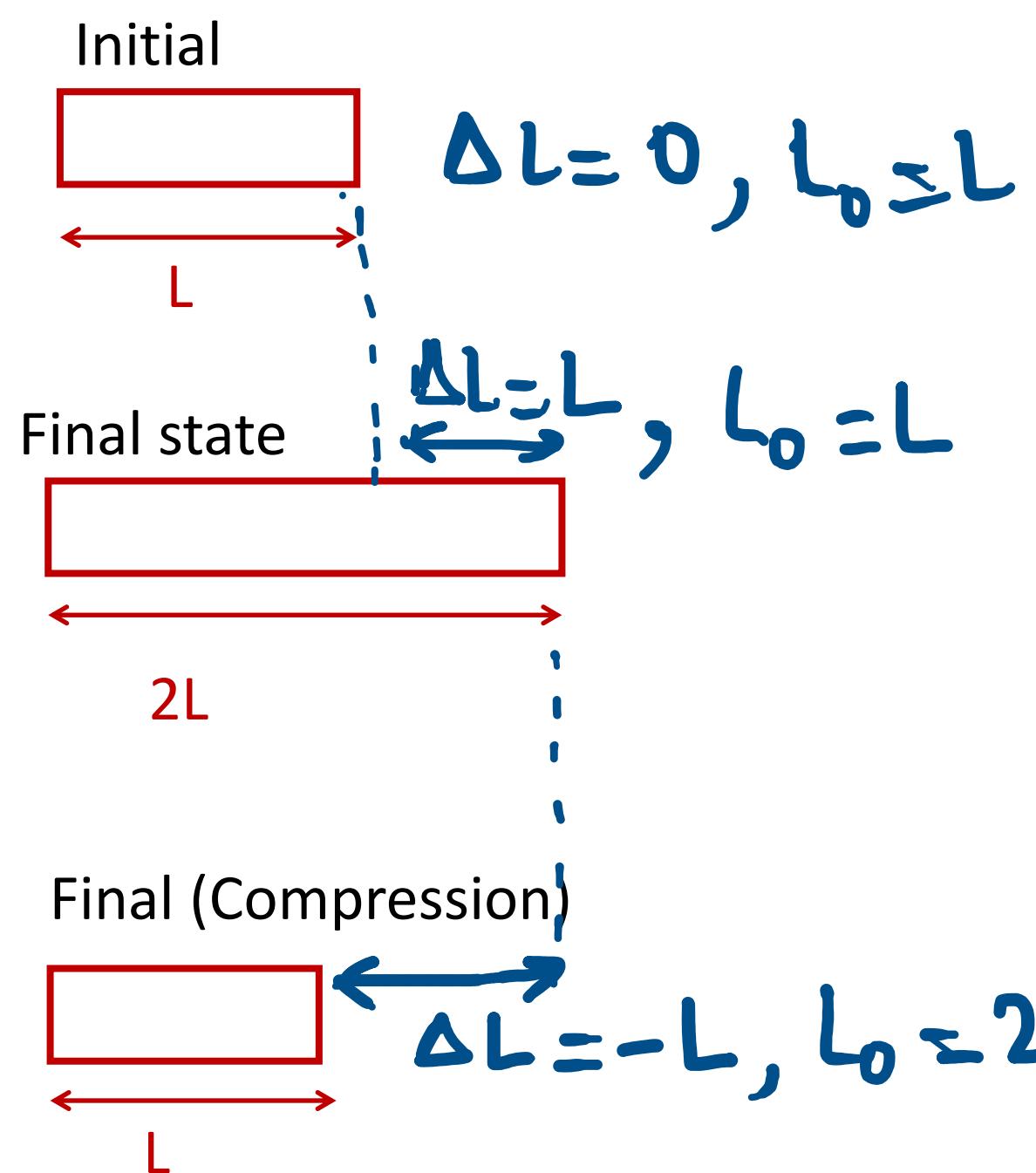
$$\sigma_T = \sigma_E (1 + \epsilon_E)$$

$$\text{True strain, } \epsilon_T = \ln (1 + \epsilon_E) = \ln \frac{L}{L_0}$$

$$\text{Engineering strain, } \epsilon_E = \frac{\Delta L}{L_0}$$

Implications

True strain is the real strain: for practical purposes



Engineering strain

$$\varepsilon_E = \frac{\Delta L}{L_0} = 0$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{L}{L} = 1$$

$$\varepsilon_E = \frac{\Delta L}{L_0} = \frac{-L}{2L} = -0.5$$

$$\text{Net } \varepsilon_E = 0.5$$

True strain

$$\varepsilon_T = \ln \frac{L}{L_0} = 0$$

$$\varepsilon_T = \ln \frac{2L}{L} = \ln 2 = 0.69$$

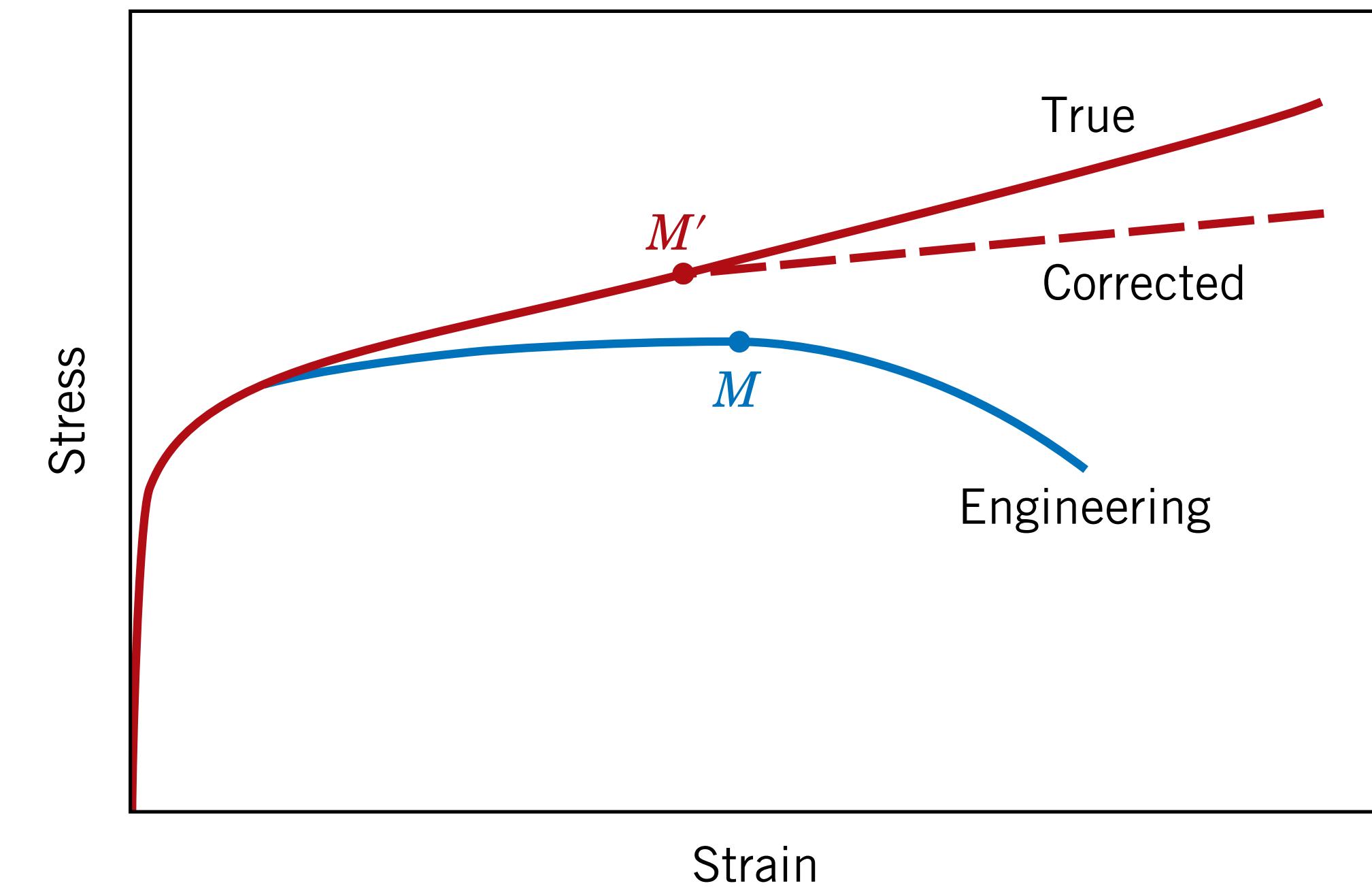
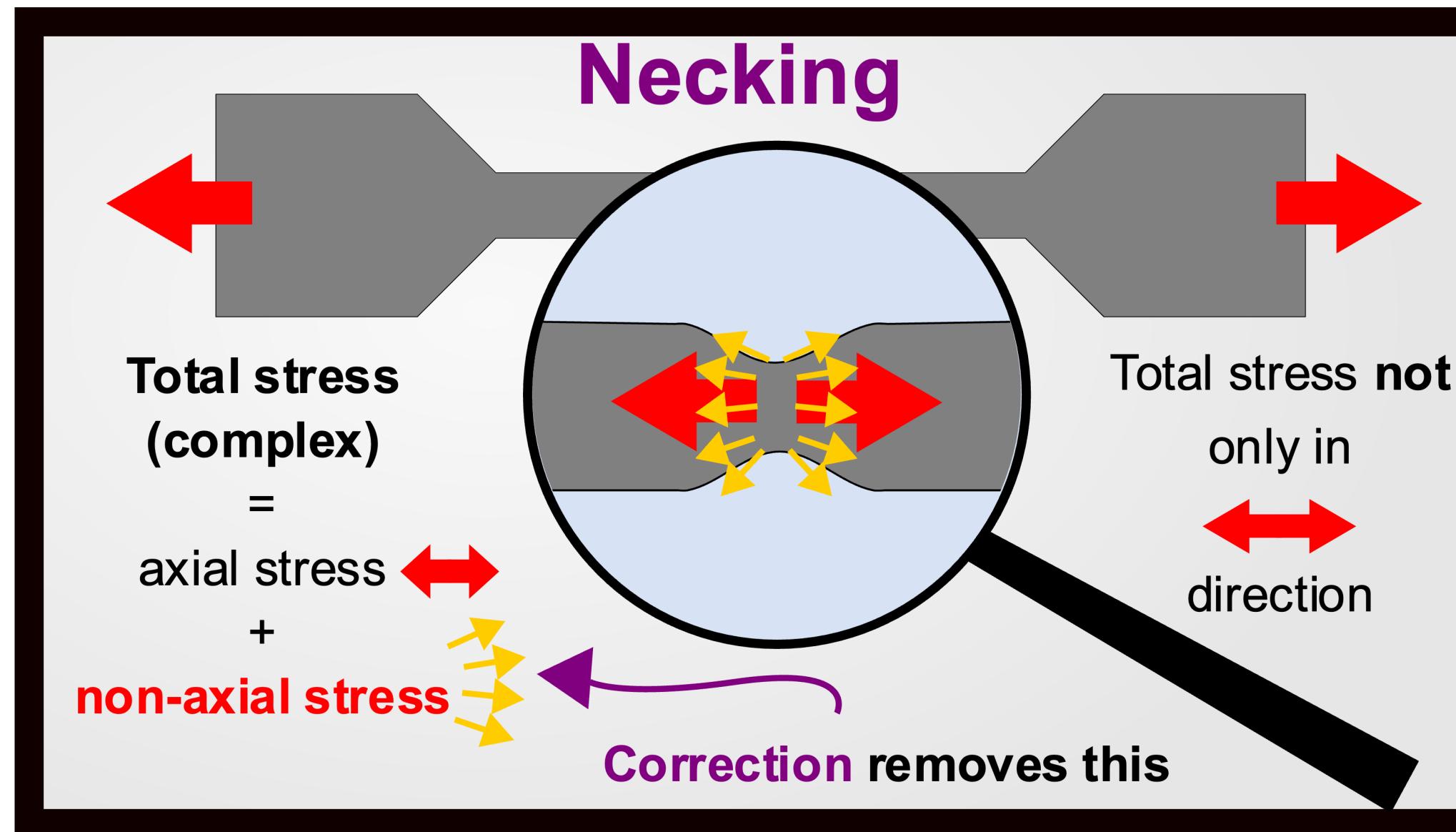
$$\varepsilon_T = \ln \frac{L}{2L} = -\ln 2 = -0.69$$

$$\text{Net } \varepsilon_T = 0$$

True vs Engineering stress-strain

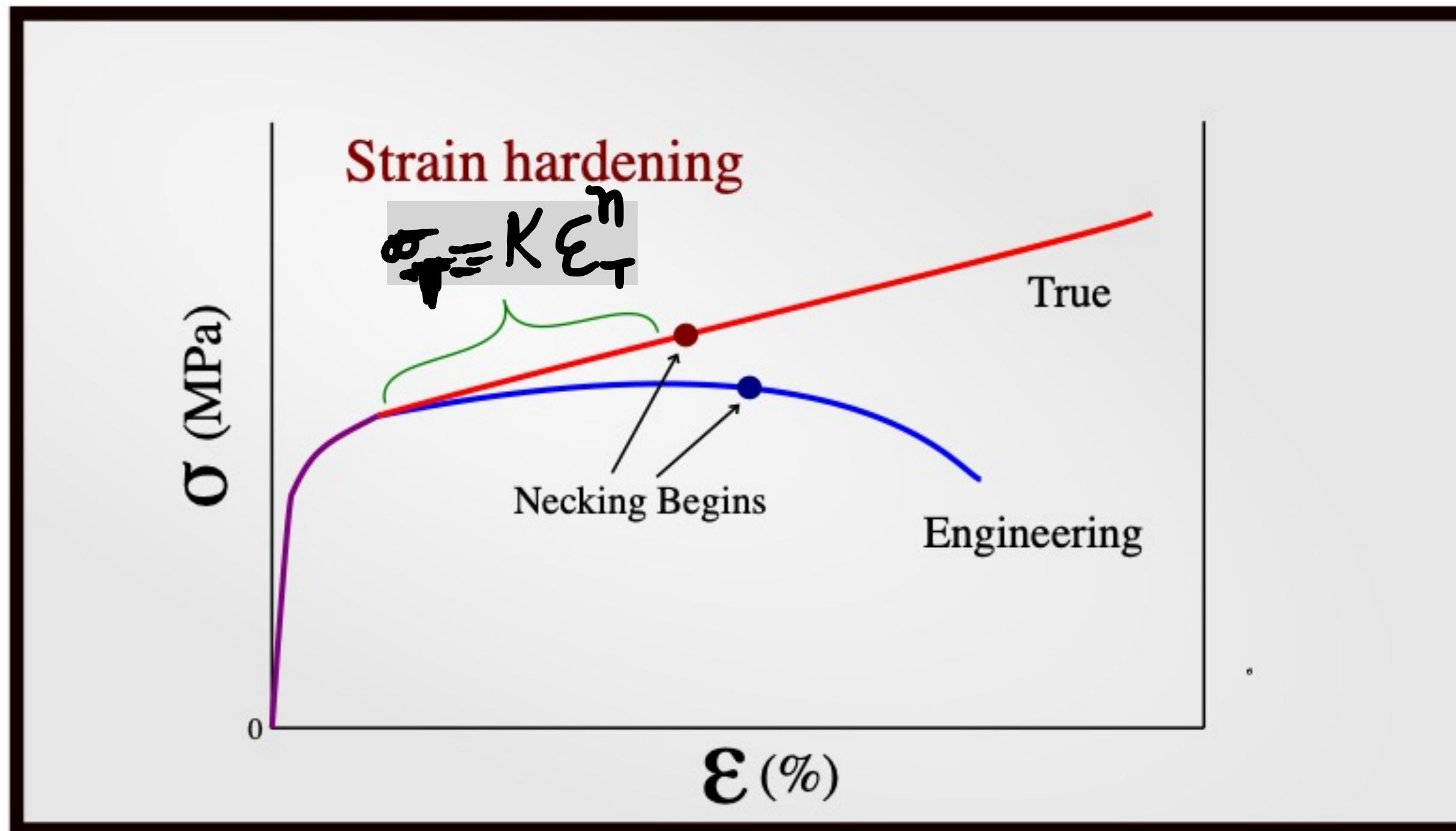
Necking region: existence of other stress components in addition to the axial stress

The “correct” stress (axial) within the neck is slightly lower than the stress computed from the applied load and neck cross- sectional area.



Strain hardening

Region of the true stress–strain curve from the onset of plastic deformation to the point at which necking begins



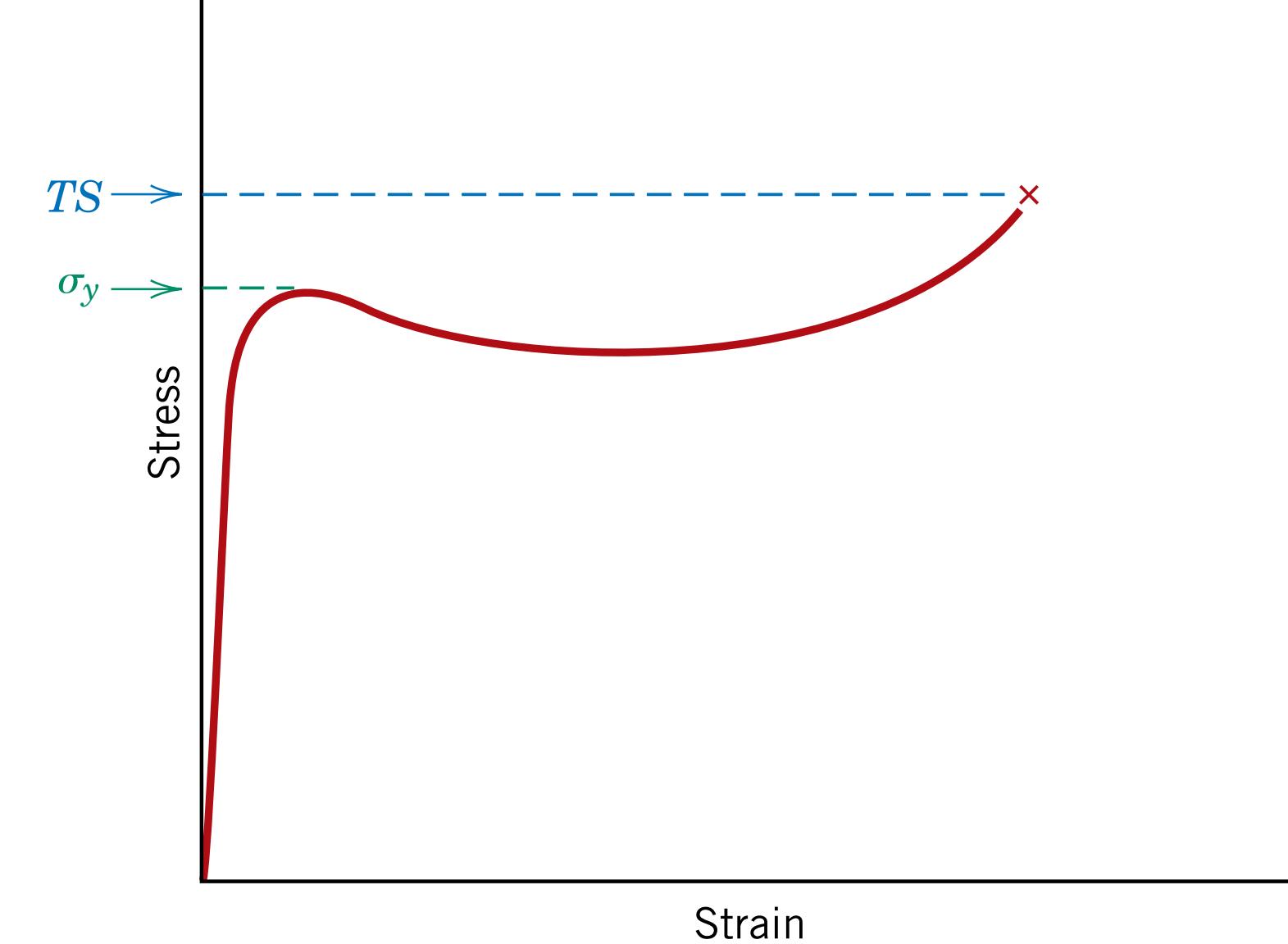
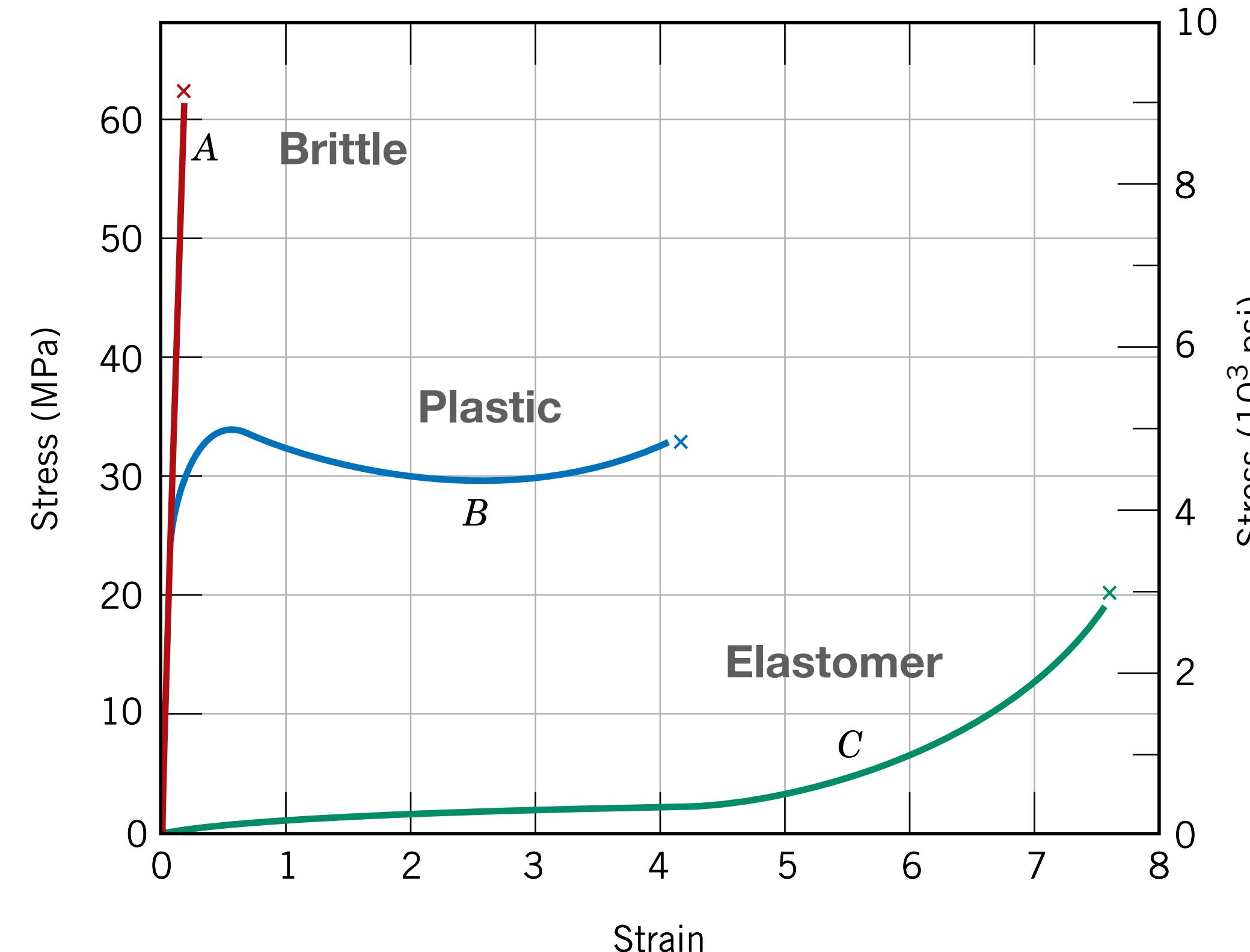
$$(n < 1)$$

n = strain hardening exponent (we will do this when we learn more about plastic deformation)
 K = strength coefficient

Stress-strain curve for Polymers

Three categories

- Fibres (A)
- Plastics (B)
- Elastomers (C)



Stress-strain curve for Polymers

Three categories



Plastics



Elastomers



Fibres

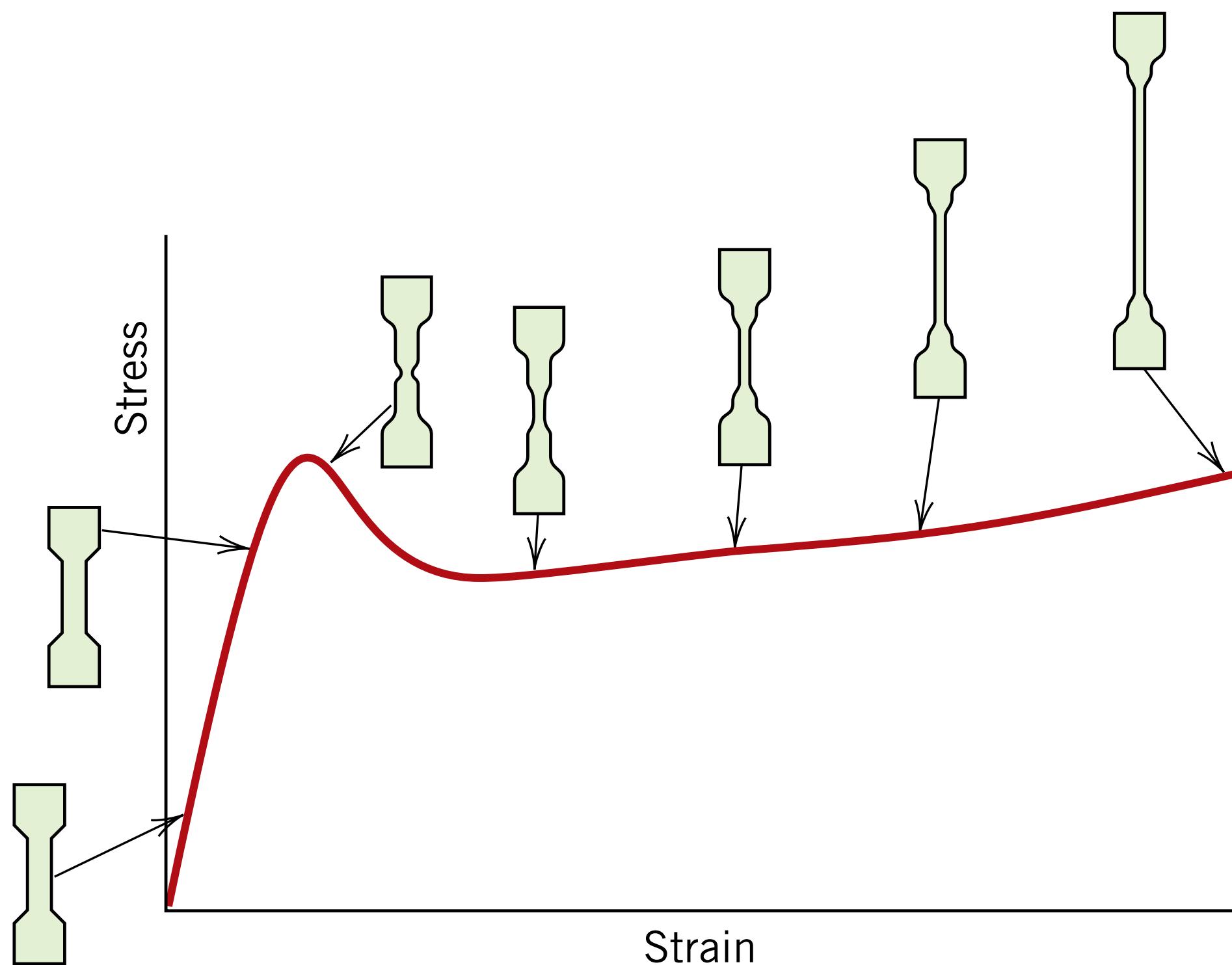
Plastics: are materials that have some structural rigidity (stiffness) under load. Examples: Polyethylene, polypropylene, poly(vinyl chloride), polystyrene, and the fluorocarbons, epoxies, phenolics, and polyesters.

- Can be rigid (stiff) and brittle
- Can be flexible (elastic and plastic deformation)
- May have any degree of crystallinity
- All molecular structures and configurations (linear, branched, isotactic, etc.) are possible.
- Thermoplastic or thermosetting

Viscoelasticity

Viscous-liquid+ elastic behaviour

- Found in materials which respond to an applied stress by both recoverable and permanent deformations, which are time dependent
- Very common in non-crystalline organic polymers
- Time-dependent permanent deformation is called viscous flow
- In elastic deformation, the rate of strain or strain is not important



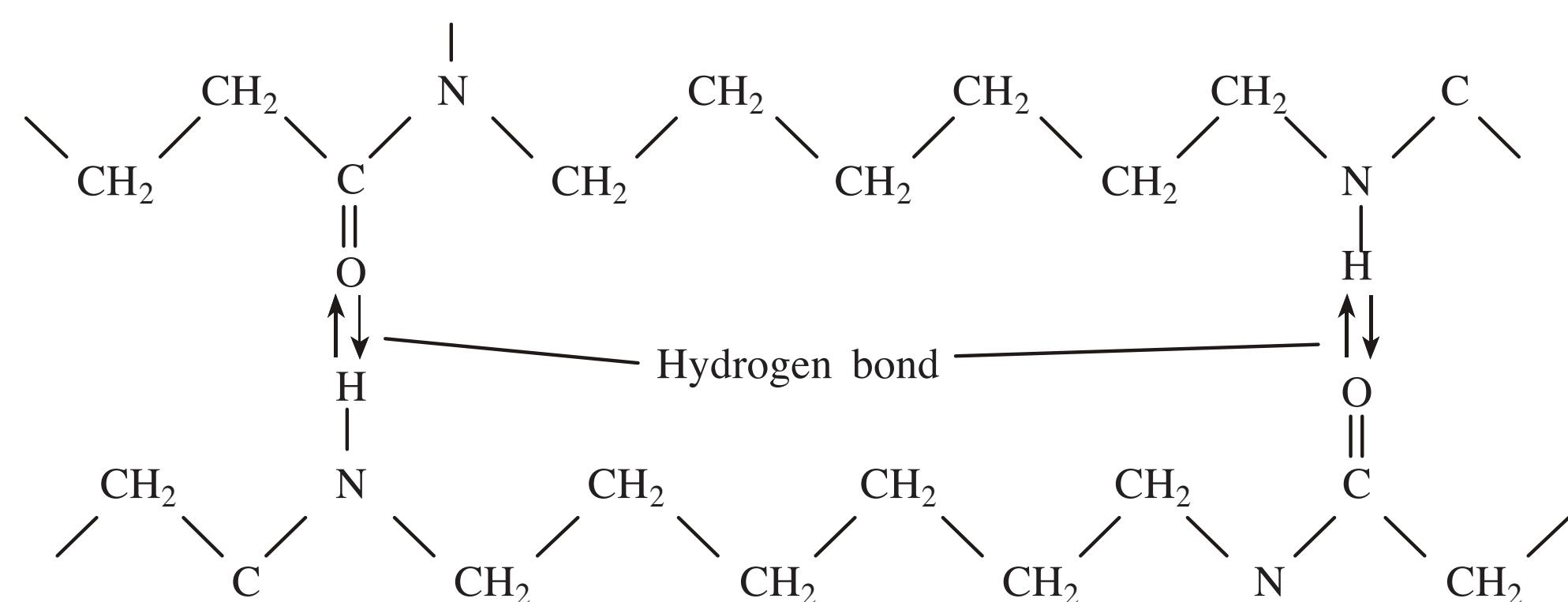
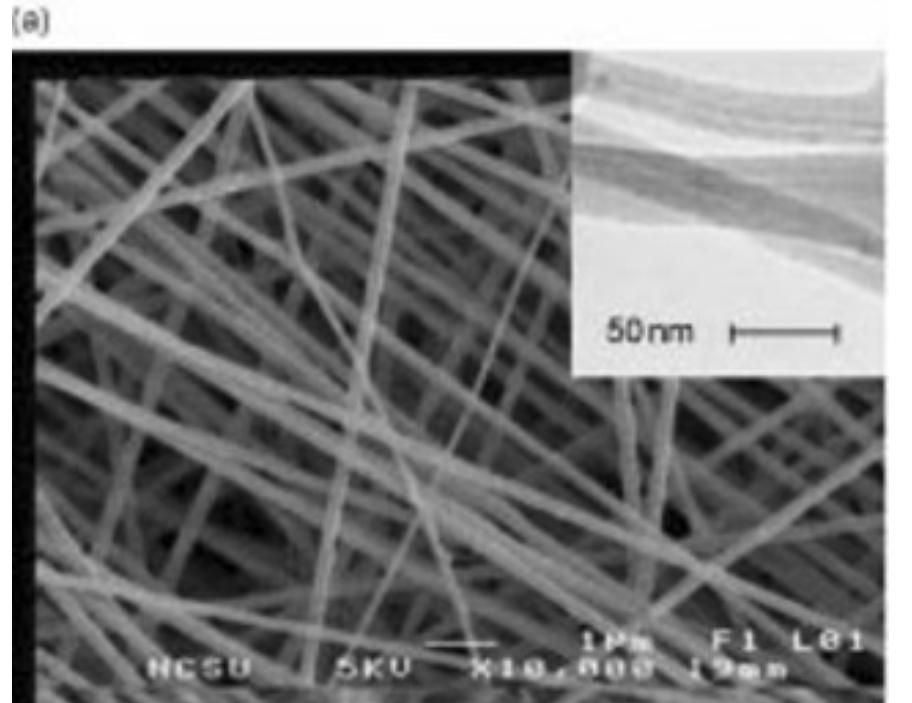
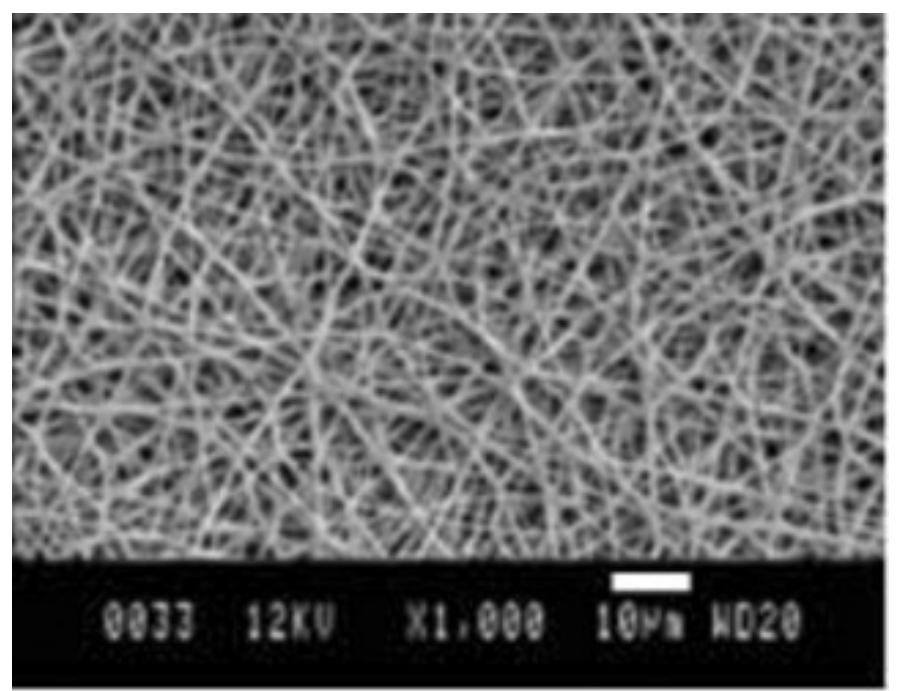
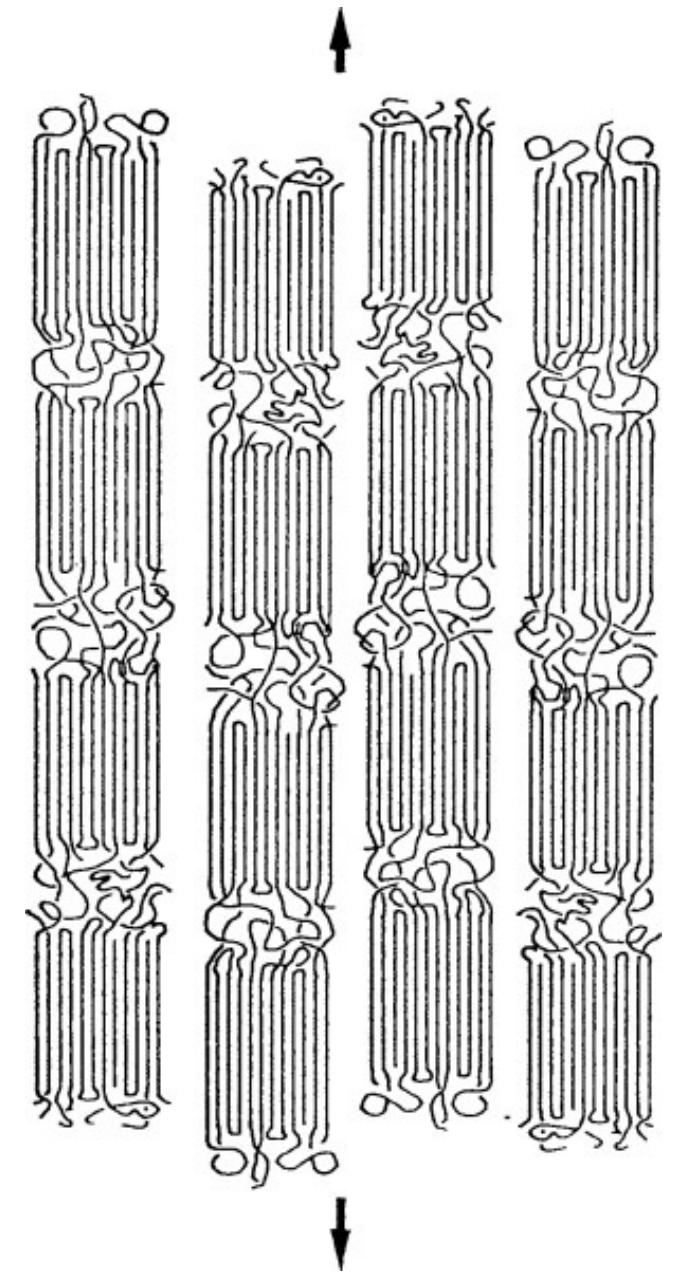
Amorphous material:

- Glass at low temperatures: not all molecular motion is frozen
 - Rubbery solid above glass transition temperature: conformational changes
 - Viscous liquid at high temperature: segments between entanglements can recover
-
- At low temperature: elastic (Hooke's law)
 - At high temperature: viscous liquid-like behaviour
 - At intermediate temperatures: combined mechanical characteristics:

Viscoelasticity

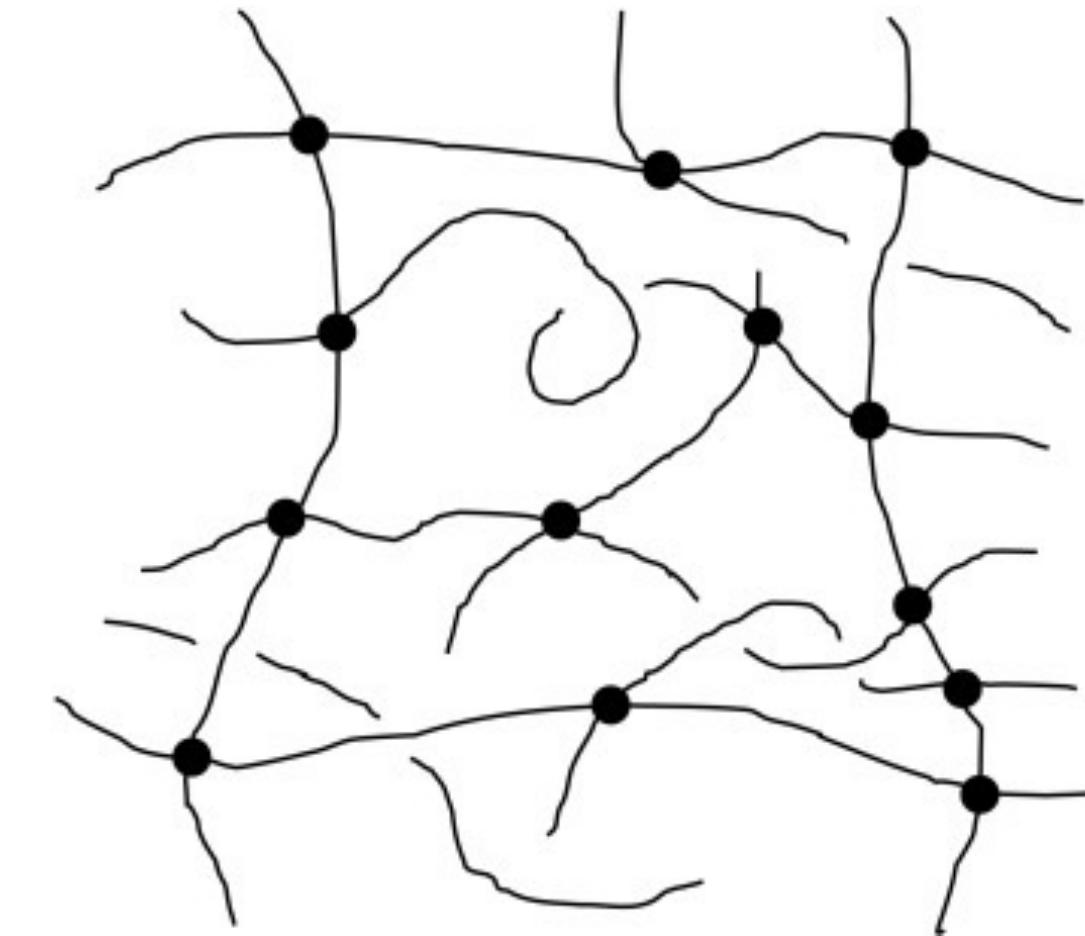
Fibers

- Polymers are capable of being drawn into long filaments having at least a 100:1 length-to-diameter ratio.
- All the chains are more or less aligned in the long direction of the fibre
- High elastic modulus: Their strength and elastic modulus in a direction parallel to the fibre length are an order of magnitude larger as compared to the nonaligned structure.
- High degree of crystallinity leads to high tensile strength: linear and unbranched polymer chains, polar groups increase inter-chain intermolecular forces
- Examples: Nylon– polyamide fiber



Elastomers

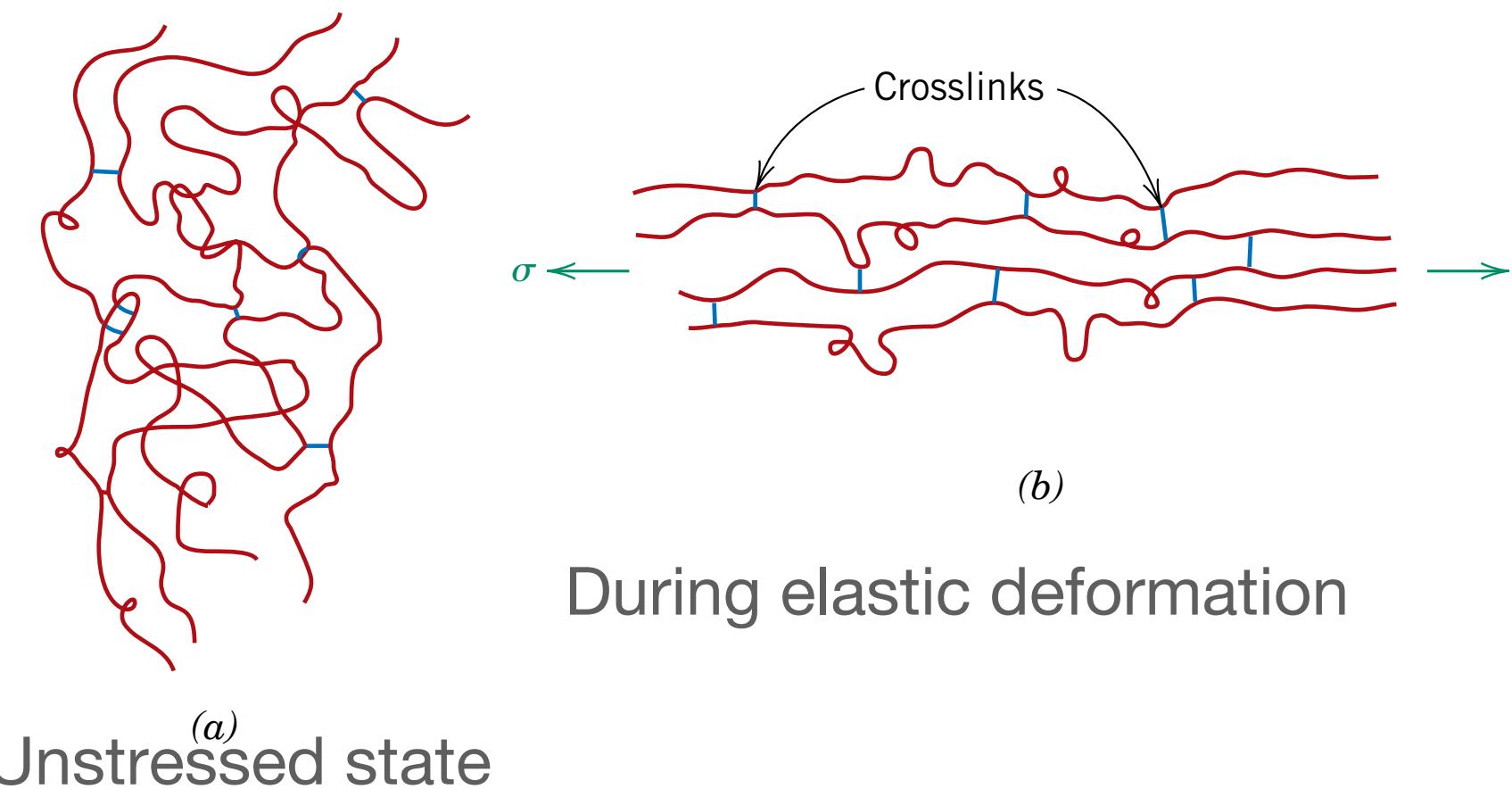
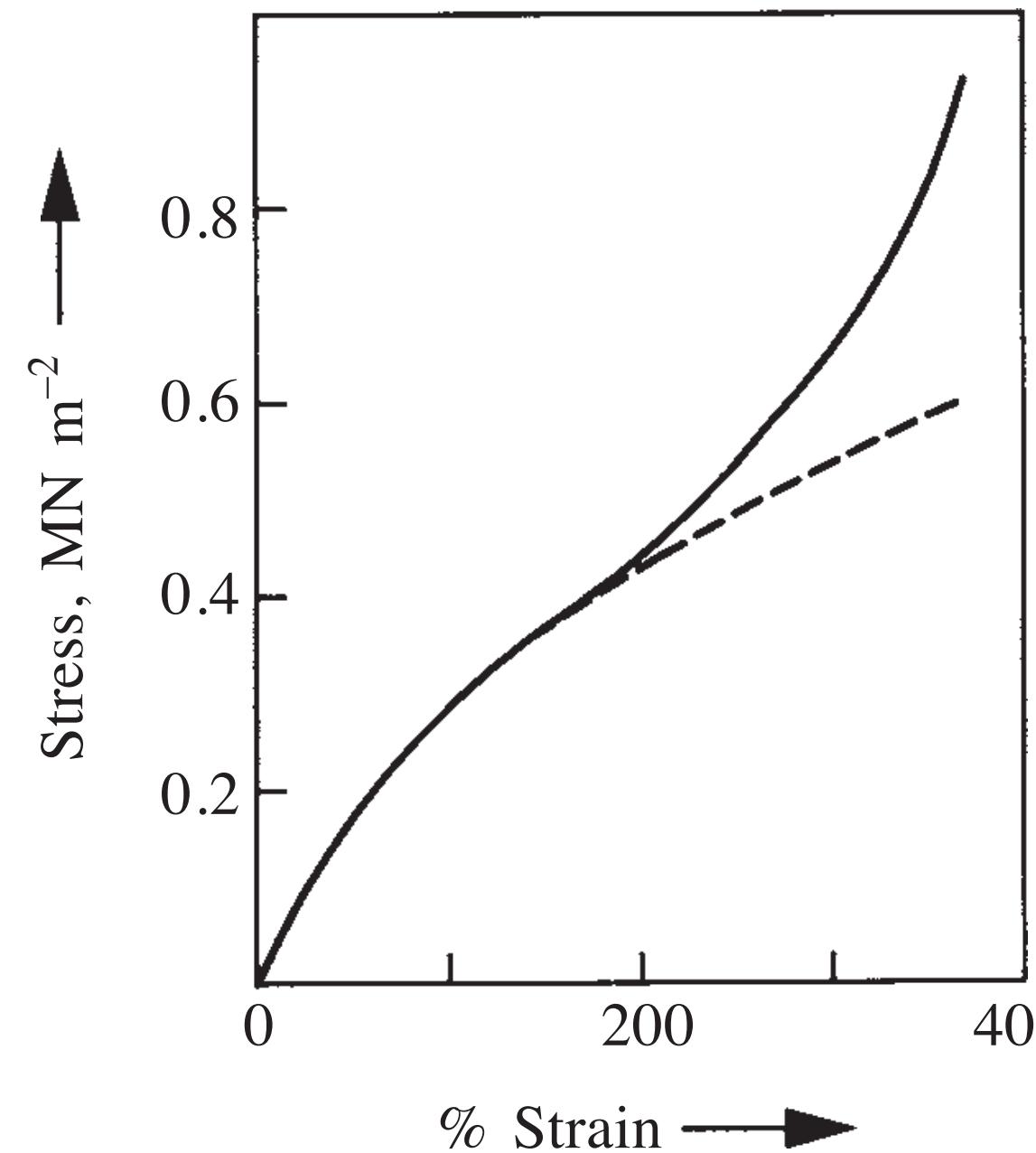
Rubber-like elasticity



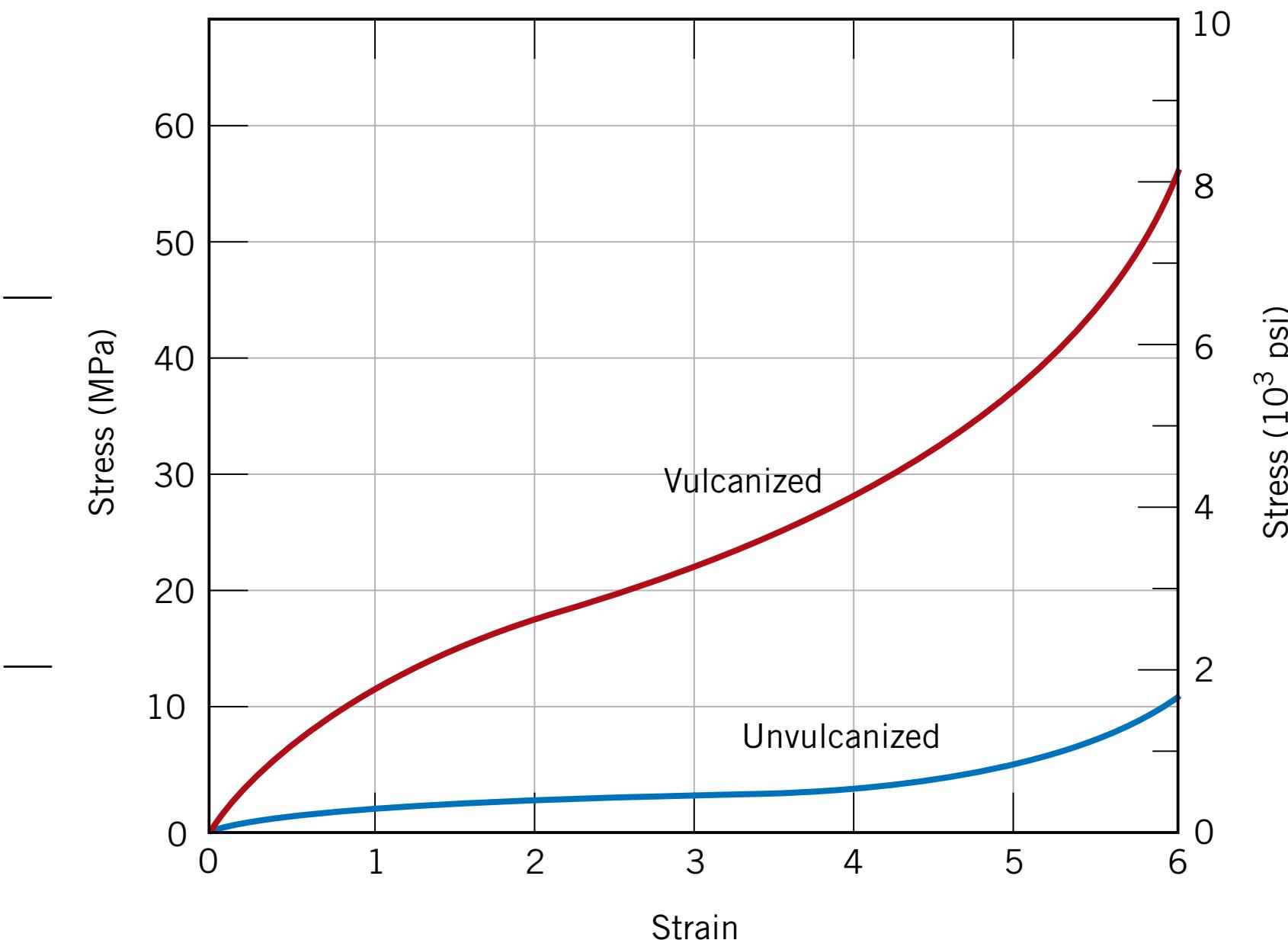
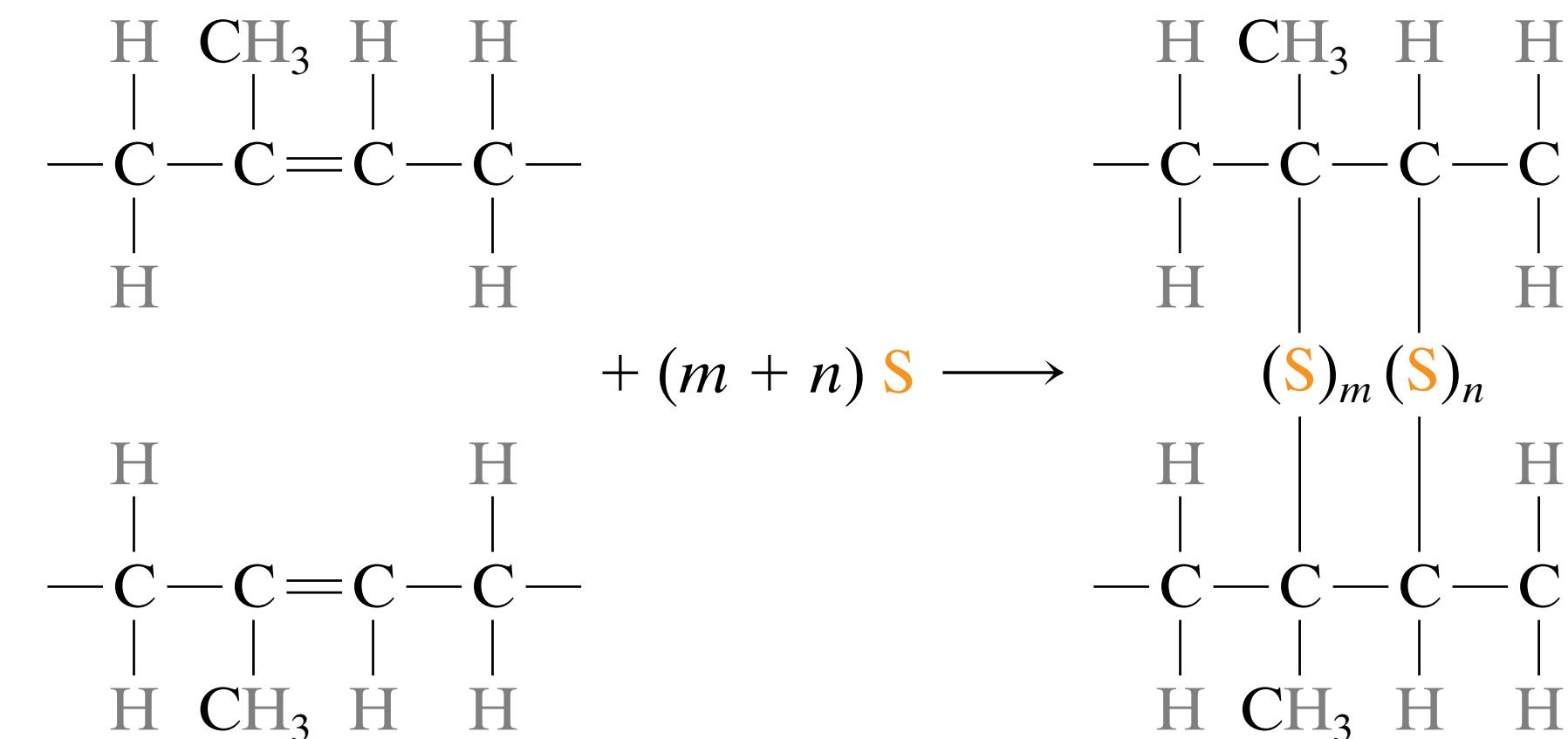
- Materials which undergo recoverable deformation of *a few hundred per cent* are called *elastomers* and exhibit rubber-like elasticity.
- The stress is not proportional to strain in these materials, in contrast to ordinary elastic materials.
- Long chain polymers with some *cross-linking* between the chains.
- This feature is what keeps the molecules from slipping past one another permanently during stretching
- After cross-linking, the translational motion of chains gets restricted to segmental mobility between cross-linking points. When a stress is applied to an elastomer, equilibrium in the molecular configuration is established fairly quickly so that we can ignore the time dependent aspects of stretching as a first approximation.
- Do not easily crystallize
- Amorphous
- Onset of plastic deformation is delayed: restricting the motions of chains

Elastomers

Stress-strain curve



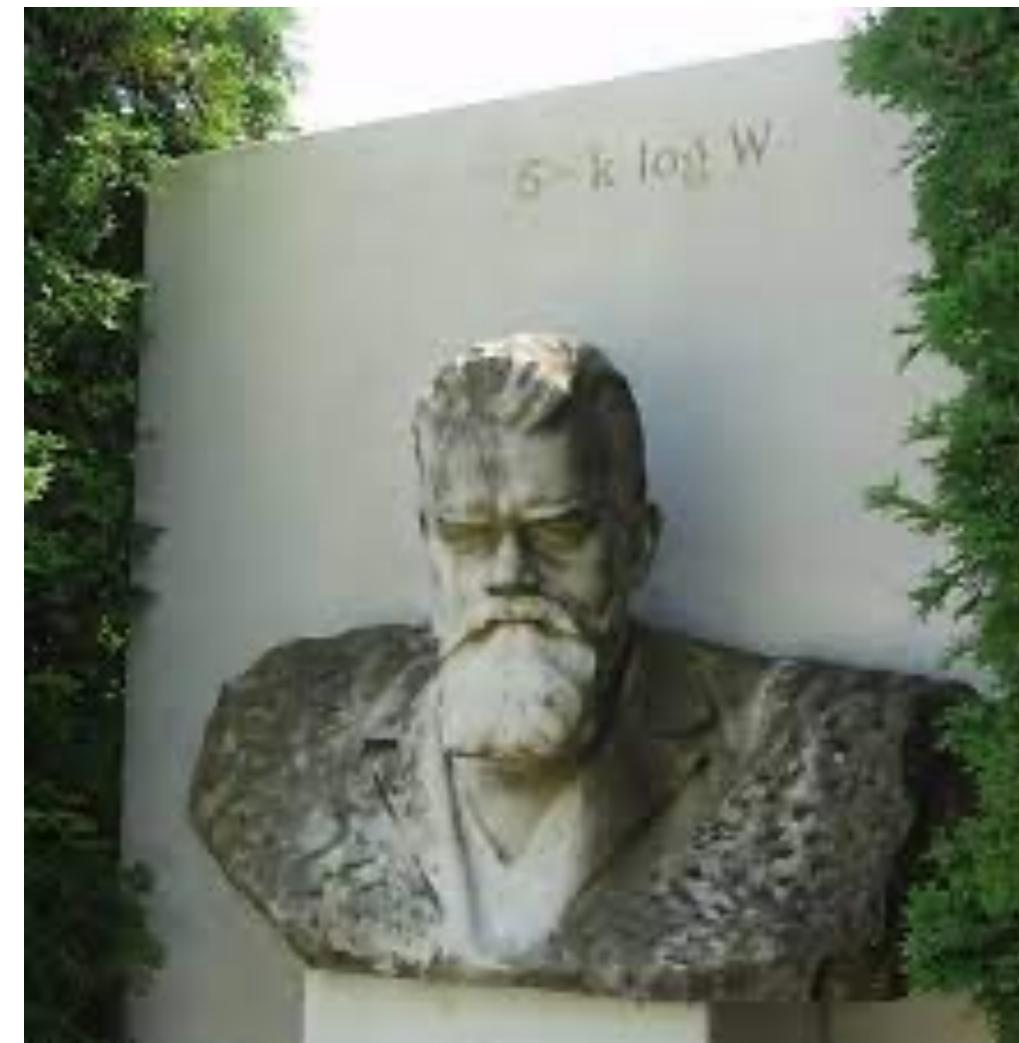
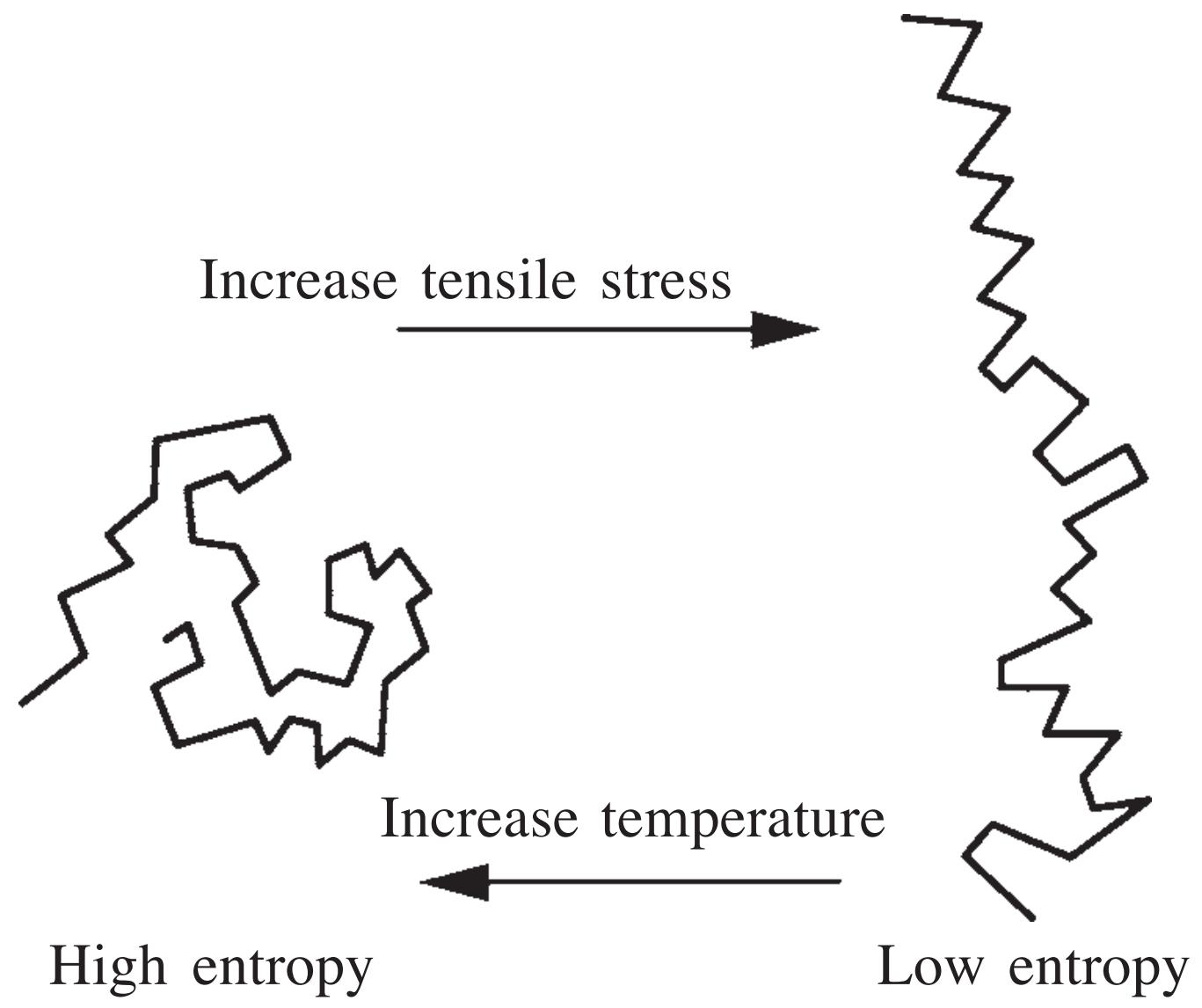
Vulcanization: crosslinking process in elastomers



- Sulfur compounds are added to the heated elastomer; chains of sulfur atoms bond with adjacent polymer backbone chains and crosslink them
- Unvulcanized rubber, which contains very few crosslinks, is soft and has poor resistance to abrasion.
- Elastic modulus increases with increasing temperature.
- Magnitude of elastic modulus \propto density of cross-links.

Driving force for elastic deformation in elastomer is entropy

Thermodynamics



Ludwig Boltzmann

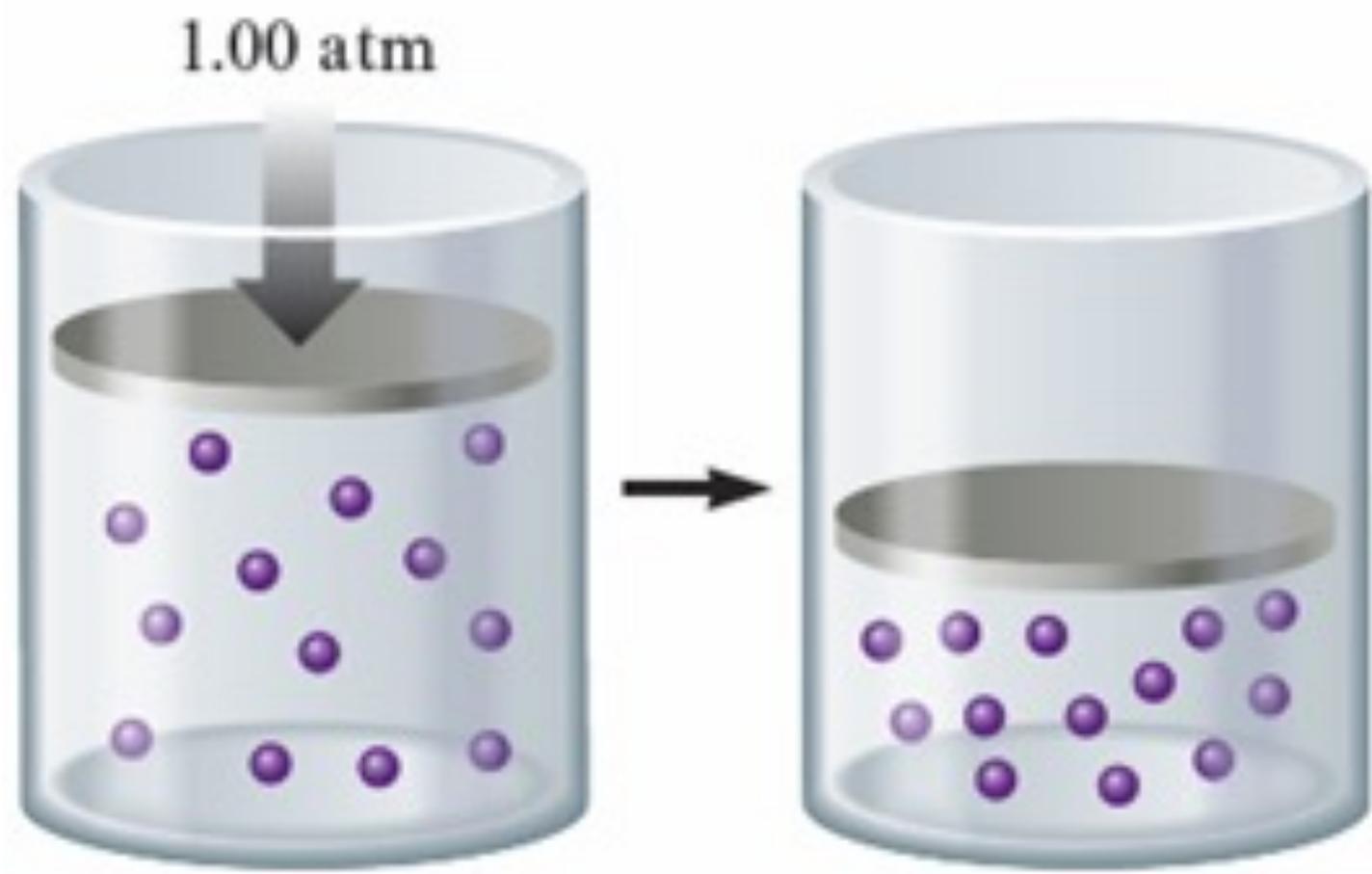
A new definition of entropy
 $S = k \log W$

The stretching process merely uncoils the coiled molecules, but does not change the bond lengths or bond angles. This behaviour is in contrast to what happens in an ordinary elastic material, where bond lengths are clearly changed

W = number of ways of arrangement of molecules
 S = Entropy is a measure of the possible number of ways in which the energy of the system can be distributed among the molecules.

Good reads: "Anxiety and Equation" by Eric Johnson
"Entropy Demystified" by A. Ben Naim

Food for thought..



Why does gas in a container expand spontaneously?

Why does not the gas contract on its own spontaneously?

Why does a hot coffee mug get cold spontaneously on keeping for sometime?

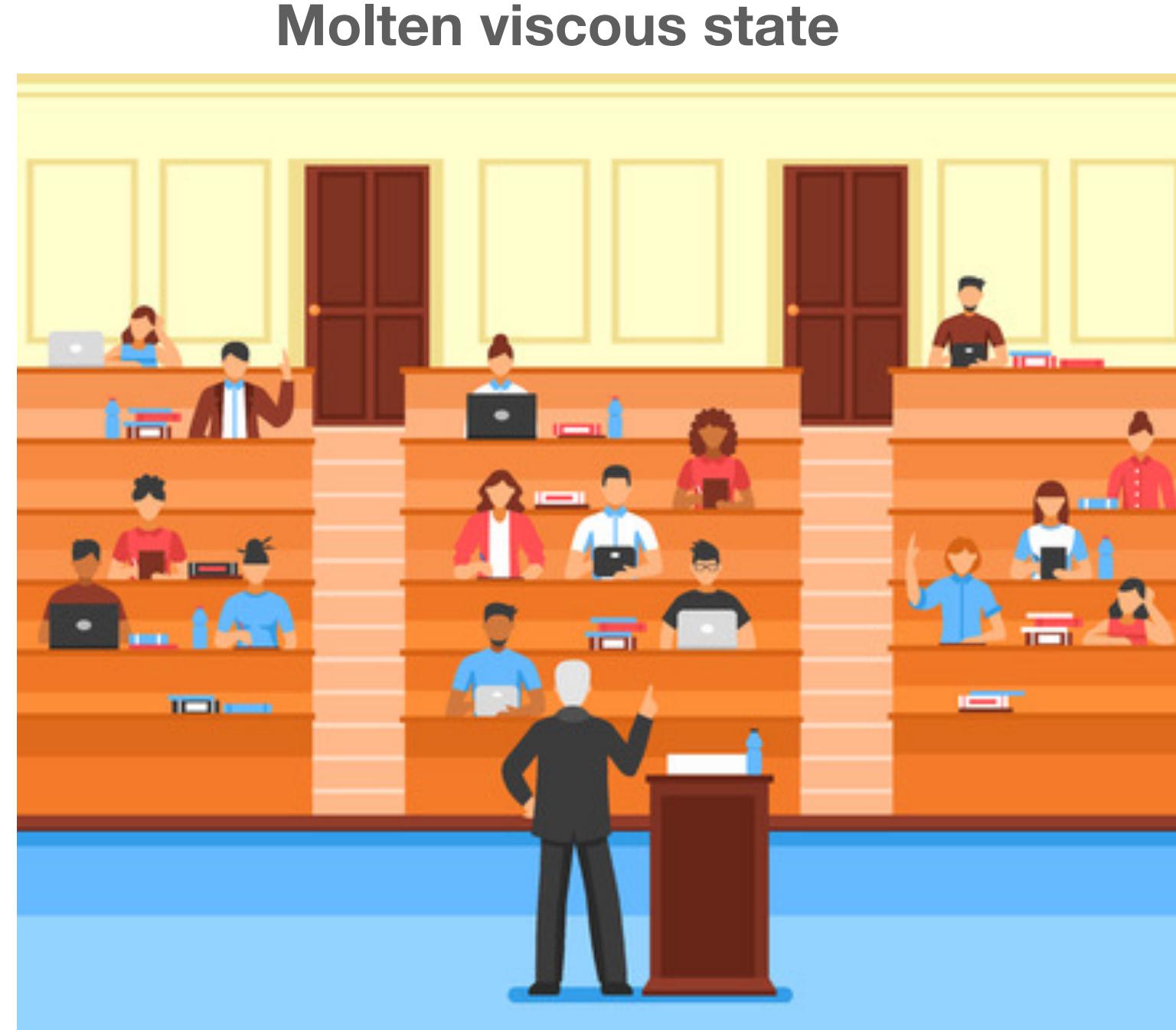
If you keep a cold coffee mug on table, why doesn't it get hot on its own spontaneously?

Dispersal of energy (*distribution of energy*) → spontaneity → entropy

The statistical or *molecular* definition of Entropy...

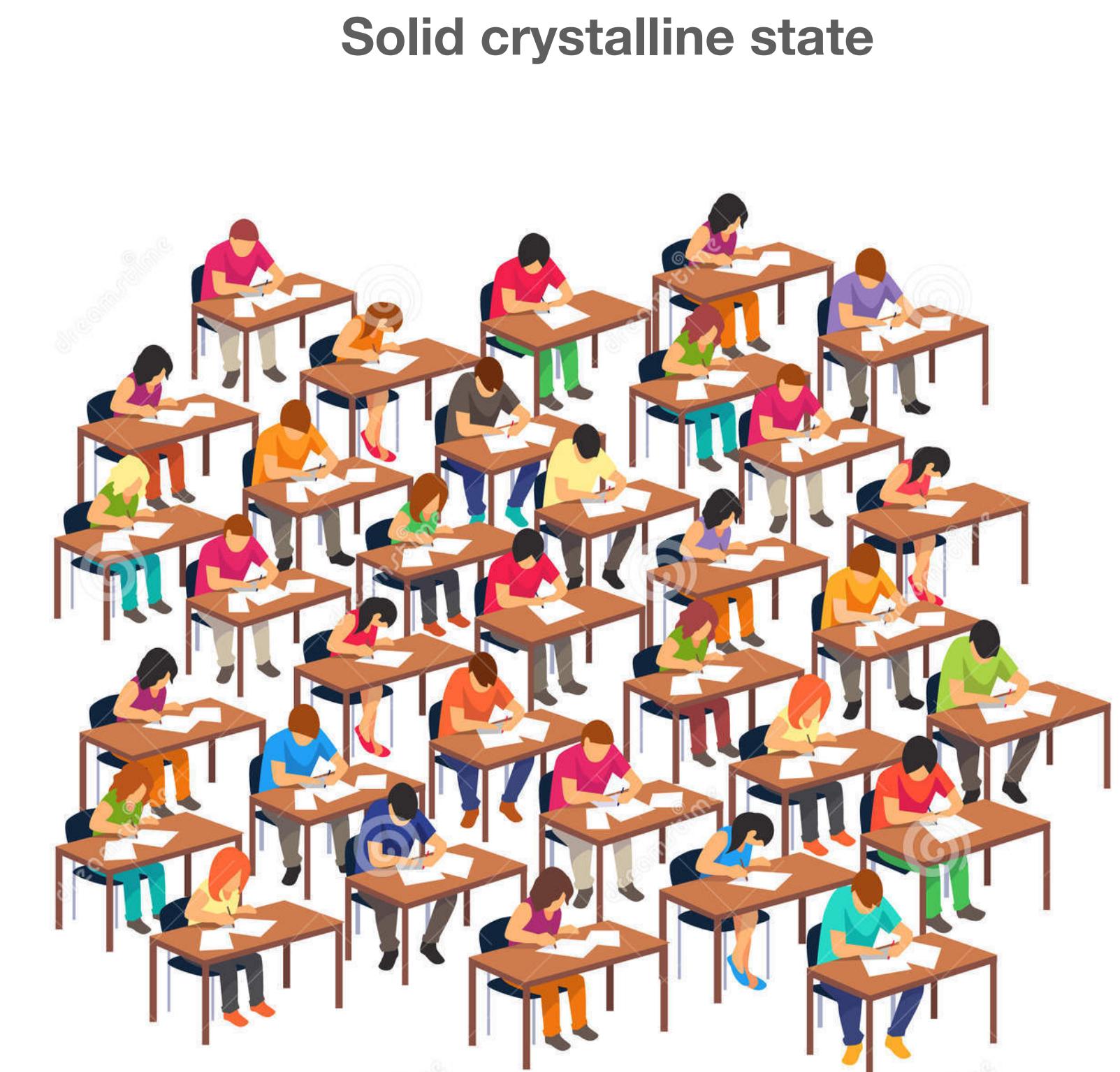


Liquid state
On a "random" lecture day



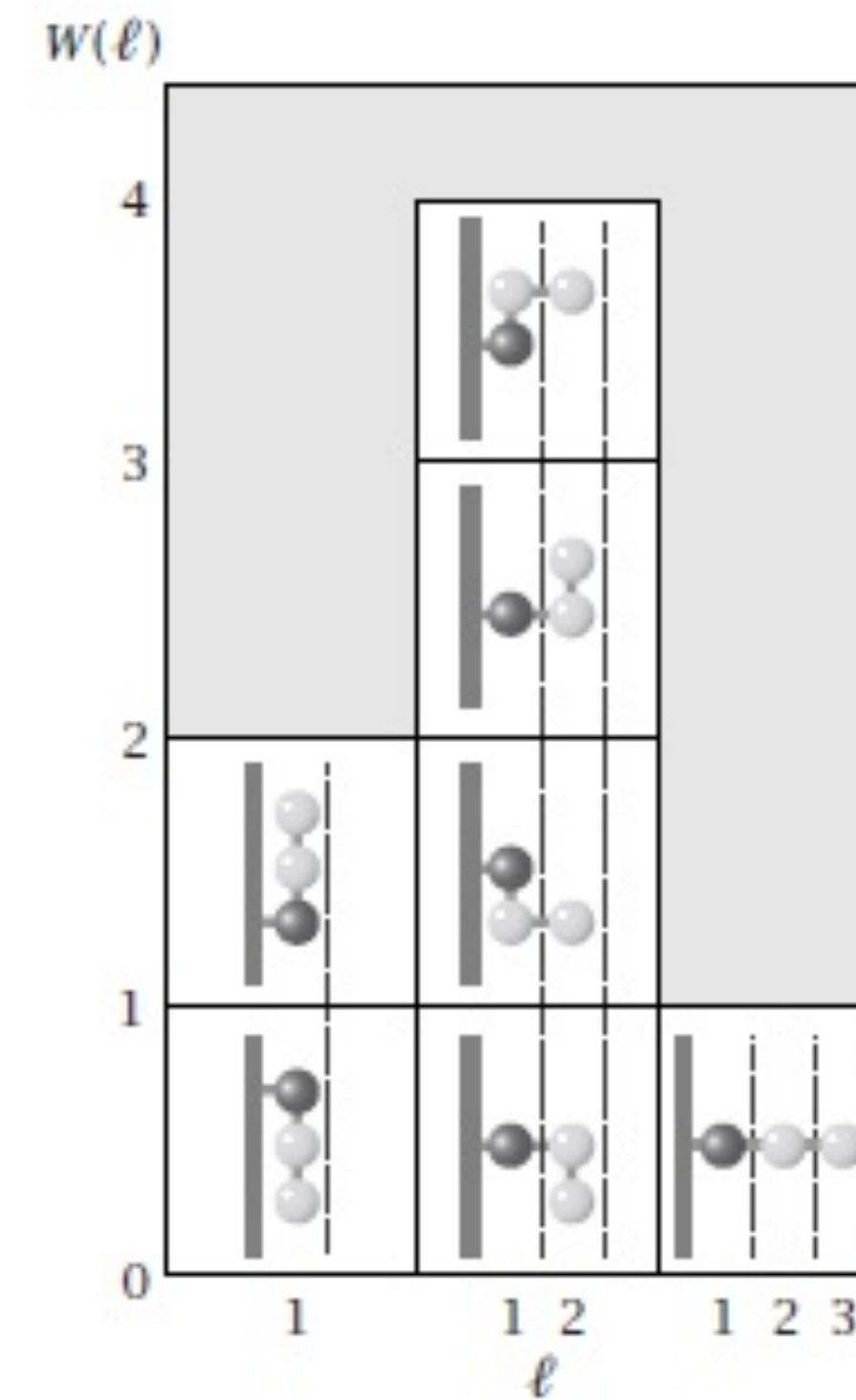
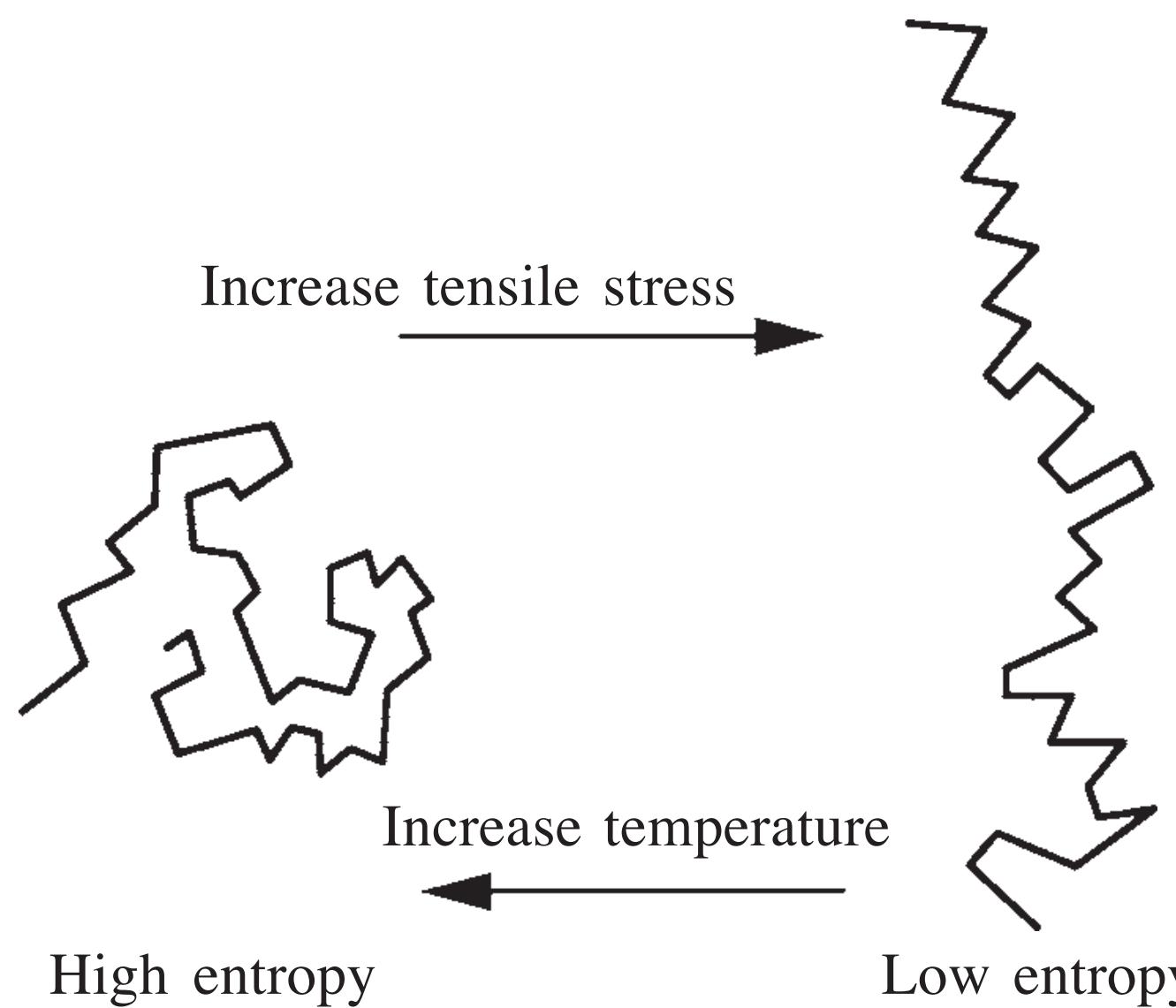
Molten viscous state
When students *prefer* to choose their company..

Decreasing Entropy



Solid crystalline state
On "exam" day:
Perfectly ordered arrangement

Driving force for elastic deformation is entropy



Case	Left	Right
A	● ● ○ ○	○ ○ ○ ○
B	● ● ● ○	○ ○ ○ ○
C	● ● ● ●	○ ○ ○ ○

Permeable Barrier →

Diffusion in materials

Stretchability in rubber

Which state will have higher entropy?

