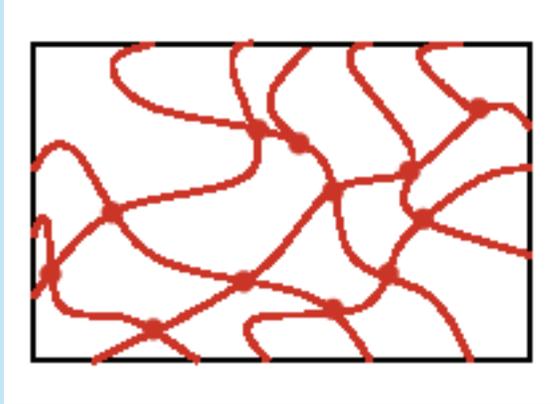


High Elasticity of Polymer Networks.

Polymer Networks.

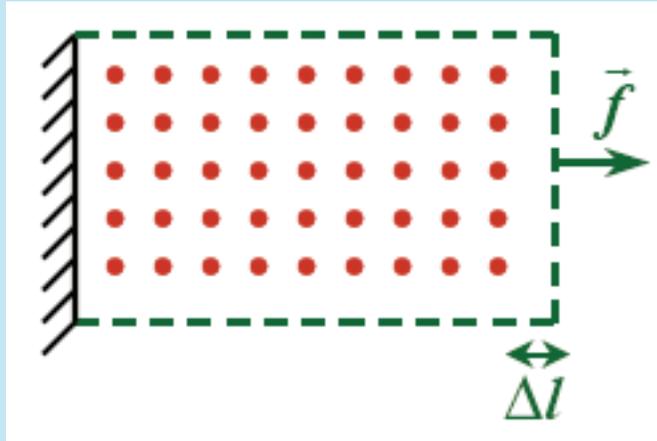


Polymer network consists of long polymer chains which are **crosslinked** with each other to form a **giant three-dimensional macromolecule**.

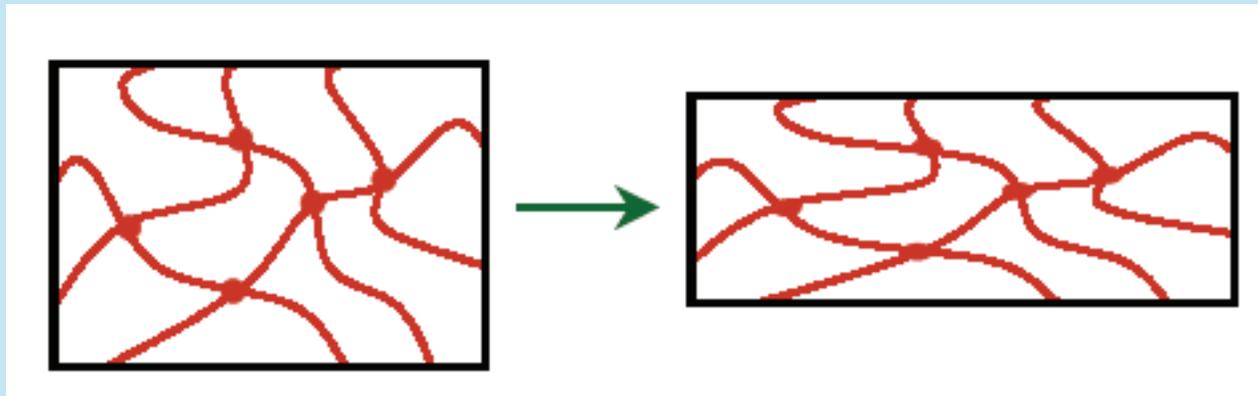
All polymer networks except those who are in the glassy or partially crystalline states exhibit the property of **high elasticity**, i.e., **the ability to undergo large reversible deformations at relatively small applied stress**.

High elasticity is the most specific property of polymer materials, it is connected with the most fundamental features of ideal chains considered in the previous lecture. In everyday life, highly elastic polymer materials are called **rubbers**.

Molecular Nature of the High Elasticity.



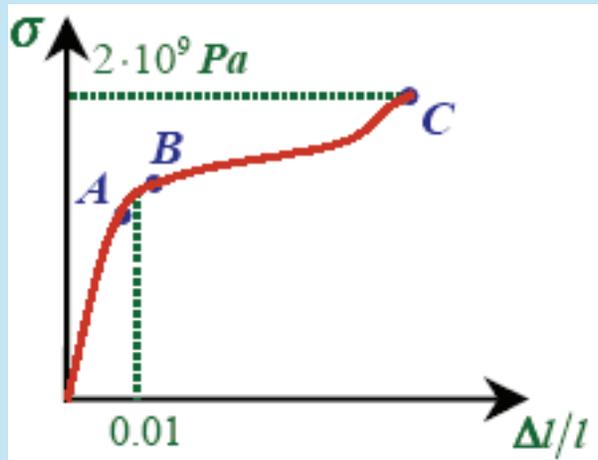
Elastic response of the crystalline solids is due to the change of the equilibrium interatomic distances under stress and therefore, the change in the **internal energy** of the crystal.



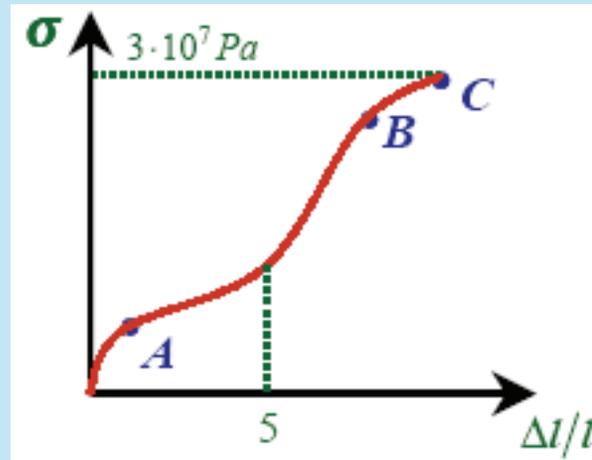
Elasticity of rubbers is composed from the elastic responses of the chains crosslinked in the network sample. External stress changes the equilibrium end-to-end distance of a chain, and it thus adopts a less probable conformation. Therefore, the elasticity of rubbers is of **purely entropic nature**.

Typical Stress-Strain Curves.

for steel



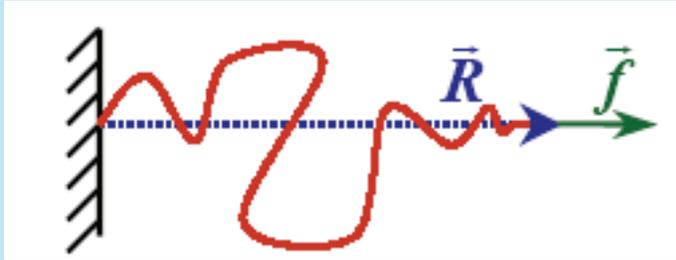
for rubbers



A - the upper limit for stress-strain linearity, B - the upper limit for the reversibility of deformations, C - the fracture point.

- the typical values of deformations $\Delta l/l$ are much larger for rubber;
- the typical values of strain σ are much larger for steel;
- the typical values of the **Young modulus** is **enormously larger for steel** than for rubber ($E \approx 10^{11} \text{ Pa}$ and $10^5 - 10^6 \text{ Pa}$, respectively);
- for steel linearity and reversibility are lost practically simultaneously, while for rubbers there is a very **wide region of nonlinear reversible deformations**;
- for steel there is a wide region of plastic deformations (between points **B** and **C**) which is all but absent for rubbers.

Elasticity of a Single Ideal Chain.



The energy of an ideal chain equals zero.

Under the external stress an ideal chain elongates and adopts a less probable conformation, its entropy therefore decreases.

Thus, the elasticity is of purely entropic nature.

According to Boltzmann the entropy takes form

$$S(\vec{R}) = k \ln W_N(\vec{R})$$

where k is the Boltzmann constant, $W_N(\vec{R})$ is the number of chain conformations compatible with the end-to-end distance \vec{R} . Obviously,

$$W_N(\vec{R}) = \text{const} \times P_N(\vec{R})$$

Elasticity of a Single Ideal Chain.

Thus,

$$S(\vec{R}) = k \ln P_N(\vec{R}) + \text{const}$$

were

$$P_N(\vec{R}) = \left(\frac{2\pi Ll}{3} \right)^{-3/2} \exp\left(-\frac{3R^2}{2Ll} \right)$$

Therefore,

$$S_N(\vec{R}) = -\frac{3kR^2}{2Ll} + \text{const}$$

And for the free energy F

$$F = E - TS = -TS = \frac{3kTR^2}{2Ll} + \text{const}$$

Finally, the force equals the derivative of the free energy with respect to R :

$$\vec{f} = \frac{\partial F}{\partial \vec{R}} = \frac{3kT}{Ll} \vec{R}$$

Elasticity of a Single Polymer Chain.

$$\vec{f} = \frac{\partial F}{\partial \vec{R}} = \frac{3kT}{Ll} \vec{R}$$

The chain elongates in the direction of the force and the elongation is proportional to the force: $\vec{f} \sim \vec{R}$ (the Hook law).

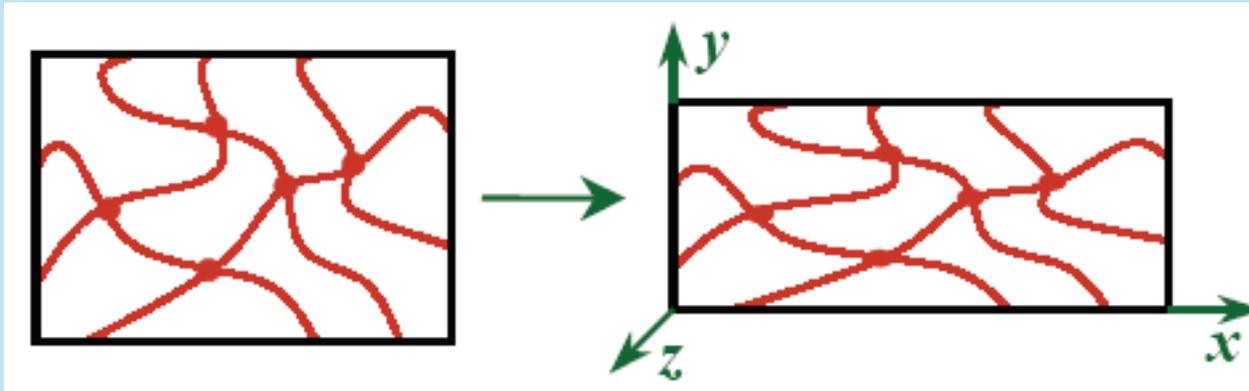
The elastic modulus $3kT/Ll$ is inversely proportional to the chain length L , and is, therefore, small for long chains.

Long polymer chains are very susceptible to external actions.

The elastic modulus is proportional to kT and, thus, increases with the increase of temperature. This indicates the entropic nature of high elasticity.

Limitations: the elongation should be small enough ($R \ll L$) for $P_N(\vec{R})$ to remain Gaussian.

Elasticity of Polymer Networks.



Consider a densely packed system of crosslinked chains. Assume chains to be freely-jointed, with the segment length l , and total contour length L .

Let deformation along the three main axes x, y, z be $\lambda_x, \lambda_y, \lambda_z$, respectively, i.e. the sample dimensions along the axes to be

$$a_x = \lambda_x a_{x0}, a_y = \lambda_y a_{y0}, a_z = \lambda_z a_{z0}$$

Affinity assumption: assume that the crosslink points are deformed affinely, i.e., for any chain, if the initial coordinates of the end-to-end vector are $\{R_{x0}, R_{y0}, R_{z0}\}$ then these coordinates in the deformed state are $\{R_x = \lambda_x R_{0x}, R_y = \lambda_y R_{0y}, R_z = \lambda_z R_{0z}\}$.

The Flory Theorem.

Until now, we have discussed only ideal chains where the links which are far from each other along the chain do not interact with each other. In the real chains it is, obviously, not the case. Therefore a natural question arises: is it reasonable to employ the results obtained for **ideal chains** when calculating the elastic response of a **real network**? The answer to this question is given by the so-called

Flory theorem: the statistical properties of a polymer chain in the melt are equivalent to those of ideal chains.

The explanation of this statement, which seems counterintuitive on the first glance, is as follows. In the melt each link of every chain is always in a dense surrounding of the other links, and thus all directions around the link are completely equivalent. Indeed, for example, any approach to a link of the same chain is completely compensated by a withdrawal from the links of the foreign chains.

Elasticity of Polymer Networks.

Thus, the change of the free energy of a chain between two crosslink points upon extension is

$$\begin{aligned}\Delta f &= \frac{3kT}{2Ll} (R^2 - R_0^2) = \frac{3kT}{2Ll} \left((R_x^2 - R_{x0}^2) + (R_y^2 - R_{y0}^2) + (R_z^2 - R_{z0}^2) \right) = \\ &= \frac{3kT}{2Ll} \left\{ R_{x0}^2 (\lambda_x^2 - 1) + R_{y0}^2 (\lambda_y^2 - 1) + R_{z0}^2 (\lambda_z^2 - 1) \right\}\end{aligned}$$

For the whole sample the change of the free energy equals

$$\Delta F = \nu V \langle \Delta f \rangle$$

where ν is the number of chains per unit volume, and V is the volume of the sample:

$$\Delta F = \frac{3kT}{2Ll} \nu V \left\{ (\lambda_x^2 - 1) \langle R_{x0}^2 \rangle + (\lambda_y^2 - 1) \langle R_{y0}^2 \rangle + (\lambda_z^2 - 1) \langle R_{z0}^2 \rangle \right\}$$

and since $\langle R_{x0}^2 \rangle = \langle R_{y0}^2 \rangle = \langle R_{z0}^2 \rangle = \langle R_0^2 \rangle / 3 = Ll/3$ we get finally

$$\Delta F = \frac{1}{2} kT \nu V (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Elasticity of Polymer Networks.

$$\Delta F = \frac{1}{2} kT \nu V (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Note that this result does not depend on the parameters L and l , which describe the individual subchains. This indicates that the theory is **universal**: it is not sensitive neither to the microscopic details of the chain flexibility, nor to the values of their **contour lengths** and **Kuhn segments**, nor to the particular form of the molecular mass distribution.

If we have another look at our calculations, we will see that the only fact we needed to draw the main conclusion is the fact that the **subchains are ideal** and the Gaussian distribution $P_N(\vec{R})$ is valid for them.

Therefore, we get the **limits of applicability** of the theory: we consider polymer **melts** (i.e., there is no solvent in the system), the network is **loosely crosslinked** and the **extensions are not too large** (i.e., even the shortest subchains remain Gaussian). Moreover, we have neglected the **topological restrictions** due to the **chain entanglements**.

The Uniaxial Extension.

$$\Delta F = \frac{1}{2} kTvV (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3)$$

Consider now the application of this formula to the case of uniaxial extension ($\lambda_x = \lambda > 1$) and compression ($\lambda_x = \lambda > 1$) along the axis x .

For rubbers the **incompressibility condition** is valid with high accuracy: their compression modulus is of the same order of magnitude as the compression modulus of the low-molecular materials (the all-around compression inevitably leads to the reduce of the distance between the molecules), while the Young modulus is 5-6 orders of magnitude lower.

Therefore, we can assume that

$$V_0 = V = \lambda_x a_{x0} \lambda_y a_{y0} \lambda_z a_{z0} = \lambda_x \lambda_y \lambda_z V_0$$

And thus, taking the symmetry considerations into account

$$\lambda_y = \lambda_z = 1/\sqrt{\lambda}$$

The Uniaxial Extension.

$$\text{Thus, } \Delta F = \frac{1}{2} kT \nu N \left\{ \lambda^2 + \frac{2}{\lambda} - 3 \right\}$$

Therefore, for the stress σ we get:

$$\sigma = \frac{1}{a_{y0} a_{x0}} \frac{\partial F}{\partial a_x} = \frac{1}{V} \frac{\partial F}{\partial \lambda} \Rightarrow \boxed{\sigma = kT \nu \left(\lambda - \frac{1}{\lambda^2} \right)}$$

The Young modulus, thus, equals $E = 3kT \nu$.

For the loosely crosslinked networks it is small since $\nu \sim 1/N \nu$ where ν is a volume of one monomer unit. This is exactly the reason of the high elasticity of rubbers.

Analogous formulae can be obtained for other kinds of deformation (shear, twist, etc).

Let us remind once again that the result obtained is universal, it does not depend on the microscopic details of the chain structure.

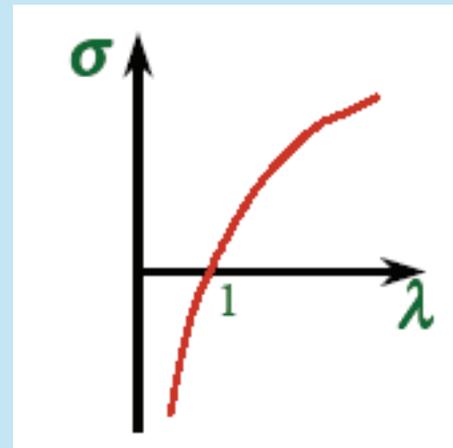
The reason is that the entropic elasticity is caused by the **large-scale properties of polymer coils**.

The Uniaxial Expansion.

$$\sigma = kT \nu \left(\lambda - \frac{1}{\lambda^2} \right)$$

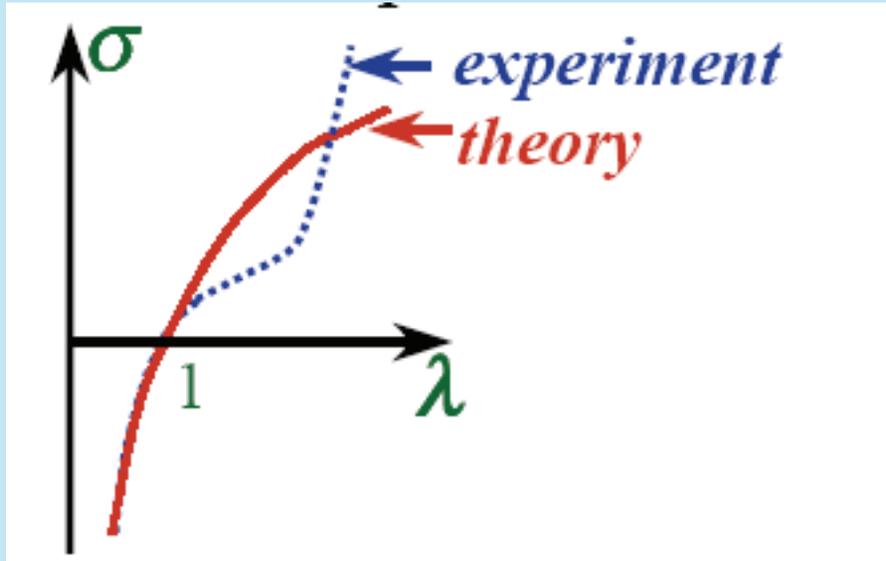
Other important conclusions:

The stress-strain curve is **substantially non-linear**:



If $\sigma = \text{const} > 0$ and temperature T increases, the value of λ should decrease. Thus, **rubbers shrink upon heating**, contrary to gases and crystalline materials. This property is connected to the **entropic nature of rubber elasticity**. Consequently, **rubbers heat up under adiabatic extension**.

Comparison with the Experiment.



$0.4 < \lambda < 1.2$ excellent agreement

$1.2 < \lambda < 5$ theory slightly overestimates stress at a given strain.
Reason: neglect of chain entanglements.

$\lambda > 5$ theory significantly underestimates stress at a given strain.
Reason: finite extensibility of the chains.