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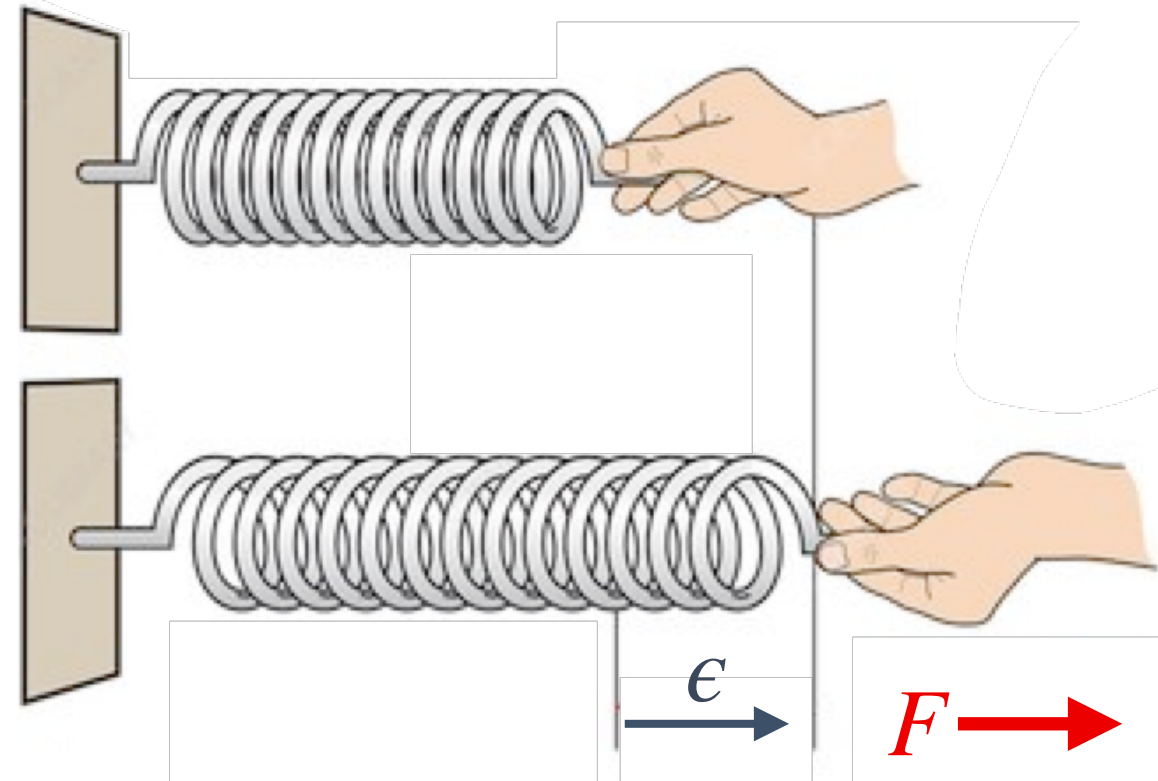
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Mechanical Properties

Elastic Springs and Dashpots

- two borderline cases for materials deformation: **elastic solids** vs. **Newtonian liquids**

elastic solids
(reversible deformation)



Hooke's law: $\sigma = E\epsilon$

viscoelastic materials
(a world in between)



see Chapter 5.2

viscous liquids
(irreversible deformation)



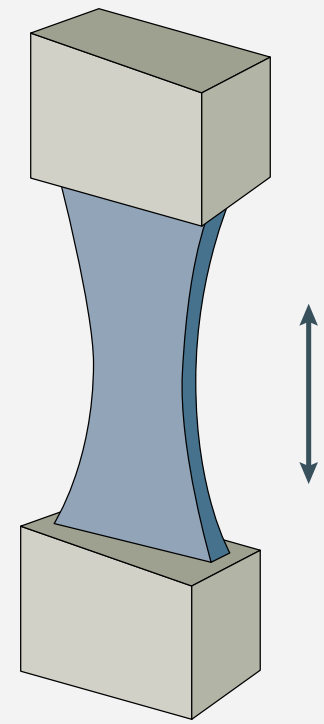
Newton's law: $\dot{\epsilon} = \frac{\sigma}{\eta}$

- depending on magnitude, duration (temperature), and velocity of the deformation, polymers show a dominant elastic behaviour or fluidic behaviour. **They are viscoelastic!**

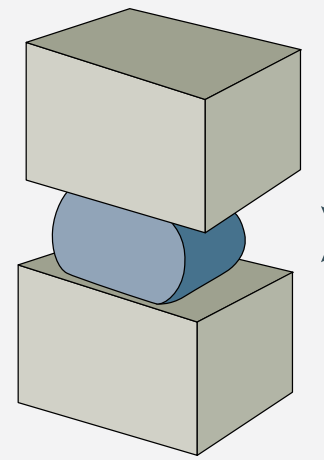
Main Mechanical Deformations and Representative Curves

- materials can deform in various ways under applied forces, each exhibiting unique characteristics

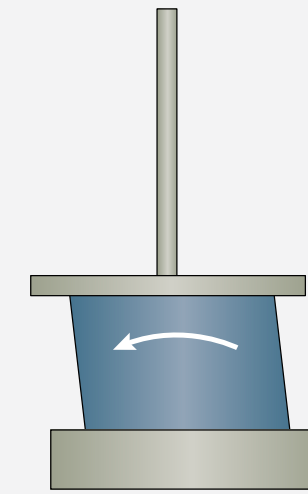
tension



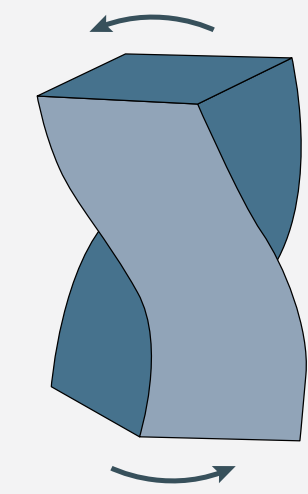
compression



shear



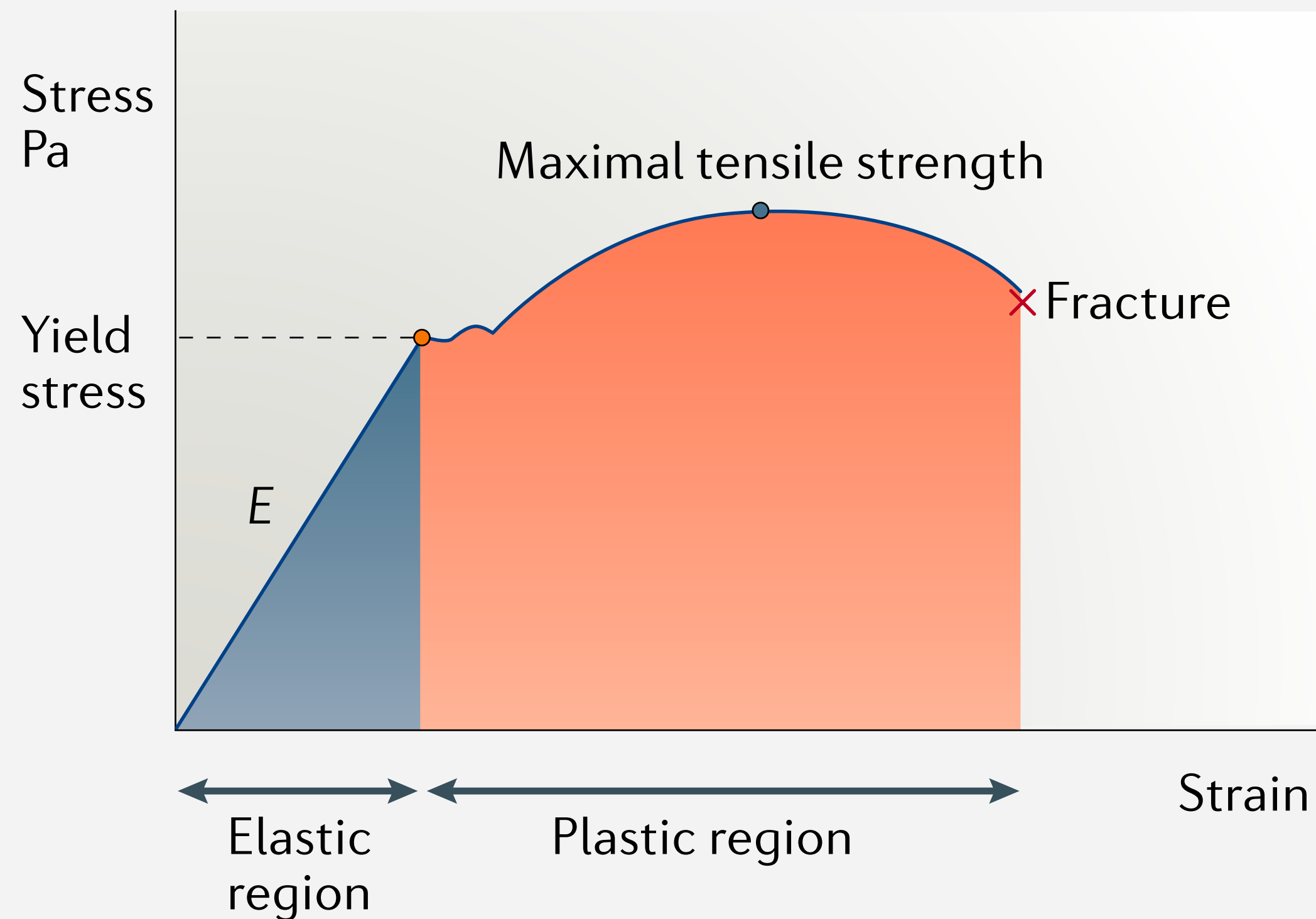
torsion



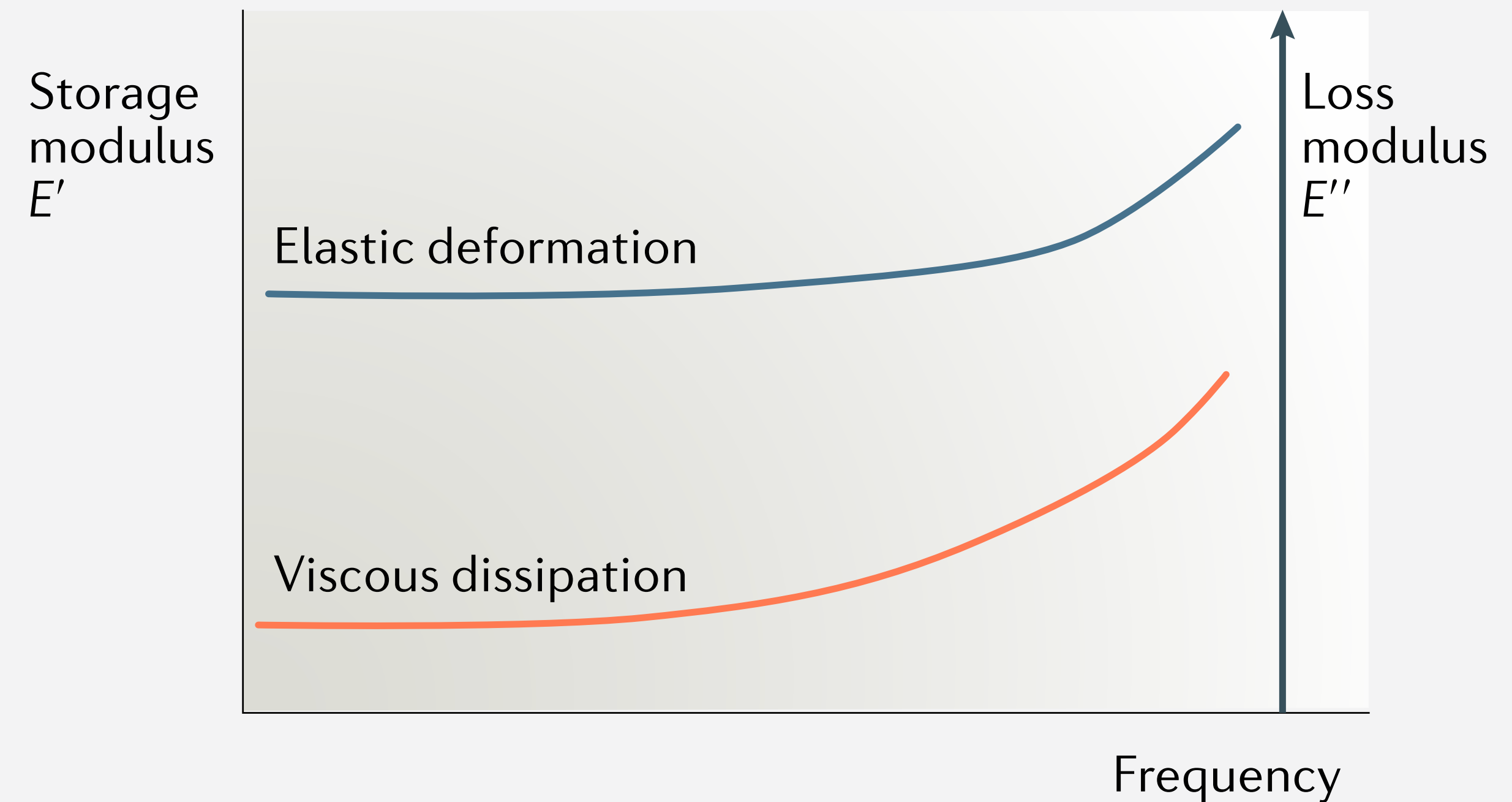
- **tension:** a force that pulls materials apart, leading to elongation and stretching
- **compression:** a force that pushes materials together, causing shortening and compacting
- **shear:** a force that causes layers of a material to slide past each other, resulting in angular distortion
- **torsion:** a twisting force applied to a material, resulting in shear deformation along its length

Static vs. Dynamic Measurements

static measurements
(see **Chapters 4.1** and **4.3**)



dynamic measurements
(see **Chapter 4.2**)



- **static measurements:** material's response under constant loads, highlighting strength and elastic limits
- **dynamic measurements:** varying (often oscillatory) loads, providing insight into viscoelastic behavior

Basic Mechanical Behavior of Polymers

- polymers can be classified according to their stress-strain behaviour under tension

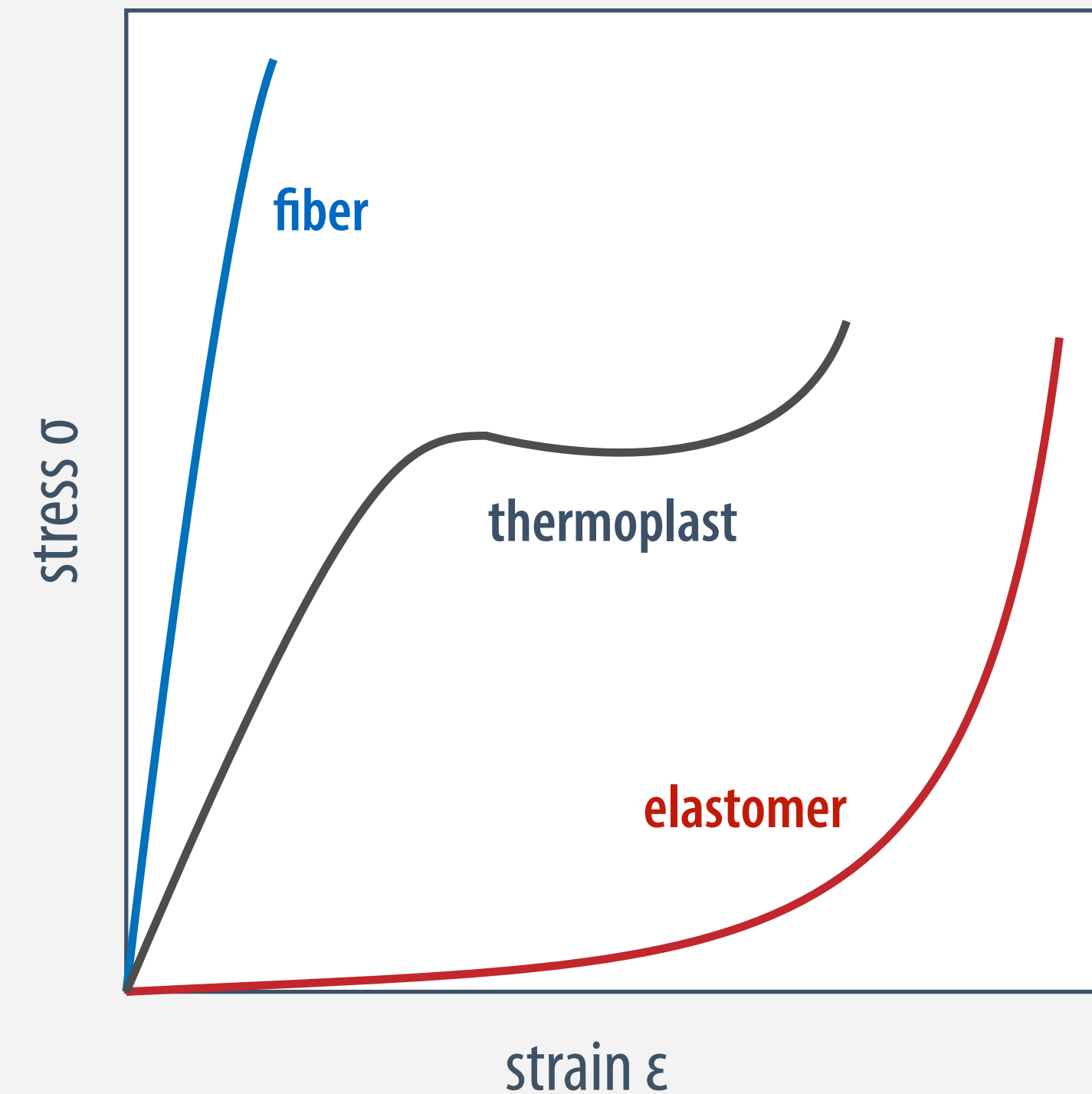


$$\sigma = \frac{\text{force}}{\text{unit area}}$$

$$\epsilon = \frac{\Delta l}{l}$$

analogy to **Hooke's law**:

$$E = \frac{\sigma}{\epsilon}$$

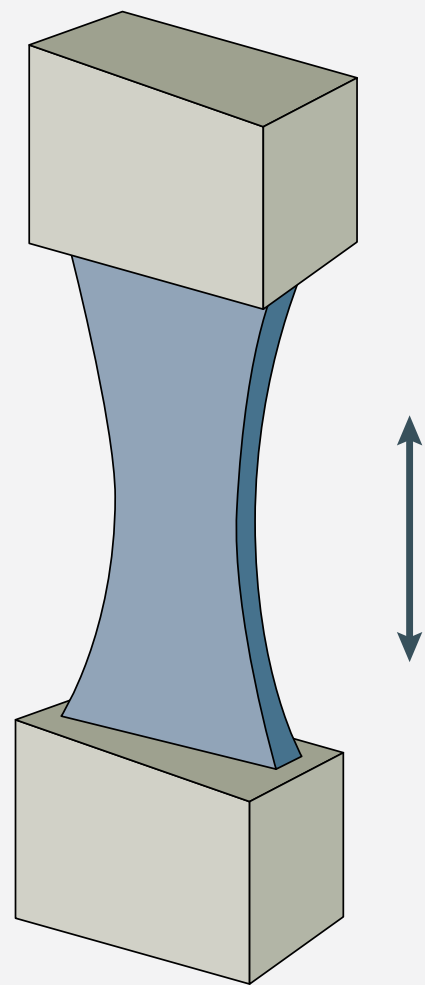


- Hooke's law is often, for polymer materials in particular, only applicable at small strains

Elastic Moduli

- different elastic moduli and compliances describing different stress situations:

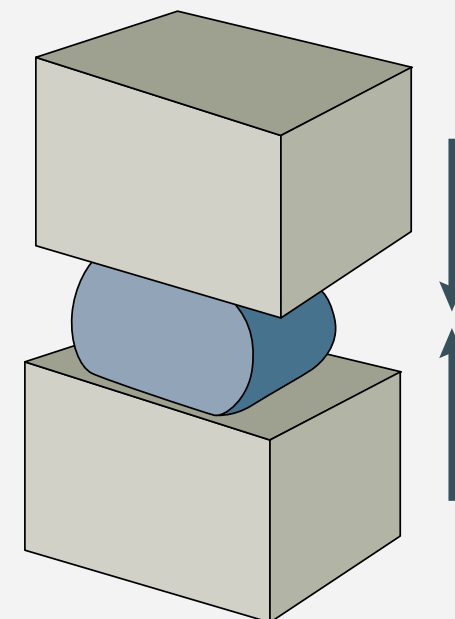
tension



Young's modulus E

tensile compliance $D = \frac{1}{E}$

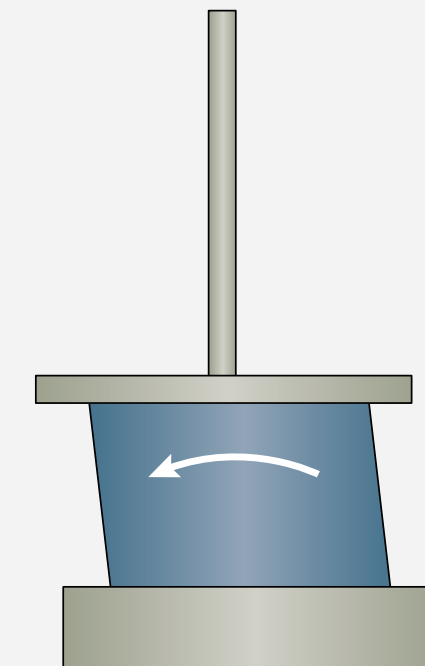
compression



bulk modulus K

bulk compliance $B = \frac{1}{K}$

shear



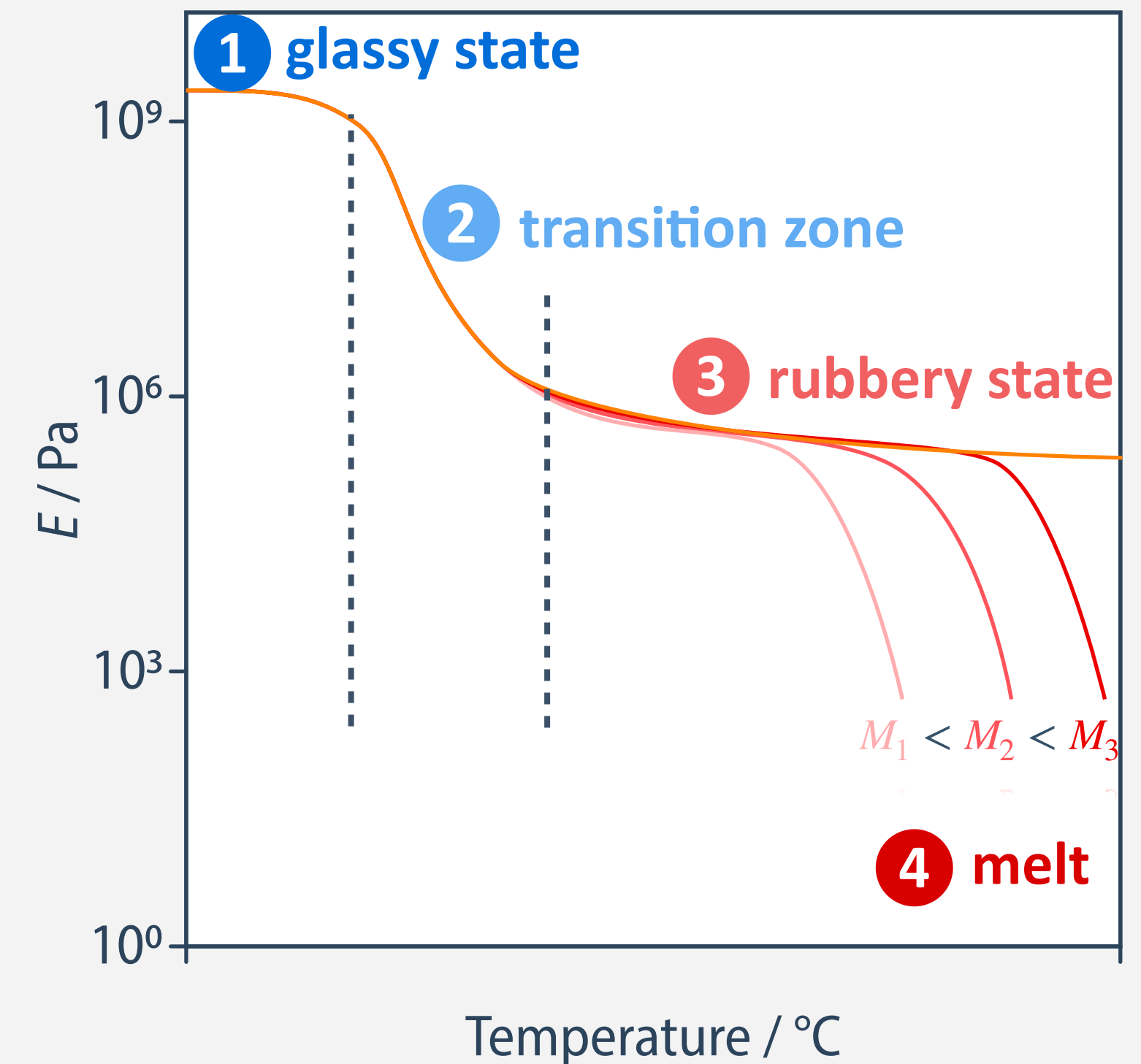
shear modulus G

shear compliance $J = \frac{1}{G}$

Small Deformation Behavior

- 1 deformation in the glassy or semi-crystalline state:** time-independent response to stress like an elastic solid
- 2 transition zone:** retarded highly elastic state at around T_g . Strongly time-dependent (viscoelasticity) (see Chapter 4.2)
- 3 rubber elasticity:** large elastic (reversible) deformations possible (see Chapter 4.1)
- 4 viscous state:** little to no elastic recovery, but viscous liquid behavior

universal trend of Young's modulus

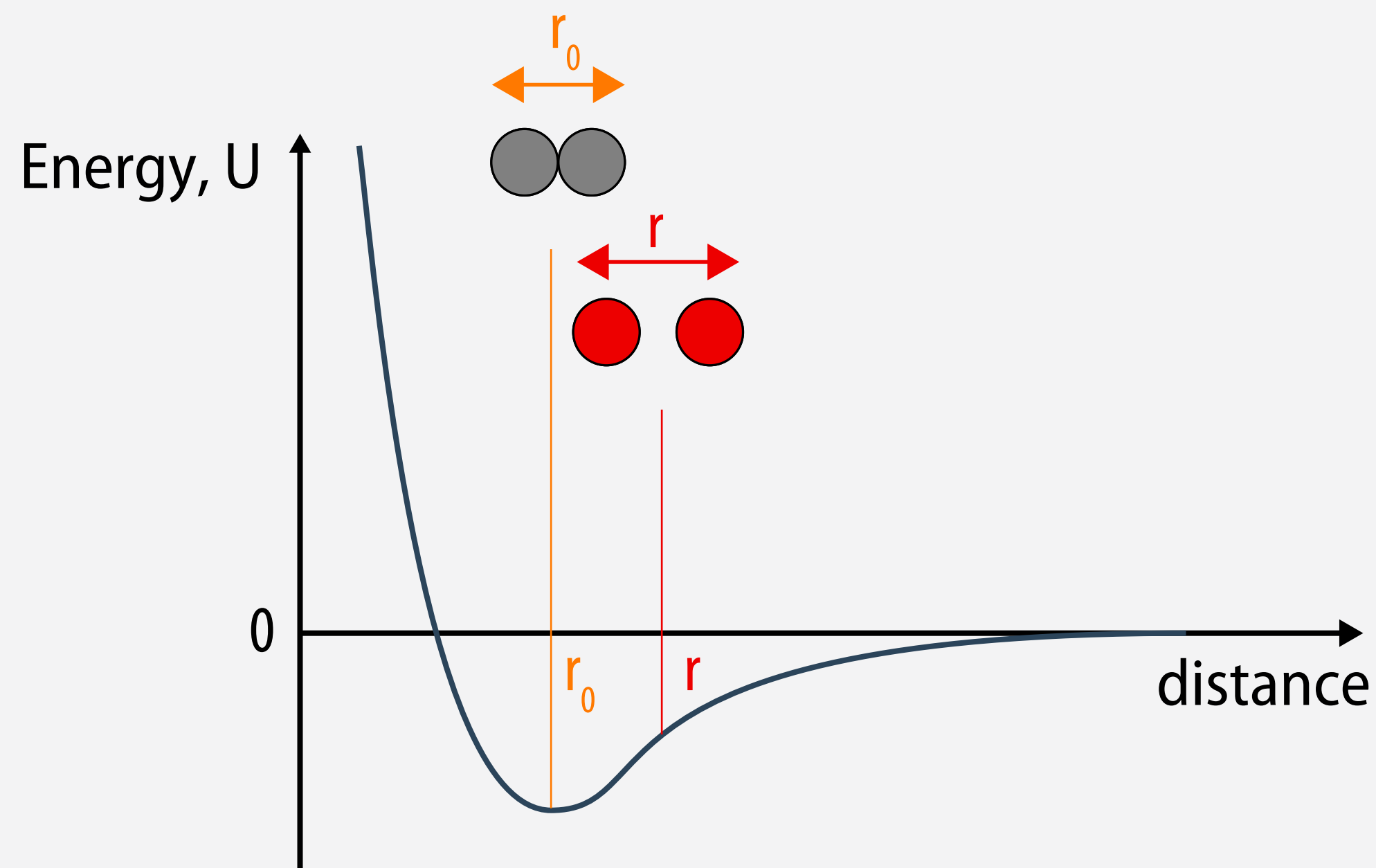


5.1

Elastic Deformation

Energy Driven Elasticity

- typical for crystalline solids, i.e. steel wires can be reversibly stretched by up to 1%



parabolic nature of the potential near equilibrium point:

$$U = C(r - r_0)^2$$

elastic force:

$$f = \frac{\partial U}{\partial r} = 2C(r - r_0)$$

stress:

$$\sigma = \frac{f}{A} = \frac{2C}{A}(r - r_0) = \frac{2Cr_0}{A} \frac{r - r_0}{r_0} = E\epsilon$$

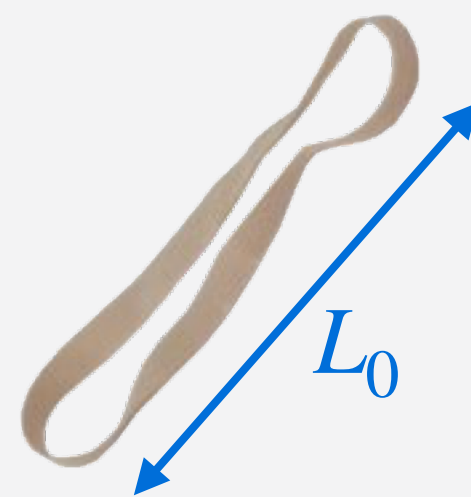
Hooke's law!

- the elastic force is of predominant enthalpic nature; entropy is a minor factor
- steel is cooling upon stretching
- the elastic modulus decreases upon temperature increase

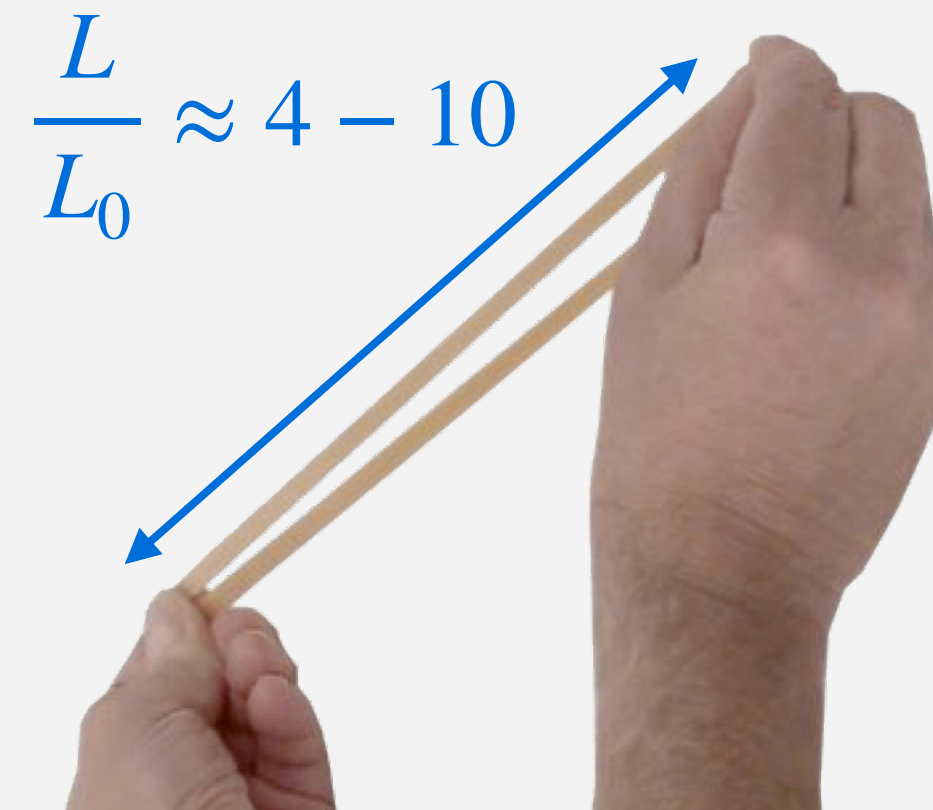
Observations on Elastomers Contradicting the Elasticity of Other Materials

- elastomers and rubbers are capable of undergoing large deformations ($\epsilon > 100\%$)

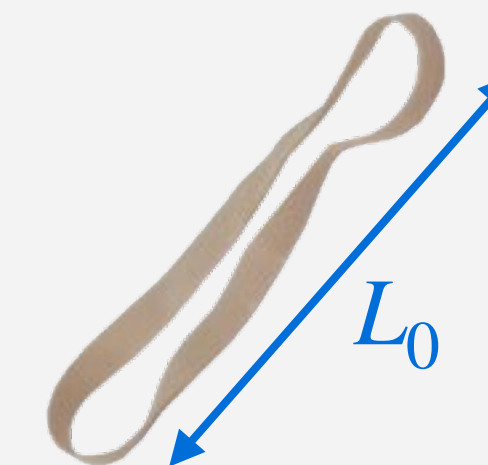
original shape



under stress



after stress

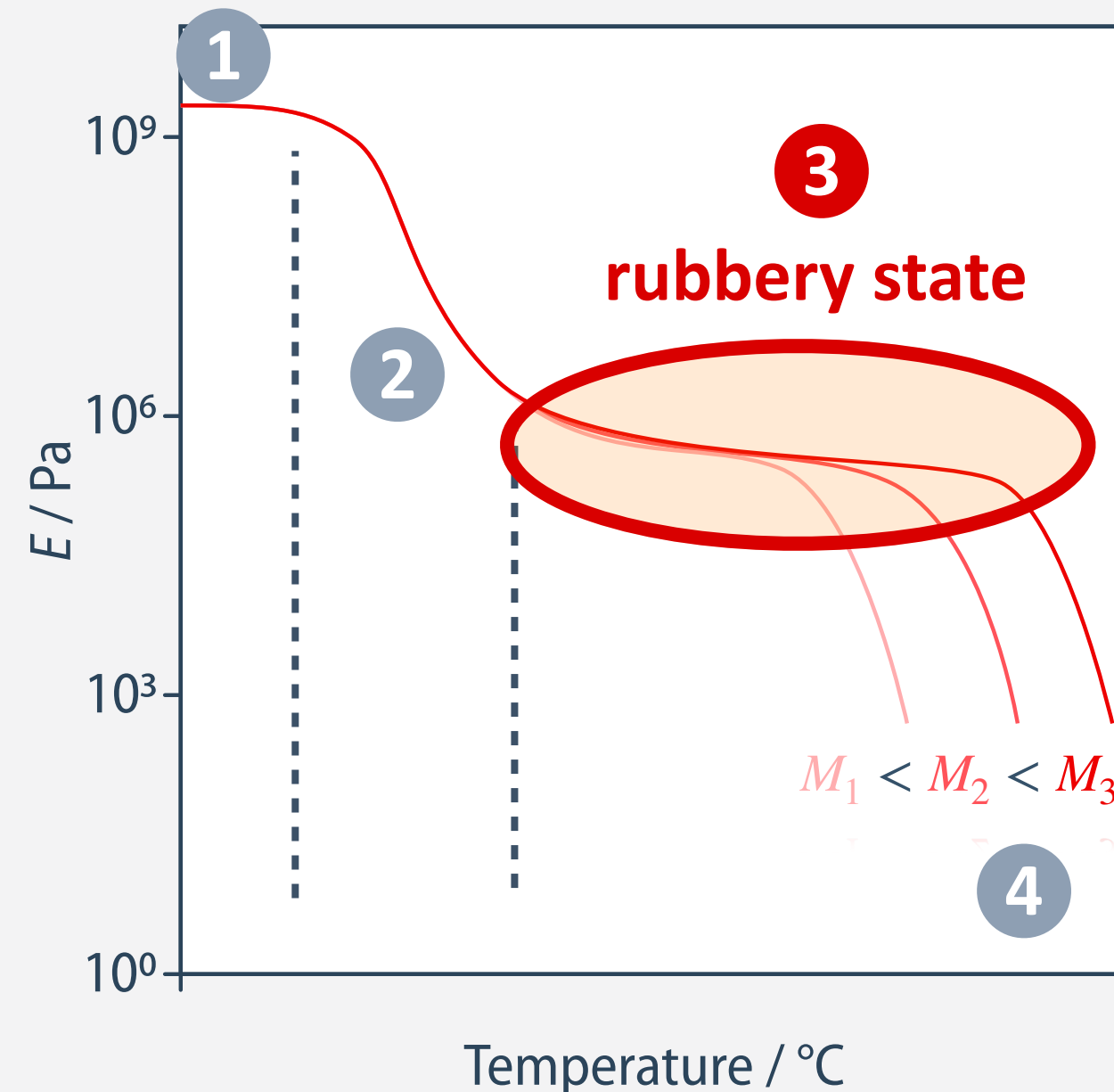


- rubbers and elastomers contract upon heating (Gough-Joule effect, reported already in 1802)
- the temperature of a rubber band increases upon rapid stretching
- the elastic modulus increases, when the temperature of the elastomer increases

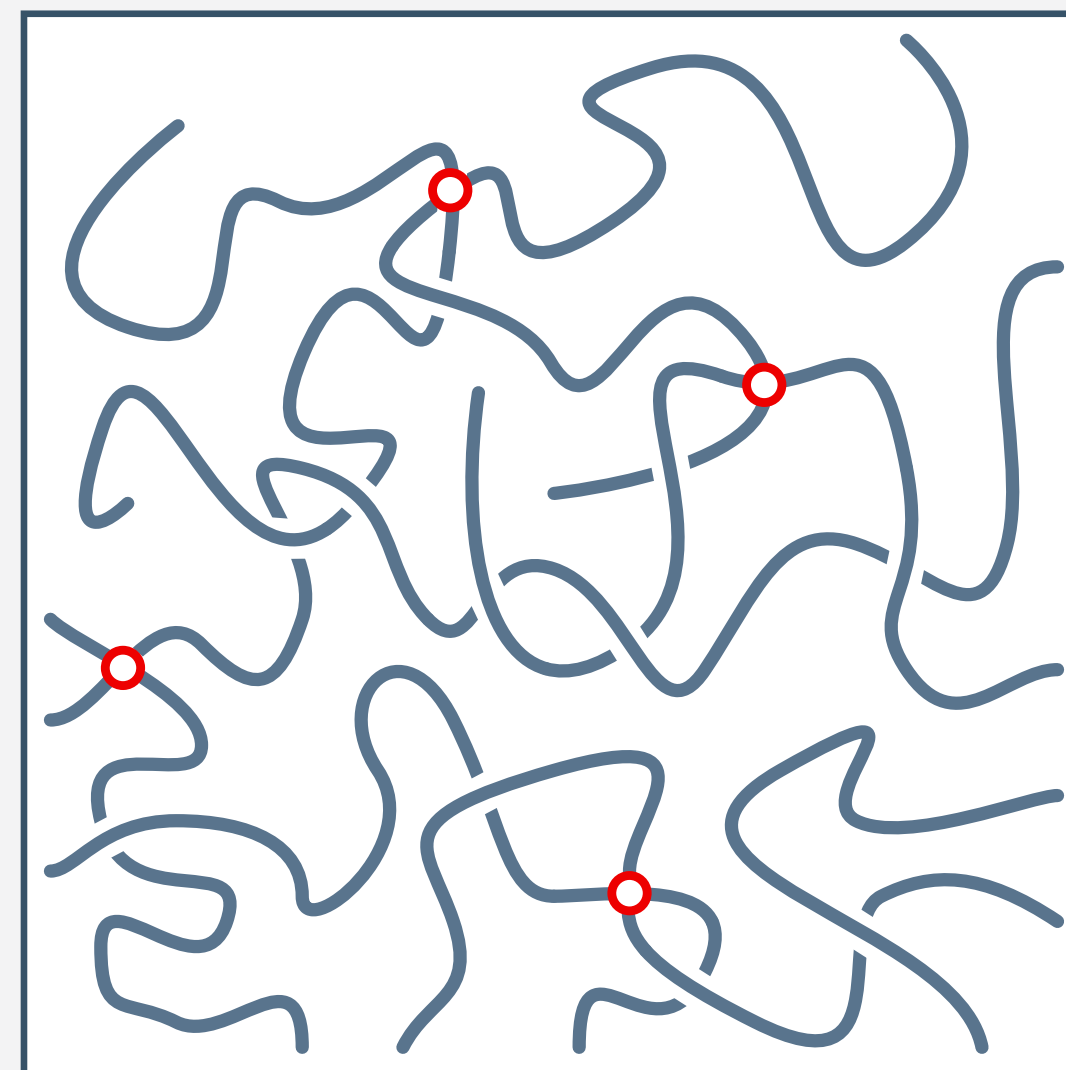
Conditions for Rubber Elasticity

- rubber elasticity is specific to organic polymers above T_g .

phenomenology

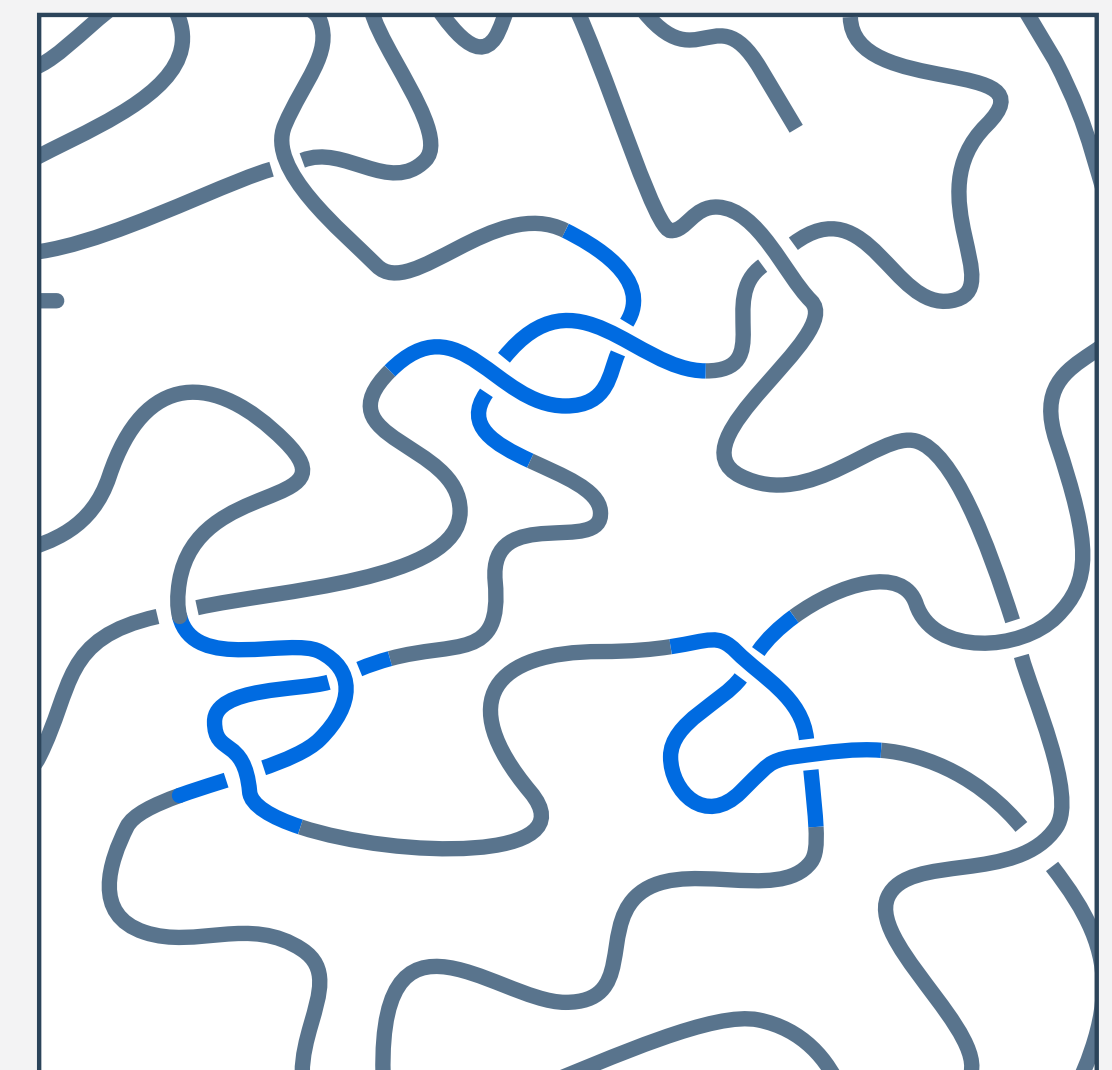


elastomers



lightly cross-linked

rubbers



operating T slightly above T_g ;
corresponds to the rubbery state

- long, flexible chains (little to no crystallisation)
- rather weak intermolecular forces
- crosslinks (**chemical** or **physical**)



the static picture representing entanglements as “knots” does not reflect the purely dynamic origin of this phenomenon!

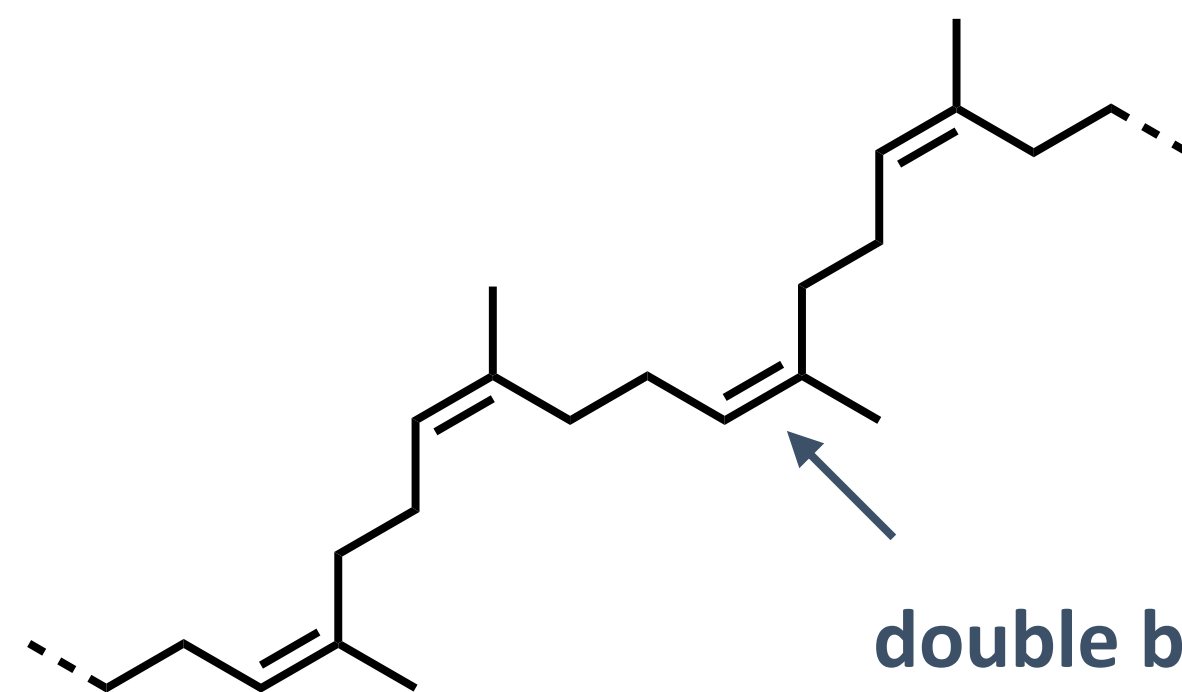
Rubbers vs. Elastomers

- in practice, we tend to confuse elastomers and rubbers...

rubbers



natural rubber (“fluid”-like)



upon vulcanisation, natural rubber is converted into an elastomer



elastomers

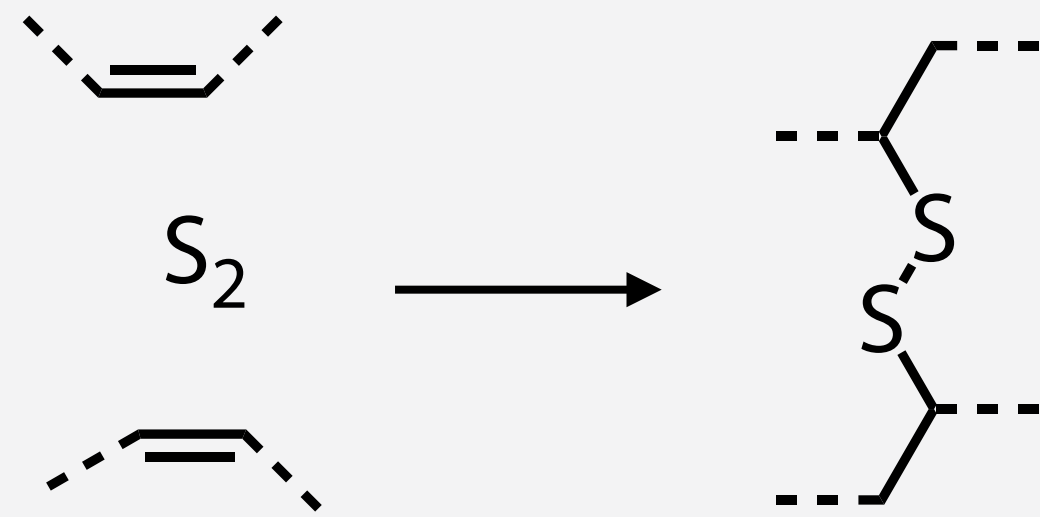


“rubber gloves”

Network Creation for Elastomers

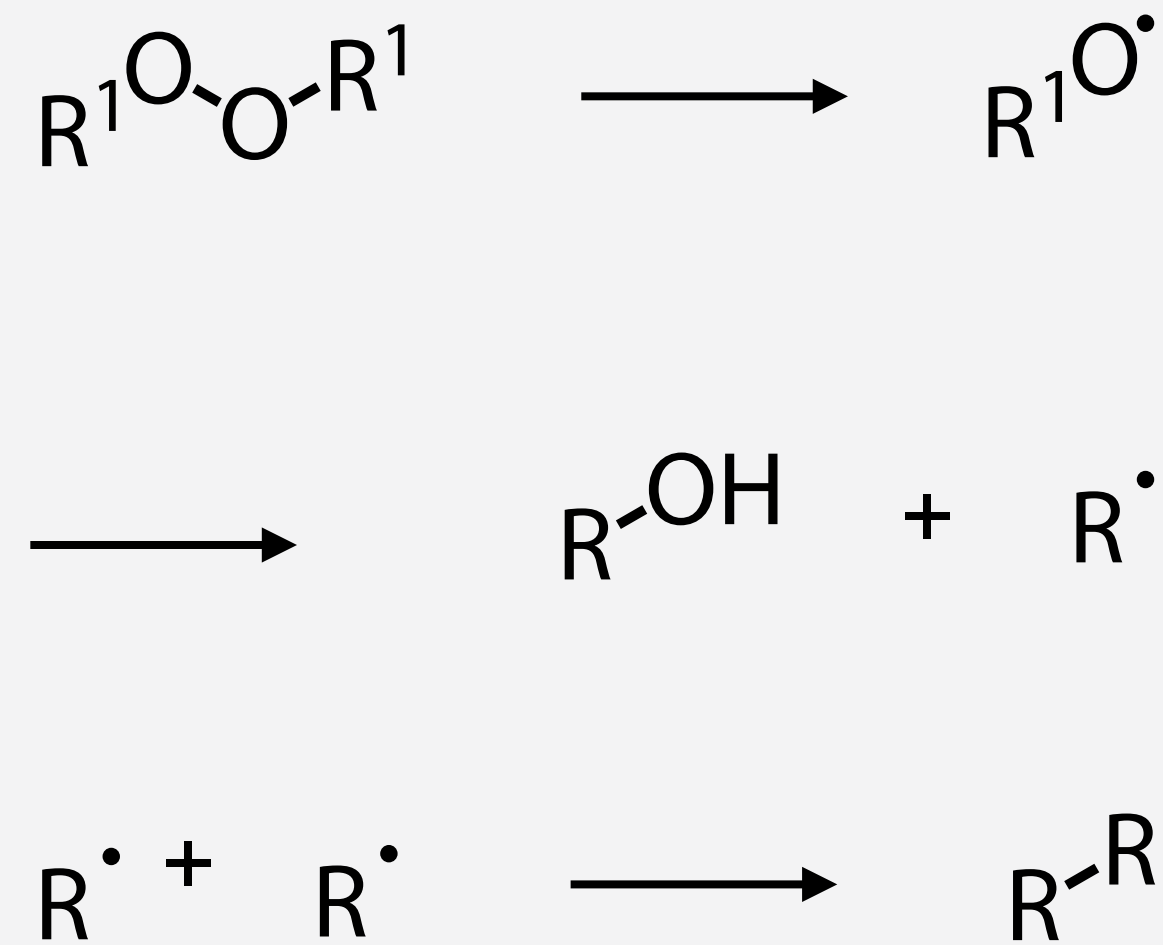
- three-dimensional networks by chemical or physical crosslinking methods

vulcanisation



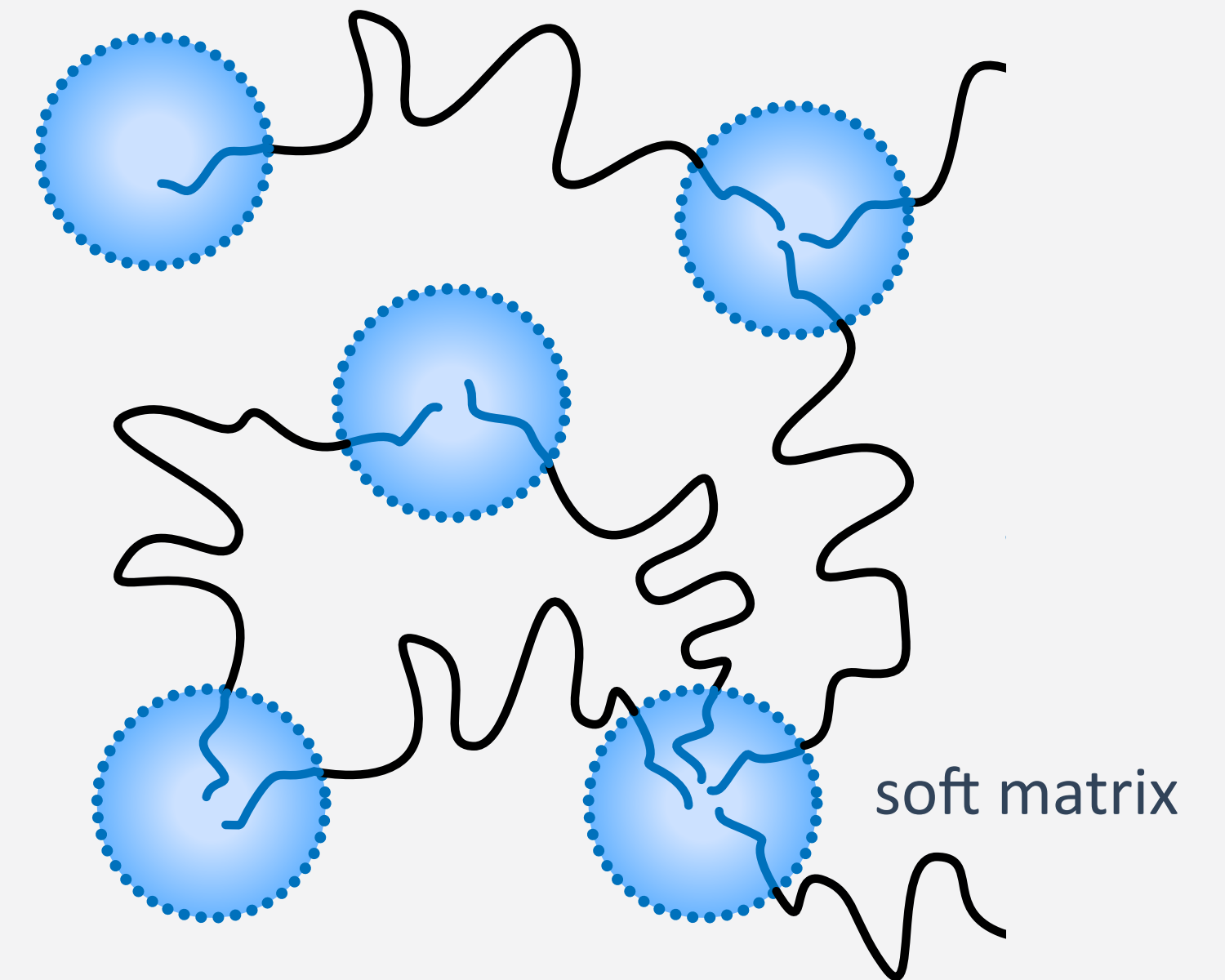
< 1%: elastomer
ca. 10%: hard “rubber”

radical mechanism



crosslinking of PE by irradiation
and formation of free radicals
(resistant to sterilisation in boiling
water)

physical crosslinks



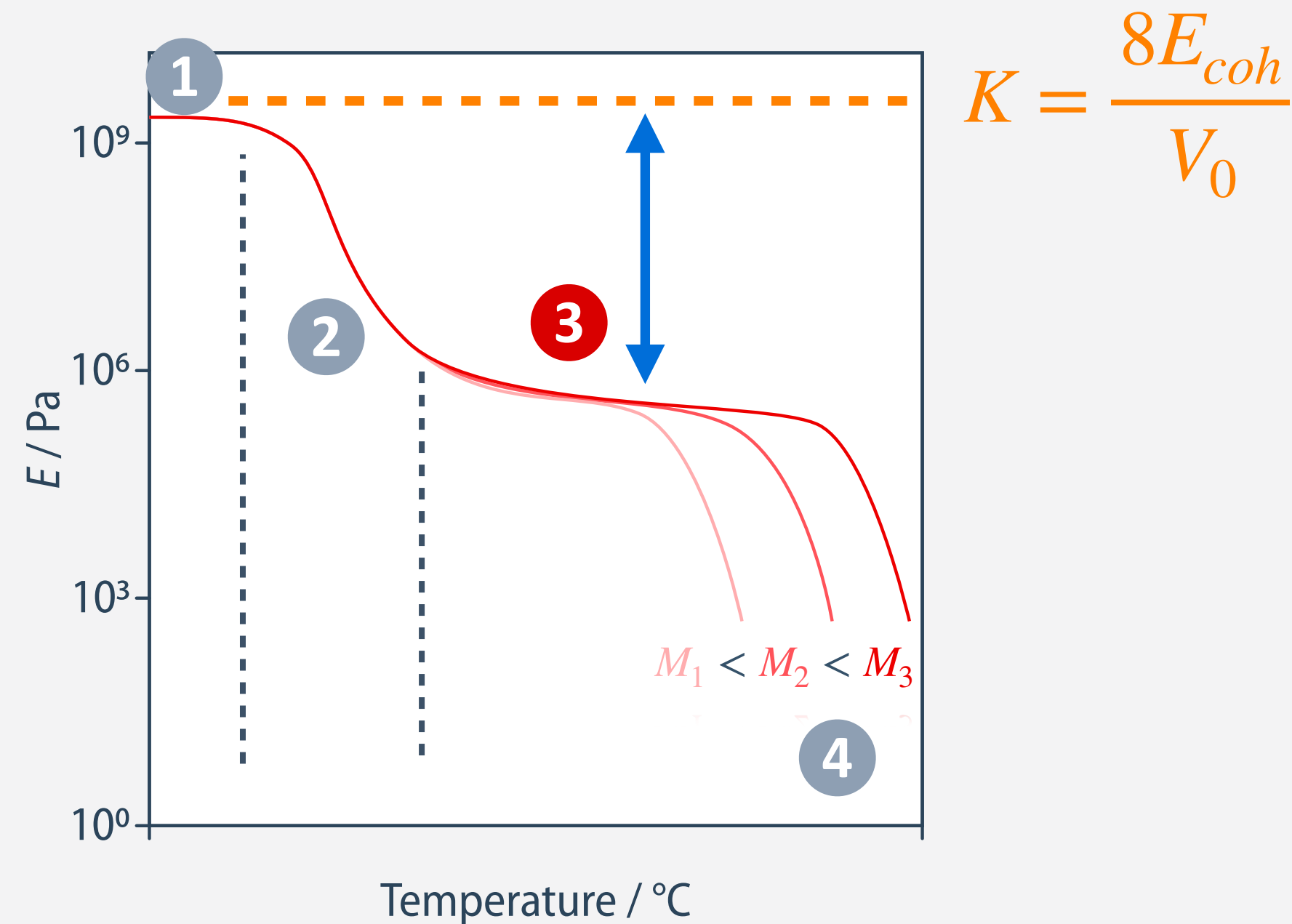
PS: glassy, hard
PUR: semicrystalline

Thermodynamic Consideration of Rubber Elasticity

Incompressible Nature of Rubbers

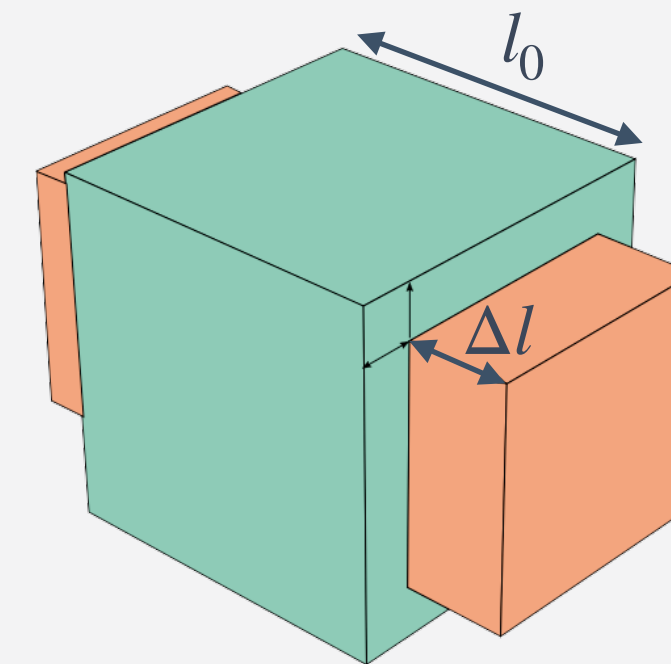
- invariant dependence of compression modulus, K , but strong dependence of elastic modulus, E , on T

phenomenology



decrease of E by a factor of 1000 above T_g

Poisson's ratio



$$\frac{\Delta V}{V_0} = (1 - 2\mu) \frac{\Delta l}{l_0} = (1 - 2\mu)\epsilon$$

$$\mu = \frac{1}{2} \left(1 - \frac{E}{3K} \right)$$

Poisson's ratio for a uniaxially deformed polymer is 0.5.

- polymers in their rubbery and melt state are considered as incompressible

Thermodynamic Considerations of Rubber Elasticity

- **1st law of thermodynamics:** change in internal energy of an isolated system, dU :

$$dU = dQ - dW = TdS - pdV + fdl$$

- Helmholtz free energy, A , and its change, dA :

$$A = U - TS$$

$$dA = dU - d(TS) = dU - TdS - SdT$$

- dA is a thermodynamic state function of variables T , V , and l :

$$dA = -SdT - pdV + fdl$$

- the complete differential is:

$$dA = \left(\frac{\delta A}{\delta T}\right)_{V,l} dT + \left(\frac{\delta A}{\delta V}\right)_{T,l} dV + \left(\frac{\delta A}{\delta l}\right)_{T,V} dl$$

- the partial derivatives of A are:

$$\left(\frac{\partial A}{\partial T}\right)_{V,l} = -S$$

$$\left(\frac{\partial A}{\partial V}\right)_{T,l} = -p$$

$$\left(\frac{\partial A}{\partial l}\right)_{T,V} = f$$

Energetics and Entropic Components of the Elastic Force

- from incompressibility, it follows:

$$\left(\frac{\partial A}{\partial T}\right)_{V,l} = -S$$

~~$$\left(\frac{\partial A}{\partial V}\right)_{T,l} = -p$$~~

$$\left(\frac{\partial A}{\partial l}\right)_{T,V} = f$$

- a second derivative of A does not depend on the order of differentiation:

$$\frac{\partial^2 A}{\partial T \partial l} = \frac{\partial^2 A}{\partial l \partial T}$$

$$-\left(\frac{\partial S}{\partial l}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{V,l}$$

- we arrive at two contributions for the force f :

$$f = \left(\frac{\partial A}{\partial l}\right)_{T,V} = \left[\frac{\partial(U - TS)}{\partial l}\right]_{T,V} = \underbrace{\left(\frac{\partial U}{\partial l}\right)_{T,V}}_{\text{energetic term}} - \underbrace{T\left(\frac{\partial S}{\partial l}\right)_{T,V}}_{\text{entropic term}}$$

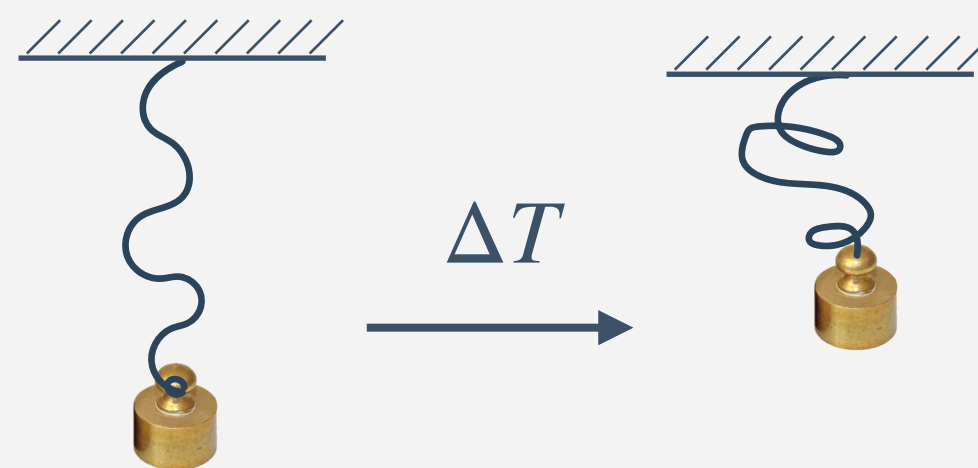
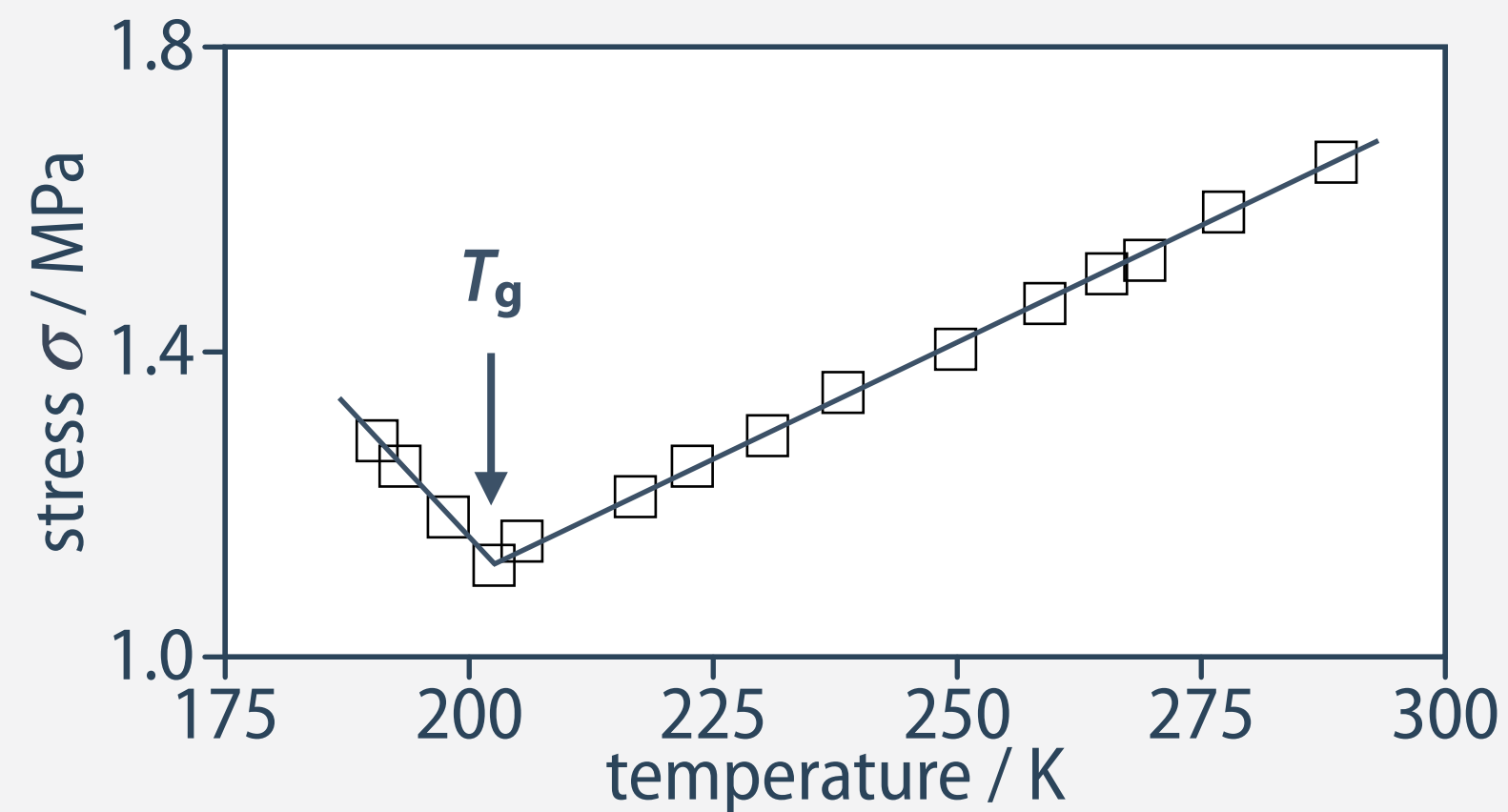
- combination of the above equations:

$$f = \underbrace{\left(\frac{\partial U}{\partial l}\right)_{T,V}}_{f_E} + \underbrace{T\left(\frac{\partial f}{\partial T}\right)_{V,l}}_{f_S} = f_E + f_S$$

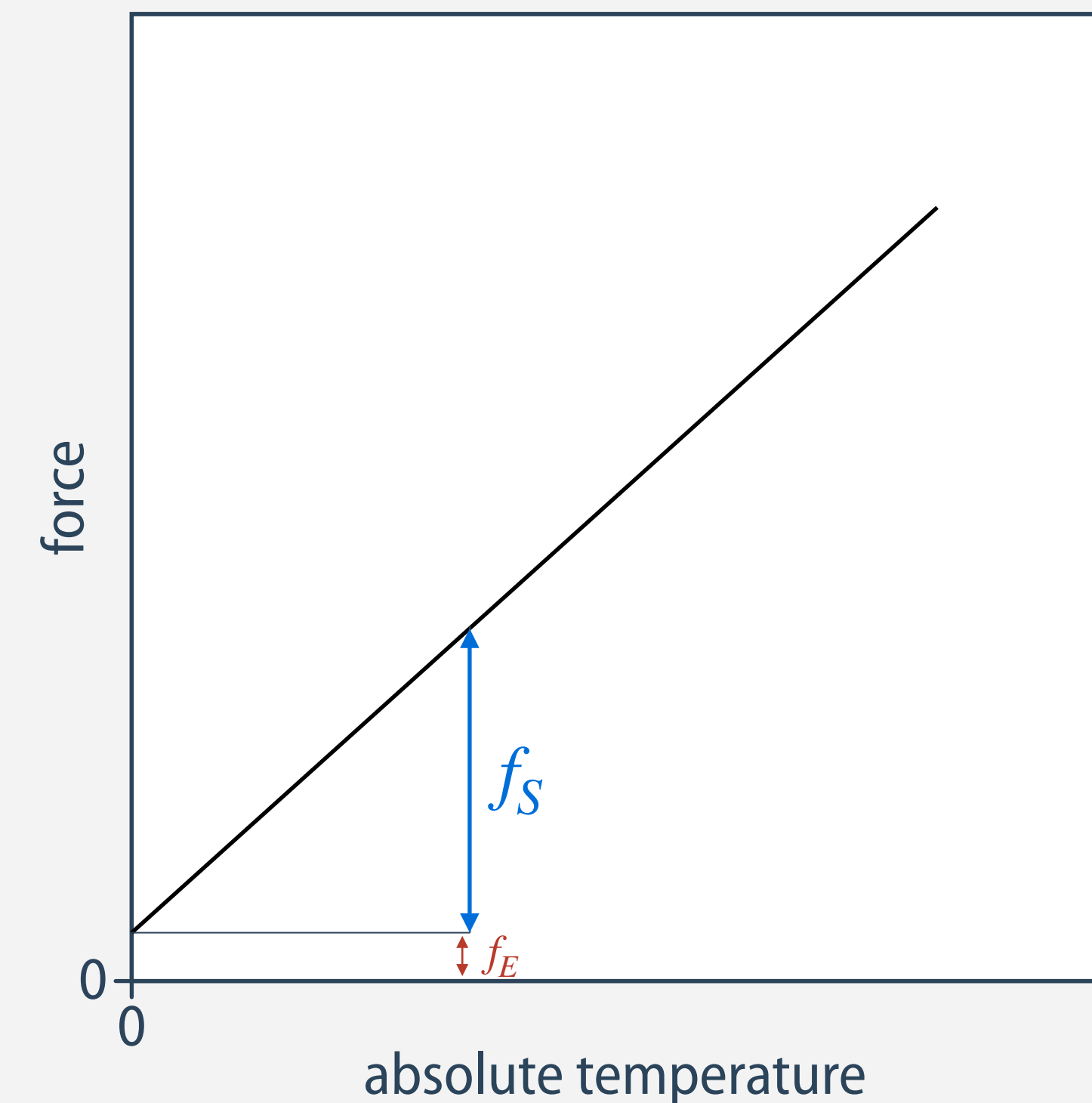
Energetics and Entropic Components of the Elastic Force

- a peculiar temperature-dependence: the retraction force, f , increases with increasing temperature!

for a (large) constant deformation



$$f = \left(\frac{\partial U}{\partial l} \right)_{T,V} + T \left(\frac{\partial f}{\partial T} \right)_{V,l} = f_E + f_S$$

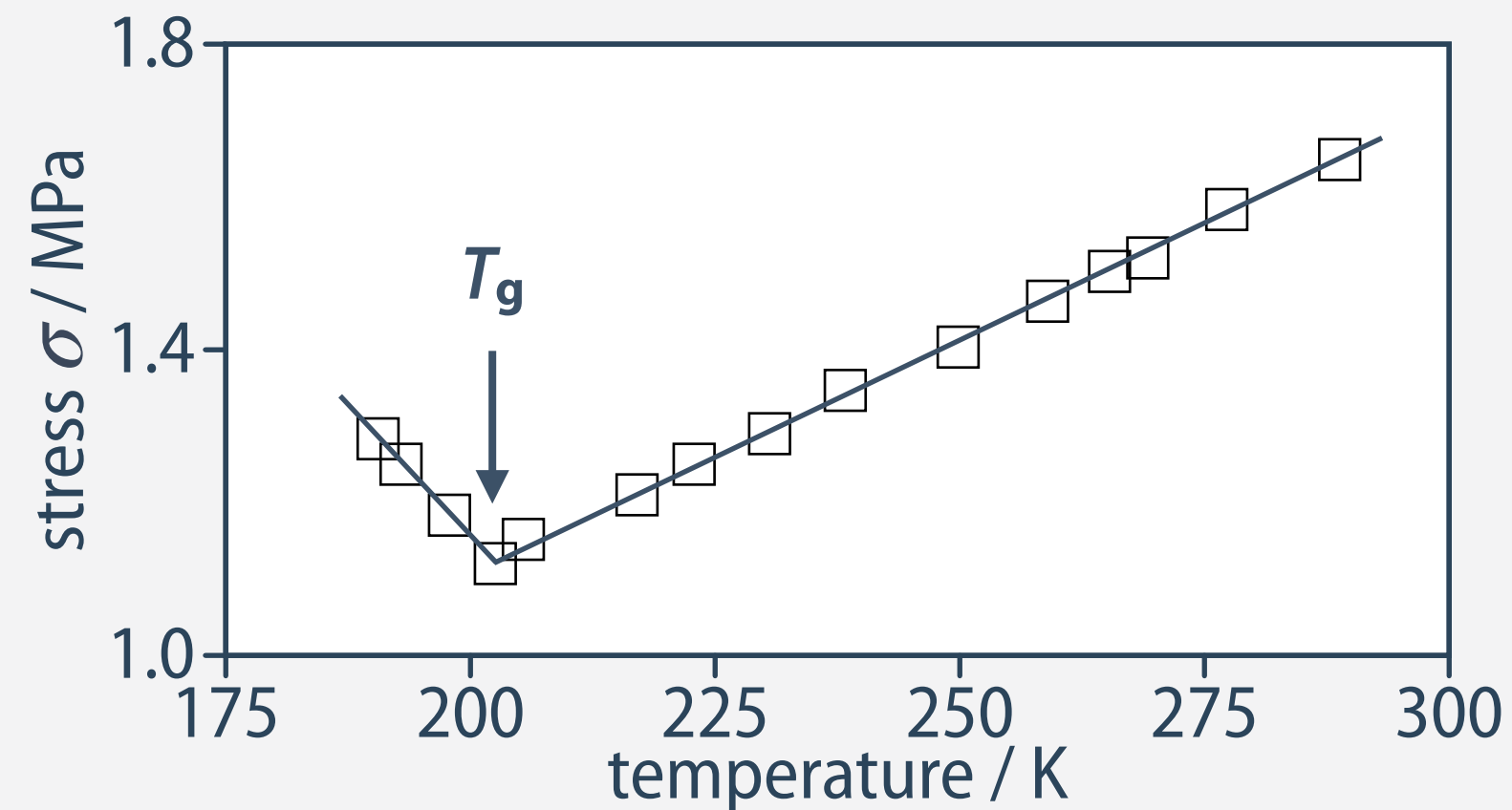


- rubber elasticity has primarily entropic origins; for ideal rubbers, $f_E = 0$!

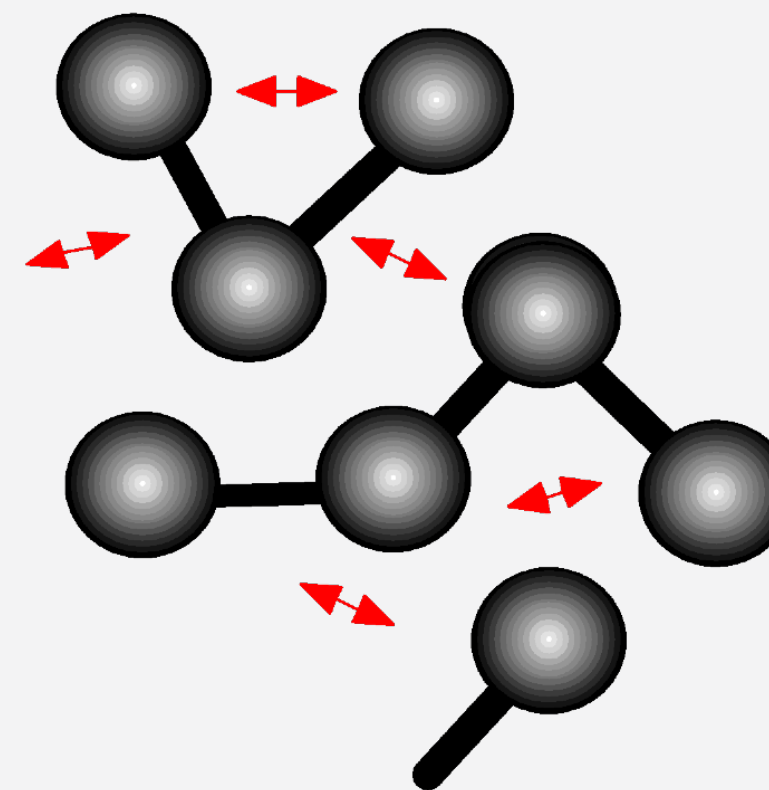
Physical Interpretation

- below T_g , too high barriers to conformational changes: deformation results in predominant changes of the internal energy (U or E_{coh}).

for a (large) constant deformation

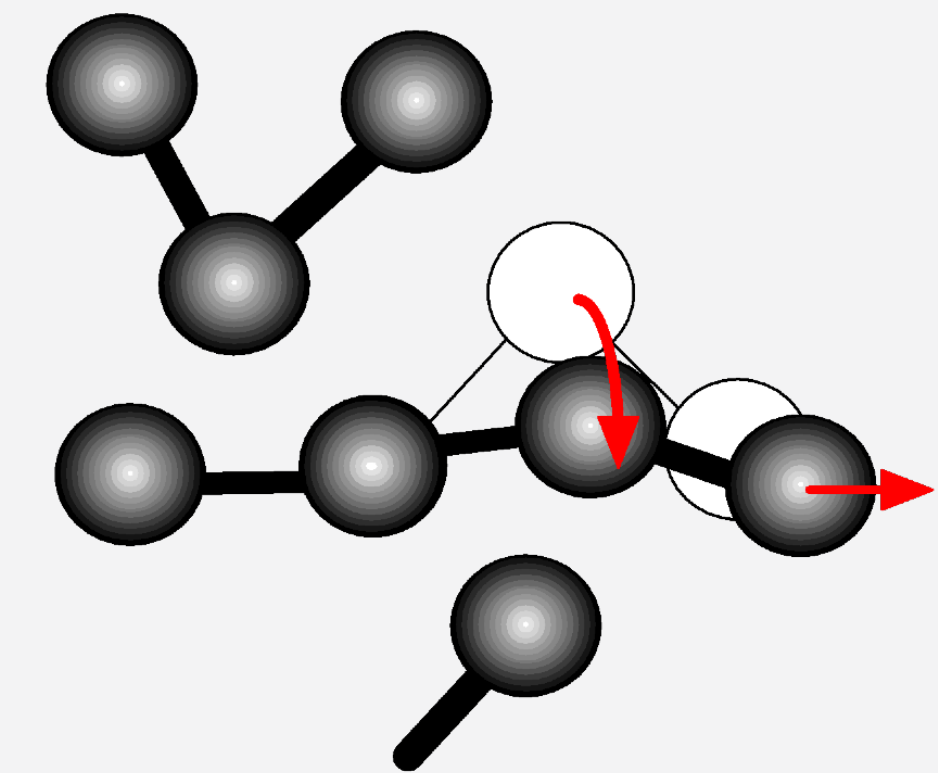


below T_g



frozen random coil
conformation

above T_g



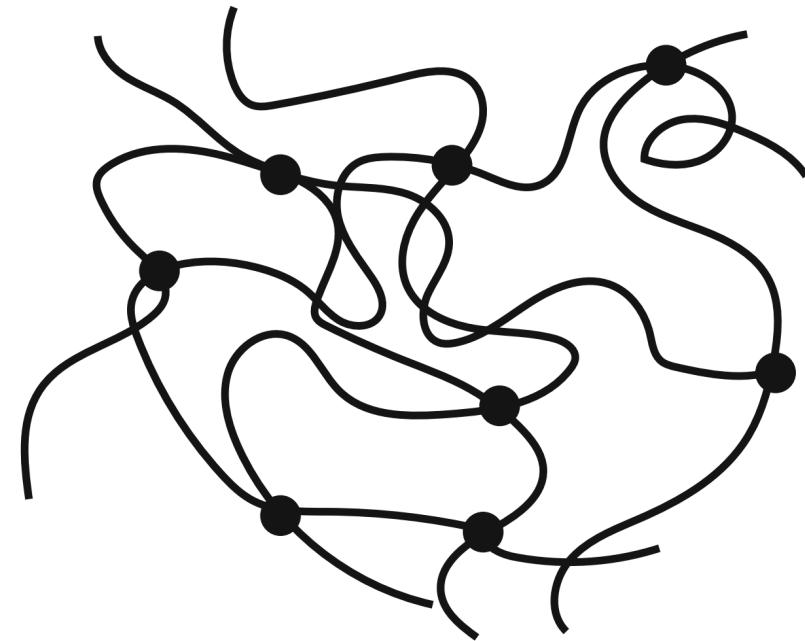
stretched conformations
possible

- above T_g , we assume that energetic barriers to changes in conformation are negligible
- deformation leads then to a decrease in entropy

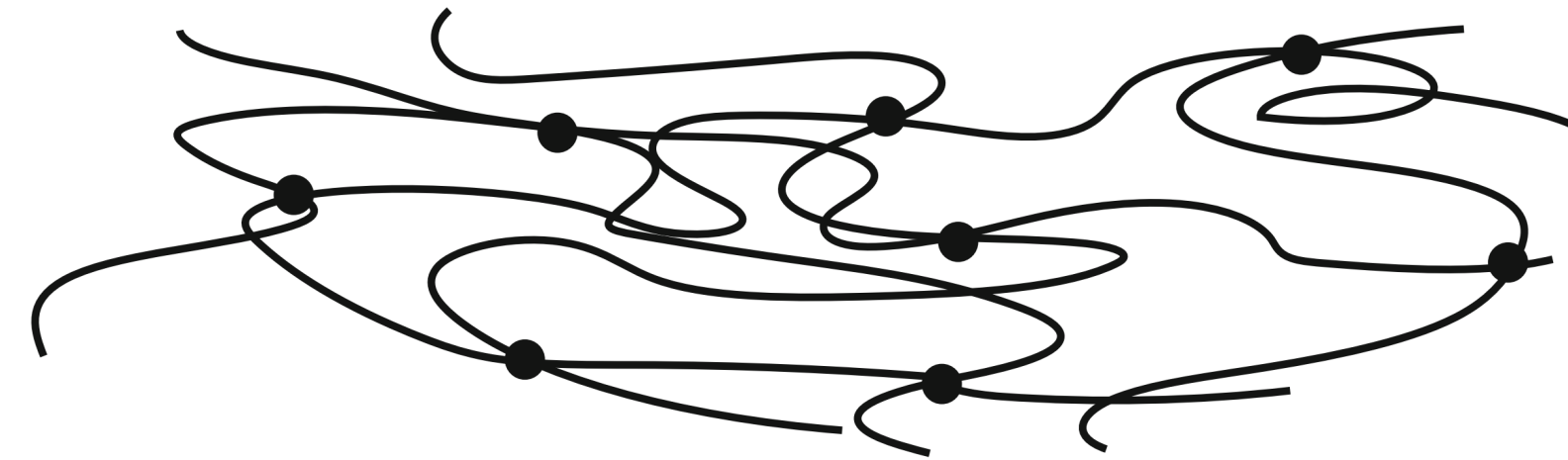
Statistical Mechanical Theory

Affine Network Model

undeformed network



affine network

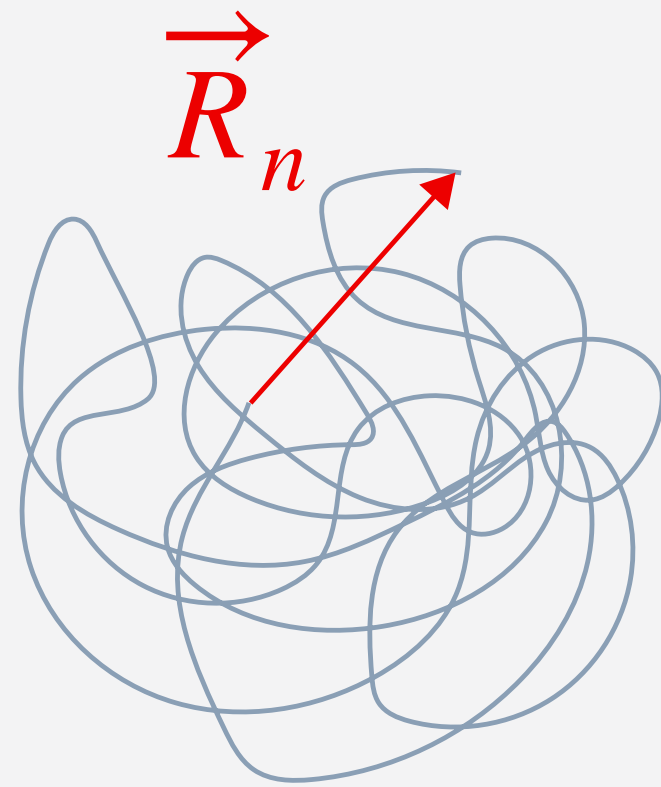


- fixed positions of junction points defined by the specimen deformation ratio
- network strands deform in the same manner with the macroscopic deformation

- **deformation is affine** (positions of crosslinks are changed precisely according to macroscopic deformation)
- **chains between crosslinks can be represented by Gaussian statistics of phantom chains**
- **the network is ideal** ($f_E = 0$)
- **chains are flexible** ($T > T_g$), no chain slip or strain-induced crystallisation (see [Slide 172](#) and [Chapter 3.3](#))
- **incompressibility**

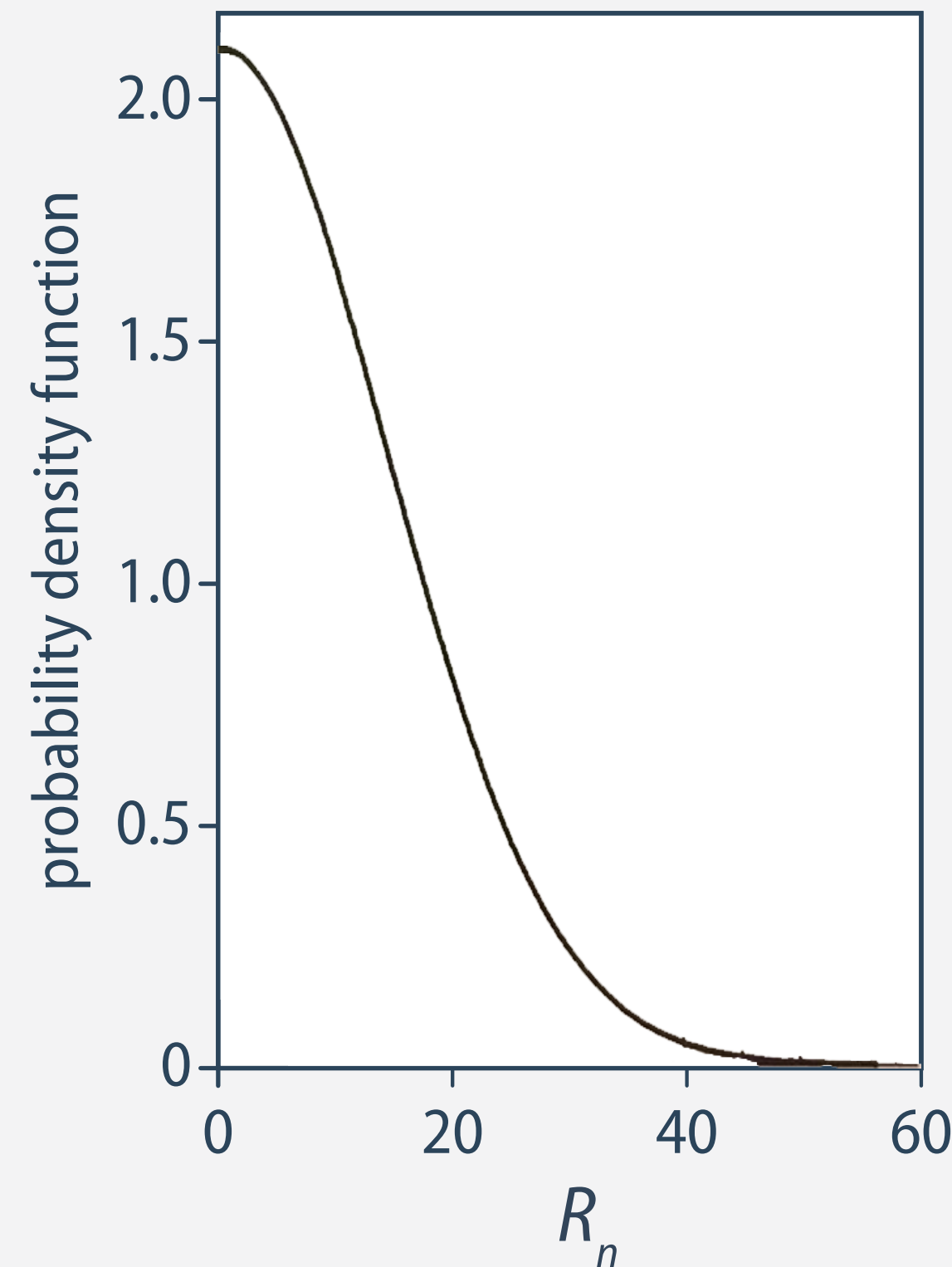
Repetition: The “Gaussian” Chain

- an ideal chain can be mapped onto a random walk and obeys Gaussian statistics (see **Chapter 2.1**)

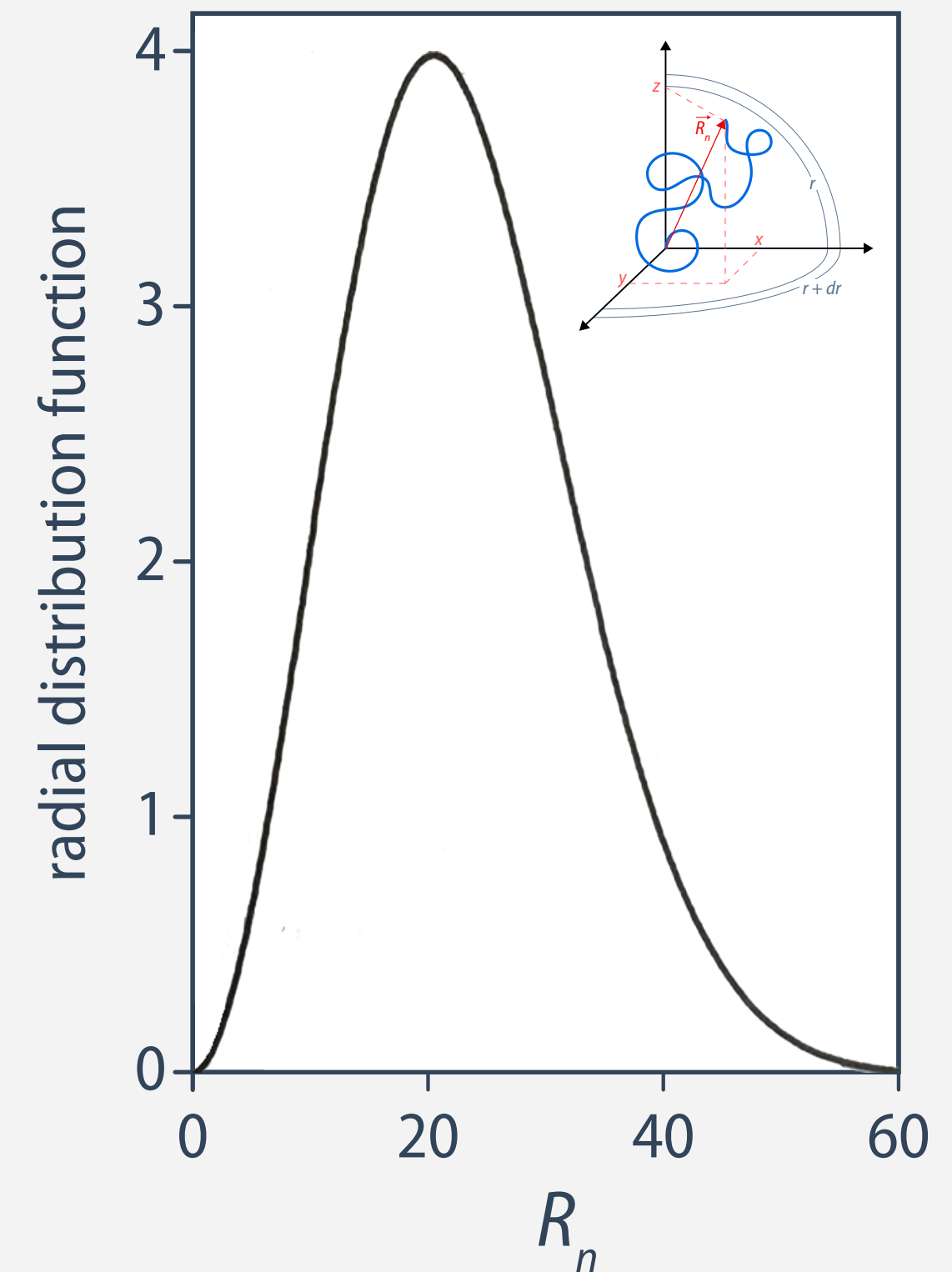


$$\langle R_n^2 \rangle^{\frac{1}{2}} \cong \sqrt{n} a$$

$$P = \left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R_n^2}{2na^2}\right)$$



$$P4\pi R^2 dr = 4\pi \left(\frac{3}{2\pi na^2}\right)^{3/2} \exp\left(-\frac{3R_n^2}{2na^2}\right) R_n^2 dr$$



- most probable are conformations with $\vec{R}_n = 0$, but it's *rms* value is finite and proportional to $\sqrt{n}$

The Entropy of an Ideal Polymer Chain

- the entropy is the product of Boltzmann's constant, k , and the logarithm of the number of states, Ω

$$S = k \ln \Omega$$

- the entropy of an ideal chain, S^c , is related to the probability density function

$$S^c = k \ln \Omega = k \ln(P \, d\tau) = C + k \ln P$$

- insertion and rearrangement leads us to

$$S^c = C + k \ln \left[\left(\frac{3}{2\pi n l^2} \right)^{3/2} \exp \left(-\frac{3R_n^2}{2nl^2} \right) \right]$$

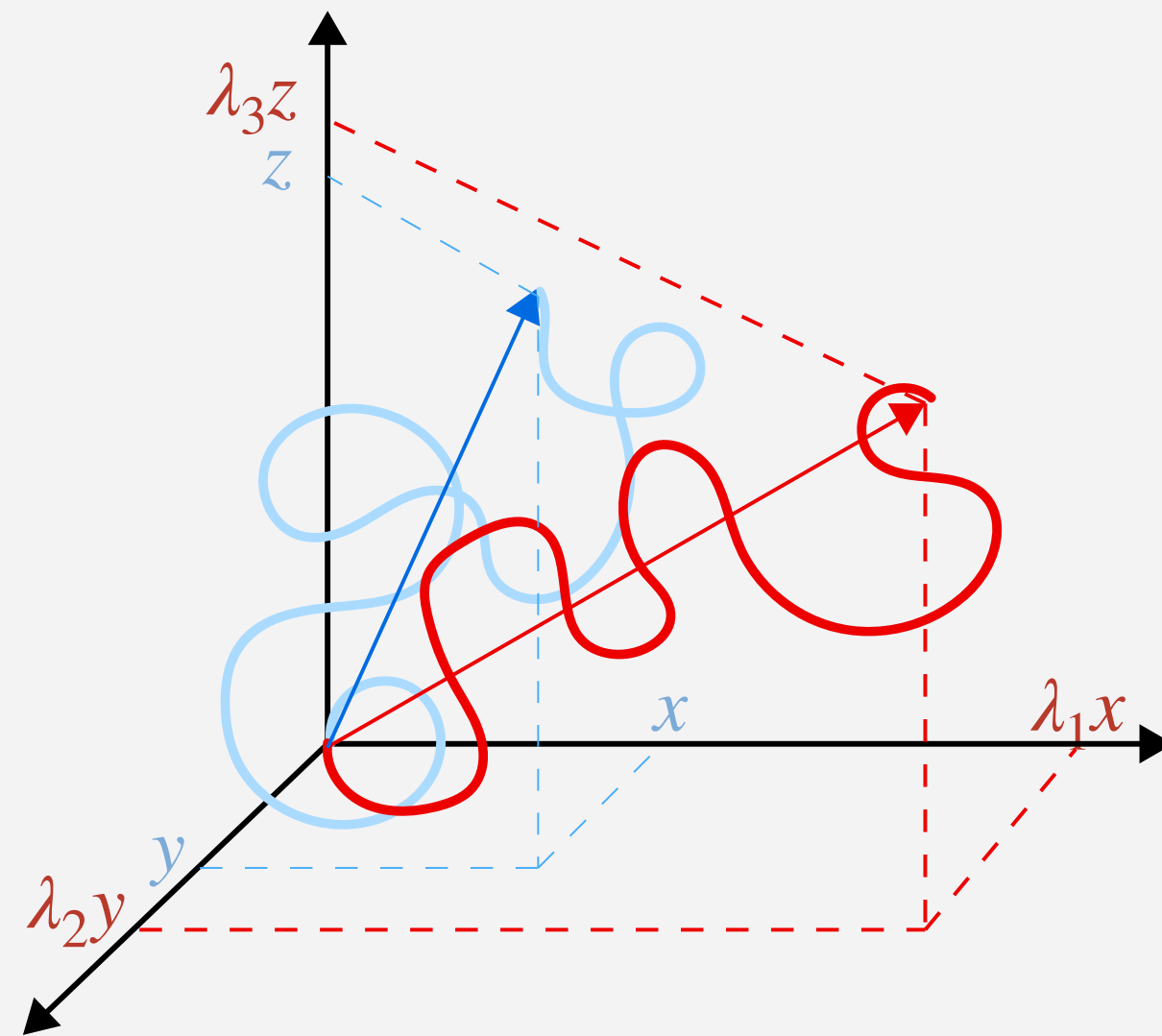
$$S^c = C + k \left(\ln \left[\left(\frac{3}{2\pi n l^2} \right)^{3/2} \right] - \frac{3R_n^2}{2nl^2} \right)$$

- only the last term depends on the end-to-end vector

$$S^c = S_0 - \frac{3kR_n^2}{2nl^2}$$

The Effect of Deformation

- the deformation, λ , displaces one junction point from (x, y, z) to $(\lambda_1 x, \lambda_2 y, \lambda_3 z)$



**before
deformation**

$$S^c = S_0 - \frac{3kR_n^2}{2nl^2}$$

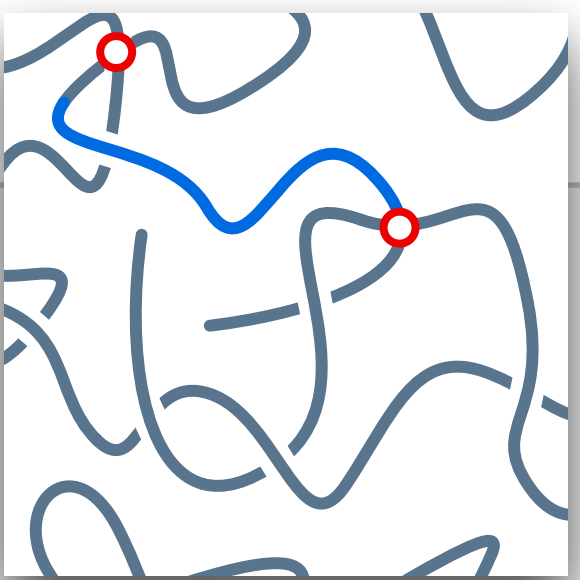
**after
deformation**

$$\Delta S^c = - \frac{3k((\lambda_1^2 - 1)x^2 + (\lambda_2^2 - 1)y^2 + (\lambda_3^2 - 1)z^2)}{2nl^2}$$

- under the assumption of no change of internal energy (i.e. for ideal rubber behavior):

$$\Delta A^c = - T \Delta S^c = \frac{3kT((\lambda_1^2 - 1)x^2 + (\lambda_2^2 - 1)y^2 + (\lambda_3^2 - 1)z^2)}{2nl^2}$$

Network Deformation



- we consider N **subchains** per unit volume (equivalent to the number of crosslinks) with n subunits and an end-to-end distance according to ideal chain statistics

before deformation

$$\langle R_n^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = na^2$$

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{na^2}{3}$$

after deformation

$$\langle \Delta A^c \rangle = \frac{kT((\lambda_1^2 - 1) + (\lambda_2^2 - 1) + (\lambda_3^2 - 1))}{2}$$

$$\Delta A = N \langle \Delta A^c \rangle = \frac{NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)}{2}$$

stretching into a single direction ($\nu = 0.5$)

$$\lambda_1 \lambda_2 \lambda_3 = 1 \quad \lambda_1 = \lambda \quad \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}$$

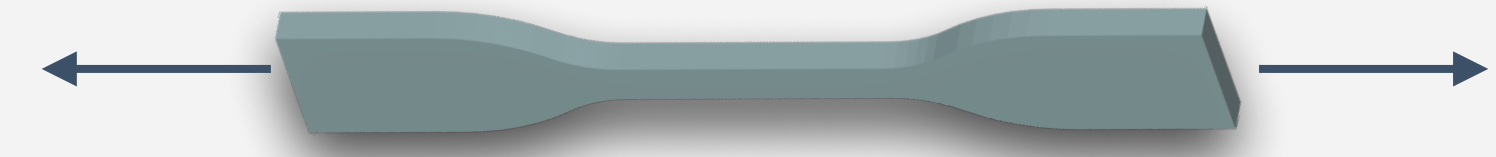
$$\Delta A = N \langle \Delta A^c \rangle = \frac{NkT(\lambda^2 + 2\lambda^{-1} - 3)}{2}$$

- the force per unit volume:**

$$f = \left(\frac{\partial A}{\partial l} \right)_T = \left(\frac{\partial A}{\partial \lambda} \right)_T = \frac{\partial}{\partial \lambda} \left(\frac{NkT(\lambda^2 + 2\lambda^{-1} - 3)}{2} \right)_T = NkT(\lambda - \lambda^{-2}) = \sigma$$

Uniaxial Deformation

- using $\epsilon = \frac{\Delta l}{l_0} = \frac{\lambda l_0 - l_0}{l_0} = \lambda - 1$,
we find a relations between stress:



$$\sigma = NKT\left(1 + \epsilon - \frac{1}{(1 + \epsilon)^2}\right) = NkT \frac{(1 + \epsilon)^3 - 1}{(1 + \epsilon)^2} = NkT \frac{\epsilon^3 + 3\epsilon^2 + 3\epsilon}{(1 + \epsilon)^2}$$

$$\epsilon \rightarrow 0 : \sigma \approx 3NkT\epsilon$$

Young's modulus, E , is accordingly:

$$E = \frac{\sigma}{\epsilon} = 3NkT$$

- rubber elasticity depends only on the number subchains, N , and the temperature, T
- stiffness increases with increasing temperature

Relationship Between Moduli and Moduli of Elasticity

- for isotropic polymers, simple relationships exist between the elastic constants:
(for small deformations, when Hooke's law applies)

Young's modulus:

$$E = 2G(1 + \nu)$$

$$E = 3K(1 - 2\nu)$$

Shear modulus:

$$G = \frac{1}{2} \frac{E}{1 + \nu}$$

$$G = \frac{3}{2} \frac{K(1 - 2\nu)}{1 + \nu}$$

Bulk modulus:

$$K = \frac{1}{3} \frac{E}{1 - 2\nu}$$

$$K = \frac{2}{3} \frac{G(1 + \nu)}{1 - 2\nu}$$

Poisson's ratio:

$$\nu = \frac{1}{2} - \frac{1E}{6K}$$

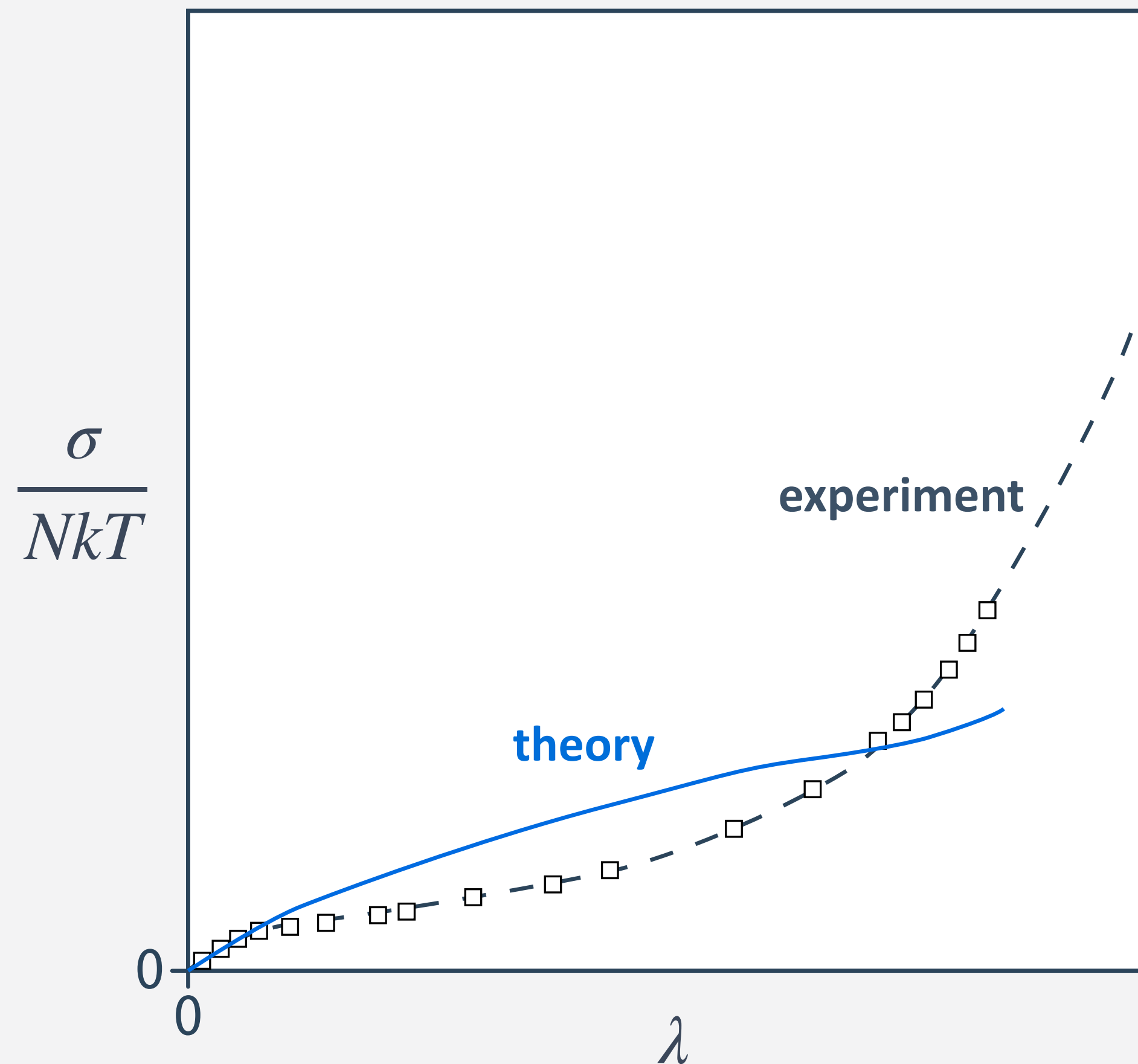
$$\nu = \frac{E}{2G} - 1$$

- for an elastomer (Poisson's ratio ≈ 0.5), the shear modulus is therefore: $G = \frac{E}{3} = NkT$

Limitation of the Molecular Theory of Rubber Elasticity

- our approach works well for small strains and low cross linking densities

comparison



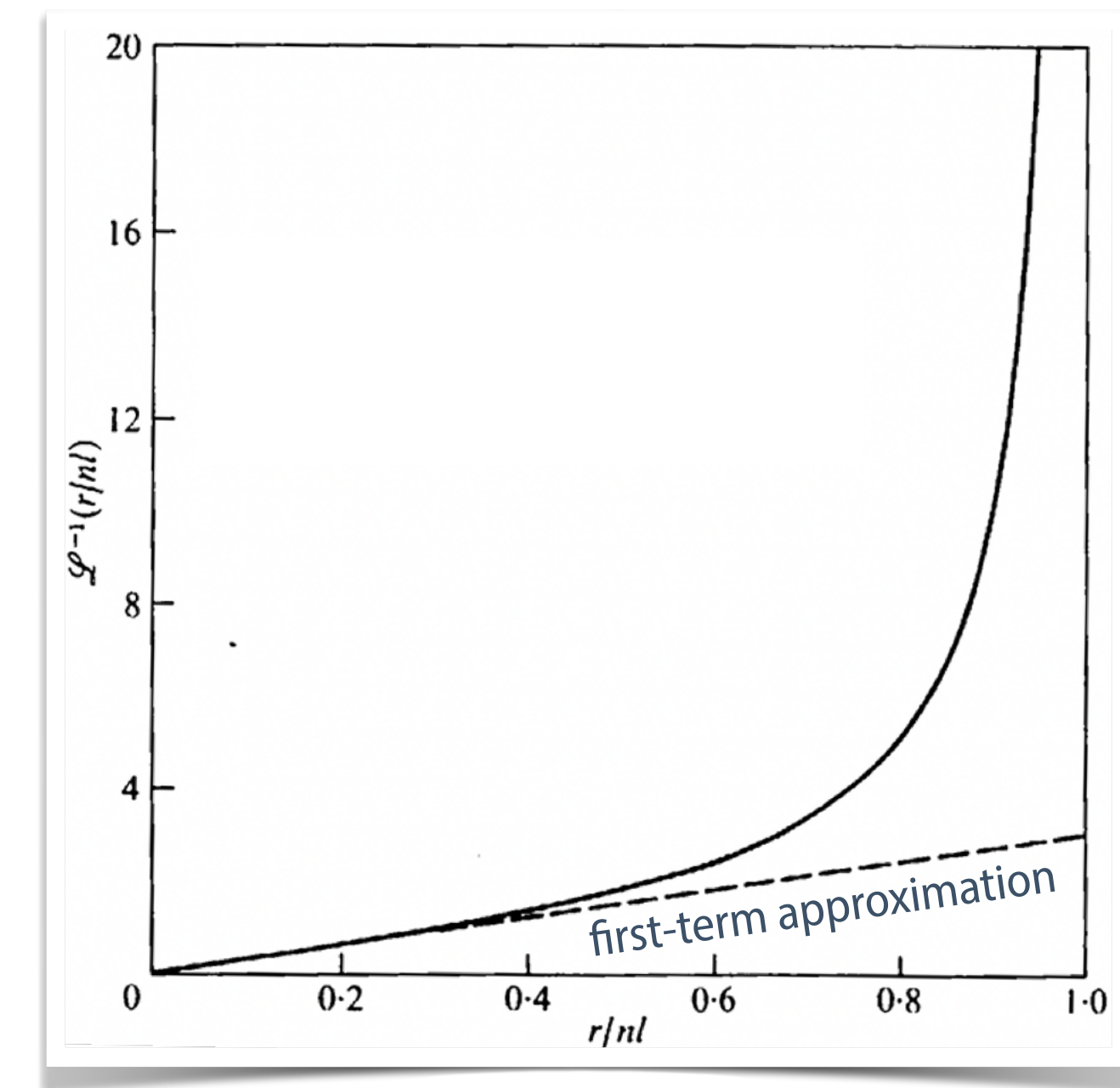
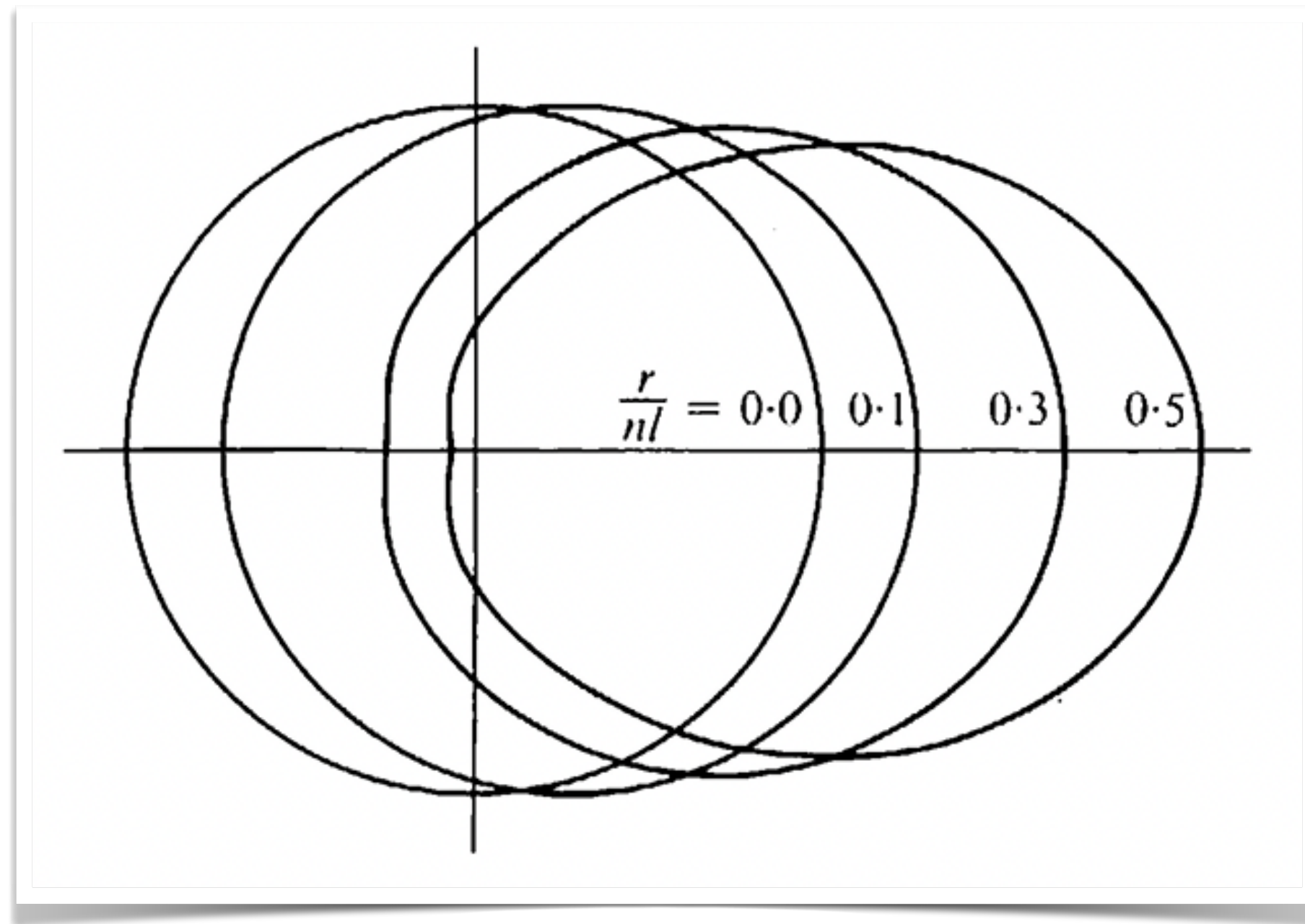
limitations

- failure of the model for high crosslinks
- phantom network: independent conformations of subchains
- strain hardening: induced crystallisation at large deformations
- Gaussian approximation fails at large strains

Non-Gaussian Statistics

- more realistic distribution functions such as the **Langevin distribution** can be used

$$\ln P(r) = \text{constant} - n \left[\frac{3}{2} \left(\frac{r}{nl} \right)^2 + \frac{9}{20} \left(\frac{r}{nl} \right)^4 + \frac{99}{350} \left(\frac{r}{nl} \right)^6 + \dots \right] \quad f = \frac{kT}{l} \left[3 \left(\frac{r}{nl} \right) + \frac{9}{5} \left(\frac{r}{nl} \right)^3 + \frac{297}{175} \left(\frac{r}{nl} \right)^5 + \frac{1539}{875} \left(\frac{r}{nl} \right)^7 + \dots \right]$$



- Langevin and Gaussian distribution are identical for $R_n \ll nl$.

Empirical Approaches

- empirical strain-energy function according to **Mooney-Rivlin** depends only on extension ratios

$$\text{strain-energy-function} = f(\lambda_1, \lambda_2, \lambda_3)$$

- invariance: independence of the choice of coordinate system

$$\lambda_1 + \lambda_2 + \lambda_3$$

$$\lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$\lambda_1\lambda_2 + \lambda_2\lambda_3 + \lambda_3\lambda_1$$

$$\lambda_1\lambda_2\lambda_3$$

- only even powers of λ to construct strain-energy function

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2$$

$$I_3 = \lambda_1^2\lambda_2^2\lambda_3^2$$

- incompressibility, i.e. $\lambda_1\lambda_2\lambda_3 = 1$:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

$$I_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2}$$

$$I_3 = 1$$

Empirical Approaches (Mooney-Rivlin)

- the change in A can be formulated as a power series with $\lambda_1 = \lambda_2 = \lambda_3 = 1$ for the non-deformed state

$$\Delta A = \sum_{m,n=0}^{\infty} C_{m,n} (I_1 - 3)^m (I_2 - 3)^n = C_{1,0} (I_1 - 3) + C_{0,1} (I_2 - 3) + \dots$$

$$\sigma = \frac{d\Delta A}{d\lambda} = \frac{d}{d\lambda} (C_{1,0}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_{0,1}(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) + \dots)$$

- for uniaxial tension, $\lambda_1 = \lambda$ and $\lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}$:

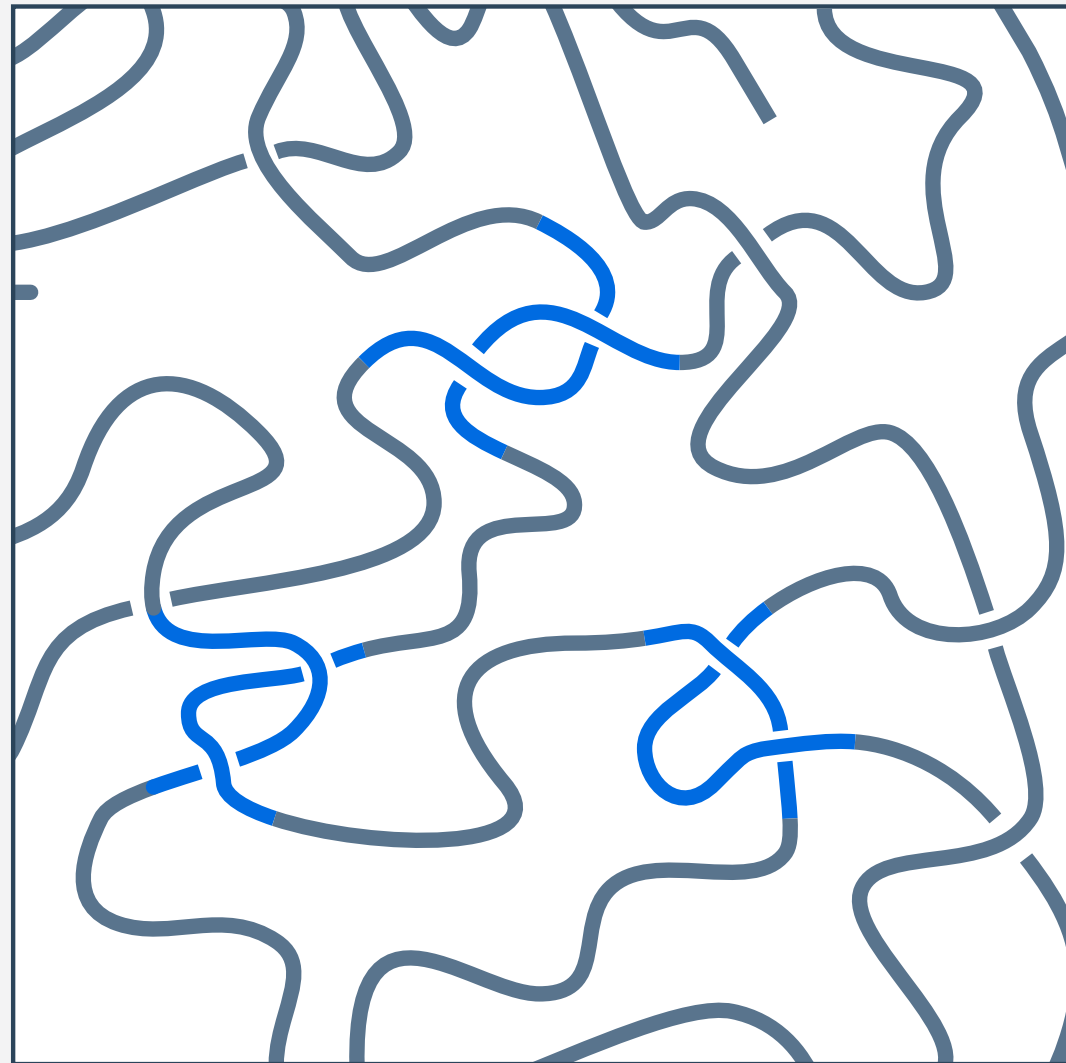
$$\sigma = C_{1,0}(2\lambda - \lambda^{-2}) + 2C_{0,1}(1 - \lambda^{-3}) + \dots$$

Slide 290: $3NkT$

- the last equation resembles our previously derived one (Slide 272), but includes correction terms with arbitrary constants to be adjusted to a more real rubber behaviour.

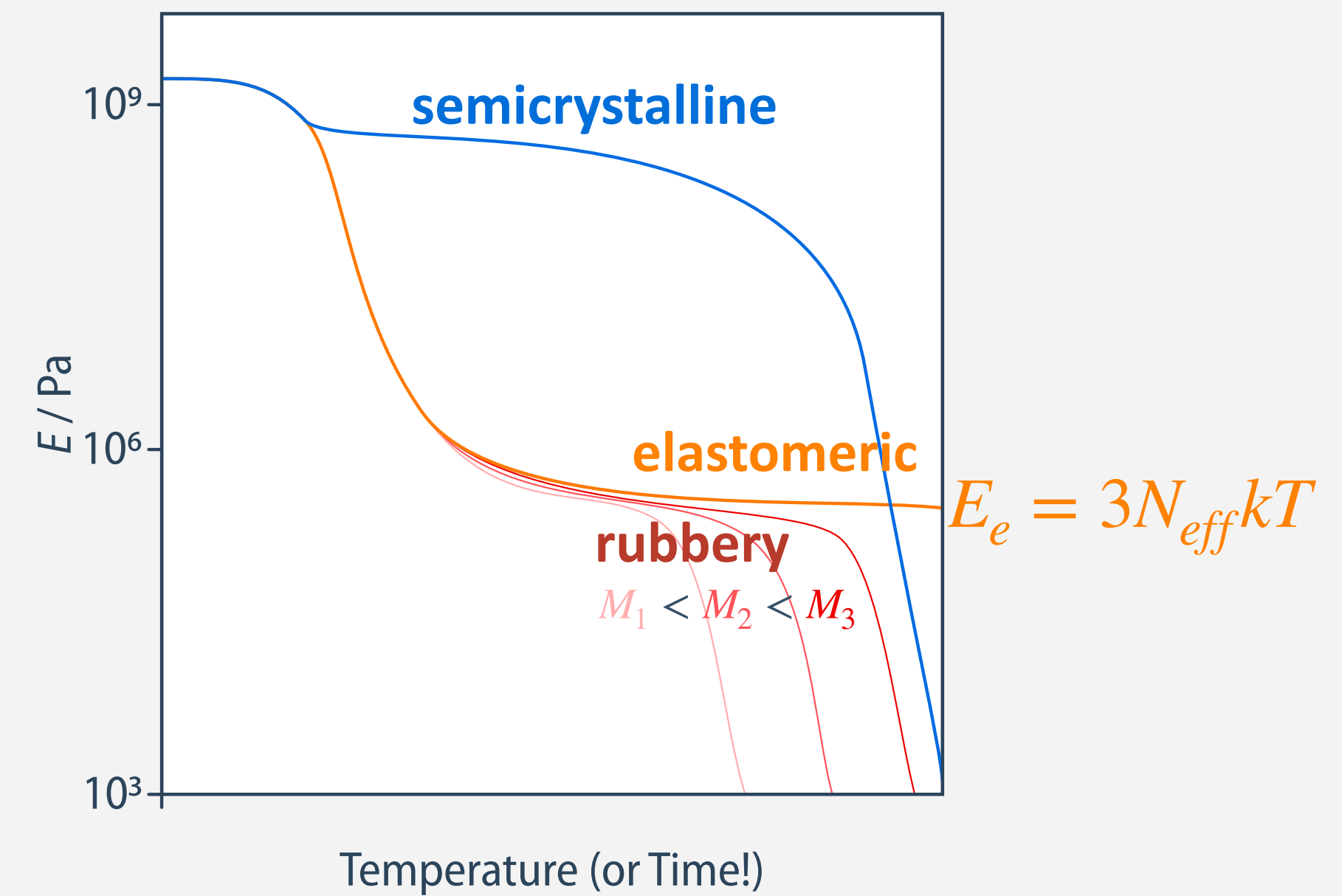
Entanglement Network

entanglement



The static picture representing entanglements as “knots” does not reflect the purely dynamic origin of this phenomenon!

entanglement network



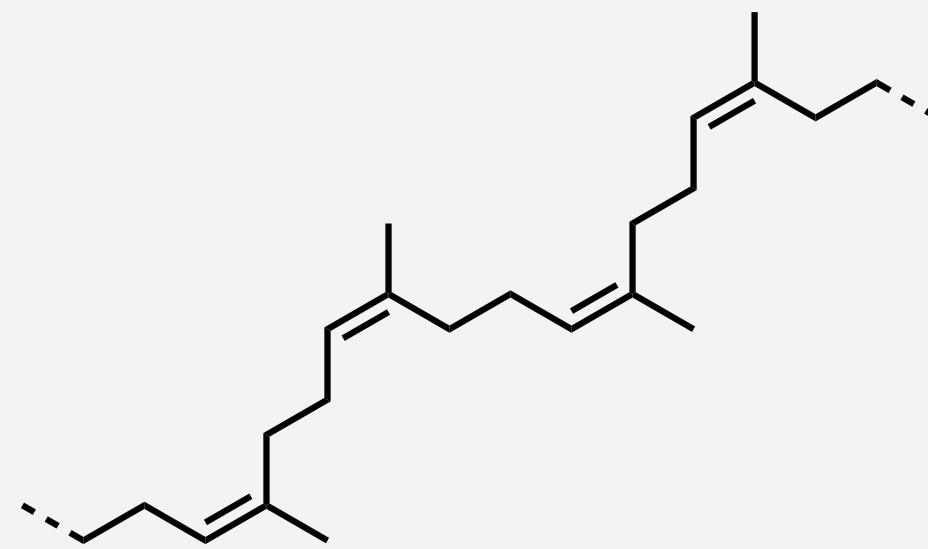
- entanglement contribute to the effective cross-linking density in elastomers $N_{eff}^{-1} = N_e^{-1} + N_x^{-1}$
 N_e : entanglement density N_x : cross-linking density

Elastomers in Practice

Natural Rubber

- commercial exploitation of natural rubber from *Hevea Brasiliensis* (> 20% of global rubber production)

Latex



(almost entirely cis-1,4-PI)

$T_g = -70\text{ °C}$

$M_w = 10^6\text{ g/mol}$

Hevea Brasiliensis



Natural Rubber

milky fluid from extremely small particles of rubber, used for products made by dipping, extruding, or coating processes.

Dry Natural Rubber

dried or milled sheets are processed by compression molding, extrusion.

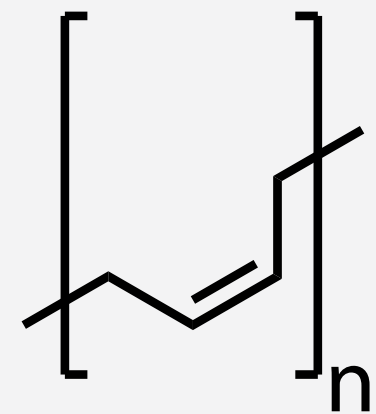
- product very resistant to breakage (crystallisation induced by deformation)
- low hysteresis during cyclic deformation
- moderately resistant to UV, oxidants, fuels

Synthetic Elastomers and Rubbers

- technologically relevant homopolymers with low T_g (ca. 60% of global rubber production)

polybutadiene (PB)

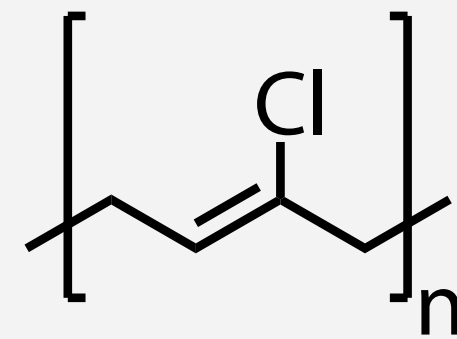
$T_g = -90\text{ °C}$



resistance to abrasion
(impact modification,
copolymers, mixtures, tires)

neoprene

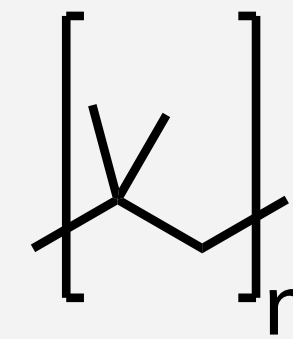
$T_g = -50\text{ °C}$



resistance to the
environment
(pipes, cables, protection)

polyisobutylene (PIB)

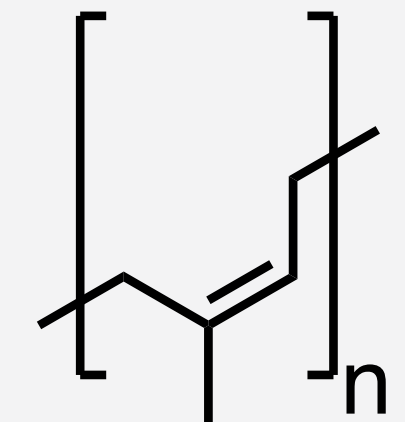
$T_g = -65\text{ °C}$



low permeability, resistance
to oxidations
(inner tubes, seals, bags)

synthetic PI

$T_g = -70\text{ °C}$



resistance to tear and abrasion,
elasticity
(tires, see [Slide 302](#))

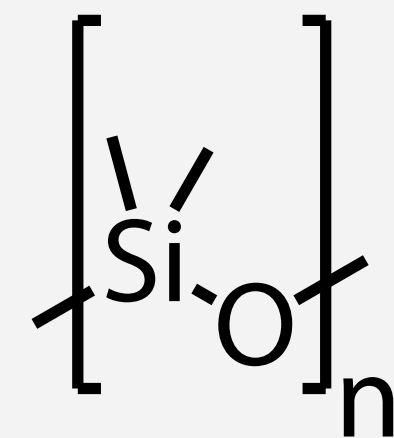
- many more that fulfil rubber criteria (low T_g , no or low T_m , well entangled)

Silicones

- heteroatom backbone from strong Si-O bonds

PDMS

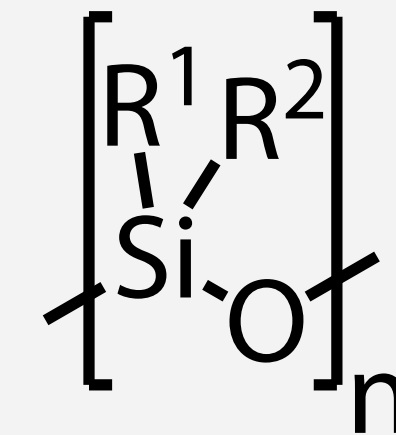
(polydimethylsiloxane)



tendence to crystallize

MPDMS

modified poly(dimethylsiloxane)



operating temperature from -130 to 250 °C;
resistant to the environment, chemically inert,
but poor mechanical properties
(moulds, electronics industry, medicine, etc..)

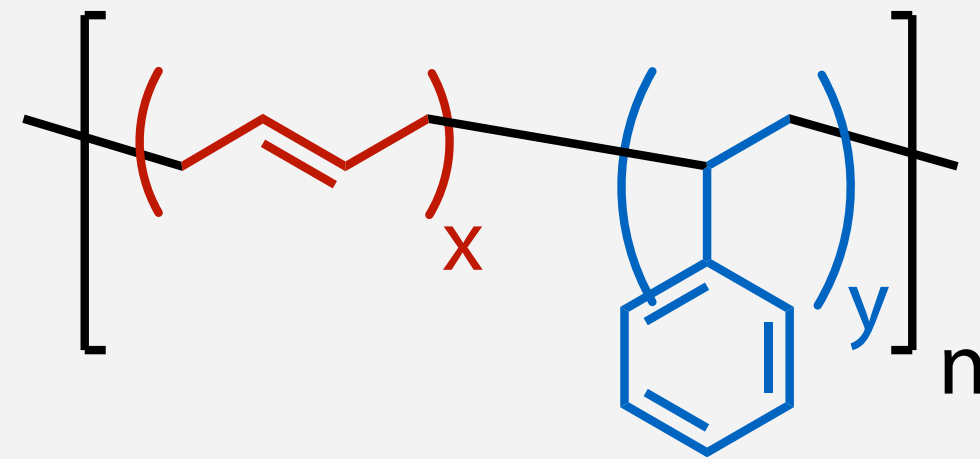
- wide-ranging applications depending on structure and properties

Synthetic Elastomers From Copolymers

- technologically relevant (random) copolymers with low glass transition temperatures

poly(styrene-co-butadiene)

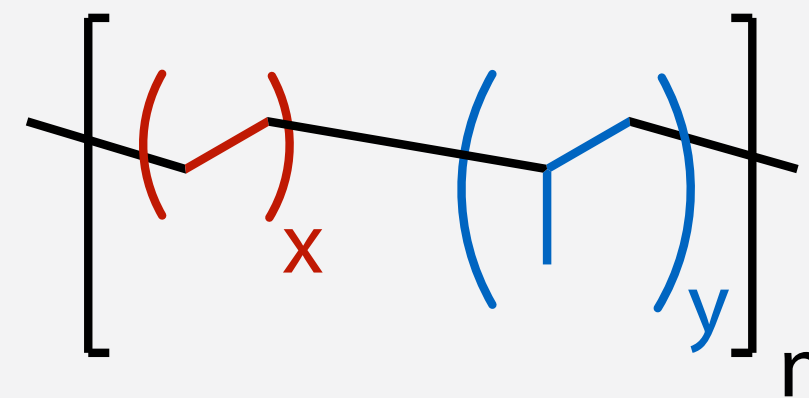
$T_g = -60\text{ }^{\circ}\text{C}$



PS domains act as physical crosslinks;
better abrasion resistance than natural rubber,
cheap
(tires, shoes, cables)

ethylene-propylene (EPR)

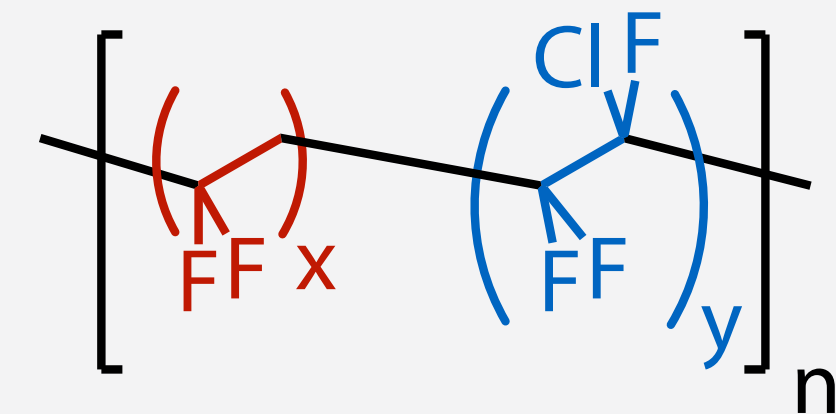
$T_g = -60\text{ }^{\circ}\text{C}$



environmentally resistant
(cables, impact modification)

fluoroelastomers

$T_g = -65\text{ }^{\circ}\text{C}$



exceptional resistance to the environment
and T -resistant, but expensive
(engineering applications)

- many other formulations, in particular block copolymers, including TPEs (PS- or PU-based)...**
(> 10% of global rubber production)

Applications of Elastomers in Tires



internal coating
(PIB)

cis 1-4 PB	35%
carbon black	65%
fuel oil	9%
others	

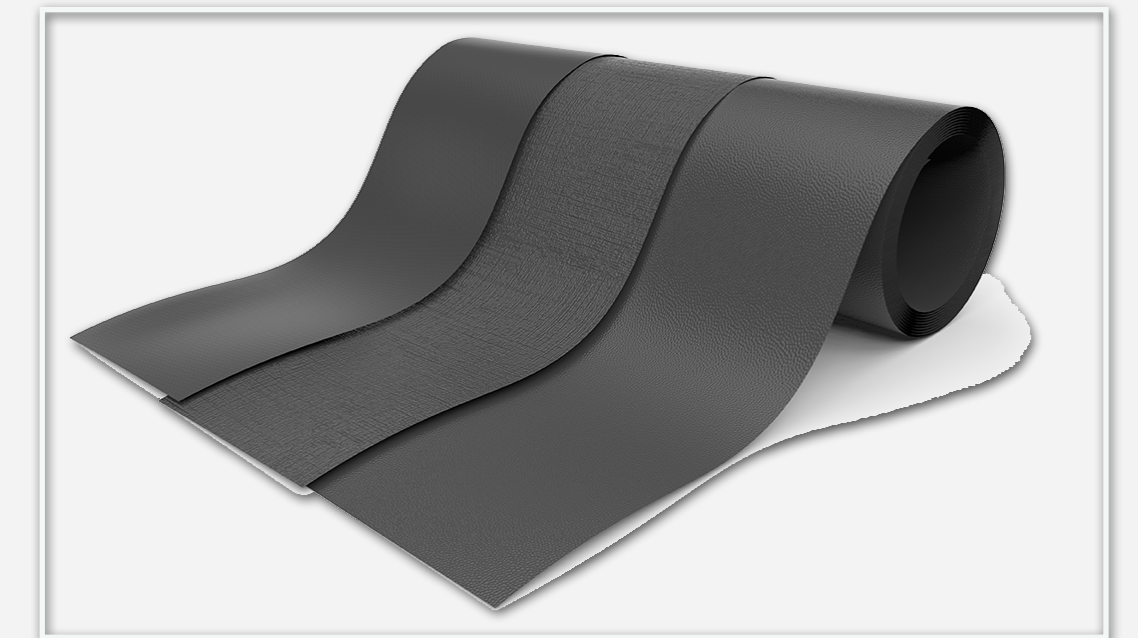
natural rubber
SB
cis 1-4 PB
carbon black

world production: 40×10^6 tonnes (2×10^{10} per year)

- **mostly tires:** optimised adhesion, resistance to indentation & abrasion, vertical damping (comfort), etc...

Other Types of Applications

- industrial applications (seals, belts, insulation, cables...)
- agriculture (animal tags, convey belts, ...)
- medical applications (gloves, implants, prosthetics, ...)
- printing applications
- consumer products, footwear, sporting goods, food storage, housing, adhesives



Summary

- elastomers are materials capable of undergoing very large reversible deformations: this phenomenon is at present limited to highly cross-linked flexible polymers above T_g .
- thermodynamic analysis indicates the dominant contribution to the stress-strain behaviour to be entropic in origin. The forces opposing deformation arise from the reduced number of conformational states available to a stretched chain (equivalent to a decrease in entropy and hence an increase in free energy).
- half of the world's rubber production currently ends up as tires (mainly NR, SBR, and PB). Since most common elastomers are miscible, there is enormous scope for adapting properties by blending. Many more types of rubbers are available for specific applications.