# Table of Contents

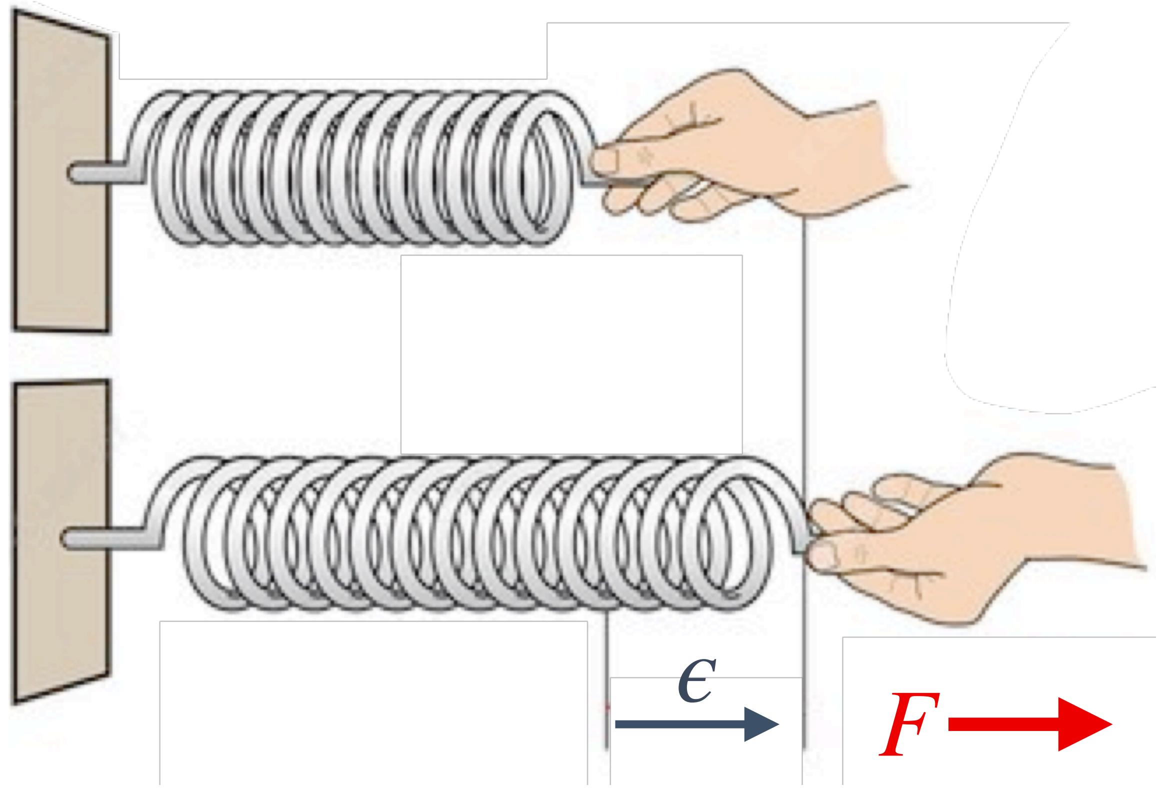
# 4

# Mechanical Properties

# Elastic Springs and Newtonian Liquids

- two limiting cases of materials response: perfectly **elastic solids** vs. purely viscous **Newtonian liquids**

**elastic solids**
(reversible deformation)



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

**viscoelastic materials**
(a world in between)

**see Chapter 4.2**

**viscous liquids**
(irreversible deformation)

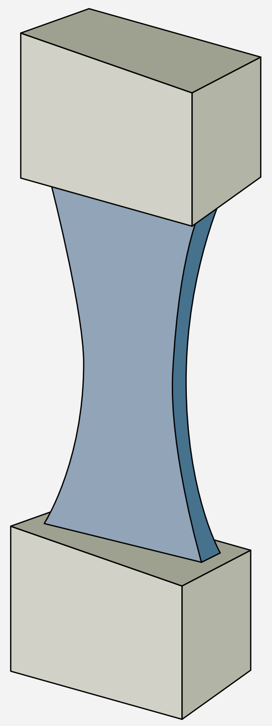
**Newton's law:** $\dot{\epsilon} = \dfrac{\sigma}{\eta}$

- **depending on deformation magnitude, duration (temperature), and rate, polymers exhibit a continuum of behaviours. They are viscoelastic materials!**

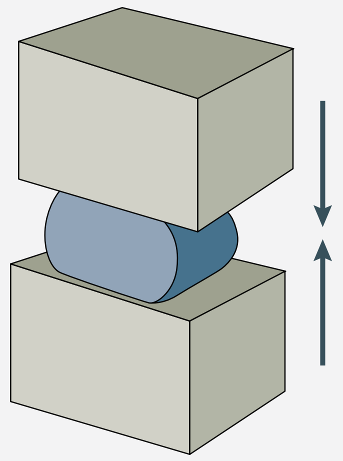
# Main Mechanical Deformations

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

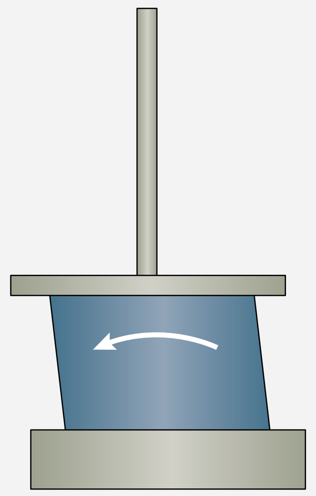
**tension**



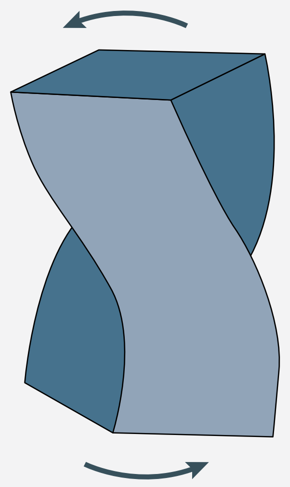
**compression**



**shear**



**torsion**

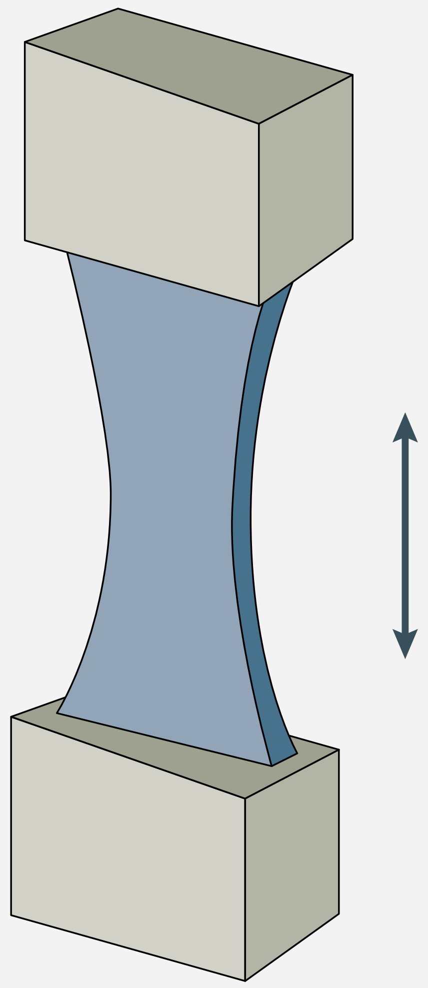


- **tension:** force pulling materials apart, leading to elongation and stretching
- **compression:** force pushing materials together, causing shortening and compaction
- **shear:** force causing layers to slide past each other, resulting in angular distortion
- **torsion:** twisting force, resulting in shear deformation along the material’s length

# Elastic Moduli

- different elastic moduli ($E$, $K$, $G$) and corresponding compliances describe specific stress-strain situations
- these moduli quantify the stiffness or resistance to deformation under defined loading modes

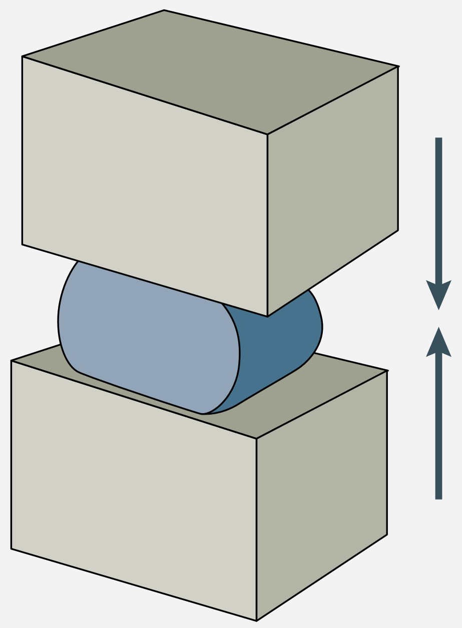
**tension**



**Young's modulus** $E$

**tensile compliance** $\mathrm{D} = \dfrac{1}{E}$

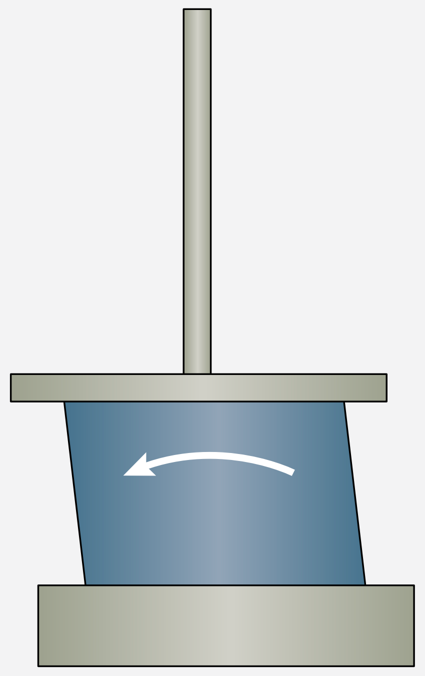
**compression**



**bulk modulus** $K$

**bulk compliance** $\mathrm{B} = \dfrac{1}{K}$

**shear**



**shear modulus** $G$

**shear compliance** $\mathrm{J} = \dfrac{1}{G}$

# Relationship Between Elastic Moduli

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

| | | |
|---|---|---|
| Young's modulus: | $E = 2G(1 + v)$ | $E = 3K(1 - 2v)$ |
| shear modulus: | $G = \frac{1}{2}\,\frac{E}{1 + v}$ | $G = \frac{3}{2}\,\frac{K(1 - 2v)}{1 + v}$ |
| bulk modulus: | $K = \frac{1}{3}\,\frac{E}{1 - 2v}$ | $K = \frac{2}{3}\,\frac{G(1 + v)}{1 - 2v}$ |
| Poisson's ratio: | $v = \frac{1}{2} - \frac{1E}{6K}$ | $v = \frac{E}{2G} - 1$ |

- **if two of the four elastic constant ($E, G, K, v$) are known, the others can be calculated**

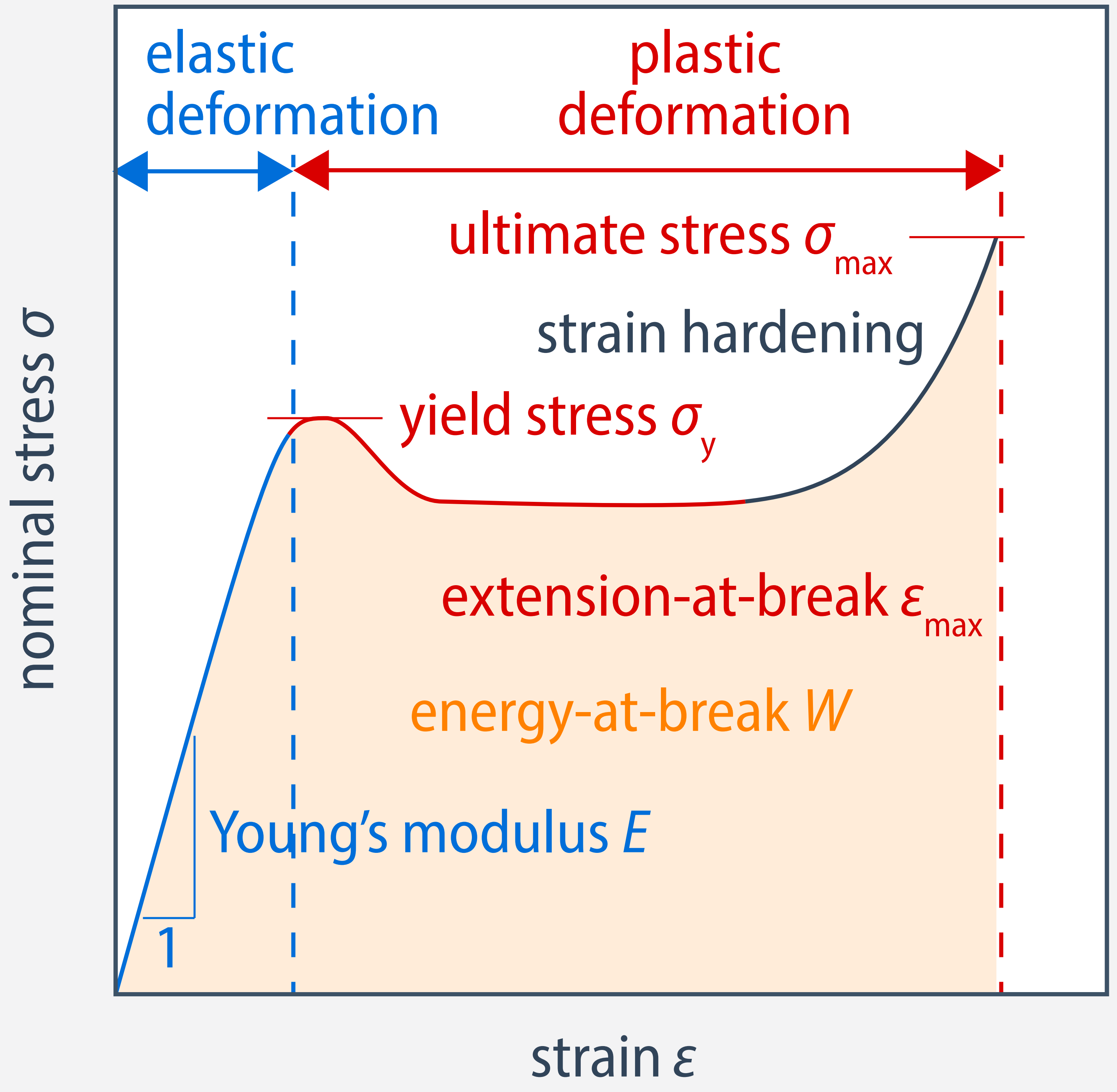
# Static Measurements

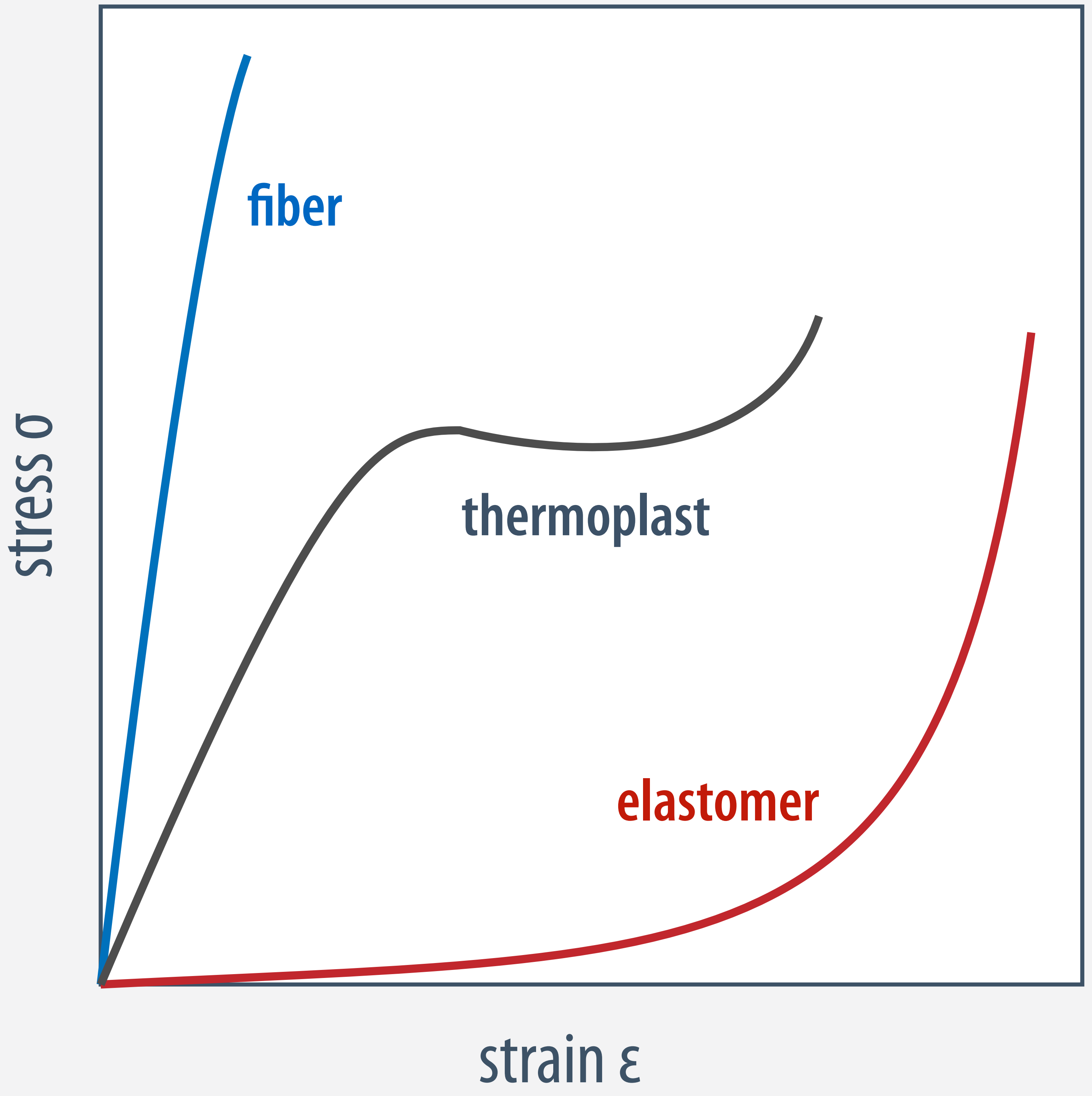
- measure of material's response under constant or slowly varying loads, revealing strength and elastic limits

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

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

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



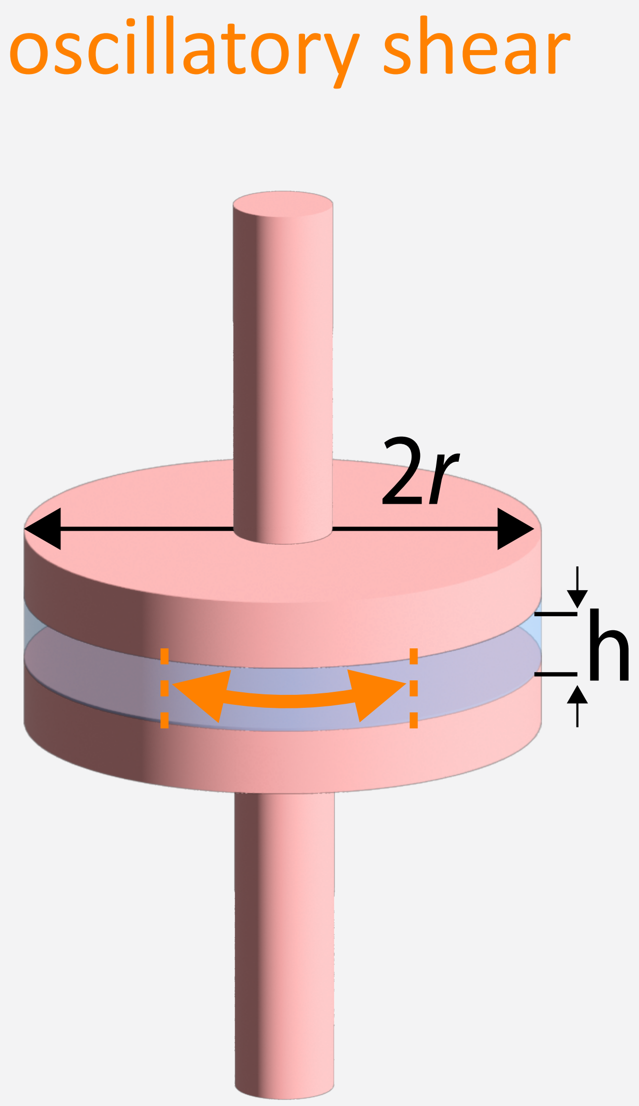


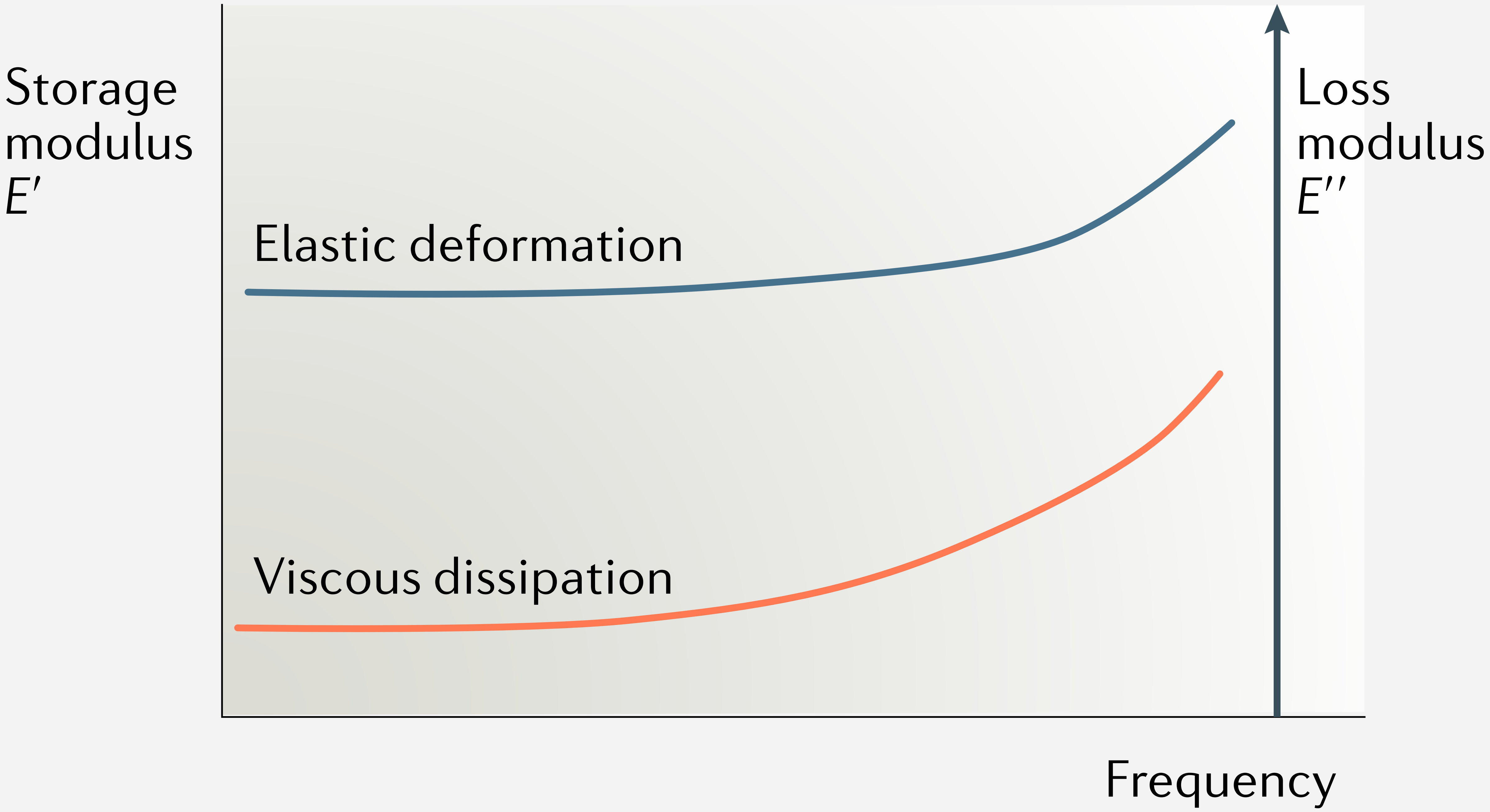
- Hooke's law applies only in the linear, small-strain regime
- polymers can be classified by their stress-strain curves under tension

see **Reading Recommendation** (Stiffness of Living Tissues)

# Dynamic Measurements

- probing the material under oscillatory (sinusoidal) deformation reveals its viscoelastic behavior





- in small-amplitude oscillatory tests, the response remains within the **linear viscoelastic regime**
- **this allows determination of viscoelastic moduli (*E*’ and *E*’’) as function of frequency or temperature**

see **Reading Recommendation** (Stiffness of Living Tissues)

# Small Deformation Behavior

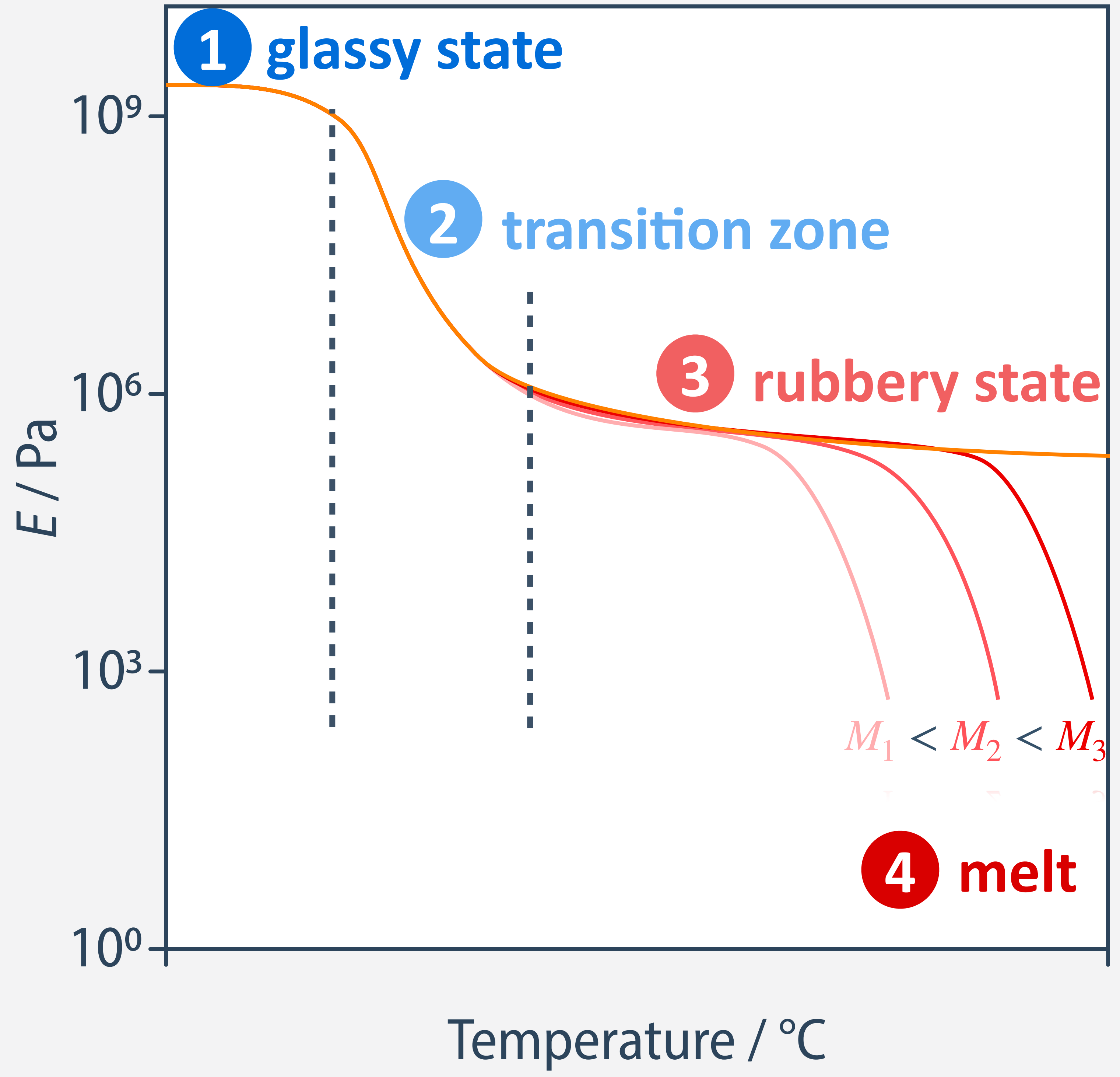
1. **deformation in the glassy or semi-crystalline state:**
   time-independent, solid-like elastic response

2. **transition zone:** highly time-dependent (viscoelastic) response near $T_g$, reflecting delayed segmental motion **(see Chapter 4.2)**

3. **rubbery state:** large, reversible deformations due to entropic elasticity **(see Chapter 4.1)**

4. **viscous state:** little or no elastic recovery, dominated by flow and energy dissipation

**universal trend of Young's modulus**

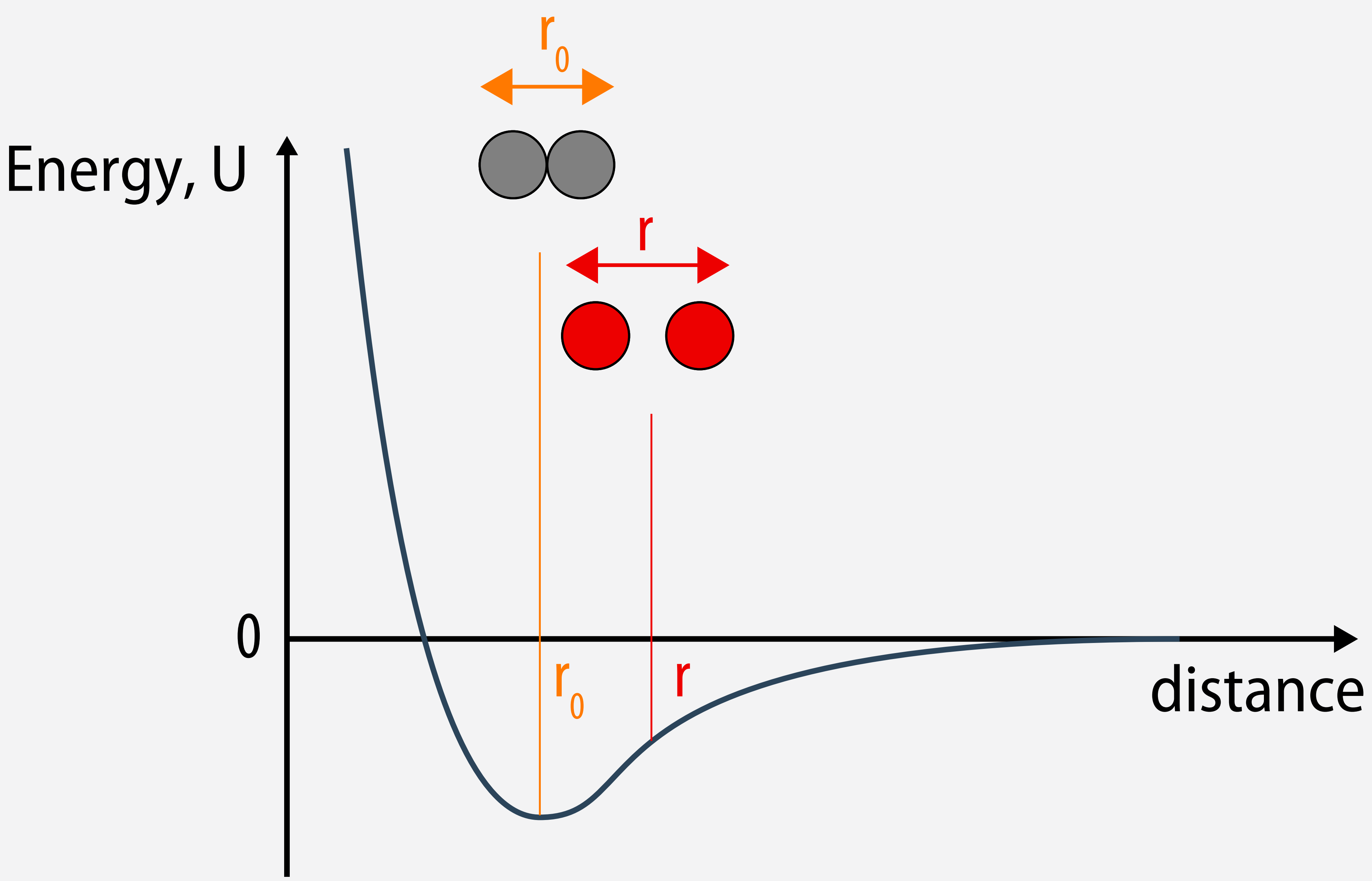


# 4.1

# Elastic Deformation

# Energy-Driven Elasticity

- typical of crystalline solids (e.g. steel wires can be reversibly stretched by up to ~1%)



**parabolic nature of the potential near equilibrium point:**

$$U = \mathrm{C}(r - r_0)^2$$

**elastic force:**

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

**stress:**

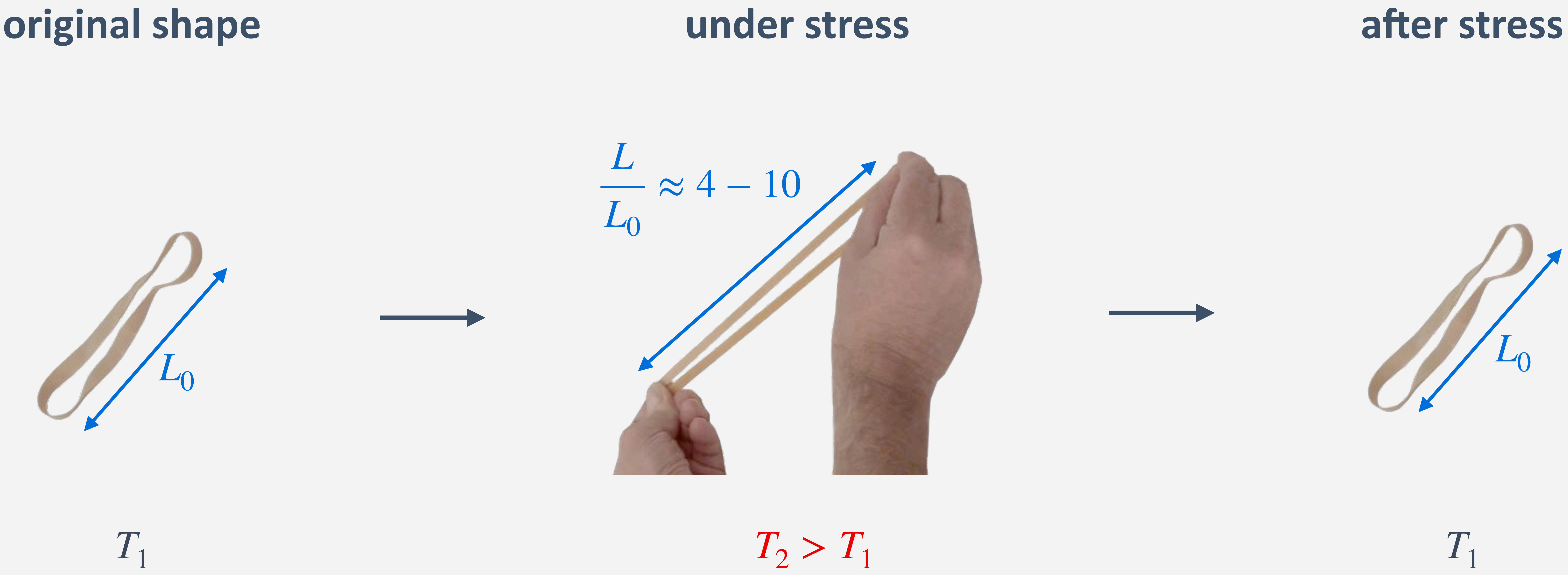
$$\sigma = \frac{f}{A} = \frac{2\mathrm{C}}{A}(r - r_0) = \frac{2\mathrm{C}r_0}{A}\,\frac{r - r_0}{r_0} = E\epsilon$$

Hooke's law!

- **the elastic restoring force is enthalpic in origin;** entropy plays a minor role
- **steel cools upon stretching,** indicating energy is stored as internal potential energy
- **the elastic modulus decreases with increasing temperature**

# Observations on Elastomers Contradicting Conventional Elasticity

- elastomers and rubbers can undergo large, reversible deformations ($\epsilon > 100\,\%$ )



**original shape** → **under stress** → **after stress**

$L_0$, $T_1$

$\frac{L}{L_0} \approx 4 - 10$, $T_2 > T_1$

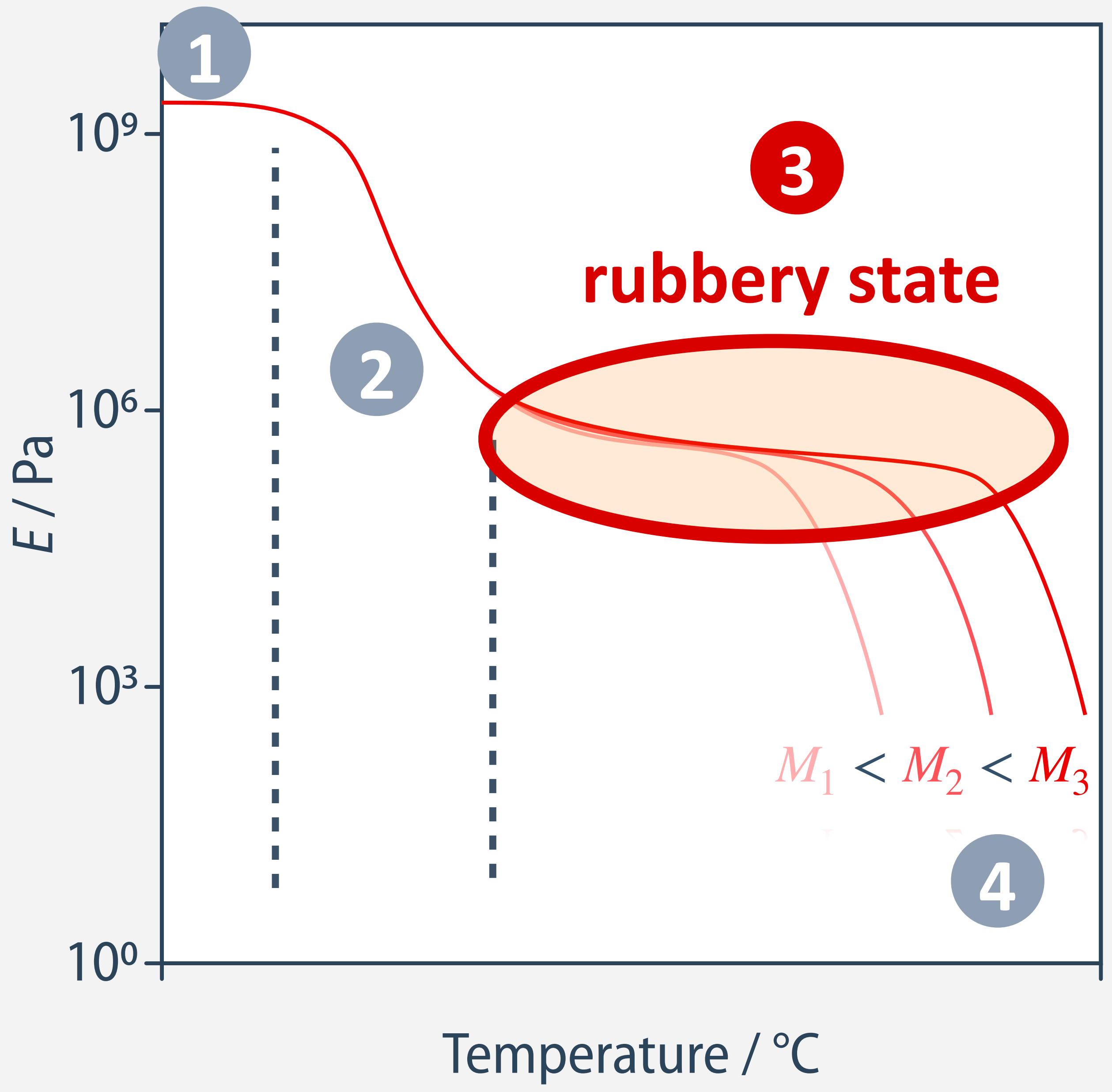
$L_0$, $T_1$

- **rubbers and elastomers contract when heated** (Gough-Joule effect, first reported in 1802)
- **the temperature of a rubber band increases upon rapid stretching**
- **the elastic modulus increases with increasing temperature**

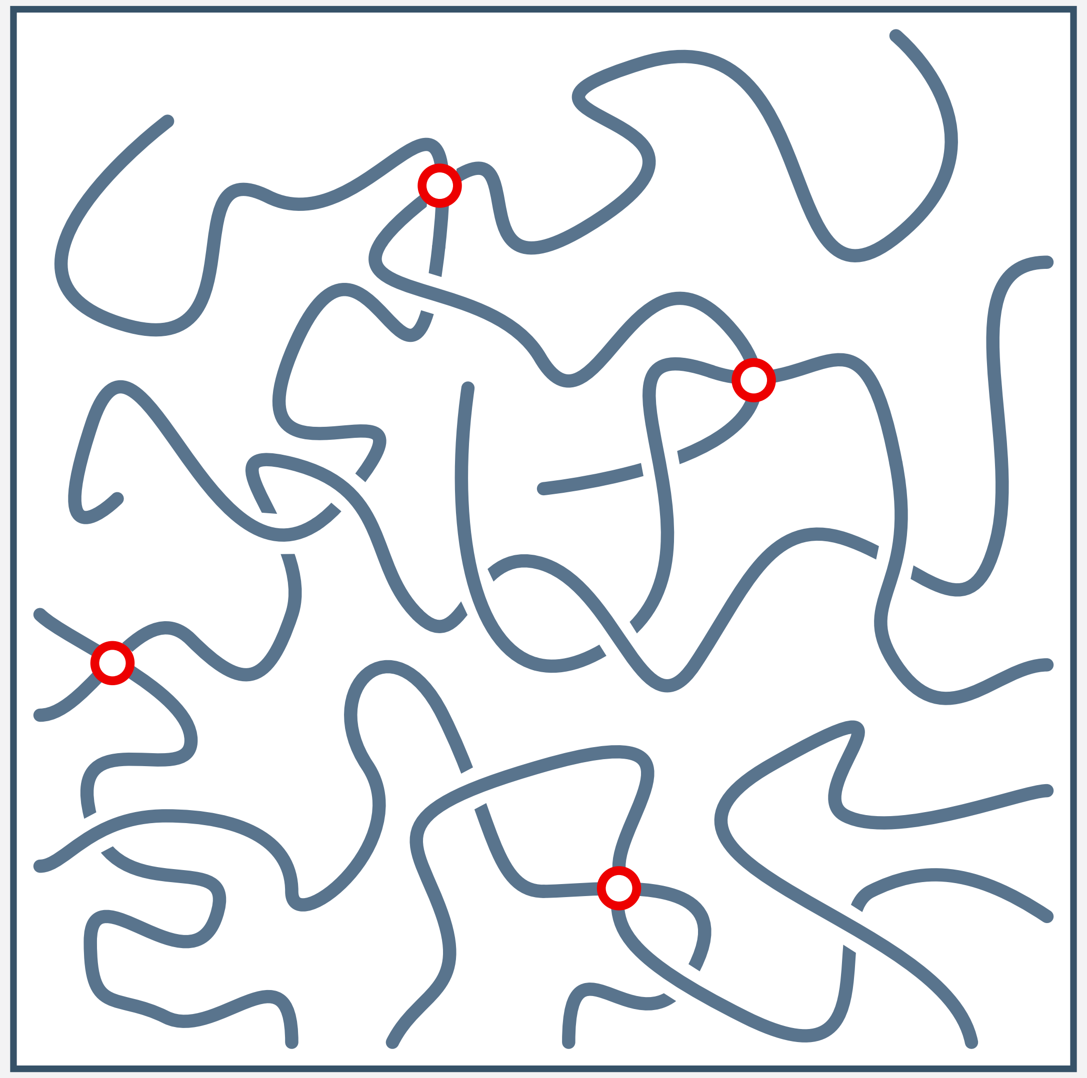
# Conditions for Rubber Elasticity

- rubber elasticity occurs in amorphous organic polymers above $T_g$

**phenomenology**

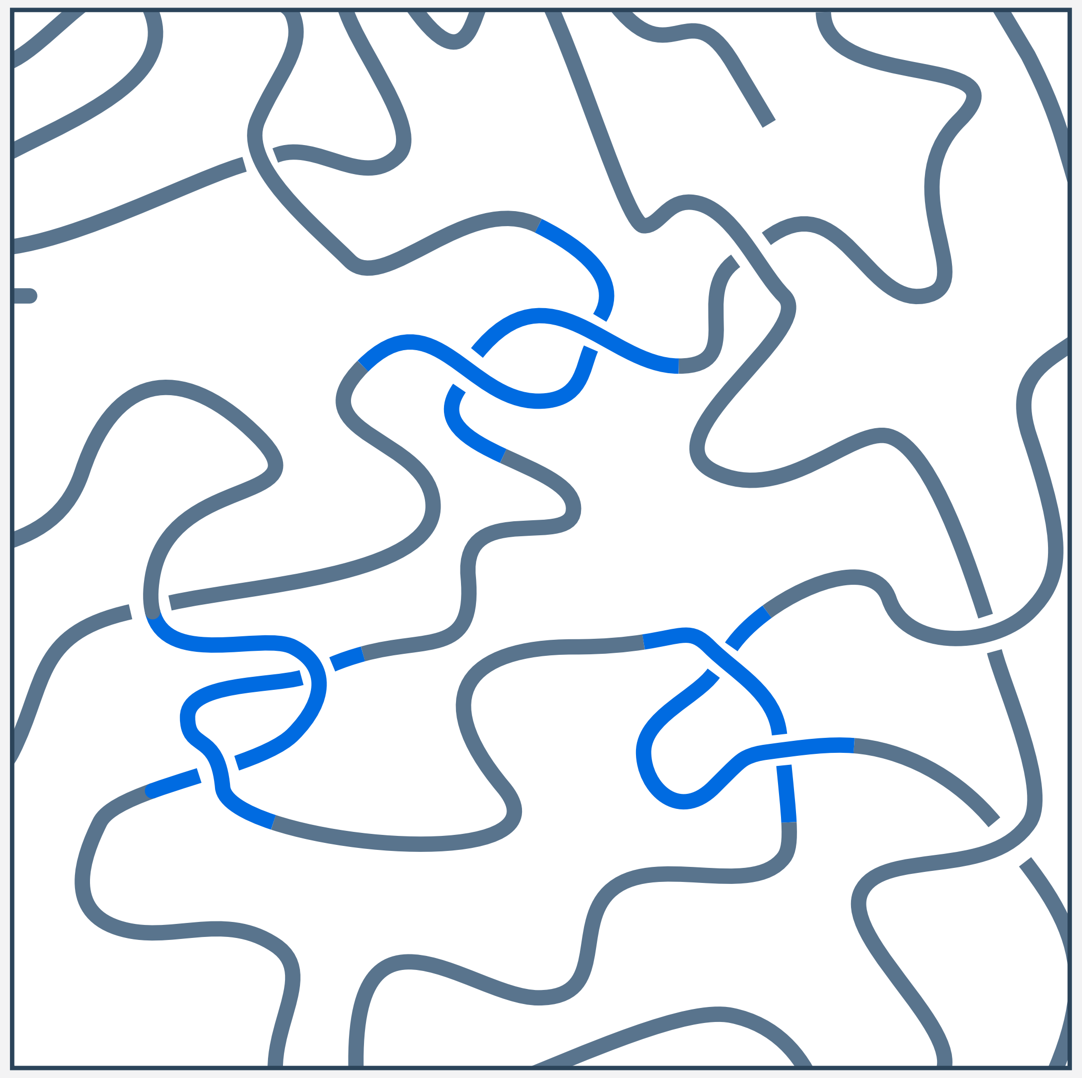


**elastomers**



lightly cross-linked

**rubbers**



operating $T$ above $T_g$;
corresponds to the rubbery state

- requires **long, flexible chains** with minimal crystallization tendency
- **weak intermolecular interactions between chains**
- **crosslinks (chemical or physical) for network integrity**

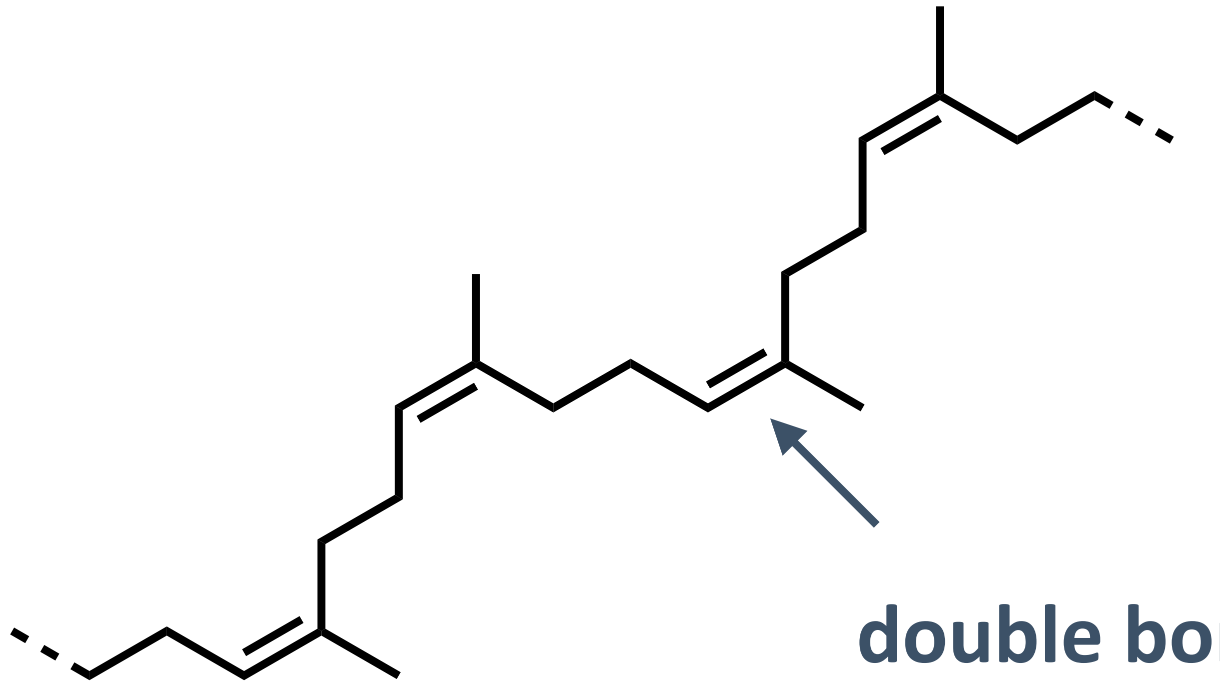
the static picture representing entanglements as “knots” does not reflect the purely dynamic origin of this phenomenon!

# Rubbers vs. Elastomers

- in everyday language, “rubber” and “elastomer” are often used interchangeably

**rubbers**

**natural rubber (“fluid”-like)**



**double bond: prone to cross-linking**

upon vulcanisation, natural rubber is converted into an elastomer

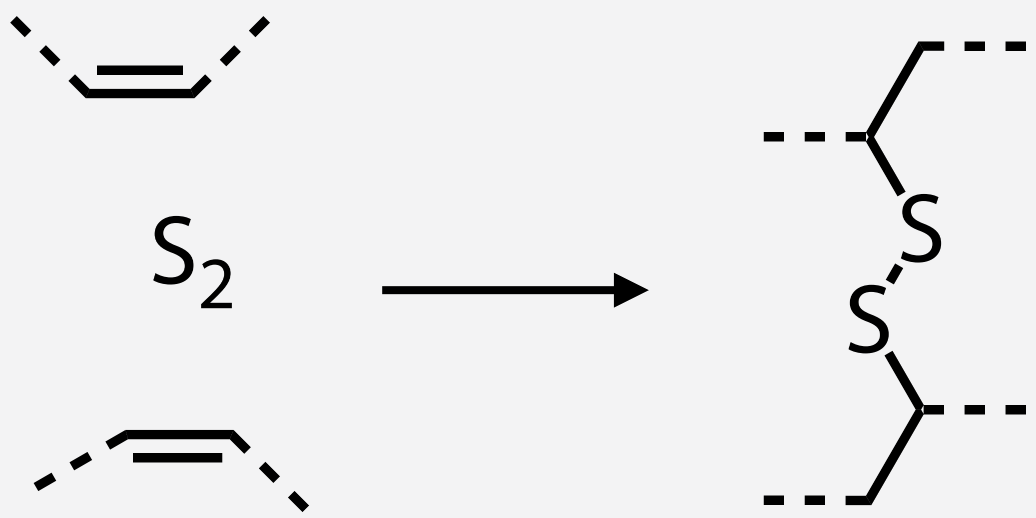
**elastomers**

**“rubber gloves”**

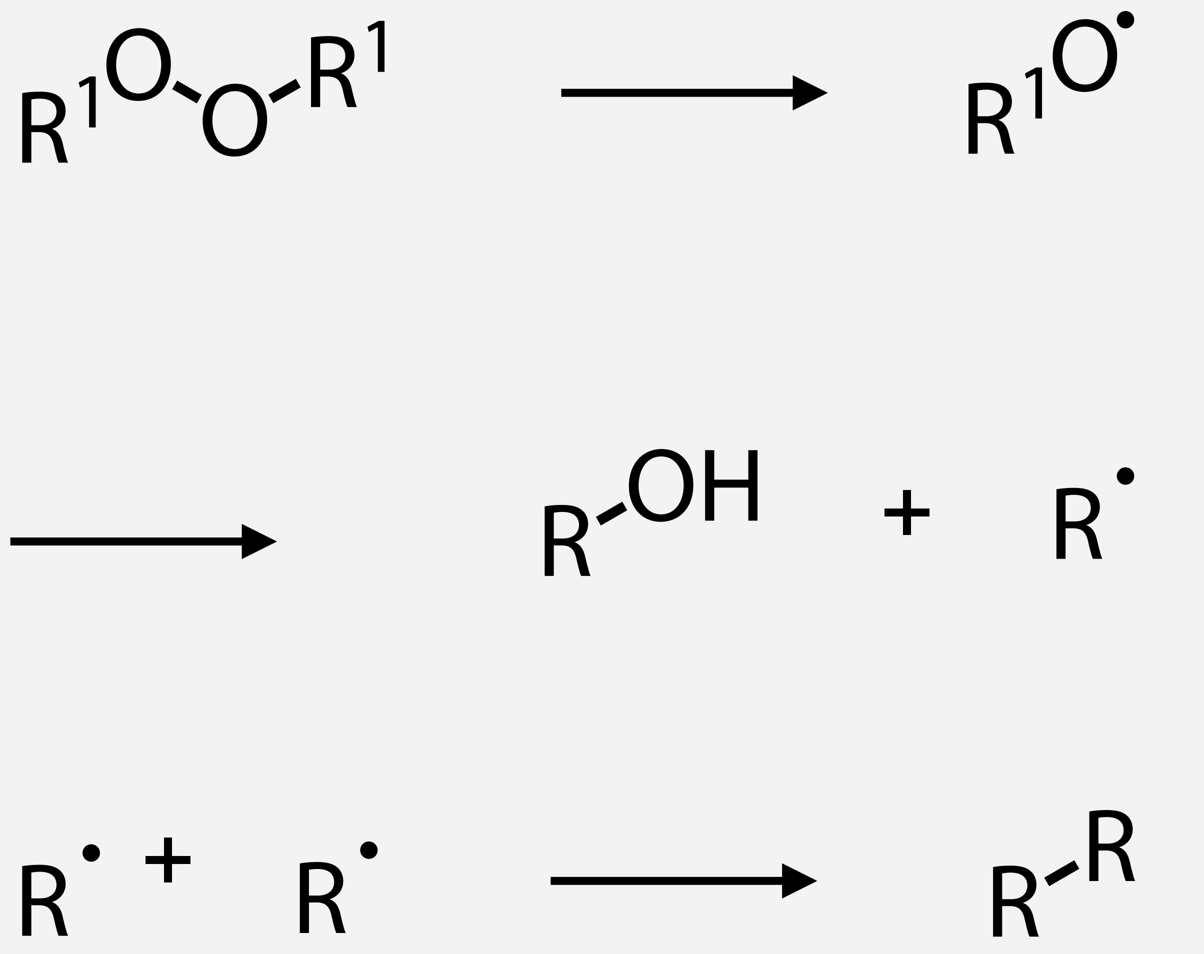
# Network Formation in Elastomers

- three-dimensional networks are created by chemical or physical crosslinking methods

**vulcanisation**



**radical mechanism**

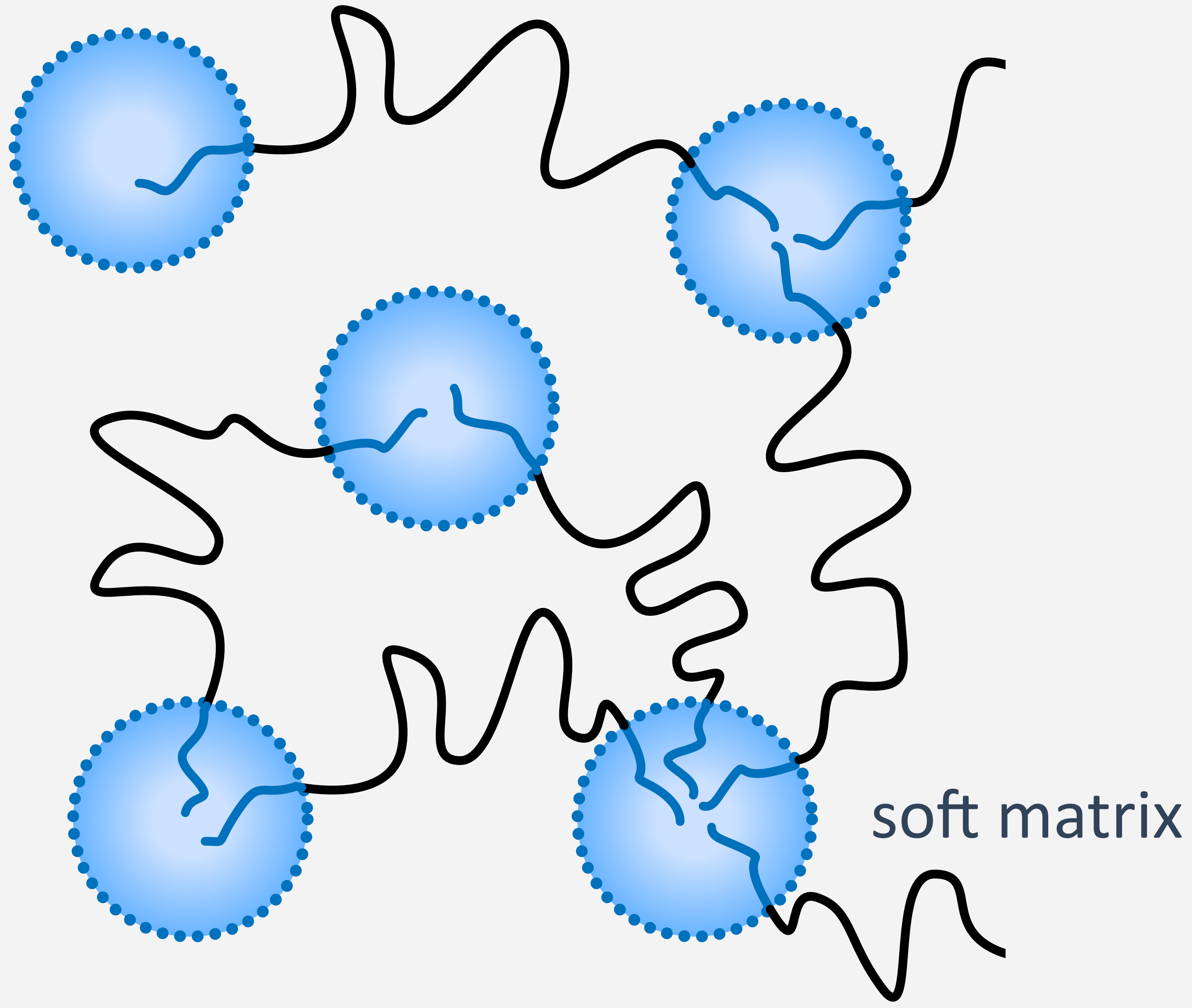


$R^1O{-}O{-}R^1 \longrightarrow R^1O^\bullet$

$\longrightarrow R{-}OH + R^\bullet$

$R^\bullet + R^\bullet \longrightarrow R{-}R$

**physical crosslinks**



**< 1%: elastomer**

**ca. 10%: hard “rubber”**

**crosslinking of PE by irradiation and formation of free radicals**

(resistant to sterilisation in boiling water)

PS: glassy, hard

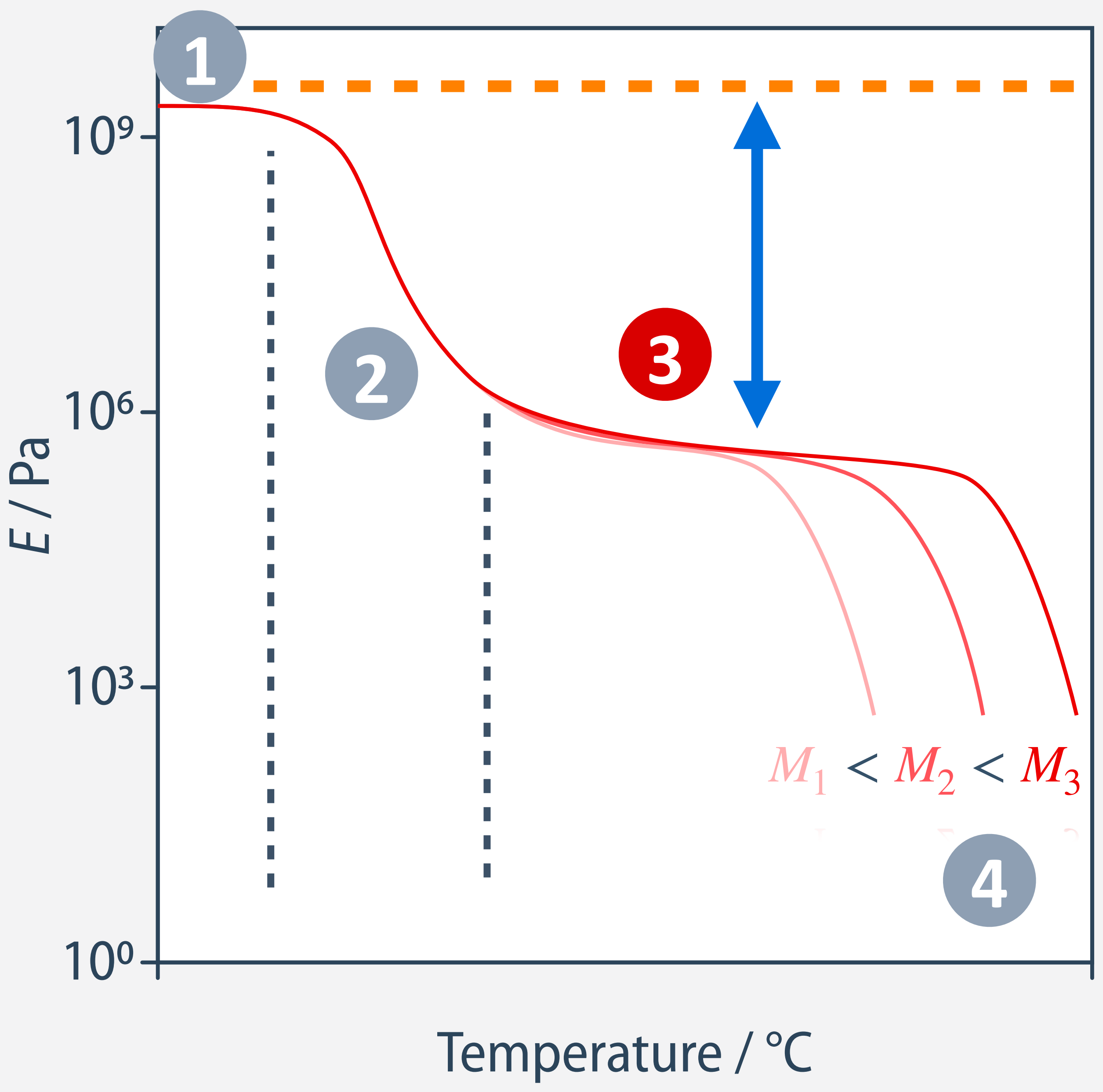
PUR: semicrystalline

# Thermodynamic Consideration of Rubber Elasticity

# Incompressible Nature of Rubbers

- the bulk (compression) modulus $K$ is nearly independent of temperature
- the elastic (tensile) modulus $E$ shows a strong temperature dependence

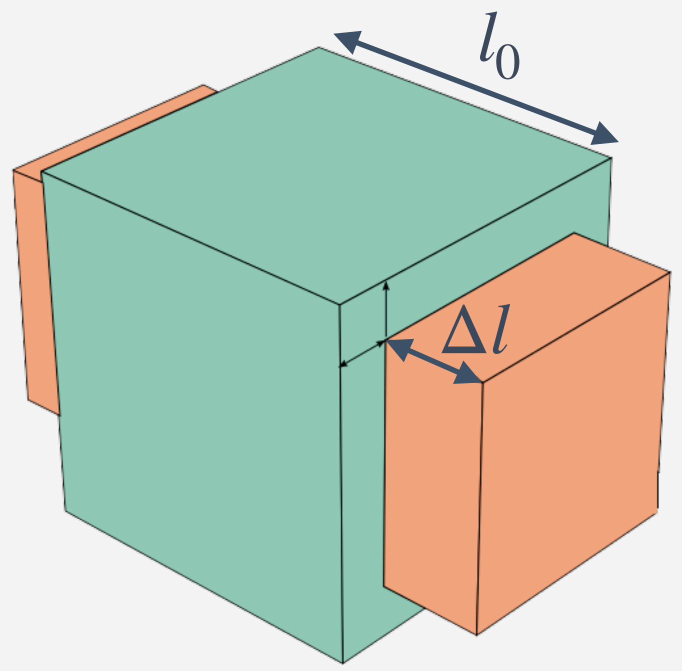
## phenomenology



$$K = \frac{8E_{coh}}{V_0}$$

**decrease of $E$ by a factor of ~1000 above $T_g$**

## Poisson’s ratio



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

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

Poisson’s ratio for a uniaxially deformed rubber is 0.5.

- **rubbery and molten polymers are therefore treated as incompressible material**

  (volume remains essentially constant during deformation)

# Thermodynamic Framework of Rubber Elasticity

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

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

- Helmholts 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:

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

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

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

# Energetic and Entropic Components of the Elastic Force

- from incompressability, it follows:

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

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

$$\frac{\partial^2 A}{\partial T \partial l} = \frac{\partial^2 A}{\partial l \partial T} \qquad -\left(\frac{\partial S}{\partial l}\right)_{T,V} = \left(\frac{\partial f}{\partial T}\right)_{V,l}$$

- we arrive at two contributions for the force $f$:

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

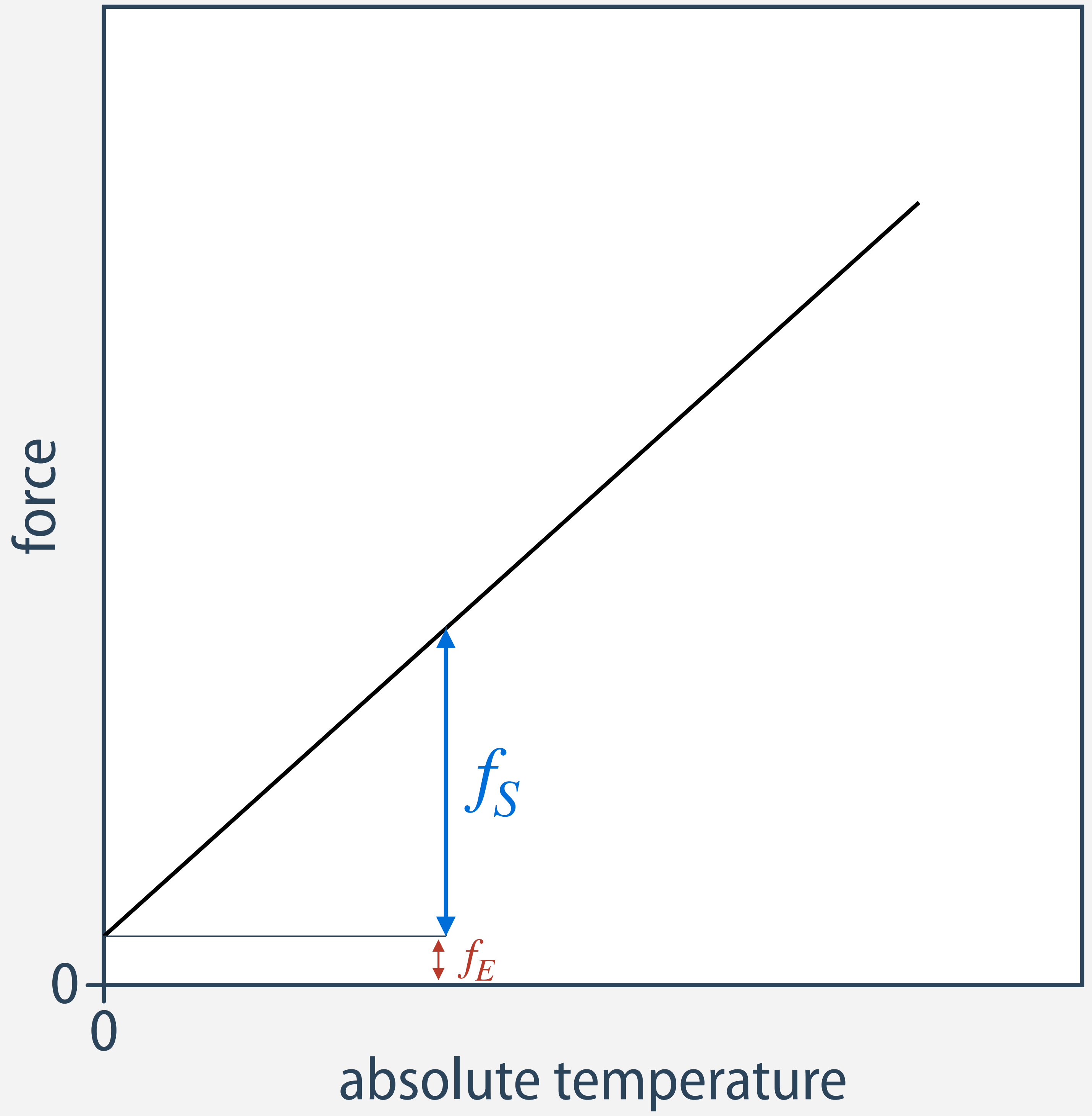
- combination of the above equations:

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

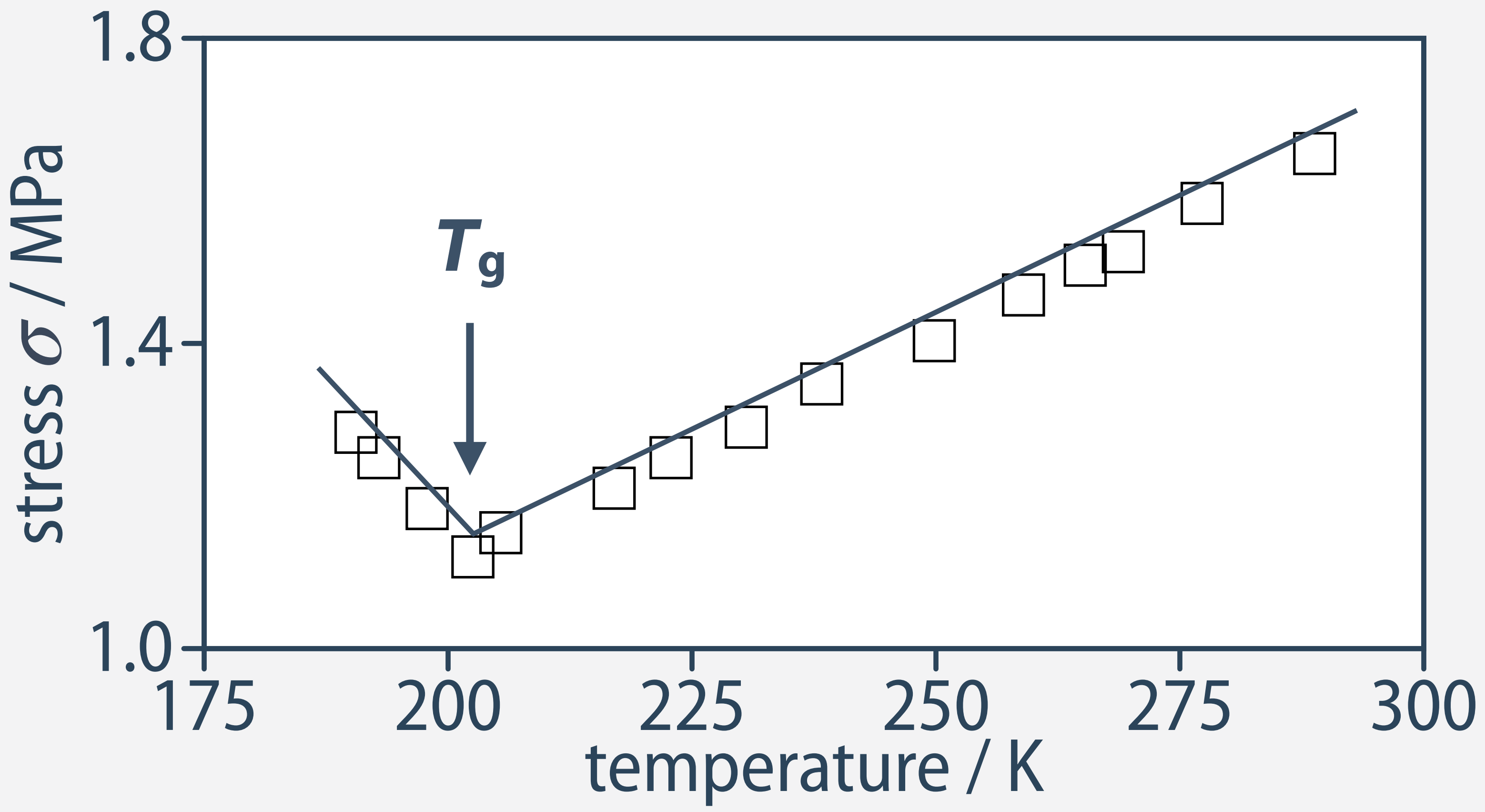
# Energetic and Entropic Components of the Elastic Force

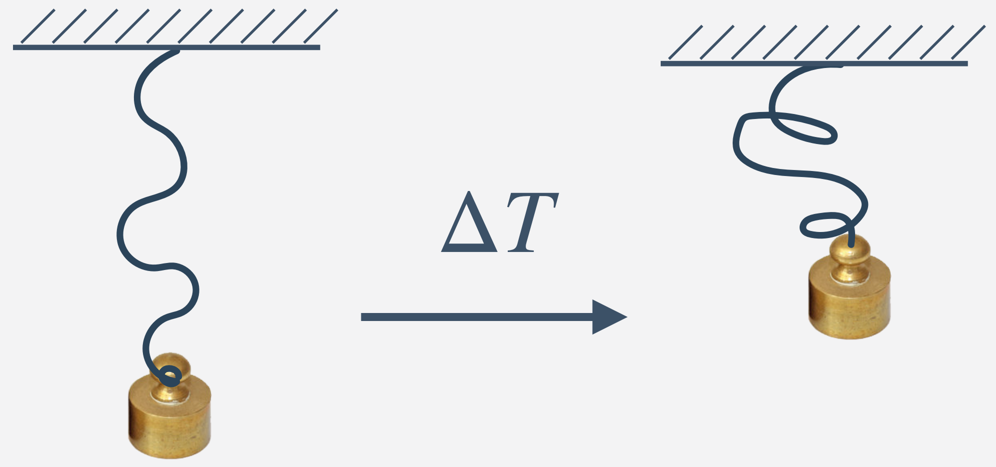
- experimentally observed temperature-dependence: the retraction force increases with increasing *T*!

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



**for a (large) constant deformation**



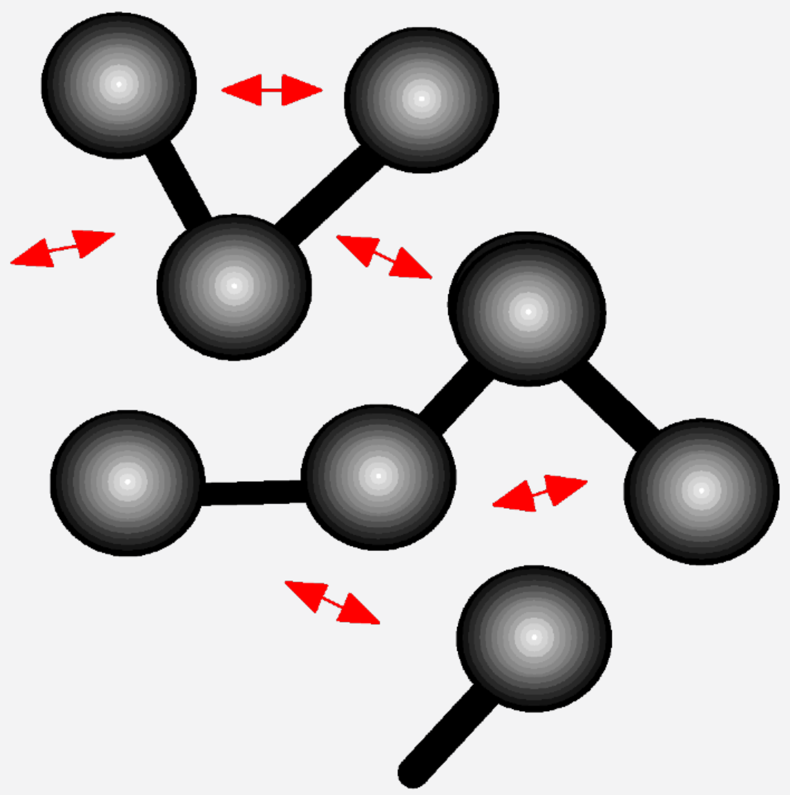


- **for an ideal rubber, $f_E = 0$, meaning elasticity is purely entropic in origins!**

# Physical Interpretation

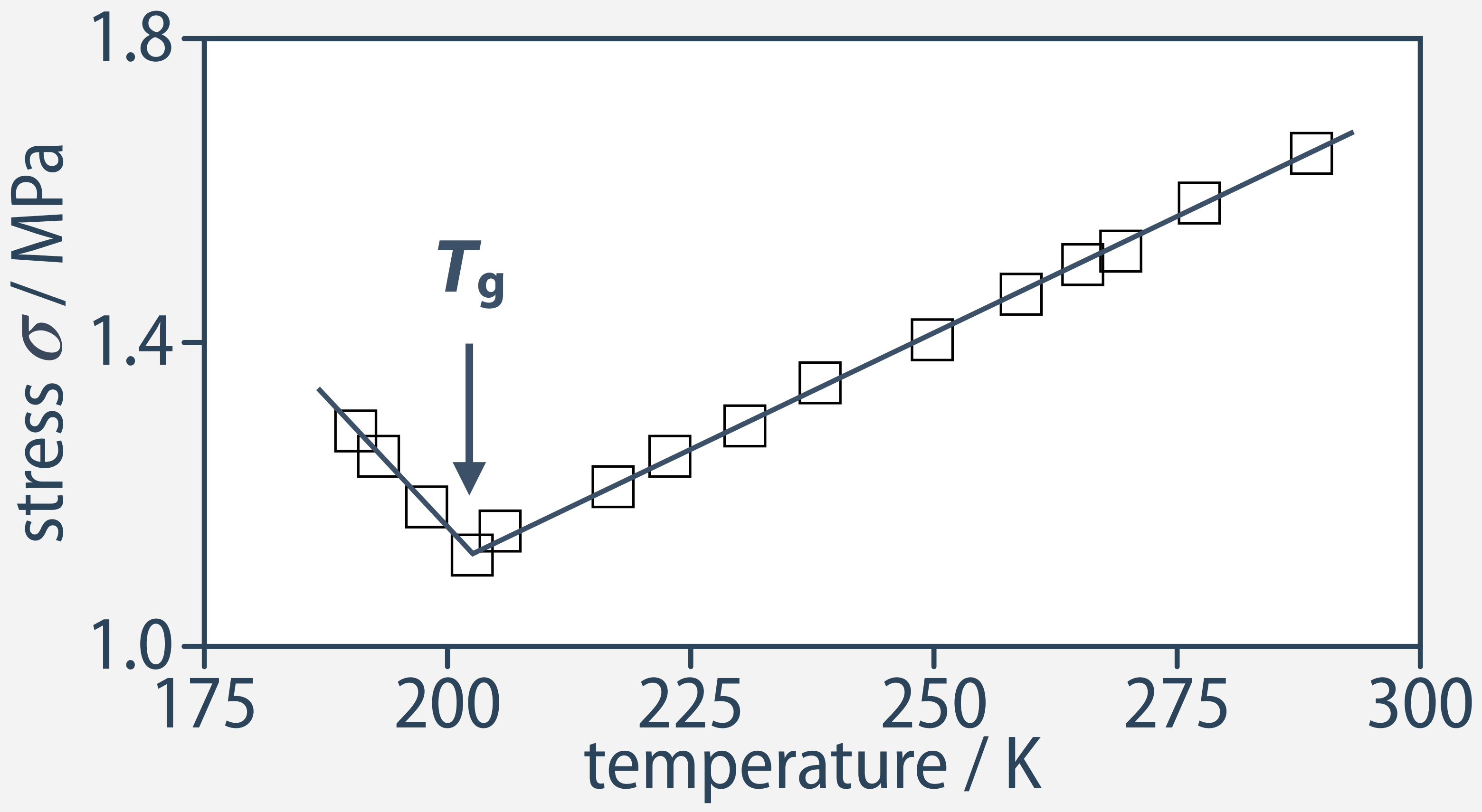
- **below $T_g$:** large energy barriers hinder conformational changes, deformation mainly changes internal energy (bond stretching, intermolecular potentials).

**below $T_g$**

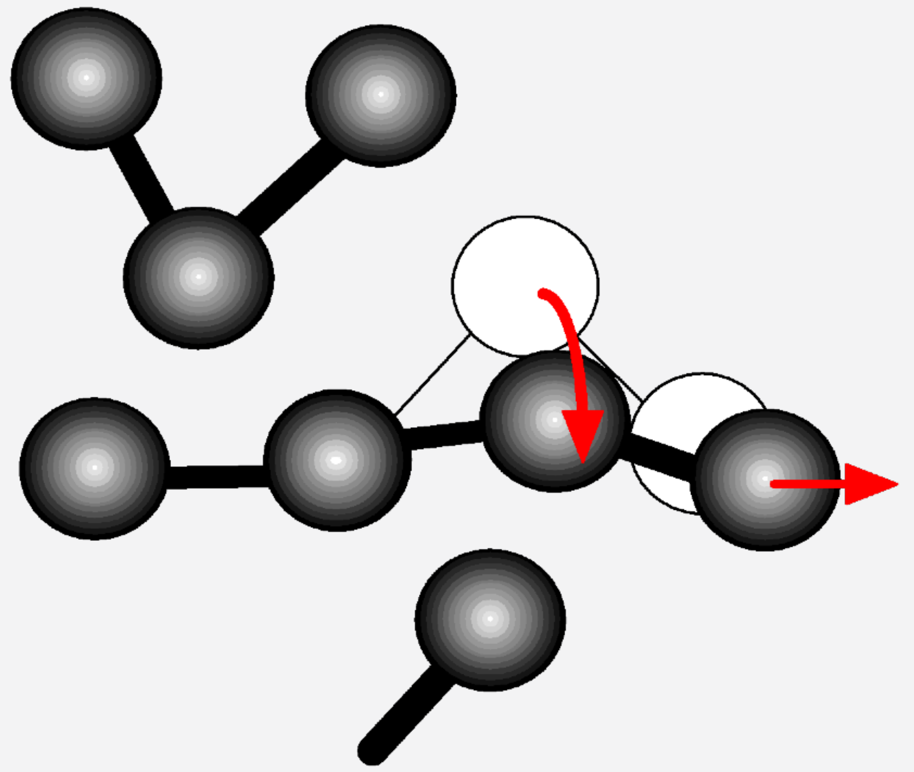


**frozen random coil conformation**

**for a (large) constant deformation**



**above $T_g$**



**stretched conformations possible**

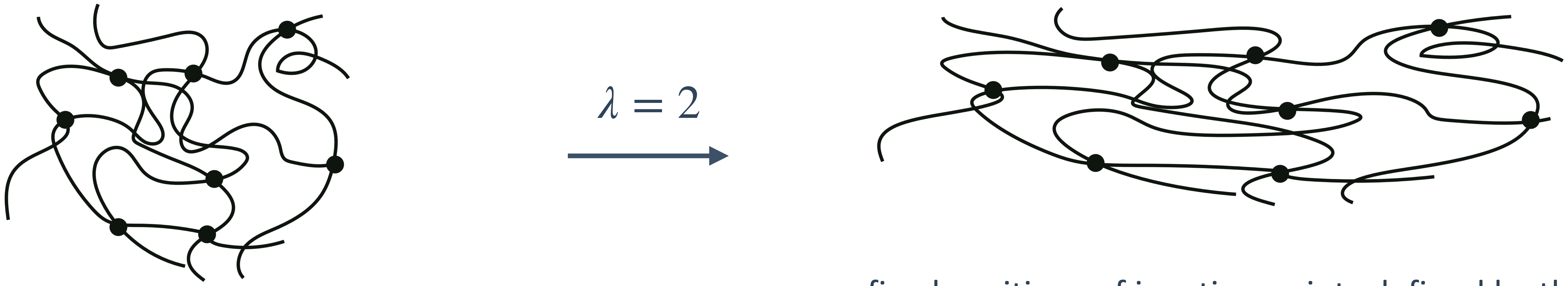
- **above $T_g$:** conformational changes are facile, deformation primarily affects entropy
- **the restoring force is thus entropic, driving the system back toward maximum disorder (random coils)**

# Statistical Mechanical Theory

# Affine Network Model

**undeformed network**

**affine network**

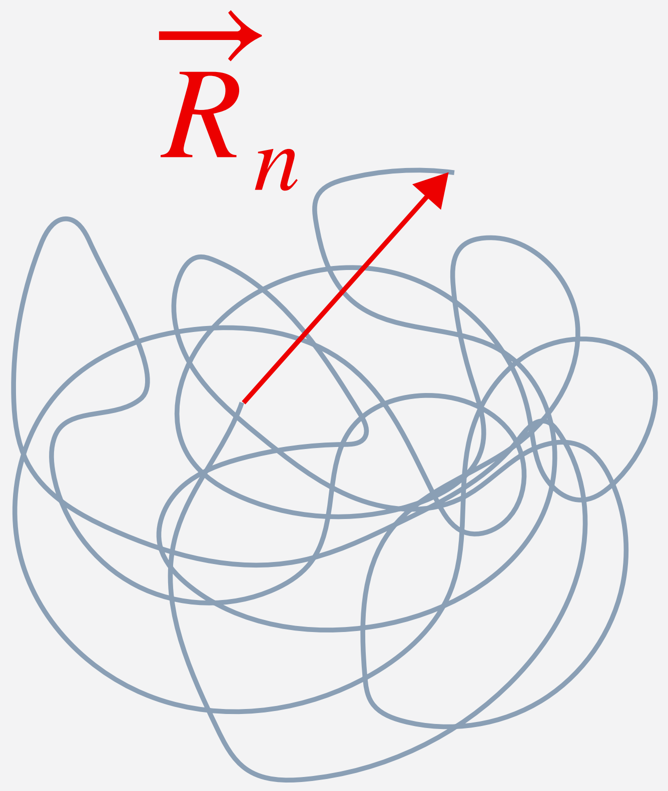


- fixed positions of junction points defined by the specimen deformation ratio
- network strands deform in the same manner with the macroscopic deformation

- **deformation is affine:** the positions of crosslinks change exactly according to the macroscopic deformation
- **chains between crosslinks obey Gaussian statistics**
- **the network is ideal** (no energetic contribution, $f_E = 0$)
- **chains are flexible ($T > T_g$), no chain slip or strain-induced crystallisation**
- **incompressability:** $\lambda_1 \lambda_2 \lambda_3 = 1$

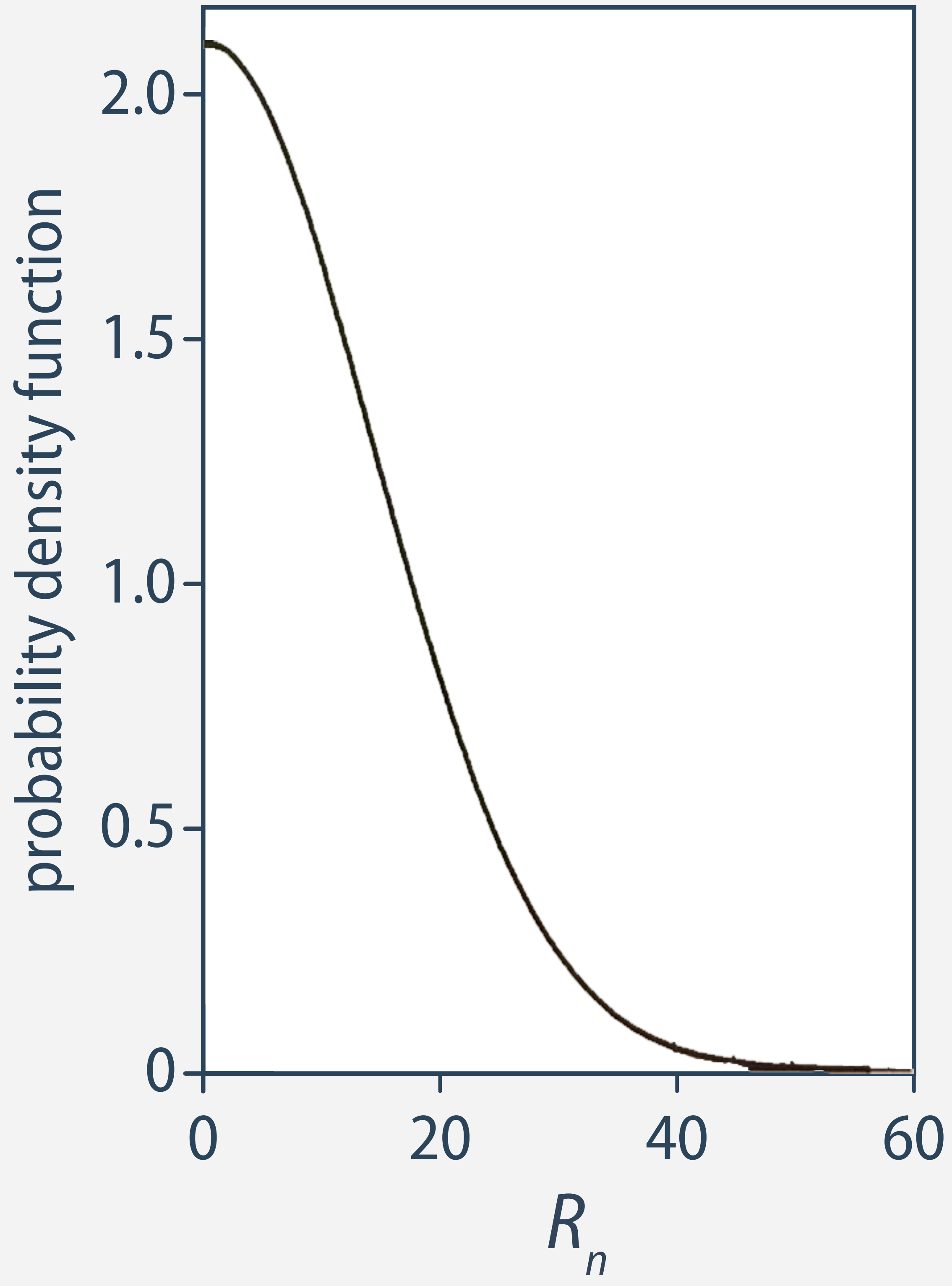
# Repetition: The “Gaussian” Chain

- an ideal chain can be represented as a 3D random walk with step length *a* and *n* steps (see **Chapter 2.1**)

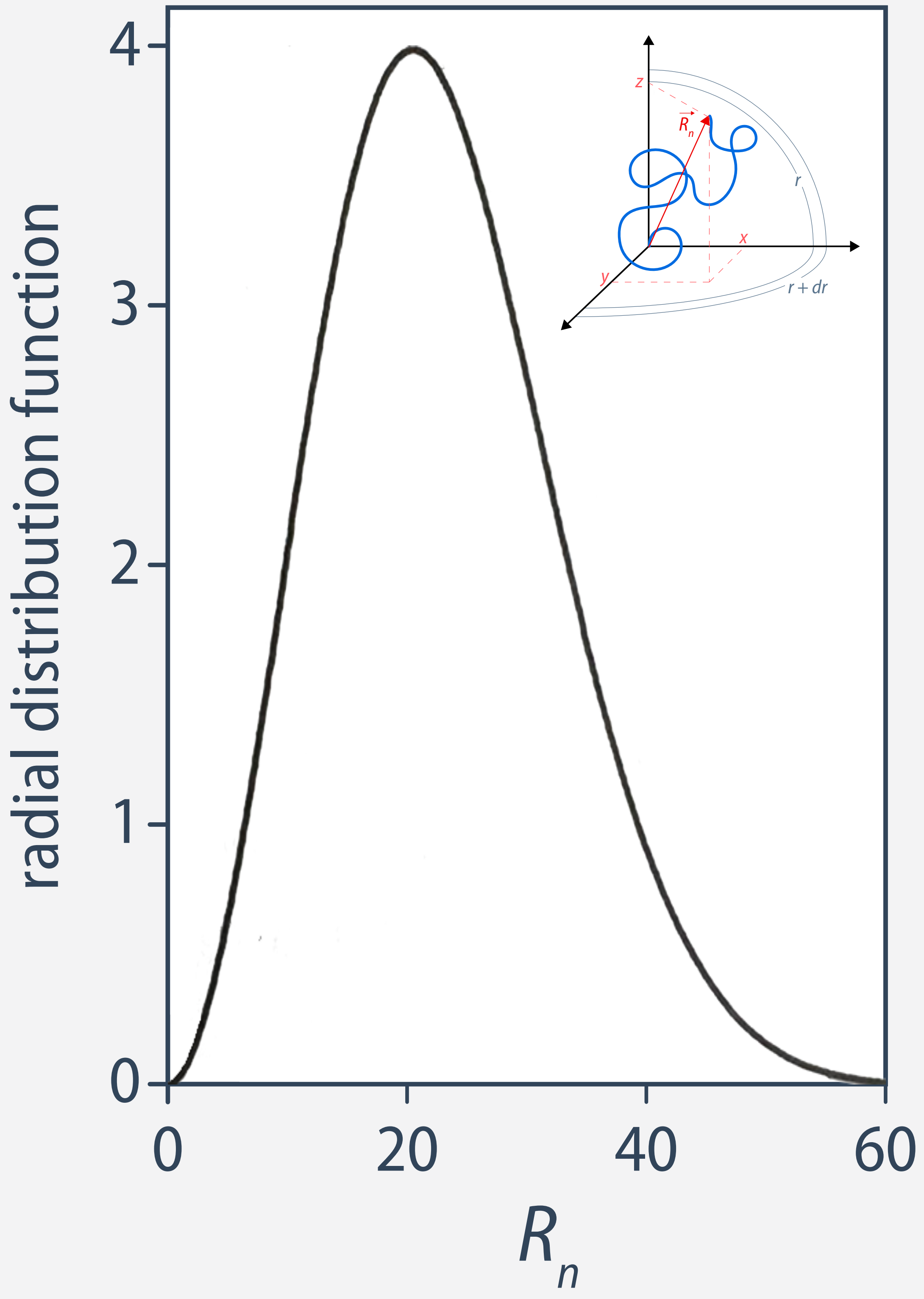


$$\boxed{< R_n{}^2 >^{\frac{1}{2}} \cong \sqrt{n}\ a}$$

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



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



- Gaussian statistics: most probable are conformations with $\vec{R}_n = 0$, but its *rms* value is finite ( $\propto \sqrt{n}$)

# 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, $\Omega$

$$\boxed{S = \mathrm{k} \ln \Omega}$$

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

$$\boxed{S^c = \mathrm{k} \ln \Omega = \mathrm{k} \ln (P \mathrm{d}\tau) = C + \mathrm{k} \ln P}$$

- insertion and rearrangement leads us to

$$\boxed{S^c = \mathrm{C} + \mathrm{k} \ln [(\frac{3}{2\pi n a^2})^{3/2} \exp(-\frac{3R_n^2}{2na^2})]}$$

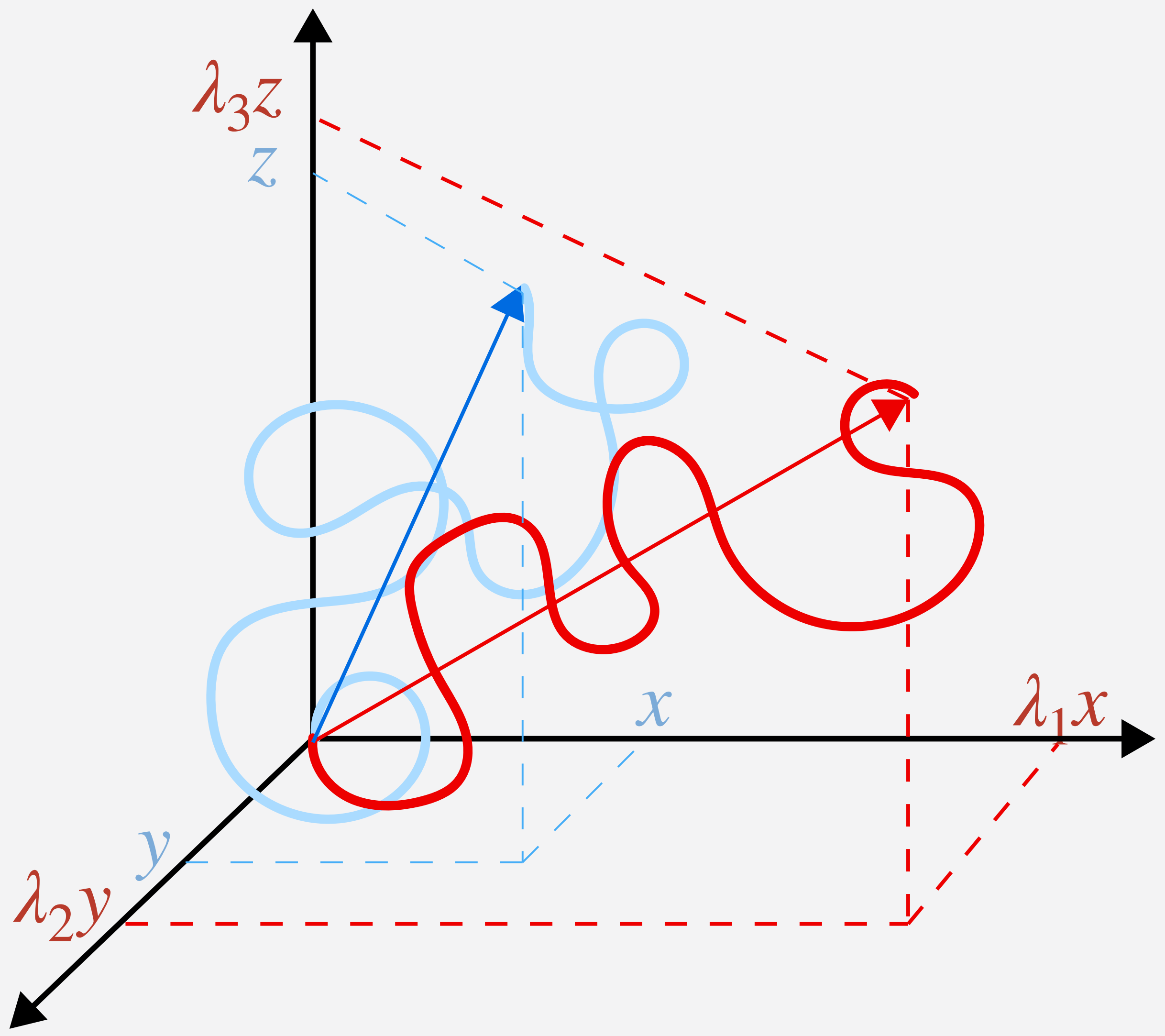
- only the last term depends on the end-to-end vector

$$\boxed{S^c = \mathrm{S}_0 - \frac{3\mathrm{k}R_n^2}{2na^2}}$$

see Reader on Rubber Elasticity

# The Effect of Deformation

- during deformation, a junction point moves from $(x, y, z)$ to $(\lambda_1 x, \lambda_2 y, \lambda_3 z)$



**before deformation**

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

**after deformation**

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

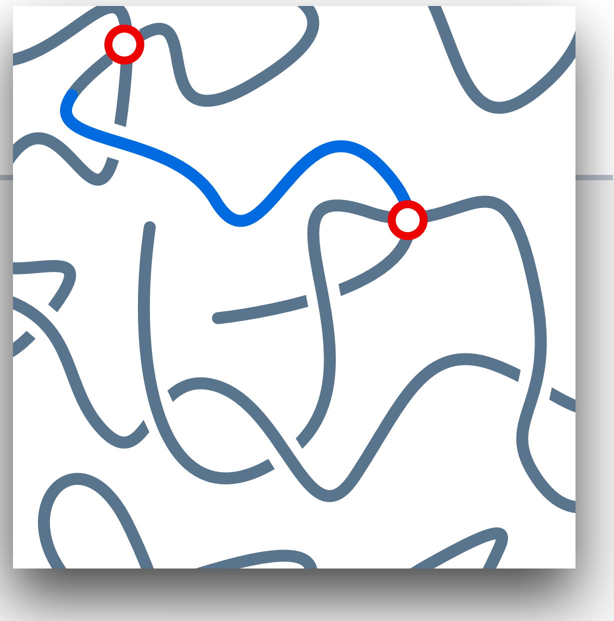
- for ideal rubber behavior ($\Delta U = 0$):

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

- **the free energy increases with stretch factor $\lambda$ due to entropy loss**

see Reader on Rubber Elasticity

# Network Deformation



- consider $N$ subchains per unit volume, each with $n$ segments and Gaussian statistics
- the total free energy change of the network is obtained by averaging over all chain orientation

**before deformation**

$$< R_n^2 > = < x^2 > + < y^2 > + < z^2 > = na^2$$

$$< x^2 > = < y^2 > = < z^2 > = \frac{na^2}{3}$$

**after deformation**

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

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

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

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

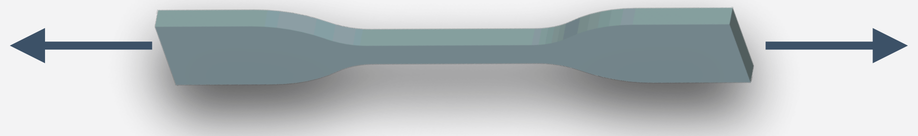
$$\Delta A = N < \Delta A^c > = \frac{NkT(\lambda^2 + 2\lambda^{-1} - 3)}{2}$$

- **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 and strain:



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

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

**Young's modulus, $E$, is accordingly:**

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

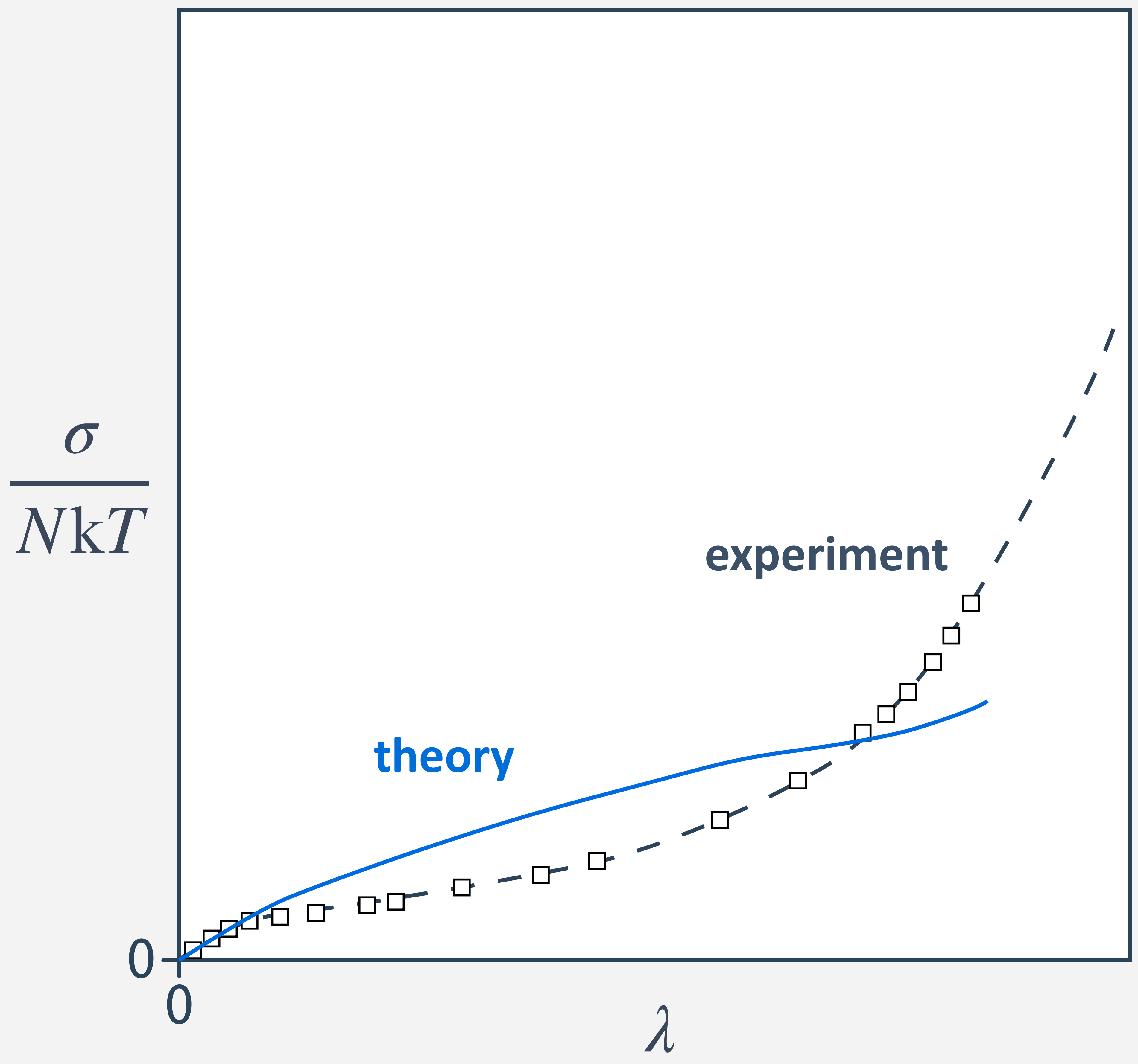
$$\boxed{G = \frac{E}{3} = NkT}$$

- **rubber elasticity depends only on the number subchains, *N*, and the temperature, *T***
- **rubber stiffness increases linearly with temperature and crosslink density *N***

# Limitation of the Molecular Theory

- valid only for small strains and low crosslink densities
- assumes Gaussian chain statistics and fine deformation

## comparison



## limitations

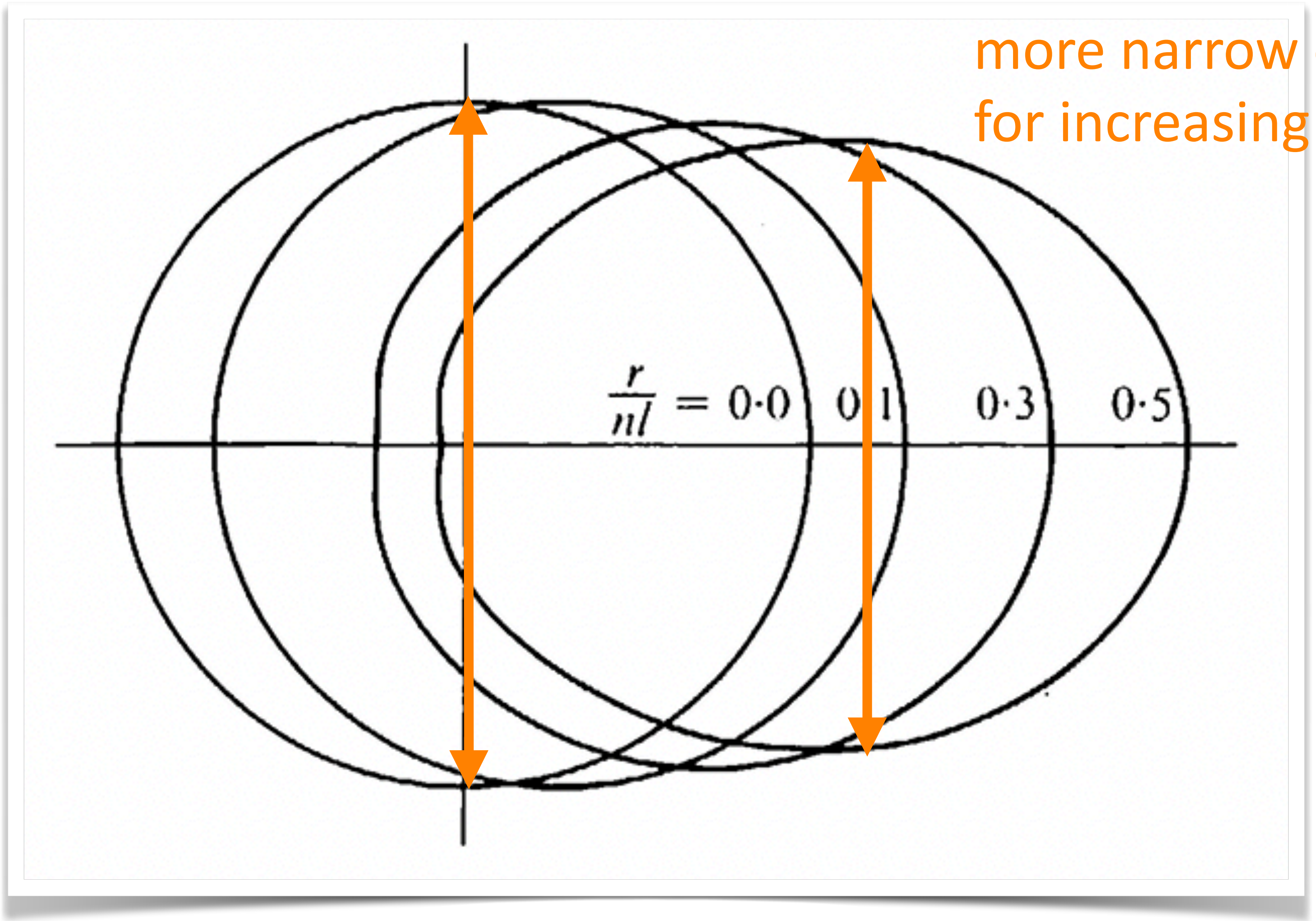
- failure of the model for high crosslinks
- phantom network: independent conformations of subchains
- strain hardening: induced crystallisation at large deformations
- Gaussian approximation fails at large strains

# Non-Gaussian Statistics

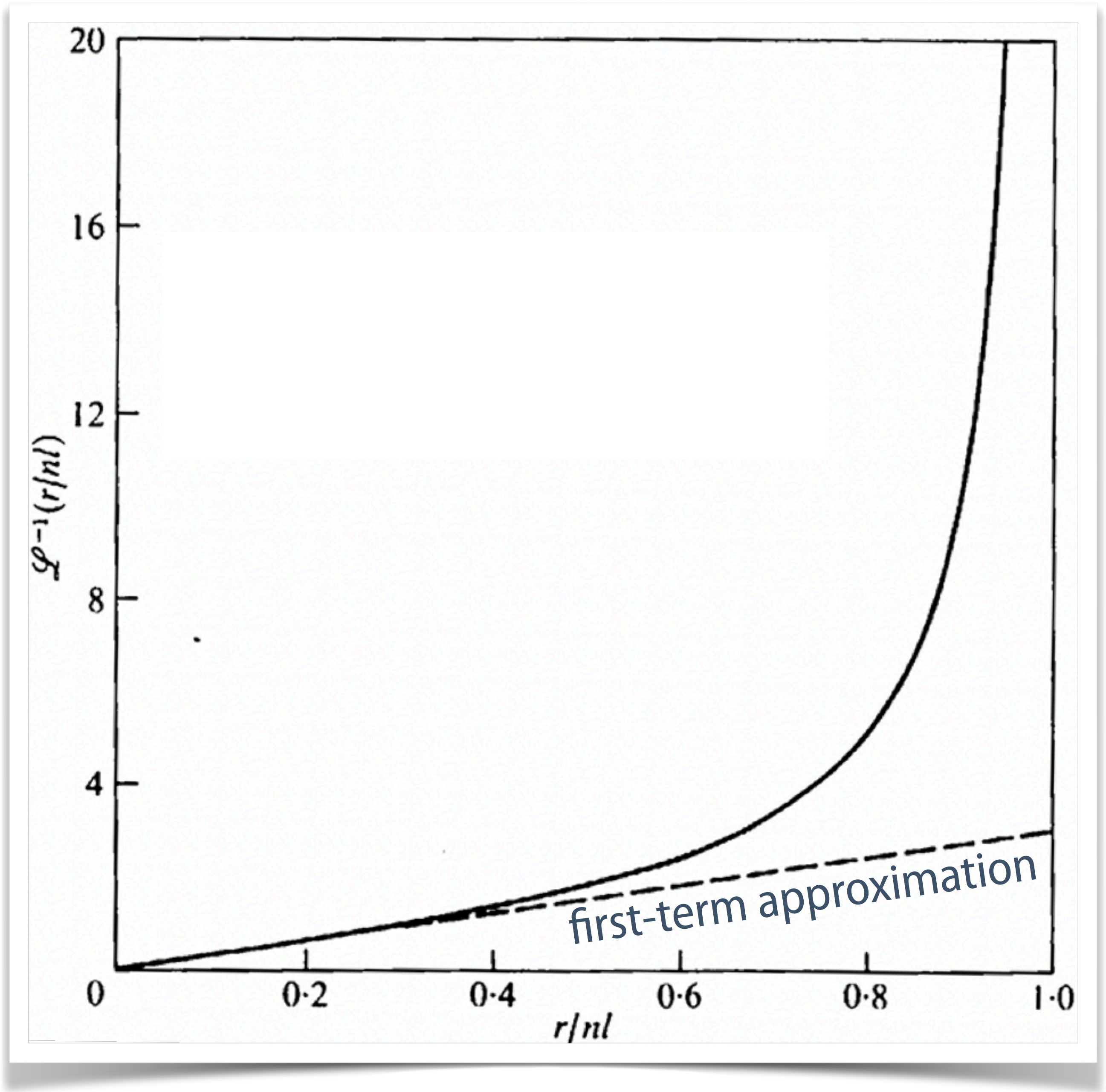
- at large extensions, the Gaussian assumption breaks down as $R_n \rightarrow nl$

$$\ln P(r) = \text{constant} - n\left[\frac{3}{2}\left(\frac{r}{nl}\right)^2 + \frac{9}{20}\left(\frac{r}{nl}\right)^4 + \frac{99}{350}\left(\frac{r}{nl}\right)^6 + \cdots\right]$$

$$f = \frac{\mathrm{k}T}{l}\left[3\left(\frac{r}{nl}\right) + \frac{9}{5}\left(\frac{r}{nl}\right)^3 + \frac{297}{175}\left(\frac{r}{nl}\right)^5 + \frac{1539}{875}\left(\frac{r}{nl}\right)^7 + \cdots\right]$$



more narrow distribution for increasing $r/nl$



first-term approximation

- **Langevin distribution accounts for finite chain extensibility and strong stiffening at high stretch ratios**
- both Gaussian and Langevin statistics coincide for $R_n \ll nl$.

# Empirical Approaches

- empirical strain-energy functions according to **Mooney-Rivlin** depend only on extension ratios

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

- based on invariance (independent of coordinate system, reflecting isotropy)

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

- use only even powers of $\lambda$ to describe large symmetric deformations

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \qquad I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \qquad I_3 = \lambda_1^2\lambda_2^2\lambda_3^2$$

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

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \qquad I_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} \qquad I_3 = 1$$

# Empirical Approaches (Mooney-Rivlin)

- the change in *A* can be expressed as a power series expansion around $\lambda_1 = \lambda_2 = \lambda_3 = 1$

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

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

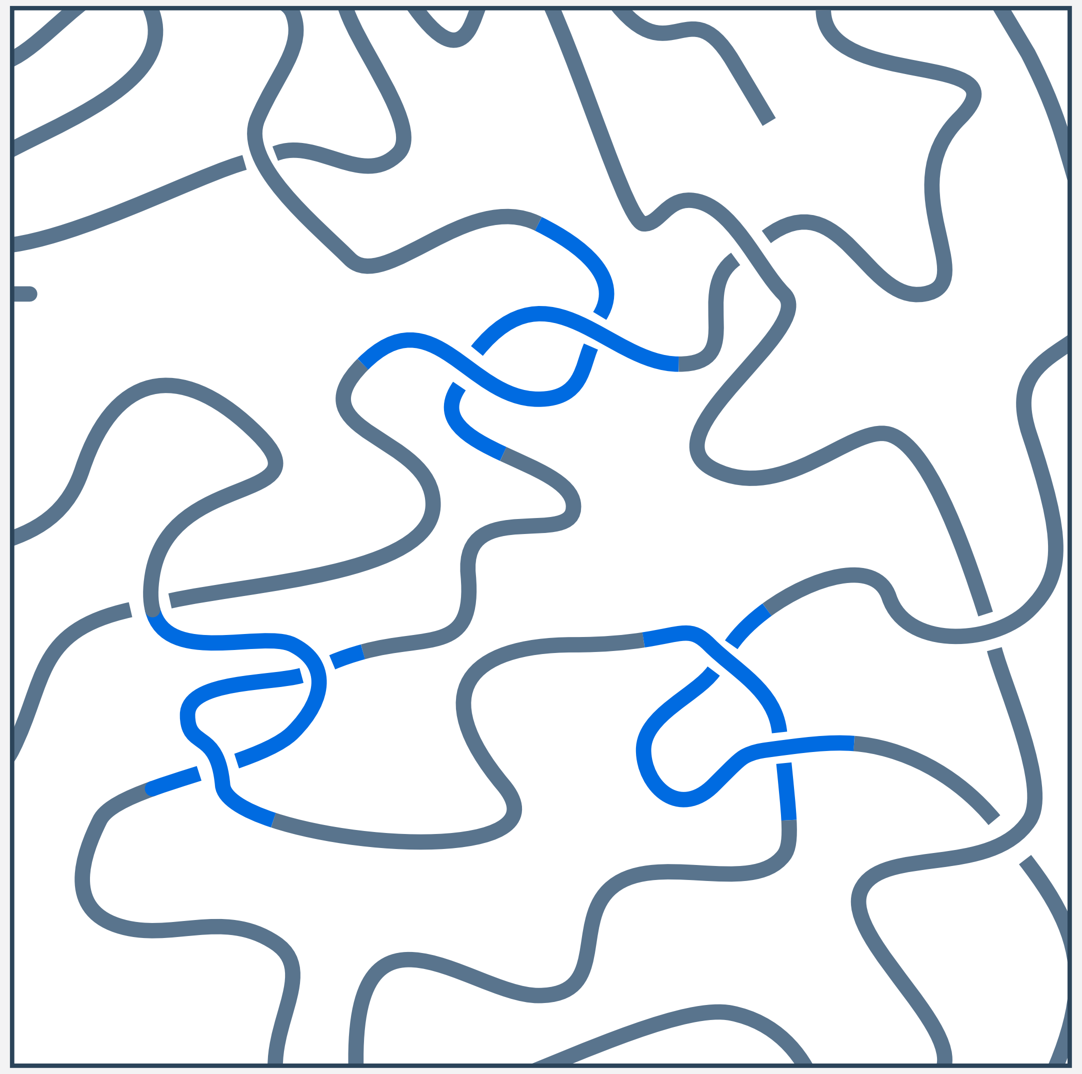
- for uniaxial tension ($\lambda_1 = \lambda$ and $\lambda_2 = \lambda_3 = 1/\sqrt{\lambda}$): $\sigma = 2C_{1,0}(\lambda - \lambda^{-2}) + 2C_{0,1}(1 - \lambda^{-3}) + \ldots$

- Resembles the ideal network expression but includes empirical correction terms for real rubbers
- $C_{1,0}$ and $C_{0,1}$ are adjustable parameters fitted to experimental data.

# Entanglement Network

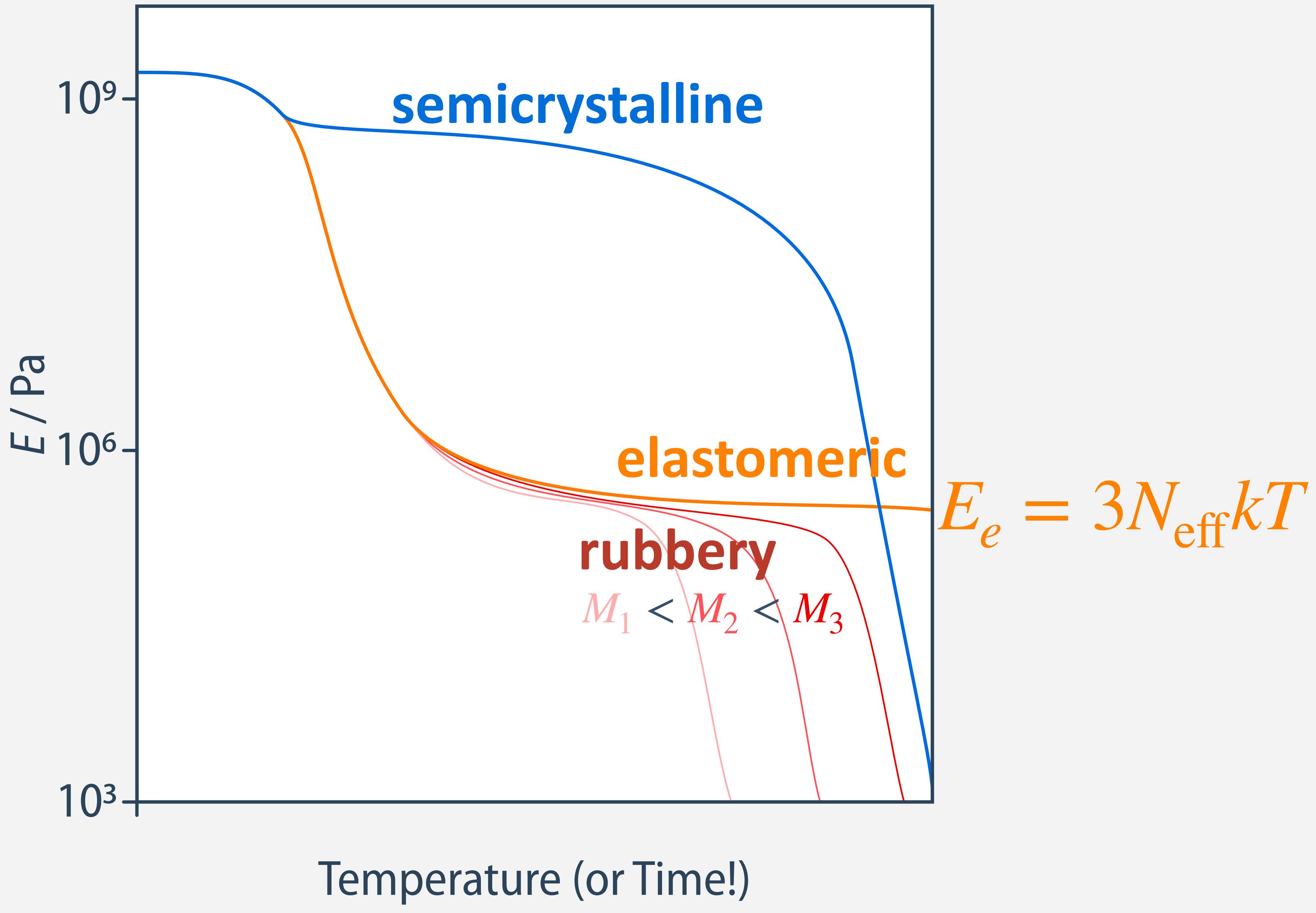
- entanglements act as temporary crosslinks, adding to the elastic response

**entanglement**



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

**entanglement network**



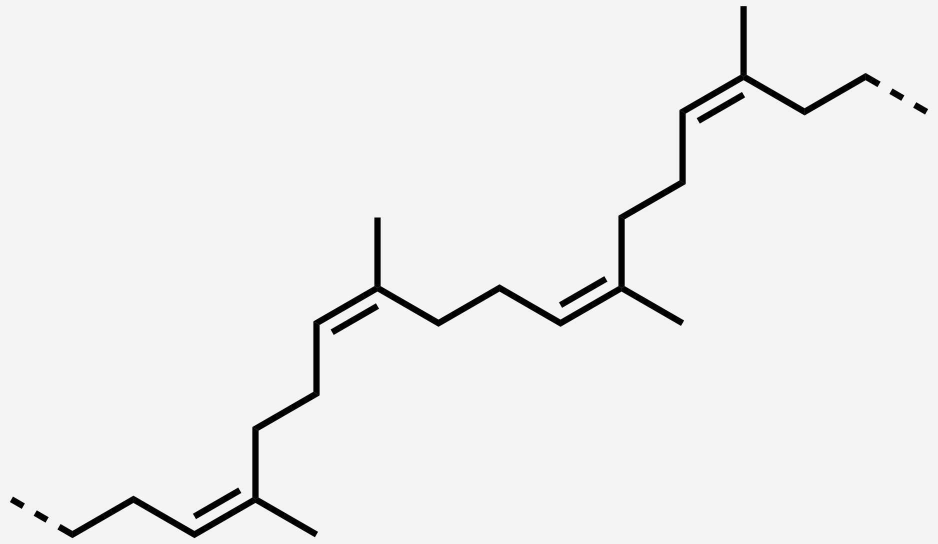
- **effective cross-linking density in elastomers:** $N_{\text{eff}} = N_{\text{e}} + N_{\text{x}}$ ($N_{\text{e}}$: entanglement density; $N_{\text{x}}$: cross-linking density)
- at high temperatures or long times, entanglements can relax, which reduces $N_{\text{eff}}$

# 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 °C**
**$M_w$ = $10^6$ 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.

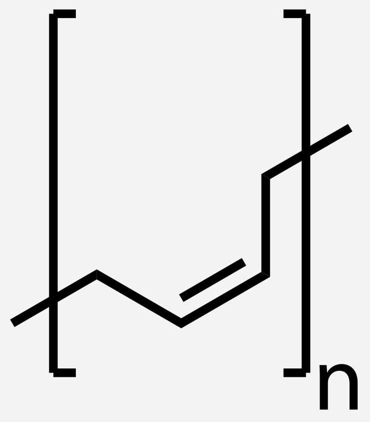
- **product very resistanced to breakage (crystallisation induced by deformation)**
- **low hysteresis during cyclic deformation**
- **moderately resistant to UV, oxidants, fuels**

# Synthetic Elastomers and Rubbers

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

**polybutadiene (PB)**

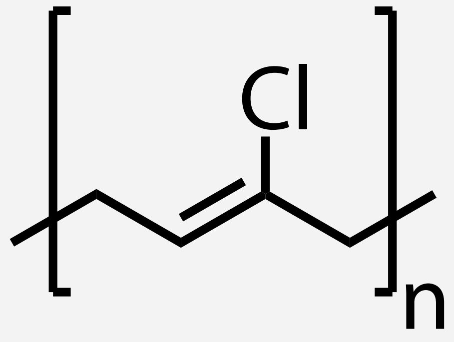
**$T_g$ = -90 °C**



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

**neoprene**

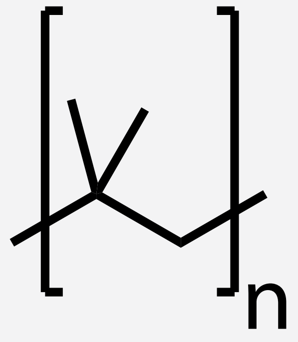
**$T_g$ = -50 °C**



resistance to the environment (pipes, cables, protection)

**polyisobutylene (PIB)**

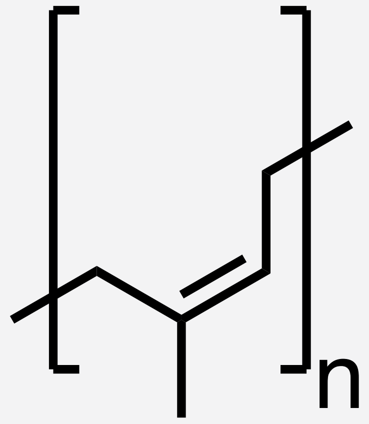
**$T_g$ = -65 °C**



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

**synthetic PI**

**$T_g$ = -70 °C**

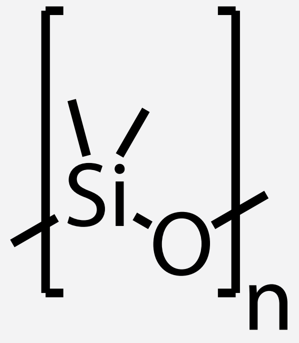


resistance to tear & abrasion, elasticity (tires)

**silicones**

(polydimethylsiloxane, PDMS)

**$T_g$ = -125 °C**



tendency to crystallize (wide-ranging applications)

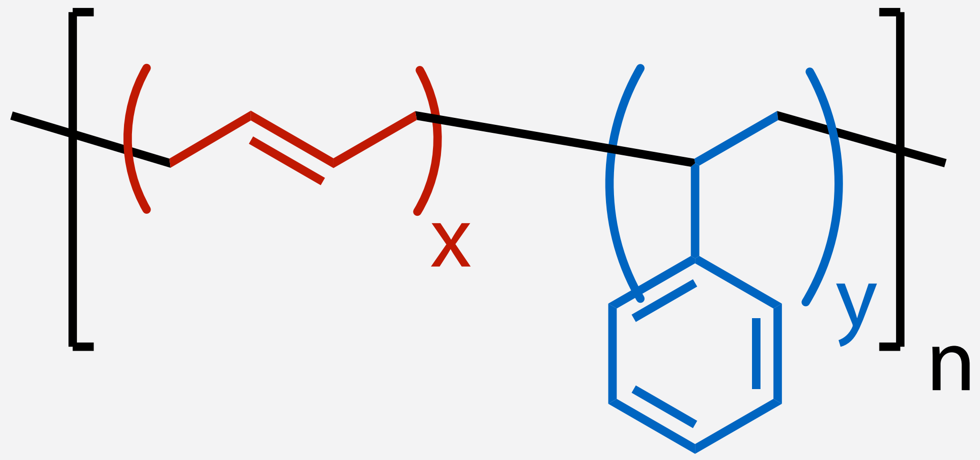
- **many more that fulfil rubber criteria (low $T_g$, no $T_m$, well entangled)**

# Synthetic Elastomers From Copolymers

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

**poly(styrene-co-butadiene)**

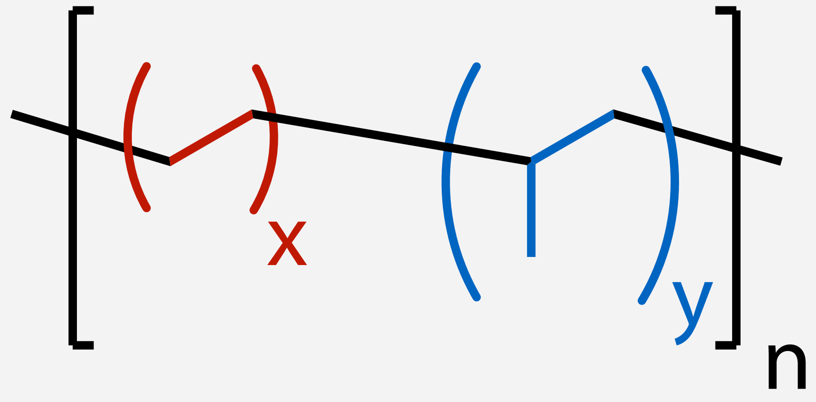
$\boldsymbol{T_g = -60\ °C}$



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

**ethylene-propylene (EPR)**

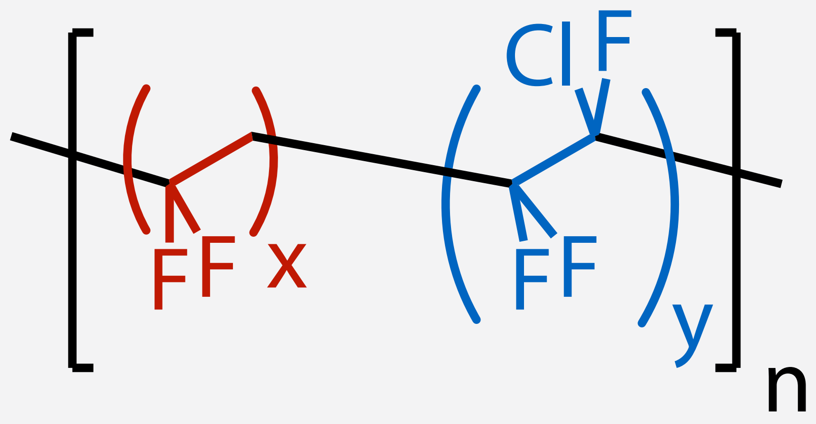
$\boldsymbol{T_g = -60\ °C}$



environmentally resistant
(cables, impact modification)

**fluoroelastomers**

$\boldsymbol{T_g = -65\ °C}$



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

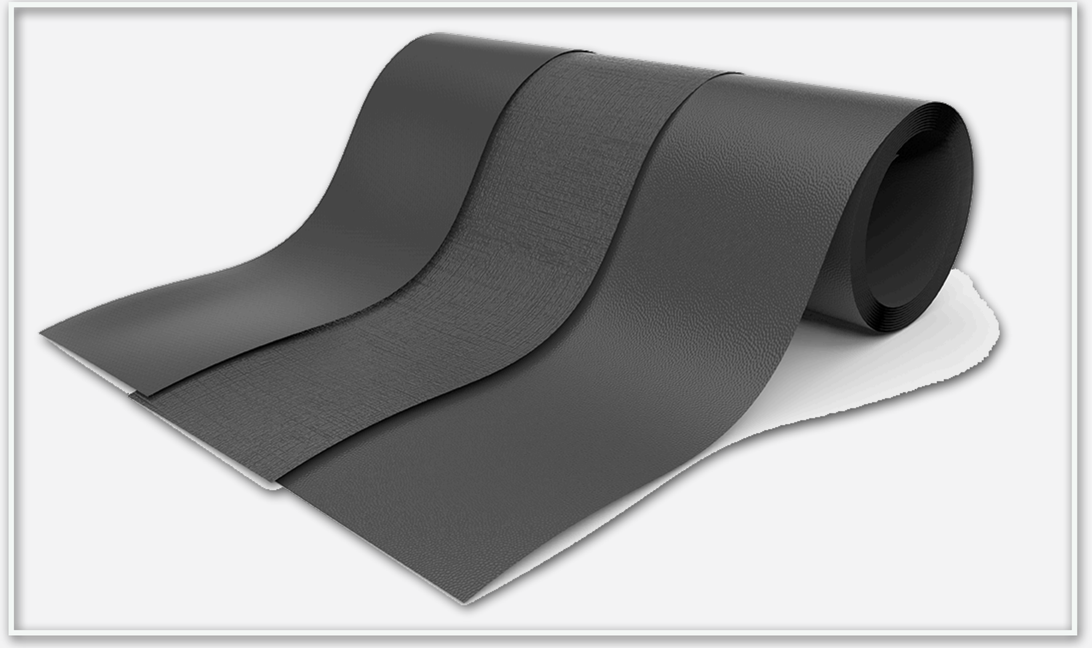
world production: **40 x $10^6$ tonnes (2 x $10^{10}$ per year)**

- **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 proudcts, 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.