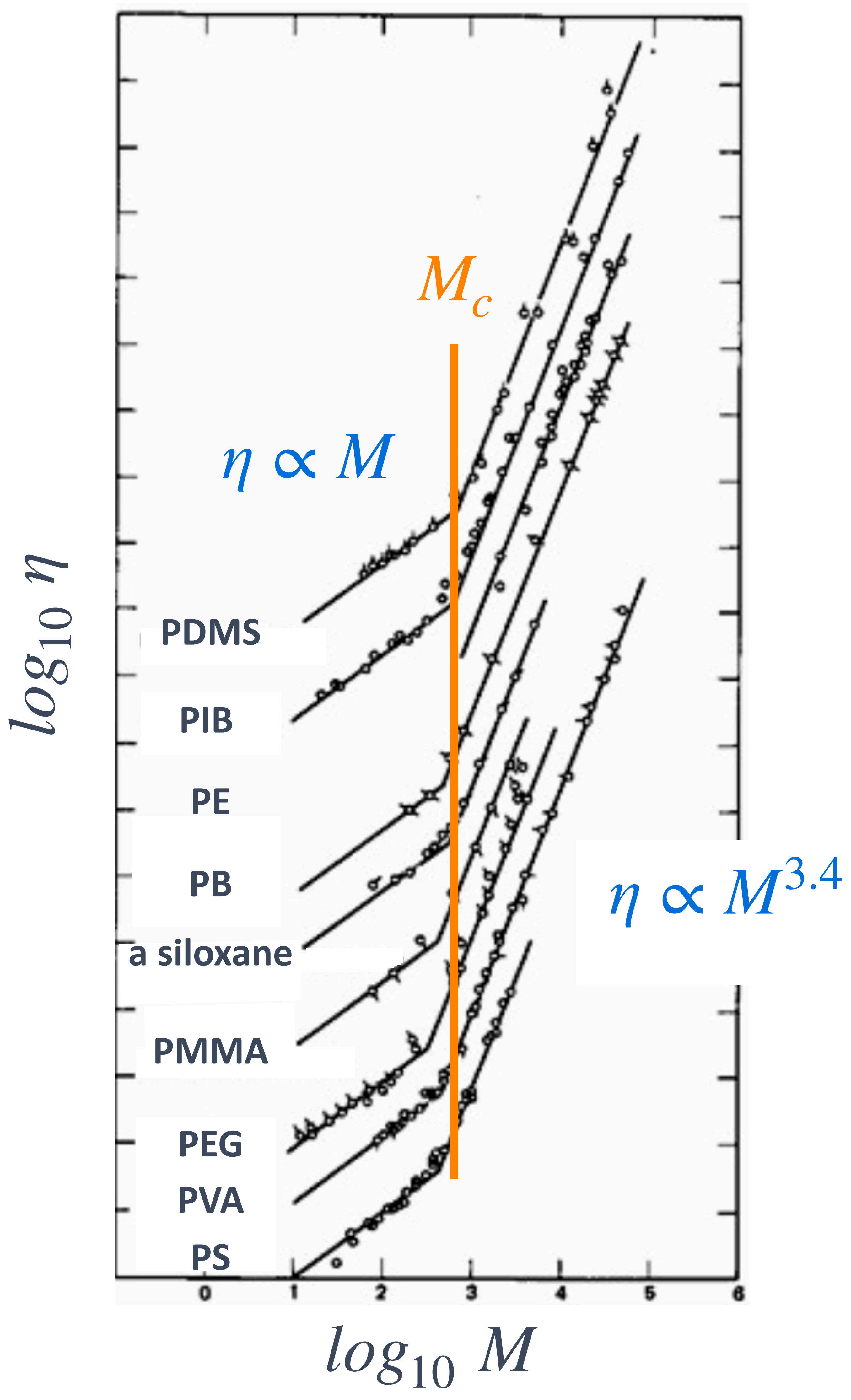
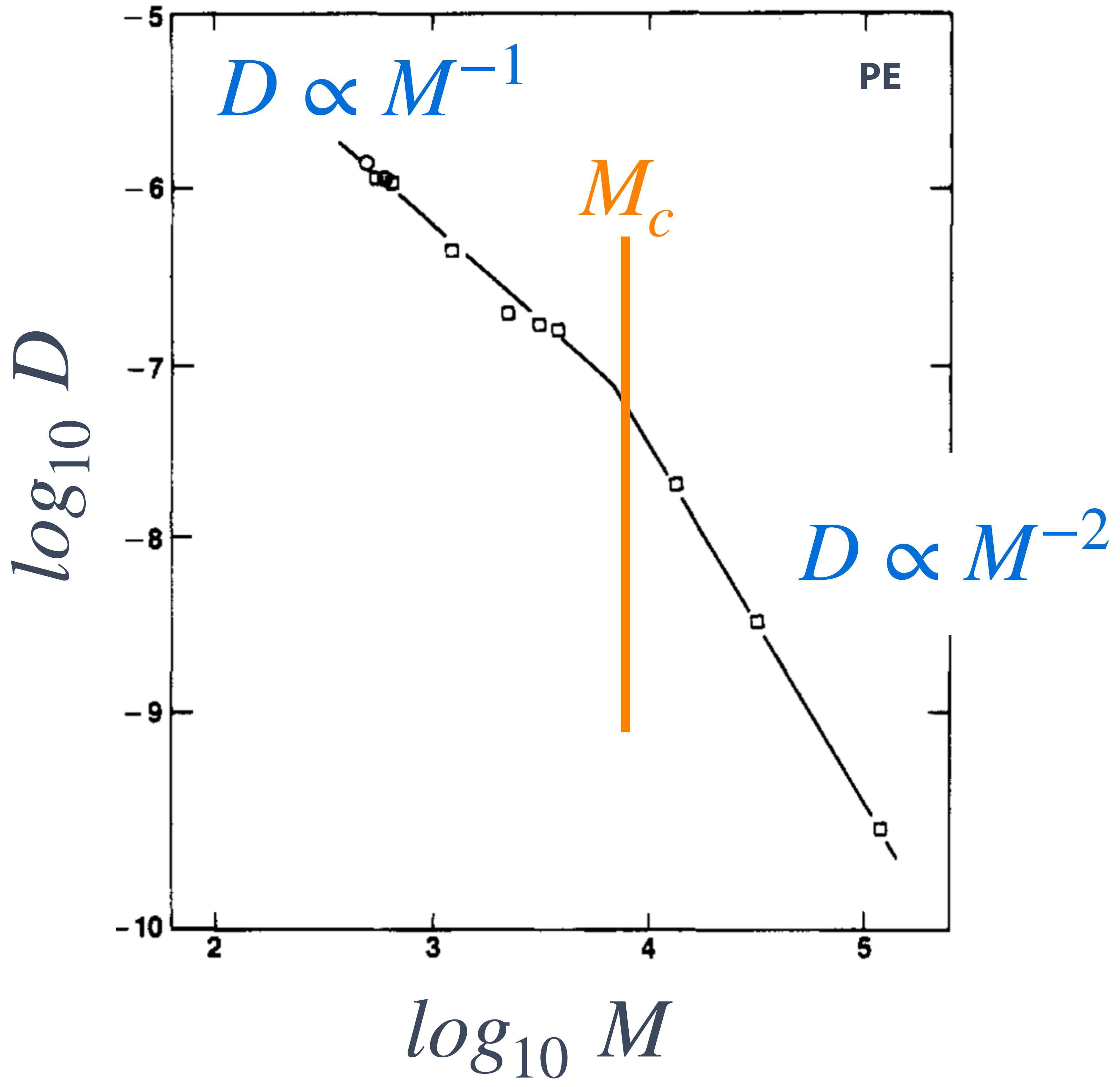
Entanglement & Reptation

Universal Molecular Weight Dependence

Viscosity



Diffusion Coefficient

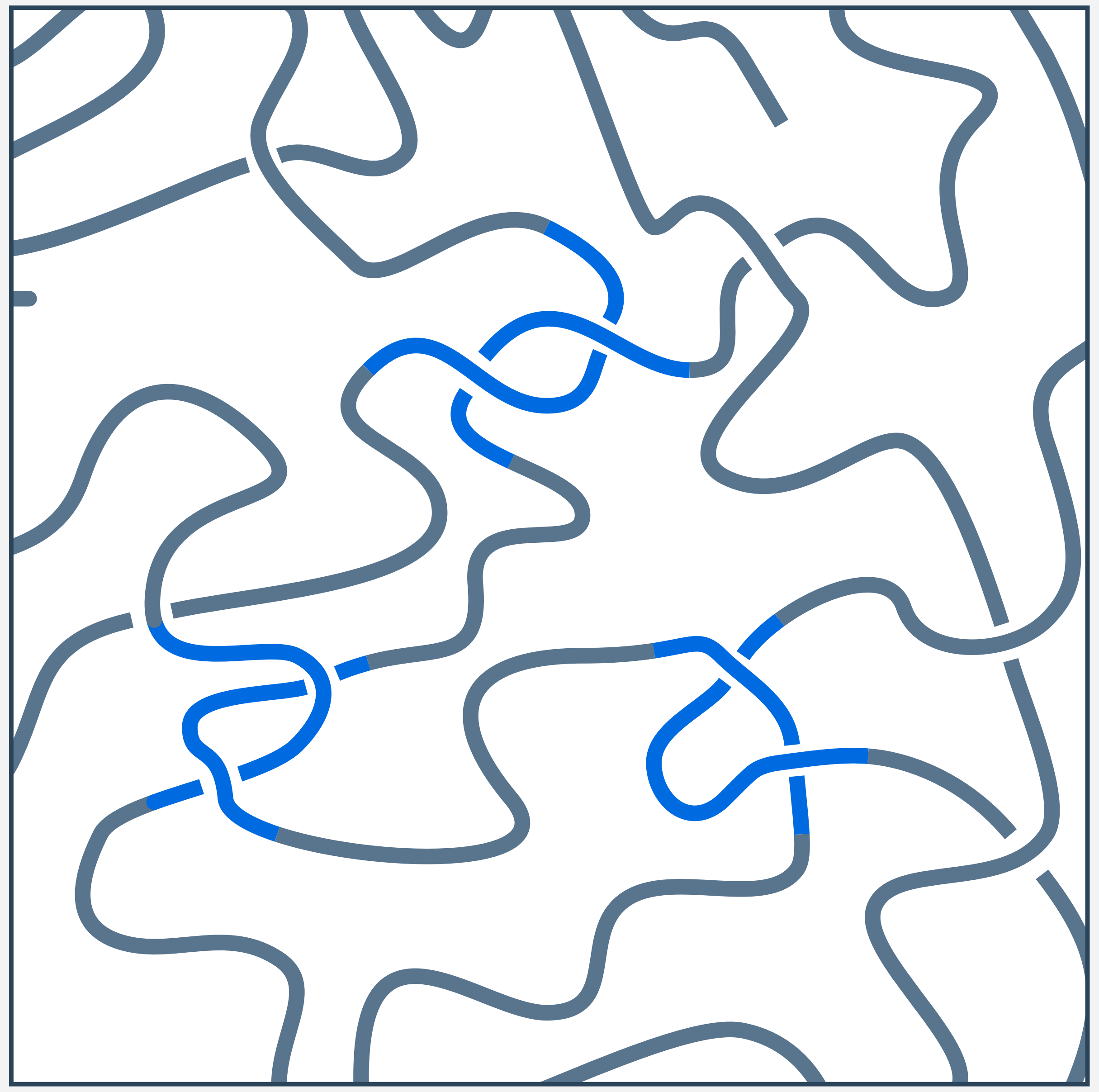


- **What is the molecular origin of these universal power laws?**

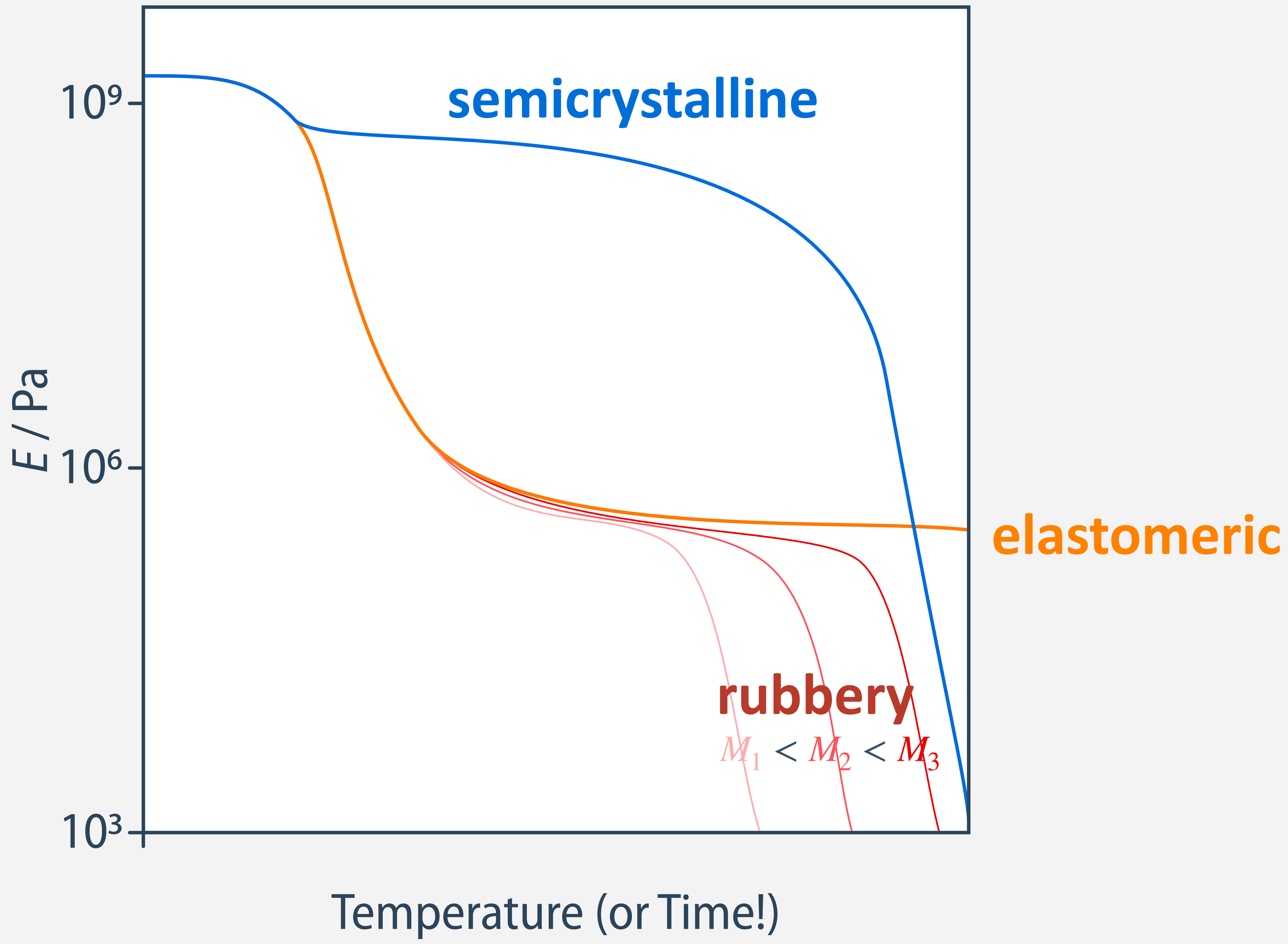
G. C. Berry, T. G. Fox, *Adv. Polym. Sci.* **1968**, *5*, 261; D. S. Paerson *et al. Macromolecules* **1987**, *20*, 1133.

Entanglement

- two chains cannot pass through one another by simple translational motion
- these topological interactions lead to the formation of an entanglement network



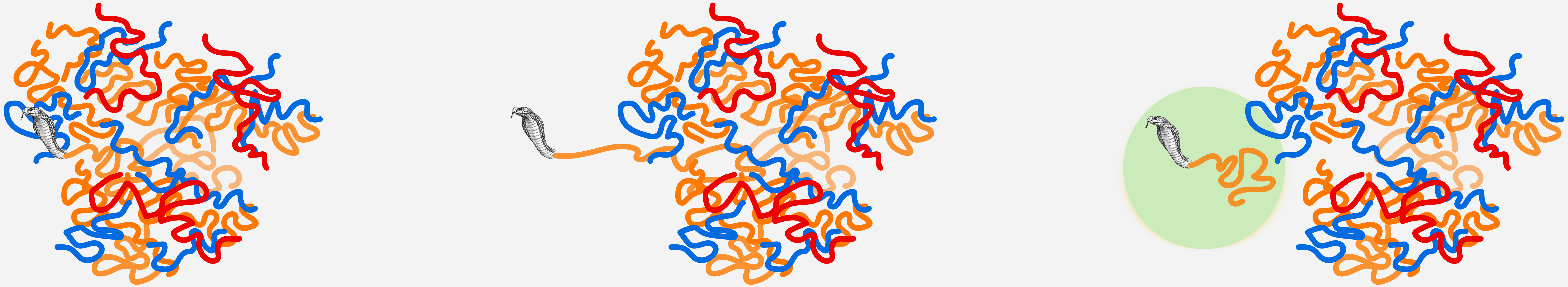
⚠ The static picture representing entanglements as “knots” does not reflect the purely dynamic origin of this phenomenon!



- entanglements are origin of the rubbery state formed by amorphous polymers

Reptation

- **if a chain can becomes entangled with its neighbours, it can also “disentangle”**
  (if its mobility is high enough due to a sufficiently high temperature or due to a sufficiently long time)

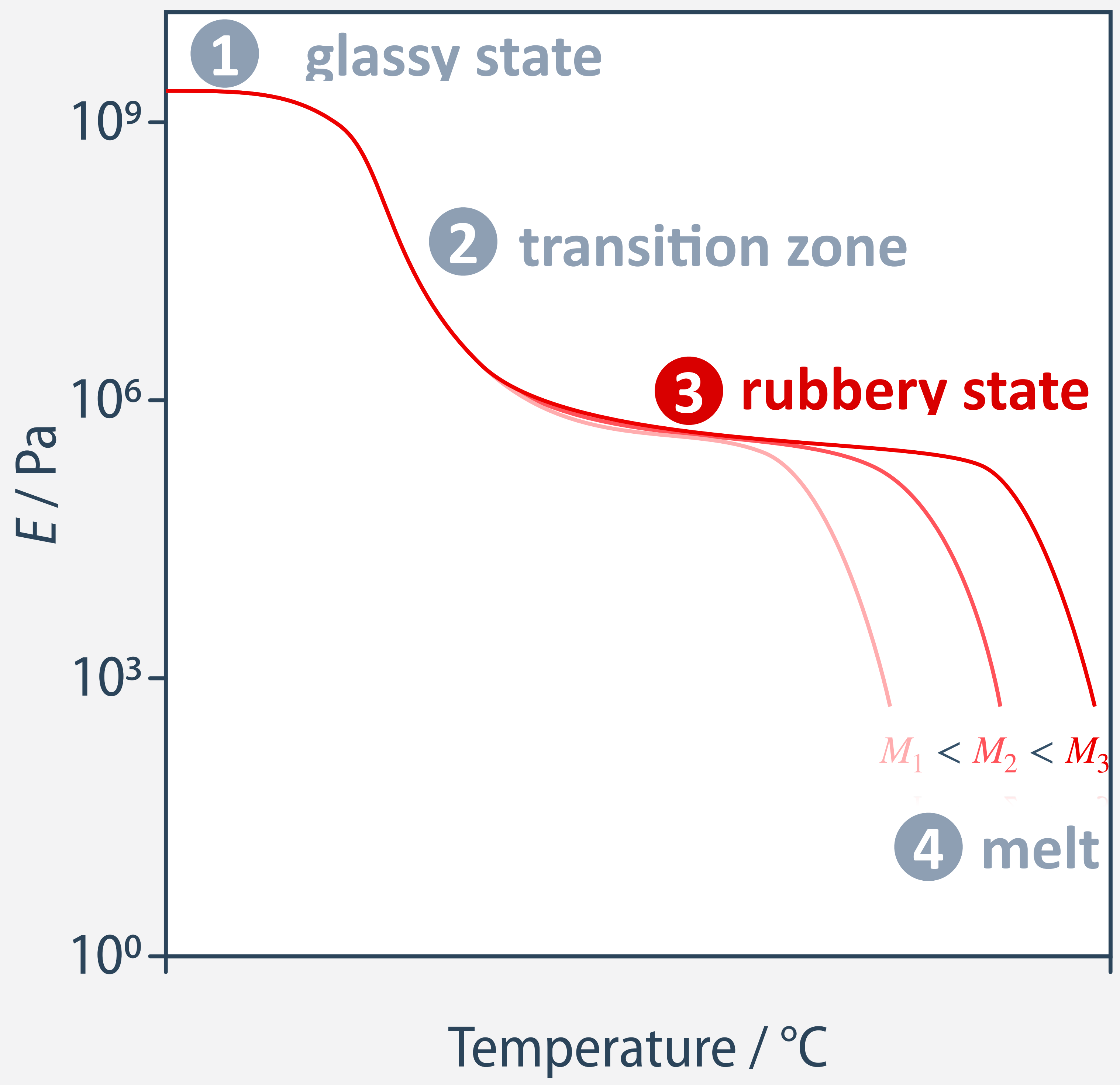


- **disentanglement often described by the term “reptation”** (evoked by the movement of a snake or reptile)

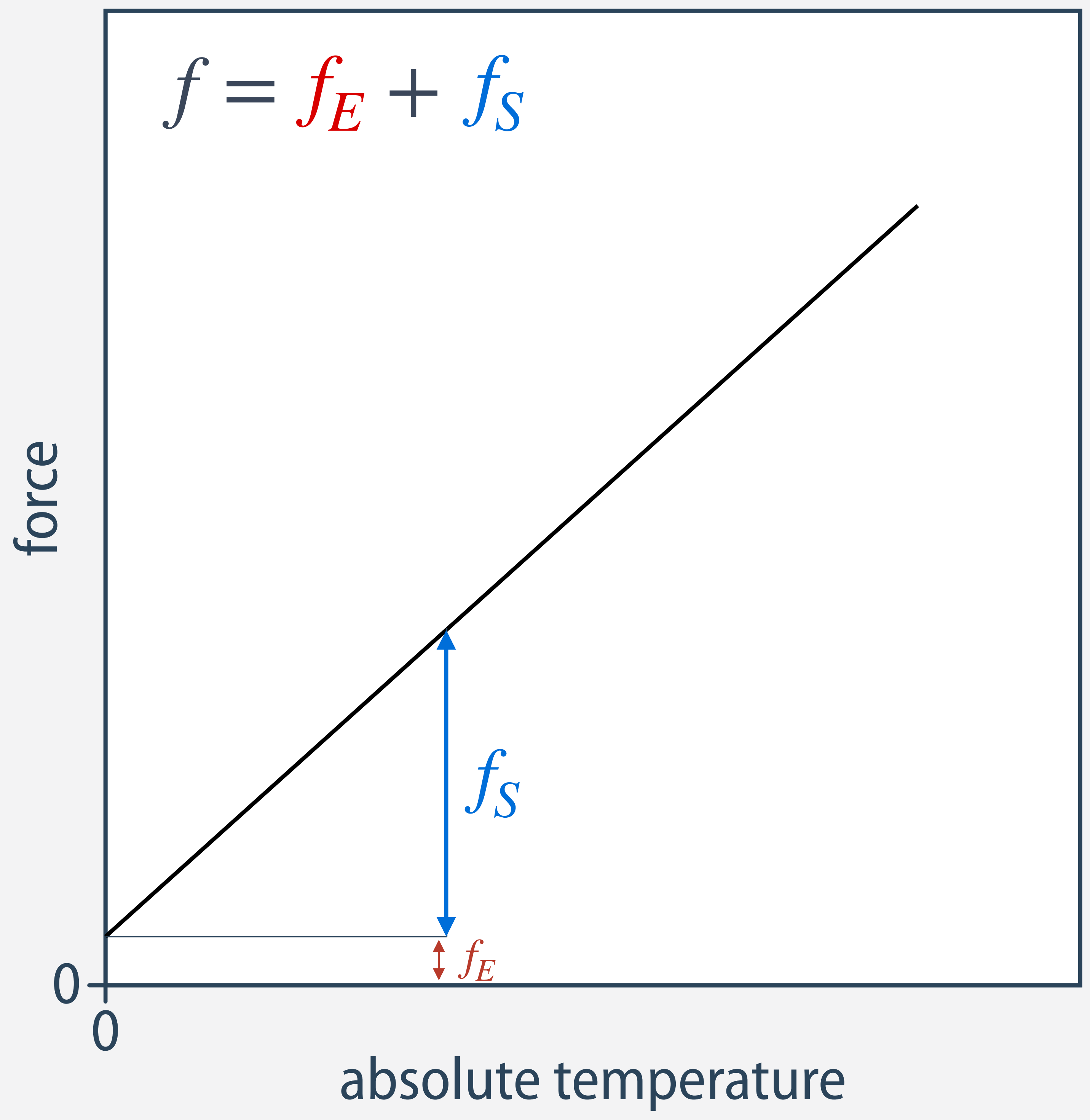
Dynamics of an Isolated Chain in a Solvent

Revision: Rubber Elasticity

universal trend of Young's modulus



energetic components of the elastic force

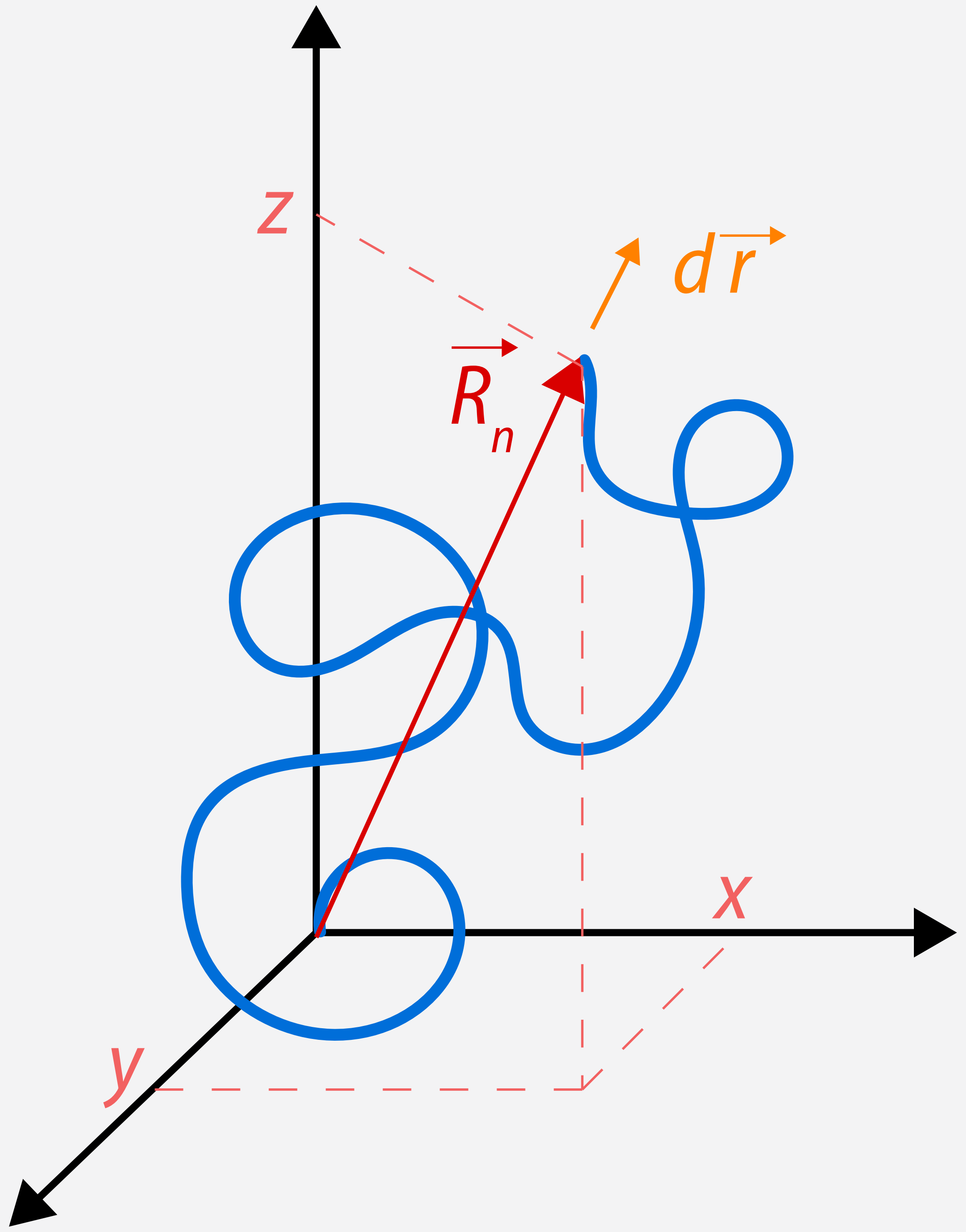


- **rubber elasticity has primarily entropic origins; for ideal rubbers, $f_E = 0$!**

Quantification of the Elastic Force

- the entropy of an ideal polymer chain is related to the Gaussian distribution function of R_n

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



before deformation: $S^c = C - \dfrac{3kR_n^2}{2na^2}$

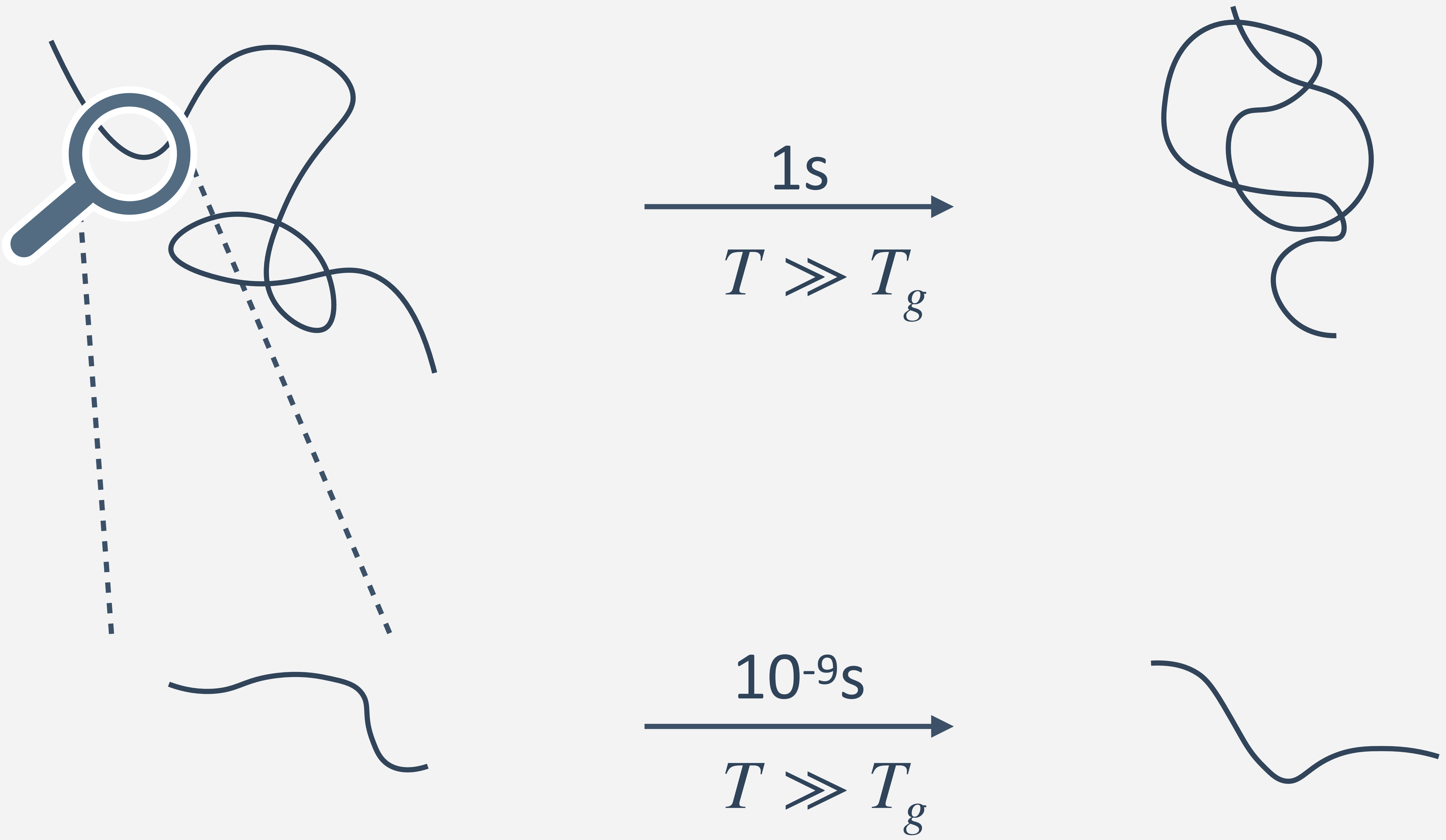
entropy change during small displacement $d\vec{r}$: $dS^c \approx -\dfrac{3k\vec{R}_n \cdot d\vec{r}}{na^2}$

force acting in the direction of this displacement $d\vec{r}$: $f^c \approx -\dfrac{3kT\vec{R}_n}{na^2}$

- **like a spring, the chain opposes its displacement**

Time-dependent Response of Molten Polymer Chains

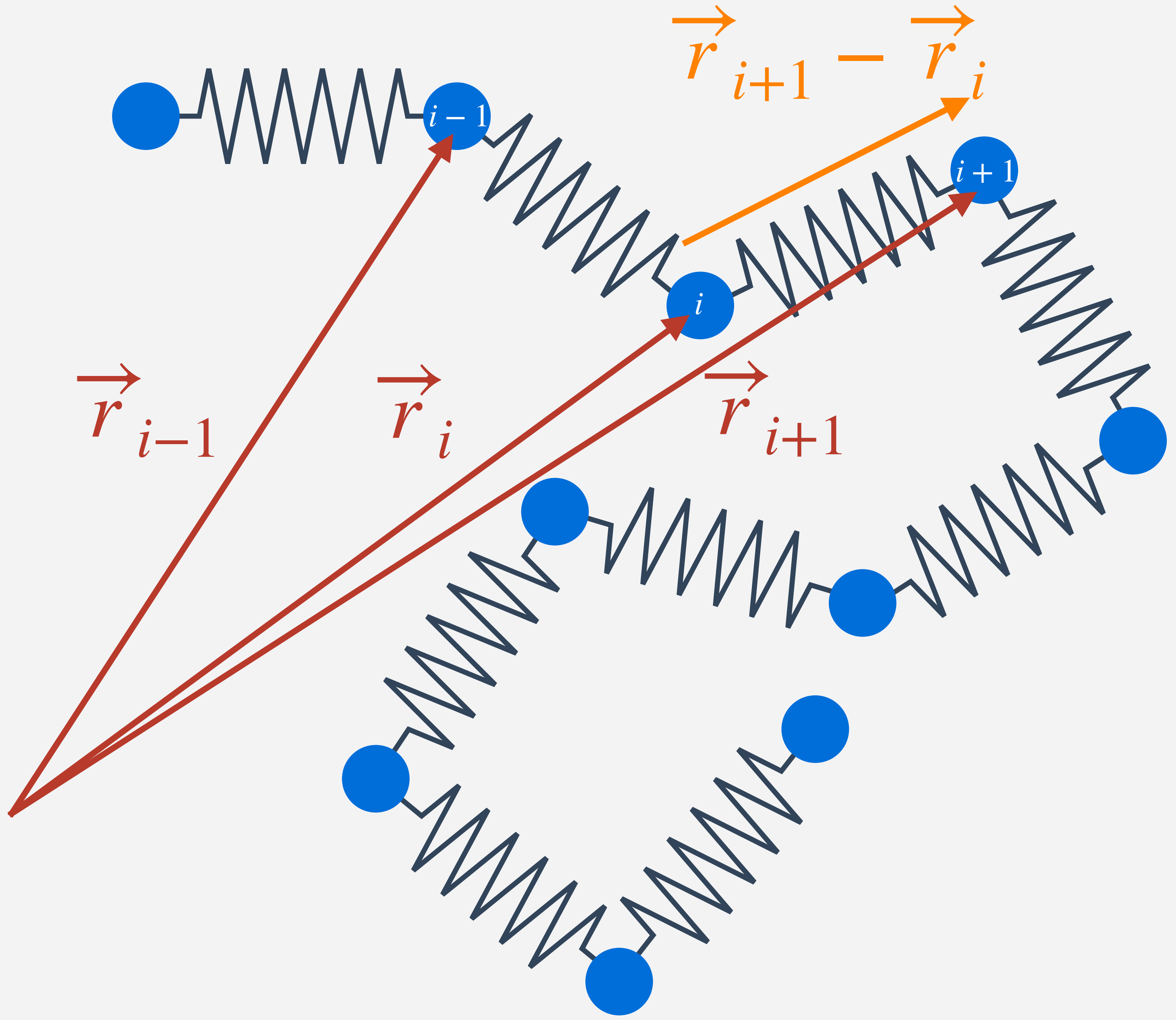
- **time scale for a certain conformational change strongly dependent on the size of the transformed group**



- **rearrangement on a local scale is rapid**
  (controlled by the nature of the repeating unit itself)
- **full equilibration of the entire polymer chain requires a time that is many orders of magnitude longer**
  (strongly dependent on global architecture, i.e. molar mass and chain branching)

Isolated Chains in a Solvent

- the viscoelastic behavior of a very dilute solution will reflect the dynamics of an isolated chain if one takes into account its interactions with the solvent
- **Rouse model: Gaussian subchains of identical length represented by m beads and $m-1$ springs**



mean-square end-to-end distance:

$$< R_s^2 > = \frac{n}{m-1} l^2$$

contraction force along the vector $\vec{r}_{i+1} - \vec{r}_i$:

$$f = \frac{3kT}{R_n^2} (\vec{r}_{i+1} - \vec{r}_i)$$

(see **exercise 6**)

The Rouse Model for Unentangled Polymers

- **balance between elastic deformation and frictional forces between bead i and solvent**

$$f = \frac{3kT}{R_n^2}(\vec{r}_i - \vec{r}_{i-1}) + \frac{3kT}{R_n^2}(\vec{r}_i - \vec{r}_{i+1}) = \frac{3kT}{R_n^2}(2\vec{r}_i - \vec{r}_{i-1} - \vec{r}_{i+1}) = -\xi\frac{d\vec{r}_i}{dt}$$

entropic elasticity due to deformation of the two springs

viscous force

- **for a whole subchain, m such coupled equations which can be solved by "normal mode transformation";** for a dilute solution containing N_m chains per volume, we get m independent equations with solutions:

$$\mathrm{G}(t) = N_m kT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}} \qquad G'(t) = N_m kT \sum_{p=1}^{m} \frac{\omega^2 {\tau_p}^2}{1 + \omega^2 {\tau_p}^2} \qquad G''(t) = N_m kT \sum_{p=1}^{m} \frac{\omega \tau_p}{1 + \omega^2 {\tau_p}^2}$$

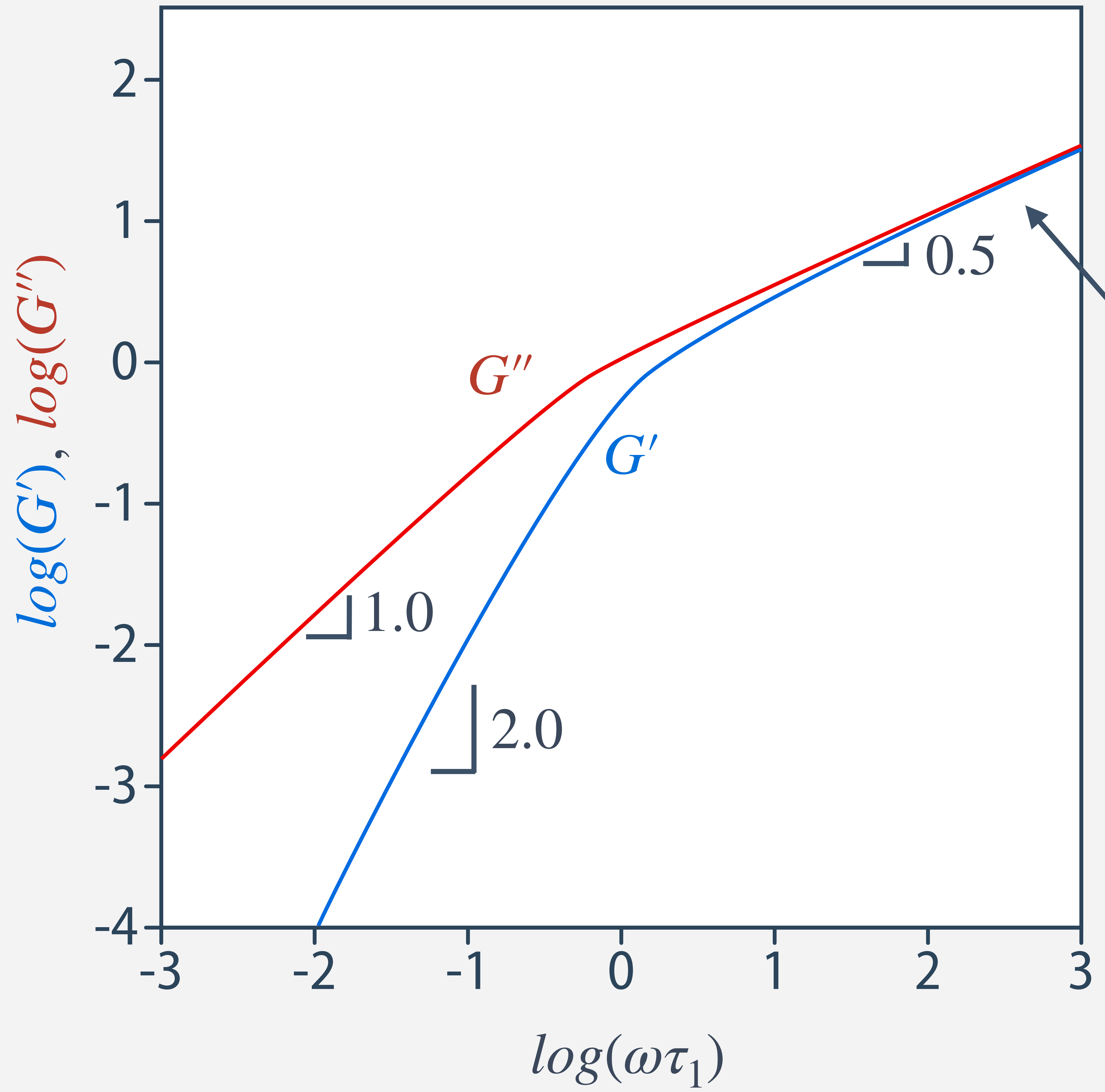
- **each relaxation time, τ_p , describes the time scale over which a different mode of vibration p decays:**

$$\tau_p = \frac{\xi R_s^2}{24kT} sin^{-2}\left(\frac{\pi p}{2(m+1)}\right) \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 kT} \quad , for\ m \gg 1,p \qquad p = 1,2,\dots m$$

Practicability of the Rouse Model

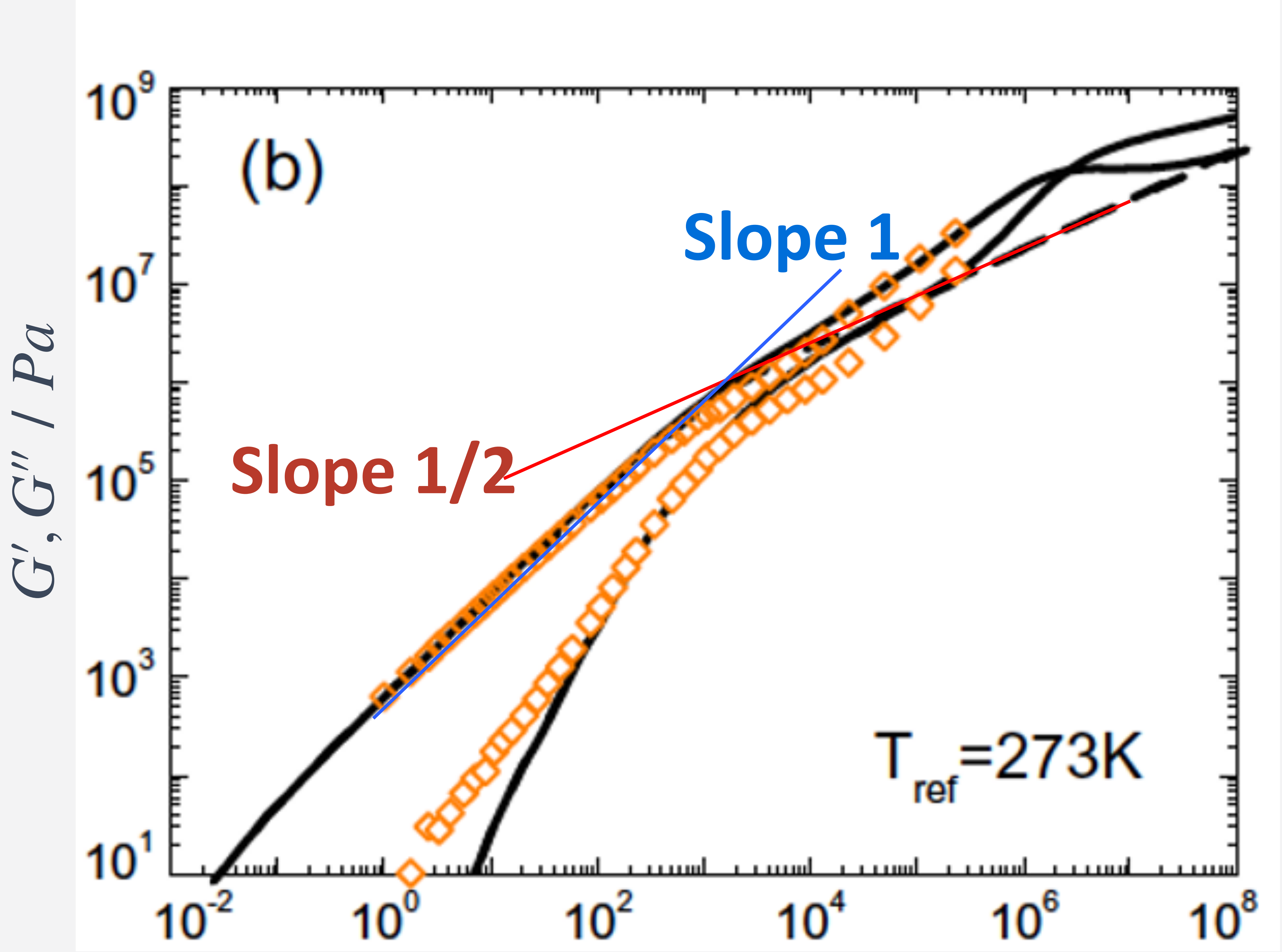
- same behavior in the terminal zone as for the Maxwell model

predicted rheology curves



here: $G' \approx G''$ are approximately proportional to $\omega^{1/2}$

linear poly(butyl acrylate), $M_n = 5'300\ g/mol$



- **polymer melts, particularly at low molecular weights, are well described with the Rouse model**

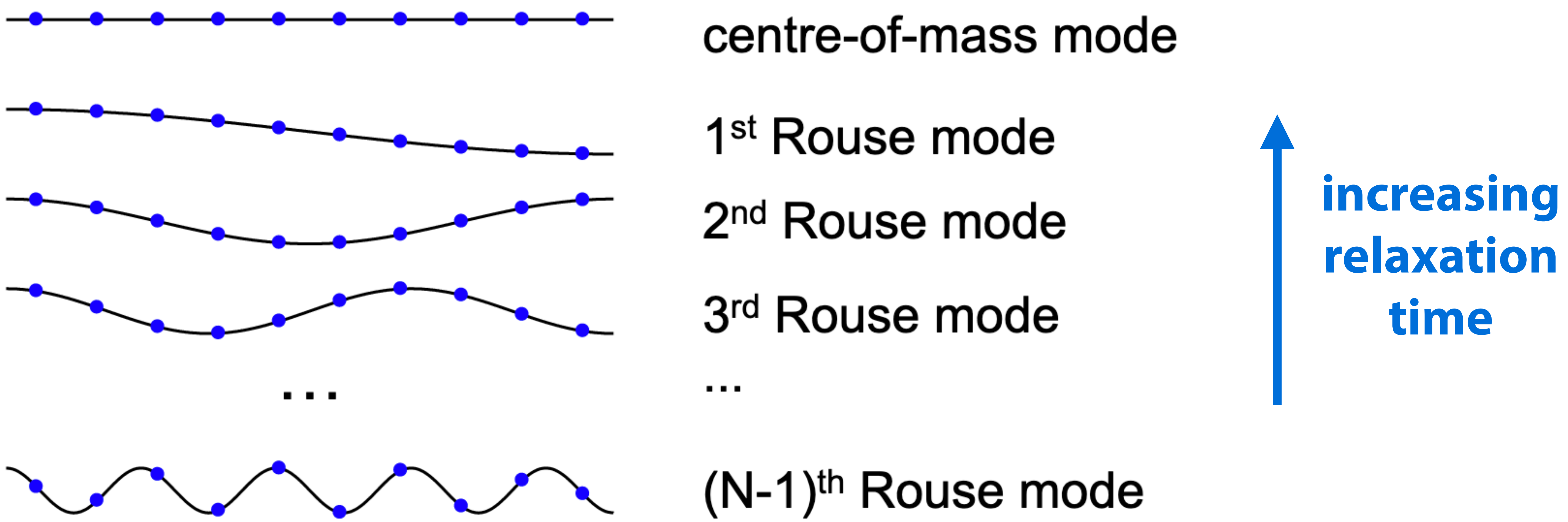
Europ. Polym. J. **2011**, *47*, 746-751.

Rouse Modes

- the different modes of vibration exhibit p nodes along the polymer chain

$$\tau_p \approx \frac{\xi m^2 R_n^2}{6\pi^2 p^2 kT}$$

$$for\ m \gg 1,p$$



centre-of-mass mode

1^{st} Rouse mode

2^{nd} Rouse mode

3^{rd} Rouse mode

...

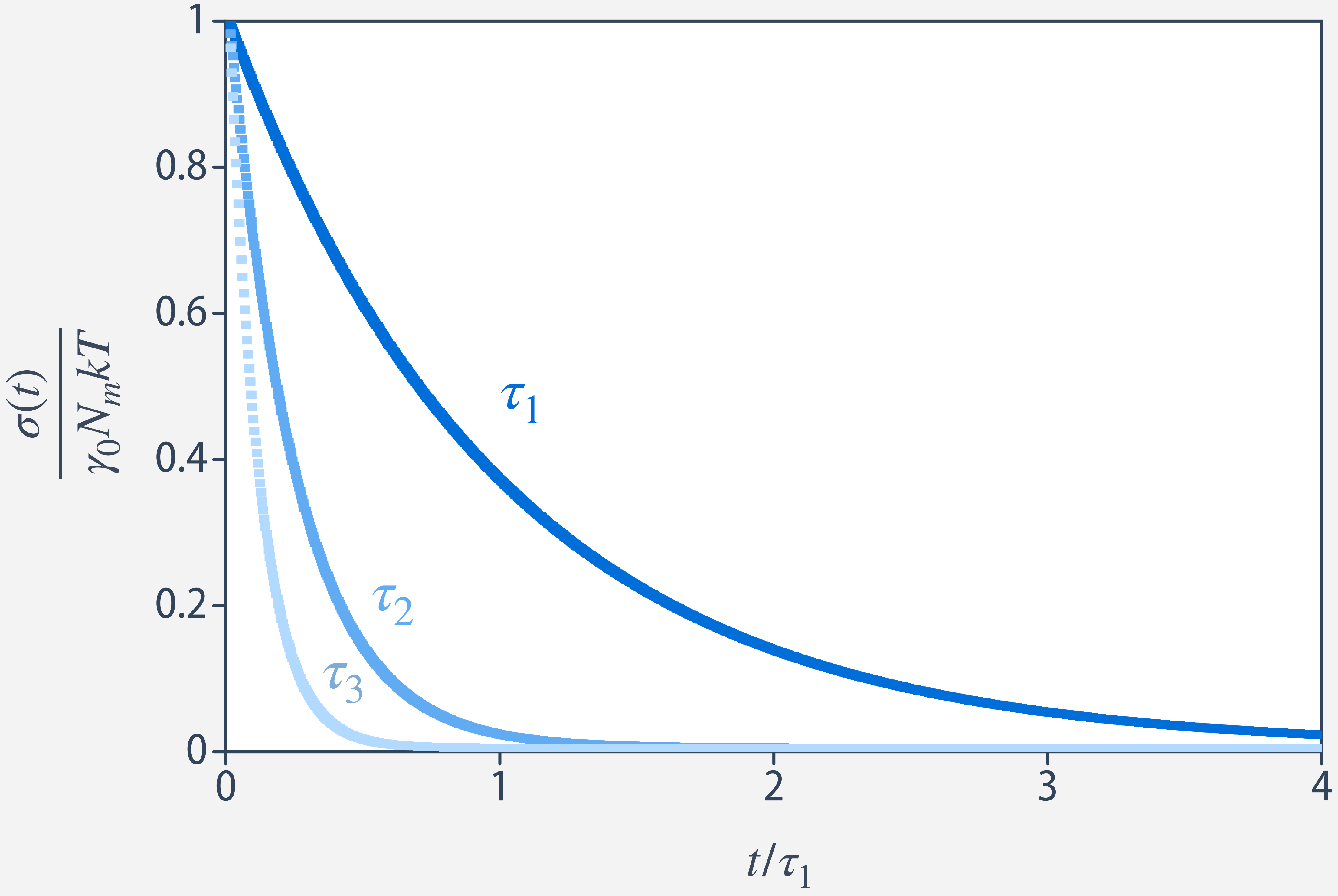
$(N-1)^{th}$ Rouse mode

increasing relaxation time

- Rouse modes characterise the motion of polymers on different lengths
- the longest relaxation time (Rouse time), τ_1, is proportional to M^2

Rouse Relaxation

$$G(t) = N_m kT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}}$$



- What is the meaning of m?
- What if $m \to n$?
- What if $\tau_1 = \infty$?

(see **exercise 8**)

- **the stress is relaxed according to a simple exponential decrease**
- **the contribution of faster relaxation times becomes negligible for for $t \geq \tau_1$**

Assumptions of the Rouse Model

- the chain is treated by a “bead and spring” model with entropic forces between nearest neighbours.

- the interaction with other surrounding chains is described by a frictional coefficient ξ

- hydrodynamic interactions are neglected (for corrections, see the Zimm model)

- the chain must be long

- as long as the molecular weight is smaller than a critical molecular weight, M_c,Rouse adequately describes the dynamics of a chain

- for $MW > M_c$, entanglement must be taken into account

Limitation of the Rouse Approach

- dilute polymer solutions are not accurately described, because bead-solvent interactions (hydrodynamics interactions) are not taken into account (see Zimm theory for a more accurate treatment)

Rouse behavior

$$\tau_1 \propto M^2$$

D is the diffusion coefficient of the centre of mass of the chain

$$\boxed{D = \frac{kt}{\xi m} = \frac{kt}{\xi_0 n} \propto \frac{1}{M}}$$

observations

(from dilute solutions)

$$\tau_1 \propto M^{3/2}$$

$$\boxed{D \propto 1M^{1/2}}$$

- **Rouse model is only valid for short time scales (high frequencies) or for low molecular weights**
- **it does not take entanglement into account!**

Entanglement

Constraints on a Chain in the Condensed State

- **the volume of a Gaussian chain is:** $V_g = 4r_g^3$ $\quad r_g^2 = \dfrac{C_\infty n l^2}{6}$

- **let's take typical values:** $C_\infty = 10, \quad l = \sqrt{2}\ \text{Å}, \quad n = 10^3, \quad \rho = 1\dfrac{g}{cm^3} = 10^6\ \dfrac{g}{m^3}$

  (example of polystyrene)

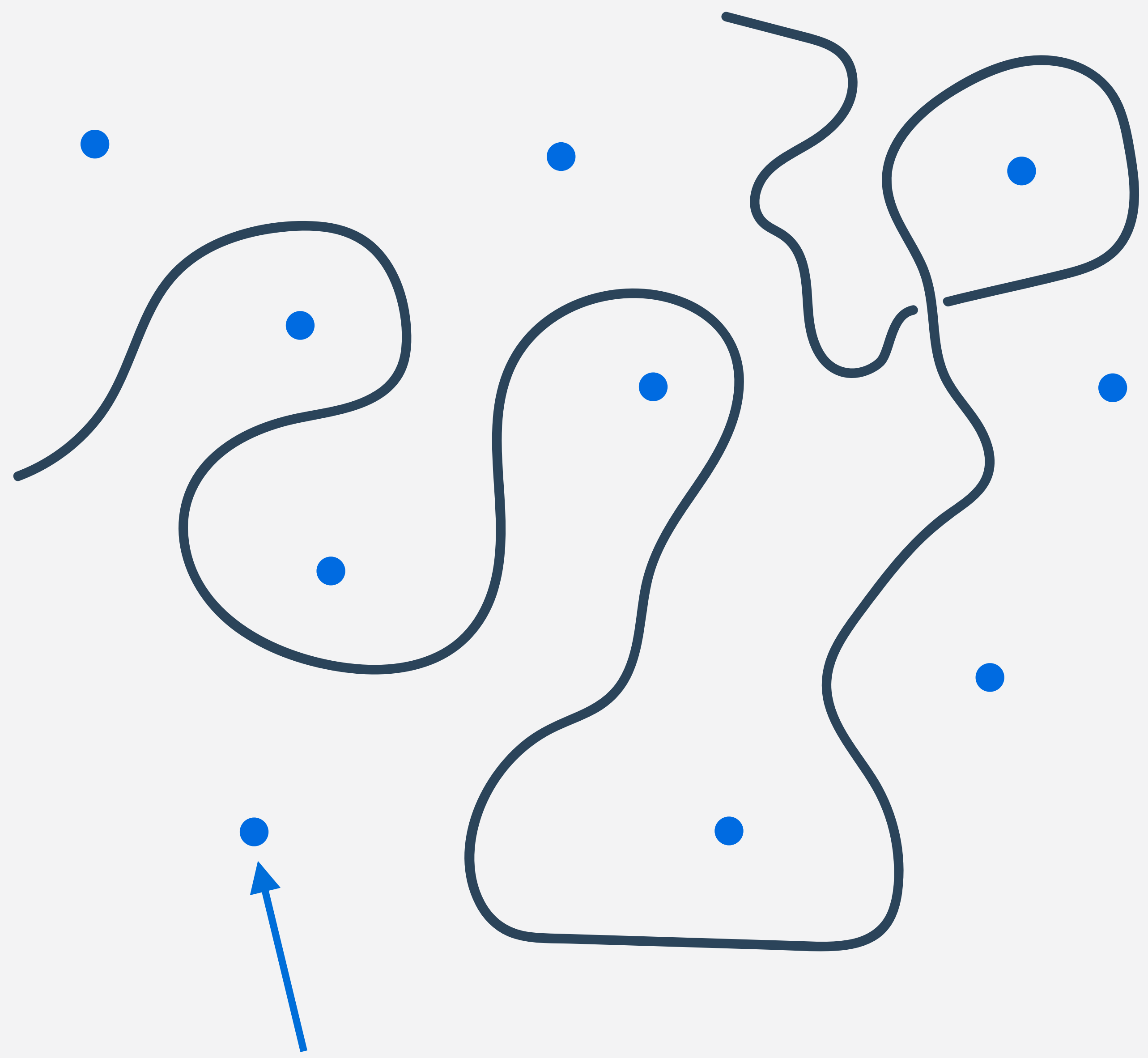
- **thus, the volume** $V_g \approx \dfrac{4}{5} \cdot 10^6 \text{Å}^3$ **corresponds to a mass** $m_g = \rho V_g \approx \dfrac{4}{5} \cdot 10^{-18}\ g$

- **comparison with one chain of PS with** $n = 10^3$**:** $m_{chain} = \dfrac{nM_0}{2N_A} \approx \dfrac{5}{6} \cdot 10^{-19}\ g$

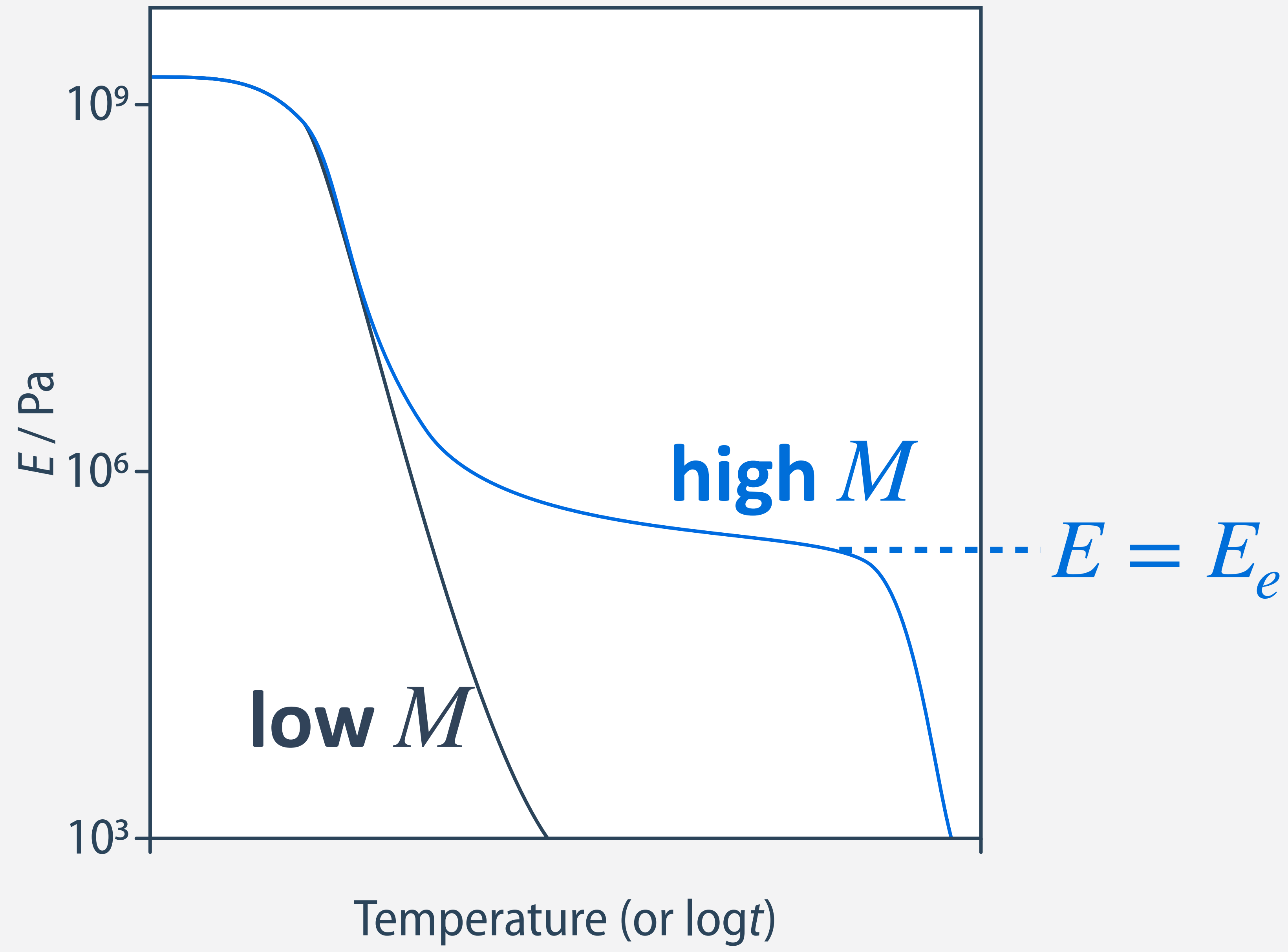
- **polymer chains are strongly interpenetrating each other, in case of our example, by an average of approximately 10 other chains:** $\dfrac{m_g}{m_{chain}} \approx 10$

Static Models of Entanglement

- **high degree of penetrations with neighbouring chains restricts the mobility of chains**



cross section of a neighbouring chain



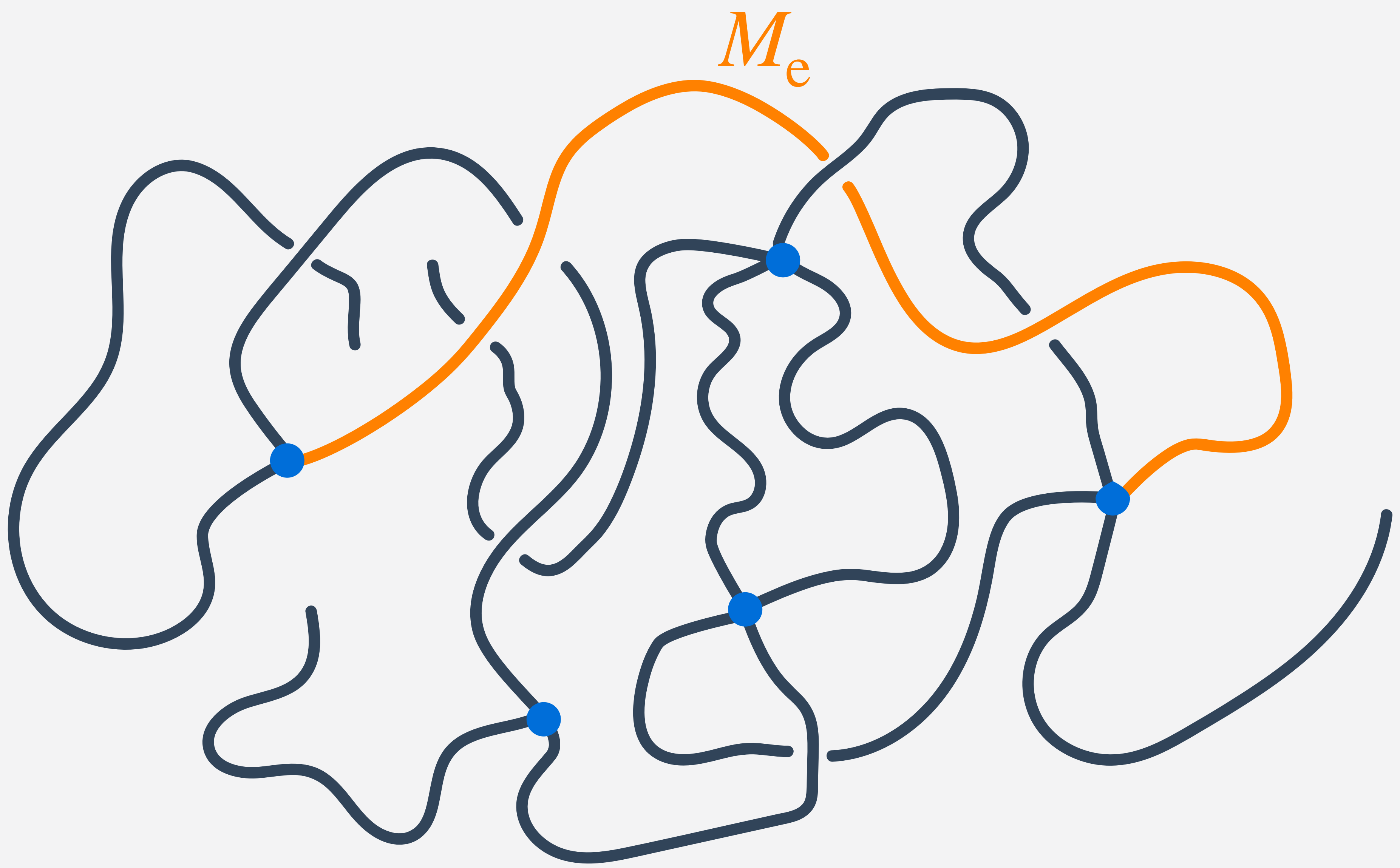
In analogy to elastomers ($E = 3NkT$), we assume:

$E_e = 3N_e kT$ N_e: **"entanglement" density**

- **the rubbery state in non-crosslinked amorphous polymers above T_g is due entanglement**

Entanglement Network

- a non-crosslinked polymer is considered as a network of subchains of average molar mass M_e linked by entanglement points



$$E_e = 3N_e kT = 3RT\frac{\rho}{M_e}$$

$$M_e = 3RT\frac{\rho}{E_e}$$

- M_e is an important parameter: only for $M > 2M_e$, characteristic properties of long polymer chains (e.g. rubber elasticity) are manifested
- if $M < 2M_e = M_c$: no entanglement and no rubbery state are obtained (compare to Exercise #4.2)

Entanglement Molecular Weight and Chain Structure

- M_e and the entanglement density, N_e , vary greatly depending on the polymer

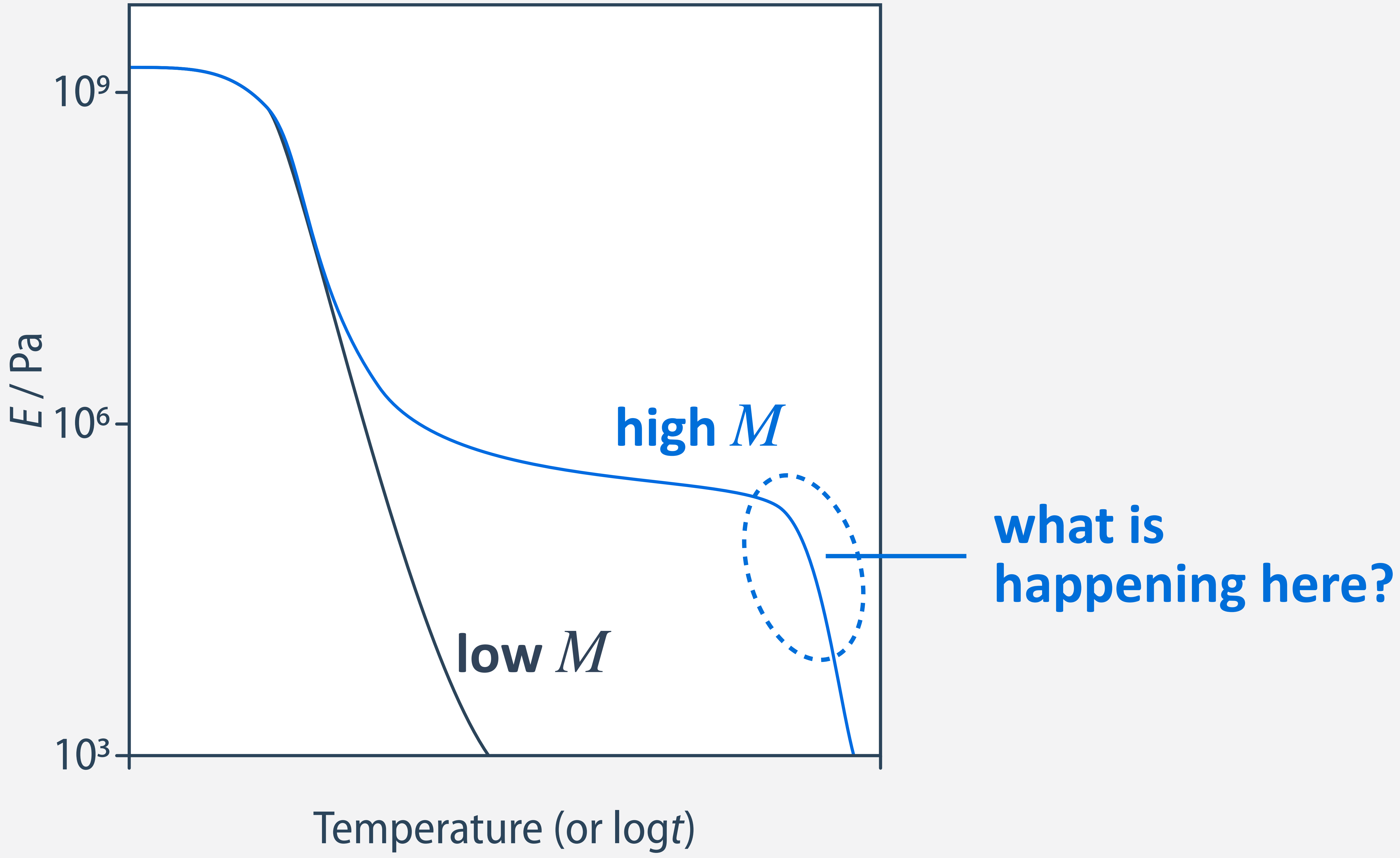
polymer	density	M_e	C_∞	N_e
	g/cm³	g/mol	GPa	mmol/cm³
PS	1.05	18'700	10.8	0.0561
PMMA	1.17	9'200	8.2	0.127
PVC	1.4	5'560	7.6	0.252
PA6	1.08	2'480	6.2	0.435
POM	1.25	2'550	7.5	0.49
PA66	1.07	1'990	6.1	0.537
PE	0.85	1'390	6.8	0.613
PC	1.2	1'790	2.4	0.725
PET	1.33	1'630	4.2	0.815

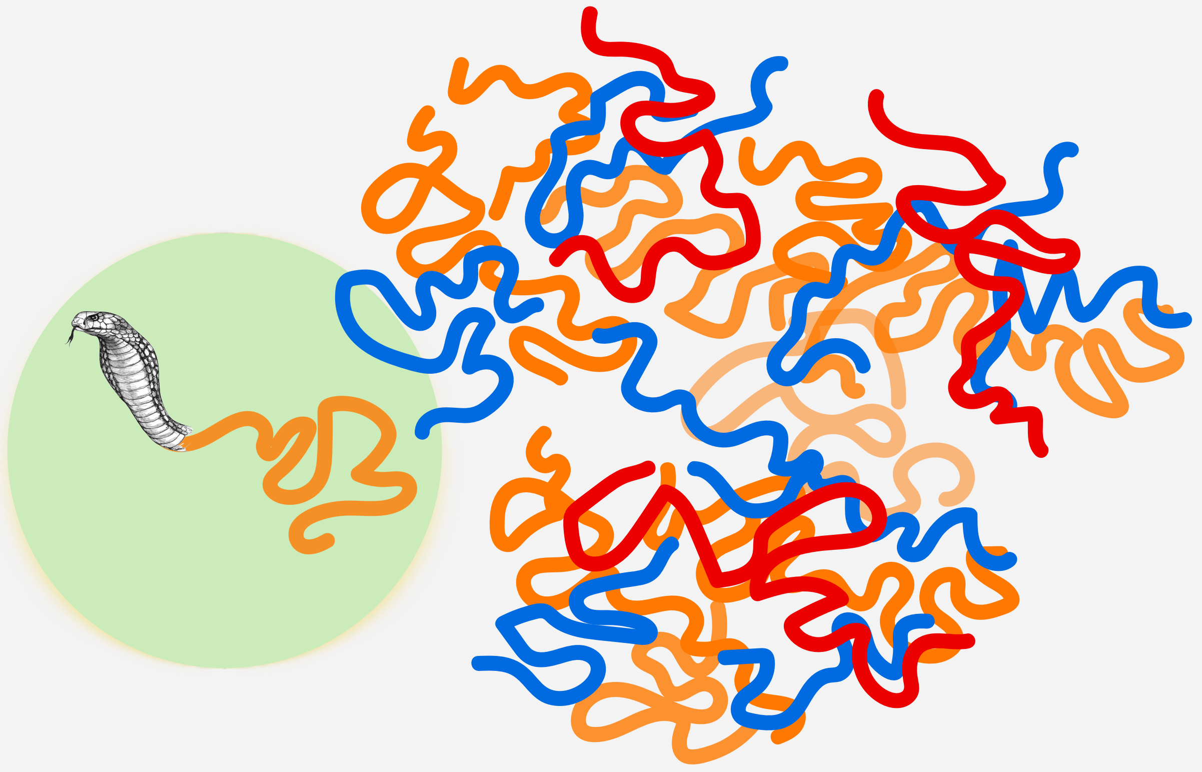
- empirical relations exist that connect M_e, C_∞, and M_0 (Wu 1990): $M_e = 3M_0{C_\infty}^2$

Reptation

Disentanglement

- **if the mobility (temperature) is high enough or time is sufficiently long, chains begin to slide versus each other**

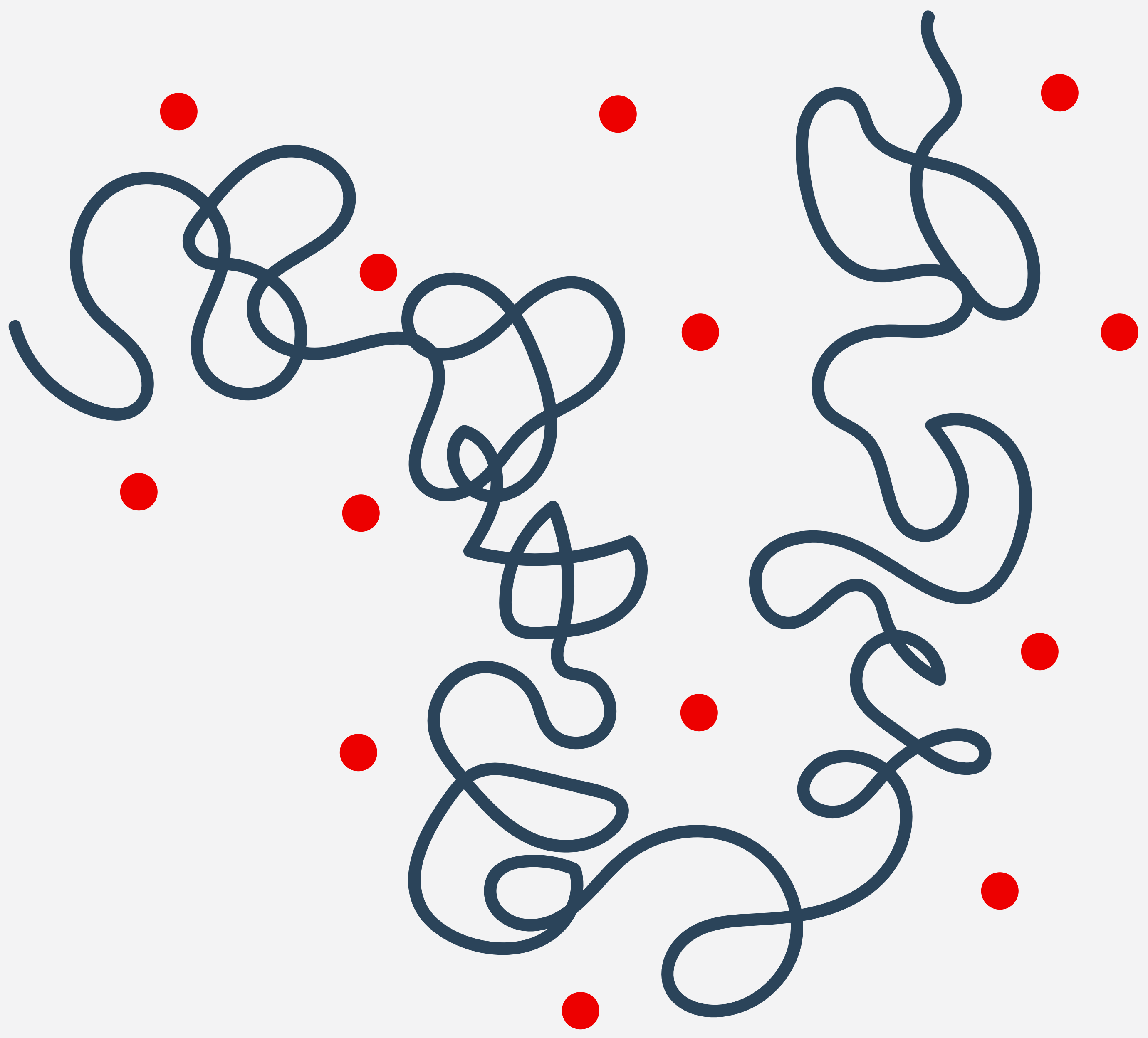


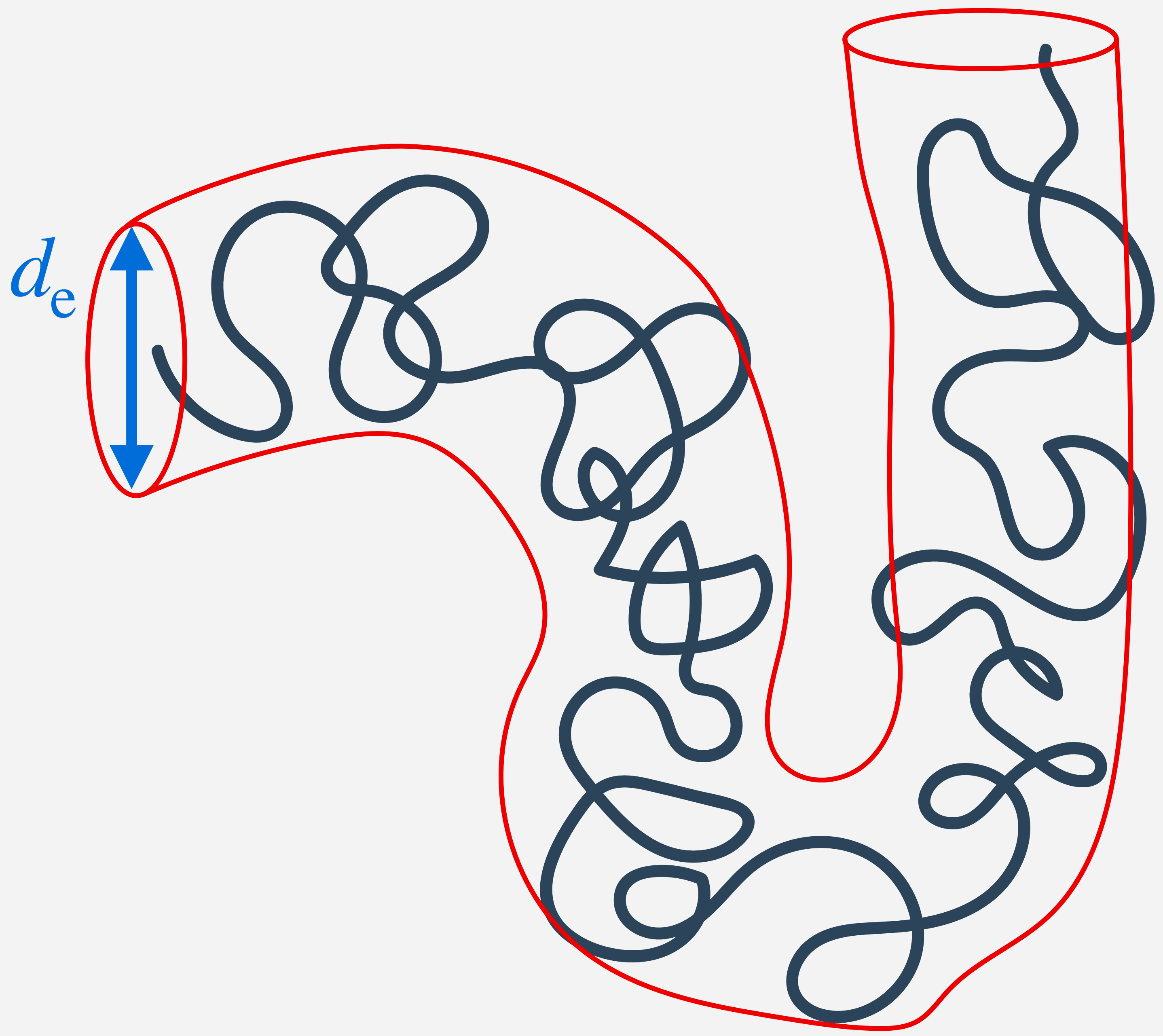


- **in the absence of cross-linking, the behavior becomes that of a viscous liquid.**

The Tube Model

- **in the tube model** (DeGennes, Doi, and Edwards)**, a given chain is assumed to be trapped in a virtual tube that represents its interactions with its neighbours**





- **the diameter of the tube, d_e , corresponds to the length of a chain with mass M_e:** $< d_e^2 > = \frac{M_e}{M_0} l^2$

The Entanglement Time

- **stress relaxation modulus and relaxation times according to the Rouse model:**

$$G(t) = N_m kT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}} \qquad \tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 kT}$$

- **hindered relaxation for long chain segments:**

$$\tau_p = \infty, \ for \ \frac{R_s^2}{p} > d_\mathrm{e}^2$$

- **cross-over time from Rouse to reptation behavior:**

$$\tau_\mathrm{e} = \frac{\xi m^2 R_s^2}{6\pi^2 kT} \cdot \frac{d_\mathrm{e}^4}{R_s^4} = \frac{\xi_0 d_\mathrm{e}^4}{6\pi^2 kT l^2} = \frac{\xi_0 l^2}{6\pi^2 kT}\left(\frac{M_\mathrm{e}}{M_0}\right)^2$$

- **the entanglement time τ_e determines the polymer's transition from Rouse to repetition behavior**
- τ_e **is a materials parameter** (dependent on M_e, but independent of the polymer molar mass M)

Relaxation According to the Tube Model

- the chain does not remain blocked in the tube, but leaves the tube after a time τ_d

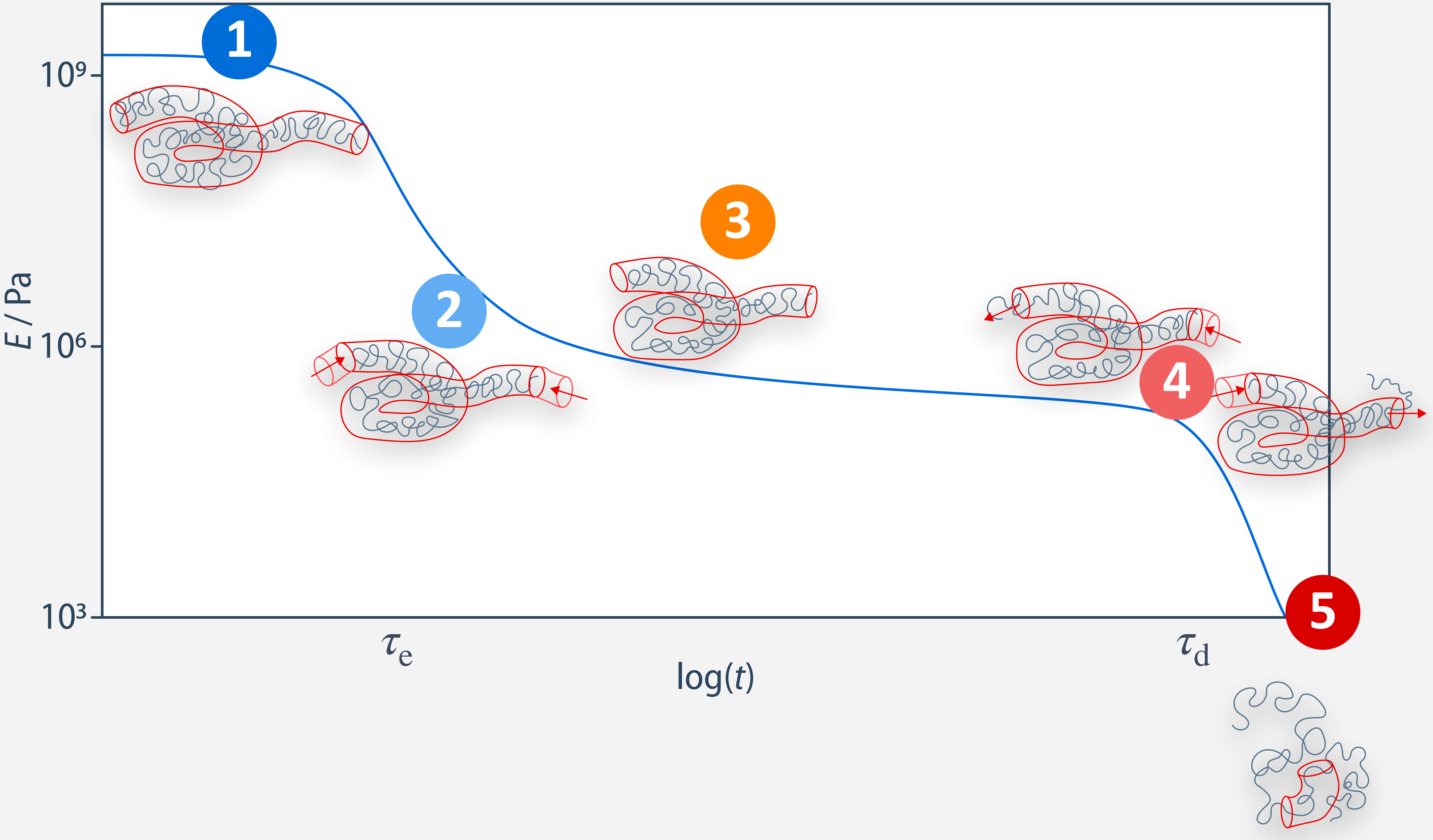
① **instant tube & chain deformation:** no relaxation, high stress

② **rapid Rouse-type relaxation inside the tube until $t = \tau_\mathrm{e}$**

③ **rubbery plateau for $\tau_\mathrm{e} < t < \tau_\mathrm{d}$**

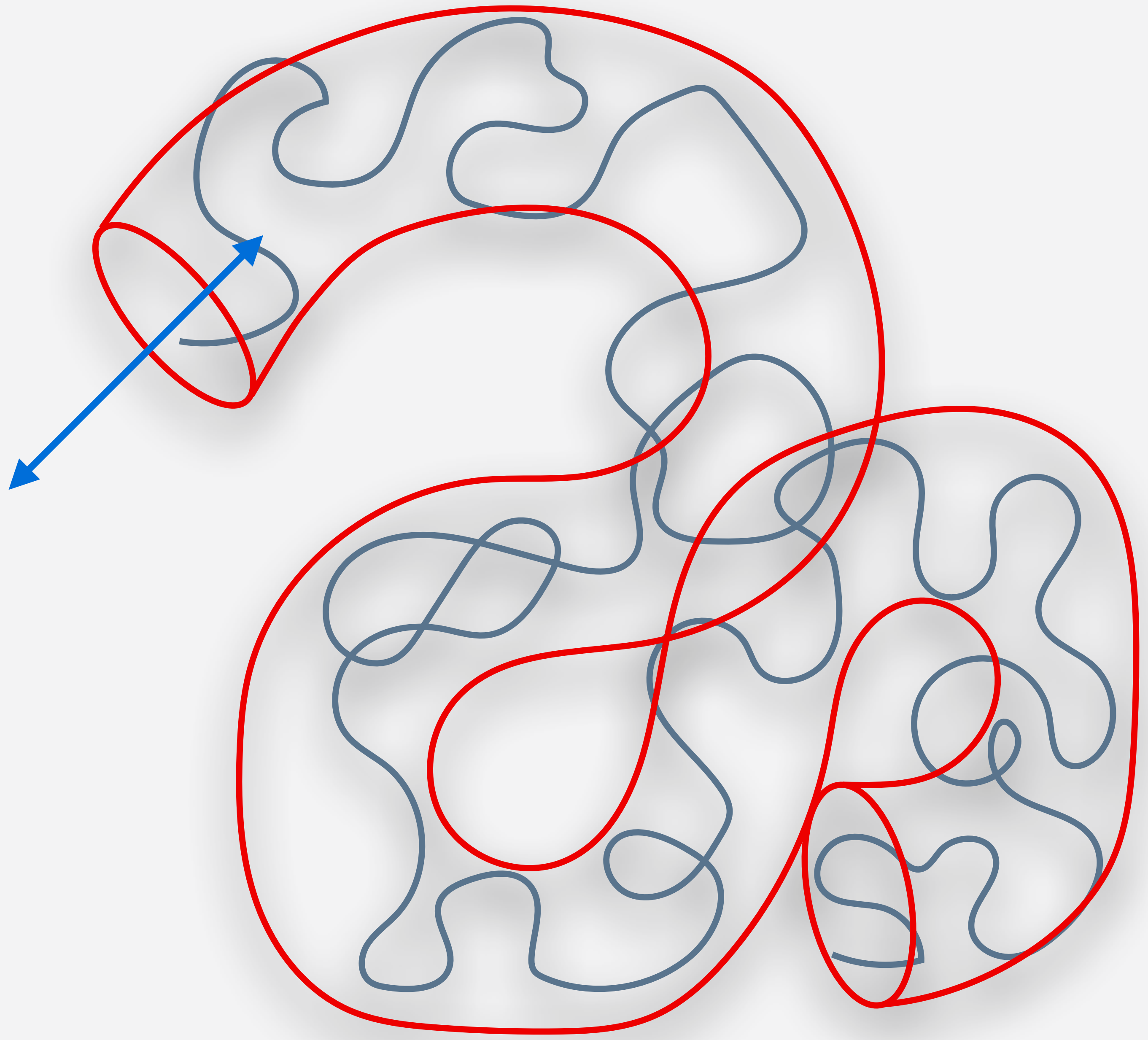
④ **chain begins to escape from the tube, when $t = \tau_\mathrm{d}$**

⑤ **random conformation fully restored:** relaxation terminated when $t \gg \tau_\mathrm{d}$



Molecular Weight Dependence of Reptation

- **Rouse model, the diffusion coefficient along the tube is inversely proportional to M:** $D_R \propto \frac{1}{M}$



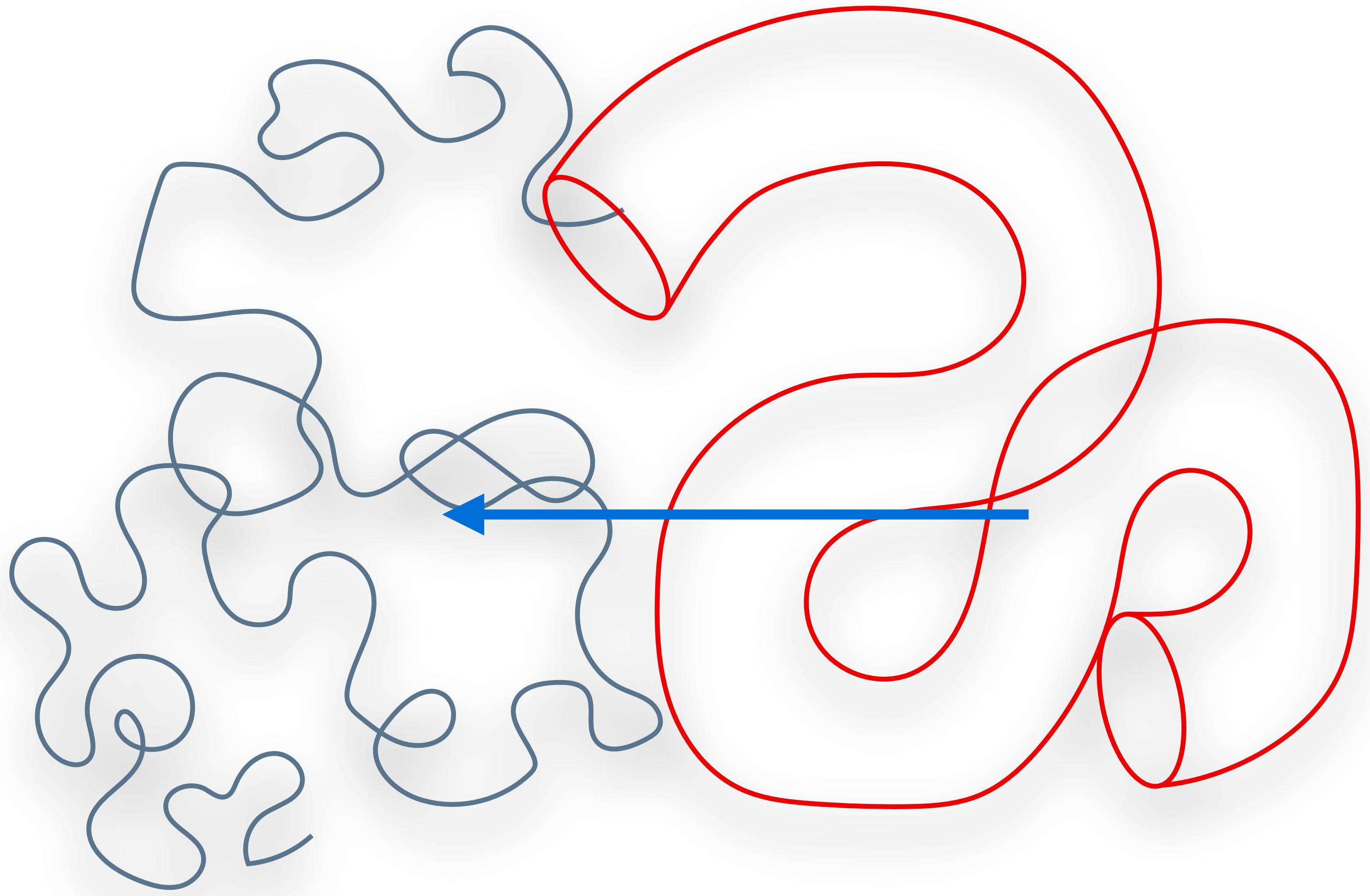
the diffusion distance
after time t (Fick's law): $x = \sqrt{D_R t} \propto \sqrt{\frac{t}{M}}$

contour length of the tube: $L = \frac{M}{M_\mathrm{e}} d_\mathrm{e}$

- **one step diffusion out of the tube after disentanglement time:** $\tau_\mathrm{d} \approx \frac{L^2}{D_R} = \frac{\xi_0 n}{kT}\left(\frac{M}{M_\mathrm{e}}\right)^2 d_\mathrm{e}^2 = 6\pi^2\left(\frac{M}{M_\mathrm{e}}\right)^3 \tau_\mathrm{e}$
- τ_e **scales with** M^3 (while τ_e is independent of M)**: strong dependence of rubbery behavior on molar mass**

Experimental Evidence

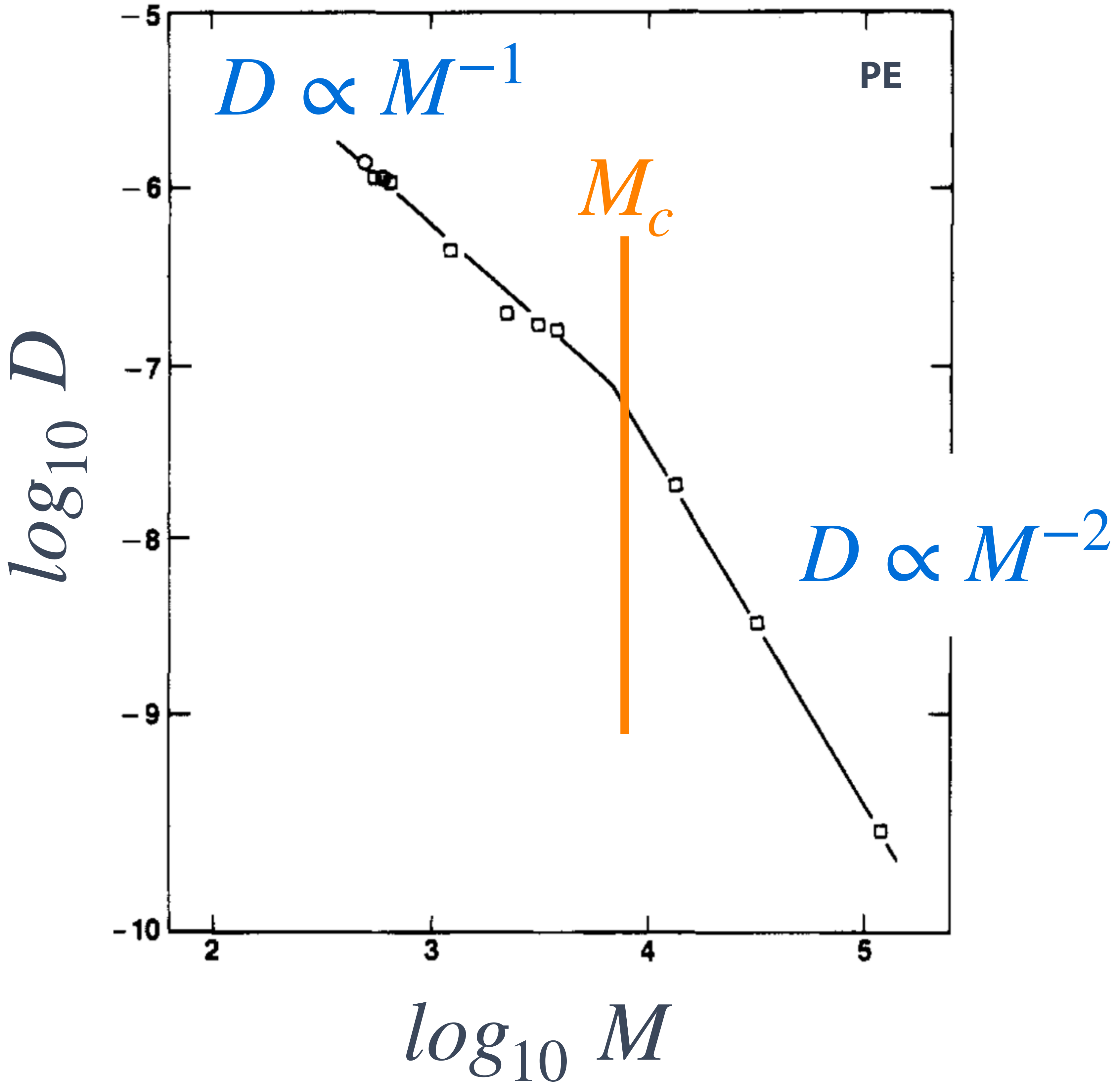
- the diffusion coefficient is a measurable quantity (Neutron scattering)



self-diffusion coefficient, D, for $M > M_c$:

$$D \approx \frac{< r_g^2 >}{\tau_\mathrm{d}} \propto \frac{M}{M^3} \propto M^{-2}$$

diffusion coefficient



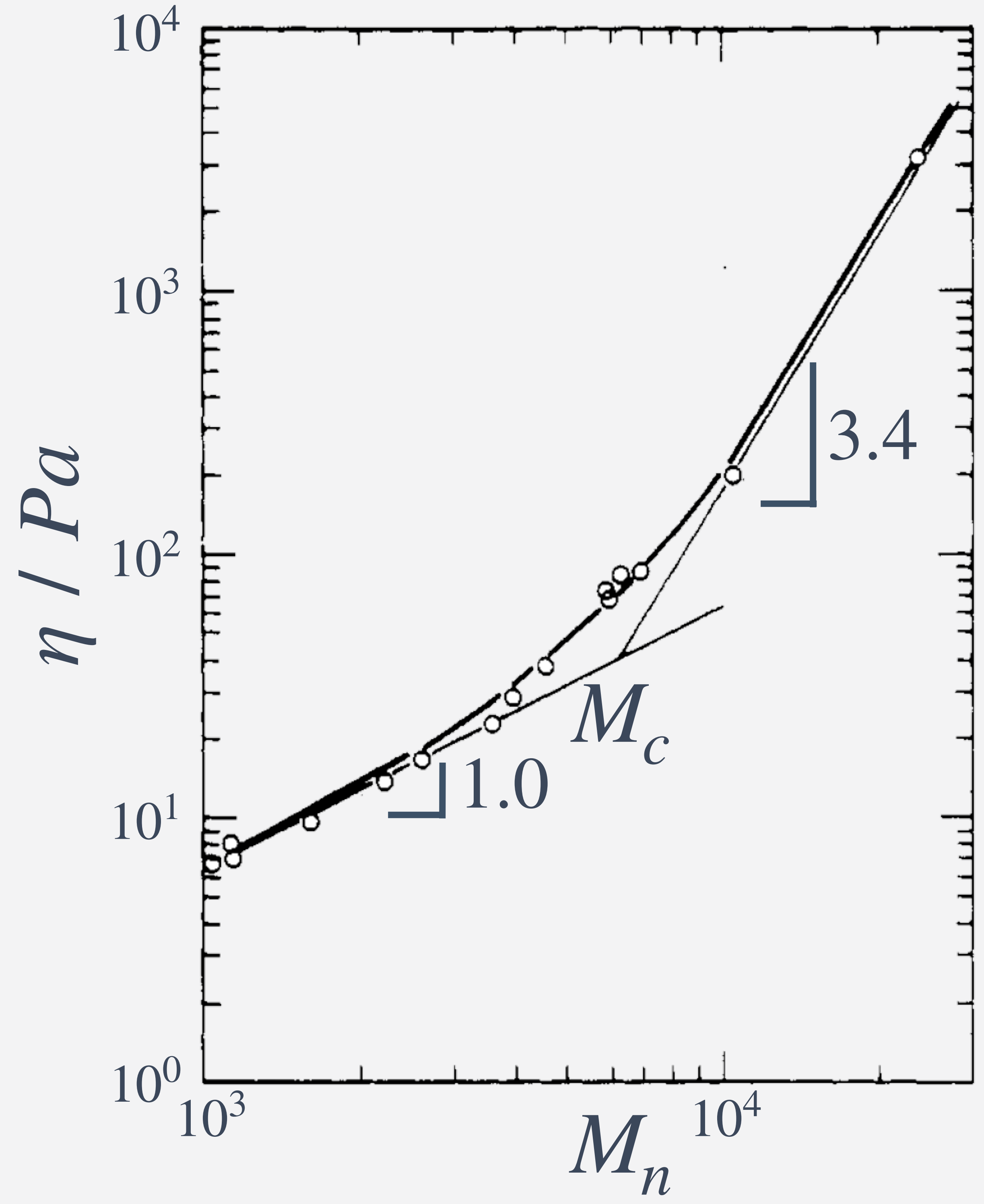
- **when the chain leaves the tube in time τ_d, its centre of mass moves by the average distance $< r_g >$**

Stress Relaxation and Viscosity

- **in the viscous behavior regime ($t \gg \tau_\mathrm{d}$), the theory of Doi & Edwards predicts:**

$$\boxed{\eta \propto \left(\frac{M}{M_\mathrm{e}}\right)^3} \qquad \text{for } M > M_c \equiv 2M_\mathrm{e}$$

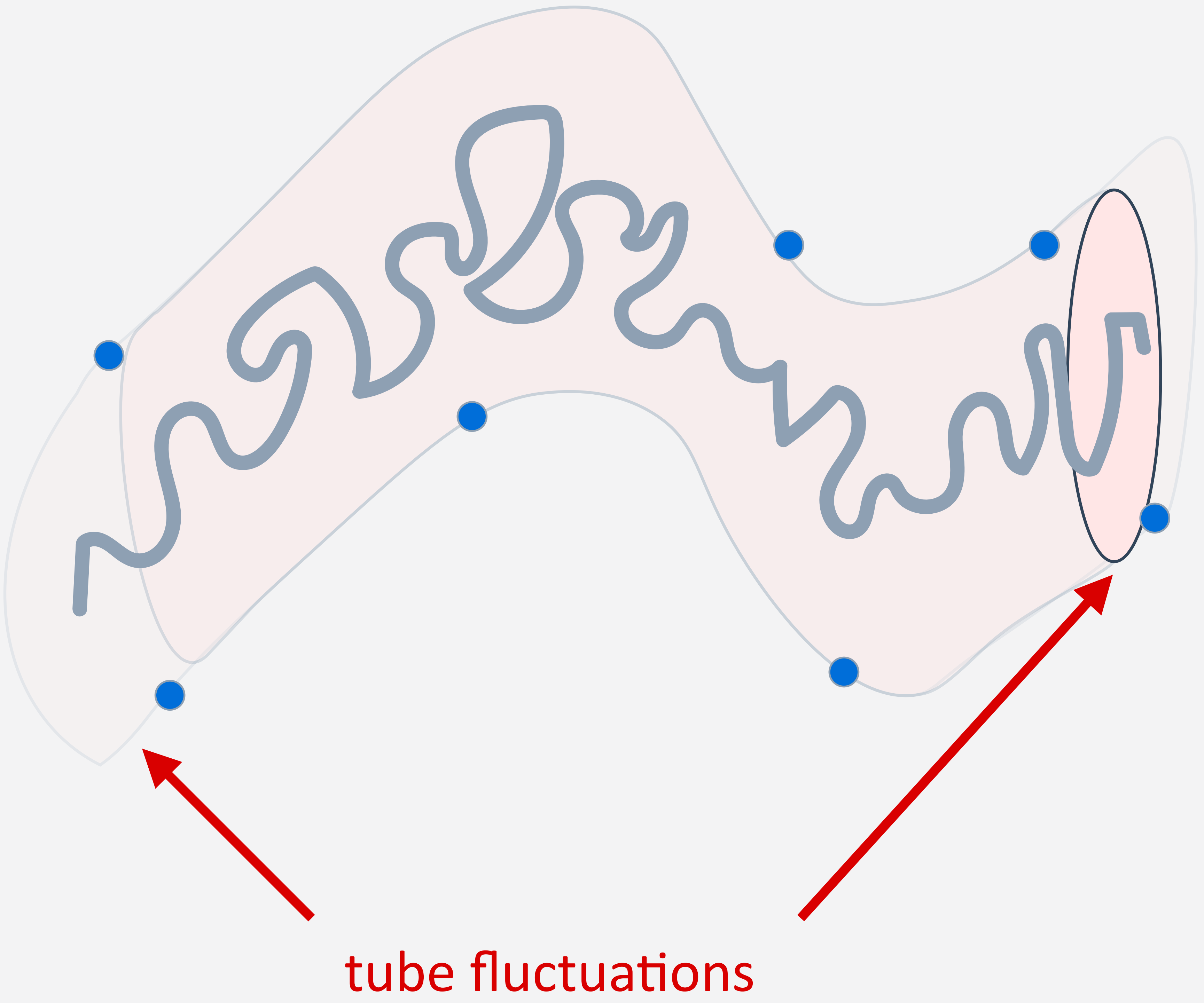
$$\boxed{\eta \propto \frac{M}{M_\mathrm{e}}} \qquad \text{for } M \leq M_c \equiv 2M_\mathrm{e}$$



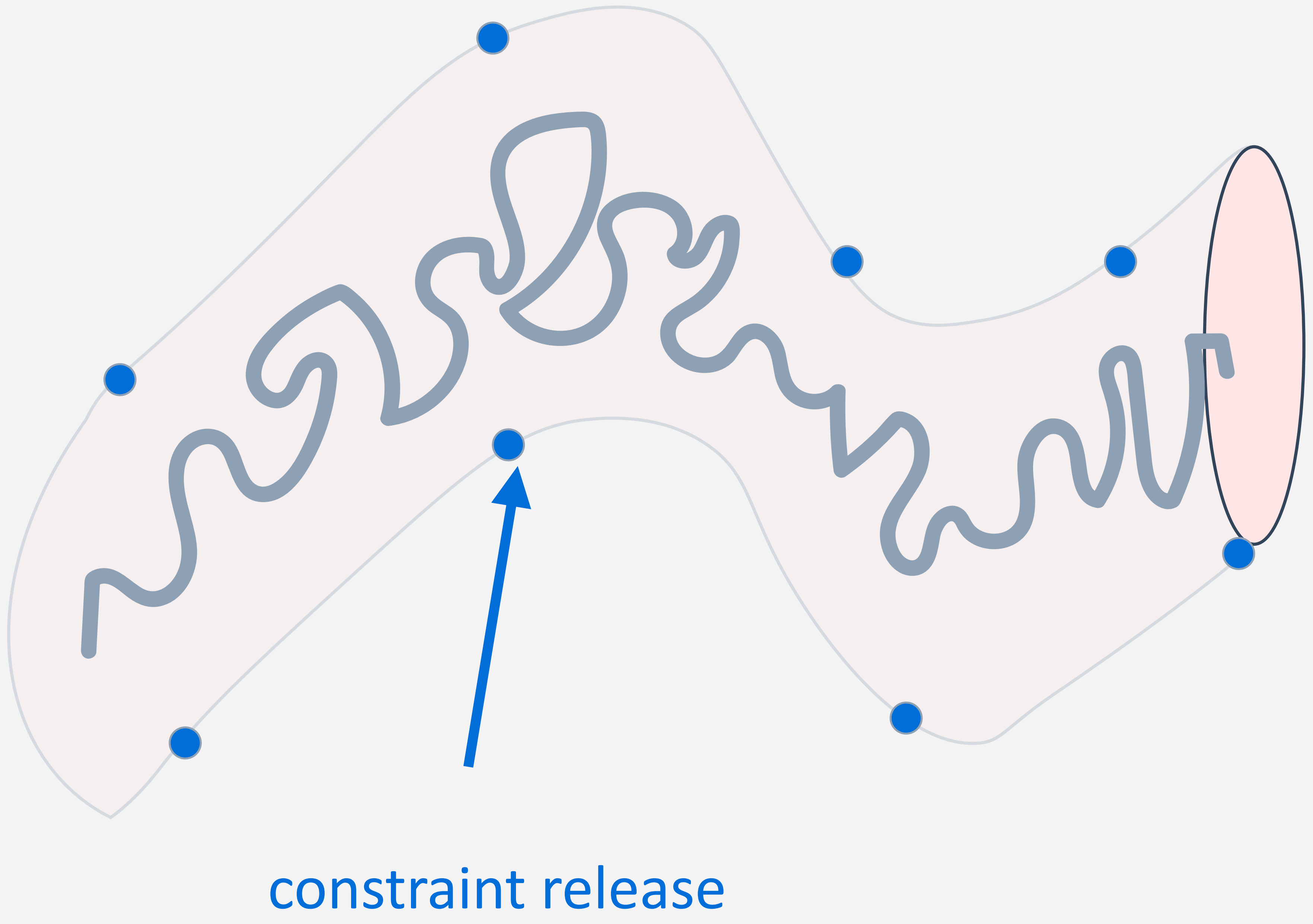
- **measurement of η as a function of M allows to determine M_e**
- the reptation theory of to DeGennes, Doi, and Edwards are applicable to the non-linear viscoelastic regime and is thus widely used, e.g. in flow simulations

Corrections to the Reptation Model

tube length fluctuation



constraint release



- **stronger molar mass dependence of diffusion coefficient, relaxation time, and viscosity**

- **leads to Rouse-like motion of the confining tube itself**

Learning Outcome

- isolated chains may be described using the Rouse approach (springs and beads): better agreement with dynamics in dilute solution when hydrodynamic interactions taken into account (Zimm model).

- for sufficiently long chains in the *condensed* state, entanglement effects must be taken into account. The existence of a rubbery plateau above T_g for non-crosslinked polymers has led to the idea of the “entanglement network” and M_e. For $M < 2M_\mathrm{e}$ entanglement effects are not seen.

- for sufficiently long times and/or at sufficiently high temperatures, entanglement can no longer be considered permanent. General descriptions of viscolesaticity use “tube models” which allow for disentanglement by *reptation*. These account for the strong influence of M on the melt viscosity, diffusion etc.