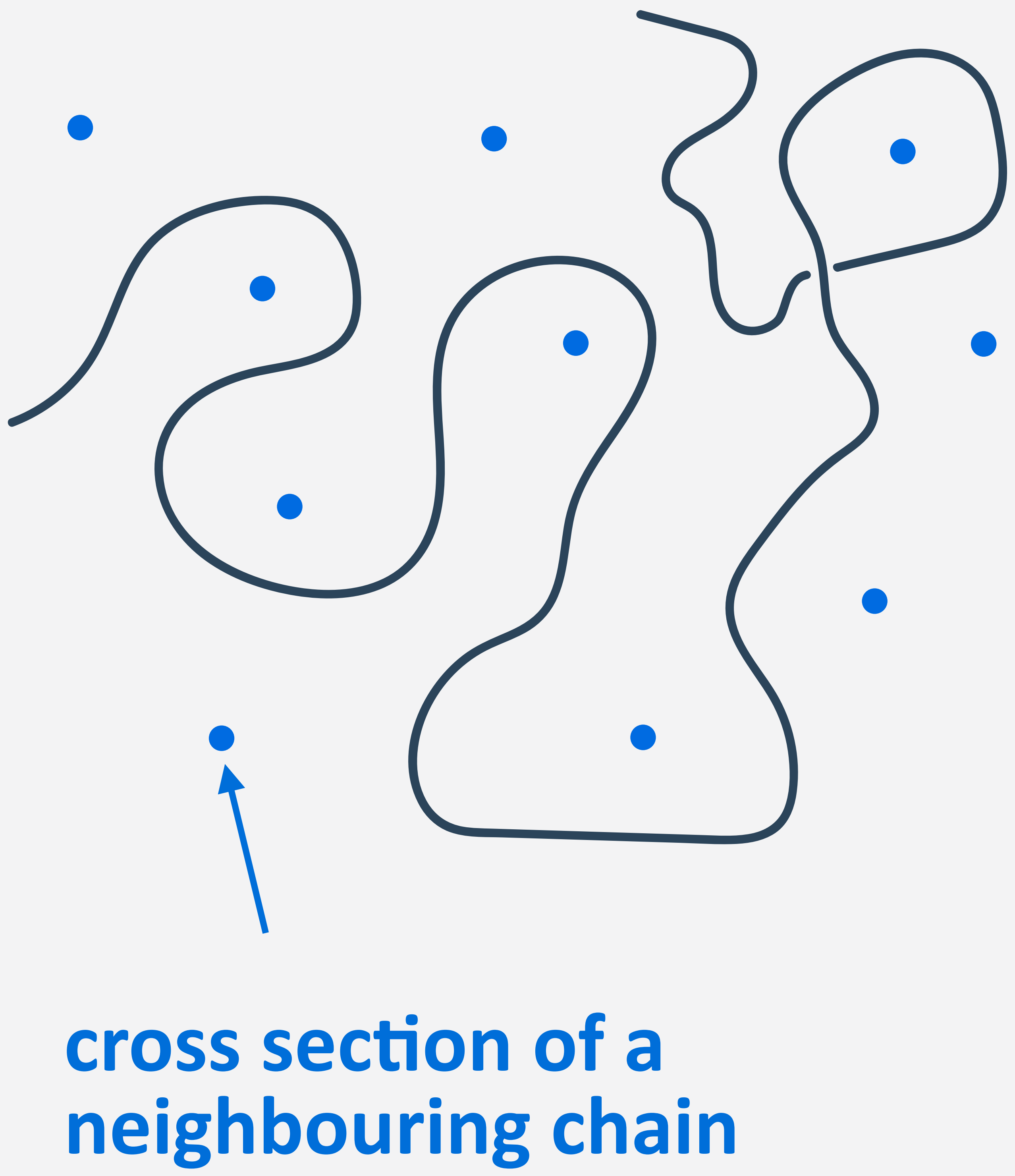
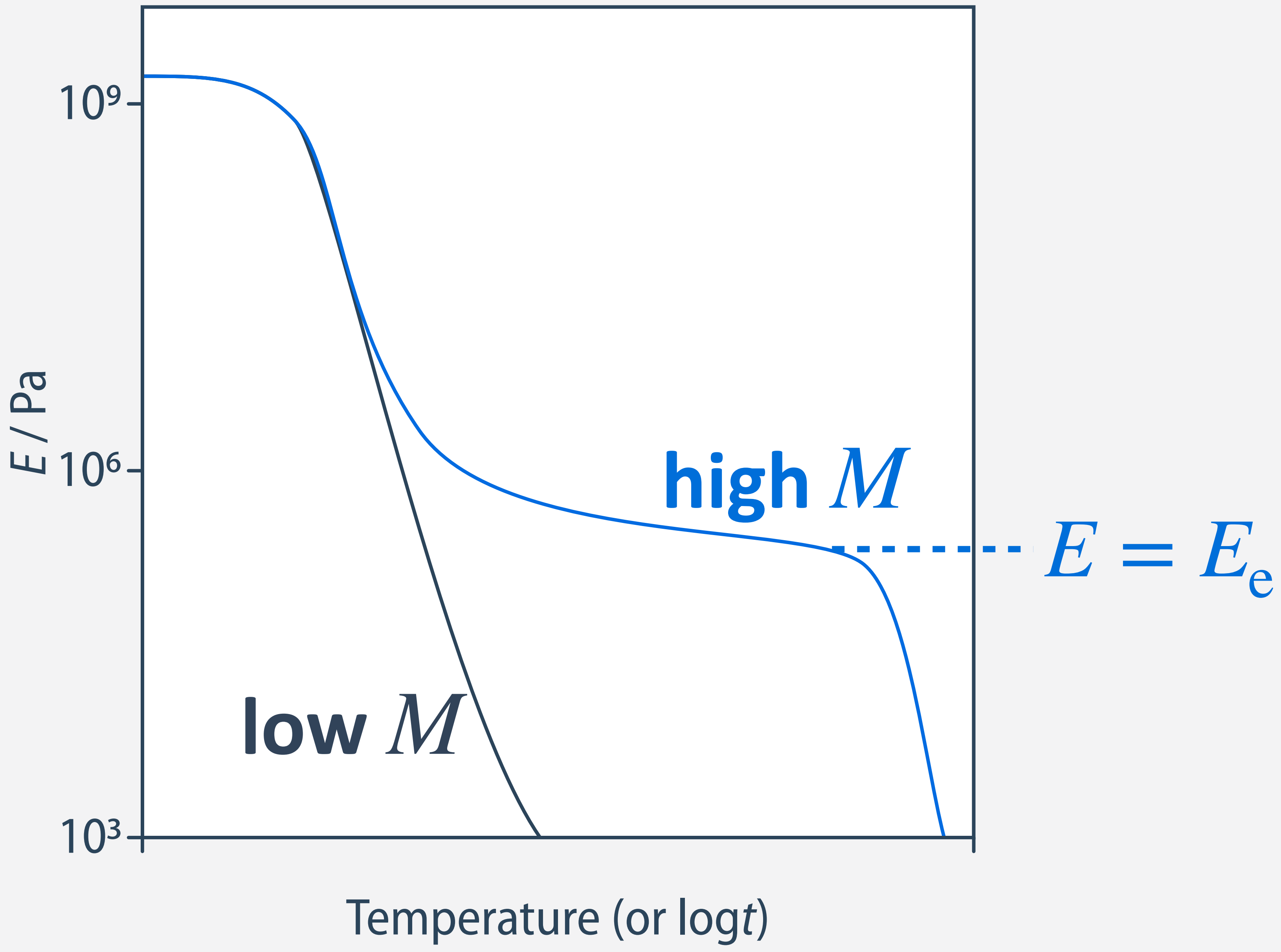
Entanglement

Constraints on a Chain in the Condensed State

Static Models of Entanglement

- strong interpenetration and interchain friction restrict polymer chain mobility
- these topological constraints give rise to an entanglement network even in non-crosslinked systems





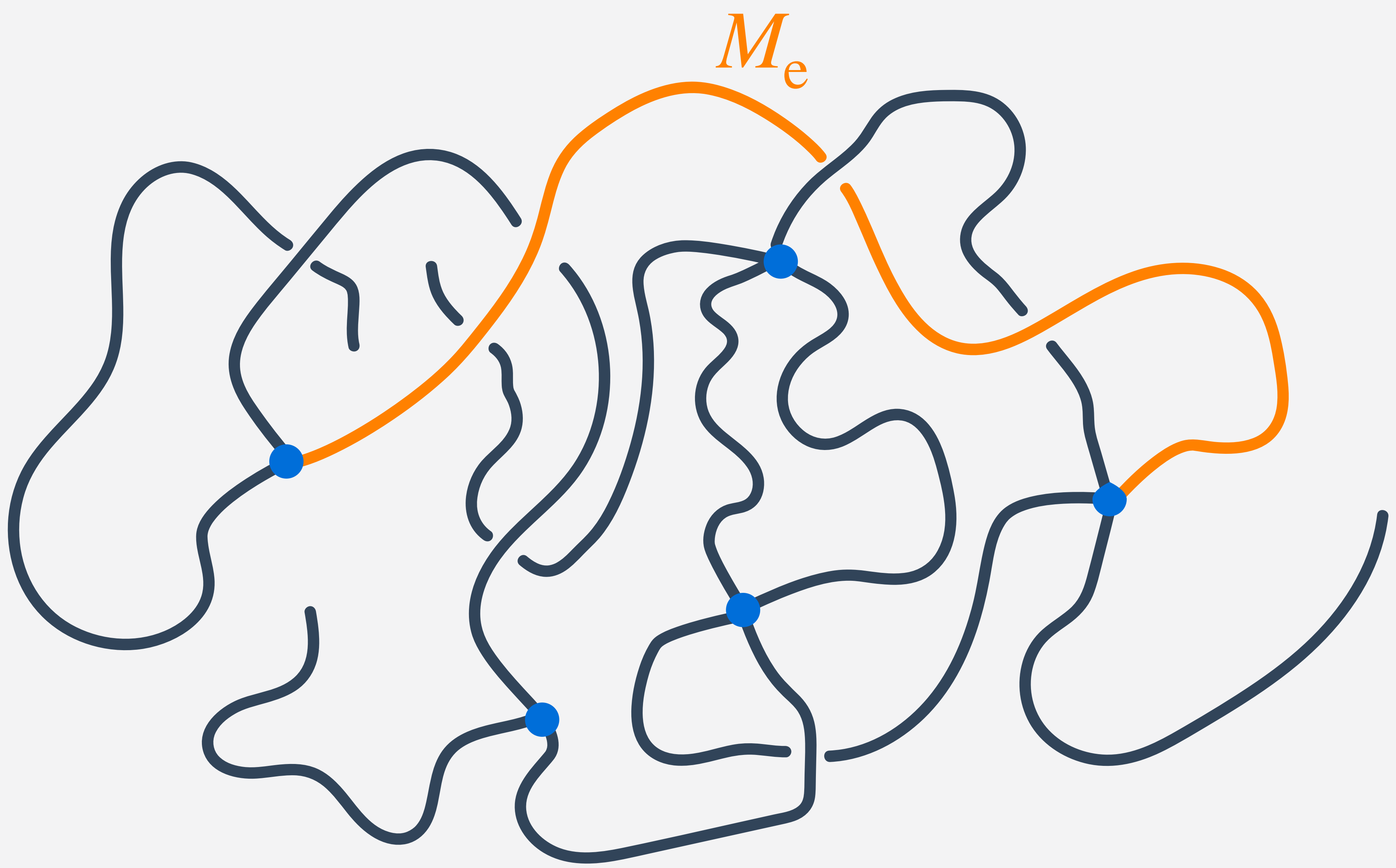
In analogy to elastomers ($E = 3NkT$), we assume:

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

- the rubbery state of amorphous polymers above T_g is therefore due to entanglements

Entanglement Network

- **a non-crosslinked polymer can be viewed as a temporary network of subchains (molar mass M_e) linked by entanglement points**



$$E_\mathrm{e} = 3N_\mathrm{e}kT = 3N_\mathrm{e}\frac{\mathrm{R}}{\mathrm{N_A}}T = 3\mathrm{R}T\boxed{\frac{\rho}{M_\mathrm{e}}}$$

mols of entanglements

$$M_\mathrm{e} = 3\mathrm{R}T\frac{\rho}{E_\mathrm{e}}$$

- **M_e is a key materials parameter:**

for $M > 2M_\mathrm{e} = M_\mathrm{c}$: characteristic long-chain behavior (e.g. rubber elasticity, plateau modulus) appears

for $M < 2M_\mathrm{e} = M_\mathrm{c}$: no entanglement and no rubbery state are obtained (compare to **Exercise #4.3**)

Entanglement Molecular Weight and Chain Structure

- **M_e and the entanglement density N_e vary strongly with polymer structure**
- empirical relations exist that connect M_e, C_∞, and M_b (Wu 1990): $M_\mathrm{e} = 3M_\mathrm{b}{C_\infty}^2$

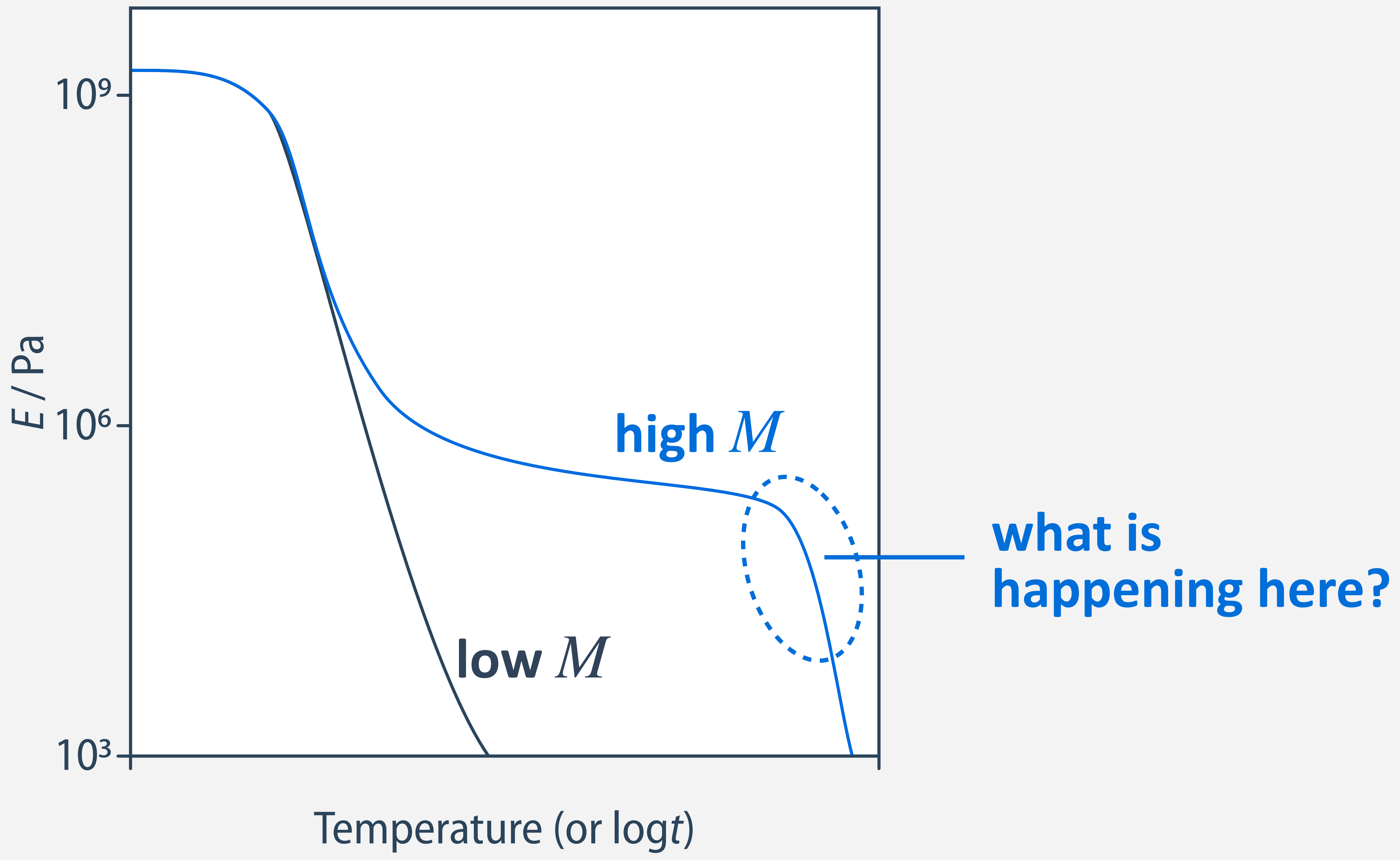
polymer	density	M_e	C_∞	N_e
	g/cm³	g/mol	GPa	mmol/cm³
PS	1.05	18'700	10.8	0.0561
PMMA	1.17	9'200	8.2	0.127
PVC	1.4	5'560	7.6	0.252
PA6	1.08	2'480	6.2	0.435
POM	1.25	2'550	7.5	0.49
PA66	1.07	1'990	6.1	0.537
PE	0.85	1'390	6.8	0.613
PC	1.2	1'790	2.4	0.725
PET	1.33	1'630	4.2	0.815

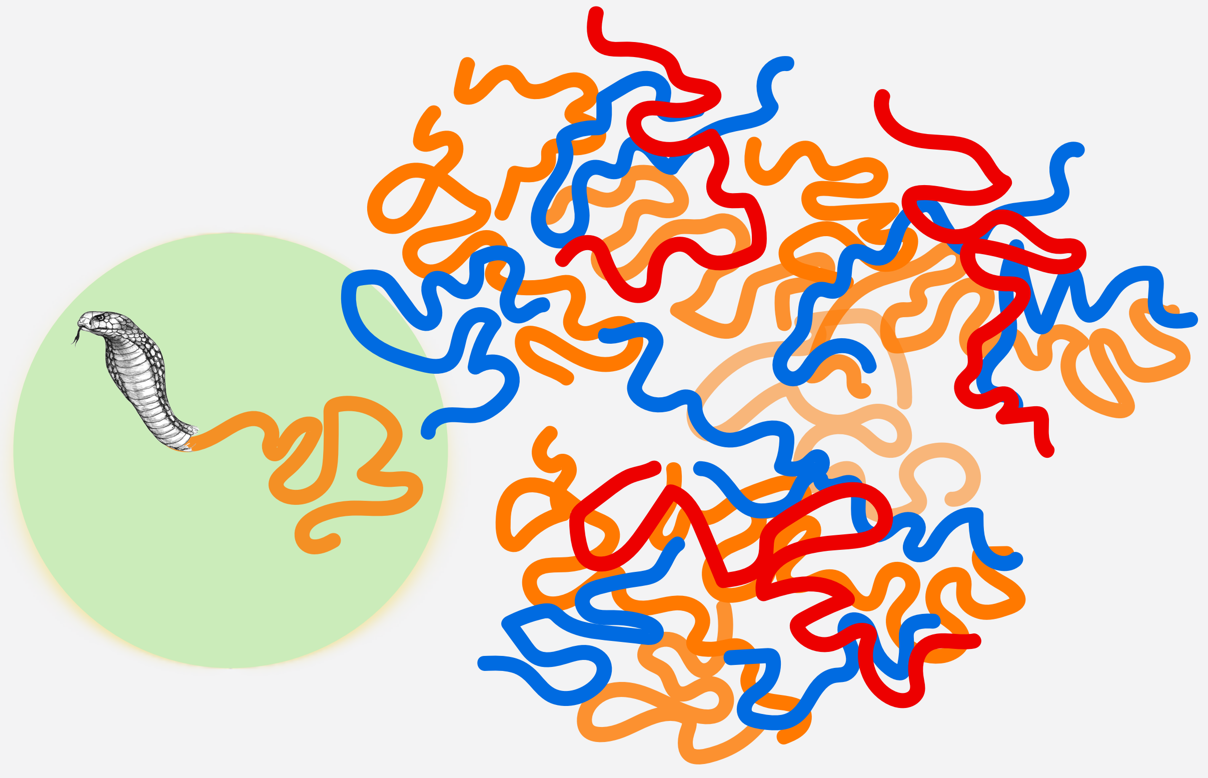
- **chain stiffness or bulky side groups (large C_∞) increase M_e**

Reptation

Disentanglement

- if mobility (temperature or time) increases sufficiently, chains begin to slide past each other

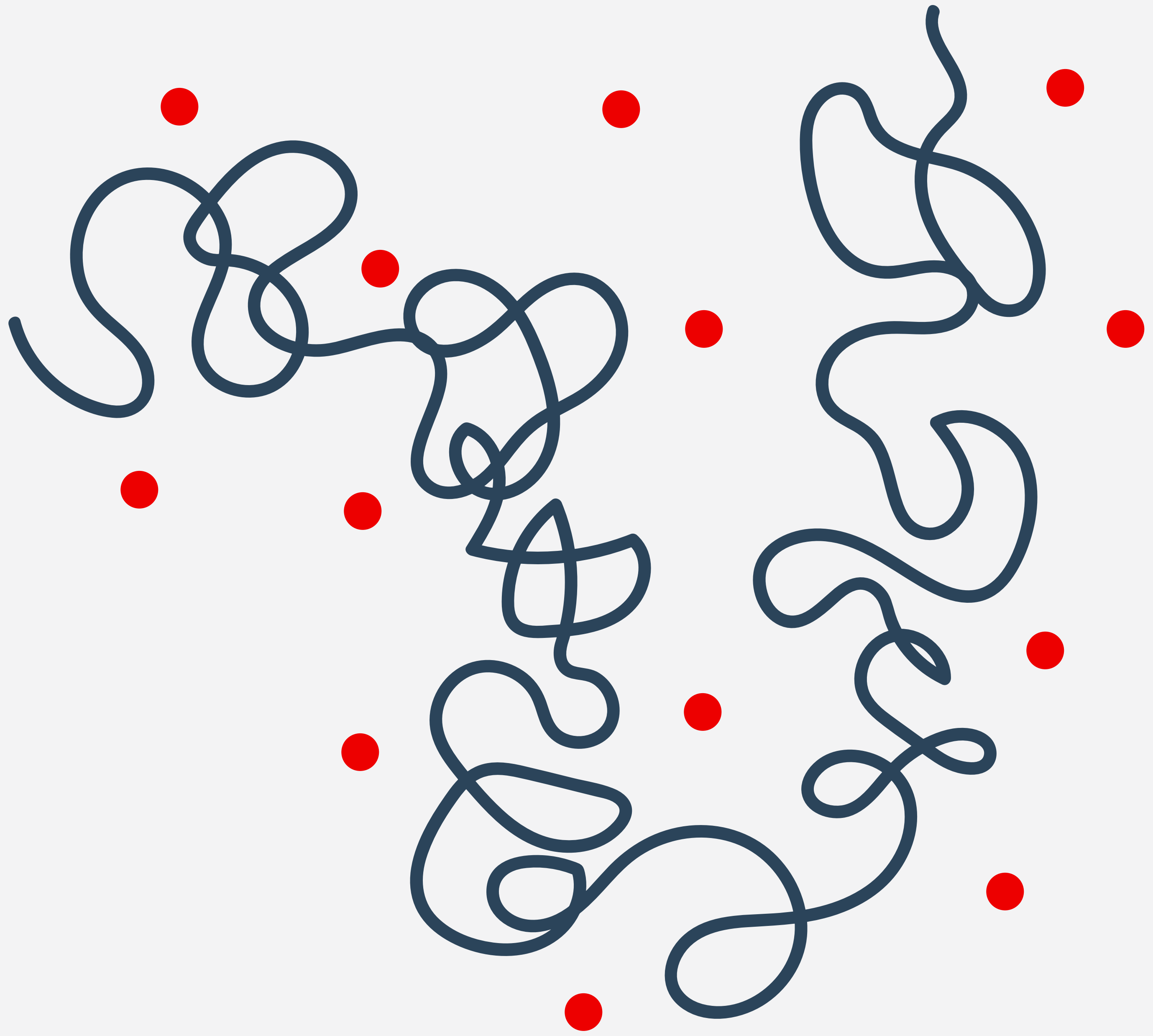




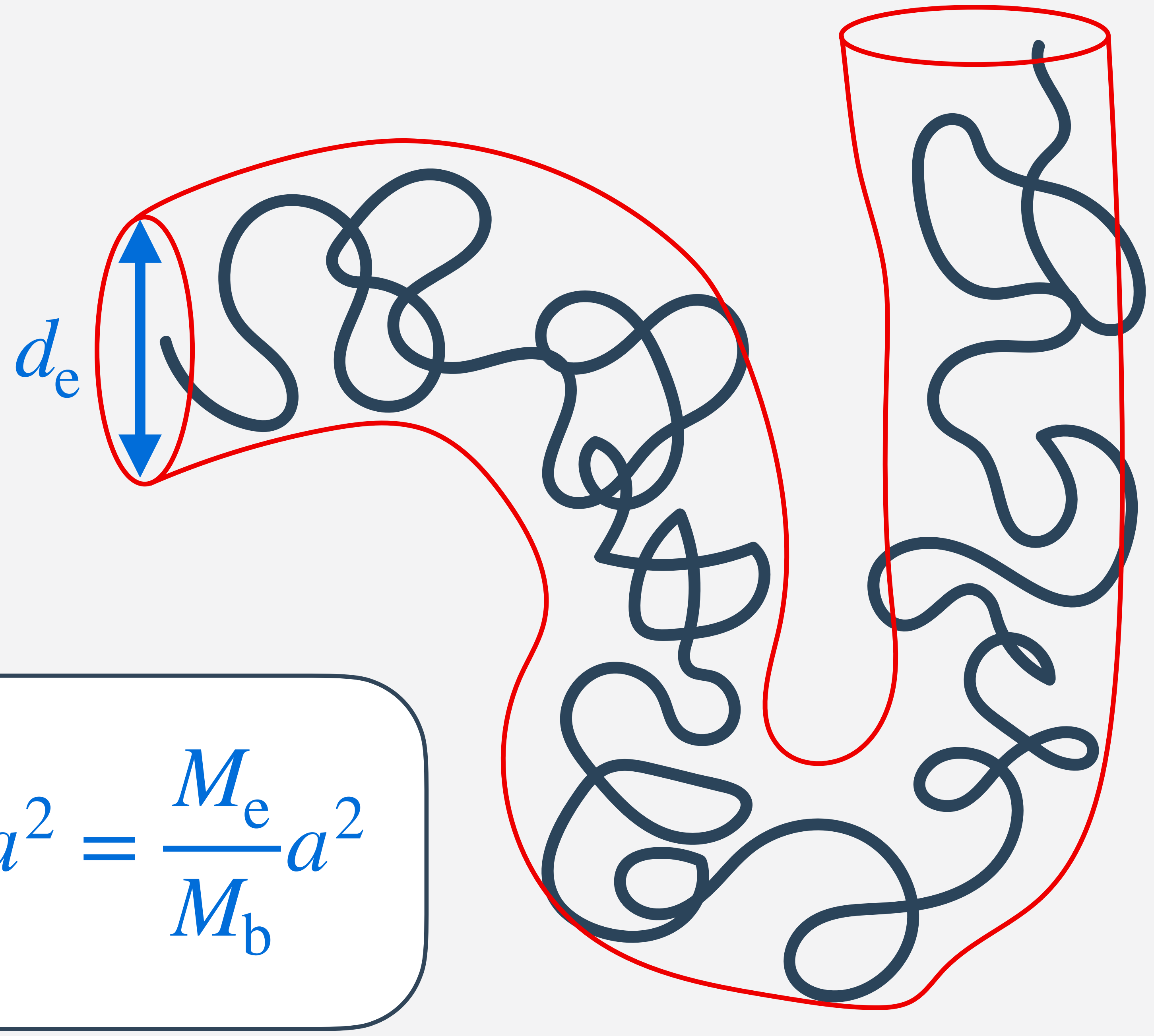
- in the absence of chemical crosslinks, the material gradually transitions from elastic to viscous behavior

The Tube Model

- eveloped by DeGennes, Doi, Edwards
- **in the tube model a chain is confined to a virtual tube representing constraints by neighbouring chains**
- **motion transverse to the tube is suppressed, diffusion along the contour (“reptation”) remains possible**



$$< d_{\mathrm{e}}^2 > = n_{\mathrm{e}} a^2 = \frac{M_{\mathrm{e}}}{M_{\mathrm{b}}} a^2$$



tube contour length:

$$L = \frac{M}{M_{\mathrm{e}}} d_{\mathrm{e}}$$

- **the diameter of the tube d_{e} corresponds to the length of a chain segment with mass M_{e}**

key concept: see Reader on Tube Model

The Entanglement Time

- stress relaxation and relaxation times follow the Rouse model for unentangled motion

$$\mathrm{G}(t) = N\mathrm{k}T\sum_{p=1}^{m} e^{-\frac{t}{\tau_p}} \qquad \tau_p \approx \frac{\xi_0 n^2 a^2}{6\pi^2 p^2 \mathrm{k}T}$$

- for long chains, relaxation of segments longer than d_e is hindered by the tube constraint:

$$\tau_p = \infty, \quad \text{for} \quad \frac{n}{p}a^2 > d_\mathrm{e}^2$$

- the **entanglement time**:

$$\tau_\mathrm{e} = \frac{\xi_0 n^2 a^2}{6\pi^2 \mathrm{k}T} \cdot \frac{d_\mathrm{e}^4}{n^2 a^4} = \frac{\xi_0 n_\mathrm{e}^2 a^2}{6\pi^2 \mathrm{k}T}$$

$$\boxed{\tau_\mathrm{e} = \frac{\xi_0 a^2}{6\pi^2 \mathrm{k}T}\left(\frac{M_\mathrm{e}}{M_\mathrm{b}}\right)^2}$$

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

key concept: see Reader on Tube Model

Stress Relaxation within the Tube

- **for $t < \tau_e$: Rouse-like modes within the tube relax local stresses**

$$G(t) = NkT \underbrace{\sum_{p=1}^{n/n_\mathrm{e}} e^{-\frac{t}{\infty}}} + NkT \underbrace{\sum_{p=n/n_\mathrm{e}}^{m} e^{-\frac{t}{\tau_p}}}$$

low Rouse modes (segments larger than an entanglement strand) are **blocked** by the tube

higher Rouse modes (segments shorter than an entanglement strand) **relax freely** within the tube

- **for $\tau_\mathrm{e} < t < \tau_\mathrm{d}$: the tube constraint persists, and stress relaxation reaches a plateau modulus**

$$G_\mathrm{e} = NkT \sum_{p=1}^{n/n_\mathrm{e}} 1 = \frac{n}{n_\mathrm{e}} NkT$$

$$\boxed{G_\mathrm{e} = N_\mathrm{e} kT}$$

N_e: entanglement density

- the remaining (unrelaxed) modes correspond to the network of entanglement strands
- **this regime corresponds to the rubbery plateau observed experimentally**

see Reader on Tube Model

Relaxation According to the Tube Model

- **the chain does not remain blocked, but gradually leaves the tube after the disentanglement time τ_d**

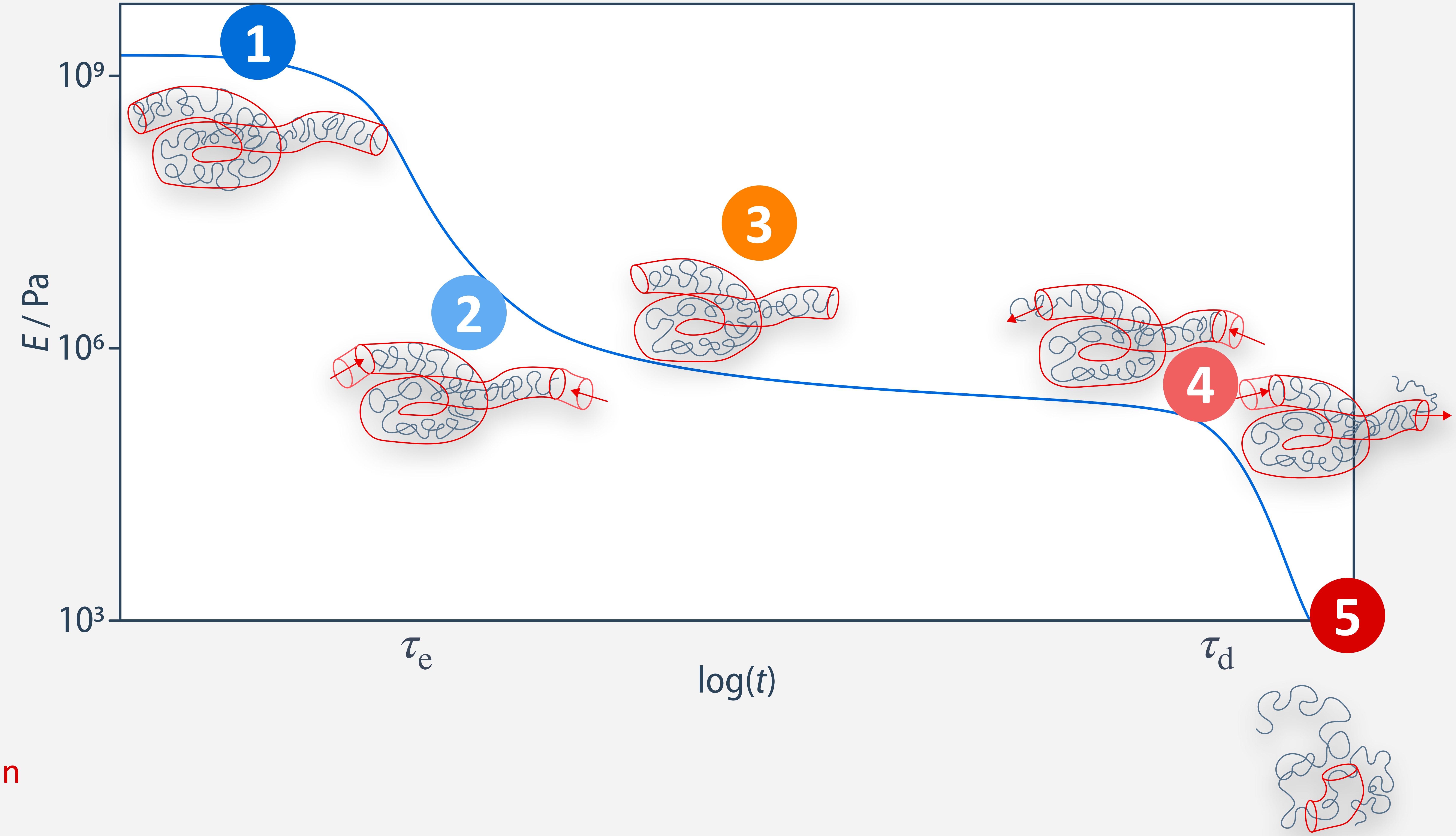
① **instant tube & chain deformation:** no relaxation, high stress

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 **reptation begins at $t = \tau_\mathrm{d}$**

⑤ **random coil conformation fully restored:** complete stress relaxation at $t \gg \tau_\mathrm{d}$



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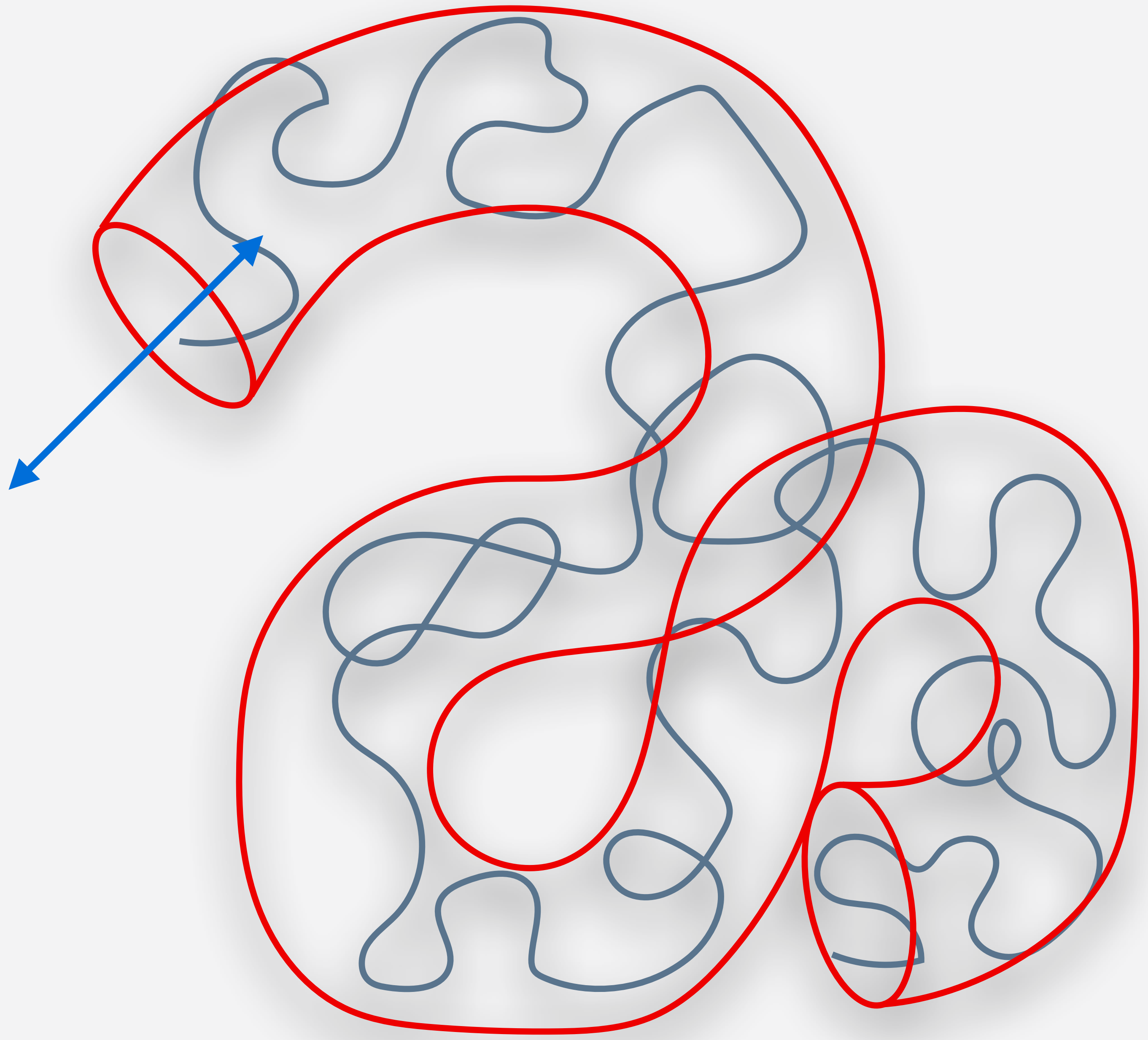
Molecular Weight Dependence of Reptation

- **in the Rouse model, the diffusion coefficient along the tube is inversely proportional to M:** $D_\mathrm{R} \propto \dfrac{1}{M}$



the diffusion distance
after time t (Fick's law):

$$x = \sqrt{D_\mathrm{R} t} \propto \sqrt{\frac{t}{M}}$$

contour length of the tube:

$$L = \frac{M}{M_\mathrm{e}} d_\mathrm{e}$$

- τ_d **corresponds to diffusion along the tube:**

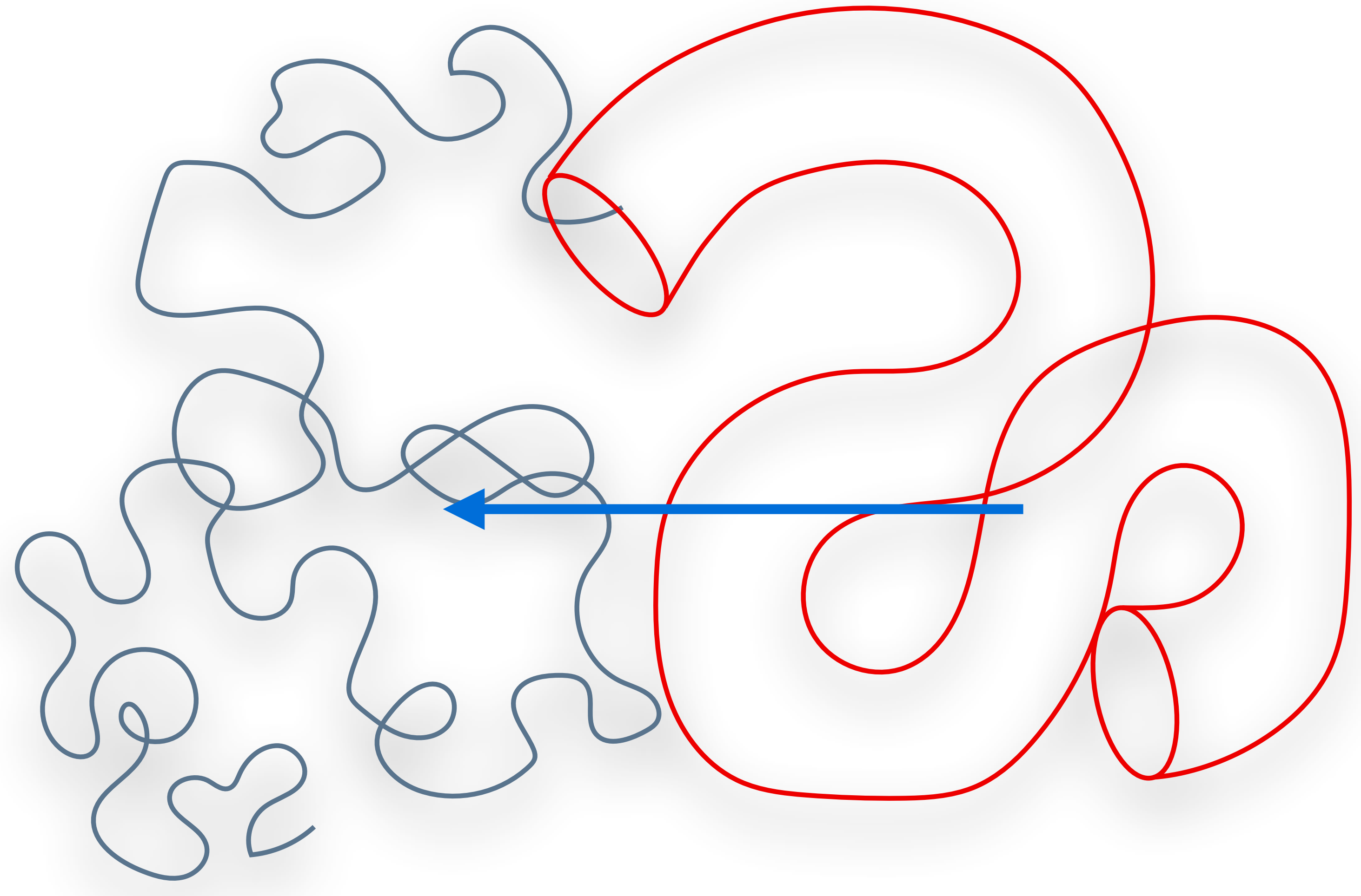
$$\tau_\mathrm{d} \approx \frac{L^2}{D_\mathrm{R}} = \frac{\xi_0 n}{\mathrm{k}T}\left(\frac{M}{M_\mathrm{e}}\right)^2 d_\mathrm{e}^2$$

$$\boxed{\tau_\mathrm{d} = 6\pi^2\left(\frac{M}{M_\mathrm{e}}\right)^3 \tau_\mathrm{e}}$$

- $\tau_\mathrm{d} \propto M^3$ (while τ_e is independent of M)**: strong molar-mass dependence of rubbery and flow behavior**

Experimental Evidence

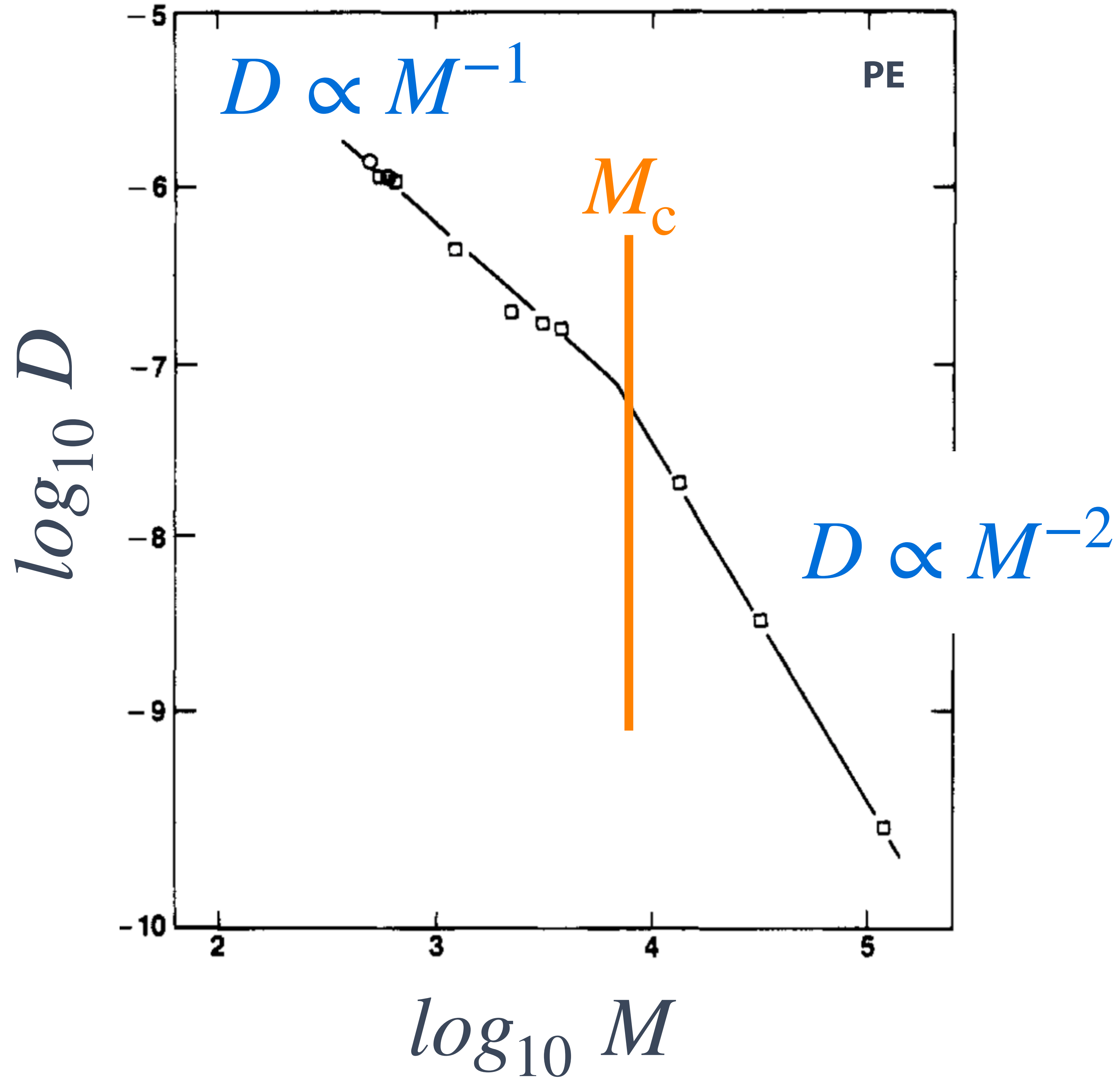
- the self-diffusion coefficient D can be measured by neutron scattering



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

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

diffusion coefficient



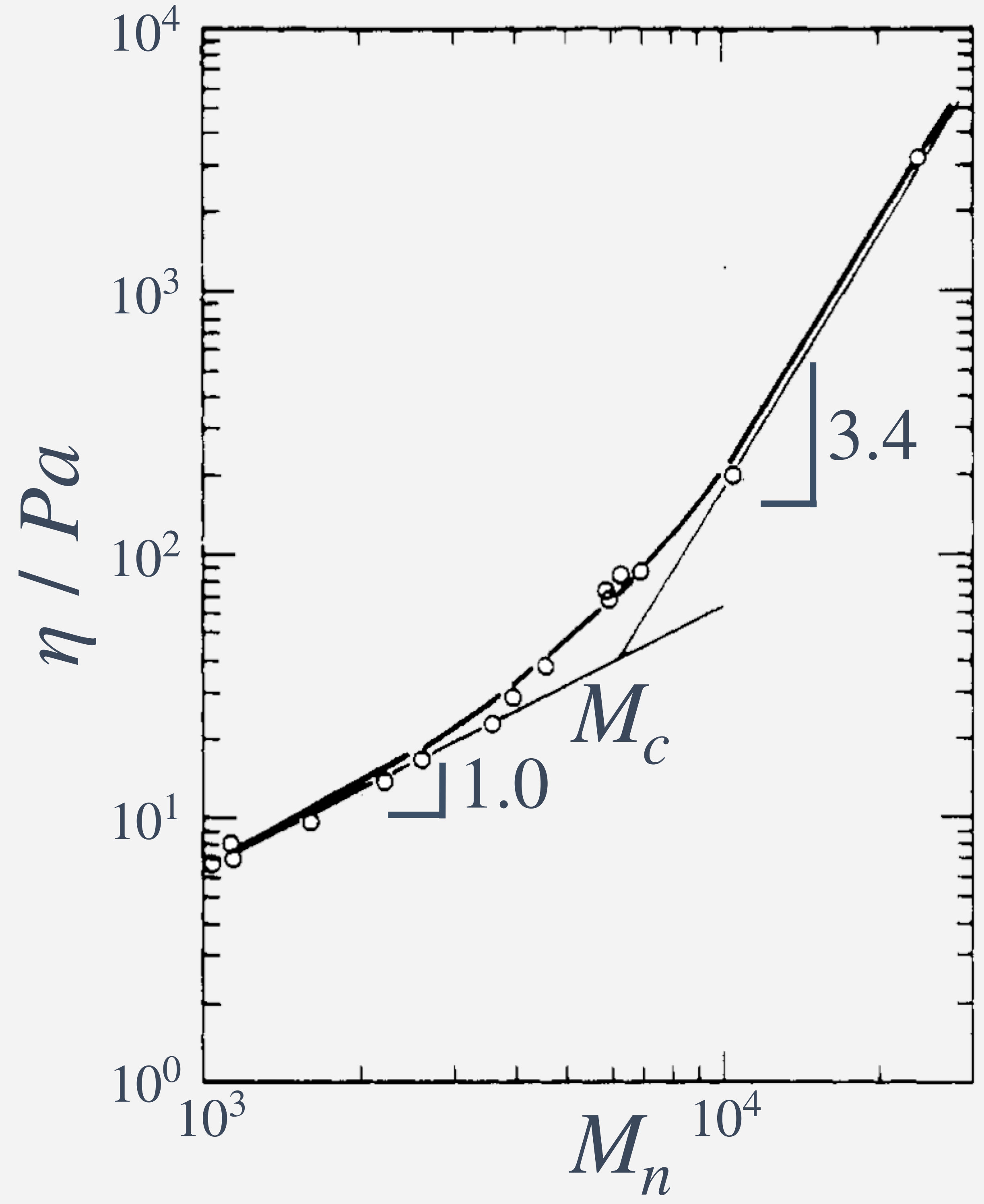
- **when the chain leaves its tube in time τ_{d}, its centre of mass moves roughly by the radius of gyration R_{g}**

Stress Relaxation and Viscosity

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

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

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



- **measurement of η as a function of M allows to determine M_e**
- the reptation theory extends into the nonlinear viscoelastic regime: widely used in flow simulations

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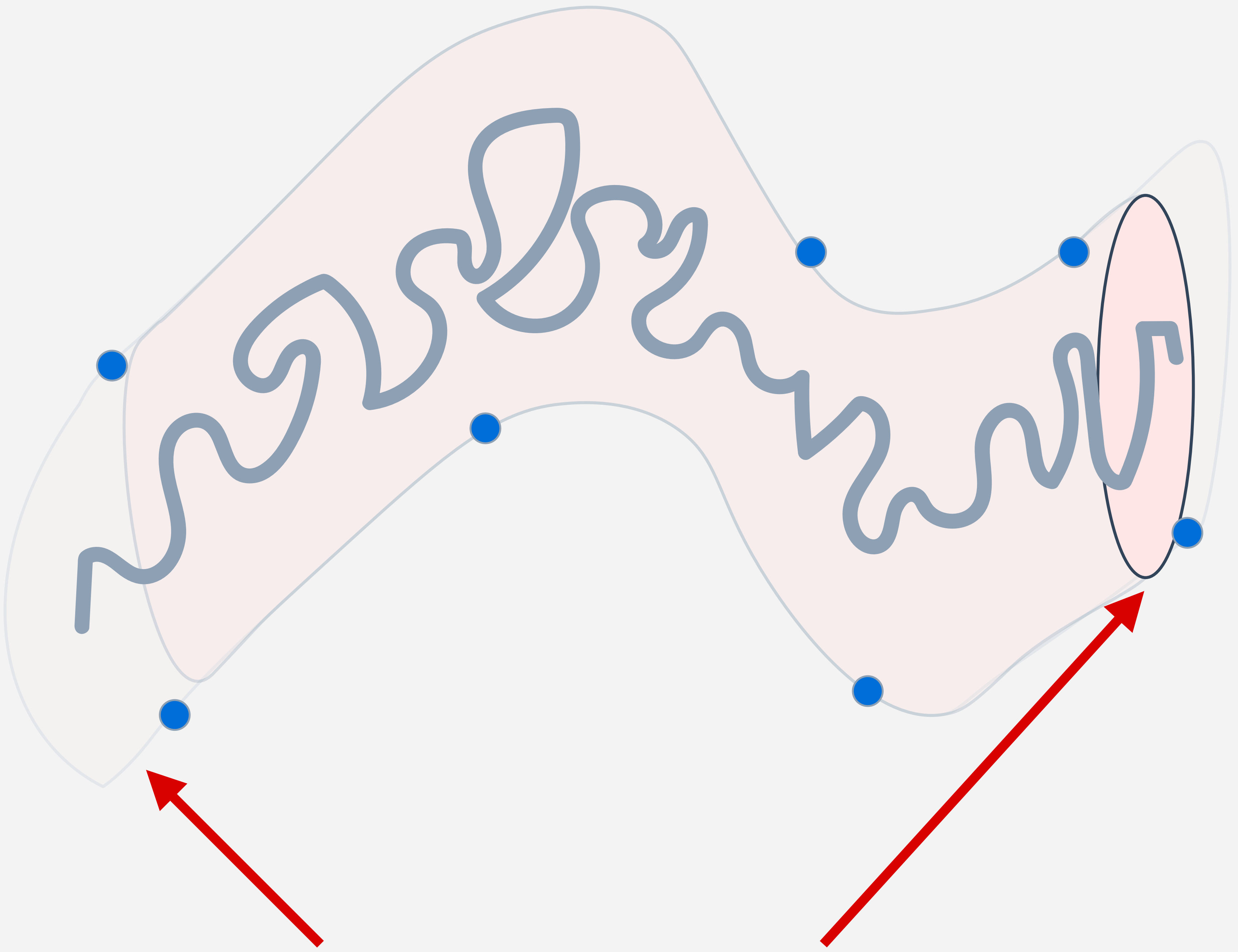
Corrections to the Reptation Model

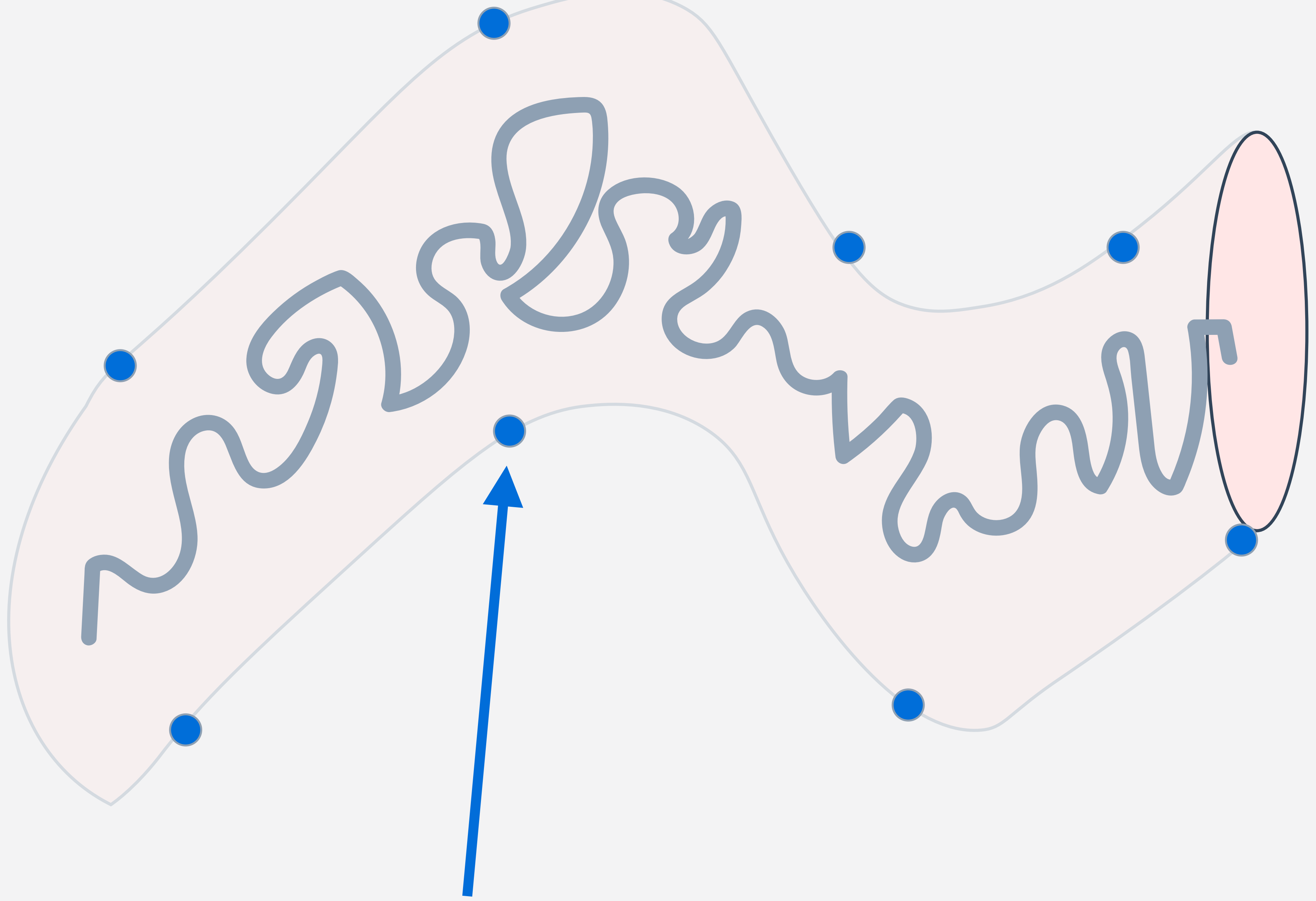
tube length fluctuation



tube length fluctuations

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

constraint release



constraint release:
neighbouring chains also move

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

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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.