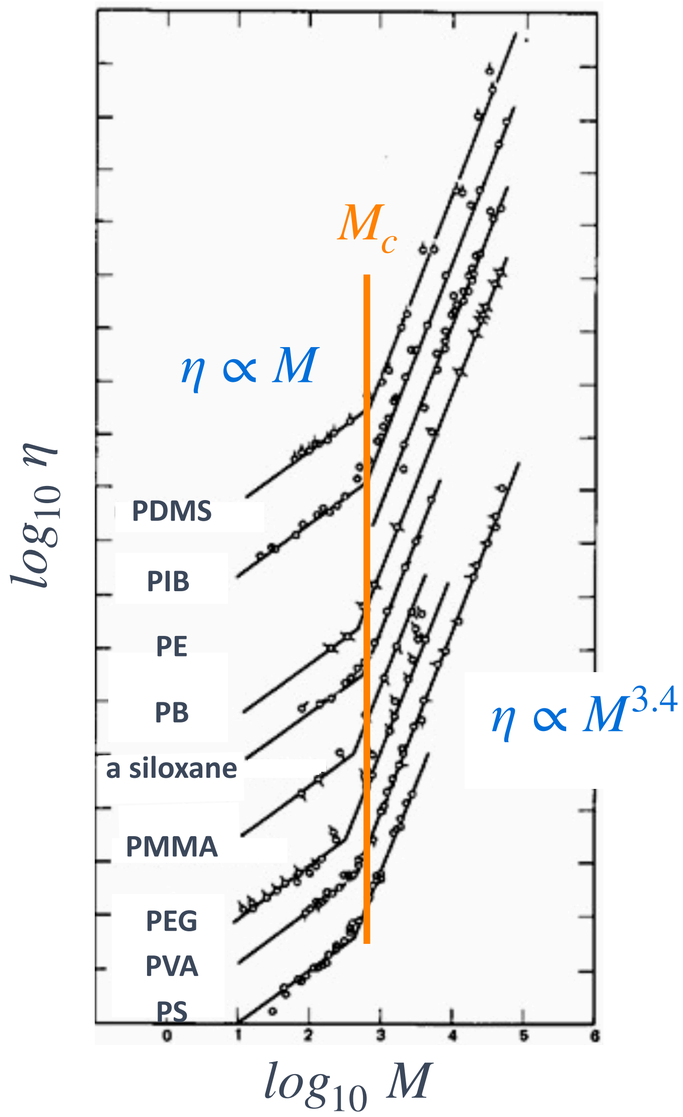
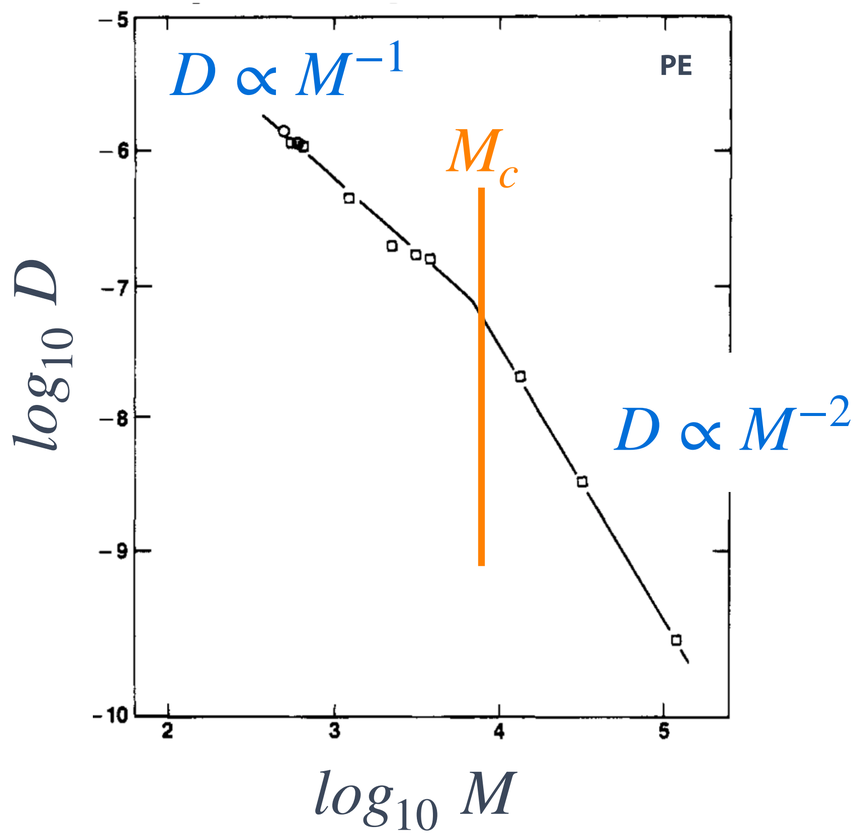
Entanglement & Reptation

Universal Molar Mass Dependence

Viscosity



Diffusion Coefficient

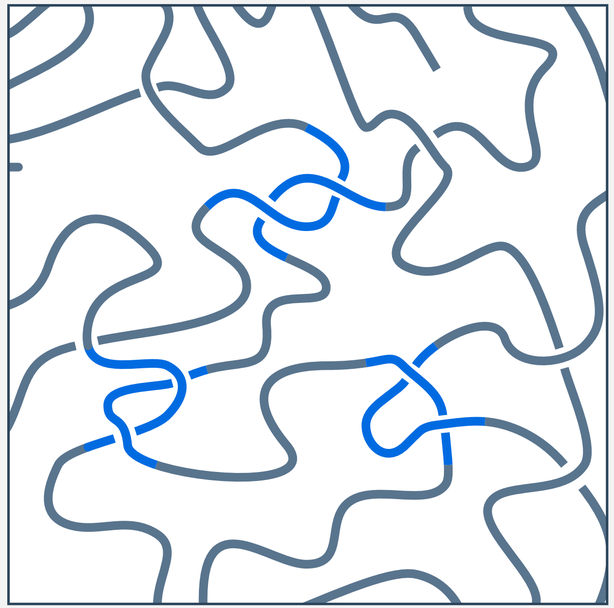


- polymer dynamics exhibit universal power laws with *M*
- what is the molecular origin of these dependencies?

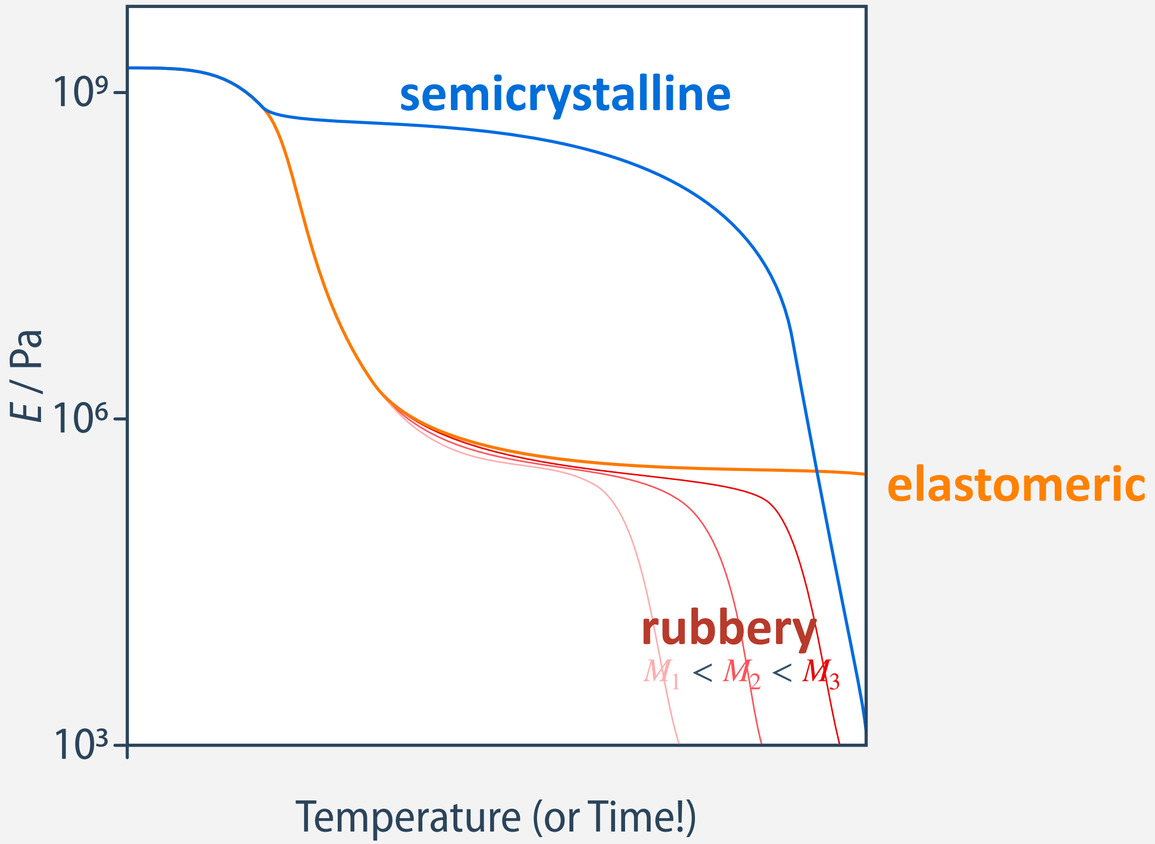
G. C. Berry, T. G. Fox, *Adv. Polym. Sci.* **1968**, *5*, 261; D. S. Paerson *et al*. *Macromolecules* **1987**, *20*, 1133.

Entanglement

- polymer chains cannot pass through one another by simple translational motion
- such topological constraints lead to the formation of an entanglement network



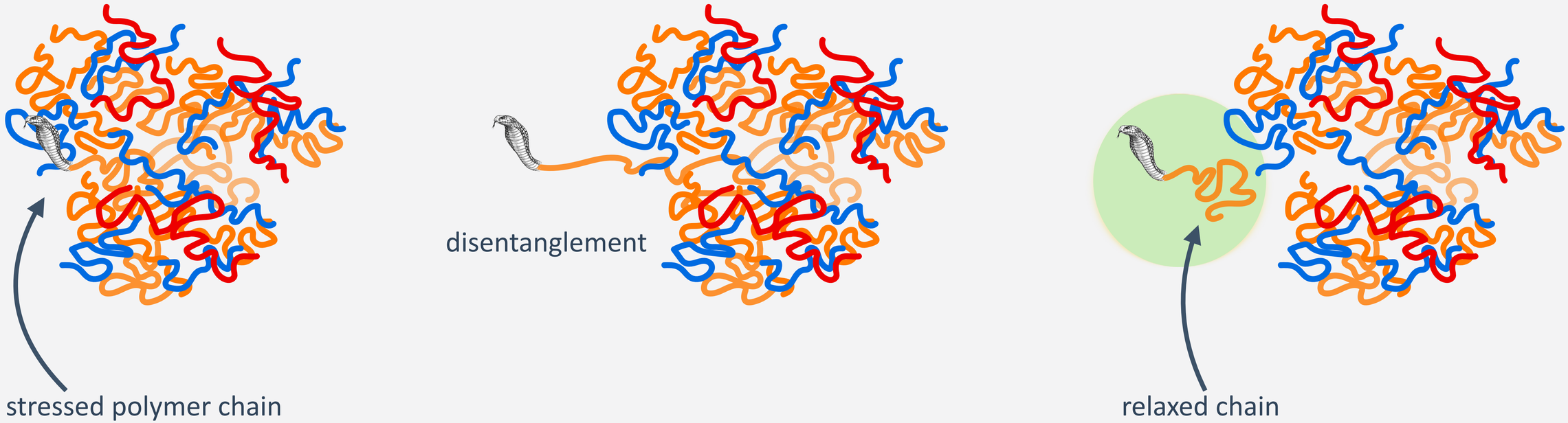
The static picture representing entanglements as “knots” does not reflect the purely dynamic origin of this phenomenon!



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

Reptation

- **entangled chains can still move by disentangling over time or at high T**

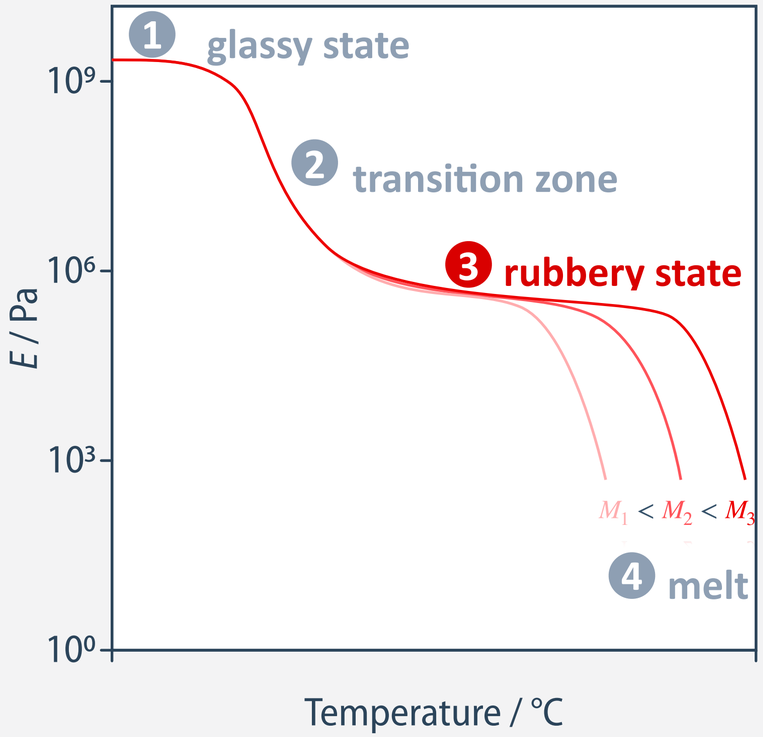


- **this snake-like motion is called “reptation”** (from *reptare*, to creep)

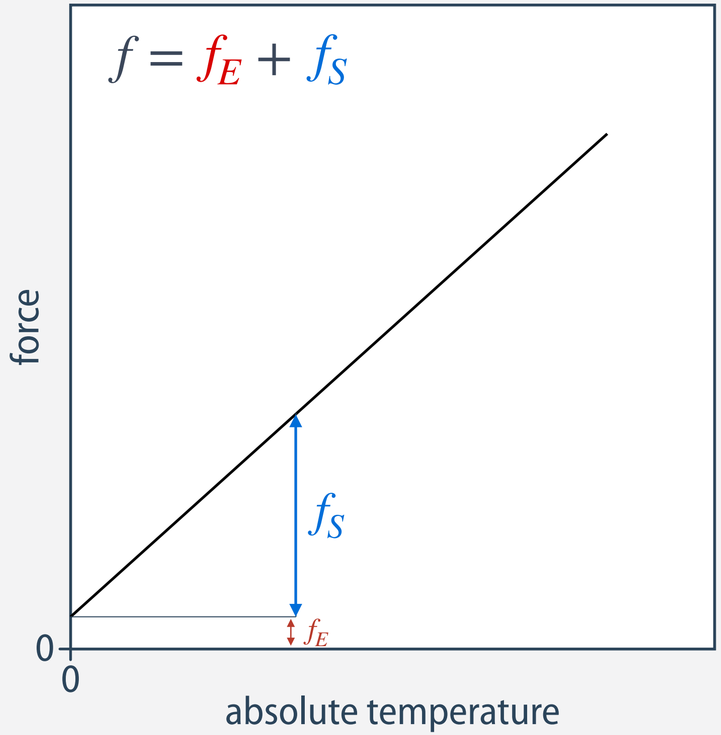
Dynamics of an Isolated Chain in a Solvent

Revision: Rubber Elasticity

universal trend of Young's modulus



energetic components of the elastic force

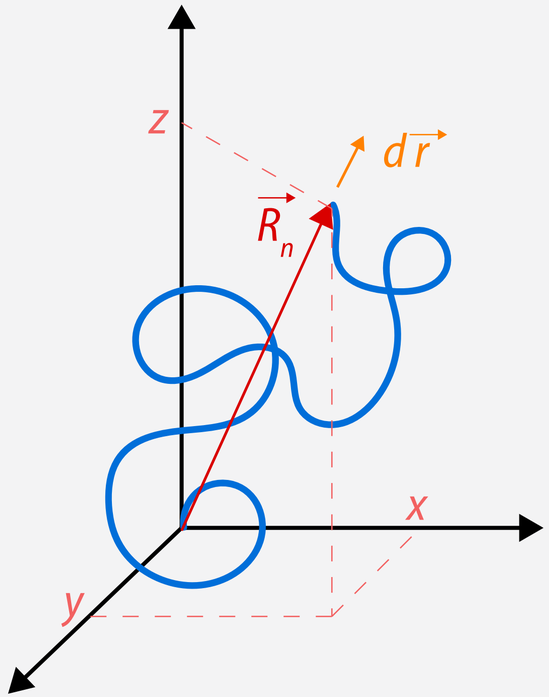


- rubber elasticity is primarily entropic in origin; for ideal rubbers, $f_E = 0$!
- the restoring force arises from reduced chain configurational entropy during stretching

Quantification of the Elastic Force

- the entropy of an ideal polymer chain follows a **Gaussian distribution** of end-to-end distances:

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



before deformation:

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

entropy change during small displacement $\mathrm{d}\vec{r}$:

$$\mathrm{d}S^c \approx -\frac{3\mathrm{k}\vec{R}_n \cdot \mathrm{d}\vec{r}}{na^2}$$

force acting in the direction of this displacement $\mathrm{d}\vec{r}$:

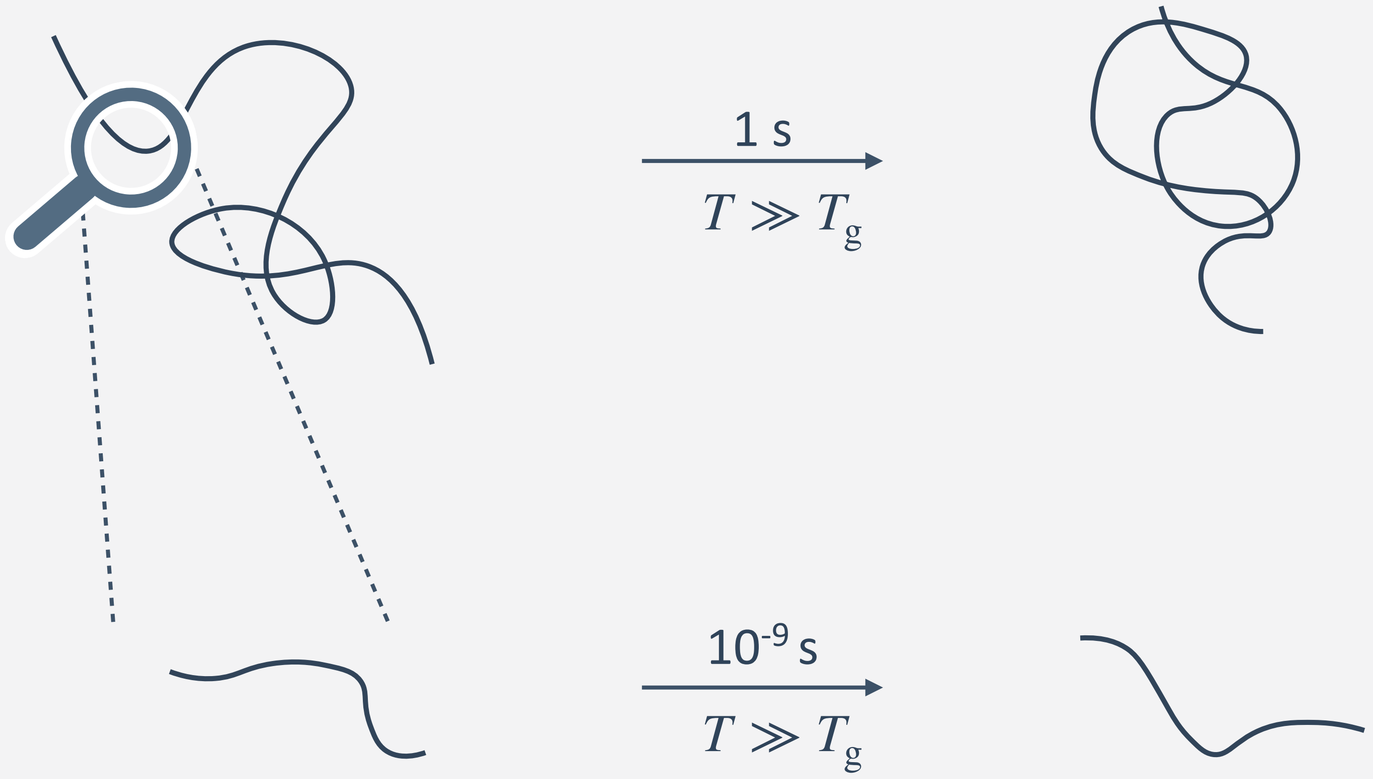
$$f^c \approx -\frac{3\mathrm{k}T\vec{R}_n}{na^2}$$

- **like a spring, the chain resists stretching or compression and opposes its displacement**

see Exercise 7

Time-dependent Response of Molten Polymer Chains

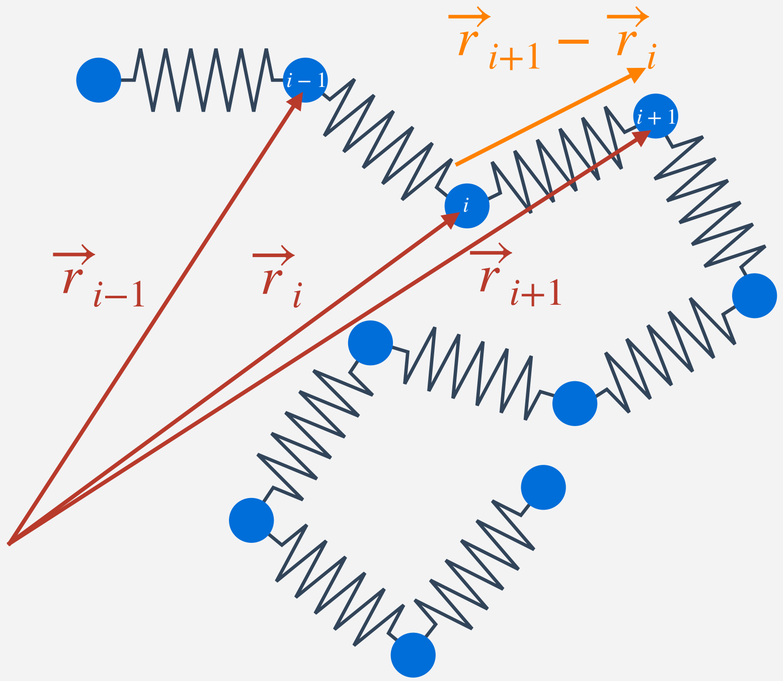
- **relaxation times depend strongly on the size of the moving segment**



- **local rearrangements are fast** (controlled by the nature of the repeating unit itself)
- **global equilibration of the full chain that is much slower and dependent on *M***

Isolated Chains in a Solvent

- the viscoelastic response of a dilute solution reflects **single-chain dynamics**
- the **Rouse model** represents a chain with n bonds of length a as m beads connected $m-1$ springs
- **each represents a Gaussian subchain of n_s bonds**



mean-square end-to-end distance:

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

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

$$f = -\frac{3\mathrm{k}T}{n_s a^2}(\vec{r}_{i+1} - \vec{r}_i)$$

(see **exercise 7**)

The Rouse Model for Unentangled Polymers

- **balance between elastic deformation and frictional drag on each bead i:**

$$f = \frac{3\mathrm{k}T}{R_s^2}(\vec{r}_i - \vec{r}_{i-1}) + \frac{3\mathrm{k}T}{R_s^2}(\vec{r}_i - \vec{r}_{i+1}) = \frac{3\mathrm{k}T}{R_s^2}(2\vec{r}_i - \vec{r}_{i-1} - \vec{r}_{i+1}) = -\xi\frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t}$$

entropic elasticity due to deformation of the two springs

viscous force

- **for a whole chain: m coupled equations; solved via normal mode transformation;**
  for a dilute solution containing N_m chains per volume, we get m independent equations with solutions:

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

- **each vibrational mode p relaxes on its own time scale τ_p (Rouse relaxation spectrum):**

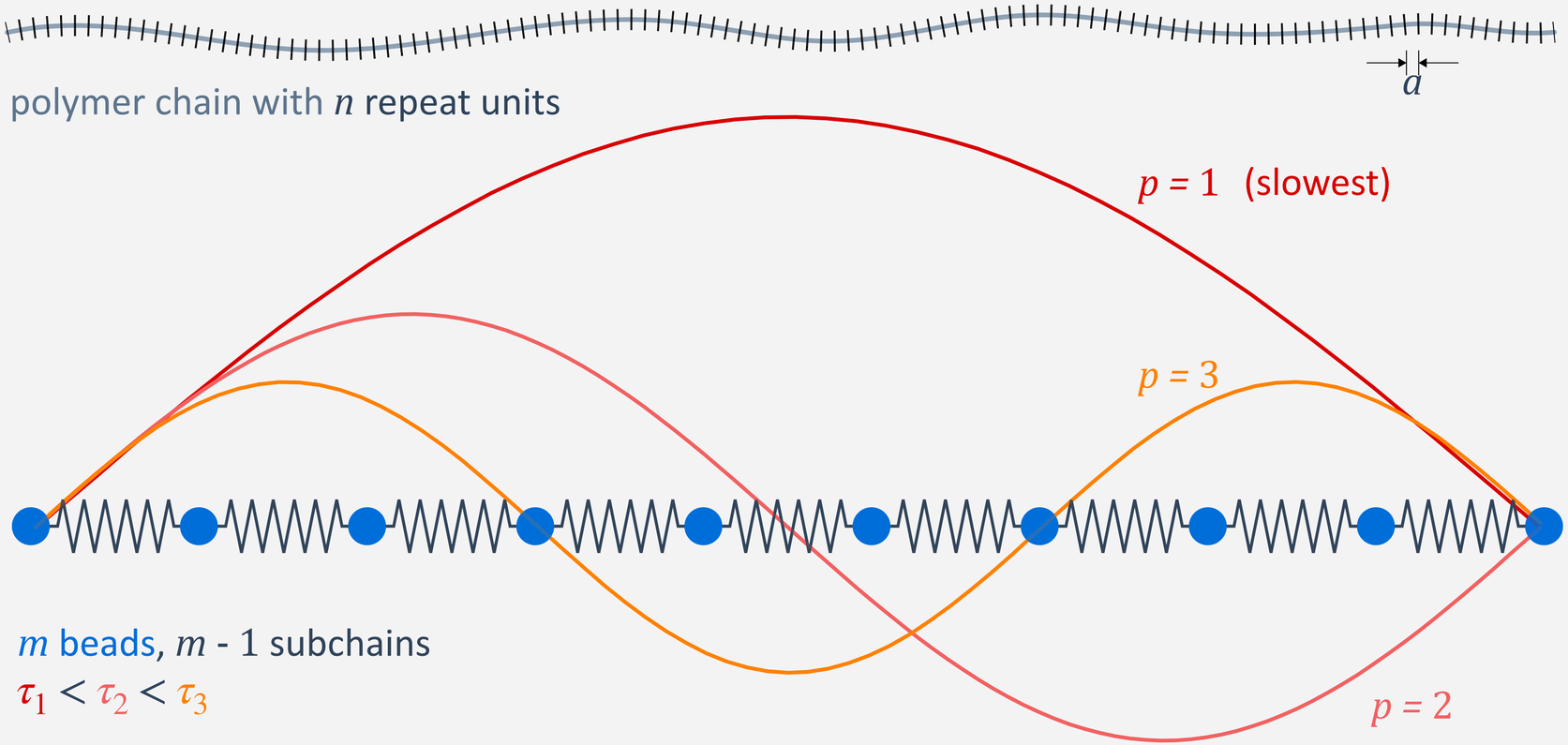
$$\tau_p = \frac{\xi R_s^2}{24\mathrm{k}T}\sin^{-2}\left(\frac{\pi p}{2(m+1)}\right) \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 \mathrm{k}T}\ \text{, for } m \gg 1, p \qquad p = 1,\ 2,\ \ldots,\ m$$

Rouse Modes

- **the normal modes of vibration have p nodes along the polymer contour**

$$\tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 \mathrm{k}T} \propto \frac{M^2}{p^2}$$

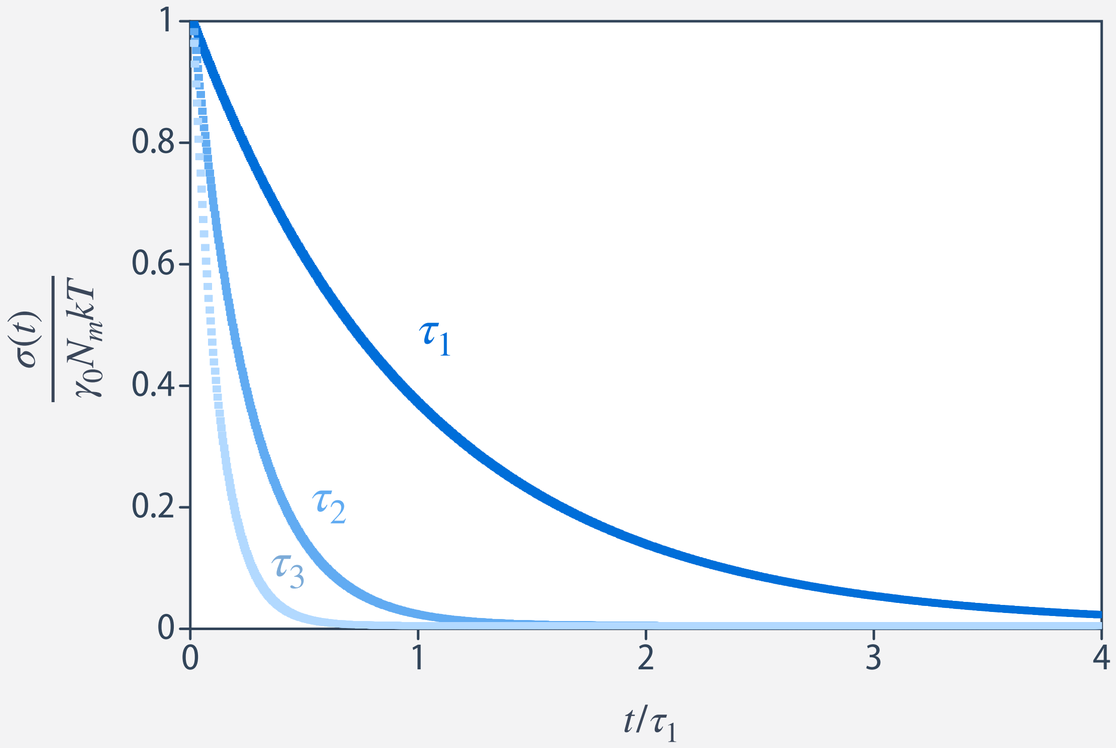
for $m \gg 1$, p



- **Rouse modes describe relaxation on different length scales: higher *p* ⟶ more local and faster relaxation**
- **the slowest mode (*p* = 1) defines the Rouse relaxation time (τ_1), which scales with 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**)

- **stress relaxes exponentially; the overall response equals the sum of all exponential decays**
- **for $t \geq \tau_1$, faster relaxation modes are negligible**

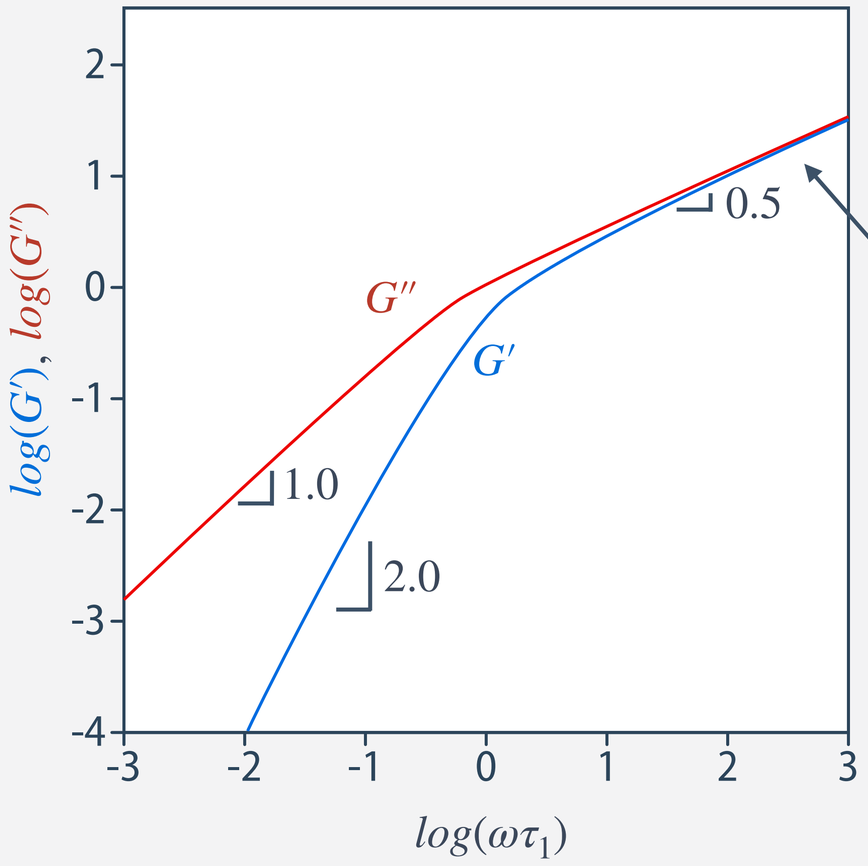
Assumptions of the Rouse Model

- the chain is treated by a “bead and spring” model with entropic forces between beads
- the interaction with surrounding chains (or solvent) is described by a friction coefficient ξ
- hydrodynamic interactions are neglected (for corrections, see the Zimm model)
- the chain must be long enough for Gaussian statistics
- valid for molar masses smaller than a critical molar mass M_c (no entanglements)

Practicability of the Rouse Model

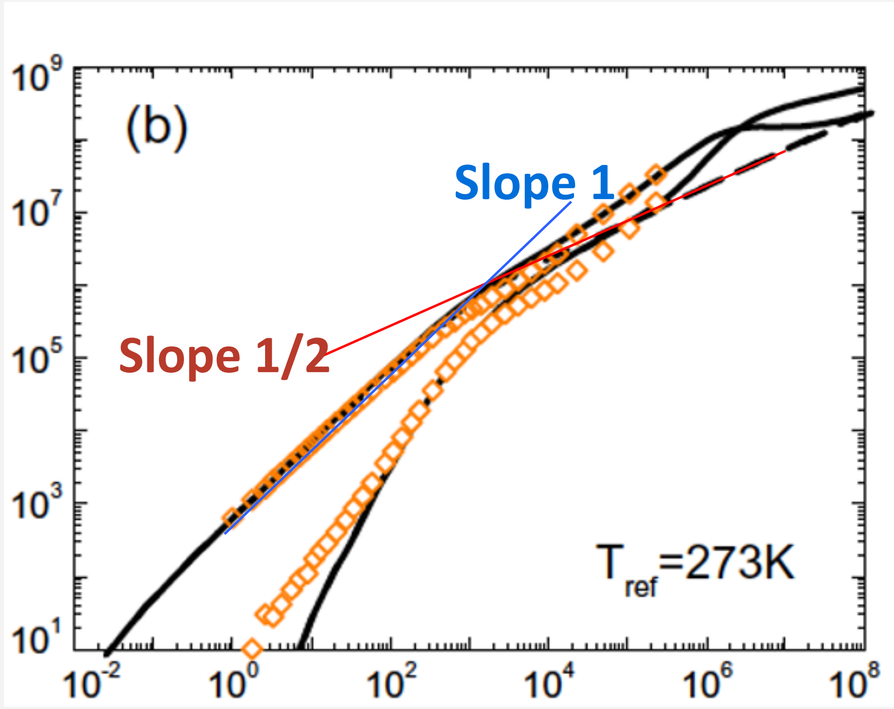
- predicts the same terminal behavior as the Maxwell model

predicted rheology curves



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

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



- **accurately describes unenntangled melts and low molar mass polymers**

Limitations of the Rouse Approach

- fails for dilute solutions, neglects hydrodynamic interactions (see Zimm for a more accurate theory)

	Rouse behavior	**observations** (from dilute solutions)
	$\tau_1 \propto M^2$	$\tau_1 \propto M^{3/2}$
D is the diffusion coefficient of the centre of mass of the chain	$D = \frac{kt}{\xi m} = \frac{kt}{\xi_0 n} \propto \frac{1}{M}$	$D \propto \frac{1}{M^{1/2}}$

- **valid only for short time / high frequencies or for low molar masses**
- **it cannot describe entanglement or plateau behavior**