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The Rouse Model

1. Concept and Physical Picture

The Rouse model describes the dynamics of a single polymer chain in a viscous medium. It assumes that the chain is flexible and that its segments interact only through connectivity and friction with the surrounding fluid. Originally, it was developed for **very dilute polymer solutions**, where each chain moves independently and the flow disturbances created by the motion of one chain do not affect others, i.e. inter-chain hydrodynamic interactions are neglected.

The model represents a chain containing n bonds as a sequence of m beads connected by $m - 1$ **Gaussian subchains** (or "springs"). Each subchain contains $n_s = n/(m-1)$ repeat units and must be sufficiently long for Gaussian statistics to hold. If this is the case, its mean-square end-to-end distance is

$$\langle R_s^2 \rangle = n_s a^2 = \frac{n}{m-1} a^2 \quad , \tag{1}$$

where a is the length of a bond. **The choice of the number of beads m is somewhat arbitrary**: it serves as a coarse-graining parameter that defines how finely the polymer contour is subdivided. Increasing m improves the spatial resolution of the model, but the overall chain dynamics remain unchanged as long as the shortest subchains (i.e., the fastest modes) relax much faster than the timescale of interest (i.e. $t \gg \tau_m$).

If m is too small, the fastest internal fluctuations are not properly represented, and the model underestimates the contribution of local chain flexibility. If m is too large, the subchains become too short for Gaussian statistics to remain valid. Thus, m must be chosen as a compromise:

- large enough that the fastest mode relaxes well within the observation window,
- small enough that each subchain still represents many bonds.

Each bead interacts with the solvent through viscous drag, characterized by a friction coefficient ξ (unit: N s/m). Physically, this means that whenever a bead moves relative to the surrounding fluid (for instance, due to Brownian motion), the solvent exerts a frictional resistance proportional to the bead velocity. **This interplay between entropic elasticity and viscous damping governs the time-dependent relaxation of the polymer conformation.**

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2. Force Balance on a Bead

For a given subchain with end positions $\vec{r}_i$ and $\vec{r}_{i+1}$, the **entropic restoring force** is linear in its extension $\vec{R}_s = \vec{r}_{i+1} - \vec{r}_i$ (see Exercise 7):

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

The prefactor can be interpreted as an **effective spring constant** that increases with temperature, reflecting the stronger restoring force at higher T. Each bead i experiences a net elastic force from its two neighboring subchains:

$$f_i = f_{i-1 \to i} + f_{i \leftarrow i+1} = \frac{3\mathrm{k}T}{n_s a^2}(\vec{r}_i - \vec{r}_{i-1}) + \frac{3\mathrm{k}T}{n_s a^2}(\vec{r}_i - \vec{r}_{i+1}) = \frac{3\mathrm{k}T}{n_s a^2}(2\vec{r}_i - \vec{r}_{i-1} - \vec{r}_{i+1}) \quad . \tag{3}$$

In equilibrium, this elastic force is balanced by the **viscous drag** exerted by the solvent on the bead as described by Stokes' law:

$$-\xi \frac{\mathrm{d}\vec{r}_i}{\mathrm{d}t} = \frac{3\mathrm{k}T}{R_s^2}(2\vec{r}_i - \vec{r}_{i-1} - \vec{r}_{i+1}) \quad , \tag{4}$$

where $\mathrm{d}\vec{r}_i/\mathrm{d}t$ is the bead velocity. The minus sign indicates that the drag opposes the direction of motion. This force balance constitutes the fundamental force-balance equation of the **Rouse model**.

3. Normal Modes and Relaxation Spectrum

Equation (4) yields m coupled linear differential equations – one for each bead coordinate. The parameter m defines the level of coarse-graining: the larger m, the more internal modes (and shorter subchains) are represented.

These coupled equations describe how each bead is connected to its neighbors through spring-like forces. To solve them, it is convenient to express the bead positions in terms of collective motion patterns (called *normal coordinates*), which describe how the entire chain moves rather than individual beads. This is analogous to expressing a system of coupled oscillators or vibrating strings in terms of independent vibration modes, which is a familiar approach from mechanics or molecular vibration analysis in physical chemistry, where a set of normal modes replaces the coupled equations of motion.

This mathematical transformation removes the coupling between beads and reduces the system to m **independent equations**, each describing a specific mode of motion (indexed by p = 1,2, …, m). Each mode, or **Rouse mode**, relaxes with its own characteristic relaxation time τ_p:

$$\tau_p = \frac{\xi R_s^2}{24\mathrm{k}T} \sin^{-2}\left(\frac{\pi p}{2(m+1)}\right) \quad , \qquad p = 1,2,\ldots,m \quad . \tag{5}$$

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For long chains ($m \gg 1$), this expression simplifies to

$$\tau_p \approx \frac{\xi m^2 R_s^2}{6\pi^2 p^2 kT}, \qquad (m \gg 1) \quad . \tag{6}$$

Each mode p corresponds to a collective fluctuation pattern with p nodes along the contour length of the chain. The lowest mode (p = 1) represents the slowest, global motion of the entire chain, i.e. the relaxation of its overall conformation. Higher modes describe progressively faster, more localized fluctuations of shorter wavelength.

The **longest relaxation time**, often called the **Rouse relaxation time**, therefore corresponds to p = 1 (involving motion of the entire chain):

$$\tau_1 \approx \frac{\xi m^2 R_s^2}{6\pi^2 \mathrm{k}T} = \frac{\xi m^2 n_s a^2}{6\pi^2 \mathrm{k}T} \quad . \tag{7}$$

Let us introduce the monomeric friction coefficient ξ_0 (such that $\xi = \xi_0 n/m$), which represents the friction experienced by a single repeat unit (or monomer). Since each bead in the Rouse model represents a subchain of $n_s = n/(m-1)$ links, the total friction acting on a bead is the sum of the monomeric frictions within that subchain:

$$\xi = \xi_0 n_s \approx \xi_0 \frac{n}{m} \quad . \tag{8}$$

Recalling again that $n_s = n/(m-1) \approx n/m$ for long chains, we can rewrite the Rouse relaxation time as:

$$\tau_1 \approx \frac{\xi_0 \left(\frac{n}{m}\right) m^2 \left(\frac{n}{m}\right) a^2}{6\pi^2 \mathrm{k}T} = \frac{\xi_0 n^2 a^2}{6\pi^2 \mathrm{k}T} \propto n^2 \propto M^2 \quad . \tag{9}$$

The quadratic scaling of the Rouse relaxation time with molar mass is one of the key predictions of the Rouse model. It reflects that, in the absence of hydrodynamic interactions or entanglements, each monomer experiences an independent drag force, while the relaxation of the chain involves collective motion of all monomers. As a result, the overall relaxation slows down dramatically with increasing chain length.

Experimentally, this M^2 scaling is observed **for unentangled polymer melts** and **for dilute solutions of short chains**. For longer, entangled polymers, however, deviations occur: the relaxation becomes much slower, following $\tau \sim M^{3.4}$. Thus, the Rouse model provides the reference framework for understanding polymer dynamics in the unentangled regime (before entanglement effects set in) and provides a baseline from which more complex behaviors such as reptation are developed.

Note: the special case p = 0 corresponds to uniform translation of the entire chain (the center-of-mass motion) and therefore does not contribute to internal stress relaxation.

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4. Stress Relaxation and Moduli

Each Rouse mode p behaves as an independent Maxwell element with its own relaxation time τ_p. If a small step strain is applied, the stress associated with mode p decays exponentially as

$$\mathrm{G}_p(t) = N\mathrm{k}T e^{-\frac{t}{\tau_p}} \quad , \tag{10}$$

Where $N\mathrm{k}T$ represents the elastic energy density per mode (since each mode stores on the order of kT per chain). **According to Boltzmann's superposition principle, valid in the linear viscoelastic regime (small deformations), the total stress is simply the sum of the stresses that each independent relaxation process would produce if it acted alone.** Since the Rouse modes relax independently, the total stress relaxation modulus is obtained by summing over all modes:

$$\mathrm{G}(t) = N\mathrm{k}T \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}} \quad , \tag{11}$$

This exponential decay reflects that each mode relaxes independently and linearly, with the total response given by the superposition of all modes. The number of terms m corresponds to the number of beads in the chain, and hence the number of distinct relaxation mechanisms available.

In oscillatory shear, the frequency-dependent moduli follow from Fourier transforming G(t):

$$\mathrm{G}'(t) = N\mathrm{k}T \sum_{p=1}^{m} \frac{\omega^2\tau_p^2}{1+\omega^2\tau_p^2} \tag{12}$$

$$\mathrm{G}''(t) = N\mathrm{k}T \sum_{p=1}^{m} \frac{\omega\tau_p}{1+\omega^2\tau_p^2} \tag{13}$$

These expressions are formally identical to those of the generalized Maxwell model with equal spring constants $E_\mathrm{i} = NkT$, meaning that each Rouse mode contributes equally to the total elastic energy but relaxes on its own timescale τ_p.

From the mode spectrum (the set of all relaxation times τ_p), three characteristic regimes can be identified:

- **terminal regime** (low ω): dominated by the longest time τ_1
- **intermediate regime:** several modes contribute equally, leading to $\mathrm{G}'(t) \approx G''(t) \sim \omega^{1/2}$
- **high-frequency regime:** only the fastest modes (shortest subchains) respond; beyond this limit, the model ceases to be valid.

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Finally, since all relaxation times scale with temperature as

$$\tau_p \propto \frac{\xi(T)}{\mathrm{k}T} \quad , \tag{14}$$

the Rouse model is naturally consistent with the **time-temperature superposition principle**.

5. Comparison with Experiments

The Rouse model was first developed for dilute polymer solutions, but experimental tests revealed inconsistencies. For example, it predicts that the longest relaxation time scales with the squared molar mass (see Equation (9)). Experimentally, however, a weaker dependence ($\tau_1 \propto M^{3/2}$) dependence is observed.

Moreover, the diffusion coefficient of the chain's center of mass follows from the Einstein relation between diffusion and total friction:

$$D = \frac{\mathrm{k}T}{\xi m} \approx \frac{\mathrm{k}T}{\xi_0 \left(\frac{n}{m}\right) m} = \frac{\mathrm{k}T}{\xi_0 n} \propto \frac{1}{M} \quad , \tag{15}$$

showing that diffusion slows down inversely with the number of bonds, and hence with the molar mass M. Experimentally, however, diffusion decreases somewhat more slowly, with $D \propto M^{-1/2}$, indicating that hydrodynamic coupling between chain segments reduces the effective friction compared to the Rouse prediction.

These discrepancies arise because the Rouse model neglects intra-chain hydrodynamic interactions between different chain segments. Including these long-range interactions leads to the **Zimm model**, which correctly reproduces the experimental scaling in dilute solutions.

Nevertheless, the Rouse model remains extremely valuable for describing polymer melts above the glass transition T_g, where the "solvent" effectively consists of other chains. In this case, the surrounding medium transmits friction but not long-range hydrodynamic coupling. Under such conditions, the Rouse model provides a good description as long as:

- the molar mass M is not too high (chains are unentangled, no rubbery plateau appears);
- or, for high-molar-mass systems, one considers timescales shorter than the entanglement time (before topological constraints become relevant);
- the timescales are not too short that the corresponding subchains become too short for the Gaussian assumption of Equation (2) to hold (since m would then have to be chosen very large).

Within these limits, the Rouse model serves as the fundamental reference case for **understanding viscoelastic relaxation in unentangled polymers** and as the baseline for more advanced theories such as the Zimm and reptation models.

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Additional Reading

M. Rubinstein, R. H. Colby. *Polymer Physics*, Oxford University Press, 2003, Chapter 8 ("Unentangled polymer dynamics").

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