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The Tube Model

1. Dynamic Constraints by Entanglements

In earlier discussions, we introduced the **network model of entanglements**, which explains the existence of the rubbery plateau in polymer melts and thermoplastics. However, this **static picture**, where chains are connected by permanent "entanglement points", cannot explain why the rubbery plateau has a finite modulus and how stress relaxation eventually occurs.

To capture these dynamic effects, we need to abandon the idea of localized, permanent "knots" between chains. Instead, the **Tube Model** describes the motion of a chain dynamically confined by its neighbors:

- The surrounding chains form a virtual cage, restricting lateral motion.
- For long chains, this cage extends along the contour of the chain, thus forming a **tube** through which the chain can move only along its axis by reptation.
- The tube ends remain open, allowing the chain to gradually escape from its confining environment.

This picture was formalized in the 1970s by de Gennes and Doi-Edwards and forms the theoretical basis of modern polymer rheology and viscoelastic modeling.

The **tube diameter d_e** corresponds to the distance between neighboring entanglements. It equals the root-mean-square end-to-end distance of a subchain with molar mass M_e, the **entanglement molar mass**:

$$d_e = \sqrt{n_e}a = \sqrt{\frac{M_e}{M_b}}a \;, \tag{1}$$

where n_e is the number of bonds per entanglement strand and M_b is the molar mass of a statistical segment. A long chain can therefore be viewed as a random walk of M/M_e entanglement strands, each of size d_e. The **tube contour length** L of the tube is therefore proportional to the polymer molar mass M:

$$L = \frac{M}{M_e}d_e = \frac{n}{n_e}\sqrt{n_e}a = \frac{1}{\sqrt{n_e}}na \propto M \quad , \tag{2}$$

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Hence, the tube contour is shorter than the total chain contour na by factor of $1/\sqrt{n_e}$, because it represents the primitive path, i.e. a smoothed backbone obtained by averaging over the chain's local conformations between entanglements.

2. Stress Relaxation within the Tube

Consider a stress relaxation experiment: at $t = 0$, the sample is suddenly deformed, thereby deforming both the polymer chains and their confining tubes. To relax the stress, the chains must return to random coil conformations.

However, as long as they remain trapped within their tubes, chain segments cannot cross the tube walls. **Only chain segments shorter than or equal to the tube diameter d_e can relax locally:**

$$\frac{n}{p}a^2 \leq d_e^2 \quad , \tag{3}$$

where n/p is the number of bonds per segment, and a is the bond length. **Segments longer than this remain topologically constrained.**

The **Rouse model** provides an adequate description of such local, short-wavelength motions inside the tube and thus serves as the microscopic basis of the tube model:

$$\mathrm{G}(t) = NkT \sum_{p=1}^{m} e^{-\frac{t}{\tau_p}} \quad , \tag{4}$$

where N is the number of chains per unit volume, k is Boltzmann's constant, p is the Rouse mode index, m the number of internal relaxation modes, and τ_p is the relaxation time of mode p. **Only Rouse modes corresponding to segment sizes (mean-square end-to-end distance) smaller than the tube diameter can contribute to stress relaxation:**

$$\tau_p \approx \frac{\xi_0 n^2 a^2}{6\pi^2 p^2 \mathrm{k}T}, \qquad \text{for} \quad \frac{n}{p}a^2 \leq d_e^2 \quad . \tag{5}$$

Here, ξ_0 is the monomeric friction coefficient (see Reader on Rouse Model for details). Modes with larger spatial extent are effectively frozen:

$$\tau_p = \infty, \qquad \text{for} \quad \frac{n}{p}a^2 > d_e^2 \quad . \tag{6}$$

The borderline condition in Equation (3) defines the transition between Rouse-like local relaxation and entanglement-dominated dynamics. Substituting this condition into Equation (5) gives the **entanglement time**:

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$$\tau_\mathrm{e} = \frac{\xi_0 n^2 a^2}{6\pi^2 \mathrm{k}T} \cdot \frac{d_\mathrm{e}^4}{n^2 a^4} = \frac{\xi_0 d_\mathrm{e}^4}{6\pi^2 \mathrm{k}T a^2} = \frac{\xi_0 {n_\mathrm{e}}^2 a^4}{6\pi^2 \mathrm{k}T a^2} = \frac{\xi_0 {n_\mathrm{e}}^2 a^2}{6\pi^2 \mathrm{k}T} = \frac{\xi_0 a^2}{6\pi^2 \mathrm{k}T}\left(\frac{M_\mathrm{e}}{M_\mathrm{b}}\right)^2 \quad . \tag{7}$$

where n_e is the number of bonds per entanglement strand, M_e its molar mass, and M_b the molar mass of one statistical segment (i.e. the repeating unit). **τ_e is a materials parameter: it depends on M_e but is independent of the overall polymer molar mass. Materials with a lower entanglement molar mass M_e become dynamically constrained earlier, that is they reach the entangled regime at shorter chain lengths.**

At times longer than τ_e, the chain is effectively trapped within its tube: internal Rouse modes have relaxed, and further stress relaxation can occur only by **reptation**, i.e., diffusion of the entire chain along the tube contour.

3. The Rubbery Plateau Modulus

In this time regime ($\tau_\mathrm{e} < t < \tau_\mathrm{d}$), modes with $p > n/n_\mathrm{e}$ (wavelengths shorter than d_e) have relaxed, while the lower modes remain frozen ($\tau_\mathrm{p} = \infty$). The relaxation modulus can thus be written as:

$$\mathrm{G}(t) = N\mathrm{k}T \sum_{p=1}^{n/n_\mathrm{e}} e^{-\frac{t}{\infty}} + N\mathrm{k}T \sum_{p=n/n_\mathrm{e}}^{m} e^{-\frac{t}{\tau_p}} \quad . \tag{8}$$

The first term remains constant, while the second term decays rapidly and tends to zero in the long-time limit ($t \gg \tau_\mathrm{p}$):

$$\mathrm{G}_\mathrm{e} = N\mathrm{k}T \sum_{p=1}^{n/n_\mathrm{e}} 1 = \frac{n}{n_\mathrm{e}} N\mathrm{k}T = N_\mathrm{e}\mathrm{k}T \quad , \tag{9}$$

which corresponds to the experimentally observed **rubbery plateau modulus**. Since each chain contains n/n_e entanglement strands, the total number of entanglement strands per unit volume (the entanglement density) is $N_\mathrm{e} = Nn/n_\mathrm{e}$. This result is valid in the range $\tau_\mathrm{e} < t < \tau_\mathrm{d}$, where $p \ll n$ (i.e. each segment between beads still behaves as a Gaussian subchain). For times longer than the **disentanglement (reptation) time τ_d**, the chain escapes its tube and the stress finally relaxes to zero.

The plateau modulus connects to **entanglement molar mass M_e** via the density ρ. Each statistical segment has a molar mass M_b and therefore a mass of $M_\mathrm{b}/\mathrm{N_a}$, where $\mathrm{N_a}$ is Avogadro's number. The mass density is then:

$$\rho = (Nn)\frac{M_\mathrm{b}}{\mathrm{N_a}} \quad \rightarrow \quad Nn = \frac{\rho \mathrm{N_a}}{M_\mathrm{b}} \quad . \tag{10}$$

Since $M_\mathrm{e} = n_\mathrm{e} M_\mathrm{b}$, substitution into Equation (9) gives:

$$\mathrm{G_e} = \frac{n}{n_\mathrm{e}} N\mathrm{k}T = \frac{M_\mathrm{b}}{M_\mathrm{e}} \frac{\rho \mathrm{N}_a}{M_\mathrm{b}} \mathrm{k}T = \frac{\rho \mathrm{kN}_a T}{M_\mathrm{e}} = \frac{\rho \mathrm{R}T}{M_\mathrm{e}} \quad . \tag{11}$$

Therefore, the entanglement molar mass M_e can be determined directly from the experimentally measured rubbery plateau modulus $\mathrm{G_e}$.

4. Disentanglement

The chain does not remain trapped in the tube forever. **Over time, it escapes its original tube by diffusion along its contour, a process known as *reptation*.** Diffusion is in general described by Fick's law,

$$x = \sqrt{Dt} \quad , \tag{12}$$

where x is the diffusion distance, D the diffusion coefficient, and t the time.
For the chain to completely leave its tube, it must diffuse a distance comparable to the tube contour length L. The corresponding **disentanglement time** is therefore:

$$\tau_\mathrm{d} \approx \frac{L^2}{D_\mathrm{R}} \quad , \tag{13}$$

Inserting the Rouse diffusion coefficient (see Equation (15) in the Reader on the Rouse Model) and the tube length from Equation (2), and subsequently rearranging using ($n = M/M_\mathrm{b}$), gives:

$$\tau_\mathrm{d} = \frac{\xi_0 n}{\mathrm{k}T}\left(\frac{M}{M_\mathrm{e}}\right)^2 d_\mathrm{e}^2 = \frac{\xi_0 n}{\mathrm{k}T}\left(\frac{M}{M_\mathrm{e}}\right)^2 \left(\sqrt{\frac{M_\mathrm{e}}{M_\mathrm{b}}}\, a\right)^2 = \frac{\xi_0 n M^2}{\mathrm{k}T M_\mathrm{e} M_\mathrm{b}} a^2 = \frac{\xi_0 M^3}{\mathrm{k}T M_\mathrm{e} {M_\mathrm{b}}^2} a^2 \quad . \tag{14}$$

To relate this to the entanglement time τ_e (Equation (7)), we multiply and divide by τ_e:

$$\tau_\mathrm{d} = \frac{\xi_0 M^3}{\mathrm{k}T M_\mathrm{e} {M_\mathrm{b}}^2} a^2 \frac{\tau_\mathrm{e}}{\tau_\mathrm{e}} = \frac{\xi_0 M^3}{\mathrm{k}T M_\mathrm{e} {M_\mathrm{b}}^2} a^2 \frac{6\pi^2 \mathrm{k}T}{\xi_0 a^2}\left(\frac{M_\mathrm{b}}{M_\mathrm{e}}\right)^2 \tau_\mathrm{e} = 6\pi^2 \left(\frac{M}{M_\mathrm{e}}\right)^3 \tau_\mathrm{e} \quad . \tag{15}$$

The numerical prefactor $6\pi^2$ arises from the longest Rouse mode ($p = 1$). **Several important conclusions follow:**

- $\tau_\mathrm{d} \propto M^3$. The **disentanglement time increases steeply with molar mass**, explaining why long-chain polymers exhibit extended rubbery plateaus.

- **onset of the rubbery plateau**: the plateau appears only when $M > M_e$, i.e. when the chain is long enough to contain several entanglement segments (then, $\tau_d > \tau_e$).
- **temperature dependence**: both τ_e and τ_d share the same temperature dependence through kT and the friction coefficient $\xi_0(T)$. Thus, **the tube model is consistent with the time-temperature superposition principle**.

Once the chain has escaped its tube, it can return to its random conformation, and the stress is fully relaxed. A compact expression for the stress relaxation modulus combines a short-time (Rouse) part, describing modes that relax inside the tube, with a plateau term multiplied by the tube-survival probability $\mu(t)$, which is the probability that the chain still occupies its original tube at time t:

$$\mathrm{G}(t) = N\mathrm{k}T \sum_{p=n/n_e} e^{-\frac{t}{\tau_p}} + \mathrm{G_e}\mu(t) \ , \tag{16}$$

where the critical mode $p = n/n_e$ corresponds to an entanglement strand (i.e. a wavelength of d_e). The Rouse contributions decay for $t \gtrsim \tau_e$.

The model captures the full relaxation behavior of non-crosslinked polymers with $M > M_e$:

- $t < \tau_e$: **local Rouse relaxations** inside the tube dominate, $\mathrm{G}(t)$ falls from the instantaneous modulus to the plateau $\mathrm{G_e}$.
- $\tau_e < t < \tau_d$: **rubbery plateau** (chain segments fluctuate, but the overall tube constraint remains fixed), The Rouse part in Equation 15 tends to zero, $\mu(t) \approx 1$, and $\mathrm{G}(t) \approx \mathrm{G_e}$.
- $t \approx \tau_d$: **reptation begins** (the chain starts to escape the tube)
- $t \gg \tau_d$: **terminal flow** (complete relaxation, viscous behavior dominates)

For **elastomers**, where the chain ends are permanently crosslinked, $\tau_d \to \infty$, and stress relaxation stops in the rubbery plateau.

5. Consequences and Scaling Laws

Self-Diffusion Coefficient

When the chain leaves its tube after the time τ_d, its center of mass has diffused by a distance of order R_g. According to Fick's law (Equation 12), the self-diffusion coefficient is therefore inversely proportional to the squared molar mass,

$$D = \frac{R_g^2}{\tau_d} \propto \frac{M}{M^3} \propto M^{-2} \ , \tag{17}$$

since $R_g \propto \sqrt{M}$ and $\tau_d \propto M^3$. **This implies a much slower motion than predicted by the Rouse model** ($D \propto M^{-1}$).

Zero Shear Viscosity

In the **terminal regime** of viscous behavior ($t \gg \tau_d$), the tube survival probability is dominated by the first mode p = 1 and the function can be approximated as a single exponential.

$$\mathrm{G}(t) \approx \mathrm{G_e} e^{-\frac{t}{\tau_\mathrm{d}}} \quad . \tag{18}$$

Using the Boltzmann superposition principle,

$$\sigma(t) = \int_0^t \mathrm{G}\,(t-t')\frac{\mathrm{d}\gamma}{\mathrm{d}t'}\mathrm{d}t' = \int_0^t \mathrm{G_e} e^{-\frac{t-t'}{\tau_\mathrm{d}}}\dot{\gamma}\mathrm{d}t' = \mathrm{G_e}\dot{\gamma}\int_0^t e^{-\frac{t-t'}{\tau_\mathrm{d}}}\mathrm{d}t' \quad , \tag{19}$$

where $\dot{\gamma}$ is constant. Note that either 0 or $-\infty$ can be taken as the lower bound of the integral. Integration yields:

$$\sigma(t) = \mathrm{G_e}\dot{\gamma}\left[\tau_\mathrm{d} e^{-\frac{t-t'}{\tau_\mathrm{d}}}\right]_0^t = \mathrm{G_e}\dot{\gamma}\tau_\mathrm{d}\left(1 - e^{-\frac{t}{\tau_\mathrm{d}}}\right) \approx \mathrm{G_e}\dot{\gamma}\tau_\mathrm{d} \quad , \tag{20}$$

for $t \gg \tau_d$. The zero-shear viscosity is therefore:

$$\eta = \frac{\sigma(t)}{\dot{\gamma}} = \mathrm{G_e}\tau_\mathrm{d} \propto M^3 \qquad \text{for } M > M_\mathrm{e} \quad , \tag{21}$$

Hence, viscosity increases dramatically with molar mass. Experimentally, it often scales slightly more steeply ($\propto M^{3.4}$) because the tube itself (i.e. the surrounding chains) undergoes dynamic processes such as contour-length fluctuations, constraint release, and effects resulting from polydispersity. As a result, ultra-high molecular weight polyethylene (UHMWPE), though mechanically exceptional, cannot be processed in the melt due to its extremely high viscosity. Conversely, low-molar mass HDPE is easy to process but exhibits poor creep resistance.

For linear, unentangled polymers, the Rouse model predicts $\eta \propto M$ (see Appendix). **The crossover molar mass M_c at which entanglement become visible is empirical and often lies near $2M_e$. It marks a gradual transition rather than a sharp boundary.**

In summary, the tube model transforms the vague concept of "entanglements" into a quantitative dynamic constraint. It explains the finite rubbery plateau, predicts how viscosity and diffusion scale with molar mass, and provides a coherent framework linking molecular architecture, molecular motion, and macroscopic rheology.

Additional Reading

M. Rubinstein, R. H. Colby. *Polymer Physics*, Oxford University Press, 2003, Chapter 9 ("Entangled polymer dynamics").

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Appendix

For low-molar mass, unentangled polymer melts ($M < M_e$), the dynamics are described by the Rouse model. At long times $t \gg \tau_1$, stress relaxation is governed by the slowest Rouse mode with relaxation time τ_1. The shear relaxation modulus then reads:

$$G(t) = NkTe^{-\frac{t}{\tau_1}} \quad , \tag{A1}$$

where N is the number of chains per unit volume. According to the Boltzmann superposition principle, the stress under a constant shear rate $\dot{\gamma}$ is given by:

$$\begin{aligned} \sigma(t) &= \int_0^t G\,(t-t')\frac{d\gamma}{dt'}dt' = \int_0^t NkTe^{-\frac{t-t'}{\tau_1}}\dot{\gamma}dt' = NkT\dot{\gamma}\int_0^t e^{-\frac{t-t'}{\tau_1}}dt' \\ &= NkT\dot{\gamma}\left[\tau_1 e^{-\frac{t-t'}{\tau_1}}\right]_0^t = NkT\dot{\gamma}\tau_1\left(1-e^{-\frac{t}{\tau_1}}\right) \quad . \end{aligned} \tag{A2}$$

For long times ($t \gg \tau_1$), this expression approaches:

$$\sigma(t) \approx NkT\dot{\gamma}\tau_1 \quad , \tag{A3}$$

Hence, the zero-shear viscosity is:

$$\eta = \frac{\sigma(t)}{\dot{\gamma}} = NkT\tau_1 \quad , \tag{A4}$$

Since $N = \rho N_a / M$ (number of chains per unit volume) and the Rouse relaxation time scales as $\tau_1 \propto M^2$ (see Reader on the Rouse Model), it follows that:

$$\eta \propto \frac{1}{M}M^2 = M \qquad \text{for } M < M_e \quad . \tag{A5}$$

This linear scaling holds up to $M_c = 2M_e$ and reflects the absence of topological constraints: each chain relaxes independently via internal Rouse modes, and the viscosity increases only linearly with chain length. Beyond M_c entanglement effects lead to the much stronger M^3 dependence.

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