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Course Notes of Chapter 4.2 (Part 2)

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1. Molecular Approach to and Physical Origin of Viscoelasticity

In the previous part of this course, we described viscoelastic behavior using **phenomenological models** (springs, dashpots). These models can reproduce the observed relaxation behavior but contain no direct information on molecular structure.

Polymers are made of long, flexible chains, and their viscoelastic response must therefore originate from the conformational dynamics of these chains.

We have already seen that lightly crosslinked rubbers behave as entropic springs, with a modulus

$$E = 3NkT \quad , \tag{1}$$

where N is the crosslink density. This modulus is recovered experimentally in the long-time limit ($t \gg \tau_i$) of a generalized Maxwell model, but in that model the relaxation times τ_i and moduli E_i are purely empirical.

A key question therefore remains: **can we relate the macroscopic behavior to chain structure and dynamics?**

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2. Isolated Chain Dynamics in a Solvent – the Rouse Model (see *Reader on Rouse model*)

The **Rouse model** provides the simplest molecular description of chain dynamics and viscoelasticity. It treats a polymer chain as a series of **beads** (representing frictional units) connected by **harmonic springs** (representing entropic elasticity of chain segments). The beads experience Brownian forces and viscous drag from their surroundings that damps their motion.

Each collective motion of the chain can be decomposed into **Rouse modes**. These are normal modes of relaxation that correspond to motions of decreasing wavelength along the chain contour. The slowest mode (p = 1) involves motion of the entire chain, while the fastest modes correspond to local segmental motions. Each mode relaxes exponentially with a relaxation time

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

where ξ is the friction coefficent per bead and R_s the segment length.

Key results:

- the longest relaxation time (the **Rouse time τ_1**) scales as $\tau_1 \propto M^2$.
- the diffusion coefficient of the chain's center of mass follows $D \propto M^{-1}$.
- the model predicts Maxwell-type behavior at low frequencies, and characteristic frequency dependences $G' \sim \omega^{1/2}$ and $G'' \sim \omega^{1/2}$ at intermediate frequencies.

Main limitation:

The Rouse model assumes that chains move independently and neglects topological constraints from surrounding chains. It therefore describes well unentangled melts ($M < 2\,M_e$), or the short-time regime ($t < \tau_e$) of entangled melts ($M > 2\,M_e$).

At higher molar masses or longer times, **entanglements** dominate the dynamics, leading to the **rubbery plateau** and **reptation behavior**.

3. Entanglement – Molecular Origin of the Rubbery Plateau

In polymers above their glass transition temperature T_g, molecular motion occurs over a wide range of timescales:

- **short times**: local bond rotations and segmental motions (governed by frictional drag)
- **intermediate times**: collective motions of chain segments (Rouse-type relaxations)
- **long times**: large-scale chain motions that are increasingly constrained by neighboring chains (entanglement and reptation).

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These molecular mechanisms together give rise to the observed **spectrum of relaxation times**, the **rubbery plateau**, and **the strong molar mass dependence of viscosity**.

Above T_g, non-crosslinked polymers exhibit an elastic response over an intermediate time window (the rubbery plateau) even though no chemical crosslinks are present. This apparent network behavior originates from topological constraints, or entanglements, between interpenetrating chains.

A simple static model treats the melt as a transient network of subchains with an average molar mass between entanglements M_e, connected at entanglement points:

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

where N_e is the entanglement density.

If the total chain molar mass M is smaller than roughly twice M_e, the chains are too short to form a percolating network, and the rubbery plateau disappears. Thus, M_e marks the crossover from **unentangled (Rouse-like)** to **entangled (rubber-like)** behavior.

4. Disentanglement and the Tube Model (see *Reader on Tube Model*)

Entanglements are not permanent: on sufficiently long timescales, a chain can move out of its local constraints. This process, called **disentanglement**, and is well described by the **tube model** according to De Gennes, Doi, and Edwards (for details, see the *Reader on Tube Model*).

In this picture, each chain is confined to a virtual tube formed by surrounding chains.

- **short times** ($t < \tau_e$): the chain relaxes locally inside the tube (Rouse-like modes).
- **intermediate times** ($\tau_e < t < \tau_d$): the tube constraint persists, leading to the rubbery plateau in the relaxation modulus $G(t)$.
- **long times** ($t \gg \tau_d$): the chain escapes its tube by reptation, and the stress fully relaxes.

The characteristic times are:

$$\tau_e = \frac{\xi_0 a^2}{6\pi^2 kT}\left(\frac{M_e}{M_b}\right)^2 \quad and \quad \tau_d = 6\pi^2\left(\frac{M}{M_e}\right)^3 \tau_e \quad . \tag{4}$$

Hence, the rubbery plateau appears only when $M > M_e$, i.e. when the chain is long enough to contain several entanglement segments (then, $\tau_d > \tau_e$). The M^3-dependence of the disentanglement time directly explains why long-chain polymers exhibit extended rubbery plateaus.

Moreover, in the **terminal (viscous) regime** ($t \gg \tau_d$), the zero-shear viscosity increases dramatically with molar mass.

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$$\eta \propto M^3 \qquad \text{for } M > M_e \quad . \tag{5}$$

In real polymers, dynamic effects such as tube-length fluctuations and constraint release lead to a slightly higher exponent of 3.4.

Experimental Manifestations:

- rubbery plateau in $G'(t)$ or $E'(t)$ for $M > 2\ M_e$.
- self-diffusion coefficient in the entangled regime: $D \propto M^{-2}$
- zero-shear viscosity: $\eta \propto M^3$ (or $M^{3.4}$ in practice)
- absence of a plateau with $\eta \propto M$ and $D \propto M^{-1}$ for $M < 2\ M_e$

These relationships provide direct ways to extract M_e experimentally, even for semicrystalline polymers where the plateau modulus is obscured by matrix crystallinity.

5. Summary

- Phenomenological models describe viscoelasticity but lack molecular meaning.
- The Rouse model explains viscoelasticity of short, unentangled chains.
- The tube model extends this to long, entangled chains ($M > 2M_e$) and explains the existence and limits of the rubbery plateau.
- The molecular approach therefore provides a quantitative link between chain structure (M, M_e, stiffness) and macroscopic rheological behaviour ($G(t)$, η, D).

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