Molecular Theories of Linear Viscoelasticity
THE TUBE MODEL

De Gennes recognized that the complex many body problem of an entangled polymer diffusing in the melt is simple if we focus on a single chain, with the surrounding chains effectively confining the chain to a tube-like region.

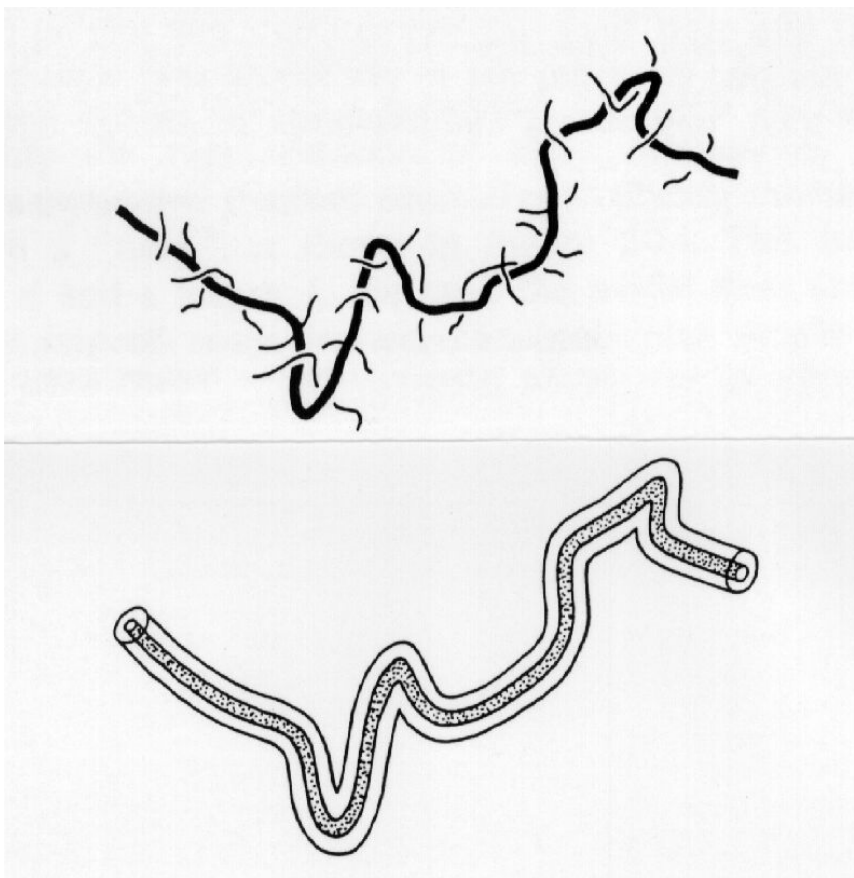

Figure 1: The Tube Model. Surrounding chains confine every chain to move in a tube-like region.

P. G. de Gennes, J. Chem. Phys., vol. 55, p. 572 (1971).

Molecular Theories of Linear Viscoelasticity
REPTATION SCALING

The chain moves by **Rouse motion** confined to a tube.

$$\text{Curvilinear Diffusion Along Tube is} \qquad D_C = \frac{kT}{\zeta N} \sim \frac{1}{N}$$

To move a distance equal to its size $R \sim N^{1/2}$, the chain must diffuse along the tube a distance equal to the contour length of the tube $L \sim N$.

$$\text{Tube Disengagement Time} \qquad \lambda_d \cong \frac{L^2}{D_C} \sim N^3$$

Recall the Plateau Modulus

$$G_N^0 = \frac{\rho RT}{M_e} \qquad \text{independent of M} \tag{2-20}$$

The tube disengagement time is the terminal time.
The plateau modulus is the terminal modulus.

$$\text{Viscosity } \eta_0 \cong \lambda_d G_N^0 \sim N^3$$

is close to the experimental result.

$$\eta_0 \propto M^{3.4} \qquad (M > M_C) \tag{2-107}$$

The through-space diffusion coefficient

$$D \cong \frac{R^2}{\lambda_d} \sim \frac{1}{N^2}$$

is in excellent agreement with experiment.

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DOI-EDWARDS THEORY (P. 1)

On short time scales the chain relaxes by **unrestricted Rouse motion**. The Rouse relaxation time of an entanglement strand is λ_e.

Recall the Rouse relaxation time of a chain of N beads.

$$\lambda_R = \frac{a^2 N^2 \zeta}{6\pi^2 kT}$$

The Rouse time of an entanglement strand is

$$\lambda_e = \frac{a^2 N_e^2 \zeta}{6\pi^2 kT}$$

The plateau modulus is the value of the Rouse relaxation modulus when the entanglement strand has relaxed.

$$G_N^0 \cong G(\lambda_e) \tag{2-108}$$

The Rouse model describes relaxation of long chains up to time scale λ_e.

$$G(t) = G_N^0 (\lambda_e / t)^{1/2} \qquad t < \lambda_e \tag{2-109}$$

At λ_e, the chain finds out it is trapped in a tube!

All Rouse motion for times longer than λ_e is restricted to the tube.

The chain wriggles back and forth in the tube until it abandons the tube.

Tube disengagement takes a long time, so there is a large period of time where essentially no relaxation takes place (the **entanglement plateau**).

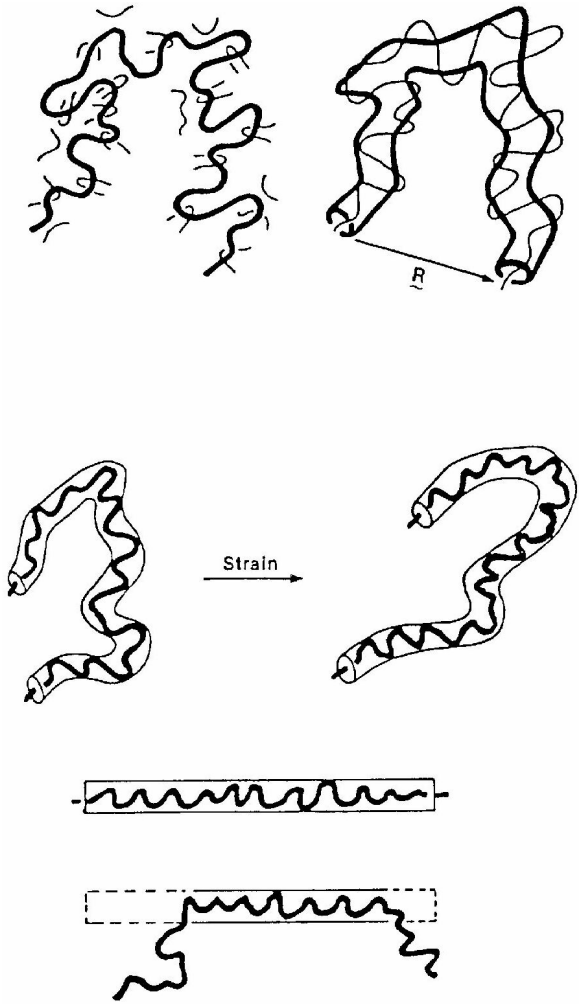

Figure 2: The Tube Model and Tube Disengagement.

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DOI-EDWARDS THEORY (P. 3)

Stress is proportional to the fraction of initial tube still occupied at time t.

$$G(t) = G_N^0 \frac{8}{\pi^2} \sum_{p \text{ odd}}^{N} \frac{1}{p^2} e^{-p^2 t/\lambda_d} \qquad t > \lambda_e \tag{2-110}$$

Compare to the Rouse result.

$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^{N} e^{-p^2 t/\lambda_R} \tag{2-94}$$

The N modes of the Rouse model are all equally weighted.

The $1/p^2$ inside the sum in (2-110) and the fact that the sum is only over odd p, makes the Doi-Edwards model close to the Maxwell model with a single relaxation time.

The relaxation time is the tube disengagement time λ_d.

$$\lambda_d = \frac{a^2 \zeta M^3}{M_e M_0^2 \pi^2 kT} \tag{2-111}$$

Compare to the Rouse time.

$$\lambda_R = \frac{a^2 \zeta M^2}{6\pi^2 M_0^2 kT}$$

The reptation time is longer by

$$\frac{\lambda_d}{\lambda_R} = \frac{6M}{M_e}$$

Recall the Rouse time of an entanglement strand

$$\lambda_e = \frac{a^2 \zeta M_e^2}{6\pi^2 M_0^2 kT}$$

The entanglement plateau spans a time range

$$\frac{\lambda_d}{\lambda_e} = 6 \left(\frac{M}{M_e} \right)^3$$

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DOI-EDWARDS THEORY (P. 4)

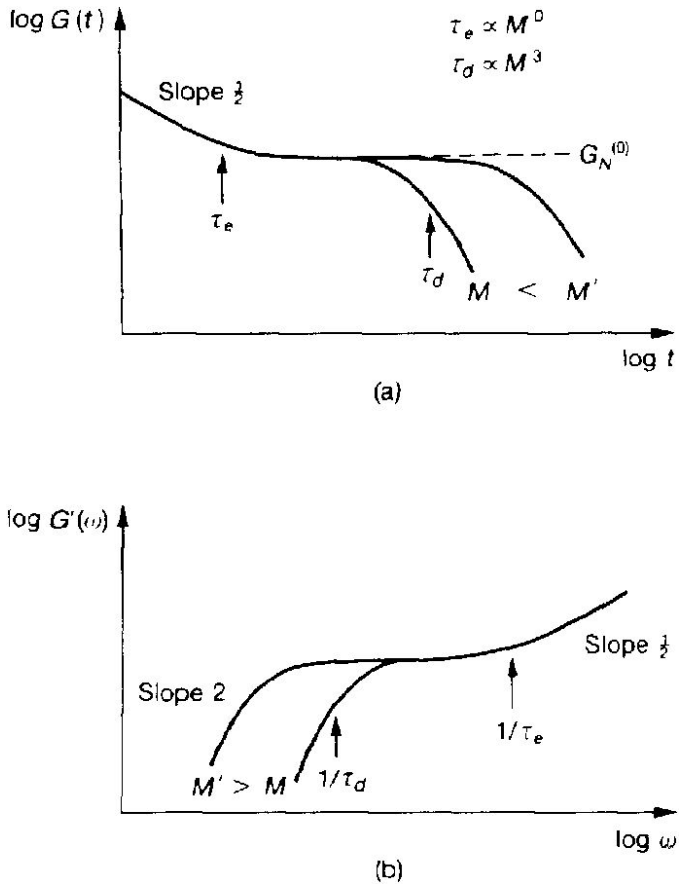

Figure 3: Doi-Edwards Reptation Predictions. (a) Relaxation Modulus (b) Storage Modulus

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DOI-EDWARDS THEORY (P. 5)

$$G(t) = G_N^0 \frac{8}{\pi^2} \sum_{p \text{ odd}}^{N} \frac{1}{p^2} e^{-p^2 t/\lambda_d} \tag{2-110}$$

$$\lambda_d = \frac{a^2 \zeta M^3}{M_e M_0^2 \pi^2 kT} \tag{2-111}$$

Viscosity

$$\eta_0 = \int_0^\infty G(t)dt \tag{2-19}$$

$$\eta_0 = \frac{1}{12} \frac{\rho N_0 a^2 \zeta M^3}{M_e^2 M_0^2} = \frac{\pi^2}{12} G_N^0 \lambda_d \qquad \text{text has typo!} \tag{2-112}$$

Steady State Compliance

$$J_S^0 = \frac{1}{\eta_0^2} \int_0^\infty G(t) t dt \tag{2-33}$$

$$J_S^0 = \frac{6}{5} \frac{M_e}{\rho RT} = \frac{6}{5 G_N^0} \qquad \text{text has typo!} \tag{2-113}$$

independent of chain length.

Longest Relaxation Time

$$\lambda_d = \frac{12 M_e \eta_0}{\pi^2 \rho RT} = \frac{10}{\pi^2} \eta_0 J_S^0 \qquad \text{text has typo!} \tag{2-114}$$

Thus both Rouse and Reptation Models predict

$$\lambda \cong \eta_0 J_S^0$$

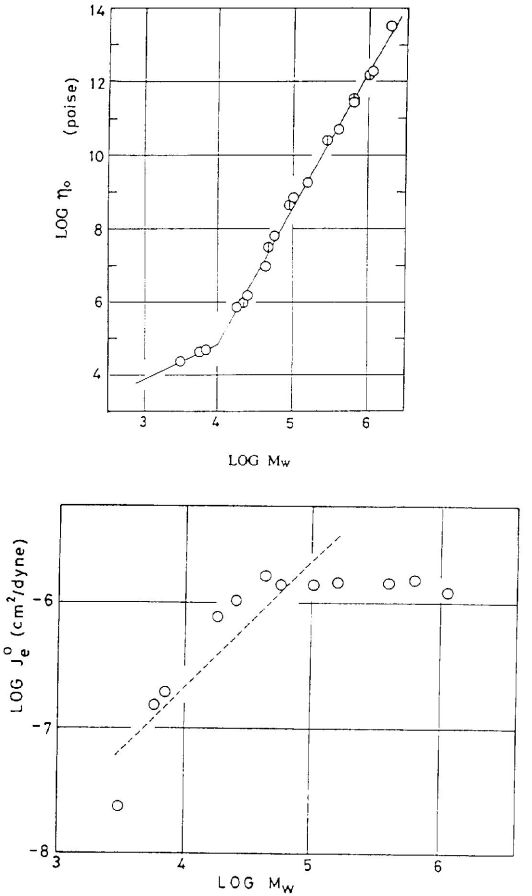

Figure 4: Viscosity and Steady State Compliance

Significance of $\lambda \cong \eta_0 J_S^0$

λ, η_0 and J_S^0 are **terminal properties** associated with **liquid flow**.

$$G''(\omega) = \eta_0 \omega$$

$$G'(\omega) = J_s^0 \eta_0^2 \omega^2$$

These power laws intersect at

$$\omega_x = \frac{1}{J_s^0 \eta_0} = \frac{1}{\lambda} \quad \text{and} \quad G'(\omega_x) = G''(\omega_x) = \frac{1}{J_s^0}$$

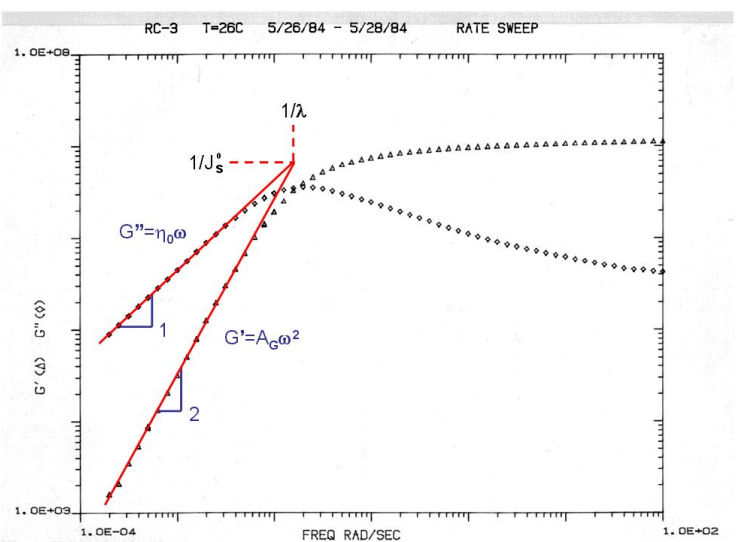

Figure 5: Storage and Loss Moduli Terminal Slopes of 2 and 1.