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9.1 Entanglements in polymer melts

The Edwards tube model of polymer entanglements was already discussed in Section 7.3.1. The topological constraints imposed by neighbouring chains on a given chain restrict its motion to a tube-like region (see Fig. 7.10) called the confining tube. The motion of the chain along the contour of the tube (the primitive path) is unhindered by topological interactions. Displacement of monomers in the direction perpendicular to the primitive path is restricted by surrounding chains to an average distance a, called the tube diameter. The number of Kuhn monomers in a strand of size equal to the amplitude of transverse fluctuations (the tube diameter) is N_{e} , the number of monomers in an entanglement strand. For melts, excluded volume interactions are screened (see Section 4.5.2) and the tube diameter is determined by ideal chain statistics:

$$a \approx b\sqrt{N_{\rm e}}.$$
 (9.1)

The tube can be thought of as being composed of N/N_e sections of size *a*, with each section containing N_e monomers. The chain can be considered as either a random walk of entanglement strands (N/N_e strands of size *a*) or a random walk of monomers (*N* monomers of size *b*).

$$R \approx a \sqrt{\frac{N}{N_{\rm e}}} \approx b \sqrt{N}. \tag{9.2}$$

The average contour length $\langle L \rangle$ of the primitive path (the centre of the confining tube, see Fig. 7.10) is the product of the entanglement strand length *a* and the average number of entanglement strands per chain N/N_e .

$$\langle L \rangle \approx a \frac{N}{N_{\rm e}} \approx \frac{b^2 N}{a} \approx \frac{b N}{\sqrt{N_{\rm e}}}.$$
 (9.3)

The average primitive path contour length $\langle L \rangle$ is shorter than the contour length of the chain bN by the factor $a/b \approx \sqrt{N_e}$ because each entanglement strand in a melt is a random walk of N_e Kuhn monomers.

One manifestation of entanglement in long chains $(N \gg N_e)$ is the appearance of a wide region in time (or frequency) where the modulus is

almost constant in a stress relaxation (or oscillatory shear) experiment. In analogy with crosslinked rubbers, this region is referred to as the **rubbery plateau**, and the nearly constant value of the modulus in this plateau regime is called the **plateau modulus** G_e . In analogy with an affine network, whose modulus is of order kT per network strand [Eq. (7.31)], the plateau modulus is of order kT per entanglement strand [Eq.(7.47)]. The numberaverage molar mass of an entanglement strand is called the entanglement molar mass M_e . The occupied volume of an entanglement strand with molar mass M_e in a melt with density ρ is the product of the number of Kuhn monomers per strand N_e and the Kuhn monomer volume v_0 :

$$\frac{M_{\rm e}}{\rho \mathcal{N}_{\rm Av}} = v_0 N_{\rm e} \approx v_0 \frac{a^2}{b^2} \approx \frac{v_0}{b^3} a^2 b. \tag{9.4}$$

Since monomers are space-filling in the melt, the number density of entanglement strands is just the reciprocal of the entanglement strand volume, leading to a simple expression for the plateau modulus of an entangled polymer melt [Eq. (7.47)].

$$G_{\rm e} \approx \frac{\rho \mathcal{R}T}{M_{\rm e}} \approx \frac{kT}{\mathbf{v}_0 N_{\rm e}} \approx \frac{b^3}{\mathbf{v}_0} \frac{kT}{a^2 b}.$$
 (9.5)

The number of chains P_e within the confinement volume a^3 is determined from the fact that monomers in the melt are space-filling:

$$P_{\rm e} \approx \frac{a^3}{v_0 N_{\rm e}} \approx \frac{b^3}{v_0} \sqrt{N_{\rm e}}.$$
(9.6)

Table 9.1 shows N_e and P_e calculated from the measured plateau modulus. All flexible polymers have $P_e \cong 20$ overlapping entanglement strands defining the entanglement volume a^3 , which is the overlap criterion for entanglement in polymer melts.

Table 9.1 Entanglement parameters for flexible linear polymer melts

Polymer	G _e (MPa)	$M_{\rm c}~({\rm gmol^{-1}})$	$N_{\rm e}$	b (Å)	a (Å)	v_0 (Å ³)	$P_{\rm e}$
Polyethylene at 140 °C	2.6	1000	7	14	36	320	21
Poly(ethylene oxide) at 80 °C	1.8	1700	13	11	37	210	19
1,4-Polybutadiene at 25°C	1.15	1900	18	10	41	190	19
Polypropylene at 140 °C	0.47	5800	32	11	62	380	20
1,4-Polyisoprene at 25°C	0.35	6400	53	8.4	62	220	20
Polyisobutylene at 25 °C	0.34	6700	24	13	62	500	19
Polydimethylsiloxane at 25 °C	0.20	12 000	32	13	74	650	20
Polystyrene at 140 °C	0.20	17000	23	18	85	1200	22
Polyvinylcyclohexane at 160 °C	0.068	49 000	81	14	130	1100	22

9.2 Reptation in polymer melts

At first glance, understanding the motion of a polymer in the melt is daunting. Since roughly \sqrt{N} other polymers share the pervaded volume of a given chain in the melt, chain motion appears to be a difficult manybody problem. However, by utilizing the Edwards tube concept, de Gennes cleverly reduced this many-body problem to the motion of a single chain confined to a tube of surrounding chains. Models that consider chain motion as being restricted to a tube-like region are referred to as **tube models**. The simplest tube model was proposed by de Gennes in 1971 for the motion of linear entangled polymers, and is called the **reptation model**.

9.2.1 Relaxation times and diffusion

In de Gennes' reptation model, an entangled chain diffuses along its confining tube in a way analogous to the motion of a snake or a worm (see Fig. 9.1). This motion of the chain consists of diffusion of small loops, along the contour of the primitive path. This curvilinear motion of a polymer along its tube satisfies the topological constraints imposed by surrounding chains and is characterized by the Rouse friction coefficient $N\zeta$. The curvilinear diffusion coefficient D_c that describes motion of the chain along its tube is simply the Rouse diffusion coefficient of the chain [Eq. (8.12)].

$$D_{\rm c} = \frac{kT}{N\zeta}.\tag{9.7}$$

The time it takes for the chain to diffuse out of the original tube of average length $\langle L \rangle$ is the reptation time:

$$\tau_{\rm rep} \approx \frac{\langle L \rangle^2}{D_{\rm c}} \approx \frac{\zeta b^2}{kT} \frac{N^3}{N_{\rm e}} = \frac{\zeta b^2}{kT} N_{\rm e}^2 \left(\frac{N}{N_{\rm e}}\right)^3.$$
(9.8)

Here, Eq. (9.3) was used for the average contour length of the tube. The reptation time τ_{rep} is predicted to be proportional to the cube of the molar mass. The experimentally measured scaling exponent is higher than 3:

$$\tau \sim M^{3.4}.\tag{9.9}$$

We will discuss the possible reasons for the disagreement between the simple reptation model and experiments in Section 9.4.5.

The first part of the final relation of Eq. (9.8) is the Rouse time of an entanglement strand containing N_e monomers:

$$\tau_{\rm e} \approx \frac{\zeta b^2}{kT} N_{\rm e}^2. \tag{9.10}$$



Fig. 9.1

Reptation steps: (a) formation of a loop at the tail of the snake and elimination of the tail segment of the confining tube; (b) propagation of the loop along the contour of the tube; (c) release of the loop at the head of the snake and formation of a new section of the confining tube.



Fig. 9.2

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Molar mass dependence of the diffusion coefficient for melts of hydrogenated polybutadiene at 175 °C. Data compiled in T. P. Lodge *Phys. Rev. Lett.* **83**, 3218 (1999).

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The ratio of the reptation time τ_{rep} and τ_e is the cube of the number of entanglements along the chain:

$$\frac{\tau_{\rm rep}}{\tau_{\rm e}} \approx \left(\frac{N}{N_{\rm e}}\right)^3.$$
 (9.11)

The chain moves a distance of order of its own size R in its reptation time τ_{rep} , since this is the time scale at which the tube is abandoned:

$$D_{\rm rep} \approx \frac{R^2}{\tau_{\rm rep}} \approx \frac{kT N_{\rm e}}{\zeta N^2}.$$
 (9.12)

The diffusion coefficient of entangled linear polymers is predicted to be reciprocally proportional to the square of the molar mass, which also disagrees with experiments, as shown in Fig. (9.2):

$$D \approx \frac{R^2}{\tau} \sim M^{-2.3}.$$
(9.13)

9.2.2 Stress relaxation and viscosity

The reptation ideas discussed above will now be combined with the relaxation ideas discussed in Chapter 8 to describe the stress relaxation modulus G(t) for an entangled polymer melt. On length scales smaller than the tube diameter a, topological interactions are unimportant and the dynamics are similar to those in unentangled polymer melts and are described by the Rouse model. The entanglement strand of N_e monomers relaxes by Rouse motion with relaxation time τ_e [Eq. (9.10)]:

$$\tau_{\rm e} = \tau_0 N_{\rm e}^2. \tag{9.14}$$

The Rouse model predicts that the stress relaxation modulus on these short time scales decays inversely proportional to the square root of time [Eq. (8.47)]:

$$G(t) \approx G_0 \left(\frac{t}{\tau_0}\right)^{-1/2} \quad \text{for } \tau_0 < t < \tau_e.$$
(9.15)

The relaxation time of the Kuhn monomer τ_0 is the shortest stress relaxation time in the Rouse model, given by Eq. (8.56) with p = N:

$$\tau_0 = \frac{\zeta b^2}{6\pi^2 kT} \approx \frac{\zeta b^2}{kT}.$$
(9.16)

The stress relaxation modulus at τ_0 is the Kuhn modulus (kT per Kuhn monomer):

$$G_0 \approx G(\tau_0) \approx \frac{kT}{\mathbf{v}_0}.\tag{9.17}$$





Consider for example, a melt of 1,4-polybutadiene linear chains with $M = 130\,000\,\mathrm{g\,mol^{-1}}$. The molar mass of a polybutadiene Kuhn monomer is $M_0 = 105\,\mathrm{g\,mol^{-1}}$ (see Table 2.1) so this chain has $N = M/M_0 = 1240$ Kuhn monomers. At 25 °C, this polymer is 124 K above its glass transition and its oscillatory shear master curve is shown in Fig. 9.3. The time scale for monomer motion is $\tau_0 \cong 0.3$ ns, An entanglement strand of 1,4-polybutadiene has molar mass $M_e = 1900\,\mathrm{g\,mol^{-1}}$ (see Table 9.1) and therefore contains $N_e = M_e/M_o = 18$ Kuhn monomers. The whole chain has $N/N_e = M/M_e = 68$ entanglements. The Rouse time of the entanglement strand $\tau_e \cong 0.1\,\mu$ s [Eq. (9.10)].

At the Rouse time of an entanglement strand τ_e , the chain 'finds out' that its motion is topologically hindered by surrounding chains. Free Rouse motion of the chain is no longer possible on time scales $t > \tau_e$. The value of the stress relaxation modulus at τ_e is the plateau modulus G_e , which is kTper entanglement strand [Eq. (9.5)]:

$$G_{\rm e} = G(\tau_{\rm e}) = \frac{G_0}{N_{\rm e}} = \frac{kT}{v_0 N_{\rm e}}.$$
 (9.18)

The Rouse time of the chain is $\tau_{\rm R} \cong 0.5$ ms:

$$\tau_{\rm R} = \tau_0 N^2 = \tau_{\rm e} \left(\frac{N}{N_{\rm e}}\right)^2. \tag{9.19}$$

In the simple reptation model, there is a delay in relaxation (the rubbery plateau) between τ_e and the reptation time of the chain τ_{rep} [Eq. (9.11)]. By restricting the chain's Rouse motions to the tube, the time the chain takes to diffuse a distance of order of its size is longer than its Rouse time by a factor of $6 N/N_e$. This slowing arises because the chain must move along the confining tube. The reptation time of the chain $\tau_{rep} = 0.2 \text{ s}$ is measured experimentally as the reciprocal of the frequency at which G' = G'' in Fig. 9.3 at low frequency (see Problem 9.8). In practice, this time is determined experimentally and τ_0 , τ_e and τ_R are determined from τ_{rep} .



Fig. 9.4

Schematic representation of the stress relaxation modulus of entangled linear polymers on logarithmic scales.

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The stress relaxation modulus is summarized schematically in Fig. 9.4. For long linear chains, the rubbery plateau can span many decades in time.

The diffusion coefficient of the chain is controlled by the reptation time [Eq. (9.12)]. The linear polybutadiene chain with $M = 130\,000\,\mathrm{g\,mol^{-1}}$ has N = 1240 Kuhn monomers, with Kuhn length $b = 10\,\mathrm{\AA}$ and coil size $R = b\sqrt{N} \cong 350\,\mathrm{\AA}$. Since linear polymers move a distance of order their own size in their reptation time, the reptation time of $\tau_{\rm rep} \cong 0.2\,\mathrm{s}$ at $25\,^{\circ}\mathrm{C}$ enables estimation of the diffusion coefficient $D \approx R^2/\tau_{\rm rep} \cong 6 \times 10^{-15}\,\mathrm{m}^2\,\mathrm{s}^{-1}$. Physically, this means that at $25\,^{\circ}\mathrm{C}$ this polybutadiene chain moves about $350\,\mathrm{\AA}$ in a random direction every 0.2 s.

The stress relaxation modulus in the reptation model is proportional to the fraction of original tube remaining at time t (see Fig. 9.1). As time goes on, sections of the original tube are abandoned when the chain end first visits them. Such a problem is called a first-passage time problem. The stress relaxation modulus G(t) for the reptation model was calculated by Doi and Edwards in 1978 by solving the first-passage problem for the diffusion of a chain in a tube (see Problem 9.6):

$$G(t) = \frac{8}{\pi^2} G_{\rm e} \sum_{\text{odd}\,p} \frac{1}{p^2} \exp\left(-\frac{p^2 t}{\tau_{\rm rep}}\right). \tag{9.20}$$

The longest relaxation time in this model is the reptation time required for the chain to escape from its tube

$$\tau_{\rm rep} = 6\tau_0 \frac{N^3}{N_{\rm e}} = 6\tau_{\rm e} \left(\frac{N}{N_{\rm e}}\right)^3 = 6\tau_{\rm R} \frac{N}{N_{\rm e}}$$
(9.21)

where the Rouse time τ_R is the longest relaxation time of the Rouse model [Eq. (8.18)], which is half the end-to-end vector correlation time.

The main contribution¹ comes from the first mode p = 1 and the function is almost a single exponential [Eq. (7.111)]:

$$G(t) \approx G_{\rm e} \exp(-t/\tau_{\rm rep}).$$
 (9.22)

The **Doi–Edwards equation** [Eq. (9.20)] is the first attempt at a molecular model for viscoelasticity of entangled polymers. It ignores tube length fluctuation modes that relax some stress on shorter time scales. These modes significantly modify dynamics of entangled polymers, as described in Section 9.4.5.

The reptation model prediction for the viscosity of an entangled polymer melt is determined by integrating Eq. (9.20):

$$\eta = \int_{0}^{\infty} G(t) \, \mathrm{d}t = \frac{8}{\pi^2} G_{\rm e} \sum_{\text{odd}\,p} \frac{1}{p^2} \int_{0}^{\infty} \exp\left(-\frac{p^2 t}{\tau_{\rm rep}}\right) \, \mathrm{d}t = \frac{\pi^2}{12} G_{\rm e} \tau_{\rm rep}.$$
 (9.23)

¹ Fraction $8/\pi^2$ of the terminal relaxation is associated with the first mode with relaxation time $\tau_{\rm rep}$ (see Problem 9.7).

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The final result was obtained from the fact that $\sum_{\text{odd}p} 1/p^4 = \pi^4/96$. Since the stress relaxation is nearly a single exponential, the scaling prediction of the viscosity as the product of the plateau modulus [Eq. (9.5)] and the reptation time [Eq. (9.8)] is nearly quantitative:

$$\eta \approx G_{\rm e} \tau_{\rm rep} \approx G_{\rm e} \tau_{\rm e} \left(\frac{N}{N_{\rm e}}\right)^3 \approx \frac{kT}{v_0 N_{\rm e}} \frac{\zeta b^2 N_{\rm e}^2}{kT} \left(\frac{N}{N_{\rm e}}\right)^3 \approx \frac{\zeta b^2}{v_0} \frac{N^3}{N_{\rm e}^2}.$$
 (9.24)

The viscosity of a polymer melt is predicted to be proportional to molar mass for unentangled melts (the Rouse model) and proportional to the cube of molar mass for entangled melts (the reptation model).

$$\eta \sim \begin{cases} M & \text{for } M < M_{\rm c}, \\ M^3 & \text{for } M > M_{\rm c}. \end{cases}$$
(9.25)

As Fig. 8.17 shows, the critical molar mass M_c for entanglement effects in viscosity [defined in Eq. (8.136)] is typically a factor of 2–4 larger than the entanglement molar mass M_e [defined in Eq. (9.5)]. As shown in Fig. 9.5, the exponent in the entangled regime is $\cong 3.4$ for all linear entangled polymers. This exponent is significantly larger than the prediction of 3 by the simple reptation model [Eq. (9.24)]:

$$\eta \approx G_{\rm e} \tau \sim M^{3.4}.\tag{9.26}$$

The deviations from the 3.4 power law at low molar masses ($M < M_c$) are because those chains are too short to be entangled (see Section 8.7.3). The deviations at very high molar mass are consistent with a crossover to pure reptation (see Section 9.4.5).

The simple reptation model does not properly account for all the relaxation modes of a chain confined in a tube. This manifests itself in all measures of terminal dynamics, as the longest relaxation time, diffusion coefficient and viscosity all have stronger molar mass dependences than the reptation model predicts. In Sections 9.4.5 and 9.6.2, more accurate analytical and numerical treatments of this problem are given with results that are in reasonable agreement with the experimental dependence of terminal dynamics on the molar mass of the chain [Eqs (9.9), (9.13), and (9.26)].

9.3 Reptation in semidilute solutions

9.3.1 Length scales

Consider a semidilute solution with polymer volume fraction ϕ . The concentration dependence of the correlation length was discussed in Chapter 5:

$$\xi \approx b\phi^{-\nu/(3\nu-1)}.\tag{9.27}$$



Fig. 9.5

Molar mass dependence of viscosity for polymer melts reduced by their critical molar mass. Open circles are polyisobutylene with $M_c = 14\,000\,\mathrm{g\,mol^{-1}}$, from T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.* **70**, 2384 (1948) and *J. Phys. Chem.* **55**, 221 (1951). Open squares are polybutadiene with $M_c = 6700\,\mathrm{g\,mol^{-1}}$, from R. H. Colby *et al.*, *Macromolecules* **20**, 2226 (1987). Open triangles are hydrogenated polybutadiene with $M_c = 8100\,\mathrm{g\,mol^{-1}}$, from D. S. Pearson *et al.*, *Macromolecules* **27**, 711 (1994).

In an athermal solvent the exponent $\nu \approx 0.588$ and the correlation length decreases with concentration as $\xi \approx b\phi^{-0.76}$, while in a θ -solvent the exponent $\nu = 1/2$ and the correlation length has a stronger concentration dependence $\xi \approx b\phi^{-1}$ [Eq. (5.52)]. The number of monomers g in a correlation volume ξ^3 was also determined in Chapter 5 [Eq. (5.24)]:

$$g \approx \frac{\phi \xi^3}{b^3} \approx \phi^{-1/(3\nu - 1)}.$$
(9.28)

In an athermal solvent, the number of monomers in a correlation volume decreases with concentration as $g \approx \phi^{-1.3}$, while in a θ -solvent a stronger concentration dependence is expected with $g \approx \phi^{-2}$. The chain is always a random walk of correlation blobs, with end-to-end distance *R* [Eq. (5.26)]:

$$R \approx \xi \left(\frac{N}{g}\right)^{1/2} \approx b N^{1/2} \phi^{-(2\nu-1)/(6\nu-2)}.$$
(9.29)

In a good solvent, the chain size decreases with concentration as $R \approx b N^{1/2} \phi^{-0.12}$. In a θ -solvent ($\nu = 1/2$) there is no concentration dependence of chain size, as the chain is nearly ideal at all concentrations $R \approx b N^{1/2}$.

To understand the dynamics of entangled solutions, another length scale, the tube diameter *a*, must be specified. Just as in the melt, the confinement volume a^3 must contain multiple chains. Entanglements between chains are controlled by binary intermolecular contacts. In the athermal solvent limit, the number density of binary intermolecular contacts is proportional to the reciprocal of the correlation volume $\xi^{-3} \sim \phi^{3\nu/(3\nu-1)}$, and the distance between binary contacts is the reciprocal cube root of this number density $\xi \sim \phi^{-\nu/(3\nu-1)}$. Hence, the correlation length describes the distance between binary intermolecular contacts. *The tube diameter a in an athermal solvent is proportional to, but larger than, the correlation length* ξ :

$$a(\phi) \approx a(1)\phi^{-\nu/(3\nu-1)} \approx a(1)\phi^{-0.76}$$
 for an athermal solvent. (9.30)

The tube diameter in the melt, $a(1) \approx b\sqrt{N_e(1)}$, is given by Eq. (9.1) in terms of the number of Kuhn monomers in an entanglement strand in the melt $N_e(1)$. Notice that a(1) > b, which makes $a > \xi$ at all concentrations. Since the chain is a random walk of correlation blobs on scales larger than ξ , the entanglement strand is a random walk of correlation blobs, as depicted in Fig. 9.6.

In a θ -solvent, the correlation length is determined by ternary contacts between chains (see Section 5.4). This is because the effects of binary contacts on the free energy (or osmotic pressure) exactly cancel at the θ -temperature. The solvent-mediated energetic interaction between monomers exactly compensates for the hard core repulsion at the θ -temperature. Binary contacts between chains still occur, they simply have



Fig. 9.6

The confining tube in a semidilute solution. Thick circles are the correlation blobs of the chain. Thin empty circles are the correlation blobs of surrounding chains.

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no effect on the free energy, and this directly leads to nearly ideal chain statistics at all concentrations in a θ -solvent, and the applicability of mean-field theory. However, binary contacts still control entanglements between chains. The number density of space-filling correlation volumes in a θ -solvent is given by the mean-field result $\xi^{-3} \sim \phi^3$. The same mean-field ideas determine the number density of binary intermolecular contacts to be proportional to ϕ^2 . Just as in the good solvent, the average distance between binary contacts is given by the reciprocal cube root of this number density, and in a θ -solvent the distance is proportional to, but larger than, the distance between binary contacts:

$$a(\phi) \approx a(1)\phi^{-2/3}$$
 for a θ -solvent. (9.31)

The length scales ξ , a, and *R* are plotted as a function of concentration for a typical good solvent in Fig. 9.7. All three length scales change their concentration dependences from athermal to ideal at the concentration $\phi^{**} \approx v/b^3$ separating semidilute and concentrated solutions.

9.3.2 Entanglement concentration

The concentration at which the correlation length ξ is of the order of the coil size $R \approx bN^{\nu}$ is the overlap concentration ϕ^* , given by Eq. (5.19):

$$\phi^* \approx \frac{Nb^3}{R^3} \approx N^{1-3\nu}.$$
(9.32)

In an athermal solvent $\phi^* \approx N^{-0.76}$, while in a θ -solvent $\phi^* \approx N^{-1/2}$.

The concentration at which the tube diameter a [from Eqs (9.30) or (9.31)] equals the coil size R [Eq. (9.29)] is the entanglement concentration ϕ_e :

$$\phi_{\rm e} \approx \begin{cases} [N_{\rm e}(1)/N]^{(3\nu-1)} \approx [N_{\rm e}(1)/N]^{0.76} & \text{for an athermal solvent,} \\ [a(1)/b]^{3/2} N^{-3/4} \approx [N_{\rm e}(1)/N]^{3/4} & \text{for a } \theta\text{-solvent,} \end{cases}$$
(9.33)

where $N_{e}(1)$ is the number of Kuhn monomers in an entanglement strand in the melt. Note that the predictions for both solvents are very similar.

For $\phi > \phi_e$, entanglement effects control chain dynamics and the reptation model must be used as described below. Between the overlap concentration and the entanglement concentration ($\phi^* < \phi < \phi_e$), the solution is semidilute but not entangled, and the unentangled solution model of Section 8.5 describes dynamics. The width of this semidilute unentangled regime is given by the ratio of Eqs (9.33) and (9.32):

$$\frac{\phi_{\rm e}}{\phi^*} \approx \begin{cases} [N_{\rm e}(1)]^{3\nu-1} \approx [N_{\rm e}(1)]^{0.76} & \text{for an athermal solvent,} \\ ([N_{\rm e}(1)]^{3/4})/N^{1/4} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.34)



Fig. 9.7

Chain size *R*, tube diameter *a*, and correlation length ξ in a good solvent. The semidilute unentangled regime is $\phi^* < \phi < \phi_e$; the semidilute entangled regime is $\phi_e < \phi < \phi^{**}$ and; the concentrated regime is $\phi^{**} < \phi < 1$.

Table 9.1 shows that the number of Kuhn monomers in an entanglement strand in the melt state varies over a wide range $(7 < N_e(1) < 80)$ making $4 < \phi_e/\phi^* < 30$ for solutions in an athermal solvent. Since the entanglement concentration ϕ_e cannot be lower than the overlap concentration ϕ^* , the expressions for a θ -solvent [Eqs (9.31), (9.33), and (9.34)] are valid for $N < [N_e(1)]^3$. This condition is not very restrictive and it is satisfied for all experimental studies to date.

9.3.3 Plateau modulus

Owing to the fact that the tube diameter is always larger than the correlation length $(a > \xi)$, the entanglement strand is a random walk of correlation volumes in any solvent:

$$a \approx \xi \sqrt{\frac{N_{\rm e}}{g}},$$
 (9.35)

where N_e/g is the number of correlation volumes per entanglement strand. The above relation can be solved for the concentration dependence of the number of monomers in an entanglement strand:

$$N_{\rm e}(\phi) \approx g \left(\frac{a}{\xi}\right)^2 \approx N_{\rm e}(1) \begin{cases} \phi^{-1/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{-4/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.36)

The two predictions are nearly identical, since $1/(3\nu - 1) \cong 1.3$.

The occupied volume of an entanglement strand is $\xi^3 N_e/g \approx a^2 \xi$. Since the correlation volumes are space-filling in solution, the number density of entanglement strands is simply the reciprocal of this volume. Analogous to Eq. (9.5), the plateau modulus of an entangled polymer solution is once again of the order of kT per entanglement strand,

$$G_{\rm e}(\phi) \approx \frac{kT}{a^2 \xi} \approx \frac{kT\phi}{b^3 N_{\rm e}(\phi)} \approx G_{\rm e}(1) \begin{cases} \phi^{3\nu/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{7/3} & \text{for a } \theta\text{-solvent,} \end{cases}$$
(9.37)

where $G_{e}(1)$ is the plateau modulus of the melt, given by Eq. (9.5). The predictions for athermal and θ -solvents are essentially the same (the concentration dependence exponents are $\cong 2.3$ in both cases). This interesting result is experimentally confirmed, as shown in Fig. 9.8.

9.3.4 Relaxation times and diffusion

Topological constraints do not influence polymer motion on length scales smaller than the size of an entanglement strand. In entangled polymer solutions, chain sections with end-to-end distance shorter than the tube



Fig. 9.8

Dilution effect on the plateau modulus of linear polymers. Filled diamonds are polystyrene in cyclohexane at $34.5 \,^{\circ}C (\theta$ -solvent), open squares are polystyrene in benzene at $25 \,^{\circ}C$ (good solvent), filled circles are polybutadiene in dioctylphthalate at $25 \,^{\circ}C$ (near θ -solvent) and open triangles are polybutadiene in phenyloctane (good solvent). PS data from M. Adam and M. Delsanti, *J. Phys. France* **44**, 1185 (1983); **45**, 1513 (1984). PB data from R. H. Colby *et al.*, *Macromolecules* **24**, 3873 (1991).

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diameter *a* move as they would in an unentangled solution. On length scales smaller than the correlation length ξ , hydrodynamic interactions are not screened. As with unentangled chains, the relaxation time τ_{ξ} of the strand within each correlation volume is determined by the Zimm result [Eq. (8.75)]:

$$\tau_{\xi} \approx \frac{\eta_{s}}{kT} \xi^{3} \approx \frac{\eta_{s} b^{3}}{kT} \left(\frac{\xi}{b}\right)^{3} \approx \tau_{0} \left(\frac{\xi}{b}\right)^{3} \approx \tau_{0} \phi^{-3\nu/(3\nu-1)}.$$
(9.38)

On length scales larger than the correlation length ξ but smaller than the tube diameter *a*, hydrodynamic interactions are screened, and topological interactions are unimportant. Polymer motion on these length scales is described by the Rouse model. The relaxation time τ_e of an entanglement strand of N_e monomers is that of a Rouse chain of N_e/g correlation volumes [Eq. (8.76)]:

$$\tau_{\rm e} \approx \tau_{\xi} \left(\frac{N_{\rm e}}{g}\right)^2 \approx \tau_0 [N_{\rm e}(1)]^2 \begin{cases} \phi^{-3\nu/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{-5/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.39)

On length scales larger than the tube diameter, topological interactions are important and the motion is described by the reptation model with the chain relaxation time given by the reptation time:

$$\tau_{\rm rep} \approx \tau_{\rm e} \left(\frac{N}{N_{\rm e}}\right)^3 \approx \tau_0 \left(\frac{\xi}{b}\right)^3 \left(\frac{N_{\rm e}}{g}\right)^2 \left(\frac{N}{N_{\rm e}}\right)^3. \tag{9.40}$$

Using Eqs (9.27), (9.28), and (9.36) transforms this into a simple relation for the concentration dependence of the reptation time:

$$\tau_{\rm rep} \approx \tau_0 \frac{N^3}{N_{\rm e}(1)} \begin{cases} \phi^{3(1-\nu)/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{7/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.41)

The reptation time has a considerably weaker concentration dependence in athermal solvent than in θ -solvent, since $3(1 - \nu)/(3\nu - 1) \cong 1.6$. Note that Eq. (9.41) reduces to Eq. (9.20) when $\phi = 1$.

The diffusion coefficient in semidilute polymer solutions is determined from the fact that the chain diffuses a distance of order of its own size in its reptation time:

$$D \approx \frac{R^2}{\tau_{\rm rep}} \approx \frac{b^2}{\tau_0} \frac{N_{\rm e}(1)}{N^2} \begin{cases} \phi^{-(2-\nu)/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{-7/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.42)

The reptation prediction of the concentration dependence of diffusion coefficient in athermal solvent is slightly weaker than in θ -solvent, since

 $(2 - \nu)/(3\nu - 1) \cong 1.85$. Figure 8.9 already showed that there is a low concentration regime that is semidilute but unentangled that is described by Eq. (8.85). That regime persists for roughly one decade in good solvent, as expected by Eq. (9.34). Above the entanglement concentration ϕ_e , the athermal solvent prediction of Eq. (9.42) applies for a range of concentration (see Fig. 8.9). At still higher concentrations, an even stronger concentration dependence is noted for the two highest concentrations in Fig. 8.9, consistent with the θ -solvent scaling prediction of Eq. (9.42) in concentrated solution (for $\phi > \phi^{**}$):

$$D \sim \begin{cases} \phi^{-0.54} & \text{for } \phi^* < \phi < \phi_e, \\ \phi^{-1.85} & \text{for } \phi_e < \phi < \phi^{**}, \\ \phi^{-7/3} & \text{for } \phi^{**} < \phi < 1. \end{cases}$$
(9.43)

9.3.5 Stress relaxation and viscosity

There are three different regimes of polymer dynamics on three different length and time scales for an entangled polymer solution in an athermal solvent. The stress relaxation modulus of such a solution is shown in Fig. 9.9. Two of the regimes are identical to those discussed in Section 9.2.2 and the other regime was discussed in Section 8.5.

Between τ_0 and the relaxation time of a correlation blob τ_{ξ} , both static and dynamic properties are similar to those in a dilute solution. Hydrodynamic interactions are important and dynamics of these small sections of chains are described by the Zimm model. The stress relaxation modulus on time scales between τ_0 and τ_{ξ} is similar to the Zimm result for unentangled solutions discussed in Section 8.5 [Eq. (8.88)]. The stress relaxation modulus decays with time as a power law with exponent $-1/(3\nu)$. This time dependence is $G(t) \sim t^{-0.57}$ in a good solvent with Flory exponent $\nu \cong 0.588$ and is $G(t) \sim t^{-2/3}$ in a θ -solvent. The stress relaxation modulus in this regime decays from the Kuhn modulus G_0 (kT per Kuhn monomer) to the osmotic pressure Π [kT per correlation blob, see Eq. (8.89)].

On intermediate length scales between the correlation length ξ and the tube diameter *a*, hydrodynamic interactions are screened and topological interactions are not important. The dynamics on these intermediate scales (for $\tau_{\xi} < t < \tau_{e}$) are described by the Rouse model with stress relaxation modulus similar to the Rouse result for unentangled solutions [Eq. (8.90) with the long time limit the Rouse time of an entanglement strand τ_{e}]. At τ_{e} , the stress relaxation modulus has decayed to the plateau modulus $G_e[kT]$ per entanglement strand, Eq. [(9.37), see Fig. 9.9)]. The ratio of osmotic pressure and plateau modulus at any concentration in semidilute solution in athermal solvents is proportional to the number of Kuhn monomers in an entanglement strand in the melt. In θ -solvents this ratio is considerably smaller and concentration dependent:

$$\frac{\Pi}{G_{\rm e}} \approx \left(\frac{a}{\xi}\right)^2 \approx \begin{cases} N_{\rm e}(1) & \text{for an athermal solvent,} \\ N_{\rm e}(1)\phi^{2/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.44)



Fig. 9.9

Schematic representation of the stress relaxation modulus of an entangled polymer solution in an athermal solvent on logarithmic scales. At the Rouse time of an entanglement strand τ_e , the chain in semidilute solution 'finds out' that it is trapped in the confining tube. The stress relaxation modulus between τ_e and the reptation time τ_{rep} is almost constant and equal to the plateau modulus (see Fig. 9.9). At the reptation time [Eq. (9.41)], the stress relaxation modulus decays to zero exponentially [Eq. (9.22)].

The polymer contribution to the viscosity of an entangled polymer solution is estimated as the product of the plateau modulus [Eq. (9.37)] and the reptation time [Eq. (9.41)]:

$$\eta - \eta_{\rm s} \approx G_{\rm e} \tau_{\rm rep} \approx \eta_{\rm s} \frac{N^3}{\left[N_{\rm e}(1)\right]^2} \begin{cases} \phi^{3/(3\nu-1)} & \text{for an athermal solvent,} \\ \phi^{14/3} & \text{for a } \theta\text{-solvent.} \end{cases}$$
(9.45)

The concentration dependence of viscosity is $\eta \sim \phi^{3.9}$ in an athermal solvent with Flory exponent $\nu \simeq 0.588$ and $\eta \sim \phi^{4.7}$ in a θ -solvent. The 14/3 $\simeq 4.7$ exponent is demonstrated for poly(ethylene oxide) in water at 25.0 °C in Fig. 8.11. There are two different scaling regimes for the specific viscosity in an athermal solvent, corresponding to unentangled and entangled semidilute solutions:

$$\eta_{\rm sp} \approx \begin{cases} (\phi/\phi^*)^{1/(3\nu-1)} & \text{for } \phi^* < \phi < \phi_{\rm e}, \\ (\phi/\phi^*)^{3/(3\nu-1)}/[N_{\rm e}(1)]^2 & \text{for } \phi_{\rm e} < \phi < 1. \end{cases}$$
(9.46)

Data for different molar masses of the same polymer species combine into a single plot in good solvent [Fig. 9.10(a)] if specific viscosity $\eta_{sp} = (\eta - \eta_s)/\eta_s$ is plotted as a function of reduced concentration ϕ/ϕ^* . This simple data collapse works in a good solvent because the correlation length and the tube diameter are proportional to each other, with the same concentration exponents. The line in Fig. 9.10(a) has the slope of 3.9 expected by Eq. (9.46) for semidilute entangled solutions.

In a θ -solvent, the correlation length ξ and the tube diameter *a* have different concentration dependences [$\xi \approx b\phi^{-1}$, Eq. (9.27), with $\nu = 1/2$ and $a \approx a$ (1) $\phi^{-2/3}$, Eq. (9.31)]. The simple plot of relative viscosity η/η_s vs. ϕ/ϕ^* will only collapse data for different molar masses in unentangled solutions, but *not* in entangled solutions in a θ -solvent.

$$\eta_{\rm sp} \approx \begin{cases} (\phi/\phi^*)^2 & \text{for } \phi^* < \phi < \phi_{\rm e}, \\ (\phi/\phi^*)^{14/3} N^{2/3} / [N_{\rm e}(1)]^2 & \text{for } \phi_{\rm e} < \phi < 1. \end{cases}$$
(9.47)

Construction of a reduced data plot for the viscosity of entangled solutions of a given type of polymer in θ -solvents requires plotting $\eta_{sp}/N^{2/3}$ as a function of reduced concentration, as demonstrated in Fig. 9.10(b). This complicated form of data reduction is a direct consequence of the two length scales *a* and ξ having different concentration dependences in θ -solvent. The line in Fig. 9.10(b) has the slope predicted by Eq. (9.47).



Fig. 9.10

Concentration dependence of viscosity in semidilute solutions of polystyrene at 35 °C. (a) Solutions in the good solvent toluene have ϕ/ϕ^* reduce data for different molar masses to a universal curve, using data from M. Adam and M. Delsanti, J. Phys. France 44, 1185 (1983). (b) Solutions in the θ -solvent cyclohexane must have specific viscosity divided by $N^{2/3}$ for ϕ/ϕ^* to reduce data to a universal curve, using data from M. Adam and M. Delsanti, J. Phys. France 45, 1513 (1984). Open triangles are $M = 171000 \text{ g mol}^{-1}$, filled triangles are $M = 422\,000\,\mathrm{g\,mol}^{-1}$ open circles are $M = 1260000 \text{ g mol}^{-1}$ filled circles are $M = 2\,890\,000\,\mathrm{g\,mol^{-1}}$. open squares are $M = 3840000 \text{ g mol}^{-1}$ filled squares are $M = 6770000 \,\mathrm{g \, mol^{-1}}$, and open inverted triangles are $M = 20\,600\,000\,\mathrm{g\,mol^{-1}}$.

The entangled viscosity data in both good solvent and θ -solvent show stronger concentration dependences than predicted by the simple reptation model. The steeper experimental slopes are consistent with the additional relaxation modes discussed in Section 9.4.5 (see Problem 9.14).

In order to construct a universal plot for the viscosity of all entangled polymer solutions in a given class of solvent, it is necessary to also multiply the ordinates of Fig. 9.10 by $[N_e(1)]^2$ because different polymers have different numbers of Kuhn monomers in their entanglement strands in the melt (see Table 9.1). Such universal plots have indeed been constructed successfully in the literature.

9.4 Dynamics of a single entangled chain

9.4.1 Chain in an array of fixed obstacles

Chains in polymer melts and entangled polymer solutions form an effective entanglement network. Since chains in melts and solutions are free to diffuse, the entanglements they form with their neighbours are temporary and have finite lifetime. Any given chain can disentangle from its neighbours by its own motion (reptate away) or by the motion of its neighbours. Effects of the motion of surrounding chains on the dynamics of a given chain will be discussed in Section 9.5.

A simple case to consider first is a single chain diffusing through a network, where the network only imposes permanent topological obstacles² that retard the motion of the chain. Consider an ideal chain in an array of fixed topological obstacles. A two-dimensional schematic representation of this problem, a giant snake in a forest, is presented in Fig. 9.11a. The snake randomly meanders through the forest and each of its conformations are assumed to be as likely as any other (an ideal snake). If the snake gets tired of being in a certain conformation, it is difficult for it to get into a completely different one because of the trees in the forest. These trees constrain this poor reptile to move primarily along its contour. Sideways excursions, although possible, put the snake into uncomfortable conformations with loops. The topological constraints imposed by the trees determine that the preferred path for the motion of the snake is along the confining tube.

The primitive path is the centre line of the confining tube. It can be visualized by hiring one smart student and one brave student to reel in the snake at its ends (Fig. 9.11b). The final contour of the snake, when pulled taut, is the primitive path—the shortest path with the same 'topology' as the original conformation of the snake. A long-exposure photograph of the wiggling snake, taken by a curious student, depicts the whole confining tube in Fig. 9.12.

The reptation model assumes the contour length of the primitive path is fixed at its average value $\langle L \rangle$. In reality, the primitive path length



Fig 9.11

Frame (a) shows a two-dimensional model of a chain in a permanent entanglement network: a giant snake in a forest. Frame (b) shows two students reeling-in the ends of the snake to construct the primitive path.



Fig. 9.12

A long-exposure photograph of the giant snake in the forest clearly defines its confining tube.

 $^{^2\,}$ Real networks can lead to correlation and excluded volume effects on chain conformation that we ignore here.

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L fluctuates in time as the chain (or snake) moves. A full description of chain dynamics requires knowledge of the probability distribution of the primitive path lengths. This problem has been solved exactly by Helfand and Pearson in 1983 for a lattice model of a chain in a regular array of topological obstacles, but here we present a simple estimate of the probability distribution of primitive path lengths.

If an ideal linear chain is confined to a cylindrical pore of diameter *a*, it occupies a section of the pore of length $R_{\parallel} \approx b\sqrt{N}$ [Eq. (3.47)]. Entangled chains occupy a much longer length of confining tube $\langle L \rangle \approx bN/\sqrt{N_e} \gg b\sqrt{N}$, making them strongly stretched. The source of this stretching is the entropy gain at each tube end because each end segment of the primitive path is free to choose from multiple possible directions. This entropy gain leads to an approximately linear contribution to the free energy of a chain in a confining tube³ of order kT per primitive path step,

$$F_{\rm ent}(L) \approx -\Upsilon kT \frac{L}{a},$$
 (9.48)

where Υ is a numerical constant of order unity. This approximately linear potential can be thought of as arising from nearly constant entropic forces of order kT/a acting on the chain at the tube ends. The chain in its confining tube is effectively under a tension kT/a and can be represented as an array of Pincus blobs of size *a* (see Section 3.2.1). Stretching an ideal chain along the contour of its tube to length *L* raises its free energy by $\gamma kTL^2/(2Nb^2)$, where γ is an effective dimensionless spring constant of order unity. The total free energy of a chain in a tube is the sum of these two effects:

$$F(L) \approx \frac{\gamma k T L^2}{2Nb^2} - \Upsilon k T \frac{L}{a}$$

$$\approx \frac{\gamma k T}{2Nb^2} \left[L^2 - \frac{2\Upsilon Nb^2}{\gamma a} L + \left(\frac{\Upsilon Nb^2}{\gamma a}\right)^2 \right] - \frac{k T \Upsilon^2 Nb^2}{2\gamma a^2}$$

$$\approx \frac{\gamma k T}{2Nb^2} (L - \langle L \rangle)^2 - \frac{k T \Upsilon^2}{2\gamma} \frac{N}{N_e}.$$
(9.49)

In the second line of Eq. (9.49), the term $kT\Upsilon^2Nb^2/(2\gamma a^2)$ was added and subtracted so as to complete the square inside the square brackets, in order to recover the expression for the equilibrium tube length $\langle L \rangle \approx$ $\Upsilon Nb^2/(\gamma a)$ [Eq. (9.3)]. This quadratic approximation for the free energy of tube length fluctuations around the average value $\langle L \rangle$ was first proposed by Doi and Kuzuu in 1980:

$$F(L) = \frac{\gamma kT}{2Nb^2} (L - \langle L \rangle)^2.$$
(9.50)

The constant term $kT\Upsilon^2 N/(2\gamma N_e)$ in Eq. (9.49) does not affect the dependence of the free energy F(L) on the contour length L of the primitive

 $^{^3}$ The contribution to the free energy is not strictly linear because for each primitive path length L, the entropy of not only the ends, but of the rest of the chain in an entanglement network needs to be considered.

path. The quadratic approximation of the free energy leads to a Gaussian probability distribution of the tube length L for a chain with N monomers:

$$p(N,L) \sim \exp\left[-\frac{F(L)}{kT}\right] \sim \exp\left[-\frac{\gamma}{2Nb^2}(L-\langle L \rangle)^2\right].$$
 (9.51)

The average length of a tube with diameter *a* is $\langle L \rangle \approx aN/N_e$ [Eq. (9.3)]. A typical fluctuation in the tube length corresponds to a free-energy change of order $F(L) - F(\langle L \rangle) \approx kT$:

$$\sqrt{\langle (L - \langle L \rangle)^2 \rangle} \approx b\sqrt{N} = R \approx a\sqrt{N/N_{\rm e}}.$$
 (9.52)

Thus, a typical tube length fluctuation is of the order of the root-meansquare end-to-end distance R of the chain and the confining tube has a wide range of typical lengths:

$$L \approx \langle L \rangle \pm R \approx a \left(\frac{N}{N_{\rm e}} \pm \sqrt{\frac{N}{N_{\rm e}}} \right).$$
 (9.53)

These thermal fluctuations of the tube length are the basis of the Doi fluctuation model, leading to significant modifications of reptation dynamics for entangled linear chains. Linear chains in a permanent network relax stress by abandoning tube sections via tube length fluctuations and reptation. Since the branch point of a branched polymer prohibits its reptation, branches relax only by fluctuations in tube length. For this reason, we next consider relaxation of simple branched polymers: star polymers (next section), H-polymers and comb polymers (Section 9.4.3). Star polymers in particular relax primarily by fluctuations in tube length. The ideas of tube length fluctuations and reptation will be combined in Sections 9.4.4 and 9.4.5 to treat linear polymers relaxing in a permanent network.

9.4.2 Entangled star polymers

All the discussions of entangled polymer dynamics above were limited to linear chains. The molecular architecture of the chain (star vs. linear vs. ring) significantly modifies polymer dynamics. Snake-like reptation is impossible for *f*-arm star polymers because they would have to drag f - 1 arms along the tube of a single arm, significantly reducing the entropy of the star polymer. Therefore, the branch point of a star is usually localized in one cell of an entanglement net. Stars relax stress and diffuse by arm retractions, which are large (exponentially unlikely) fluctuations of the tube lengths of their arms. This is analogous to an octopus entangled in an array of topological constraints (a fishing net), sketched in Fig. 9.13.

The easiest way for the octopus to change the conformation of any of its arms without crossing the obstacles, represented by gray circles in Fig. 9.13, is by retracting that arm. Such arm retraction reduces the length L_a of its primitive path by forming loops. In Section 9.4.1, we demonstrated that such conformations with primitive path reduced by



Fig. 9.13

Arm retraction of entangled star polymers demonstrated by an octopus in a fishing net. The circles are permanent topological constraints.

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more than the root-mean-square fluctuation *R* from its equilibrium length $\langle L_a \rangle$ are exponentially unlikely [Eq. (9.51)]. Arm retraction by distance $s = \langle L_a \rangle - L_a$ along the contour of the tube can be analysed as a thermally activated process in an effective potential $U(s) \equiv F(L_a)$ (see Fig. 9.14). This potential is typically approximated by a parabola [Eq. (9.50)]:

$$U(s) \approx \frac{\gamma kT}{2} \frac{(L_{\rm a} - \langle L_{\rm a} \rangle)^2}{N_{\rm a} b^2} \approx \frac{\gamma kT}{2} \frac{s^2}{N_{\rm a} b^2}.$$
(9.54)

The number of Kuhn monomers in each arm of the star is N_a and the effective spring constant of this harmonic potential is γ . Most of the time, the length L_a of the confining tube of an arm is close to its equilibrium value $\langle L_a \rangle$ with deviations from it $|s| \leq R = b\sqrt{N_a}$ [Eq. (9.53)] corresponding to an effective potential change of order kT.

Occasionally, there are large atypical fluctuations of the tube length (with $|s| = |L - \langle L \rangle| \gg R$) that are exponentially unlikely [Eq. (9.51)] because of the restricted number of conformations that allow such a state. The probability of the tube length to be reduced by *s* can be estimated by the Boltzmann weight in the effective potential U(s) [Eq. (9.51)]:

$$p(s) \sim \exp\left(-\frac{U(s)}{kT}\right) \sim \exp\left(-\frac{\gamma}{2}\frac{s^2}{N_{\rm a}b^2}\right).$$
 (9.55)

The average time between these large fluctuations $\tau(s)$ is inversely proportional to their probability p(s):

$$\tau(s) \sim \exp\left(\frac{\gamma}{2} \frac{s^2}{N_a b^2}\right). \tag{9.56}$$

The coefficient in front of the exponential depends on the degree of polymerization N of the arm as well as on the magnitude of arm retraction s, but the average retraction time is dominated by the exponential [Eq. (9.56)]. For these large tube length fluctuations, it is important to remember that the quadratic potential [Eq. (9.50)] and the related Gaussian distribution [Eq. (9.51)] are approximations valid for small tube length fluctuations $|L - \langle L \rangle| \ll L$. The probability of large tube length fluctuations deviates from the simple Gaussian form [Eq. (9.51)]. For example, Eq. (9.51) predicts that the probability for the primitive path to be reduced to L = 0 and for the chain to form a single loop is exponentially low in the number of entanglements per chain (exp $[-\gamma N/(2N_e)]$). The actual probability indeed has an exponential dependence on the average number of entanglements per chain,

$$p(N,0) \sim \exp\left(-\frac{\gamma' N_a}{2 N_e}\right),$$
 (9.57)

but with a different coefficient in the exponential $\gamma' \neq \gamma$.

The relaxation time of a star in an array of fixed topological obstacles is equal to the time it takes to completely retract its arms, written here



Fig. 9.14

(a) Effective potential for arm retraction for an entangled star polymer. The thin curves are harmonic approximations for small and large arm retractions. (b) Numerical results for the dependence of the effective spring constants γ (solid curves) and γ' (dashed curves) on the number of Kuhn monomers per entanglement strand on square (two-dimensional) and cubic (three-dimensional) lattices.

by including the power law 'prefactor' in the number of entanglements per arm:⁴

$$\tau_{\rm arm} = \tau(\langle L \rangle) \sim \left(\frac{N_{\rm a}}{N_{\rm e}}\right)^{5/2} \exp\left(\frac{\gamma'}{2} \frac{\langle L \rangle^2}{N_{\rm a} b^2}\right) \sim \left(\frac{N_{\rm a}}{N_{\rm e}}\right)^{5/2} \exp\left(\frac{\gamma'}{2} \frac{N_{\rm a}}{N_{\rm e}}\right). \tag{9.58}$$

The relaxation time of a star grows exponentially with the number of entanglements N_a/N_e per arm and is independent of the number of arms *f* in the star. The coefficient in the exponential is weakly dependent on the relative amount of arm retraction $s/\langle L \rangle$, changing from γ at small retractions to γ' at full retraction, because the harmonic potential is only an approximation of the actual potential. For polystyrene (with $N_e = 23$), the cubic lattice model predicts the spring constant of the harmonic potential to increase from $\gamma = 0.63$ for abandoning the first few tube sections to $\gamma' = 0.75$ for complete retraction of the arm $s = \langle L_a \rangle$ [see Fig. 9.14(b)]. However, this small change of γ to γ' changes the relaxation time of strongly entangled star polymers enormously. For example, a star with $N_a/N_e = 100$ entanglements per arm changes its relaxation time by a factor of $\exp(6) = 400$.

The stress relaxation modulus is proportional to the average fraction of entanglements per arm that have not yet relaxed by having the free end of the arm visiting that tube section. If *s* is the length of the tube that has been retracted and relaxed during time $t = \tau(s)$ then the stress relaxation modulus at time *t* is

$$G(t) \approx G_{\rm e} \frac{\langle L_{\rm a} \rangle - s}{\langle L_{\rm a} \rangle} \quad \text{for } \tau_{\rm e} < t < \tau_{\rm arm},$$
 (9.59)

where G_e is the plateau modulus [Eq. (9.18)]. The stress relaxation modulus of a star polymer has a time dependence similar to that of a linear polymer with molar mass 2 M_a (the span molar mass of the star polymer) for times shorter than the Rouse time of the span, as shown in the frequency dependence of the complex modulus in Fig. 9.15. At the terminal time τ_{arm} ,



⁴ See the Appendix of L. J. Fetters, et al., Macromolecules 26, 647 (1993).

Fig. 9.15

Storage modulus (filled symbols) and loss modulus (open symbols) for linear 1,4-polybutadiene with $M_w = 160\ 000\ \mathrm{g}\ \mathrm{mol}^{-1}$ (squares) and a 6-arm star 1,4-polybutadiene with $M_a = 77\ 000\ \mathrm{g}\ \mathrm{mol}^{-1}$ (circles), both at a reference temperature of 28 °C. The linear polymer was chosen because it's molar mass is approximately the span molar mass of the star polymer. Data courtesy of L. Archer.

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there is of order one unrelaxed entanglement left per arm and the stress relaxation modulus is lower than the plateau modulus by the number of entanglements per arm:

$$G(\tau_{\rm arm}) \approx \frac{N_{\rm e}}{N_{\rm a}} G_{\rm e}.$$
 (9.60)

The viscosity of entangled stars can be estimated as the product of the relaxation time and the terminal modulus:

$$\eta \approx G(\tau_{\rm arm})\tau_{\rm arm} \sim \left(\frac{N_{\rm a}}{N_{\rm e}}\right)^{3/2} \exp\left(\frac{\gamma' N_{\rm a}}{2 N_{\rm e}}\right).$$
 (9.61)

The main feature is the exponential growth of the viscosity with the number of entanglements per arm N_a/N_e . Another interesting feature of the viscosity of entangled stars is that it is independent of the number of arms f. An experimental verification of this prediction is presented in Fig. 9.16. Viscosity of three-arm stars is ~ 30% lower than for stars with the same arm molar mass, but larger number of arms $f \ge 4$. This effect might be due to additional diving modes of a branch point down the tube of a three-arm star (see Problem 9.28).

Naively, one may think that for a branch point to hop between neighbouring entanglement cells, f - 2 of the arms must simultaneously retract, forming essentially linear tube and f - 2 large loops. This simultaneous retraction is an extremely unlikely event and its probability is the product of the already very low retraction probabilities for each of the f - 2 arms. The problem with this naive approach is that it is indeed hard for an octopus to put on a sweater by pulling in all arms and then pushing them all out at the same time. It would be much easier for the octopus to retract one arm at a time. This way, in several steps of arm retraction it could form a favourable arrangement of tubes near the branch point for a successful hop of this branch point between neighbouring cells of an entanglement net.



Fig. 9.16

Viscosity of polyisoprene star polymers with various numbers of arms at 60 °C. The left plot shows that viscosity is only a function of the number of entanglements per arm and that the viscosity of entangled linear polyisoprene (line with $M_a \equiv M/2$) is always lower. The right plot shows that Eq. (9.61) describes all star polymer viscosity data with the effective spring constant of the quadratic potential $\gamma' = 0.96$. Data from L. J. Fetters *et al.*, *Macromolecules* **26**, 647 (1993).



Linear polymers move a distance of order of their own size during their relaxation time, leading to a diffusion coefficient $D \approx R^2/\tau$ [Eq. (9.12)]. However, the diffusion of entangled stars is different because at the time scale of successful arm retraction, the branch point can only randomly hop between neighbouring entanglement cells by a distance of order one tube diameter *a*. For this reason, diffusion of an entangled star is *much slower* than diffusion of a linear polymer with the same number of monomers:

$$D \approx \frac{a^2}{\tau_{\rm arm}} \sim \left(\frac{N_{\rm a}}{N_{\rm e}}\right)^{-5/2} \exp\left(-\frac{\gamma'}{2}\frac{N_{\rm a}}{N_{\rm e}}\right). \tag{9.62}$$

The main feature of the diffusion coefficient of stars [Eq. (9.62)] is its exponential dependence on the number of entanglements per arm N_a/N_e related to the arm retraction time τ_{arm} . This prediction is in good agreement with experiments, as illustrated in Fig. 9.17(a) for diffusion of threearm star hydrogenated polybutadienes. The product of viscosity [Eq. (9.61)] and diffusion coefficient [Eq. (9.62)] decreases with the number of entanglements per arm:

$$\eta D \approx G(\tau_{\rm arm})a^2 \sim \frac{N_{\rm e}}{N_{\rm a}}$$
(9.63)

as shown in Fig. 9.17(b).

9.4.3 H-polymers and combs

The arm retraction mechanism of star dynamics can be applied to other entangled branched polymers, such as H-polymers and comb polymers (see Fig. 1.5) in an array of fixed topological obstacles. In the simplest case, all side branches of an H-polymer or a comb polymer are the same and contain N_a monomers (Fig. 9.18). The delineation of the comb into the backbone (thick line) and branches is done so that the ends of the backbone coincide with the branch points at the two ends of the polymer.

Fig. 9.17

(a) Diffusion coefficients of three-arm star hydrogenated polybutadienes at 165 °C. The slope determines $\gamma' = 0.82$. (b) The product of viscosity and diffusion coefficient is inversely proportional to the number of entanglements on each arm. Data are from C. R. Bartels *et al.*, *Macromolecules* **19**, 785 (1986).



Fig. 9.18

(a) Entangled comb polymer with q = 7 branches and N_a monomers per branch and a backbone (thick line) with N_{bb} monomers. (b) Reptating backbone of a comb with N_{bb} monomers (thick line) and q - 2 = 5 high friction points (black circles) in its confining tube (dashed lines).

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The retraction time of an arm τ_{arm} in an array of fixed obstacles is the same as the relaxation time of a star polymer with N_a monomers per arm [Eq. (9.58)]. On time scales shorter than τ_{arm} , the branch points are localized and cannot move between neighbour cells of the entanglement net. The branch points begin to hop between neighbouring cells of the entanglement net on the time scale of arm retraction τ_{arm} . Similar to star polymers, the length scale of these hops is of the order of the tube diameter *a*, allowing the effective friction coefficient for motion of the branch points to be determined by the retraction time of an arm:

$$\zeta_{\rm br} \approx kT \frac{\tau_{\rm arm}}{a^2}.$$
(9.64)

The backbone of the polymer moves by reptation along the contour of its tube, with curvilinear diffusion dominated by the branch point friction ζ_{br} . An H-polymer is the simplest comb polymer with q=4 branches per molecule. For any trifunctional comb polymer ($q \ge 4$) the number of branch points is q-2 since each end of the backbone has two branches. The total number of monomers in the reptating backbone is N_{bb} . We assume that branches are well-entangled, so that the branch points dominate the friction:

$$(q-2)\zeta_{\rm br} \gg \zeta(N_{\rm bb} + qN_{\rm a}), \tag{9.65}$$

where ζ is the monomeric friction coefficient and $N_{bb} + qN_a$ is the total number of monomers in the whole chain. The curvilinear diffusion coefficient of the backbone along its confining tube is given by the Rouse model [Eq. (9.7)] with friction from the q - 2 branch points:

$$D_{\rm c} \approx \frac{kT}{(q-2)\zeta_{\rm br}} \approx \frac{a^2}{(q-2)\tau_{\rm arm}}.$$
 (9.66)

The length of the confining tube of the backbone is $L_{bb} \approx a N_{bb}/N_e$ leading to the reptation time of the backbone:

$$\tau_{\rm rep} \approx \frac{L_{\rm bb}^2}{D_{\rm c}} \approx \tau_{\rm arm} (q-2) \left(\frac{N_{\rm bb}}{N_{\rm e}}\right)^2. \tag{9.67}$$

The diffusion coefficient of entangled H-polymers and combs is the meansquare size of the backbone divided by its reptation time:

$$D \approx \frac{N_{\rm bb}b^2}{\tau_{\rm rep}} \approx \frac{a^2}{\tau_{\rm arm}(q-2)} \left(\frac{N_{\rm e}}{N_{\rm bb}}\right). \tag{9.68}$$

The stress relaxation modulus of combs and H-polymers consists of an arm-retraction part at shorter times ($t < \tau_{arm}$) and a reptation part at longer times ($\tau_{arm} < t < \tau_{rep}$).

9.4.4 Monomer displacement in entangled linear melts

On time scales shorter than the relaxation time of an entanglement strand τ_e , the sections of a linear chain involved in coherent motion are

Fig. 9.19

Curvilinear displacement of a monomer (labelled by a dark circle) along the contour of the tube between two conformations is Δs . Only a short section of the tube is shown.

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shorter than the entanglement strand and are not aware of the topological constraints. Since hydrodynamic interactions are screened in polymer melts, the motion on very short time scales $t < \tau_e$ is Rouse-like with mean-square monomer displacement given by the subdiffusive motion of the Rouse model [Eq. (8.58)].

$$\langle [\overrightarrow{r}(t) - \overrightarrow{r}(0)]^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{1/2} \text{ for } t < \tau_e.$$
 (9.69)

On longer time scales $t > \tau_e$, topological constraints restrict polymer motion to the confining tube. Displacements of monomers tangential to the axis of the tube (primitive path) on length scales larger than the tube diameter *a* are suppressed by surrounding chains. Monomer displacement along the contour of the tube is unconstrained and follows the subdiffusive motion of the Rouse model [Eq. (8.58)] *along the primitive path*.

For times shorter than the Rouse time of the chain $(t < \tau_R)$, each monomer participates in coherent motion of a chain segment consisting of $\sqrt{t/\tau_0}$ neighbouring monomers. The time-dependent curvilinear coordinate of a monomer along the contour of the tube is s(t) (Fig. 9.19). The mean-square monomer displacement *along the tube* is of the order of the mean-square size of this section in three-dimensional space [Eq. (8.58)]:

$$\langle [s(t) - s(0)]^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{1/2} \approx a^2 \left(\frac{t}{\tau_e}\right)^{1/2} \quad \text{for } \tau_e < t < \tau_R.$$
(9.70)

Since the tube itself is a random walk with step length *a*, the mean-square displacement of a monomer in three-dimensional space $\langle \Delta r^2 \rangle$ is the product of the step length *a* and the contour length displacement $\sqrt{\langle \Delta s^2 \rangle}$:

$$\langle \Delta r^2 \rangle \approx a \sqrt{\langle \Delta s^2 \rangle}.$$
 (9.71)

Thus, the mean-square monomer displacement in space exhibits a weak one-fourth power law in time when the chain is confined to a tube:

$$\langle [\vec{r}(t) - \vec{r}(0)]^2 \rangle \approx a \sqrt{\langle [s(t) - s(0)]^2 \rangle} \approx a^2 \left(\frac{t}{\tau_e}\right)^{1/4} \quad \text{for } \tau_e < t < \tau_R.$$
(9.72)

This time dependence is slower than for unrestricted Rouse motion [Eq. (8.58)] because displacement along the contour of the tube leads to a smaller displacement in space [Eq. (9.71)]. At the Rouse time of the chain,

$$\tau_{\rm R} \approx \tau_0 N^2 \approx \tau_{\rm e} \left(\frac{N}{N_{\rm e}}\right)^2,$$
(9.73)

each monomer participates in coherent Rouse motion of the whole chain along the tube. The mean-square displacement of a monomer along the

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tube at the Rouse time of the chain is of the order of the mean-square size of the *whole chain*:

$$\langle [s(\tau_{\mathbf{R}}) - s(0)]^2 \rangle \approx b^2 N \approx R^2.$$
 (9.74)

Note that the root-mean-square magnitude of these fluctuations is in perfect agreement with the value of tube length fluctuations derived above [Eq. (9.52)]. Even though this magnitude seems large, it is a small fraction of the contour length of the tube [Eq. (9.3)]:

$$\frac{R}{L} \approx \frac{bN^{1/2}}{bNN_{\rm e}^{-1/2}} \approx \left(\frac{N_{\rm e}}{N}\right)^{1/2}.$$
(9.75)

At times longer than the Rouse time $\tau_{\rm R}$, all monomers move coherently with the chain. The chain diffuses along the tube, with a curvilinear diffusion coefficient given by the Rouse model $D_{\rm c} \approx R^2/\tau_{\rm R}$:

$$\langle [s(t) - s(0)]^2 \rangle \approx D_c t \approx b^2 N \frac{t}{\tau_R} \approx a^2 \frac{N}{N_e} \frac{t}{\tau_R} \quad \text{for } t > \tau_R.$$
 (9.76)

In entangled polymer melts this diffusion occurs along the contour of the tube, with the mean-square monomer displacement in space determined using Eq. (9.71):

$$\left\langle \left[\vec{r}(t) - \vec{r}(0) \right]^2 \right\rangle \approx a \sqrt{\left\langle \left[s(t) - s(0) \right]^2 \right\rangle} \\ \approx a^2 \left(\frac{N}{N_{\rm e}} \right)^{1/2} \left(\frac{t}{\tau_{\rm R}} \right)^{1/2} \quad \text{for } \tau_{\rm R} < t < \tau_{\rm rep}.$$
(9.77)

This curvilinear motion continues up to the reptation time τ_{rep} where the chain has curvilinearly diffused the complete length of the tube, of order aN/N_e . At times longer than the reptation time $(t > \tau_{rep})$ the mean-square displacement of a monomer is approximately the same as the centre of mass of the chain and is a simple diffusion with diffusion coefficient D [Eq. (9.12)].

There are four different regimes of monomer displacement in entangled linear polymer melts, shown in Fig. 9.20. The $t^{1/4}$ subdiffusive regime for the mean-square monomer displacement is a unique characteristic of Rouse motion of a chain confined to a tube, which has been found in both NMR experiments and computer simulations.

9.4.5 Tube length fluctuations

Displacements of monomers at the two ends of the tube are unrelated to each other on time scales shorter than the Rouse time of the chain $(t < \tau_R)$. These incoherent curvilinear displacements lead to tube length fluctuations [Eq. (9.70)]:

$$\langle [L(t) - L(0)]^2 \rangle \approx b^2 \left(\frac{t}{\tau_0}\right)^{1/2} \approx a^2 \left(\frac{t}{\tau_e}\right)^{1/2} \quad \text{for } \tau_e < t < \tau_R.$$
 (9.78)



Fig. 9.20

Time dependence of the mean-square monomer displacement predicted by the reptation model for a melt of long entangled linear chains, on logarithmic scales.

Doi was the first to point out that the decrease of tube length due to these fluctuations leads to partial relaxation of stress. The stress relaxation modulus G(t) is not quite constant in the rubbery plateau, but decreases slightly with time. The weak time dependence of the stress relaxation modulus corresponds to the rate at which sections of the tube are vacated by the fluctuating chain. Subdiffusive Rouse dynamics along the contour of the tube [Eq. (8.58)] implies a $t^{1/4}$ time dependence of vacated sections of the tube [see Eq. (9.70)]:

$$G(t) \approx G_{\rm e} \frac{L(t)}{\langle L \rangle} \approx G_{\rm e} \frac{\langle L \rangle - \sqrt{\langle [L(t) - L(0)]^2 \rangle}}{\langle L \rangle}$$
$$\approx G_{\rm e} \left[1 - \frac{b}{\langle L \rangle} \left(\frac{t}{\tau_0} \right)^{1/4} \right]$$
$$\approx G_{\rm e} \left[1 - \frac{N_{\rm e}}{N} \left(\frac{t}{\tau_{\rm e}} \right)^{1/4} \right] \quad \text{for } \tau_{\rm e} < t < \tau_{\rm R}. \tag{9.79}$$

The last relation made use of the fact that $\langle L \rangle \approx aN/N_e \approx bN/\sqrt{N_e}$ and $\tau_e \approx \tau_0 N_e^2$. The tube length fluctuations grow and the stress relaxation modulus decreases up to the Rouse time of the whole chain [Eq. (8.17)]. Consequently, the stress relaxation modulus at the Rouse time of the chain is lower than G_e :

$$G(\tau_{\rm R}) \approx G_{\rm e} \left[1 - \frac{N_{\rm e}}{N} \left(\frac{\tau_{\rm R}}{\tau_{\rm e}} \right)^{1/4} \right] \approx G_{\rm e} \left[1 - \mu_{\rm V} \sqrt{\frac{N_{\rm e}}{N}} \right].$$
(9.80)

The final result was obtained using Eq. (9.19) $(\tau_R/\tau_e \approx (N/N_e)^2)$ and μ is a coefficient of order unity. The fraction $\sqrt{N_e/N}$ of the tube is vacated, and therefore relaxed, at the Rouse time of the chain by tube length fluctuations. The modulus at the relaxation time of the chain is also lower by the same factor:

$$G(\tau_{\rm rep}) \approx G_{\rm e} \left[1 - \mu_{\star} \sqrt{\frac{N_{\rm e}}{N}} \right]. \tag{9.81}$$

Since the distance that the chain must diffuse along the tube has been shortened by tube length fluctuations, the relaxation time is shorter than in the Doi–Edwards reptation model [Eq. (9.8)]:

$$\tau_{\rm rep} \approx \frac{\langle L \rangle^2 [1 - \mu \sqrt{N_{\rm e}/N}]^2}{D_{\rm c}} \approx \tau_0 \frac{N^3}{N_{\rm e}} \left[1 - \mu \sqrt{\frac{N_{\rm e}}{N}} \right]^2.$$
(9.82)

The stress relaxation modulus then decays exponentially at the reptation time [Eq. (9.22)]. The terminal relaxation time can be measured quite precisely in linear viscoelastic experiments.⁵ Hence, Eq. (9.82) provides the simplest direct means of testing the Doi fluctuation model and evaluating

 $^{^5}$ The modulus scale typically has a $\pm 5\%$ uncertainty owing to imperfect sample geometry which also affects viscosity but not relaxation times.

the parameter μ , as shown in Fig. 9.21. Requiring each data set to have an intercept of unity in Fig. 9.21 provides a correction to Eq. (9.21) for estimating τ_0 . We conclude from Fig. 9.21 that $\mu \cong 1.0$, based primarily on computer simulations of the repton model (Section 9.6.2.6) because the experimental data are noisy owing to the usual $\pm 5\%$ uncertainties in determination of molar mass.

Recall that Fig. 9.3 showed the linear viscoelastic response of a polybutadiene melt with $M/M_e \cong 68$. The squared term in brackets in Eq. (9.82) is the tube length fluctuation correction to the reptation time. With $\mu = 1.0$ and $N/N_e = 68$, this correction is 0.77. Hence, the Doi fluctuation model makes a very subtle correction to the terminal relaxation time of a typical linear polymer melt. However, this subtle correction imparts stronger molar mass dependences for relaxation time, diffusion coefficient, and viscosity.

Tube length fluctuation modes significantly modify the rheological response of entangled polymers. The effect of these modes is most clearly observed in the shape of the loss modulus $G''(\omega)$. The Doi–Edwards equation ignores tube length fluctuations and predicts an almost single exponential stress relaxation modulus with small contribution from higher order modes [Eq. (9.21)]. The corresponding loss modulus is obtained from the Doi–Edwards equation by integration using Eq. (7.150) (see Problem 9.8):

$$G''(\omega) = \frac{8G_{\rm e}}{\pi^2} \sum_{p:\rm odd} \frac{\omega \tau_{\rm rep}}{(\omega \tau_{\rm rep})^2 + p^4}.$$
(9.83)

In the rubbery plateau (for $3 \le \omega \tau_{\rm rep} \le 300$ in Fig. 9.22), this Doi–Edwards reptation prediction gives $G'' \sim \omega^{-1/2}$. In contrast, a single exponential G(t) leads to $G'' \sim \omega^{-1}$ at high frequencies. The shorter time modes, corresponding to $p = 3, 5, 7, \ldots$, make the reptation prediction of the loss modulus larger than that of a single exponential relaxation at high frequencies. The Doi fluctuation model has even more relaxation in the rubbery plateau, with $G'' \sim \omega^{-1/4}$ for frequencies larger than the reciprocal of the Rouse time of the chain (see Problem 9.36). Experimental data appear to obey a power law that is independent of polymer species (see Fig. 9.22) but with an intermediate exponent⁶ ($G'' \sim \omega^{-0.3}$). At higher frequencies, differences between the two polymers are noted (particularly in G'') that are consistent with their 20% difference in M/M_e that creates a factor of 1.8 difference in $\tau_{\rm rep}/\tau_e$. These differences show up at high frequencies.

In Fig. 9.23(a), the loss moduli of two nearly monodisperse polybutadiene samples are simultaneously fitted by the predictions of the Doi–Edwards reptation model [Eq. (9.83)]. Experimental peaks are much



Fig. 9.21

Experimental verification of the Doi fluctuation model using data for polystyrene as open squares, from S. Onogi *et al.*, *Macromolecules* **3**, 109 (1970) and A. Schausberger *et al.*, *Rheol. Acta* **24**, 220 (1985), polybutadiene as open circles from R. H. Colby *et al.*, *Macromolecules* **20**, 2226 (1987) and filled circles from the repton model described in Section 9.6.2.6, courtesy of D. Shirvanyants. The line is Eq. (9.82) with $\mu = 1.0$.



Fig. 9.22

Oscillatory shear data for two nearly monodisperse linear polymers with $M/M_e = 40$, reduced by their terminal loss modulus maximum. Triangles are the storage modulus G' and circles are the loss modulus G''. Filled symbols are for polybutadiene with $M_w = 70\,900 \,\mathrm{g \,mol^{-1}} \,(M/M_c = 37)$ from M. Rubinstein and R. H. Colby, J. Chem. Phys. **89**, 5291 (1988). Open symbols are for polystyrene with $M_w = 750\,000 \,\mathrm{g \,mol^{-1}} \,(M/M_c = 44)$ from A. Schausberger *et al.*, *Rheol. Acta* **24**, 220 (1985).

 $^{^{6}}$ Longitudinal Rouse modes of the chain along the tube may affect the value of this exponent.

Fig. 9.23

Simultaneous fit of loss modulus data for the two monodisperse polybutadiene samples at 30 °C by (a) the Doi–Edwards equation and (b) the Doi tube length fluctuation model. Lines are the fitting results. Open circles are data for $M = 355\,000\,\mathrm{g\,mol^{-1}}$. Filled squares are data for $M = 70\,900\,\mathrm{g\,mol^{-1}}$. Data from M. Rubinstein and R. H. Colby, J. Chem. Phys. **89**, 5291 (1988).



Fig. 9.24

Dependence of viscosity, reduced by the cube of molar mass, on the number of entanglements per chain. Filled circles are data from the 'Repton model' of Section 9.6.2, courtesy of D. Shirvanyants. Open symbols are experimental data for the three polymers in Fig. 9.5, shifted parallel to the η_0/M^3 axis to coincide with the 'Repton model' data. The curve is the Doi fluctuation model [Eq. (9.84)] with $\mu = 1.0$.

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broader, especially at high frequencies (short times). The breadth of the experimental peaks of the loss modulus increases with decreasing molar mass. This comparison suggests that the Doi–Edwards equation underestimates stress relaxation by ignoring tube length fluctuation modes [Eq. (9.79)]. The complete stress relaxation modulus due to motion of a chain in its tube consists of two parts:

- (1) Rouse modes of the chain, including tube length fluctuations and longitudinal Rouse modes, are active at times shorter than the Rouse time of the chain.
- (2) Reptation modes are active at times longer than the Rouse time of the chain.

The results of models that include tube length fluctuation modes [Fig. 9.23(b)] are in much better agreement with the experimentally measured loss modulus $G''(\omega)$ of monodisperse melts than the prediction of the Doi–Edwards reptation model [Eq. (9.83)]. Tube length fluctuation corrections predict that the loss peak broadens with decreasing molar mass because the fraction of the stress released by fluctuations is larger for shorter chains.

The viscosity can again be estimated as the product of the terminal modulus and the reptation time:

$$\eta \approx \tau_{\rm rep} G(\tau_{\rm rep}) \approx \frac{\tau_0 k T N^3}{v_0 N_e^2} \left[1 - \mu \sqrt{\frac{N_e}{N}} \right]^3.$$
(9.84)

Doi's estimate of the effect of tube length fluctuations [Eq. (9.84)] predicts a molar mass dependence that approximates $\eta \sim N^{3.4}$ over a reasonable range of molar masses. Viscosity data from experiments and Repton model simulations are compared with the predictions of the Doi fluctuation model in Fig. 9.24. The Doi fluctuation model with $\mu = 1.0$ (solid curve) is in good agreement with both experimental and simulation data for $M > 10M_e$. The data exhibit departures from the 3.4 power law (dashed line in Fig. 9.24) for long chains ($M > 300M_e$) that are well described by the Doi fluctuation model.

Many-chain effects: constraint release

Other computer simulations, such as the Evans–Edwards model of a chain in an array of fixed obstacles (described in detail in Section 9.6.2) exhibit fluctuations of the tube length and also find stronger molar mass dependences of relaxation time $\tau \sim M^{3.3\pm0.2}$ and diffusion coefficient $D \sim M^{-2.4\pm0.1}$ than the simple reptation model without tube length fluctuations [Eqs (9.8) and (9.12)]. These results of computer simulations of a single chain in an array of fixed obstacles are in good agreement with experiments on entangled polymer solutions and melts over the entire range of molar masses covered by simulations ($M < 600M_e$). Tube length fluctuations are responsible for the stronger molar mass dependences of diffusion coefficient (Fig. 9.2), relaxation time [Eq. (9.9)], and viscosity (Fig. 9.5) than predicted by the simple reptation model.

9.5 Many-chain effects: constraint release

In Section 9.4, the motion of a single chain in an array of fixed topological constraints was discussed. Such models apply to dynamics of a chain in a network or in a melt of extremely long chains. In a melt of shorter chains, the topological constraints that define the confining tube are formed by neighbouring chains, which also move along their respective tubes. As chain B moves away, the topological constraint it once imposed on chain A disappears (Fig. 9.25). A new set of conformations is now available for chain A. A third chain moves in and imposes a new topological constraint on chain A. The constraints hence fluctuate in time, keeping the time-average total number of topological constraints imposed on a given chain by its neighbours constant. As some neighbours move away and remove their constraints from a given chain, others move in and place new constraints on it.

The exchange of neighbours and their topological constraints imposed on a given chain leads to a modification of the tube that a given polymer is confined to and is called **constraint release**. When a neighbouring chain B moves away, chain A can explore an additional volume of the order of an entanglement mesh size a^3 . If a new chain C moves in, it can locally confine chain A to this new volume, changing the conformation of the tube of A. This process can be modelled by a local jump of the tube, analogous to an elementary move of the Rouse model. The rate of these local jumps of the primitive path is reciprocally proportional to the lifetime τ of the topological constraints. Thus, constraint release leads to Rouse-like motion of the confining tube and its primitive path.



Fig. 9.25

Constraint release mechanism: when chain B reptates away, it releases the constraint on chain A. Later, this constraint is replaced by chain C, which confines chain A in a displaced tube.

9.5.1 Relaxation times and diffusion

Consider a single linear chain with P monomers in a melt of shorter N-mers. The P-mer has two relaxation mechanisms occurring simultaneously:

- (1) Single-chain motion of the *P*-mer within its confining tube by reptation and tube length fluctuations.
- (2) Constraint release as a Rouse motion of the tube confining the *P*-mer.

Whichever process relaxes the chain faster is the one that controls terminal dynamics.

The constraint release process for the *P*-mer can be modelled by Rouse motion of its tube, consisting of P/N_e segments, where N_e is the average number of monomers in an entanglement strand. The average lifetime of a topological constraint imposed on a probe *P*-mer by surrounding *N*-mers is the reptation time of the *N*-mers $\tau_{rep}(N)$. The relaxation time of the tube confining the probe chain by constraint release is the Rouse time of P/N_e tube segments [Eq. (8.17)] with segment relaxation time $\tau_{rep}(N)$ dictated by the reptation time of the surrounding *N*-mers:

$$\tau_{\rm tube} \approx \tau_{\rm rep}(N) \left(\frac{P}{N_{\rm e}}\right)^2.$$
 (9.85)

The diffusion coefficient of a *P*-mer in a melt of *N*-mers can be written as a sum of contributions from each of these two types of motion, assuming that each contributes independently to diffusion:

$$D \approx \frac{R^2}{\tau_{\rm rep}(P)} + \frac{R^2}{\tau_{\rm tube}}.$$
(9.86)

The reptation time of the *P*-mer is $\tau_{rep}(P)$ and the constraint release time τ_{tube} given in Eq. (9.85). The faster of the two types of motion controls the diffusion of the *P*-mer. For constraint release to significantly affect terminal dynamics, the Rouse relaxation time of the confining tube τ_{tube} must be shorter than the reptation time of the *P*-mer $\tau_{rep}(P)$:

$$\tau_{\rm rep}(P) > \tau_{\rm tube} \approx \tau_{\rm rep}(N) \left(\frac{P}{N_{\rm e}}\right)^2.$$
(9.87)

Very long *P*-mers have the constraint release time [Eq. (9.85)] shorter than their reptation time.⁷ Such very long *P*-mers relax and diffuse by constraint release (Rouse motion of their tubes) before they get a chance to reptate out of their confining tubes. For shorter *P*-mers, the reptation time $\tau_{rep}(P)$ is shorter than the constraint release time τ_{tube} and reptation dominates the diffusion of these chains. Reptation certainly dominates diffusion in monodisperse solutions and melts (for P = N).

⁷ Constraint release controls the terminal relaxation in the reptation model if $P/N_e > (N/N_e)^3$ and in the Doi fluctuation model if $(P/N_e)^{1.4} > (N/N_e)^{3.4}$.

Many-chain effects: constraint release

Experiments on diffusion of deuterated polystyrene into a melt of hydrogenated polystyrene (Fig. 9.26) confirm the crossover assumed in Eq. (9.86). For very long matrix chains (large N), the terminal dynamics of the *P*-mer are controlled by reptation and consequently the diffusion coefficient of the *P*-mer only depends on the molar mass of the *P*-chains and is independent of N:

$$D \approx \frac{R^2}{\tau_{\rm rep}(P)}$$
 for large N. (9.88)

On the other hand, if the matrix chains are short enough (small N) constraint release controls the terminal dynamics of the *P*-chains [Eq. (9.85)] and the diffusion coefficient of the *P*-mers depends strongly on N:

$$D \approx \frac{R^2}{\tau_{\text{tube}}}$$
 for small N. (9.89)

The solid line in Fig. 9.26 is the crossover between Eqs (9.88) and (9.89), and divides the data nicely into a regime of constraint release control, where *D* is strongly dependent on N/N_e for short-chain matrices [described by Eq. (9.89)] and a regime of reptation control, where *D* is independent of *N* for diffusion into long-chain matrices [described by Eq. (9.88)].

9.5.2 Stress relaxation

Constraint release has a limited effect on the diffusion coefficient: it is important only for the diffusion of very long chains in a matrix of much shorter chains and can be neglected in monodisperse solutions and melts. The effect of constraint release on stress relaxation is much more important than on the diffusion and cannot be neglected even for monodisperse systems. Constraint release can be described by Rouse motion of the tube. The stress relaxation modulus for the Rouse model decays as the reciprocal square root of time [Eq. (8.47)]:

$$G(t) \sim (t/\tau)^{-1/2}.$$
 (9.90)

Thus, a finite fraction of the stress relaxes by constraint release at time scales of the order of the constraint lifetime in the Rouse model of constraint release. This is also the time scale at which the stress relaxes by reptation in monodisperse entangled solutions and melts. Both processes simultaneously contribute to the relaxation of stress. Therefore, constraint release has to be taken into account for a quantitative description of stress relaxation even in monodisperse systems. The contribution of constraint release to stress relaxation in polydisperse solutions and melts is even more important as will be discussed below.

9.5.2.1 Stress relaxation in binary blends

Single-chain models, such as the Doi–Edwards reptation model [Eq. (9.21)] or the Doi tube length fluctuation model, assume a linear contribution to



Fig. 9.26

Diffusion coefficient of trace amounts of deuterium-labelled polystyrene *P*-mers into polystyrene *N*-mer melts at 174 °C for six *P*-mers: open circles $M = 55000 \text{ g mol}^{-1}$; filled circles $M = 110000 \text{ g mol}^{-1}$; open squares $M = 255000 \text{ g mol}^{-1}$; filled squares $M = 520000 \text{ g mol}^{-1}$; open triangles $M = 915000 \text{ g mol}^{-1}$; and filled triangles have $M = 2000000 \text{ g mol}^{-1}$. Data from P. F. Green and E. J. Kramer, *Macromolecules* **19**, 1108 (1986).

the stress relaxation modulus from each component of a polydisperse system:

$$G(t) = \sum_{N} \phi_N G_N(t), \qquad (9.91)$$

where ϕ_N is the volume fraction of *N*-mers and $G_N(t)$ is the single-chain stress relaxation modulus of *N*-mers. For a binary blend of long (L) and short (S) chains, these models predict a simple linear addition of the stress relaxation moduli of the two components weighted by their volume fractions:

$$G(t) = \phi_{\mathrm{L}}G_{\mathrm{L}}(t) + \phi_{\mathrm{S}}G_{\mathrm{S}}(t). \qquad (9.92)$$

However, many experiments observe that the amount of stress relaxed at the time scale of the reptation time $\tau_{\rm S}$ of shorter chains is much larger than the volume fraction of short chains. This is shown in Fig. 9.27(a), where the loss moduli of binary blends are compared with the predictions of Eq. (9.92) using the Doi–Edwards reptation model predictions for G(t)[Eq. (9.21)] for the $G_{\rm L}(t)$ and $G_{\rm S}(t)$ relaxation functions. Recall from Section 7.6.5 that the magnitude of $G''(\omega)$ directly reflects the amount of relaxation occurring at each frequency ω . Hence, Eq. (9.92) strongly underestimates the amount of relaxation occurring when the short chains relax [the high-frequency peak in $G''(\omega)$].

Some of the stress relaxed at time scale τ_S occurs by release of constraints imposed on long chains by short ones, which makes a significant contribution to the stress relaxation at the reptation time of the short chains τ_S .

Topological constraints are often assumed to be *pairwise* entanglements between chains. There are three types of these pairwise entanglements in a binary blend: between two long chains (L–L); between two short chains (S–S), and between a short and a long chain (S–L). If the dynamics of each chain along its tube is approximated by the Doi–Edwards reptation model, there are two time scales in the problem—reptation times of long (τ_L) and short (τ_S) polymers. The constraint on a given chain, caused by a long neighbour, has lifetime τ_L , while the constraint imposed by a short neighbour has lifetime τ_S . The constraint release process in a binary blend can be represented by a Rouse model with two mobilities of the effective beads:

(1) slow, corresponding to entanglements with long chains;

(2) fast, corresponding to entanglements with short chains.

These two mobilities can be assumed to be randomly distributed along the tube with relative concentrations corresponding to the probabilities of entanglement with a chain of each type. The simplest assumption is that these relative concentrations are proportional to the volume fractions of each type of chain (for pairwise entanglements).

The combined stress relaxation modulus for both reptation and constraint release of a binary blend is

$$G(t) = \phi_{\rm L} G_{\rm L}(t) \Lambda_{\rm L}(t) + \phi_{\rm S} G_{\rm S}(t) \Lambda_{\rm S}(t), \qquad (9.93)$$



Fig. 9.27

Comparison of the loss modulus data for three blend compositions of the two polybutadiene samples in Fig. 9.23 at 30 °C with the predictions of (a) Doi–Edwards reptation model and (b) self-consistent constraint release model. Dotted lines are the predictions and open circles are the data for $\phi_L = 0.882$. Solid lines and filled squares are for $\phi_L = 0.768$. Dashed lines and open triangles are for $\phi_L = 0.638$. Data from M. Rubinstein and R. H. Colby, *J. Chem. Phys.* **89**, 5291 (1988).