

Doi and Edwards

6

DYNAMICS OF A POLYMER IN A FIXED NETWORK

6.1 Tube model

6.1.1 Tube model in crosslinked systems

As mentioned in Section 5.4.3, the highly entangled state of polymers can be effectively described by the tube model. The idea of the tube model originated in studying the problem of rubber elasticity.^{1,2} A rubber is a huge molecular network which is formed when a polymeric liquid is crosslinked by chemical bonds.³ An important problem in the theory of rubber elasticity is to calculate the entropy, which is essentially the number of allowed conformations of the chains constituting the rubber. The topological constraints play an important role in such a problem.

Consider a lightly crosslinked rubber which consists of long strands of polymers between crosslinks. A strand in such a rubber is schematically shown in Fig. 6.1. In Fig. 6.1b the strand is placed on a plane and the cross-sections of other strands are shown by dots. Due to the topological constraints, the strand cannot cross the dots, so that the number of conformations allowed for the strand is much less than that in free space. How can we estimate it?

Suppose for a moment that the other chains are frozen, then the dots can be regarded as fixed obstacles. One can see that the allowed conformation of the strand is almost confined in a tube-like region shown by the dotted lines: the conformations which go outside the tube are likely to violate the topological constraints. The axis of the tube can be defined as the shortest path connecting the two ends of the strand with the same topology as the strand itself relative to the obstacles. Such a path represents a group of conformations which are accessible to each other without violating the topological constraints imposed by the other chains, and is called the primitive path.⁴ If the topological constraints are replaced by the tube, the number ω of the allowed conformations can be calculated easily by the method described in Chapter 2 (see Section 6.4).

In real rubbers, the situation is more complicated since the other strands are mobile. However, even in such a case, a self-consistent picture will be that the range in which each part of the strand can move around will remain finite. The range is perhaps larger than the mean separation between the frozen strands discussed above. What diameter one should assign to the tube is a question which has not been answered with absolute certainty. However, as long as the strand is long enough, the diameter is determined by local conditions, and will be independent

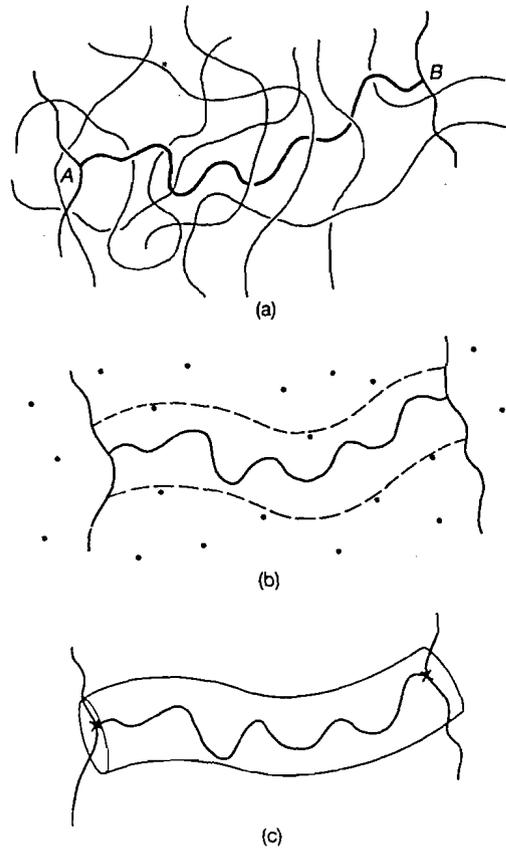


Fig. 6.1. (a) A strand in a rubber. **A** and **B** denote the crosslinks. (b) Schematic picture of (a): the strand under consideration is placed on a plane and the other strands intersecting the plane are shown by dots. (c) The tube model.

of the length of the strand. Detailed discussions^{1,2,4} on rubber elasticity based on this idea and its appraisals^{5,6} are given in the literature. An important point here is the proposition that the tube concept will be a self-consistent picture in the system of topologically interacting system.

6.1.2 Tube model in uncrosslinked systems

The idea of the tube is intuitively appealing, and one can imagine that the same picture will be useful for uncrosslinked system such as polymer melts. However, one has to face a new problem that, in melts, the tube itself changes with time because all conformations in a melt are accessible. A key concept to solve this problem was introduced by de Gennes⁷ who discussed the Brownian motion of an unattached chain

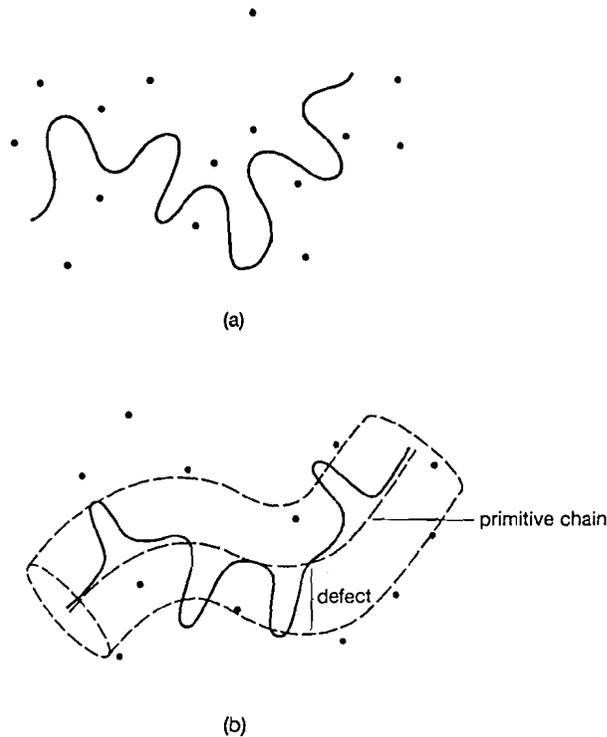


Fig. 6.2. (a) A chain in a fixed network of obstacles (denoted by dots). (b) The defects and the primitive chain (dashed line).

moving through a fixed network (see Fig. 6.2). His idea was that in the situation shown in Fig. 6.2a, the motion of the chain is almost confined in a tube-like region denoted by dotted lines in Fig. 6.2b. Since the chain is rather longer than the tube, the slack will constitute a series of 'defects' which can flow up and down the tube (Fig. 6.2b). De Gennes visualized this as a gas of non-interacting defects running along like the arch in a caterpillar (see Fig. 6.3a). As a result of such motion, the tube itself changes with time (Fig. 6.3b): for example if the chain moves right; the part B_0B can choose a random direction, and create a new part of the tube which will be a constraint for the rest of the chain, while the part of the previous tube A_0A becomes empty and disappears. This type of motion was called reptation by de Gennes after the Latin *reptare*, to creep.

Our current understanding of the dynamics of the highly entangled state is based on the concept of reptation. This picture is rigorously correct for the system that has been presented, i.e., a single chain in a

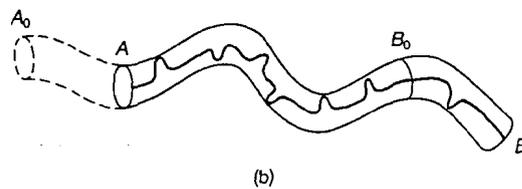
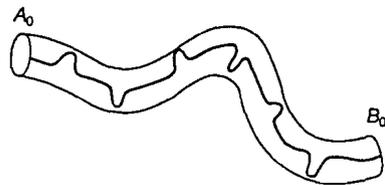
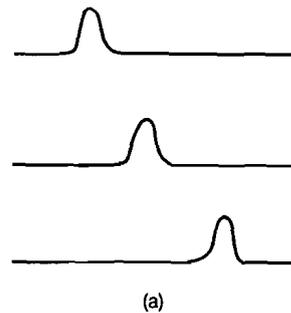


Fig. 6.3. (a) Motion of a single defect (b) Motion of the tube.

fixed network. Whether the picture does indeed hold for concentrated polymer solutions or melts still remains a matter for debate, but many experimental results suggest that reptation is the dominant mechanism for the dynamics of a chain in the highly entangled state. Leaving the detailed discussion of this problem to the next chapter, we shall first consider the simple situation of a chain moving in a fixed network.

6.2 Reptation

6.2.1 Primitive chain

Let us consider a polymer moving in a fixed network of obstacles. For the convenience of later discussion, we shall specify the problem in slightly

different terms from those used by de Gennes. We assume that the intrinsic properties of the polymer are represented by the Rouse model consisting of N segments with bond length b and friction constant ζ . The obstacles are assumed to be thin lines, so they have no effect on static properties, but have a serious effect on dynamical properties by imposing topological constraints.

The characteristic feature of the dynamics can be visualized by the tube model. For a given conformation of the polymer, we can draw the primitive path, *i.e.*, the shortest path connecting the two ends of the chain with the same topology as the chain itself relative to the obstacles (see the dashed line in Fig. 6.2*b*). In the short time-scale the motion of the polymer is regarded as wriggling around the primitive path. On a longer time-scale, the conformation of the primitive path changes as the polymer moves, creating and destroying the ends of the primitive path.

Even though such a picture is clear, the mathematical treatment of the problem is still complicated since the time evolution of the primitive path is governed by the wriggling motion of the polymer, and the wriggling motion itself is limited by the primitive path. However, if we are interested in the large-scale motion of long chains, we may disregard the small-scale fluctuations, and discuss only the time evolution of the primitive path. Since the primitive path at any moment represents the conformation of the chain with the small-scale fluctuations omitted, we shall use the term 'primitive chain' to denote the dynamical equivalent of the primitive path. At this level of description, the details of the wriggling motion are irrelevant, and we can start with a simpler model.

To denote a point on the primitive chain, we use the contour length s measured from the chain end and call this the primitive chain segment s . If $\mathbf{R}(s, t)$ is its position at time t , the vector

$$\mathbf{u}(s, t) = \frac{\partial}{\partial s} \mathbf{R}(s, t) \quad (6.1)$$

is the unit vector tangent to the primitive chain.

The dynamics of the primitive chain is characterized by the following assumptions.

- (i) The primitive chain has constant contour length L .
- (ii) The primitive chain can move back and forth only along itself with a certain diffusion constant D_c .
- (iii) The correlation of the tangent vectors $\mathbf{u}(s, t)$ and $\mathbf{u}(s', t)$ decreases quickly with $|s - s'|$.

The first assumption corresponds to neglecting the fluctuations of the contour length. The second states that the motion of the primitive chain is reptation. The third guarantees that the conformation of the primitive

chain becomes Gaussian? on a large length-scale. This assumption introduces a new parameter into the problem. Since the mean square distance between two points on the Gaussian chain is proportional to $|s - s'|$, it is written as

$$\langle (\mathbf{R}(s, t) - \mathbf{R}(s', t))^2 \rangle = a |s - s'| \quad \text{for } |s - s'| \gg a. \quad (6.2)$$

The length a is called the step length of the primitive chain.

The primitive chain is thus characterized by three parameters L , D_c and a , which must be expressed by the Rouse model parameters N , b , ξ and the parameters characterizing the network. The parameter D_c can be identified as the diffusion coefficient of the Rouse model

$$D_c = \frac{k_B T}{N \xi} \quad (6.3)$$

because the motion of the primitive chain corresponds to the overall translation of the Rouse chain along the tube. The length L is expressed by a since the mean square end-to-end vector of the primitive chain, which is La according to eqn (6.2), must be the same as that of the Rouse chain Nb^2 . Thus

$$L = \frac{Nb^2}{a}. \quad (6.4)$$

We are left with a single parameter a , which depends on the statistical nature of the network. Though precise calculation of this parameter is difficult, it is obvious that a is of the order of the mesh size of the network and much less than L . This knowledge is enough for the purpose of the present discussion.

6.2.2 Simple application

We now study the dynamics of the primitive chain and show that certain time correlation functions can be calculated by a straightforward method.[†] For example, consider the time correlation function of the end-to-end vector $\mathbf{P}(t) \equiv \mathbf{R}(L, t) - \mathbf{R}(0, t)$. Figure 6.4 explains the principle of calculating this correlation function. At $t = 0$, the chain is trapped in a certain tube. As time passes, the primitive chain reptates and at a certain later time (Fig. 6.4d), the part of the chain CD remains in the original tube while the parts AC and DB are in a new tube. To calculate

[†] It must be remembered that despite the Gaussian behaviour with a large length-scale, the primitive chain cannot be modelled by a continuous Gaussian chain since the contour length of the continuous Gaussian chain is infinite and has no physical significance, while the contour length of the primitive chain has a definite physical significance and appears in various dynamical results.

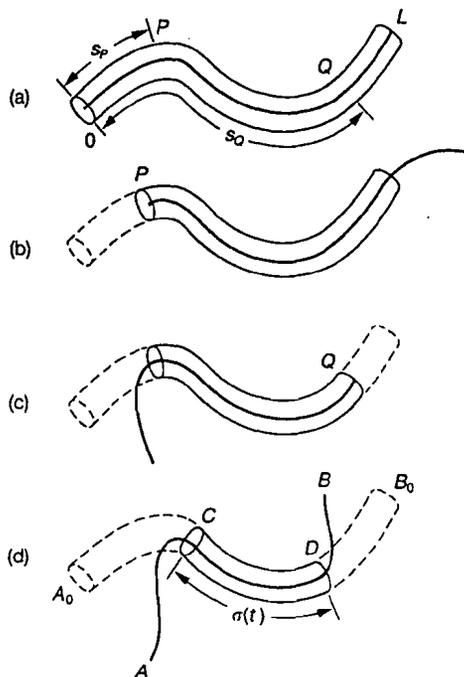


Fig. 6.4. Four successive situations of a reptating chain. (a) The initial conformation of the primitive chain and the tube which we call the original tube. (b) and (c) As the chain moves right or left, some parts of the chain leave the original tube. The parts of the original tube which have become empty of the chain disappear (dotted line). (d) The conformation at a later time t . The tube segment vanishes when it is reached by either of the chain ends: e.g., the tube segment P and Q vanish at the instance (b) when $\xi(t) = s_p$ and at (c) when $\xi(t) = s_Q - L$, respectively.

$\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle$, we express $\mathbf{P}(t)$ and $\mathbf{P}(0)$ as

$$\mathbf{P}(0) = A_0C + \overline{CD} + \overline{DB}_0 \quad (6.5)$$

$$\mathbf{P}(t) = \overline{AC} + \overline{CD} + \overline{DB} \quad (6.6)$$

Since the vectors \overline{AC} and \overline{DB} are uncorrelated with $\mathbf{P}(0)$, $\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle$ will have the form

$$\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle = \langle \overline{CD}^2 \rangle = a \langle \sigma(t) \rangle \quad (6.7)$$

where $\sigma(t)$ is the contour length of \overline{CD} , i.e., the part in the original tube.

To calculate $\langle \sigma(t) \rangle$ we focus attention on a certain segment s of the original tube. This tube segment disappears when it is reached by either end of the primitive chain. Let $\psi(s, t)$ be the probability that this tube

segment remains at time t . The average $\langle \sigma(t) \rangle$ is calculated as

$$\langle \sigma(t) \rangle = \int_0^L ds \psi(s, t). \quad (6.8)$$

Let $\Psi(\xi, t; s)$ be the probability that the primitive chain moves the distance ξ while its ends have not reached the segment s of the original tube. The probability satisfies the one-dimensional diffusion equation

$$\frac{\partial \Psi}{\partial t} = D_c \frac{\partial^2 \Psi}{\partial \xi^2} \quad (6.9)$$

with the initial condition

$$\Psi(\xi, 0; s) = \delta(\xi). \quad (6.10)$$

When $\xi = s$, the tube segment s is reached by the end of the primitive chain and $\Psi(\xi, t; s)$ vanishes (see Fig. 6.4). Similarly when $\xi = s - L$, the tube segment is reached by the other end and $\Psi(\xi, t; s)$ vanishes.† Thus

$$\Psi(\xi, t; s) = 0 \quad \text{at} \quad \xi = s \quad \text{and} \quad \xi = s - L. \quad (6.11)$$

The solution of eqn (6.9) with these boundary conditions is

$$\Psi(\xi, t; s) = \sum_{p=1}^{\infty} \frac{2}{L} \sin\left(\frac{p\pi s}{L}\right) \sin\left(\frac{p\pi(s-\xi)}{L}\right) \exp(-p^2 t / \tau_d) \quad (6.12)$$

where

$$\tau_d = L^2 / D_c \pi^2. \quad (6.13)$$

For the tube segment s to remain, ξ can be anywhere between $s - L$ and s , so that

$$\begin{aligned} \psi(s, t) &= \int_{s-L}^s d\xi \Psi(\xi, t; s) \\ &= \sum_{p; \text{odd}} \frac{4}{p\pi} \sin\left(\frac{p\pi s}{L}\right) \exp(-p^2 t / \tau_d). \end{aligned} \quad (6.14)$$

Thus from eqns (6.7), (6.8), and (6.14)

$$\langle P(t) \cdot P(0) \rangle = La\psi(t) = Nb^2\psi(t) \quad (6.15)$$

where

$$\psi(t) = \frac{1}{L} \int_0^L ds \psi(s, t) = \sum_{p; \text{odd}} \frac{8}{p^2 \pi^2} \exp(-p^2 t / \tau_d). \quad (6.16)$$

† Strictly speaking this argument is valid in the limit of $a \rightarrow 0$. If a is finite, the boundary condition is not written in a simple form, but the correction is of the order of a/L .

The longest relaxation time of $\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle$ is given by τ_d . This is called the reptation or disengagement time, since it is the time needed for the primitive chain to disengage from the tube it was confined to at $t=0$.

Equation (6.15) can be compared with eqn (4.35) for the Rouse chain without constraints:

$$\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle = Nb^2 \sum_{p, \text{ odd}} \frac{8}{p^2 \pi^2} \exp(-p^2 t / \tau_R) \quad (6.17)$$

where τ_R is the Rouse relaxation time,

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}. \quad (6.18)$$

On the other hand, eqn (6.13) is rewritten by eqns (6.3) and (6.4) as

$$\tau_d = \frac{1}{\pi^2} \frac{\zeta N^3 b^4}{k_B T a^2}. \quad (6.19)$$

Note that τ_d is proportional to N^3 and becomes much larger than τ_R for large N . This demonstrates the crucial effect of topological constraints on the conformational change of polymers.

Let us define the number of steps in a primitive chain by

$$Z = \frac{L}{a} = \frac{Nb^2}{a^2}. \quad (6.20)$$

Then the ratio between τ_d and τ_R is written as

$$\tau_d / \tau_R = 3Z. \quad (6.21)$$

Equation (6.19) has been confirmed by computer simulation.⁸⁻¹⁰

The function $\psi(s, t)$ will appear frequently in the subsequent discussions. This function has been defined as the probability that the original tube segment s remains at time t . As will be shown in Section 6.3.3, $\psi(s, t)$ also represents the probability that the primitive chain segment s is in the original tube at time t . (Note the distinction between the *tube segment* and the *primitive chain segment*; the former is fixed in space, while the latter moves with the primitive chain.)

The behaviour of $\psi(s, t)$ is shown in Fig. 6.5. The tube segments in the middle ($s \approx L/2$) have long lifetimes of order τ_d , while the tube segments near the chain ends have very short lifetimes: the end segment is almost instantaneously replaced. This fact will be used in the subsequent discussions. The function $\psi(t)$ represents the average fraction of the original tube that remains at time t . This function is also equal to the average fraction of the primitive chain contour that remains in the original tube.