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The effect of entanglements on diffusion in a polymer melt

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Abstract. The motion of a macromolecule in a polymer melt is considerably restricted by interchain entanglements. This paper considers the topological constraints on the motion of a chain using the Wiener integral model. Two methods are considered: (i) a pipe constraint, (ii) the exact topological invariants. A Smoluchowsky-like equation is obtained by both methods and it is found that a point $r(s, t)$ on the chain has a correlation function $\langle (r(s, t) - r(s, t'))^2 \rangle \propto |t - t'|^{1/4}$ as opposed to the $|t - t'|^{1/2}$ dependence of a free Rouse-like chain. The type of diffusion considered is called cooperative diffusion and is contrasted to the reptative diffusion of de Gennes.

1. Introduction

The motion of a long chain molecule in bulk polymeric material is considerably restricted by interchain entanglements. This is demonstrated by the marked increase in molecular weight dependence of viscosity above a critical value M_c . The experimental situation is reviewed by Porter and Johnson (1966) and by Ferry (1970). Since bulky side groups do not seem to inhibit entanglement coupling it would appear that considerable chain lengths are involved, as opposed to the point action of cross links.

There is no satisfactory statistical mechanical theory of entanglement effects on diffusive motions. Attempts have been made to modify the Rouse model (see Rouse 1953) by supposing the local friction constant to be increased depending on the degree of entanglement (see eg Ferry *et al* 1955 and Bueche 1955). These theories are not derived in an *a priori* fashion, and assume that the friction coefficient is the same for all modes of motion.

This cannot be true since the longer the mode of motion, the more inhibited it must be. Chompff and Duiser (1966) and Chompff and Prins (1968) have performed a normal mode analysis for an entangled network, but their treatment assumes the entanglements to be acting at a point. The same criticism can be raised of the transient network model as advanced by Lodge (1964) and others.

If one chain is considered to move in frozen surroundings one can easily obtain an estimate of the diffusion of a point on the chain, provided the chain is very long (de Gennes 1971). In this paper we shall always work with the gaussian chain in its continuum limit, that is, the monomers labelled r_1, r_2, \dots are replaced by the continuous function $r(s, t)$, and the freely hinged condition is translated into the Wiener functional probability, that is, the probability of finding a configuration $r(s)$ is given by

$$P([r]) = \mathcal{N} \exp\left(-\frac{3}{2l} \int r'^2(s) ds\right), \quad (1.1)$$

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where \mathcal{N} is the normalization and l the step length. Now consider at any one time t_0 a chain which has a configuration $\mathbf{R}(s, t_0)$ as shown in figure 1. The circles represent

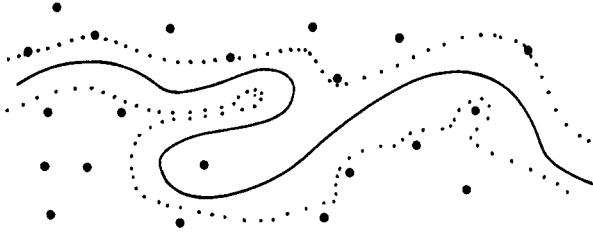


Figure 1.

frozen obstacles. Suppose the motion is now essentially one dimensional, that is, at a subsequent time

$$\mathbf{r}(s, t) = \mathbf{R}(s_1, t_0) \quad (1.2)$$

so that the motion of the chain just maps different points of the chain to points of the original chain or near them. It must be emphasized that \mathbf{R} and \mathbf{r} are random walks and the diagram grossly oversimplifies the true complexity of the configuration. Now it is known (and the result will be reproduced below in (3.6)) that if one point on a free chain is considered say $\mathbf{r}(a, t)$

$$\langle (\mathbf{r}(a, t) - \mathbf{r}(a, t_0))^2 \rangle \propto \sqrt{(t - t_0)}$$

which is true also in one dimension

$$\langle (\mathbf{x}(a, t) - \mathbf{x}(a, t_0))^2 \rangle \propto \sqrt{(t - t_0)}. \quad (1.3)$$

If we assume that the same argument will apply along $\mathbf{R}(s, t)$, then call the distance along \mathbf{R} , S , that is,

$$S(s, t_0) = s. \quad (1.4)$$

Then

$$\langle (S(s, t) - S(s, t_0))^2 \rangle \propto \sqrt{(t - t_0)}. \quad (1.5)$$

But \mathbf{R} is itself a random walk, so the distance

$$\langle (\mathbf{r}(s, t) - \mathbf{R}(s, t_0))^2 \rangle \propto |S(s, t) - S(s, t_0)| \quad (1.6)$$

the normal result. Hence

$$\langle (\mathbf{r}(s, t) - \mathbf{R}(s, t_0))^2 \rangle \propto (t - t_0)^{1/4}. \quad (1.7)$$

The precise coefficient will be a constant times $l^{5/4}(kT/\nu)^{1/4}$. This motion has been named reptation by de Gennes. In a real melt however the whole network is not frozen and will also be changing by diffusion, and a treatment of these cooperative effects seems necessary to calculate the viscosity of the system. We will consider, therefore, a model in which the chain moves in a statistically defined 'pipe', which itself diffuses. The pipe will firstly be introduced in an intuitive way, and self-consistency arguments will be used to calculate the time scales, a method which needs some arbitrary constants to be employed. The second approach will be a direct attack *ab initio*, leading to much more

difficult mathematics, but which evaluates the constants in terms of step length, kT , ν intrinsic molecular viscosity and ρ the density. These approaches agree and again give point diffusion to go like $|t - t_0|^{1/4}$, but now obtain also the structure of the coefficient

$$\langle (r(s, t) - r(s, t'))^2 \rangle = A|t - t'|^{1/4} \quad (1.8)$$

where A is a numerical constant. The viscosity is discussed in the second paper.

2. The pipe constraint

As a first attempt to incorporate topological constraints on the diffusion motions of a chain, we consider it to be 'hemmed in' by a pipe, composed of the other chains of the system. This is shown in figure 1. The chain can clearly move by two possible mechanisms.

(i) It can reptate its way back and forth along the pipe in the manner considered by de Gennes. If the system is densely packed, the chain width ($\sim 5 \text{ \AA}$) may be comparable with the diameter of the pipe ($\sim 8 \text{ \AA}$), and reptation may be severely inhibited, since it will be hard for very much length to be stored in the pipe by, for example, de Gennes' defects. At higher temperatures we would expect the density of the system to decrease, widening the pipe and perhaps allowing reptation.

(ii) The pipe is composed of other chains. As these chains move so does the pipe. In turn the chain constrained by the pipe moves, and so on. This type of motion, which we will term cooperative diffusion, will be the dominant mechanism for a densely packed system. As the chain moves, the pipe tends to constrain it to where it was at an earlier time. A free chain would have an entropy $S \propto -(3k/2l) \int r'^2 ds$ from (1.1), hence a free energy $F = (3kT/2l) \int r'^2 ds$ will appear in its lagrangian. The Langevin equation resulting will have the form

$$m\ddot{r}(s, t) + \nu\dot{r}(s, t) - \epsilon r''(s, t) = \phi(s, t), \quad (2.1)$$

where the dots denote differentiation with respect to time t and primes with respect to arc parameter s . The frictional term $\nu\dot{r}$ arises from the friction of the chain rubbing against the other chains. $\epsilon r''$ is the intramolecular entropic force, that is, $\epsilon = 3kT/l$, $\phi(s, t)$ is a random force arising from the microbrownian motion of the system, and $m\ddot{r}(s, t)$ is the inertial term, which will be small and neglected in the following calculations. The pipe constraint is now expressed by assuming the pipe causes an harmonic force on the chain centred where the chain was an earlier time. To do this we note that (2.1) is put in normal mode form by employing the Fourier transform

$$r(\omega, t) = \frac{1}{2\pi} \int e^{i\omega s} r(s, t) ds.$$

It is only reasonable to suppose that different normal modes will notice the time drift of the pipe on different time scales so that if $\tau(\omega)$ is introduced as the memory time, we can postulate an equation

$$\nu\dot{r}(\omega, t) + \epsilon\omega^2 r(\omega, t) + \mu(r(\omega, t) - r(\omega, t - \tau(\omega))) = \phi(\omega, t). \quad (2.2)$$

We could choose much more complicated forms, and have indeed chosen the simplest

form we could think of which still retains the essence of the problem. However it is to be noted that μ is taken independent of ω , since in previous calculations in rubbers, where the chains do not diffuse on a long time scale because of vulcanization, one can evaluate μ directly using the methods of the second part of this paper (eg Edwards and Kerr 1972) and μ is *not* a function of ω . (It turns out to be proportional to $\rho^{1/2}$ where ρ is the density of material, a result reproduced below.)

If we consider the chain $\mathbf{r}(s, t)$ to be of finite length L , we must use the Fourier series in n rather than a transform; however the latter form is more convenient and we can use it provided we remember that by $(L/2\pi)\int d\omega$ we really mean Σ_n and by ω , $2\pi n/L$.

Taking the Fourier transform E , on t , (2.2) becomes

$$\epsilon\omega^2\mathbf{r}(\omega, E) + iE\nu\mathbf{r}(\omega, E) + \mu\{1 - \exp(-iE\tau(\omega))\}\mathbf{r}(\omega, E) = \Phi(\omega, E). \quad (2.3)$$

From this equation we can solve the motion in terms of $\tau(\omega)$, and then apply a self-consistency argument to determine $\tau(\omega)$. This argument will reflect the cooperative diffusion mechanism.

We could alternatively regard the chain $\mathbf{r}(\omega, t)$ as moving quickly, while its surroundings, the chains forming the pipe, move more slowly. The chain would then be expected to feel a potential between $\mathbf{r}(\omega, t)$ and its average over a collision time with the pipe. Thus the new term of (2.2) would now be

$$\mu' \left(\mathbf{r}(\omega, t) - \frac{1}{\tau(\omega)} \int_{t-\tau(\omega)}^t \mathbf{r}(\omega, \lambda) d\lambda \right),$$

leading to the Langevin equation,

$$\epsilon\omega^2\mathbf{r}(\omega, E) + iE\nu\mathbf{r}(\omega, E) + \mu' \left(1 + \frac{\exp(-iE\tau(\omega)) - 1}{iE\tau(\omega)} \right) \mathbf{r}(\omega, E) = \Phi(\omega, E). \quad (2.5)$$

A similar argument could be applied to determine $\tau(\omega)$ in this case. For $\tau(\omega)$ small,

$$1 - \exp(-iE\tau(\omega)) \simeq 2 \left(1 + \frac{\exp(-iE\tau(\omega)) - 1}{iE\tau(\omega)} \right) \simeq iE\tau(\omega). \quad (2.6)$$

Thus if $\mu' = 2\mu$ we have the same approximation to the Langevin equation

$$\{\epsilon\omega^2 + iE(\nu + \mu\tau(\omega))\}\mathbf{r}(\omega, E) = \Phi(\omega, E) \quad (2.7)$$

for both cases. We will work with (2.2) rather than (2.5), but the latter may represent an interesting alternative view of the problem.

3. The case when τ is small

The long time-scale motions of the chain are those for which E is small in equation (2.3). If we further suppose τ to be small we can make the approximation of equation (2.6). The effect of the entanglements is now seen to be an increased friction coefficient $\nu + \mu\tau(\omega)$ which is ω , and hence mode dependent. The chain in equilibrium has a random-walk configuration and we require

$$\langle (\mathbf{r}(s, t) - \mathbf{r}(s', t))^2 \rangle = |s - s'|, \quad (3.1)$$

where l is the effective monomer length. Now,

$$\langle (r(s, t) - r(s', t))^2 \rangle = \frac{L}{2\pi} \int \int \langle r(\omega, E) r^*(\omega, E) \rangle 2(1 - \cos \omega |s - s'|) d\omega dE \quad (3.2)$$

with

$$\langle r(\omega, E) r^*(\omega, E) \rangle = \frac{\langle \phi(\omega, E) \phi^*(\omega, E) \rangle}{\epsilon^2 \omega^4 + E^2(v + \mu\tau(\omega))^2} \quad (3.3)$$

from (2.7). Thus

$$\langle \phi(\omega, E) \phi^*(\omega, E) \rangle = \frac{2\epsilon(v + \mu\tau(\omega))l}{L}. \quad (3.4)$$

Hence,

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle &= \frac{L}{2\pi} \int \int_{-\infty}^{\infty} \frac{\langle \phi(\omega, E) \phi^*(\omega, E) \rangle \{1 - \cos E(t - t')\} d\omega dE}{E^2(v + \mu\tau(\omega))^2 + \epsilon^2 \omega^4} \\ &= l \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \left\{ 1 - \exp\left(-\frac{\epsilon\omega^2}{v + \mu\tau(\omega)} |t - t'| \right) \right\} \end{aligned} \quad (3.5)$$

on integrating over E . The unentangled free Rouse chain is the special case $\mu = 0$, $\tau = 0$, for which

$$\langle (r(s, t) - r(s, t'))^2 \rangle = l \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \left\{ 1 - \exp\left(-\frac{\epsilon\omega^2}{v} |t - t'| \right) \right\} \propto |t - t'|^{1/2} \quad (3.6)$$

using the substitution $x = \omega^2 |t - t'|$. Equations (3.5) and (3.6) have relaxation times

$$\frac{v + \mu\tau(\omega)}{\epsilon\omega^2}, \quad \frac{v}{\epsilon\omega^2} \quad (3.7)$$

for the entangled and free chains respectively. The entangled chain is seen to have an additional relaxation of characteristic time τ' , where

$$\frac{1}{\tau'} = \left(\frac{1}{v} - \frac{1}{v + \mu\tau(\omega)} \right) \epsilon\omega^2. \quad (3.8)$$

For cooperative diffusion, we would expect the relaxation of the pipe to be this additional relaxation, that is, $\tau = \tau'$. Since τ is positive for all ω ,

$$\tau(\omega) = \frac{v}{2\epsilon\omega^2} \left\{ 1 + \left(1 + \frac{4\epsilon\omega^2}{\mu} \right)^{1/2} \right\} \quad (3.9)$$

on solving for $\tau(\omega)$. The entangled chain thus has relaxation times $\lambda(\omega)$,

$$\lambda(\omega) = \frac{v + \mu\tau(\omega)}{\epsilon\omega^2} = \frac{v}{2\epsilon^2\omega^4} \left[2\epsilon\omega^2 + \mu \left\{ 1 + \left(1 + \frac{4\epsilon\omega^2}{\mu} \right)^{1/2} \right\} \right]. \quad (3.10)$$

This has the long (ω small) and short (ω large) wavelength limits

$$\frac{\mu v}{\epsilon^2 \omega^4}, \quad \frac{v}{\epsilon \omega^2} \quad (3.11)$$

respectively.

The former times correspond to configurational rearrangements beyond the entanglements, and the latter to the free rearrangements between entanglements. These are then the two sets of relaxation times, characteristic of viscoelastic properties, but there is a transition between them via (3.10). Since μ is an entanglement parameter depending on the number and strength of the entanglements, the larger the value of μ , the sharper is the transition between the two sets of relaxation times. Substituting (3.9) into (3.5)

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle &= l \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \left\{ 1 - \exp \left(\frac{-(\epsilon\omega^2/\nu)|t-t'|}{1 + (\mu/2\epsilon\omega^2)\{1 + (1 + \mu\epsilon\omega^2/\mu)^{1/2}\}} \right) \right\} \\ &\simeq l \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \left\{ 1 - \exp \left(\frac{-\epsilon^2\omega^4|t-t'|}{\mu\nu} \right) \right\}, \end{aligned} \tag{3.12}$$

since the long time-scale behaviour is dominated by the long wavelength modes. Hence

$$\langle (r(s, t) - r(s, t'))^2 \rangle = l \left(\frac{\epsilon^2}{\mu\nu} \right)^{1/4} |t-t'|^{1/4} \tag{3.13}$$

and the displacements of one point on the chain obey a $t^{1/4}$ diffusion as opposed to the $t^{1/2}$ diffusion of a free chain. This coefficient differs by the factor μ from that of reptation. If μ , as is derived later, varies as $kT(\rho l^3)^{1/2}$, the coefficient contains $(kT/\nu)^{1/4} l^{5/4} / (\rho l^3)^{1/8}$ as against the reptation expression $(kT/\nu)^{1/4} l^{5/4}$.

4. The case when τ is large

In general E and τ may not be small and instead we should consider all of (2.3) rather than its approximation (2.7). Then

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle &= \frac{L}{2\pi} \iint_{-\infty}^{\infty} \frac{\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle \{1 - \cos E(t-t')\} d\omega dE}{\{\epsilon\omega^2 + \mu(1 - \cos E\tau)\}^2 + (\nu E + \mu \sin E\tau)^2}, \end{aligned} \tag{4.1}$$

where $\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle$ will have a new value to be calculated. If we consider the long time-scale motions which have $E \rightarrow 0$, but make no restrictions on τ , the denominator of the integrand of (4.1), that is,

$$\{\epsilon\omega^2 + \mu(1 - \cos E\tau)\}^2 + (\nu E + \mu \sin E\tau)^2 \simeq \epsilon^2\omega^4 + E^2\{(v + \mu\tau)^2 + \mu\epsilon\omega^2\tau^2\} \tag{4.2}$$

for small E . For τ also small we obtain the approximation $\epsilon^2\omega^4 + E^2(v + \mu\tau)^2$ used above. For large τ , a better approximation is

$$\epsilon^2\omega^4 + E^2\mu\tau^2(\epsilon\omega^2 + \mu). \tag{4.3}$$

The condition that, at any one instant, $r(s, t)$ be a random walk in this case gives

$$\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle = \frac{2\epsilon l}{L} \{\mu\tau^2(\epsilon\omega^2 + \mu)\}^{1/2} \tag{4.4}$$

and thus

$$\langle (r(s, t) - r(s, t'))^2 \rangle = l \int_{-\infty}^{\infty} \frac{d\omega}{\omega^2} \left\{ 1 - \exp\left(\frac{-\epsilon\omega^2 t}{\{\mu\tau^2(\epsilon\omega^2 + \mu)\}^{1/2}} \right) \right\}. \quad (4.5)$$

The same self-consistent technique of solving for $\tau(\omega)$ gives

$$\tau(\omega) = v \left(\frac{1}{\epsilon\omega^2} + \frac{1}{\mu^{1/2}(\epsilon\omega^2 + \mu)^{1/2}} \right) \quad (4.6)$$

and hence the relaxation times $\lambda(\omega)$,

$$\lambda(\omega) = \frac{v}{\epsilon\omega^2} \left(\frac{\mu^{1/2}(\epsilon\omega^2 + \mu)^{1/2}}{\epsilon\omega^2} + 1 \right) \quad (4.7)$$

with the same asymptotic limits as (3.11). Identical behaviour is obtained as that when τ was assumed small except in the intermediate range of ω , which is unimportant. It would appear that we have chosen a satisfactory criterion for $\tau(\omega)$ in cooperative diffusion.

5. Short time-scale behaviour

For shorter times, $|t - t'|$, we must consider the Langevin equation for larger values of E . As $E \rightarrow \infty$ the left-hand side of (4.2) is better approximated by

$$\epsilon^2\omega^4 + v^2E^2 + 2\mu(\epsilon\omega^2 + \mu) \quad (5.1)$$

on replacing $\cos E\tau$ and $\sin E\tau$ by their average value which is zero. Clearly as $E\tau \rightarrow \infty$ $\cos E\tau$ and $\sin E\tau$ oscillate increasingly rapidly, and such averaging is possible. Thus

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle &= \frac{2}{v^2} \frac{L}{2\pi} \int \int_{-\infty}^{\infty} \frac{\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle \{1 - \cos E(t - t')\} d\omega dE}{E^2 + \epsilon^2\omega^4/v^2 + (2\mu/v^2)(\epsilon\omega^2 + \mu)}. \end{aligned} \quad (5.2)$$

Again using the criterion that $r(s, t)$ be a random walk,

$$\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle = \frac{2vl}{L\omega^2} \{(\epsilon\omega^2 + \mu)^2 + \mu^2\}^{1/2} \quad (5.3)$$

and

$$\langle (r(s, t) - r(s, t'))^2 \rangle = l \int_{-\infty}^{\infty} (1 - \exp[-\{(\epsilon\omega^2 + \mu)^2 + \mu^2\}^{1/2} t/v]) d\omega. \quad (5.4)$$

As $\omega \rightarrow 0$ we have a factor $(1 - \exp(-2\mu^2 t/v))$, independent of ω , in the integrand. This corresponds to the chain relaxing back to its original state, there being no net diffusion of the longest wavelength modes. The only motions are on the short length scale between entanglements, as can be seen on substituting $\omega \rightarrow \infty$ in (5.4), when we get Rouse-like behaviour of the shortest modes.

Thus, on a short time scale, there is no overall motion of the chain, but short length Rouse-like behaviour occurs between entanglements. On a longer time scale, long scale motions occur causing a very slow $t^{1/4}$ net diffusion of a point on the chain.

6. The Smoluchowski equation

The dynamics of an unentangled chain can be expressed in the diffusional limit by a Smoluchowski equation, the Rouse equation, which for a continuous chain of length L can be written (see Edwards 1970, Edwards and Goodyear 1972) in Fourier form

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta \mathbf{r}(\omega)} \frac{kT}{v} \left(\frac{\delta}{\delta \mathbf{r}(-\omega)} + \frac{3L}{2\pi l} \omega^2 \mathbf{r}(\omega) \right) \right\} G(\mathbf{r}, \mathbf{r}', t, t') = \prod_{\omega} \delta(\mathbf{r}(\omega) - \mathbf{r}(\omega')) \delta(t - t') \quad (6.1)$$

and so each mode has the diffusion coefficient kT/v .

We can write down a similar equation for an entangled chain, but from § 3 we note that we must have the friction coefficient v replaced by $v + \mu\tau(\omega)$ with the equilibrium solution maintained as

$$\exp\left(-\frac{3}{2l} \int \mathbf{r}^{1/2} ds\right) = \exp\left(-\frac{3L}{2\pi l} \int \omega^2 |\mathbf{r}(\omega)|^2 d\omega\right),$$

that is,

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta \mathbf{r}(\omega)} \mathcal{D}(\omega) \left(\frac{\delta}{\delta \mathbf{r}(-\omega)} + \frac{3L}{2\pi l} \omega^2 \mathbf{r}(\omega) \right) \right\} G(\mathbf{r}, \mathbf{r}', t, t') = \prod_{\omega} \delta(\mathbf{r}(\omega) - \mathbf{r}(\omega')) \delta(t - t'), \quad (6.2)$$

where

$$\mathcal{D}(\omega) = \frac{kT}{v} \left[1 + \frac{\mu}{2\epsilon\omega^2} \left\{ 1 + \left(1 + \frac{4\epsilon\omega^2}{\mu} \right)^{1/2} \right\} \right]^{-1}. \quad (6.3)$$

The value of the mode diffusion coefficient is seen to be mode dependent.

From § 4, we can again satisfy equation (6.2), by replacing v of (6.1) by $\mu^{1/2}(\epsilon\omega^2 + \mu)^{1/2}$ with $\tau(\omega)$ given by (4.6). Then,

$$\mathcal{D}(\omega) = \frac{kT}{v} \left(\frac{\epsilon\omega^2}{\epsilon\omega^2 + \mu^{1/2}(\epsilon\omega^2 + \mu)^{1/2}} \right). \quad (6.4)$$

Both (6.3) and (6.4) give the same limiting behaviour for small and large ω . For small ω

$$\mathcal{D}(\omega) = \frac{kT}{\mu v} \epsilon\omega^2, \quad (6.5)$$

while for large ω

$$\mathcal{D}(\omega) = \frac{kT}{v} \quad (6.6)$$

independent of ω , corresponding to the fact that short scale motions are uninhibited by entanglements. The Smoluchowski equation (6.3) is valid in the long-time limit considered in §§ 3 and 4. It does not describe the short-time behaviour of § 5.

The entangled chain has been shown to have two sets of relaxation behaviour. For large ω , corresponding to the short wavelength modes between entanglements, the chain shows Rouse-like behaviour. For small ω , the motion beyond entanglement spacings, the motion is seen to be severely inhibited. The method of representing the

topology by a gaussian pipe is so far somewhat arbitrary, and so in the following sections we consider the direct use of topological invariants (Edwards 1967, 1968) and how they can be applied to cooperative diffusion. We will obtain results similar to those of these sections.

7. Topological invariants

Entanglements can be categorized by an infinite series of invariants. The topology of the curves $r_1(s)$ and $r_2(s)$ of figure 2 can be described by the first invariant I_{12} ,

$$I_{12} = \oint \oint \frac{dr_1 \times dr_2}{|r_{12}|^3} \cdot r_{12}; \quad r_{12} = r_1 - r_2 \quad (7.1)$$

which takes the value $4\pi n$, where n is the net number of times the curve r_2 passes through the surface S , with r_1 as perimeter. For (a) clearly $n = 0$, whilst for (b) $n = \pm 1$, the sign depending on the convention of direction of the integrations. A similar result can be shown for infinitely long but open curves and will be approximately true for open finite length curves. I_{12} then represents the constraint that the two curves cannot pass through one another, if I_{12} is fixed. In general there is an infinite set of such invariants, but the vital one is the first and we confine ourselves to it. It represents the simple direct entanglement between two chains. Considering only I_{12} is analogous to ignoring all but two-body forces in a many-body calculation.

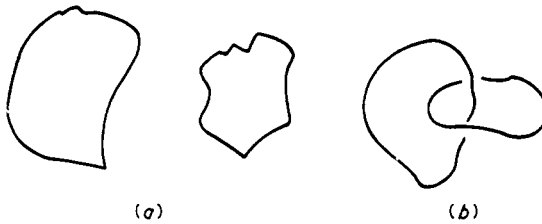


Figure 2.

The chain $r(s, t)$ in the molten polymer, is considered to have the constraint

$$I_i = n_i \quad (7.2)$$

imposed on it, for all $i = 1, \dots, N$, where

$$I_i = \frac{1}{4\pi} \oint \oint (dr \times dR_i) \nabla \frac{1}{|r - R_i|} \quad (7.3)$$

and is the first invariant between $r(s, t)$ and $R(s, t)$ divided by 4π . We assume that $r(s, t)$ has N entanglements at various places along its length, and that these act essentially independently of one another. This being so, we relax the constraint (7.2) slightly, giving

$$\sum_{i=1}^N I_i = I = n = \sum_{i=1}^N n_i. \quad (7.4)$$

This makes the constraint somewhat easier to handle when we come to average over all

initial entanglement distributions. We can now write down the equilibrium distribution of a chain originally set up with entanglement parameter n ,

$$p_n[\mathbf{r}(s)] = \mathcal{N} \exp\left(-\frac{3}{2l} \int_0^L \mathbf{r}'^2(s) ds\right) \delta_{I,n}. \quad (7.5)$$

The Kronecker delta function can be parametrized to give

$$p_n[\mathbf{r}(s)] = \frac{\mathcal{N}}{2\pi} \int_{-\pi}^{\pi} d\lambda \exp\left(-\frac{3}{2l} \int \mathbf{r}'^2(s) ds + i\lambda(I-n)\right). \quad (7.6)$$

The free chain distribution $p[\mathbf{r}(s)]$ can be recovered by summing over all the possible values of n weighted by the probability distribution function, $P(n)$, of their initial occurrence,

$$p[\mathbf{r}(s)] = \sum_n p_n[\mathbf{r}(s)] P(n). \quad (7.7)$$

If $G_n(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2)$ is the Green function corresponding to $p_n[\mathbf{r}(s)]$ we can write

$$G_n(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) = \frac{1}{2\pi} \int_{-\pi}^{\pi} d\lambda e^{-i\lambda n} G_\lambda(\mathbf{r}_1, \mathbf{r}_2, s_1, s_2) \quad (7.8)$$

which defines G_λ

$$G_\lambda = \mathcal{N} \int_{\mathbf{r}_1(s_1)}^{\mathbf{r}_2(s_2)} \delta\mathbf{r} \exp\left(-\frac{3}{2l} \int_{s_1}^{s_2} \mathbf{r}'^2(s) ds + i\lambda I\right). \quad (7.9)$$

G_λ will be the Green function for the diffusive motion arising from a Langevin equation with a Lagrange multiplier λ referring to the topology,

$$v\dot{\mathbf{r}}(s, t) + \epsilon \mathbf{r}''(s, t) + \phi(s, t) + i\lambda \nabla_r I = 0. \quad (7.10)$$

The Lagrange multiplier λ has a value determined by the solution of the equation. I has some value, n , for a particular solution $\mathbf{r}(s, t)$, and in general, n will depend on the initial configuration, specifying its topology. Associated with n is $P(n)$, and thus

$$\lambda = \lambda(n, [\mathbf{r}(s, t)]). \quad (7.11)$$

We will assume that we can average over an ensemble of chains with topology n in such a way that λ is merely a function of n and not in addition a functional of $\mathbf{r}(s, t)$. In this case λ itself is a measure of the topology of the chain, and there exists a probability distribution function $Q(\lambda)$ of λ . Then

$$G_\lambda = \sum_n e^{i\lambda n} G_n \quad (7.12)$$

and λ and n constitute a Fourier pair. It is straightforward to show that $Q(\lambda)$ and $P(n)$ are Fourier conjugates, with the knowledge that $P(n) = P(-n)$, I being as likely positive as negative. Assuming the chains were set up originally at random, we would expect $P(n)$ to be gaussian

$$P(n) \propto \exp(-\gamma n^2) \quad \text{hence} \quad Q(\lambda) \propto \exp(-\Gamma \lambda^2). \quad (7.13)$$

If the chains are very long, and there are many entanglements, N , contributing to I , we

would expect $P(n)$ to have a large variance, tending to proportionality with N . Then

$$\gamma \propto \frac{1}{N}, \quad \Gamma \propto N \quad (7.14)$$

and

$$\overline{n^2} \propto N, \quad \overline{\lambda^2} \propto \frac{1}{N}. \quad (7.15)$$

The importance of this is that we may treat λ , as opposed to n , as a meaningful entanglement parameter.

The term $i\lambda \nabla_r I$ in (7.10) is a 'mixing term' in that it couples many different modes of motion. We have seen however that we can in many ways regard $\nabla_r I$ as a random variable. As such we can apply the standard techniques for deriving transport equations, but must always bear in mind the fact that many assumptions go into the standard theory, and the difficulty of calculating higher order terms leaves a question mark over the validity of the standard methods. We can now argue that G_λ can be shown to satisfy the modified Smoluchowski equation

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta \mathbf{r}(\omega)} \mathcal{D}_\lambda(\omega) \left(\frac{\delta}{\delta \mathbf{r}(-\omega)} + \frac{3L}{2\pi l} \omega^2 \mathbf{r}(\omega) |\alpha_\lambda(\omega)| \right) \right\} G_\lambda = \prod_\omega \delta(\mathbf{r}(\omega) - \mathbf{r}(\omega')) \delta(t - t'), \quad (7.16)$$

where

$$\mathcal{D}_\lambda(\omega) = \frac{kT}{v} - \lambda^2 \left(\frac{kT}{v} \right)^2 h(\omega) \quad (7.17)$$

$$h(\omega) = \int dt \langle \nabla_{-\omega} I(\mathbf{r}(0)) \nabla_{\omega} I(\mathbf{r}(t)) \rangle \quad (7.18)$$

$$\alpha_\lambda(\omega) = 1 + \frac{\lambda^2 l}{3\omega^2} \left(\frac{kT}{v} \right)^2 \frac{k(\omega)}{\mathcal{D}_\lambda(\omega)} \quad (7.19)$$

and

$$k(\omega) = \frac{L}{2\pi} \int \left\langle \frac{\delta}{\delta \mathbf{r}(\eta)} \nabla_{-\omega} I(\mathbf{r}(0)) \frac{\delta}{\delta \mathbf{r}(\omega, t)} \nabla_{-\eta} I(\mathbf{r}(t)) \right\rangle dt d\eta. \quad (7.20)$$

The averages are over the self-consistent distribution of the entangled chains. Equation (7.16) has been derived by Kerr (1971) and by Grant (1972). $h(\omega)$ is a diffusive force, whereas $k(\omega)$ is a dynamical friction and represents a kind of excluded volume effect, since the equilibrium solution

$$\left(\frac{\delta}{\delta \mathbf{r}(-\omega)} + \frac{3L}{2\pi l} \omega^2 \mathbf{r}(\omega) \alpha_\lambda(\omega) \right) P_\lambda = 0$$

is the probability distribution of a walk of entanglement level λ . We will find that h dramatically alters the behaviour of the whole equation, whereas α_λ does little more than produce a λ dependent effective step length. To the accuracy used in the next section we can replace α_λ by unity and concentrate on the effect of $h(\omega)$.

8. The self-consistent method for $\mathcal{D}_\lambda(\omega)$

If the entanglements are independent of one another

$$\begin{aligned} h(\omega) &= \int dt \sum_{\alpha=1}^N \langle \nabla_{-\omega} I_\alpha(0) \nabla_\omega I_\alpha(t) \rangle \\ &= N \int dt \langle \nabla_{-\omega} I_\alpha(0) \nabla_\omega I_\alpha(t) \rangle, \end{aligned} \quad (8.1)$$

where

$$I_\alpha = \frac{1}{4\pi} \iint d\mathbf{r} \times d\mathbf{R}_\alpha \nabla \frac{1}{|\mathbf{r} - \mathbf{R}_\alpha|}. \quad (8.2)$$

Now

$$\begin{aligned} \frac{\delta}{\delta \mathbf{r}(\omega)} (\mathbf{dr} \times d\mathbf{R}_\alpha) \nabla \frac{1}{|\mathbf{r} - \mathbf{R}_\alpha|} \\ = (\mathbf{dr} \times d\mathbf{R}_\alpha) \frac{\delta}{\delta \mathbf{r}(\omega)} \nabla \frac{1}{|\mathbf{r} - \mathbf{R}_\alpha|} + \text{terms in } \frac{\delta}{\delta \mathbf{r}(\omega)} \mathbf{dr} \text{ etc} \end{aligned} \quad (8.3)$$

$$= (\mathbf{dr} \times d\mathbf{R}_\alpha) \delta(\mathbf{r} - \mathbf{R}_\alpha) e^{i\omega s_1} + \dots \quad (8.4)$$

and this first term will be the dominant term, so that

$$\begin{aligned} h(\omega) &= \frac{N}{16\pi^2} \int dt \left\langle \left(\frac{d\mathbf{r}}{ds_1} \times \frac{d\mathbf{R}_\alpha}{ds_2} \right) \left(\frac{d\mathbf{r}}{ds'_1} \times \frac{d\mathbf{R}_\alpha}{ds'_2} \right) \delta(\mathbf{r} - \mathbf{R}_\alpha)_t \right. \\ &\quad \left. \times \delta(\mathbf{r}' - \mathbf{R}'_\alpha) \exp\{i\omega(s_1 - s'_1)\} \right\rangle ds_1 ds'_1 ds_2 ds'_2. \end{aligned} \quad (8.5)$$

The important point to notice is that $h(\omega)$ is proportional to N , for a sufficiently large number of entanglements, and that it can be expressed as an integral over the s . This will also be true if we consider the other terms of (8.3).

To ensure the convergence of the integrals, two types of restriction on the range of the variables must be imposed. (i) After a very long period of time, the chain will wriggle out of its particular original topology. The head and tail of the chain ensure a finite lifetime of one particular grouping of cooperative diffusion. Thus the range of t must be finite. (ii) The minimum meaningful length on a chain is l , the effective step length. Thus we must restrict the range of s_1, s'_1, s_2, s'_2 to (l, L) .

With these restrictions, $h(\omega)$ converges for all finite ω , and is therefore analytic. This being so we can express it as a power series in ω .

$$h(\omega) = h_0 + h_2\omega^2 + h_4\omega^4 + \dots, \quad (8.6)$$

where h_2 will be negative. The series contains even powers of ω only, because $h(\omega)$ is the Fourier transform of a real function. Thus

$$\mathcal{D}_\lambda(\omega) = \frac{kT}{v} - \lambda^2 \left(\frac{kT}{v} \right)^2 (h_0 + h_2\omega^2 + h_4\omega^4 + \dots). \quad (8.7)$$

The assumption of the independence of the entanglements implies that $h(\omega)$, and hence h_i for all i , are proportional to N , the number of entanglements. For N large, we have said that $\lambda^2 \propto 1/N$, and for most chains $\lambda^2 \propto 1/N$. We would thus expect $\mathcal{D}_\lambda(\omega)$ to be

independent of N . However, for small values of N , we may be unable to assume the gaussian nature of I , or the independence of the entanglements. Clearly if no entanglements are present, $\lambda^2(kT/v)^2h(\omega)$ is zero; but this term will have a large finite value independent of N for a high entanglement density. We might expect $\lambda^2h(\omega)$ to be proportional to N for very small N , becoming asymptotically constant for N greater than some N_0 . We can write equation (8.7) in the form

$$\mathcal{D}_\lambda(\omega) = \frac{kT}{v} - \lambda^2 \mathcal{D}_0 + \lambda^2 \mathcal{D}_2 \omega^2 + \lambda^2 \mathcal{D}_4 \omega^4 + \dots, \tag{8.8}$$

where clearly,

$$\mathcal{D}_0 = \left(\frac{kT}{v}\right)^2 h_0, \quad \mathcal{D}_2 = -\left(\frac{kT}{v}\right)^2 h_2 \text{ etc.} \tag{8.9}$$

An infinite chain would be expected to show no diffusion of the $\omega = 0$ mode, since it contains an infinite number of entanglements. As such,

$$\lambda^2 \mathcal{D}_0 = \lambda^2 \left(\frac{kT}{v}\right)^2 h_0 = \frac{kT}{v} \tag{8.10}$$

giving

$$\mathcal{D}_\lambda(\omega)|_{\omega=0} = 0. \tag{8.11}$$

Now $\mathcal{D}_\lambda(\omega)$ cannot be negative for any ω , as such kT/v must be the upper limiting value, the asymptotic limit of $\lambda^2 \mathcal{D}_0$ for any length of chain for which $N > N_0$. Thus,

$$\lambda^2 \mathcal{D}_0 \simeq kT/v$$

and

$$\mathcal{D}_\lambda(\omega) = \lambda^2 \mathcal{D}_2 \omega^2 + \lambda^2 \mathcal{D}_4 \omega^4 + \dots, \tag{8.12}$$

where \mathcal{D}_2 must be positive.

We can, in principle, now obtain the values of $\mathcal{D}_2, \mathcal{D}_4$ etc by a self-consistent argument. Take as a first approximation

$$\mathcal{D}_\lambda(\omega) = \lambda^2 \mathcal{D}_2^{(1)} \omega^2, \tag{8.13}$$

then we have the Smoluchowski equation,

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta r(\omega)} \lambda^2 \mathcal{D}_2^{(1)} \omega^2 \left(\frac{\delta}{\delta r(-\omega)} + \frac{3L}{2\pi l} \omega^2 r(\omega) \right) \right\} G_\lambda = \prod_{\omega} \delta(r(\omega) - r(\omega')) \delta(t - t'), \tag{8.14}$$

to describe the motion of the chain. Thus, to a first approximation, $h(\omega)$ can be averaged against the distribution given by this equation. In this case

$$h(\omega) = h(\omega, \mathcal{D}_2^{(1)}) \tag{8.15}$$

and hence

$$\mathcal{D}_\lambda(\omega) \simeq \frac{kT}{v} - \lambda^2 \mathcal{D}_0^{(1)} (\mathcal{D}_2^{(1)}) + \lambda^2 \mathcal{D}_2^{(1)} \omega^2 + \dots \tag{8.16}$$

However from (8.12) we required

$$\lambda^2 \mathcal{D}_0^{(1)}(\mathcal{D}_2^{(1)}) = kT/v \quad (8.17)$$

which can be inverted to give

$$\mathcal{D}_2^{(1)} = \mathcal{D}_2^{(1)}(\mathcal{D}_0^{(1)}) = \mathcal{D}_2^{(1)} \left(\frac{kT}{v\lambda^2} \right) \quad (8.18)$$

and the value of $\mathcal{D}_2^{(1)}$ determined. The condition (8.12) implies the value of $\mathcal{D}_2^{(1)}$ and \mathcal{D}_2 is known to a first approximation.

To calculate \mathcal{D}_4 , a second approximation of (8.12)

$$\mathcal{D}_\lambda(\omega) = \lambda^2 \mathcal{D}_2^{(1)} \omega^2 + \lambda^2 \mathcal{D}_4^{(2)} \omega^4 \quad (8.19)$$

needs to be considered. By a similar argument $\mathcal{D}_4^{(2)}$ can be calculated since $\mathcal{D}_2^{(1)}$ is known and then, using $\mathcal{D}_4^{(2)}$, the more accurate value of \mathcal{D}_2 namely $\mathcal{D}_2^{(2)}$ can be calculated and so on. This argument leads to $\mathcal{D}_\lambda = \lambda^2 \mathcal{D}_2 \omega^2$ for small ω , and is based on the analyticity of $\mathcal{D}_\lambda(\omega)$. This in its turn depends on the existence of the cut-offs, in particular the large L cut-off. Experience in other branches of statistical mechanics like critical phenomena and excluded volume problems suggests that one will be able to let $L \rightarrow \infty$ but the limiting process destroys the analyticity so that one expects the leading power to be

$$\mathcal{D}_\lambda \sim \lambda^2 \mathcal{D}_2 \omega^{2+\gamma}, \quad (8.20)$$

where γ is small, but nonzero. To take $\gamma = 0$ is a similar assumption to the molecular field theory of magnetization, or the Ornstein-Zernicke theory of correlations. We shall continue to assume (8.13), but comment again on (8.20) particularly with reference to the 0.4 in the 3.4 power appearing in the viscosity.

A similar comment applies to $\alpha_\lambda(\omega)$. It may be that an accurate calculation could alter the dynamical friction term from ω^2 to $\omega^{2+\delta}$ but one again will expect δ to be small and this is not such a dramatic effect as that found in $h(\omega)$. Thus the Smoluchowski equation can be taken to be

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta r(\omega)} \lambda^2 \mathcal{D}_2 \omega^2 \left(\frac{\delta}{\delta r(-\omega)} + \frac{3L}{2\pi l} \omega^2 r(\omega) \right) \right\} G_\lambda = \prod_{\omega} \delta(r(\omega) - r(\omega')) \delta(t - t') \quad (8.21)$$

and this equation will be taken to describe the behaviour of the long wavelength modes.

9. The correlation function $\langle (r(s, t) - r(s, t'))^2 \rangle$

The calculations of the previous two sections have obtained a separable Smoluchowski equation. This could have been derived from a Langevin equation of the form

$$\frac{kT}{\lambda^2 \mathcal{D}_2 \omega^2} \dot{r}(\omega, t) + \epsilon \omega^2 r(\omega, t) = \phi(\omega, t). \quad (9.1)$$

In other words, the Langevin equation (7.10) has been made separable, a chain whose topology is represented by the Lagrange multiplier λ , having an effective friction coefficient $kT/\lambda^2 \mathcal{D}_2 \omega^2$; this is clearly both mode and topology dependent. For a chain picked

at random, λ may be unknown, and so we wish to average over the topology in some way.

The correlation function $\langle (r(s, t) - r(s, t'))^2 \rangle_\lambda$ can be derived from (9.1) for a chain with topology λ . Now

$$\langle r(\omega, E) r^*(\omega, E) \rangle_\lambda = \frac{\langle \Phi(\omega, E) \cdot \Phi^*(\omega, E) \rangle_\lambda}{(EkT/\lambda^2 \mathcal{D}_2 \omega^2)^2 + \epsilon^2 \omega^4}, \quad (9.2)$$

where, if the criterion

$$\langle (r(s, t) - r(s', t))^2 \rangle_\lambda = l|s - s'| \quad (9.3)$$

for a random walk is to be satisfied

$$\langle \Phi(\omega, E) \Phi^*(\omega, E) \rangle_\lambda = \frac{2\epsilon kTl}{\lambda^2 \mathcal{D}_2 \omega^2 L}. \quad (9.4)$$

Then

$$\langle (r(s, t) - r(s, t'))^2 \rangle_\lambda = l \int \frac{d\omega dE [1 - \exp\{iE(t - t')\}] \beta \omega^2}{E^2 + \beta^2 \omega^8} \quad (9.5)$$

with

$$\beta = \frac{\lambda^2 \mathcal{D}_2}{kT}. \quad (9.6)$$

Hence

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle_\lambda &= l \int \frac{d\omega}{\omega^2} [1 - \exp\{-\beta \omega^4 |t - t'| \}] \\ &= K \left(\frac{\lambda^2 \mathcal{D}_2}{kT} \right)^{1/4} |t - t'|^{1/4} = \text{constant} \times \beta^{1/4} |t - t'|^{1/4}. \end{aligned} \quad (9.7)$$

We are now in a position to average over the topology λ to consider the average behaviour of a chain picked at random in the melt. If $Q(\lambda)$ is the probability distribution function,

$$Q(\lambda) \propto e^{-\Gamma \lambda^2} \quad (9.8)$$

then,

$$\begin{aligned} \langle (r(s, t) - r(s, t'))^2 \rangle &= \int_{-\pi}^{\pi} Q(\lambda) d\lambda \langle (r(s, t) - r(s, t'))^2 \rangle_\lambda \\ &= K |t - t'|^{1/4} \left(\frac{\overline{\lambda^2} \mathcal{D}_2}{kT} \right)^{1/4}. \end{aligned} \quad (9.9)$$

We know that $\lambda^2 \mathcal{D}_2$ is independent of N , for $N > N_0$. We would expect that on the average, a chain would obey the Smoluchowski and Langevin equations,

$$\left\{ \frac{\partial}{\partial t} - \frac{L}{2\pi} \int d\omega \frac{\delta}{\delta r(\omega)} \overline{\mathcal{D}_2} \omega^2 \left(\frac{\delta}{\delta r(-\omega)} + \frac{3L}{2\pi l} \omega^2 r(\omega) \right) \right\} G = \prod_{\omega} \delta(r(\omega) - r(\omega')) \delta(t - t') \quad (9.10)$$

and

$$\frac{kT}{\overline{\mathcal{D}}\omega^2} \dot{r}(\omega, t) + \epsilon\omega^2 r(\omega, t) = \Phi(\omega, t), \quad (9.11)$$

respectively, where $\overline{\mathcal{D}} = \overline{\lambda^2} \mathcal{D}_2$.

These equations represent the motion of a chain with the average topology. It must be remembered that a real chain will have qualitatively the $|t-t'|^{1/4}$ behaviour, but the magnitude of the diffusion will depend to some extent on the particular topology involved.

10. Conclusions

The same type of behaviour results from the constraint represented by the topological invariants, as from that represented by the pipe considered in the first half of this paper. Both of the constraints refer to cooperative diffusion as opposed to the reptative diffusion considered by de Gennes. The majority of chains will have friction and mode diffusion coefficients close to the average values of (9.10) and (9.11). Some chains, because of their nonaverage topology, will have different values for these coefficients. However their form, and the type of motions of the chains will be the same as that of the average.

This calculation has ignored the dynamical friction term; this term would cause a slight modification in the behaviour of the chains. Being dependent on λ , it may cause slight differences in the form of behaviour for chains of differing topology.

We have only considered ω to be small. This is apparent from the power series expansion for $\mathcal{D}_2(\omega)$. For large ω , we would expect $h(\omega)$ to tend to zero, giving the second set of relaxation times for the short scale Rouse-like motions between entanglements.

The sections on topological invariants are to be viewed as justifying the form of behaviour of $\tau(\omega)$ and $\mathcal{D}(\omega)$ of the pipe constraint. It is now clear that μ will not depend on N , the total number of entanglements the chain has, but rather on the density and strength of entanglements per unit length of the chain.

Since $\mathcal{D}(\omega) \propto \omega^2$ it is tempting to conclude that the chain has an overall diffusion, \mathcal{D} proportional to $1/L^3$ in the same way that the Rouse chain, which has $\mathcal{D}(\omega) = kT/\nu$, has $\mathcal{D} = kT/\nu L$. We note that $\omega = 2\pi n/L$. A calculation has been given by Grant. The difficulty however is that the $\omega = 0$ mode has been implicitly excluded in our calculations and the overall diffusion coefficient really refers to this translational mode. If \mathcal{D} can be defined, and is proportional to $1/L^3$, and hence to $1/M^3$ where M is the polymer molecular weight, then it is interesting to compare this with the $1/M^2$ reptate diffusion coefficient of de Gennes. Clearly if the latter occurs it will dominate the cooperative diffusion, but as we considered earlier, reptation may be effectively suppressed. Unfortunately there is little experimental evidence as to \mathcal{D} for an entangled polymer melt although Bueche (1968) considers the best fit to experiment is $\mathcal{D} \sim 1/M^{3.4}$.

In a following paper we show how the diffusive motions can be used to derive an expression for the zero shear coefficient of viscosity. We will find that this is proportional to M^3 .

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