Relaxation and Viscosity Anomaly of Melts Made of Long Entangled Polymers. Time-Dependent Reptation

J. des Cloizeaux

Service de Physique Théorique[†] *de Saclay, F-91191 Gif-sur-Yvette, Cedex, France*

Received February 6, 1990; Revised Manuscript Received April 10, 1990

ABSTRACT: The stress relaxation function, $G(t)$ (t = time), of a melt made of long entangled polymers is calculated by applying a modified version of the reptation concept introduced by de Gennes. The complex motions of a polymer along a stress point are simulated by considering that they are simply equivalent to a diffusion of the stress point along the polymer. A time-dependent diffusive equation describing the process is deduced from elementary considerations. The function $G(t)$ obtained for a melt made of monodisperse polymers of molecular mass M depends not only on a relaxation time τ proportional to M^3 but also on a pure number H proportional to M. For blends made of polydisperse polymers belonging to the same species, $G(t)$ is calculated in the same way, by direct application of the double reptation principle. The theoretical results are in rather good agreement with experimental data obtained by Colby for polybutadiene. A simpler semi-phenomenological diffusion equation is also studied and it leads to fairly similar results. The viscosity η associated with $G(t)$ is calculated for both equations, as a function of H. A large crossover region appears, and this effect explains qualitatively and quantitatively why the experimentalists find a dependence of η with respect to M of the form $\eta \propto M^\alpha$ with $\alpha \simeq 3.4$.

I. Introduction

The relaxation properties of a polymer melt are given by the stress relaxation function, $G(t)$. Here, we want to give a theoretical expression of $G(t)$ and to compare it with experimental results.

Actually, the experimentalists do not obtain $G(t)$ directly, but they measure

$$G''(\omega) = \omega \int_0^\infty \mathrm{d}t \cos \omega t \, G(t)$$

$$G'(\omega) = \omega \int_0^\infty \mathrm{d}t \sin \omega t \, G(t) \qquad (1)$$

Here, to test our theoretical results, we shall use values of $G''(\omega)$ obtained by Colby[1] for polymer melts made of long polybudadiene molecules of masses M_L = 355 000 and M_S = 70 900 (L for very long and S for shorter).

To calculate $G(t)$ for entangled chains, we shall use the reptation concept introduced by de Gennes[2] and developed by Edwards and Doi.[3,4] However, in practive, this concept can be applied in different manners. Thus, in previous articles[5,6] the author introduced the double reptation idea, which tells us that, in first approximation, the relaxation function $G(t)$ of blends (or of monodisperse melts) must be represented by an expression of the form[7]

$$G(t)/G_0 = [\sum \varphi_A \, p_A(t)]^2 \qquad (2)$$

where φ_A is the volume fraction of polymers of type A and $p_A(t)$ is the corresponding average fraction of tube conserved after a time t (thus $p_A(0) = 1$ and $G(0) = G_0$). In other words, if two polymers of types A and B are entangled at time zero, $p_A(t)\, p_B(t)$ is the probability that they remain entangled at time t.

A direct application of the reptation concept leads to the formula

$$p_A(t) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)t/\tau_A] \qquad (3)$$

which was derived by de Gennes[2] a long time ago. Moreover, the corresponding theory tells us that the relaxation time τ_A must be proportional to $M_A{}^3$ (M_A = molecular mass of polymers A). However, the experiments performed on polymer melts definitely show[1,6] that $G(t)$ cannot depend only on one relaxation time, even when the polymers in the melt are very long and entangled. This observation is in contradiction with eq 3 and shows that a more sophisticated theory is needed.

The elasticity of the polymers has to be taken into account and, several years ago, Doi[8] tried to deal with this effect. However, when the situation is attacked in this way, the problem is very difficult.

For this reason, the author suggested another approach. Instead of trying to describe the complex motion of a polymer near a stress point, where the polymer interacts with another polymer, he assumed that this effect can be simulated by considering that the stress point diffuses along the polymer. In this way, the (infinitely) numerous parameters corresponding to the polymer modes, are replaced only by one parameter defining the coordinate s of the stress point along the chain ($0 < s < S$). Thus, the apparent motion of the stress point along the polymer can be described by a diffusion equation.

Then, let $P(t,s)$ be the probability distribution of a stress point on a chain. We can assume that $P(0,s) = 1/S$, an equation that means that, at time zero, the density of stress points is uniform on the chain, and we can also assume that $p(t)$ is given by

$$p(t) = \int_0^S \mathrm{d}s \, P(t,s) \qquad (4)$$

The diffusion equation can be written in the form

$$\frac{\partial}{\partial t}P(t,s) = \frac{\partial}{\partial s}\left[D(t,s)\frac{\partial}{\partial s}P(t,s) + F(t,s)\, P(t,s) \right] \qquad (5)$$

with the boundary conditions

$$P(0,s) = 1/S \qquad P(t{>}0,0) = P(t{>}0,S) = 0 \qquad (6)$$

In the right-hand side of eq 5, the first term is purely diffusive and the second one describes sliding effects.

In a preceding article,[6] we considered the case where the diffusion process does not depend on time

$$D(t,s) = D(s)$$

[†] Laboratorie de l'Institut de Recherche Fondamentale du Commissariat à l'Energie Atomique.

0024-9297/90/2223-4678$02.50/0

$$F(t,s) = F(s) \tag{7}$$

We also gave an explicit solution of an equation of the form

$$\frac{\partial P(t,s)}{\partial s} = \frac{\partial}{\partial s}\left[A(s,\beta)\frac{\partial}{\partial s}[A(s,\beta)\, P(t,s)] \right] \tag{8}$$

where $A(s,\beta)$ is a function depending on a parameter β with singularities at $s = 0$ and $s = S$.

The form of this function (for our BD1 model[5]) was chosen "ad hoc" and β was given a value β_L (=0.30) for the polymers of mass M_L and a value β_S (=0.45) for the polymers of mass M_S. Thus, we could reproduce the experimental results rather well, and this fact showed us clearly that simple diffusion equations are able to describe the relaxation properties of melts made of long entangled polymers, in a proper fashion.

However, the preceding approach was not completely satisfactory for the following reasons. First, our choice of $A(s,\beta)$ was arbitrary, and we did not know how to establish a relation between the parameter β and the molecular mass of a polymer. Second, one may believe that the diffusion process should be time-dependent and not space-dependent as was assumed in eq 8. At least, this objection was raised by the reviewers of the preceding article. The author tried to answer the objection, by arguing that the introduction of a time-dependent diffusion constant would destroy the time symmetry of the problem and that it was not a thing to do. The argument would be valid if the diffusion process was a real one; however, one must recall that the diffusion equation is introduced only to simulate the motion of a polymer along the stress point. Thus, time zero, at which one starts observing the relaxation of the melt, plays a very special role.

Here, we reconsider the problem and we shall derive a time-dependent diffusion equation from elementary considerations. Thus, $p(t)$ will depend not only on a relaxation time τ proportional to M^3 but also on a dimensionless parameter H, proportional to M. This time-dependent diffusion (TDD) equation that we consider is of the form

$$\frac{\partial}{\partial t}P(t,s) = D(t)\frac{\partial^2}{\partial t^2}P(t,s) \tag{9}$$

where $D(t)$ is proportional to $t^{-1/2}$ for small t and becomes constant ($D(t) \simeq D$) for large t. Thus, rather realistic values of $G''(\omega)$ are obtained. However, the theory applies only for molecular masses above the entanglement threshold.

We also associate a viscosity η with the function $G(t)$ by setting

$$\eta = \int_0^\infty \mathrm{d}t\; G(t) \tag{10}$$

and consequently, for monodisperse melts, we write

$$\eta = \int_0^\infty \mathrm{d}t\; p^2(t) \tag{11}$$

in agreement with eq 2.

In the classical case, $p(t)$ is given by eq 2 and we find

$$\eta = A\tau \propto M^3 \qquad A = \text{constant} \tag{12}$$

Here, we shall find for η an expression of the form

$$\eta / G_0\tau = f(H) \tag{13}$$

Thus, $f(H)$ will define a crossover region, and, in this way, we shall explain why the experimental values of η can be fitted for large M by expressions of the form $\eta \propto M^\alpha$ with $\alpha \simeq 3.4$.

In section II, we derive the time-dependent diffusion (TDD) equation associated with the apparent motion of a stress point along a polymer. In section III, we solve this equation, we define the parameter H (proportional to the molecular mass M), and we obtain an approximate expression for $G(t)$. In section IV, we compare the results of this TDD theory with experimental data concerning $G''(\omega)$ for polybutadiene samples. In section V, we introduce a simpler (semiphenomenological) time-dependent diffusion (STDD) equation and we compare the corresponding values of $G''(\omega)$ to the same experimental data. Finally, in section VI, we present calculations of the viscosity η of a monodisperse melt, for the TDD and the STDD models, and we compare them with experiments.

II. Derivation of the Time-Dependent Diffusion Equation (TDD)

The reptation concept relies on the fact that, in a melt, each polymer moves in a (renewable) tube made of the other polymers. In the absence of a better description of reality, we can assume that in this tube a polymer moves like a one-dimensional Rouse chain. This assumption will be our starting point.[9]

We shall derive a simple time-dependent diffusion equation, which will be characterized by a time-dependent diffusion constant $D(t)$. Then, this equation will be solved, and from its solution $P(s,t)$, which must obey proper boundary conditions, $p(t)$ will be deduced.

Our first aim is to calculate $D(t)$, which defines the whole diffusion process. For this purpose, we consider a stress point on a polymer and, at time t, the point P, which coincides with the stress point. It will be assumed that the motion of P is of Rouse type; this motion can be easily determined, and it defines an apparent diffusion constant. Thus, by saying that the motion of P near the stress point is equivalent to a diffusion of the stress point along the polymer, we shall deduce $D(t)$ from the *free* Rouse motion. This $D(t)$ will then be introduced in the diffusion equation *with boundary conditions.*

Let us now describe the whole process in detail.

We consider a point P belonging to the one-dimensional Rouse chain representing the polymer; let s be the abscissa defining the position of P on the chain ($0 < s < S$), and let $x(t,s)$ be the coordinate of P, at time t, on the axis that bears the chain. This function $x(t,s)$ is a solution of a Rouse equation of the form

$$\frac{\partial}{\partial t}x(t,s) = \gamma\frac{\partial^2}{\partial s^2}x(t,s) + f(t,s)$$

where γ is a constant and $f(t,s)$ a Gaussian random force defined by the averages

$$\langle f(t,s)\rangle = 0$$

$$\langle f(t,s)\, f(t',s')\rangle = 2\gamma\, \delta(s-s')\, \delta(t-t')$$

The properties of this Rouse chain are classical and can be derived in a straightforward manner by introducing the chain modes. In particular, we have

$$\langle [x(t,S) - x(t,0)]^2\rangle = S \tag{14}$$

Thus, S is a Brownian area that can be considered as proportional to the number of links N (the mass M) of the polymer. In the same way, s is proportional to the number of links contained in the portion of chain joining P to the origin of the chain.

On the other hand, we have

$$\langle [x(t,s) - x(0,s)]^2 \rangle = \frac{2\gamma}{S}\left[t + 2\mathrm{t}\sum_{n=1}^{\infty}\frac{1 - e^{-n^2t/\iota}}{n^2}\cos^2(n\pi s/S)\right] \quad (15)$$

where ι is an internal time (Rouse time) defined by

$$\iota = S^2/\pi^2\gamma \qquad \iota \text{ for internal} \quad (16)$$

We may also set

$$D = \gamma/S \quad (17)$$

Thus for large t

$$\langle [x(t,s) - x(0,s)]^2 \rangle = 2Dt + \text{constant} \quad (18)$$

and we see that D is the diffusion constant of the chain along the tube (note that D is inversely proportional to M).

It is well-known that $x(t,s)$ is a Gaussian variable. Consequently, its probability distribution is a Gaussian function that could be considered as a solution of a time-dependent diffusion equation, which we shall not write. This consideration and the preceding equations suggest the introduction of an effective diffusion constant $D(t,s)$, depending on time and space. To define it, we set

$$\langle [x(t,s) - x(0,s)]^2 \rangle = 2\int_0^t \mathrm{d}t'\, D(t',s) \quad (19)$$

and therefore

$$D(t,s) = \frac{\gamma}{S}[1 + 2\sum_{n=1}^{\infty} e^{-n^2t/\iota}\cos^2(n\pi s/S)] \quad (20)$$

Now, we remark that $D(t,s)$, which is singular with respect to t (at $t = 0$), has only a slow dependence with respect to s. Therefore, it will be convenient for further developments to introduce the average $D(t)$ of $D(t,s)$ over the chain

$$D(t) = \frac{1}{S}\int_0^S \mathrm{d}s\, D(t,s) \quad (21)$$

Thus, we have

$$D(t) = \frac{\gamma}{S}[1 + \sum_{n=1}^{\infty} e^{-n^2t/\iota}] \quad (22)$$

Let us now analyze the reptation process. When the reptation concept is applied in the simplest way, the polymer is considered as a nonelastic string, whose parts all diffuse simultaneously along the chain tube with a diffusion coefficient D. The stress points where the polymer interacts with other polymers are considered as fixed. However, we can simulate this physical situation by saying that the polymer remains fixed and that the stress point P diffuses on this polymer with a diffusion constant D. Thus, in this simple case, the diffusion equation reads

$$\frac{\partial}{\partial t}\mathcal{P}(t,l) = D\frac{\partial^2}{\partial l^2}\mathcal{P}(t,l) \quad (23)$$

where now L is the length of the polymer and l is the length of the segment joining P to the origin of the polymer. Moreover, the solution must obey the boundary conditions

$$\mathcal{P}(0,l) = 1/L \qquad \mathcal{P}(t{>}0,0) = \mathcal{P}(t{>}0,L) = 0 \quad (24)$$

These relations determine $\mathcal{P}(t,l)$, and, in agreement with eq 4, we obtain the classical result

$$p(t) = \int_0^L \mathrm{d}l\, \mathcal{P}(t,l) = \frac{8}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2 t/\tau] \quad (25)$$

where

$$\frac{1}{\tau} = \frac{D\pi^2}{L^2} \quad (26)$$

We can now generalize eq 22. We have only to replace D by $D(t)$ in this equation and to observe that $l/L = s/S$. The new diffusion equations reads

$$\frac{\partial P}{\partial t}(t,s) = D(t)\frac{S^2}{L^2}\frac{\partial^2}{\partial s^2}P(t,s) \quad (27)$$

where $D(t)$ is given by eq 21, the boundary conditions being given by eq 6.

Incidentally, the reader might think that, to derive the diffusion equation, it would be better to use $D(t,s)$ than $D(t)$ and that the problem has been oversimplified. This matter is discussed in Appendix A (and also in section VII); the conclusion is that a more sophisticated equation leads in first approximation to the same answer as eq 27. Thus, this TDD equation seems realistic in spite of its simplicity.

III. Solution of the Time-Dependent Diffusion Equation. Definition of H and Calculation of $p(t)$

In order to calculate the probability $p(t)$ corresponding to our TDD model, we want the solution $P(t,s)$ of eq 24.

We can write

$$P(t,s) = \frac{1}{S}\int_0^S \mathrm{d}s_0\, P(t,s,s_0) \quad (28)$$

where $P(t,s,s_0)$ is the solution of the equation

$$\frac{\partial}{\partial t}P(t,s,s_0) = D(t)\frac{S^2}{L^2}\frac{\partial^2}{\partial s^2}P(t,s,s_0) \quad (29)$$

with the boundary conditions

$$P(0,s,s_0) = \delta(s-s_0) \qquad P(t{>}0,0,s_0) = P(t{>}0,S,s_0) = 0 \quad (30)$$

This solution is

$$P(t,s,s_0) = \frac{2}{S}\sum_{m=1}^{\infty}\sin\left(m\pi\frac{s}{S}\right)\sin\left(m\pi\frac{s_0}{S}\right)\exp[-m^2U(t)] \quad (31)$$

where

$$U(t) = \frac{\pi^2}{L^2}\int_0^t \mathrm{d}t'\, D(t') \quad (32)$$

and this fact can be easily verified by noting that the eigenfunctions associated with eq 29 are

$$\varphi_m(t,s) = (2/S)^{1/2}\sin\left(m\pi\frac{s}{S}\right)\exp[-m^2U(t)]$$

The probability $p(t)$ is given by eqs 4 and 28

$$p(t) = \frac{1}{S}\int_0^S \mathrm{d}s\int_0^S \mathrm{d}s_0\, P(t,s,s_0)$$

We obtain

$$p(t) = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2U(t)] \quad (33)$$

and $U(t)$ is given by eqs 22 and 32.

$$U(t) = \frac{\pi^2\gamma}{SL^2}\left[t + \iota\sum_{n=1}^{\infty}\frac{1 - e^{-n^2t/\iota}}{n^2}\right] \tag{34}$$

We can now express $U(t)$ in terms of more physical constants. We define the relaxation time τ by setting

$$1/\tau = D\pi^2/L^2 = \pi^2\gamma/SL^2 \tag{35}$$

in agreement with eqs 17 and 26, and we see that $\tau \propto M^3$ as expected.

We define the parameter H by setting

$$H = \tau/\iota = L^2/S \tag{36}$$

in agreement with eqs 15 and 29. Thus we see that H is a dimensionless number, which is proportional to M, since the length L and the area S are both proportional to M. Thus, H can be interpreted as a number of entanglements per polymer (we use H to represent this quantity because the letter H looks like the letter N, which is commonly used to represent the number of links of a polymer).

We can also define an intrinsic relaxation time, τ_0, by setting

$$\tau = H^3\tau_0 \tag{37}$$

Thus, τ_0 does not depend on M since we have

$$\tau_0 = \frac{1}{\pi^2\gamma}\left(\frac{S}{L}\right)^4 \tag{38}$$

Now $U(t)$ can be written in the form

$$U(t) = \frac{t}{\tau} + \frac{1}{H}g(Ht/\tau) \tag{39}$$

where $g(x)$ is defined by the equality

$$g(y) = \sum_{n=1}^{\infty}\frac{1 - e^{-n^2y}}{n^2} \tag{40}$$

Incidentally, we note that

$$g(y) \simeq \pi^2/6 \quad \text{for } y \gg 1$$
$$g(y) \simeq \pi^{1/2}y^{1/2} \quad \text{for } 0 < y \ll 1 \tag{41}$$

Thus eqs 33, 39, and 40 define $p(t)$ completely. However, we note that the form of eq 39 can be expected to be rather general. The value of $g(y)$ that we give is only approximate, since to derive it, we used a Rouse equation that does not seem completely valid in the present case. Better expressions for $g(y)$ could probably be found. What is really important is the fact that $g(y)$ has a dominant singularity at $y = 0$. Thus, for short times, the second term in eq 33 becomes much more important than the first one: this is the essential effect and it corresponds to quick local reptation motions of the polymer.

IV. Comparison of Predictions of the TDD Theory with Experimental Results

In the preceding section, we calculated $p(t)$ in terms of the relaxation time τ and of a parameter H, which is proportional to the molecular mass. Thus, $G(t)/G_0$ is given by explicit expressions for monodisperse or polydisperse melts (see eq 2). On the other hand, according to eq 1, $G''(\omega)/G_0$ is a Fourier transform of $G(t)/G_0$ and can be calculated on a computer. However, as $G(t)$ is singular and as we need $G''(\omega)$ for very large values of ω, the transformation requires some care (see Appendix B).

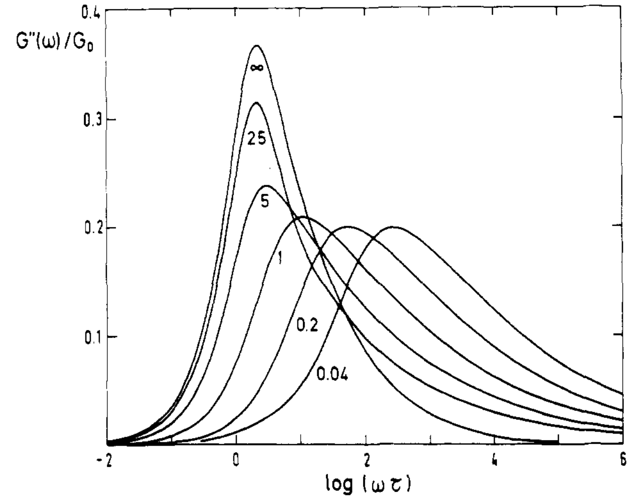

Figure 1. TDD model with double reptation. Here log $[G''(\omega)/G_0]$ is plotted against log ($\omega\tau$) for various values of H; τ is the main relaxation time for reptation ($\tau \propto M^3$), and H can be interpreted as a number of entanglements per polymer. The limit $H \rightarrow \infty$ corresponds to the classical (double) reptation theory.

In the case of monodisperse melts

$$G(t)/G_0 = p^2(t) \tag{42}$$

In order to see how $G''(\omega)/G_0$ depends on H, we plotted log $[G''(\omega)/G_0]$ against log ($\omega\tau$), in Figure 1, for various values of H. The case $H = \infty$ corresponds to the classical "double reptation" theory. We see that when H diminishes, two effects appear: (1) the curves become flatter and broader; (2) the peak is displaced toward the right. Both effects are in qualitative agreement with experimental observations, and, in particular, the second one explains why the main relaxation time of a long entangled polymer seems to increase faster than M^3.

We can now try to fit the experimental results obtained by Colby[1] for two monodisperse polybutadiene samples of molecular masses M_L = 355 000 and M_S = 70 900. Values of $G''(\omega)$ were measured at three temperatures, +30, −2, and −51 °C, and the data were superimposed to a reference temperature of 30 °C via time–temperature shifting. These results appear in Figure 2 with the corresponding theoretical curves. These curves were fitted by choosing the following values for the parameters

$$H_L = 15$$
$$H_S = 15(M_S/M_L) = 2.996$$
$$\tau_L = 6.5\text{ s}$$
$$\tau_S = 6.5(M_S/M_L)^3 = 5.18 \times 10^{-2}\text{ s}$$
$$G_0 = 12.53 \times 10^6\text{ dyn/cm}^3$$

Thus, two intrinsic constants characterizing the relaxation properties of polybutadiene samples can be determined, namely

$$M_0 = M/H \simeq 23667\text{ Da}$$
$$\tau_0 = \tau/H^3 \simeq 1.926 \times 10^{-3}\text{ s}$$

We note that the agreement is good but not perfect. Actually, the results obtained in a previous article,[6] with the BD1 model mentioned in section I, was slightly better. However, this BD1 model was partly phenomenological, and we had two parameters β_L and β_S that could be fitted independently. Here, on the contrary, H_S is always related to H_L since $H_S/H_L = M_L/M_S$, and this is a severe con-

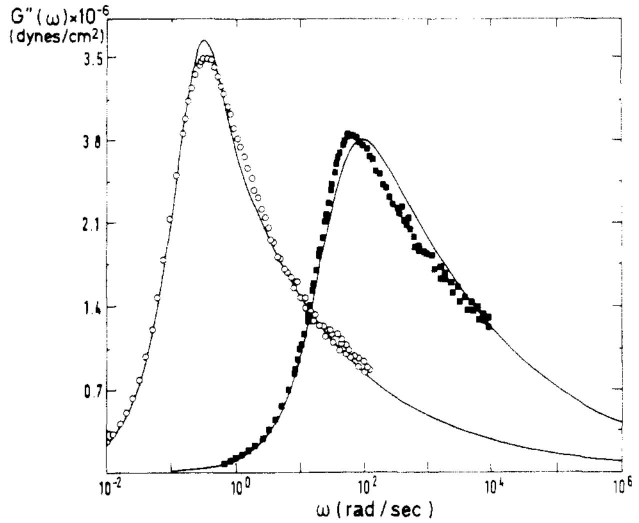

Figure 2. Loss modulus data for two polybutadiene samples L and S of masses M_L = 355 000 and M_H = 70 900. The experimental data (Colby[1]) are represented by open circles for polymer L and by filled squares for polymer S. The two theoretical curves correspond to the TDD theory and result from a simultaneous fit. The values of the three independent parameters are $H_L = 15$, $\tau_L = 6.5$ s, and $G_0 = 12.53 \times 10^6$ dyn/cm².

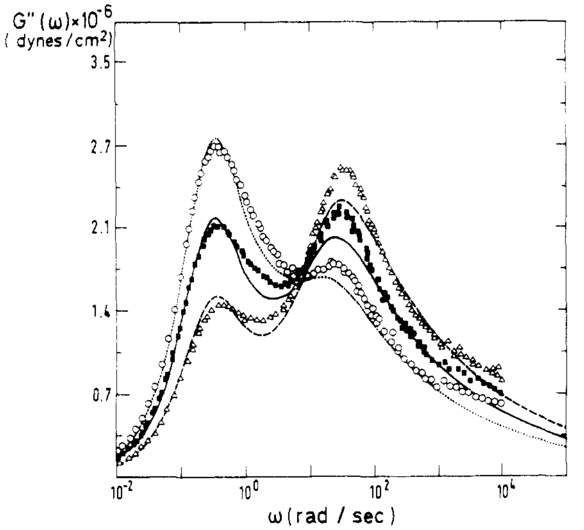

Figure 3. Loss modulus data for three mixtures of polybutadienes of masses M_L = 355 000 and M_S = 70 900. The theoretical curves correspond to the TDD model, and the values of the parameters are the same as those in Figure 2. Open circles are the data, and the dotted line is the prediction for $\varphi_L = 0.882$; filled squares are the data, and the solid line is the prediction for $\varphi_L = 0.768$; open triangles are the data, and the dashed line is the prediction for $\varphi_L = 0.638$.

straint. However, H_L itself is not very precisely defined (we may have a variation of the order of 10% in the value of M_0).

Now, let us consider the experimental results obtained by Colby for mixtures of polybutadiene molecules of molecular masses M_L = 355 000 and M_S = 70 900. The volume fractions are φ_L and φ_S with

$$\varphi_L + \varphi_S = 1$$

and Colby studied three samples for which he had $\varphi_L = 0.882$, $\varphi_L = 0.768$, and $\varphi_L = 0.638$. The experimental results appear in Figure 3 with the corresponding theoretical curves. In the present case, we write

$$G(t)/G_0 = [\varphi_L p_L(t) + \varphi_S p_S(t)]^2$$

The theoretical curves corresponding to the mixtures were drawn by using the values of H_L, H_S, τ_L, and τ_S introduced previously to get a reasonable fit in the monodisperse case. Again the agreement is not perfect, but nevertheless it can be considered as satisfactory, if one considers the simplicity of our theory, the fact that it uses only a minimal number of parameters, and the improvement thus obtained.

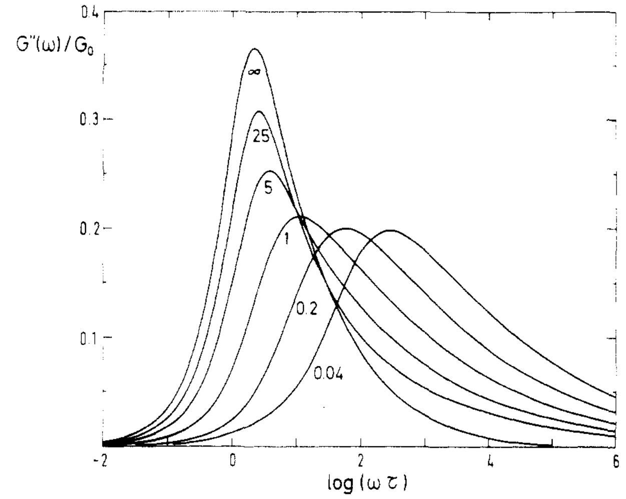

Figure 4. STDD model with double reptation. Here, log $[G''(\omega)/G_0]$ is plotted against log $(\omega\tau)$ for various values of H. Compare this figure with Figure 1.

V. A Semiphenomenological Expression of $p(t)$

At the end of section III, we noted that the singularities in $g(y)$ are essential, but the expression that we give for $g(y)$ (see eq 40) is perhaps not the best one.

This suggests that we represent $g(y)$ by a simpler formula preserving the essential features of this function. Thus, we shall define the STDD model (simplified time-dependent diffusion) by setting

$$g(y) = -y + y^{1/2}[y + (\pi y)^{1/2} + \pi]^{1/2} \tag{43}$$

a function that for small y and large y has about the same properties as the previous expression of $g(y)$ (see eqs 40 and 41). Then, everything is known, and we can calculate $G(t)$.

Let us consider monodisperse melts. In Figure 4, log $[G''(\omega)/G_0]$ is plotted against log $(\omega\tau)$ for various values of H. Thus, we see that Figure 4 is very analogous to Figure 1.

Now, we can try to get a fit with the experimental results obtained by Colby. Thus, for monodisperse melts, we obtain Figure 5, which is very analogous to Figure 2. However, here the theoretical curves were fitted by choosing slightly different values for the parameters, namely

$$H_L = 15$$

$$H_S = 15(M_S/M_L) = 2.996$$

$$\tau_L = 7.5 \text{ s}$$

$$\tau_S = 7.5(M_S/M_L)^3 = 5.97 \times 10^{-2} \text{ s}$$

$$G_0 = 12.05 \times 10^6 \text{ dyn/cm}^2$$

For this model, the values of the intrinsic constants M_0 and τ_0 of polybutadiene are

$$M_0 = M/H = 23677$$

$$\tau_0 = \tau/H = 2.222 \times 10^{-3} \text{ s}$$

Again, the agreement is good but not perfect. However,

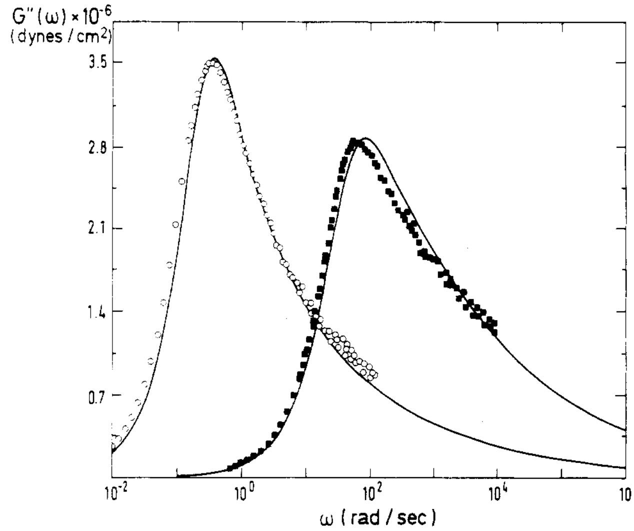

Figure 5. Loss modulus data for two polybutadiene samples L and S of masses M_L = 355 000 and M_S = 70 900. The experimental data are represented by open circles for polymer L and by filled squares for polymer S. The two theoretical curves correspond to the STDD model, and they result from a simultaneous fit. The values of the three independent parameters are $H_L = 15$, $\tau_L = 7.5$ s, and $G_0 = 12.05 \times 10^6$ dyn/cm². Compare this figure with Figure 2.

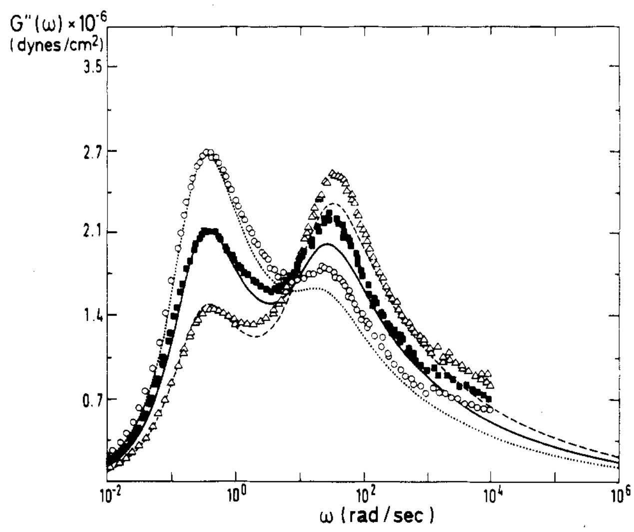

Figure 6. Loss modulus data for three mixtures of polybutadienes of masses M_L = 355 000 and M_S = 70 900. The theoretical curves correspond to the STDD model, and the values of the parameters are the same as those in Figure 5. Open circles are the data, and the dotted line is the prediction for $\varphi_L = 0.882$; filled squares are the data, and the solid line is the prediction for $\varphi_L = 0.768$; open triangles are the data, and the dashed line is the prediction for $\varphi_L = 0.638$. Compare this figure with Figure 3.

by comparing Figures 2 and 5, we note that, with the present semiphenomenological expression of $g(y)$, we can obtain a slightly better fit than previously.

Now let us consider polybutadiene mixtures. The experimental results obtained by Colby for $\varphi_L = 0.882$, $\varphi_L = 0.768$, and $\varphi_L = 0.638$ appear in Figure 6, with the theoretical curves. To draw these curves, the same values of H_L, H_S, τ_L, τ_S, and G_0 were used as in the monodisperse case. Figure 6 is very similar to Figure 3. The fit is slightly better in certain regions but slightly worse in others.

Briefly, the simplified theory (STDD) gives about the same results as the original (TDD) theory.

VI. An Explanation of the Viscosity Anomaly in Polymer Melts

For many years, experimentalists measured the viscosity of melts made of long entangled polymer and they found[7] that their results were consistent with a power law of the form

$$\eta \equiv M^{\alpha}$$

where α takes values around 3.4.

This fact was a puzzle for theoreticians because reptation theory predicts that η cannot increase faster than M^3 and because it is not easy to find simple mechanisms able to reduce the viscosity for high molecular masses. However, with Graesseley, we may think that α is an effective exponent, that the real exponent is 3, and that the experimentalists observe only a crossover behavior. This view seems reasonable, but it seems that until now it has not been justified in a completely convincing manner, in spite of interesting attempts made by Doi[8] in this direction.

Here, we shall reconsider this question by using the results obtained in the previous section, and we shall see that these results demonstrate the existence of a crossover that explains the anomaly very clearly.

We define the viscosity η by setting

$$\eta = \int_0^\infty \mathrm{d}t\, G(t) \tag{44}$$

Then, let us consider a monodisperse melt; eqs 33 and 42 give

$$\eta/G_0 = \int_0^\infty \mathrm{d}t\, p^2(t) = \int_0^\infty \mathrm{d}t \left[\frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 U(t)] \right]^2$$

Now eq 39 enables us to express η in terms of $g(y)$. Setting

$$\tau = H^3 \tau_0$$

$$G_0 \tau_0 = \eta_0$$

We find

$$\eta/\eta_0 = H^3 \int_0^\infty \mathrm{d}T \left[\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left\{ -(2n+1)^2 \left[T + \frac{1}{H} g(HT) \right] \right\} \right]^2 \tag{45}$$

Thus, if we put $g(y) = 0$ in this formula, we find the classical result

$$\eta/\eta_0 = (64/\pi^4) A H^3 \equiv M^3 \tag{46}$$

where

$$A = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left[\frac{1}{(2m+1)^2} \right] \left[\frac{1}{(2n+1)^2} \right] \times \left[\frac{1}{(2m+1)^2 + (2n+1)^2} \right] \simeq 0.528 \tag{47}$$

Now, we can replace $g(y)$ by the function eq 40 for TDD and by the function eq 43 for STDD. We computed η/η_0 in both cases; thus, log (η/η_0) is plotted against log H, in Figure 7 for TDD and in Figure 8 for STDDD. We see that the two corresponding curves look very similar. In particular each curve has the same two asymptotes of slopes 3 and 4, and it defines a crossover between two scaling laws corresponding to these asymptotes.

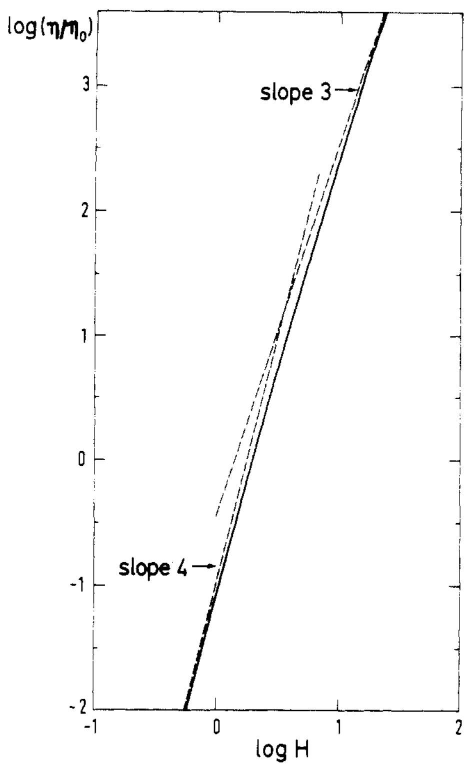

Figure 7. Viscosity of a monodisperse polymer melt: log (η/η_0) is plotted against H for the TDD model. The curve has two asymptotes with a crossover region.

The behavior of η for large H and for small H is the same for the two models, because in both cases, the behavior of $y + g(y)$ for large y and for small y is the same (see eqs 41 and 43).

When H becomes infinite, $(1/H)g(HT)$ goes to zero. Thus, in this limit, we recover the classical result

$$\eta/\eta^0 = (64/\pi^4)AH^3$$

where A is given by eq 47. In this way, we find the first asymptote.

When H goes to zero, the theory breaks down because this limit corresponds to short chains and we know that, in this domain, we have $\eta \equiv M$ as a consequence of short-range viscous processes, which have nothing to do with reptation. However, it is useful to consider the limit $H \rightarrow 0$ in the framework of the present theory because it gives a trend. For small y, $g(y) \simeq (\pi y)^{1/2}$ according to eqs 41 and 43, and therefore for small H

$$T + \frac{1}{H}g(HT) \simeq (\pi T/H)^{1/2}$$

Bringing this expression in eq 45, we find

$$\eta/\eta_0 = (128/\pi^5)BH^4 \qquad (48)$$

where

$$B = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\left[\frac{1}{(2m+1)^2}\right]\left[\frac{1}{(2n+1)^2}\right] \times \left[\frac{1}{[(2n+1)^2 + (2m+1)^2]}\right]^2 \simeq 0.252 \qquad (49)$$

In this way, we find the second asymptote.

Thus the effective

$$\alpha = \frac{\partial \log(\eta/\eta_0)}{\partial \log H} \qquad (50)$$

is a number that decreases from 4 to 3 when H goes from zero to infinity. This α is the exponent that the experimentalist measures, in the crossover region, for values of H ($H > 1$) corresponding to the entanglement domain.

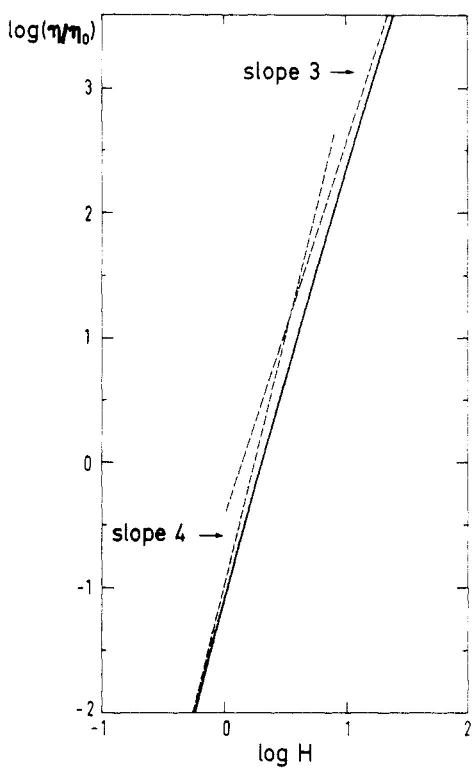

Figure 8. Viscosity of a monodisperse polymer melt: log (η/η_0) is plotted against H for the STDD model. The curve has two asymptotes (the same as in Figure 7) with a crossover region.

In Figure 9, we compare the theoretical curve of the TDD model with values of the viscosity of polybutadiene samples at 25 °C, reported by Colby, Fetters, and Graesseley. Though, the reference temperature is now 25 °C and not 30 °C, as in the preceding experiments, we use the same constants as in a section IV, namely

$$M_0 = 23667$$

$$\eta_0 = G_0 T_0 = 24125P$$

The experimental viscosities that we use are extracted from Table XI of ref 11. They are reproduced in Table I with the corresponding values of $H = M/M_0$ and of η/η_0. We see looking at Figure 9 that the agreement between the theory and the experiments is very good. We note that for small values of H the experimental points are slightly above the theoretical curve, but this was to be expected since the value $H = 1$ should correspond approximately to the entanglement threshold.

VII. Summary and Conclusion

In the preceding section, we studied the relaxation of long entangled polymers and we presented a modified reptation theory, which explains why the shape of the relaxation function $G(t)$ (or of $G''(\omega)$) changes when M varies. The effect comes from a competition between the internal time ι, which is proportional to M^2, and the reptation time τ, which is proportional to M^3. Thus, we had to introduce the parameter $H = \tau/\iota$, which can be interpreted as the number of entanglements per polymer.

The problem was simplified by using the idea that instead of considering a polymer as mobile and a stress

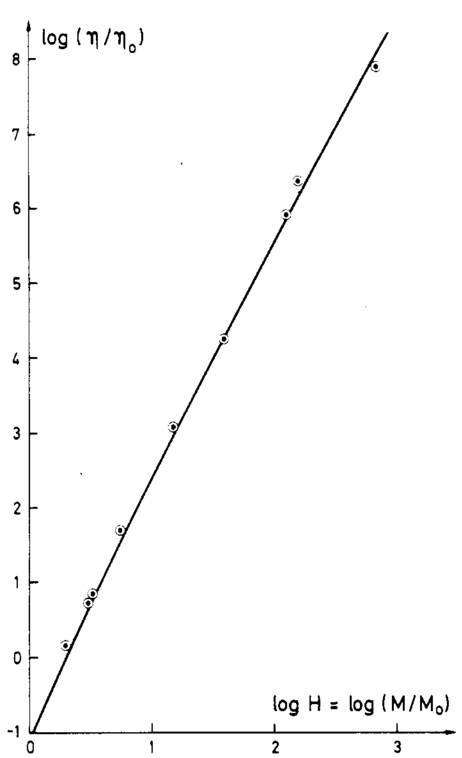

Figure 9. Viscosity of a monodisperse polymer melt: a comparison between the theoretical result obtained with the TDD theory and experimental data, given in ref 11, for polybutadiene samples (M_0 = 23 667, η_0 = 24 125, $H = M/M_0$).

Table I
Viscosities of Polybutadiene Samples at 25 °C[a]

sample	M	η	$H = M/M_0$	η/η_0
CDS-30	4.60×10^4	3.53×10^4	1.944	1.463
B_1	7.09	1.33×10^5	2.996	5.51
C20	7.60	1.73	3.211	7.17
B_2	1.30×10^5	1.21×10^6	5.49	50.15
B_3	3.55	3.0×10^7	15	1243
B_4	9.25	4.4×10^8	39.08	1.824×10^4
B_5	2.95×10^6	2.0×10^{10}	124.6	8.29×10^5
B_6	3.74	5.7	158.0	2.362×10^6
B_7	1.65×10^7	1.9×10^{12}	697	7.87×10^7

[a] We take M_0 = 23 677 and η_0 = 24 155.

point as fixed, one could do the reverse. Thus, the number of degrees of freedom is greatly reduced since the complex reptation motions of a polymer along a stress point are simulated by a simple diffusion of the stress point along the polymer. This diffusion is characterized by a time-dependent diffusion coefficient, $D(t)$, which breaks the time symmetry in the system.

Physically, the phenomenon can be interpreted as follows. At time zero, the melt is strained. At a stress point that can be considered as fixed, two polymers interact. When t increases, each polymer moves along the stress point. When an end point reaches a stress point, the corresponding stress is relaxed. When t is small, we observe quick local motions that are fluctuations and occur at every point of the chain. If we consider the real process, we may say that the only important motion is the motion of the end points. Thus, the difference between our method and Doi's approach can be considered as purely technical.

The phenomenon can also be interpreted in the framework of the diffusive process, which simulates the real events, but the two interpretations must be carefully dissociated; otherwise, they may look contradictory. Thus, for instance, it must be understood that eq 2 for $s = 0$ (or $s = S$) cannot determine alone the details of the motion of the end points and consequently the relaxation that occurs at these points. In other words, $G(t)$ is not a functional of $D(t,0)$ but a functional of $D(t,s)$ because all modes participate nontrivially in the relaxation process. This is why it is not very wrong to replace $D(t,s)$ by its average $D(t)$.

We may explain this in a different way. Recalling that we try to interpret the diffusive process, we note that *now distances are measured along the polymer.* Thus, diffusion and adsorption at the end points play a direct role, but diffusion in the central part of the polymer also plays a role that is indirect but nonnegligible. This role can be easily understood from a physical point of view: because of central fluctuations, a stress point that at time zero is at the center of the polymer may come nearer to one end, at time t, even if the end points do not move; consequently, intermediary motions of this kind may contribute to accelerate the final disentanglement process. In particular, this fact may explain why corrections to the usual reptation theory can be observed for very high molecular masses, many times larger than the mass corresponding to the entanglement threshold.

What is really important is that $D(t)$ is singular at $t = 0$. This fact is related to the existence of the quick motions that occur everywhere on the polymer for small t and that, in the middle of the polymer, would be about the same if the polymer was infinite. Consequently, during some time, $D(t)$ is proportional to $t^{-1/2}$ and therefore decreases with t. However, after a period of time of the order of ι, the end points began to play a role and $D(t)$ stops diminishing. Finally, when $t \rightarrow \infty$, $D(t)$ has a finite limit D, which is the diffusion coefficient of the whole polymer.

The theory is deduced from first principles and uses a minimal number of parameters, since H is the only dimensionless parameter and since it is proportional to M.

This theory combined with the double reptation principle is rather successful. First, it enables us to calculate $G''(\omega)$ rather accurately for monodisperse and polydisperse melts, and it shows how $G''(\omega)$ depends on the molecular masses of the constituents. Second, it explains the well-known viscosity anomaly (the 3.4 law), which is currently observed in monodisperse melts.

The agreement between the theoretical results and the experiments is good but not perfect. The origin of the discrepancies can be the following:

(1) We did not take into account the viscous corrections, which play an essential role for large values of ω (Rouse motions).

(2) The values of the molecular masses given by the experimentalists may differ slightly from the real ones.

(3) The polydispersity effects have been neglected.

(4) The form of the function $g(y)$ that we use is not exactly correct.

(5) The double reptation principle is only a good approximation, and interactions involving three polymers may lead to corrections.

(6) The computation is less precise for large ω than for small ω.

We are pretty sure that all these uncertainties play a nonnegligible role. We think that point (1) and also point (5) might lead to the largest effects, but this is only a feeling. We also note that, in spite of defects, the space-dependent diffusion equations studied in a preceding article[6] give results that in some respects, are slightly better than the time-dependent diffusion equations presented here. However, we do not know whether this fact is significant or not.

The fact that the relaxation properties of polymer melts, which are very complex systems, can be predicted with a good precision by using very few parameters is surprising, but it is probably possible to do even better; in particular, it would be useful to take into account the viscous effects, which play an essential role for small t (and large ω).

Let us also make a few comments concerning possible experiments. To test the theories, one needs very precise measurements made under similar conditions on sets of good monodisperse (or polydisperse) samples corresponding to different and well-defined molecular masses. It would also be interesting (but difficult!) to explore the local dynamics of chains in melts. Thus, a fraction of the polymers might contain labeled parts (for instance, by deuteration), whose motions could be studied by scattering effects. In brief, very interesting experiments could certainly be made, and the author would be glad if the present article could have a stimulating effect.

Appendix A. Refinements Concerning the Diffusion Equation

In section II, we introduced a function $D(t,s)$ given by eq 20, but our time-dependent diffusion eq 27 uses only the function $D(t)$, which is an average of $D(t,s)$ over s. The reader might think that it would be better to avoid this simplification and to study the diffusion equation associated with $D(t,s)$. However, the problem is ambiguous because $\partial/\partial s$ does not commute with $D(t,s)$.

In spite of this difficulty, we think that it is reasonable to generalize eq 27 as follows

$$\frac{\partial}{\partial t}P(t,s) = \frac{S^2}{L^2}\frac{\partial}{\partial s}\Big[\,(D(t,s))^{1/2}\frac{\partial}{\partial s}[(D(t,s))^{1/2}P(t,s)]\,\Big] \qquad \text{(A.1)}$$

with the usual boundary conditions (eq 6).

There are two reasons for that:

(1) In a preceding article,[6] it was shown by comparison with experiment that the BD models that correspond to equations of the type

$$\frac{\partial}{\partial t}P(t,s) = \frac{\partial}{\partial s}\Big[A(s)\frac{\partial}{\partial s}\Big[A(s)\frac{\partial}{\partial s}P(t,s)\Big]\Big]$$

give a better description of reality than other models.

(2) These BD models correspond to simple Langevin equations.[6]

Now, we should solve eq A.1, but the problem is not easy. Therefore, since $D(t,s)$ varies slowly with s, we shall content ourselves with a first-order approximation. Even so, we might think that we would get a better approximation than by solving eq 27. However, we shall now show that this approximation leads to the same answer. Thus, eq 27 is probably better than it looks, and this is the essential result of this Appendix.

To solve eq A.1, we can introduce the biorthogonal set of functions $\varphi_n(t,s)$ and $\bar{\varphi}_m(t,s)$, which are eigenfunctions of the equations

$$E_n(t)\,\varphi_n(t,s) = -\frac{\partial}{\partial s}\Big[\,(D(t,s))^{1/2}\frac{\partial}{\partial s}[(D(t,s))^{1/2}\varphi_n(t,s)]\,\Big]$$

$$E_n(t)\,\bar{\varphi}_n(t,s) = -(D(t,s))^{1/2}\frac{\partial}{\partial s}\Big[\,(D(t,s))^{1/2}\frac{\partial}{\partial s}\bar{\varphi}_n(t,s)\,\Big] \qquad \text{(A.2)}$$

with the boundary conditions

$$\varphi_n(t,0) = \varphi_n(t,S) = 0$$

$$\bar{\varphi}_n(t,0) = \bar{\varphi}_n(t,S) = 0$$

The normalization condition reads

$$\int_0^S \bar{\varphi}_m(t,s)\,\varphi_n(t,s) = \delta_{nm} \qquad \text{(A.3)}$$

Then, $P(t,s)$ is given by

$$P(t,s) = \frac{1}{S}\sum_{n=1}^{\infty}\exp\left(-\frac{S^2}{L^2}\int_0^t \mathrm{d}t\,E_n(t')\right)\times \varphi_n(t,s)\int_0^S \mathrm{d}s'\,\bar{\varphi}_n(t,s') \qquad \text{(A.4)}$$

In particular, if $D(t,s)$ is replaced by $D(t)$ in eq A.1, we have

$$\varphi_n(t,s) = \bar{\varphi}_n(t,s) = (2/S)^{1/2}\sin(\pi ns/S)$$

$$E_n(t) = \frac{\pi^2 n^2}{S^2}D(t) \qquad \text{(A.5)}$$

To first order, we can replace the exact $\varphi_n(t,s)$ and $\bar{\varphi}(t,s)$ by their unperturbed values (eq A.5), and from eqs A.2, we get

$$E_n(t) = -\frac{2}{S}\int_0^{\infty}\mathrm{d}s\,\sin(\pi ns/S)\times \frac{\partial}{\partial s}\Big[\,(D(t,s))^{1/2}\frac{\partial}{\partial s}[(D(t,s))^{1/2}\sin(\pi ns/S)]\,\Big]$$

Integrating by parts as many times as needed, we obtain

$$E_n(t) = \frac{\pi^2 n^2}{S^3}\int_0^{\infty}\mathrm{d}s\,D(t,s) = \frac{\pi^2 n^2}{S^2}D(t)$$

Thus, to first order, the $P(t,s)$ solution of eq A.2 coincides with the $P(t,s)$ solution of eq 27.

Appendix B. Calculation of $G''(\omega)$

The function $G''(\omega)$ defined by the integral

$$G''(\omega) = \omega\int_0^{\infty}\mathrm{d}t\,\cos\omega t\,G(t) \qquad \text{(B.1)}$$

must be calculated over a large range of values of ω (several decades). Thus, a direct calculation of $G''(\omega)$ leads to two difficulties:

(1) $G(t)$ is singular for $t = 0$, and this singularity can produce anomalies in the computation. To avoid this effect, we can subtract the singular part of $G(t)$ and integrate it analytically independently of the remaining part.

(2) For very large values of ω, cos ωt has strong oscillations and the convergence is poor. Fortunately, $G(t)$ is given by an analytic expression for which we can find an analytic continuation in the complex t plane. Thus, by transforming eq B.1, we find that $G''(\omega)$ is also given by the integral

$$G''(\omega) = \frac{\omega}{2}\int_0^{\infty}\mathrm{d}T\,e^{-a\omega T}[(1+ia)e^{i\omega T}G((1+ia)T) + \text{complex conjugate}]$$

where a is arbitrary. In this way, for large ω, we get rapidly converging expressions.

References and Notes

(1) Rubinstein, M.; Colby, R. *J. Chem. Phys.* **1989**, *89*, 5291.

(2) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.

(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.

(4) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986; Chapter 6.

(5) des Cloizeaux, J. *Europhys. Lett.* **1988**, *5*, 437; Erratum, *Europhys. Lett.* **1988**, *6*, 475.

(6) des Cloizeaux, J. *Macromolecules* **1990**, *23*, 3992.

(7) An equation of this form had been proposed previously, but for

different reasons by: Marucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 159. Marucci's approach is interesting but more complicated and less convincing than the double reptation idea.

(8) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265; *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.

(9) The same assumption was also the starting point of a computer simulation made by: Ketzmerick, R.; Ottinger, H. C. *Continuum Mech. Thermodyn.* **1989**, *1*, 113.

(10) Berry, G. C.; Fox, T. C. *Adv. Polym. Sci.* **1968**, *5*, 261. See also: Reference 4; Chapter 7, p 232.

(11) Colby, R. H.; Fetters, L. J.; Graesseley, W. W. *Macromolecules* **1987**, *20*, 226.