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Lateral Diffusion Model for Polymer Dynamics in the Melt: Mean-Squared Displacement for Monodisperse and Polydisperse Systems

Michael F. Herman

Department of Chemistry and Quantum Theory Group, Tulane University,
New Orleans, Louisiana 70118

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ABSTRACT: A model is developed for the dynamics of linear chain polymer systems in the melt. Monodisperse and polydisperse systems are considered. The basic premise of the model is that the polymer chains move by sliding along the backbones of the neighboring chains with which they are in contact. Since the various chains are entangled over distances on the order of the chain radius of gyration, this sliding contact motion along the contours of neighboring chains must occur over distances on the order of the chain contour. The constraining nature of the interchain contacts is included in an effective single-bead friction coefficient, which is found to be an increasing function of time. The effective friction coefficient is averaged over the distribution of contact lifetimes. The resulting averaged time-dependent single-bead friction coefficient is employed in a Rouse model for the chain dynamics. Calculations show that $D_{CM} \sim N^{-2}$ and $t_f \sim N^3$ for monodisperse systems within this model. The mean-squared bead displacement displays a $t^{1/3}$ dependence at early times and crosses over to the simple diffusion $6D_{CM}t$ form for $t > t_f$. The mean-squared displacement of the center of mass behaves as $t^{2/3}$ for $t < t_f$, before crossing over to the simple diffusion form. Numerical calculations are also performed for the case of a single probe polymer of length N_p in a melt of host chains, each of length N_m. It is found that D_{CM} only depends weakly on N_m.

I. Introduction

The reptation model of polymer dynamics[1-7] and its refinements[8-22] have been highly successful in explaining a great deal of dynamic and viscoelastic data for polymer systems in the melt and concentrated solutions.[23-33] This model is based on the premise that the lateral motion of a polymer chain is suppressed by the obstacles imposed by neighboring chains and that each chain diffuses primarily along its own backbone. Despite its general success, some questions persist concerning the validity of the reptation model. The shear viscosity is found experimentally to scale with chain length roughly as $N^{3.4}$, rather than the $N^{3.0}$ as predicted by reptation. This difference may be real, or it may result merely from the experimental systems not being in the true large N asymptotic region.[9] Some computer simulations have also raised doubts concerning the validity of the reptation hypothesis.[34-37] However, these simulations consider only lightly entangled systems, and there is disagreement as to the conclusions that should be drawn from them.[34-40] Since the justification for the reptation model lies mainly in its ability to reproduce phenomenology, it is of interest to explore whether other models[41-44] reproduce the phenomenology as well.

In this paper we consider the consequences of a model based on the alternate assumption that the chain lateral motion does play a significant role in the chain dynamics. A preliminary account of this model has been presented previously.[45,46] In this paper we refine and generalize the development of the model to allow for polydisperse systems of linear chains. In a companion paper,[47] we consider the linear viscoelastic response of these systems within the context of this model.

A pair of neighboring chains in the melt has on the order of $N^{1/2}$ contacts with each other. In the course of these many contacts, these two chains randomly wind around each other and entangle. As a result the chains cannot easily separate. Each chain entangles in this way with on the order of $N^{1/2}$ neighboring chains. Reptation provides one possible mechanism for the chains to untangle. Alternatively, the chains could move laterally, sliding along the contours of neighboring chains until reaching the chain ends. Both mechanisms could also take place together. In this work we explore the consequences of a model based on the lateral motion premise. The motion of each chain along the contours of its neighboring chains is treated as Brownian, with a friction coefficient ζ_c. On short time scales nearby chains impose obstacles to the sliding motion of one chain along the contour of a second chain. It is assumed that the chain can wriggle past these moving additional chains. If the correlation time for these many-chain interactions is short compared with the terminal relaxation for the polymer system, then the use of a friction coefficient to account for the average effects of these obstacles is reasonable for times long compared with this correlation time.

We show that, due to the Gaussian coil nature of the chain contours, the three-dimensional mean-squared bead displacement for a polymer chain, $g(t)$, is related to the mean-squared contour displacement of one chain along the backbone of a neighboring chain, $\langle L^2(t)\rangle$. The relationship is $g(t) \sim b\langle L^2(t)\rangle^{1/2}$, where b is the segment length along the contour. To illustrate the consequences of this relationship, consider the example in which the contact points between chains are replaced by simple random walkers on the contours. In this case, the motion of the walkers along the contour is simple diffusion, which gives $\langle L^2\rangle \sim t$. This results in $g(t) \sim t^{1/2}$. Thus, the increase in $g(t)$ is slower when the walkers are constrained to follow the Gaussian random coils than when they are freely diffusing walkers. This result for $g(t)$ is equivalent to having a time-dependent friction coefficient for the three-dimensional motion of the walker which behaves as $\zeta(t) \sim t^{1/2}$. This last expression shows that for this simple case $\zeta(t) \sim g(t)$.

Because of the coupling between segments along a chain, the Brownian motion of the contact points along the chain contours is not simple diffusion. However, we show that the relationship $\zeta(t) \sim g(t)$ still holds for the bead friction coefficient in monodisperse samples, and we also provide

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a generalization of this expression for polydisperse samples. Once the bead friction coefficient has been evaluated, the intrachain coupling can be included by means of a Rouse model. Since the constraining effects of the neighboring chains have been incorporated into $\zeta(t)$, a Rouse model is reasonable for the chain dynamics. A contact between chains influences the friction felt by each chain as long as the contact exists. Therefore, the effective friction coefficient must be averaged over the distribution of contact lifetimes before it is employed in the Rouse model.

Section II.A develops the basic relationships between the mean-squared bead displacement for the chains, the contour displacement of the contact point along the chains, and the effective time-dependent single-bead friction coefficient. The model employed for the contact survival probability is presented in section II.B, and it is used to average the effective friction coefficient. This average friction coefficient is employed in a Rouse model for chain dynamics. The results of numerical calculations are presented in section III for monodisperse systems and for the case of a single probe chain in a system of host chains of different length. These results are summarized and discussed in section IV.

II. Theory

A. Relationship between g, $\bar{L}$, and ζ. In this section we first derive a relationship between g and $\bar{L}$ and then use this to obtain expressions for the time derivative of $\bar{L}^2$ and an effective bead friction coefficient, which account for the constrained nature of the chain motion in this model. The Brownian motion along the chain contours must be related to the three-dimensional motion of the chain segments. Consider a point A_0 on the contour of a particular chain, chain A. Suppose at time zero this point is a point of contact with another chain, chain B. At some time t later this point on the contour of chain A has moved from $\mathbf{R}_{A_0}(0)$ to $\mathbf{R}_{A_0}(t)$. During this time the point of contact with chain B has moved along the contour of A from A_0 to A_1. The displacement of the contact point from $\mathbf{R}_{A_0}(0)$ to $\mathbf{R}_{A_1}(t)$ can be expressed as

$$\Delta\mathbf{R}_{cp}(t) = [\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)] + [\mathbf{R}_{A_0}(t) - \mathbf{R}_{A_0}(0)] \quad (1)$$

The first term is the distance between the points A_0 and A_1 along the contour of A at time t, while the second term is the displacement of the point A_0 on chain A during the time interval. We can divide the motion of $\mathbf{R}_{A_0}$ into a reptation motion along the contour and a lateral motion. For pure reptation motion, the vectors $\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)$ and $\mathbf{R}_{A_0}(t) - \mathbf{R}_{A_0}(0)$ are completely correlated, since the motion of A is completely along its own backbone. For pure lateral motion these two vectors are totally uncorrelated. Since we are assuming that lateral motion dominates, we ignore the correlation between these two vectors. This yields the mean-squared displacement of the contact point as

$$\langle \Delta\mathbf{R}_{cp}^2\rangle = \langle[\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)]^2\rangle + g_A(t) \quad (2)$$

where $g_A(t)$ is the mean-squared displacement of a bead in chain A in time t. In general, $g_A(t)$ depends on location along the contour. In particular, $g_A(t)$ is larger for points near the chain ends. However, it does not change too much over the central portion of the chain. In order to simplify the model, we ignore the variations in $g_A(t)$ with location on the chain. These variations can be accounted for, but a much more complex model results.[48]

The quantity $\langle[\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)]^2\rangle$ is the mean-squared distance between two points along the contour of A. This quantity is averaged over configurations and all motions of A and B. We can perform the average in two steps. The first step is an average over all configurations and motions of chains A and B which result in a contour displacement of L_A between A_0 and A_1. In the melt the chain contours can be treated as Gaussian random coils.[49,50] Therefore, the value of $[\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)]^2$ after performing this restricted average is bL_A, where b is the effective segment length. This quantity must then be averaged over the distribution of contour lengths L_A. If this average is performed for any of a number of simple distributions, we obtain[51]

$$\langle[\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)]^2\rangle = b_1\bar{L}_A \quad (3)$$

where $\bar{L}_A = \langle L_A^2\rangle^{1/2}$ and b_1 depends on the particular distribution of L_A. Since the shape of this distribution can in general vary with time, b_1 can have some small time dependence. However, this time dependence is negligible compared with the time dependence of $\bar{L}_A$, and we simply take $\langle[\mathbf{R}_{A_1}(t) - \mathbf{R}_{A_0}(t)]^2\rangle$ to be given by (3) with $b_1 = (2/\pi)^{1/2}b$, which corresponds to a Gaussian distribution for L_A.

Substituting (3) into (2) yields

$$\langle\Delta\mathbf{R}_{cp}(t)^2\rangle = b_1\bar{L}_A(t) + g_A(t) \quad (4)$$

The same relationship could also been derived in terms of chain B. Therfore

$$g_A(t) + b_1\bar{L}_A(t) = g_B(t) + b_1\bar{L}_B(t) \quad (5)$$

We are not necessarily taking the motion of the two chains to be the same. For instance, one could be stiffer and less mobile than the other.

Over a relatively short time interval τ, we can decompose the changes in quantities into changes due to the motion of chain A and changes due to the motion of chain B. The lateral motion of chain A produces a change in $\langle L_B^2\rangle$ and also a change in $\langle L_A^2\rangle$. We refer to these as $\delta\langle L_B^2\rangle_A$ and $\delta\langle L_A^2\rangle_A$, respectively. The quantities $\delta\langle L_B^2\rangle_A$ and $\delta\langle L_A^2\rangle_A$ should be proportional. The value of the proportionality constant does not qualitatively effect the results of the model. Throughout we choose $\delta\langle L_A^2\rangle_A = (1/3)\delta\langle L_B^2\rangle_A$ in order to be definite.[52]

The changes in (5) during the time interval τ are given by

$$\delta g_A + \frac{b_1}{2\bar{L}_A}(\delta\langle L_A^2\rangle_A + \delta\langle L_A^2\rangle_B) = \delta g_B + \frac{b_1}{2\bar{L}_B}(\delta\langle L_B^2\rangle_A + \delta\langle L_B^2\rangle_B) \quad (6)$$

If we separately equate all changes due to the motion of A, we obtain

$$\delta g_A = (1/2)b_1\delta\langle L_B^2\rangle_A\left[\frac{1}{\bar{L}_B} - \frac{1}{3\bar{L}_A}\right] \quad (7)$$

where $\delta\langle L_A^2\rangle_A = (1/3)\delta\langle L_B^2\rangle_A$ has been employed. Likewise

$$\delta g_B = (1/2)b_1\delta\langle L_A^2\rangle_B\left[\frac{1}{\bar{L}_A} - \frac{1}{3\bar{L}_B}\right] \quad (8)$$

using $\delta\langle L_B^2\rangle_B = (1/3)\delta\langle L_A^2\rangle_B$. If we divide by τ to formally obtain time derivatives, we can obtain after a little manipulation

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle {L_A}^2\rangle = \frac{\mathrm{d}}{\mathrm{d}t}\langle {L_A}^2\rangle_A + \frac{\mathrm{d}}{\mathrm{d}t}\langle {L_A}^2\rangle_B = \frac{2\dot{g}_A\bar{L}_A\bar{L}_B}{(3\bar{L}_A - \bar{L}_B)b_1} + \frac{6\dot{g}_B\bar{L}_A\bar{L}_B}{(3\bar{L}_B - \bar{L}_A)b_1} \tag{9}$$

where the dot over g_A and g_B denotes time derivatives. This expression relates the time dependence of the contour displacement for the contact point between chains A and B to the rate of change of g_A and g_B. A similar expression for the time derivative of $\langle L_A^2\rangle$ is obtained by interchanging the A and B subscripts.

In order to obtain a simple model, we want to evaluate a friction coefficient for the three-dimensional motion of a point on a given chain. This friction coefficient should incorporate the effect of constraining the chain motion to be along the random-coil contours of neighboring chains. This bead friction should not include the effect of the coupling to adjacent beads in the same chain, since this is included directly in the Rouse model. If this coupling is neglected, the motion of one chain along the other is purely diffusive. Therefore

$$\delta\langle {L_B}^2\rangle_{A_0} = 2(K_BT/\zeta_{C,A})\tau \tag{10a}$$

$$\delta\langle {L_A}^2\rangle_{B_0} = 2(K_BT/\zeta_{C,B})\tau \tag{10b}$$

where $\zeta_{C,A}$ is the friction coefficient for the sliding of chain A along the contour of chain B, and $\zeta_{C,B}$ is defined analogously. The subscript zero on $\delta\langle L_B^2\rangle_{A_0}$ and $\delta\langle L_A^2\rangle_{B_0}$ indicates the neglect of intrachain couplings. The effective friction coefficient for the *three-dimensional* motion of the chain segments can be defined in terms of the bead mean-squared displacement from

$$\delta g_{A_0} = 6[K_BT/\zeta_A(t)]\tau \tag{11a}$$

$$\delta g_{B_0} = 6[K_BT/\zeta_B(t)]\tau \tag{11b}$$

The bead friction coefficients $\zeta_A(t)$ and $\zeta_B(t)$ are written as time-dependent quantities, anticipating the result below.

Equations 7 and 8 must hold for the dynamics whether the intrachain couplings are included or not. After substituting (10) and (11) into (7) and (8) and rearranging, we find

$$\zeta_A(t) = 18\zeta_{C,A}\bar{L}_A\bar{L}_B/[b_1(3\bar{L}_A - \bar{L}_B)] \tag{12a}$$

$$\zeta_B(t) = 18\zeta_{C,B}\bar{L}_A\bar{L}_B/[b_1(3\bar{L}_B - \bar{L}_A)] \tag{12b}$$

Since the intrachain couplings are neglected when defining the friction coefficients, the motion along the contours is purely diffusive, and $\zeta_{C,A}$ and $\zeta_{C,B}$ are time independent. The time dependence of $\zeta_A(t)$ and $\zeta_B(t)$ arises from the time-dependent nature of $\bar{L}_A$ and $\bar{L}_B$.

B. Contact Survival Probability, Average Friction Coefficient and Rouse Model. In this model, a contact point between two chains is treated as moving along the chain contours which have an effective length of $L_{\mathrm{eff}} = cbN$. bN is the actual contour length of the chain. The parameter c is included to compensate for the fact that, in real systems, the chain ends tend to be more mobile than the rest of the chain. Thus, they provide less of a constraint on the chain motion. Furthermore, some contacts can break before reaching the end of the chain. This is pictured in Figure 1. By choosing $c < 1$, we allow for somewhat faster contact breaking than is the case for $c = 1$.

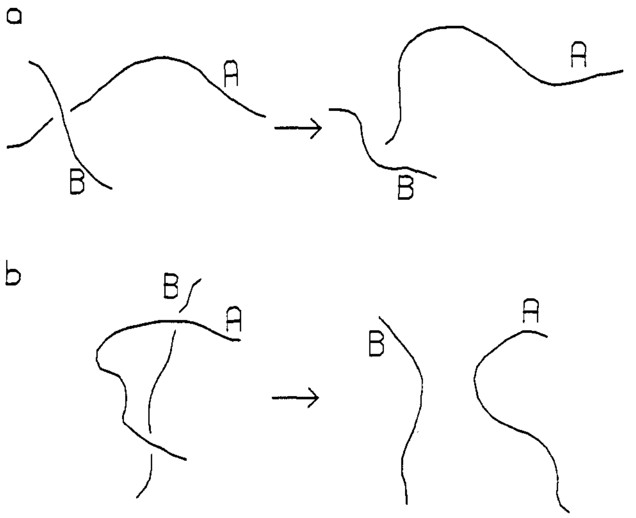

Figure 1. Breaking of a contact between chains A and B. In a, the contact is broken as it slides past the end of chain A. In b, the contact is broken at a point along each chain which is not a chain end.

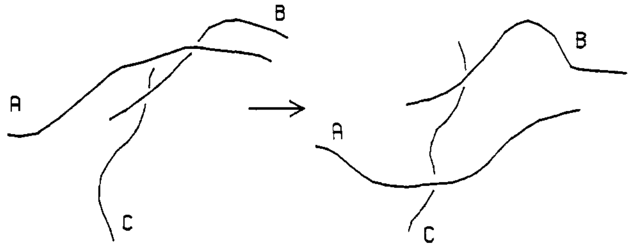

Figure 2. Chain A slides past the end of chain B. As this occurs the constraint on the motion of chain A is continued due to the contact with chain C.

Consider the function $P_A(t)$, which is the probability that a contact between chain A and B has not slid past the end of the contour of chain A. The contact point is taken to be distributed along this contour with uniform probability at time zero. We model $P_A(t)$ as

$$P_A(t) = \sum_{j=1,3,\ldots} \frac{8}{j^2\pi^2}\exp\left[\frac{-j^2\pi^2\langle {L_A}^2\rangle}{2{L_{e,A}}^2}\right] \tag{13}$$

If the contact point were a simple random walker on the chain contours, then $\langle L_A^2\rangle = 2Dt$, and (13) is the well-known expression for a one-dimensional walker with absorbing boundary conditions. In our model the contact point is not a simple random walker, and this expression is only approximate. However, it should be qualitatively correct and is sufficient to demonstrate the important behavior of this lateral motion model.

As chain A moves past the end of chain B, there are other chains which constrain its motion in the same direction as chain B did. This is sketched in Figure 2. As chain A moves off of chain B, it establishes contact with chain C, and the effective constraint on A is continued rather than broken. In this view the influence of this event on the constrained dynamics of chain A is rather slight. Chain A may be able to take a small additional three-dimensional displacement as it switches from chain B to chain C. This should add a contribution to $g_A(t)$ in much the same manner as constraint release[5,7] adds an additional contribution to $g(t)$ in the reptation model. On the other hand, as the contact slides past the end of chain B, it no longer effects the dynamics of chain B. Therefore, contacts are considered broken for the purpose of evaluating the $\zeta_A(t)$ only when the contact point reaches the end of chain A, and the contact survival probability for chain A is $P_A(t)$.

A model for the contact survival probability is required because the relationship between the effective bead friction coefficients and the contour displacements, (12), persists only as long as the contact survives. The average number of interchain contacts involving chain A in an equilibrium system is independent of time. For each contact that breaks, on the average another is formed. The effective single-bead friction coefficient for chain A at time t, averaged over contact lifetimes, is given by

$$\overline{\zeta_A(t)} = P_A(t)\, \zeta_A(t) + \int_0^t dt_1\, f_A(t_1)\, \zeta_A(t_1) \tag{14}$$

The quantity $f_A(t_1)$ is the probability density that a contact that exists at time t was formed at time $t - t_1$. The first term on the right-hand side of (14) is the contribution from contacts which exist at t and were formed before time zero. The second term is the contribution for contacts which were formed after time zero. For an equilibrium system, the probability distribution that a contact exists at a given time t and was formed at $t - t_1$ must be the same as the probability distribution that a contact existing at a specific time will break at a time t_1 later. This quantity is just the negative of the time derivative of $P_A(t)$

$$f_A(t_1) = -\frac{\partial}{\partial t_1} P_A(t_1) \tag{15}$$

P_A, f_A, and $\bar{L}_A$ are quantities defined for a contact point between two chains. They depend on the motion of both chains through (9). The averaging in (14) is over the distribution of lifetimes for a specific pair of chains involved in a contact. The average $\zeta_A(t)$ employed in the Rouse model for $g_A(t)$ must be averaged over all possible types and lengths of B chains, as well as over the distribution of contact times for each specific A–B pair.

$$\langle \zeta_A \rangle = \langle [P_A(t)\, \zeta_A(t) + \int_0^t dt_1\, f_A(t_1)\, \zeta_A(t_1)] \rangle_B \tag{16}$$

where $\langle\ \rangle_B$ denotes the averaging over all lengths and types of B chains.

Since the effects of the interactions between neighboring chains have been incorporated into the effective single-bead friction coefficient, a Rouse model can be used to account for the intrachain couplings. The single-bead friction coefficient employed in the Rouse model is the time-dependent bead friction coefficient, (16). In this work the effective friction coefficient $\zeta_A(t)$ is independent of location on the chain. This is consistent with the use of an averaged mean-squared bead displacement, $g_A(t)$. As a result, the normal modes of the chain are simply the standard Rouse modes. The location of the jth monomer in an N bead chain can be expressed as[1]

$$\mathbf{R}_j = \mathbf{a}_0 + 2\sum_{p=1}^{\infty} \mathbf{a}_p \cos\frac{jp\pi}{N} \tag{17}$$

where $\mathbf{a}_0$ is the location of the center of mass and $\mathbf{a}_p$ is the amplitude of the pth Rouse model. The amplitude $\mathbf{a}_p$ obeys the equation

$$\zeta_p \dot{\mathbf{a}}_p = -K_p \mathbf{a}_p + \mathbf{f}_p \tag{18}$$

where $\mathbf{f}_p$ is the fluctuating random force, $\zeta_p = 2N\langle \zeta_A(t) \rangle$ and $K_p = 6\pi^2 K_B T p^2/Nb^2 = p^2 K_1$ in the large N limit. The fluctuating force satisfies the fluctuation–dissipation theorem $\langle f_p(t)\, f_q(t_2) \rangle = 2K_B T \zeta_p \delta_{pq} \delta(t_1 - t_2)$. Equation 18 can be easily integrated. The result, together with $\langle \mathbf{a}_p{}^2(t) \rangle = 3K_B T/K_P$, which follows from the fluctuation–dissipation theorem, yields the mean-squared bead displacement

$$g_A(t) = g_{cm,A}(t) + \frac{12K_B T}{K_{1,A}} \sum_p \frac{1}{p^2} (1 - \exp[-\int_0^t dt_1/\tau_{p,A}]) \tag{19}$$

with $\tau_{p,A} = \zeta_{p,A}/K_{p,A} = \tau_{1,A}/p^2$. The center-of-mass mean-squared displacement is given by

$$g_{cm,A}(t) = \frac{6K_B T}{N} \int_0^t dt_1/\zeta_{cm,A}(t) \tag{20}$$

where $\zeta_{cm,A}(t) = N_A\langle \zeta_A(t) \rangle$. The relaxation time for the pth mode, $\tau_{p,A}$, depends on time through $\zeta_{p,A}(t) = 2N\langle \zeta_A(t) \rangle$. At long times $\langle \zeta_A(t) \rangle$ and $\zeta_{cm,A}(t)$ approach asymptotic values, $\langle \zeta_A(\infty) \rangle$ and $\zeta_{cm,A}(\infty)$, respectively, and $g_{cm,A}(t)$ assumes the simple diffusion form. The center-of-mass diffusion constant is given by $D_{cm,A} = K_B T/\zeta_{cm,A}(\infty)$.

III. Results

In this section we present the results of numerical calculations for monodisperse melts and for a probe polymer of length N_p in an otherwise monodisperse multichain system with chain length N_m. A calculational procedure correct through second order in the time step δt is employed. For the monodisperse case, $\bar{L}_A = \bar{L}_B$, $g_A = g_A$, etc. At each time step an initial estimate of $\overline{L_A(t+\delta t)}$ is obtained from the two most recent values of $\bar{L}_A$ (except, of course, on the first time step). This can then be used in (13) to obtain P_A at $t + \delta t$. Equations 12 and 16 can then be employed to obtain $\langle \zeta_A \rangle$, which in turn can be substituted into (19) and (20) to yield g_A and $g_{cm,A}$. These then provide a better estimate of $\langle L_A{}^2 \rangle$ through (9). This is iterated to self-consistency for each time step. For the case of a probe chain with a different length than that of the host chains, the monodisperse calculation provides all quantities for the host chains. A second calculation must be performed for the probe chain quantities. In this calculation the A chain in each contact is the probe chain, and the B chain is a host chain. Therefore, $g_B(t)$, $g_{cm,B}(t)$, and $\overline{L_B(t)}$ are already known, and the iterative procedure described for the monodisperse case can be employed to evaluate P_A, $\langle \zeta_A \rangle$, g_A, $g_{cm,A}$, and $\langle L_A{}^2 \rangle$. The time step δt is chosen to be a fixed fraction (0.004 in all calculations reported) of the total time t before that step. At very early times the bead friction is treated as a constant, and its value is set to $\zeta_{C,A}$ of (10). This is done because the expression for the time-dependent friction coefficient is only appropriate for $g(t) > b^2$. The crossover time between the constant behavior and the time-dependent behavior is chosen so that $\zeta_A(t)$ is continuous. The length scale is chosen so that $b_1 = 1$, and the time scale is defined such that $K_B T/\zeta_{C,A} = 1$.

The values of the center-of-mass diffusion constant are presented in Figure 3 for monodisperse systems with N ranging from 50 to 204 800. A value of $L_e = Nb_1/2 = Nb/(2\pi)^{1/2}$ is used for the effective chain contour length in all calculations. Also shown in Figure 3 is the time at which the mean-squared displacement of the center of mass equals twice the squared radius of gyration. We equate this time, which we call t_f, with the terminal time. The results are well described by the forms $D_{cm} \sim N^{-2}$ and $t_f \sim N^3$. Figure 4 presents $g_{cm}(t)$ and $g(t)$ from the calculation for monodisperse chains with $N = 800$. The function $g(t)$ is approximated very well by $t^{1/3}$ and $g_{cm}(t)$

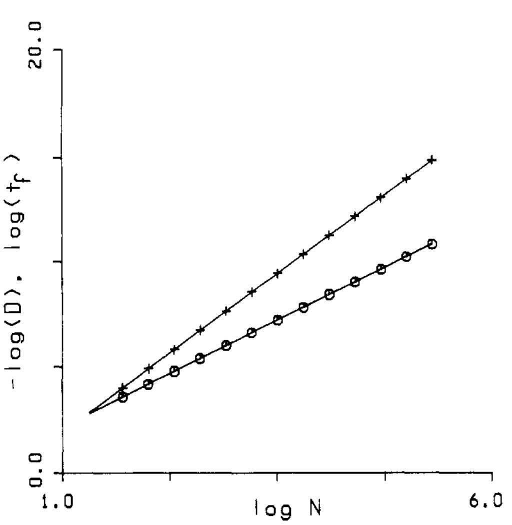

Figure 3. Dependence of D_{cm} and t_f on N for monodisperse samples for $N = 50$ to $N = 204\,800$. The circles are the D_{cm} data, and the pluses are the data for t_f. The straight lines have slope 2 for the $-\log D_{cm}$ data and slope 3 for the $\log t_f$ data and pass through the data points for $N = 204\,800$.

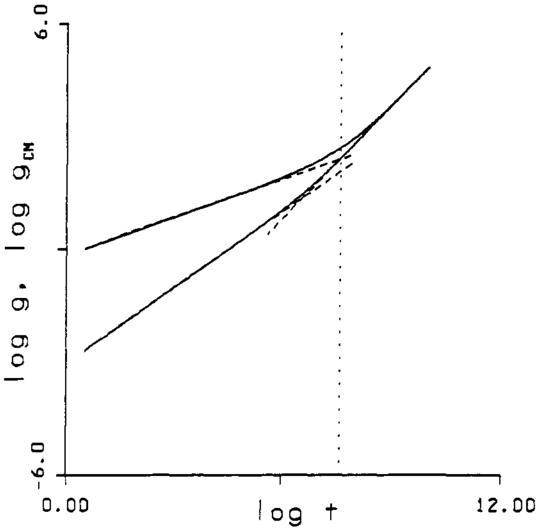

Figure 4. log-log plot of g_{cm} (lower curve) and g (upper curve) versus t for $N = 800$. The dashed straight lines have slopes $^1/_3$ (early times, upper curve), $^2/_3$ (early times, lower curve), and 1 (later times). The dotted vertical line is located at $t = t_f$.

by $t^{2/3}$ at early times, and then they switch over to the simple diffusion $6D_{cm}t$ form at longer times. Figure 5 plots the results for the center-of-mass diffusion coefficient of a probe chain of length N_p in an otherwise monodisperse system of chains of length N_m. D_{cm} is essentially independent of N_m for $N_m > N_p$, and it is only weakly dependent on N_m for $N_m < N_p$.

IV. Discussion

We have presented a model for the dynamics of dense systems of linear polymers which is based upon the assumption that the primary mechanism for chain motion is a sliding of each chain along the contours of neighboring chains. A time-dependent effective single-bead friction coefficient is derived which accounts for the constraining nature of the neighboring chains on the motion of a given chain. For monodisperse systems, at times short compared with the average contact lifetime, $g(t)$ and $g_{cm}(t)$ have the forms $g \sim t^{1/3}$ and $g_{cm} \sim t^{2/3}$. For times long compared with the averaged contact survival time, $g(t)$ and $g_{cm}(t)$ cross over to the simple diffuson form $6D_{cm}t$, with D_{cm} having an N^{-2} dependence on the chain length. The model also produces $t_f = N^3$ dependence for the time at which g_{cm} is equal to twice the radius of gyration for the chain. If we were to employ a contact survival probability which is unity until $g_{cm} = 2R_g^2$ and then abruptly drops to zero, then $\zeta(t)$ is proportional to $g(t)$ for $t < t_f$, and it is constant for $t > t_f$. In this case[45] the model provides results which are not qualitatively different from the numerical results in Figure 4. This demonstrates that the basic results of the model are not very sensitive to the form employed for $P_A(t)$. Rather they are a direct consequence of the time-dependent form of the friction coefficient, (12). On the other hand, the time dependence of the relaxation modulus, which is discussed in the following paper,[47] does depend on the details of $P_A(t)$.

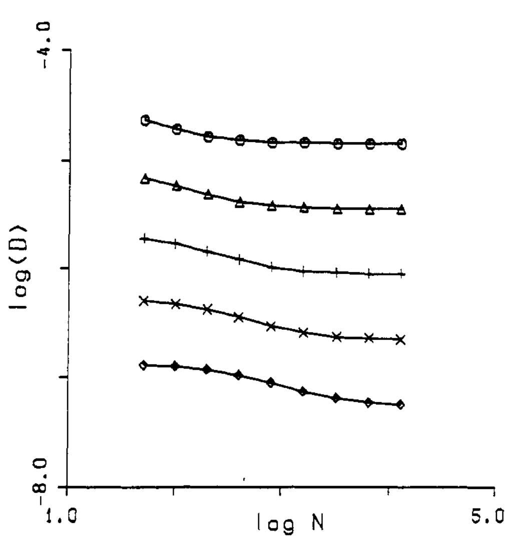

Figure 5. log D_{cm} for a probe polymer of length N_p plotted versus log N for the host polymer chains. The data are for $N_p = 200$ (○), $N_p = 400$ (△), $N_p = 800$ (+), $N_p = 1600$ (×), and $N_p = 3200$ (◇).

Our calculations show that to a very good approximation $D_{cm} \sim N^{-2}$ and $t_f \sim N^3$ for this model. This is the same level of qualitative agreement with experimental results as obtained by the reptation model.[1] As with the reptation model, the question arises of the discrepancy with the experimentally observed dependence of the terminal relaxation time $\tau_f \sim N^{3.4}$. There have been numerous explanations[9,53,54] purposed for this apparent discrepancy with regard to reptation. Many of these explanations apply to the model described in this paper as well as to reptation. Since both the current model for lateral motion and reptation result in the same scaling behavior, this raises the possibility that both mechanisms can contribute in polymer systems in varying degrees.

There have been a number of recent interesting computer simulations of multichain systems.[34-40] Skolnick and co-workers have performed lattice-based Monte Carlo simulations for systems with chain lengths ranging up to 800 segments.[34-37] They find $g \sim t^{\alpha}$ and $g_{cm} \sim t^{\beta}$ for their simulations at early times, and then these quantities cross over to the simple diffusion $6D_{cm}t$ form at long times. The exponents α and β depend on the chain length. They have values near the Rouse values, $\alpha = {}^1/_2$ and $\beta = 1$, for short chains, and they seem to approach the values predicted by the model presented here, $\alpha = {}^1/_3$ and $\beta = {}^2/_3$, for longer chains. The values $\alpha = 0.36$ and $\beta = 0.71$ are obtained for $N = 800$. Skolnick and co-workers have also evaluated mean-squared single-bead displacements parallel and perpendicular to the "primitive path".[35-37] They find that the dynamics is *not* dominated by motion parallel to this primitive path. This result is in qualitative agreement with the model presented here.

Grest et al.[38,39] have recently reported very extensive molecular dynamics calculations for dense multichain systems with chain lengths as high as $N = 200$. The data for $g(t)$ display a short Rouse-like $t^{1/2}$ region at early times, which crosses over to a t^{α} region. The $g(t)$ they report is averaged over the central five beads in the chain, so as not to include the more mobile end beads. For $N = 150$, they fit this region with a $t^{0.28}$ curve. They attribute the difference between their observations and those of Skolnick and co-workers to the higher density in their system. On the other hand, Skolnick and co-workers also observe a $t^{0.28}$ region in their $N = 800$ simulations, if they average only over the middle region of the chain. This suggests that the simulations of the two groups are comparable.[55] Grest et al. conclude that the motion parallel to the primitive path dominates, although they only report these quantities for relatively short times compared with the terminal relaxation time. Skolnick and co-workers consider these quantities for longer times. They observe the dominance of the parallel motions at early times as well but find that the motion becomes isotropic at later times.[35-37,55]

Our data for a single probe chain of length N_p in a system of host chains of length N_m are in qualitative agreement with the rather limited range of simulation data available.[36] The data on actual experimental systems[23,24,27] also display a very weak dependence of D_{cm} on N_m for sufficiently large values for N_m. For smaller N_m, there is a crossover to a rather strong dependence on N_m. This crossover occurs at a value of N_m which depends weakly on N_p. In our model calculations D_{cm} is only very weakly dependent on N_m over the entire range of N_m considered. Although we do not include it in the calculations presented in this work, there should be an independent contribution to $g(t)$ and D_{cm} for a chain due to the moving of the contact point past the end of the other chain in the contact. This contribution is quite analogous to the constraint-release contribution[5,7] in the reptation model. It is known that the experimental data are well fit by reptation with constraint release,[24,27] and the model present here should give comparable results.

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References and Notes

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1987.
(2) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1802.
(4) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1818.
(5) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(6) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(7) Klein, J. *Macromolecules* **1986**, *19*, 105.
(8) Rubinstein, M.; Helfand, E. *J. Chem. Phys.* **1985**, *82*, 2477.
(9) Doi, M. *J. Polym. Sci., Lett.* **1981**, *19*, 265.
(10) Doi, M. *J. Polym. Sci.* **1983**, *21*, 667.
(11) Evans, K. E.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1891.
(12) Evans, K. E.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1929.
(13) Helfand, E.; Pearson, D. S. *J. Chem. Phys.* **1983**, *79*, 2054.
(14) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(15) Marrucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 159.
(16) Watanabe, H.; Tirrell, H. *Macromolecules* **1989**, *22*, 927.
(17) Han, C. D.; Kim, J. K. *Macromolecules* **1989**, *22*, 1914.
(18) Rubinstein, M.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 822.
(19) Rubinstein, M.; Colby, R. H. *J. Chem. Phys.* **1988**, *89*, 5291.
(20) Merrill, W. W.; Tirrell, M.; Tassin, J.-F.; Monnerie, L. *Macromolecules* **1989**, *22*, 896.
(21) Doi, M.; Pearson, D. S.; Kornfield, J.; Fuller, G. G. *Macromolecules* **1989**, *22*, 1488.
(22) Doi, M.; Grassley, W. W.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 1900.
(23) Green, P. F.; Mills, P. J.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.
(24) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(25) Bartels, C. R.; Crist, B.; Graessley, W. W. *Macromolecules* **1984**, *17*, 2702.
(26) Bartels, C. R.; Crist, B.; Fetters, L. J.; Graessley, W. W. *Macromolecules* **1986**, *19*, 785.
(27) Antonietti, M.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(28) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(29) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
(30) Kim, H.; Chang, T.; Yohanan, Y. M.; Wang, L.; Yu, H. *Macromolecules* **1986**, *19*, 2737.
(31) Tead, S. F.; Kramer, E. J. *Macromolecules* **1988**, *21*, 1513.
(32) Tassin, J. F.; Monnerie, L.; Fetters, L. J. *Macromolecules* **1988**, *21*, 2404.
(33) Ylitalo, C. M.; Kornfield, J. A.; Fuller, G. G.; Pearson, D. S. *Macromolecules* **1991**, *24*, 749.
(34) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *84*, 1922.
(35) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 1567.
(36) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 7164.
(37) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 7174.
(38) Kremer, K.; Grest, G. S.; Carmesin, I. *Phys. Rev. Lett.* **1988**, *61*, 566.
(39) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, *92*, 5057.
(40) Pakula, T.; Greyler, S. *Macromolecules* **1987**, *20*, 2909.
(41) Bird, R. B.; Curtis, C. F. *J. Chem. Phys.* **1981**, *74*, 2016, 2026.
(42) Schweizer, K. S. *J. Chem. Phys.* **1989**, *91*, 5802, 5822.
(43) Hess, W. *Macromolecules* **1986**, *19*, 1395; **1987**, *20*, 2587; **1988**, *21*, 2620.
(44) Loring, R. F. *J. Chem. Phys.* **1991**, *94*, 1505. Szleifer, I.; Loring, R. F. *J. Chem. Phys.* **1991**, *95*, 2080. Szleifer, I.; Wilson, J. D.; Loring, R. F. *J. Chem. Phys.* **1991**, *95*, 8474.
(45) Herman, M. F. *J. Chem. Phys.* **1990**, *92*, 2043.
(46) Herman, M. F. *J. Non-Cryst. Solids* **1991**, *131-133*, 715.
(47) Herman, M. F. *Macromolecules*, following paper in this issue.
(48) Herman, M. F., unpublished results.
(49) Freed, K. F.; Edwards, S. F. *J. Chem. Phys.* **1974**, *61*, 3626.
(50) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(51) The delta function distribution gives $b_1 = b$, while the Gaussian distribution gives $b_1 = (2/\pi)^{1/2}b$. If a distribution which is uniform up to a maximum value of L_A is employed, then $b_1 = 3^{1/2}b/2$. For an exponential distribution, $b_1 = b/2^{1/2}$. All of these cases give b_1 between $0.7b$ and b.
(52) This choice of $^1/_3$ for the proportionality constant is the result that is obtained for motions on such a small scale that the contours can be treated as straight lines, and the motion of chain A is taken to be perpendicular to its own backbone. In this case the proportionality constant is just the average of $\sin^2\theta$ in spherical polar coordinates, where θ is the angle between the contours of the two chains.
(53) Fixman, M. *J. Chem. Phys.* **1988**, *89*, 3892, 3912.
(54) Weiss, G. W.; Bendler, J. T.; Shlesinger, M. F. *Macromolecules* **1989**, *21*, 521.
(55) Skolnick, J. Presented at the International Discussion Meeting on Relaxations in Complex Systems, Heraklion, Crete, Greece, June 1990.