barrier heights for radical cation interconversions and in the detailed characterization of the photochemical interconversions.

It is a pleasure to acknowledge the invaluable contributions of Marcia L. Schilling and Christopher J. Abelt to the major body of this research and to express my appreciation to R. C. Haddon, P. G. Gassman, T. Miyashi, T. Mukai, K. Raghavachari, and C. C. Wamser, who contributed to individual facets of this work. This article is dedicated to Professor William v. E. Doering, in whose laboratory I received much inspiration, on the occasion of his 70th birthday.

Monte Carlo Studies of the Long-Time Dynamics of Dense Polymer Systems. The Failure of the Reptation Model

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Received February 16, 1987 (Revised Manuscript Received June 5, 1987)

Introduction

Imagine a very large bowl of overcooked spaghetti that is subject to constant random jiggling. Suppose one picks a given spaghetti strand. How on average does this strand move across the bowl? The strand sees a matrix comprised of the other spaghetti strands which it cannot cross. Thus, one has in principle a very complicated many-body (many-strand) problem. This is a simple realization of the problem that has over the past 15 years occupied a central position in the study of concentrated polymer solutions (analogous to a bowl of spaghetti with tomato sauce) and melts (analogous to a bow of spaghetti drained of all other liquids).[1-4] Namely, what is the microscopic mechanism by which a highly entangled collection of polymers moves? The answer to this question has practical applications to, among other areas, polymer rheology, polymer adhesion, and polymer failure.

Any successful theory of polymer melt motion must be able to rationalize the following experimental results.[1-6] For a linear polymer composed of n bonds, the center-of-mass self-diffusion coefficient of the polymer, D, behaves like

$$D \sim n^{-1} \qquad \text{if } n < n_c \tag{1a}$$

$$D \sim n^{-2} \qquad \text{if } n > n_c \tag{1b}$$

with n_c a critical degree of polymerization, although recently other exponents α in $D \sim n^{-\alpha}$ have also been reported.[7] Furthermore, the zero-frequency shear viscosity η scales like

$$\eta \sim n \qquad \text{if } n < n_c' \tag{2a}$$

$$\eta \sim n^{3.4} \qquad \text{if } n > n_c' \tag{2b}$$

with $n_c > n_c'$.[5,6] The source of the difference between n_c and n_c' is not at all understood.[8] (For the convenience of the reader a compilation of various parameters employed in this article may be found in Table I.) The above experimental behavior indicates that as the molecular weights of the chains increase, entanglements between the chains become important. Thus, another important feature of a successful theory is to elucidate the nature of these intermolecular entanglements.

Table I.
Compilation of Parameters

parameter	definition
n	degree of polymerization, i.e., the number of beads (monomer units) per polymer chain
n_c	degree of polymerization above which D is proportional to n^{-2}
n_c'	degree of polymerization above which the shear viscosity is proportional to $n^{3.4}$
N	number of polymers in the Monte Carlo box
n_M	degree of polymerization of the larger volume fraction (matrix) component in a bidisperse melt
n_P	degree of polymerization of the smaller volume fraction (probe) component in a bidisperse melt
n_B	average number of monomers down a given chain in the melt where the excluded-volume effect is screened out
n_e	the average distance between dynamic entanglements
n_b	number of beads in the subchain or blob used in the averaging process to construct the equivalent path
τ_R	terminal or longest relaxation time of the end-to-end vector

One of the most striking consequences of the experimental observations embodied in eq 1 and 2 is that for

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sufficiently low molecular weights a polymer in the melt behaves like a Rouse chain, the simplest model of the long-time dynamic properties of a polymer at infinite dilution.[9] In a Rouse chain (a bead–spring model of a polymer in a continuum solvent that exerts frictional forces on the polymer beads), the motion on average is locally as well as globally isotropic, and hydrodynamic interactions between beads (the perturbation of the solvent flow about one bead due to the other beads) are ignored.[10] In a low molecular weight polymer melt, the surrounding matrix behaves identically to a small-molecule fluid with the important exception that hydrodynamic interactions are screened out.[2,6] Thus, whatever the nature of the entanglements between chains, they are unimportant in the low molecular weight limit.

The Rouse model exhibits the following features which we will require in subsequent discussion.[9,10] The mean-square displacement of the center of mass

$$g_{\mathrm{cm}}(t) = 6Dt \tag{3}$$

for all times t with $D \sim n^{-1}$. In the long-chain limit, the mean-square displacement of a single bead[2,9]

$$g(t) \sim t^{1/2} \qquad t < \tau_{\mathrm{Rouse}} \tag{4a}$$

$$g(t) \sim t \qquad t > \tau_{\mathrm{Rouse}} \tag{4b}$$

with τ_{Rouse} the terminal or longest relaxation time for the decay of the end-to-end vector which is proportional to n^2 and is the time constant for the decay of the longest wavelength internal relaxation mode of the system.

As n is further increased, as implied by eq 1 and 2, a polymer melt changes from a viscous to a viscoelastic liquid.[6] Consider the response of a polymer melt to a sudden deformation. At very short times, before the entanglements have had a chance to disengage, the behavior of the melt is similar to a cross-linked collection of chains,[11] i.e., a rubber, which behaves as one huge macromolecule.[12] What differentiates the two is the behavior of the network at longer times. In a rubber, the network linked by chemical bonds is infinitely long lived. In a melt, the chains eventually slide past each other, and the system then behaves like a normal viscous liquid. The essential question, then, is, what is the time scale for the matrix relaxation relative to the motion of a given individual chain?

In the highly ingenious reptation model of de Gennes,[1,2] which was later refined by Doi and Edwards,[11] it is assumed that the surrounding matrix of linear chains that produces the entanglements remains static on the order of the relaxation time of the end-to-end vector. Thus, the many-body problem has been reduced to a single-chain problem. A schematic picture of the motion is depicted in Figure 1. The chain of interest finds itself confined to a tube composed of the entanglements, and the only way it can move long distances is by slithering out the ends of its tube, hence the name reptation. Thus, the dominant long-distance motion is longitudinal and down the chain contour defined at zero time. Lateral fluctuations are unimportant. Because of the tortuous path a given chain must take to move with respect to the laboratory-fixed frame, the terminal relaxation time (longest) of the end-to-end vector, τ_{rep}, is proportional to n^3.[1,2] τ_{rep} is frequently called the tube renewal time. When coupled with the assumption of rubberlike behavior at short times,[11] one obtains $\eta \sim \tau_{\mathrm{rep}} \sim n^3$. Similarly, the self-diffusion coefficient $D_{\mathrm{rep}} \sim n^{-2}$. Thus, this simple model almost reproduces the experimental behavior of D and η.

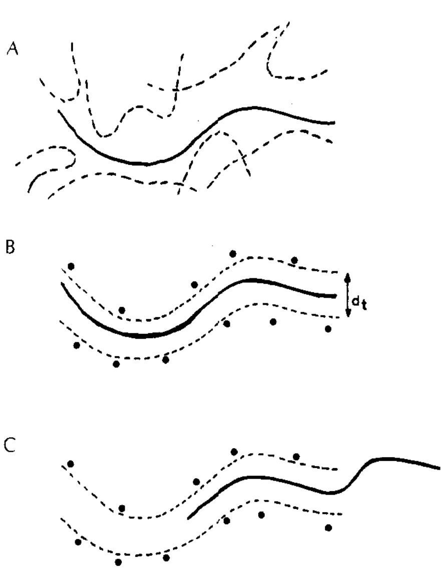

Figure 1. (A) In reptation theory, the matrix of chains (dashed curves) surrounding the test chain (solid curve) is replaced by rigid posts as in (B) which act to confine the chain of interest into a tube of diameter d_T. The chain moves by slithering out the tube as in (C).

In the reptation model,[1-4,13] $g(t)$ is predicted to behave differently than a free Rouse chain. For distances less than d_T, the chain of interest does not experience the confining effects of the tube, so it still behaves like a free Rouse chain (see eq 4a). Then, there is relaxation of the chain within the tube giving

$$g(t) \sim t^{1/4} \qquad t < \tau_{\mathrm{Rouse}} \tag{5a}$$

Once the internal degress of freedom have relaxed to their equilibrium values, one is left with center-of-mass motion down the tube

$$g(t) \sim t^{1/2} \qquad t < \tau_{\mathrm{rep}} \tag{5b}$$

Finally, the free chain diffusion limit is reached where

$$g(t) = 6D_{\mathrm{rep}}t \tag{5c}$$

Similarly[14]

$$g_{\mathrm{cm}}(t) \sim t^{1/2} \qquad t < \tau_{\mathrm{rep}} \tag{6a}$$

$$g_{\mathrm{cm}}(t) \sim 6D_{\mathrm{rep}}t \qquad t > \tau_{\mathrm{rep}} \tag{6b}$$

Observe that "pure" reptation theory treats the matrix as fixed while the test chain moves. To remove this nonequivalent treatment, reptation theory has been made self-consistent.[15,16] Thus, the posts depicted as solid circles in Figure 1B also reptate. In addition, tube leakage, which is the formation of relatively small loops between the posts, has also been included.[3,17] Thus,

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in all its variants, the crucial assumptions of reptation theory are that the tube is very well defined and that the dominant long-distance motion is the slithering out the ends of the tube defined by the chain contour at zero time. Hence, lateral motions of the chains are negligible. The question is, are these assumptions really valid for a melt?

While reptation theory has been able to rationalize a wide variety of,[2-4] although by no means all,[7] experimental data, measurement of quantities such as the diffusion coefficient does not directly probe the mechanism of polymer melt motion.[18] The existence of a spatially fixed tube has been questioned for melts[19] as well as for concentrated solutions of rodlike polymers.[20] Computer simulations are ideally suited for this purpose.[20,21] and thus, to establish the mechanism of polymer melt motion and the nature of dynamic entanglements, we have embarked on a series of dynamic Monte Carlo (MC) simulations.[22-25] We view these as computer experiments designed to test the validity of reptation theory and, if the central assumptions of reptation are found not to hold (as turns out to be the case), to guide the development of alternative theories.

Description of the Model

In the context of diamond and cubic lattice models of a polymer melt, we have examined the nature of polymer motion. The lattice is enclosed in a periodic MC box of volume L^3 subject to periodic boundary conditions. We always choose $L > \langle R^2 \rangle^{1/2}$, with $\langle R^2 \rangle$ the equilibrium mean-square end-to-end distance, to ensure that the interactions of a chain with its image are unimportant. Each polymer chain occupies n lattice sites and there are N polymers per MC box, with ϕ the volume fraction of occupied sites. In all cases, to model excluded-volume effects, multiple occupancy of lattice sites is prohibited. The dynamic properties of homopolymeric diamond lattice polymers were studied over a range of ϕ from 0 to 0.75 for chain lengths up to n = 216; cubic lattice polymers were studied at fixed ϕ = 0.5, but for n ranging from 64 to 800 for the homopolymeric melt and for a probe chain of length n_p = 100 in a matrices of chains ranging from n_m = 50 to 800.

One begins by constructing an equilibrated dense melt that has a specific molecular weight distribution (either mono- or bidisperse for the systems described below).[22] Next, one chooses a set of lattice moves that locally introduce new random conformations into the middle of the chain.[26-29] Otherwise, if new orientations can only arise in the chain interior by diffusion from the chain ends, an artificial n^3 time scale having nothing to do with realistic polymer motion can be built into the model.[26,27] For diamond and cubic lattices, the set of elementary jumps[22,23,29,30-32] we employed satisfies the above requirements and is reasonable in that a large fraction of the jumps are successful.[22] For each attempt at a particular move, the chain and bead are randomly selected. The fundamental unit of time is taken to be that required for each of the allowed lattice moves on average to be attempted per bead. In actual implementation, the choice of elementary moves are randomly mixed, and any given move is rejected if the local conformation is such that the move is not allowed or if excluded-volume restrictions prohibit it. In fact, while one specifies the a priori ratio of moves, at high density, the system itself, due to excluded-volume restrictions, chooses the fraction of successful moves.

The use of a lattice confers both advantages and disadvantages. The advantages are that one can simulate much longer polymers, at much higher densities, for much longer times than the corresponding off-lattice systems. The disadvantage is that we must demonstrate that the results are physically meaningful and not a lattice artifact; the hope is that the character of the long-distance motion is insensitive to local details. While we have not been able to prove this, whenever possible we have compared our results to the corresponding off-lattice simulations and have found qualitative agreement.[33,34] Moreover, both the diamond[23] and cubic lattice[24] models under similar conditions yield identical results when corrected for differences in local persistence length (a chain of length n on a diamond lattice has dynamic behavior like a chain of length $n/2$ on a cubic lattice), even though the local elementary moves are very different.

Equilibrium Properties

While the detailed study of the equilibrium properties is beyond the scope of this article, nevertheless one must be sure that they are correct before proceeding to an analysis of the dynamics. In the ϕ = 0 limit in agreement with others,[35,36] both the diamond and cubic lattices give $\langle R^2 \rangle \sim n^{1.18}$, consistent with the self-avoiding, random walk model appropriate to the description of polymer dimensions in a good solvent. As the density increases, these chains obey ideal statistics,[2] viz. $\langle R^2 \rangle \sim \langle S^2 \rangle \sim n$ (with $\langle S^2 \rangle$ the mean-square radius of gyration). The crossover of $\langle S^2 \rangle$ and $\langle R^2 \rangle$ from $n^{1.18}$ to n^1 scaling allows us to estimate n_B, which is the number of monomers down a given chain in a melt after which the excluded-volume effect is screened out. For both diamond[23] and cubic lattice systems[24] at ϕ = 0.5, $n_B \cong 17$, and for the diamond lattice when ϕ = 0.75, $n_B \cong 12$. This quantity is of interest in that n_B has been employed as an estimate of the mean distance between dynamic entanglements n_e.[11,14,32] For the n = 800, ϕ = 0.5 case in particular, if n_B is in fact the correct measure of dynamic entanglements, then n/n_B = 47, and by every criterion of reptation theory[3,14-16] these chains should reptate. However, even if $n_e > n_B$,[32] it is evident from the above that the systems studied here are very dense and should be appropriate to qualitatively examine the validity of reptation theory.

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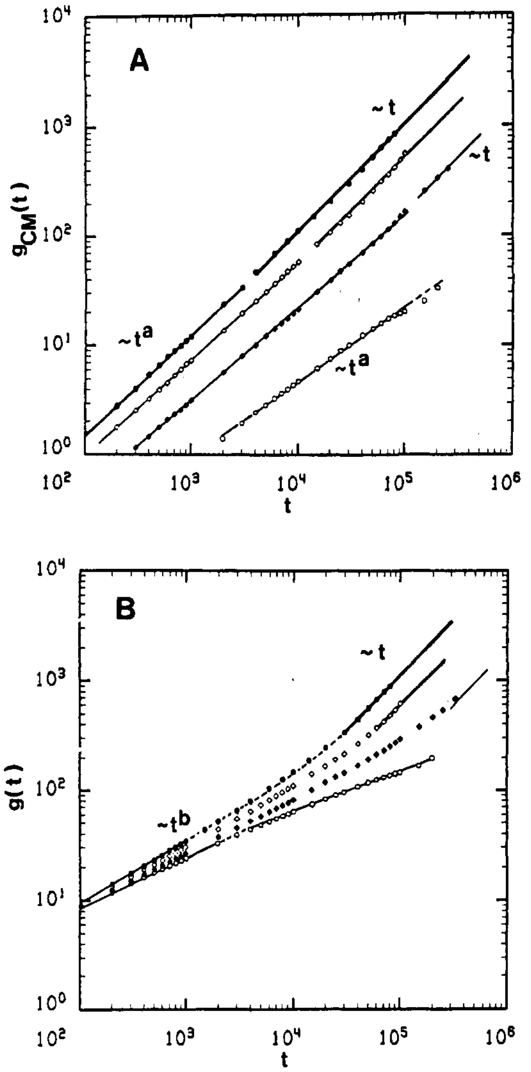

Figure 2. (A) and (B) log–log plots of the center-of-mass autocorrelation function $g_{CM}(t)$ vs. time t and the single bead autocorrelation function $g(t)$ vs. t, respectively, for n = 64, 100, 216, and 800 chains reading from left to right (or top to bottom). The $g(t)$ are averaged over all the beads in the system. ϕ = 0.5 in all cases.

Dynamic Properties

Center-of-Mass Motion and Terminal Relaxation Times. We must first demonstrate that these systems are in the regime where the diffusion constant and terminal relaxation time of the end-to-end vector are consistent with eq 1b and 2b, respectively. We begin by discussing the center-of-mass motion and in Figure 2A plot on a log–log scale $g_{cm}(t)$ vs t for homopolymeric, cubic lattice systems. Two regimes are evident in $g_{cm}(t)$ vs. t. For distances such that $l^2 \leq g_{cm}(t) \leq 2\langle S^2\rangle$ (with l the bond length) $g_{cm}(t) \sim t^a$ with the values of the exponents a decreasing from 0.91 when n = 64 to 0.71 when n = 800. These systems behave neither like a simple Rouse chain having a uniform bead friction constant (eq 3) nor like reptating chains (eq 6). Qualitively, identical behavior was seen in diamond lattice simulations[22,32] as well as in off-lattice simulations.[34] A value of a less than unity may indicate that there is coupling of the center-of-mass motion of the chain into the internal relaxation modes. This is also consistent with the fact that $2\langle S^2\rangle$ is the distance over which all the internal modes of a Rouse chain relax to their equilibrium values.[23]

Table II.
Chain Length Dependence of the Self-Diffusion Coefficient, $D \sim (n-1)^{-\alpha}$, and the Terminal Relaxation Time, $\tau_R \sim (n-1)^{\beta}$, on Cubic and Diamond Lattices

ϕ	α	β	range of n fit
	Cubic Lattice		
0.5	1.52 (±0.006)	2.63 (±0.04)	64–216
	Diamond Lattice		
[b]	1.154 (±0.010)[a]	2.349 (±0.018)[a]	12–216
0.25	1.372 (±0.021)[a]	2.563 (±0.061)[a]	12–49
0.50	1.567 (±0.017)[a]	2.677 (±0.035)[a]	12–216
0.75	2.055 (±0.016)[a]	3.364 (±0.082)[a]	12–96

[a] Standard deviation of the slope obtained from linear least square fit of log–log plots. [b] Single chain.

The long-time limit of $g_{cm}(t)$ was employed to obtain D by fitting to[13]

$$g_{cm}(t) = 6Dt + c \qquad (7)$$

with c a small positive constant that reflects the faster motion of the center of mass at shorter times. Fitting the data for the n = 64–216 chains, we find $D \sim n^{-1.52}$. However, there is a systematic deviation in the direction of increasing exponent. Lacking the computational resources to run the n = 800 system up to the free diffusion limit, we employed various extrapolation procedures to obtain D for this system, thereby allowing us to determine whether α in $D \sim n^{-\alpha}$ has crossed over from a value of unity to a value of two (eq 1b).[24] A previous study of cubic lattice chains up to n = 48 provides α = 1.2–1.25.[37] The present system when n = 64–100 gives $\alpha \simeq 1.4$, when n = 100–216, α = 1.6, and finally, a very conservative estimate for the n = 216–800 regime gives α = 2.05. This further suggests that the n = 800, ϕ = 0.5 system is a very good place to look for the existence of reptation. The values of α for all the cubic and diamond lattice systems studied are summarized in Table II.

We next examined the terminal relaxation time τ_R of the end-to-end vector, $\mathbf{R}(t)$, obtained from the long-time decay of

$$g(R,R(t)) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle \qquad (8)$$

After a very rapid initial relaxation, $g(R,R(t))$ is invariably well fit by a single exponential. The scaling of $\tau_R \sim n^{\beta}$ on cubic and diamond lattices is summarized in Table II, column three. Note that the diamond lattice, ϕ = 0.75 system is in accord with the experimentally observed dependence of D and η on n, if η scales with τ_R.

Observe that, for all concentrations, the product $D\tau_R$ in the diamond (cubic) lattice systems scales like $n^{1.2}$ ($n^{1.1}$) rather than the expected n^1 (the product $D\tau_R$ is on the order of the radius of gyration which is proportional to n).[2] One possible explanation of this discrepancy is the coincidence of statistical uncertainties in the estimation of both α and β (about 0.05 for each exponent at high densities). Another is that one is observing a crossover to the $D\tau_R \sim n$ limit. If so, this implies that the experimental $\eta \sim n^{3.4}$ behavior is indicative of a crossover regime that, consistent with the simulation, is rather broad. The justification of this statement is as follows: The observed τ_R is always below times when $g_{cm}(t) \sim t$. In other words, consistent with

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experiment (see eq 1 and 2), the diffusion constant experiences the onset of dynamic constraints at smaller values of n than τ_R does, and the anomalous scaling of $D\tau_R$ may merely reflect this.

Single Bead Motion. We next turn to a discussion of the finer details of the chain motion and present in Figure 2B log–log plots of $g(t)$ vs. t for chains confined to a cubic lattice. Two different regimes of behavior in $g(t)$ vs. t are evident. In the first time regime, which extends up to $2\langle S^2\rangle$, $g(t)$ behaves like t^b, with b decreasing gradually from 0.54 when n = 64 to 0.48 when n = 216. Thus, these chains exhibit a Rouse-like dependence of $g(t)$ on t (see eq 4). Similar behavior was seen for all the diamond lattice chains studied. However, the n = 800 case is distinctly different from all previous cases examined; a decreased slope whose minimum value is 0.36 is evident and is indicative of the more constrained dynamics of these very long chains. One's first response is to suspect that the $t^{0.36}$ regime is similar to the $t^{1/4}$ regime predicted from reptation theory (see eq 5). However, we shall demonstrate below that the microscopic picture of chain motion is distinctly different.

Construction of the Equivalent Path. In their treatment of reptation, Doi and Edwards[11] employed the idea of a primitive path which basically involves the replacement of the actual chain by an equivalent one in which all the local fluctuations irrelevant to the long-distance motion are averaged out. Thus, we construct the equivalent chain path and follow its motion as a function of time. Every bead on the original chain is replaced by a point on the equivalent path which is the center of mass of a subchain or "blob" composed of n_b beads. Thus, a smooth path composed of partially overlapping blobs is generated which should be very close to the primitive path of Doi and Edwards[11] if n_b is close to the entanglement length.

At each time t, we generate the equivalent path and look at displacements down (the reptation component) and orthogonal to the primitive path defined at zero time. If in fact the chains are reptating, there should be substantial memory of the initial primitive path conformation, especially in the middle of the chain. To examine whether or not this is the case, we then compute the average mean-square displacement down, $g_{\parallel}(t)$ (the reptation component), and perpendicular to the original primitive path, $g_{\perp}(t)$. Since a reptating chain has a maximum in $g_{\perp}(t)$ of $(2/3)d_T^2$ for times t less than the tube renewal time, the ratio $g_{\perp}(t)/g_{\parallel}(t)$ vs. t should monotonically decrease with increasing time. On the other hand, if the motion is globally isotopic with no memory whatsoever of a tube defined at zero time, $g_{\perp}(t)/g_{\parallel}(t)$ should monotonically increase.

By simulating a chain in a partially frozen environment where chains are known to reptate,[13,33,34] we have demonstrated that $g_{\perp}(t)/g_{\parallel}(t)$ monotonically decreases with time;[23] thus, this procedure correctly demonstrates the presence of reptation when it is the dominant mechanism for long-distance motion. Moreover, our set of elemental moves do not somehow artificially suppress reptation.

In Figure 3A we plot $g_{\perp}(t)/g_{\parallel}(t)$ vs. t for n = 216 and 800 chains on a cubic lattice at ϕ = 0.5 for times below the tube renewal time of reptation theory. We set n_b equal to the excluded-volume screening value n_B; that is, n_b = 17. But we have also set n_b equal to 101 and find no qualitative difference in the behavior of $g_{\perp}/g_{\parallel}$. We remind the reader that if n_B corresponds to the dynamic entanglement length, then by every theoretical criterion the n = 800 chains should reptate.[3,15] The qualitative features displayed here are identical with those seen for shorter chains on a diamond lattice at equivalent and higher densities.[23] At short times, transverse chain motion is clearly preferred; this arises from both chain connectivity and the nature of cooperative motion at high density. Consider the following:[22] Suppose a given piece of chain has undergone a three-bond (two-bead) jump. Now, the probability that correlated motion in a neighboring bond occurs is the product of the probability that (i) the bond is in a conformation that can undergo a jump and (ii) there are unoccupied sites which the beads can jump into. (i) is the same for both down and cross-chain motion. (ii) is unity for cross-chain motion and, to lowest order, $(1 - \phi)^2$ for down chain motion. Thus, as the density increases, cross-chain motion dominates at short times.

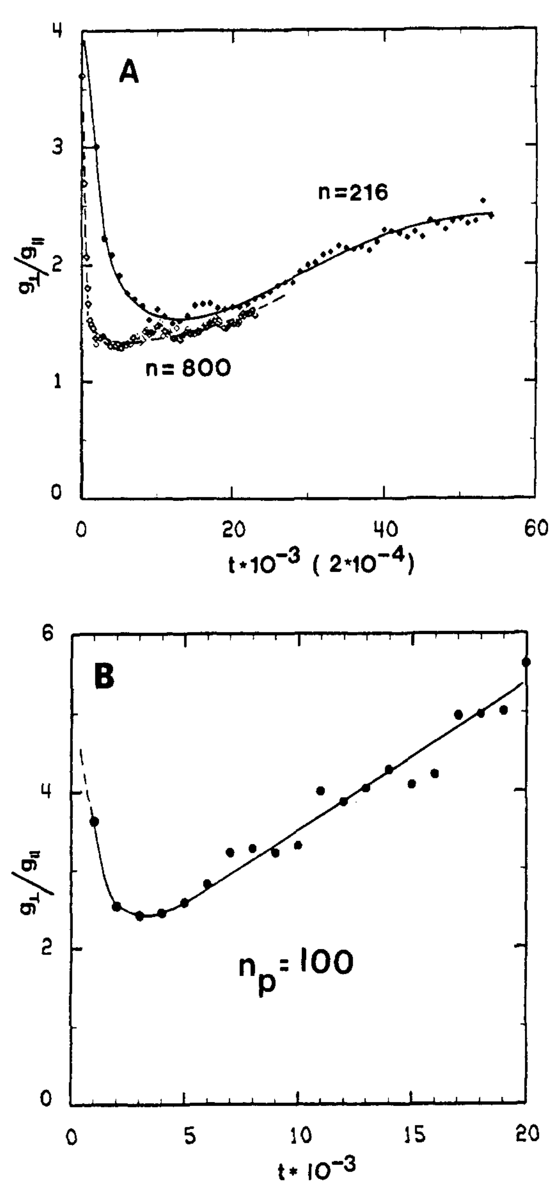

Figure 3. Plot of the ratio $g_{\perp}(t)/g_{\parallel}(t)$ vs. time for n = 216 (upper curve) and n = 800 (lower curve) homopolymeric melt in (A), and a n_P = 100 probe chain in a n_M = 800 matrix in (B). In all cases, the simulations were done on a cubic lattice at ϕ = 0.5.

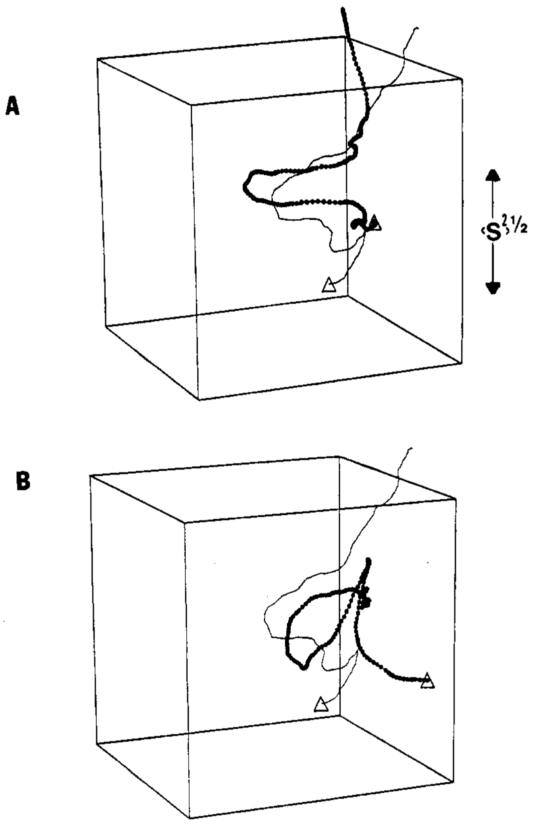

Figure 4. Snapshot projections of the "primitive path" of a chain with $n = 800$ in the melt, with $\phi = 0.5$. Triangles indicate one of the chain ends. (A) The displacement after (A) 6×10^4 steps and (B) 2×10^5 steps. Every bead in the plot corresponds to the center of mass of a blob, and for clarity only every fourth bead is plotted. The density of the beads reflects the density of the chain beads (in addition to the effect of the projection from three onto two dimensions).

Subsequent to the short-time preference for transverse motion, there is a period when down chain motion becomes somewhat more important (the minimum in the two curves). This corresponds to distances on the order of the excluded-volume blob size. Finally, at longer times the longitudinal component becomes increasingly less important. Therefore, we conclude that reptation-like motions down the chain are in fact strongly damped, and the motion of the equivalent chain is essentially isotropic. In other words, *there is no tube confining the chain of interest*! This is graphically illustrated in Figure 4A,B where the dynamic evolution of one of the $n = 800$ chains is presented. The thin curve depicts the initial configuration of the equivalent path, and the solid curves show the equivalent path at a time $t = 6 \times 10^4$ (2×10^5) later in Figure 4A (4B). For ease of visualization, n_b was set equal to 101, a very conservative value. As anticipated from the ratio $g_\perp(t)/g_\parallel(t)$, significant transverse fluctuations are apparent, and the motion down the original path is hardly noticeable. Thus, we once again conclude that these model chains simply do not know that they are in a tube. We hasten to point out that the snapshots presented here are typical ones. Thus, for the homopolymeric melt we see no evidence of reptation as the dominant mechanism of long-distance motion.

We next examined the case of a probe polymer of size n_P dissolved in a matrix of polymers, each containing n_M beads. In all cases, the total volume fraction of probe plus matrix polymers was kept essentially constant at $\phi = 0.5$. We chose $n_P = 100$ and allowed $n_M = 50, 100, 216$, and 800. This series of simulations was undertaken because an essential assumption of reptation theory that there is a time scale separation of the matrix and the probe chain certainly holds when $n_M = 800$ and $n_P = 100$; their diffusion constants differ by about 2 orders of magnitude. Moreover, the variation of D of the probe with n_M has been experimentally examined, and we wished to see whether these model systems exhibit the same qualitative behavior. We found that the behavior of D vs. n_M is qualitatively consistent with real experimental self-diffusion constant measurements of Green et al.[38] and Antonietti et al.[39] on polystyrene (PS) in matrices of different degrees of polymerization and decreases by about 25% as n_M goes from 50 to 800.

The mechanism of the probe chain motion in the $n_M = 800$ environment was further analyzed by decomposing the equivalent chain motion into the reptation component, $g_\parallel(t)$, and $g_\perp(t)$ as described above for the homopolymeric melt. The results are displayed in Figure 3B. Again, reptation does not dominate probe chain motion. Even in an environment whose *diffusion constant is 2 orders of magnitude less*, the surrounding matrix is not fixed and once again *there is no tube*! Snapshots of the equivalent path trajectory are similar to those shown in Figure 4 and show no difference in qualitative behavior when $n_M = n_P$ as compared to that when $n_M > n_P$.

This behavior may be qualitatively rationalized if the dynamic entanglements between chains are rare and are not fixed with respect to the laboratory frame, as assumed in reptation theory, but rather "slosh" around. The probe chain, while somewhat slowed down by the globally slower moving matrix (or more to the point the dynamic contacts on the probe chains when $n_M > n_P$ are longer lived), undergoes isotropic motion precisely because the environment itself is not reptating. Whatever their exact microscopic nature, if a contact between two chains is short-lived (much like in a small-molecule fluid), apart from modifying the local friction constant, it cannot change the scaling of the D and τ_R with n. Only those dynamic contacts that are long-lived, i.e., which persist on the order of the terminal relaxation time of the end-to-end vector, can change the molecular weight dependence of single-chain, long-time dynamic variables. A search of the simulation for the dynamic contacts bears out this qualitative picture and provides an n_e of about 133.

Concluding Remarks

The present series of dynamic Monte Carlo simulations has attemped to examine the validity of reptation theory at its most fundamental level. In particular, the assertion of reptation theory that in a melt the dominant long-wavelength motion is highly anisotropic and consists of the slithering of a chain down the tube formed by the matrix of neighboring chains does not survive scrutiny. For the range of chain lengths studied, which qualitatively mimic real experiments remarkably well, we find that the motion is isotropic, and the polymers simply do not know that they are confined in

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(38) Green, P. F.; Mills, P. J.; Palmstrom, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145.

(39) Antonietti, M. A.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.

a tube. Thus, these studies cast severe doubt on the validity of reptation as applied to finite-length polymer melts. Indeed, even when the probe and matrix diffusion constants differ by 2 orders of magnitude, reptation fails to dominate. While we cannot rule out the possibility that these chains will reptate with increasing n, such a crossover would not be evident from standard experimental measurements of viscosity and diffusion; we have found systems where η is proportional to $n^{3.4}$ and $D \sim n^{-2}$, and yet the chains do not reptate. These studies clearly indicate that the widely accepted reptation model of polymer melt dynamics does not adequately describe the motion in these model systems and alternative models are required.

Physically, then, what are the dynamic entanglement contacts? Although we recognize that further, more detailed analysis is required, the physical picture that emerges is as follows. In order to have a long-lived dynamic contact, two requirements must be satisfied: First, the pair of chains must be in contact at short times and have a topology that admits the possibility of a long-lived contact, as, for example, when one chain loops around the other. Second, the pair happen to move together in a direction that leads to a long-lived dynamic contact. Thus, a dynamic entanglement results when one chain drags the other through the melt for times on the order of τ_R. Such dynamic entanglements are created and destroyed by the random motion of the chains. This picture rationalizes why short chains in a melt behave like simple Rouse chains. They are not long enough for the dynamic entanglements to live a time on the order of τ_R. As n increases, so does the likelihood of long-lived contacts. Thus, one has a crossover from simple Rouse-like behavior to entangled behavior in which a given chain behaves at short times like a rubber due to these dynamic entanglements and at longer times like a Rouse chain with some slow-moving points. This simple physical idea forms the basis of a phenomenological theory of polymer motion that is in the process of being developed. This is one step in the process of understanding the nature of the viscoelastic behavior of polymeric liquids.

This research was supported in part by grants from the Polymer Program of the National Science Foundation. J.S. acknowledges the support of the Alfred P. Sloan Foundation.