

DYNAMICS OF DENSE POLYMER SYSTEMS
DYNAMIC MONTE CARLO SIMULATION RESULTS AND ANALYTIC THEORY

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Abstract

Dynamic Monte Carlo simulations of long chains confined to cubic and tetrahedral systems as a function of both volume fraction and chain length were employed to investigate the dynamics of entangled polymer melts. It is shown for a range of chain lengths there is a crossover from a much weaker degree of polymerization (n) dependence of the self-diffusion coefficient to a much stronger one, consistent with $D \sim n^{-2}$. Similarly, systems have been identified having a terminal relaxation time that varies as $n^{3.4}$. Since such scaling with molecular weight signals the onset of highly constrained dynamics, an analysis of the character of chain contour motion was performed. No evidence whatsoever was found for the existence of a well defined tube required by the reptation model. Lateral motions of the chain contour are remarkably large, and the motion appears to be essentially isotropic in the local coordinates. Results from this simulation indicate that the motion of a polymer chain is essentially Rouse-like, albeit, slowed down. Motivated by the simulation results, an analytic theory for the self-diffusion coefficient and the viscoelastic properties have been derived which is in qualitative agreement with both experimental data and the simulations.

I. Introduction

A long standing problem of polymer physics is the elucidation of the microscopic mechanism by which a given chain in an entangled polymer melt moves.¹ Although this problem has been a central one in polymer science for over the past forty years, the mechanism, in fact, remains unclear.² The answer to this question has practical applications to, among other areas, polymer flow rheology, polymer adhesion and polymer failure.¹

Among the phenomenological properties that any microscopic theory must rationalize, in order to be considered a candidate for a correct

theory, are the following: Imagine a linear polymer composed of n bonds. The center of mass self-diffusion coefficient of the polymer, D , must scale like

$$\begin{aligned} D &\sim n^{-1} \text{ when } n < n'_c \\ D &\sim n^{-2} \text{ when } n > n'_c \end{aligned} \quad (1)$$

n'_c is a crossover value of the degree of polymerization.¹ More recently, other values of the molecular weight dependence of D have been reported, and the situation is not quite as clear as it appeared a few years ago.³ The degree of polymerization dependence of the zero frequency shear viscosity η is better characterized and is given by⁴

$$\begin{aligned} \eta &\sim n \text{ if } n < n_c \\ \eta &\sim n^{3.4} \text{ if } n > n_c \end{aligned} \quad (2)$$

One of the mysteries which remains unresolved is why n_c the crossover value for viscosity is smaller than that for self-diffusion. Whatever the microscopic mechanism giving rise to this behavior, however, it is clear that as the molecular weight of the chains increases, entanglements of some nature become important.

What are these entanglements? Computer simulations can be a particularly powerful technique for elucidating, at least in a qualitative sense, the microscopic mechanism of various physical processes and motion in polymers is no exception. This paper describes the results of simulations on melts of linear chains and describes a simple theory of melt dynamics that is suggested by those simulations.

One of the most remarkable, and in fact, surprising consequences of the experimental observations embodied in the dependence at low molecular weight of the self-diffusion coefficient and the viscosity is that the polymer chain in a melt behaves like a Rouse chain.⁵ This is the simplest model for the properties of a polymer chain at infinite dilution. In a Rouse chain, which is just a bead-spring model of a polymer dissolved in a continuum solvent that exerts a high frequency, frictional force on the beads, the overall motion is locally, as well as globally, isotropic, and one can neglect hydrodynamic interactions between beads. Hydrodynamic interactions arise from the perturbation of the solvent flow about a bead due to the presence of the other beads. Thus, if the molecular weight of the polymer melt is sufficiently small, it behaves not only as if it is not entangled, but it behaves remarkably simpler than if it were at infinite dilution where hydrodynamic interactions must be considered.⁶

In subsequent discussion we will require various scaling properties of the Rouse model⁷. The mean square displacement of the center of mass

$$g_{cm}(t) = 6Dt. \quad (3)$$

In the long chain limit, the mean square displacement of a single bead,

$$g(t) \sim t^{\frac{1}{2}} \quad t < \tau_{\text{Rouse}} \quad (4)$$

with τ_{Rouse} the terminal or longest internal relaxation time; $\tau_{\text{Rouse}} \propto n^2$.

As n increases, the polymer changes its response from a viscous liquid to a viscoelastic liquid. Probably the most widely accepted model to describe the scaling behavior of D vs. n is the reptation model of de Gennes⁸, which was later modified and elaborated on by Doi and Edwards.⁹⁻¹² Basically, one imagines 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. Thereby, an extremely complicated many body problem is reduced to an effective single particle picture. The matrix of chains is replaced by a tube, which is defined by the static entanglements. In the reptation picture, the only way the chain can move appreciable distances is by slithering out the ends of the tube; hence, the name reptation.

In the original reptation model, and in all its subsequent variants, the dominant long distance motion is longitudinal down the chain contour defined at zero time.¹ Lateral fluctuations are always of limited extent. Because of the torturous path that the chain must take with respect to the laboratory fixed frame, the longest internal relaxation time of the system τ_{Rep} turns out to be proportional to n^3 . This is typically called the tube renewal time.

If one further assumes that there is a rubber-like elastic response of the polymer at short times¹⁰, then $\eta \sim n^3$ as well. Observe that this is a slightly weaker molecular weight dependence than experiment indicates (see eq. 2). Similarly, the self-diffusion constant scales as n^{-2} . Thus, at face value it would seem that this simple model of polymer melt motion quite closely reproduces the experimentally observed behavior of the self-diffusion coefficient and the shear viscosity. In subsequent developments, however, it turns out that $D \sim n^{-2}$ is a ubiquitous property that is quite insensitive to the microscopic details of the motion, a point we will return to later.

Let us contrast the behavior of the single bead autocorrelation function $g(t)$ for a reptating chain with that of a Rouse chain. For distances less than the tube diameter, $g(t)$ scales like $t^{\frac{1}{2}}$. In this time regime the chain has absolutely no information about whether there is a tube or not, and so it will still behave like a pure Rouse chain. For somewhat longer times, the chain behaves like a Rouse chain confined to a tube which itself is a Gaussian random walk, and therefore, the $t^{\frac{1}{2}}$ behavior is further diminished so that $g(t)$ is proportional to $t^{\frac{1}{2}}$ times for up to τ_{Rouse} . Next, one is left with the center of mass motion down the tube. Thus $g(t)$ is proportional to $t^{\frac{1}{2}}$ for times less than the reptation time. Finally, in the free diffusion limit $g(t)$ is proportional to t . Similar considerations indi-

cate that there is a range of times for which the mean square displacement of the center of mass scales not like t , but $t^{1/2}$ for times less than the reptation time, but longer than τ_{Rouse}^7 . For $t > \tau_{\text{rep}}$, $g_{\text{cm}}(t) \sim t$.

All this is extremely plausible for a regular gel for which, in fact, reptation was originally derived.⁸ It is not at all clear that this picture holds for polymer melts where everything is moving on the same time scale. The reality of a spatially fixed tube has been previously questioned by Phillies¹³ and Fujita and Einaga¹⁴ for melts, and by Fixman for concentrated solutions of rod-like polymers.¹⁵

The existence of reptation as the dominant mechanism in a polymer melt forms the focus of the present paper, the outline of the remainder of which is as follows: We shall begin with the description of the microscopic model of the polymer dynamics and then turn to the dynamics of homopolymeric linear chains. Subsequently, we summarize the results of a recent analytic theory which is in qualitative agreement with both experiment and simulation.¹⁶⁻¹⁷

II. DESCRIPTION OF THE MODEL

Both diamond and cubic lattice models of a polymer melt have been employed.¹⁸⁻¹⁹ A lattice representation is used for a number of reasons. First of all, it allows one to do the calculations in integer arithmetic, thereby affording a factor of 10 to 100 speedup over floating point calculations. Second of all, it allows one to rigorously insure that no bond cutting occurs and thereby that the excluded volume effect exerted by one chain upon another is rigorously implemented. As in all simulations of this type, the lattice is enclosed in a periodic box of volume L^3 .⁷ To avoid the problem of a given polymer chain interacting with its image, we always chose $L > \langle R^2 \rangle^{1/2}$ (the equilibrium root mean square end-to-end distance) to insure that interactions of the chain with itself cannot occur. Each polymer chain is assumed to occupy n consecutive lattice sites, and ϕ is the volume fraction of occupied sites. In all cases, excluded volume is implemented by prohibiting the multiple occupancy of any given lattice site. The dynamic properties of homopolymeric diamond lattice polymers were studied over a range of volume fractions ϕ from zero to 0.75 for chains up to $n = 216$.¹⁸ The corresponding cubic lattice polymers were studied at fixed $\phi = 0.5$, but for n ranging from 64 to 800 for homopolymeric melts of linear chains.¹⁹

The first problem one faces in attempting to undertake such a simulation is the construction of an equilibrated dense melt. Procedures for constructing such systems have been discussed in detail elsewhere and need not concern us further.²⁰ The next problem encountered in studying the dynamics of the melt by Monte Carlo techniques is that one must choose a set of local moves. One wants to make the moves as local as possible, to avoid either distorting the time scale

of motion or somehow building in an artificial and unphysical dynamics.^{7,18-19}

The crucial properties of the chain dynamics are as follows: One has to choose a set of moves on any given lattice that not only can diffuse local orientations down the chain but also has the possibility of locally introducing new random conformations into the chain. Otherwise, the dynamics of even an isolated chain would be non-physical. That is, if new chain orientations can only arise by diffusion from the free ends, an now artificial n^3 time scale is built into the algorithm which has absolutely nothing whatsoever to do with entangled dynamics.²¹⁻²² For the case of both diamond²³ and cubic lattices,^{19,21-22,24} the set of elementary jumps depicted in Figures 1 and 2 respectively satisfy the above requirements and are useful in that a reasonable fraction of the jumps are successful.

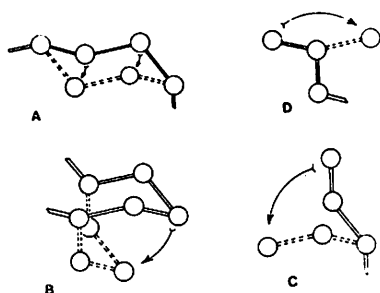


Figure 1. Elementary conformational jumps for tetrahedral polymers: (a) three-bond motion $g^+ \rightarrow g^-$, (b) four-bond motion (with a random choice of the new orientation of the bonds), (c) two-bond motion of end units (with a random choice of the new orientation of the bonds), (d) one-bond motion of end units (with a random choice of the new orientation of the bonds).

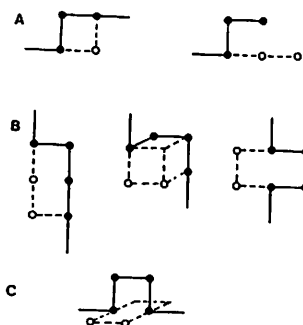


Figure 2. Elementary conformational jumps for cubic lattice polymers. (A) The normal bead motion and an example of chain end motion. (B) Examples of three-bond permutations. (C) The 90° -crankshaft motion of a U-shaped fragment of the chain.

The simulation proceeds as follows: A chain is picked at random and then a given bead is chosen. One then attempts to make each of

the various kinds of moves per bead on average. The fundamental time unit is taken to be that required such that on average each of the lattice moves is attempted once per bead. Of course, in actual implementation, we randomly mixed the moves, and any move is rejected if such a move is not allowed. For example, in the case of a diamond lattice, if a three bond flip from one half of a cyclohexane ring to the other is attempted and the conformation of the selected three bonds is trans, as opposed to a gauche plus (g+) or gauche minus (g-) conformation, the move cannot occur. Similarly, the move will be rejected if the site(s) to which the jump is attempted is (are) already occupied. One of the nice things about doing simulations at high density is that while one may specify an *a priori* choice of any given type of move, the system itself due to excluded volume restrictions chooses the fraction of successful moves for a wide range of *a priori* probabilities.¹⁸⁻²⁰

At this point, it is appropriate to review the relative advantages and disadvantages of using a lattice representation of a polymer melt. One uses a lattice as mentioned above because it allows one to simulate much longer polymers at much higher densities for longer times than corresponding off lattice systems. The disadvantage, of course, is that one has to demonstrate that the results obtained from such a simulation are physically meaningful and not an artifact of the lattice. While we cannot prove this, in fact, when comparisons can be made with off-lattice simulations,²⁵ all the qualitative conclusions are identical. Moreover, we have obtained identical results for both cubic and diamond lattices when corrections for differences in local persistence length and lattice coordination number are made.

III. SIMULATIONS ON HOMOPOLYMERIC LINEAR CHAINS

CENTER MASS MOTION AND THE LONGEST INTERNAL RELAXATION TIMES

The first problem that one faces when doing computer simulations is demonstrating that the scaling behavior of the self diffusion constant and terminal relaxation time are consistent with experiment. Thus we start by an examination of the center of mass motion, and in the Figure 3, plot, on a log-log scale, the mean square displacement of the center of mass, $g_{cm}(t)$ vs. t for homopolymeric cubic lattice systems at $\phi = 0.5$. Clearly, two regimes are evident. For distances such that $g_{cm}(t) \leq 2\langle S^2 \rangle$ ($\langle S^2 \rangle$ is the mean square radius of gyration), $g_{cm}(t) \sim t^a$ with the values of a monotonically decreasing from about 0.91 when $n = 64$ to 0.71 when $n = 800$. Thus, we conclude that these systems behave neither like a Rouse chain having a uniform friction constant where $g_{cm}(t)$ is always proportional to time, nor like reptating chains which have a $t^{3/2}$ regime. Qualitatively identical behavior is seen in diamond lattice simulations,¹⁸ as well as in off-lattice simulations.²⁵ The existence of a t^a regime where $a < 1$ indicates coupling between the center of mass of motion and

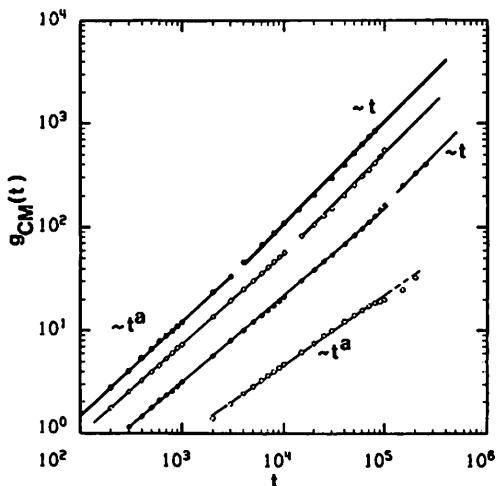


Figure 3. Log-log plots of the center-of-mass autocorrelation function $g_{cm}(t)$ vs. t for $n = 64, 100, 216$ and 800 melts reading from left to right (or top to bottom). $\phi = 0.5$ in all cases. The shorter time t^a regime is to be distinguished from the long time diffusion regime.

the internal relaxation modes. This is also consistent with the fact that $2\langle S \rangle^2$ is the maximum distance over which the internal modes of the chain relax to their equilibrium values if, in fact, one can treat the chains as statistically independent. The self-diffusion constant was obtained by fitting $g_{cm}(t)$ equal to the following functional form: $g_{cm}(t) = 6Dt + c$, with c a small positive constant that arises from the fast motion of the center of mass at shorter times. If the data is fit over the regime from $n = 64$ to $n = 216$, then $D \sim n^{-1.52}$. Unfortunately, during the time these simulations were run we lacked the computer resources to run the $n = 800$ system out into the free diffusion limit. Thus, a number of extrapolation procedures were employed to obtain D for this system. These have been discussed in detail elsewhere,¹⁹ but basically we feel that by $n = 800$, D is well into the n^{-2} regime.

We next examined the scaling of the longest relaxation time of the end-to-end vector obtained from the long-time decay of $\langle R(t) \cdot R(0) \rangle$ where $R(t)$ is the end-to-end vector at a time t . Following a period of very rapid initial relaxation we find that the autocorrelation function vector is rather well fit by a single exponential.

The scaling of $D \sim (n-1)^{-\alpha}$ and $\tau_R \sim (n-1)^\beta$ on diamond and cubic lattice systems are summarized in Table I.

TABLE 1. Chain Length Dependence of the Self-Diffusion Coefficient $D \sim (n-1)^{-\alpha}$ and Terminal Relaxation Time $\tau_R \sim (n-1)^\beta$

ϕ	α	β
Diamond Lattice		
Single Chain	1.154 (± 0.010) ^a	2.349 (± 0.018) ^a
0.25	1.372 (± 0.021) ^a	2.563 (± 0.061) ^a
0.50	1.567 (± 0.017) ^a	2.677 (± 0.035) ^a
0.75	2.055 (± 0.016) ^a	3.364 (± 0.082) ^a
Cubic Lattice		
0.5 ^b	1.52 (± 0.06) ^a	2.63 (± 0.04) ^a

^a Standard deviation of the slope obtained from a linear least square fit of the log-log plots of D vs. n and τ_R vs. n , respectively.

^b Fit over the $n = 64$ to 216 range, i.e., in the crossover region.

We point out that the diamond lattice system at $\phi = 0.75$ is in accord with the experimentally observed dependence of η on n if $\eta \sim \tau_R$. That is, η is proportional to the 3.4 power of n . We further point out that a given $\phi \leq 0.5$ on the diamond lattice the chains are in the crossover region. One would expect that on increasing n similar values of the exponents α and β should be seen as in the $\phi = 0.75$ case. One of the more interesting results that were obtained from this series of simulations is that at all concentrations the product $D\tau_R$ scales like $n^{1.2}$ on a diamond lattice and $n^{1.1}$ on a cubic lattice rather than the expected n^1 . Based on elementary scaling considerations $D\tau_R$ should be on the order of the radius of gyration of the chain, which in linear polymer melts is proportional to n . A possible origin of this discrepancy might be the coincidence of statistical uncertainties in the estimation of both α and β , which is approximately ± 0.05 for both exponents at high densities. A second explanation is that one is observing a crossover to $D\tau_R \sim n$ in the infinite chain limit. If this were to be true, this would imply that the experimentally determined scaling of the shear viscosity, $\eta \sim n^{3.4}$, would be indicative of a crossover regime, and consist with the simulations it would be rather broad. Some recent experiments by Colby, Fetters and Graessley are not inconsistent with this particular conclusion, but by no means demand it.²⁶ A final alternative explanation is, in fact, that $D\tau_R$ always scales like $n^{1+\epsilon}$ with ϵ greater than zero. That is to say, configurational relaxation is rapid relative to the

disentanglement between the chains. This idea has been put forth in a recent theory of Fixman.²⁷

Having established that our simulations are on chains sufficiently large that the experimentally observed scaling with molecular weight of D vs. n obtains we next turn to a finer characterization of the dynamics, namely, single bead motion. In Figure 4A the log-log plots of the average mean square of the displacement per bead, $g(t)$ vs. t for chains confined to a cubic lattice is displayed. Clearly, two different regimes of behavior are evident. The first regime, which extends once again up to $2\langle S^2 \rangle$, $g(t) \sim t^b$ with b decreasing gradually from the Rouse exponent of about 0.54 when n is equal to 64 to 0.48 when n is equal to 216. Thus, within the statistical error of the simulation one might conclude that these chains exhibit a Rouse-like dependence of $g(t)$ on t . However, the $n = 800$ curve exhibits distinctly different behavior from all of the previous cases. There is a region where $g(t) \sim t^{0.36}$, indicative of more constrained dynamics in these chains.

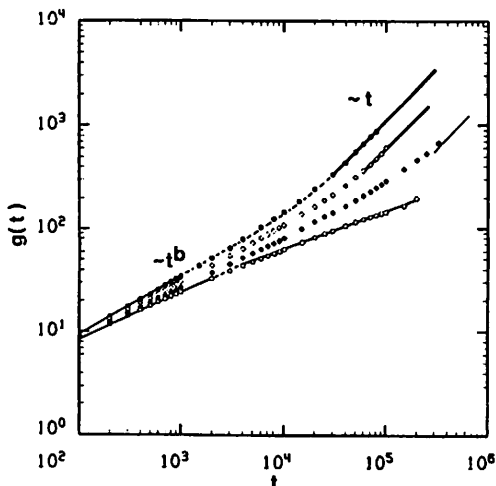
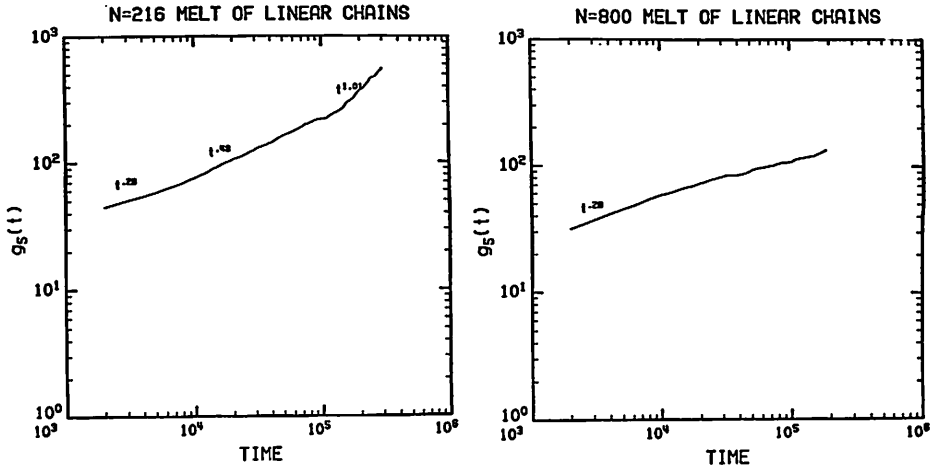


Figure 4A. Log-log plots of the single bead autocorrelation function $g(t)$ vs. time t for $n = 64, 100, 216$ and 800 melts reading from top to bottom. The $g(t)$ are averaged over all the beads in the system. $\phi = 0.5$ in all cases.

One's first response is to suspect the $t^{0.36}$ regime is similar to the t^k regime predicted by reptation theory, and that these chains are reptating. However, getting slightly ahead of the story, microscopic examination of the motion demonstrates that the character of the chain motion is distinctly different. One might expect that the central beads of the chain, in fact, would cross over to the t^k first. Thus, in Figures 4B and 4C, we plot present log-log plots of the average mean square displacement of the central five beads of the chain, $g_5(t)$, vs. t for $n = 216$ and $n = 800$. A t^k regime is clearly evident (actually, $g_5(t) \sim t^{0.28}$). Thus, one is left with the question: Are these chains, in fact, reptating or is the character of their motion, in fact, different?



Figures 4B and 4C. Log-log plot of the single bead autocorrelation functions of the central five beads, $g_5(t)$ vs. t for $n = 216$ and $n = 800$ in Figures 4B and 4C respectively. In all cases $\phi = 0.5$.

EXAMINATION OF THE PRIMITIVE PATH DYNAMICS

In the classic treatment of polymer melt dynamics, assuming that reptation is the dominant mode of chain motion, Doi and Edwards used the idea of a primitive path.⁹⁻¹² This basically involves the replacement of the actual chain by an equivalent one in which all of the local fluctuations in chain contour irrelevant to the long distance motion are averaged out. Basically, one could imagine taking the chain and reeling in the slack and then looking at the resultant path. In what follows, we construct an equivalent chain which is quite close to the primitive path and follow its motion as a function time.

The basic outline of the procedure is as follows: Each bead in the original chain is replaced by a point on the equivalent path which is the center of mass of a subchain composed of n_b beads. Thus, one replaces the actual contour of the chain by a smooth path composed of these partially overlapping subchains which should be very close to the primitive path of Doi and Edwards, if n_b is close to the number of monomers between entanglements. At every time, we generate the equivalent path and look at the displacements down the original path defined at zero time. This corresponds to the reptation component.

What is left over is the non-reptation component which should be small if reptation is dominant. To determine whether, in fact, this is true we compute the average mean square displacement, $g_{\parallel}(t)$ down the original primitive path and perpendicular to the primitive path, $g_{\perp}(t)$. It is trivial to demonstrate that a reptating chain has a maximum value of $g_{\perp}(t)$ equal to one half the mean square tube radius for times less than the tube renewal time. Thus, the ratio $g_{\perp}(t)/g_{\parallel}(t)$ should monotonically decrease in time. On the other hand, if the motion is, in fact, globally isotropic and liquid-like with no memory whatsoever of a tube defined at zero time, $g_{\perp}(t)/g_{\parallel}(t)$ should monotonically increase with time. It is interesting to point out that reptation theory assumes a kind of glass transition has already occurred in the melt. That is to say, the motion of a chain perpendicular to the original path is essentially frozen out due to the existence of entanglements.

The question immediately arises whether, in fact, somehow we have not artificially suppressed reptation in our choice of moves, and if our particular criteria of the ratio of $g_{\perp}(t)/g_{\parallel}(t)$ vs. t would provide the signature of reptation when it exists. It has long been established that if a chain is in a fixed mesh and if it is sufficiently long, the chain should reptate.^{25,28-29} Basically, the origin of the force that tends to keep the chain from having large lateral displacements is as follows: If a chain attempts to move between a set of fixed obstacles then the allowed number of configurations of the chain are reduced. In the asymptotic limit one could imagine that this forms a constrained ring whose configurational entropy is greatly reduced relative to the case when one takes the equivalent chain length and pokes it out the end of the tube. Thus, one would expect in the asymptotic limit that reptation should dominate.

To demonstrate that this is true for our simulation we have simulated a chain in a partially frozen environment.¹⁸ Basically, what one does is take the original $n = 216$ diamond lattice polymer melt and freeze all the chains but a test chain. However, if one does this, since the tube is not very porous, one finds grid lock. Thus a partially frozen environment is used. We took every 18 beads in the matrix chains and pinned them. This provides for a set of local dynamics which is extremely close to that of the original polymer melt, but here all chains but the test chain of interest are constrained from moving appreciable distances. Looking at pictures of the primitive path, these chains reptate, and $g_{\perp}(t)/g_{\parallel}(t)$ vs. t monotonically decreases with increasing time. Thus, the signature of reptation is recovered, and one finds the presence of reptation when it is the dominant mechanism of long distance motion. Furthermore, since the chains do reptate when placed in a partially frozen environment, our choice of local Monte Carlo moves does not somehow artificially suppress reptation.

In Figure 5, we plot for the melt where everything moves $g_{\perp}(t)/g_{\parallel}(t)$ vs. t for $n = 216$ and 800 chains on a cubic lattice at

a $\phi = 0.5$ for times below the tube renewal time of reptation theory. We have set $n_b = 17$ as well as 101 and find no qualitative difference.

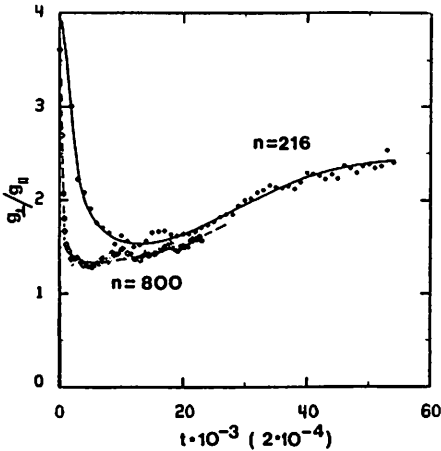


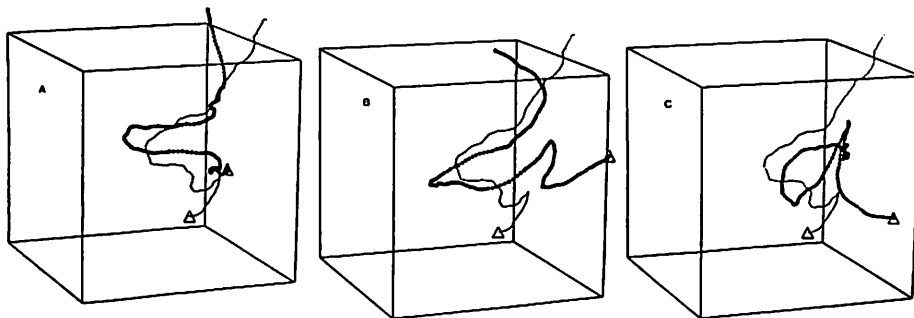
Figure 5. The plot of the ratio $g_1(t)/g_{||}(t)$ vs. time for the $n = 216$ (upper curve) and $n = 800$ (lower curve) melt. See the text for more details.

The qualitative features displayed here are identical to those seen for shorter chains on a diamond lattice at higher density. At short times, transverse motion of a chain is preferred. This is an effect due to the nature of cooperative motions in high density systems whose origin is the following:²⁰ Imagine a chain has undergone a conformational rearrangement. Now the probability of the chain undergoing correlated motion is a product of two quantities. (1) The intrinsic probability that the chain is in a conformation such that it can undergo a jump. (2) The probability there are unoccupied sites the chain can jump into. For both down and cross chain motion, the intrinsic probabilities of undergoing a jump are identical. For cross chain motion, given that the chain has undergone a jump, there is now an unoccupied volume into which the neighboring chain can jump into and, therefore, the conditional probability that it can undergo a jump is now one. However, for down chain motion, this probability is roughly proportional (on a lattice) to $(1-\phi)$ raised to the power of the number of sites involved in the motional unit. Therefore, one would expect that with an increase in density, cross chain motion should dominate at short times, as is indeed observed.

Subsequent to the short time preference for transverse motion, there is a period when down chain motion becomes somewhat more important. This corresponds to, in fact, distances on the order of the excluded volume decay length. Basically what is happening is that the chain is starting to feel the effect of the environmental, topological constraints on this distance scale and has slowed down. There is a

certain incubation period before the collective motion giving rise to the larger scale lateral motion takes over. Finally, at longer times the reptation component becomes increasing less important and the lateral component grows. In fact, it becomes increasingly difficult to follow the original primitive path and project onto it. We point out, however, that for the displacements shown, the maximum time is on the order of a tenth of the terminal relaxation time, and the tube (if it indeed exists) should have been well defined. An interesting point observed on comparison of Figure 5 with Figure 4B is that the minimum in $g_1(t)/g_{||}(t)$ occurs when the chains are crossing out of the $t^{1/4}$ regime in the $g_5(t)$ vs. t plot. Thus, if one were to merely look at $g_1(t)/g_{||}(t)$ for times just up to the end of the $t^{1/4}$ regime, but for times and distances still short relative to the radius of gyration, one would incorrectly conclude that reptation dominates. One still has to go out further into the second $t^{3/4}$ regime where reptation, in fact, becomes at most a minor component of the motion with respect to the original primitive path defined at zero time. Thus, we conclude that there is no tube confining chain of interest. We will return to this point in subsequent discussion.

A more pictorial illustration of the character of the chain motion is presented in Figures 6A-6C, where the trajectory of one of the $n = 800$ chains is presented.



Figures 6A-C. Snapshot projections of the primitive path of a $n = 800$ chain within the melt, at $\phi = 0.5$. The thinner line corresponds to the conformation at the initial time. The thicker line at a time t (indicated below) later. Triangles indicate one of the chain ends. (A) The displacement after 6×10^4 steps; (B) after 1.2×10^5 steps; (C) after 2×10^5 steps. The equivalent chain has been constructed as described in the text with $n_b = 101$. Every bead in the plot corresponds to the center-of-mass of such a blob, and for clarity only every fourth bead is plotted. The density of the beads reflects the density of the chain beads.

The behavior of all of the other chains are qualitatively the same. The thin curve is the initial configuration of the primitive path defined at zero time and the thick solid curve, the path at times

$t = 6 \times 10^4$, 1.2×10^5 and 2×10^5 for Figures 6A-6C, respectively. For ease of visualization, $n_b = 101$ a very conservative value. It is entirely evident and consistent with the ratio of $g_i(t)/g_{||}(t)$ that significant transverse fluctuations of the chain are observed, and the motion down the original path is basically insignificant. One is forced to conclude, based both on the examination of the primitive path and from the $g_i(t)/g_{||}(t)$ analysis that the chains simply do not know they are confined to a fixed network or tube.

THE ORIGIN OF DYNAMIC ENTANGLEMENTS

Whatever their physical origin, in order to have an important effect on the long distance motion, entanglement constraints must live for times on the order of a terminal relaxation time. Otherwise, they can be subsumed into an effective molecular weight independent monomeric friction coefficient. Based on the simulations which behave much like slowed down, Rouse chains, one might conjecture that the slow down is due to dynamic entanglement contacts - that is, where one chain drags another chain for times on the order of the terminal relaxation time. Eventually, of course, we would expect these two chains to diffuse apart. However, this disengagement process would occur on a very long time scale. We next examine what the simulations have to say about this conjecture.

BEAD DISTRIBUTION PROFILES

Some further insight into the nature of dynamic entanglements emerges from Fig. 7, where we plot the time dependence of the average mean square displacement of the bead, $g_i(t)$, as a function of the position i along the chain. In the curves denoted by a through d, the time equals 3×10^4 , 6.9×10^4 , 1.35×10^5 and 2.1×10^5 time steps for the $\phi = 0.5$, $n = 216$ homopolymeric diamond lattice melt. The smooth curves through the data correspond to the values produced from the Rouse model obtained employing an apparent diffusion constant defined as $g_{cm}(t)/6t$.

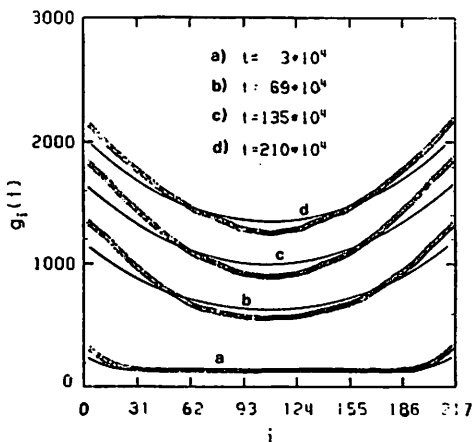


Figure 7. Plot for $n = 216$ chains in a melt having $\phi = 0.5$ of $g_i(t)$ vs. i , at times indicated in the figure, in the open circles, and calculated assuming that the Rouse eigenvectors form a good basis set, in the solid lines. See the text for additional details.

The Rouse model over-estimates the mobility of the chain interior and somewhat underestimates the mobility of the ends. Overall, though, the bead distribution profiles are rather good. In fact, in general, it should be pointed out that even for a long isolated Rouse chain in the absence of any constraints the bead distribution profile is parabolic, with the ends moving more than the middle. This is a general result for linear chains that is independent of the particular model of dynamics.

NATURE OF THE DYNAMIC CONTACTS BETWEEN CHAINS

In order to examine the time evolution of contacts between chains the following procedure was employed. (1) We replaced each chain by a series of non-overlapping blobs, each having $n_b = 18$ monomers; thus the resulting chain is analogous to a pearl necklace. (2) Next we searched for pairs of blobs belonging to different chains whose centers of mass are at a distance less than a distance $r_{\min} = 5$ from each other at zero time (the length of a bond equals unity). (3) We count the number of such contacts. Let $n_c(t)$ be the fraction of such dynamic contacts that survive up to a time t later, given that the chains were at contact at time zero. In Figure 8, we plot $n_c(t)$ vs. t for the $n = 216$, $\phi = 0.5$ homopolymeric cubic lattice chains. $n_c(t)$ is found to be decomposable into a sum of three exponentials. While we realized that our three exponential decomposition is by no means unique, the time constants which are obtained, nevertheless, are highly suggestive. The majority of the

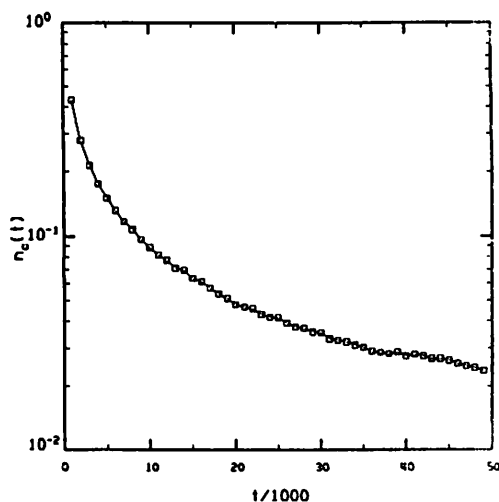


Figure 8. Log-log plot of the number of dynamic contacts that survive up to a time t , $n_c(t)$ vs. t for a $n = 216$ homopolymeric cubic lattice melt with $\phi = 0.5$, $n_b = 18$, and $r_{\min} = 5$. See the text for further details.

contacts (64%) decay within 1% of τ_R , 91% of the contacts decay within 9% of τ_R , and the remaining 9% decay on the order of τ_R . Therefore, we conclude that dynamic entanglement events are very rare and approximately 10% of these contacts in an $n = 216$ chain are long lived. This translates into one dynamic entanglement for every 133 beads. This compares remarkably well with the estimate of the number of monomers between entanglements obtained from the self diffusion constant (see below, eq. 5) which equals 125. The mean lifetime of these contacts is consistent with the idea that contacts between polymers slow down the motion. Most local contacts, however, are rather short-lived, and apart from modifying the local friction constants have no effect on the long time dynamics. Thus, the first conclusion that emerges from these simulations is that the long-lived dynamic entanglement contacts have a distance scale which is order of a magnitude larger than the static screening length. In real polymer melts the static excluded volume screening length is on the order of a monomer unit or so, whereas, based on estimates of the plateau modulus, the mean number of monomers between dynamic entanglements is on the order of 100.¹ Moreover, we have also established that all entanglements are in fact moving with respect to the laboratory fixed frame. Thus, there is no fixed cage.

What then are the dynamic entanglements? Suppose that at zero time, a pair of chains are in a configuration where one chain forms a loop around the other chain - this is a necessary but not sufficient condition for an entanglement. They then subsequently have to move together in a direction that causes the contact to be long-lived. That is to say, one chain drags another chain. Currently we are in the process of examining the nature of the dynamic entanglement process in far more detail.

IV. RECENT ANALYTIC WORK

THE SELF-DIFFUSION CONSTANT

It is possible using the Mori projection operator treatment to calculate the effective friction constant of a polymer due to the presence of all of the other polymers. This was done in a recent elegant article by Hess.³⁰ If one then assumes that one need only consider two body terms, (consistent with the fact that the entanglements are rather dilute), and thus the propagator between collisions has a free Rouse component, then it is quite easy to show that¹⁶

$$D = \frac{d_0}{n+n^2/n_0} \quad (5)$$

with d_0 the monomeric diffusion constant and n_0 is the mean number of monomers between dynamic entanglements. Thus, based on these relatively benign assumptions we conclude that the n^{-2} dependence of D is very general and will, in fact, be independent of the microscopic

details of the mechanism of motion. In other words $D \sim n^{-2}$ is not a unique signature of reptation.

What then must any successful theory say about the internal dynamics of polymer melts? It must rationalize the experimental molecular weight dependence of the self-diffusion coefficient and the shear viscosity (see eq. 1 and 2). It must also be consistent with the simulations which indicate that the motion appears to Rouse like, but slowed down and that there is no tube. $g(t)$ has a t^b regime with $b < \frac{1}{2}$; $g_{cm}(t)$ has a t^a regime with a less than one when $g_{cm}(t) < 2\langle S^2 \rangle$. The product $D\tau_R/n \sim n^\epsilon$ with ϵ between 0.1 and 0.2. Furthermore, it must rationalize the single bead, mean square displacement profiles which says that the ends are more mobile than the corresponding equivalent Rouse chain and the middle is less mobile.

We summarize below the features of a recent phenomenological theory that accounts for the above facts.¹⁷ The following assumptions need to be made. (1) At short times a la Doi and Edwards,¹⁰ we treat the response of a melt as identical to that of a rubber. We then focus on the motion of an average reporter chain. We are further going to assume that the long time relaxation behavior of a given chain in a polymer melt is adequately described by a Rouse model. However, due to the presence of dynamic entanglements there are some slow moving points.

Qualitatively, what might one expect from the crossover behavior of such a physical picture? Let us consider the behavior of a chain having a single dynamic entanglement. Physically one would expect that the longest lived dynamic entanglement contact to be located in the center of the chain. Clearly, the terminal relaxation time in this system does not change by much; basically, the slow moving point behaves like a local defect. However, in the absence of the entanglement, the self-diffusion is constant is d_0/n and in the presence of the entanglement it is $d_0/2n$. Therefore, one would expect the crossover regions of D and τ_R to be different. Moreover, the center of mass and the center of resistance are not identical. Basically, the center of mass motion couples into the internal coordinates and this gives rise to $g_{cm}(t) \sim t^a$ regime with $a < 1$ for distances less than $2\langle S^2 \rangle^{\frac{1}{2}}$. Similarly, $g(t) \sim t^b$ with $b < \frac{1}{2}$. One can show is that as n goes to infinity, the dynamic properties behave as if the monomer friction constant can be replaced by the average friction constant per bead equal to $\zeta_0 (1+n/n_e)$, with ζ_0 the friction constant in the absense of chain connectivity. The shear viscosity equals $4/15$ of the Doi and Edwards value³¹ and ultimately scales as n^3 . Thus, we would predict that $\eta \sim n^{3+\delta}$ where δ goes to zero as n goes to infinity. And finally, the product of the plateau modulus times the shear compliance equals $10/7$. Doi and Edward theory gives a value of $6/5$ and experiments are in the range from $2\frac{1}{2}$ to 3 .³¹

As shown in Figure 9 where the circles denote the calculated values and the dashed line is the fit through the points giving $\eta \sim n^{3.44}$ the

crossover value of $\eta \sim n^3$ should be around 40 to 50 entanglements. This is not inconsistent with the recent work of Colby, Fetters and Graessley²⁶ although by no means demanded by it. We find in the present theory that the value of n'_c , in eq. 1 equals about $4.5 n_c$. Thus, the resulting regime where η depends on the 3.4 power of the molecular weight occurs at smaller chain lengths than for diffusion. Finally, $D\tau_R/\langle S^2 \rangle$ has an n' regime with $\epsilon = 0.1$ or 0.2 regime, depending on the particular distribution of friction constants.

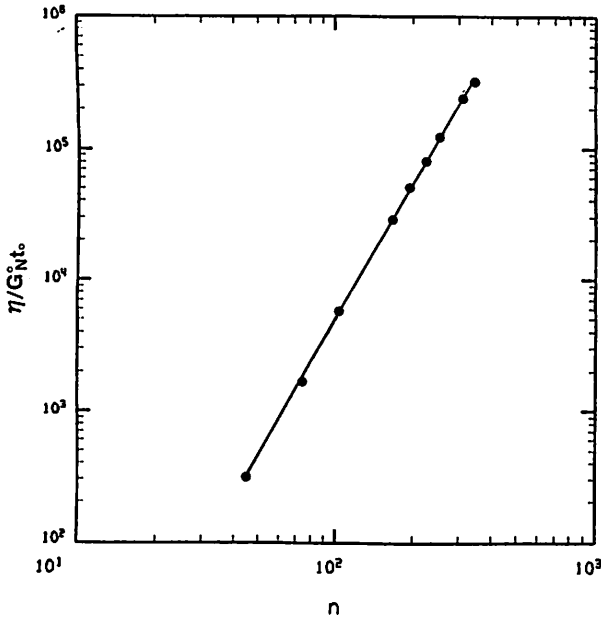


Figure 9. Plot of the shear viscosity in reduced units vs. n . The circles are the calculated values and the solid line is the least square fit through the data giving $\eta \sim n^{3.44}$. G_N^0 is the plateau modulus and t_0 is the time it takes a monomer to diffuse a distance equal to a bond length.

Finally, in Figure 10, log-log plots of $g_{cm}(t)$ and $g(t)$ vs. t are presented for the case of a chain having $n = 255$ with a mean distance between entanglements of 15; $\tau_R = 1.88 \times 10^5$. We point out that τ_R of a Rouse chain of corresponding molecular weight will be 1.3×10^4 . In the top solid curve, there are $t^{1/2}$, t^1 and $t^{3/2}$ regimes in $g(t)$. Clearly, however, these chains do not reptate. Thus, we have demonstrated that the existence of a $t^{3/2}$ regime in $g(t)$ is indicative of some kind of slow down in the dynamics of this system, but no means demands the existence of reptation as the dominant mechanism of polymer motion.

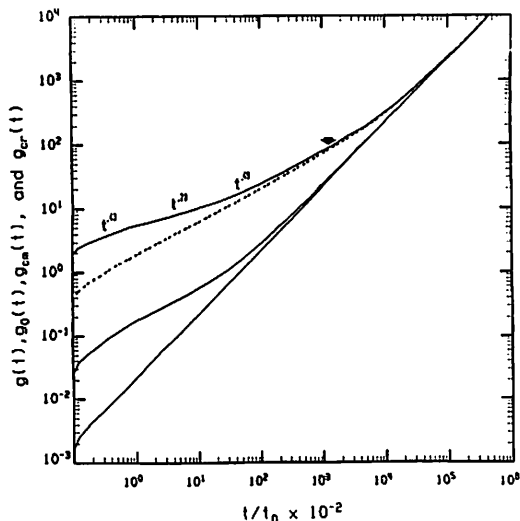


Figure 10. Going from top to bottom in reduced units, log-log plots of the mean square displacement per bead $g(t)$, the mean square displacement per bead if the friction constant were smeared uniformly over the entire chain, $g_0(t)$, the mean square displacement of the center of mass $g_{cm}(t)$, and the mean square displacement of the center of frictional resistance, $g_{cr}(t)$. $n = 255$ and $n_0 = 15$. The arrow denotes $2\langle S^2 \rangle$.

V. SUMMARY

The computer simulations provide no evidence whatsoever that reptation is the dominant mode of polymer melt motion. There is no spatially fixed tube; rather to a very good approximation the character of the long-distance motion is essentially isotropic. Furthermore, there are two relevant distance scales in polymer melts. One is associated with the distance over which static excluded volume effects are screened out and a second, much longer distance, is associated with the mean distance between dynamic entanglements. These dynamic entanglements appear to be rare, and are the result of topological constraints. From an analytical viewpoint, the motion of the chain can be phenomenologically treated as that of a Rouse chain having a few less mobile points, corresponding to the long dynamic entanglements. Theory further indicates that the scaling $D \sim n^{-2}$ is due to the onset of some kind of constrained dynamics and nothing more.

Perhaps in the asymptotic limit chains reptate. If so, the transition to reptation behavior will be transparent to experiment. We have found cases in the simulation where D is proportional to n^{-2} and τ_R is proportional to $n^{3.4}$ and yet these chains do not reptate. Clearly, however, this is by no means a solved problem. One has to now examine

the nature of dynamic entanglements more closely and establish whether, in fact, ultimately there is some kind of moving tube where the long-lived entanglements somehow disengage by a reptating or slipping mechanism of one chain past the other. Refinements of the analytic theory are also required.

Acknowledgement

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