Monte Carlo studies on the long time dynamic properties of dense cubic lattice multichain systems. II. Probe polymer in a matrix of different degrees of polymerization

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The dynamics of a probe chain consisting of $n_P = 100$ segments in a matrix of chains of length of $n_M = 50$ up to $n_M = 800$ at a total volume fraction of polymer $\phi = 0.5$ have been simulated by means of cubic lattice Monte Carlo dynamics. The diffusion coefficient of the probe chain over the range of n_M under consideration decreases by about 30%, a behavior rather similar to that seen in real melts of very long chains. Furthermore, the analysis of the probe chain motion shows that the mechanism of motion is not reptation-like and that the cage effect of the matrix is negligible. That is, the local fluctuations of the topological constraints imposed by the long matrix chains (even for $n_M = 800$) are sufficiently large to provide for essentially isotropic, but somewhat slowed down, motion of the probe, $n_P = 100$, chains relative to the homopolymer melt. The results of these MC experiments are discussed in the context of theoretical predictions and experimental findings for related systems.

I. INTRODUCTION

Since the ingenious ideas of de Gennes[1-3] combined with the elegant formalism of Doi and Edwards[4] to change the way of thinking about the dynamics of multichain systems, a large effort has been directed towards verifying the reptation theory of the dynamic properties of polymeric melts.[5-18] In the context of reptation theory, a most interesting case is the consideration of the dynamics of a "single" (or rather a small volume fraction or concentration) probe polymer of degree of polymerization n_P immersed in a matrix of chemically identical (or similar) monodisperse (or "nearly" monodisperse) polymers of another degree of polymerization n_M. Both situations, of fixed n_P with varying n_M and fixed n_M with changing n_P have been theoretically analyzed in the context of self-consistent reptation theories[19-22] and experimentally examined in a series of studies on carefully prepared, bidisperse polymer melts.[16,17]

In the present work, we have attempted to simulate by means of lattice Monte Carlo (MC) dynamics, the experimental situation where a flexible probe polymer of given n_P is placed in a matrix of exactly monodisperse chains of length n_M. Only the variation of degree of polymerization of the matrix chains is considered, with n_P equal to 100 in all the model systems examined. The value of $n_P = 100$ in the cubic lattice representation of the configuration of the system should correspond to a few times larger degree of polymerization in real polymers due to the fact that the equivalent segment length (or the persistence length) of a cubic lattice chain is small in comparison with the chain diameter. Thus, these model chains are more flexible than typical real synthetic polymers, and it is hoped that $n_P = 100$ corre-

sponds to the case of "long polymers," near the critical entanglement length at the relevant density. The details of the model of the dynamics are exactly the same as described in the preceding paper for monodisperse systems and hereafter referred to as paper I.[23] Both the diffusion coefficient D as well as the terminal relaxation of the end-to-end vector τ_R are estimated for the probe polymer as a function of the length of matrix chains n_M. The results are discussed in the context of the reptation model[1-4,19-22] as well as the recent experimental findings.[16,17] We conclude by summarizing the conclusions that have emerged from our studies of various long chain lattice systems by the method of MC dynamics.

II. MODEL

All the computational MC experiments were performed at a single, total volume fraction of polymer $\phi = 0.5$, where $\phi = \phi_P + \phi_M$ is the sum of contributions from probe polymers and matrix polymers, respectively. The value of ϕ_P was always much lower (by a factor of 32 to 40) than ϕ_M. The summary of the properties of the model systems under consideration are given in Table I. As one can see, the fraction of probe polymers has been kept at a value even lower than that in many real experiments on approximately bidisperse systems.[16,17] Thus, the interactions between the probe polymers (in the cases where there is more than one $n_P = 100$ polymer per MC box) are presumably negligible. Furthermore, the size of the MC box is sufficiently large to prevent the unphysical interaction of the polymers with their replicas resulting from the imposed periodic boundary conditions. The thermal equilibration of the system under consideration has been achieved by the following procedure: Well equilibrated, monodisperse systems from previous studies have been used as the input state. Then, one of the long polymers was divided into pieces each of length $n_P = 100$. For example, the system of $N = 40$ chains of length $n = 800$ as changed into a

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TABLE I. Equilibrium dimensions of a polymer with $n_P = 100$ in various linear chain matrices of length n_M. The total volume fraction $\phi = 0.5$.

| | System $n_P = 100$ | | | |
	$n_M = 50$ $L = 20^a$	$n_M = n_P = 100$ $L = 20^a$	$n_M = 216$ $L = 24^a$	$n_M = 800$ $L = 40^a$
ϕ_P	0.0125	$\cdots$	0.0145^b	0.0125
ϕ_M	0.4874	$\cdots$	0.4844	0.4875
N_P	1	$\cdots$	2	8
$\langle |\mathbf{R}| \rangle^c$	12.4	12.7	12.7	12.7
$\langle R^2 \rangle^c$	178	187	188	185
$\langle |\mathbf{S}| \rangle^d$	5.29	5.42	5.34	5.42
$\langle S^2 \rangle^d$	29.5	30.8	30.0	30.7

^{a} L is the MC box length.
^{b} $\phi = \phi_P + \phi_M$ in this particular case equals $\simeq 0.499$; and the system consists of 31 chains of length $n_M = 216$ plus 2 chains of length $n_P = 100$.
^{c} R is the end-to-end vector.
^{d} S is the radius-of-gyration vector.

system of $N_M = 39$ matrix chains with $n_M = 800$ plus $N_P = 8$ probe chains of $n_P = 100$. In the next step, the reptation algorithm was applied to the entire collection of chains in order to obtain an equilibrium distribution of shorter chains in the MC box. Eventually, the MC dynamic simulation algorithm (the same as used for the further investigation of the dynamics; see Sec. II of paper I) was applied to ensure final equilibration of the system of interest. The above procedure is presumably much more efficient in the cases when $n_P \gg n_M$, than growing the new system from scratch (see Ref. 24) due to the fact that the relaxation of the matrix polymers controls the relaxation of the entire system. Since the presence of some shorter polymers (at constant density) only marginally disturbs the distribution of the longer polymers; the entire equilibration process is relatively fast. On the other hand, when $n_p > n_M$ the above is, of course, not true, but then the entire system becomes small and equilibration is rapid. In the case $n_P > n_M$ the matrix polymers are obtained by the decomposition of a system of monodisperse longer chains, and only the final step of the equilibration procedure was performed since the equilibration of the centers-of-mass distribution over the MC box of the small chains is extremely fast (here $N_P = 1$).

Table I also displays some equilibrium data for the probe chain. Note that there is no systematic dependence of the coil dimensions of the $n_P = 100$ chain on the degree of polymerization of the matrix. This shows that both the probe chain as well as the matrix chains are always significantly longer than the critical length required for the screening of the excluded volume effect. The data of Table I come from an ensemble average collected only during the MC-dynamics run. Of course there exist more efficient methods (for instance, the reptation algorithm) for sampling the equilibrium properties, but this is not the main purpose of the present work. The somewhat lower values of the coil dimensions observed in the case of $n_M = 50$ lie within the range of the statistical error. In the last case only one polymer contributes to the average (however, these averages were collected over a relatively long MC run). The differences in the equilibrium dimensions of the probe chain in the various matri-

ces are rather small; compare, for example, the results given in Table I with the dimensions of a self-avoiding (SAW), five choice, single chain of $n = 100$ (the model of a single chain in an athermal solvent). For this case, $\langle R^2 \rangle_{SAW}$ is about 261 and $\langle S^2 \rangle_{SAW} \cong 41$.[25]

Finally, it should be noted that the model of lattice dynamics and the chain time scale are exactly the same as used previously.[23] The fundamental time unit is the time interval required to attempt one normal two-bond cycle (including a modification of the chain end orientations) plus two attempts at a three-bond permutation, plus two attempts at 90° three-bond kink motions for every single polymer bead, on average, in the system. (See Fig. 1 of paper I for a schematic representation of the allowed moves.) The observed acceptance ratios are very close to those reported for the cubic lattice representation of a monodisperse model melt.[23]

III. RESULTS

Various autocorrelation functions for the probe chain of length $n_P = 100$ were computed from trajectories obtained in a long series of MC runs. The mean square displacement of the center of mass, $g_{CM}(t)$, has been used to estimate the diffusion coefficient D by fitting the simulation results when $g_{CM}(t) > 2\langle S^2 \rangle$ to

$$g_{CM}(t) = 6Dt + c \qquad (1)$$

with c a constant. This corresponds to the pure diffusive regime reached after complete relaxation of the internal chain configuration. Values of D so obtained are shown in Table II, row one. Below $2\langle S^2 \rangle$, there is a regime of faster diffusion reflected in the presence of the constant c in the above asymptotic form. The faster diffusion regime is fit very well by the form $g_{CM}(t) \sim t^a$; the exponent a is less than unity and depends on the matrix chain length n_M. However, as shown in row two of Table II, the variation in a, which presumably reflects the coupling of the center-of-mass motion of the chain to the internal modes of the probe chain and perhaps to the matrix chains, is surprisingly small over the relatively broad range of n_M studied. This suggests a small coupling of the probe dynamics to the matrix, since no qualitative difference between the extreme cases is evident. Sample plots of $g_{CM}(t)$ vs t on a log–log scale together with plots for $g(t)$, the single bead autocorrelation function for $n_P = n_M = 100$ ($n_P = 100$, $n_M = 800$) are given in Fig. 1 in the curves depicted by the solid (open) diamonds and circles, respectively. Again, the average mean-square, single bead displacement $g(t)$ obtained from the average over all the beads of probe chain, does not exhibit any qualitative change on changing the matrix chain length.[1,4,19] There is no indication of a $t^{1/4}$ regime predicted for the monomer $g(t)$ of a reptating chain ($\xi_B = 4$–5 is the static estimate for the blob dimensions).[2] Rather, for $\xi_B^2/3 < g(t) < \langle S^2 \rangle$, $g(t) \sim t^b$, with values of b (displayed in row 3 of Table II) quite close to 1/2. Hence, these systems do not behave like that of a probe chain moving in a fixed cage (for example, a chain in a crosslinked gel, or the MC experiments when all the chains, but one, are partially frozen).[26,27,29-32] On the contrary, the time course of $g(t)$ follows the predictions of the Rouse model very closely. Therefore, one may speculate that the

TABLE II. Dynamic properties of a probe polymer with $n_P = 100$ in various linear chain matrices of length n_M. Total volume fraction $\phi = 0.5$.

	$n_M = 50$	$n_M = n_P = 100$	$n_M = 216$	$n_M = 800$
$D*10^4$	9.44 ± 0.69	9.03 ± 0.21	8.57 ± 0.27	7.04 ± 0.38
a^a	0.958	0.890	0.883	0.825
b^b	0.551	0.522	0.518	0.504
τ_R*10^{-4}	0.567 ± 0.042	0.605 ± 0.029	0.669 ± 0.029	0.797 ± 0.021

[a] Exponent in the t^a regime of $g_{CM}(t)$.
[b] Exponent in the t^b regime of $g(t)$ (see the text).

dramatic change in the time scale of the *global* motion of the matrix polymers as one goes from $n_M = 50$ to $n_M = 800$ has little influence on the motion of the probe polymer. Consequently, the local fluctuations of topological constraints in the high molecular matrix case must be sufficiently large to allow relatively fast disentanglement of the probe polymer, and the cage effect (if indeed it is present) is not felt by the probe chain. Only the effect of changes in the effective local friction constant appear to be present.

In addition to the diffusion coefficient D, we estimated the longest relaxation time for the end-to-end vector of the probe polymer. The autocorrelation function

$$g_R(t) = \langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle / \langle R^2 \rangle \qquad (2)$$

has been used for this purpose. After a short period of fast relaxation, $g_R(t) \sim e^{-t/\tau_R}$. Therefore, τ_R, has been estimated from a semilog plot of $g_R(t)$ vs t over a window of good linear behavior. Again the $g_R(t)$ vs t behavior is similar to that in the monodisperse system. Numerical values of τ_R are given in Table II, row four.

The matrix chain length dependence of the diffusion coefficient D and the terminal relaxation time τ_R of the probe chain are shown in Fig. 2. The change of D in the range of n_M

$= 50$ to $n_M = 800$ is rather moderate. Presumably the $n = 800$ case is close (as far as the probe chain dynamics is concerned) to the $n_M \to \infty$ limit. This conjecture is based on the comparison of the self-diffusion coefficients of $n = 100$ and $n = 800$ polymers at $\phi = 0.5$ which differ by about two orders of magnitude. (D for $n = 800$ is about 2.0×10^{-5}.[23])

Comparison of the present computer studies with the real experiments of Antonietti *et al.* on photolabeled polystyrene in matrices of various degrees of polymerization[16] and the related experiments of Green *et al.*[13] suggest that our choice of $n_P = 100$ corresponds to a relatively high degree of polymerization, n_P (PS), of real polymers. This very qualitative statement results from mapping the MC results onto the experimental curves obtained for various fixed values of n_P (PS) as a function of changing the degree of polymerization of the matrix. Namely, using the $n_P = n_M$ case from the MC dynamics as a reference state, we compared the relative change of the diffusion coefficient D in the range $n_M = n_P/2$ to $n_M = 8 n_P$. The best agreement is obtained with the highest degree of polymerization studied in Ref. 16 where n_P (PS) $= 960$. A similar value for n_P emerges from comparison with the data of Green *et al.*[13] From the plateau modulus for the polystyrene melt, the critical entanglement
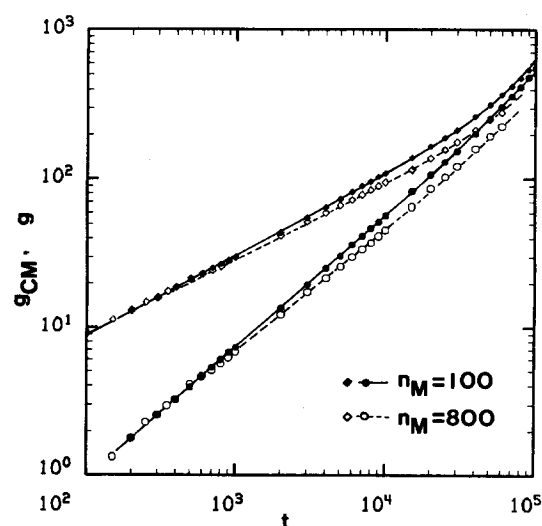

FIG. 1. Comparison on a log–log plot of the single bead autocorrelation function $g(t)$ (diamonds) and the center-of-mass autocorrelation function $g_{CM}(t)$ (circles) vs time for the case of $n_P = n_M = 100$ (solid symbols) and $n_P = 100$, $n_M = 800$ (open symbols), respectively.
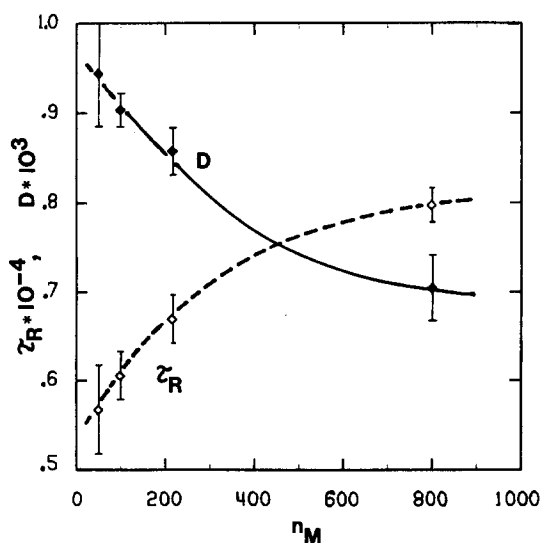

FIG. 2. Matrix chain length dependence of the diffusion coefficient D (solid diamonds) and the longest relaxation time τ_R (open diamonds) of a probe chain of $n_P = 100$. The lines are an arbitrary interpolation of the MC data.

length may be estimated as n_e (PS) = 174. Therefore, the number of entanglements in the real experiment equals 960/174 = 5.5. This value nicely coincides with that estimated for our model system (100/17) = 5.9, at the density $\phi = 0.5$.

These analogies to the real physical system are not, however, as faithful as might appear at first glance. The cubic lattice model melt of monodisperse polymers at $\phi = 0.5$ does not yet exhibit the $D \sim n^{-2}$ behavior when $n_P = n_M = 100$, but rather is in the crossover regime ($D \sim n^{-1.6}$). The onset of "melt dynamics" ($D \sim n^{-2}$) has been seen for the higher degrees of polymerization, namely $n \geqslant 216$. However, real polystyrene melts in range of n(PS) = 960 seem to be well into the $D \sim n^{-2}$ regime.[13,16] The question of how serious is this discrepancy can perhaps be clarified in a series of computational experiments that vary n_P over a wide range of values with fixed n_M. Unfortunately, this kind of simulation appears to be much more expensive due to the necessity of keeping the volume fraction of probe polymers low. Thus, one must run a very long trajectory on a large system to obtain satisfactory statistics.

The aforementioned observations may, in fact, result from some ambiguity in matching the volume fraction of the model chains in a lattice system with the density (and/or temperature) in a real polymer melt. It is well known that the critical chain length of the crossover to $D \sim n^{-2}$ dynamics is temperature dependent, and there is even some evidence that the exponent itself seems to vary with temperature prior to the crossover to long chain dynamics.[16] If one considers the fact that every critical dynamic crossover (with increasing chain length, and/or with increasing temperature) in model lattice systems appears to be somewhat smoother than that obtained from experimental studies,[6-18] there may be some differences in the scaling behavior of D in the vicinity of the cross-over transition. Therefore only *qualitative* agreement with experiment should be concluded.

The character of motion of the probe chain can be analyzed in more detail by decomposing the chain contour migration into the reptation component (down the chain) and the remaining, locally, tranverse displacement. This is done by the method previously described in paper I. First, the chain is transformed into the equivalent smooth path, where every original bead is replaced by the center-of-mass of the blob of $n_B = 17$ beads (the bead under consideration is the middle one for such a blob when one counts down the chain). The value of $n_B = 17$ is a conservative estimate of the static screening length of the excluded volume at $\phi = 0.5$ (see Ref. 23). Second, the middle quarter of the equivalent chains are used to compute the distance of longitudal displacement represented by the shift factor ($i - j$) for a given probe molecule as a function of time. Therefore, the reptation component

$$g_{\parallel}(t) = l_P^2 \langle (\overline{i-j})^2 \rangle , \qquad (3)$$

with the bar denoting the average of $i - j$ over a single chain, the brackets denoting the ensemble average over all the chains. l_P^2 is the mean-square persistence length of the equivalent chain; it is a function of the chain bond length, geometry of the chain, density, and n_B ($l_P^2 = 0.103$). The

remaining component of the motion of the equivalent chain $g_{\perp}(t)$ is not reptation-like and is computed for the middle half of every probe chain.

As shown in Fig. 3(A), similar to a monodisperse melt, the dependence of $g_{\perp}(t)/g_{\parallel}(t)$ on time first exhibits a fast decrease on the distance scale in the range of a blob diameter or less, then monotonically increases, thereby demonstrating the nonexistence of a fixed tube surrounding the chain. Probably some additional information may be extracted from the comparison of log-log plots of $g_{\perp}(t)$ and $g_{\parallel}(t)$ vs t with theoretical predictions. As can be seen in Fig. 3(B), where we plot $g_{\perp}(t)$ and $g_{\parallel}(t)$ for a chain of $n_P = 100$ with $n_M = 800$ there is a significant preference for tranverse, non-reptation-like motion that increases with increasing time. Actually, the $g_{\perp}(t)$ component accounts for most of the
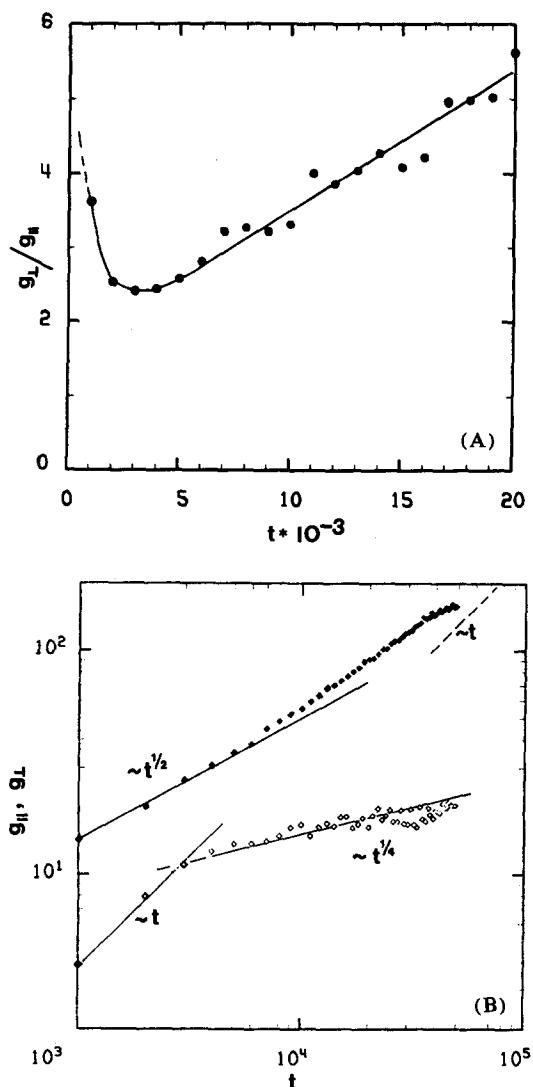

FIG. 3. (A) The course of $g_{\perp}(t)/g_{\parallel}(t)$ vs time of the computer experiment for the case $n_P = 100$, $n_M = 800$. (B) Log–log plot of the mean-square-displacement of the longitudinal component of the beads of the equivalent chain $g_{\parallel}(t)$ (lower curve) and the tranverse component $g_{\perp}(t)$ (upper curve) vs time t for the chain of $n_P = 100$ in a matrix of $n_M = 800$ chains at a total $\phi = 0.5$. See the text for more details.

chain motion. The course of $g_\perp(t)$ is consistent with Rouse-chain, $t^{1/2}$, motion[2] of a single bead over the range $g_\perp(t) < \langle S^2 \rangle$ and then smoothly crosses over into the free diffusion t regime (the center-of-gravity motion asymptote is marked in upper part of the plot).

The motion down the chain is more complicated. At very short distances [note that $g_\parallel(t)$ is considerably less than $g_\perp(t)$ even here] there seems to be free motion of the blob. Since the relevant distance scale is below the blob diameter, the connectivity effect is not yet felt. Hence, due to the averaging procedure we performed over the $n_B = 17$ units of the original chain, the blob moves as a free "chain." At longer times, instead of the $t^{1/2}$ behavior expected for a one-dimensional (in the local curvilinear coordinates) Rouse chain, we observe a much slower motion behaving like t^γ with the approximate exponent $\gamma = 0.25$. The small value of γ reflects the very strong damping of motion of the "defects" down the chain contour, in strong contradiction to the reptation picture.[1-3] A possible explanation is the fact that due to fluctuations of polymer density (on the blob size scale), the hypothetical tube is also partially filled with the segments of other chains. If this is true, then there is no reason to assume that entanglements more effectively slow down the transverse motion in comparison with the longitudinal motion of the entire chain. The substantially slower, in comparison with reptation theory, longitudinal motion, when compensated by the significant lateral fluctuations of the chain contour, may lead to a similar phenomenology for the transport coefficients as provided by reptation theory in spite of a completely different microscopic physical picture of the motion.

To further buttress the above characterization of the probe dynamics, in Figs. 4(A) and 4(B) we present a comparison of the motions of equivalent chains in the monodisperse melt with $n = 100$, and a probe chain of $n_P = 100$ in a $n_M = 800$ melt. The thin curve depicts the equivalent path at zero time and the bold curve depicts the equivalent chain configuration at times close to the terminal relaxation time. Qualitatively, the motion in both cases is very similar. Large scale transverse fluctuations are evident and little memory of the original primitive path is seen. Clearly, in both cases the probe chain is not reptating.

We hasten to add that we cannot exclude the possibility of the onset of reptation for very long chains (large n_P and n_M). However, if this is true then the magnitudes of the various correlation lengths currently predicted from reptation theory must be reconsidered. Certainly, if there is some dynamic (topological ?) limit to the relative extent of the lateral fluctuation of the polymer contour, it must be at least an order of magnitude larger than the static screening length.[27,28]

IV. DISCUSSION

The present MC study of the behavior of a cubic lattice chain composed of $n_P = 100$ lattice "monomers" in various monodisperse matrices, where n_M varied from 50 to 800 and at fixed total volume fraction of polymer $\phi = 0.5$, does not provide any evidence for a transition from Rouse-type chain dynamics to reptation dynamics of the probe chain over a
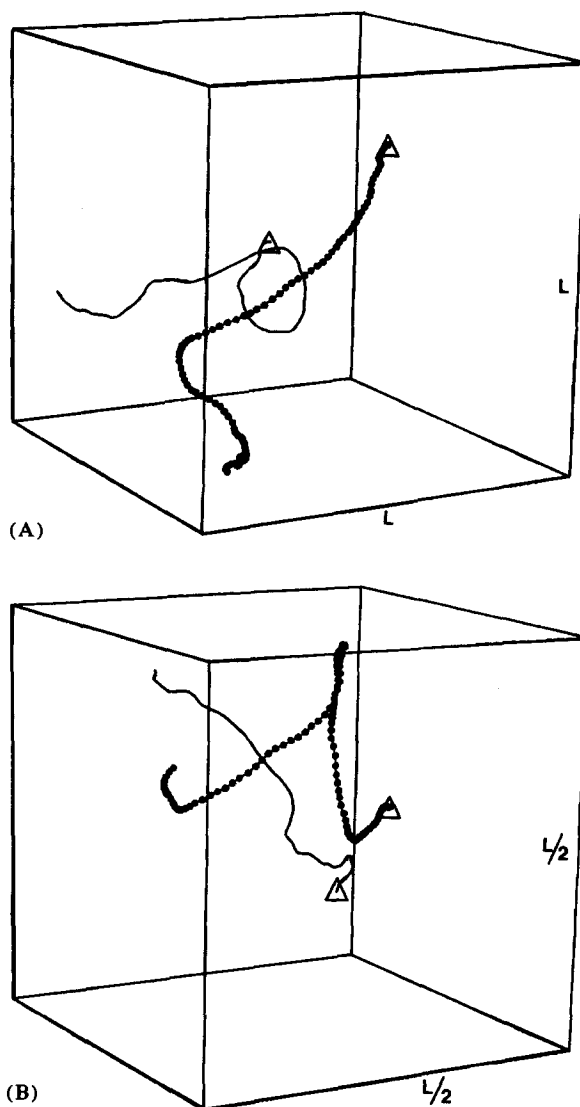

(A)

(B)

FIG. 4. The comparison of the motion of equivalent chains in the monodisperse melt $n = 100$ (A) and in the case of $n_P = 100$, $n_M = 800$ (B). In both cases, the thinner line corresponds to the initial time, the bold curve (formed from filled circles) to the time close to the relaxation time (when $g_R(t)$ decays to $1/e$ of its initial value); $t = 6 \times 10^3$ time steps in (A), and 8×10^3 steps in (B). (A) shows the full size of the MC box, while (B) displays only 1/8 of the MC-box volume in order to maintain the similarity of scales with respect to the $n = 100$ chains.

broad range of n_M. The time course of the single bead autocorrelation function and the center-of-mass autocorrelation function exhibit only a small quantitative variation with the change of chain environment. Since the probe polymer, with $n_P = 100$, is itself sufficiently long to be close to the crossover regime where the dynamics are characterized by $D \sim n^{-2}$, and on other hand, the self-diffusion coefficient of the longest matrix chains $n_M = 800$ is, at $\phi = 0.5$, about two orders of magnitude smaller than that for $n_M = 100$, one might expect quite a strong cage effect. However, this is not observed in the simulations. Moreover, the large ratio of the diffusion coefficients of probe chain to that of matrix for the most extreme case studied here ($n_M = 800$) strongly suggests that it is very unlikely that any further increase of n_M will change the physical picture of the motion of the probe

chain in the melt. Of course, what may happen when one significantly increases *both* n_P and n_M is an open question.

Why chains of length $n_P = 100$ do not reptate is easy to explain if one considers the character of motion of the long chains. As was shown in our studies of the monodisperse melt,[23] while the self-diffusion coefficient in the range $n = 216-800$ at $\phi = 0.5$ is qualitatively consistent with $D \sim n^{-2}$, there is no apparent evidence of a well-defined memory of the chain configuration (a tube) that is required for reptation-like motion to dominate. On the contrary, large lateral fluctuations of the primitive path as a function of time are observed. The amplitude of these fluctuations, and what may be more important, their frequency, are sufficient to create changes in the topology of the chain entanglements which allow the shorter chains to diffuse without following the motion of the matrix chain. The above description is further supported by the observed damping of the down chain motion of the defects characteristic of the reptation mode. As a result, the motion of the probe chain is basically Rouse-like, albeit slowed down. On the other hand, the observed dependence of the probe diffusion coefficient on matrix chain length seems to be in reasonable agreement with experimental data. To some extent, the behavior of the present lattice model may be similar to that deduced from real experiments in the "tube formation"[16–18] regime, with, however, here the complete absence of any evidence for a tube. A more precise idea of the range of n required to go beyond this regime (to see if a longer chain, '"reptating regime" in fact exists) would require simulations on a longer (a series of n_P) probe chains. This is unfortunately beyond our present computational resources. However, present experiments with $n_P = 100$ when combined with the observed lack of tube memory in a melt of $n = 800$ matrix chains strongly suggest the possibility that nonreptating motion of the shorter probe chain in a matrix of longer chains would be expected to persist for significantly larger values of n_P and that perhaps there is no physically realizable regime where reptation is the dominant motion.

The results of the present MC experiments taken together with our previous studies of lattice systems[23,28] of long polymers packed at high density may be summarized as follows.

(1) The experimentally measured features of polymer melt dynamics, namely $D \sim n^{-2 \pm 0.2}$ ($\tau_R \sim n^{3.4 \pm 0.2}$) may be qualitatively reproduced in these computer experiments on well defined lattice models. There is no evidence for the existence of a time scale separation of the longitudinal and transverse motion of the chain contour. Thus, we do not see the onset of reptation as the dominant mode of long wavelength motion.

(2) The computer simulations confirm the microscopic picture provided by reptation theory when the separation of time scales of the test chain and the surrounding matrix is enforced by a fixed, nonrelaxing cage[26,27,29–32] (that is, motion in a frozen or partially frozen environment or a gel).

(3) There is no evidence for reptation of a short chain (whose length is close to the regime of entangled melt dynamics characterized by $D \sim n^{-2}$) in a matrix of long chains. Presumably the MC results are consistent with the existence of what has previously been denoted by the "tube formation" regime.[16] However, unlike the picture provided by reptation theory, neither the probe chain nor the matrix chains reptate. Increasing n_P to values where $D \sim n_P^{-2}$ will further clarify the character of the dynamics beyond the crossover regime. However, further, even qualitative, MC studies of significantly longer polymers would be extremely difficult. Due to the relaxation time scale already reached ($\tau_R \sim n^{3.4}$) in the "crossover" regime, the cost of computation increases at least as n^4 when one takes into consideration the necessary increase in the number of chains. Finally, further real experiments in the crossover regime when D changes from n^{-1} to n^{-2} scaling are called for, and the width and smoothness of the crossover needs to be better established. Based on the MC simulations reported here a smooth rather than abrupt change in the scaling exponent is expected.

(4) This series of *computer experiments on lattice systems* indicates that the situation in a polymer melt (monodisperse, or bidisperse) where the transverse motion of the cage (the surrounding media) is small in comparison to the longitudinal motions of the entire polymer (a fundamental requirement for reptation) is very unlikely.

(5) Regardless of whether reptation subsequently emerges as the dominant motion in the limit of "very long chains," these computer simulations strongly suggest that the various dynamic correlation length scales need to be reconsidered. Over a wide range of chain lengths and densities (in various lattice models studied) estimates of the number of entanglements per chain lead to results which contradict reptation theory[1–4,19–22]; namely, every theoretically calculated critical number of entanglements predicted to be sufficient to observe the onset of reptation appear to be significantly too low, i.e., the MC chains should have long since passed into the pure reptation regime and yet in reality they have not.

Finally, let us exercise the following words of caution. A broad class of simplified mathematical models of polymer solutions and melts comprising lattice and off-lattice approaches seem to be consistent with physical models considered by various theories of polymer dynamics. However, there is always a chance that some important features are missed. For example, one may ask if a preference for local parallelism of semiflexible chains or even the fuzzy domain structure[33] in the polymer melt could result in a kind of local cooperativity of motion which exerts an important influence on longer distance dynamic correlations. Due to the extreme complexity of the polymer many body problem, many of these questions remain to be addressed.

ACKNOWLEDGMENTS

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