Investigations of model polymers: Dynamics of melts and statics of a long chain in a dilute melt of shorter chains

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We report additional results on a simple model of polymers, namely the diffusion in concentrated polymer systems and the static properties of one long chain in a dilute melt of shorter chains. It is found, for the polymer sizes and time scales amenable to our computer calculations, that there is as yet no evidence for a "reptation" regime in a melt. There is some indication of reptation in the case of a single chain moving through fixed obstacles. No statistically significant effect of the change, from excluded volume behavior of the long chain to ideal behavior as the shorter chains grow, is observed.

INTRODUCTION

In a number of previous publications, we have reported on the statics\textsuperscript{1,2} and dynamics\textsuperscript{3,4} of a continuum polymer model. All "beads" in the system interact by a shifted Lennard-Jones potential and \( l \) beads are linked into \( N \) chains by a modified harmonic potential. In this note we report results for two important polymer problems:

(a) diffusion in concentrated polymer systems and

(b) static properties of one long chain in a dilute melt of shorter chains which mimics the behavior in a dilute athermal solution.

It is found, for the polymer sizes and time scales amenable to our computer calculations, that there is as yet no evidence for a "reptation" regime in a melt. There is some indication of reptation in the case of a single chain moving through fixed obstacles. No statistically significant effect of the change from excluded volume behavior of the long chain to ideal behavior as the shorter chains grow is observed.

METHOD

The difficulties in simulating polymer systems, stem from the long relaxation times these systems display. Long runs are needed in order to ensure adequate equilibration. We have employed a reptation Monte Carlo technique\textsuperscript{5} in order to study static properties and to provide equilibrated systems for initializing dynamics calculations. This technique, originally proposed by Wall and Mandel\textsuperscript{6} for lattice systems and extended by Ceperley\textsuperscript{7} and Webman, Lebowitz and Kalos\textsuperscript{8} for continuum models, consists in removing a bead from one end of a chain and attempting to place it in a random direction near the other end of the chain. It is an efficient method for sampling phase space in an algorithm of the Metropolis type. We emphasize that it is not introduced explicitly as a dynamical model. The time dependent behavior is generated by a kind of Brownian dynamics which may or may not exhibit reptation behavior. To be specific, a Smoluchowski equation can be written for the time evolution of the polymer probability density \( f(R,t) \)

\[
\frac{\partial f(R,t)}{\partial t} = D \sum_{i=1}^{l} \nabla_{i} \cdot [\nabla_{i} f(R,t) + \beta f(R,t) V_{i} U(R)],
\]

in which \( D \) is the diffusion constant of a monomer, \( \beta \) the reciprocal temperature and \( U \) the intermolecular potential. The diffusion equation was solved by a Monte Carlo random walk.\textsuperscript{3} The time step was selected to be 0.01 in units of \( \sigma^{2}/D \); distances are measured in units of \( \sigma \). This step size was shown to be appropriate by calculating the end-to-end distance correlation function for trajectories using different time steps. With this model chain crossing is not excluded. However, because of the potential parameters chosen (maximum bond extension 1.95), the probability of such a crossing is very small. We cannot, however, strictly exclude the possibility that this could influence the long time behavior of the results.

DIFFUSION IN CONCENTRATED POLYMER SYSTEMS

The nature of entanglements in concentrated polymer systems is still an open question.\textsuperscript{10} De Gennes\textsuperscript{11} has proposed a reptation model as a way of describing motion in entangled systems. In his original treatment he
considered a single, ideal chain trapped inside a rigid three-dimensional network such as a polymeric gel. The chain could wiggle along inside of the "tube" formed by the fixed obstacles, i.e., a "cage." He concluded that the self-diffusion coefficient $D$ scaled as $l^{-2}$ and the dynamic segment self-correlation function as $l^{1/4}$.

This model has been studied in two dimensions by computer simulation. Ågren used a hexagonal lattice with embedded obstacles to examine the motion of a single nonexcluded volume chain. Dynamics involved letting one or two beads in the chain jump to neighboring positions unless this was forbidden by the obstacles. The difference of the $D$ behavior ($-l^{-3}$) from the reptation prediction was ascribed to the shortness of the runs. Later Dol studied a similar lattice model for longer times and a square lattice and obtained $D \sim l^{-2}$.

The extension of the tube concept to a melt was made by Edwards and Grant, Doi and Edwards, and Klein. In these, a chain was assumed to move through a tube formed by geometrical constraints imposed by neighboring polymers. The shape of the tube changes with time, but this process was found to be much slower than the time necessary for the chain to disengage from the initial tube. Klein, and Klein and Brisco obtained experimental evidence for reptation in an entangled polymer melt using IR microdensitometry. Deuterated polyethylene chains were followed as they moved through undeterated polyethylene. It was found that $D$ for the labeled chain was proportional to $l^{-2}$. In experiments by Hervet, Leger, and Rondel a photochrome was attached to the probe chain and $D$ was obtained by forced Rayleigh scattering. De Gennes' prediction of the concentration dependence ($D \sim C^{1/3}$) was verified. However, Richter, Bäumgartner, Binder, Ewen, and Hayter found no evidence of reptation when they obtained the dynamic structure factor both by neutron spin-echo techniques and by Monte Carlo computer simulation. Their results were in qualitative agreement with the Rouse model.

We have investigated the nature of diffusion in concentrated polymer systems by monitoring the positions of individual beads and the center of mass. Let $R_i^k(j)$ be the position of the $i$th bead on the $k$th chain at time $j$. Then the center of mass of the $k$th chain at time $j$ $R_k^c(j)$ is given by

$$ R_k^c(j) = \frac{1}{N_k} \sum_i R_i^k(j). $$

(2)

Also the center of mass $\langle \Delta R_k^c(t) \rangle$ and segment $\langle \Delta R_k^s(t) \rangle$ self-correlation functions are defined by

$$ \langle \Delta R_k^c(t) \rangle = \frac{1}{N_k N_c} \sum_{i,j} \sum_{t} (R_i^c(j+t) - R_i^c(j))^2 $$

(3a)

and

$$ \langle \Delta R_k^s(t) \rangle = \frac{1}{N_k N_c} \sum_{i,j} \sum_{t} (R_i^s(j+t) - R_i^s(j))^2, $$

(3b)

where $N_k$ is the number of time steps the data is averaged over and $N_c$ is the number of chains.

The models were modified so as to cause the simulations to behave in particular ways. First, we set potential parameters appropriate for generating behavior characteristic of a Rouse chain. An excluded volume single chain is a natural behavior of the model, as is a melt. A cage can be generated by freezing all but one chain.

A Rouse chain was created by dropping the Lennard-Jones potential terms and setting the maximum bond extension to infinity. In the units defined in Ref. 1, we kept $k$ (the spring constant) as 20 and the temperature as 10. The self-correlation functions of the Rouse chain are presented in Figs. 1, 2(a), and 2(b).

In Figs. 2(a) and 2(b) "middle beads" refers to quantities obtained by averaging over the middle half of the chains. Improvement of statistics requires averaging over a number of beads. In doing so it is important to avoid the effect of known edge effects. Naturally, no beads are omitted in computing the center of mass. The time dependence of the functions were determined from log-log plots and exponents read from those are listed in Table I.

The single particle diffusion has three time regimes. At short times, before neighboring beads have moved as much as the bond separation, one can show from Eq. (1) that $\langle \Delta R_k^c(t) \rangle = 6Dt + O(t^2)$. At intermediate times the Rouse model predicts proportionality to $t^{1/2}$. This is the regime in which the correlation of nearest neighbors has relaxed from its initial configuration but the center of mass has diffused less than a radius of gyration. At longer times, the single bead motions will be dominated by the center-of-mass motion and $\langle \Delta R_k^c(t) \rangle \sim (6D/t)^{1/2}$. For our realizations of a Rouse chain, the
measured exponents, 0.54 and 1.06 for the segment and center-of-mass diffusion, respectively, are in good agreement with theoretical predictions for the Rouse model.

Single, excluded volume, chain data were available from a previous study. The results are contained in Figs. 1 and 2 and Table I. The \( \langle \Delta R_z^2(t) \rangle \) exponents are consistent with the \( t^{1/2} \) law and the \( \langle \Delta R_z^2(t) \rangle \) exponents are consistent with the \( t^{3/2} \) law except for the small 5 unit chain. For chains of this size, the center of mass diffused several times the radius of gyration in the total time shown. Hence, the exponent of the segment correlation is between 1/2 and 1. The other chains (\( t \geq 10 \)) all fall essentially on the same curve with an exponent close to 1/2. So in the longer chains, the diffusion of the central beads is independent of the length of the chain within the time scale shown in Fig. 2. Single particle diffusion is not yet dominated by the center-of-mass motion and the results are therefore typical of very long chain. The slopes of the center-of-mass curves give \( D \) proportional to \( t^{1} \) (the Rouse result).

Runs involving a melt were started from our previously equilibrated states. These results are presented in Figs. 3–6 and Table II. Exponents at densities 0.1 and 0.5 are very similar to those obtained for the single chain. However, at the higher density, there seems to be a decrease in the exponents as the chains lengthen. In both cases, \( D \) is still proportional to \( t^{1} \). Again, we note that the segment correlation function for the 5 unit chain displays the influence of the center-of-mass motion. In Figs. 4 and 6 there is a crossover from one linear regime to another. The exponent changes from 0.70 to 0.82 at density of 0.1 and from

### Table I. Graphical fit of data to \( \langle \Delta R_z^2(t) \rangle = b(t)^{\alpha} \) (\( t \) = center of mass or segment) for the single chain results: Rouse and excluded volume. \( T \) is the total simulation time (in units of \( \sigma^2/D \)).

<table>
<thead>
<tr>
<th>( I )</th>
<th>Center-of-mass exponent</th>
<th>Segment exponent</th>
<th>( T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 (Rouse)</td>
<td>1.06</td>
<td>0.54</td>
<td>1250</td>
</tr>
<tr>
<td>5</td>
<td>1.01</td>
<td>0.76</td>
<td>5000</td>
</tr>
<tr>
<td>10</td>
<td>0.96</td>
<td>0.59</td>
<td>5000</td>
</tr>
<tr>
<td>20</td>
<td>1.02</td>
<td>0.60</td>
<td>7500</td>
</tr>
<tr>
<td>33</td>
<td>0.94</td>
<td>0.54</td>
<td>10000</td>
</tr>
<tr>
<td>48</td>
<td>0.96</td>
<td>0.58</td>
<td>110000</td>
</tr>
</tbody>
</table>

0.67 to 0.90 at density of 0.5. The time that the chain of length 50 was run is considerably shorter than required (by a factor of 2–10) for its center of mass to diffuse a multiple of the radius of gyration. Thus, the time dependence of the correlation function given in Table II may not yet be indicative of its long time behavior.

We have also examined the case of the motion of one chain through a “frozen” network of neighbors which we call a cage model. Using an equilibrated configuration of $M$ chains, one chain is allowed to diffuse through the matrix formed by the others. The results are illustrated in Figs. 7 and 8 and Table II. We have tested the results by averaging over several different cage configurations. At the lower density of 0.1, the exponents are very similar to the single chain and melt cases. This is clearly seen in Figs. 3 and 4. However, at a
TABLE II. Graphical fit of data to $\langle \Delta R(t) \rangle = b(t)^{1/2} \rho^{\alpha} \mu$ (where $\mu$ = center-of-mass or segment for the No. 1 melt and cage runs at $\rho = 0.1$ and 0.5) $T$ is the total simulation time (in units of $a^2/D$). Numbers in parentheses give the exponent values after crossover. Different cage configurations were generated by 1500 reptation steps.

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$l$</th>
<th>$N$</th>
<th>Center-of-mass exponent</th>
<th>Segment exponent</th>
<th>$T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5</td>
<td>25</td>
<td>0.98</td>
<td>0.70 (0.82)</td>
<td>250</td>
</tr>
<tr>
<td>0.1</td>
<td>10</td>
<td>20</td>
<td>0.96</td>
<td>0.66</td>
<td>250</td>
</tr>
<tr>
<td>0.1</td>
<td>20</td>
<td>20</td>
<td>0.97</td>
<td>0.64</td>
<td>250</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>50</td>
<td>0.92</td>
<td>0.67 (0.90)</td>
<td>250</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>25</td>
<td>0.91</td>
<td>0.60</td>
<td>250</td>
</tr>
<tr>
<td>0.5</td>
<td>20</td>
<td>25</td>
<td>0.88</td>
<td>0.56</td>
<td>150</td>
</tr>
<tr>
<td>0.5</td>
<td>50</td>
<td>20</td>
<td>0.86</td>
<td>0.55</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>cage</td>
<td></td>
<td>0.93</td>
<td>0.58</td>
<td>2500</td>
</tr>
<tr>
<td>0.5</td>
<td>10</td>
<td>25</td>
<td>0.60</td>
<td>0.39</td>
<td>2500</td>
</tr>
<tr>
<td>0.5</td>
<td>20</td>
<td>25</td>
<td>0.60 + 0.05</td>
<td>0.36 + 0.02</td>
<td>2500</td>
</tr>
<tr>
<td>0.5</td>
<td>32</td>
<td>16</td>
<td>0.62</td>
<td>0.37</td>
<td>2500</td>
</tr>
</tbody>
</table>

density of 0.5 even a chain of 10 beads has a slower motion (see Figs. 7 and 8, and Table II) at this density $D$ is found to be proportional to $t^{1/2}$. It has been conjectured by de Gennes that the reptation tube has a radius $d = (\rho a)^{1/2}$ where $\rho$ is the system density and $a$ the monomer diameter. In our model $a = 1$, $d(\rho = 0.1) = 3.16$ and $d(\rho = 0.5) = 1.41$. Hence, the tube through which the chain can move is very narrow at our higher density.

As a chain moves through a tube within fixed obstacles the "hole" left at one end remains available while an opening at the other end may or may not exist. This effect slows the diffusion by an amount which depends on the ratio of bead diameter to chain length.

![Image](https://example.com/figure7.jpg)

FIG. 7. The center-of-mass self-correlation function for the cage.

![Image](https://example.com/figure8.jpg)

FIG. 8. The segment self-correlation function for the cage.

Our results agree with the recent work of Bäumgärtner and Binder. They used freely jointed, rigid link, Lennard-Jones chains and introduced dynamics by allowing for stochastic rotations of chain bonds. They found Rouse behavior for single chains and for a melt, and reptation behavior for a chain moving in a frozen network. Their calculations used chains with 17 beads, (segment length = 2.5$\sigma$) and densities of 0.17 and 0.70 (expressed in our units). Moreover, they explicitly excluded chain crossings. The combination of dynamic rules which favor motions perpendicular to the chain axis, explicit geometrical constraints, and larger link lengths (our segment length is 1.2$\sigma$) make entanglements more likely in their model than ours. We suspect that these features are responsible for the clear reptation behavior found in their cage study. However, even at a high density of 0.70, they did not find reptation behavior in the melt.

ONE LONG CHAIN AMONG SHORTER CHAINS

Flory and de Gennes and Joanny, Grant, Turkevich, and Pincus have all studied the end-to-end distance $R_N$ of one long chain of $N$ units immersed in a solution of shorter chains, each with $P$ units. They found that when $P$ increases beyond $N^{1/2}$, $R_N$ crosses over from an excluded volume behavior ($R_N \sim N^{1/2}$) to an ideal behavior ($R_N \sim N^{1/3}$). Neutron scattering experiments by Kirste and Lehner indicate that a long chain will change from an expanded size to its theta point size as the number of units on the smaller chains increases to the number on the longer chains. We have examined this effect by using our reptation Monte Carlo technique on systems containing one long probe chain immersed in different sized polymer hosts.
TABLE III. The mean square end-to-end distance ($R^2$) and radius of gyration ($S^2$) for different densities. Systems 1, 2, 3, and 8 have one long chain in a melt of short chains. Systems 4, 5, 6, 7, 9, and 10 contain only one type of chain (see Ref. 1). NEQ and EQ are the number of equilibration and equilibrium steps in $10^5$ per chain.

<table>
<thead>
<tr>
<th>System</th>
<th>$l$</th>
<th>$N$</th>
<th>$R^2$</th>
<th>$S^2$</th>
<th>NEQ($10^5$)</th>
<th>EQ($10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32</td>
<td>1</td>
<td>89.55 ± 2.38</td>
<td>14.01 ± 0.42</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>5</td>
<td>48.66 ± 0.95</td>
<td>7.92 ± 0.12</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>32</td>
<td>1</td>
<td>88.82 ± 2.89</td>
<td>14.06 ± 0.24</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>20</td>
<td>7.42 ± 0.02</td>
<td>1.35 ± 0.01</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>1</td>
<td>218.05 ± 13.49</td>
<td>35.28 ± 1.68</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>10</td>
<td>7.46 ± 0.06</td>
<td>1.35 ± 0.01</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>25</td>
<td>7.35 ± 0.06</td>
<td>1.34 ± 0.01</td>
<td>6</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>20</td>
<td>50</td>
<td>49.50 ± 0.54</td>
<td>7.93 ± 0.07</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>9</td>
<td>32</td>
<td>10</td>
<td>88.58 ± 2.73</td>
<td>14.07 ± 0.25</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>70</td>
<td>15</td>
<td>217.99 ± 2.99</td>
<td>35.44 ± 0.25</td>
<td>180</td>
<td>180</td>
</tr>
</tbody>
</table>

The results are presented in Table III along with data on previously studied homogeneous systems. At the lower density of 0.1, there is no change in either the end-to-end distance ($R^2$) or the radius of gyration ($S^2$). At the higher density, when the degree of polymerization of the small chain (5) is less than the square root of the degree of polymerization of the large chain (5.37), there is a change. The disagreement, is 1.36 standard errors of the difference, not statistically significant.

Clearly by our current methods we can only check the single long chain, dilute region where the reduced volume fraction $\phi_p$ defined by Eq. (23) of Ref. 28, is smaller than one. The homogeneous 70 bead polymer system has a ($R^2$) which itself has not reached the ideal Flory regime, i.e., it is already somewhat expanded. To the extent that our 70 bead chain has conformed to the Flory prediction our mixture results agree with the theoretical predictions.

CONCLUSIONS

There is some evidence for reptation in fixed hosts and very slight evidence for the crossover behavior in ($R^2$) and ($S^2$). One needs to look at much longer chains at higher densities in order to clarify the effects. But when one considers that the Brownian dynamics runs for $l = 50$, $N = 20$ at $p = 0.5$ required lengthy calculations and that the relaxation times scale as $N^2$, one concludes that it is unlikely that such effects can be tested on the computing machines we currently use. We appear to be approaching the results obtained in Ref. 25 for the cage model. We have also checked the predicted conformations of dilute, polydisperse polymer solutions.

Note added in proof: K. E. Evans and S. F. Edwards, J. Chem. Soc. Faraday Trans. 2 77, 1891, 1929 (1981) have reported on their computer simulations of a single Rouse chain moving through a three-dimensional network of obstacles. The reptation predictions were confirmed. In addition, they examined the static properties of a "primitive" chain and obtained excellent agreement with theoretical calculations. Finally, they combined these two studies to show that the primitive chain model can be applied to polymer dynamics.

ACKNOWLEDGMENTS

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6D. Ceperley (private communication).