chemical shift. Also in this case, the linear relationship was observed. Thus the complexation of K^+–PEO must be associated with the preferential solvation similar to that of Na^+–PEO. The effect of the cations is shown in Figure 7. The slope of the linear relationship in the K^+–PEO system was smaller than that in the Na^+–PEO system. K_0 of Na^+–PEO was larger than that of K^+–PEO in NM, while the situation is reverse in AN. This may be explained as follows. The ionic radius of Na^+ is smaller than that of K^+, so that the ion–dipole interaction of PEO with Na^+ is stronger than that with K^+. Therefore, in low-donicity NM where the interaction between cation and solvent is small, the interaction of PEO–Na^+ is stronger than that of PEO–K^+. On the other hand, Na^+ is more solvated than K^+ in high-donicity solvent, so that the interaction between PEO and Na^+ becomes weak. As the result of this ion solvation effect, K_0 of Na^+–PEO is smaller than that of K^+–PEO in AN.

Conclusion

The solvent effect of the complexation between PEO and alkali-metal ions was quantitatively correlated with the dielectric constant and the donor number using binary solvent mixtures. The strength of the complexation was found to be mainly governed by the donor number. The cation size effect is also explained from this viewpoint.

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Relaxation in Bead-Jump Polymer Simulations

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ABSTRACT: A new algorithm for the generation of equilibrium configurations of polymers is described. The algorithm involves nonlocal moves and is suitable for end-restricted polymers. It is shown to reproduce the correct equilibrium properties of both ideal and self-avoiding polymers. A naive analysis shows that the equilibration time τ for this algorithm should scale with the polymer length N as $\tau \propto N^2$, with the time measured in terms of the computer steps. Simulations in one, two, and three dimensions indicate that the dynamics is considerably slower than expected both for ideal and self-avoiding polymers, although it is still faster than algorithms involving local moves. A novel "stretch relaxation" mechanism is found to be responsible for this anomalous slowness; its origin, however, has not been clearly identified.

I. Introduction

Increasingly, computer simulations are being used to study statistical properties of polymer liquids.[1-3] Certain important properties, such as scaling behavior with molecular weight, may be simulated with very simple models of the polymer chains. Indeed for such properties, any type of self-avoiding walks with finite mean-square step length is adequate.[4] This has led to a growing interest in how a polymer system may be simulated most efficiently.[5,6] For a dilute polymer liquid the most efficient Monte Carlo algorithm for many purposes is the "slithering snake", or reptation[2,7] dynamics. In this scheme one chooses one of the chain ends at random and transfers a monomer from this end to the other repeatedly. If the transferred monomer touches another, the move is rejected. This scheme applied to an N-bead chain leads to a statistically independent configuration in a computer time of order N^2.

For many situations, however, reptation dynamics is not appropriate. If the system is so concentrated that free-volume effects become important, the time for a successful reptation step may become unmanageably large. In such situations, molecular dynamics[3,8] methods appear to be more practical. Another case where reptation dynamics cannot be used is in polymers whose ends are attached to something. In such cases a common approach[9,10] is to use algorithms involving local moves. In such schemes (which we shall call "local algorithms"), a monomer is chosen at random and is moved to a nearby lattice site while preserving the connectivity of the chain. (Such a move is typically possible for only a fraction of the mono-

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mers.) Relaxation to a new configuration for a chain of average size R now requires on the order of R^2N^2 time steps.[11]

This dynamics is considerably slower than reptation dynamics. Here disturbances are required to diffuse locally along the chain. That is, if a monomer is externally displaced by one unit and the simulation is continued in parallel with both the disturbed and undisturbed chains, the two chains remain identical except for a gradually growing region near the disturbance. The effect of the disturbance cannot relax until this region has expanded to include the whole chain. By contrast, in reptation dynamics the same disturbance relaxes as soon as the end of the chain has reptated to the disturbed site. In the local schemes beads are moved only locally; in the reptation scheme they are moved globally.

Recently, some new schemes involving nonlocal moves have been introduced. One is the global pivoting scheme originally introduced by Lal,[12] independently rediscovered by MacDonald et al.,[13] and extensively analyzed by Madras and Sokal.[5] In this scheme a site of the chain is chosen at random and the entire chain segment beyond that site is rotated rigidly by, e.g., 90 deg, so that the rotated section again fits on the lattice. For self-avoiding chains, the monomers of the rotated section are then checked for contacts with the unrotated section. If there are any contacts, this move is rejected. The global properties of the chains, such as the radius of gyration or the end-to-end distance relax extremely rapidly; computer time of $O(N)$ is enough to relax these properties for ideal chains. The constraint of self avoidance merely increases this time approximately by a factor of $N^{0.2}$. The detailed (local) structure of the chains relaxes more slowly by an additional factor of N. Thus, for these properties, this scheme is slightly slower than the slithering snake algorithm. Furthermore, if one starts the simulation with an unequilibrated configuration, at least $10N^2$ steps are needed to reach an equilibrated one. Nevertheless, this is an extremely rapid algorithm applicable for many purposes.

Another scheme preserves the global quality of the moves without moving an extensive fraction of the chain at each step. This "bead-jump" scheme involves removing a monomer at a site chosen arbitrarily and then inserting it at another arbitrary point. A method similar to this bead-jump dynamics was used by Pakula[14] to simulate a polymer melt. A grandcanonical version was studied extensively by Caracciolo and Sokal.[6,15] Our aim here is to show that this method is an efficient and reliable one for simulating polymer chains with constrained ends. We exhibit a way of implementing the procedure that satisfies detailed balance. We find that by several measures the equilibration time is on the order of $N^{1/2}$ faster than that in local algorithms. The absolute relaxation times for the chain lengths we studied were 1 order of magnitude faster using the bead-jump method. We check that the bead-jump method reproduces the same chain statistics as the local methods.

The paper is organized as follows. After defining the process and showing that it satisfies detailed balance, we estimate by various simple arguments that the relaxation time should be on the order of N^2 as in reptation. These arguments assume that the removed and inserted beads move independently. We point out a defect in this assumption, which may lead to a retardation in the relaxation. Then we present the simulation data. We find that the relaxation time indeed increases more rapidly with N than the simple arguments predict. The discrepancy persists in one, two, and three dimensions and on two types of lattices. It persists with or without self-avoidance. It persists for ring polymers as well as for simple chains. By studying short-time motion along the chain, we find that the moves occur independently for short times. But as anticipated, the independence of the moves breaks down on a time scale on the order of N. We find that this breakdown is caused by a slow decay of the local stretches formed along the chain. We have not, however, succeeded in understanding this slow decay by analytical means.

II. Definition of Algorithm

The algorithm involves removing an arbitrary monomer and placing it at random somewhere else along the chain. Such a move is not intended to represent any physical motion of the chain. It merely is used as a means of moving efficiently in the configuration space of the chain. When implemented on hypercubic lattices, two or more bond lengths are needed to enable the dynamics.[16] In one and two dimensions we allow nearest and next nearest bonds. In three dimensions, third neighbor bonds are allowed as well.

We start with an arbitrary configuration of the chain with the monomers numbered in sequence from 1 to N. We arbitrarily choose one end of the chain as the beginning. This directionality is used only to define the algorithm. Initially a bond is directed from monomer n to monomer $n + 1$. A "ghost" bond is assumed to connect a fictitious $n = 0$ monomer to monomer $n = 1$. For a ring polymer there is no ghost bond; instead there is a real bond from monomer N to monomer 1. An elementary move is then made in two steps: we choose at random one of the monomers and remove it. The two neighbors of the removed monomer are connected by a new bond. If this bond is longer than the allowed maximum bond length, the move is rejected and the monomer is returned to its previous position, restoring the previous bonds. If the removal is allowed, one then chooses a monomer at random in the range $[0, N]$ (or $[1, N]$ for ring polymers) excluding the removed monomer. One also chooses a neighboring site of that monomer. A neighboring site is defined as being at a distance not larger than the maximum allowed bond length. The removed monomer is placed at the chosen neighboring site and the bond leading from the chosen monomer to its successor is replaced by two new bonds so as to insert a monomer in the chain after the chosen monomer (Figure 1). This procedure is slightly modified if the chosen monomer is the $n = 0$ or $n = N$ monomer of a chain polymer, since no bond is discarded in such cases. The move is rejected when any of the new bonds is of too large a length; the removed monomer is returned to its original place. In addition, when the chosen neighboring site is already occupied by another monomer, the move is again rejected to ensure self-avoidance for nonideal chains.

We note that the whole move is canceled if any one of its steps violates a rule. This assures detailed balance, since the probability of a single move that leads from configuration A to any other one, B, is the same as the one leading from B to A. For the example shown in Figure 1 (or between any two configurations on a square lattice), this probability is $1/(8N^2)$. Furthermore when a move is unsuccessful, the unchanged configuration of the polymer is included in the sample space for averaging of the static quantities an additional time. For dynamical studies, the time is incremented for such moves also. This is needed to ensure an unbiased sampling of equilibrium configurations.

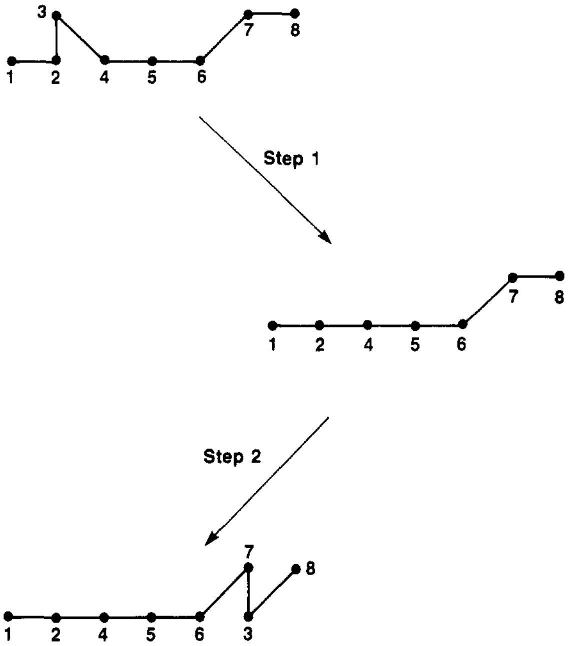

Figure 1. Elementary move of the algorithm. In step 1, monomer 3 is chosen to be removed. A new bond is formed between monomers 2 and 4. In step 2, monomer 3 is placed at a randomly chosen neighboring site of monomer 7. The bond between monomers 7 and 8 is replaced by a bond between 7 and 3, and another one between 3 and 8.

III. Relaxation Time Estimates

One crude measure of the relaxation time is the time for the chain to diffuse its own diameter. In the bead-jump dynamics, the center of mass moves a distance on the order of R/N in a move. If the moves are independent, the center of mass should move a distance on the order of the radius of gyration R_g in a time on the order of N^2, as in reptation dynamics. An independent configuration should be reached within this time.

To estimate the relaxation time more convincingly, we modify the simulation by fixing the end bead of the chain. Although this bead may not jump, it will still lose its position at the end when another bead is added to its free end. Because of these additions and removals, the fixed bead moves randomly up and down the chain. At length, it has moved to the opposite end of the chain. Evidently at this point the chain is in a configuration statistically independent of its initial state. Thus the relaxation time is the transit time for the fixed bead.

When the bead is at a fractional distance f from one end of the chain, the probability that its position moves on the next bead-jump is $f(1-f)$. Over most of the chain this probability is of order unity. Thus, if the moves are independent, the transit time is on the order of N^2, in agreement with the more naive estimate above. The random-walk motion of the fixed bead is slowed substantially near the ends because the factor $f(1-f)$ becomes small there. But this slowdown is not sufficient to alter the scaling for the mean transit time.

We now examine our assumption that the moves of the chosen bead are statistically independent. This assumption must be valid for early times. If, e.g., the fixed bead is initially at the center of an equilibrium chain, the first two attempted moves of the fixed bead must be essentially uncorrelated. There can be no correlation unless the two corresponding bead jumps involve the same vicinity of the chain. Here the "vicinity" of a bead means those beads either chemically or physically adjacent to it. Evidently, only a limited number of beads may be in the vicinity of a bead, regardless of the chain length N. Since the removals and insertions are sampled uniformly, the chance that the second move is affected by the first is on the order of $1/N$ and may be neglected.

As the simulation proceeds, the chance that a jump occurs in the vicinity of a previous jump increases. To analyze the effects to be expected, we imagine making a number of bead jumps from ahead of the fixed bead to beyond it, with no jumps within the section ahead of or beyond the fixed bead. After these jumps, the two sides are no longer in equilibrium with each other. This produces two effects. Some bonds in the first part of the chain are "stretched". Removal from a site next to such a bond is more likely than average to be disallowed, because it would result in too great a distance between succeeding beads. The probability of a successful removal next to a stretched bond is smaller than average by a factor of order unity. The vicinity of an inserted bead is similarly affected. Such a bead can always be removed; there is a smaller than average probability that removal will be disallowed. With self-avoidance imposed, there is a further effect. It is more likely than average that a subsequent insertion next to the bead in question will fail because the insertion site is occupied. We term such a site "overfull"; the probability of removal from such a site is increased by a factor of order unity over that of a generic site. The probability of insertion there is reduced by a comparable factor.

These perturbations of the chain eventually affect the random motion of the fixed bead. Again we imagine allowing only bead jumps from one side of the fixed bead to the other. But now we allow both directions equally. Still, after a small number of moves k, there is a net displacement of the fixed bead of order $k^{1/2}$. This implies that there are on the order of $k^{1/2}$ stretched bonds on one side of the fixed bond and $k^{1/2}$ overfull sites on the other side. This leads to an increased probability that the next move will be back toward the center. The walk is biased.

The amount of bias is proportional to the probability that a stretched or overfull site will be selected, i.e., $k^{1/2}/N$. Such a bias acting over k steps would result in a displacement on the order of $k^{3/2}/N$. This becomes comparable to the displacement $k^{1/2}$ of the random-walk motion when k is on the order of N.

If the bias from stretching and overfilling remains on the order of the displacement from the center, then this displacement is confined to a region on the order of $N^{1/2}$. This is the same type of bias one would encounter in a simulation of a particle at position x confined in a harmonic potential x^2/N. Thus in our polymer simulations, the fixed bead cannot move throughout the chain unless the stretching and overfilling can relax.

We now investigate the relaxation of stretching and overfilling. We imagine an equilibrium ring chain of $N+1$ beads, from which a single bead has been removed to form a stretched bond. Then as the bead-jump process proceeds, the bias resulting from this stretch will ultimately relax. A substantial fraction of this bias relaxes in a time on the order of N. To see this explicitly, we analyze the special case of a one-dimensional ring polymer without self-avoidance. Each succeeding bead is at the same position as its predecessor or is one step to the left or right. Now, the two beads adjacent to a bond of length 1 are harder to remove than average. If such a bead is selected for removal, there is a one-in-three chance that it will not be removable. This is the probability that this bead lies between two bonds in the same direction. A bead next to a bond of length zero may always be removed. Similarly, adding a bead at a bond of length 1 is forbidden with probability 1/3 relative to adding one to a bond of length 0.

Most of the effect of an extra bond of length 1 dies out in on the order of N steps. If one of the adjacent beads is removed, the average change in number of bonds of length 1 is −2/3. Such changes have a probability of $(8/9)N^{-1}$ per time step. If a bead is inserted at the extra bond, then there is a net addition of 1/3 bond of length unity. In view of the $(2/3)N^{-1}$ probability of this insertion, the increase of unit bonds averages $(2/9)N^{-1}$. Evidently, the net effect is to reduce the number of extra unit bonds by a substantial fraction in a time on the order of N.

This reasoning suggests that the stretch relaxes to an arbitrarily small fraction of its initial value in times on the order of N. But we have not been able to show this explicitly. Indeed, we expect some parts of the relaxation to occur on longer time scales. For example, the time required for the effect of the initial stretch to be distributed among all the beads is at least on the order of N^2. We have not succeeded in finding an estimate of how important this time scale is.

A small part of the perturbation lasts until the chain relaxes completely. Thus, if a bead is removed from an equilibrium chain of length $N + 1$, the resulting chain has on average too large a size for its chain length. Until relaxation of the end-to-end distance takes place, there will be a small excess of unit bonds. For every bead removed, the mean-squared end-to-end distance is roughly one square bond length too long as compared to the relaxed state. Even if the chain relaxes into the most random state consistent with this stretch, it must have a small excess of unit bonds. For each bead initially removed, this residual excess is on the order of $1/N$, that is, much less than one in the chain. We show that such a small excess should have negligible effects on our measurements.

We now consider the effect of these relaxations on the stretched and overfull bonds of our fixed-bead simulation. We have seen that a time on the order of N steps is required to make the stretching and overfilling important for the displacement of the fixed bead. We have seen that the majority of the stretch or overfilling present should relax on this same time scale, so that any lack of relaxation should only retard the motion by a finite factor. The residual stretches or overfull bonds have a negligible biasing effect on the fixed bead. Indeed, this bias, given a net displacement k, is the fraction of the stretched bonds, i.e., $(k/N)(1/N)$, so that the bias itself produces a net displacement after t steps on the order of $(k/N^2)t$. This only becomes comparable to the displacement produced by the random walk of the fixed bead for times t on the order of N^2. By this time the fixed bead has explored a finite fraction of the chain. We conclude that the residual stretch cannot influence the fixed bead for times less than the overall relaxation time.

Considering all these effects, we are led to two alternative estimates for the overall relaxation time τ. If we suppose that internal stretching (and overfilling) relaxes in times on the order of N, then this relaxation is not rate-limiting and the scaling of τ should conform to our naive estimates: $\tau \propto N^2$. Alternatively, the stretch relaxation may require times of on the order of $\tau_s \propto N^s$, with $s > 1$. In this case stretch relaxation *is* the rate-limiting process. The effect of this anomalous stretch relaxation on the overall relaxation time can be estimated as follows: On time scales $t < N$, the relative motion of the fixed bead along the chain is diffusive as in our naive estimates ($k^2 \sim t$). Beyond this time scale the fixed bead is confined to a zone of width $\Delta k \sim N^{1/2}$ limited by stretching and overfilling. Equilibrium fluctuations in the stretching and overfilling cause this confinement zone to move randomly along the chain. These fluctuations should have a correlation time on the order of τ_s. Thus we expect the confinement zone to execute random steps along the chain of size $N^{1/2}$ and at a rate τ_s^{-1}. With such steps the whole chain is then explored in a time $\tau \simeq \tau_s(N/N^{1/2})^2 \propto N^{s+1}$.

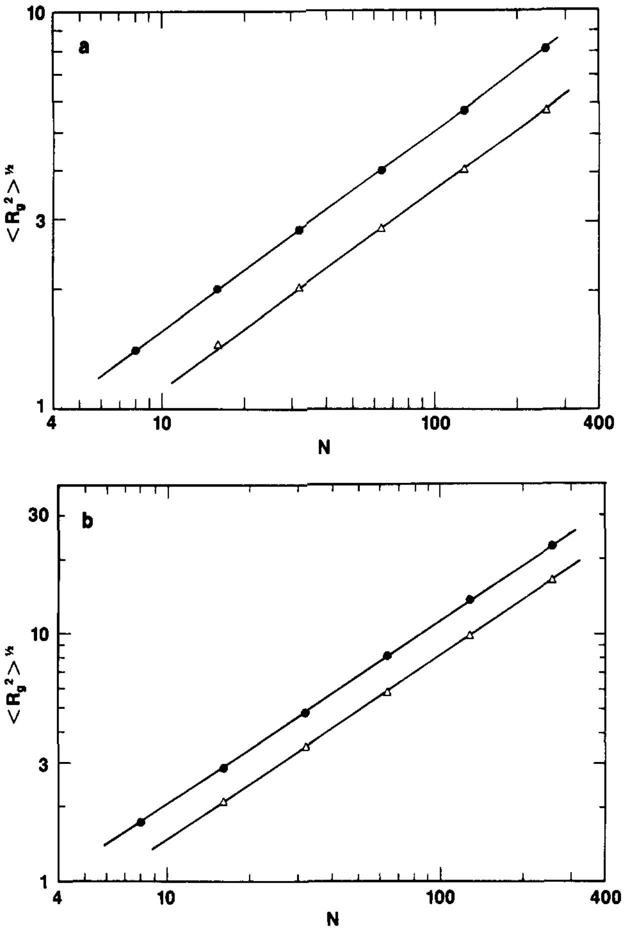

Figure 2. (a) Root-mean-squared radius of gyration as a function of polymer length in two dimensions for (●) ideal chains and (△) ideal ring polymers. The solid lines both have a slope of 0.5. (b) Same as in (a) for self-avoiding polymers. The slope of the solid lines is 0.75.

IV. Simulations

Simulations were carried out in one, two, and three dimensions with and without excluded volume (self-avoiding and ideal walks, respectively). In two dimensions both ring and chain geometries were simulated.

We first present the results for the static properties obtained by our method. Figure 2 shows the root-mean-squared (rms) radius of gyration as a function of the number of monomers, N, for two-dimensional simulations. The results show the expected $\langle R_g^2\rangle \propto N^{2\nu}$ behavior, with $\nu = 0.75$ and 0.50 for the self-avoiding and the ideal cases, respectively. The ratio $\langle R_g^2\rangle_{\text{ring}}/\langle R_g^2\rangle_{\text{chain}}$ for the ideal case is found to be 0.5 for $16 \leq N \leq 256$, in agreement with the exact ratio.[17] The values for the rms radii of gyration were obtained after averaging over the configurations encountered in a run whose length varied between 4000τ for $N = 8$ and 70τ for $N = 256$. Here τ is the relaxation time (number of computer steps to get to an

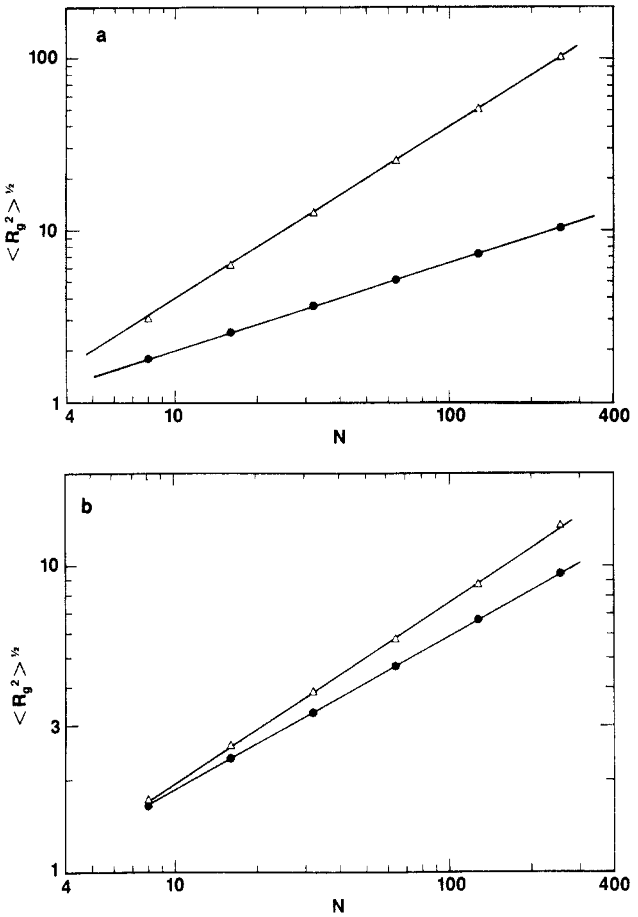

Figure 3. (a) Rms radius of gyration vs polymer length N for (●) ideal and (△) self-avoiding chain polymers in 1D. The slopes of the solid lines are 0.5 and 1.0, respectively. (b) Same as in (a) for 3D chain polymers. The lines have slopes of 0.5 (ideal) and 0.59 (self-avoiding).

independent configuration) that will be quantitatively defined later. Figure 3 presents the same quantity for the 1D and the 3D simulations of chains. The data are consistent with $\nu = 0.59$ and 0.50 for the cases with and without excluded volume, respectively, in three dimensions and $\nu = 0.5$ and 1.0 in one dimension. The statistical errors, which we estimate by averaging over different parts of the run are less than 5% and are within the size of the symbols shown. Despite the relatively short runs, these exponents agree reasonably well with the known values[18] in one, two, and three dimensions.

The relaxation times for our algorithm were measured using two different methods. One of these is to observe the diffusive motion of the polymer during the simulation and identify the time it takes the polymer to diffuse its own radius of gyration as the relaxation time. We emphasize that this motion is not intended to represent the real diffusive motion of the chain; it is being used as a means of estimating the equilibration time of our algorithm. We estimate (see section III) that this time, $\tau(N)$ should scale with the number of monomers as $\tau(N) \propto N^2$. The results, however, show a more complicated behavior.

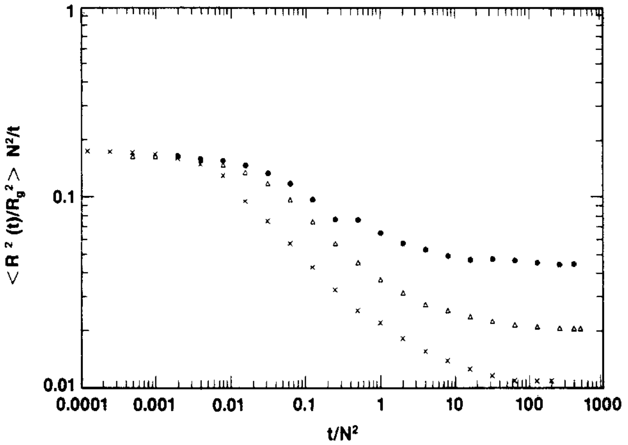

Figure 4. Mean-squared displacement of chains of length (●) $N = 64$, (△) $N = 128$, and (×) $N = 256$ vs time. The ordinate is scaled in such a way that it gives the diffusion constant multiplied by N^2. The time is also scaled by N^2.

We first present the results for two-dimensional chains with excluded volume. Figure 4 shows on a double logarithmic plot the mean-squared displacement, scaled by the radius of gyration squared and multiplied by N^2/t, for three different chain lengths. The time is also scaled by the expected relaxation time, N^2. The mean-squared displacement, $R^2(t)$ is defined as

$$R^2(t) = \langle(\vec{R}_{\mathrm{CM}}(t) - \vec{R}_{\mathrm{CM}}(0))^2\rangle$$

Here, $\vec{R}_{\mathrm{CM}}$ is the position vector of the center of mass and t is the number of attempted moves of the algorithm. (The success ratio, defined as the fraction of the number of the successful moves to the number of all the attempted ones, is a very slowly varying function of the polymer size and saturates for the larger polymers simulated. The variation comes from the fact that the two end monomers are easier to remove and moves involving these monomers have a higher probability to succeed. The effect is almost completely absent in the ring polymers.) The brackets denote the average over different starting states. It can be seen that at very early times and for times $t \gg N^2$, the curves have zero slope, indicating diffusive motion in these two time regimes. Furthermore, at the early times, all three curves converge to the same horizontal line, confirming the expected N^2 dependence of the relaxation time (rather of R_g^2/D). This behavior persists for a very short time and crosses over to a subdiffusive behavior which continues up to times $t \simeq N^2$. At even later times, the motion becomes diffusive again; however, the curves do not overlap. Instead they are displaced from each other by a constant proportional to N. This indicates a relaxation time that scales with the chain length as N^3.

The relaxation times for individual chains are measured from the value of the ordinate at the latter diffusive regime. In fact, the relaxation times are given by $N^2/y(N)$, where $y(N)$ is the limiting value of the ordinate as $t \rightarrow \infty$. Figure 5 shows the relaxation times obtained for chains of length $8 \leq N \leq 256$ and rings with $16 \leq N \leq 256$. Both exhibit a power law behavior, $\tau(N) \propto N^x$, with $x \simeq 3.1$ for both cases, much larger than the expected behavior with $x = 2$.

In order to make sure that the dynamics is not affected by having bonds of two different lengths, we repeated the simulation on a triangular lattice for $N = 32$ and 64 using only nearest-neighbor bonds. The relaxation times found were almost identical with those on a square lattice.

To further investigate the subdiffusive regime, we modified our simulation in the following manner: We designated one of the monomers as "fixed", so that it is never removed. The other monomers were free to be removed and placed elsewhere. The position of the labeled monomer relative to the others performs a stochastic motion

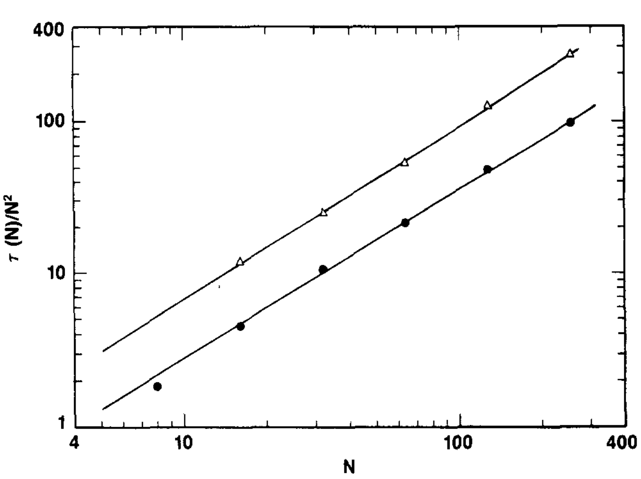

Figure 5. Relaxation times for self-avoiding (●) chains and (△) rings in two dimensions vs the polymer size. The times are scaled by the expected N dependence. The solid lines shown have a slope of 1.1.

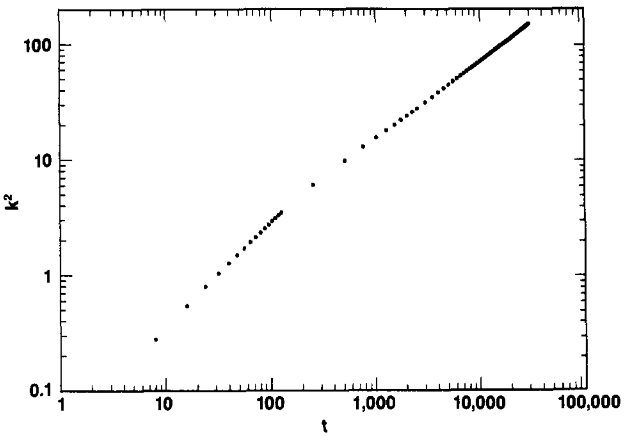

Figure 6. Mean-squared displacement of the relative position of the "fixed" monomer on a self-avoiding chain of length 64 at time t.

in one dimension (along the polymer) with a mean-squared displacement, k^2, that should saturate at $N^2/4$ because of the finite length of the chain. Figure 6 shows this motion for a chain of length 64. Again for very small times, the motion is diffusive. After $O(N)$ steps, a sub-diffusive motion with a slope of approximately 0.67 sets in. Requiring that the curve be continuous at $t = N$, we obtain $k^2 \propto N^{0.33}t^{0.67}$ for this regime. The labeled monomer should have a displacement $k^2 \simeq N^2$ (i.e., move along the whole length of the chain) before a completely independent configuration is reached. This corresponds to a relaxation time $\tau(N) \propto N^{1.67/0.67} = N^{2.5}$. Although this exponent does not agree with the one found from the center of mass motion, both simulations demonstrate a slowing down of the motion after a rapid start. In order to be in accord with our observation that $\tau \propto N^3$, the t exponent should be 1/2 rather than 0.67. It seems likely that this apparent $t^{0.67}$ is a crossover effect.

A second method of estimating the relaxation time is to observe the decay of the autocorrelation of the radius of gyration

$$C(t) = (\langle R_g(t)R_g(0)\rangle - \langle R_g\rangle^2)/(\langle R_g^2\rangle - \langle R_g\rangle^2)$$

We expect the longest relaxation time of the internal modes to have the same N dependence as the diffusive relaxation time. That this is the case is demonstrated in Figure 7, in which $C(t)$ is shown as a function of time for three different chains, with time scaled with $N^{3.1}$. All the $C(t)$ curves follow the same line down to the noise level of the correlations.

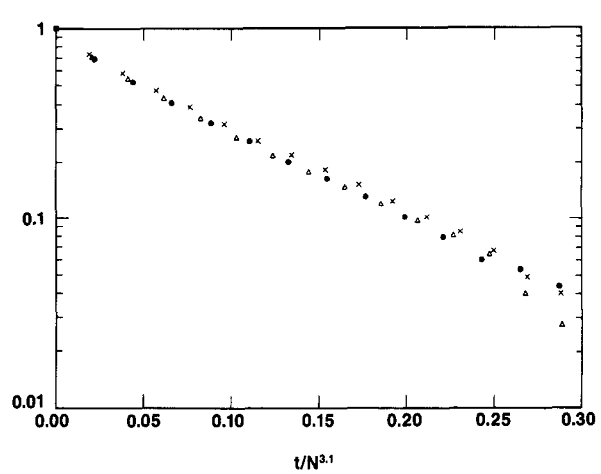

Figure 7. Autocorrelation function of the radius of gyration as a function of time on a semilogarithmic plot. The time is scaled by $N^{3.1}$. The curves for (●) $N = 32$, (△) $N = 64$, and (×) $N = 128$ collapse, confirming the proposed scaling.

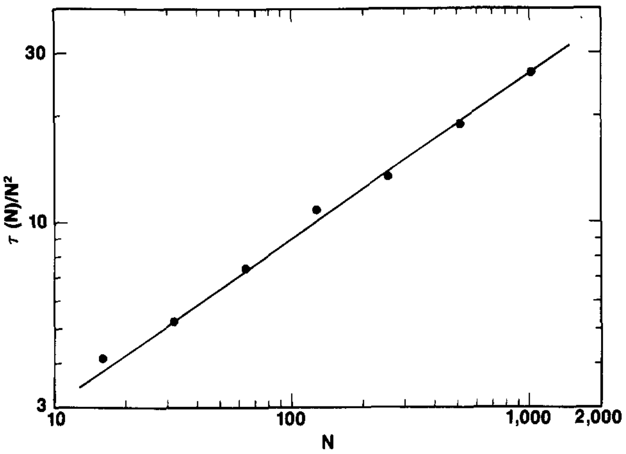

Figure 8. Relaxation times for ideal rings in two dimensions as a function of polymer size. The relaxation times are scaled by the expected N dependence. The slope of the solid line is 0.5.

The relaxation times for the ideal chains and rings exhibit a milder N dependence. Figure 8 shows this time obtained from the diffusive motion of ring polymers with $16 \leq N \leq 1024$. The behavior is consistent with $\tau(N) \propto N^{2.5}$ with no systematic change in the local slope with increasing N. The same scaling behavior is found from the decay of $C(t)$. We also measured the relaxation times for chain polymers of length $8 \leq N \leq 256$. The scaling behavior is identical with the one found for rings. Thus the naive expectation is apparently ruled out both in the ideal and the nonideal polymers.

In order to identify a possible cause for the deviation from the expected behavior, we performed a modified simulation in which an artificial stretch was formed in one portion of the polymer. We then followed the relaxation of this stretch and tried to find the dependence of the relaxation behavior on the polymer length. The simulation was performed in the following manner: We started with an equilibrium configuration of a chain of length N and labeled the monomer at position $N/2$. We then moved n monomers from one side of the labeled monomer to the other, thus forming a stretch on one side and over-filling the other. We then ran the algorithm without moving the labeled monomer and allowing only moves within each of the two sides. However, we counted the at-

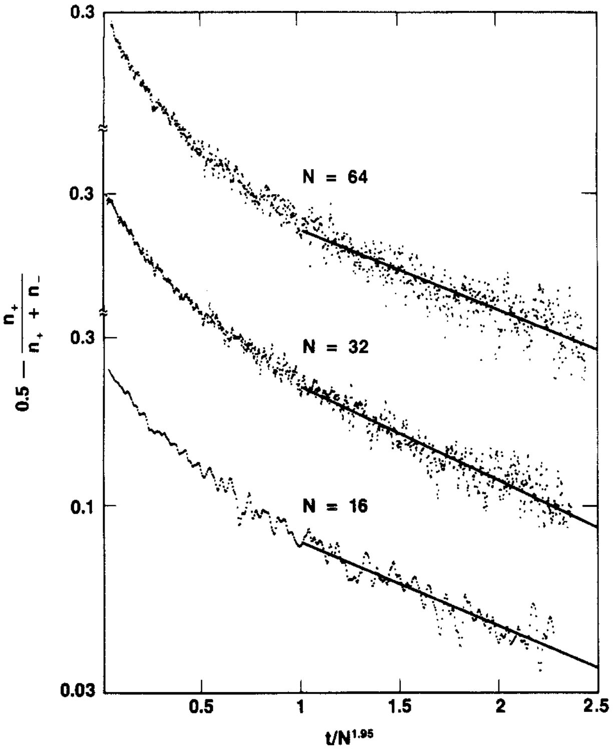

Figure 9. Relaxation of stretch on self-avoiding chains of length N = 16, 32, and 64. n_+ and n_- are the *attempted* moves from the "stretched" and "overfilled" parts, respectively, at time t. The curves are displaced vertically for clarity. Note the logarithmic vertical axis and the scaling of the time. The solid lines are linear fits to the data for $t > N^{1.95}$. They are displayed to emphasize that the curves are roughly parallel for those times.

tempted moves from the overfilled side to the stretched one and vice versa. Initially there will be more attempts from the overfilled side since it is difficult to remove a monomer from the already stretched side. Later, however, both sides will relax their initial distortions, and the frequency of the attempts in the two directions will equalize. Figure 9 shows this deviation from equality as a function of time on a semilogarithmic plot for chains with N = 16, 32, and 64. The points shown are averages over 40 000 runs with different starting configurations for N = 16 and 32 and over 10 000 runs for N = 64. The behavior obviously cannot be described by a single-exponential decay; however, the curves are parallel for longer times when the time is scaled by $N^{1.95}$. This indicates that the stretch relaxes in a time that scales with the chain length in this fashion.

We also calculated the relaxation times through center of mass diffusion for ideal and self-avoiding chains in one and three dimensions. In the range $8 \le N \le 256$, the data are consistent with a power law behavior, $\tau(N) = N^x$ with x = 2.75 and x = 2.95 for the ideal and the nonideal chains, respectively. In 1D we find x = 2.5 for the ideal chains. The linear dependence of R_g on N for the self-avoiding chains makes it difficult to observe the diffusive motion for displacements larger than R_g, but we find x to be at least 3.0 for this case.

V. Discussion

Our algorithm reproduces the correct scaling for the static properties of chain and ring polymers both with and without excluded volume. This suggests that a good statistical sampling was achieved by the algorithm. We assured this point by identifying all the possible configurations of a N = 4 chain on a square lattice (360 distinct configurations) and counting the number of times each of these was visited by the algorithm. We found that all the configurations were equally frequently visited, with a spread in the frequency of each configuration that decreases as the square root of the total length of run.

The relaxation time increases much faster than our estimates for all the cases studied. Our estimates relied upon the assumption that the moves are mutually independent. From our results, however, it is evident that they are correlated in such a way that most of the moves effectively undo the previous ones. This probably has to do with local stresses formed. These stresses are formed (see section III) even when the moves are totally uncorrelated. Unlike uncorrelated moves, which should cause stresses that relax in a time proportional to N, the stresses in our algorithm are found to relax within a time that scales as $N^{1.95}$ (for self-avoiding walks). As stated in section III, this corresponds to an overall relaxation time on the order of $N^{2.95}$, in excellent agreement with the results found by other methods. Numerically, the stretch relaxation times, τ_s fall into the "subdiffusive" region of Figure 4.

Recently Caracciolo and Sokal[6] introduced an algorithm involving moves in which a pair of monomers is locally destroyed or created. This results in an algorithm that is similar to a grandcanonical analogue of the one presented here. Their simulations for the two-dimensional self-avoiding walks give $x = 3.0 \pm 0.4$, very similar to the result we obtain using different methods, x = 2.9–3.1. Their result for the nonreversal random walk, $x = 2.2 \pm 0.5$, is also consistent with our x = 2.5 for random walks.

We believe that our measured results are not inconsistent with the expectations discussed in section III. The short-time motion confirms our prediction of independent bead-jump behavior. This motion is seen in both center of mass displacement R^2 and in the displacement k. It takes place over times up to $O(N)$ steps, as predicted. This time appears to be followed by one in which the motion is subdiffusive, with mean-squared displacement varying as a power of time less than 1. But according to section III, the rms displacement should be constant until the stress relaxation time. We believe that this discrepancy between our predictions and our measurements stems from the shortness of our chains. The apparent sublinear region never extended over more than 1 order of magnitude in R^2 or in k^2.

This apparent sublinear region extends only to times substantially shorter than the final relaxation time. These times are consistent with the stretch relaxation time. Thus, e.g., for N = 64, the end of the sublinear region occurs (see Figure 4) for $t \simeq 10\,000$, while the stretch relaxation time (see Figure 9) for this N is about 4500. For the same N, the relaxation time from the center of mass motion is approximately 90 000. This leads us to identify the subdiffusive region as that in which stretch relaxation is occurring. Further, this hypothesis, together with the measured stretch relaxation time, predicts correctly the final relaxation time τ.

Our results for the behavior of the stretch relaxation, however, cannot be explained by our estimates. Using a model variation of our algorithm in one dimension, we had predicted (section III) that any local stretch that may randomly form should decay substantially within a time on the order of N. We could not show that any longer stretch relaxation times were important. Our simulation results, on the other hand, indicate that some slower relaxation process is important. Thus although we can identify the stretch relaxation as the mechanism responsible for the anomalous slowness of the overall dynamics, we have not been able to elucidate its origin.

An interesting result of our simulations is that the relaxation time for the self-avoiding walks has the same $\tau \propto N^3$ scaling in one, two, and three dimensions. This fits naturally with the explanation that the stretch relaxation requires a time on the order of N^2. The relaxation time exponent for the ideal case seems to increase from 2.5 in one and two dimensions to 2.75 in three dimensions. This may imply that the stretch relaxation time has a different chain length dependence for ideal chains in different dimensions. It may also be interesting to see if the exponents for the ideal and self-avoiding polymers are identical in four dimensions. We have not checked these points.

In order to compare our algorithm with one involving local dynamics, we performed simulations in which monomers are allowed to make local moves, without altering the connectivity between them. This results in a relaxation time $\tau(N) \propto N^{3.5}$ for two-dimensional polymers, as expected (see section I). The actual relaxation times for this dynamics were approximately 3 times larger than ours for $N = 16$. This ratio increased to 6.3 for $N = 64$. Thus, despite the fact that the scaling behavior of our dynamics is slower than expected, it offers a considerable reduction in computation time in simulations involving large chains.

VI. Conclusion

This work shows that the bead-jump dynamics considered here is an efficient and reliable technique for simulating polymers in situations where reptation dynamics is inappropriate. Further, we have identified a novel relaxation mechanism that appears to be responsible for the peculiar relaxation properties seen in the dynamics. This mechanism is "stretch relaxation" or the relaxation of stored length along the chain. We have not succeeded in explaining the slow decay of such stretches. We believe that the same mechanism may explain the relaxation properties seen by others[6] in previous simulations.

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Evolution of Structure and Viscoelasticity in an Epoxy near the Sol-Gel Transition

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ABSTRACT: The divergences of the average molecular weight, average cluster size, and bulk viscosity as the gel point is approached and the power law behavior of the dynamic shear moduli at the gel point were measured for a cross-linked epoxy. The critical exponents describing the evolution of static structure were found to be significantly different from the predictions of mean-field theory and in reasonable agreement with percolation. The exponents describing the viscoelastic behavior in the critical region were found to be significantly different from the predictions of the de Gennes electrical analogy and in good agreement with our scaling theory.

Introduction

It is difficult to overstate the technological importance of cross-linked elastomers and thermosets, and yet the evolution of structure and viscoelastic properties during cure in these systems is not well understood theoretically nor has it been thoroughly studied experimentally. The general features of structural evolution during gelation such as the divergences of molecular weight and cluster size as the gel point is approached were cap-

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