Effect of Coordination Number on the Dynamics of Lattice Models for Polymer Chains

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ABSTRACT: A body-centered-cubic (BCC) lattice model for polymer chain dynamics is developed and used to study the relaxation of the first three Rouse coordinates of isolated chains. We find that the relaxation times obey the relation $\tau_k \sim (N-1)^{2.2}/k^{2.14}$ in the presence of excluded volume. These results are essentially identical with those obtained previously for the simple cubic (SC) and face-centered-cubic (FCC) lattice models. A detailed comparison of the dynamics of all three lattice models is presented in the context of the general relationship $\tau \sim \langle R^2 \rangle (N-1)$. We find that all three models conform to this relationship for chains of length $N \geq 36$.

Introduction

In a series of recent papers[1,2] we have studied both the chain length and mode number dependence of the dynamics of both simple cubic (SC) and face-centered-cubic (FCC) lattice models for polymer chains using a Monte Carlo simulation method. The original work on isolated SC lattice chains[1] confirmed that, in the absence of excluded volume, the model shows essentially Rouse-like[3] behavior in both the chain length, N, and mode number, k, dependence of the relaxation times. In the presence of excluded volume, a deviation from Rouse-like behavior is seen in both the N and k dependence. The N dependence is consistent with dynamic scaling.[4,5] The k dependence, however, has not yet had a theoretical explanation.

The cubic lattice model, however, requires two type of elementary motions, the two-bond "normal bead" motion and the three-bond "90° crankshaft", in order to create proper dynamical algorithm. In our SC algorithm both motions are assumed to occur on the same time scale. In order to test whether this assumption is reasonable we developed an FCC lattice model[2] in which only two-bond motions are required in the dynamical algorithm. The FCC model gave results that were slightly closer to both the Rouse model in the absence of excluded volume and the dynamic scaling prediction in the presence of excluded volume than the SC model. In the excluded volume case the FCC model also shows a k dependence similar to that of the SC model.

It has also been suggested by Romiszowski and Stockmayer[6] that the time scale in our SC algorithm might be distorted because the algorithm attempts a crankshaft motion whenever a normal bead motion is blocked by a second-nearest-neighbor bead. This question was explored by Stokely, Crabb, and Kovac,[7] who compared the original Crabb–Kovac[1] algorithm with an algorithm in which the normal bead and crankshaft motions are completely decoupled. They found that as long as reasonable choices were made for the relative frequencies of normal bead and crankshaft motions that the chain length dependence of the end-to-end vector relaxation time, τ_R, is the same in the coupled and the decoupled algorithms. This strongly suggests that there is no distortion of the time scale in our SC model.

In the present paper we develop a body-centered-cubic (BCC) lattice model for polymer chains and use it to study both the chain length and mode number dependence of the relaxation times of an isolated polymer chain. There are two reasons for doing this. First, a dynamical algorithm can be developed for the BCC model using only two-bond motions. This allows us to further explore the issue of the proper definition of the time scale in the dynamical Monte Carlo method. Second, since the BCC lattice has a coordination number of 8, comparison of the dynamics of BCC chains with previous results for SC and FCC chains will allow us to study the effect of lattice coordination number on the chain dynamics. Whenever a lattice model is used to represent a continuous system it is important to carefully check whether the results depend on the particular lattice chosen. Comparison of the 8-choice BCC lattice model with the 6-choice SC and the 12-choice FCC lattice model will be a good test of the effects of lattice coordination number on the chain dynamics.

In the following sections we will present the details of our BCC lattice model for polymer chains and show results for the dynamics of single chains both with and without excluded volume. We have studied both the end-to-end vector relaxation time and, as a more detailed probe of the chain dynamics, the relaxation of the first three normal modes. We will then present a comparsion of the dynamics of the BCC model with the SC and FCC models developed in earlier papers. We find that the scaling behavior of the BCC model is essentially the same as that of the other models. We also find that any deviation from either the Rouse model or dynamic scaling prediction for the chain length dependence of the relaxation times seems to be due to finite chain effects and not to problems of the Monte Carlo time scale being dependent on chain length. The deviation from the Rouse value for the k dependence of the relaxation times in the presence of excluded volume occurs for all three models, and the exponent is essentially independent of the lattice coordination number.

Body-Centered-Cubic Lattice Model

The chain is modeled as a random walk of $(N-1)$ steps of unit length on an eight-choice body-centered-cubic lattice. Each of the steps is referred to as a bond. The chain occupies N lattice junctions, each of which is called a bead. A representative chain conformation is shown in Figure 1. The chain is moved according to the following algorithm, which is similar to both the SC and FCC algorithms described in previous papers. The initial description is for the case when excluded volume is present.

First, a bead is chosen at random. If it is an end bead there are seven possible motions corresponding to the seven possible locations lying one lattice unit from the next to the last bead. One of these seven positions is chosen at random and a check made to see if the new position is occupied. If the new position is unoccupied, the end bead is moved and the cyclic terminates. If the new position is occupied then the end bead remains at its original position and the cycle is terminated.

If an interior bead is chosen the conformation of the two adjacent bonds is determined. In the presence of excluded volume these two bonds can form three different angles:

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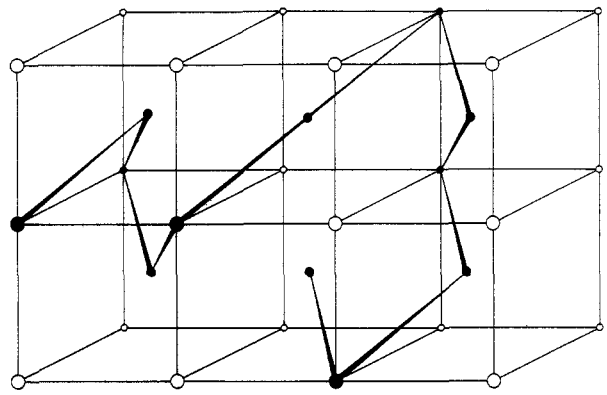

Figure 1. Representative conformation of a body-centered lattice (BCC) polymer chain.

Figure 2. Elementary motion for two bonds with a bond angle of 120°.

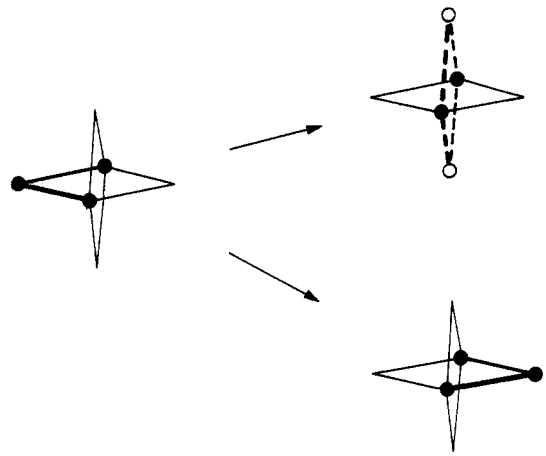

Figure 3. Elementary motions for two bonds with a bond angle of 60°.

60°, 120°, and 180°. The allowed elementary motions depepnd on the bond angle. If the angle is 180° the bonds are collinear and no motion is possible. If this conformation is found the cycle is terminated. If the bonds form a 120° angle, then there is one possible motion analogous to the normal bead motion in the cubic lattice model. This is illustrated in Figure 2. The bead is moved to the new position if that position is unoccupied.

For the 60° case there are more possibilities. There is one in-plane motion as shown in Figure 3. In addition there are two out-of-plane, crankshaft-type motions. These are also shown in Figure 3. It is these motions that introduce new bond directions into the interior of the chain. A random choice is made among the three possible motions in the 60° case. If the new position is occupied, the original conformation is retained; if it is unoccupied, the bead is moved.

If excluded volume is absent the new bead position is not checked and all motions are accepted. An additional modification in the absence of excluded volume is the possibility of a 0° angle between adjacent bonds. This "spike" conformation is treated in the same way as the end bead.

From time to time the coordinates of all the beads are sampled and recorded for later analysis. The elementary time unit is taken to be N bead cycles. All the computations were performed on our Hewlett Packard 1000 series A900 computer using FORTRAN source codes.

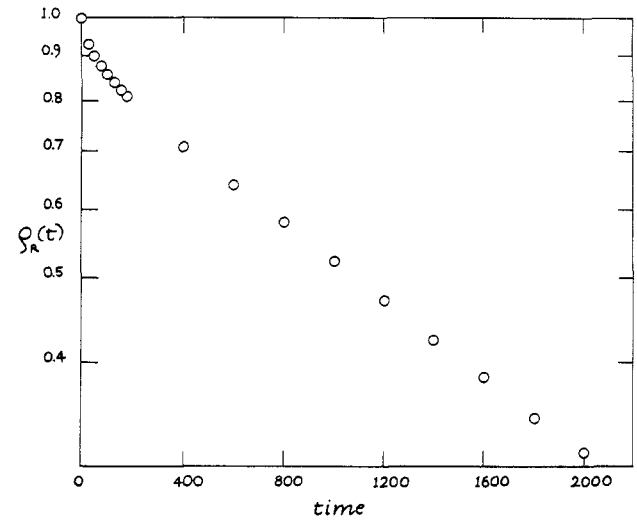

Figure 4. Semilogarithmic plot of the end-to-end vector autocorrelation function $\rho(t)$ vs. t for a chain of length $N = 60$ in the presence of excluded volume.

To analyze the dynamics of the chain we used the values of the end-to-end vector, $\mathbf{R}(t)$, to compute the autocorrelation function, $\rho_R(t)$, defined by

$$\rho_R(t) = \langle \mathbf{R}(t)\cdot\mathbf{R}(0)\rangle / \langle R^2\rangle \quad (1)$$

where the broken brackets represent an equilibrium ensemble average. The ensemble average was computed as a time average over a trajectory begun from a fully equilibrated chain conformation. The relaxation time, τ_R, was estimated by fitting an unweighted least-squares line to the linear, long-time region of a semilog plot of $\rho_R(t)$ vs. time. The inverse of the relaxation time is the negative of the slope of the line.

To analyze the dynamics in more detail we also studied the relaxation of the first three normal modes. The normal modes $\mathbf{U}_k(t)$ are given by the Rouse formula[8]

$$\mathbf{U}_k(t) = \sum_{j=1}^{N} \left(\frac{2-\delta_{k0}}{N}\right)^{1/2} \cos\left[(j-\tfrac{1}{2})\pi k/N\right]\mathbf{R}_j(t) \quad (2)$$

where $\mathbf{R}_j(t)$ is the position of the j-th bead with respect to the origin. The Rouse coordinates have proven to be an excellent set of normal coordinates for both the SC and FCC models. The autocorrelation function of the k-th normal mode, $\rho_k(t)$, is given by

$$\rho_k(t) = \langle \mathbf{U}_k(t)\cdot\mathbf{U}_k(0)\rangle / \langle U_k^2\rangle \quad (3)$$

The equilibrium ensemble average was again computed as a time average. The relaxation time of the k-th mode, τ_k, is computed by fitting a least-squares line to a semilog plot of $\rho_k(t)$ vs. time. The negative of the relaxation time is the inverse of the slope of this line.

Results and Discussion

Simulation runs were performed on chains of length 12, 24, 36, 48, and 60 beads both in the absence and presence of excluded volume. At least four runs were done for each case. Figure 4 shows a typical end-to-end vector autocorrelation function $\rho_R(t)$ for a chain with excluded volume. It is clear from this semilog plot that the autocorrelation function is a single exponential at long times. The relaxation times, τ_R, calculated from the long-time slopes of the ln $\rho_R(t)$ vs. t plots are collected in Table I. These values are the averages of at least four simulation runs. Also given in Table I is the scaling exponent, α_R, obtained from a

Table I
Values of the Relaxation Time, τ_R, as a Function of Chain Length, N, for Both Non-Excluded Volume and Excluded Volume Cases[a]

N	τ_R	
	no excluded volume	excluded volume
12	18.3 (0.8)	52.2 (2.6)
24	76.5 (1.7)	289 (45)
36	176 (18)	776 (72)
48	309 (11)	1460 (165)
60	190 (41)	2330 (130)

[a] Standard deviations are given in parentheses. The scaling exponents, α_R, are 1.98 in the non-excluded volume case and 2.27 in the presence of excluded volume.

least-squares fit of ln τ_R vs. ln $(N-1)$. This slope corresponds to a scaling exponent given by the relation

$$\tau_R \sim (N-1)^{\alpha_R} \tag{4}$$

In the absence of excluded volume the value of α_R is 1.96, which is very close to the Rouse value of 2.0. In the presence of excluded volume the value of α_R is 2.27, which is fairly close to the scaling theory prediction of 2.2. These exponents are similar to those obtained for both the SC and FCC models.

In Figure 5 are shown representative semilog plots of the normal-mode autocorrelation functions $\rho_k(t)$ for the first three modes for a chain with excluded volume. The semilog plots are extremely linear, indicating that the Rouse coordinates are an excellent set of normal coordinates for this model as they were for the SC and FCC models. The relaxation times, τ_k, obtained from the least-squares slopes of the ln $\rho_k(t)$ vs. t plots are collected in Table II.

As in previous papers the scaling properties of the normal-mode relaxation times were determined by making plots of ln τ_k vs. ln $(N-1)$ at constant k and ln τ_k vs. ln k at constant N. The slopes of these plots correspond to the scaling exponents α_k and γ_N defined by the relationships

$$\tau_k \sim (N-1)^{\alpha_k} \tag{5}$$

$$\tau_k \sim k^{-\gamma_N} \tag{6}$$

The values of α_k and γ_N are collected in Table III. As in the FCC case we have computed the value of α_k both including and excluding the value for $N = 12$.

The values of α_k and γ_N are essentially the same as the Rouse values of 2.0 in the absence of excluded volume. In the presence of excluded volume the values of α_k are fairly close to the scaling theory value of 2.2, although not quite as close as in the FCC case. As in the FCC case the exponents computed without the values for $N = 12$ are closer to the scaling prediction than those which include $N = 12$. The values of γ_N in the excluded volume case are significantly different from the Rouse value of 2.0 and are similar to those obtained in the SC and FCC cases.

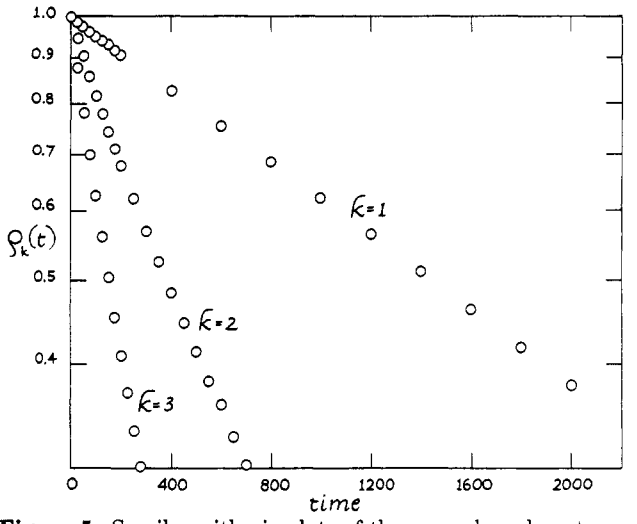

Figure 5. Semilogarithmic plots of the normal-mode autocorrelation function $\rho_k(t)$ vs. t for the first three modes for a chain of length $N = 60$ in the presence of excluded volume.

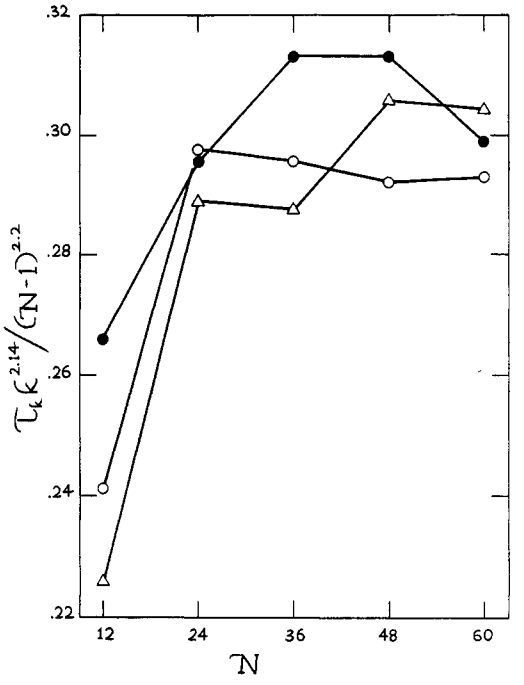

Figure 6. Plot of the quantity $[\tau_k k^{2.14}/(N-1)^{2.2}]$ vs. N for excluded volume chains [$k = 1$ (●), $k = 2$ (○), $k = 3$ (△)].

Following the example of our previous work, we have computed the quantities $[\tau_k k^2/(N-1)^2]$ for the non-excluded volume case and $[\tau_k k^{2.14}/(N-1)^{2.2}]$ for the excluded volume case as a function of both N and K. The numerical values are collected in Table IV. In Figures 6 and 7 we have plotted the excluded volume values. In the non-excluded volume case we have used the Rouse theory to determine the compact formula for the relaxation times.

Table II
Values of the Normal-Mode Relaxation Times τ_k as a Function of Chain Length, N, and Mode Number, k, for Both the Non-Excluded Volume and Excluded Volume Cases[a]

N	no excluded volume			excluded volume		
	τ_1	τ_2	τ_3	τ_1	τ_2	τ_3
12	1896 (0.9)	4.7 (0.1)	2.1 (0.1)	51.9 (2.5)	10.7 (0.6)	4.21 (0.23)
24	76.5 (1.6)	20.1 (0.4)	8.5 (0.2)	293 (44)	66.8 (3.3)	27.2 (1.6)
36	177 (19)	45.0 (2.8)	20.1 (1.0)	781 (70)	167 (7)	68.3 (3.3)
48	310 (16)	78.8 (2.1)	37.5 (2.2)	1460 (130)	316 (16)	139 (10)
60	495 (51)	126 (1.3)	55.6 (2.2)	2350 (97)	523 (27)	228 (13)

[a] Standard deviations are given in parentheses.

Table III
Scaling Exponents α_k and γ_N as a Function of Mode Number and Chain Length Respectively for Both the Non-Excluded Volume and Excluded Volume Cases

k	no excluded volume α_k	excluded volume α_k	
		incl N = 12	excl N = 12
1	1.95	2.28	2.21
2	1.95	2.31	2.18
3	1.97	2.37	2.27

N	no excluded volume γ_N	excluded volume γ_N
12	1.98	2.29
24	1.99	2.16
36	1.98	2.22
48	1.93	2.15
60	1.99	2.13

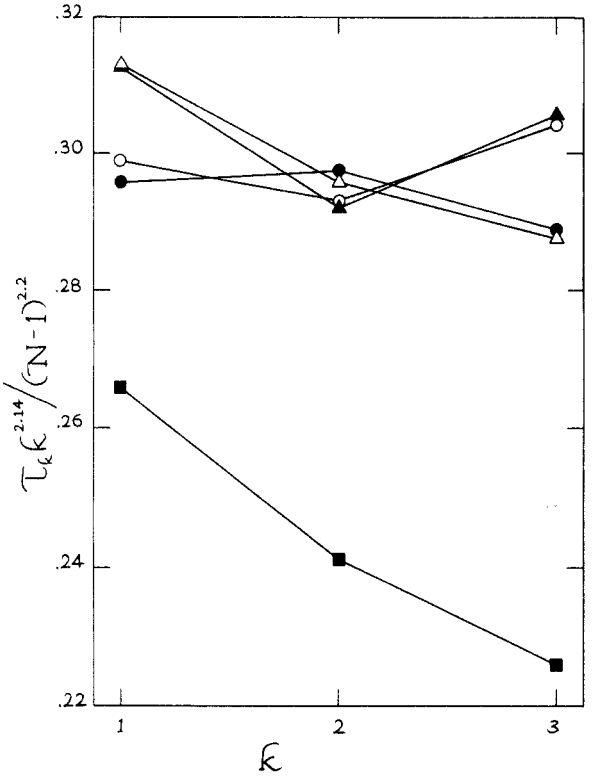

Figure 7. Plot of the quantity $[\tau_k k^{2.14}/(N-1)^{2.2}]$ vs. k for excluded volume chains of lengths N = 12 (■), N = 24 (●), N = 36 (△), N = 48 (▲), and N = 60 (○).

In the excluded volume case we used the scaling theory value for α_k and adjusted γ_N to qualitatively obtain the minimum scatter at large values of N. The graphs and the table clearly show that the Rouse theory gives an excellent description of the relaxation times in the absence of excluded volume. In the presence of excluded volume the relaxation times are well described by the relationship

$$\tau_k(N) \sim (N-1)^{2.2}/k^{2.14}$$

which is similar to that obtained for both the SC and FCC models.

Comparison with the SC and FCC Lattice Models

Dynamic scaling arguments[4,5] suggest that the relaxation time of a free draining polymer chain should scale with the chain dimensions as

$$\tau \sim \langle R^2 \rangle (N-1) \quad (7)$$

This relationship provides a framework with which we can compare the results of the three different lattice models that we have studied. Any effects of finite chain length or of an N dependence of the time scale should be evident in a plot of the quantity $\tau/[\langle R^2 \rangle (N-1)]$ vs. N. We have computed the ratio $S_k = \tau_k/[\langle R^2 \rangle (N-1)]$ for the SC, BCC and FCC models. Plots of these quantities as a function of chain length for both the non-excluded volume and excluded volume cases are shown in Figures 8–10 and the numerical values are collected in Table V.

As expected, in the absence of excluded volume, the ratio S_k is very nearly constant for all three lattice models and

Table IV
Values of the Quantity $\tau_k k^2/(N-1)^2$ in the Absence of Excluded Volume and $\tau_k k^{2.14}/(N-1)^{2.2}$ in the Presence of Excluded Volume as a Function of Chain Length, N, and Mode Number, k

N	k = 1	k = 2	k = 3
$\tau_k k^2/(N-1)^2$ (No Excluded Volume)			
12	0.153	0.157	0.157
24	0.145	0.145	0.145
36	0.145	0.147	0.148
48	0.141	0.143	0.145
60	0.142	0.145	0.144
$\tau_k k^{2.14}/(N-1)^{2.2}$ (Excluded Volume)			
12	0.266	0.241	0.226
24	0.296	0.298	0.289
36	0.313	0.296	0.288
48	0.313	0.292	0.306
60	0.299	0.293	0.304

Table V
Values of the Ratio $S_k = \tau_k = \tau_k/[\langle R^2 \rangle (N-1)]$ as a Function of Chain Length N and Mode Number for the SC, FCC, and BCC Lattices for the Non-Excluded Volume and Excluded Volume Cases

N	S_1	S_2	S_3
Simple Cubic (SC) No Excluded Volume			
12	0.153	0.0269	0.0074
24	0.145	0.0340	0.0138
36	0.139	0.0338	0.0141
48	0.135	0.0337	0.0147
60	0.141	0.0341	0.0146
Simple Cubic (SC) Excluded Volume			
12	0.176	0.0317	0.0061
24	0.170	0.0359	0.0123
36	0.159	0.0380	0.0143
48	0.160	0.0368	0.0155
60	0.159	0.0376	0.0150
Face-Centered-Cubic (FCC) No Excluded Volume			
12	0.156	0.0388	0.0183
24	0.155	0.0363	0.0179
36	0.159	0.0364	0.0170
48	0.142	0.0381	0.0165
60	0.163	0.0368	0.0173
Face-Centered-Cubic (FCC) Excluded Volume			
12	0.257	0.0541	0.0211
24	0.275	0.0622	0.0248
36	0.282	0.0651	0.0263
48	0.283	0.0691	0.0290
60	0.287	0.0666	0.0280
Body-Centered-Cubic (BCC) No Excluded Volume			
12	0.147	0.0374	0.0165
24	0.140	0.0356	0.0169
36	0.152	0.0385	0.0172
48	0.143	0.0376	0.0160
60	0.152	0.0389	0.0174
Body-Centered-Cubic (BCC) Excluded Volume			
12	0.272	0.0560	0.0220
24	0.304	0.0695	0.0283
36	0.334	0.0176	0.0292
48	0.323	0.0700	0.0308
60	0.328	0.0729	0.0318

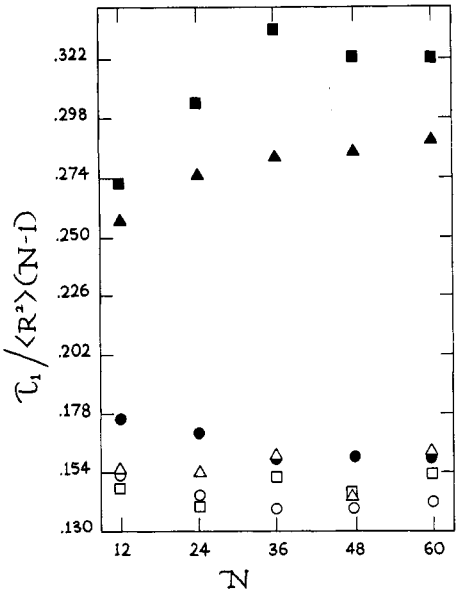

Figure 8. Plot of the quantity $\tau_1/[\langle R^2\rangle(N-1)]$ vs. N for SC (○), FCC (△), and BCC (□) chains. Open symbols indicate no excluded volume; filled symbols indicate excluded volume.

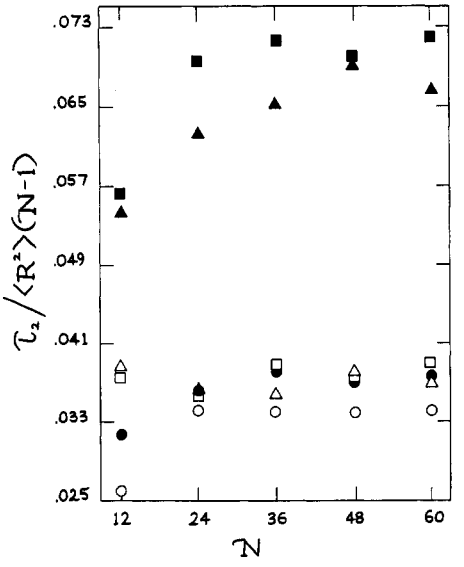

Figure 9. Plot of the quantity $\tau_2/[\langle R^2\rangle(N-1)]$ vs. N for SC (○), FCC (△), and BCC (□) chains. Open symbols indicate no excluded volume; filled symbols indicate excluded volume.

for all three modes. The largest amount of scatter is seen for the $k = 3$ mode for very short chains ($N - 1 = 11$ or 23). This scatter is easy to understand, since for these cases the length scale of the normal mode has become comparable to the short-range correlations in the chain and hence will be strongly influenced by the details of the elementary motions and by local stiffness.

In the presence of excluded volume the ratio S_k is not constant at short chain lengths, but the plots appear to level off to constant values by a chain length of $(N - 1) \simeq 35$. For $(N - 1) \geq 35$ a log–log plot of the ratio $\tau_k/[\langle R^2\rangle(N-1)]$ vs. $(N - 1)$ would show a slope indistinguishable from zero. This strongly suggests that all three lattice models obey the dynamic scaling hypothesis expressed in eq 7. There is a deviation for short chain lengths, but it is fairly small. These plots also provide further evidence that there is no distortion of the time scale in the SC model.

It is clear from Figures 8–10 that the three-bond crankshaft motion used in the SC model has a significant

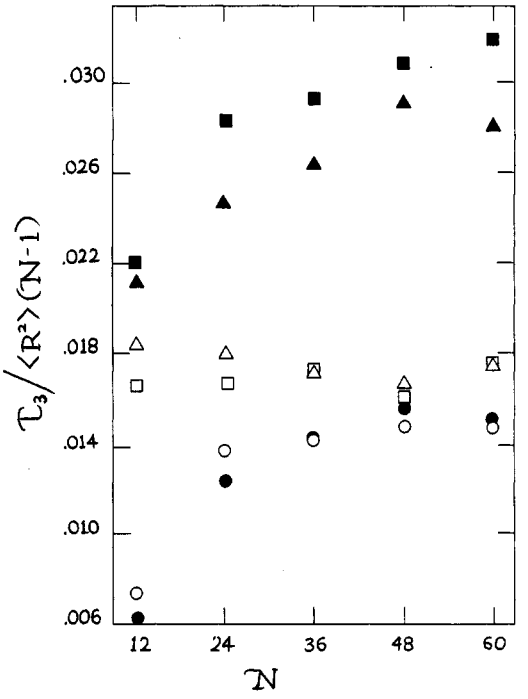

Figure 10. Plot of the quantity $\tau_3/[\langle R^2\rangle(N-1)]$ vs. N for SC (○), FCC (△), and BCC (□) chains. Open symbols indicate no excluded volume; filled symbols indicate excluded volume.

effect on the absolute value of the relaxation time. For both the BCC and FCC models the ratio S_k increases by approximately a factor of 2 when the excluded volume constraint is included. For the SC model the increase is much more modest, only 15–20%. This effect is seen for all three modes. It is also interesting to note that the relaxation of the first mode is relatively faster at short chain lengths for the SC model but relatively slower for both the BCC and FCC models. The three-bond crankshaft must be particularly efficient in relaxing the first mode of the short SC chains. This effect, however, does not occur for modes 2 and 3. Figure 8 also shows why the exponent α_R is less than 2.2 in the SC case but larger than 2.2 for the BCC and FCC cases. The deviations are due to short-chain effects. To avoid such short-chain effects one should use chains of length 36 and longer.

It is also interesting to compare the compact formulas found for the relaxation times for the three different models. In all three cases the non-excluded volume results conformed very closely to a Rouse formula

$$\tau_k \sim N^{2.0}/k^{2.0} \tag{8}$$

In the presence of excluded volume all three models were fit to an expression of the form

$$\tau_k \sim N^{2.2}/k^{\gamma} \tag{9}$$

where γ has a value a little larger than 2.1 in all cases. The exponent γ may have a universal value for all free draining chains with excluded volume. It is possible that this value for γ is either an artifact of the lattice or an artifact of the particular Monte Carlo simulation model we have used. It may also be a result of the neglect of the hydrodynamic interactions. In any case it is an interesting effect that deserved further study both theoretically and by simulation.

Conclusions

Comparison of the BCC model developed here with the SC and FCC models shows that the dynamic Monte Carlo lattice models are a useful tool with which to study the

effects of excluded volume on isolated polymer chain dynamics in the free draining case. The chain length and mode number dependence of the relaxation times are both essentially independent of the lattice coordination number. Finite chain effects on the dynamics seem to disappear for $N > 36$. The relaxation times obey dynamic scaling in the presence of excluded volume. The absolute value of the time scale does depend on the set of elementary motions chosen, but the existence of two types of elementary motions in the algorithm does not appear to introduce a chain length dependence to the time scale, at least for single chains. We, therefore, conclude that for single-chain properties the choice of the particular lattice model is mostly a question of convenience.

For a multiple chain simulations particularly at high concentrations the situation may be different. All multiple chain simulations done so far[9-13] have used either the cubic lattice or the diamond lattice and there is some evidence[14] that the need for two kinds of elementary motions in these models might strongly effect the results. It is important therefore that the study of the effect of lattice coordination member be extended to investigate the effects of concentration.

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Simulation of Polymer Chain Dynamics by Lattice Models with Excluded Volume: Lattice Dependence

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ABSTRACT: The effects of varying the lattice and the elementary move rules upon the dynamical behavior of bead-stick models of polymer chains with excluded volume have been studied by computer simulation. Long relaxation times and translational diffusion constants are reported for chains on body-centered cubic, face-centered cubic, and simple cubic lattices, for chains not constrained to lie on a lattice, for one-bead and two-bead elementary moves, and for random mixtures of one- and two-bead moves. The chain-length dependence of the effects of excluded volume upon long relaxation times is similar for all three lattices: When only one kind of elementary move (one-bead or two-bead) is employed, the chain-length dependence of the long relaxation times is increased by somewhat more than the first power of chain length for all three lattices. When a mixture of two kinds of elementary moves is employed, the increase in chain-length dependence drops to somewhat more than the 0.5 power. However, when the requirement of lying on a lattice is removed altogether from chains using both kinds of elementary move, the chain-length dependence increases to roughly the common value found for lattice chain simulations using only one kind of elementary move. The behavior of the translational diffusion constants parallels that of the long relaxation times.

Introduction

Lattice models have long been used to study the behavior of random-coil polymer chains in solution. They have proven especially useful for the study, via direct computer simulation, of hard core excluded volume interactions. These repulsive interactions between segments of the polymer chain give rise to expansion of chain dimensions, lengthening of relaxation times, and ultimately, chain entanglements for sufficiently long chains and/or high segment densities. These interactions are extremely difficult to treat analytically. Significant progress has been made using expansion techniques about the no-excluded volume limit, tube-snake models for the entanglement limit, scaling, and a variety of averaging techniques. Nevertheless, the problem of developing a single excluded volume model to treat continuously the effect of chain length and chain density on chain dynamics remains.

Computer models are a particularly effective means for simulating and studying the effects of excluded volume upon chain dynamics. Early simulations[1-5] have studied

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