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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the increase in the chain-length dependence of the longest relaxation times due to excluded volume interactions for single chains in solution. The results suggest that the increase due to excluded volume can be significantly greater than the familiar one-fifth power of chain length observed for the mean-square end-to-end length and predicted by some of the theoretical models. Deutch and co-workers suggested that this additional increase was an artifact due to an interaction between the constraints imposed by the simple cubic lattice employed in the simulations and the use of a single one-bead[6] or two-bead[7] move rule. To address this possibility, a simulation study[8] was carried out in which random mixtures of one-bead and two-bead moves were employed to remove the specific constraints noted by Deutch et al. The results appeared to suggest that for sufficiently long chains, the chain-length dependence of the lengthening is independent of the details of the move rules. However, more recently a preliminary study[9] in which both the lattice and the move rules were varied suggests that the chain-length dependence of the lengthening can indeed depend significantly upon the move rules. In particular, the results of this work showed an increase which is less than that found in the earlier work employing only one kind of bead move but is still significantly larger than the theoretical predictions. In addition, simulations reported by Kovac and co-workers[10,11] using move rules inherently different in nature from those employed in our work show appreciably weaker dependence of long relaxation times upon chain length than those we obtain. Thus, the effects of lattice constraints and the details of move rules upon the simulation results remain open to question.

The purpose of this paper is to examine the effects of varying the type of lattice upon the chain dynamics simulation results and the possible cross-couplings of lattice constraints with move rules. In addition, the behavior of chains completely free of lattice constraints is compared with that of the lattice models. Specifically, we report the effects of exluded volume upon long relaxation times and translational diffusion constants for chains on body-centered cubic (BCC), face-centered cubic (FCC), and simple cubic (SC) lattices, with one-bead, two-bead, and a random mixture of one- and two-bead movement rules, and for chains not constrained to lie on a lattice, with the same random mixture of one- and two-bead rules.

Model

The dynamical lattice models employed in this work have been described previously.[1,8,9,12] A random-coil polymer chain (N − 1) units long is modeled by a string of N connected beads. For models constrained to lie on lattices, the bead centers lie on the vertices of a simple cubic lattice, the bead diameter is taken equal to the length of a cube edge, and the connections between beads lie along cube edges, cube face diagonals, and cube body diagonals, for simple cubic (SC), face-centered cubic (FCC), and body-centered cubic (BCC) lattices, respectively. For the off-lattice chains, the connection vectors may point in any direction, there is no restriction on the angle between successive connection vectors, and the bead diameter is taken equal to the length of the connection vector. Both on and off lattices, Brownian motion of the chain is simulated by sequences of elementary moves, which we shall call move cycles, each of which consists of selecting a region of the chain at random[13] and attempting a local move on the selected region. Two types of elementary moves are used. One type is a one-bead move, in which the vectors between a selected bead and its two nearest neighbors along the chain are interchanged. Thus, if the beads are numbered along the chain from 1 to N, and if we let σ_j be the vector from bead j to bead $(j + 1)$, then, the one-bead move may be described by

$$\sigma'_j = \sigma_{j-1}$$
$$\sigma'_{j-1} = \sigma_j \qquad 1 \le j \le N \tag{1}$$

where the primes denote values after the move, and σ_0 and σ_N are "phantom" vectors chosen at random (from the set of allowed vectors for the particular lattice for lattice models and from the set of vectors of all possible directions for the off-lattice models) each time an end bead is selected. The second type of move is a two-bead move, in which an adjacent pair of beads is selected, rather than a single bead, and the move is described by

$$\sigma'_{j-1} = \sigma_{j+1}$$
$$\sigma'_j = \sigma_j$$
$$\sigma'_{j+1} = \sigma_{j-1} \qquad 0 \le j \le N \tag{2}$$

where subscripts −1, 0, N and $(N + 1)$ denote phantom vectors chosen at random. Thus, the on-lattice and off-lattice chains use exactly the same move rules; the only difference between them lies with the allowed values of σ, which belong to small sets of allowed lattice vectors in the first case and are entirely unrestricted in the other.

At the start of each move cycle, a random choice is made of the type of move to be attempted, with a preset probability p of choosing a two-bead move. Thus, $p = 0$, 1, and 0.5, the three values empoyed in this study, correspond to one-bead moves only, two-bead moves only, and an equal mixture of one- and two-bead moves, respectively. After the type of move has been determined, a bead on the chain (for a one-bead move) or an adjacent pair of beads (for a two-bead move) is chosen at random, and the move described by eq 1 or 2 is attempted. If the proposed move would result in beads overlapping each other, then no move is made. If the proposed move results in no bead overlap, the move is made. In either case, the move cycle is complete and a new move cycle starts with a new random choice of type of move. For chains constrained to lie on a lattice, "bead overlap" of course becomes just multiple occupancy of one or more lattice sites.

As the simulation proceeds, the chain configuration is sampled and stored at intervals. After the simulation is complete, the sampled chain configurations are used to generate sample values of the end-to-end vector l, its square l^2, and the position of the center of mass of the chain. These sampled values are used to form estimates of the autocorrelation $\rho(l,l,t)$ in the end-to-end vector:

$$\rho(l,l,t) = \langle l(0)\cdot l(t)\rangle / \langle l^2\rangle \tag{3}$$

and the translational diffusion constant

$$D = \frac{1}{6}\langle d^2\rangle / T_D \tag{4}$$

where $\langle d^2\rangle$ is the mean-square displacement of the center of mass of the chain in a time interval T_D much larger than the longest internal relaxation time τ_1 of the chain.

Results

Relaxation Times. Simulations were carried out on BCC, FCC, and SC lattices, for p equal to 0, 0.5, and 1. In addition, simulations were carried out for chains not constrained to lie on a lattice, for p equal to 0.5. Several lengths of chains were employed, with from 9 to 99 beads. Where appropriate, data for chains on the SC lattice were combined with data previously reported[8] for this lattice. Semilogarithmic plots for the autocorrelation functions for

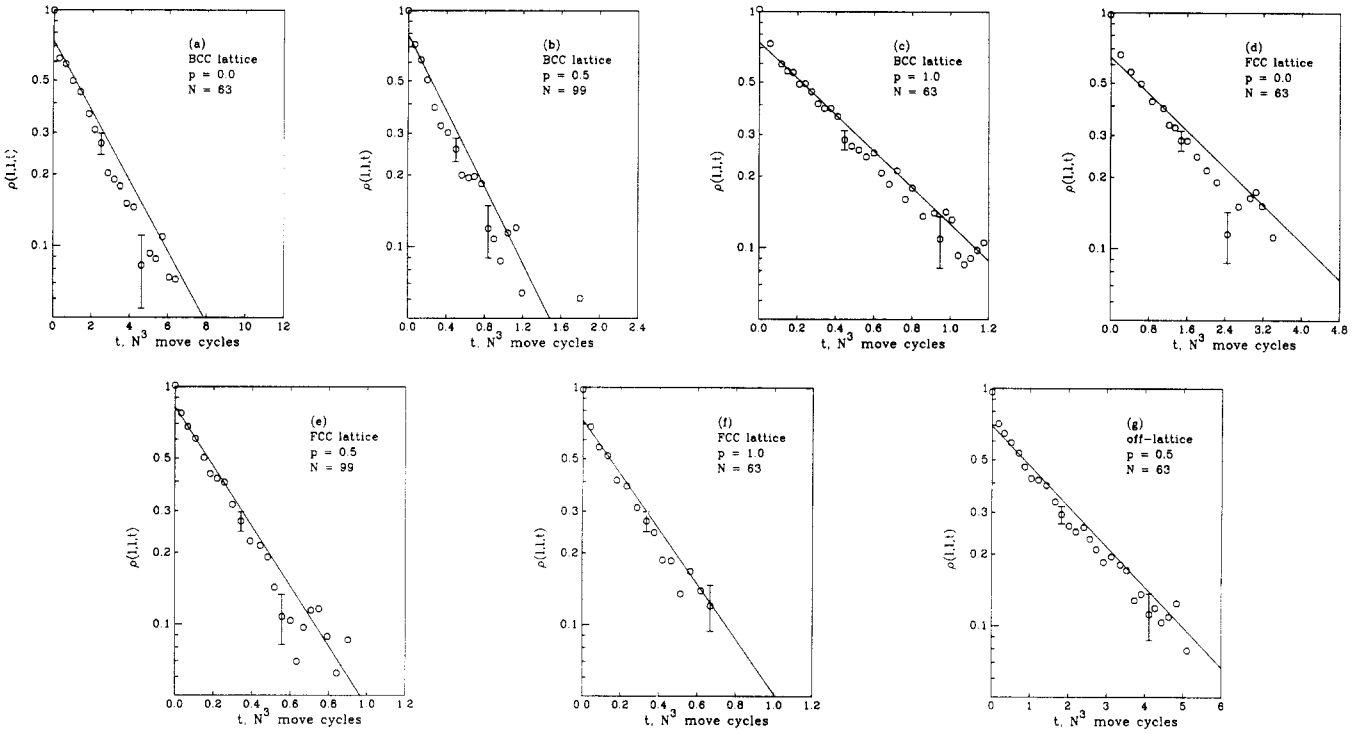

Figure 1. Semilogarithmic plots of autocorrelation functions $\rho(l,l,t)$ for end-to-end vector l for chains of N beads on body-centered cubic (BCC) and face-centered cubic (FCC) lattices and for chains not constrained to lie on lattices, with fractions p of two-bead moves. The time t is in units of N^3 move cycles. The error bars extend upward and downward one standard deviation of the mean values of ρ shown. For clarity, only a fraction of the sampled values of ρ are shown, and the plots stop as soon as a value of ρ less than 0.05 occurs.

the end-to-end vector for seven typical systems of chains on BCC and FCC lattices and chains not on a lattice are shown in Figure 1. Like the plots for simulations on SC lattices reported earlier,[8] they appear to exhibit limiting linear behavior at sufficiently long times, indicating the existence of unique longest relaxation times. As before, we have therefore extracted relaxation times, τ_1, by fitting the autocorrelation functions, ρ, by unweighted least squares to the form

$$\rho = a \exp(-t/\tau_1) \tag{5}$$

at times t after ρ has dropped below 0.6. This range appears to be safely within the limiting linear region in ln ρ vs. t. The values of a and τ_1 so obtained are given in Table I.

Standard deviations in a and τ_1 were obtained by dividing the total length of simulation for each system into a number n_s (usually 12) of equal subintervals. Values a and τ_1 were determined from the data in each subinterval. Mean values and sample standard deviations of the mean were then calculated from the sets of n_s values. The values of a and τ_1 so obtained are given in Table I. The values of n_s and the ratios T/τ_1 of the total length T of each simulation to the corresponding value of τ_1 are also shown.

In order to examine the effects of excluded volume upon the long relaxation times, we form the ratio $R_\tau = \tau_1/{}^0\tau_1$ of each value of τ_1 to the corresponding longest relaxation time ${}^0\tau_1$ for a system with the same values of p and N but with no excluded volume restrictions. The relaxation times, ${}^0\tau_1$, which do not depend upon the lattice, were obtained[14] by the methods described in ref 8. The values of R_τ obtained are given in Table II, together with their standard deviations inferred from the standard deviations in τ_1. log–log plots of these values of R_τ vs. N are shown in Figure 2. First, it is seen that on all three lattices, for models with only one kind of move rule ($p = 0$ and $p = 1$, parts a and c of Figure 2) R_τ varies as something greater

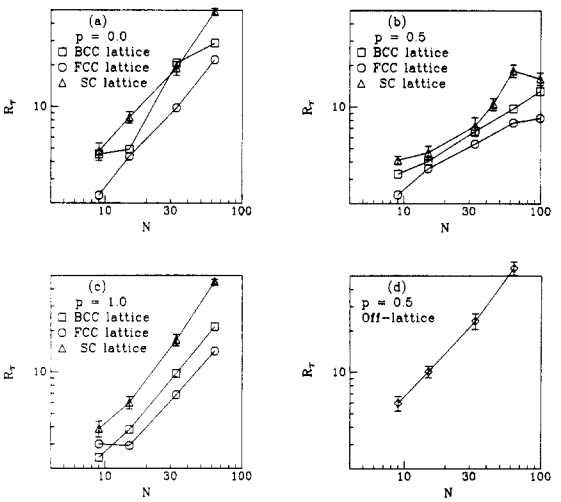

Figure 2. log–log plots of ratios R_τ of longest relaxation times τ_1 for chains with excluded volume to relaxation times ${}^0\tau_1$ for chains of the same length, move rules, and lattice but without excluded volume constraints. The error bars, shown for simplicity only for chains on the SC lattice and off-lattice chains, extend upward and downward one sample standard deviation of the mean.

than the first power of N. Second, as shown in Figure 2b, the use of two kinds of move rule ($p = 0.5$) causes this dependence to drop to about the 0.6 power. Finally, as shown in Figure 2d, eliminating the lattice constraint entirely causes it to return to a power greater than one.

Diffusion Constants and Equilibrium Dimensions. Values of the mean-square end-to-end length $\langle l^2 \rangle$ are reported in Table III. Figure 3 shows log–log plots of $\langle l^2 \rangle/(N-1)$ vs. $(N-1)$. The non-zero slopes show the additional excluded volume power-law dependence of $\langle l^2 \rangle$ on chain length which occurs when joint occupancy of space is prohibited. The additional excluded volume

Table I
Values of p, N, a, τ_1, n_s, and T/τ_1 for the Various Lattices[a]

lattice	p	N	a	τ_1	n_s	T/τ_1
BCC	0.0	9	0.793 (0.054)	0.46 (0.12)	12	166
		15	0.834 (0.049)	0.497 (0.057)	12	386
		33	0.767 (0.092)	2.09 (0.80)	12	220
		63	0.741 (0.049)	2.92 (0.36)	12	421
BCC	0.5	9	0.864 (0.082)	0.165 (0.030)	12	582
		15	0.902 (0.083)	0.187 (0.030)	12	513
		33	0.870 (0.093)	0.288 (0.039)	12	534
		63	0.740 (0.040)	0.407 (0.037)	12	660
		99	0.787 (0.049)	0.538 (0.083)	12	428
BCC	1.0	9	1.029 (0.056)	0.085 (0.013)	12	267
		15	0.870 (0.045)	0.118 (0.014)	12	487
		33	0.780 (0.052)	0.270 (0.034)	12	398
		63	0.738 (0.042)	0.565 (0.050)	12	544
FCC	0.0	9	0.899 (0.053)	0.231 (0.024)	12	237
		15	0.781 (0.040)	0.443 (0.056)	12	325
		33	0.88 (0.15)	0.99 (0.25)	12	427
		63	0.645 (0.035)	2.21 (0.31)	12	295
FCC	0.5	9	1.23 (0.25)	0.117 (0.017)	12	655
		15	0.910 (0.085)	0.165 (0.025)	12	464
		33	0.861 (0.032)	0.233 (0.019)	60	3301
		63	0.802 (0.058)	0.322 (0.038)	12	834
		99	0.824 (0.049)	0.344 (0.038)	12	503
FCC	1.0	9	0.89 (0.11)	0.106 (0.015)	12	179
		15	0.895 (0.053)	0.090 (0.007)	12	637
		33	0.782 (0.052)	0.189 (0.020)	12	447
		63	0.727 (0.042)	0.376 (0.045)	12	340
SC	0.0	9	0.793 (0.038)	0.483 (0.071)	12	293
		15	0.712 (0.033)	0.850 (0.079)	12	301
		33	0.760 (0.030)	1.92 (0.22)	12	359
		63	0.728 (0.014)	4.95 (0.27)	16	1303
SC	0.5	9	0.855 (0.037)	0.208 (0.014)	12	368
		15	0.943 (0.071)	0.216 (0.024)	12	356
		33	0.880 (0.060)	0.314 (0.048)	12	367
		45	0.834 (0.055)	0.445 (0.043)	12	603
		63	0.752 (0.025)	0.769 (0.079)	48	998
		99	0.835 (0.047)	0.665 (0.067)	12	636
SC	1.0	9	1.04 (0.15)	0.137 (0.018)	12	559
		15	0.813 (0.055)	0.186 (0.019)	12	413
		33	0.738 (0.033)	0.473 (0.044)	12	325
		63	0.672 (0.012)	1.198 (0.048)	22	1852
none	0.5	9	0.098 (0.11)	0.301 (0.036)	12	382
		15	0.804 (0.054)	0.466 (0.044)	12	330
		33	0.787 (0.038)	1.01 (0.013)	12	304
		63	0.697 (0.035)	2.55 (0.33)	9	432

[a] Values of a and τ_1 are obtained by fitting the limiting long-time behavior of autocorrelation functions, $\rho(l,l,t)$, for the end-to-end vector, l, for chains of N beads with a fraction, p, of two-bead moves on the lattices shown, with excluded volume, to the form $\rho(l,l,t) = a \exp(-t/\tau_1)$ by least squares. The values of τ_1 are in units of N^3 move cycles. Values in parentheses are sample standard deviations of the mean. Also shown are the numbers n_s of subintervals into which the simulations were divided for estimating sample standard deviations of the mean and ratios T/τ_1 of the total lengths T of the simulations to the long relaxation times, τ_1.

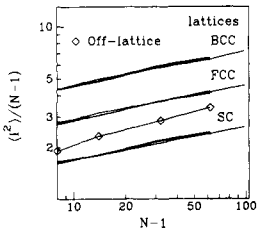

Figure 3. log–log plots of ratios $\langle l^2\rangle/(N-1)$ of mean-square end-to-end length $\langle l^2\rangle$ to number of steps $(N-1)$ vs. $(N-1)$ for chains on BCC, FCC, and SC lattices (no plotting symbols) and for chains not on a lattice (diamonds).

power-law dependence for all three lattices (SC, FCC, and BCC) and all three bead movement rules (p = 0.0, 0.5, and 1.0) is similar. Unweighted least-squares fits of $\ln[\langle l^2\rangle/(N-1)]$ to a linear function of $\ln(N-1)$ give slopes consistent with the well-known result of 0.20. The off-lattice simulation with p = 0.5 gives a slightly higher value of 0.26 for this slope. The difference between this value and the value obtained on lattices is slight. A plausible interpretation of the difference in slopes could be that an off-lattice "pearl necklace" chain requires a larger number of beads than its lattice counterpart to reach the region of the limiting long-chain results. The nonreversal of allowed chain configurations gives rise to an apparent short-range stiffness. This effect is exhibited most readily by considering the values of $\langle \sigma_1 \cdot \sigma_2\rangle/\langle \sigma^2\rangle$ for chains of three beads—too short to exhibit any excluded volume effects except simple self-reversal prohibition. It is readily seen that the values obtained for SC, FCC, BCC, and off-lattice chains are $^1/_5$, $^1/_{11}$, $^1/_7$, and $^1/_4$, respectively. Thus, by this measure, the local stiffness of the off-lattice chains is greater than that of any of the lattice chains, and it may well be that the properties of the relatively short chains studied here fall between those of flexible chains and rigid rods. As shown in Figure 2d, the chain-length dependence

Table II
Ratios, R_τ, of the Longest Relaxation Time, τ_1, with and without Excluded Volume[a]

		lattice			
p	N	BCC	FCC	SC	none
0.0	9	4.5 (1.2)	2.28 (0.24)	4.75 (0.70)	
	15	4.89 (0.56)	4.36 (0.55)	8.38 (0.78)	
	33	20.6 (7.9)	9.8 (2.5)	19.0 (2.1)	
	63	28.8 (3.6)	21.8 (3.0)	48.8 (2.6)	
0.5	9	3.27 (0.60)	2.31 (0.34)	4.12 (0.27)	5.97 (0.71)
	15	4.05 (0.65)	3.58 (0.53)	4.67 (0.53)	10.09 (0.95)
	33	6.69 (0.90)	5.41 (0.45)	7.3 (1.1)	23.49 (0.30)
	45			10.5 (1.0)	
	63	9.74 (0.88)	7.71 (0.90)	18.4 (1.9)	61.0 (7.9)
	99	13.0 (2.0)	8.32 (0.93)	16.1 (1.6)	
1.0	9	2.41 (0.37)	3.01 (0.44)	3.88 (0.52)	
	15	3.82 (0.45)	2.92 (0.21)	6.00 (0.62)	
	33	9.7 (1.2)	6.81 (0.70)	17.0 (1.6)	
	63	21.3 (1.9)	14.2 (1.7)	45.1 (1.8)	

[a] Ratios, R_τ, of the longest relaxation times, τ_1, for models with a fraction, p, of two-bead moves and chains of N beads, with excluded volume, on the lattices shown, to the longest relaxation times ${}^0\tau_1$ for models with the same values of p and N but without excluded volume. Numbers in parentheses are sample standard deviations inferred from the sample standard deviations in the values of τ_1.

of the relaxation time, τ_1, for off-lattice chains is stronger than that of its lattice counterparts, Figure 2b, a result which is consistent with an analytical calculation of the effects of stiffness in bead-spring chains.[15]

Translational diffusion constants D of the centers of mass of the chains were sampled by using eq 4. The values obtained are given in Table III, together with the ratios T_D/τ_1 of the times T_D over which the mean-square displacements of the centers of mass of the chains were sampled to the long relaxation times, τ_1, the reciprocals of ratios, R_D, of diffusion constants with excluded volume to those without excluded volume, and ratios $D\tau_1/\langle l^2\rangle$. log–log plots of the reciprocal ratios, R_D^{-1}, vs. N are shown in Figure 4.

The behavior of R_D^{-1} in Figure 4 is qualitatively similar to that of the ratios R_τ shown in Figure 2. The slopes in Figure 4 are somewhat less than the corresponding slopes in Figure 2 in all cases. For all three lattices, the slopes are near unity for $p = 0.0$ and $p = 1.0$ and decrease to about 0.3 for $p = 0.5$. For the off-lattice simulations, the slope of R_D^{-1} in Figure 4 is approximately 0.7, to be compared with a slope of R_τ in Figure 2 slightly greater than unity. In general, the R_τ slopes are observed to differ from the R_D^{-1} slopes by roughly the slopes of ln $\langle l^2\rangle$ vs. ln $(N - 1)$ shown in Figure 3. This observation is reinforced by examining the values of the dimensionless ratio $D\tau_1/\langle l^2\rangle$ reported in Table III. While the values of this ratio show appreciable fluctuations, due to the imprecision of their component factors, they show no evidence of dependence upon lattice, move rules, or chain length. In fact, they remain in the range 0.02–0.07, bracketing the value of 0.036 which may be calculated for the Rouse bead-spring model.[16] Similar values of $D\tau_1/\langle l^2\rangle$ were also observed in a nondilute solution simultion study[17] of chains on a SC lattice with $p = 0.5$, in which the bead density (i.e., the fraction of lattice sites occupied by beads) varied from 0 to 0.8.

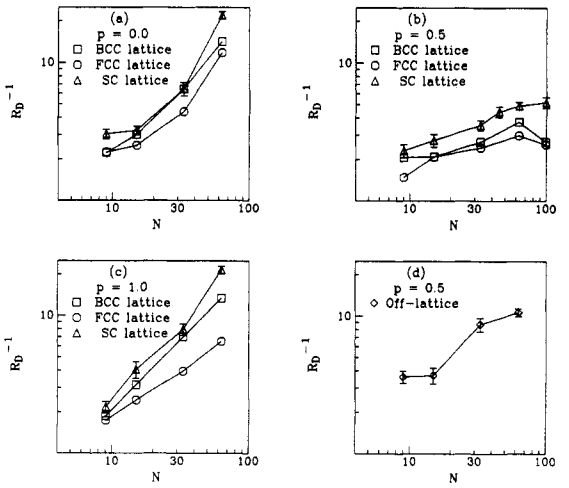

Figure 4. log–log plots of reciprocal ratios R_D^{-1} of translational diffusion constants ${}^0D$ for chains without excluded volume to diffusion constants for chains of the same length, move rules, and lattice but with excluded volume constraints. The error bars extend upward and downward one sample standard deviation of the mean.

Conclusions

Excluded volume constraints appreciably increase the chain-length dependence of the long relaxation times, τ_1. The effects of excluded volume upon relaxation behavior do not appear to depend on the type of lattice for chains on BCC, FCC, and SC lattices but do depend upon the number of kinds of elementary move rules employed. When only one kind of elementary move is allowed, excluded volume increases the chain-length dependence of τ_1 by something more than the 1st power; with two kinds of elementary moves, the increase is about the 0.6 power. Thus, the suggestion of Deutch and co-workers[6,7] that the combination of a lattice with the use of only one type of elementary move can give rise to an artificial increase in chain-length dependence appears to have some merit. However, it is clearly not the whole story; with two kinds of elementary moves, a strong increase in chain length dependence still remains. Further, when chains with two kinds of elementary moves are removed from the constraints of a lattice, the chain-length dependence, instead of decreasing still more, increases to a value close to that found for chains on lattices with only one kind of elementary move. The chain-length dependence of the mean-square end-to-end length of off-lattice chains indicates a certain amount of short-range chain stiffness, a fact which is consistent with the value of $\langle \sigma_1 \cdot \sigma_2\rangle/\langle \sigma^2\rangle$ being larger for off-lattice chains than for chains on lattices. This raises the possibility that the off-lattice chains are farther from their limiting long-chain behavior than are chains of the same numbers of beads on lattices.

Romiszowski and Stockmayer[18] and Kovac and co-workers[10,11] have reported the results of simulations of the dynamical behavior of bead-stick models on simple cubic lattices. Romiszowski and Stockmayer use the same move

Table III
Values of p, N, D, T_D/τ_1, R_D^{-1}, $\langle l^2 \rangle$, and $D_{\tau 1}/\langle l^2 \rangle$ for the Various Lattices[a]

lattice	p	N	D	T_D/τ_1	R_D^{-1}	$\langle l^2 \rangle$	$D_{\tau_1}/\langle l^2 \rangle$
BCC	0.0	9	4.06 (0.43)	4.0	2.22 (0.23)	34.48 (0.82)	0.055
		15	5.00 (0.45)	8.6	3.00 (0.27)	68.2 (1.0)	0.037
		33	5.12 (0.54)	5.1	6.44 (0.68)	191.4 (3.7)	0.056
		63	4.45 (0.40)	9.3	14.2 (1.3)	410.6 (4.6)	0.032
BCC	0.5	9	9.54 (0.76)	12.6	2.07 (0.16)	34.75 (0.54)	0.046
		15	16.5 (1.9)	11.2	2.10 (0.24)	69.68 (0.96)	0.045
		33	29.7 (2.3)	11.6	2.68 (0.21)	185.7 (2.2)	0.046
		63	41.2 (6.2)	14.3	3.75 (0.57)	400.0 (5.8)	0.042
		99	91 (12)	9.4	2.68 (0.35)	705.9 (9.7)	0.070
BCC	1.0	9	16.4 (1.4)	6.1	1.86 (0.16)	34.50 (0.74)	0.041
		15	17.4 (2.4)	10.6	3.13 (0.44)	67.28 (1.00)	0.031
		33	18.1 (1.9)	8.8	6.99 (0.75)	187.5 (3.8)	0.026
		63	18.4 (2.7)	11.8	13.4 (2.0)	402.1 (5.1)	0.026
FCC	0.0	9	2.68 (0.23)	5.4	2.24 (0.20)	21.69 (0.52)	0.029
		15	3.99 (0.52)	7.3	2.51 (0.32)	42.80 (0.77)	0.042
		33	5.00 (0.93)	9.4	4.40 (0.82)	118.2 (2.7)	0.042
		63	3.57 (0.41)	6.6	11.8 (1.4)	254.0 (3.5)	0.031
FCC	0.5	9	8.9 (1.1)	14.1	1.48 (0.19)	22.43 (0.45)	0.047
		15	11.0 (1.2)	10.2	2.10 (0.22)	42.63 (0.74)	0.043
		33	21.8 (1.6)	14.3	2.44 (0.18)	118.66 (0.68)	0.043
		63	34.5 (5.2)	17.9	2.99 (0.45)	258.1 (3.5)	0.043
		99	63.4 (4.8)	11.0	2.57 (0.19)	446.6 (6.9)	0.049
FCC	1.0	9	11.8 (1.4)	4.2	1.73 (0.20)	21.90 (0.57)	0.060
		15	14.9 (1.6)	13.8	2.43 (0.27)	44.33 (0.62)	0.031
		33	21.4 (2.1)	9.8	3.94 (0.39)	117.5 (1.0)	0.035
		63	25.3 (4.9)	7.6	6.5 (1.3)	262.3 (5.7)	0.036
SC	0.0	9	0.987 (0.077)	6.6	3.04 (0.24)	12.90 (0.21)	0.040
		15	1.55 (0.11)	6.8	3.22 (0.23)	25.38 (0.47)	0.053
		33	1.70 (0.19)	8.0	6.46 (0.73)	70.4 (1.5)	0.047
		63	0.958 (0.060)	14.1	21.9 (1.4)	151.8 (1.3)	0.031
SC	0.5	9	2.84 (0.31)	8.2	2.32 (0.25)	13.30 (0.22)	0.045
		15	4.20 (0.44)	7.9	2.75 (0.29)	25.17 (0.33)	0.036
		33	7.46 (0.60)	8.1	3.56 (0.29)	67.7 (1.5)	0.035
		45	8.20 (0.72)	13.1	4.45 (0.39)	99.4 (1.6)	0.037
		63	10.49 (0.66)	5.7	4.91 (0.31)	148.2 (1.9)	0.055
		99	15.7 (1.4)	13.7	5.20 (0.47)	255.9 (3.6)	0.041
SC	1.0	9	4.71 (0.44)	12.1	2.17 (0.20)	13.14 (0.14)	0.050
		15	4.48 (0.62)	9.1	4.05 (0.56)	25.09 (0.42)	0.033
		33	5.29 (0.50)	7.3	7.95 (0.75)	69.7 (1.4)	0.036
		63	3.81 (0.24)	14.5	21.5 (1.4)	150.3 (1.1)	0.030
none	0.5	9	1.83 (0.19)	8.5	3.62 (0.37)	15.26 (0.17)	0.036
		15	3.13 (0.41)	7.4	3.70 (0.49)	32.43 (0.57)	0.045
		33	3.04 (0.35)	6.8	8.7 (1.0)	91.00 (0.90)	0.034
		63	4.83 (0.31)	3.4	10.67 (0.68)	210.1 (2.4)	0.054

[a] Translational diffusion constants, D, are given for models with a fraction, p, of two-bead moves and chains of N beads with excluded volume, in units of (lattice unit)^2/(N^3 move cycles), on the lattices indicated. Also shown are ratios T_D/τ_1 of the times T_D over which displacements of the centers of mass of the chains were sampled to estimate the diffusion constants to the long relaxation times, τ_1; reciprocal ratios $R_D^{-1} = {}^0D/D$ of the diffusion constants, ${}^0D$, calculated for chains without excluded volume constraints to the values of D found for chains of the same length and value of p and on the same latttice with excluded volume constraints; mean-square end-to-end lengths, $\langle l^2 \rangle$, in units of (lattice unit)^2; and values of the dimensionless ratio $D\tau_1/\langle l^2 \rangle$. Numbers in parentheses are sample standard deviations of the mean.

rules as ours, except that multiple occupancy of lattice sites is discouraged by a preset Boltzmann factor instead of being totally forbidden. As one might expect, their results become similar to ours as the repulsive energy becomes large. Kovac and co-workers employ two kinds of bead move, one similar to our one-bead move and the other to a two-bead move which cannot be described as an interchange of bead connection vectors. In addition, they choose move type on a contingent basis, attempting one type of move if the other is found to be blocked. Their models show a much weaker dependence of long relaxation time upon chain length for chains with excluded volume than do ours. However, the appropriateness of their model's move rules has been questioned[18] on the grounds that allowing moves on a contingent basis might be expected to distort the time scale. Indeed, one might construct a model with a whole hierarchy of kinds of move, in which at each cycle one kind of move after another was attempted until an unblocked one was found. Depending upon the set of moves chosen, this could easily lead to a model in which long relaxation times were actually decreased by the excluded volume constraint, a rather unphysical result. Thus, the selection of a particular set of move rules predetermines the effect of excluded volume on the time scale and the corresponding lengthening of relaxation times.

The effects of excluded volume upon chains are complex, even in the case of equilibrium dimensions. The same hard-core repulsive interactions which expand chains in dilute solution eventually cause contraction back (approximately) to the nonexcluded volume values at sufficiently high bead densities. The effects of excluded volume upon such dynamical properties as viscosity appear to depend even more strongly upon chain length and bead

density than do equilibrium dimensions. The finding reported in this paper that lattice type does not materially affect the dynamical behavior, but that bead movement rules do, is perhaps not surprising in this regard. Further, these results raise the possibility that universal chain-length dependences of dynamical properties analogous to those found for equilibrium dimensions may simply not exist; i.e., nontrivial dependence upon move rules may be unavoidable.

Lastly, the chain-length dependences of D, τ_1, and $\langle l^2 \rangle$ track in such a way that the dimensionless ratio $D\tau_1/\langle l^2 \rangle$ stays more or less constant, with about the same value calculated for a Rouse bead-spring model, independent of lattice, move rules, chain length, or excluded volume constraints. This ratio may be the sole universal quantity for dynamical properties.

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(13) Throughout this paper, the word "random" with reference to computer simulations means the result of using a pseudorandom number generator. The generator employed in the present work was of the multiplicative congruential type, with a multiplier of 5^{13} and a modulus of 2^{35}.
(14) For $p = 0.5$ and $N = 99$, we obtain the value 0.0413 in units of N^3 move cycles. The correct value of ${}^0\tau_1$ for $p = 0.0$ and $N = 63$ is 0.1013, not 0.1010 as given in ref 8. (The corresponding ratio R in Table III of ref 8 should be 47.5 instead of 47.7.) The remaining values of ${}^0\tau_1$ are as reported in ref 8.
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Investigation of Local Motions in Polymers by the Dynamic Rotational Isomeric State Model

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ABSTRACT: The internal dynamics of a short sequence in a chain is studied according to the dynamic isomeric state scheme. Conformational transitions with dynamic pair correlations are considered. Resistance to dynamic rearrangements resulting from environmental effects and constraints operating at the ends of a sequence is incorporated into the calculation scheme. Calculations for a short sequence in a polyethylene chain showed that pair correlations do not significantly affect the orientational relaxation of a vector affixed to a bond of the sequence. Contribution from constraints, on the other hand, is dominant and slows down the orientational motions.

Introduction

The Rouse–Zimm model,[1,2] though successful in representing the low-frequency motions of polymeric chains, is unsuitable for rapid relaxation processes that are attributed to local conformational transitions of the backbone. These motions are studied by techniques such as NMR, dielectric relaxation, fluorescence anisotropy decay, ESR, ultrasonic relaxation, dynamic light scattering, giving information about the orientation correlation functions and/or the corresponding spectral densities. A common feature deduced from experimental evidence is the occurrence of a nonexponential relaxation associated with local backbone rearrangements. To explain the observed departure from Debye behavior, on a molecular basis, stochastic jump models, both numerical[3-7] and analytical,[8-12] have been developed. In dynamic Monte Carlo techniques, Verdier and Stockmayer[3,4] and Gêny and Monnerie[5] adhered to the postulate of local coordinated motion leaving unchanged the tails surrounding the mobile segment. Such crankshaft motions were first conceived by Boyer and Schatzki.[13] On the other hand, Helfand et al.[6-9] concentrated on the transitions of a single bond, accompanied by some distortion and deformation spread over the neighboring units, in order to accommodate the newly created isomeric state. In fact, the experimentally observed[14-16] activation energies and Brownian simulations[6,7] suggest the crossing of but a single rotational barrier during local motions. According to their kinetic theory, which employs an extension of Kramer's rate theory,[17] compensating pair transitions are between second neighbors and occur only when the intervening bond is in the trans position. The two-state model proposed by Hall and Helfand[7] treats two types of transitions, cooperative and individual, leading respectively to compensating motions of neighboring units and translation of chain ends.

The basic physical and mathematical character of local chain dynamics is delineated in the above studies and in several references cited therein. The local dynamics may conveniently be described by the orientational relaxation of a vector affixed to a bond of the chain. That this relaxation progresses through correlated rotational transitions of the bonds of the sequence is now well established. However two fundamental points brought out by these studies still remain unsettled. First, the effect of neighbor

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