Computer Simulation of Shape Relaxation in Cubic Lattice Models of Linear Polymers

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Introduction

The study of shape fluctuations of polymer chains was initiated long ago by Šolc, Stockmayer, and Gobush[1-3] following the work of Koyama.[4] The equilibrium shapes of linear polymers have continued to attract some attention, particularly in the context of random walk theory.[5] The dynamics of shape fluctuations in polymer chains were first studied by Kranbuehl, Verdier, and Spencer[6] and by Kranbuehl and Verdier.[7] They used a dynamic Monte Carlo method to calculate the autocorrelation functions of the eigenvalues of the radius-of-gyration tensor of cubic lattice chains of lengths 9, 15, 33, and 63 beads, both with and without excluded volume. After a long hiatus there has been some recent interest in the dynamics of shape fluctuations of uniform star polymers.[8-10]

In this note we report a study of the dynamics of shape fluctuations of cubic lattice models of linear polymer chains using a dynamic Monte Carlo method.[11] Since the model employed in this study has given quite different results from the algorithm of Kranbuehl and Verdier, it seemed worthwhile to see whether these differences persist for the case of shape fluctuations. We were also interested in comparing these results with those of a concurrent study of star polymers.[10]

There are two kinds of motions of the instantaneous ellipsoidal shape of a polymer coil. The first is fluctuations of the extensions of the segment density along the three principal axes of the ellipsoid. These are termed breathing motions. The second is rotation of the ellipsoid without significant change of the principal axis extensions. Both can be studied by diagonalizing the radius-of-gyration tensor. The eigenvalues provide a measure of the asphericity of the segment density while the eigenvectors are related to the angles that the principal axes make with respect to a fixed laboratory coordinate system. We have studied both processes. In the case of the breathing motions we are able to compute a simple exponential relaxation time and study the dynamic scaling relations. The rotations, however, seem to relax in a nonexponential fashion and, therefore, are much harder to understand.

Model

The simple cubic lattice model developed by Gurler, Crabb, Dahlin, and Kovac[11] was used in this study. Five or more simulation runs for chains of lengths of 23, 35, 47, 59, and 71 bonds were carried out. The time unit was taken to be N bead cycles as in previous work.

The chain motions were studied by first computing the radius-of-gyration tensor S_{ij} defined by Šolc.[2] The elements of S_{ij} are given by the formula

$$S_{ij} = N^{-1}\sum_k x_i^k x_j^k - N^{-2}\sum_k x_i^k \sum_k x_j^k \qquad (1)$$

where i and j designate the coordinate axes and k is the index designating the kth unit of the chain. The tensor S_{ij} is numerically diagonalized. The eigenvalues, λ_i, represent the extensions of the radius of gyration along the principal axes. From the numerically determined eigenvectors we can extract the angles of rotation (θ,ϕ) of the principal axes with respect to the fixed laboratory coordinate system. We then compute the second-order spherical harmonics, $Y_i(\theta,\phi)$, of these angles. The dynamics of the chain are then monitored by calculating the autocorrelation functions of the various quantities according to the formula

$$\rho_A(t) = (\langle A(t)A(0)\rangle - \langle A\rangle^2)/(\langle A^2\rangle - \langle A\rangle^2) \qquad (2)$$

where $A = \lambda_1, \lambda_2, \lambda_3, Y_1^2, Y_2^2$, and Y_3^2. The squares of the spherical harmonics are used because the numerical diagonalization procedure does not produce a consistent direction for the principal axes. A switch in direction introduces a nonphysical jump in the value of the spherical harmonic. Use of the square neatly eliminates this problem.

Table I
Equilibrium Values of the Eigenvalues of the Radius-of-Gyration Tensor, λ_i, as a Function of the Chain Length, N, for both the Ideal Chain and Excluded Volume Cases

	ideal chain			excluded volume		
$N-1$	$\langle\lambda_1\rangle$	$\langle\lambda_2\rangle$	$\langle\lambda_3\rangle$	$\langle\lambda_1\rangle$	$\langle\lambda_2\rangle$	$\langle\lambda_3\rangle$
23	3.00	0.722	0.261	5.85	1.17	0.384
35	4.69	1.04	0.389	9.72	1.94	0.638
47	6.67	1.40	0.519	13.7	2.76	0.910
59	8.64	1.78	0.650	18.0	3.63	1.20
71	10.5	2.17	0.782	22.5	4.58	1.51

Results and Discussion

The equilibrium values for the eigenvalues of the radius-of-gyration tensor are given in Table I. The average ratio of the eigenvalues is 12.77:2.75:1.00 in the ideal chain case and 15.11:3.04:1.00 in the excluded volume case. These ratios compare fairly well with the results of Šolc and Stockmayer[1] for ideal chains, those of Mazur, Guttman, and McCrackin[12] for the excluded volume case, and the comparable ratios for both cases obtained by Kranbuehl and Verdier.[7]

We have also studied the chain length dependence of the eigenvalues by computing the static scaling exponent, 2ν. For ideal chains the exponents are 1.09, 0.98, and 0.97 for the three eigenvalues, while for excluded volume chains they are 1.19, 1.21, and 1.21. The agreement with the expected values is excellent.

The relaxation times, τ_{λ_i}, for the autocorrelation functions of the eigenvalues, which correspond to the breathing motions, were computed by fitting an unweighted least-squares line to the linear long-time portion of a semilogarithmic plot of $\rho_{\lambda_i}(t)$ vs t. These eigenvalue relaxation times are collected in Table II.

The eigenvalue relaxation times were analyzed in two ways. First, we computed the scaling exponent a_i which gives the chain length dependence of the relaxation times according to the relation

$$\tau_{\lambda_i} \sim (N-1)^{a_i} \qquad (3)$$

The values of a_i are 2.05, 1.99, and 1.95 for $i = 1$, 2, and 3, respectively, in the ideal chain case and 2.23, 2.17, and 2.18 in the excluded volume case. These values correspond well to the expected values of 2.0 and 2.2 for the two cases. The results of Kranbuehl and Verdier show an exponent of 2.0 in the ideal chain case, but an exponent greater than 3.0 in the presence of excluded volume. The difference

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Table II
Relaxation Times, τ_{λ_i}, for the Breathing Motions as a Function of the Chain Length, N, in both the Ideal Chain and the Excluded Volume Cases[a]

	excluded volume			ideal chain		
$N-1$	τ_{λ_1}	τ_{λ_2}	τ_{λ_3}	τ_{λ_1}	τ_{λ_2}	τ_{λ_3}
23	39.9 (8.7)	10.9 (2.2)	4.13 (0.72)	31.0 (7.9)	7.46 (0.55)	2.12 (0.23)
35	104 (12)	25.7 (2.3)	9.71 (0.71)	86.6 (20)	16.8 (2.3)	5.13 (1.3)
47	216 (35)	47.8 (8.9)	19.2 (2.3)	152 (20)	28.0 (4.0)	7.91 (2.4)
59	344 (35)	89.6 (12)	32.7 (3.8)	237 (40)	48.16 (5.3)	13.3 (1.2)
71	472 (88)	119 (13)	47.0 (1.7)	310 (60)	70.7 (13)	20.0 (2.3)

[a] Standard deviations are shown in parentheses.

Table III
Values of the Ratio $R_i = \tau_{\lambda_i}/[\lambda_i(N-1)]$ as a Function of the Chain Length, N, for both the Ideal Chain and the Excluded Volume Cases

	ideal chain			excluded volume		
$N-1$	$i=1$	$i=2$	$i=3$	$i=1$	$i=2$	$i=3$
23	0.433	0.449	0.352	0.296	0.405	0.468
35	0.528	0.463	0.377	0.307	0.378	0.435
47	0.484	0.429	0.324	0.336	0.369	0.500
59	0.465	0.440	0.346	0.323	0.418	0.462
71	0.416	0.460	0.359	0.306	0.367	0.440

between the two stimulation models has been seen before[11] and analyzed by Deutch and co-workers.[13]

In a study of the shape fluctuations of star polymers[10] we found that a generalized dynamic scaling relation of the form

$$\tau_{\lambda_i} \sim \lambda_i(N-1) \tag{4}$$

held for the relaxation times of the eigenvalues. To test this relation we computed the ratio $R_i = \tau_{\lambda_i}/[\lambda_i(N-1)]$. The values of R_i are shown in Table III. It is clear from the table that this ratio is essentially independent of chain length but does depend weakly on the eigenvalue being considered. For the excluded volume case there is a consistent increase in this ratio as the size of the eigenvalue increases. This means that the relaxation times for the fluctuations along the smallest axis are relatively longer than along the other two axes. This may be an indication of local chain rigidity, since the average extension along this direction is so small that the segment density is nearly planar.

The autocorrelation functions of the spherical harmonics $\rho_{Y_i^2}(t)$ are a measure of the rigid-body rotational motions of the polymer coil. A semilogarithmic plot of a typical rotational autocorrelation function is shown in Figure 1. This function does not have an obvious linear region even at the longest times. This behavior was observed for all three spherical harmonics and for all chain lengths studied, both with and without excluded volume. It is consistent with the rotational relaxation behavior of star polymers.[10] For this reason we did not attempt to extract a relaxation time from the decay of the autocorrelation functions,

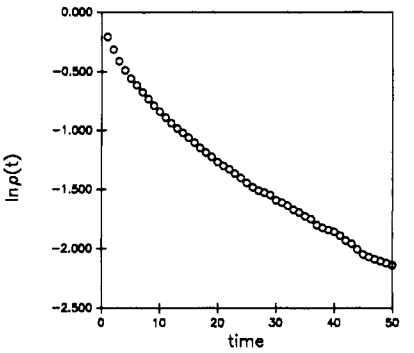

Figure 1. Semilogarithmic plot of a typical autocorrelation function for the rotational relaxation.

although this could be done with a Kohlrausch–Williams–Watts function. The origin of this nonexponential time dependence is not obvious and deserves further study.

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