Monte Carlo Studies of Self-Interacting Polymer Chains with Excluded Volume. II. Shape of a Chain

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ABSTRACT: The principal moments of the squared radius of gyration of polymer chains with excluded volume were computed for chains on the simple cubic and face-centered cubic lattices. The moments were ordered for each configuration by their magnitude, then averaged over a large number of chain configurations and divided by the squared radius of gyration to yield shape factors of the chain. These shape factors were found to be independent of chain length for long chains. The shape factors showed that the instantaneous shape of a polymer chain is very asymmetrical. With increasing interaction energy between the segments of the chains, the chains became less asymmetrical; at the Θ point the shape factors became equal to those of the random coil as previously calculated by Šolc and Stockmayer. The relative variations of the principal moments were also calculated. The largest principal moments were found to have the largest relative variations.

Kuhn[1] in the early thirties was able to show that for the freely jointed model of a polymer in solution, the instantaneous shape of the molecule is not spherical. However, he provided no picture of its instantaneous shape.

Recently, Šolc and Stockmayer[2] and Šolc[3] have presented both analytical and Monte Carlo calculations on the random-coil polymer model which gave quantitative estimates on the deviations from sphericity. However, the random-coil model of a polymer in solution does not take into account the effects of either excluded volume or attractive energies between segments of the polymer. In this paper, we investigate the effects of excluded volume and attractive energy between nearest-neighbor segments on the deviations from sphericity of chains on a lattice generated by the Monte Carlo method.

Description of Calculation

In the first paper in this series[4] (paper I) we presented Monte Carlo calculations of the mean-squared radius of gyration[5] and of the mean squared end-to-end distance on a three-dimensional lattice model of a polymer chain with excluded volume and nearest-neighbor attractive energies. We shall not repeat the details of the model employed or of calculational techniques here. Suffice it to say that chains with N segments are laid on a three-dimensional lattice which is either simple cubic or face-centered cubic. No two polymer beads are allowed to occupy the same lattice point (excluded volume); nonbonded beads on nearest-neighbor sites are assumed to interact with each other *via* a fixed energy ϵ. Our results are presented as functions of the interaction parameter $\Phi = -\epsilon/k_B T$, where k_B is Boltzmann constant and T is the temperature. More details of the model, of calculational techniques and of other results appeared in paper I.[4]

Let s_{xi}, s_{yi}, and s_{zi} be the coordinates of the vector $\mathbf{s}_i$ from the center of gravity of the chain to the ith bead of the chain. Following Šolc,[3] for each chain we computed the symmetrical tensor with components given as averages over the chain of products of the components of $\mathbf{s}_i$.

$$X_{xx} = \frac{1}{N}\sum_{i=1}^{N} s_{xi}^2 \qquad X_{xy} = \frac{1}{N}\sum_{i=1}^{N} s_{xi}s_{yi}$$
$$X_{xz} = \frac{1}{N}\sum_{i=1}^{N} s_{xi}s_{zi} \tag{1}$$

This tensor is related to the tensor of inertia by

$$N\bar{X} = NS^2\bar{E} - \bar{I} \tag{2}$$

where $\bar{X}$ is the matrix defined by eq 1, $\bar{E}$ is the unit matrix, $\bar{I}$ is tensor of inertia of the chain considered as a rigid body with beads of unit mass, and S^2 is the squared radius of gyration of the chain given by

$$S^2 = \frac{1}{N}\sum_{i=1}^{N}(s_{xi}^2 + s_{yi}^2 + s_{zi}^2) \tag{3}$$

The trace of $\bar{X}$ is seen to be equal to the squared radius of gyration of the chains:

$$S^2 = X_{xx} + X_{yy} + X_{zz} \tag{4}$$

For each chain configuration generated, $\bar{X}$ was diagonalized to yield the moments along the principal axes of the chain. These principal moments were ordered and called L_1^2, L_2^2, and L_3^2 so that $L_3^2 \geq L_2^2 \geq L_1^2$. The averages of the ordered quantities were obtained in a manner similar to other averages discussed in paper I. The average squared radius of gyration $\langle S^2\rangle = \langle L_1^2\rangle + \langle L_2^2\rangle + \langle L_3^2\rangle$ was also computed. The dimensionless ratios $\langle L_1^2\rangle/\langle S^2\rangle$, $\langle L_2^2\rangle/\langle S^2\rangle$, and $\langle L_3^2\rangle/\langle S^2\rangle$, which we shall call shape factors, are used to characterize the shape of the chains.

Results

The average principal moments were computed for a range of values of the interaction parameter Φ on the simple cubic and face-centered cubic lattices for chain lengths N from 50 to 500. The coefficients of variation of the averages, estimated by the method of paper I, were less that 5% for $\langle L_1^2\rangle$, $\langle L_2^2\rangle$, and $\langle L_3^2\rangle$. The shape factors $\langle L_1^2\rangle/\langle S^2\rangle$, $\langle L_2^2\rangle/\langle S^2\rangle$ and $\langle L_3^2\rangle/\langle S^2\rangle$ were then computed to characterize the shape of the chains.

Within the accuracy of the data, no variation with chain length from N = 50–500 for the ratios $\langle L_1^2\rangle/\langle S^2\rangle$, $\langle L_2^2\rangle/\langle S^2\rangle$, or $\langle L_3^2\rangle/\langle S^2\rangle$ was observed. Therefore the values of each ratio for the same values of Φ but for different values of N were collected and averaged, and the averages are shown in Table I for the face-centered cubic and simple cubic lattices.

For spherically symmetric chains, the ratios shown in Table I would all equal 1/3. Since the values deviate greatly from this value, the chains with excluded volume and nearest neighbor interaction remain asymmetrical. The chains with excluded volume but without interaction energies (Φ = 0) are seen to be the most asymmetrical.

As the interaction between segments increases (increasing Φ) the chains become more symmetrical although they remain very asymmetrical even for large values of Φ.

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(5) Radius of gyration is used in the sense commonly employed in chain statistics instead of its meaning in mechanics.

Table I
Ratios of Principal Moments to Radius of Gyration Squared for Chains with Excluded Volume and Interactions and for Random-Coil Chains (Chains without Excluded Volume or Interactions)

	$\Phi = 0$	0.1	0.2	0.25	0.3	0.4	Random Coil[a]
			Simple Cubic Lattice				
$\langle L_3^2\rangle/\langle S^2\rangle$	0.785	0.784	0.774	0.767	0.757	0.731	0.760
$\langle L_2^2\rangle/\langle S^2\rangle$	0.162	0.162	0.167	0.170	0.176	0.189	0.175
$\langle L_1^2\rangle/\langle S^2\rangle$	0.053	0.054	0.059	0.062	0.067	0.079	0.065
	$\Phi = 0$	0.05	0.1	0.125	0.15	0.2	
			Face-Centered Cubic Lattice				
$\langle L_3^2\rangle/\langle S^2\rangle$	0.779	0.776	0.769	0.762	0.751	0.706	
$\langle L_2^2\rangle/\langle S^2\rangle$	0.164	0.166	0.170	0.174	0.180	0.204	
$\langle L_1^2\rangle/\langle S^2\rangle$	0.056	0.057	0.061	0.064	0.069	0.091	

[a] Sŏlc and Stockmayer.[2]

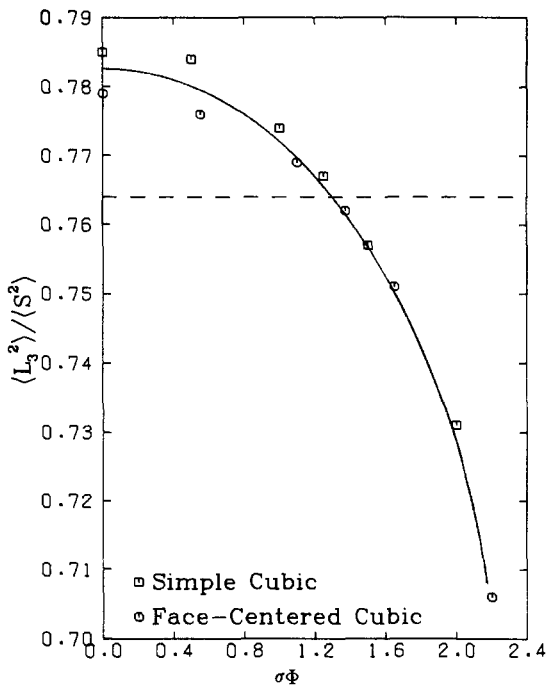

Figure 1. The largest shape factor $\langle L_3^2\rangle/\langle S^2\rangle$ *vs.* $\sigma\Phi$ for face-centered cubic and simple cubic lattices. The dashed line shows the value for a random coil (ref 2).

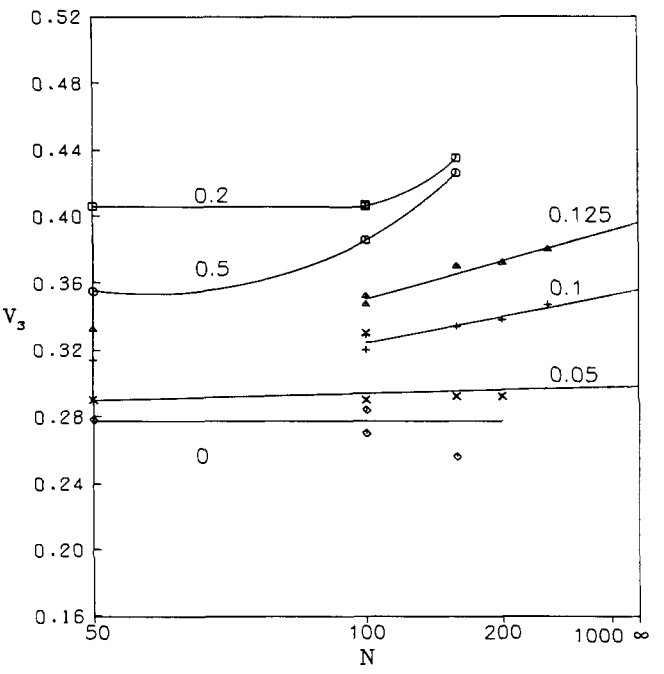

Figure 2. The relative variance of L_3^2, $V_3 = \langle L_3^4\rangle/\langle S^2\rangle^2 - 1$, for the face-centered cubic lattice *vs.* chain length N on a reciprocal scale. The curves are labeled by the interaction parameter Φ. The data are extrapolated to $N = \infty$ whenever possible.

Let σ be the number of choices for a step of the chain on the lattice so that $\sigma + 1$ is the coordination number of the lattice. For the simple cubic and face-centered cubic lattices, σ is 5 and 11, respectively. A number of parameters related to $\langle R^2\rangle$ and $\langle S^2\rangle$ were found in paper I to be independent of the lattice when plotted *vs.* $\sigma\Phi$. Therefore, $\langle L_3^2\rangle/\langle S^2\rangle$ for both lattices is shown plotted *vs.* $\sigma\Phi$ in Figure 1.

The values for both lattices are seen to lie near a single curve. For $\sigma\Phi = 1.3$, they equal the value obtained by Šolc and Stockmayer for the random-coil model without excluded volume or attractive energies between segments. This value is less than the critical value of $\sigma\Phi = 1.37$ found in paper I at which $\langle R^2\rangle$ and $\langle S^2\rangle$ are proportional to the chain length N.

The magnitude of fluctuation of any one of the principal moments may be estimated by

$$V_i = \frac{\langle L_i^4\rangle - \langle L_i^2\rangle^2}{\langle L_i\rangle^2} \qquad (5)$$

where $i = 1$, 2, or 3. The quantity V_i measures the relative variance in elongation squared along the principal axes. Figure 2 shows values of V_3 for the face-centered cubic lattice *vs.* chain length N for various values of Φ. The chain length N is plotted on a reciprocal scale so that the point $N = \infty$ is at the right of the scale. Significant dependence of the V_3 values upon chain length at a fixed value of Φ was found. The data were extrapolated to $N = \infty$ whenever possible. For example, in Figure 2, V_3 was extrapolated to $N = \infty$ for $\Phi = 0.05$, 0.1, and 0.125 as shown, while the data for $\Phi = 0$, 0.15, and 0.2 were considered to be insufficient for extrapolation. In order to extrapolate the data for $\Phi = 0$, 0.15, and 0.2, more data for larger values of N are required.

The values of V_1, V_2, and V_3, extrapolated to infinite chain length for the face-centered cubic and simple cubic lattice, are shown *vs.* $\sigma\Phi$ in Figure 3. The most striking feature of the V_i is that $V_3 > V_2 > V_1$; that is, the fractional variation of the moments is greater, the greater the magnitude of the moment. Furthermore, V_3 is much greater than either V_2 or V_1 and seems to be increasing as

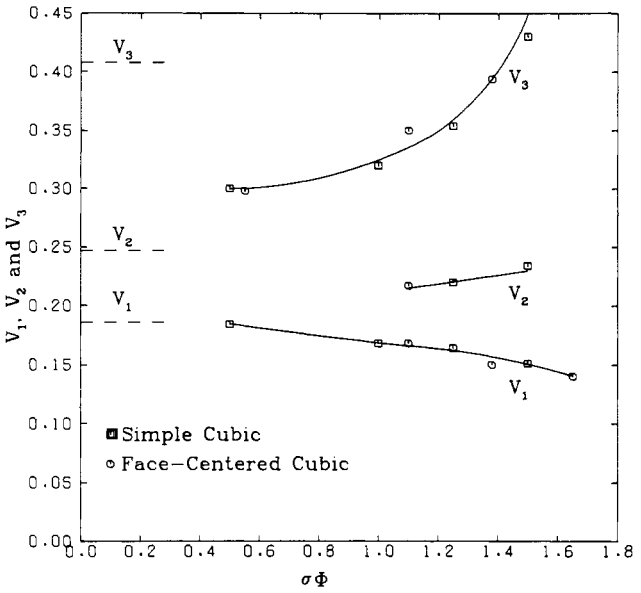

Figure 3. The relative variances of the principal moments for chains *vs.* $\sigma\Phi$.

Φ increases. These results say that the absolute variance along the long direction of the molecules is much greater than that along the other two directions.

In Figure 3 we have also noted by dashed lines the random-coil values of V_i as computed from the data of Šolc for five-choice chains of 200 segments.

Conclusions

The asymmetry of a random chain with excluded volume and attractive energies between segments was investigated for chains on the face-centered cubic and simple cubic lattices. The ratios of the ordered principal moments to the radius of gyration of the chains, the shape factors, differed greatly from the value of 1/3 for a symmetrical chain when viewed on their principal axes.

The shape factors have been found to be independent of the chain length in the range of N = 50–500. The shape factors are seen by Table I and Figure 1 to get slightly closer to the value 1/3 of a symmetrical polymer as Φ increases. Thus the chains become slightly more symmetrical with increasing attractive energies between segments. For Φ between 0.25 and 0.3 on the simple cubic lattice, the shape factors have the values for a random coil previously calculated by Stockmayer and Šolc.[2] This is the critical range of Φ in which other properties of the chain have been found in paper I to equal the random-coil values. The shape factors were also found to be independent of the lattice when plotted *vs.* $\sigma\Phi$. $\langle L_3^2\rangle/\langle S^2\rangle$ was found to have the value of a random coil at $\sigma\Phi$ = 1.29, while $\langle S^2\rangle$ has the value of a random coil at $\sigma\Phi$ = 1.39. However, the shape factors show much less variation with Φ than does $\langle S^2\rangle$ and do not deviate greatly from the random-coil values.

The relative variations (V_1, V_2, and V_3) among chain configurations of the principal moments have also been calculated. Some dependence on the chain length was found, so the variations of the moments were extrapolated to infinite chain lengths whenever possible. The variation V_3 of the largest principal moment is seen in Figure 3 to be much larger than the variations of the other principal moments, and to increase with increasing interaction parameter Φ. Also, the variations of the principal moments are independent of lattice when plotted *vs.* $\sigma\Phi$.

Intrinsic Viscosity Measurements on Rodlike Poly(n-butyl isocyanate) and Poly(n-octyl isocyanate)

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ABSTRACT: Previous calculations of the molecular length of rodlike poly(n-butyl isocyanate), $(-CO-NC_4H_9-)_n$, from dielectric relaxation time measurements have not shown satisfactory agreement with the results from X-ray and light-scattering measurements. Here, we examine this conflict by extending our hydrodynamic experiments to include intrinsic viscosity measurements on well-characterized low molecular weight samples of poly(n-butyl isocyanate) (PBIC) and poly(n-octyl isocyanate) (POIC), $(-CO-NC_8H_{17}-)_n$. Using the Kirkwood-Auer-Riseman equation relating intrinsic viscosity and rod dimensions, the intermonomer translation along the rod axis is calculated to be 1.66 ± 0.12 Å. This is lower than the 1.94-Å result from X-ray measurements, but higher than the 1.33 ± 0.12 Å result from dielectric relaxation time measurements. The root of the problem appears to be the application of hydrodynamic equations to a physical situation which does not satisfy the model assumptions.

The rodlike molecular posture of low molecular weight poly(n-butyl isocyanate) (PBIC) in solution has been the object of measurement in many experiments. These measurements, dielectric,[2a,b,3] light scattering,[4] electric dichroism,[5,6] electric birefringence,[7,8] rotatory diffusion,[8] and intrinsic viscosity,[8] demonstrate the rigid rod conformation of the polymer molecule. However, the quantita-

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