Statistics of polymer chains embedded on a diamond lattice.\textsuperscript{a)\text} 

I. Exact results for the lattice version of the freely rotating chain

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A polymer of finite length is embedded on a diamond lattice where the angle between adjacent monomers is \(\cos^{-1}(-1/3) = 109^\circ\). We show that the characteristic function \(C_n(k)\) can be calculated in closed form for an \(n\) link chain if all configurations (i.e., \textit{trans} and \textit{gauche}) are given equal weights. It is necessary to do a spherical average to get rid of the cubic symmetry artificially imposed by the diamond lattice. This represents the only model, other than the freely \textit{jointed} chain, for which the characteristic function is known in closed form. This model may be regarded as the \textit{lattice version of the freely rotating chain}. From the characteristic function we extract the first few moments \(\langle R^2 \rangle_n\), \(\langle R^4 \rangle_n\), and \(\langle R^6 \rangle_n\). We show that the results for the second and fourth moments are identical to those for the freely rotating chain, but the sixth moment is different. Various approximations to the probability distribution function \(W_n(R)\) [the Fourier transform of \(C_n(k)\)] are tested against the exact result.

I. INTRODUCTION

The standard statistical problem in polymer physics is the calculation of the distribution function for a polymer with \(n\) monomer units having an end-to-end separation of \(R\).\textsuperscript{1} This is usually designated \(W_n(R)\). The Fourier transform of this function \(C_n(k)\) is known as the \textit{characteristic function}. The characteristic function is only known in closed form for one model, the freely jointed chain,\textsuperscript{2} where adjacent monomers can point in any direction with equal probability.\textsuperscript{1} It is also known for equivalent models to the freely jointed chain on lattices where all nearest-neighbor steps are allowed and each step is independent of the previous step.\textsuperscript{3} These models are not very different from the freely jointed chain but have the serious drawback that a finite fraction of the neighboring monomers lie on top of one another because of immediate returns.

In this paper we show that the characteristic function can be obtained for a polymer embedded on a diamond lattice, if \textit{trans} and \textit{gauche} weightings are all made equal to \(\frac{1}{2}\). This corresponds to doing a random walk on the diamond lattice with immediate returns disallowed. This model system is interesting because the angle between adjacent monomers is \(\cos^{-1}(-\frac{1}{2}) = 109^\circ\) which is close to the value observed for many polymers that contain singly bonded C atoms in the spine as in polyethylene. This model is the \textit{lattice version of the freely rotating chain} where the angle between adjacent monomers is fixed. The characteristic function is not known for the freely rotating chain and so it is useful to have the solution given in this paper for the \textit{lattice version of the freely rotating chain}. In the freely rotating chain each monomer can lie on a cone whose axis is defined by the previous monomer, whereas in the lattice version of this model only three discrete equally spaced positions on the cone are allowed. The characteristic function is found by setting up recursion relations between the characteristic functions with different \(n\). This is done in Sec. II and the equations are solved. The solution shows that the characteristic function \(C_n(k)\) depends on \(k\) as the system has cubic rather than isotropic symmetry. This function \(C_n(k)\) has a very simple form and can be expanded in powers of \(k\) to give the first few moments. This is done in Sec. III where it is shown that the moments \(\langle R^2 \rangle_n\) and \(\langle R^4 \rangle_n\) are the same as for the freely rotating chain, whereas \(\langle R^4 \rangle_n\) and the higher moments are slightly different and indeed exhibit an odd-even effect because of the two sublattice nature of the diamond lattice.

In the course of evaluating \(\langle R^4 \rangle_n\) we discovered a mistake in the work of Porod\textsuperscript{4} for the freely rotating chain. We give the correct result in Sec. IV.

In Sec. V we show how \(C_n(k)\) can be spherically averaged and Fourier transformed numerically to give \(W_n(R)\). The Gaussian quadrature procedure for doing this is explained in the appendix. In Sec. VI we compare the exact results for \(W_n(R)\) with various approximations for \(W_n(R)\) based on the first few moments. It can be seen how the chain becomes Gaussian for large \(n\).

Although this model is very simple and probably is not applicable to most real polymers, it is useful to have another closed form solution for the characteristic function to add to the one already known (the freely jointed chain). In a subsequent paper we will explore the extension of this model to more complex weightings (e.g., \textit{gauche} and \textit{trans} weighted differently).

II. CALCULATION OF THE CHARACTERISTIC FUNCTION

The model for the polymer is an \(n\) step walk on a diamond lattice with no immediate returns allowed. This kind of random walk has been considered before although much more attention has been given to random walks with no restrictions.\textsuperscript{3}

The key to the solution of this problem, is that eliminating immediate returns requires that a memory of the \textit{single previous step} be retained. The polymer is embedded on a diamond lattice, a small piece of which is shown in Fig. 1. The two sublattices A and B are shown

\textsuperscript{a)}Work supported in part by the N.S.F.
as solid and open circles, respectively. Every A site is surrounded by B sites and vice versa. When a polymer is embedded on this lattice, it alternates A, B, A, B etc. The four nearest neighbors of an A site are

\[ r_1 = a(1, 1, 1), \]
\[ r_2 = a(1, -1, 1), \]
\[ r_3 = a(-1, 1, 1), \]
\[ r_4 = a(-1, -1, 1), \]

where \( l = a\sqrt{3} \) is the length of a monomer or nearest-neighbor distance. The four nearest neighbors of B site are just the negatives of Eq. (1).

The characteristic function \( C_n(k) \) is defined as

\[
C_n(k) = \langle e^{i k \cdot r_n} \rangle_n = \frac{1}{z} \sum_{r_1} e^{i k \cdot r_1} \frac{1}{(z-1)} \sum_{r_2} e^{i k \cdot r_2} \ldots \frac{1}{(z-1)^{n-1}} \sum_{r_n} e^{i k \cdot r_n},
\]

where the angular bracket \( \langle \cdots \rangle \) denotes an average over all configurations. This average is written out explicitly in Eq. (2) where \( z = 4 \) is the number of nearest neighbor sites and

\[ R = \sum_{i=1}^{n} r_i \]

is the chain vector composed of \( n \) monomer units each described by a vector \( r_i \) of length \( l \). The first monomer unit starts at an A site and can be in any one of \( z = 4 \) directions with no restrictions; all other monomers have \( z-1 = 3 \) choices. A polymer chain is sketched in Fig. 2.

Recurrence relations can be written from Eq. (2) by performing the summations over \( r_n \) and \( r_{n-1} \) to give

\[
(z-1) C_n = \gamma_n C_{n+1} - C_{n-2} \quad \text{for odd } n \geq 3,
\]

\[
(z-1) C_n = \gamma_n C_{n+1} - C_{n-2} \quad \text{for even } n \geq 4,
\]

where we suppress the \( k \) dependence of the \( C_n \) in these equations and \( \gamma_n \) is given by

\[
\gamma_n = 4 \left[ \cos(k_x a) \cos(k_y a) \cos(k_z a) + i \sin(k_x a) \sin(k_y a) \sin(k_z a) \right],
\]

where we have used Eq. (1). The quantity \( \gamma_n^* \) is the complex conjugate of \( \gamma_n \) and \( k = (k_x, k_y, k_z) \).

The recurrence relations Eqs. (3) and (4) can be solved with the boundary conditions

\[ z C_1 = \gamma_1, \]

and

\[ z(z-1) C_2 = \gamma_2 \gamma_1^* - z. \]

These equations can be solved by searching for “normal modes” such that

\[ (C_n - \alpha C_{n+1}) = \beta (C_{n-1} - \alpha^* C_{n+2}) \]

for odd \( n \geq 3 \),

where from Eq. (3),

\[ \alpha + \beta = \gamma_1 / (z - 1) \]

and

\[ \alpha^* \beta = 1 / (z - 1). \]

Similarly

\[ (C_n - \alpha^* C_{n+1}) = \beta^* (C_{n-1} - \alpha C_{n+2}) \]

for even \( n \geq 4 \).

From Eqs. (8) and (9), we find that there are two roots \( \alpha^* \) with their corresponding two roots \( \beta^* \), where

\[ \alpha^* = [\gamma_1 \gamma_1^* z \pm \sqrt{z(\gamma_1^* - 4(z-1))}] / \gamma_1^* \]

and

\[ \beta^* = \alpha^*. \]

We may write

\[ (C_n - \alpha^* C_{n+1}) = |\beta^*| \gamma_1 (C_{n-1} - \alpha C_{n+2}) \]

for even \( n \geq 0 \).

Using the initial values for \( C_2 \) and \( C_4 \) from Eq. (6) we find the complete solution

\[ C_{n+1}(k) = \frac{\gamma_n}{2z} \left( \left[ \frac{(\gamma_n R_n^* - x)^2}{4(z-1) \gamma_n^*} \right]^{n/2} \left( 1 - \frac{\gamma_n R_n^*}{x} + \frac{2z}{x} \right) + \left[ \frac{(\gamma_n R_n^* + x)^2}{4(z-1) \gamma_n^*} \right]^{n/2} \left( 1 + \frac{\gamma_n R_n^*}{x} - \frac{2z}{x} \right) \right) \]

for even \( n \geq 0 \).
\[ C_{m1}(k) = \sqrt{\gamma_k x^2 \left[ \left( \frac{\gamma_k x^2 - x^2}{4(x - 1) \gamma_k x^2} \right) \right]^{n/2} \left( 1 - \frac{\gamma_k x^2}{x} + \frac{2x}{x} \right) + \left[ \frac{(\gamma_k x^2 + x)^2}{4(x - 1) \gamma_k x^2} \right]^{n/2} \left( 1 + \frac{\gamma_k x^2}{x} - \frac{2x}{x} \right)} \] for odd \( n \geq 1 \).

These two equations represent the main results of this paper. Note that \( C_n(k) \) is an even function of \( x \) and so depends on \( x^2 \). This is important as \( x \) [see Eq. (11)] can be either real or imaginary but \( C_n(k) \) is always real for \( n \) even because \( \gamma_k x^2 \) is real and from Eq. (5) is given by

\[ \gamma_k x^2 = 4(1 + \cos(2k_x)/\cos(2k_y) + \cos(2k_x) / \cos(2k_y) \cos(2k_z)). \] (15)

This factor involving the sums of products of pairs of cosines is characteristic of the fcc lattice which is the Bravais lattice for the diamond lattice. The diamond lattice can be regarded as an fcc lattice with two atoms per lattice point. Note that if the first monomer unit had started at a B site rather than an A site, the factors \( \gamma_k \) and \( \gamma_k \) would be interchanged with the net result that the prefactor \( \gamma_k \) would be replaced by \( \gamma_k \) in Eq. (13) and Eq. (14) would be unaltered. For odd \( n \), \( C_n(k) \) has a real and imaginary part because of the \( \gamma_k \) prefactor in Eq. (13). Only the real part has any significance as the imaginary part drops out when either an average is taken over A and B starting sites or a spherical average is done as described in Sec. V.

In order to illustrate these results, we have plotted \( C_n(k) \) for \( n = 4 \) and 5 in Figs. 3 and 4 along the principle symmetry directions. It can be seen that \( C_n(0) = 1 \) as we would expect from the definition (2) and the function is periodic as governed by Eq. (15) for \( n = 4 \) and Eqs. (5) and (15) for \( n = 5 \).

III. MOMENTS

The first few moments can be extracted from our solution. Expanding both sides of Eq. (2), we get

\[ C_n(k) = \langle e^{i \mathbf{k} \cdot \mathbf{R}} \rangle = \left( 1 - \frac{1}{2!} (\mathbf{k} \cdot \mathbf{R})^2 + \frac{1}{4!} (\mathbf{k} \cdot \mathbf{R})^4 - \frac{1}{6!} (\mathbf{k} \cdot \mathbf{R})^6 + \cdots \right). \] (16)

Equation (16) displays the cubic symmetry associated with the lattice. This symmetry makes the odd terms in Eq. (16) equal to zero. In order to extract meaningful moments, we do a spherical average of both sides of Eq. (16) over the surface of a sphere in \( k \) space. Denoting this spherical average by a bar, we obtain on the right-hand side of Eq. (16) terms like

\[ \langle k^p R^q \rangle = \langle k^p (R^q) \rangle / (p + 1). \] (17)

The left-hand side of Eq. (16) is expanded in powers of \( k \) using Eqs. (13), (14), and (15). We also need to spherically average quantities like

\[ \langle k^2 \rangle = k^2 / 5, \]
\[ \langle k^4 \rangle = k^4 / 15, \]
\[ \langle k^6 \rangle = k^6 / 7, \]
\[ \langle k^8 \rangle = k^8 / 35, \]
\[ \langle k^{10} \rangle = k^{10} / 105. \] (18)

The result is that

\[ \frac{\langle R^2 \rangle}{l^2} = 2n - \frac{3}{2} - \frac{3}{2}, \] (19)
\[ \frac{\langle R^4 \rangle}{l^4} = \frac{20}{3} n^2 - \frac{64}{3} n^2 + \frac{57}{2} - \frac{2n}{2} - \frac{57}{2} \frac{1}{3}, \] (20)
\[ \frac{\langle R^6 \rangle}{l^6} = \frac{280}{9} n^2 - \frac{686}{9} n^2 + \frac{7240}{9} n - \frac{21667}{18} - \frac{4}{9} (-1)^n + \frac{70}{3} n^2 + \frac{518}{3} n + \frac{7225}{6} \frac{1}{3}. \] (21)

It is necessary to do a spherical average because the direction of the first monomer unit establishes the cubic symmetry of the whole polymer. The spherical average corresponds to letting this first monomer unit take all possible orientations.

[FIG. 3. Showing \( C_n(k) \) along the three principle symmetry directions. The distance \( a = l / \sqrt{3} \) where \( l \) is the length of a monomer.]

[FIG. 4. Showing the real part of \( C_n(k) \) along the three principle symmetry directions. The distance \( a = l / \sqrt{3} \) where \( l \) is the length of a monomer.]
The second moment \( \langle R^2 \rangle_n \) and fourth moment \( \langle R^4 \rangle_n \) are identical to those for the freely rotating chain with same angle \( \theta = \cos^{-1}(-\frac{1}{3}) \) between adjacent monomers.\(^4\) (Although see comments in the next section.) This is not surprising as the freely rotating chain corresponds to a monomer being able to take up all possible positions on a cone whose axis is defined by the previous monomer. In our model only three discrete positions that are symmetrically placed on the cone are allowed. Ratios of those moments are shown as functions of \( n \) in Fig. 5.

The sixth moment \( \langle R^6 \rangle_n \) is the lowest moment to exhibit an odd-even effect as we would expect on the diamond lattice. This is manifested through the \( 4(-1)^n/9 \) term in Eq. (21). It is extremely small in magnitude.

The sixth moment for this model and the freely rotating chain are not exactly the same. The sixth moment is not available for the freely rotating chain. However we can see they are different by considering \( n=3 \). From Eq.

\[
\frac{3}{2}D_n = \frac{2k}{(1+k)(1-k)^2} (27k^4 + 7k^3 - 4k^2 + 8k + 16) + \frac{2}{(1+k)(1-k)^2} (-3k^5 + 3k^4 + k^3 - 5k^2 - 5k + 1) \\
- \frac{4p^2}{1-p} \left[ 1 + \frac{8k}{(1-k)^2} + \frac{1+k}{(1-k)^2} \right] n \left[ 2 + \left( \frac{1+k}{1-k} \right)^2 \left( 1 - \frac{4p^2}{1-p} + \frac{6k^4}{(1-k)^2} \right) + \frac{16k}{(1-k)^2} \right] \\
+ n^2 \left[ \frac{1+k}{1-k} \right] \left[ \frac{3k}{(1-k)^2} \left( -1 - 2k^2 + k^2 \right) - n(1 + 3k^2) + \frac{2p^2}{(k-p)^2} [k(3k - 2p - 1) + n(1-k)(k-p)] \right] \\
- k^2 \left[ \frac{6k^2}{(1-k)^2} + \frac{4p^2}{1-p} \left[ -1 + 2 \left( \frac{1+k}{1-k} \right)^2 - \frac{8k}{(1-k)^2} \right] + \left( \frac{1+k}{1-k} \right)^2 + \frac{8k}{(1-k)^2} \right] + \frac{16k^2p^2}{(1-k)^2} [2p - k(p + 1)],
\]

where

\[
D_n = \langle R^4 \rangle_n - \langle R^2 \rangle_n^2.
\]  

The errors in the final expression do not appear to be just simple typing errors. We are surprised that this error does not appear to have been reported in the literature before as this result is widely quoted.\(^1\)

If we put \( k = \frac{1}{3} \) and \( p = -\frac{1}{3} \) in this general result Eq. (22) and in the expression for \( \langle R^2 \rangle_n \) [see Porod Eq. (6)], then the results for the fourth moments from Eqs. (20) and (22) are identical with \( l = 1 \).

V. CALCULATION OF \( W_n(R) \)

The probability distribution \( P_n(R) \) for an \( n \) link polymer to have an end to end separation \( R \) is given by

\[
P_n(R) = \frac{1}{(2\pi)^3} \int C_n(k) e^{i R \cdot k} \, dk ,
\]

where \( C_n(k) \) is defined by Eq. (2) and given explicitly by Eqs. (13) and (14). If this integral is evaluated exactly \( P_n(R) \) is only nonzero at discrete \( R \) corresponding to sites in the diamond lattice. This occurs when \( C_n(k) \) is Fourier transformed in Eq. (24) because \( C_n(k + g) = C_n(k) \) for even \( n \) where \( g \) are the reciprocal lattice vectors for the fcc lattice.\(^6\) There is a similar although more complicated periodicity to \( C_n(k) \) for odd \( n \) (see Fig. 4).

As explained earlier it is necessary to do a spherical average so that the first monomer unit points in all possible directions. This is similar to a polycrystalline average in solid state physics.

We find that \( \langle R^2 \rangle_n = 85689/729 \), whereas the result for the freely rotating chain obtained by performing the integration\(^5\) is \( \langle R^2 \rangle_n = 84665/729 \).

IV. FOURTH MOMENT FOR FREELY ROTATING CHAIN

In the course of this work we compared the fourth moment with that of a freely rotating chain. Porod\(^4\) has claimed to have calculated \( \langle R^4 \rangle_n \) for a freely rotating chain as a function of \( k = \cos \theta \) and \( p = (3(\cos^2 \theta) - 1)/2 \), where \( \theta \) is the polymer bond angle. Note that this angle \( \theta \) is the supplement of the angle we have been using. We have repeated this calculation following his method from the initial formulation to the final closed form expression. We have found that the method is correct and that his results are correct up to his penultimate equation (17). However the final expression is incorrect. The correct result is given here:

\[
W_n(R) = \frac{1}{(2\pi)^3} \int_0^\infty S_n(k) \sin \frac{kR}{hR} \, 4\pi k^2 \, dk,
\]

where

\[
S_n(k) = \frac{1}{4\pi} \int_0^\pi \int_0^{2\pi} C_n(k) \sin \theta \, d\theta \, d\phi \sin \theta,
\]

and

\[
e^{-\frac{i R \cdot k}{hR}} = \sin \frac{kR}{hR}.
\]

Thus \( S_n(k) \) is given by averaging \( C_n(k) \) over the surface of a sphere in \( k \) space. This of course has to be done...
numerically. It is explained in detail in the Appendix as it is a most important part of the procedure. Results for \( n = 4 \) and \( n = 5 \) are shown in Figs. 6 and 7, respectively. Although these small values of \( n \) are not so interesting, we show the results so that the small oscillations can be seen. For larger \( n \) the function \( S_n(k) \) becomes close to Gaussian and the ripples become insignificant. Comparing Figs. 3 and 6 and Figs. 4 and 7, it can be seen how the spherical averaging eliminates the periodicity in \( k \) space and gives a function that is strongly peaked around \( k = 0 \). Note that because \( P_n(R) \) is normalized to one, we have \( S_n(0) = 1 \). The behavior of \( S_n(k) \) for small \( k \) is determined by the moments calculated in Sec. III.

The final step in calculating \( W_n(R) \) is to do the one-dimensional integral over \( S_n(k) \) in Eq. (25). The result for \( n = 15 \) is shown by the solid line in Fig. 8. We have chosen to show a relatively small value of \( n \) so that there are substantial deviations from a Gaussian distribution. Strictly speaking, this result should consist of \( \sim (2 \cdot 15)^{1/4} \) closely spaced delta functions. The integration procedure smoothes these out to give a continuous curve. This would not be the case for very small \( n \). In order to help with the convergence of the integral (25) it was found useful to include a convergence factor \( \exp(-\alpha k^4) \) in the integrand where \( \alpha = 0.01 \). If \( \alpha \) is too large the function is distorted and if \( \alpha \) is too small the integral converges too slowly so that \( \alpha = 0.01 \) represents a compromise. The upper limit of integration in Eq. (25) was taken to be large enough so that \( W_n(R) \) did not change significantly by increasing it further.

VI. APPROXIMATIONS TO \( W_n(R) \)

With the existence of an exact solution we can check various approximation schemes involving the low moments.\(^1\) We examine one of these in this section.

We approximate \( S_n(k) \) by

\[
S_n(k) = \exp(-\alpha k^2 - \beta k^4 - \gamma k^6) ,
\]

(28)

where the coefficients \( \alpha \), \( \beta \), and \( \gamma \) can be obtained by noting that

\[
S_n(k) = \frac{\sigma^4(R \phi \rho)^n}{1 - k^2 (R^2)^n/6 + k^4 (R^4)^n/120 - k^6 (R^6)^n/5040}
\]

(29)

where we have used Eq. (17) to do the spherical averaging. Expanding Eq. (28) and equating powers of \( k^2 \) in Eqs. (26) and (29) we find that

\[
\begin{align*}
\alpha &= \langle R^2 \rangle R^2 /6 , \\
\beta &= \langle R^4 \rangle R^2 /120 , \\
\gamma &= \langle R^6 \rangle R^2 /5040 .
\end{align*}
\]

(30)

In our first approximation we put \( \beta = \gamma = 0 \) in Eq. (28) and get the Gaussian approximation for \( S_n(k) \) and hence for \( W_n(R) \) via Eq. (25). This is shown by the dot–dash line in Fig. 8. A better approximation is obtained by keeping \( \beta \) and putting \( \gamma = 0 \) and numerically integrating Eq. (25) to give the dashed line in Fig. 8. Finally, we use all three terms in the exponent of Eq. (28) and numerically integrate to obtain the dotted curve in Fig. 8. This final approximation is very close to the exact result even for such a small value of \( n \) as 15. The deviations from Gaussian behavior are greatest at small \( R \) as we would expect.

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**FIG. 6.** Showing \( S_n(k) \) which is the spherical average of \( C_n(k) \) shown in Fig. 3.

**FIG. 7.** Showing \( S_n(k) \) which is the spherical average of \( C_n(k) \) shown in Fig. 4.

**FIG. 8.** The exact probability distribution \( W_n(R) \) is shown by the solid line. The horizontal axis is plotted in units where the monomer length \( l = 1 \) and the function \( W_n(R) \) is by definition normalized to 1 over \( 4 \pi R^2 dR \). The vertical scale is in units of \( 10^{-4} \). The other lines represent various approximations based on moments as described in Sec. VI. The dot–dashed line is based on the second moment (i.e., Gaussian), the dashed line is based on the second and fourth moments and the dotted line is based on the second, fourth, and sixth moments.
By exploiting the 48-fold cubic symmetry of the diamond lattice we were able to reduce the limits of integration to

$$S_n(k) = \frac{4}{\pi} \int_0^{\pi/4} \int_0^{\pi/2} C_n(k, \theta, \phi) \sin \theta \, d\theta \, d\phi.$$

Instead of integrating over 1/48 of the cube, we selected the ranges of $\theta$ and $\phi$ such that 3/48 of the cube was used. The reason for this is that 3 is the smallest number of segments for which $\theta$ and $\phi$ are not functionally interrelated. This extension of the integration zone greatly simplified the evaluation of the integral and was actually more computing-time efficient than if we had integrated over only one region.

The Gaussian quadrature method used is the standard type as in Abramowitz and Stegun. That $S_n(k)$ is of the form

$$\int_{\epsilon_1}^{\epsilon_2} \int_{\phi_1}^{\phi_2} f(\theta, \phi) d\theta \, d\phi.$$  \hspace{1cm} (A2)

This was transformed to the usual Gaussian quadrature sum

$$S_n(k) = \left( \frac{\epsilon_2 - \epsilon_1}{4} \right) \left( \phi_2 - \phi_1 \right) \sum_{i=1}^{r} \sum_{j=1}^{r} \omega_{\epsilon_i} \omega_{\phi_j} f(\theta_{\epsilon_i}, \phi_{\phi_j}),$$  \hspace{1cm} (A3)

where the transformed coordinates are given by

$$\theta_i = \left( \frac{\epsilon_2 - \epsilon_1}{2} \right) X_{\epsilon_i} + \left( \frac{\epsilon_2 + \epsilon_1}{2} \right); \quad \phi_j = \left( \frac{\phi_2 - \phi_1}{2} \right) X_{\phi_j} + \left( \frac{\phi_2 + \phi_1}{2} \right)$$  \hspace{1cm} (A4)

and $\omega_{\epsilon_i}$, $\omega_{\phi_j}$, $X_{\epsilon_i}$, $X_{\phi_j}$ are the tabulated weights and coordinates, respectively, for an $r$-point Gaussian quadrature. Typically $r$ was 12 and the largest value of $r$ used was 32. Employing the above simplifications due to symmetry our integral became

$$S_n(k) \approx \frac{\pi}{8} \sum_{i=1}^{r} \sum_{j=1}^{r} \omega_{\epsilon_i} \omega_{\phi_j} C_n(k, X_{\epsilon_i}, X_{\phi_j}) \sin X_{\epsilon_i},$$  \hspace{1cm} (A5)

where

$$\epsilon_i = \frac{\pi}{8} (X_{\epsilon_i} + 1); \quad \phi_j = \frac{\pi}{8} (X_{\phi_j} + 1).$$  \hspace{1cm} (A6)

This expression is evaluated for various values of $k$ from 0 to $k_{\text{max}}$, where $k_{\text{max}}$ is that value of $k$ where the oscillations of $S_n(k)$ have sufficiently diminished and is generally on the order of $\pi/2a$.

An $r$-point Gaussian quadrature routine will integrate a 2$r$-1 order polynomial exactly and therefore the order of the Gaussian quadrature was selected in accordance with the number of oscillations $C_n(k)$ made in the integration zone.

VII. CONCLUSIONS

We have shown that the characteristic function $C_n(k)$ can be calculated exactly for an $n$ link polymer embedded on a diamond lattice and the probability distribution function $W_n(R)$ obtained by doing a spherical average and a one-dimensional Fourier transform. This model may be regarded as the lattice version of the freely rotating chain.

The expression $C_n(k)$ was expanded in powers of $k$ and the moments $(R^2)_{\epsilon_i}$, $(R^4)_{\epsilon_i}$, and $(R^6)_{\epsilon_i}$ obtained in closed form. The first two of these moments were shown to be identical to the freely rotating chain but $(R^6)_{\epsilon_i}$ and higher moments are different.

We hope that this exact result will be useful in various applications and it provides an alternative to the freely jointed chain for testing approximate theories of polymer statistics.

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APPENDIX

Gaussian quadrature was used to spherically average the characteristic function $C_n(k)$ [see Eq. (26)]:

$$S_n(k) = \frac{1}{4\pi} \int_0^{\pi} \int_0^{2\pi} C_n(k, \theta, \phi) \sin \theta \, d\theta \, d\phi.$$  \hspace{1cm} (A1)


2Lord Rayleigh, Philos. Mag. 37, 321 (1919).


