Finite-Chain Corrections to the Unperturbed End-to-End Vector Distribution Function

Marc L. Mansfield*

Michigan Molecular Institute, Midland, Michigan 48640

Jia-Lin Syi

Department of Chemical and Nuclear Engineering, University of Maryland, College Park, Maryland 20742. *Received September 2, 1986*

ABSTRACT: When unperturbed chains are sufficiently long that the directional correlation between the two chain ends is negligible, the moment $\langle R^{2k}\rangle$ is a kth order polynomial in N, the number of bonds. This fact is sufficient to demonstrate that a distribution of the same form as the wormlike chain Daniels distribution, i.e., a series expansion about the Gaussian distribution in powers of R^2 and N^{-1}, exists for any unperturbed chain. A few such series are obtained for several different random walks and compared with either exact or with Monte Carlo generated distributions. The approach seems to be successful in generating accurate approximations if the true distribution is not too far from Gaussian.

Introduction

The distribution function of the end-to-end distance of a chain is determined completely by the set of even moments: $\langle R^{2m}\rangle$, $m = 1, 2, 3, ...$, for R, the end-to-end distance.[1] Therefore, by calculating a set of the lower even moments and selecting a function that exactly reproduces these moments, one approximates the exact distribution with a precision that usually improves with the number of moments employed. Two different approaches have been developed for computing the moments of unperturbed chains, namely, the generator matrix techniques[2-5] discussed by Nagai and by Flory and co-workers and the Fixman–Skolnick technique[6] based on matrix representations of rotation operators. The generator matrix approach works well for $m = 1$ or 2, but beyond $m = 3$ or 4 the Fixman–Skolnick approach becomes more efficient.[6] The distribution function is usually inferred by expanding the unknown function in terms of an appropriate orthonormal basis set and selecting contributions from each basis function so as to force agreement with the previously calculated moments. For example, Nagai has developed an approach based on a Hermite polynomial expansion.[2,4] Since the Hermite polynomial weight function is Gaussian, this approach works well when the desired distribution is approximately Gaussian, although convergence problems are encountered otherwise. A number of authors discuss the problem of inferring the distribution function from its moments.[2,4,6-13]

The complexity of either the Fixman–Skolnick or the generator matrix computations of the even moments conceals a striking simplicity. If an unperturbed chain is sufficiently long that the directions of the bonds at either end are uncorrelated, then the moments $\langle R^{2m}\rangle$ are mth order polynomials in N, the number of bonds in the chain

$$\langle R^{2m}\rangle = \sum_{j=0}^{m} C_{mj}N^j \qquad (1)$$

This was proven in a papar by Nagai in 1963.[2,14] He considers a polymer chain of total length $N = N_1 + \nu + N_2$. The quantity ν is the length of an internal section of the chain chosen to be sufficiently large to "be capable of making $[\mathbf{V}_3\cdot\mathbf{A}^{\nu}\cdot\mathbf{U}_3]_{1,1}$ negligible", i.e., so that the correlation in direction between two bonds separated by ν bonds is negligible. N_1 and N_2 are the numbers of bonds in each of the two subsections external to the section of length ν and can be assumed to be arbitrary. Nagai proves directly that the quantities he calls g_{2k}' are polynomials (see eq 89 of ref 2), but by consulting his eq 5, 9, 10, and 86–88, we see that the even moments are also polynomials, permitting us to write eq 1. For flexible polymer chains, we can expect the end-bond correlation to be effectively negligible after only 20 or 30 bonds, so that eq 1 should represent a valid approximation over a large molecular weight range.

Equation 1 neglects terms of the general form e^{-aN} that decay about as rapidly as the end-vector correlation, where e^{-a} represents an eigenvalue of the transfer matrix permitting computation of the end-vector correlation.[15] The dominant term at large N is of course of the required form to generate Gaussian statistics

$$C_{mm} = \frac{(2m+1)!}{6^m m!}C_{11}{}^m \qquad (2)$$

Additional terms in eq 1 represent finite-chain corrections to the Gaussian moments, expanded in a series in N^{-1}. The quantity C_{11} is proportional to the characteristic ratio, since

$$C_{11} = \lim_{N\to\infty} \langle R^2\rangle/N \qquad (3)$$

One might consider expanding the exponential terms not shown explicitly in eq 1 in a power series in N^{-1} and including these in the expression. However, since e^{-N} is nonanalytic in N^{-1} such an expansion cannot be done. Equation 1 represents the exact asymptotic expansion of each moment in powers of N^{-1} about their Gaussian values; each expansion terminates after a finite number of terms. Due to the neglect of these nonanalytic terms, eq 1 becomes invalid at lower N.

The behavior described above is observed in all cases for which exact expressions for the lower moments have been obtained. For example, moments of the freely jointed chain are given exactly by polynomials in N, with none of the nonanalytic terms discussed above.[16] Such terms are not expected since the freely jointed chain exhibits no end-bond correlation for any N. Another example, the wormlike chain, has terms $e^{-n(n+1)L\lambda}$ appearing in its moment expressions, where n is an integer and where L and λ represent the contour length and stiffness parameter, respectively. When these terms are neglected, polynomials in L result.[8] Additionally, random walks on the diamond lattice, in which end-bond correlation decays as 3^{-N}, also have polynomial moments when terms in 3^{-nN}, for integral n, are neglected.[17]

This behavior explains[18] the observation of Maeda, Saito, and Stockmayer[19] that by an appropriate choice of "shift factor" $\langle R^2\rangle$ of many flexible RIS chain models could be forced to follow the equation for $\langle R^2\rangle$ of the wormlike chain over a large molecular weight range. By adjusting

0024-9297/87/2220-0894$01.50/0 © 1987 American Chemical Society

the two independent parameters of the wormlike chain, L and λ, one can bring the wormlike chain equivalent of eq 1 for $\langle R^2 \rangle$, $\langle R^2 \rangle = L/\lambda - 1/(2\lambda^2)$, into agreement with the corresponding equation of any other model, provided that the constant term has the correct sign. They also observed that fourth-moment shift factors can be obtained. This is, of course, equivalent to forcing agreement between the two leading terms in the fourth-moment polynomials and also explains their observation that the second-moment shift factor is in general different from the fourth-moment shift factor.

Equation 1, when employed in the Hermite polynomial expansion, yields

$$P(\rho) = \pi^{-3/2} e^{-\rho^2} \{1 + \sum_{\mu=1}^{\infty} \sum_{\nu=0}^{\infty} B_{\mu\nu} N^{-\mu} \rho^{2\nu}\} \qquad (4)$$

for the distribution of the reduced end-to-end distance $\rho = [3/(2NC_{11})]^{1/2} R$. Equation 4 represents the exact series expansion of $P(\rho)$ about the Gaussian distribution in powers of ρ^2 and N^{-1} and has been previously derived by Nagai.[2] Such expansions are well-known for the wormlike chain, namely, the various Daniels distributions.[1,20,21] In this paper we show how eq 1 yields eq 4 and derive a series expansion for the quantities $B_{\mu\nu}$ in terms of the C_{mj}. Then we show how to obtain accurate approximations to $P(\rho)$ in the form of a Daniels-type series expansion.

Inference of the Distribution Function

As stated above, Nagai[2] has already demonstrated the validity of a series of the form of eq 4. In this section, we show how the polynomials in eq 1 yield eq 4 directly, and we derive a series expansion relating the coefficients $B_{\mu\nu}$ and C_{mj} of the two equations. We employ the standard Hermite polynomial expansion[2,4] of the end-to-end vector distribution function in terms of its even moments.

Let

$$\rho = [3/(2NC_{11})]^{1/2} R \qquad (5)$$

be a reduced end-to-end distance.[22] As has been shown,[4] the distribution function obeys

$$P(\rho) = \pi^{-3/2} e^{-\rho^2} \sum_{\nu=0}^{\infty} h_\nu \rho^{-1} H_{\nu+1}(\rho) \qquad (6)$$

where $H_m(\rho)$ is the mth Hermite polynomial and where

$$h_\nu = (2)^{-\nu-2} [(\nu + 1)!]^{-1} \langle \rho^{-1} H_{\nu+1}(\rho) \rangle \qquad (7)$$

for even ν, while $h_\nu = 0$ for odd ν. Therefore

$$P(\rho) = \pi^{-3/2} e^{-\rho^2} \sum_{j=0}^{\infty} (2)^{-2j-2} [(2j + 1)!]^{-1} \langle \rho^{-1} H_{2j+1}(\rho) \rangle \rho^{-1} H_{2j+1}(\rho) \qquad (8)$$

In the above, $\rho^{-1} H_{2j+1}(\rho)$ is a jth order polynomial in ρ^2. Let E_{jk} denote its coefficients

$$\rho^{-1} H_{2j+1}(\rho) = \sum_{k=0}^{j} E_{jk} \rho^{2k} \qquad (9)$$

Then[23]

$$E_{jk} = (-1)^{j-k} 2^{2k+1} \frac{(2j + 1)!}{(j - k)!(2k + 1)!} \qquad (10)$$

and

$$P(\rho) = \pi^{-3/2} e^{-\rho 2} \sum_{j=0}^{\infty} \sum_{k=0}^{j} \sum_{m=0}^{j} 2^{-2j-2} [(2j + 1)!]^{-1} E_{jk} E_{jm} \langle \rho^{2k} \rangle \rho^{2m} \qquad (11)$$

By combining eq 1 and 5, we obtain

$$\langle \rho^{2k} \rangle = (3/2)^k \sum_{m=0}^{k} D_{km} N^{m-k} \qquad (12)$$

where

$$D_{km} = C_{km}/C_{11}{}^k \qquad (13)$$

By combining eq 11 and 12 and rearranging the sums, we obtain

$$P(\rho) = \pi^{-3/2} e^{-\rho^2} \sum_{\mu=0}^{\infty} \sum_{\nu=0}^{\infty} B_{\mu\nu} N^{-\nu} \rho^{2\nu} \qquad (14)$$

with

$$B_{\mu\nu} = \sum_{j=\max(\mu,\nu)}^{\infty} \sum_{k=\mu}^{j} 3^k 2^{-(2j+k+2)} [(2j + 1)!]^{-1} E_{jk} E_{j\nu} D_{k,k-\mu} \qquad (15)$$

where the sum over j begins at the greater of μ or ν. Consider the quantity $B_{0\nu}$. Setting $\mu = 0$ in eq 15 and rearranging yield

$$B_{0\nu} = \sum_{j=\nu}^{\infty} \frac{(-1)^j E_{j\nu}}{2^{2j+1} j!} \sum_{k=0}^{j} \frac{(-1)^k j!}{k!(j - k)!} \qquad (16)$$

The sum over k is just the binomial expansion of $(1 - 1)^j = \delta_{j0}$, for δ_{jk} the Kroneker δ. Therefore

$$B_{0\nu} = E_{00} \delta_{\nu 0}/2 = \delta_{\nu 0} \qquad (17)$$

and eq 4 is then obtained. As long as eq 4 converges, it *represents the exact distribution for all values of N* for which the moments are polynomials, i.e., for which the end-bond correlation is negligible.

An integration over eq 4 yields

$$\langle R^{2\alpha} \rangle = \sum_{j=0}^{\infty} C_{\alpha,\alpha-j} N^{\alpha-j} \qquad (18)$$

for α any real number greater than $-^3/_2$ and where

$$C_{\alpha\alpha} = 2\pi^{-1/2} (2C_{11}/3)^\alpha \Gamma\left(\frac{2\alpha + 3}{2}\right) \qquad (19)$$

and

$$C_{\alpha,\alpha-j} = 2\pi^{-1/2} (2C_{11}/3)^\alpha \sum_{\nu=0}^{\infty} B_{j\nu} \Gamma\left(\frac{2\alpha + 2\nu + 3}{2}\right) \qquad (20)$$

Above, $\Gamma(x)$ represents the gamma function. Equation 19 becomes eq 2 for positive integral α. Equation 18 contains an infinite number of terms for general α, but for α a positive integer, the series terminates after a finite number of terms, since eq 1 must be recovered.

Approximation to the End-to-End Distance Distribution Function

The derivation in the last section demonstrates that a series of the form of eq 4 can always be given for an unperturbed polymer. As it stands, however, the series has questionable utility, since the series for $B_{\mu\nu}$ in eq 15 has an infinite number of terms requiring the specification of $D_{k,k-\mu}$, i.e., of the polynomial coefficients of $\langle R^{2k} \rangle$ for all values of k. Unless the convergence of eq 15 is particularly good, accurate computations of the $B_{\mu\nu}$ terms would probably require knowledge of a rather large number of the $\langle R^{2k} \rangle$ polynomials. Instead, we consider the following approach.

Assume that all the $\langle R^{2k} \rangle$ polynomials are given through $\langle R^{2M} \rangle$ for some M. Then assume that the series in eq 4 is truncated after a finite number of terms

$$P(\rho) = \pi^{-3/2} e^{-\rho^2} \{1 + \sum_{\mu=1}^{M} \sum_{\nu=0}^{M} B_{\mu\nu}{}^{(M)} N^{-\mu} \rho^{2\nu}\} \qquad (21)$$

Equation 21 contains $M(M + 1)$ unknown quantities, the

Table I
Coefficients C_{mj} for the Freely Jointed Chain

	j					
m	0	1	2	3	4	5
1	0	1				
2	0	$^{-2}/_{3}$	$^{5}/_{3}$			
3	0	$^{16}/_{9}$	$^{-14}/_{3}$	$^{35}/_{9}$		
4	0	$^{-48}/_{5}$	$^{404}/_{15}$	−28	$^{35}/_{3}$	
5	0	$^{256}/_{3}$	$^{-2288}/_{9}$	$^{2684}/_{9}$	$^{-1540}/_{9}$	$^{385}/_{9}$

Table II
Coefficients $B_{\mu\nu}^{(M)}$ for the Freely Jointed Chain

	ν					
μ	0	1	2	3	4	5
			$M = 3$			
1	$^{-3}/_{4}$	1	$^{-1}/_{5}$	0		
2	−1	2	$^{-4}/_{5}$	$^{8}/_{105}$		
3	0	0	0	0		
			$M = 4$			
1	$^{-3}/_{4}$	1	$^{-1}/_{5}$	0	0	
2	$^{29}/_{160}$	$^{-23}/_{20}$	$^{109}/_{100}$	$^{-149}/_{525}$	$^{1}/_{50}$	
3	$^{-81}/_{40}$	$^{27}/_{5}$	$^{-81}/_{25}$	$^{108}/_{175}$	$^{-18}/_{525}$	
4	0	0	0	0	0	
			$M = 5$			
1	$^{-3}/_{4}$	1	$^{-1}/_{5}$	0	0	0
2	$^{29}/_{160}$	$^{-23}/_{20}$	$^{109}/_{100}$	$^{-149}/_{525}$	$^{1}/_{50}$	0
3	$^{117}/_{40}$	$^{-111}/_{10}$	$^{249}/_{25}$	$^{-552}/_{175}$	$^{202}/_{525}$	$^{-8}/_{525}$
4	$^{-27}/_{5}$	18	$^{-72}/_{5}$	$^{144}/_{35}$	$^{-16}/_{35}$	$^{32}/_{1925}$
5	0	0	0	0	0	0

$B_{\mu\nu}^{(M)}$, which can be determined by solving $M(M + 1)$ simultaneous linear equations, each of the form of eq 20. One obtains $M(M + 1)$ equations by setting $\alpha = 0, 1, 2, ..., M$ and $j = 1, 2, ..., M$ in eq 20 and using $C_{\alpha,\alpha-j} = 0$ whenever $j > \alpha$. One writes $B_{\mu\nu}^{(M)}$ with a superscript (M) since the values obtained are, of course, M-dependent. The resulting series does not represent the true function since we have no guarantee that it gives the exact moments $\langle R^{2k}\rangle$ for $k > M$. When $k > M$, it continues to give polynomials, but only the leading term C_{mm} is correct. We also expect

$$\lim_{M\to\infty} B_{\mu\nu}^{(M)} = B_{\mu\nu} \qquad (22)$$

Although the series is not exact, we can still expect a good approximation if M is sufficiently large and if the true $P(\rho)$ is at least approximately Gaussian, simply because we have selected a function that reproduces the first M even moments. To demonstrate the approach, we have determined $B_{\mu\nu}^{(M)}$ quantities for four models: the freely jointed chain, the wormlike chain, and two closely related RIS models of polyethylene.

Freely Jointed Chain. We obtained expressions for the even moments through $\langle R^{10}\rangle$ by a computer algebra expansion of the characteristic function $(k^{-1} \sin k)^N$. The polynomial coefficients are given in Table I. In Table II we give the $B_{\mu\nu}^{(M)}$ values that are obtained for $M = 3$–5. Note that for $\mu = 1$ and 2, the $B_{\mu\nu}^{(M)} \to B_{\mu\nu}$ convergence seems to be complete. Exact expressions for $P(R)$ are available for small values of N;[16,24,25] in Figure 1 we compare the exact expressions with the $M = 5$ approximation. It is evident that for $N \geq 6$, very good agreement is obtained. A $R = 0$ for $N = 6$, the two disagree by only 0.36%. These series of figures also indicate that the approximation seems to work well only if the exact curve is at least qualitatively Gaussian. At $N = 6$ and at $R = 0$, the contribution to the approximation due to the correction terms is about 11% of the leading Gaussian term $e^{-\rho^2}$. The $M = 5$ approximation to $\langle R^{-1}\rangle$ for the freely jointed chain is

$$\langle R^{-1}\rangle = \left(\frac{6}{\pi N}\right)^{1/2}\left[1 - \frac{3}{20N} - \frac{13}{1120N^2} + \frac{9}{40N^3} - \frac{27}{55N^4}\right] \qquad (23)$$

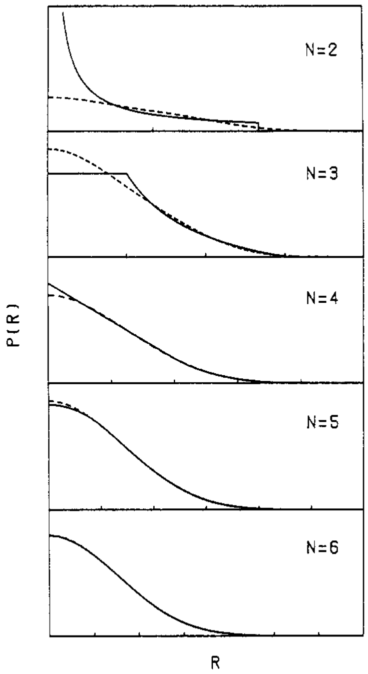

Figure 1. Comparison between exact and approximate distribution functions for the freely jointed chain. The solid curves are the exact distributions; the dashed curves are the approximations by eq 21 with $M = 5$. The tics along the horizontal axis are spaced one bond length apart. N is the number of bonds.

Wormlike Chain. When units are taken such that λ, the stiffness parameter, is unity and by the use of L, the contour length, in place of N, the above arguments apply to the wormlike chain. The polynomial coefficients C_{mj} are taken from the known expressions[8] for the first five even moments and are given in Table III, while Table IV gives the resulting $B_{\mu\nu}^{(M)}$ coefficients, for M = 3–5. Once again the convergence $B_{\mu\nu}^{(M)} \to B_{\mu\nu}$ appears to be complete for $\mu = 1$ or 2. The entries in Table IV are to be compared with the Daniels distribution[1,20]

$$P(\rho) = \pi^{-3/2}e^{-\rho^2}\left[1 + L^{-1}\left(-\frac{5}{8} + \frac{4}{3}\rho^2 - \frac{11}{30}\rho^4\right) + ...\right] \qquad (24)$$

Table III
C_{mj} Coefficients of the Wormlike Chain

	j					
m	0	1	2	3	4	5
1	$^{-1}/_{2}$	1				
2	$^{107}/_{54}$	$^{-26}/_{9}$	$^{5}/_{3}$			
3	$^{-6143}/_{324}$	$^{226}/_{9}$	$^{-259}/_{18}$	$^{35}/_{9}$		
4	$^{123\,403}/_{375}$	$^{-281\,183}/_{675}$	$^{3554}/_{15}$	$^{-224}/_{3}$	$^{35}/_{3}$	
5	$^{-164\,016\,904}/_{18\,225}$	$^{67\,421\,951}/_{6075}$	$^{-2\,545\,708}/_{405}$	$^{169\,301}/_{81}$	$^{-22\,715}/_{54}$	$^{385}/_{9}$

Table IV
$B_{\mu\nu}^{(M)}$ Coefficients of the Wormlike Chain[a]

μ	ν = 0	1	2	3	4	5
$M = 3$						
1	−0.625 000	1.333 33	−0.366 667	0		
2	−4.093 75	9.673 61	−4.463 89	0.481 746		
3	1.066 49 (1)	−2.132 99 (1)	8.531 94	−0.812 566		
$M = 4$						
1	−0.625 000	1.333 33	−0.366 667	0	0	
2	−0.123 437	−0.913 889	1.888 61	−0.728 254	0.067 222 2	
3	−2.921 26 (1)	8.501 01 (1)	−5.527 21 (1)	1.134 006 (1)	−0.675 175	
4	6.941 42 (1)	−1.851 04 (2)	1.110 63 (2)	−2.115 48 (1)	1.175 27	
$M = 5$						
1	−0.625 000	1.333 33	−0.366 667	0	0	0
2	−0.123 437	−0.913 889	1.888 61	−0.728 254	0.067 222 2	0
3	1.724 95 (1)	−6.986 36 (1)	6.862 69 (1)	−2.405 91 (1)	3.258 13	−0.143 029
4	−2.511 20 (2)	8.833 42 (2)	−7.436 95 (2)	2.230 62 (2)	−2.595 99 (1)	0.986 733
5	5.695 03 (2)	−1.898 34 (3)	1.518 68 (3)	−4.339 07 (2)	4.821 19 (1)	−1.753 16

[a] The power of 10 multiplying each entry is shown in parentheses.

Table V
C_{mj} Coefficients for RIS Model Polyethylene, Case 1[a]

m	j = 0	1	2	3	4	5
1	−3.6101 (1)	6.8916				
2	1.0758 (4)	−1.4603 (3)	7.9155 (1)			
3	−7.6946 (6)	9.4797 (5)	−5.0444 (4)	1.2728 (3)		
4	9.9561 (9)	−1.1737 (9)	6.1957 (7)	−1.8101 (6)	2.6316 (4)	
5	−2.0164 (13)	2.3281 (12)	−1.2262 (11)	3.7790 (9)	−7.0427 (7)	6.6497 (5)

[a] The power of 10 multiplying each entry is shown in parentheses.

Table VI
$B_{\mu\nu}^{(M)}$ Coefficients for RIS Model Polyethylene, Case 1[a]

μ	ν = 0	1	2	3	4	5
$M = 3$						
1	−7.089 45	1.469 10 (1)	−3.985 92	3.736 32 (−6)		
2	−4.824 18 (2)	1.134 73 (3)	−5.218 46 (2)	5.617 16 (1)		
3	1.322 38 (4)	−2.644 75 (4)	1.057 90 (4)	−1.007 52 (3)		
$M = 4$						
1	−7.089 71	1.469 18 (1)	−3.986 34	8.444 77 (−5)	−4.483 97 (−6)	
2	−1.290 97 (1)	−1.172 97 (2)	2.293 67 (2)	−8.691 67 (1)	7.949 35	
3	−3.703 26 (4)	1.075 69 (5)	−6.983 12 (4)	1.430 87 (4)	−8.509 01 (2)	
4	9.310 51 (5)	−2.482 80 (6)	1.489 68 (6)	−2.837 49 (5)	1.576 38 (4)	
$M = 5$						
1	−7.091 81	1.469 87 (1)	−3.991 93	1.682 56 (−3)	−1.820 52 (−4)	6.457 00 (−6)
2	−1.195 65 (1)	−1.204 74 (2)	2.319 09 (2)	−8.764 30 (1)	8.030 05	−2.934 38 (−3)
3	2.207 22 (4)	−8.944 66 (4)	8.778 17 (4)	−3.072 35 (4)	4.152 68 (3)	−1.819 48 (2)
4	−3.425 51 (6)	1.203 91 (7)	−1.012 78 (7)	3.035 54 (6)	−3.530 46 (5)	1.341 13 (4)
5	8.208 44 (7)	−2.736 15 (8)	2.188 92 (8)	−6.254 05 (7)	6.948 94 (6)	−2.526 89 (5)

[a] The power of 10 multiplying each entry is shown in parentheses.

for $\rho = (3/2L)^{1/2}R$. The coefficients in eq 24 agree exactly with the $B_{1\nu}^{(M)}$ coefficients in Table IV. We also obtain, employing the $M = 5$ expansion

$$\langle R^{-1}\rangle = (6/\pi L)^{1/2}[1 - (2.5 \times 10^{-2})L^{-1} - (1.6296 \times 10^{-2})L^{-2} + (1.3165)L^{-3} - (21.427)L^{-4} + (51.772)L^{-5}] \tag{25}$$

which is to be compared with the Daniels distribution result[1]

$$\langle R^{-1}\rangle = (6/\pi L)^{1/2}(1 - 1/40L) \tag{26}$$

RIS Polyethylene, Case 1. We here consider the three-state RIS model with symmetric rotational potential proposed by Flory as being appropriate for polyethylene.[4] The model parameters employed are as follows: $\sigma = 0.54$, $\omega = 0.088$, $\psi = 1$, $\theta = 68°$, $\phi_{\text{trans}} = 0°$, $\phi_{\text{gauche}} = 120°$, and bonds of unit length. The moments $\langle R^{2k}\rangle$, $k = 1$–5, were calculated by the Fixman–Skolnick technique,[6] with results displayed in Figure 2. Values of C_{mj} were obtained by polynomial least-squares fits of the $\langle R^{2k}\rangle$ data, with results given in Table V. The resulting $B_{\mu\nu}^{(M)}$ values are given in Table VI. The convergence $B_{\mu\nu}^{(M)} \rightarrow B_{\mu\nu}$, at least for $\mu = 1$ and 2, is again observed but is not complete as in the previous cases. At $M = 5$, the $\langle R^{-1}\rangle$ series obtained is

$$\langle R^{-1}\rangle = (6/\pi C_{11}N)^{1/2}[1 - 0.370\,42N^{-1} - 2.1008N^{-2} + 1678.3N^{-3} - (2.9261 \times 10^{5})N^{-4} + (7.462\,34 \times 10^{6})N^{-5}] \tag{27}$$

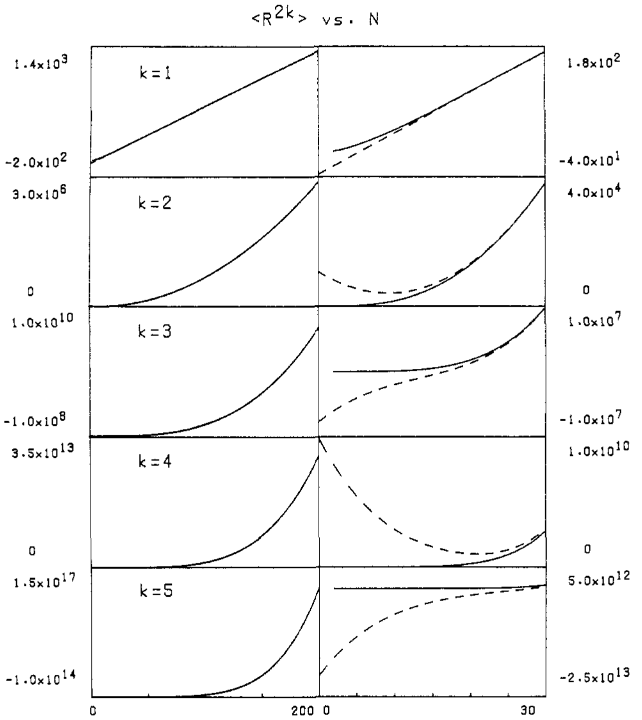

Figure 2. First five even moments, $\langle R^{2k}\rangle$ for $k = 1$–5 of RIS model polyethylene plotted as a function of N, the number of bonds. Solid curves are the exact values of the moments; the dashed curves are the polynomial approximations given in Table V. The panels on the left display the behavior of the moments in the range $N \le 200$. Each panel on the right is a magnification of the panel to its left and displays behavior in the range $N \le 30$. Dashed curves have been plotted on both the left and right, but the resolution on the left is too low to distinguish the dashed curves except when $k = 1$. The numbers to the right and left give the range of each graph.

There is a possibility that some imprecision may be generated by obtaining C_{mj} values by least-squares fitting, at least for the least significant terms of the higher moments (i.e., for large m and small j). To avoid biasing the fit in the low-N region where the polynomial expressions are invalid, one must neglect values of $\langle R^{2m}\rangle$ below a certain value of N. On the other hand, the least significant terms in the polynomials are only important at smaller N. For example, in the above polyethylene example, the polynomials were fit over the range $50 \le N \le 200$. For $N \ge 50$ we can probably assume with all confidence that the moments are given accurately by the polynomials. However, the C_{50} term in the $\langle R^{10}\rangle$ polynomial has an absolute value less that 10% of $\langle R^{10}\rangle$ for all $N > 67$ and less that 1% for all $N > 97$. Therefore, the possibility exists that C_{50} given in Table V is not too precise. Of course, from the practical standpoint of obtaining useful approximations, little damage results from the imprecise evaluation of relatively insignificant terms. As Figure 2 indicates, the polynomial coefficients in Table V provide very adequate fits to the moments whenever $N \ge 50$.

RIS Polyethylene, Case 2. This model differs from the previous one only in the value of the bond angle. The tetrahedral value, $\theta = 70.53°$, was employed so that the results could be compared with a Monte Carlo estimation of the distribution of diamond lattice chains. The C_{mj} values were once again obtained by least-squares polynomial fits to the moments computed by the Fixman–Skolnick technique. The distribution function was also estimated for various values of N by a Monte Carlo sampling technique. A million samples were generated at each value of N by performing single bond rotations with Metropolis biasing. Details of this calculation are given elsewhere.[28] We found that eq 21 does well for $N \ge 60$, and in every case it improves upon the Gaussian distribution.

Conclusions

When unperturbed chains become so long that they exhibit negligible correlation between the directions of the bonds at either end, they enter a regime in which the even moments $\langle R^{2k}\rangle$ are kth-order polynomials in N (see eq 1) and in which the end-to-end vector distribution function can be given as a series expansion in powers of N^{-1} and R^2 about the Gaussian distribution (see eq 4). The exact coefficients in the series expansion appear difficult to determine in general, but a truncated series, eq 21, can be obtained by using existing techniques which ensure exact agreement with each term in the polynomials representing the first M even moments and exact agreement with the leading term in the polynomials representing all the higher even moments. For $M = 5$ the truncated series accurately represents the freely jointed chain distribution for all $N \ge 6$ and the RIS model polyethylene distribution for all $N \ge 60$. Better agreement should be available by going to larger M; however, as discussed above, if the polynomial coefficients are obtained from a least-squares fit of raw moment data, one should expect inaccurate determinations of the less significant terms in the higher moment polynomials. The problem of inferring the distribution of unperturbed chains would benefit greatly from the development of techniques permitting direct computation of either the coefficients C_{jm} or $B_{\mu\nu}$. At present, only C_{11}, C_{10}, and C_{mm} can be calculated directly.[18,26,27]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Partial support was also provided by the National Science Foundation, Grant No. DMR-8451928.

Registry No. Polyethylene, 9002-88-4.

References and Notes

(1) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(2) Nagai, K. *J. Chem. Phys.* **1963**, *38*, 924.
(3) Flory, P. J.; Jernigan, R. L. *J. Chem. Phys.* **1965**, *42*, 3509.
(4) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Wiley: New York, 1969.
(5) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(6) Fixman, M.; Skolnick, J. *J. Chem. Phys.* **1976**, *65*, 1700.
(7) Jernigan, R. L.; Flory, P. J. *J. Chem. Phys.* **1969**, *50*, 4185.
(8) Nagai, K. *Polym. J.* (*Tokyo*) **1973**, *4*, 35.
(9) Fixman, M.; Alben, R. *J. Chem. Phys.* **1973**, *58*, 1553.
(10) Fixman, M. *J. Chem. Phys.* **1973**, *58*, 1559.
(11) Freire, J.; Fixman, M. *J. Chem. Phys.* **1978**, *69*, 634.
(12) Freire, J. J.; Rodrigo, M. M. *J. Chem. Phys.* **1980**, *72*, 6376.
(13) Rubio, A. M.; Freire, J. J. *Macromolecules* **1982**, *15*, 1411.
(14) For a simple proof of eq 1 for second moments see also Appendix 2 of: Mansfield, M. L. *Macromolecules* **1986**, *19*, 1421.
(15) It actually appears that the moments of chains confined to lattices can in some instances exhibit additional weak N dependencies, which are not expected to be present in off-lattice systems. For example, see: Baram, A. *J. Chem. Phys.* **1982**, *77*, 5255.
(16) Bagchi, B. *J. Phys. Chem.* **1981**, *85*, 4040.
(17) Thorpe, M. F.; Schroll, W. W. *J. Chem. Phys.* **1981**, *75*, 5143.
(18) Mansfield, M. L. *Macromolecules* **1981**, *14*, 1822.
(19) Maeda, J.; Saito, N.; Stockmayer, W. H. *Polym. J.* (*Tokyo*) **1971**, *2*, 94.
(20) Gobush, W.; Yamakawa, H.; Stockmayer, W. H.; Magee, W. S. *J. Chem. Phys.* **1972**, *57*, 2839.
(21) Yamakawa, H. *Annu. Rev. Phys. Chem.* **1984**, *35*, 23.
(22) In separate treatments, Nagai (ref 2) and Jernigan and Flory (ref 4) employ different definitions for a reduced end-to-end distance. Ours is that of Nagai and is preferable from the standpoint of mathematical simplicity. The alternative would lead to a more complicated N dependence.

(23) Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1965; Chapter 22.
(24) Rayleigh *Philos. Mag.* **1919**, *37*, 321.
(25) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.
(26) Matsuo, K. *Macromolecules* **1977**, *10*, 498.
(27) Matsuo, K. *Macromolecules* **1980**, *13*, 1712.
(28) Syi, J.-L., Doctoral Dissertation, University of Maryland at College Park, College Park, MD, 1986.

Notes

Small-Angle X-ray Scattering Studies of Polymer Colloids: Nonaqueous Dispersions of Poly(isobutylene)-Stabilized Poly(methyl methacrylate) Particles

MITCHELL A. WINNIK and BRETT WILLIAMSON

Department of Chemistry and Erindale College, University of Toronto, Toronto, Canada M5S 1A1

THOMAS P. RUSSELL*

IBM Almaden Research Center,
San Jose, California 95120-6099. *Received June 2, 1986*

Several years ago, we began an investigation into the internal structure of colloidal polymer particles thought to be of the core-shell type.[1] The core-shell model for a particle composed of two different and incompatible polymers pictures a structure with one material in the center forming the core and the other as a spherical exterior shell. This model treats the system as though minimization of surface energy were the controlling factor in determining particle structure during its synthesis.

Our studies focused on nonaqueous dispersions of poly(methyl methacrylate) (PMMA) particles, sterically stabilized by poly(isobutylene) (PIB).[1] These materials were prepared in a two-step process where MMA was polymerized to low conversion in the presence of PIB (degraded butyl rubber) containing 2% unsaturation. This process produces a graft copolymer stabilizer, which is then added to a large excess of MMA plus initiator in an aliphatic hydrocarbon solvent (here isooctane). Free radical polymerization leads to the formation of spherical particles.[2] Alternatively, the same particles can be produced in a one-pot synthesis where, presumably, the graft copolymer stabilizer is generated in situ. These recipes produce particles with a fairly narrow size distribution. The mean particle diameters range from 0.3 to 2 μm, depending upon the ratio of reactants. The particles prepared for the experiments reported here had a mean diameter of 0.6 μm and a composition of approximately 90 mol % MMA. According to the core-shell model, these particles should consist of a sphere of (glassy) PMMA coated with a shell of PIB. Problems with the core-shell model for these materials first became apparent during fluorescence energy-transfer studies on particles containing naphthalene (N) groups as fluorescent labels.[3,4] These groups were incorporated covalently into the PMMA phase of the particles by adding a comonomer, 1-naphthalmethyl methacrylate, to the particle synthesis step. When dispersions of these particles in cyclohexane were exposed to low concentrations of anthracene, efficient energy transfer could be observed. This process

$$\underset{\substack{\text{emits at}\\ 340\ \text{nm}}}{N^*} + A \rightarrow N + \underset{\substack{\text{emits at}\\ 400\ \text{nm}}}{A^*} \qquad (1)$$

requires the A molecules to approach to within 20–40 Å of the N* species. Analysis of the data indicated that most, if not all, of the N in the particle were able to transfer energy to A.

Since the N groups are statistically distributed throughout the particles and the light penetrates into them to a depth of at least its wavelength, these observations require that the A molecules have access to a pathway to penetrate rapidly (seconds or minutes) into the deepest reaches of the particle core.

As a consequence, we rejected the core-shell model for this system and replaced it with an alternative model that presumes extensive grafting between PMMA and PIB during particle synthesis.[4] These covalent bonds oppose macroscopic separation of phases but permit local phase separation. Under such circumstances, much of the PIB would be located in the particle interior where it might form an interconnecting network of channels. These could be swollen by hydrocarbon solvents and thereby permit rapid diffusion of certain substances into and out of the particles. We call this the *microphase model* of polymer colloid structure.[4] One might note similarities between this model and the traditional view of the morphology of interpenetrating networks.[5]

Since this is a new model, it would be particularly useful to see if the structure it suggests would be consistent with experiments involving other analytical techniques. Light scattering techniques, in view of the particle size, would be well suited for differentiating between these two models. However, quantitative use of light scattering is somewhat difficult due to the large amount of scattering arising from the surface. Small-angle X-ray scattering (SAXS), on the other hand, probes a much smaller size scale. Evaluation of the structure factor of the core-shell model or of the microphase model by SAXS is not possible. However, the two models differ dramatically in the homogeneity of the phases within the particles. In the core-shell model, the particle consists of two homogeneous phases, whereas in the microphase model, the structure is heterogeneous. This difference should give rise to a discernible difference in the SAXS profiles. In order to enhance the contrast, we chose to treat the particles with a small amount of tetraphenyllead, a hydrocarbon-soluble heavy metal derivative. We assumed that under mild conditions this derivative would diffuse rapidly into the PIB regions of the particle, whereas the time scale for diffusion into the glassy PMMA phase would be very long. For tetraphenyllead with a molecular diameter of ca. 10 Å, the diffusion constant in PMMA at room temperature would be quite small and would take years to fully saturate the particles.[6]

Experimental Section

PMMA–PIB particles were prepared in isooctane according to the one-pot recipe previously reported.[2] In order that the same batch of material could be analyzed by several different methods, the recipe included ca. 2 mol % 1-naphthylmethyl methacrylate in the methyl methacrylate feed. The dispersions were purified

0024-9297/87/2220-0899$01.50/0 © 1987 American Chemical Society