Shape of a Random-Flight Chain*

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An analysis is made of the distribution function and its moments for a linear combination of three randomly chosen orthogonal components of the so-called radius of gyration of an unrestricted random-flight chain, and certain averages of moments are obtained of the three-dimensional distribution $W(L_1^2L_2^2L_3^2)$, where $L_1 \leq L_2 \leq L_3$ are the orthogonal components of the radius of gyration along the principal axes of inertia of the chain. The strong departures of the chain shape from spherical symmetry indicated by these results are confirmed and complemented by Monte Carlo studies of unrestricted random walks on a simple cubic lattice. A surprisingly high ratio of principal components is found for chains with 50 and 100 bonds, $\langle L_3^2 \rangle : \langle L_2^2 \rangle : \langle L_1^2 \rangle \simeq 11.7:2.7:1$.

I. INTRODUCTION

During the last decade several papers[1–6] have been published dealing with the distribution functions for the square radius of gyration S^2 of a random chain and for its orthogonal components. While Fixman[1] in the first paper of this kind directed attention mainly to the statistical moments of the S^2 distribution for an infinitely long chain, and investigated in detail only certain regions of the distribution function itself, the more recent papers contain more complete descriptions of the distribution functions even for finite chain lengths. In a series of papers, Forsman and Hughes[2] and Hoffman and Forsman[5] developed and used a multiple integration technique for numerical computation of the distribution functions of S^2 and its orthogonal components, and Forsman[4] showed that the two-dimensional problem (i.e., the distribution of the sum of two orthogonal components) can be treated exactly. Although not quite general, their results apply even for finite, sufficiently long chains. Finally, Coriell and Jackson[6] examined in detail the properties of the distribution function of an orthogonal component of the radius of gyration and derived a rigorous expression for it in the form of a contour integral, valid for any length of the random-flight chain. The distribution functions treated so far thus describe in one way or another the size distribution of the random coils; however, no attempt has been made to estimate their shape distribution. The first difficulty encountered here is obviously the very definition of the shape. Many years ago Kuhn[7] drew attention to the strong asymmetry of the random-flight chain following from consideration of the average loci of several special segments in the chain relative to its end-to-end vector. But this estimate can hardly characterize the average shape of the chain, which should be based on the positions of all segments rather than on those of certain specially chosen segments. A similar objection would apply to the definition of the shape as the envelope of certain geometrical form (e.g., ellipsoidal) encompassing all the segments of a particular chain. We therefore chose a more democratic (and mathematically feasible) way of characterizing the shape of a random chain by the three specific orthogonal components of the radius of gyration $L_1 \leq L_2 \leq L_3$ taken along its principal axes of inertia. These will be referred to as the principal components of S. The advantage of this choice lies also in its close relation to the three principal moments of inertia of the chain.

In the next section the distribution function and its moments are derived for a linear combination of the three orthogonal components of the radius of gyration for two cases: (1) for a random-flight chain, (2) for an ensemble of bodies with the three-dimensional shape distribution $W(L_1^2L_2^2L_3^2)$ of the squares of principal components of S. By comparison of the two results in Sec. III, some average moments of the shape distribution are found for the random-flight chain. Finally, Sec. IV describes some Monte Carlo calculations of the shape distribution of two types of random chain on simple cubic lattices, which complement the analytical results. A preliminary report of the principal results has already appeared.[8]

II. DISTRIBUTION FOR THE LINEAR COMBINATION OF ORTHOGONAL COMPONENTS OF RADIUS OF GYRATION

A. Random-Flight Chain

Consider a homogeneous random-flight chain consisting of $N-1$ segments and N beads of unit mass, the first of which is located at the origin of the Cartesian coordinate system x_1, x_2, x_3 fixed in space. Denoting the coordinates of the mth bead by $x_k^{(m)}$, $k=1, 2, 3$, we define the symmetrical tensor $\mathbf{X}$ by the relation

$$X_{kl} = N^{-1} \sum_{m=1}^{N} x_k^{(m)} x_l^{(m)} - N^{-2} \sum_{m=1}^{N} x_k^{(m)} \sum_{m=1}^{N} x_l^{(m)}. \quad (1)$$

It is noted that $\mathbf{X}$ is closely related to the tensor of inertia $\mathbf{T}$ of our chain: the products of inertia are proportional to corresponding off-diagonal terms of $\mathbf{X}$,

$$T_{kl} = -NX_{kl}, \qquad k \neq l, \quad (1a)$$

while the moments of inertia are given as

$$T_{kk} = N(X_{ll} + X_{mm}), \qquad k \neq l \neq m \neq k. \quad (1b)$$

Furthermore, the trace of $\mathbf{X}$ equals the square radius of gyration[9] S^2. As mentioned above, so far attention has been paid mostly to the size distribution of the random coils; and only the distribution functions of one orthogonal component[2,3,5,6] $S_1^2(\equiv X_{11})$ and of the sum of two,[4,5] $S_2^2(\equiv X_{11}+X_{22})$, or three,[1,5] $S_3^2(\equiv S^2\equiv X_{11}+X_{22}+X_{33})$, orthogonal components of the square radius of gyration, respectively, have been investigated.

We thought that a more general analysis might reveal some information about the shape distribution of the random coils and so we turned to the distribution function $P(Q)$ of a quantity Q, defined generally as a linear combination of orthogonal components of the square radius of gyration,

$$Q\equiv \sum_{k=1}^{3} C_k X_{kk}. \tag{2}$$

Sometimes, especially when comparison is made for different chain lengths, the more convenient reduced forms of Q and $P(Q)$ will be used, where $Q_r=Q/N\sigma^2$, $P_r(Q_r)=N\sigma^2P(Q)$, and σ^2 denotes the mean square length of a segment. The correlation between $P(Q)$ and the shape of the coil becomes obvious when we choose, for instance, the coefficients C_k such that $\sum C_k=0$; then for a spherically symmetrical cloud of segments Q is identically equal to zero, and therefore any nonzero distribution $P(Q)$ found for random coils would reflect somehow the departures of their shapes from spherical symmetry. Assuming a Gaussian segment length distribution for our freely jointed chain,

$$P(\mathbf{x}^{(m)}-\mathbf{x}^{(m-1)})=(2\pi\sigma^2/3)^{-3/2} \times \exp[-(3/2\sigma^2)(\mathbf{x}^{(m)}-\mathbf{x}^{(m-1)})^2], \tag{3}$$

we can write the distribution function $P(Q)$, using Eqs. (1)–(3), as a $3(N-1)$-multiple integral:

$$P(Q)=\left(\frac{2\pi\sigma^2}{3}\right)^{-(3/2)(N-1)} \times\int_{-\infty}^{+\infty}\cdots\int_{-\infty}^{+\infty}\delta[Q-N^{-1}\sum_{k,m}C_k(x^{(m)})^2 +N^{-2}\sum_k C_k(\sum_m x_k^{(m)})^2] \times \exp\left(-\frac{3}{2\sigma^2}\sum_{k,m}(x_k^{(m)}-x_k^{(m-1)})^2\right)\prod_{k,m}dx_k^{(m)} \tag{4}$$

where the ranges of indices are $k=1, 2, 3$; $m=2, 3, \cdots, N$. After introducing the Fourier representation of the Dirac delta function $\delta(x)$, the expression can be integrated[10] yielding

$$P(Q)=(2\pi)^{-1}2^{-(3/2)(N-1)} \times\int_{-\infty}^{+\infty}\exp(i\lambda Q)(|A_1||A_2||A_3|)^{-1/2}d\lambda, \tag{5}$$

where $|A_k|$ is the determinant of the matrix $\mathbf{A}_k$ defined by

$$(\mathbf{A}_k)_{mn}=\delta_{mn}(1+i\lambda'C_k)-i\lambda'C_kN^{-1} -\tfrac{1}{2}(\delta_{m,n+1}+\delta_{m,n-1})-\tfrac{1}{2}\delta_{mN}\delta_{nN}, \tag{6}$$

and λ' is the reduced integration variable of Eq. (5),

$$\lambda'=\lambda\sigma^2/3N. \tag{7}$$

Finally, the application of Coriell and Jackson's generating-function method[6] for the determination of characteristic polynomials of the matrices $\mathbf{A}_k$ gives the following relation for $P(Q)$:

$$P(Q)=(2\pi)^{-1}N^{3/2} \times\int_{-\infty}^{+\infty}\exp(i\lambda Q)\prod_k U_{N-1}^{-1/2}(1+i\lambda'C_k)d\lambda, \tag{8}$$

where $U_N(x)$ is the Chebyshev polynomial of the second kind.

The integrand in Eq. (8) has in general $3(N-1)$ branch points, located on the imaginary axis in the complex plane, with coordinates

$$\lambda_k'^{(m)}=iC_k^{-1}[1-\cos(m\pi/N)], \quad k=1, 2, 3;\ m=1, 2, \cdots, N-1, \tag{9}$$

as follows readily from an alternative expression of Chebyshev polynomials,[11]

$$U_{N-1}(1+i\lambda'C_k)=\sin(N\theta)/\sin\theta, \tag{10}$$

where

$$\theta=\arccos(1+i\lambda'C_k).$$

For each particular choice of the coefficients C_k, the distribution function $P(Q)$ can thus be computed by integrating along the branch cuts as the sum of a finite number of definite integrals, as shown by Coriell and Jackson[6] for their special case $C_1=1$, $C_2=C_3=0$. Though it does not seem useful to follow this procedure further in general, the results for a special class of Q distributions are probably worth mentioning. The calculation is simplified when two of the three coefficients C_k become identical, e.g., $C_1=C_2=C$, and the third one is either of the opposite sign or zero, respectively; then the branch points in the complex half-plane corresponding to $C_1=C_2=C$ degenerate into isolated singularities and the function $P(Q)$, in the interval where $\operatorname{sign}Q=\operatorname{sign}C$, can be calculated simply as a sum of $N-1$ terms (see Appendix):

$$P_r(Q_r)=\frac{6N^{5/2}}{|C|}\sum_{m=1}^{N-1}(-1)^{m+1}v_m^{-N} \times\sin^2\left(\frac{m\pi}{N}\right)\left[\frac{y_m(1+y_m^2)^{1/2}}{1-v_m^{-4N}}\right]^{1/2}\exp\left(\frac{6N^2y_m^2Q_r}{C_3}\right), \tag{11}$$

where

$$y_m=(-C_3/C)^{1/2}\sin(\tfrac{1}{2}m\pi/N),$$

$$v_m=y_m+(1+y_m^2)^{1/2}.$$

The analytically accessible distribution $P(S_2^2)$ of the sum of two orthogonal components of the square radius of gyration, investigated with a different method by Forsman,[4] obviously belongs to this class ($C=1$, $C_3=0$). The results obtained from Eq. (11) for this distribution and its moments,

$$P_r(S_{2,r}^2)=3N^2\sum_m (-1)^{m+1}\sin^2(m\pi/N)\times\exp[-6N^2S_{2,r}^2\sin^2(m\pi/2N)], \quad (11a)$$

$$\langle S_2^{2n}\rangle_r=2n!(6N^2)^{-n}\sum_m(-1)^{m+1}\times\cos^2(m\pi/2N)\sin^{-2n}(m\pi/2N), \quad (11b)$$

deviate at finite N from those given by Forsman [Eqs. (16) and (27), Ref. 5]. The reason should be probably sought in the approximation $N\simeq N+1$ made in the basic general Eq. (8), Ref. 2. On the other hand, our relation for the first moment,

$$\langle S_2^2\rangle_r=(3N^2)^{-1}\sum_m(-1)^{m+1}\cot^2(m\pi/2N), \quad (11c)$$

is in agreement with Coriell and Jackson's result[6] for $\langle S_1^2\rangle$. Note that $\langle S_2^2\rangle=2\langle S_1^2\rangle$.

The investigation of the moments $\langle Q^n\rangle$ appears to be more rewarding than that of the distribution $P(Q)$ itself. They are obtained by differentiation[10] of the characteristic function $K(\lambda)$ of the distribution $P(Q)$ [see Eq. (8)], where

$$K(\lambda)=N^{3/2}\prod_k U_{N-1}^{-1/2}(1+i\lambda' C_k). \quad (12)$$

We thus get

$$\langle Q^n\rangle_r=(-N\sigma^2)^{-n}[d^nK(\lambda)/d(\lambda i)^n]|_{\lambda=0}$$
$$=(-3)^{-n}N^{-2n+(3/2)}\sum_{j=0}^{n}\sum_{l=0}^{j}\binom{n}{j}\binom{j}{l}\times C_1^{n-j}C_2^{j-l}C_3^{l}F_{N-1}^{(n-j)}F_{N-1}^{(j-l)}F_{N-1}^{(l)}, \quad (13)$$

where

$$F_N^{(l)}=d^lU_N^{-1/2}(x)/dx^l|_{x=1}$$

and the derivatives of Chebyshev polynomials can be expressed conveniently by means of Gegenbauer polynomials

$$d^lU_N(x)/dx^l=2^l l!C_{N-l}^{(l+1)}(x).$$

Specifically, the first three moments are seen to be

$$2\langle Q\rangle_r=3^{-1}(1-N^{-2})\langle C\rangle,$$
$$2\langle Q^2\rangle_r=3^{-2}(1-N^{-2})\times[(1-N^{-2})(\tfrac{1}{2}\langle C^2\rangle+\tfrac{1}{3}\langle CC\rangle)-\tfrac{1}{5}(1-4N^{-2})\langle C^2\rangle],$$
$$2\langle Q^3\rangle_r=3^{-3}(1-N^{-2})\times[\tfrac{1}{2}(1-N^{-2})^2(\tfrac{5}{6}\langle C^3\rangle+\langle C^2C\rangle+\tfrac{1}{9}\langle CCC\rangle)-\tfrac{1}{5}(1-N^{-2})(1-4N^{-2})(\tfrac{3}{2}\langle C^3\rangle+\langle C^2C\rangle)+(1/35)(1-4N^{-2})(1-9N^{-2})\langle C^3\rangle], \quad (14)$$

where the averages of the constants C_k are defined as

$$6\langle C^uC^vC^w\rangle=C_1^uC_2^vC_3^w+C_1^uC_2^wC_3^v+C_1^vC_2^uC_3^w+C_1^vC_2^wC_3^u+C_1^wC_2^uC_3^v+C_1^wC_2^vC_3^u. \quad (14a)$$

The relations (14) reduce to Coriell and Jackson's[6] moments $\langle S_1^{2n}\rangle$ of the one-dimensional distribution for $C_1=1$, $C_2=C_3=0$, and the moments of two- and three-dimensional distributions, Eqs. (14b) and (14c) agree in the limit $N\to\infty$ with the results of Forsman[4] and Fixman[1]:

$$\langle S_2^2\rangle_r=(1/9)(1-N^{-2}),$$
$$\langle S_2^4\rangle_r=(1/405)(7-5N^{-2}-2N^{-4}),$$
$$\langle S_2^6\rangle_r=(1/8505)(31-21N^{-4}-10N^{-6}), \quad (14b)$$
$$\langle S^2\rangle_r=(1/6)(1-N^{-2}),$$
$$\langle S^4\rangle_r=(1/540)(19-20N^{-2}+N^{-4}),$$
$$\langle S^6\rangle_r=(1/68\,040)(631-399N^{-2}-231N^{-4}-N^{-6}). \quad (14c)$$

As a first rough measure of the nonsphericity of random coils we examined specifically the quantity

$$Q^*=2X_{33}-X_{11}-X_{22}, \quad (15)$$

identically equal to zero for any body of spherical symmetry. Its first several moments for a chain with $N\to\infty$, obtained from Eqs. (14) and compared with the mean square radius of gyration,

$$\langle Q^*\rangle=0, \qquad \langle Q^{*2}\rangle=(8/15)\langle S^2\rangle^2,$$
$$\langle Q^{*3}\rangle=(128/315)\langle S^2\rangle^3, \quad (16)$$

do suggest that the departures from spherical symmetry are far from negligible and worthy of further study. The evaluation of $P(Q^*)$ for $Q^*\leq 0$, using Eq. (11) for finite N, also shows that for physically significant negative values of Q^* [those for which $P(Q^*)/P_{\max}(Q^*)>10^{-3}$] the convergence of the reduced distribution function $P_r(Q_r^*)$ with increasing N to a limiting form for $N\to\infty$ is quite rapid. The difference between chains with 50 and 500 bonds in this interval is always less than 0.265% and the trend of $P_r(Q_r^*)$ for $Q_r^*\to 0$ suggests similar behavior in the positive region. The most probable value of Q_r^* is negative; e.g., for $N=500$ it is $(Q_r^*)_{\max}\simeq -0.016$.

However, the $P(Q)$ distributions and their moments reflect not only the shape distribution of random coils but also their random orientation, because of the choice of a fixed coordinate system x_1, x_2, x_3. In order to isolate the shape factor alone, we will derive in the next section the relations for the moments $\langle q^n\rangle$ of an ensemble of randomly oriented bodies with a three-dimensional distribution $W(L_1^2L_2^2L_3^2)$ of the squares of their three principal components of the radius of gyration $L_1\leq L_2\leq L_3$ (i.e., three orthogonal components of the radius of gyration along the principle axes of the ellipsoid of inertia), hoping that the comparison of the two results might yield some information about the shape distribution of random coils in terms of the moments of the distribution of equivalent ellipsoids. Here the definition of q is, of course, equivalent to that of Q for random coils [Eq. (2)].

B. Ensemble of Equivalent Ellipsoids

Let us first consider the quantity q for a single cloud of N beads of unit mass. The principal components L_k of the radius of gyration of the cloud are given by the relation

$$L_k^2 = N^{-1} \sum_m (\xi_k^{(m)})^2, \qquad k=1,2,3, \tag{17}$$

where $\xi_k^{(m)}$ are coordinates of the mth bead relative to the principal axes of the ellipsoid of inertia of the cloud. Denoting by α, β, γ the three Eulerian angles transforming this ξ-coordinate system into the fixed system x, we can write for each of the N beads the equation

$$\mathbf{x}^{(m)} = \mathbf{M}\boldsymbol{\xi}^{(m)}, \tag{18}$$

where

$$\mathbf{M} \equiv \begin{pmatrix} \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma & \sin\alpha\cos\gamma + \cos\alpha\cos\beta\sin\gamma & \sin\beta\sin\gamma \\ -\cos\alpha\sin\gamma - \sin\alpha\cos\beta\cos\gamma & -\sin\alpha\sin\gamma + \cos\alpha\cos\beta\cos\gamma & \sin\beta\cos\gamma \\ \sin\alpha\sin\beta & -\cos\alpha\sin\beta & \cos\beta \end{pmatrix}$$

and, subsequently, by means of Eqs. (1), (2), and (17) also the relation for q (as observed in the fixed coordinate system) of this specifically oriented cloud of beads[12]:

$$q = N^{-1} \sum_k C_k \sum_m (x_k^{(m)})^2 = \sum_l L_l^2 \sum_k C_k M_{kl}^2. \tag{19}$$

Since q depends upon the orientation of the equivalent ellipsoid through the matrix elements M_{kl}, it turns out that mere randomization of the orientation of the cloud (without varying its principal components L_l) creates already a distribution function, though in a restricted interval of q (except the invariant case $C_1 = C_2 = C_3$):

$$P_1(q) = (8\pi^2)^{-1} \times \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^{\pi} \sin\beta d\beta\, \delta(q - \sum_l L_l^2 \sum_k C_k M_{kl}^2). \tag{20}$$

For instance, for q^* defined analogously to Q^* in Eq. (15), the following distribution function is obtained:

$$\begin{aligned} P_1(q_r^*) &= \pi^{-1}(3\eta)^{-1/2} K(\tau/\eta) \quad \text{if} \quad \xi - 2 \le q_r^* \le 1 - 2\xi, \\ &= \pi^{-1}(3\tau)^{-1/2} K(\eta/\tau) \quad \text{if} \quad 1 - 2\xi \le q_r^* \le 1 + \xi, \end{aligned} \tag{21}$$

where $\eta = (1-\xi)(1+\xi-q_r^*)$, $\tau = \xi(2-\xi+q_r^*)$, $q_r^* \equiv q^*/(L_3^2 - L_1^2)$, the parameter $0 \le \xi \le 1$ is defined as $\xi = (L_3^2 - L_2^2)/(L_3^2 - L_1^2)$, and $K(x)$ is the complete elliptic integral of the first kind.[11] The distribution function has a very sharp maximum reaching infinity at the coordinate $(q_r^*)_{\max} = 1 - 2\xi$, which is positive if $L_2^2 - L_1^2 > L_3^2 - L_2^2$ (e.g., for an oblate ellipsoid of revolution) and negative in the opposite case. The small negative $(Q_r^*)_{\max}$ observed for the random coil thus suggests that the most probable shape of the random coil is slightly closer to the prolate than to the oblate ellipsoid.

Let us now turn our attention to the $P(q)$ function observed for an ensemble of randomly oriented clouds of beads with the probability distribution $W(L_1^2 L_2^2 L_3^2)$ of the squares of their principal components of S. The three-dimensional distribution function $W(L_1^2 L_2^2 L_3^2)$ can be visualized conveniently as a scalar field in the subspace cut out from a Cartesian coordinate system L_k^2 by three planes $L_1^2 = 0$, $L_1^2 = L_2^2$, $L_2^2 = L_3^2$ (see Fig. 1), where each point represents a different equivalent ellipsoid. The distribution function $P(q)$ is now given as the weighted average of the previously defined $P_1(q)$ [Eq. (20)] over all possible ellipsoids:

$$P(q) = (8\pi^2)^{-1} \int_0^{2\pi} d\alpha \int_0^{2\pi} d\gamma \int_0^{\pi} \sin\beta d\beta \times \int_0^{\infty} dL_3^2 \int_0^{L_3^2} dL_2^2 \int_0^{L_2^2} dL_1^2 W(L_1^2 L_2^2 L_3^2) \times \delta(q - \sum_l L_l^2 \sum_k C_k M_{kl}^2). \tag{22}$$

From this relation it is seen that the contribution to $P(q)$ made by equivalent ellipsoids with a specified orientation α, β, γ comes from surface integrals of $W(L_1^2 L_2^2 L_3^2)$ over parallel planar sections of our subspace. Since by varying the coefficients C_k of the examined quantity q, we have an unlimited possibility of changing the orientation of this set of sampling planes, it might seem that, on the other hand, by analyzing a sufficient number of $P(q)$ functions for

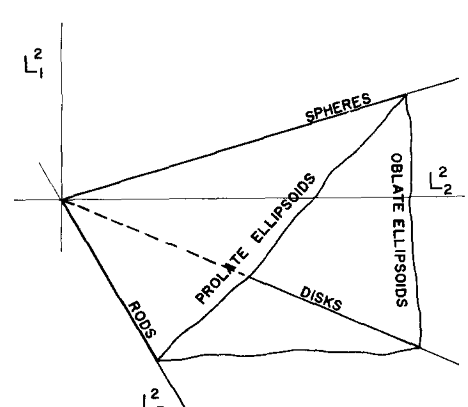

FIG. 1. The subspace used for the representation of the shape distribution function $W(L_1^2 L_2^2 L_3^2)$.

random-flight chain, one could obtain any information required about its distribution $W(L_1^2L_2^2L_3^2)$. Unfortunately, this impression is erroneous: the random orientation of equivalent ellipsoids (and random chains) allowed for in this treatment mixes together to a certain degree the sampling data from planes with different orientation even for a single triplet of coefficients C_k [as follows from the presence of the rotation matrix elements M_{kl} in $\delta(x)$ in Eq. (22)], thus destroying a part of the information; and, therefore, only certain averages can be obtained analytically.

The moments $\langle q^n\rangle$ of the distribution $P(q)$ are calculated from Eq. (22). Using integral properties of the Dirac delta function, we get

$$\langle q^n\rangle=(8\pi^2)^{-1}\sum_{ml}\binom{n}{m}\binom{m}{l}\langle L_1^{2(n-m)}L_2^{2(m-l)}L_3^{2l}\rangle\int_0^{2\pi}d\alpha\int_0^{\pi}\sin\beta d\beta\int_0^{2\pi}d\gamma \times(\sum_k C_kM_{k1}^2)^{n-m}(\sum_k C_kM_{k2}^2)^{m-l}(\sum_k C_kM_{k3}^2)^{l}, \quad (23)$$

where the multidimensional moments are defined in the usual way:

$$\langle L_1^{2u}L_2^{2v}L_3^{2w}\rangle=\int_0^{\infty}L_3^{2w}dL_3^2\int_0^{L_3^2}L_2^{2v}dL_2^2\int_0^{L_2^2}L_1^{2u}W(L_1^2L_2^2L_3^2)dL_1^2, \quad (24)$$

or, after expressing the integrals in terms of beta functions,

$$\langle q^n\rangle=(2\pi^2)^{-1}\sum_{ml}\binom{n}{m}\binom{m}{l}\langle L_1^{2(n-m)}L_2^{2(m-l)}L_3^{2l}\rangle\sum_{abcdgh}\binom{n-m}{a}\binom{a}{b}\binom{m-l}{c}\binom{c}{d}\binom{l}{g}\binom{g}{h}C_1^n\left(\frac{C_2}{C_1}\right)^{a+c+g}\left(\frac{C_3}{C_2}\right)^{b+d+h}$$
$$\times\sum_{ijkp}(-1)^{i+p}\binom{2(n-m-a)}{i}\binom{2(a-b)}{j}\binom{2(m-l-c)}{k}\binom{2(c-d)}{p}B[n-b+f+\tfrac{1}{2},\, b-l-f+\tfrac{1}{2}]$$
$$\times B[n-h-r+\tfrac{1}{2},\, r-b-d+\tfrac{1}{2}]B[h+\tfrac{1}{2}(i+j+k+p+1),\, b+d+l-h+1], \quad (25)$$

where

$$f=d-m+\tfrac{1}{2}(k+p-i-j),$$
$$r=a+l+c-g+\tfrac{1}{2}(i+k-j-p).$$

In the last equation, the summation limits follow from the properties of the combinatorial terms, and the integers i, j, k, p are such that their sum is an even number. From Eq. (25) it is observed that the coefficient of $\langle L_1^{2u}L_2^{2v}L_3^{2w}\rangle$ is invariant to the permutation of the exponents in the product; i.e., it is identical to those of $\langle L_1^{2u}L_2^{2w}L_3^{2v}\rangle$, $\langle L_1^{2w}L_2^{2u}L_3^{2v}\rangle$, etc. This simplifies considerably the numerical evaluation of $\langle q^n\rangle$, since the average moments $\langle L^{2u}L^{2v}L^{2w}\rangle$ can be introduced analogously to the relation (14a). The number of average moments is then restricted by the condition

$$0\leq u\leq v\leq w\leq n, \qquad u+v+w=n; \quad (26)$$

however, this small convenience is overbalanced by the impossibility of separating the average moments into their components.

III. AVERAGE MOMENTS OF PRINCIPAL COMPONENTS OF RADIUS OF GYRATION FOR RANDOM-FLIGHT CHAIN

By equating the expression for $\langle q^n\rangle$, Eq. (25), to that for $\langle Q^n\rangle$, Eq. (13), it is possible now to find relations for the average moments $\langle L^{2u}L^{2v}L^{2w}\rangle$ of a random-flight chain. These relations must be independent of a specific choice of the coefficients C_k; therefore, after rearrangement of the order of summation in the rhs of Eq. (25) into a form analogous to rhs of Eq. (13), each pair of corresponding terms in the summations over $C_1^xC_2^yC_3^z$ on both sides of equation can be put equal each other, yielding thus finally

$$\sum_{uvw}A\frac{\langle L^{2u}L^{2v}L^{2w}\rangle}{u!v!w!}\sum_{abcd}\binom{w}{a}\binom{a}{b}\binom{v}{c}\binom{c}{d}\binom{u}{y+z-a-c}\binom{y+z-a-c}{z-b-d}$$
$$\times\sum_{ijkp}(-1)^{i+p}\binom{2(w-a)}{i}\binom{2(a-b)}{j}\binom{2(v-c)}{k}\binom{2(c-d)}{p}$$
$$\times B[v+w+s+\tfrac{1}{2},\, u-z-s+\tfrac{1}{2}]B[w+t+\tfrac{1}{2},\, v-t+\tfrac{1}{2}]B[z-b-d+\tfrac{1}{2}(j+k+p+i+1),\, u+2b+2d-z+1]$$
$$=(-1)^n2\pi^2N^{3/2-n}\left(\frac{\sigma^2}{3}\right)^n(x!y!z!)^{-1}F_{N-1}^{(x)}F_{N-1}^{(y)}F_{N-1}^{(z)}, \quad (27)$$

TABLE I. The moments of the principal components distribution for the random-flight chains.

	Five-choice walk Monte Carlo					Six-choice walk Monte Carlo					
	$N-1$	$i=1$	$i=2$	$i=3$	Average	$N-1$	$i=1$	$i=2$	$i=3$	Average	Analytical average
$\langle L_i^2\rangle_r\times10^2$	100	1.555	4.225	18.80	8.195	50	1.075	2.906	12.70	5.562	5.553
	200	1.549	4.219	18.79	8.185	100	1.077	2.916	12.56	5.517	5.555
$\langle L_i^4\rangle_r\times10^4$	100	2.848	22.16	486.1	170.4	50	1.347	10.41	226.3	79.37	80.27
	200	2.845	22.19	497.1	174.1	100	1.361	10.70	223.5	78.53	80.25
$\langle L_i^2L_{i+1}^2\rangle_r\times10^4$	100	6.954	82.33	29.52	39.60	50	3.313	38.68	13.76	18.58	18.48
	200	6.988	82.46	29.44	39.63	100	3.342	38.96	13.98	18.76	18.51
$\langle L_i^6\rangle_r\times10^6$	100	6.188	143.8	16 470	5540	50	1.975	45.24	5371	1806	1858
	200	6.274	143.0	17 738	5962	100	2.018	49.87	5351	1801	1857
$\langle L_i^4L_{i+1}^2\rangle_r\times10^6$	100	13.65	449.5	763.5		50	4.442	145.8	245.1		
	200	13.95	457.0	783.2	577.6	100	4.523	154.3	255.4	187.0	190.8
$\langle L_i^4L_{i-1}^2\rangle_r\times10^6$	100	54.95	36.91	2147	599.5	50	17.29	12.41	697.0	193.7	191.0
	200	54.99	38.97	2249		100	18.25	12.95	717.0		
$\langle L_1^2L_2^2L_3^2\rangle_r\times10^6$	100		136.5		136.5	50		44.24		44.24	43.85
	200		138.3		138.3	100		46.05		46.05	44.03

where

$$A=1 \quad \text{if} \quad u=v=w,$$
$$=6 \quad \text{if} \quad u\neq v\neq w\neq u,$$
$$=3 \quad \text{otherwise},$$
$$s=y+b+d-2a-2c+\tfrac{1}{2}(j+p-k-i),$$
$$t=d-b+\tfrac{1}{2}(k+p-i-j).$$

Here u, v, w are subject to the condition (26) and i, j, k, p are restricted similarly as in Eq. (25).

The relation (27) represents actually an infinite number of sets of equations: for any particular n required, by choosing the integers $0\leq x\leq y\leq z\leq n$ satisfying also the relation $x+y+z=n$, a set of n linear independent equations is obtained for n sought average moments of the nth order, and this set of equations can be solved. We calculated the moments up to the third order; their reduced values, $\langle L^{2u}L^{2v}L^{2w}\rangle_r=\langle L^{2u}L^{2v}L^{2w}\rangle(N\sigma^2)^{-n}$, are given as follows:

$$\langle L^2\rangle_r=(1/18)(1-N^{-2}),$$
$$\langle L^4\rangle_r=(1/1620)(13+10N^{-2}-23N^{-4}),$$
$$\langle L^2L^2\rangle_r=(1/540)(1-5N^{-2}+4N^{-4}),$$
$$\langle L^6\rangle_r=(1/204\,120)\times(379+609N^{-2}+21N^{-4}-1009N^{-6}),$$
$$\langle L^4L^2\rangle_r=(1/68\,040)\times(13-42N^{-2}-63N^{-4}+92N^{-6}),$$
$$\langle L^2L^2L^2\rangle_r=(1/22\,680)\times(1-14N^{-2}+49N^{-4}-36N^{-6}). \quad (28)$$

The moments of the principal components confirm strong departures of random coils from spherical symmetry, as follows from the great differences among various average moments of the same order, e.g.,

$$\langle L^4\rangle:\langle L^2L^2\rangle=[13+75(N^2-4)^{-1}]:3,$$
$$\langle L^6\rangle:\langle L^4L^2\rangle:\langle L^2L^2L^2\rangle$$
$$=[379+35(169N^2-361)(N^2-4)^{-1}(N^2-9)^{-1}]:$$
$$:3[13+140(N^2-9)^{-1}]:3^2. \quad (29)$$

All the moments given in Eqs. (28) show monotonous dependence on N in physically relevant regions. The first moment $\langle L^2\rangle_r$, depicting the size of the random coil, increases steadily with increasing N. However, the higher moments do not exhibit unique behavior: The homogeneous moments $\langle L^{2u}\rangle_r$, most sensitive to the

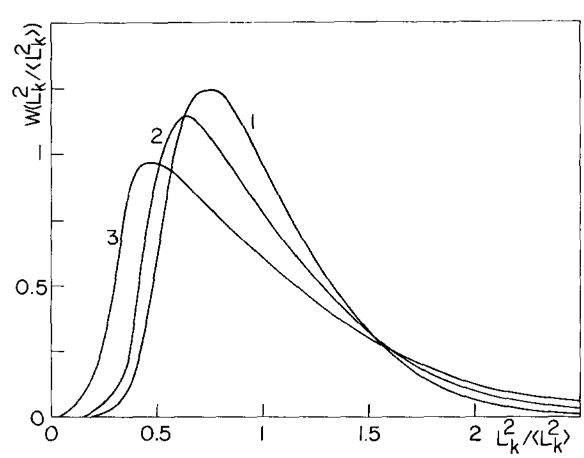

FIG. 2. The approximate one-dimensional distributions of the three principal components of the radius of gyration. The subscript k is indicated at each curve.

longest axis L_3, decrease with increasing N, while the inhomogeneous ones show an increase, thus indicating that the shape of random coil becomes more symmetrical with increasing chain length N (although it never attains spherical symmetry).

As mentioned before, the average moments of the principle components of the radius of gyration cannot be separated because of the allowed random orientation of the random coil. However, the separate moments can be evaluated numerically by the Monte Carlo method,[8] and the average moments can then be used to test the precision and consistency of this numerical method.

IV. MONTE CARLO METHOD

Two types of random walks were generated on a simple cubic lattice, using the Dartmouth GE-635 Computer: 100-step random walk with six choices at each step yielding a completely unrestricted random chain, and 200-step random walk with five choices at each step, where the return to the nearest neighbor site occupied by the preceding bead was forbidden. We chose a longer walk for the five-choice chain because of the larger effective step length. Comparison of the results obtained in the two cases offers a check of randomness of the random numbers generated by the computer, since the correspondence between the random integers and the direction of the step is different in the two cases: in the six-choice walk, the six integers are firmly associated with six directions of the fixed coordinate system, while in the other case the five integers determine the direction of the step relative to that of the preceding step. In both cases, 1000 walks were generated.

For each walk, the elements of the tensor **X** were computed from Eq. (1), and then the principal components L_k^2 appearing in the diagonalized form of **X** were determined: The smallest root $(L_1^2)_r$ of the reduced secular equation

$$L_r^6+a_2L_r^4+a_1L_r^2+a_0=0, \qquad (30)$$

$$a_0=N^{-3}\sum_{k}\sum_{l<m}\sum_{m\neq k\neq l}\left[X_{kk}(X_{ml}^2-\tfrac{1}{3}X_{mm}X_{ll})-\tfrac{2}{3}X_{mk}X_{kl}X_{lm}\right],$$

$$a_1=N^{-2}\sum_{k<l}\sum(X_{kk}X_{ll}-X_{kl}^2),$$

$$a_2=-N^{-1}\sum X_{kk},$$

was found by trial to a precision better than 5×10^{-7} (corresponding to a relative error smaller than 10^{-3} % in most cases), while the other two roots $(L_2^2)_r$ and $(L_3^2)_r$ were determined by solving the quadratic equation

$$L_r^4+L_r^2[a_2+(L_1^2)_r]-a_0(L_1^2)_r^{-1}=0. \qquad (31)$$

The squares of the principal components of the radius of gyration thus obtained were stored for further statistical treatment. To save computer time when investigating the chain-length dependence, the longest random chain generated can serve as the source of data for shorter chains. For instance, in our case 1000 walks of 100 steps each were used to yield data for 2000 walks of 50 steps each. The calculation of the first 50-step walk in each 100-step walk is trivial, while for the computation of the second walk the only additional data needed to be stored are the coordinates of the 51st bead $x_k^{(51)}$ and the sums

$$\sum_{m=1}^{51}x_k^{(m)}, \qquad \sum_{m=1}^{51}x_k^{(m)}x_l^{(m)}$$

(which are being continuously evaluated anyway). The corresponding sums $\sum y_k^{(m)}$, $\sum y_k^{(m)}y_l^{(m)}$ related to the 51st bead as the origin, which are needed for the evaluation of the tensor elements for the second chain,

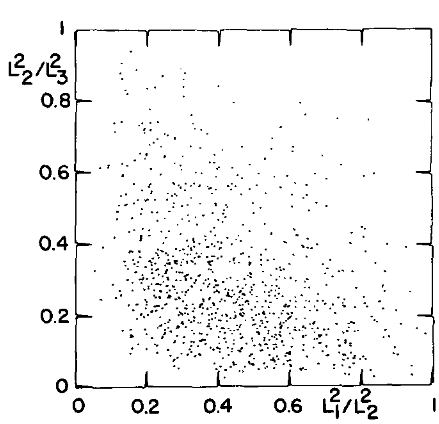

FIG. 3. The shape distribution in the ensemble of 1000 random cubic-lattice chains of 100 bonds each, expressed by square ratios of principal components of each chain.

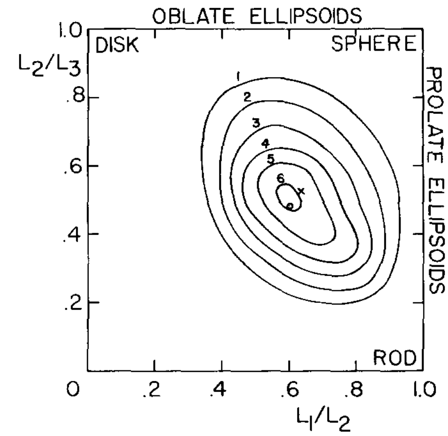

FIG. 4. The distribution of the principal component ratios for a random cubic-lattice chain of 50 bonds. The probability density is indicated at each contour line. The coordinates of two special points are: circle, $(\langle L_1^2\rangle^{1/2}/\langle L_2^2\rangle^{1/2};\ \langle L_2^2\rangle^{1/2}/\langle L_3^2\rangle^{1/2})$; cross, $(\langle L_1/L_2\rangle;\ \langle L_2/L_3\rangle)$.

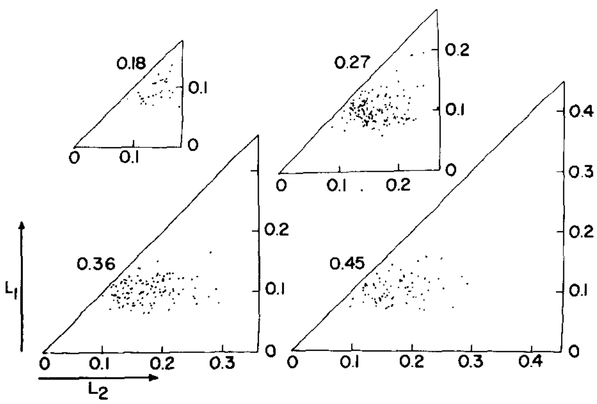

FIG. 5. The representative points contained in the four sections of the reduced subspace $L_{k,r}$ by vertical planes $L_{3,r}=$ const for the random cubic lattice chain of 50 bonds. The positive directions of the axes $L_{1,r}$ and $L_{2,r}$ are denoted by arrows. The number at each triangle indicates $L_{3,r}$.

can then be calculated as

$$\sum_{m=51}^{101} y_k^{(m)}=\sum_{m=1}^{101} x_k^{(m)}-\sum_{m=1}^{51} x_k^{(m)}-50x_k^{(51)}, \quad (32)$$

$$\sum_{m=51}^{101} y_k^{(m)}y_l^{(m)}=\sum_{m=1}^{101} x_k^{(m)}x_l^{(m)}-\sum_{m=1}^{51} x_k^{(m)}x_l^{(m)}-50x_k^{(51)}x_l^{(51)}-x_k^{(51)}\sum_{m=51}^{101} y_l^{(m)}-x_l^{(51)}\sum_{m=51}^{101} y_k^{(m)}. \quad (33)$$

Analogous procedures were used to obtain data for 2000 walks of 100 steps each on the five-choice lattice.

Table I shows the reduced moments of the principal components distribution up to the third order for all cases examined.[13] The good agreement between the average values for the six-choice walk obtained by Monte Carlo method and the analytical values calculated from Eqs. (28) attests to fairly good randomness of the generated random numbers and the consistency of the results (e.g., the deviations of $\langle L^2\rangle$ for $N=50$ and $N=100$ are only $+0.16\%$ and -0.68%, respectively). Although the analytical random-flight model and Monte Carlo lattice model are basically different as regards the number of allowed orientations in each step as well as the type of the bond-length distribution assumed, the first moments $\langle L^2\rangle$ turn out to be identical for both models even for very low chain lengths (e.g., $N=2$ and 3), and the differences observed for higher moments at low N decrease rapidly with its growing value. Chains with $N=51$ and $N=101$ are obviously too long to show any significant difference, and both models yield equivalent results. Surprising is the high ratio among the principal components found to be $\langle L_3^2\rangle:\langle L_2^2\rangle:\langle L_1^2\rangle=11.82:2.704:1$ for $N=51$ and 11.66:2.706:1 for $N=101$, which corresponds to the square-root ratios $\langle L_3^2\rangle^{1/2}:\langle L_2^2\rangle^{1/2}:\langle L_1^2\rangle^{1/2}=3.438:1.644:1$ and 3.414:1.645:1, respectively. Though the observed difference between the two chains is probably insignificant, it is nevertheless in accord with the expected decrease of asymmetry with increasing chain length. As expected, these ratios of the average squares of the principal components of the radius of gyration taking into account the positions of all beads in the chain, differ from the ellipsoid axis ratio 2.8:2.2:1 obtained by Kuhn[7] from the most probable positions of some specifically selected beads; however, they still indicate very strong average departures of the random coils from spherical symmetry. As a matter of fact, none of the 1000 chains generated for $N=101$ showed even approximate spherical symmetry; the closest one was a chain with the ratio $L_3^2:L_2^2:L_1^2\simeq 1.60:1.20:1$.

For the five-choice chain with $\langle\cos\theta\rangle=\frac{1}{5}$, the only quantity available analytically so far[14,15] is $\langle L^2\rangle_r$. Its calculated values 8.231×10^{-2} for $N=101$ and 8.282×10^{-2} for $N=201$ are again in reasonable agreement with Monte Carlo results (the deviations being -0.44% and -1.17%, respectively). However, both these figures and the average higher moments seem to indicate that in this case the dispersion of the Monte Carlo results is broader than that found for the symmetrical six-choice walk, and more walks would be needed in order to obtain results of comparable quality. The principal-component ratios found here for the chains $N=101$ and $N=201$, $\langle L_3^2\rangle:\langle L_2^2\rangle:\langle L_1^2\rangle=12.09:2.717:1$ and 12.13:2.723:1, respectively, are only slightly higher than those for the symmetrical six-choice walk and confirm the previously found high asymmetry of the random coil. The figures in Table I suggest that for long enough chains, the ratio of the principal-axis moments of the nth order of two chains with different short-range restrictions is roughly equal to the nth power of the constant $K\equiv\langle L^2\rangle_2/\langle L^2\rangle_1$.

The more reliable data on six-choice chains, especially the larger ensemble for $N=51$, were submitted to a closer examination. The one-dimensional distributions of the three square principal components L_k^2 (always considered regardless of the other two) show marked differences. Their approximate distribution functions reduced by $\langle L_k^2\rangle$ for the purpose of comparison, shown in Fig. 2 for $N=51$, indicate that the relative distribution of the shortest axis $W(L_1^2/\langle L_1^2\rangle)$ is narrower, with its peak higher and closer to unity, than that of the longest axis $W(L_3^2/\langle L_3^2\rangle)$. The shape distribution alone (irrespective of the size of coils) is illustrated in Figs. 3 and 4 by means of the diagrams of the square principal-component ratios L_2^2/L_3^2 vs L_1^2/L_2^2 and their square roots, respectively. As apparent from Fig. 3, where each point represents one of 1000 random chains generated for $N=101$, coils with square axis ratios $L_2^2/L_3^2<0.04$ and $L_1^2<L_2^2<0.1$ occur extremely rarely, as do coils with symmetrical shapes (spheres and ellipsoids of revolution). The vast majority of points occupies the left lower quarter of the diagram, with rather sharp boundaries on the left and bottom sides and diffuse diagonal boundary when moving up right. In the square-root plot in Fig. 4, contour lines of constant probability density are approximately drawn for the larger population of chains with $N=51$. The lines are roughly elliptical, with the most probable values $(L_1/L_2)_{\max}\simeq 0.60$, $(L_2/L_3)_{\max}\simeq 0.50$, which are quite close to the averages $\langle L_1^2\rangle^{1/2}/\langle L_2^2\rangle^{1/2}=0.608$, $\langle L_2^2\rangle^{1/2}/\langle L_3^2\rangle^{1/2}=0.478$ and $\langle L_1/L_2\rangle=0.635$, $\langle L_2/L_3\rangle=0.524$. (The corresponding averages found for $N=101$ are 0.608, 0.482, 0.636, and 0.525, respectively.)

We have examined also to some degree the correlations among the distributions of different principal components. Figure 5 shows the individual representative points for the chain length $N=51$ contained in the volume elements of constant thickness $\Delta L_{3,r}=0.02$, cut out from the subspace $L_{k,r}$ (analogous to that in Fig. 1) by two vertical planes, as functions of $L_{3,r}$. Examination of the number of points in each section would yield the one-dimensional distribution $W(L_{3,r})$; however, here we are rather interested in the distribution of the points within the section as a function of $L_{3,r}$. It is surprising to see that the distribution of the shortest axis $L_{1,r}$ is to a considerable extent independent of the longest axis $L_{3,r}$, unless $L_{3,r}$ becomes so small that it efficiently imposes an upper limit on $L_{1,r}$ due to the condition $L_1\leq L_2\leq L_3$. However, even then, the population of points does not shift to lower values of $L_{1,r}$ (its sharp lower boundary at $L_{1,r}\simeq 0.07$ rather slightly increases than decreases with diminishing $L_{3,r}$) and is only cut away by the previously mentioned condition in the region of L_1 comparable with L_3. A similar conclusion can be drawn about the relation between L_2 and L_3 distributions, though here the inequality appears to be much more restrictive. The average values $\langle L_1\rangle_r$ and $\langle L_2\rangle_r$ given in Table II as functions of $L_{3,r}$ comprising 98.6% of the 2000 chains generated, confirm these qualitative considerations: Following the 440% increase of $L_{3,r}$ from 0.15 to 0.66, it is seen that the average value $\langle L_1^2\rangle_r$ is increased only by ~9%, while that of $\langle L_2^2\rangle_r$ by ~37%. A weak correlation is suggested also by the ratios of the average moments from Table I:

$$\langle L_1^2L_2^2\rangle\langle L_1^2\rangle^{-1}\langle L_2^2\rangle^{-1}\simeq 1.06,$$

$$\langle L_1^2L_3^2\rangle\langle L_1^2\rangle^{-1}\langle L_3^2\rangle^{-1}\simeq 1.01,$$

and

$$\langle L_2^2L_3^2\rangle\langle L_2^2\rangle^{-1}\langle L_3^2\rangle^{-1}\simeq 1.05.$$

TABLE II. The dependence of the average moments $\langle L_1\rangle_r$ and $\langle L_2\rangle_r$ on the length of the third principal component $L_{3,r}$ for the random chain of 50 bonds. The interval width is $\Delta L_{3,r}=0.03$.

$L_{3,r}\times 10^2$	Number of chains	$\langle L_1\rangle_r\times 10^2$	$\langle L_2\rangle_r\times 10^2$
12	1	7.1	10.9
15	13	9.6	12.8
18	54	9.6	13.8
21	153	10.1	14.6
24	212	10.2	15.7
27	232	10.2	16.4
30	230	10.3	16.8
33	207	10.3	18.0
36	189	10.3	17.3
39	196	10.4	17.3
42	138	10.4	17.6
45	116	10.0	17.2
48	80	10.5	17.9
51	54	10.5	17.3
54	35	10.5	17.8
57	32	10.5	17.5
60	23	10.3	17.2
66	8	10.4	17.4

The results obtained can be interpreted also in terms of the moments of inertia T_{kk} of the random coils, using Eq. (1b) for the transcription. For instance, for the unrestricted six-choice random chain with $N=51$, there is obtained from Table I: $\langle T_{11}\rangle_r=0.159$, $\langle T_{22}\rangle_r=0.141$, $\langle T_{33}\rangle_r=0.0406$, $\langle T_{11}^2\rangle_r=0.0327$, $\langle T_{22}^2\rangle_r=0.0266$, $\langle T_{33}^2\rangle_r=0.00191$, etc.

It thus seems that the deviations of the random-coil shape from spherical symmetry are of such extent that they could distort significantly the theoretical relations derived for some experimental properties of dilute polymer solutions on the assumption of a spherically symmetrical segment distribution. In an improved version, the random coils should be replaced either by the average ellipsoids with average parameters following from the present treatment, or more elaborately by an ensemble of ellipsoids with mutually independent distributions of their three axes; however, the proposal of a specific form of such distributions would require much more computer data than we have in hand thus far.

ACKNOWLEDGMENT

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APPENDIX

If we choose, for instance, $C_1=C_2=C>0$ and $C_3<0$, then the integrand in Eq. (8) shows [see Eq. (9)] $N-1$ isolated singular points $\lambda_\alpha'^{(m)}$ on the positive imaginary axis,

$$\lambda_\alpha'^{(m)}=iC^{-1}[1-\cos(m\pi/N)], \qquad (A1)$$

and $N-1$ branch points $\lambda_\beta'^{(m)}$ on the negative imaginary axis,

$$\lambda_\beta'^{(m)}=iC_3^{-1}[1-\cos(m\pi/N)],$$

$$m=1, 2, \cdots, N-1. \qquad (A2)$$

The integral in Eq. (8) for nonnegative Q can thus be calculated simply by completing the integration contour by an infinite semicircle in the upper half-plane and applying the residue theorem,

$$P(Q)=(3/2)\pi^{-1}\sigma^{-2}N^{5/2}\times\sum_{m=1}^{N-1}\oint_{\lambda_\alpha'^{(m)}}\exp(i\lambda Q)\,U_{N-1}^{-1}(1+i\lambda'C)\times U_{N-1}^{-1/2}(1+i\lambda'C_3)\,d\lambda', \quad \text{(A3)}$$

where the contour integrals in Eq. (A3) are taken around each of $N-1$ singular points $\lambda_\alpha'^{(m)}$.

For the evaluation of the individual contour integrals it is convenient to substitute the Chebyshev polynomials in Eq. (A3) in the form of products

$$U_{N-1}(1+i\lambda'C)=(2C)^{N-1}\prod_{m=1}^{N-1}[i(\lambda'-\lambda_\alpha'^{(m)})],$$

$$U_{N-1}(1+i\lambda'C_3)=(2C_3)^{N-1}\prod_{m=1}^{N-1}[i(\lambda'-\lambda_\beta'^{(m)})], \quad \text{(A4)}$$

where $\lambda_\alpha'^{(m)}$ and $\lambda_\beta'^{(m)}$ correspond to the zeros of the polynomials, given by Eqs. (A1) and (A2). Expressing then the integration variable λ' in the contour integral around $\lambda_\alpha'^{(m)}$ as $\lambda'=\lambda_\alpha'^{(m)}+\rho e^{i\phi}$ and taking the limit of the integral for $\rho\rightarrow 0$, we get the result for the contour integral in terms of reciprocal products of differences among the zeros of the Chebyshev polynomials,

$$\oint_{\lambda_\alpha'^{(m)}}\exp(i\lambda Q)\,U_{N-1}^{-1}(1+i\lambda'C)\,U_{N-1}^{-1/2}(1+i\lambda'C_3)\,d\lambda'$$
$$=2\pi 2^{-3(N-1)/2}C^{-(N-1)}C_3^{-(N-1)/2}\times\exp(i\lambda_\alpha^{(m)}Q)\prod_{l=1,l\neq m}^{N-1}[i(\lambda_\alpha'^{(m)}-\lambda_\alpha'^{(l)})]^{-1}\times\prod_{l=1}^{N-1}[i(\lambda_\alpha'^{(m)}-\lambda_\beta'^{(l)})]^{-1/2}. \quad \text{(A5)}$$

The first homogeneous product can be calculated from the relation (A6), which follows from comparison of Eqs. (10) and (A4),

$$\prod_{l=1}^{N-1}[i(\lambda'-\lambda_\alpha'^{(l)})]^{-1}=(2C)^{N-1}\frac{\sin\alpha}{\sin(N\alpha)}, \quad \text{(A6)}$$

where

$$\alpha=\arccos(1+iC\lambda'),$$

by taking the limit for $\lambda'\rightarrow\lambda_\alpha'^{(m)}$:

$$\prod_{l=1,l\neq m}^{N-1}[i(\lambda_\alpha'^{(m)}-\lambda_\alpha'^{(l)})]^{-1}$$
$$=(2C)^{N-1}\sin\alpha_m\lim_{\lambda'\rightarrow\lambda_\alpha'^{(m)}}\frac{i(\lambda'-\lambda_\alpha'^{(m)})}{\sin[N\arccos(1+iC\lambda')]}$$
$$=(-1)^{m+1}2^{N-1}C^{N-2}N^{-1}\sin^2(m\pi/N). \quad \text{(A7)}$$

Similarly to Eq. (A6), the product involving $\lambda_\beta'^{(l)}$ terms may be written in general as

$$\prod_{l=1}^{N-1}[i(\lambda'-\lambda_\beta'^{(l)})]=(2C_3)^{N-1}\frac{\sin\beta}{\sin(N\beta)}, \quad \text{(A8)}$$

where

$$\beta=\arccos(1+iC_3\lambda');$$

however, since in the region of our interest $(\lambda'\rightarrow\lambda_\alpha'^{(m)})$ the quantity $iC_3\lambda'$ is never negative, the angle β is imaginary, as can be seen from its definition above. The product occurring in Eq. (A5) can be thus expressed in terms of hyperbolic functions,

$$\Lambda\equiv\prod_{l=1}^{N-1}[i(\lambda_\alpha'^{(m)}-\lambda_\beta'^{(l)})]^{-1}$$
$$=(2C_3)^{N-1}\frac{\sinh\gamma}{\sinh(N\gamma)}, \quad \text{(A9)}$$

where the real quantity γ can be calculated from equation

$$\sinh\left(\frac{\gamma}{2}\right)=\left(-\frac{C_3}{C}\right)^{1/2}\sin\left(\frac{m\pi}{2N}\right),$$

or, after transcription in terms of goniometric functions,

$$\Lambda=2^NC_3^{N-1}y_m(1+y_m^2)^{1/2}v_m^{-2N}(1-v_m^{-4N})^{-1}, \quad \text{(A10)}$$

where y_m and v_m are defined in the same way as in Eq. (11). Finally, the substitution of products (A7) and (A10) into the relation for the contour integrals (A5) and their summation as indicated in (A3) yields the distribution function $P(Q)$ given by Eq. (11).

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[1] M. Fixman, J. Chem. Phys. **36**, 306 (1962).
[2] W. C. Forsman and R. E. Hughes, J. Chem. Phys. **38**, 2118 (1963).
[3] W. C. Forsman, J. Chem. Phys. **42**, 2829 (1965).
[4] W. C. Forsman, J. Chem. Phys. **44**, 1716 (1966).
[5] R. F. Hoffman and W. C. Forsman, J. Chem. Phys. **50**, 2316 (1969).
[6] S. R. Coriell and J. L. Jackson, J. Math. Phys. **8**, 1276 (1967).
[7] W. Kuhn, Kolloid Z. **68**, 2 (1934).
[8] K. Šolc and W. H. Stockmayer, J. Chem. Phys. **54**, 2756 (1971).

[9] The term "radius of gyration" is not related to any particular direction as defined in mechanics; it is here used rather in the sense commonly employed in chain statistics, $S^2=N^{-1}\Sigma r_m^2$, where r_m is the displacement of the mth bead from the center of mass of the coil.

[10] H. Cramér, *Mathematical Methods of Statistics* (Princeton U. P., Princeton, N.J., 1958), Chap. 11.
[11] Natl. Bur. Std. Appl. Math. Ser. **55**, (1968).

[12] The second term of Eq. (1) is equal to zero for the quantity q since the origin of ξ-coordinate system is identical to the center of mass of the cloud of beads.

[13] The slight difference between the values given in the preliminary report[8] and those in Table I is due to the different definition of the reduction: in the former case the figures were related to the number of bonds while here they refer more conveniently to the number of beads.

[14] R. A. Sack, Nature **171**, 310 (1953).
[15] H. Benoit and P. M. Doty, J. Phys. Chem. **57**, 958 (1953).