A recently obtained estimate of β is 1.722 ± 0.005,[4] leading to

$$\alpha \geq 0.722 \pm 0.005 \quad (6)$$

which is consistent with (5). Furthermore it is not unreasonable to expect the equality $\delta = \beta + \gamma$ to hold (this is equivalent to assuming the existence of scaling laws for self-avoiding walks). In this case we get independently α = 0.722 ± 0.005 in agreement with (5), the most probable value being α = 0.72. Incidentally let us notice a simple (and certainly too naîve) way for estimating α: assuming an n-mer to be equivalent to a hard sphere of radius $\sim\langle r^2\rangle_0^{1/2}$, we get by scaling

$$\beta = 3\gamma/2,\ \delta = 5\gamma/2,\ \alpha = (3/2)\gamma - 1$$

Exact enumerations of self-avoiding walks on various three-dimensional lattices indicate that γ = 1.2,[5] hence the result α = 0.8, slightly higher than (5).

In an earlier investigation Bluestone and Vold[6] computed $\langle r^2\rangle$ by a Monte-Carlo method for an n-mer on a simple cubic lattice on which another n-mer is already present, in the special case n = 101. From the dependence of $\langle r^2\rangle$ upon the distance separating the centers of mass of the two chains, they estimated that, at sufficiently low concentrations

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 \simeq 1 - 3\varphi + \ldots$$

in qualitative agreement with our own results. Several questionable assumptions are involved in establishing the coefficient of φ in this expression, so that it should not be taken too literally; our own estimate, according to (5), is

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 \simeq 1 - (1.2 \pm 0.2)\varphi$$

On the other hand a certain number of theoretical expressions have been proposed for $\langle r^2\rangle_\varphi/\langle r^2\rangle_0$ in the literature, a recent review of which is given by Yamakawa;[7] they all agree in predicting that this quantity decreases as φ increases; they cannot however be directly compared to our results because they strictly apply in the vicinity of the θ temperature. On the experimental side, it has been observed for polystyrene in cyclohexane that the mean radius of gyration decreases with increasing concentration;[8] a quantitative comparison with the model used here is precluded by the fact that it only takes repulsive effects into account.

Not much can be said about highly concentrated solutions. First of all our computer experiments become very lengthy because of the difficulty of generating new configurations by the pseudobrownian motion described earlier, when the n-mers get tightly packed. Care has to be taken that the system is not stuck in some metastable state; that this was not the case at the highest concentrations studied here has been checked by starting from a different type of initial configuration where all n-mers were partially stretched (instead of randomly coiled) and by verifying that the same value of $\langle r^2\rangle$ was ultimately reached. From Figure 2 it appears that the compression of the chain is maintained up to $\varphi \simeq 1$ for the cases n = 6 and 10, though it seems to slow down as φ increases. No serious conclusions can be drawn for n = 20 and 30 at the present time.

The tentative conclusion of this paper is that at relatively low concentrations one has for athermal polymer solutions

$$\langle r^2\rangle_\varphi/\langle r^2\rangle_0 \simeq 1 - An^{0.72}\varphi$$

with A depending on the specific structure of the system. Extensions of this work both to higher concentrations and to nonathermal mixtures are presently in progress.

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Statistical Mechanics of Random-Flight Chains. VI. Distribution of Principal Components of the Radius of Gyration for Two-Dimensional Rings[1,2]

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ABSTRACT: The distribution of principal components L_1^2,L_2^2 of the square radius S^2 for two-dimensional random-flight chains of any structure can be calculated in the form of a Bessel–Fourier series, provided the number of beads, N, is greater than 3. The ensemble of such chains is found to contain neither extremely asymmetrical (L_1^2 = 0, $L_2^2 = S^2$) nor perfectly symmetrical ($L_1^2 = L_2^2 = S^2/2$) chains but chains of only intermediate elliptical shapes. These general conclusions are complemented by a thorough study of cyclic chains. For Gaussian rings of three bonds (*i.e.*, three beads connected by three springs) the most probable shape is a rod, and the asymmetry distribution is independent of instantaneous extension described by S^2. On the other hand in longer cyclic chains, N > 3, the asymmetry distribution depends on the square radius S^2 of the chain, the more so the higher N is. Smaller tightly coiled chains have a higher chance of being more symmetrical than highly extended chains. The principal component moments for rings can be calculated in the form of fast converging series.

In a series of recent papers, it has been shown that the shape of random-flight chains on the average is quite asymmetrical[3,4] and that the proper consideration of the asymmetry improves the agreement between the smoothed-density model theory of the second virial coefficient and the experimental data.[5] Since the effect of shape is important for other properties as well,[6] it seems worthwhile to investigate the shape distributions of random-flight chains in more detail.

At present, the most detailed information on the shape distribution of random-flight chains comes from Monte Carlo studies on lattice chains. The partial results obtained so far by analytical methods, though valuable for checking the accuracy of Monte Carlo data, do not really yield any usable information on the shape distribution or its individual statistical moments. The Monte Carlo method gives us reasonable estimates of several statistical moments of the shape distribution and a rough idea about the overall distribution itself. However, unless extremely large ensembles of chains are generated, many intimate relations remain undisclosed, as for instance, the correlations between the shape and instantaneous size of the chains, the behavior of the shape distribution in the regions of both highly symmetrical and highly asymmetric shapes which are hard to generate by an unbiased random procedure, etc. It is obvious that such questions could be better and more fully answered by an analytical solution.

Since the extension of our present approach to three dimensions is not obvious at this time, we report in this paper on the analytical solution for two-dimensional chains, keeping in mind that some of the conclusions may apply to three dimensions as well. The direct analytical calculation of the shape distribution for random-flight chains seems to be extremely difficult. The shape of each chain for our purpose is characterized by two *principal* orthogonal components L_1^2 and L_2^2 of its radius of gyration S^2 which are obtained by decomposing S^2 along principal axes of inertia of the chain. Evidently, it would be easy to numerically compute L_k^2 for each particular chain with a given set of bead coordinates by finding the eigenvalues of its tensor of radius of gyration (in fact, this procedure is used in Monte Carlo studies[3-6]); however, it is difficult to adopt such a method for a general analytical treatment. Our method rather tries to filter this information from that contained in the distribution functions of *random* orthogonal components S_1^2 and S_2^2 of the radius of gyration taken along a fixed coordinate system. Such distribution functions can be evaluated by the Wang–Uhlenbeck method and have been the subject of investigation by many authors (for review, see ref 7). Physically they express the probability density of finding a chain with particular values of S_1^2 and S_2^2 in an ensemble of randomly oriented random-flight chains of different shapes and sizes. The distributions of principal and random components have to be closely related; one can easily visualize the latter one being created by summing up the contributions made to the fixed axes-based random components by randomly rotating chains conforming to some principal component distribution. In section I this approach is thoroughly investigated and a way of calculating the principal component distribution from a known random component distribution is proposed. In section II the general relations of section I (which are not necessarily restricted to random-flight chains) are applied to random-flight chains with Gaussian segment–length distribution, particularly to chains of cyclic structure which yield mathematically simple results. Finally, section III deals with the statistical moments of the principal component distribution. Although, in principle, these moments could be obtained as integrals over the principal component distributions known from section II, such procedure is not convenient because of the relatively slow convergence of resulting series. Therefore, alternate ways are investigated in section III.

I. Relation between the Distributions of Random and Principal Components of the Square Radius

Consider a two-dimensional particle consisting of N points of unit mass, with its center of mass located at the origin of a fixed orthogonal coordinate system x_1,x_2. The components S_k^2 obtained by decomposing the square radius S^2 of the particle along these coordinate axes will be called the random components of the square radius since the relative orientation of the particle with respect to such a coordinate system is arbitrary, *i.e.*, random. They can be easily calculated from the relation

$$S_k^2 = N^{-1}\sum_{m=1}^{N}(x_k^{(m)})^2 \qquad k = 1, 2 \tag{1}$$

where $x_k^{(m)}$ is the kth coordinate of the mth mass point referred to the fixed coordinate system x_1,x_2. It is evident, however, that the random components alone cannot disclose any information on the shape of the particle since they also depend upon the orientation between the particle and the coordinate system x_1,x_2. In order to get rid of the orientation effect and to isolate the shape alone, the coordinate system for decomposing S^2 has to be selected in a unique way, closely related to the instantaneous orientation of the particle. This can be done, for instance, by always identifying the coordinate system with the principal axes of inertia ξ_1,ξ_2 of the particle. The principal components L_k^2 of the square radius obtained in this way

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

are then independent of orientation and characterize both the shape and the size of the particle. In order to distinguish the two principal components it is required that $L_1^2 \le L_2^2$.

The coordinates of the mass points in these two coordinate systems are related by

$$\mathbf{x}^{(m)} = \mathbf{M}\xi^{(m)} \qquad m = 1, 2, \ldots, N \tag{3}$$

where $\mathbf{M}$ is the rotation matrix transforming one system into the other. This relation can be used to eliminate the coordinates of individual mass points and to express the random components of a particle with a specified orientation as functions of its principal components (*i.e.*, of its shape) and of its orientation α with respect to the fixed system x_1,x_2

$$S_1^2 = L_1^2\cos^2\alpha + L_2^2\sin^2\alpha$$
$$S_2^2 = L_1^2\sin^2\alpha + L_2^2\cos^2\alpha \tag{4}$$

It is immediately obvious, however, that the calculation of principal components L_k^2 from the given set of $\mathbf{x}^{(m)}$ coordinates will be more complex than the calculation of random components S_k^2; in order to apply eq 2 or 4 for this purpose, one has first to determine the principal axes of inertia ξ_1,ξ_2 of the particle, or their orientation α with respect to the fixed system x_1,x_2. It is also apparent from eq 4 that the randomization of orientation alone, of a particle of a fixed shape L_1^2,L_2^2, will generate a whole spectrum of S_1^2,S_2^2 values ranging from L_1^2 to L_2^2.

There is a great deal of information available in the literature on distribution functions of the square radius S^2 and of its random components S_k^2 for ensembles of randomly oriented random-flight chains of different structures (for review, see ref 7), and a question arises how this information could be utilized to obtain the distribution functions of principal components L_k^2 of the square radius. It is not difficult to formulate the normalized distribution function of random components $P(S_1^2,S_2^2)$ for an ensemble of randomly oriented particles of various sizes and shapes, conforming to some yet unknown principal component distribution $W(L_1^2,L_2^2)$. Since a particle of any size, shape, and orientation may contribute to $P(S_1^2,S_2^2)$, provided that eq 4 are satisfied, this distribution is given by the triple integral

$$P(S_1^2, S_2^2) = \frac{2}{\pi}\int_0^\infty dL_2^2 \int_0^{L_2^2} dL_1^2 W(L_1^2, L_2^2) \times \int_0^{\pi/2} d\alpha\,\delta(S_1^2 - L_1^2\cos^2\alpha - L_2^2\sin^2\alpha) \times \delta(S_2^2 - L_1^2\sin^2\alpha - L_2^2\cos^2\alpha) \quad (5)$$

where the normalized principal component distribution $W(L_1^2,L_2^2)$ appears as a statistical weight, and the product of two Dirac delta functions $\delta(x)$ assures that the conditions spelled out in eq 4 are met. As mentioned above, however, we need the inverse relation, *i.e.*, we wish to solve the integral eq 5 for $W(L_1^2,L_2^2)$.

Upon introducing the integral representation of two δ-functions and applying the inversion theorem for Fourier transforms, the following relation is obtained from eq 5

$$\int_0^\infty dL_2^2 \int_0^{L_2^2} dL_1^2 W(L_1^2, L_2^2) \int_0^\pi d(2\alpha) \exp\{\tfrac{1}{2} i[(L_2^2 - L_1^2)(\kappa - \lambda)\cos(2\alpha) - (L_2^2 + L_1^2)(\kappa + \lambda)]\} = \pi \int_0^\infty \int_0^\infty dS_1^2 dS_2^2 P(S_1^2, S_2^2) \exp[-i(\kappa S_1^2 + \lambda S_2^2)] \quad (6)$$

where κ and λ are the integration variables of the originally introduced δ functions. The lower integration limits in the right-hand side of (6) are written as zeros instead of $-\infty$ since by definition the distribution function $P(S_1^2,S_2^2)$ is zero for $S_1^2 < 0$ and/or $S_2^2 < 0$. Equation 6 can now be simplified by integrating over α and switching to a new set of variables and parameters, using the substitutions[8]

$$S^2 = L_1^2 + L_2^2 = S_1^2 + S_2^2$$
$$\Delta_L^2 = L_2^2 - L_1^2 \qquad \Delta_S^2 = S_2^2 - S_1^2 \quad (7)$$
$$2\mu = \kappa + \lambda \qquad 2\nu = \kappa - \lambda$$

we obtain

$$\int_0^\infty dS^2 \int_0^{S^2} d\Delta_L^2 W^*(S^2, \Delta_L^2) \exp(-i\mu S^2) J_0(\nu\Delta_L^2) = \int_0^\infty dS^2 \int_{-S^2}^{S^2} d\Delta_S^2 P^*(S^2, \Delta_S^2) \exp[i(\nu\Delta_S^2 - \mu S^2)] \quad (8)$$

where $J_0(x)$ is the zeroth order Bessel function of the first kind. Since the Jacobian of the transformation is not unity, the following identities apply between the normalized distributions of eq 6 and 8

$$2W^*(S^2, \Delta_L^2) \equiv W(L_1^2, L_2^2)$$
$$2P^*(S^2, \Delta_S^2) \equiv P(S_1^2, S_2^2) \quad (9)$$

The parameter μ can now be eliminated from (8) by arguing that the equality of Fourier transforms of two functions of S^2 necessarily implies the equality of the original functions as well, with the simple result

$$\int_0^{S^2} d\Delta_L^2 W^*(S^2, \Delta_L^2) J_0(\nu\Delta_L^2) = 2\int_0^{S^2} d\Delta_S^2 P^*(S^2, \Delta_S^2)\cos(\nu\Delta_S^2) \quad (10)$$

The assumption of $P^*(S^2,\Delta_S^2)$ being an even function of Δ_S^2, used in eq 10, follows from both physical and mathematical reasons. Equation 10 defines the close relation between the two types of distribution in a much simpler way than eq 5 did.

There are three distinct cases for which we would like to discuss the consequences following from the integral eq 10.

(i) If the ensemble contains only bodies of identical size and shape characterized by parameters S_0^2 and $\Delta_{L,0}^2$, *i.e.*, if the principal component distribution is represented by the product of two δ functions, $W^*(S^2,\Delta_L^2) \equiv \delta(S^2 - S_0^2)\delta(\Delta_L^2 - \Delta_{L,0}^2)$, then the corresponding random component distribution is due to only random orientation, and it is necessarily of the following discontinuous form

$$P^*(S^2, \Delta_S^2) = (\pi\Delta_{L,0}^2)^{-1}[1 - (\Delta_S^2/\Delta_{L,0}^2)^2]^{-1/2}\delta(S^2 - S_0^2) \quad \text{if } |\Delta_S^2| < \Delta_{L,0}^2$$
$$= 0 \quad \text{otherwise} \quad (11)$$

Therefore any random component distribution other than that obviously implies that the corresponding ensemble is heterogeneous as regards the size and/or shape of its bodies.

(ii) In the very special yet physically significant case (as shown later) that the distribution $P^*(S^2,\Delta_S^2)$ does not depend on Δ_S^2 in the interval $-S^2 \le \Delta_S^2 \le S^2$, *i.e.*, $P^*(S^2,\Delta_S^2) \equiv \frac{1}{2}P(S^2)/S^2$, the principal component distribution has to satisfy the relation

$$\int_0^{S^2} d\Delta_L^2 W^*(S^2, \Delta_L^2) J_0(\nu\Delta_L^2) = \frac{\sin(\nu S^2)}{\nu S^2} P(S^2)$$

and can be identified as

$$W^*(S^2, \Delta_L^2) = \Delta_L^2[1 - (\Delta_L^2/S^2)^2]^{-1/2} S^{-4} P(S^2) \quad \text{if } 0 \le \Delta_L^2 < S^2$$
$$= 0 \quad \text{otherwise} \quad (12)$$

where $P(S^2)$ is the normalized distribution function of the two-dimensional square radius S^2. As follows from eq 12, such ensemble does not contain any symmetrical bodies ($\Delta_L^2 = 0$); on the other hand, the most probable shape found is a rod ($\Delta_L^2 = S^2$).

(iii) The form of the left-hand side of eq 10 suggests that in some cases this integral equation for $W^*(S^2,\Delta_L^2)$ could be solved by expanding the sought distribution function into a Bessel–Fourier series

$$W^*(S^2, \Delta_L^2) = \frac{\Delta_L^2}{S^2}\sum_{m=1}^{\infty} c_m(S^2)\frac{J_0(\beta_m\Delta_L^2/S^2)}{J_1^2(\beta_m)} \quad (13)$$

where β_m is the mth zero of the Bessel function of the zeroth order, $J_0(\beta_m) = 0$. The unknown functions $c_m(S^2)$ of the square radius of gyration can be identified from eq 10 and 13 by the standard procedure utilizing the orthogonal properties of Bessel functions[9]

$$c_m(S^2) = 4S^{-2}\int_0^{S^2} d\Delta_S^2 P^*(S^2, \Delta_S^2)\cos(\beta_m\Delta_S^2/S^2) \quad (14)$$

Two characteristic features of the distribution in (13) are immediately evident, provided that the Fourier–Bessel series in (13) converges, (a) $W^*(S^2,\Delta_L^2) = 0$ for $\Delta_L^2 = S^2$ since β_m are the roots of $J_0(x)$, and (b) $W^*(S^2,\Delta_L^2) = 0$ for $\Delta_L^2 = 0$. Physically this means than an ensemble yielding a converging series in (13) must contain neither perfectly symmetrical ($\Delta_L^2 = 0$, *i.e.*, $L_1^2 = L_2^2$) nor extremely asymmetric ($\Delta_L^2 = S^2$, *i.e.*, $L_1^2 = 0$, $L_2^2 = S^2$) bodies. Note that formally the functions $c_m(S^2)$ can be calculated from eq 14 for any ensemble with any principal component distribution $W^*(S^2,\Delta_L^2)$ since the integral of eq 14 is always finite; however, the attempt to substitute these functions into the series in (13) for ensembles not conforming to the two above conditions would result in a diverging series. Indeed, for instance the special case (ii) representing an ensemble which contains rods would lead to a diverging series $\Sigma\beta_m^{-1}J_1^{-2}(\beta_m)\sin\beta_m$ for $\Delta_L^2 = S^2$.

II. Principal Component Distribution for Random-Flight Chains

In analogy to three dimensions,[4a] the conformation probability distribution function for a two-dimensional random-flight chain with Gaussian segment-length distribution consisting of N beads can be written briefly as

$$P_{\mathrm{conf}}(\mathbf{y}_1, \mathbf{y}_2) = \mathrm{const}(\pi\sigma^2)^{-(N-1)}\exp[-(2/\sigma^2)(\mathbf{y}_1{}^T\mathbf{V}\mathbf{y}_1 + \mathbf{y}_2{}^T\mathbf{V}\mathbf{y}_2)] \quad (15)$$

In this formulation, the first bead of the chain rather than the center of mass is located at the origin of the fixed coordinate system x_1,x_2 so that only $N - 1$ remaining beads are free to move. The mean square bond length is denoted by σ^2, $\mathbf{y}_k$ is the $(N - 1)$-dimensional vector of the kth coordinates of beads, *e.g.*, $\mathbf{y}_1 \equiv x_1^{(2)}, x_1^{(3)}, \ldots, x_1^{(N)}$ where $x_1^{(m)}$ is the first coordinate of the mth bead, and the normalization constant is equal to unity for chains containing no rings, whereas const = N_c for chains containing a ring of N_c bonds. The $(N - 1)\times(N - 1)$ conformation matrix $\mathbf{V}$ contains the information about the structure of the chains; *e.g.*, for linear chains $V_{kl} = \delta_{kl} - \frac{1}{2}(\delta_{k,l+1} + \delta_{k,l-1} + \delta_{k,N}\delta_{l,N})$. The rules for constructing the matrix $\mathbf{V}$ for a particular type of chain are given elsewhere.[4a]

The distribution function $P^*(S^2, \Delta_S^2)$ required for eq 10 can now be obtained directly from eq 15 as a multiple integral over all bead coordinates

$$P^*(S^2, \Delta_S^2) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{d}\mathbf{y}_1\mathrm{d}\mathbf{y}_2 P_{\mathrm{conf}}(\mathbf{y}_1, \mathbf{y}_2)\delta[S^2 - N^{-1}(\mathbf{y}_2{}^T\mathbf{G}\mathbf{y}_2 + \mathbf{y}_1{}^T\mathbf{G}\mathbf{y}_1)]\,\delta[\Delta_S^2 - N^{-1}(\mathbf{y}_2{}^T\mathbf{G}\mathbf{y}_2 - \mathbf{y}_1{}^T\mathbf{G}\mathbf{y}_1)] \quad (16)$$

In eq 16, the random components S_k^2 of the square radius have been expressed in a quadratic form, *i.e.*, $S_k^2 = N^{-1}\mathbf{y}_k{}^T\mathbf{G}\mathbf{y}_k$, where for the matrix $\mathbf{G}$ we have $G_{mn} = \delta_{mn} - N^{-1}$.[4a] After introducing the integral representation for δ functions, the expression can be integrated over $\mathbf{y}_1,\mathbf{y}_2$ and compared to eq 8. This yields the integral equation for $W^*(S^2,\Delta_L^2)$ of random-flight chains, which is a special case of eq 10.

$$\int_0^{S^2} \mathrm{d}\Delta_L{}^2 W^*(S^2, \Delta_L{}^2)J_0(\nu\Delta_L{}^2) = \frac{\mathrm{const}}{\pi 2^N} \times \int_{-\infty}^{+\infty} \frac{\mathrm{d}\mu\,\exp(i\mu S^2)}{|\mathbf{V} + i(\mu' + \nu')\mathbf{G}|^{1/2}|\mathbf{V} + i(\mu' - \nu')\mathbf{G}|^{1/2}} \quad (17)$$

The primed quantities in (17) are reduced, *i.e.*, $\mu' = \mu\sigma^2/2N$, $\nu' = \nu\sigma^2/2N$. In this case, it is also preferable to introduce reduced size and shape parameters, *e.g.*, $S_{kr}^2 = S_k^2/(N\sigma^2)$, $L_{kr}^2 = L_k^2/(N\sigma^2)$, which remain finite even if $N \to \infty$. Using the same method as in section I, case iii, we can then write the reduced principal component distribution in the form of a Fourier–Bessel series

$$W_r^*(S_r^2, \Delta_{Lr}^2) = \frac{\Delta_{Lr}^2}{S_r^2}\sum_{m=1}^{\infty} c_m'(S_r^2)\frac{J_0(\beta_m\Delta_{Lr}^2/S_r^2)}{J_1^2(\beta_m)} \quad (18)$$

$$c_m'(S_r^2) = \frac{\mathrm{const}}{2^{N-2}\pi S_r^2} \times \int_{-\infty}^{+\infty} \frac{\mathrm{d}\mu\,\exp(2i\mu S_r^2)}{|\mathbf{V} + iN^{-2}(\mu + \beta_m')\mathbf{G}|^{1/2}|\mathbf{V} + iN^{-2}(\mu - \beta_m')\mathbf{G}|^{1/2}} \quad (18a)$$

where $\beta_m' = \beta_m/2S_r^2$.

Since each of the determinants of eq 18a can be represented as a polynomial of the order $N - 1$ in β_m, and $J_1^2(\beta_m)$ is proportional to β_m^{-1} for $m \gg 1$, it is evident that the series of eq 18 will converge whenever N is larger than three. Physically it means that the ensemble of two-dimensional random-flight chains of four or more beads of any structure does contain only chains of intermediate asymmetry, *i.e.*, of elliptical shapes, whereas the probability of the two extreme forms (*i.e.*, chains with a perfect symmetry and rod-like chains) is zero. Perhaps this result is not as surprising as it might seem at first sight; the requirements for a perfect symmetry or a rod are so strict that none of the longer chains with four or more beads can meet them.

The determinants needed for eq 18a are known for several different chain structures: for linear chains[3b,10,11] as well as for rings, stars, and combs.[4a,12] Unfortunately, in most cases one cannot avoid the numerical integration over μ. For instance, for linear chains and $N \to \infty$, the function $c_m'(S_r^2)$ is given by the integral

$$\lim_{N\to\infty} c_m'(S_r^2) = \frac{2}{\pi S_r^2}\int_{-\infty}^{\infty}\mathrm{d}\mu\,\exp(2i\mu S_r^2) \times \left\{\frac{[2i(\mu + \beta_m')]^{1/2}[2i(\mu - \beta_m')]^{1/2}}{\sinh[2i(\mu + \beta_m')]^{1/2}\sinh[2i(\mu - \beta_m')]^{1/2}}\right\}^{1/2} \quad (19)$$

Only for rings with an odd number of bonds N is an analytical solution of eq 18a feasible, and this case will be discussed in detail in the next paragraph.

Rings with Odd Number of Bonds. The simplest way to obtain the principal component distribution function for rings with $N > 3$ is to use the general formulas, eq 13 and 14, with the two-dimensional analog $P_r^*(S_r^2,\Delta_{Sr}^2)$ of the known distribution function for the reduced random components of the square radius of cyclic macromolecules[12]

$$P_r^*(S_r^2, \Delta_{Sr}^2) = \tfrac{1}{2}P(S_{1r}^2, S_{2r}^2) = \tfrac{1}{2}\Sigma_k\Sigma_l a_k a_l \times \exp[-(b_k S_{1r}^2 + b_l S_{2r}^2)] = \tfrac{1}{2}\Sigma_k\Sigma_l a_k a_l \times \exp[-(b_k + b_l)S_r^2/2]\cosh[(b_k - b_l)\Delta_{Sr}^2/2] \quad (20)$$

where $a_k = (-1)^{k+1}8N^2\sin^2\gamma_k\cos\gamma_k$, $b_k = 4N^2\sin^2\gamma_k$, $\gamma_k \equiv k\pi/N$, and the double sum over k and l runs from 1 to $N_1 \equiv (N - 1)/2$. This procedure yields the function $c_m'(S_r^2)$ of eq 18 in the form of a double sum

$$c_m'(S_r^2) = 2\sum_{k,l}\frac{a_k a_l}{S_r^4(b_k - b_l)^2 + 4\beta_m^2}[S_r^2(b_k - b_l)(e^{-b_l S_r^2} - e^{-b_k S_r^2})\cos\beta_m + 2\beta_m(e^{-b_l S_r^2} + e^{-b_k S_r^2})\sin\beta_m] \quad (21)$$

Because of the trigonometric identity $\Sigma_k a_k = 0$ which holds for N odd if $N > 3$, it is evident that the functions $c_m'(S_r^2)$ of eq 21 fast approach zero as soon as

$$\beta_m \gg \max[S_r^2(b_k - b_l)/2] \approx 2N^2S_r^2 \quad (22)$$

and hence it is legitimate to use the Fourier–Bessel expansion (eq 18); this merely confirms the previously reached general conclusion. Actually, for numerical purposes the sum over m in eq 18 can be broken off much earlier than eq 22 would suggest.

For higher N, however, the calculation of $c_m'(S_r^2)$ in the form of double sum (eq 21) is inconvenient; for instance, in order to get meaningful results for $N = 49$ and m up to 20, the double precision operation is required on the IBM-370 computer. The limiting form of eq 21 for $N \to \infty$ is not handy either since its convergence in k and l is very slow.

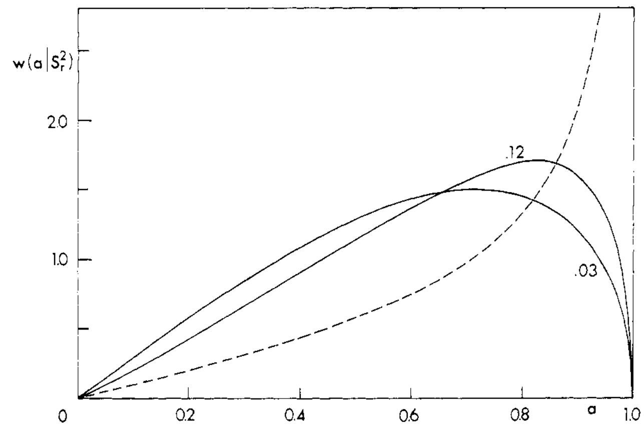

Figure 1. Asymmetry distribution $w(a|S_r^2)$ for rings with $N = 3$ (dotted line) and $N = 5$ (full line). S_r^2 is displayed at each curve for $N = 5$.

For this reason we also calculated the functions $c_m'(S_r^2)$ for rings directly from eq 18a. As shown in Appendix I, this method yields $c_m'(S_r^2)$ in the form of a single fast converging sum which is much easier to apply than its equivalent eq 21

$$c_m'(S_r^2) = 2^{11/2} N^3 S_r^{-2} \sum_{k=1}^{N_1} (-1)^{k+1} A^{-1} C \sin^3\gamma_k \cos\gamma_k \times \exp(-4N^2 S_r^2 \sin^2\gamma_k) \quad (23)$$

where

$$C = \frac{\cos\beta_m[B_s(s+1)^{1/2} + B_c(s-1)^{1/2}] + \sin\beta_m[B_s(s-1)^{1/2} - B_c(s+1)^{1/2}]}{1 - 2A^{-2}\cos(2\Psi) + A^{-4}}$$

$$B_s = (1 + A^{-2})\sin\Psi \qquad B_c = (1 - A^{-2})\cos\Psi$$

$$A = \{c\cos^2\gamma_k + s\sin^2\gamma_k + \sin\gamma_k\cos\gamma_k[(c+1)^{1/2}(s-1)^{1/2} + (c-1)^{1/2}(s+1)^{1/2}]\}^{N/2}$$

$$\Psi = N\arctan\frac{(c-1)^{1/2}\cos\gamma_k + (s+1)^{1/2}\sin\gamma_k}{(c+1)^{1/2}\cos\gamma_k + (s-1)^{1/2}\sin\gamma_k}$$

$$c = [1 + \beta_m^2(2N^2S_r^2\cos^2\gamma_k)^{-2}]^{1/2}$$

$$s = [1 + \beta_m^2(2N^2S_r^2\sin^2\gamma_k)^{-2}]^{1/2}$$

In the limit for $N \to \infty$ we have then simply

$$\lim_{N\to\infty} c_m'(S_r^2) = 2^{11/2} S_r^{-2} \sum_{k=1}^{\infty} (-1)^{k+1} A^{-1} C (k\pi)^3 \times \exp(-4k^2\pi^2 S_r^2) \quad (24)$$

$$A = \exp\{k\pi[(s-1)/2]^{1/2}\}$$

$$\Psi = k\pi[(s+1)/2]^{1/2}$$

$$s = [1 + \beta_m^2(2k^2\pi^2S_r^2)^{-2}]^{1/2}$$

where C is identical with that of eq 23.

The random-flight ring chains of three bonds have to be treated differently since the Fourier–Bessel series, eq 18, does not converge in this case. It might have been observed from earlier results that the behavior of these short rings is distinctly different from that of longer rings.[12] They are the only type of chains for which the one-dimensional distribution function $P_1(S_1^2)$ of a random component S_1^2 is a monotonically decreasing function of S_1^2, *i.e.*, for which $P_1(S_1^2) > 0$ for $S_1^2 = 0$, necessarily implying the presence of chains deformed to rods. This qualitative conclusion can now be confirmed quantitatively. It is evident from (20) that for $N = 3$ the distribution $P^*(S^2, \Delta_S^2)$ is independent of Δ_S^2, hence the reduced principal component distribution is given by an analog of eq 12.

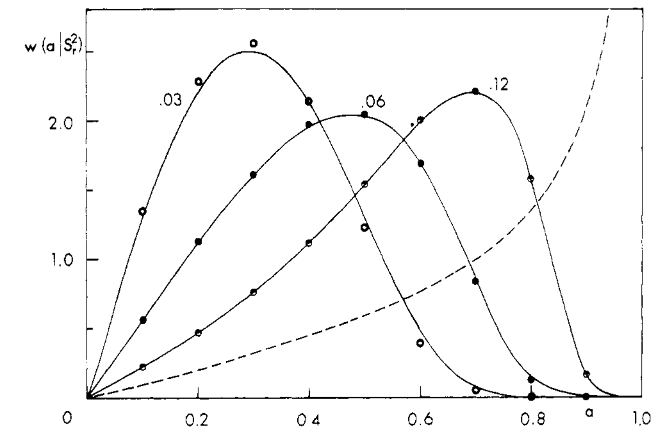

Figure 2. Asymmetry distribution $w(a|S_r^2)$ for rings with $N = 49$ (full line) and $N \to \infty$ (points). S_r^2 is indicated at each curve. Dotted curve gives again the distribution for $N = 3$.

$$W_r^*(S_r^2, \Delta_{Lr}^2) = 3^6[(S_r^2/\Delta_{Lr}^2)^2 - 1]^{-1/2}\exp(-27S_r^2)$$

$$W_r(L_{1r}^2, L_{2r}^2) = 3^6[(L_{2r}^2/L_{1r}^2)^{1/2} - (L_{1r}^2/L_{2r}^2)^{1/2}] \times \exp[-27(L_{1r}^2 + L_{2r}^2)] \quad (25)$$

The most probable shape of a three-membered random-flight ring chain appears to be a rod. This somewhat unexpected result has been brought on by the spring-like character of bonds as assumed in eq 15; a ring with undeformable bonds of constant length would necessarily form an equilateral triangle. The discrepancy between shapes of the two types of chains, so significant for $N = 3$, of course fades out with growing N.

A convenient way to illustrate the relation between the shape distribution and the size (expressed by S_r^2) of ring chains is to plot the asymmetry distribution $w(a|S_r^2)$ for several different reduced square radii S_r^2, where a is the asymmetry of the chain, $a = \Delta_L^2/S^2$, and its distribution is defined by

$$w(a|S_r^2) = S_r^2\frac{W_r^*(S_r^2, \Delta_{Lr}^2)}{P_r(S_r^2)} = a\frac{\Sigma c_m'(S_r^2) J_0(\beta_m a)/J_1^2(\beta_m)}{\Sigma c_m'(S_r^2)/[\beta_m J_1(\beta_m)]} \quad (26)$$

Such curves run always from zero to one, are normalized, and can be easily compared. It is apparent from Figure 1 that for short rings the asymmetry distribution does not vary much with the degree of expansion of the chain: for $N = 3$ (dotted line) $w(a|S_r^2)$ does not depend on S_r^2 at all, and also for $N = 5$ the distributions for $S_r^2 = 0.03$ and $S_r^2 = 0.12$ do not differ greatly. On the other hand, in the case of longer chains with $N = 49$ (Figure 2), the asymmetry distribution depends considerably on the square radius: for small tightly coiled chains the maximum of $w(a|S_r^2)$ is in the region of more symmetrical shapes, whereas highly extended chains tend to be strongly asymmetric. The points on Figure 2 correspond to an infinitely long ring chain, as described by eq 24. It appears that at high extensions, the asymmetry distribution of a chain with $N = 49$ is practically indistinguishable from the asymptotic distribution for $N \to \infty$. There is, however, a noticeable difference in distributions for tightly coiled chains. It can be concluded, therefore, that (i) the variation of the asymmetry distribution with the degree of extension is stronger for longer chains, and (ii) the variation of the asymmetry distribution with the chain-length N is stronger for tightly coiled chains.

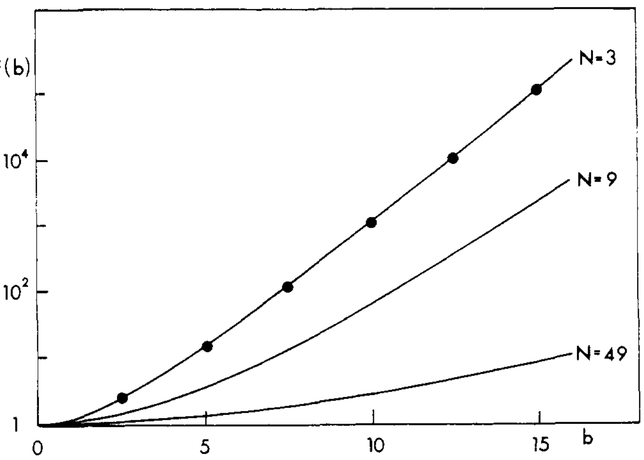

Figure 3. The right-hand side of the integral equation for the asymptotic asymmetry distribution $w(a|0)$ as a function of b. Curves correspond to the approximate eq 30; points correspond to the exact equation for $N = 3$.

In order to put these qualitative statements in more definite terms, we will examine the asymptotic asymmetry distributions for $S_r^2 \to \infty$ and $S_r^2 \to 0$. It is convenient to start with the integral equation for the asymmetry distribution $w(a|S_r^2)$ which is obtained from eq 17 and 26.

$$\int_0^1 w(a\,|\,S_r^2)\,J_0(\beta a)\,\mathrm{d}a = I(2N^2S_r^2, \beta/2N^2S_r^2)/I(2N^2S_r^2, 0) \quad (27)$$

The symbol $I(x,y)$ serves here as an abbreviation of the integral appearing in (18a), and it is defined and calculated in Appendix I, eq A1 and A9. The denominator of (27) represents the distribution $P_r(S_r^2)$ of the reduced square radius of eq 26. It is evident from (A9) that for $S_r^2 \to \infty$ only the first term of the series over k will be important, and after taking its limit for $S_r^2 \to \infty$ we have the simple result

$$\int_0^1 \mathrm{d}a\,w(a\,|\,\infty)\,J_0(\beta a) = (\sin\beta)/\beta \quad (28)$$

with the solution [*cf.* eq 12]

$$w(a\,|\,\infty) = a(1 - a^2)^{-1/2} \quad (29)$$

The asymptotic asymmetry distribution $w(a|S_r^2)$ for $S_r^2 \to \infty$ is thus independent of N, the number of bonds in the ring, and it is identical with the asymmetry distribution for rings of three bonds of any square radius. Of course, the same conclusion could have been drawn directly from eq 20 since, regardless of N, for $S_r^2 \to \infty$ the distribution function $P^*(S_r^2, \Delta_{Sr}^2)$ becomes independent of Δ_{Sr}^2. As follows from eq 29 and Figures 1 and 2, $w(a|\infty)$ approaches infinity for $a \to 1$. Physically this means that the most probable shape of an extremely expanded chain is a rod, although it is not the only form present; virtually all possible shapes are represented though to a much lesser extent. The absolute number of such rod-like chains in an ensemble of random-flight chains of $N > 3$, however, approaches zero since the probability of finding an infinitely expanded chain is zero.

The approximate integral equation for the asymptotic asymmetry distribution for $S_r^2 \to 0$ can be obtained by the method of steepest descent (see Appendix II)

$$\int_0^1 \mathrm{d}a\,w(a\,|\,0)I_0(ab) \approx 2^{(N/2)-1}\frac{\exp[(B - 1)(N - 1)/2]}{B^{1/2}(1 + B)^{(N/2)-1}} \equiv F(b) \quad (30)$$

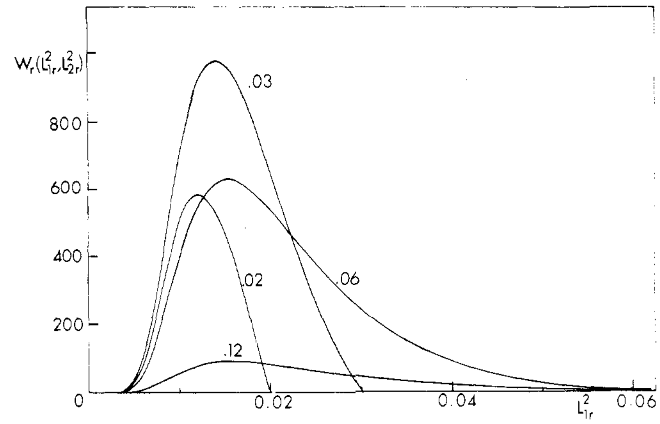

Figure 4. Reduced principal component distributions for rings with $N = 49$ for several different L_{2r}^2 (as indicated at each curve).

where $B = [1 + 4b^2/(N - 1)^2]^{1/2}$, $I_0(x)$ is the modified Bessel function, $I_0(x) = J_0(ix)$, and b is a real parameter. Although we have not been able to find the solution to this integral equation, some conclusions can be drawn directly from eq 30.

(i) In our case the method of steepest descent gives only an approximate solution. The quality of this approximation can be assessed by comparing the right-hand side of eq 30 for $N = 3$ with the expression $b^{-1}\sinh(b)$ which corresponds to the exact asymmetry distribution for $N = 3$, $w(a|S_r^2) = a(1 - a^2)^{-1/2}$ [*cf.* eq 25 and 29]. Curves in Figure 3 represent the right-hand side of the integral eq 30 plotted for several different values of N, and it may be noted with satisfaction that on this scale the curve for $N = 3$ is indistinguishable from the simple function $b^{-1}\sinh(b)$ represented by points. The approximation is not good enough, however, to yield identical moments. For instance, the approximate second moment of the asymmetry distribution function, obtained from (30), is $\langle a^2\rangle = 2(N - 2)(N - 1)^{-2}$ which for $N = 3$ gives $\langle a^2\rangle_{N=3} = \frac{1}{2}$. On the other hand, from the exact formula for $N = 3$, eq 29, we have $\langle a^2\rangle_{N=3} = \frac{2}{3}$.

(ii) Integral eq 30 and Figure 3 show that unlike in the case of the asymptote for $S_r^2 \to \infty$, the asymptotic asymmetry distribution for $S_r^2 \to 0$ depends on the number of bonds N in the ring chain. With increasing N, the maximum of the asymmetry distribution function shifts to smaller values of a, *i.e.*, the most probable shape is getting more symmetrical. It is apparent that in the limit for $N \to \infty$, the right-hand side of eq 30 becomes independent of the parameter b indicating that the asymmetry distribution takes the form of a δ function

$$\lim_{\substack{S_r^2 \to 0 \\ N \to \infty}} w^*(a) = \delta(a)$$

It is only in this double limit that the chains would become perfectly symmetrical; their amount, however, again approaches zero. The same conclusion is indicated by the aforementioned approximate formula for the second moment $\langle a^2\rangle$.

The shape distributions can also be expressed in terms of the principal components L_1^2 and L_2^2 by means of eq 9 and 18. Figure 4 shows $W_r(L_{1r}^2, L_{2r}^2)$ for $N = 49$ plotted as a function of L_{1r}^2 for several different L_{2r}^2. These curves are not normalized, and the area under each of them indicates the probability density of finding a chain with the corresponding L_{2r}^2 component. Two characteristic features of this distribution are worth noting. (i) Similar to $w(a|S_r^2)$, there is a significant difference in the behavior at the borders of the interval in which these distributions are defined. While in the symmetrical region (*i.e.*, for $L_{1r}^2 \to L_{2r}^2$), the distributions drop to zero almost linearly, they approach practically zero long before L_1^2 reaches its limit in the asymmetrical region of the interval. There are virtually no chains present with $L_{1r}^2 < 0.003$. (ii) The maxima of all distributions plotted in Figure 4 are located in the narrow interval $0.012 < L_{1r}^2 < 0.017$ although L_{2r}^2 varies from 0.02 to 0.12. A similar "almost independent" behavior of the three principal components was detected from Monte Carlo data on three-dimensional linear chains,[3b] and it led us to propose that for practical purposes the shape distribution might be approximated by a product of three functions, one for each principal direction.[5] In retrospect, however, such form ignores the fact demonstrated here for two dimensions, that the probability density of finding a perfectly symmetrical chain is zero.

III. Statistical Moments of the Principal Component Distribution

Since the moments of random component distribution are well known for random-flight chains of many different structures, the easiest way to obtain the moments of principal component distribution might be to find the relationship between the two kinds of moments. Unfortunately, a finite number of random component moments does not contain sufficient information for this purpose. For instance, we may try to start from eq 10 by expanding $J_0(\nu\Delta_L^2)$ and $\cos(\nu\Delta_S^2)$ and comparing the coefficients at each power of ν. This procedure, however, would yield only relations between even moments of Δ_L^2 and Δ_S^2 and, consequently, we would not be able to resolve the individual principal component moments, *e.g.*, $\langle L_1^2\rangle$ and $\langle L_2^2\rangle$. A similar situation has been observed in our previous papers[3,4a] although the results were obtained by a different method. It is the consequence of allowing unrestricted random orientation of chains in spacs which results in unresolvable symmetrical relations with respect to fixed coordinates x_1 and x_2.

The undesired symmetry can be simply removed by letting the particles rotate only in the interval $0 \le \alpha \le \pi/4$. With such restriction the upper integration limit for $d(2\alpha)$ in eq 6 is $\pi/2$, and the right-hand side integral is taken only over the region where $S_2^2 \ge S_1^2$, as follows from eq 4. With this modification, we get after transformation [using eq 7] the equivalent of eq 10

$$\int_0^{S^2} d\Delta_L^2 W^*(S^2,\Delta_L^2)\left\{J_0(\nu\Delta_L^2) + 2i/\pi\sum_{k=0}^{\infty}\frac{(-1)^k(\nu\Delta_L^2)^{2k+1}}{[(2k+1)!!]^2}\right\} = \int_0^{S^2} d\Delta_S^2 P_{\rm rst}^*(S^2,\Delta_S^2)\exp(i\nu\Delta_S^2) \quad (31)$$

where the distribution $P_{\rm rst}^*(S^2,\Delta_S^2)$ is normalized in the restricted region, *i.e.*

$$\begin{aligned} P_{\rm rst}^*(S^2,\Delta_S^2) &= 2P^*(S^2,\Delta_S^2) \quad \text{if } \Delta_S^2 > 0 \\ &= 0 \quad \text{if } \Delta_S^2 < 0 \end{aligned} \quad (32)$$

Equation 31 then yields the relation between the two types of moments which holds independently of whether n is even or odd.

$$\langle S^{2m}\Delta_L^{2n}\rangle = \{S^{2m}\Delta_S^{2n}\}2^n\Gamma^2(\tfrac{1}{2}n+1)/\Gamma(n+1) \quad (33)$$

Recalling now the definitions of newly substituted variables, eq 7, we can reintroduce the original physically significant principal component moments with the result

$$\langle L_1^{2u}L_2^{2v}\rangle = 2^{-(u+v)}\sum_{n=0}^{u+v}\{S_1^{2n}S_2^{2(u+v-n)}\}\sum_{j=0}^{u+v}2^j\frac{\Gamma^2(\tfrac{1}{2}j+1)}{\Gamma(j+1)}\times F(u,v,j)F(j,u+v-j,n) \quad (34)$$

where

$$F(i,j,k) \equiv \sum_m(-1)^m\binom{i}{m}\binom{j}{k-m}$$

For instance, for moments of the first and second order, we have

$$\begin{aligned}
\langle L_1^2\rangle &= (\{S_1^2\}+\{S_2^2\})/2 - \pi(\{S_2^2\}-\{S_1^2\})/4 \\
\langle L_2^2\rangle &= (\{S_1^2\}+\{S_2^2\})/2 + \pi(\{S_2^2\}-\{S_1^2\})/4 \\
\langle L_1^4\rangle &= 3(\{S_1^4\}+\{S_2^4\})/4 - \pi(\{S_2^4\}-\{S_1^4\})/4 - \{S_1^2S_2^2\}/2 \quad (35) \\
\langle L_2^4\rangle &= 3(\{S_1^4\}+\{S_2^4\})/4 + \pi(\{S_2^4\}-\{S_1^4\})/4 - \{S_1^2S_2^2\}/2 \\
\langle L_1^2L_2^2\rangle &= 3\{S_1^2S_2^2\}/2 - (\{S_1^4\}+\{S_2^4\})/4
\end{aligned}$$

It should be remembered, however, that the moments $\{S_1^{2u}S_2^{2v}\}$ appearing in eq 34 and 35 have been obtained by integration over a restricted interval $0 \le S_1^2 \le S_2^2$, and therefore, in general, they differ from unrestricted moments $\langle S_1^{2u}S_2^{2v}\rangle$ commonly occurring in the literature on random-flight chain statistics. (Only if $u = v$, we have $\langle S_1^{2u}S_2^{2v}\rangle \equiv \{S_1^{2u}S_2^{2v}\}$.) To avoid any possible misunderstanding, they will be referred to as the restricted moments of the random component distribution. It is also evident that there is no feasible way to calculate the restricted moments from only the unrestricted moments since the latter do not contain sufficient information. This is even more apparent from the moments in S^2,Δ_S^2 coordinates: while $\{S^{2m}\Delta_S^{2n}\} \equiv \langle S^{2m}\Delta_S^{2n}\rangle$ for n even, we have $\langle S^{2m}\Delta_S^{2n}\rangle$ identically equal to zero for n odd, *i.e.*, the unrestricted moments $\langle S^{2m}\Delta_S^{2n}\rangle$ do not provide any information on $\{S^{2m}\Delta_S^{2n}\}$ for n odd.

Having the general relations, eq 34 and 35, for principal component moments, we will now formulate the restricted random component moments for random-flight chains. It is convenient to define the normalized restricted random component distribution, $P_{\rm rst}(S_1^2,S_2^2)$, which is identically equal to zero for $S_2^2 < S_1^2$ [*cf.* eq 32]. Similar to eq 16, we have

$$P_{\rm rst}(S_1^2,S_2^2) = 2\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}{\rm d}\mathbf{y}_1{\rm d}\mathbf{y}_2P_{\rm conf}(\mathbf{y}_1,\mathbf{y}_2)\delta(S_1^2 - N_1^{-1}\mathbf{y}_1^T\mathbf{G}\mathbf{y}_1)\delta(S_2^2 - N^{-1}\mathbf{y}_2^T\mathbf{G}\mathbf{y}_2)H(\mathbf{y}_2^T\mathbf{G}\mathbf{y}_2 - \mathbf{y}_1^T\mathbf{G}\mathbf{y}_1) \quad (36)$$

where for the unit step function $H(x)$ we will use the integral representation

$$H(x) = \tfrac{1}{2}\left\{1 - (i/\pi)\int_0^{\infty}\frac{{\rm d}t}{t}[\exp(ixt) - \exp(-ixt)]\right\}$$

After integration over $\mathbf{y}_1,\mathbf{y}_2$ we get

$$P_{\rm rst}(S_1^2,S_2^2) = P(S_1^2,S_2^2) - \frac{i\text{const}}{2^{N+1}\pi^3}\iint_{-\infty}^{+\infty}{\rm d}\mu{\rm d}\nu\exp[i(\mu S_1^2+\nu S_2^2)]I_t(\mu',\nu') \quad (37)$$

where

$$I_t(\mu',\nu') = \int_{-\infty}^{+\infty}\frac{{\rm d}t}{t|\mathbf{V}+i(\mu'+t')\mathbf{G}|^{1/2}|\mathbf{V}+i(\nu'-t')\mathbf{G}|^{1/2}} \quad (37a)$$

$P(S_1^2,S_2^2)$ is the common unrestricted distribution of random components and the primed quantities are reduced as in eq 17. The reduced restricted moments $\{S_1^{2u}S_2^{2v}\}_r$ can now be expressed from (37) in terms of the reduced unrestricted moments $\langle S_1^{2u}S_2^{2v}\rangle_r$ and the derivatives of the two-dimensional characteristic function of the second term of eq 37.

$$\{S_1^{2u}S_2^{2v}\}_r = \langle S_1^{2u}S_2^{2v}\rangle_r - \frac{i\text{const}}{\pi 2^{N-1}(-2N^2)^{u+v}} \left.\frac{\partial^{u+v}I_t(\mu',\nu')}{\partial(i\mu')^u\partial(i\nu')^v}\right|_{\mu'=\nu'=0} \quad (38)$$

Equation 38 indicates that unlike the common unrestricted random component moments, the restricted random component moments (as well as the principal component moments) require evaluation of a complex integral which in most cases has to be performed numerically. Again, only for rings with an odd number of bonds is a simple analytical solution feasible. In this case, the integrand of (37a) has N simple poles: a pole at the origin, N_1 poles in the upper, and N_1 poles in the lower half-plane of the complex plane. The integral can be calculated from the residue theorem, using similar methods as in Appendix I

$$I_t(\mu',\nu') = 2^{N-1}\pi i\left\{N\frac{\sin(\tau/2)\sin(\omega/2)}{\sin(N\tau/2)\sin(N\omega/2)} + 8\sum_{k=1}^{N_1}(-1)^k\frac{\sin^2\gamma_k\cos\gamma_k\sinh(\phi_k)'}{[2\sin^2\gamma_k + i\mu']\sinh(N\phi_k)}\right\} \quad (39)$$

where $\cos\tau = 1 + i\mu'$, $\cos\omega = 1 + i\nu'$, $\sinh\phi_k = [\sin^2\gamma_k + \frac{1}{2}i(\mu'+\nu')]^{1/2}$. It is now only a matter of routine to take the derivatives of the integral I_t, eq 39, and substitute in (38). For instance, for the restricted random component moments of the first and second order we get after some simplification (see Appendix III)

$$\begin{aligned}24\{S_1^2\}_r &= 1 - N^{-2} - 12Z_1\\ 24\{S_2^2\}_r &= 1 - N^{-2} + 12Z_1\\ 5760\{S_1^4\}_r &= 12(1 - N^{-4}) - 720Z_2\\ 5760\{S_2^4\}_r &= (1 - N^{-2})(16 + 56N^{-2}) + 720Z_2\\ 576\{S_1^2S_2^2\}_r &= 576\langle S_1^2S_2^2\rangle_r = (1 - N^{-2})^2\end{aligned} \quad (40)$$

where

$$Z_1 = N^{-1}\sum_{k=1}^{N_1}(-1)^{k+1}\frac{\cos\gamma_k}{\sin\gamma_k\sinh(N\Phi_k)}$$

$$Z_2 = N^{-2}\sum_{k=1}^{N_1}(-1)^{k+1}\frac{\cos\gamma_k\cosh(N\Phi_k)}{\sin^2\gamma_k\cosh(\Phi_k)\sinh^2(N\Phi_k)}$$

$$2\phi_k = \text{arcsinh}(\sin\gamma_k)$$

In the limit for $N \to \infty$, Z_1 and Z_2 reduce to simple infinite series

$$Z_1 = \Sigma_k(-1)^{k+1}[k\pi\sinh(k\pi)]^{-1} \simeq 2.698 \times 10^{-2}$$

$$Z_2 = \Sigma_k(-1)^{k+1}\cosh(k\pi)[k\pi\sinh(k\pi)]^{-2} \simeq 8.713 \times 10^{-3}$$

Although for finite N, Z_1 and Z_2 can be written as rational numbers, we were not able to identify a general formula and they have to be evaluated as series. Fortunately, the convergence of these series is very fast.

The principal component moments are now calculated from eq 35 and 40.

$$\begin{aligned}24\langle L_1^2\rangle_r &= 1 - N^{-2} - 6\pi Z_1\\ 24\langle L_2^2\rangle_r &= 1 - N^{-2} + 6\pi Z_1\\ 5760\langle L_1^4\rangle_r &= 16 + 40N^{-2} - 56N^{-4} - \pi(1 + 10N^{-2} - 11N^{-4} + 360Z_2)\\ 5760\langle L_2^4\rangle_r &= 16 + 40N^{-2} - 56N^{-4} + \pi(1 + 10N^{-2} - 11N^{-4} + 360Z_2)\\ 720\langle L_1^2L_2^2\rangle_r &= 1 - 5N^{-2} + 4N^{-4}\end{aligned} \quad (41)$$

It may be noted that unlike the random component moments, the principal component moments of the type $\langle L_1^{2u}L_2^{2v}\rangle$, $u \neq v$, are given by irrational numbers. The ratio of the first to the second average principal component depends strongly on the number of bonds N; *e.g.*, with growing N, the ratio $\langle L_2^2\rangle/\langle L_1^2\rangle$ decreases from 8.32 for $N = 3$ to 3.07 for $N \to \infty$.

It is apparent from eq 13 that the principal component moments can also be calculated in the form of Fourier–Bessel series. Such procedure, however, does not seem particularly interesting in view of the complexity of resulting relations, as compared to those presented in this section.

IV. Conclusions

(1) A natural system of coordinates for expressing the shape distribution of random-flight chains appears to be the system S^2,Δ_L^2 rather than the original physically important system L_1^2,L_2^2.

(2) Random-flight chains of more than three bonds are never perfectly symmetrical ($L_1^2 = L_2^2$) or extremely asymmetric ($L_1^2 = 0$, $L_2^2 = S^2$) but rather assume an intermediate elliptical shape. Although $W^*(S^2,\Delta_L^2) = 0$ for both $\Delta_L^2 = 0$ and $\Delta_L^2 = S^2$, there is a very distinct difference in the way this function behaves in the neighborhood of these limits. In the symmetrical region (*i.e.*, for $\Delta_L^2 \to 0$), the distribution function $W^*(S^2,\Delta_L^2)$ decreases nearly linearly to zero over an appreciable interval of Δ_L^2. On the other hand, in the asymmetric region with Δ_L^2 decreasing from S^2, the function $W^*(S^2,\Delta_L^2)$ stays virtually at zero for a long time before it starts to increase into physically significant values (see Figure 2). A similar observation can be made in terms of the distribution function $W(L_1^2,L_2^2)$ (see Figure 4) which for small values of L_1^2 resembles very much the behavior of $P_1(S_1^2)$.

(3) The asymmetry distribution generally varies with the degree of expansion of the chain as characterized by its radius of gyration S^2. This variation is stronger for longer chains.

(4) Most of the statistical moments of the principal component distribution are given by irrational numbers. They cannot be calculated from the well-known unrestricted random component moments since the latter ones do not contain sufficient information.

(5) Independently of N, the most probable shape of an extremely expanded ($S_r^2 \to \infty$) ring chain is a rod. On the other hand, the most probable shape of an extremely shrunken ring chain ($S_r^2 \to 0$) is still an ellipse, the asymmetry of which decreases with growing length of the chain N. Only in the limit for $N \to \infty$ does it reach the perfect symmetry ($L_1^2 = L_2^2$).

(6) We feel that all of the conclusions formulated in this paragraph for two-dimensional chains can be generalized to three dimensions. It is important that any artificially constructed empirical form of the shape distribution complies with statement 2. The lack to do so is a misrepresentation of the shape distribution which may result in misleading conclusions. In retrospect, this may partly account for the disparity between the three-dimensional Flory–Fisk type[13] shape distribution and the Monte Carlo generated ensembles of chains in the calculation of the mean-square radius expansion factor.[5]

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Appendix I

We wish to evaluate the integral of the type

$$I(x,y) = \int_{-\infty}^{+\infty} \frac{\mathrm{d}z \exp(izx)}{|\mathbf{V} + i(z+y)\mathbf{G}|^{1/2}|\mathbf{V} + i(z-y)\mathbf{G}|^{1/2}} \quad \text{(A1)}$$

which appears in eq 18a and 27. For rings with an odd number of bonds N, the determinants are given by the relation[4a,12]

$$2^{N_1}N^{1/2}|\mathbf{V} + iu\mathbf{G}|^{1/2} = [U_{N_1}(1+iu) + U_{N_1-1}(1+iu)] = \frac{\sin(N\alpha/2)}{\sin(\alpha/2)} \quad \text{(A2)}$$

where $U_n(1+iu)$ are Chebyshev polynomials of the second kind, $\alpha = \arccos(1+iu)$ and $N_1 = (N-1)/2$, $N-1$ being the size of the determinant. From (A2) it is apparent that the square root of the determinant, $|\mathbf{V} + iu\mathbf{G}|^{1/2}$, has N_1 different zeros located at $\alpha_k = 2k\pi/N$, *i.e.*, $u_k = 2i\sin^2(k\pi/N)$, where $k = 1, 2, \ldots, N_1$, and that it can be decomposed into the product

$$|\mathbf{V} + iu\mathbf{G}|^{1/2} = N^{-1/2}\prod_{k=1}^{N_1}[i(u-u_k)] \quad \text{(A3)}$$

Therefore, the integrand of eq A1 has $N-1$ simple poles located in the upper half-plane

$$z_k^+ = -y + 2i\sin^2\gamma_k \qquad z_k^- = y + 2i\sin^2\gamma_k \qquad k = 1, 2, \ldots, N_1 \quad \text{(A4)}$$

where $\gamma_k \equiv k\pi/N$, and the integral can be calculated by closing the integration path by a counterclockwise semicircle of radius R, where $R \to \infty$, and applying the residue theorem

$$I(x,y) = 2\pi N\sum_{k=1}^{N_1}\{\exp(ixz_k^+)\prod_{l\neq k}[i(z_k^+ - z_l^+)]^{-1} \times \prod_m[i(z_k^+ - z_m^-)]^{-1} + \exp(ixz_k^-)\prod_{l\neq k}[i(z_k^- - z_l^-)]^{-1}\prod_m[i(z_k^- - z_m^+)]^{-1}\} \quad \text{(A5)}$$

where the subscripts l and m run from 1 to N_1.

The products needed for eq A5 can now be calculated from equations analogous to (A2) and (A3). For instance, the first of the incomplete products is calculated as the limit

$$\prod_{l\neq k}[i(z_k^+ - z_l^+)] = -2^{-N_1}i\lim_{z\to z_k^+}\frac{\sin(N\theta^+/2)}{(z - z_k^+)\sin(\theta^+/2)} = (-1)^{k+1}2^{-(N_1+2)}N(\sin^2\gamma_k\cos\gamma_k)^{-1} \quad \text{(A6)}$$

where $\theta^+ = \arccos[1 + i(z+y)]$, while the complete product is simply

$$\prod_m[i(z_k^- - z_m^+)] = 2^{-N_1}\frac{\sin(N\theta_k^+/2)}{\sin(\theta_k^+/2)} \quad \text{(A7)}$$

where $\theta_k^+ = \arccos[1 + i(z_k^- + y)] = \arccos[1 - 2\sin^2\gamma_k + 2iy]$. The expression $\sin(N\theta_k^+/2($ FOR EQ A7 can be obtained by using the Euler's formula and De Moivre's theorem by the following succession of steps

$$\cos\theta_k^+ = 1 - 2\sin^2\gamma_k + 2iy$$

$$\exp(i\theta_k^+/2) = (\cos^2\gamma_k + iy)^{1/2} + i(\sin^2\gamma_k - iy)^{1/2}$$

$$|\exp(i\theta_k^+/2)| = \{c\cos^2\gamma_k + s\sin^2\gamma_k + \sin\gamma_k\cos\gamma_k[(c+1)^{1/2}(s-1)^{1/2} + (c-1)^{1/2}(s+1)^{1/2}]\}^{1/2} \equiv A^{1/N}$$

$$\arg[\exp(i\theta_k^+/2)] = \arctan\left[\frac{(c-1)^{1/2}\cos\gamma_k + (s+1)^{1/2}\sin\gamma_k}{(c+1)^{1/2}\cos\gamma_k + (s-1)^{1/2}\sin\gamma_k}\right] \equiv \Psi/N$$

$$c = (1 + y^2\cos^{-4}\gamma_k)^{1/2} \qquad s = (1 + y^2\sin^{-4}\gamma_k)^{1/2}$$

$$\exp(iN\theta_k^+/2) = A\exp(i\Psi)$$

$$2\sin(N\theta_k^+/2) = (A + A^{-1})\sin\Psi - i(A - A^{-1})\cos\Psi \quad \text{(A8)}$$

Substitution of relations A6–A8 into eq A5 then yields the result

$$I(x,y) = 2^N 2^{7/2}\pi\sum_{k=1}^{N_1}(-1)^{k+1}A^{-1}C\sin^3\gamma_k\cos\gamma_k \exp[-2x\sin^2\gamma_k]$$

where

$$C = \frac{\cos(xy)[B_s(s+1)^{1/2} + B_c(s-1)^{1/2}] + \sin(xy)[B_s(s-1)^{1/2} - B_c(s+1)^{1/2}]}{1 - 2A^{-2}\cos(2\Psi) + A^{-4}} \quad \text{(A9)}$$

$$B_s = (1 + A^{-2})\sin\Psi \qquad B_c = (1 - A^{-2})\cos\Psi$$

Appendix II

The method of steepest descent[14] has often been used in the chain statistics for evaluation of the distribution functions of the radius of gyration for small values of argument. It approximates the integral I in the complex plane by the expression

$$I = \int_{-\infty}^{\infty}\exp[f(u)]\mathrm{d}u \approx [-2\pi/f''(u_0)]^{1/2}\exp[f(u_0)] \quad \text{(A10)}$$

where the coordinate u_0 of the saddle point is determined from the condition

$$f'(u_0) \equiv [\partial f(u)/\partial u]_{u=u_0} = 0 \quad \text{(A11)}$$

Since we are interested in the asymptotic behavior of the integral $I(x,y)$ of eq A1 for $x \to 0$ and $y \to \infty$ [*cf.* eq 27], it is convenient to redefine here y as $y = \beta/x$, with β of eq 27, and write instead of (A1)

$$xI(x,\beta/x) = \int_{-\infty}^{+\infty}\frac{\exp(iu)\mathrm{d}u}{|\mathbf{V} + ix^{-1}(u+\beta)\mathbf{G}|^{1/2}|\mathbf{V} + ix^{-1}(u-\beta)\mathbf{G}|^{1/2}} = N2^{N-1}\int_{-\infty}^{\infty}\mathrm{d}u\exp(iu)\frac{\sinh(\omega^+/2)\sinh(\omega^-/2)}{\sinh(N\omega^+/2)\sinh(N\omega^-/2)} \quad \text{(A12)}$$

where $\cosh\omega^{\pm} = 1 + ix^{-1}(u \pm \beta)$. The function $f(u)$ of eq A10 is then

$$f(u) = \ln (N2^{N-1}) + iu + \ln \frac{\sinh (\omega^+/2) \sinh (\omega^-/2)}{\sinh (N\omega^+/2) \sinh (N\omega^-/2)} \quad \text{(A13)}$$

and its derivatives $f'(u)$ and $f''(u)$ are not difficult to obtain. Since we wish to investigate only the region for $x \to 0$, we may simplify the obtained relations by neglecting all terms of the order $O(x)$ and higher, which leads to simple results for saddle points u_0 and the second derivative $f''(u_0)$.

$$(u_0)_{1,2} = -\tfrac{1}{2}i(N-1)\{1 \pm [1 - 4\beta^2/(N-1)^2]^{1/2}\} \quad \text{(A14)}$$

$$f''(u_0) = (N-1)(u_0^2 + \beta^2)(u_0^2 - \beta^2)^{-2} \quad \text{(A15)}$$

We also note from eq A12 that for $x \to 0$, the $N - 1$ simple poles of the integrand degenerate into only two poles located at $u_{1,2} = \mp\beta$.

A closer examination of these results yields the following conclusions. If β is real, the two poles are always on the real axis. The position of the saddle points, however, depends upon the absolute value of β. For $\beta = 0$, the first saddle point is on the imaginary axis at $(u_0)_1 = -i(N-1)$ while the second saddle point (in this special case superimposed with the pole) is located at the origin. With $|\beta|$ increasing, two saddle points move along the imaginary axis and approach each other, until for $\beta = \pm(N-1)/2$ they meet at $(u_0)_{1,2} = -\tfrac{1}{2}i(N-1)/2$. As follows from eq A15, the second derivative $f''(u_0)$ is negative for the first and positive for the second saddle point, *i.e.*, the crossing of the saddle point in the direction of the real axes is possible only at $(u_0)_1$. However, the absolute values of $f''(u_0)$ decrease as the saddle points come closer, and for $\beta = \pm(N-1)/2$ we have $f''(u_0) = 0$. For $|\beta| > (N-1)/2$ the saddle points split again and move apart in the direction parallel to the real axes. It is obvious that in the neighborhood of $|\beta| = (N - 1)/2$ the method of the steepest descent must not be used since $f''(u_0)$ approaches zero. This is unfortunate since in order to solve the integral eq 27, the complex integral, eq A12, is needed as a function of β in the whole interval of absolute values $|\beta|$.

This failure can be avoided by requesting that β is imaginary, *i.e.*, $\beta = bi$, where b is real. It is apparent that in such case both the poles and the saddle points are always located on the imaginary axis

$$u_{1,2} = \mp bi \quad \text{(A16)}$$

$$(u_0)_{1,2} = -\tfrac{1}{2}i(N-1)\{1 \pm [1 + 4b^2/(N-1)^2]^{1/2}\} \quad \text{(A17)}$$

and the second derivative at both saddle points is negative

$$f''(u_0) = (N-1)(u_0^2 - b^2)(u_0^2 + b^2)^{-2} \quad \text{(A18)}$$

Since the second saddle point on the positive imaginary axis behaves pathologically for $b \to 0$ (it coincides with a pole), the only possibility is to deflect the integration path into the negative half-plane and to cross the first saddle point, eq A17. Then the approximation eq A10 with eq 27 yield the result given in eq 30.

Appendix III

The derivatives of the integral I_t, eq 39, needed for eq 38, can be simplified by employing some identities following from physically necessary conditions. For instance, from the condition $I_t(0,0) = 0$ we have

$$\sum_{k=1}^{N_1} (-1)^{k+1} \frac{\sin (k\pi/N) \cos (k\pi/N)}{\sinh (N\Phi_k)} = (4N)^{-1} \quad \text{(A19)}$$

where $\Phi_k = \text{arcsinh}\,[\sin (k\pi/N)]$. From the condition $\{S_1^2\} + \{S_2^2\} = \langle S^2 \rangle$ we get

$$\sum_{k=1}^{N_1} (-1)^{k+1} \frac{\cos (k\pi/N) \cosh (N\Phi_k)}{\cosh (\Phi_k) \sinh^2 (N\Phi_k)} = (1 - N^{-2})/12 \quad \text{(A20)}$$

while a similar condition for the moments of the fourth order yields

$$\sum_{k=1}^{N_1} (-1)^{k+1} \frac{\cos (k\pi/N)}{\sin^3 (k\pi/N) \sinh (N\Phi_k)} = (2N^3 + 20N - 22N^{-1})/720 \quad \text{(A21)}$$

References and Notes

(1) The authors dedicate this paper to Professor Walter H. Stockmayer of Dartmouth College, Hanover, N.H., on the occasion of his 60th birthday, in recognition of his important contributions to the field of physical chemistry of polymers as well as of his inspiration to other scientists.

(2) This paper was presented in part at the Symposium on Configurational Characteristics of Chain Molecules at the American Chemical Society Meeting in Detroit, May 1–4, 1973.

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(8) Note that Δ_S^2 and Δ_L^2 are not squares but rather differences of square quantities. The Δ_L^2 has to be nonnegative due to the restriction $L_2^2 \geq L_1^2$; on the other hand, Δ_S^2 may be negative if the full range of orientation angles α is allowed [*cf.* eq 4].

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