Distribution Function and Principal Components for a Polymer Chain with Excluded Volume

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ABSTRACT: The excluded-volume effect on the distribution function of the square radius of gyration, $P(S^2)$, and the principal components ($\lambda_1 \geq \lambda_2 \geq \lambda_3$) of a linear chain is investigated by using the ϵ-expansion method developed by Jasnow and Moore. For $P(S^2)$, the unperturbed distribution function is obtained, provided that S^2 is rescaled by the perturbed square radius of gyration, $\langle S^2 \rangle$; furthermore, a value of 0.162 for $\langle S^2 \rangle / \langle R^2 \rangle$ is obtained. The results for the principal components are improved: the undesirable divergence of λ_1 in the limit of large N which was reported in the previous work is removed. The improved λ_1:λ_2:λ_3 ratio is 11.3:2.47:1.00. In spite of the asphericity being smaller than that found in the Monte Carlo methods, it is found that the aspherical distribution is strengthened by the introduction of the excluded volume, as predicted by the Monte Carlo methods.

Equilibrium properties of a single polymer chain immersed in dilute solution are characterized by various quantities: the mean-square radius of gyration, the mean-square end-to-end distance, orthogonal principal components,[1] span,[2] distribution functions, etc. These quantities can be completely known when based on a random flight chain model, provided that self-interactions between units constituting a backbone chain are not considered. The existence of repulsive interactions in a real polymer chain, however, changes the laws which are held to be valid for the random flight chain. This problem, called "excluded volume", has attracted much interest in polymer physics in the past 30 years, and the history of its investigation is summarized in a textbook by Yamakawa.[3]

In particular, for the important quantities of end-to-end distance and its distribution function, Edwards has investigated their asymptotic behavior by the self-consistent-field method,[4] and the results are in close agreement with experimental predictions. The explicit form, however, of the distribution function of the square radius of gyration in the perturbed state has not yet been obtained, because a major difficulty in treating it lies in the fact that it is not Gaussian even in the unperturbed state, notwithstanding the fact that the end-to-end distribution function is Gaussian. We attacked this problem by using a first-order perturbation method within the usual two-parameter theory[5] and obtained the explicit expression for the distribution function of the square radius of gyration for a ring chain in two dimensions.[6]

The concept of "principal components" of a polymer chain, i.e., the components of the radius of gyration along the axes of inertia, is a very important one, as it describes the aspherical distribution of segments around the center of mass.[7] Recent development is due to Šolc and Stockmayer,[1] who showed, by Monte Carlo methods, that in the absence of the excluded-volume effect surprisingly high ratios of principal components are found:

$$\lambda_1:\lambda_2:\lambda_3 \simeq 12:2.7:1 \tag{1}$$

Doi and Nakajima[8] proposed a method for theoretically estimating the principal components by considering chain conformations in Fourier space and showed that it reproduces the ratios in eq 1 fairly well. It has been shown that the aspherical distribution of segments plays an important role in the theory of chain statistics, excluded volume, and nonequilibrium properties of polymer solutions.[9–13]

We[14,15] have considered the effect of excluded volume on the principal components themselves, based on the approximate model proposed by Doi and Makajima and on the phenomenological expansion parameter which appears in the boson operator formalism of polymer dynamics developed by Fixman.[16,17] There, it has been shown that the asphericity is further strengthened by the introduction of excluded volume, as predicted by Monte Carlo studies etc.[12,18,19] The asphericity has been, however, accompanied by the undesirable result that the longest component, λ_1, increases infinitely with the increase in excluded-volume parameter z while the other two components, λ_2 and λ_3, converge to finite values as z approaches infinity.

In order to solve these excluded-volume problems, the renormalization group (RG) approach, based upon scaling concepts,[20] has offered us a new clue.[21] As is well-known, many valuable results in polymer physics have been derived by this approach, and these are summarized in the monograph of de Gennes.[21] In the RG approach, the "critical" exponents play an especially important role.

Dynamical aspects of polymer chains in solution are described in terms of the exponent z (which is different from the excluded-volume parameter z and must not be confused with it), by which, for example, the characteristic times τ of the internal relaxation modes can be described, leading to a power law dependence on z as $\tau \sim N^{z\nu}$. Jasnow and Moore[23] have obtained z for a single polymer to the order of ϵ (=4 − d) for the bead-and-spring (Rouse–Zimm[24]) model in d-dimensional space by an approximation of the ϵ expansion in the RG method. Their result insists that the effective force constant, α_k, behaves as $\alpha_k^2 \simeq (k/N)^{2+\epsilon/8}$ up to the order of ϵ in the presence of excluded volume, where k (=1, 2, ..., N) specifies the mode number and N is the number of beads in the Rouse–Zimm model. The α_k are, of course, related not only to the internal relaxation of Rouse modes but also to the instantaneous, aspherical distribution of segments.

In this paper, we discuss two problems: the problem of the distribution function and the problem of the principal components of the ellipsoidal form of a chain. In these problems, the excluded volume is treated by the ϵ expansion of the RG method, where the method employed is similar to, but somewhat different from, that of Jasnow and Moore. In the first problem, our attention will be focused on obtaining the characteristic function of the distribution of the square radius of gyration, from which the shape of the distribution function and its nth moment can be obtained. In the second problem, which is closely related to that of the square radius of gyration, our aim is directed to an improvement of the result reported in the previous work.[14,15]

0024-9297/81/2214-1035$01.25/0

Perturbed State Vector near Four Dimensions

Let us start with the usual bead-and-spring model represented by the creation and annihilation operators, i.e., $\mathbf{b}^\dagger$ and $\mathbf{b}$, introduced by Fixman.[16,17] In this formalism the perturbed state vector $|\rho\rangle$ and the operator L^a acting on it

$$L^a = \sum_{k=1}^{N}\sum_{l=1}^{N}\mathbf{b}_k^\dagger\cdot\Lambda_{kl}\cdot[\mathbf{b}_l + (\mathbf{b}_l,V)_-] \tag{2}$$

satisfy the equation

$$L^a|\rho\rangle = 0 \tag{3}$$

with

$$\Lambda_{kl} \equiv 2kT\alpha_k\alpha_l\sum_{i=1}^{N}\sum_{j=1}^{N}Q_{ki}Q_{lj}[\beta^{-1}\delta_{ij} + \mathbf{T}(\mathbf{r}_{ij})] \tag{4}$$

where $(,)_-$ represents the commutation relation in the boson system and $\mathbf{T}$ is the Oseen tensor. Here, in the d-dimensional space, the creation and annihilation operators have d components:

$$\mathbf{b}_k^\dagger \equiv \sum_{i=1}^{d}\mathbf{b}_{ki}^\dagger\mathbf{e}_i \qquad \mathbf{b}_k \equiv \sum_{i=1}^{d}\mathbf{b}_{ki}\mathbf{e}_i \tag{5}$$

with $\mathbf{e}_i$ being a unit vector in the x, y, ..., $d-1$ and d directions. $\mathbf{b}_k$ and $\mathbf{b}_k^\dagger$ are related to $\mathbf{q}_k$ through the relation

$$\mathbf{q}_k = (1/\alpha_k)2^{-1/2}(\mathbf{b}_k + \mathbf{b}_k^\dagger) \tag{6}$$

where $\mathbf{q}_k$ are normal coordinates ($k = 1, 2, ..., N$). The $\mathbf{q}_k$ are used to obtain the real-space coordinates $\mathbf{r}_k$, representing bead conformations, as follows:

$$\mathbf{r}_i = \sum_{k=1}^{N}Q_{ik}\mathbf{q}_k \qquad \mathbf{q}_k = \sum_{l=1}^{N}Q_{kl}\mathbf{r}_l \tag{7}$$

where

$$Q_{ik} = 1/N^{1/2}(2-\delta_{k0})^{1/2}\cos(ik\pi/N) \tag{8}$$

Further, α_k in eq 4 is given by

$$\alpha_k^2 = 2db^{-2}\sin^2(k\pi/2N) \simeq (d/2b^2)(k\pi/N)^2 \tag{9}$$

where b is the averaged spring length and the second relation is caused by the large values of N. Of course, the "excited" state $|\rho\rangle$ deviates from the ground state $|0\rangle$ due to the perturbation V in eq 2, such as excluded-volume forces.

Now, following Jasnow and Moore,[23] we represent the interaction term, V, by using terms of the creation and annihilation operators in the d-dimensional space. Here, for simplicity, we assume that the interaction potential between beads is a δ function. Thus, V can be written as

$$V = \beta\sum_i\sum_j\delta(\mathbf{r}_{ij}) \equiv \beta\sum_i\sum_j\sum_{\mathbf{p}}e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{r}_j)} \tag{10}$$

By using eq 7, the exponential part in eq 10 becomes

$$e^{i\mathbf{p}\cdot(\mathbf{r}_i-\mathbf{r}_j)} = \exp[-(p^2/2)\sum_k f_k^2]\exp[i\mathbf{p}\cdot\sum_k f_k(\mathbf{b}_k + \mathbf{b}_k^\dagger)] \tag{11}$$

where we have used the relations

$$f_k = (1/\sqrt{2}\alpha_k)(Q_{ki} - Q_{kj}) \tag{12}$$

and

$$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j = \sum_k f_k(\mathbf{b}_k + \mathbf{b}_k^\dagger) \tag{13}$$

Thus, we have

$$\delta(\mathbf{r}_{ij}) = \beta K_d\int_0^\infty \mathrm{d}p\, p^{d-1}\exp(-c_{ij}p^2 - i\mathbf{p}\cdot\mathbf{r}_{ij}) \tag{14}$$

where we have used the notation

$$c_{ij} = (1/2)\sum_k f_k^2 \tag{15}$$

and the identity

$$\sum_{\mathbf{p}}... = K_d\int_0^\infty \mathrm{d}p\, p^{d-1}... \tag{16}$$

Expanding the right-hand side of eq 14 in powers of $\mathbf{r}_{ij}$ and retaining only the term $\mathbf{r}_{ij}^2$, we obtain

$$V = -(\beta K_d/2)\sum_{ij}\mathbf{r}_{ij}^2\int_0^\infty \mathrm{d}p\, p^{d+1}\exp(-c_{ij}p^2) \tag{17}$$

$$= -d(\beta K_d/8)\sum_k(\mathbf{b}_k + \mathbf{b}_k^\dagger)^2\alpha_k^2\sum_{ij}(c_{ij})^{-(d+2)/2}(Q_{ki} - Q_{kj})^2 \tag{18}$$

where the diagonal approximation has been used;[25] i.e.

$$f_kf_{k'}(\mathbf{b}_k + \mathbf{b}_k^\dagger)\cdot(\mathbf{b}_{k'} + \mathbf{b}_{k'}^\dagger) \simeq f_k^2(\mathbf{b}_k + \mathbf{b}_k^\dagger)^2 \tag{19}$$

Here we notice that, in the limit of large N, the following relation is available:

$$c_{ij} \simeq |i-j|b^2/2d \tag{20}$$

As discussed by Jasnow and Moore,[23] the summations over i and j in eq 17 are very sensitive to the space dimensionality d. When we examine the N and k dependences of the summations, we can find different behaviors, depending on whether $d < 4$ or $d > 4$. At the special dimensionality $d = 4$, the leading corrections are logarithmic ones, and thus, by using eq 9, we can easily obtain the following relations, valid for large values of N:

$$V = (1/2)\sum_k G_k(\mathbf{b}_k + \mathbf{b}_k^\dagger)\cdot(\mathbf{b}_k + \mathbf{b}_k^\dagger) \tag{21}$$

with[26]

$$G_k = 128K_4\beta b^{-4}\ln(k\pi/N) + ... \tag{22}$$

After calculating the commutation relation $(\mathbf{b}_k,V)_-$ and substituting the result into eq 2, we can obtain L^a of eq 2 in terms of $\mathbf{b}^\dagger$ and $\mathbf{b}$, and finally the solution of eq 3 can be given for the case of the special dimensionality $d = 4$ by

$$|\rho\rangle = \exp[-(1/2)\sum_k G_k(1 + G_k)^{-1}\mathbf{b}_k^\dagger\cdot\mathbf{b}_k^\dagger]|0\rangle \tag{23}$$

Detailed derivation of eq 23 and approximations contained there are fully discussed in Fixman's paper.[16,17]

Now, we consider how the coefficient of $\mathbf{b}_k^\dagger\cdot\mathbf{b}_k^\dagger$ in eq 23 can be determined. For this, we consider the case when the space dimensionality d is slightly smaller than 4, i.e., when $\epsilon = 4 - d > 0$. In any case, of course, it should be chosen so as to make observable quantities, such as the mean-square radius of gyration, have the correct power laws for small deviations from $d = 4$; i.e., the following relation should hold:

$$\langle S^2\rangle = b^2N^{2\nu} \simeq b^2N^{1+\epsilon/8} \tag{24}$$

to the order of ϵ. From this, the coefficient of $\ln(k\pi/N)$ in eq 22, i.e., $128K_4\beta b^{-4}$, must be taken to be equal to $\epsilon/8$ (see ref 26). Thus, we have

$$1 + G_k = (k\pi/N)^{\epsilon/8} \tag{25}$$

Finally, eq 23 can be written as

$$|\rho\rangle = \exp\{-(1/2)\sum_k[1 - (N/k\pi)^{1+\epsilon/8}]\mathbf{b}_k^\dagger\cdot\mathbf{b}_k^\dagger\}|0\rangle \tag{26}$$

This is our desired form which is valid for small values of ϵ.

Characteristic Function

The distribution function of the square radius of gyration for a linear chain in d-dimensional space is defined by

$$P(S^2) = \langle 0|\delta(S^2 - (1/N)\sum_k \mathbf{q}_k^2)|\rho\rangle \quad (27)$$

Here, we will define the characteristic function, $C(\mu)$, from

$$P(S^2) = (2\pi)^{-d}\int_{-\infty}^{+\infty} d\mu \exp(-i\mu S^2)C(\mu) \quad (28)$$

Then, $C(\mu)$ can be written with terms of the creation and annihilation operators as

$$C(\mu) = \prod_k \langle 0|\exp[-(i\mu/2N\alpha_k^2)(\mathbf{b}_k + \mathbf{b}_k^\dagger)\cdot(\mathbf{b}_k + \mathbf{b}_k^\dagger)]|\rho\rangle \quad (29)$$

We can easily evaluate the above matrix elements. By using eq 9, we have the following result valid for large values of N:

$$C(\mu) = \prod_k \left[1 - \frac{2b^2 i\mu}{dN}\left(\frac{N}{k\pi}\right)^{2+\epsilon/8}\right]^{-d/2} \quad (30)$$

State vector $|\rho\rangle$ has all of the information about the shape of the distribution function, $P(S^2)$, and its moments, $\langle S^{2n}\rangle$ (n is an integer). For example, the second moment, $\langle S^2\rangle$, can be given by the cumulant expansion as

$$\langle S^2\rangle \simeq N^{1+\epsilon/8}\sum_k (1/k\pi)^{2+\epsilon/8} \quad (31)$$

$$\simeq 0.1353N^{1.125} \quad \text{for } \epsilon = 1 \quad (32)$$

and the mean-square end-to-end distance, $\langle R^2\rangle$, can also be calculated as[16,17]

$$\langle R^2\rangle \simeq N^{1+\epsilon/8}\sum_k [1 - (-1)^k](1/k\pi)^{2+\epsilon/8} \quad (33)$$

$$\simeq 0.8346N^{1.125} \quad \text{for } \epsilon = 1 \quad (34)$$

Now the perturbed distribution function itself, $P(S^2)$, can be obtained from the Fourier transform of eq 30 in either the analytical or the numerical way, and since these problems have been discussed in pertinent literature,[27] we will not refer to them in this paper. We will, however, point out that, up to the order of ϵ, the perturbed distribution function $P(S^2)$ has the same form as the unperturbed distribution $P_0(S^2)$, which itself is a function of $S^2/\langle S^2\rangle_0$, provided that the rescaled variable $S^2/\langle S^2\rangle$ is used in $P(S^2)$ instead of the original variable, $S^2/\langle S^2\rangle_0$. Here, $\langle S^2\rangle_0$ represents the unperturbed mean-square radius of gyration and $\langle S^2\rangle$ is given by eq 31.

Principal Components λ_1, λ_2, and λ_3

The three principal components, λ_1, λ_2, and λ_3, are quantitative measures of the asphericity of the distribution of beads (segments), and they are also affected by excluded volume. All of the Monte Carlo experiments[18,19] as well as the theories developed by Gobush, Šolc, and Stockmayer[12] and by us[14,15] predict that the introduction of excluded-volume forces further strengthens the asymmetry of the distribution of beads. Our previous calculations, however, have contained the undesirable result of an anomalous increase of λ_1 (i.e., the longest component) with an increase in the excluded-volume parameter z.

In this section we will remove this deficiency by applying the preceding results. In order to do this, we will put $\epsilon = 1$, i.e., $d = 3$. Then, the principal components are given approximately by[8,14,15]

$$\lambda_1 = N^{-1}\langle 0|[\mathbf{q}_1\cdot\mathbf{q}_1 + \sum_{k=2}^{N}(\mathbf{q}_k\cdot\mathbf{q}_1)^2/|\mathbf{q}_1|^2]|\rho\rangle \quad (35)$$

$$\lambda_2 = N^{-1}\langle 0|\left\{[\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2 + \sum_{k=3}^{N}\frac{[\mathbf{q}_k\cdot\mathbf{q}_2 - \mathbf{q}_k\cdot\mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2}{|\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2|^2}\right\}|\rho\rangle \quad (36)$$

$$\lambda_3 = N^{-1}\langle 0|\sum_{k=3}^{N}[\mathbf{q}_k\cdot(\mathbf{q}_1 \times \mathbf{q}_2)^2/|\mathbf{q}_1 \times \mathbf{q}_2|^2]|\rho\rangle \quad (37)$$

By using the explicit expression for $|\rho\rangle$ as given by eq 23, we obtain the following relations after calculation of the matrix elements:

$$\lambda_1 = N^{-1}\left[\frac{3}{2\alpha_1^2(1 + G_1)} + \sum_{k=2}^{N}\frac{1}{2\alpha_k^2(1 + G_k)}\right] \quad (38)$$

$$\lambda_2 = N^{-1}\left[\frac{1}{\alpha_2^2(1 + G_2)} + \sum_{k=3}^{N}\frac{1}{2\alpha_k^2(1 + G_k)}\right] \quad (39)$$

$$\lambda_3 = N^{-1}\left[\sum_{k=3}^{N}\frac{1}{2\alpha_k^2(1 + G_k)}\right] \quad (40)$$

where $\alpha_k^2 = 3k^2\pi^2/2N^2b^2$ (see ref 14 and 15).

Having discussed in the preceding sections terms up to the order of ϵ, we can now state that the force constant in d-dimensional space changes from the unperturbed ones, α_k, to the effective ones, $\tilde{\alpha}_k$, as

$$\tilde{\alpha}_k^2 = \alpha_k^2(1 + G_k) \simeq (d/2b^2)(k\pi/N)^{2+\epsilon/8} \quad (41)$$

Thus, putting $\epsilon = 1$ (i.e., $d = 3$) in eq 41 and substituting eq 41 into eq 38–40, we can rewrite λ_i by using the renormalized force constant, $\tilde{\alpha}_k$, as

$$\lambda_1 = N^{-1}[3/2\tilde{\alpha}_1^2 + \sum_{k=2}^{N}1/2\tilde{\alpha}_k^2] \quad (42)$$

$$\lambda_2 = N^{-1}[1/\tilde{\alpha}_2^2 + \sum_{k=3}^{N}1/2\tilde{\alpha}_k^2] \quad (43)$$

$$\lambda_3 = N^{-1}\sum_{k=3}^{N}1/2\tilde{\alpha}_k^2 \quad (44)$$

After the summations over k, we obtain the following results, which are expected to hold for large values of N:

$$\lambda_1 \simeq 1.1805N^{1.125}b^2 \quad (45)$$

$$\lambda_2 \simeq 0.2569N^{1.125}b^2 \quad (46)$$

$$\lambda_3 \simeq 0.1041N^{1.125}b^2 \quad (47)$$

These results are correct to the order of ϵ. In the present treatment the anomalous behavior of λ_1 is eliminated. The improved ratios of the principal components in the perturbed state are

$$\lambda_1:\lambda_2:\lambda_3 = 11.3:2.47:1 \quad (48)$$

This result should be compared with that obtained for the unperturbed state:[8,14,15]

$$\lambda_1:\lambda_2:\lambda_3 = 9.22:2.27:1 \quad (49)$$

The comparison with the previously obtained results is tabulated in Table I. .

The asphericity in the present result is smaller than those from the Monte Carlo method and the theory, as

Table I
Ratios of the Three Principal Components

method/model[a]	N[b]	λ_1:λ_2:λ_3	ref
Monte Carlo/RW	50	11.8:2.70:1	1
Monte Carlo/RW	100	11.7:2.71:1	1
Monte Carlo/(five-choice walk) RW	200	12.1:2.72:1	1
Monte Carlo/RW	63	11.7:2.70:1	19
Monte Carlo/SAW	9	14.6:3.04:1	19
Monte Carlo/SAW	15	15.0:3.04:1	19
Monte Carlo/SAW	33	14.6:3.04:1	19
Monte Carlo/SAW	63	14.7:3.00:1	19
Monte Carlo/SAW	∞	14.8:3.06:1	18
smooth-density model			
Monte Carlo procedure: $z = 3.75$	∞	14.9:3.08:1	12
empirical distribution function: $z = 3$	∞	16.7:3.28:1	12
empirical distribution function: $z \to \infty$	∞	28.7:4.75:1	12
analytical RW	∞	9.22:2.27:1	8
previous work SAW	∞	∞:3.62:1	15
this work SAW	∞	11.3:2.47:1	

[a] RW = random walk; SAW = self-avoiding walk. [b] N = the number of steps (segments).

shown in Table I. This disagreement may be mainly attributed to the approximate nature of the present model.

Conclusion and Comment

In this paper, we have been concerned with the square radius of gyration, its distribution function, and the principal components which are closely related to the square radius of gyration, using the ϵ expansion of the renormalization group method within the order of ϵ. The results obtained are summarized as follows: (i) The characteristic function of the distribution of S^2 is given by eq 30, from which we find that the distribution function, $P(S^2)$, in the perturbed state has the same form as that in the unperturbed state, provided that S^2 is rescaled by the perturbed square radius of gyration, $\langle S^2 \rangle$, which is given by eq 31. (ii) $\langle S^2 \rangle / \langle R^2 \rangle$ in the perturbed state is 0.162, as compared to 0.167 for the perturbed state and to 0.155 obtained from Monte Carlo studies on lattice chains.[28] (iii) The values of the principal components in the perturbed state are given by eq 45–47, and λ_1:λ_2:λ_3 = 11.3:2.47:1, which is an improvement over the previous result.

Finally, we give a comment. We have recently performed a Monte Carlo simulation by a model which is different from the lattice chain model. There, a soft-core potential between segments is assumed. Then, the result for $\langle R^2 \rangle$ is slightly different from that of the lattice chain model, and it seems that it is rather similar to that of the first order of ϵ. This will be published elsewhere.[29]

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