Table IV
Parameters in Flory's Equation of State

Substance	v^*, cm^3/g	T^*, K	P^*, bar	$\sigma(v_{sp}) \times 10^4$,[a] cm^3/g
HMDS	0.9995	4468	3253	33
PDMS 3	0.8780	5070	3078	23
PDMS 10	0.8694	5288	3133	20
PDMS 20	0.8531	5395	3156	18
PDMS 100	0.8412	5470	3230	19
PDMS 350	0.8403	5554	3115	18
PDMS 1000	0.8403	5554	3115	18

[a] σ = standard deviation.

compressible liquids, HMDS and PDMS 3, within the experimental accuracy. Flory's equation of state represents well the PVT behavior of all liquids with characteristic parameters determined using all PVT data reported here. Equation-of-state parameters evaluated from volumetric data at 1 bar only differ significantly from those in Table IV and do not allow good representation of the data at high pressures. Although agreement between fitted and experimental PVT data is good, the deviations may be significant for polymer–solution thermodynamics since equation-of-state contributions may be important in calculating excess functions of polymer mixtures. We made no attempt to test other equations of state for polymer liquids.

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Supplementary Material Available: Experimental results for specific volume and relative volume at 25, 40, 55, and 70 °C at pressures to 900 bars for all seven dimethylsiloxanes in this work (8 pages). Ordering information can be found on any current masthead page.

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Excluded Volume Effect on the Principal Components of Polymer Chains. 1

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ABSTRACT: The excluded volume effect on the principal components is discussed by a perturbation method with the aid of a method of second quantization introduced by Fixman. The perturbation series of the excluded volume parameter z for the square radius of gyration is decomposed, up to the term linear in z, into the three orthogonal components along the principal axis of inertia of a polymer chain. The ratio of coefficients of z is 1.91:1.33:1. This represents that the effect of excluded volume forces is very anisotropic; this effect has the tendency to strengthen further the asymmetrical distribution of segments in the unperturbed state.

It has been well known that the distribution of segments about the center of mass is not spherically symmetric but may be regarded as approximately ellipsoidal. The ratios of the principal orthogonal components of a ellipsoid are a quantitative measure of this asymmetrical distribution. Since the sum of three principal components equals the square radius of gyration S^2, the problem of determining the values of principal components equals that of decomposing the square radius of gyration S^2 into its three orthogonal components λ_i ($\lambda_1 \geq \lambda_2 \geq \lambda_3$) along the principal axis of inertia of the chain.

Many years ago Kuhn[1] drew attention to strong asymmetry of a random-flight chain following from consideration of average loci of several special segments in the chain relative to its end-to-end vector. A priori or a qualitative introduction of this asymmetrical distribution has played an important role in the theory of the excluded volume effect[2] and nonequilibrium properties of dilute polymer solutions such as viscosity and diffusion coefficient of flexible chains with and without the excluded volume effect.[3]

Recent works on the shape of a random-flight chain clearly reveal this asymmetry from quantitative points of view. In 1971 Šolc[4] showed, by the Monte Carlo method, that in the absence of the excluded volume effect, the intersegmental hydrodynamic interaction, and external perturbations (such as shear flow), a surprisingly high ratio of principal components is found to be

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

A little later Doi and Nakajima[5] proposed a method, as mentioned below, for a theoretical estimation of principal components, based on the spring bead model (Rouse model[6]), and showed that it reproduces fairly well the above high ratio.

It is expected, however, that owing to the presence of the

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excluded volume effect and shear flow with the hydrodynamic interaction, the values of principal components may alter from those for an ideal chain to the corresponding values for a perturbed chain. In particular, the problem of the excluded volume effect has been investigated by a perturbation method within the framework of the two-parameter theory.[7] For example, the end-to-end expansion parameter α_R and the gyration radius expansion parameter α_S may be expressed as a power series in the parameter of z up to third and second order, respectively, as follows:[7]

$$\alpha_R^2 = 1 + 1.333z - 2.075z^2 + 6.459z^3 - \ldots \quad (2)$$

$$\alpha_S^2 = 1 + 1.276z - 2.082z^2 + \ldots \quad (3)$$

where z is the usual excluded volume parameter.

Therefore, there arises a new, interesting problem of decomposition of the coefficients of z^n (n is integer) in eq 3 into the three orthogonal components. That is, each of three principal components may also be expanded in a power series of z as

$$\lambda_i = \lambda_i^0 + \lambda_i^1 z - \lambda_i^2 z^2 + \ldots \qquad (i = 1, 2, 3) \quad (4)$$

where subscript 0 refers to the unperturbed chain. In eq 4 the ratios of magnitude of coefficients λ_i^n in each order represent the anisotropy of appearance of excluded volume forces for an unperturbed chain.

On the other hand, Fixman[8,9] developed a method of second quantization for the discussion of polymer dynamics, based on the fact that the Rouse model is a coupled oscillator system. Since a coupled oscillator system is, as is well known in statistical physics, the collection of harmonic oscillators, it can be described systematically in terms of creation and annihilation operators.

It is the purpose of the present paper to study the effect of excluded volume forces on principal components of the ellipsoid formed by a chain with a special attention payed for obtaining the values of coefficients of the linear term of z in eq 4, combining Doi and Nakajima's approximate scheme and the method of second quantization. First, a method of operator representation satisfying boson commutation rules is described following Fixman's theory. Second, Doi and Nakajima's idea for principal components is given. Third, using the method of second quantization, first-order correction terms in eq 4 are calculated in practice. Finally, a few comments on the result obtained are presented.

Boson Representation

In this section we describe in brief a method of operator representation satisfying the boson commutation relation which was introduced by Fixman.[8,9] The introduction of this technique makes not only explicit consideration of the excluded volume but also of shear flow with intersegmental hydrodynamic interactions. The time-dependent distribution function $\psi(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N;t)$ satisfies the quation[10,11]

$$(\partial\psi/\partial t) + L\psi = 0 \quad (5)$$

where

$$L\psi = \nabla^{tr}\{v^0\psi - D[kT\nabla\psi + \psi\nabla(U + W)]\} \quad (6)$$

Here, ∇ is a column matrix whose elements are the vector components of $\partial/\partial\mathbf{r}_i$, with $\mathbf{r}_i$ the position of the ith bead referred to a Cartesian coordinate system having its origin at the center of mass; ∇^{tr} is the transpose of ∇; v^0 is a column matrix whose elements are the velocity components of the unperturbed flow field, evaluated at the bead positions. The number of rows is three times the number of beads. U is the intersegmental potential energy; U is the sum of two potentials

$$U = S + E \quad (7)$$

where S is the potential of interaction between beads close together along the backbone and E is the excluded volume potential. W is an external potential. Finally, D is a square matrix whose elements are the dyadic components of

$$\mathbf{D}_{ij} = \beta^{-1}\delta_{ij} + \mathbf{T}(\mathbf{r}_{ij}) \quad (8)$$

$$\mathbf{T}(\mathbf{r}_{ij}) = (8\pi\eta_0 r_{ij})^{-1}(1 + \mathbf{r}_i\mathbf{r}_j/r_{ij}^2) \quad (9)$$

We first put $\psi = \psi^\alpha\rho$, where ψ^α forms a zeroth approximation to the equilibrium distribution function ψ and is related to an effective intersegmental potential S as

$$\psi^\alpha \propto \exp(-S^\alpha/kT) \quad (10)$$

where ψ^α is normalized to unity over the space of bead coordinates. The new ρ satisfies

$$\partial\rho/\partial t + \tilde{L}\rho = 0 \quad (11)$$

$$\tilde{L} = \tilde{L}^a + \tilde{L}^b \quad (12)$$

where

$$\tilde{L}^a = -kT[\nabla^{tr} - (\nabla^{tr}S^\alpha/kT)]D\{\nabla + [\nabla(U - S^\alpha + W)]\} \quad (13)$$

$$\tilde{L}^b = [\nabla^{tr} - (\nabla^{tr}S^\alpha/kT)]v^0 \quad (14)$$

The operators and functions in eq 13 and 14 have thus far been expressed in bead coordinates, $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N$, for each polymer molecule presented. In these coordinates ψ^α is chosen to be a modified Gaussian distribution and S^α is given by a spring potential as

$$S^\alpha = \frac{3kT}{2b^2}\sum_{i=1}^{N}(\mathbf{r}_i - \mathbf{r}_{i+1})^2 \quad (15)$$

The flexibility in the distribution is contained in the parameter b, or more specifically in an expansion factor α:

$$b = b_0\alpha \quad (16)$$

where α measures the expansion relative to a reference length b_0 and is used to obtain the closed expressions for various expansion factors such as α_R and α_S.[7,8,13]

Here, for large N the orthogonal transformation (Fourier cosine transformation) which diagonalizes S^α

$$\mathbf{r}_i = \sum_{k=0}^{N} Q_{ik}\mathbf{q}_k, \qquad \mathbf{q}_k = \sum_{i=1}^{N} Q_{ki}\mathbf{r}_i \quad (17)$$

$$Q_{ik} = N^{-1/2}(2 - \delta_{k,0})^{1/2}\cos(ik\pi/N) \quad (18)$$

is introduced, and it gives

$$S^\alpha = kT\sum_{l=1}^{N}\alpha_l^2|\mathbf{q}_l^2| \quad (19)$$

where

$$\alpha_l^2 = 6b^{-2}\sin^2(l\pi/2N) \quad (20)$$

In terms of these "normal" coordinates the operator $\tilde{L}^a$ assumes the form

$$\tilde{L}^a = -kT\sum_{l,k=1}^{N}\sum^{N}\left(\frac{\partial}{\partial\mathbf{q}_k} - 2\alpha_k^2\mathbf{q}_k\right)\cdot\mathbf{F}_{kl}\cdot\left(\frac{\partial}{\partial\mathbf{q}_l} + \frac{\partial V}{\partial\mathbf{q}_l}\right) \quad (21)$$

where

$$\mathbf{F}_{kl} \equiv \sum_{i=1}^{N}\sum_{j=1}^{N} Q_{ki}Q_{lj}\mathbf{D}_{ij}, \qquad V \equiv (kT)^{-1}(U - S^\alpha + W) \quad (22)$$

For the presentation of $\tilde{L}^b$, let simple shear flow be specified for which

$$\mathbf{v}_i^0 = \kappa\mathbf{e}_x\mathbf{e}_y\cdot\mathbf{r}_i \quad (23)$$

so that eq 14 becomes

$$\tilde{L}^b = \kappa \sum_{l=1}^{N} \left(\frac{\partial}{\partial \mathbf{q}_l} - 2\alpha_l{}^2\mathbf{q}_l\right) \cdot (\mathbf{e}_x \mathbf{e}_y) \cdot \mathbf{q}_l \qquad (24)$$

Equations 21 and 24 are the fundamental equations in terms of "normal" coordinates $\mathbf{q}_k$.

In essence second quantization is to regard "normal" coordinates $\mathbf{q}_k$ and their derivatives $\partial/\partial \mathbf{q}_k$ as operators acting on a orthonormal complete system.[12] For this purpose, we introduce the usual creation, annihilation operators, and orthonormal basis set in boson systems. Then the defining equation for the creation operator is

$$b_{li}|n\rangle = (n+1)^{1/2}|n\rangle, \qquad \langle m|b_{li}|n\rangle = (n+1)^{1/2}\delta_{m,n+1} \qquad (25)$$

Similarly, the annihilation operator is defined to have the property

$$b_{li}|n\rangle = n^{1/2}|n-1\rangle, \qquad \langle m|b_{li}|n\rangle = n^{1/2}\delta_{m,n-1} \qquad (26)$$

The ket and bra vectors satisfy

$$\langle n|m\rangle = \delta_{n,m} \qquad (27)$$

On the other hand, using the Hermite polynomial function with weight function ψ^α, the matrix element of $\partial/\partial q_{ki}$ is given by

$$\left(\frac{\partial}{\partial q_{ki}}\right)_{mn} = (2^m 2^n n! m!)^{-1/2} \frac{\alpha_1}{\pi^{1/2}} \int_{-\infty}^{+\infty} \mathrm{d}q_{ki} \exp(-\alpha_k{}^2 q_{ki}{}^2) \times H_m(\alpha_k q_{ki}) \frac{\partial}{\partial q_{ki}} H_n(\alpha_k q_{ki}) = (2n)^{1/2}\alpha_k \delta_{m,n-1} \qquad (28)$$

Similarly

$$(q_{ki})_{mn} = (1/\alpha_k 2^{1/2})[n^{1/2}\delta_{m,n-1} + (n+1)^{1/2}\delta_{m,n+1}] \qquad (29)$$

In eq 28 and 29, k specifies the mode number, i stands for 1, 2, 3 (x, y, z), and we have used for ψ^α

$$\psi^\alpha = \prod_{k=1}^{N} \prod_{i=1}^{3} \left[\frac{\alpha_k}{\pi^{1/2}} \exp(-\alpha_k{}^2 q_{ki}{}^2)\right] \qquad (30)$$

given from eq 10 and 19. Comparison of eq 25 and 26 with eq 28 and 29 gives

$$(\partial/\partial \mathbf{q}_l) = \alpha_l 2^{1/2}\mathbf{b}_l, \qquad \mathbf{q}_l = (1/\alpha_l 2^{1/2})(\mathbf{b}_l + \mathbf{b}_l{}^\dagger) \qquad (31)$$

where

$$\mathbf{b}_l \equiv \sum_{i=1}^{3} b_{li}\mathbf{e}_i, \qquad \mathbf{b}_l{}^\dagger \equiv \sum_{i=1}^{3} b_{li}{}^\dagger \mathbf{e}_i \qquad (32)$$

and $\mathbf{e}_i$ is a unit vector in the x, y, or z direction. From eq 25 and 26 follow the usual commutation properties of boson operators:

$$(b_{li}, b_{kj}) = b_{li}b_{kj} - b_{kj}b_{li} = 0, \qquad (b_{li}{}^\dagger, b_{kj}{}^\dagger) = 0, \qquad (b_{li}, b_{kj}{}^\dagger) = \delta_{k,l}\delta_{i,j} \qquad (33)$$

With the understanding that all functions of "normal" coordinates are given by a boson representation through eq 31, $\tilde{L}^a$ and $\tilde{L}^b$ are written in the form,

$$\tilde{L}^a = \sum_{k=1}^{N} \sum_{l=1}^{N} \mathbf{b}_k{}^\dagger \cdot \mathbf{\Lambda}_{kl} \cdot [\mathbf{b}_l + (\mathbf{b}_l, V)] \qquad (34)$$

$$\tilde{L}^b = -\kappa \Sigma \mathbf{b}_1{}^\dagger \cdot (\mathbf{e}_x \mathbf{e}_y) \cdot (\mathbf{b}_1 + \mathbf{b}_1{}^\dagger) \qquad (35)$$

where $(\partial V/\partial \mathbf{q}_l) = (\partial/\partial \mathbf{q}_l, V)$ and

$$\mathbf{\Lambda}_{kl} \equiv 2kT\alpha_k\alpha_l \mathbf{F}_{kl} = 2kT\alpha_k\alpha_l \sum_i \sum_j Q_{ki}Q_{lj}[\beta^{-1}\delta_{ij} + \mathbf{T}(\mathbf{r}_{ij})] \qquad (36)$$

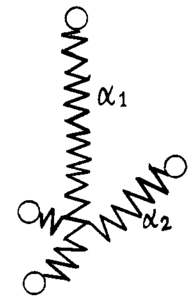

Figure 1. Schematic representation of the spring bead system in a Fourier space.[5]

The average of any function P of "normal" coordinates is written as

$$\langle P\rangle = \int \psi^\alpha \rho P(\mathbf{q}_1, \mathbf{q}_2, \ldots, \mathbf{q}_N)\, \mathrm{d}\mathbf{q}_1\, \mathrm{d}\mathbf{q}_2 \ldots \mathrm{d}\mathbf{q}_N = \langle 0|P|\rho\rangle \qquad (37)$$

with P and $|\rho\rangle$ expressed in the boson representation, where $|0\rangle$ designates the ground state defined by

$$\mathbf{b}_l|0\rangle = 0 \qquad (\langle 0|\mathbf{b}_l{}^\dagger = 0) \qquad (38)$$

Therefore, if $|\rho\rangle$ is given under suitable conditions and the observable P is defined, the average of P will be obtained by straightforward algebraic calculations with the use of commutation relations and eq 38.

The next step is to obtain the perturbed state vector in the boson representation. For the case of the presence of the excluded volume effect only, $\tilde{L}^b$ vanishes and ρ satisfies

$$\tilde{L}^a \rho = 0 \qquad (39)$$

Then Fixman showed, using the boson representation for a δ function $\delta(\mathbf{r}_{ij})$ which interacts between beads, that the boson representation of $|\rho\rangle$ is given by

$$|\rho\rangle = \exp\left[-\tfrac{1}{2} \sum_{k=1}^{N} G_k(1+G_k)^{-1}\mathbf{b}_k{}^\dagger \cdot \mathbf{b}_k{}^\dagger\right]|0\rangle \qquad (40)$$

with

$$G_k = (\alpha^2 - 1) - (z/\alpha^3)g_k \qquad (41)$$

where

$$z = (3/2\pi b_0{}^2)^{3/2}XN^{1/2} \qquad (42)$$

$$g_k = \tfrac{1}{2}N^{-3/2}\left(\sin\frac{k\pi}{2N}\right)^{-2} \sum_{i<j} \left(\cos\frac{kj\pi}{N} - \cos\frac{ki\pi}{N}\right)^2 |j-i|^{-5/2} \qquad (43)$$

The parameter z is one which has been frequently used to measure excluded volume forces (X is the strength of a δ function). The g_k are numbers independent of N for large N and are related to Fresnel integrals. Detailed derivation of eq 40 and approximations contained there are fully discussed in Fixman's paper,[8,9] so we do not reproduce them here.

Doi and Nakajima's Idea for Principal Components[5]

As shown in a previous section, a system of beads coupled with nearest neighbors by a spring, by the introduction of Fourier transformation, is transformed into that of a product of independent harmonic oscillators. Each of those are bound to the center of mass in $\mathbf{q}_k$ space (Fourie space) by force constants α_k (see eq 19 and 20), as shown in Figure 1 schematically. For such a system, if the directions of principal axis of the ellipsoid can be determined, the principal components may be given by the sum of the square of projection of vectors $\mathbf{q}_k$ ($k = 1, 2, \ldots, N$) on them. Since an effective force constant is smallest for $k = 1(\alpha_k \propto k^2)$, the major axis may be parallel to the direction of vector $\mathbf{q}_1$. Doi and Nakajima thus assumed that (1) the major axis is parallel to the $\mathbf{q}_1$ vector, (2) the second axis is perpendicular to the $\mathbf{q}_1$ vector and lies on the plane that the $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors make, and (3) the third axis is perpendicular to both $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors. That is, a determining factor of the instantaneous shape of the ellipsoid formed by a chain is, in essence, two vectors $\mathbf{q}_1$, $\mathbf{q}_2$.

From the above assumptions unit vectors $\mathbf{u}_1$, $\mathbf{u}_2$, $\mathbf{u}_3$ along three principal axes are given in terms of $\mathbf{q}_1$ and $\mathbf{q}_2$ as

$$\mathbf{u}_1 = \mathbf{q}_1/|\mathbf{q}_1|, \qquad \mathbf{u}_2 = \frac{\mathbf{q}_2 - \mathbf{u}_1(\mathbf{u}_1\cdot\mathbf{q}_2)}{|\mathbf{q}_2 - \mathbf{u}_1(\mathbf{u}_1\cdot\mathbf{q}_2)|}, \qquad \mathbf{u}_3 = \frac{\mathbf{q}_1 \times \mathbf{q}_2}{|\mathbf{q}_1 \times \mathbf{q}_2|} \tag{44}$$

We are now in a position to consider the effect of excluded volume forces.

Calculation of λ_i

As discussed already, the principal components λ_i are given by the sum of the square of projection of vectors $\mathbf{q}_k$ ($k = 1, 2, \ldots, N$) on the directions of unit vectors $\mathbf{u}_1$, $\mathbf{u}_2$, and $\mathbf{u}_3$. However, the spring bead system takes many conformations, so λ_i ($i = 1, 2, 3$) are given by the average over all conformations in $\mathbf{q}_k$ space. Therefore, λ_1 is given from eq 37 and 44 as

$$\lambda_1 = (Nb_0)^{-2}\left\{\langle 0|(\mathbf{q}_1\cdot\mathbf{q}_1) + \sum_{k=2}^{N}\frac{(\mathbf{q}_k\cdot\mathbf{q}_1)^2}{(\mathbf{q}_1\cdot\mathbf{q}_1)}|\rho\rangle\right\} \tag{45}$$

where $\mathbf{q}_k$ ($k = 1, 2, \ldots, N$) are operators defined by eq 31. As long as we are concerned with the linear term of z, it is sufficient to use the expansion of the exponential in eq 40 up to fourth order

$$|\rho\rangle = |\rho\rangle_1 - |\rho\rangle_2 + |\rho\rangle_3 - |\rho\rangle_4 + \ldots \tag{46}$$

where

$$|\rho\rangle_1 = |0\rangle, \qquad |\rho\rangle_2 = \tfrac{1}{2}\sum_k G_k(1+G_k)^{-1}\mathbf{b}_k{}^\dagger\cdot\mathbf{b}_k{}^\dagger|0\rangle,$$
$$|\rho\rangle_3 = \tfrac{1}{8}\sum_k\sum_m G_kG_m(1+G_k)^{-1}(1+G_m)^{-1} \times \mathbf{b}_k{}^\dagger\cdot\mathbf{b}_k{}^\dagger\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger|0\rangle, \text{etc.}, \ldots \tag{47}$$

and $G_k = -zg_k$ given from eq 41 with $\alpha = 1$.

By the use of eq 31, eq 45 is written as

$$\lambda_1 = (Nb_0)^{-2}\Bigg[\frac{1}{2\alpha_1{}^2}\Big\{\langle(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\rangle - \tfrac{1}{2}\sum_m G_m(1+G_m)^{-1}\langle(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \tfrac{1}{8}\sum_m\sum_n G_mG_n(1+G_m)^{-1}(1+G_n)^{-1}\langle(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\mathbf{b}_n{}^\dagger\cdot\mathbf{b}_n{}^\dagger\rangle\Big\}$$
$$+ \sum_{k=2}^{N}\frac{B}{4\alpha_1{}^2\alpha_k{}^2}\Big\{\langle[(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\rangle - \tfrac{1}{2}\sum_m G_m(1+G_m)^{-1}\langle[(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)]^2\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \tfrac{1}{8}\sum_m\sum_n G_mG_n(1+G_m)^{-1}(1+G_n)^{-1} \times \langle[(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)]^2\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\mathbf{b}_n{}^\dagger\cdot\mathbf{b}_n{}^\dagger\rangle\Big\}\Bigg] \tag{48}$$

where the notation $\langle\ldots\rangle$ in place of $\langle 0|\ldots|0\rangle$ has been introduced for simplicity and the denominator of the second term in eq 45 is regarded as a c-number scalar quantity defined by

$$B^{-1} = \langle 0|(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)|\rho\rangle \tag{49}$$

The reason why we replace the denominator of the second term in eq 45 by its average is that the absolute value of the $\mathbf{q}_1$ vector or its square is meaningless because of fluctuations of the $\mathbf{q}_1$ vector. The matrix elements in eq 48 and 49 are evaluated easily with the use of the commutation rule and eq 38 noting that a product of creation and annihilation operators can be transformed into the sum of a product of the contraction.[12]

For example, the fifth term in eq 48 is calculated as

$$\langle[(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)]^2\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle = \langle\mathbf{b}_k\cdot\mathbf{b}_1\mathbf{b}_k\cdot\mathbf{b}_1{}^\dagger\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \langle\mathbf{b}_k\cdot\mathbf{b}_1\mathbf{b}_k{}^\dagger\cdot\mathbf{b}_1\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle$$
$$\equiv 3\{2\langle b_{1x}b_{1x}{}^\dagger\rangle\langle b_{kx}b_{mx}{}^\dagger\rangle\langle b_{kx}b_{mx}{}^\dagger\rangle + 2\langle b_{kx}b_{kx}{}^\dagger\rangle\langle b_{1x}b_{mx}{}^\dagger\rangle\langle b_{1x}b_{mx}{}^\dagger\rangle\} = 6\delta_{k,m} + 6\delta_{m,1} \tag{50}$$

where in the right-hand side of the first line, all terms except the above two terms vanish on account of the property of the ground state, i.e., eq 38, factor 2 arises from the fact that two annihilation operators $\mathbf{b}_k\mathbf{b}_k(\mathbf{b}_1\mathbf{b}_1)$ can be contracted in two different ways with two creation operators $\mathbf{b}_m{}^\dagger\mathbf{b}_m{}^\dagger(\mathbf{b}_m{}^\dagger\mathbf{b}_m{}^\dagger)$, and the commutation rule

$$(b_{ki}, b_{mj}{}^\dagger) = \delta_{k,m}\delta_{i,j} \qquad (i, j = 1, 2, 3) \tag{51}$$

has been used.

Equation 48 thus becomes the following simple form:

$$\lambda_1 = (Nb_0)^{-2}\left[\frac{3}{2\alpha_1{}^2(1+G_1)} + \frac{1}{2}\sum_{k=2}^{N}\frac{1}{\alpha_k{}^2(1+G_k)}\right] \tag{52}$$

For large N, $\alpha_k{}^2$ approximates to

$$\alpha_k{}^2 = 3k^2\pi^2/2(Nb_0)^2 \tag{53}$$

Using this and $G_k = -zg_k$, we obtain after the expansion of the denominator in eq 52 in a power series of z

$$\lambda_1 = \frac{1}{\pi^2} + \sum_{k=2}^{N}\frac{1}{3\pi^2k^2} + \left(\frac{g_1}{\pi^2} + \sum_{k=2}^{N}\frac{g_k}{3\pi^2k^2}\right)z - 0(z^2) \tag{54}$$

Next we shall consider λ_3. The defining equation is

$$\lambda_3 = (Nb_0)^{-2}\left\{\sum_{k=3}^{N}\langle 0\left|\frac{[\mathbf{q}_k\cdot(\mathbf{q}_1\times\mathbf{q}_2)]^2}{(\mathbf{q}_1\times\mathbf{q}_2)^2}\right|\rho\rangle\right\} = (Nb_0)^{-2}\langle(\mathbf{q}_1\times\mathbf{q}_2)^2\rangle^{-1}\left\{\sum_{k=3}^{N}\langle 0|[\mathbf{q}_k\cdot(\mathbf{q}_1\times\mathbf{q}_2)]^2|\rho\rangle\right\} \tag{55}$$

where the denominator is replaced by its average. Equation 55 is written explicitly in terms of boson operator as

$$\langle 0|[\mathbf{q}_k\cdot(\mathbf{q}_1\times\mathbf{q}_2)]^2|\rho\rangle = \frac{1}{8\alpha_k{}^2\alpha_1{}^2\alpha_2{}^2}\langle 0|(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot[(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\times(\mathbf{b}_2+\mathbf{b}_2{}^\dagger)]^2\Big\{1 - \tfrac{1}{2}\sum_m G_m(1+G_m)^{-1}\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger + \tfrac{1}{8}\sum_m\sum_n G_mG_n(1+G_n)^{-1}(1+G_m)^{-1}\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\mathbf{b}_n{}^\dagger\cdot\mathbf{b}_n{}^\dagger + \ldots\Big\}|0\rangle \tag{56}$$

The term order z in eq 56 is evaluated as follows:

$$\langle\{(\mathbf{b}_k+\mathbf{b}_k{}^\dagger)\cdot[(\mathbf{b}_1+\mathbf{b}_1{}^\dagger)\times(\mathbf{b}_2+\mathbf{b}_2{}^\dagger)]\}^2\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle$$
$$= \langle[\mathbf{b}_k\cdot(\mathbf{b}_1\times\mathbf{b}_2)][\mathbf{b}_k{}^\dagger\cdot(\mathbf{b}_1\times\mathbf{b}_2{}^\dagger)]\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \langle[\mathbf{b}_k\cdot(\mathbf{b}_1\times\mathbf{b}_2)][\mathbf{b}_k{}^\dagger\cdot(\mathbf{b}_1{}^\dagger\times\mathbf{b}_2)]\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \langle[\mathbf{b}_k\cdot(\mathbf{b}_1\times\mathbf{b}_2)][\mathbf{b}_k\cdot(\mathbf{b}_1{}^\dagger\times\mathbf{b}_2{}^\dagger)]\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle$$
$$= 3\{\langle b_{kx}(b_{1y}b_{2z} - b_{1z}b_{2y})b_{kx}{}^\dagger(b_{1y}b_{2z}{}^\dagger - b_{1z}b_{2y}{}^\dagger)\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\rangle + \langle b_{kx}(b_{1y}b_{2z} - b_{1z}b_{2y})b_{kx}{}^\dagger(b_{1y}{}^\dagger b_{2z} - b_{1z}{}^\dagger b_{2y})\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger + b_{kx}(b_{1y}b_{2z} - b_{1z}b_{2y})b_{kx}(b_{1y}{}^\dagger b_{2z}{}^\dagger - b_{1z}{}^\dagger b_{2y}{}^\dagger)\mathbf{b}_m{}^\dagger\cdot\mathbf{b}_m{}^\dagger\}$$

$$= 6\{\langle b_{kx}b_{1y}b_{2z}b_{kx}{}^{\dagger}b_{1y}b_{2z}{}^{\dagger}b_{my}{}^{\dagger}b_{my}{}^{\dagger}\rangle + \langle b_{kx}b_{1y}b_{2z}b_{kx}{}^{\dagger}b_{1y}{}^{\dagger}b_{2z}b_{mz}{}^{\dagger}b_{mz}{}^{\dagger}\rangle + \langle b_{kx}b_{1y}b_{2z}b_{kx}b_{1y}{}^{\dagger}b_{2z}{}^{\dagger}b_{mx}{}^{\dagger}b_{mx}{}^{\dagger}\rangle\} = 12\delta_{m,1} + 12\delta_{m,2} + 12\delta_{k,m} \quad (57)$$

In a similar way, all the matrix elements in eq 56 can be evaluated. As the final expression for λ_3, we have

$$\lambda_3 = (Nb_0)^{-2}\left\{\frac{1}{2}\sum_{k=3}^{N}\frac{1}{\alpha_k{}^2(1+G_k)}\right\} \quad (58)$$

Furthermore eq 58 becomes

$$\lambda_3 = (Nb_0)^{-2}\left\{\frac{1}{2}\sum_{k=3}^{N}\frac{1}{\alpha_k{}^2} + \frac{z}{2}\sum_{k=3}^{N}\frac{g_k}{\alpha_k{}^2} - 0(z^2)\right\} = \frac{1}{3\pi^2}\sum_{k=3}^{N}\frac{1}{k^2} + \left(\frac{1}{3\pi^2}\sum_{k=3}^{N}\frac{g_k}{k^2}\right)z - 0(z^2) \quad (59)$$

where eq 53 has been used.

Finally, λ_2 is given by

$$\lambda_2 = \langle 0|[\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2 + \frac{\sum_{k=3}^{N}[\mathbf{q}_k\cdot\mathbf{q}_2 - \mathbf{q}_k\cdot\mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2}{[\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2}|\rho\rangle \quad (60)$$

The denominator of the second term in eq 60 also is replaced by its average; that is, it equals the first term. Though the calculation of the matrix elements in eq 60 is very tedius, we obtain

$$\langle[\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2\rangle = \frac{1}{\alpha_2{}^2(1+G_2)}$$
$$\times\langle[\mathbf{q}_k\cdot\mathbf{q}_2 - \mathbf{q}_k\cdot\mathbf{q}_1(\mathbf{q}_1\cdot\mathbf{q}_2)/|\mathbf{q}_1|^2]^2\rangle = \frac{1}{2\alpha_k{}^2\alpha_2{}^2(1+G_k)(1+G_2)} \quad (61)$$

Thus

$$\lambda_2 = (Nb_0)^{-2}\left\{\frac{1}{\alpha_2{}^2(1+G_2)} + \sum_{k=3}^{\infty}\frac{1}{2\alpha_k{}^2(1+G_k)}\right\} \quad (62)$$

With the use of eq 53, eq 62 is written up to order z as

$$\lambda_2 = (Nb_0)^{-2}\left\{\frac{1}{\alpha_2{}^2} + \frac{1}{2}\sum_{k=3}^{N}\frac{1}{\alpha_k{}^2} + \left(\sum_{k=3}^{N}\frac{g_k}{2\alpha_k{}^2} + \frac{g_2}{\alpha_2{}^2}\right)z + 0(z^2)\right\} = \frac{1}{6\pi^2} + \frac{1}{3\pi^2}\sum_{k=3}^{N}\frac{1}{k^2} + \left(\frac{1}{3\pi^2}\sum_{k=3}^{N}\frac{g_k}{k^2} + \frac{g_2}{6\pi^2}\right)z + 0(z^2) \quad (63)$$

Results and Discussion

The purpose of the present paper was to decompose the perturbation series of z for α_S, up to the term linear in z, into three orthogonal components along the principal axis. The results are given by eq 54, 59, and 63. In order to compare these series expansions, we need values of g_1, g_2, and $\Sigma_{k=3}^{N}g_k/k^2$. These were obtained by the numerical computation as follows:[8,13]

$$g_1 = 1.5157, \qquad g_2 = 1.1705, \qquad (6/\pi^2)\sum_{k=1}^{\infty}g_k/k^2 = 1.2762 \quad (64)$$

In the limit of $N \to \infty$, eq 54, 59, and 63 thus become

$$\lambda_1 = \frac{1}{18} + \frac{2}{3\pi^2} + \left(\frac{2g_1}{3\pi^2} + \sum_{k=1}^{\infty}\frac{g_k}{3\pi^2k^2}\right)z - \ldots \quad (65)$$
$$= 0.1231 + 0.1732z - \ldots \quad (65')$$

$$\lambda_2 = \frac{1}{18} - \frac{1}{4\pi^2} + \left(\frac{g_2}{12\pi^2} - \frac{g_1}{3\pi^2} + \sum_{k=1}^{\infty}\frac{g_k}{3\pi^2k^2}\right)z - \ldots \quad (66)$$
$$= 0.3022\times10^{-1} + 0.2959\times10^{-1}z - \ldots \quad (66')$$

$$\lambda_3 = \frac{1}{18} - \frac{5}{12\pi^2} + \left(\sum_{k=1}^{\infty}\frac{g_k}{3\pi^2k^2} - \frac{g_1}{3\pi^2} - \frac{g_2}{12\pi^2}\right)z - \ldots \quad (67)$$
$$= 0.1334\times10^{-1} + 0.9826\times10^{-2}z - \ldots \quad (67')$$

where the sum $\Sigma_{k=1}^{k=\infty}k^{-2} = \pi^2/6$ has been used. Adding eq 65, 66, and 67, we have

$$\lambda_1 + \lambda_2 + \lambda_3 = \frac{1}{6}\left(1 + \frac{6}{\pi^2}\sum_{k=1}^{\infty}\frac{g_k}{k^2}\cdot z - \ldots\right. \quad (68)$$

and it agrees exactly with the expression of the perturbation series for the square radius of gyration obtained by Stidham and Fixman.[13] Furthermore, anisotropy of the excluded volume effect for λ_i can be seen from the following expressions:

$$\alpha_{\lambda_1} = \lambda_1/\lambda_1{}^0 = 1 + 1.4069z - \ldots \quad (69)$$

$$\alpha_{\lambda_2} = \lambda_2/\lambda_2{}^0 = 1 + 0.9791z - \ldots \quad (70)$$

$$\alpha_{\lambda_3} = \lambda_3/\lambda_3{}^0 = 1 + 0.7365z - \ldots \quad (71)$$

These show that the effect of excluded volume forces on principal components λ_i is very anisotropic, that is, it has the tendency to strengthen further the asymmetrical distribution of segments in the unperturbed state.[15] The ratio of coefficients of z is 1.91:1.33:1.

Though the present calculation is based on Doi and Nakajima's idea, it is thought that the result obtained here holds in general for random flight chains. As pointed out by Doi and Nakajima, however, the present method does not give quantitative agreement with computer calculations by Šolc for $\lambda_2{}^0$ and $\lambda_3{}^0$. Šolc[4] obtained that $\lambda_1{}^0 = 0.1256$, $\lambda_2{}^0 = 0.2916\times10^{-1}$, and $\lambda_3{}^0 = 0.1077\times10^{-1}$. These disagreements may be due to the ambiguity of selections of both major and second axis in a Fourier space. Therefore, if they are chosen to give satisfactory estimations for $\lambda_2{}^0$ and $\lambda_3{}^0$, the method used here may give more reliable information about the effect of excluded volume forces on them.

For the present model, of course, the calculation of coefficients of higher order of z or the closed expressions of z for λ_i may clearly reveal the effect of excluded volume forces on principal components.[15a] Furthermore, it is of interest to investigate the behavior of principal components under external perturbations, such as shear flow with hydrodynamic interaction. This problem can also be treated along the line mentioned in previous sections. The result will be reported in a separate paper.[14]

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