Excluded Volume Effect on the Principal Components of Polymer Chains. 2

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ABSTRACT: The excluded volume effect on the principal components ($\lambda_1 \geq \lambda_2 \geq \lambda_3$) is discussed based on the result obtained in a previous paper. The perturbation series of the excluded volume parameter z for the square radius of gyration is decomposed, up to the term quadratic in z, into three orthogonal components along the principal axis of inertia of a polymer chain. The ratio of coefficients of z^2 is 1.49:1.22:1.00. Furthermore, it is found that for large values of z, only λ_1/N diverges, obeying the so-called fifth power type law, while both λ_2/N and λ_3/N converge. Here N is the number of segments.

In a previous paper[1] (hereafter referred to as 1), the present authors have proposed a method, based on the model suggested by Doi and Nakajima,[2] for taking account of the excluded volume forces to the principal components λ_i (i = 1, 2, 3) of inertia of an unperturbed polymer chain.[3] It was assumed that the perturbation series of the excluded volume parameter z for the square radius of gyration can be decomposed into its three orthogonal components λ_i along the principal axis of inertia of the chain. That is, the λ_i are expressed as a power series in the parameter z as

$$\lambda_i = \lambda_i{}^0 + \lambda_i{}^1 z - \lambda_i{}^2 z^2 + \dots \qquad (i = 1, 2, 3) \tag{1}$$

The terms $\lambda_i{}^0$ independent of z and the coefficients $\lambda_i{}^1$ of terms linear in z are evaluated by a method of second quantization introduced by Fixman[4] to give

$$\lambda_1 = 0.1231 + 0.1732z - \dots \tag{2}$$

$$\lambda_2 = 0.3022 \times 10^{-1} + 0.2959 \times 10^{-1}z - \dots \tag{3}$$

$$\lambda_3 = 0.1334 \times 10^{-1} + 0.9826 \times 10^{-1}z - \dots \tag{4}$$

These results show, as expected, that the asphericity of the chain is increased by the introduction of excluded volume forces (also see eq 69–70 in 1). This behavior has been recently confirmed by the Monte Carlo method by Kranbuhl and Verdier.[5] However, the behavior of λ_i for an entire range of z cannot be seen from the above first-order perturbation theory.

Therefore the purpose of the present paper is twofold: first, the coefficients $\lambda_i{}^2$ of terms quadratic in z are estimated approximately, and second, the asymptotic behavior for large values of z is examined.

Main Results of 1

As shown in 1, a system of beads coupled with nearest neighbors by a spring (Rouse model), 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 Fourier space by a spring with force constant α_k (k = 1,2,..., N). For such a system, Doi and Nakajima[2] assumed that (1) the major axis of the ellipsoid formed by a product of independent harmonic oscillators 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 the $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors make, and (3) the third axis is perpendicular to both the $\mathbf{q}_1$ and $\mathbf{q}_2$ vectors. Here $\mathbf{q}_k$ denotes the vector coordinate ("normal coordinate") of the kth bead in Fourier space.

These assumptions immediately lead to the following expressions for λ_i:

$$\lambda_1 = N^{-1}\left[\mathbf{q}_1 \cdot \mathbf{q}_1 + \sum_{k=2}^{N} \frac{(\mathbf{q}_k \cdot \mathbf{q}_1)^2}{|\mathbf{q}_1 \cdot \mathbf{q}_1|}\right] \tag{5}$$

$$\lambda_2 = N^{-1}\left\{\left[\mathbf{q}_2 - \frac{\mathbf{q}_1(\mathbf{q}_1 \cdot \mathbf{q}_2)}{|\mathbf{q}_1|^2}\right]^2 + \sum_{k=3}^{N} \frac{[\mathbf{q}_k \cdot \mathbf{q}_2 - \mathbf{q}_k \cdot \mathbf{q}_1(\mathbf{q}_1 \cdot \mathbf{q}_2)/|\mathbf{q}_1|^2]^2}{|\mathbf{q}_2 - \mathbf{q}_1(\mathbf{q}_1 \cdot \mathbf{q}_2)/|\mathbf{q}_1|^2|^2}\right\} \tag{6}$$

$$\lambda_3 = N^{-1} \sum_{k3}^{N} [\mathbf{q}_k \cdot (\mathbf{q}_1 \times \mathbf{q}_2)]^2/|\mathbf{q}_1 \cdot \mathbf{q}_2|^2 \tag{7}$$

where factor N^{-1} is chosen in place of $(Nb_0)^{-2}$ in 1 as the sum of λ_i in the unperturbed state gives the correct mean square radius of gyration $\langle S^2 \rangle$ ($= Nb_0{}^2/6$). In a method of second quantization, "normal" coordinates $\mathbf{q}_k$ are regarded as operators acting on the orthonormal basis system, written explicitly in terms of creation and annihilation operators as

$$\mathbf{q}_k = (1/2^{1/2}\alpha_k)(\mathbf{b}_k + \mathbf{b}_k{}^\dagger) \tag{8}$$

where $\mathbf{b}_k{}^\dagger$ and $\mathbf{b}_k$ are the usual creation and annihilation operators in boson systems, respecitvely.

The observed λ_i are given by the average over all conformations and written in the boson representation as

$$\langle\lambda_i\rangle = \langle 0|\lambda_i|\rho\rangle \tag{9}$$

where the perturbed state vector $|\rho\rangle$ represented by boson operators was given already in 1 as

$$|\rho\rangle = \exp\left[-\frac{1}{2}\cdot\sum_m G_m(1 + G_m)^{-1}\mathbf{b}_m{}^\dagger \cdot \mathbf{b}_m{}^\dagger\right]|0\rangle \tag{10}$$

with

$$G_m = (\alpha^2 - 1) - (z/\alpha^3)g_m \tag{11}$$

where α is a parameter frequently used to measure the expansion relative to a reference length b_0, the g_m are numbers independent of N for large N, and $|0\rangle$ designates the ground state in boson systems. The matrix elements in the right-hand side of eq 9 were evaluated to give

$$\langle\lambda_1\rangle = N^{-1}\left[\frac{3}{2\alpha_1{}^2(1 + G_1)} + \sum_{k=2}^{N} \frac{1}{2\alpha_k{}^2(1 + G_k)}\right] \tag{12}$$

$$\langle\lambda_2\rangle = N^{-1}\left[\frac{1}{\alpha_2{}^2(1 + G_2)} + \sum_{k=3}^{N} \frac{1}{2\alpha_k{}^2(1 + G_k)}\right] \tag{13}$$

$$\langle\lambda_3\rangle = N^{-1}\left[\sum_{k=3}^{N} \frac{1}{2\alpha_k{}^2(1 + G_k)}\right] \tag{14}$$

where

$$\alpha_k{}^2 = 6b^{-2}\sin^2(k\pi/2N) \tag{15}$$

with $b = b_0\alpha$. Equations 12–14 with eq 15 are very important results of 1 and are used in subsequent sections.

Calculation of $\lambda_i{}^2$

First we shall consider the choice of parameter α. Following Fixman's work, α must be chosen so as to maintain $|\rho\rangle$ as near

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to $|0\rangle$ as possible. It is obvious, however, that all G_k cannot be made to vanish by the same value of α, since g_k decreases with increasing k. Therefore α is chosen to make G_1 vanish.[9] From this requirement, we get for α and G_k $(k \neq 1)$

$$\alpha^2 - 1 - (z/\alpha^3)g_1 = 0 \quad (16)$$

$$G_k = (g_1 - g_k)z/\alpha^3 \quad (17)$$

For small values of z, eq 16 and 17 become[6]

$$\alpha^2 = 1 + zg_1 - (3z^2g_1^2/2) + (33z^3g_1^3/8) + 0(z^4) \quad (18)$$

$$(1 + G_k)^{-1} = 1 + (g_k - g_1)z + (g_k - g_1)(g_k - \tfrac{5}{2}g_1)z^2 + 0(z^3) \quad (19)$$

We note that for large values of N, eq 15 approximates to

$$\alpha_k^2 \simeq 3k^2\pi^2/2(Nb)^2 \quad (20)$$

Substituting eq 20 into eq 12–14 yields

$$\langle\lambda_1\rangle/Nb_0^2 = \frac{\alpha^2}{\pi^2} + \sum_{k=2}^{N} \frac{\alpha^2}{3\pi^2k^2(1 + G_k)} \quad (21)$$

$$\langle\lambda_2\rangle/Nb_0^2 = \frac{\alpha^2}{6\pi^2(1 + G_2)} + \sum_{k=3}^{N} \frac{\alpha^2}{3\pi^2k^2(1 + G_k)} \quad (22)$$

$$\langle\lambda_3\rangle/Nb_0^2 = \sum_{k=3}^{N} \frac{\alpha^2}{3\pi^2k^2(1 + G_k)} \quad (23)$$

where $G_1 = 0$ has been used.

Equations 18 and 19 permit expansions of eq 21–23 as already sketched by Fixman[4] and Stidham and Fixman.[6] We thus have resulting equations up to the term quadratic in z:

$$\frac{\langle\lambda_1\rangle}{Nb_0^2} = \frac{1}{\pi^2} + \sum_{k=2}^{N} \frac{1}{3\pi^2k^2} + \left(\frac{g_1}{\pi^2} + \sum_{k=2}^{N} \frac{g_k}{3\pi^2k^2}\right) z + \frac{z^2}{3\pi^2}(C_2 - \tfrac{9}{2}g_1^2) \quad (24)$$

$$\frac{\langle\lambda_2\rangle}{Nb_0^2} = \frac{1}{6\pi^2} + \sum_{k=3}^{N} \frac{1}{3\pi^2k^2} + \left(\frac{g_2}{6\pi^2} + \sum_{k=3}^{N} \frac{g_k}{3\pi^2k^2}\right)z + \frac{z^2}{3\pi^2}[C_3 + \tfrac{1}{2}(g_2 - g_1)(g_2 - \tfrac{3}{2}g_1) - \tfrac{3}{4}g_1^2] \quad (25)$$

$$\frac{\langle\lambda_3\rangle}{Nb_0^2} = \sum_{k=3}^{N} \frac{1}{3\pi^2k^2} + \left(\sum_{k=3}^{N} \frac{g_k}{3\pi^2k^2}\right)z + \frac{z^2}{3\pi^2}(C_3) \quad (26)$$

where

$$C_j = \sum_{k=j}^{N} k^{-2}[(g_k - g_1)(g_k - \tfrac{3}{2}g_1) - \tfrac{3}{2}g_1^2] \quad (27)$$

For large N, all terms in eq 24–27 can be evaluated with the use of values of g_k given from numerical computations by Stidham and Fixman. The final results are given as

$$\frac{\langle\lambda_1\rangle}{Nb_0^2} = 0.1231 + 0.1732z - 0.4043z^2 + 0(z^3) \quad (28)$$

$$\frac{\langle\lambda_2\rangle}{Nb_0^2} = 0.03022 + 0.2959 \times 10^{-1}z - 0.8109 \times 10^{-1}z^2 + 0(z^3) \quad (29)$$

$$\frac{\langle\lambda_3\rangle}{Nb_0^2} = 0.01334 + 0.9826 \times 10^{-2}z - 0.2933 \times 10^{-1}z^2 + 0(z^3) \quad (30)$$

The above equations show that the perturbation series of z for the square radius of gyration $\langle S^2\rangle$ was decomposed into its three orthogonal components λ_i up to the order quadratic in z. However, the present method developed by Fixman[4] does not give correct estimations for the coefficients of z^2 in the perturbation series for both the end-to-end expansion parameter and the gyration radius expansion parameter. Therefore, the coefficients of z^2 in eq 28–30 are not exact, but

Table I
Comparison of Ratios of $\langle\lambda_i\rangle$ Given from Computer Experiments with Those Given from the Present Method

	N	$\langle\lambda_1\rangle:\langle\lambda_2\rangle:\langle\lambda_3\rangle$
Computer expt	9^5	14.6:3.04:1.00
	15^5	15.0:3.04:1.00
	33^5	14.6:3.04:1.00
	63^5	14.7:3.00:1.00
	∞^7	14.8:3.05:1.00
This work	∞	∞:3.62:1.00

they are sufficient for our discussion of the qualitative behaviors of eq 28–30 as a function of z.

Asymptotic Behavior of $\langle\lambda_i\rangle$ for large z

In this section we shall consider the the behaviors of $\langle\lambda_i\rangle$ for large values of z. For such z eq 16 becomes

$$\alpha^5 \simeq g_1z \quad (31)$$

Furthermore note that for large z

$$\frac{\alpha^2}{k^2(1 + G_k)} = \frac{\alpha^5}{k^2(\alpha^5 - zg_k)} \simeq \frac{1}{k^2(1 - g_k/g_1)} \quad (32)$$

Thus eq 21–23 are written in the form

$$\langle\lambda_1\rangle/Nb_0^2 = \pi^{-2}(g_1z)^{2/5} + \sum_{k=2}^{\infty} \frac{1}{3\pi^2k^2(1 - g_k/g_1)} \quad (33)$$

$$\langle\lambda_2\rangle/Nb_0^2 = \frac{1}{6\pi^2(1 - g_2/g_1)} + \sum_{k=3}^{\infty} \frac{1}{3\pi^2k^2(1 - g_k/g_1)} \quad (34)$$

$$\langle\lambda_3\rangle/Nb_0^2 = \sum_{k=3}^{\infty} \frac{1}{3\pi^2k^2(1 - g_k/g_1)} \quad (35)$$

The sums in eq 34 and 35 are evaluated numerically in the same way as Fixman and Stidham[6] did. The results are

$$\langle\lambda_1\rangle/Nb_0^2 = 0.1196z^{2/5} + 0.06540 \quad (36)$$

$$\langle\lambda_2\rangle/Nb_0^2 = 0.1025 \quad (37)$$

$$\langle\lambda_3\rangle/Nb_0^2 = 0.2831 \times 10^{-1} \quad (38)$$

These results show that in the limit of $z \rightarrow \infty$, only $\langle\lambda_1\rangle/Nb_0^2$ diverges obeying the so called fifth power type law, while both $\langle\lambda_2\rangle/Nb_0^2$ and $\langle\lambda_3\rangle/Nb_0^2$ approach certain constant values.

Results and Discussion

One of the purposes of this paper was to decompose the perturbation series of z for the square radius gyration into three orthogonal components along the principal axis of inertia up to the term quadratic in z. The results are given by eq 28, 29, and 30. These equations can be rewritten in the following forms:

$$\alpha_{\lambda_1} = \langle\lambda_1\rangle/\langle\lambda_1^0\rangle = 1 + 1.4079z - 3.2842z^2 + \ldots \quad (39)$$

$$\alpha_{\lambda_2} = \langle\lambda_2\rangle/\langle\lambda_1^0\rangle = 1 + 0.9791z - 2.6833z^2 + \ldots \quad (40)$$

$$\alpha_{\lambda_3} = \langle\lambda_3\rangle/\langle\lambda_3^0\rangle = 1 + 0.7365z - 2.1986z^2 + \ldots \quad (41)$$

The ratio of coefficients of z is that 1.91:1.33:1, while that of z^2 is that 1.49:1.22:1. The relative ratio of these coefficients in the perturbation series for the expansion factors α_{λ_i} decreases with an increase in the order of z. The contribution of $\langle\lambda_1\rangle$ itself to the perturbation series for the square radius of gyration, however, increases with increasing the order of z as is easily seen from eq 28–30.

On the other hand, for the limit of $z \rightarrow \infty$, α_{λ_1} diverges, while α_{λ_2} and α_{λ_3} approach 3.39 and 2.12, respectively. That is, $\langle\lambda_1\rangle$ increases without limit, while $\langle\lambda_2\rangle$ and $\langle\lambda_3\rangle$ become 3.39 and 2.12 times as large as $\langle\lambda_0^2\rangle$ and $\langle\lambda_0^3\rangle$, respectively. This shows that the asphericity of instantanuous shape of the chain increases without limit as z increases.

However, recent Monte Carlo studies[5,7] of asphericity in lattice model chains with excluded volume forces do not show such a behavior, as shown in Table I. In addition, Gobush, Šolc, and Stockmayer[3] considered this problem from a different point of view, based on a smooth density model. Although they obtained the larger asphericity for large z, that is, $\langle\lambda_1\rangle:\langle\lambda_2\rangle:\langle\lambda_3\rangle = 28.7:4.75:1.00$, it could not be found that only $\langle\lambda_1\rangle$ increases without limit. This discrepancy may be attributed not only to our selection of the major axis chosen to be parallel to the $\mathbf{q}_1$ vector in a Fourier space but also to the condition of $G_1 = 0$ in the present treatment. It is very difficult, however, to relax the above two conditions.

Summary

It seems very difficult to estimate analytically, under the presence of excluded volume forces, the eigenvalues of the symmetric tensor[8] which characterizes the instantanious shape of the chain. We therefore are forced to consider the model easy to handle. In particular, for the model introduced by Doi and Nakajima, we have shown in 1 and this paper that it is possible to introduce explicitly the effect of excluded volume forces to it. The results obtained, however, do not agree with those of computer experiments and other approaches. More precise theoretical and experimental studies are necessary for the discussion of the excluded volume forces on the principal components $\langle\lambda_i\rangle$.

References and Notes

(1) T. Minato and A. Hatano, *Macromolecules*, preceding paper in this issue.
(2) M. Doi and H. Nakajima, S.P.S.J, Symposium on Macromolecules, Tokyo, 23, 1023 (1974), and *Chem. Phys.*, **6**, 124 (1974).
(3) W. Gobush, K. Šolc, and W. H. Stockmayer, *J. Chem. Phys.*, 60, 12 (1974). These authors considered this problem based on a smooth density model.
(4) (a) M. Fixman, *J. Chem. Phys.*, **45**, 785 (1966); (b) **45**, 793 (1966).
(5) D. Kranbuhl and P. H. Verdier, *J. Chem. Phys.*, **67**, 361 (1977), or see ref 3 and 7.
(6) H. Stidham and M. Fixman, *J. Chem. Phys.*, **48**, 3092 (1968).
(7) J. Mazur, C. Guttaman, and F. MaCrackin, *Macromolecules*, **6**, 872 (1973).
(8) K. Šolc, *J. Chem. Phys.*, **55**, 335 (1971).
(9) The physical meaning of this approximation is discussed in detail in Fixman's paper.[4a]

Laser Light Scattering from Soft Gels

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ABSTRACT: Photon correlation spectroscopy has been used to probe standing displacement waves set up in cuvettes exposed to mechanical vibrations. The dependence of mode frequencies on cuvette dimensions agrees with predictions of a simple theoretical model. Time behavior of the oscillating portion of the measured photon autocorrelation functions is found to be independent of **Q** (the Bragg wave vector), also in accord with theory. Values of longitudinal sound speed are obtained and corresponding values of elastic moduli are determined. Agarose and polyacrylamide gels of differing concentration have been investigated, establishing that materials whose elastic moduli fall within the range 10^2–10^5 dyn/cm^2 can be studied by this technique. Elastic moduli of agarose are found to vary with weight percentage of polymer ρ according to $E \sim \rho^m$, where $m \simeq 4.1$. Corroborative measurements have been made with instrumentation designed to analyze the frequency distribution of scattered light.

I. Introduction

Various materials of biological origin possess rheological properties characteristic of weakly cross-linked polymer networks. Examples are the lens and *vitreous humor* of the eye,[2] sputum,[3] and mucus,[4] constituents of connective tissue such as hyaluronic acid,[5] and the cytoplasm of motile cells.[6,7] In the present paper we describe a procedure involving laser inelastic light scattering which can be used to study the mechanical properties of such gel-like materials. The method differs from prior laser light scattering techniques[8–12] in that it probes low-frequency displacement waves which are selected by the mechanical resonant cavity defined by the gel boundaries, whereas other techniques detect short-lived thermally induced density fluctuations.

A theory for interpreting these light scattering measurements is presented in an accompanying paper.[13] We show that the material parameter which can be extracted from the data is the low-frequency longitudinal sound velocity, which can be related to elastic coefficients (the compressibility and shear moduli). Based on preliminary measurements, we envision that the technique can be used to probe materials whose elastic moduli fall within the range 10^2–10^5 dyn/cm^2. Illustrative data are given primarily for agarose gels, but similar observations have been made when measuring other materials such as specially prepared collagen gel networks, *vitreous humor* obtained from the eyes of fetal calves, and polyacrylamide gels of appropriate composition. The longitudinal sound velocity is determined from the frequencies of observed oscillatory components of photon autocorrelation functions. Oscillations previously were noted by Wun, Feke, and Prins[10] when they, too, used laser light scattering to investigate agarose gels.

Other rheological techniques which are used to study the properties of soft gels generally measure the response which the material shows to an imposed macroscopic mechanical disturbance.[14] Such methods have the disadvantage of causing significant perturbation of the gel structure and, therefore, are not suitable for studying pressure-dependent polymeric systems such as cytoplasmic extracts near a sol-gel transition.[15] Light scattering techniques, being noninvasive, do not suffer from such limitations. Furthermore, light scattering measurements oftentimes are extremely rapid (of the order of a minute or less) so that the kinetics of gelation can be studied and have the advantage that in principle only very small volumes of material are needed.

II. Materials and Methods

Agarose gels were prepared by heating aqueous suspensions

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