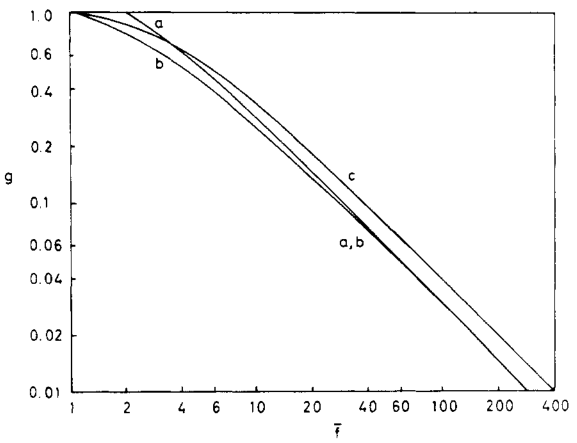

Figure 6. Limiting values of g as a function of the average number of branches for (a) stars with homodisperse branches ($\alpha = 0.1$); (b) regular homodisperse stars ($\alpha = 1$); (c) stars with polydisperse branches (most-probable length distribution) ($\alpha = 1$).

In the limit of large and small central units the curves of Figure 5 can be easily interpreted. Large compact spheres have small dimensions compared with those of linear chains of the same molecular weight. Hence, g starts at a very low value for short chains and gradually approaches a limiting value for very long chains. This limiting value is identical for all types of central units in the star, because at large chain lengths weight and dimensions of the central unit become negligible compared with those of the branches. For stars with small central units this limiting value of g is approached from larger values for short branches, because here the bond lengths of the central unit and the side chain units have approximately the same size, resulting in g factors close to 1 for very short side chains. The behavior of stars with moderately large centers is rather complicated and appears not accessible to interpretation in simple terms.

The limiting g values are given by

$$g \longrightarrow 4\frac{1 + (f - 1)\alpha}{[2 + (f - 1)\alpha]^2} \tag{34}$$

(polydisperse branches)

$$g \longrightarrow \frac{1 + 3(f - 1)\alpha}{[1 + (f - 1)\alpha]^2} \tag{35}$$

(homodisperse branches)

and these equations hold exactly for star molecules with point centers.[16]

It is of interest that for large numbers of branches g depends uniquely on the number average $\alpha f = \bar{f}$ of branches per molecule, while at small $\bar{f}$ it also depends on the probability α. See Figure 6.

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Polymer Normal Mode Analysis by Inelastic Light Scattering

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ABSTRACT: We have analyzed theoretically the autocorrelation function and spectrum of light inelastically scattered from a dilute solution of flexible polymer chains, each of which has a small but strongly scattering "label" conjugated to one or both ends or to the middle. Scattering from the polymer itself is nulled by refractive index matching. The label is postulated to be small enough that its influence on the hydrodynamic normal modes of the polymer is insignificant. Calculations indicate that intramolecular normal modes of the polymer chain, as they are manifested in the motion of the label, contribute strongly to the scattering spectrum at moderate chain lengths and scattering angles.

I. Introduction

In his fundamental paper of 1964,[1] and in several later ones,[2,3] Pecora raised the goal of using inelastic laser light scattering to detect intramolecular modes of motion in flexible polymer chains. This goal has been steadily pursued, notably by Frederick and coworkers,[4-6] but the pursuit has been difficult, because of the low scattering intensity contributed by the internal modes relative to translational diffusion and the stringent requirements for very high polymer molecular weight and monodispersity.

This paper presents a theoretical analysis of a new approach to this problem. We imagine that a dense, strongly scattering "label" is conjugated to the polymer chain at one or two points and that the solvent refractive index is chosen to match that of the polymer. Then scattering arises only from the label, which is supposed to have a substantial excess polarizability relative to the solvent. At the same time, the label is postulated to be small enough that its influence on the hydrodynamic normal modes of the polymer chain is insignificant. Our analysis of this model demonstrates that intramolecular normal modes of the polymer chain, as they are manifested in the motion of the label, contribute strongly to the autocorrelation function or spectrum of scattered light. Only moderate chain lengths and scattering angles are required.

II. Theory and Results

We follow the development and notation of Pecora[1-3] as closely as possible. Readers are directed to these papers for background, derivations of basic equations, and further details.

Consider a solution of polymer molecules, sufficiently dilute that each molecule scatters independently. There are $Z + 1$ segments in each chain, numbered from 0 to Z, connected by Z bonds. The excess polarizability of the jth segment, relative to solvent, is α_j. Then the autocorrelation function for light scattered from the polymer chain is proportional to

$$P(\mathbf{K}, t) = \left\langle \sum_{l=0}^{Z} \sum_{j=0}^{Z} \alpha_l \alpha_j \exp[i\mathbf{K}\cdot(\mathbf{r}_l^0 - \mathbf{r}_j)] \right\rangle \tag{1}$$

Here $\mathbf{K}$ is the difference between incident and scattered wave vectors, $\mathbf{r}_l^0$ is the position of segment l at time zero, $\mathbf{r}_j$ is the position of segment j at time t, and the angular brackets denote an ensemble average.

Expression of the segmental coordinates in terms of the polymer normal modes[7] and suitable averaging transforms eq 1 to

$$P(K, t) = \exp(-DK^2 t) \sum_{l=0}^{Z} \sum_{j=0}^{Z} \alpha_l \alpha_j \exp\left\{-(2x/\pi^2) \sum_{k=1}^{Z} \frac{1}{k^2} \times [R_{jk}^2 + R_{lk}^2 - 2R_{lk}R_{jk}e^{-t/\tau_k}]\right\} \tag{2}$$

The translational diffusion coefficient of the polymer chain is D, and $x = K^2\langle l^2\rangle_e/6$, where $\langle l^2\rangle_e$ is the equilibrium mean-square end-to-end length. The suitably normalized coefficients of segment j in normal mode k are R_{jk}. For free-draining chains, and to a good approximation for nondraining chains

$$\begin{aligned} R_{jk} &= \sin \pi k[(j/Z) - (1/2)] \quad k \text{ odd} \\ &= \cos \pi k[(j/Z) - (1/2)] \quad k \text{ even} \end{aligned} \tag{3}$$

The relaxation time of the kth normal mode is τ_k, which for the long-wavelength modes ($k \ll Z$) of free-draining chains equals

$$\tau_k = \langle l^2\rangle_e / 3\pi^2 k^2 D \tag{4}$$

To display more explicitly the effect of the internal relaxations on the autocorrelation function, one may expand the last term in the first exponential in eq 2, obtaining

$$P(x, t) = \exp(-DK^2 t) \sum_{N=0}^{\infty} P_N(x, t) \tag{5}$$

where

$$P_N(x, t) = \sum_{l=0}^{Z} \sum_{j=0}^{Z} \alpha_l \alpha_j \exp\left[-(2x/\pi^2) \sum_{k=1}^{Z} k^{-2}(R_{jk}^2 + R_{lk}^2)\right] \frac{1}{N!}\left[(4x/\pi^2) \sum_{k=1}^{Z} k^{-2} R_{\ell k} R_{jk} e^{-t/\tau_k}\right]^N \tag{6}$$

The spectral density $S(K,\omega)$ of scattered light whose frequency is shifted by ω from the incident light is

$$S(K, \omega) = (1/2\pi) \int P(K, t) \exp(-i\omega t) dt \tag{7}$$

The development up to this point has been quite general. It is now customary to assume that all the segmental polarizabilities are identical; $\alpha_l = \alpha_j = \alpha/Z$, where α is the molecular polarizability. However, we shall investigate in this paper the consequences of setting all of the excess segmental polarizabilities, except one or two, to zero.

If only one of the segments, say the mth, has nonzero polarizability, then eq 6 becomes

$$P_N(x, t) = \alpha_m^2 \times \exp\left[-(4x/\pi^2) \sum_{k=1}^{Z} k^{-2} R_{mk}^2\right] (N!)^{-1} \left[(4x/\pi^2) \sum_{k=1}^{Z} k^{-2} R_{mk}^2 e^{-t/\tau_k}\right]^N \tag{8}$$

Utilizing the trigonometric identities

$$\left\{\begin{matrix} \sin^2 \\ \cos^2 \end{matrix}\right\} u = \frac{1}{2}(1 \pm \cos 2u) \tag{9}$$

and

$$\cos(u - v) = \cos u \cos v + \sin u \sin v \tag{10}$$

we see that

$$R_{mk}^2 = \frac{1}{2}[1 + \cos(2\pi k m/Z)] \tag{11}$$

The first summation in eq 8 may now be evaluated if the upper limit is extended from Z to ∞.[8]

$$(4x/\pi^2) \sum_{k=1}^{\infty} k^{-2} R_{mk}^2 = 2x(1/3 - (m/Z) + (m^2/Z^2)) \tag{12}$$

The contributions of the various terms in eq 5 to the total intensity of scattered light are obtained by evaluating eq 8 at $t = 0$. Using eq 12, we obtain

$$\begin{aligned} P_N(x) &\equiv P_N(x, 0) \\ &= \alpha_m^2 \exp[-2x(1/3 - (m/Z) + (m^2/Z^2))](N!)^{-1}[2x(1/3 - (m/Z) + (m^2/Z^2)]^N \end{aligned} \tag{13}$$

The total scattered intensity from all modes is proportional to

$$P(x) \equiv P(x, 0) = \alpha_m^2 \tag{14}$$

Thinking in terms of constructing such a polymer chain, it would certainly be most likely that the label be attached at the beginning or end of the chain ($m = 0$ or Z). In that case eq 13 becomes simply

$$\begin{aligned} P_N(x) &= \alpha_m^2 \exp(-2x/3)(N!)^{-1}(2x/3)^N \\ &= P_0(x)(N!)^{-1}(2x/3)^N \end{aligned} \tag{15}$$

where $P_0(x)$, the intensity of the purely translational mode, is

$$P_0(x) = \alpha_m^2 \exp(-2x/3) \tag{16}$$

The normalized intensities of the first four terms, as well as the intensity of scattering from higher terms, $P_s'(x) = P(x) - \Sigma_{i=0}^{3} P_i(x)$, are shown in Figure 1.

If, on the other hand, the label were attached in the middle of the chain, at $m = Z/2$, then

$$\begin{aligned} P_N(x) &= \alpha_m^2 \exp(-x/6)(N!)^{-1}(x/6)^N \\ &= P_0(x)(N!)^{-1}(x/6)^N \end{aligned} \tag{17}$$

where

$$P_0(x) = \alpha_m^2 \exp(-x/6) \tag{18}$$

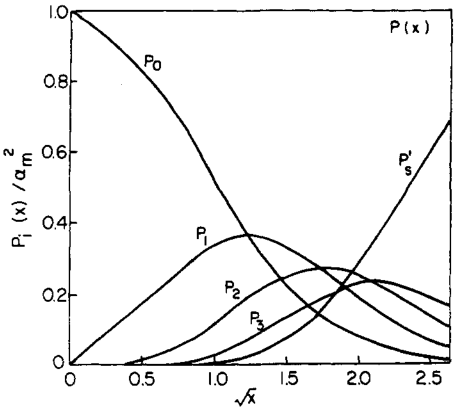

Figure 1. Normalized intensities of the first four terms $P_0(x)$, . . . , $P_3(x)$ in the expansion, eq 5, of the scattering autocorrelation function of a chain labeled at one end. Also plotted are the total intensity $P_s'(x)$ from terms higher than P_3.

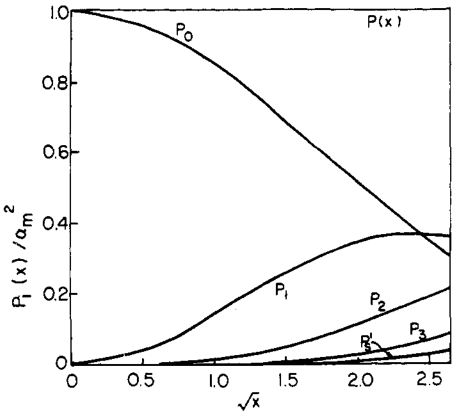

Figure 2. Same as Figure 1, for a chain labeled in the middle.

These intensities are plotted in Figure 2.

We may also imagine a label being conjugated to each end of the chain. In that case we let $\alpha_0 = \alpha_z = \alpha_m$, all others $\alpha_j = 0$, and eq 6 becomes

$$P_N(x, t) = 2\alpha_m^{\ 2} \exp(-2x/3)(N!)^{-1}(4x/\pi^2)^N \left\{\left[\sum_{k=1}^{Z} k^{-2} e^{-t/\tau_k}\right]^N + \left[\sum_{k=1}^{Z} (-1)^k k^{-2} e^{-t/\tau_k}\right]^N\right\} \quad (19)$$

Then we see that for the doubly end-labeled chain

$$P_0(x) = 2\alpha_m^{\ 2} \exp(-2x/3) \quad (20)$$

and

$$P_N(x) = 2\alpha_m^{\ 2} \exp(-2x/3)(N!)^{-1}(2x/3)^N[1 + (-1/2)^N] \quad (21)$$

while the integrated scattering is proportional to

$$P(x) = (2\alpha_m)^2(1 + e^{-x})/2 \quad (22)$$

The scattering intensities from the first four normal modes of the doubly labeled chain, and the scattering P_s' from higher modes, are shown in Figure 3.

It is evident that all of these expressions have the same basic form. The individual normal modes will emerge most clearly from $P_1(x,t)$, where cross terms between modes do not arise. In each case the kth mode has weight proportional to k^{-2}, except that only the even modes will appear in the middle labeled or doubly labeled chains, according to eq 11 and 19.

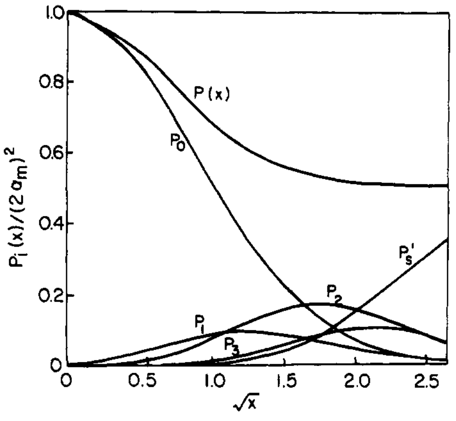

Figure 3. Same as Figure 1, for a chain labeled at both ends.

If the scattering is studied in the frequency rather than the time domain, eq 7 indicates that the spectrum corresponding to the pure translational mode will in each case be a single Lorentzian with half-width K^2D

$$S_0(x, \omega) = (2\pi)^{-1}P_0(x) \int \exp(-K^2Dt)\exp(-i\omega t)\mathrm{d}t$$
$$= (\pi)^{-1}P_0(x)\{K^2D/[\omega^2 + (K^2D)^2]\} \quad (23)$$

where $P_0(x)$ is given by eq 16, 18, or 20. The spectral distribution corresponding to P_1 will be a sum of Lorentzian line shapes, each with half-width equal to the sum of K^2D and a reciprocal relaxation time

$$S_1(x, \omega) = (\pi)^{-1}\sum_k \frac{(K^2D + \tau_k^{-1})}{\omega^2 + [K^2D + \tau_k^{-1}]^2} P_1(x, k) \quad (24)$$

where $P_1(x,k)$ is the coefficient of the kth term in eq 8 or 19. The sum in eq 24 runs over all k for chains labeled at one end and over even k for chains labeled in the middle or at both ends.

Discussion

We have analyzed the autocorrelation function and spectrum of light scattered from a dilute solution of flexible polymer chains, each of which has a small but strongly scattering label conjugated to one or both ends or to the middle. Scattering from the polymer itself is nulled by refractive index matching. The foregoing calculations indicate that the correlation function should be strongly affected by the long wavelength, intramolecular normal modes of motion. For example, it can be seen from Figure 1 that at $x^{1/2} = 1.22$, the intensities of scattering from the pure translational mode (P_0) and from a linear combination of internal modes (P_1) are equal to each other and to 0.368 of the total scattering intensity. This should be contrasted to the behavior of the chain with uniform scattering density,[3] for which the most important scattering intensity from internal modes (P_2) has a maximum only about 0.08 of the total scattering intensity at zero angle.

Furthermore, the contribution of intramolecular normal modes becomes more important for smaller chains (or at lower scattering angles) in the case analyzed here than in the uniform polymer case. As Pecora[3] points out, from the definition of x it may be shown that

$$\langle l^2\rangle_e^{\ 1/2} = 1.22 \times 10^{-5}x^{1/2} \text{ cm}$$

at $K = 2 \times 10^5$ cm^{-1} (corresponding roughly to 90° scattering of He–Ne laser light in a typical organic solvent). From Figures 1–3, it is seen that scattering from internal modes becomes important at $x^{1/2} \leq 1$, so that root-mean-square end-to-end lengths of about 1000 Å (compared to 2000 Å for uniform chains[3]) should be adequate to observe scattering from internal modes. Since $\langle l^2 \rangle_e^{1/2}$ is proportional to $Z^{1/2}$ for random coils, this means that degree of polymerization Z can be decreased fourfold.

Comparison of Figures 1–3 indicates that the most favorable case is that with the chain labeled at one end. However, the other labeling patterns are also predicted to give rise to significant scattering from internal modes. Since each weights the various normal modes differently, it would be desirable to employ all three labeling patterns to help unravel the many components of the scattering spectrum.

The experimental feasibility of this approach remains to be demonstrated. Hopefully, by using clusters of heavy metal atoms conjugated to organic moieties, as in strongly scattering markers used in electron microscopy, it will be possible to satisfy the dual criteria for the label of high scattering power and small size ($\ll \langle l^2 \rangle_e^{1/2}$). The latter criterion ensures that the hydrodynamic perturbation from the label is negligible. It must also be possible to find a solvent in which the polymer is soluble, which has the same refractive index as the polymer, and in which the label is stable. Work along these lines is in progress in our laboratory.

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A Distribution Function for Polymer Lengths[1]

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ABSTRACT: Taking cognizance of excluded volume effects in the theory of macromolecular configurations, a simple distribution function is proposed for describing end-to-end separations of flexible polymer chains. The function, when projected on one axis, is $C(1 + \beta^2x^2)\exp(-\beta^2x^2)$ where β is a parameter simply related to the mean-square end-to-end separation and C is a normalization constant. This simple modification of the Gaussian distribution provides excellent agreement with exact counts for short chains and moderately good agreement for reduced moments extrapolated to chains of infinitely long contour lengths. The one-component distribution function can easily be converted into a spherically symmetric radial distribution function. The tractability of the proposed formula is such that it should prove useful in describing actual high polymer length distributions.

Flexible polymer chains exhibit a great many distinguishable configurations, so it is quite natural that statistical methods are used for describing them. Mean-square end-to-end separations and average moments of inertia are among the quantities used to characterize flexible polymers, although the distributions of such lengths and moments would be even more useful.[2a] It is the purpose of this paper to present a simple distribution function that can be applied to polymer chain lengths. In establishing this function, we take limited cognizance of the excluded volume effect, a constraint that has generally proved to be frustrating in the theoretical treatment of polymer dimensions.[2b]

The distribution function that we shall describe is a one-parameter function which we believe will be useful for characterizing polymer molecules. The one parameter involved is the mean-square end-to-end distance, a quantity we should like, of course, to be able to predict. If, however, that average distance can be obtained or estimated by other means, then the distribution of lengths can be set forth with reasonable confidence.

In our discussions, we shall initially be concerned with components of lengths and their distribution in one dimension, let us say the x direction of a Cartesian coordinate system. When work on this subject was first initiated by numerous investigators years ago, there was a natural disposition to assume a Gaussian distribution, which would be correct were it not for the effect of excluded volume which precludes double occupancy of any sites in space. A Gaussian distribution is readily derived from the completely random walk model which is often used as a first approximation for describing a polymer chain.[3,4] On the other hand, a better description of a flexible polymer is a non-self-intersecting random walk or string of beads, a model that implies a volume constraint sufficient to render non-Gaussian the distribution of component lengths along some axis.

If $F(x)\mathrm{d}x$ is the probability that a polymer chain possesses an x component of end-to-end separation in the range x to $x + \mathrm{d}x$, then it can be shown for non-self-intersecting chains that[5,6]

$$(\mathrm{d}^2F/\mathrm{d}x^2)_{x=0} = 0 \tag{1}$$

To derive eq 1, it is only necessary to assume spherical symmetry for the three dimensional distribution and to stipulate that the end of a polymer chain cannot occupy the same site as its beginning. Spherical symmetry is reasonable to expect for long chains and the noncoincidence of the beginning and end of the chain is inherent in the excluded volume constraint. Since the Gaussian function does not satisfy eq 1, it appears that requiring the second derivative of F to vanish for $x = 0$ may lead to a better description.

To develop a suitable distribution function, we shall modify the Gaussian by multiplying it by a polynomial. The simplest symmetrical, even powered, polynomial that comes to mind consistent with eq 1 is a two-term quadratic consisting of a constant and a second degree term. Hence we shall write

$$F(x) = C(1 + \beta^2x^2)\exp(-\beta x^2) \tag{2}$$