nearly the same $LiClO_4$ concentrations. The conductivity was higher in the PEUU-3000·$LiClO_4$ complex at the same concentration, whereas profiles of the temperature dependence were similar. The latter fact is also confirmed by the similar WLF parameters, as shown in Table IV. In this case the activation energy for n is considered to be the same. Therefore the difference in the conductivity is assumed to be determined by that in μ. T_g's of the PEUU-2000·$LiClO_4$ complexes were higher than those of the PEUU-3000·$LiClO_4$ complexes. The higher T_g's in the PEUU-2000·$LiClO_4$ complexes result in the lower μ values.

References and Notes

(1) (a) Department of Chemistry. (b) Department of Electrical and Electronic Engineering.

(2) For example: Wang, C. B.; Cooper, S. L. *Macromolecules* **1983,** *16,* 775.

(3) Santaniello, E.; Manzocchi, A.; Sozzani, P. *Tetrahedron Lett.* **1979,** *47,* 4581.

(4) Moacanin, J.; Cuddihy, E. F. *J. Polym. Sci., Part C* **1966,** *14,* 313.

(5) Wright, P. V. *Br. Polym. J.* **1975,** *7,* 319.

(6) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In "Fast Ion Transport in Solids"; Vashishta, P., Mundy, J. N., Shenoy, G. K., Eds.; North-Holland Publishing Co.: Amsterdam, 1979; pp 131–136.

(7) Dupon, R.; Papke, B. L.; Ratner, M. A.; Whitmore, D. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982,** *104,* 6247.

(8) Killis, A.; LeNest, J. F.; Cheradame, H.; Gandini, A. *Makromol. Chem.* **1982,** *183,* 2835.

(9) Watanabe, M.; Nagaoka, K.; Kanba, M.; Shinohara, I. *Polym. J. (Tokyo)* **1982,** *14,* 877.

(10) Watanabe, M.; Ikeda, J.; Shinohara, I. *Polym. J. (Tokyo)* **1983,** *15,* 65.

(11) Watanabe, M.; Ikeda, J.; Shinohara, I. *Polym. J. (Tokyo)* **1983,** *15,* 175.

(12) Watanabe, M.; Sanui, K.; Ogata, N.; Kobayashi, T.; Ohtaki, Z. *J. Appl. Phys.* **1985,** *57,* 123.

(13) Robitaille, C.; Prud'homme, J. *Macromolecules* **1983,** *16,* 665.

(14) Sung, C. S. P.; Smith, T. W.; Sung, N. H. *Macromolecules* **1980,** *13,* 117.

(15) Cohen, H. *J. Chem. Soc.* **1952,** 4282.

(16) (a) Macdonald, J. R. *J. Chem. Phys.* **1973,** *58,* 4982. (b) Macdonald, J. R. *J. Chem. Phys.* **1974,** *61,* 3977.

(17) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955,** *77,* 3701.

(18) Sasabe, H.; Saito, S. *Polym. J. (Tokyo)* **1972,** *3,* 624.

Calculation of the Fourth-Order Correlation Function of a Polymer Coil (As Measured by Cross-Correlation Light Scattering)

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ABSTRACT: We calculate some properties of $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$, the normalized fourth-order correlation function of the electric field amplitude of light scattered by a *single* isolated polymer coil. This quantity can be measured in an experiment where the light intensities scattered in two directions (defined by scattering vectors **K** and **Q**) by a *small volume* of a *dilute* polymer solution are cross correlated. As expected $f^{(4)}$, which describes conformational fluctuations of the polymer coil, contains more information than the second-order function usually measured in dynamic light scattering experiments. We consider both the amplitude $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ of the conformational fluctuations and their initial time dependence $\lim_{\tau\to 0}\,[\mathrm{d}f^{(4)}(\mathbf{K},\mathbf{Q},\tau)/\mathrm{d}\tau]$. This work provides a theoretical basis for a recent experiment of Kam and Rigler (*Biophys. J.* **1982,** *39,* 7–13) as well as suggesting some new experiments.

I. Introduction

In this paper we consider the theory underlying an experiment[1] in which fluctuations in the light scattered by a small volume of a dilute solution of random-coil polymers are analyzed by a cross-correlation technique. In this situation, where the volume contains on average a relatively small number of macromolecules, conformational fluctuations (i.e., changes in the instantaneous shape) of the polymer coils modulate the "number fluctuation term" (see below) in the temporal correlation function of the scattered light intensity. As we will show explicitly in section II, the function describing these conformational fluctuations (eq 2.17) is essentially the *correlation function of the intensity scattered by a single polymer coil* or, equivalently, the *fourth-order* correlation function of the scattered light field. Thus this type of experiment provides, in principle at least, rather more detailed information on the nature and time evolution of the conformational fluctuations than does a more conventional large-scattering-volume dynamic light scattering experiment, which gives only *second-order* properties of the scattered field.

We start here with a qualitative description of the principles underlying the experiment; quantitative details are given in section II. Consider first the familiar situation where coherent light is scattered by a large volume V of a solution containing many (noninteracting) rigid spherical particles. As is well-known the intensity scattered by such a solution fluctuates in time due to the changing interference between the light fields scattered by different particles. If D_T is the translational diffusion constant of the particles and K the magnitude of the scattering vector, the typical fluctuation time of the intensity is $(D_TK^2)^{-1}$, roughly the time taken by a particle to diffuse a distance (K^{-1}) equal to the reciprocal of the scattering vector. Furthermore the fluctuations in the scattered light field are only correlated within one "coherence solid angle", $\sim(\lambda/V^{1/3})^2$, where λ is the light wavelength. Thus if two detectors are set in the far field and separated by an angle greater than $\lambda/V^{1/3}$, no cross correlation is observed between their outputs. If the particles are nonspherical and/or flexible, then rotational motions and conformational changes can contribute to fluctuations in the scattered intensity especially when $KR_G \gtrsim 1$, R_G being the particle's radius of gyration. In many cases, however, the time constants of the interference intensity fluctuations caused by rotational and conformational motions are sim-

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ilar to those caused by translational diffusion and it can be difficult to separate the different contributions to the measured temporal intensity correlation function.

Even today most dynamic light scattering experiments are performed in this large-scattering-volume limit. However, some 12 years ago Schaefer and Berne[2] recognized that if a focused laser beam and high-resolution detection optics were used so that the scattering volume V seen by the detector was small enough to contain, on average, a relatively small number of particles, then fluctuations in this number would cause measurable fluctuations in the scattered intensity.[3] The intensity fluctuations caused by these "number fluctuations" differ from those caused by interference effects in several important respects. First they are much slower since it takes a time $\sim V^{2/3}/D_T$ for a particle to diffuse across the scattering volume V and thereby change the number of particles in V; generally $V^{1/3} \gg K^{-1}$ so that the time constant $V^{2/3}/D_T$ of number fluctuations (typically of order seconds) is much longer than that $(D_T K^2)^{-1}$ of interference fluctuations (typically microseconds to milliseconds). Second the intensity fluctuations caused by number fluctuations are correlated over much larger solid angles than those caused by interference fluctuations. In the case of rigid spherical particles, for example, after averaging over the rapid interference fluctuations, the intensity scattered in any direction is proportional to the instantaneous number of particles seen by the detector. Thus number fluctuation correlations will be observed between the signals registered by well-separated detectors (provided these both observe the same scattering volume). Both these properties of number fluctuations allow one to distinguish them experimentally from interference effects.

Following Schaefer and Berne's[2] work on colloid statistics, the use of number fluctuation light scattering has been exploited in several areas:[3] the study of motile microorganisms,[4] the measurement of macromolecular weights,[5] and in the technique of fluorescence correlation spectroscopy.[6] It was also soon recognized[3,7,8] that, if small volumes of solutions containing nonspherical and/or flexible particles were studied by light scattering, rotational and conformational motions of the particles, which of course modulate the intensity scattered by a single particle, would also modulate the intensity fluctuations associated with number fluctuations. The study of such motions by number fluctuation light scattering has at least two potential advantages compared to conventional dynamic light scattering. First, because number fluctuations evolve slowly it is easy to separate experimentally the effects of rotations and configurational motions from translational diffusion of the particle's center of mass. Second, as noted above and shown explicitly in section II, whereas conventional dynamic light scattering is described entirely by *second-order* properties of the scattered light field, the modulation of the number fluctuation term in the intensity (cross) correlation function is determined by *fourth-order* properties. Generally a fourth-order correlation function will contain more information about the process under study than the second-order function. However, as we will see (section III onward), this extra information comes at a cost since the theory of the fourth-order correlation function is considerably more complicated than that, itself not trivial, of the second-order function.

At least three experiments have been reported in which modulation of the number fluctuations is observed. Griffin and Pusey[8] studied rotational motions of the rod-shaped particle tobacco mosaic virus. For several reasons[8] only qualitative agreement between experiment and theory was obtained. Rarity and Randle[9] observed rotational diffusion of doublets in a suspension of aggregating colloidal spheres and found good agreement between experiment and theory. Of relevance here is the experiment of Kam and Rigler,[1] who studied, among other things, conformational motions of DNA polymers. While their experimental results provided a convincing demonstration of the cross-correlation technique applied to flexible macromolecules, Kam and Rigler did not give a detailed theory. The aim of the present paper is to fill this gap as well as to investigate further the potential of cross-correlation light scattering experiments in the study of polymer solutions.

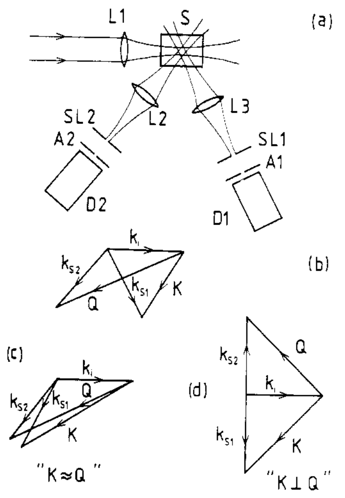

Figure 1. (a) Plan view of a typical cross-correlation light scattering experiment. The various components are identified and discussed in the text. (b) Scattering vectors $\mathbf{K}$ and $\mathbf{Q}$ for the configuration of Figure 1a; $\mathbf{k}_i$ is the propagation vector of the incident light, $\mathbf{k}_{S1}$ and $\mathbf{k}_{S2}$ are propagation vectors of the light scattered to detectors D_1 and D_2, respectively. (c) "$\mathbf{K} \approx \mathbf{Q}$" configuration; the detectors are separated by a small angle to render negligible the effect of interference fluctuations. (d) "$\mathbf{K} \perp \mathbf{Q}$" configuration.

Figure 1a shows, in outline, a plan view of a typical experiment of the type under consideration here. The incident laser light beam passes through lens L1 (frequently a microscope objective) to form a diffraction-limited waist in the sample S. Similar lenses, L2 and L3, form diffraction-limited images of this focal region on narrow slits SL1 and SL2. Thus the scattered light passing through these slits originates from the same small scattering volume V. This scattered light is collected by detectors D1 and D2 (typically photon-counting photomultiplier tubes) through detection apertures A1 and A2. The outputs of D1 and D2 are then fed to a digital correlator which constructs their normalized intensity cross-correlation function (eq 2.10). Figure 1b defines the scattering vectors $\mathbf{K}$ and $\mathbf{Q}$ associated with the scattering geometry of Figure 1a. In parts c and d of Figure 1 we note, for future reference, two experimental configurations which are useful and relatively easy to set up. In the "$\mathbf{K} \approx \mathbf{Q}$" configuration[1] (Figure 1c) the scattered light is most easily collected by a single lens–slit combination and then divided by a beam splitter. The detectors observing the two scattered beams obtained in this way can then be separated by more than the coherence angle (to render negligible interference fluctuations) but will still be at approximately the same scattering angle (i.e., $\mathbf{K} \approx \mathbf{Q}$). In the "$\mathbf{K} \perp \mathbf{Q}$" ($\mathbf{K}\cdot\mathbf{Q} = 0$) configuration[8] (Figure 1d) the two detectors are set at 90° either side of the incident beam. In all cases the magnitudes of $\mathbf{K}$ and $\mathbf{Q}$ can be changed somewhat, without altering the scattering geometry, simply by varying the wavelength of the incident laser light.

The paper is arranged as follows. In section II results of the quantitative light scattering theory are given. We also describe how the quantity of interest here, $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ (eq 2.17), the cross-correlation function of the intensity scattered by a *single polymer coil*, can be obtained from $g^{(2)}(\mathbf{K},\mathbf{Q},\tau)$, the measured cross-correlation function of the intensity scattered from a *small volume of the polymer solution* (here τ is the correlation delay time). Sections III–VI are then devoted to evaluating $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$. In section III the zero-time amplitude $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ of the cross correlation is calculated for a many-unit random-flight (Gaussian) coil; various limiting cases are considered. In section IV $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ is calculated in the low $\mathbf{K},\mathbf{Q}$ limit (KR_G, $QR_\mathrm{G} \ll 1$) for a polymer coil having arbitrary statistical properties. In sections V and VI we turn to dynamic properties, concentrating on the initial decay (or first cumulant) of $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ (section V) and a characteristic decay rate Γ derived from this initial decay (section VI). If (Oseen) hydrodynamic interactions are included we have so far only been able to evaluate Γ for a Gaussian coil in a few limiting cases. However, for a free-draining coil (no hydrodynamic interactions) the short-time dynamics can be obtained for all values of $\mathbf{K}$ and $\mathbf{Q}$. Finally in section VII we summarize and discuss the results.

While we will not consider experimental procedures in detail it should be admitted that experiments of the type considered here are much more difficult to perform than conventional dynamic light scattering experiments. High-resolution, stable optics are required. Because dilute solutions are necessary to provide a relatively small number of polymers in the scattering volume, the intensity of light scattered by the solvent alone can be comparable to or greater than that scattered by the polymers. This results in a low signal-to-noise ratio; consequently long counting times (of the order of hours) can be necessary for good statistics in the experimental data. Furthermore, other complications such as diffraction spreading of the scattered light, which are neglected in the theoretical development of section II, may in fact have appreciable effects in practice. Despite these difficulties, the new information potentially provided by these experiments seems to justify this work (for the present, at least).

Finally, for completeness, we mention that cross-correlation light scattering techniques, first discussed in detail by Cantrell,[10] have already been used in a quite wide range of experimental applications[11-14] rather different from those considered here.

II. Light Scattering Theory

The theory of dynamic light scattering from a small volume of a solution of distinct particles or macromolecules has been considered by several authors.[1-6,8,9,15] Here, with some adaptation to the problem at hand, we simply state the assumptions entering the theory and the results obtained. We then discuss the physical content of these results.

The assumptions are as follows:

(i) The volume V_T of the sample contains a large number M_T of identical, linear, random-coil polymers, each viewed as N beads connected by springs. The solution is dilute enough that correlations between the positions of the centers of mass of different polymer molecules can be neglected.

(ii) Two detectors observe light scattered from the same scattering volume V ($\approx\sigma^3$, where $\sigma \approx V^{1/3}$), much smaller than the total sample volume V_T (see Figure 1). The amplitude of the light field illuminating V is $b[\mathbf{r}]$, determined by the profile of the incident laser beam and by the characteristics of the optics collecting the scattered light. Frequently $b[\mathbf{r}]$ is taken to be a "three-dimensional Gaussian" of radius σ;[3,4,15] i.e.

$$b[\mathbf{r}] = \exp[-r^2/\sigma^2] \tag{2.1}$$

where the coordinate origin is at the center of V. In fact, provided inequality 2.2 (below) is satisfied, it is not necessary for the development of this paper to assume a particular form for $b[\mathbf{r}]$; (2.1) is chosen simply for convenience.

(iii) The polymer coils are small enough (or V large enough) that $b[\mathbf{r}]$ does not vary significantly over the spatial extent of a single coil; i.e.

$$V^{1/3} \approx \sigma \gg R_\mathrm{G} \tag{2.2}$$

where R_G is the coil's average radius of gyration. We also assume that σ is much larger than the reciprocals of the scattering vectors $\mathbf{K}$ and $\mathbf{Q}$; i.e.

$$\sigma \gg K^{-1},\ Q^{-1} \tag{2.3}$$

For typical values $\sigma \gtrsim 2\ \mu\mathrm{m}$, $R_\mathrm{G} = 0.2\ \mu\mathrm{m}$, and K, $Q \approx 20\ \mu\mathrm{m}^{-1}$, inequalities 2.2 and 2.3 are quite well satisfied.

(iv) Although V is small, the illuminating light is assumed to be "plane wave" within V.

With use of these assumptions, the amplitude $E(K,t)$ of the light field scattered at time t in the direction defined by scattering vector $\mathbf{K}$ (Figure 1b) can be written

$$E(K,t) = \sum_{\alpha=1}^{M_\mathrm{T}} b[\mathbf{r}_\alpha(t)] \exp[i\mathbf{K}\cdot\mathbf{r}_\alpha(t)]a_\alpha(K,t) \tag{2.4}$$

Here $\mathbf{r}_\alpha(t)$ is the instantaneous position of the center of mass of coil α and $a_\alpha(K,t)$ is the field amplitude scattered by coil α:

$$a_\alpha(K,t) = \sum_{i=1}^{N} \exp\{i\mathbf{K}\cdot[\mathbf{r}_{i\alpha}(t) - \mathbf{r}_\alpha(t)]\} = \exp[-i\mathbf{K}\cdot\mathbf{r}_\alpha(t)]\sum_{i=1}^{N}\exp[i\mathbf{K}\cdot\mathbf{r}_{i\alpha}(t)] \tag{2.5}$$

where $\mathbf{r}_{i\alpha}(t)$ is the instantaneous position of the ith bead in coil α. In eq 2.4 and 2.5 constants that disappear ultimately through normalization (see below) have been omitted.

The intensity received by a single detector is

$$I(K,t) \equiv |E(K,t)|^2 \tag{2.6}$$

Thus, with use of eq 2.5 and the assumptions listed above, the average scattered intensity becomes

$$\langle I(K,t)\rangle = M_\mathrm{T}\langle b^2[\mathbf{r}(t)]\rangle\langle|a(K,t)|^2\rangle \tag{2.7}$$

where the angular brackets represent an (ensemble) average over all possible positions of the molecules in V_T and over all molecular configurations. Thus, for example,

$$\langle b^2[\mathbf{r}]\rangle = \frac{1}{V_\mathrm{T}}\int \mathrm{d}^3r\ b^2[\mathbf{r}] \tag{2.8}$$

The last factor in (2.7) can be written

$$\langle|a(K)|^2\rangle = N^2P(K) \tag{2.9}$$

where $P(K)$ is the usual normalized ($P(0) = 1$) single-coil form factor. In eq 2.7 (as in eq 2.14 and 2.17 below) we have dropped the subscript α since, for noninteracting identical molecules, the average intensity and intensity correlation functions depend only on properties of a single coil.

The quantity measured in a cross-correlation light scattering experiment is the normalized temporal correlation function of the intensities received at two detectors whose positions are described by scattering vectors $\mathbf{K}$ and $\mathbf{Q}$ (Figure 1b), defined by

$$g^{(2)}(\mathbf{K},\mathbf{Q},\tau) \equiv \frac{\langle I(\mathbf{K},0)I(\mathbf{Q},\tau)\rangle}{\langle I(\mathbf{K})\rangle\langle I(\mathbf{Q})\rangle} \tag{2.10}$$

Here τ is the correlation delay time. By following the procedures outlined in ref 2–4 and 15, using assumptions i–iv above, we get

$$g^{(2)}(\mathbf{K},\mathbf{Q},\tau) = 1 + h^2(\mathbf{K}-\mathbf{Q})|f^{(2)}(K,\tau)|^2 + \frac{1}{\langle M\rangle} g_{\mathrm{NF}}(\tau) f^{(4)}(\mathbf{K},\mathbf{Q},\tau) \tag{2.11}$$

Equation 2.11 provides a quantitative basis to the qualitative discussion of section I. The first term in (2.11) is the "background" to which $g^{(2)}$ must decay at long times. The second term is the usual "interference" term observed in large-scattering-volume experiments. The function $h(\mathbf{K} - \mathbf{Q})$ is sharply peaked around $\mathbf{K} = \mathbf{Q}$ ($h(0) = 1$) and decays to zero when $|\mathbf{K} - \mathbf{Q}|V^{1/3} \gg 1$; it describes the coherence solid angle of the interference fluctuations and is defined by

$$h(\mathbf{K}-\mathbf{Q}) = \frac{\langle b^2(\mathbf{r}) \exp[i(\mathbf{K}-\mathbf{Q})\cdot\mathbf{r}]\rangle}{\langle b^2(r)\rangle} \tag{2.12}$$

For a Gaussian illumination profile[15] (eq 2.1)

$$h(\mathbf{K}-\mathbf{Q}) = \exp(-|\mathbf{K}-\mathbf{Q}|^2\sigma^2/8) \tag{2.13}$$

Thus h^2 decays to $1/e$ when $|\mathbf{K} - \mathbf{Q}|\sigma = 2$. For $\sigma = 2$ μm and a scattering angle of 90° ($K \approx 20$ μm^{-1}) this corresponds to a detector separation of about $^1/_{10}$ radian or 6°. Therefore, if the detectors are separated by more than about 6° (or less for larger scattering volumes), the second term in (2.11) is negligible; essentially this term is only observed in the "autocorrelation" configuration with the two detectors optically superimposed. The usual second-order function describing the interference fluctuations is

$$f^{(2)}(K,\tau) \equiv F^{(2)}(K,\tau)/F^{(2)}(K,0) \tag{2.14a}$$

where

$$F^{(2)}(K,\tau) \equiv \langle a(K,0)a^*(K,\tau) \exp\{i\mathbf{K}\cdot[\mathbf{r}(0) - \mathbf{r}(\tau)]\}\rangle \tag{2.14b}$$

With use of eq 2.5 we see that generally $F^{(2)}(K,\tau)$ depends on the correlated motion of pairs of beads within the same coil; in the low-K limit, $|a(K,t)| \rightarrow N$ (eq 2.5) and $F^{(2)}(K,\tau)$ simply describes the average motion of the center of mass of a single molecule.

The third term in (2.11) reflects (slow) fluctuations in the number of molecules in the scattering volume V, modulated by (rapid) fluctuations in the scattering cross section of a single molecule. $\langle M\rangle$ is an appropriate defined average number of molecules in V and the number fluctuation correlation function $g_{\mathrm{NF}}(\tau)$ decays from one to zero with characteristic time roughly equal to the time take by a single coil to diffuse a distance $V^{1/3}$, i.e., across V. For a three-dimensional Gaussian volume (eq 2.1)

$$\langle M\rangle = M_{\mathrm{T}}(\pi^{3/2}\sigma^3/V_{\mathrm{T}}) \tag{2.15}$$

and

$$g_{\mathrm{NF}}(\tau) = (1 + 4D_{\mathrm{T}}\tau/\sigma^2)^{-3/2} \tag{2.16}$$

where D_{T} is the translational diffusion coefficient of the polymer molecule.[3] The quantity of interest for the remainder of this paper is $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$, defined by

$$f^{(4)}(\mathbf{K},\mathbf{Q},\tau) \equiv \frac{F^{(4)}(\mathbf{K},\mathbf{Q},\tau)}{\langle|a(K,0)|^2\rangle\langle|a(Q,0)|^2\rangle} \tag{2.17a}$$

where

$$F^{(4)}(\mathbf{K},\mathbf{Q},\tau) \equiv \langle|a(\mathbf{K},0)|^2|a(\mathbf{Q},\tau)|^2\rangle \tag{2.17b}$$

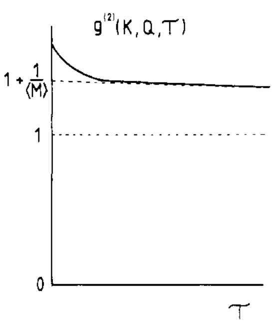

Figure 2. Typical measured normalized intensity cross-correlation function $g^{(2)}(\mathbf{K},\mathbf{Q},\tau)$. The lower dashed line represents the background term (the first term in eq 2.11); the upper dashed line is $1 + \langle M\rangle^{-1}g_{\mathrm{NF}}(\tau)$, the correlation function which would reflect number fluctuations in a suspension of rigid spherical particles; the solid line shows the modulation of the number fluctuation term due to conformational fluctuations of aspherical or flexible particles.

With use of eq 2.5, 2.6, and 2.17 we see that $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ can be identified as the function, normalized to its *long-time* value ($f^{(4)}(\mathbf{K},\mathbf{Q},\infty) = 1$), describing the correlation between intensities scattered by a *single coil* in directions defined by the scattering vectors $\mathbf{K}$ and $\mathbf{Q}$ (Figure 1b). It is a *fourth-order* correlation function depending purely on the *relative* positions and motions of four beads within the same coil. Thus it describes "conformational fluctuations" and *does not* reflect center-of-mass motions. These considerations substantiate quantitatively claims made in section I.

We conclude this section with a few comments on the determination of $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ from an experimental measurement. As mentioned above, after employing standard normalization procedures we obtain from the correlator the function $g^{(2)}(\mathbf{K},\mathbf{Q},\tau)$ (eq 2.11). If the two detectors are separated spatially by more than the coherence angle (eq 2.13 and subsequent discussion), the second term in (2.11) can be neglected. For the third term to be measurable the average number $\langle M\rangle$ of particles in the scattering volume V must not be too large (hence the requirements of dilute solution and small V). For this case a typical correlation function $g^{(2)}(\mathbf{K},\mathbf{Q},\tau)$ (for spatially separated detectors) is sketched in Figure 2. After subtraction of the background term "1", we obtain simply the third term in (2.11) which consists of a slowly decaying number fluctuation component $\langle M\rangle^{-1}g_{\mathrm{NF}}(\tau)$ multiplied by the more rapidly decaying conformational fluctuation term $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$. With suitable choice of correlator sample time it is usually possible to observe both the whole rapid decay of $f^{(4)}$ and the initial slow decay of $\langle M\rangle^{-1}g_{\mathrm{NF}}$. The latter may appear essentially flat on this time scale, or it can be approximated by its initial decay (from eq 2.16)

$$\langle M\rangle^{-1}g_{\mathrm{NF}}(\tau) = \langle M\rangle^{-1}[1 - 6D_{\mathrm{T}}\tau/\sigma^2 + ...] \tag{2.18}$$

Division of the experimentally measured third term in (2.11) by (2.18) then yields the quantity of interest $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$.

III. Equal-Time Correlations for a Gaussian Coil

A. Calculation. Clearly an important quantity in a cross-correlation experiment is the amplitude $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ of the modulation of the number fluctuation term (the third term in eq 2.11). This quantity is a four-bead generalization of the form factor $P(K)$ (eq 2.9) and we now calculate it for a polymer coil assumed to have a Gaussian distribution of bead separations.

With use of eq 2.17b and 2.5 we get

$$F^{(4)}(\mathbf{K},\mathbf{Q},0) \equiv \langle |a(\mathbf{K})|^2|a(\mathbf{Q})|^2\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\exp[i\mathbf{Q}\cdot(\mathbf{r}_k - \mathbf{r}_l)]\rangle \quad (3.1)$$

In eq 3.1 the sums are unrestricted in the sense that, if the beads are numbered from one end of the chain to the other, beads i, j, k, and l can appear in any order. To evaluate eq 3.1 it is convenient to consider separately the 4! = 24 possible rankings of i, j, k, and l. There are, in fact, three generic configurations (sketched in Figure 3), each containing eight of the possible orderings:

(i) Segments (i,j) and (k,l) are completely separate (Figure 3a). Examples are $i > j > k > l$, $j > i > k > l$, $l > k > j > i$, etc.

(ii) Segments (i,j) and (k,l) overlap; i.e., they contain a common subsegment (Figure 3b). Examples are $i > k > j > l$, $j > k > i > l$, etc.

(iii) One of the two segments (i,j) or (k,l) is completely contained within the other, e.g., $i > k > l > j$, $k > i > j > l$, etc. (Figure 3c).

After the average over a Gaussian distribution of bead separations (see below) it turns out that all eight contributions of type i are identical. However, contributions of type ii subdivide into four terms for which $i > j$, $k > l$ or $i < j$, $k < l$ and four terms for which $i > j$, $k < l$ or $i < j$, $k > l$. Contributions of type iii subdivide into four terms for which (i,j) lies within (k,l) and four terms for which (k,l) lies within (i,j); each group of four terms then subdivides further according to the same criteria as for the type ii terms (above). In total, therefore, for a Gaussian polymer coil there are seven distinct contributions to eq 3.1.

Details of the evaluation of eq 3.1 are given in the Appendix. As an example we consider here the term of type ii for which $i > k > j > l$ (Figure 3b), labeled J_2:

$$J_2 = \sum_{i=1}^{N}\sum_{k=1}^{i}\sum_{j=1}^{k}\sum_{l=1}^{j}\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\exp[i\mathbf{Q}\cdot(\mathbf{r}_k - \mathbf{r}_l)]\rangle \quad (3.2)$$

To proceed with the calculation we rewrite (3.2) in terms of independent (i.e., nonoverlapping) segments. From Figure 3b we clearly have

$$\mathbf{r}_i - \mathbf{r}_j = \mathbf{r}_i - \mathbf{r}_k + \mathbf{r}_k - \mathbf{r}_j \quad (3.3a)$$

$$\mathbf{r}_k - \mathbf{r}_l = \mathbf{r}_k - \mathbf{r}_j + \mathbf{r}_j - \mathbf{r}_l \quad (3.3b)$$

so that (3.2) becomes

$$J_2 = \sum_{i=1}^{N}\sum_{k=1}^{i}\sum_{j=1}^{k}\sum_{l=1}^{j}\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_k)]\rangle \times \langle \exp[i(\mathbf{K} + \mathbf{Q})\cdot(\mathbf{r}_k - \mathbf{r}_j)]\rangle\langle \exp[i\mathbf{Q}\cdot(\mathbf{r}_j - \mathbf{r}_l)]\rangle \quad (3.4)$$

where we have used the statistical independence of the three segments (i,k), (k,j), and (j,l) to partition the average. If the distribution of bead separations is Gaussian, we have, for example[16],

$$\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_k)]\rangle = \exp\left[-\frac{K^2a^2}{6}|i - k|\right] \quad (3.5)$$

where a is the average separation between neighboring beads on the chain. If the beads are connected by harmonic springs, eq 3.5 is exact for any value of K; however, in the "light scattering limit" (scattering vector × persistence length $\ll 1$), (3.5) is an excellent approximation for a random-coil polymer, whatever the form of the interbead potential.[16] Substitution of eq 3.5 into eq 3.4 gives

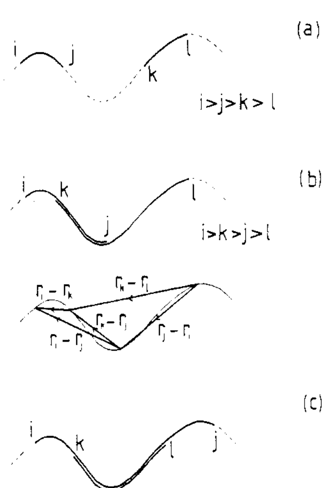

Figure 3. The three generic configurations used in the evaluation of $F^{(4)}(\mathbf{K},\mathbf{Q},0)$. (a) Segments (i, j) and (k, l), represented by solid lines, are separate. (b) Segments (i, j) and $k, l)$ contain a common subsegment ((k, j) in this case). The second part of (b) shows the decomposition of the vectors $\mathbf{r}_i - \mathbf{r}_j$ and $\mathbf{r}_k - \mathbf{r}_l$ into the vectors $\mathbf{r}_i - \mathbf{r}_k$, $\mathbf{r}_k - \mathbf{r}_j$, and $\mathbf{r}_j - \mathbf{r}_l$ which describe independent (nonoverlapping) segments (see eq 3.3). (c) Segment (k, l) is contained completely within segment (i, j).

$$J_2 = \sum_{i=1}^{N}\exp[-K^2a^2i/6]\sum_{k=1}^{i}\exp[-(Q^2 + 2\mathbf{K}\cdot\mathbf{Q})a^2k/6] \times \sum_{j=1}^{k}\exp[(K^2 + 2\mathbf{K}\cdot\mathbf{Q})a^2j/6]\sum_{l=1}^{j}\exp[Q^2a^2l/6] \quad (3.6)$$

While the summations in eq 3.6 could be performed analytically, it is simpler to realize that, in the light scattering limit $Ka \ll 1$, they can be converted to integrals; e.g.

$$\sum_{l=1}^{j}\exp(Q^2a^2l/6) \approx \int_0^j dl\,\exp(Q^2a^2l/6) \quad (3.7)$$

The results of evaluating eq 3.6 and the other terms in (3.1) are given in the Appendix. The final expression can be written in various forms, one of which is

$$F^{(4)}(\mathbf{K},\mathbf{Q},0) = N^4\left\{\frac{4}{XY} + \frac{4(X + Y)[2W^2 - (X + Y)^2]}{X^2Y^2(X + Y + W)(X + Y - W)} - \frac{4}{X^2(Y^2 - W^2)}\left[\frac{Y^2 + W^2}{Y^2 - W^2} + \frac{2W^2}{X(X - Y)}\right][\exp(-X) - 1] - \frac{4}{Y^2(X^2 - W^2)}\left[\frac{X^2 + W^2}{X^2 - W^2} - \frac{2W^2}{Y(X - Y)}\right][\exp(-Y) - 1] + \frac{4Y}{X^2(Y^2 - W^2)}\exp(-X) + \frac{4X}{Y^2(X^2 - W^2)}\exp(-Y) + \frac{2(X + Y + 2W)^2}{(X + W)^2(Y + W)^2(X + Y + W)^2}[\exp[-(X + Y + W)] - 1] + \frac{2(X + Y - 2W)^2}{(X + W)^2(Y - W)^2(X + Y - W)^2} \times [\exp[-(X + Y - W)] - 1]\right\} \quad (3.8)$$

Here

$$X = NK^2a^2/6 = K^2R_G^2 \quad (3.9a)$$

$$Y = NQ^2a^2/6 = Q^2R_G^2 \quad (3.9b)$$

and

$$W = 2N\mathbf{K}\cdot\mathbf{Q}a^2/6 = 2\mathbf{K}\cdot\mathbf{Q}R_G^2 \qquad (3.9c)$$

since, for a Gaussian coil, the average radius of gyration R_G is given by[16]

$$R_G^2 = Na^2/6 \qquad (3.10)$$

Note that

$$X + Y + W = |\mathbf{K} + \mathbf{Q}|^2 R_G^2 \qquad (3.9d)$$

and

$$X + Y - W = |\mathbf{K} - \mathbf{Q}|^2 R_G^2 \qquad (3.9e)$$

In order to obtain $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ (eq 2.17a) we need also $\langle |a(K)|^2\rangle$, which, from eq 2.9 and Debye's well-known result,[17,18] is

$$\langle |a(K)|^2\rangle = N^2P(K) = \frac{2N^2}{X^2}[\exp(-X) - 1 + X] \qquad (3.11)$$

Equations 3.8 and 3.11 can be programmed on a computer to provide $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ for arbitrary values of $\mathbf{K}$, $\mathbf{Q}$, and R_G. As it stands, however, eq 3.8 is not particularly transparent and it is instructive to consider, in the next sections, various limits.

B. $K = Q$ Limit. A limit of obvious interest is $f^{(4)}(K,K,0)$ obtained when $\mathbf{K} = \mathbf{Q}$, i.e., when the two detectors are optically superimposed. In reality they would have to be separated by a small angle in order to render negligible the second (interference) term in eq 2.11 (the $\mathbf{K} \approx \mathbf{Q}$ configuration, Figure 1c). The $\mathbf{K} \to \mathbf{Q}$ limit of (3.8) must be taken carefully because of the factors $X - Y$ and $X + Y - W$ in the denominators. Alternatively one can set $\mathbf{K} = \mathbf{Q}$ in eq 3.1 and perform the calculation from scratch. The result is

$$\langle |a(K)|^4\rangle = N^4\left[\frac{87}{2X^4} - \frac{30}{X^3} + \frac{8}{X^2} - \frac{392}{9X^4}\exp(-X) - \frac{40}{3X^3}\exp(-X) + \frac{1}{18X^4}\exp(-4X)\right] \qquad (3.12a)$$

Equation 3.12a has the limits

$$\lim_{KR_G\to 0} \langle |a(K)|^4\rangle = N^4\left(1 - \frac{2}{3}X + \frac{11}{30}X^2 + ...\right) \qquad (3.12b)$$

and

$$\lim_{KR_G\to\infty} \langle |a(K)|^4\rangle = \frac{8N^4}{X^2}\left(1 - \frac{15}{4X} + ...\right) \qquad (3.12c)$$

The quantity

$$f^{(4)}(K,K,0) \equiv \langle |a(K)|^4\rangle / \langle |a(K)|^2\rangle^2 \qquad (3.13)$$

obtained from (3.11) and (3.12) is plotted in Figure 4 as a function of $X = KR_G$. For comparison we also plot the form factor $P(KR_G)$ (eq 3.11).

We see that $f^{(4)}(K,K,0)$ starts at one as $KR_G \to 0$. This is not unexpected since, in this low-K limit, each polymer coil is effectively a point scatterer providing no modulation of the number fluctuation term (the third term in eq 2.11). At large KR_G ($KR_G \geqslant 10$), $f^{(4)}(K,K,0)$ saturates at a value of 2. This finding has a simple explanation. In this high KR_G limit, $R_G \gg K^{-1}$, the polymer coil is much larger than the typical length K^{-1} selected by a light scattering experiment. Thus the electric field $a(K,t)$ (eq 2.5) scattered by a single coil is composed of many independent contributions from regions of length K^{-1} along $\mathbf{K}$ and $a(K,t)$ itself becomes a complex Gaussian variable. The result $\lim_{KR_G\to\infty} f^{(4)}(K,K,0) = 2$ then simply represents the well-known factorization property of such a Gaussian variable. Thus the maximum modulation of the number fluctuations of a Gaussian polymer coil is a factor of 2.

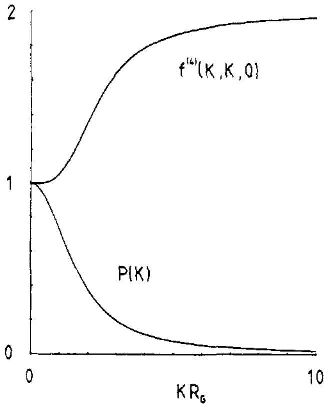

Figure 4. Upper curve: the amplitude $f^{(4)}(K,K,0)$ (eq 3.13) describing the modulation of number fluctuations by conformational motions of a Gaussian polymer coil for the "$\mathbf{K} \approx \mathbf{Q}$" scattering configuration; K is the scattering vector and R_G the radius of gyration. Lower curve: the usual particle form factor $P(K)$ (eq 3.11).

The low- and high-K limits of $f^{(4)}(K,K,0)$ can be obtained from eq 2.17, eq 3.12, and the expansions of eq 3.11

$$\lim_{KR_G\to 0} \langle |a(K)|^2\rangle^2 = N^4\left(1 - \frac{2}{3}X + \frac{5}{18}X^2 + ...\right) \qquad (3.14a)$$

and

$$\lim_{KR_G\to\infty} \langle |a(K)|^2\rangle^2 = \frac{4N^4}{X^2}\left(1 - \frac{2}{X} + ...\right) \qquad (3.14b)$$

giving

$$\lim_{KR_G\to 0} f^{(4)}(K,K,0) = 1 + \frac{4}{45}K^4R_G^4 + ... \qquad (3.15a)$$

and

$$\lim_{KR_G\to\infty} f^{(4)}(K,K,0) = 2\left(1 - \frac{7}{4K^2R_G^2} + ...\right) \qquad (3.15b)$$

C. $\mathbf{K}\cdot\mathbf{Q} = 0$. Another interesting limit is when $\mathbf{K}$ is perpendicular to $\mathbf{Q}$ i.e., $\mathbf{K}\cdot\mathbf{Q} = 0$ (Figure 1d). From the definition of $F^{(4)}(\mathbf{K},\mathbf{Q},0)$ (eq 3.1) we can immediately anticipate the result in this limit. For a Gaussian coil (viewed as a three-dimensional random-flight process of many units) the statistical behaviors of orthogonal dimensions are independent. Thus the average in eq 3.1 can be factorized:

$$F^{(4)}(\mathbf{K},\mathbf{Q},0)|_{\mathbf{K}\cdot\mathbf{Q}=0} = \sum_i\sum_j\langle\exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\rangle\sum_k\sum_l\langle\exp[i\mathbf{Q}\cdot(\mathbf{r}_k - \mathbf{r}_l)]\rangle = N^4P(K)P(Q) \qquad (3.16)$$

where eq 2.5 and 2.9 have been used. Thus, using eq 2.17a and 2.9, we get

$$f^{(4)}(\mathbf{K},\mathbf{Q},0)|_{\mathbf{K}\cdot\mathbf{Q}=0} = 1 \qquad (3.17)$$

implying no correlation between the intensities scattered by a single coil to two detectors in the $\mathbf{K}\cdot\mathbf{Q} = 0$ configuration. It is easily verified, after some algebra, that setting $W = 0$ ($\mathbf{K}\cdot\mathbf{Q} = 0$) in eq 3.8 leads to (3.16).

D. KR_G, $QR_G \to 0$. Tedious expansion of eq 3.8 and 3.11 in the limits of small X, Y, and W gives

$$\lim_{KR_G,QR_G\to 0} \langle |a(\mathbf{K})|^2 |a(\mathbf{Q})|^2\rangle = N^4\left[1 - \frac{X+Y}{3} + \left(\frac{X^2}{12} + \frac{XY}{9} + \frac{Y^2}{12} + \frac{W^2}{45}\right) + \ldots\right] \tag{3.18}$$

and

$$\lim_{KR_G,QR_G\to 0} \langle |a(K)|^2\rangle\langle |a(Q)|^2\rangle = N^4\left[1 - \frac{X+Y}{3} + \left(\frac{X^2}{12} + \frac{XY}{9} + \frac{Y^2}{12}\right) + \ldots\right] \tag{3.19}$$

Combining these two results in eq 2.17 gives, with use of eq 3.9,

$$\lim_{KR_G,QR_G\to 0} f^{(4)}(\mathbf{K},\mathbf{Q},0) = 1 + \frac{4(\mathbf{K}\cdot\mathbf{Q})^2 R_G^4}{45} + \ldots \tag{3.20}$$

a result consistent with eq 3.15a when $\mathbf{K}\cdot\mathbf{Q} = K^2$ and with eq 3.17 when $\mathbf{K}\cdot\mathbf{Q} = 0$.

E. KR_G, $QR_G \to \infty$. Further tedious algebra gives

$$\lim_{KR_G,QR_G\to\infty} \langle |a(\mathbf{K})|^2 |a(\mathbf{Q})|^2\rangle = \frac{4N^4}{XY} + N^4\frac{(X+Y-2W)^2}{(X-W)^2(Y-W)^2}P(X+Y-W) \tag{3.21}$$

which, on combination with

$$\lim_{KR_G,QR_G\to\infty} \langle |a(K)|^2\rangle\langle |a(Q)|^2\rangle = 4N^4/XY \tag{3.22}$$

gives

$$\lim_{KR_G,QR_G\to\infty} f^{(4)}(\mathbf{K},\mathbf{Q},0) = 1 + \frac{XY(X+Y-2W)^2}{4(X-W)^2(Y-W)^2}P(X+Y-W) \tag{3.23}$$

Here P is the single-coil form factor (eq 3.11) and, from eq 3.9

$$X + Y - W = (\mathbf{K} - \mathbf{Q})^2 R_G^2$$

Thus when $\mathbf{K} = \mathbf{Q}$ eq 3.23 agrees with (3.15b). Equation 3.23 is an intriguing result since it suggests that the form factor P of a large coil can be obtained from the cross-correlation coefficient $f^{(4)}$ when two initially superimposed detectors, set at large K and Q, are separated.

For future use (section VIB) we note that, in the extreme limit KR_G, $QR_G \to \infty$, $P(X + Y - W)$ is zero unless $\mathbf{K} \approx \mathbf{Q}$ so that (3.23) simplifies further to

$$\lim_{KR_G,QR_G\to\infty} f^{(4)}(\mathbf{K},\mathbf{Q},0) = 1 + P(X+Y-W) = 1 + P(|\mathbf{K} - \mathbf{Q}|) \tag{3.24}$$

IV. Equal-Time Correlations for Arbitrary Coil Statistics in the Limit KR_G, $QR_G \to 0$

The results obtained in section III apply only for a polymer coil having a Gaussian distribution of bead separations. It is well-known however that quantities such as the form factor $P(K)$ (eq 2.9) can be expanded as a power series in K^2 for arbitrary coil statistics; the coefficients in such an expansion depend on second, fourth, etc. moments of the mass distribution of the polymer. Such a procedure can be used to calculate the correlation coefficient $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ (eq 2.17) for arbitrary coil statistics. If we still assume the polymer molecule to be statistically isotropic, i.e., spherically symmetrical on average, we get, on expanding eq 3.1,

$$\langle |a(\mathbf{K})|^2 |a(\mathbf{Q})|^2\rangle = N^4\Bigg\{1 - \frac{1}{2N^2}\sum_{i,j}\langle(\mathbf{K}\cdot\mathbf{r}_{ij})^2\rangle - \frac{1}{2N^2}\sum_{k,l}\langle(\mathbf{Q}\cdot\mathbf{r}_{kl})^2\rangle + \frac{1}{24N^2}\sum_{i,j}\langle(\mathbf{K}\cdot\mathbf{r}_{ij})^4\rangle + \frac{1}{24N^2}\sum_{k,l}\langle(\mathbf{Q}\cdot\mathbf{r}_{kl})^4\rangle + \frac{1}{4N^4}\langle\sum_{i,j}(\mathbf{K}\cdot\mathbf{r}_{ij})^2\sum_{k,l}(\mathbf{Q}\cdot\mathbf{r}_{kl})^2\rangle + \ldots\Bigg\} \tag{4.1}$$

In (4.1) the summations are unrestricted and run from 1 to N and

$$\mathbf{r}_{ij} \equiv \mathbf{r}_i - \mathbf{r}_j \tag{4.2}$$

Similarly

$$\langle |a(K)|^2\rangle\langle |a(Q)|^2\rangle = N^4\Bigg\{1 - \frac{1}{2N^2}\sum_{i,j}\langle(\mathbf{K}\cdot\mathbf{r}_{ij})^2\rangle - \frac{1}{2N^2}\sum_{k,l}\langle(\mathbf{Q}\cdot\mathbf{r}_{kl})^2\rangle + \frac{1}{24N^2}\sum_{i,j}\langle(\mathbf{K}\cdot\mathbf{r}_{ij})^4\rangle + \frac{1}{24N^2}\sum_{k,l}\langle(\mathbf{Q}\cdot\mathbf{r}_{kl})^4\rangle + \frac{1}{4N^4}\sum_{i,j}\langle(\mathbf{K}\cdot\mathbf{r}_{ij})^2\rangle\sum_{k,l}\langle(\mathbf{Q}\cdot\mathbf{r}_{kl})^2\rangle + \ldots\Bigg\} \tag{4.3}$$

so that (eq 2.17)

$$f^{(4)}(\mathbf{K},\mathbf{Q},0) = 1 + K^2Q^2\{\langle(R_G^{\mathrm{I}})_K^2(R_G^{\mathrm{I}})_Q^2\rangle - \langle(R_G^{\mathrm{I}})_K^2\rangle\langle(R_G^{\mathrm{I}})_Q^2\rangle\} + \ldots \tag{4.4}$$

Here the quantity $(R_G^{\mathrm{I}})_K$, defined by

$$(R_G^{\mathrm{I}})_K^2 \equiv [R_G^{\mathrm{I}}(t)]_K^2 \equiv \frac{1}{2NK^2}\sum_{i,j}\{\mathbf{K}\cdot[\mathbf{r}_i(t) - \mathbf{r}_j(t)]\}^2 \tag{4.5}$$

is the component in the direction $\mathbf{K}/K$ of the instantaneous radius of gyration of the polymer coil[16] (i.e., the radius of gyration of the configuration of beads at time t). Thus the second term in eq 4.4 is a measure of the correlation between the instantaneous dimensions, in directions $\mathbf{K}/K$ and $\mathbf{Q}/Q$, of the polymer coil.

This realization allows the interesting possibility of studying by cross-correlation light scattering the instantaneous configuration of a polymer coil. Of course, for a Gaussian coil whose orthogonal dimensions are statistically independent, this instantaneous configuration is relatively uninteresting and it can be verified that, in this case, (4.4) reduces to (3.20). As mentioned in section IIIC this statistical independence of orthogonal dimensions stems from the picture of a Gaussian coil as an unrestricted random-flight process. Thus one might expect that for a non-Gaussian coil, such as a polymer in a good solvent where excluded volume effects are important and lead to coil expansion or swelling, instantaneous orthogonal dimensions would become correlated. Indeed one might expect a swollen coil to show a degree of "volume conservation" so that if such a coil happened at some instant to find itself more extended than average in the x direction, say, it would tend to be less extended than average in the y and z directions. Thus there would be an anticorrelation between instantaneous dimensions in orthogonal directions. Then if a solution of such polymers were studied by cross-correlation light scattering in the configuration where $\mathbf{K}$ and $\mathbf{Q}$ are perpendicular (see section I, Figure 1d), the second term in (4.4) would be negative, as opposed to zero (eq 3.17) for a Gaussian coil.

While there appear to be no direct theoretical predictions for the second term in (4.4) for swollen coils, some insight into its magnitude can be obtained from calculations performed some years ago by Stockmayer and coworkers.[19] These authors first constructed by Monte Carlo methods instantaneous configurations of *unrestricted* random-flight coils.[19a] They then determined the principal axes of inertia of each configuration and the average square components of the radius of gyration along these axes. After ranking these components in order of magnitude, they found, not surprisingly, significant correlations between them indicating considerable instantaneous asphericity of the polymer coils. It should be emphasized that these effects would not be measured for a Gaussian coil in the type of experiment considered here where we observe correlations between components of the instantaneous radius of gyration along *spaced-fixed* axes (determined by the geometry of the light scattering experiment) rather than along axes whose orientation is determined by the instantaneous configuration of each coil. (Indeed it is not easy to think up a real experiment which would measure the properties calculated by Stockmayer et al.) However, these authors went on to calculate the same properties for swollen polymer coils.[19b] They then found that the instantaneous asphericity of a swollen coil is greater, albeit only slightly, than that of an unrestricted random-flight coil. Thus this work suggests that a small effect of the type conjectured in the previous paragraph should be found experimentally.

Finally we note that it would presumably be a simple matter to estimate directly the term in braces in eq 4.4 from Monte Carlo simulations of a self-avoiding random-flight process, the simplest model for a swollen polymer coil.

V. Time-Dependence of the Fourth-Order Correlation Function

A. General Expression for the Initial Decay. In this paper we will limit our attention to what is probably the simplest quantity describing the dynamics of the cross-correlation function, namely its initial decay rate. For example, following the early work of Bixon[20] and Zwanzig,[21] Akcasu and co-workers[22] have calculated the initial decay $\lim_{\tau\to 0}\,[\mathrm{d}f^{(2)}(K,\tau)/\mathrm{d}\tau]$ of the second-order correlation function $f^{(2)}(K,\tau)$ (eq 2.14) for a variety of model polymer systems.[23]

By use of the Kirkwood–Riseman or Smoluchowski diffusion equation we have shown elsewhere[24] that the initial decay of the fourth-order correlation function $F^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ (eq 2.17b) is given by

$$\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\langle\mathbf{K}\cdot(\mathbf{D}_{ik}-\mathbf{D}_{il}-\mathbf{D}_{jk}+\mathbf{D}_{jl})\cdot\mathbf{Q}\times \exp[i\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_j)]\exp[i\mathbf{Q}\cdot(\mathbf{r}_k-\mathbf{r}_l)]\rangle \quad (5.1a)$$

$$= -4\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\langle\mathbf{K}\cdot\mathbf{D}_{ik}\cdot\mathbf{Q}\,\sin[\mathbf{K}\cdot(\mathbf{r}_i-\mathbf{r}_j)]\,\sin[\mathbf{Q}\cdot(\mathbf{r}_k-\mathbf{r}_l)]\rangle \quad (5.1b)$$

where the second form follows from the first on exchange of dummy indices. In (5.1), $\mathbf{D}_{ik}$ is the diffusion tensor which couples, through solvent-mediated hydrodynamic interactions, the motions of beads i and k. In polymer problems $\mathbf{D}_{ik}$ is usually taken to be the Oseen tensor,[25] which describes the interaction between point particles:

$$\mathbf{D}_{ik} = D_0\,\mathbf{1}\,\delta_{ik} + (1-\delta_{ik})\frac{k_{\mathrm{B}}T}{8\pi\eta r_{ik}}\left[\mathbf{1}+\frac{\mathbf{r}_{ik}\mathbf{r}_{ik}}{r_{ik}^2}\right] \quad (5.2)$$

In (5.2), D_0 is the diffusion constant of a single bead, $\mathbf{1}$ the unit dyadic, k_{B} Boltzmann's constant, T the temperature, η the shear viscosity of the solvent, and r_{ik} the magnitude of $\mathbf{r}_{ik}$ (eq 4.2)

$$r_{ik} \equiv |\mathbf{r}_{ik}| \quad (5.3)$$

Even for Gaussian coils, evaluation of eq 5.1 in the general case appears very difficult. However, some progress can be made (see the next two sections) in the limits of low and high scattering vector. In the hypothetical case of a free-draining coil in which hydrodynamic interactions are neglected, (5.1) can be evaluated quite simply (section V.D).

B. Low *K*,*Q* Limit. We expand eq 5.1b to give

$$\lim_{KR_{\mathrm{G}},QR_{\mathrm{G}},\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = -4\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\langle\mathbf{K}\cdot\mathbf{D}_{ik}\cdot\mathbf{Q}\;\mathbf{K}\cdot\mathbf{r}_{ij}\;\mathbf{Q}\cdot\mathbf{r}_{kl}\rangle \quad (5.4)$$

Even this relatively simple expression appears not to be analytically soluble for a Gaussian coil. However, we can make progress with the commonly used approximation of preaveraging the hydrodynamic interaction.[25,26] Thus, taking for simplicity $\mathbf{K} = \mathbf{Q}$, we write

$$\lim_{KR_{\mathrm{G}},\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(K,K,\tau) = -4\sum_i\sum_j\sum_k\sum_l\langle\mathbf{K}\cdot\mathbf{D}_{ik}\cdot\mathbf{K}\rangle\langle\mathbf{K}\cdot\mathbf{r}_{ij}\;\mathbf{K}\cdot\mathbf{r}_{kl}\rangle \quad (5.5)$$

Equation 5.5 can now be evaluated for a Gaussian coil by considering the 24 orderings of i, j, k, and l discussed in section IIIA and the Appendix. Clearly the second average in (5.5) is zero unless $\mathbf{r}_{ij}$ and $\mathbf{r}_{kl}$ have a common segment; for this reason, terms of type i (section IIIA) do not contribute. Evaluating the 16 terms of types ii and iii and exchanging dummy indices then lead to

$$\lim_{KR_{\mathrm{G}},\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(K,K,\tau) = -4\sum_{i=1}^{N}\sum_{j=1}^{i}\sum_{k=1}^{j}\sum_{l=1}^{k}\langle(\mathbf{K}\cdot\mathbf{r}_{jk})^2\rangle\times\langle\mathbf{K}\cdot[4\mathbf{D}_{ij}+4\mathbf{D}_{kl}-2\mathbf{D}_{ik}-2\mathbf{D}_{il}-2\mathbf{D}_{jk}-2\mathbf{D}_{jl}]\cdot\mathbf{K}\rangle \quad (5.6)$$

For a Gaussian coil[16]

$$\langle(\mathbf{K}\cdot\mathbf{r}_{jk})^2\rangle = \tfrac{1}{3}K^2a^2|j-k| \quad (5.7)$$

and, if free-draining $i = k$ terms in (5.2) are neglected,[25,26]

$$\langle\mathbf{K}\cdot\mathbf{D}_{ik}\cdot\mathbf{K}\rangle = \tfrac{3}{8}D_{\mathrm{T}}K^2N^{1/2}|i-k|^{-1/2} \quad (5.8)$$

where a is, as before, the average spacing of neighboring beads and D_{T} is the translational diffusion coefficient of the polymer

$$D_{\mathrm{T}} = \frac{8}{3\pi^{1/2}}\,\frac{k_{\mathrm{B}}T}{6\pi\eta R_{\mathrm{G}}} \quad (5.9)$$

After conversion of the summations to integrals, evaluation of eq 5.6 gives, with use of (5.7) and (5.8)

$$\lim_{KR_{\mathrm{G}},\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(K,K,\tau) = -\frac{52}{105}D_{\mathrm{T}}N^4K^4R_{\mathrm{G}}^2$$

(preaveraged hydrodynamic interaction) (5.10)

C. High *K*, *Q* Limit. We have already remarked (section IIIB) that, in the limit KR_{G}, $QR_{\mathrm{G}} \gg 1$, the light field $a(K,t)$ scattered by a single coil becomes a complex Gaussian variable so that $F^{(4)}(K,K,0)$ shows a Gaussian factorization. We also expect the time-dependent function $F^{(4)}(K,K,\tau)$ to show a similar factorization and it is instructive to consider this in a little more detail. From eq 3.1 we have

$$F^{(4)}(K,K,\tau) = \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\sum_{l=1}^{N}\langle \exp\{i\mathbf{K}\cdot[\mathbf{r}_i(0) - \mathbf{r}_j(0) + \mathbf{r}_k(\tau) - \mathbf{r}_l(\tau)]\}\rangle \tag{5.11}$$

In the limit $KR_G \gg 1$ only short segments of the polymer coil provide contributions to the scattered intensity which do not average to zero through interference. Thus in (5.11) we get nonzero contributions in only two cases, namely from short independent (nonoverlapping) segments (i,j), (k,l) and (i,l), (k,j). Thus (5.11) becomes

$$\begin{aligned}\lim_{KR_G\to\infty} F^{(4)}(K,K,\tau) = {}& \sum_i\sum_j\langle \exp\{i\mathbf{K}\cdot[\mathbf{r}_i(0) - \mathbf{r}_j(0)]\}\rangle \times \\ & \sum_k\sum_l\langle \exp\{i\mathbf{K}\cdot[\mathbf{r}_k(\tau) - \mathbf{r}_l(\tau)]\}\rangle + \\ & \sum_i\sum_l\langle \exp\{i\mathbf{K}\cdot[\mathbf{r}_i(0) - \mathbf{r}_l(\tau)]\}\rangle \times \\ & \sum_j\sum_k\langle \exp\{-i\mathbf{K}\cdot[\mathbf{r}_j(0) - \mathbf{r}_k(\tau)]\}\rangle = \\ & [F^{(2)}(K,0)]^2 + [F^{(2)}(K,\tau)]^2\end{aligned} \tag{5.12}$$

demonstrating the expected Gaussian factorization; here $F^{(2)}(K,\tau)$ is the familiar second-order correlation function defined by eq 2.14b (and $F^{(2)}(K,0) \equiv \langle|a(K)|^2\rangle$). A relatively straightforward extension of the above argument leads to

$$\lim_{KR_G,QR_G\to\infty} F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = F^{(2)}(K,0)F^{(2)}(Q,0) + [F^{(2)}(K,\tau)]^2P(|\mathbf{K} - \mathbf{Q}|) \tag{5.13}$$

After normalization, (5.13) gives the time-dependent generalization of eq 3.24.

Differentiation of eq 5.13 gives

$$\lim_{\substack{KR_G,QR_G\to\infty\\ \tau\to 0}} \frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = 2F^{(2)}(K,0)P(|\mathbf{K} - \mathbf{Q}|)\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(2)}(K,\tau) \tag{5.14}$$

Thus, as expected in this limit, the time dependence of the fourth-order correlation function is determined by that of the second-order function. We can therefore use the result[23,26,27]

$$\lim_{\substack{KR_G\to\infty\\ \tau\to 0}} \frac{\mathrm{d}}{\mathrm{d}\tau}f^{(2)}(K,\tau) = -\frac{k_BT}{16\eta}K^3 \tag{5.15}$$

obtained for a Gaussian polymer coil when free-draining terms are neglected; here $f^{(2)}(K,\tau)$ is the normalized second-order correlation function (eq 2.14a).

For completeness we show that result 5.14 is consistent with eq 5.1a (for simplicity in the $\mathbf{K} = \mathbf{Q}$ limit). To reduce (5.1) when $KR_G \gg 1$, we consider the same two contributions as above, namely $i \approx j$, $k \approx l$ and $i \approx l$, $k \approx j$. The first contribution is zero because the $\mathbf{D}$'s connect well-separated short segments. However, in the second contribution $\mathbf{D}_{il}$ and $\mathbf{D}_{jk}$ each connect beads within one of the short segments and provide the dominant terms. Thus we have

$$\begin{aligned}\lim_{\substack{KR_G\to\infty\\ \tau\to 0}} \frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(K,K,\tau) = {}& -\sum_i\sum_j\sum_k\sum_l\langle \mathbf{K}\cdot(\mathbf{D}_{il} + \mathbf{D}_{jk})\cdot\mathbf{K}\exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_l)] \times \\ & \exp[-i\mathbf{K}\cdot(\mathbf{r}_j - \mathbf{r}_k)]\rangle = \\ & -2\sum_i\sum_l\langle \mathbf{K}\cdot\mathbf{D}_{il}\cdot\mathbf{K}\exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_l)]\rangle \times \\ & \sum_j\sum_k\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_j - \mathbf{r}_k)]\rangle\end{aligned} \tag{5.16}$$

after exchange of dummy indices. Remembering the well-known result[22,23]

$$\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(2)}(K,\tau) = -\sum_i\sum_j\langle \mathbf{K}\cdot\mathbf{D}_{ij}\cdot\mathbf{K}\exp(i\mathbf{K}\cdot\mathbf{r}_{ij})\rangle \tag{5.17}$$

we see that (5.16) is equivalent to (5.14) when $\mathbf{K} = \mathbf{Q}$.

D. General Expression for Free-Draining Coil. In the free-draining approximation hydrodynamic interactions are neglected and $\mathbf{D}_{ik}$ is given by the first term in eq 5.2. Substitution of this result into eq 5.1 gives, after exchange of dummy indices,

$$\begin{aligned}\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = {}& D_0\mathbf{K}\cdot\mathbf{Q}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\langle \exp(i\mathbf{K}\cdot\mathbf{r}_{ij}) \times \\ & [\exp(i\mathbf{Q}\cdot\mathbf{r}_{ik}) - \exp(i\mathbf{Q}\cdot\mathbf{r}_{ki}) - \exp(i\mathbf{Q}\cdot\mathbf{r}_{jk}) + \exp(i\mathbf{Q}\cdot\mathbf{r}_{kj})]\rangle\end{aligned} \tag{5.18}$$

For a Gaussian coil eq 5.18 can be evaluated by following similar procedures to those outlined in section IIIA and the Appendix for $F^{(4)}(\mathbf{K},\mathbf{Q},0)$. The result is

$$\begin{aligned}\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = {}& 4N^3D_0\mathbf{K}\cdot\mathbf{Q}\Bigg\{\frac{X + Y}{XY(X + Y + W)} - \frac{X + Y}{XY(X + Y - W)} - \\ & \frac{X + Y + 2W}{(X + W)(Y + W)(X + Y + W)^2} \times [\exp[-(X + Y + W)] - 1] + \\ & \frac{X + Y - 2W}{(X - W)(Y - W)(X + Y - W)^2} \times [\exp[-(X + Y - W)] - 1] + \\ & \left[\frac{1}{X^2(Y + W)} - \frac{1}{X^2(Y - W)}\right][\exp(-X) - 1] + \\ & \left[\frac{1}{Y^2(X + W)} - \frac{1}{Y^2(X - W)}\right][\exp(-Y) - 1]\Bigg\}\end{aligned} \tag{5.19}$$

where X, Y, and W are given by eq 3.9.

Various limits of eq 5.19 are useful:

$$\lim_{KR_G,QR_G,\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = -\frac{2}{3}N^3D_0\mathbf{K}\cdot\mathbf{Q} \times W\left\{1 - \frac{X + Y}{2} + \frac{1}{60}(2W^2 + 9X^2 + 9Y^2 + 16XY)\right\} \tag{5.20}$$

$$\lim_{\substack{KR_G,QR_G\to\infty\\ \tau\to 0}}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(\mathbf{K},\mathbf{Q},\tau) = 2N^3D_0\mathbf{K}\cdot\mathbf{Q}\frac{X + Y - 2W}{(X - W)(Y - W)}P(|\mathbf{K} - \mathbf{Q}|) \tag{5.21}$$

$$\begin{aligned}\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}F^{(4)}(K,K,\tau) = {}& N^3D_0K^2\Bigg\{\frac{10}{X^2} - \frac{4}{X} + \frac{32}{3X^3}[\exp(-X) - 1] - \\ & \frac{1}{6X^3}[\exp(-4X) - 1]\Bigg\}\end{aligned} \tag{5.22}$$

VI. Characteristic Decay Rate Γ of Conformational Fluctuations

In order to interpret the results obtained in section V it is convenient to define a characteristic decay rate Γ by[1]

$$\Gamma \equiv -\lim_{\tau\to 0}\frac{\mathrm{d}}{\mathrm{d}\tau}\left\{\frac{\langle|a(\mathbf{K},0)|^2|a(\mathbf{Q},\tau)|^2\rangle - \langle|a(K)|^2\rangle\langle|a(Q)|^2\rangle}{\langle|a(\mathbf{K})|^2|a(\mathbf{Q})|^2\rangle - \langle|a(K)|^2\rangle\langle|a(Q)|^2\rangle}\right\} \tag{6.1a}$$

which, with use of eq 2.17, can be written in the equivalent forms

$$\Gamma \equiv \frac{-\lim\limits_{\tau\to 0} \dfrac{\mathrm{d}}{\mathrm{d}\tau} F^{(4)}(\mathbf{K},\mathbf{Q},\tau)}{F^{(4)}(\mathbf{K},\mathbf{Q},0) - \langle |a(K)|^2\rangle\langle |a(Q)|^2\rangle} \tag{6.1b}$$

and

$$\Gamma \equiv \frac{-\lim\limits_{\tau\to 0} \dfrac{\mathrm{d}}{\mathrm{d}\tau} f^{(4)}(\mathbf{K},\mathbf{Q},\tau)}{f^{(4)}(\mathbf{K},\mathbf{Q},0) - 1} \tag{6.1c}$$

The function in braces in eq 6.1a seems the most logical for a definition of Γ since it decays from 1 when $\tau = 0$ to 0 when $\tau = \infty$; thus if it decayed exponentially, Γ^{-1} would be the time constant of the exponential.

In the next sections we use the results of sections III and V to calculate Γ for the various cases considered there.

A. With Hydrodynamic Interactions, $KR_G = QR_G \to 0$. Combination of eq 2.17, 3.19, 3.20, and 5.10 in eq 6.1c gives

$$\Gamma = \frac{39}{7}\frac{D_T}{R_G^2} \quad \text{(Gaussian coil, } KR_G = QR_G \to 0\text{, preaveraged Oseen hydrodynamics)} \tag{6.2}$$

B. With Hydrodynamic Interactions, KR_G, $QR_G \to \infty$. Use of eq 2.14, 2.17, 3.24, 5.14, and 5.15 in 6.1c gives

$$\Gamma = (k_BT/8\eta)K^3 \tag{6.3}$$

With use of eq 5.9, eq 6.2 can be written in terms of a scaled time, R_G^2/D_T, and a scaled length, KR_G:

$$\Gamma = \frac{9\pi^{3/2}}{32}\frac{D_T}{R_G^2}(KR_G)^3 \quad \text{(Gaussian coil, } KR_G \to \infty\text{, Oseen hydrodynamics)} \tag{6.4}$$

We note that, as expected from the discussion in sections IIIB and VC, in this limit where the field scattered by a single coil is Gaussian the decay rate of $f^{(4)}$ is twice that of $f^{(2)}$ (compare eq 6.3 with eq 5.15).

C. Free-Draining Coil. Combination of eq 5.19, 3.8, and 3.11 in eq 6.1a gives general results for Γ in the case of a free-draining Gaussian coil. Use of eq 5.20, 3.19, and 3.20 in eq 6.1c gives

$$\Gamma = 15(D_0/NR_G^2) = 15(D_T/R_G^2) \quad (KR_G,\ QR_G \to 0\text{, free-draining Gaussian coil}) \tag{6.5}$$

since

$$D_T = D_0/N \tag{6.6}$$

for a free-draining coil. Use of eq 5.21, 3.22, and 3.23 in eq 6.1c gives

$$\Gamma = -2\frac{D_0}{N}\mathbf{K}\cdot\mathbf{Q}\frac{(X-W)(Y-W)}{X+Y-2W} \tag{6.7}$$

which, in the extreme high K, Q limit becomes

$$\Gamma = \frac{D_T}{R_G^2}(KR_G)^4 \quad (KR_G,\ QR_G \to \infty\text{, free-draining Gaussian coil}) \tag{6.8}$$

Finally combination of eq 5.22, 3.12, and 3.11 in eq 6.1a gives general results for Γ for a free-draining coil when $\mathbf{K} \approx \mathbf{Q}$ which are plotted in Figure 5 and discussed in section VIIB.

VII. Summary and Discussion

We have considered an experiment in which light scattered by a small volume of a dilute solution of flexible polymers is analyzed by a two-detector cross-correlation technique. We have calculated some properties of the function $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$ which describes the modulation, due to conformational fluctuations, of the number fluctuation term in the temporal cross-correlation function of the scattered light intensity.

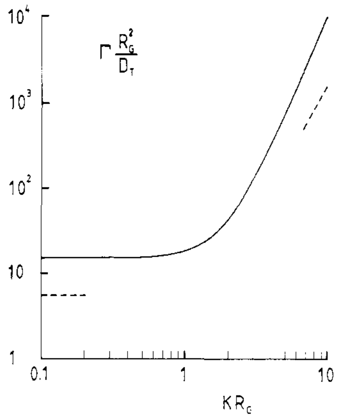

Figure 5. Initial decay rate Γ (in units of D_T/R_G^2) of $f^{(4)}(K,K,\tau)$ for a Gaussian coil in the "$\mathbf{K} \approx \mathbf{Q}$" scattering configuration. Solid line: A free-draining Gaussian coil (derived from eq 5.22 and 6.1). For $KR_G \gtrsim 5$ the asymptotic $(KR_G)^4$ behavior (a straight line on the log–log plot) is observed. Dashed lines: Limits of low KR_G (eq 6.2) and high KR_G (eq 6.4) for a Gaussian coil when Oseen hydrodynamic interactions are included. The low KR_G limit is calculated in the preaveraging approximation.

A. Amplitude $f^{(4)}(K,Q,0)$ of the Conformational Fluctuations. In section III we considered a polymer coil having a Gaussian distribution of bead separations and obtained a general expression for $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ (eq 3.8, 3.11, and 2.17). Several limiting cases were considered. In particular, the results for closely spaced detectors ("$\mathbf{K} \approx \mathbf{Q}$", Figure 1c) are plotted as a function of KR_G in Figure 4. As noted in section IIIB, $f^{(4)}(K,K,0)$ starts at one for $KR_G \ll 1$, which implies no modulation of the number fluctuation term and is the result expected for a "point" particle. At $KR_G = 1$ conformational fluctuations have an appreciable effect and at $KR_G = 10$ $f^{(4)}$ has essentially saturated at a value 2. In this limit, $KR_G \gg 1$, the amplitude of the electric field of the light scattered *by a single coil* is a complex Gaussian random variable. (We note that this last property is not limited to a Gaussian polymer coil but should be exhibited by the light scattered by any sufficiently large, irregular, inhomogeneous particle.)

An interesting prediction (also expected to apply to a wider class of scatterers than just Gaussian polymers) is embodied in eq 3.24, which shows that in the limit KR_G, $QR_G \gg 1$ the cross-correlation coefficient $f^{(4)}(\mathbf{K},\mathbf{Q},0) - 1$ is simply the single-particle form factor $P(|\mathbf{K} - \mathbf{Q}|)$. This allows the possibility of determining the form factor of large scatterers by making cross-correlation measurements away from $K \approx 0$ where conventional intensity measurements, which yield $P(K)$, could be corrupted by spurious small-angle scattering.

In section IV we calculated $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ in the limit KR_G, $QR_G \to 0$ for a scatterer having an arbitrary distribution of material. We suggested that a swollen polymer coil might show an interesting anticorrelation effect when cross-correlation scattering measurements are made in the $\mathbf{K} \perp \mathbf{Q}$ (Figure 1d) configuration.

B. Dynamics of the Conformational Fluctuations. In sections V and VI we considered the dynamics of the conformational fluctuations as characterized by a frequency Γ (eq 6.1) derived from the initial decay of $f^{(4)}(\mathbf{K},\mathbf{Q},\tau)$. For a free-draining coil (no hydrodynamic interactions) a general expression for Γ was obtained (eq

5.19 and 6.1). For the $\mathbf{K} \approx \mathbf{Q}$ configuration these results are plotted in Figure 5. At $KR_G \rightarrow 0$, Γ starts at a finite value given by eq 6.5. At $KR_G \rightarrow \infty$ it shows an asymptotic K^4 behavior (eq 6.8). Such K^4 scaling at large KR_G was predicted many years ago[23,28] for the second-order function $f^{(2)}(K,\tau)$ of a free-draining polymer. The K^4 scaling found here for $f^{(4)}$ is thus not surprising since it follows, through eq 5.14, from the Gaussian property of the light scattered by a single coil in the large KR_G limit (above and section VC).

It is well-known that hydrodynamic interactions cannot be neglected in dilute polymer solutions so that the free-draining approximation is of academic interest only. Inclusion of Oseen hydrodynamic interactions complicates the theory considerably but we have been able to obtain Γ in the low KR_G (eq 6.2, preaveraged Oseen tensor) and high KR_G (eq 6.4) limits. These limits are indicated in Figure 5.

An interesting observation, apparently first made by Schurr,[29] follows from inspection of eq 5.4 for the $\mathbf{K} \perp \mathbf{Q}$ ($\mathbf{K}\cdot\mathbf{Q} = 0$) configuration. If hydrodynamic interactions are neglected so that $\mathbf{D}_{ik} = 1\,\delta_{ik}$, the right-hand side of (5.4) is zero because $\mathbf{K}\cdot\mathbf{Q} = 0$. Furthermore, if hydrodynamic interactions are included but the preaveraging approximation applied (cf. eq 5.5), the right-hand side of (5.4) is also zero for a Gaussian coil since $\langle \mathbf{K}\cdot\mathbf{r}_{ij}\mathbf{Q}\cdot\mathbf{r}_{kl}\rangle = 0$ for $\mathbf{K} \perp \mathbf{Q}$ (from the statistical independence of orthogonal dimensions; see section IIIC). However, if hydrodynamic interactions are properly considered (i.e., without preaveraging), the right-hand side of (5.4) appears to be *nonzero* (though hard to evaluate) *even for a Gaussian coil.* Now remember that for a Gaussian coil $f^{(4)}(\mathbf{K},\mathbf{Q},0)|_{\mathbf{K}\cdot\mathbf{Q}=0} = 1$ (eq 3.17). We thus predict that if a Gaussian coil is studied by cross-correlation light scattering in the $\mathbf{K} \perp \mathbf{Q}$ configuration, there will be no equal-time modulation of the number fluctuation term (i.e., $f^{(4)}(\mathbf{K},\mathbf{Q},0) = 1$) but there is the possibility that correlations could grow (and, presumably, decay ultimately) with time (i.e., $\lim_{\tau\rightarrow 0}$ $[\mathrm{d}f^{(4)}(\mathbf{K},\mathbf{Q},\tau)/\mathrm{d}\tau] \neq 0$). It is clear from the above that this would be a purely hydrodynamic effect which can perhaps be interpreted qualitatively as follows. If, under the influence of Brownian motion, a coil happened to stretch itself in some direction over a short interval of time, this would create an inward flow of solvent in directions perpendicular to the stretch. This solvent flow could carry polymer, causing thereby the development of a time-delayed anticorrelation between orthogonal dimensions of the coil. As in the case of the equal-time anticorrelation conjectured in section IV for a *non-Gaussian coil*, the effect could well be small (but still worth an experiment).

C. Comparison with Experiment. As mentioned in section I a cross-correlation light scattering experiment on polymers has been reported by Kam and Rigler.[1] These authors studied, in the $\mathbf{K} \approx \mathbf{Q}$ configuration, a solution of DNA polymers having molecular weight 4×10^6 and radius of gyration $R_G \approx 2000$ Å. They found that the characteristic frequency Γ scaled roughly with K^3, implying that their experimental conditions corresponded to the large KR_G limit (eq 6.4). At a scattering angle of 90° and a laser wavelength of 5145 Å the magnitude of K is about 2.3×10^5 cm^{-1} so that $KR_G \approx 4.6$. Inspection of Figure 5 shows that, for a free-draining coil, the decay rate Γ at $KR_G \approx 4.6$ shows a K dependence close to that expected in the asymptotic high KR_G limit. One might guess that when hydrodynamic interactions are considered, $KR_G \approx 4.6$ might still be close to asymptotic, in agreement with Kam and Rigler's observation.

From Figure 4 we see that for a Gaussian coil the modulation amplitude $f^{(4)}(K,K,0) - 1$ at $KR_G = 4.6$ is expected to be greater than 0.8. Kam and Rigler quote an observed "4% relative mean-square fluctuations per particle". While it is not entirely clear what this means, it does seem to imply a modulation smaller than that predicted in this paper. It is of course possible that the DNA molecules were not Gaussian and/or that reduction of $f^{(4)}(\mathbf{K},\mathbf{Q},0)$ resulted from the separation of the detectors (eq 3.23). We mention however that recent unpublished cross-correlation experiments by Rarity[30] on polystyrene showed modulation amplitudes $f^{(4)}(\mathbf{K},\mathbf{Q},0) - 1$ of order 0.4, more in line with the predictions of this work.

D. Future Directions. While the experiment of Kam and Rigler clearly demonstrates the potential of the cross-correlation method in the study of polymer solutions and shows at least some qualitative agreement with the theory developed in this paper, there is a need for more detailed quantitative experiments on well-characterized polymer solutions.

One can also look further ahead to more complex systems. One phenomenon to the study of which cross-correlation light scattering techniques seem ideally suited is the collapse of a polymer coil as the quality of the solvent becomes worse. For high molecular weight polymers the collapse can be very sudden and large fluctuations in the conformation of a single coil might be expected near this critical point. This phenomenon has already been elegantly investigated by Tanaka and co-workers[31] using conventional dynamic light scattering methods. Cross-correlation experiments might elucidate further the nature of these conformational fluctuations.

A currently fashionable application of light scattering is to the study of multiscale or "fractal" aggregates of many small colloidal particles.[32-34] Here the use of cross-correlation light scattering methods, combined with some of the ideas developed in this paper, could yield more information on both the structure and dynamics of these aggregates.

Note Added in Proof: A reference overlooked in section I is: Lebedev, A. D.; Lomakin, A. V.; Noshkin, V. A.; Sharonov, B. P. *Opt. Spectrosc.* (*Engl. Transl.*) **1982**, *52*, 116–8. These authors studied, by cross-correlation spectroscopy, the rotational diffusion of a bacterium.

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Appendix. Evaluation of $F^{(4)}(\mathbf{K},\mathbf{Q},0)$ for a Gaussian Coil

As mentioned in section IIIA we evaluate $F^{(4)}(\mathbf{K},\mathbf{Q},0)$ (eq 3.1) by considering the 24 possible orderings of the indices i, j, k, and l. In section IIIA we divided these orderings into three groups of eight and we now consider these in turn.

(i) Segments (i, j) and (k, l) are completely separate (Figure 3a). The eight individual orderings in this category are $i > j > k > l$, $i > j > l > k$, $j > i > k > l$, $j > i > l > k$, $k > l > i > j$, $k > l > j > i$, $l > k > i > j$, and $l > k > j > i$. For a Gaussian coil it can easily be shown that each of these orderings gives the same contribution, J_1, to $F^{(4)}(\mathbf{K},\mathbf{Q},0)$. Thus

$$J_1 = \sum_{i=1}^{N}\sum_{j=1}^{i}\sum_{k=1}^{j}\sum_{l=1}^{k}\langle \exp[i\mathbf{K}\cdot(\mathbf{r}_i - \mathbf{r}_j)]\exp[i\mathbf{Q}\cdot(\mathbf{r}_k - \mathbf{r}_l)]\rangle \qquad \text{(A1)}$$

We follow the procedure outlined in section IIIA. Because segments (i, j) and (k, l) are separate we partition the average in (A1). Use of (3.5) gives

$$J_1 = \sum_{i=1}^{N}\exp[-K^2a^2i/6]\sum_{j=1}^{i}\exp[K^2a^2j/6] \times \sum_{k=1}^{j}\exp[-Q^2a^2k/6]\sum_{l=1}^{k}\exp[Q^2a^2l/6]$$

Conversion of sums to integrals, as in eq 3.7, followed by their evaluation then leads to

$$J_1 = N^4\left\{\frac{1}{2XY} - \frac{X+Y}{X^2Y^2} + \frac{1}{X^3(X-Y)}[\exp(-X) - 1] - \frac{1}{Y^3(X-Y)}[\exp(-Y) - 1]\right\} \qquad \text{(A2)}$$

where X and Y are defined by eq 3.9.

(ii) Segments (i, j) and (k, l) contain a common subsegment (Figure 3b). As mentioned in section IIIA the eight terms of type ii subdivide further into two groups of four. The first group, which provides contribution $4J_2$ to $F^{(4)}$ (see section IIIA), comprises $i > k > j > l$, $j > l > i > k$, $k > i > l > j$, and $l > j > k > i$, and, following the methods outlined in section IIIA and above, we get

$$J_2 = N^4\left\{\frac{1}{XY(X+Y+W)} - \frac{1}{X^2(Y+W)(X-Y)}[\exp(-X) - 1] + \frac{1}{Y^2(X+W)(X-Y)}[\exp(-Y) - 1] + \frac{1}{(X+W)(Y+W)(X+Y+W)^2} \times [\exp[-(X+Y+W)] - 1]\right\} \qquad \text{(A3)}$$

The other group of four terms of type ii is $i > l > j > k$, $j > k > i > l$, $k > j > l > i$, and $l > i > k > j$. These give a contribution $4J_3$ and it is easily shown that J_3 is obtained by replacing W by $-W$ in J_2; i.e.

$$J_3 = J_2(W \rightarrow -W) \qquad \text{(A4)}$$

(iii) One of the segments (i, j) or (k, l) is contained completely within the other (Figure 3c). This category gives four distinct contributions to $F^{(4)}(\mathbf{K},\mathbf{Q},0)$, $2J_4$, $2J_5$, $2J_6$, and $2J_7$, each composed of two terms. We have $i > k > l > j$ and $j > l > k > i$, giving

$$J_4 = N^4\left\{\frac{1}{X^2(X+Y+W)} - \frac{X-Y-W}{X^3(Y+W)^2}[\exp(-X) - 1] + \frac{1}{(Y+W)^2(X+Y+W)^2}[\exp[-(X+Y+W)] - 1] + \frac{1}{X^2(Y+W)}\left[\left(1 + \frac{1}{X}\right)\exp(-X) - \frac{1}{X}\right]\right\} \qquad \text{(A5)}$$

$i > l > k > j$ and $j > k > l > i$, giving

$$J_5 = J_4(W \rightarrow -W) \qquad \text{(A6)}$$

$k > i > j > l$ and $l > j > i > k$, giving

$$J_6 = N^4\left\{\frac{1}{Y^2(X+Y+W)} + \frac{X-Y+W}{Y^3(X+W)^2}[\exp(-Y) - 1] + \frac{1}{(X+W)^2(X+Y+W)^2}[\exp[-(X+Y+W)] - 1] + \frac{1}{Y^2(X+W)}\left[\left(1 + \frac{1}{Y}\right)\exp(-Y) - \frac{1}{Y}\right]\right\} \qquad \text{(A7)}$$

and $k > j > i > l$ and $l > i > j > k$, giving

$$J_7 = J_6(W \rightarrow -W) \qquad \text{(A8)}$$

Evaluation of the sum $8J_1 + 4(J_2 + J_3) + 2(J_4 + J_5 + J_6 + J_7)$ then gives the result quoted in eq 3.8.

References and Notes

(1) Kam, Z.; Rigler, R. *Biophys. J.* **1982**, *39*, 7–13.

(2) Schaefer, D. W.; Berne, B. J. *Phys. Rev. Lett.* **1972**, *28*, 475–8.

(3) For reviews, see: (a) Pusey, P. N. In "Photon Correlation Spectroscopy and Velocimetry"; Cummins, H. Z., Pike, E. R., Eds.; Plenum Press: New York, 1977. (b) Weissman, M. B. *Annu. Rev. Phys. Chem.* **1981**, *32*, 205–32. (c) Schaefer, D. W. In "Laser Applications to Optics and Spectroscopy"; Jacobs, S. F., et al., Eds.; Addison-Wesley: Reading, MA, 1974.

(4) Schaefer, D. W. *Science (Washington, D.C.)* **1973**, *180*, 1293–5.

(5) Weissman, M.; Schindler, H.; Feher, G. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 2776–80.

(6) Webb, W. W. *Q. Rev. Biophys.* **1976**, *9*, 49–68.

(7) Kam, Z. *Macromolecules* **1977**, *10*, 927–34.

(8) Griffin, W. G.; Pusey, P. N. *Phys. Rev. Lett.* **1979**, *43*, 1100–4.

(9) Rarity, J. G.; Randle, K. J. *Opt. Commun.* **1984**, *50*, 101–6. Rarity, J. G. Ph.D. Thesis, 1984 (Council for National Academic Awards, U.K.).

(10) Cantrell, C. D. Ph.D. Thesis, Princeton University, 1968.

(11) Pusey, P. N.; Jakeman, E. *J. Phys. A: Math. Gen.* **1975**, *8*, 392–410.

(12) Pusey, P. N. *J. Phys. D: Appl. Phys.* **1976**, *9*, 1399–409.

(13) Phillies, G. D. J. *J. Chem. Phys.* **1981**, *74*, 260–2; *Phys. Rev. A* **1981**, *24*, 1939–43.

(14) Clark, N. A.; Ackerson, B. J.; Hurd, A. J. *Phys. Rev. Lett.* **1983**, *50*, 1459–62.

(15) Drewel, M.; Pusey, P. N. *Opt. Acta* **1983**, *30*, 1483–500.

(16) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley-Interscience: New York, 1969.

(17) Debye, P. *J. Phys. Chem.* **1947**, *51*, 18–32.

(18) In this paper P will always refer to the form factor defined by eq 2.9; however, as the occasion requires, it may take arguments K, KR_G, or $X = K^2R_G{}^2$.

(19) (a) Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1971**, *54*, 2756–7. (b) Gobush, W.; Šolc, K.; Stockmayer, W. H. *J. Chem. Phys.* **1974**, *60*, 12–21.

(20) Bixon, M. *J. Chem. Phys.* **1973**, *58*, 1459–66.

(21) Zwanzig, R. *J. Chem. Phys.* **1974**, *60*, 2717–20.

(22) Akcasu, Z.; Gurol, H. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1–16.

(23) For a review, see: Schaefer, D. W.; Han, C. C. In "Dynamic Light Scattering and Velocimetry: Applications of Photon Correlation Spectroscopy"; Pecora, R., Ed.; Plenum Press: New York, 1985.

(24) Tough, R. J. A.; Pusey, P. N.; Ackerson, B. J. *J. Chem. Phys.* **1984**, *81*, 3331–3. The derivation of eq 5.1 in this reference is based on the many-particle Smoluchowski diffusion equation or on equivalent coupled Langevin equations. I am grateful to a referee for pointing out that Phillies has claimed recently that this approach is incomplete in that certain "hidden correlations" are neglected (Phillies, G. D. J. *J. Chem. Phys.* **1984**, *80*, 6234–9). Phillies' approach would lead to additional terms in eq 5.1. However, the validity of Phillies' criticisms is not yet fully accepted. It does not seem appropriate to enter this debate here and it will be assumed that eq 5.1, based on current conventional wisdom, is adequate for the purposes of this paper. In any case we note that one class of extra term

found by Phillies is proportional to $\nabla \cdot \mathbf{D}_{ik}$, which is zero for hydrodynamic interactions considered, as in this paper, at the Oseen level (eq 5.2).

(25) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.

(26) Burchard, W.; Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1980**, *13*, 580–7.

(27) Dubois-Violette, E.; de Gennes, P.-G. *Physics* (*Long Island City, N.Y.*) **1967**, *3*, 181–198.

(28) de Gennes, P.-G. *Physics* (*Long Island City, N.Y.*) **1967**, *3*, 37.

(29) Schurr, J. M., private communication (1980).

(30) Rarity, J. G., private communication.

(31) Nishio, I.; Swislow, G.; Sun, S.-T.; Tanaka, T. *Nature* (*London*) **1982**, *300*, 243–4.

(32) Schaefer, D. W.; Martin, J. E.; Wiltzius, P.; Cannell, D. S. *Phys. Rev. Lett.* **1984**, *52*, 2371–4.

(33) Martin, J. E.; Schaefer, D. W. *Phys. Rev. Lett.* **1984**, *53*, 2457–60.

(34) Weitz, D. A.; Huang, J. S.; Lin, M. Y.; Sung, J. *Phys. Rev. Lett.* **1984**, *53*, 1657–60.

Light Scattering Studies of Poly(methyl methacrylate)/[Poly(ethyl acrylate)/Poly(butyl acrylate)] Terpolymer

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ABSTRACT: The classical Bushuk–Benoit light scattering theory for solutions of copolymers is extended to solutions of (quasi)terpolymers which may be polydisperse in chain composition as well as in molecular weight. A method for determining the weight-average molecular weight of a (quasi)terpolymer with only three solvents is described. The scheme was tested by using a poly(methyl methacrylate)/[poly(ethyl acrylate)/poly(butyl acrylate)] terpolymer (PMMA/[PEA/PBA]) and five solvents: methyl ethyl ketone (MEK), dioxane (DIO), ethyl acetate (EA), cyclohexanone (CYC), and *m*-dichlorobenzene (MDCB), covering a very broad refractive index increment range. The apparent molecular weight varies from 1.37×10^6 in ethyl acetate to 1.80×10^6 in cyclohexanone. One important factor in achieving a more precise molecular weight determination is the spread of the refractive index increment from −0.0391 in *m*-dichlorobenzene to 0.122 in ethyl acetate. The (true) molecular weight of the (quasi)terpolymer was determined to be $\sim 1.2 \times 10^6$. Intensity time correlation functions of PMMA/[PEA/PBA] in MEK, dioxane, and cyclohexanone were measured at different scattering angles as a function of concentration. By using a multiexponential singular value decomposition technique in the Laplace inversion and by taking into account the difference in the scattering power of the monomer-type components in different solvents, we were able to determine simultaneously the true molecular weight distribution and the chain composition of the polymer at different representative molecular weight fractions for the PMMA/[PEA/PBA] (quasi)terpolymer, provided that the properties of [PEA/PBA] are so similar as to have an average refractive index covering both monomer types.

I. Introduction

Light scattering has been used to determine the molecular weight of synthetic high polymers for nearly 40 years.[1] The application of this technique to copolymers has met with only limited success, partly because the molecular weight determination now requires at least three times the amount of work when compared with that for a homopolymer. The light scattering theory for copolymers[2] has also been extended to terpolymers where six solvents are recommended in order to resolve the same issue.[3] Consequently, absolute molecular weight determinations of copolymers and terpolymers by light scattering studies have remained a tedious method as few investigators are tempted to spend so much effort in order to just determine the molecular weight. Nevertheless, in present-day technology, we have increased usage in materials modification at the molecular level. Characterization of copolymers, terpolymers, or even more complex multicomponent polymers may be of interest.

The theoretical treatment for determining the molecular weights of copolymers was developed by Stockmayer et al.[4] and expressed in a more useful form by Bushuk and Benoit[2] almost 25 years ago. Since then, only a handful of experiments[5-10] with some emphasis on copolymer conformation have been reported. Although a straightforward extension of the Bushuk–Benoit theory to terpolymers has been worked out by Kambe et al.,[3] to our knowledge, no definitive experiments on light scattering molecular weight characterization of a terpolymer solution have ever been reported. In this article, we want to use the Bushuk–Benoit theory for the molecular weight determination of a (quasi)terpolymer in solution and to take advantage of recent developments in the Laplace inversion technique which permits us to measure characteristic line-width distributions from intensity time correlation functions. If we take into account the effect of scattering power by different monomer types of the "terpolymer" in different solvents, we have succeeded in determining simultaneously the molecular weight distribution and the "terpolymer" composition in different representative polymer molecular weight fractions. It should be noted that we have taken PEA/PBA as a single monomer type with PMMA being the other because the refractive index increments of PEA and PBA are very similar. Thus, the notation "(quasi)terpolymer" is used and the method of analysis is essentially the same as that for a copolymer.

On the basis of the assumption of the additivity of refractive index increments of the components of a multicomponent polymer in a single solvent

$$\nu = (\mathrm{d}n/\mathrm{d}C)_{\text{polymer}} = \sum_{j=1} W_j \nu_j \tag{1}$$

where ν_j [$\equiv (\mathrm{d}n/\mathrm{d}C)_j$] is the change of the refractive index n with respect to concentration C for monomer type j and

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