

Light Scattering from Non-Gaussian Concentration Fluctuations

Dale W. Schaefer

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

Bruce J. Berne*†

Columbia University, New York, New York 10027

(Received 2 November 1971)

Quasielastic light-scattering studies from a solution of 1- μ m-diam polystyrene spheres indicate that at sufficient dilution the homodyne autocorrelation function is not consistent with the common assumption that the concentration fluctuations are Gaussian stochastic processes. In this note we show that the non-Gaussian behavior at low concentrations arises because the particles in the scattering volume are Poisson distributed.

Quasielastic light scattering has become a very useful probe for studying the dynamics of macromolecules in solution. The diffusion constants of macromolecules¹ as well as the velocity distributions of motile micro-organisms² have been measured by either homodyne or heterodyne methods. It is usually assumed that the homodyne and heterodyne techniques give essentially the same information about the system. In this note we show that the homodyne technique^{3,4} yields new information that cannot be found using the heterodyne technique.^{3,4} In particular, we have found that when the number of particles in the scattering volume is small, the amplitude of the scattered field is not a Gaussian random process. In this case, the homodyne intensity autocorrelation function decays on two widely different time scales. The slow process involves the decay of the fluctuation in the total number of particles in the scattering volume, while the fast process involves the usual microscopic motion of individual particles. In fact, the time constant of the slow part of the homodyne correlation function is so long that on the time scale of the fast decay it appears as an apparent excess background which is not directly related to the mean scattered intensity. This excess background is not present in the heterodyne correlation function. Thus the homodyne technique can be used not only to study the diffusional properties of macromolecular

solutions, but it also can be used to probe fundamental properties of colloid statistics.

In heterodyne studies the time-dependent part of the observed correlation function is, aside from the self-beat term, $I_1(\vec{K}, t) = \langle \psi^*(\vec{K}, 0)\psi(\vec{K}, t) \rangle$, where $\psi(\vec{K}, t)$ is the amplitude of the scattered field. In homodyne studies, on the other hand, the observed correlation function takes the following form, $I_2(\vec{K}, t) = \langle |\psi(\vec{K}, 0)|^2 |\psi(\vec{K}, t)|^2 \rangle$. Since the number of particles in the scattering volume is not constant, in calculating I_1 and I_2 it is necessary to allow for the fact that any particular scattering center may enter or leave the scattering volume during the course of a measurement. The expression for the amplitude of the light field scattered by a system of M identical spherical particles takes the following form^{3,4}:

$$\psi(\vec{K}, t) = \lambda \sum_{j=1}^M b_j(t) \exp[i\vec{K} \cdot \vec{r}_j(t)], \quad (1)$$

where $\vec{r}_j(t)$ is the position of the j th particle at time t . $b_j(t) = 1$ if particle j is in the scattering volume at time t , $b_j(t) = 0$ if it is not. λ is a constant that depends on the polarizability of the macromolecules, the wavelength of the light, and the geometry of the scattering system. \vec{K} is the scattering vector. For incident light of wave vector \vec{K}_0 , $K = 2K_0 \sin \frac{1}{2}\theta$, where θ is the scattering angle. If it is assumed that the particles are independent and the solution is homogeneous then I_1 and I_2 simplify considerably:

$$I_1(\vec{K}, t) = \lambda^2 \sum_{j=1}^M \langle b_j(0)b_j(t) \rangle F(\vec{K}, t) \quad (2)$$

$$I_2(\vec{K}, t) = \lambda^4 \sum_{i,j=1}^M \langle b_j^2(0)b_i^2(t) \rangle + \lambda^4 \sum_{i \neq m=1}^M \langle b_i(0)b_i(t)b_m(0)b_m(t) \rangle |F(\vec{K}, t)|^2, \quad (3)$$

where $F(\vec{K}, t)$ is the usual self-intermediate-scattering function which, for dilute macromolecular solutions, is adequately given by the diffusion approximation,³ $F(\vec{K}, t) = \exp(-K^2Dt)$, D being the self-diffusion constant.

It remains to determine the correlation functions of the quantities $b_j(t)$. This task can be accomplished by realizing that the sum over all particles of $b_j(t)$ is $N(t)$, the number of particles (occupation number) in the scattering volume. $\langle N(0)N(t) \rangle$, the correlation function of the occupation number, is then expected to decay in a time similar to that characterizing the correlation functions of the b_j 's. $\langle N(0)N(t) \rangle$, however, is expected to decay in a time of the order of $5\tau_N = L^2/24D \gg (K^2D)^{-1}$, where L is the typical dimension of the scattering volume. Therefore, on the time scale during which $F(\vec{K}, t)$ decays, $\langle N(0)N(t) \rangle = \langle N^2 \rangle$. Consequently, whenever a correlation function of the b_j 's multiplies $F(\vec{K}, t)$, we may safely replace it by its initial value. Upon making this replacement and realizing that for a Poisson process $\langle N(N-1) \rangle = \langle N \rangle^2$, Eqs. (2) and (3) can be expressed in terms of the occupation numbers,

$$I_1(\vec{K}, t) = \lambda^2 \langle N \rangle F(\vec{K}, t), \quad (4)$$

$$I_2(\vec{K}, t) = \lambda^4 \{ \langle \delta N(0) \delta N(t) \rangle + \langle N \rangle^2 [1 + |F(\vec{K}, t)|^2] \}, \quad (5)$$

where $\delta N(t) = N(t) - \langle N \rangle$ is the fluctuation in the total number of particles in the scattering volume.

There are several important points to note in connection with these formulas: (a) $\langle \delta N(0) \delta N(t) \rangle$, which can be expressed in terms of the probability after-effect function,⁵ decays in a time $\tau_N \gg (K^2D)^{-1}$ so that for times $(K^2D)^{-1} < t \ll \tau_N$ it can be approximated by its initial value $\langle N \rangle$. (b) While I_1 describes single-particle motions only, I_2 describes both single-particle motions and changes in the number of particles in the scattering volume. This difference results because only I_1 is sensitive to the phase of the scattered field. (c) The term $\langle \delta N(0) \delta N(t) \rangle$ in I_2 indicates that the scattered field is not a Gaussian random process since for a Gaussian field,⁴ $I_2(0)/I_2(\infty) = 2$. Since the scattered field is the space Fourier transform of the concentration of the macromolecules in the scattering volume, the concentration fluctuations are non-Gaussian.

We observe from Eqs. (4) and (5) that light-scattering experiments on dilute solutions can yield, in principle, important information concerning the probability after-effect function in addition to the self-diffusion function. Moreover, we conclude the experimentally relevant fact that the apparent background in homodyne experiments is not the hitherto expected background

$\lambda^4 \langle N \rangle^2$, but contains the additional factor $\lambda^4 \langle N \rangle$ which cannot be easily measured. This apparent background is of major importance in studies of solutions sufficiently dilute that $\langle N \rangle \sim \langle N \rangle^2$, but decays to the true background $\lambda^4 \langle N \rangle^2$ in a time τ_N long compared to $(K^2D)^{-1}$.

We have deliberately limited this discussion to spatially homogeneous incident light. Any real light source, however, will show some intensity variation over the scattering volume. The TEM₀₀ mode of a laser, for example, is expected to have a cylindrical Gaussian profile. The effect of such spatial inhomogeneity will slightly alter the meaning of the "scattering volume," but the essential conclusions reached above are unchanged.

The experimental verification of the effects of fluctuations in the occupation number consisted of measurement of the homodyne photocount autocorrelation function for a series of solutions of 1- μm polystyrene spheres. Two sets of data were obtained. First, a series of runs were taken on the same sample at different θ . It was verified that $\langle N \rangle$ varies as $(\sin\theta)^{-1}$ as expected from purely geometrical considerations. Second, a series of runs were taken at the fixed θ but differing $\langle N \rangle$, and it was demonstrated that $F(\vec{K}, t)$ could be successfully recovered from the data at any concentration once the net detection efficiency α had been determined self-consistently at one concentration. Because of the excessively long time constant associated with $\langle \delta N(0) \delta N(t) \rangle$, its time dependence could not be readily studied. Preliminary results on convective systems, however, indicate that $\langle \delta N(0) \delta N(t) \rangle$ does decay to zero at sufficiently long times.

The time autocorrelation function of the detected photons was measured using a twenty-channel digital correlator similar to that described by Foord *et al.*⁶ Although details of the apparatus will be published elsewhere,⁷ it should be pointed out that the limitations of the clipping procedure were circumvented by using a scaling technique.⁸ The scaled photocount autocorrelation function is expected to differ somewhat from the intensity correlation function derived above. In fact, if $n(t)$ and $n^{(s)}(t)$ are the numbers of photocounts and scaled-by- s photocounts observed in an interval T centered at time t , then for $\langle n^{(s)} \rangle \ll 1$, the scaled photocount autocorrelation function takes the following form^{8,9}

$$\langle n^{(s)}(0)n(t) \rangle = \alpha^2 [\langle N \rangle + \langle N \rangle^2 (1 + \beta e^{-2\Gamma t})] / s,$$

where β is a constant ≤ 1 . The conditions under which the spatial coherence factor β differs from 1 have been discussed elsewhere.¹⁰

Samples used in this work were prepared by dilution with filtered distilled water of concentrated solutions of 1- μm polystyrene spheres obtained from Dow Chemical Company (run no. LS-1138-B). The scattering volume used was cylindrical with a radius of approximately 25 μm and a height of 15-30 μm .

Data taken as a function of θ at constant $\langle N \rangle$ were analyzed by a linear least-squares analysis of $C(t)$ vs $C(t+T)$, where

$$C(\tau) = \frac{\langle n^{(s)}(t)n(t+\tau) \rangle_s}{\langle n \rangle^2} = \langle N \rangle^{-1} + 1 + \beta e^{-2\Gamma t}.$$

Such an analysis yields the decay rate Γ' and $\langle N \rangle$. Here the prime denotes an experimental decay rate obtained by treating the data in this way. An exponential form of $F(\vec{K}, t)$ has been assumed.

According to the preceding analysis, Γ'/K^2 should be independent of θ as should $\langle N \rangle \sin\theta$ (see Fig. 1) since the scattering volume varies as $V_{90}/\sin\theta$, where V_{90} is the scattering volume at $\theta = 90^\circ$. Also shown in Fig. 1 is the photocount efficiency α . The angle dependence of α reflects the Mie scattering function.¹¹ The apparent diffusion constant Γ_{20}'/K^2 displayed in Fig. 1 has been corrected to 20°C assuming Γ' is proportional to the ratio of absolute temperature to solvent viscosity.

A series of runs were also taken as a function

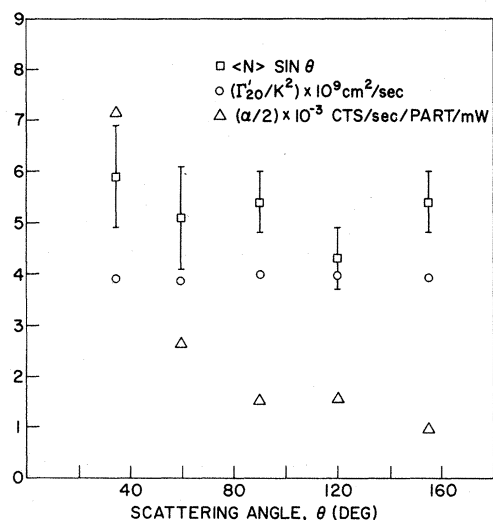


FIG. 1. Angle dependence of the reduced particle number, apparent diffusion constant, and counting efficiency.

of $\langle N \rangle$ for $1 \leq \langle N \rangle \leq 200$. These data, shown in Fig. 2, were obtained by varying the $\langle N \rangle$ at $\theta = 90^\circ$. $\langle N \rangle$ was determined as described above. Two runs are shown for $\langle N \rangle = 1.2$ to demonstrate that the excessively long time constant associated with the occupation number leads to large variations in the magnitude of the excess background especially at small $\langle N \rangle$. This variation reflects the fact that the run time was not sufficiently long to obtain a good average. These data were analyzed as a single exponential of decay rate $2\Gamma'$ plus an unknown background. The resulting average apparent diffusion constant $\bar{\Gamma}_{20}'/K^2$ was found to be $(3.79 \pm 0.10) \times 10^{-9} \text{ cm}^2/\text{sec}$ which compares satisfactorily with the value of $(3.76 \pm 0.08) \times 10^{-9} \text{ cm}^2/\text{sec}$ obtained under conditions of large scattering volume.

In order to recover $F(\vec{K}, t)$, without assuming it to be of exponential form, it is necessary to determine α . In the absence of an independent measurement of α , its value was calculated from the magnitude of the excess background at one concentration. A value of $\alpha = 7.9 \pm 0.8$ counts/sec/particle/milliwatt was obtained from the average of five runs at $\langle N \rangle \sim 16$. Using the value $\alpha = 7.9$, the normal and excess background was subtracted from the data in Fig. 2. A single exponential analysis of the resulting curves gave an apparent diffusion constant of $(3.66 \pm 0.4) \times 10^{-9} \text{ cm}^2/\text{sec}$ when averaged over the eight runs. The fact that this value is consistent with the value $3.79 \times 10^{-9} \text{ cm}^2/\text{sec}$ obtained under conditions of large scattering volume indicates that $F(\vec{K}, t)$ can be suc-

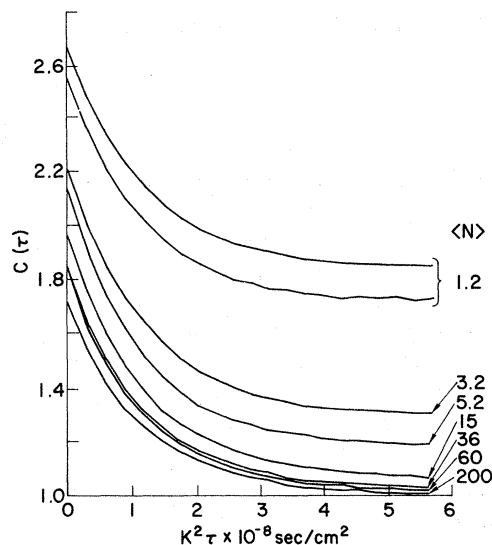


FIG. 2. Normalized photocount autocorrelation function of 1- μm polystyrene spheres. $T = 25.8^\circ\text{C}$. $\tau = 0$ values are extrapolated.

cessfully recovered even in the presence of the apparent excess background if α is accurately known.

We gratefully acknowledge helpful discussions with S. H. Koenig, D. E. Koppel, and P. N. Pusey. One of us (B.J.B.) gratefully acknowledges opportunities provided by IBM at the T. J. Watson Research Center.

*Alfred P. Sloan Foundation Fellow.

†Work partially supported by the National Science Foundation under Grant No. NSF GP22881.

¹S. B. Dubin, H. J. Lunacek, and G. B. Benedek, Proc. Nat. Acad. Sci. U. S. 57, 1164 (1967).

²P. Berge, B. Volochine, R. Billard, and A. Hamelin, C. R. Acad. Sci., Ser. D 265, 889 (1967).

³G. B. Benedek, in *Polarisation, Matière et Rayonnement, Livre de Jubilé l'honneur du Professeur A. Kast-*

ler, edited by the French Physical Society (Presses Universitaires de France, Paris, France, 1969), p. 49.

⁴H. Z. Cummins and H. L. Swinney, in *Progress in Optics*, edited by E. Wolf (North-Holland, Amsterdam, 1969), Vol. VIII, p. 135.

⁵S. Chandrasekhar, Rev. Mod. Phys. 15, 1 (1943).

⁶R. Foord, E. Jakeman, C. J. Oliver, E. R. Pike, R. J. Blagrove, E. Wood, and A. R. Peacocke, Nature 225, 242 (1970).

⁷P. N. Pusey, D. W. Schaefer, D. E. Koppel, R. C. Camerini-Otero, and R. M. Franklin, to be published. See also Proceedings of the International Conference on the Scattering of Light by Fluids, Paris, 1971 (to be published).

⁸P. N. Pusey and W. I. Goldberg, Phys. Rev. A 3, 766 (1971).

⁹D. E. Koppel, private communication.

¹⁰D. E. Koppel, J. Appl. Phys. 42, 3216 (1971).

¹¹D. T. Phillips, P. J. Wyatt, and R. M. Berkman, Colloid Interface Sci. 34, 159 (1970).

Evidence of Nonzero Critical Exponent η for a Binary Mixture from Turbidity and Scattered Light Intensity Measurements

P. Calmettes, I. Laguës, and C. Laj

Service de Physique du Solide et de Résonance Magnétique, Centre d'Etudes Nucleaires de Saclay, 91 Gif-sur-Yvette, France

(Received 12 February 1971)

Measurements of the turbidity and of the intensity of light scattered by a cyclohexane-aniline mixture in the vicinity of the critical point allow us to verify that scaling laws correctly describe the observed phenomena and yield precise values of the critical exponents γ , ν , and η , of the correlation length ξ , and of $(\partial\mu/\partial c)_{P,T}$.

Most of the optical studies of the critical properties of a binary mixture or of a pure fluid have been performed by measuring either the linewidth or the intensity of the scattered light. Puglielli and Ford,¹ however, have shown that very valuable information can also be obtained from turbidity measurements in a pure liquid. This technique has the primary advantage that the angular acceptance of the photomultiplier measuring the intensity of the transmitted light can be reduced to such an extent that any contribution due to forward or multiple scattering is completely negligible.

In the case of an aniline-cyclohexane mixture throughout the temperature range which we explored, the dominant process contributing to the turbidity is Rayleigh scattering. Furthermore, previous experiments performed in our laboratory showed that any contribution other than that due to concentration fluctuations is completely negligible.

In a wide range of temperatures above the critical temperature the intensity scattered by this binary mixture can be expressed by²

$$I_s(K) = I_0 \frac{\pi^2}{\lambda_0^4} \left(\frac{\partial n^2}{\partial c} \right)_{P,T}^2 \frac{k_B T}{(\partial\mu/\partial c)_{P,T}} \frac{\sin^2 \varphi}{(1 + K^2 \xi^2)^{1-\eta/2}}, \quad (1)$$

where all the symbols have their usual significance and η is the critical exponent introduced by Fisher to account for an eventual departure from the Ornstein-Zernicke theory. The turbidity is then readily obtained by integrating expression (1) over all angles:

$$\tau = \frac{2\pi^3}{\lambda_0^4} \left(\frac{\partial n^2}{\partial c} \right)_{P,T}^2 \frac{k_B T}{(\partial\mu/\partial c)_{P,T}} \frac{[(1+2a)^{\eta/2} - 1] [1 + a(2 - \frac{1}{2}\eta + a^2(2 + \frac{1}{2}\eta + \frac{1}{4}\eta^2))] - \eta a(1+a)}{a^3 \frac{1}{2}\eta(1 + \frac{1}{2}\eta)(2 + \frac{1}{2}\eta)}, \quad (2)$$