Statistics of Non-Gaussian Scattered Light

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The statistical distribution of the scattered light intensity is studied theoretically and experimentally for systems where $\langle N\rangle$, the average number of particles in the scattering volume, is small. An expression is obtained for the intensity distribution for the case of a uniformly illuminated scattering volume and the moments are obtained for an arbitrary illumination profile. Calculated moments are compared with those measured for dilute solutions of polystyrene spheres.

Study of the time dependence of the fluctuations in the light intensity scattered from fluid systems has provided an important new experimental tool for the study of the dynamics of molecular motion.[1,2] In many cases, interpretation of these intensity-fluctuation spectroscopy experiments has rested on the assumption that the statistical distribution of the amplitude of the scattered field is Gaussian.[3] With the exception of some turbulent systems,[4] questions concerning the validity of this Gaussian assumption have generally been either ignored, disposed of by thermodynamic fluctuation theory, or dealt with by reference to the central-limit theorem. It is the purpose of this paper to investigate the statistics for one system where the Gaussian assumption breaks down, namely when $\langle N\rangle$, the average number of scatterers in the illuminated volume V, is small. We present both a theoretical and experimental study of the non-Gaussian regime and show that measurement of the non-Gaussian statistics provides new and unique information (in this case, a measure of the number density of scatterers).

The non-Gaussian nature of the field for a finite number of scatterers was pointed out by Schaefer and Berne,[5] who showed that the correlation function of the light intensity scattered from a small number of macromolecular particles is not consistent with a Gaussian field probability distribution.[6] Moreover, they showed that in the non-Gaussian limit ($\langle N\rangle \simeq 1$) a very slowly decaying mode appears in the intensity correlation function. This mode was identified with occupation-number fluctuations (changes in the total number of scatterers in the illuminated scattering volume) and its characteristic time was found to reflect the residence time of a particle in the scattering volume (typically seconds for macromolecular solutions). In contrast, the characteristic time of the more familiar interference fluctuations is the time required for a typical particle to move the wavelength of light (typically milliseconds[1,2]).

The total field scattered by a system of M identical spherical particles is proportional to a properly weighted sum of the phase shifts (at the detector) introduced by each particle in the scattering region,

$$E(\vec{R},t)=\sum_{i=1}^{M} e(\vec{r}_i)\exp[i\vec{K}(\vec{R},\vec{r}_i)\cdot\vec{r}_i(t)], \qquad (1)$$

where $\vec{R}$ is the observation point, $\vec{r}_i(t)$ is the position of the ith particle at time t, $e(\vec{r})$ is the amplitude of the field scattered by a particle when at position $\vec{r}$, and $\vec{K}$ is the scattering vector and is a function of $\vec{R}$ and $\vec{r}_i$. For incident light of wave vector $\vec{K}_0$, $K=2K_0\sin(\theta/2)$, where θ is the scattering angle. The theoretical problem is to determine $P(E)$, the probability of observing a scattered field of amplitude E. If $P(E)$ is known, then $P(I)\propto P(|E|^2)$ follows directly. $P(n)$, the probability of observing n photocounts in a time interval of length T, is the Poisson transform[7] of $P(I)$ in the limit that T is much less than any characteristic time of the fluctuations.

The most direct approach to the solution of $P(E)$ is to realize that if the scattering volume is large compared to $1/K^3$, then the sum in Eq. (1) can be described by a two-dimensional "random" walk[2,8,9] in the complex plane. If the scatterers are independent, the angles between steps will be random and the step length will be governed by $P(e)$, the probability distribution for the magnitude of the scattered field from a single particle. $e(r)$ and therefore $P(e)$ will depend both on the illumination profile and on the details of the collection optics [$e(r)$ can be measured by a study of the dynamics of occupation number fluctuations for systems under uniform motion[8]]. In the event that there are many independent scatterers in the illuminated region (many-step random walk[8,9]) Eq. (1) leads to a Gaussian distribution for E. Here one may correctly invoke the central-limit theorem. If the particles are not independent,

the angles between steps are correlated and the Gaussian result does not necessarily follow even for a large number of scatterers. As suggested by Di Porto, Crosignani, and Bertolotti,[4] the field is Gaussian in this case only if the correlation range is small compared to the characteristic linear dimension of the scattering volume.

If the scattering volume were uniformly illuminated, Eq. (1) would be described by a finite-step walk with constant step length. This problem has been solved by Kluyver,[10,11] and adapting his work one obtains the intensity distribution[8]

$$P(I)=\tfrac{1}{2}\int_0^\infty du\, uJ_0(u\sqrt{I})\exp\{\langle N\rangle[J_0(u)-1]\}, \quad (2)$$

where J_0 is the Bessel function of order zero.[11]

Unfortunately, $P(n)$ obtained from Eq. (2) will not accurately describe experimental results reported here because (a) the scattering volume is not uniformly illuminated and (b) some spatial and temporal averaging of the fluctuations is expected because of the finite detector area and finite sampling interval. One is therefore forced to a computer simulation of Eq. (1) or to a moment method. The moment method is particularly appealing because one can identify $\langle n(n-1)\cdots(n-m+1)\rangle$, the factorial moments of the measurable $P(n)$, with $\langle I^m\rangle$, the ordinary moments of $P(I)$.[12]

Consider first of all the normalized intensity moments, $F_m\equiv\langle I^m\rangle/\langle I\rangle^m$, for uniform illumination. These moments can be obtained by multiple differentiation of the moments generating function[12] [Laplace transform of Eq. (2)] with the following results:

$$F_m=\frac{(m!)^2}{\langle N\rangle^m}\sum_{i=1}^{m}\langle N\rangle^i\sum_{\{a\}}\Big[\prod_{j=1}^{m}(j!)^{2a_j}(a_j!)\Big]^{-1}. \quad (3)$$

The summation over $\{a\}$ in Eq. (3) is performed subject to the conditions

$$\sum_{j=1}^{m}ja_j=m;\quad \sum_{j=1}^{m}a_j=i. \quad (4)$$

This result has also been obtained by Chen, Tartaglia, and Pusey[13] by a method based on combinatorial analysis.

If the restrictions leading to Eq. (2) are lifted, the moments can still be obtained by evaluating the following expression:

$$\langle I^m\rangle=(1/TA)^m\int(dt)^m\int(d\vec{\mathrm{R}})^m\langle|E(\vec{\mathrm{R}},t)|^{2m}\rangle, \quad (5)$$

where $E(\vec{\mathrm{R}},t)$ is given by Eq. (1). The integrals in Eq. (5) represent the averages over the detector area and sampling interval. The angular brackets represent an ensemble average. Evaluating Eq. (5) for $m>2$ involves a tedious exercise in term counting, but we have obtained the normalized moments to fourth order. Only the second and third moments are given here:

$$F_2=\{\Xi_4/\rho\Xi_2^{\,2}\}+1+\mathcal{S}_2\mathcal{T}_2, \quad (6)$$

$$F_3=\frac{\Xi_6}{\rho^2\Xi_2^{\,3}}+\frac{\Xi_4(3+6\mathcal{S}_2'\mathcal{T}_2)}{\rho\Xi_2^{\,2}}+1+3\mathcal{S}_2\mathcal{T}_2+2\mathcal{S}_3\mathcal{T}_3, \quad (7)$$

where ρ is the number density of scatterers and Ξ_c is a volume integral over $e^c(\vec{\mathrm{r}})$. The $\mathcal{T}_c$ are c-fold time integrals over cyclic combinations of the second-order field correlation function. $\mathcal{S}_c$ are surface integrals over cyclic combinations of the two space-point field correlation function.[12] The combination $\beta_c\equiv\mathcal{S}_c\mathcal{T}_c$ is considered here to be a measurable constant dependent only on geometry and T. $\mathcal{S}_2'$ is a new spatial factor[14] which is expressible in terms of the measurable $\mathcal{S}_2$ in the limit $\mathcal{S}_c\simeq 1$, $\mathcal{S}_2'=(11-3\mathcal{S}_2)/8+\cdots$. Moments higher than the third involve complicated coherence factors[14] and are too cumbersome to reproduce here. Note that, for uniform illumination ($\Xi_c\propto V$) and $\beta_c=1$, Eqs. (6) and (7) reduce to Eq. (3). Also if $\Xi_0\propto V$ and $\beta_c=0$ then Eqs. (6) and (7) reduce to the moments of the Poisson occupation number distribution.[9]

Experimental work consisted of measurement of the photocount probability distribution[3] for 0.234-μm-diam polystyrene spheres in water solution. The illumination profile was roughly Gaussian in all three dimensions with a volume of 3×10^5 μm^3 within the $1/e$ points of the field profile.

Apparatus used here was described by Pusey *et al.*[15] and consisted of a krypton ion laser ($\lambda=5682$ Å) focused on the center of a 1×1 cm^2 cuvette by a 3-cm focal-length lens. Collection optics consisted of an imaging lens, aperture, and slit. Diffraction at this slit determines the illumination profile in the dimension parallel to the incident beam. An ITT FW 130 photomultiplier was used as the detector. The photocount probability was analyzed by a modified version of the digital correlator described by Pusey *et al.*[15] Details of this device will be published elsewhere.[14]

Experiments were performed with two sampling intervals, $T=5\times10^{-2}$ and 5×10^{-5} sec. In the former case, interference fluctuations are effectively averaged so that $\mathcal{T}_c\to0$ in Eqs. (6) and (7). In the latter experiments, the sample cell was translated transverse to the incident beam at a

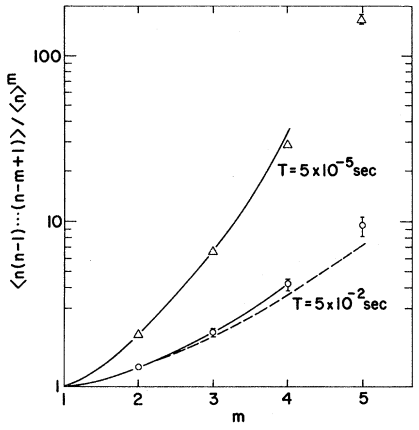

FIG. 1. Factorial moments of photocount distributions. Triangles, $T=5\times10^{-5}$ sec; circles, $T=5\times10^{-2}$ sec; solid lines, calculated moments for Gaussian illumination profile; dashed line, calculated moments for uniform illumination.

rate of about 500 μm/sec in order to reduce the time constant of occupation-number fluctuations. In both cases the actual magnitude of the coherence factors was measured through the factorial moments of the photocount distributions in the Gaussian limit (ρ large), with the result that $\beta_{2,3,4,5}=0.754$, 0.65, 0.56, 0.48 for $T=5\times10^{-5}$ sec and $\beta_{2,3,4,5}=0.025$, 0, 0, 0 for $T=5\times10^{-2}$ sec.

The measured factorial moments for a sample with about 3 particles in the illuminated volume are shown in Fig. 1. The moments calculated from Eqs. (6) and (7) are also plotted. These moments were calculated assuming a Gaussian illumination profile. In both cases, the concentration was taken as 3.37 particles within the $1/e$ points of the field profile. This value is consistent with both measured second moments. For comparison, moments calculated assuming uniform illumination are also plotted for the $T=5\times10^{-2}$-sec data. These are just the moments of a Poisson distribution with a mean of 3.1 (obtained by fitting the second moment).

Figure 1 shows that theory presented here provides a very good discription of the data for the long-interval experiments, while errors of the order of 5% occur in the third moment for the short-interval experiment. These discrepancies arise because of errors in the measured β_c which were measured in a different sample to an accuracy of no better than 3%.

Experiments were also performed at $\langle N\rangle \simeq 1$ and 8 once again excellent agreement was obtained for the long-interval experiment with discrepancies of the order of 5% arising in the third moment for the short-interval case. For the long-interval case, the number density obtained from the second moment was found to scale with the scattered intensity within experimental error while discrepancies of the order of 15% arose for the short-interval case. These results indicate that the statistics of the scattered light provide a means to determine the number density of macromolecular solutions, particularly if $\beta_c \to 0$ or $\beta_c \to 1$.

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