Multiple scattering from a system of Brownian particles

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We consider the total multiple-scattered light field from a system of Brownian diffusing particles. We assume the correlation function is due to contributions from all the independent single-scattering events leading to the multiple-scattered field. We then assume the relative magnitudes of the various orders of the multiple-scattered light are given by the Poisson distribution. For particles of radius $r \ll \lambda$, λ being the wavelength of light, we arrive at expressions for the depolarization ratio and the polarized and depolarized linewidths as functions of the average number of scattering events $\bar{n} = \sigma\rho x$, where σ is the single-particle scattering cross section, ρ is the particle concentration and x is a distance related to the scattering volume size. We give experimental data to support our contentions.

I. INTRODUCTION

Over the past few years a number of papers concerning multiple scattering from Brownian motion[1-5] and critical fluid systems[6-12] have been published. These papers have been for the most part concerned with the autocorrelation function of the multiple-scattered light. The problem is usually reduced to the study of the double-scattered light, this component being the lowest-order correction for the multiple-scattered field.

The procedure for analysis of this problem has been to consider the double-scattered field as due to two successive and independent single-scattering events. This was first suggested by Oxtoby and Gelbart[8] for the intensity of the depolarized light scattered from a fluid near the critical point, and was experimentally verified by Reith and Swinney.[10] We have considered the double-scattered autocorrelation function in terms of two independent single-scattering events and found good agreement of theory and experiment for light scattering from Brownian diffusing particles versus scattering angle.[1] We then applied this procedure to the autocorrelation function of the depolarized-scattered component from a critical fluid with apparent success.[6,7]

Quite recently Kim, Gallagher, and Armeniades[3] have considered the depolarized autocorrelation function as a function of the concentration of the Brownian particles. They found that the linewidth (inverse correlation time) increased monotonically with concentration. They also devised an ingenious experiment in which, by using two cells side by side, they changed the diffusion constant of the particles responsible for the first scattering event by a factor of approximately 2 without affecting the second scatterers. With such a change the depolarized linewidth changed only very slightly. They concluded that the depolarized linewidth is *not* affected by the motion of the first scatterers in a typical double-scattering experiment. They then developed a theory which involved mixing of the spatial and temporal coherence of the scattered light that resulted in a *double-scattered* linewidth versus concentration dependence that fit their experimental results with one free parameter. This work suggests that the concept of two independent scattering events contributing to the double-scattered linewidth is wrong.

In this paper we consider both the polarized and depolarized scattered light correlation function of the *full multiple-scattered field*. To do so, we assume the nth-order scattered field is a result of n successive and independent single-scattering events in analogy to our earlier double-scattering work,[1] but in contrast to the results of Kim *et al.*[3] Since the extent of multiple scattering is a function of the particle concentration, we shall find a concentration dependence for our linewidths. We shall show how the data of Kim, Gallagher, and Armeniades might be explained with our theory. We shall also consider the intensity of the multiple-scattered field and find a relation between the depolarization ratio and the cross section for scattering.

In Sec. II we develop our theory for multiple scattering in terms of independent single-scattering events of relative intensity given by the Poisson distribution. Section III gives preliminary experimental evidence to support our theory. In Sec. IV we consider the partitioned-cell experiment of Kim *et al.* and show how it may be explained in the context of our work. We also mention the possibility of cross-section determination from depolarization ratio measurements.

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II. THEORY

A. Multiple-scattered field

We shall consider the multiple-scattered field as a result of successive and statistically independent single-scattering events. We assume a spherical scattering geometry where the distribution of second scatterers with respect to first scatterers is taken to be spherically symmetric.[1]

Our work has not considered the effects of coherence of the field on the correlation function. Van Rijswijk and Smith,[4] however, have considered this problem. They considered two separate cells of Brownian particles. Light single scattered from one was collected at some angle and directed to the second cell and was single scattered again. The spectrum of this double-scattered light was then considered. They found, and verified experimentally, that when the cells were far apart, $R \sim 50$ cm, the light was non-Gaussian and the linewidth was independent of the *second* scatterer. However, when the cells were close together, $R \sim 1.5$ cm, the light was Gaussian and the linewidth was described by two independent single scatterings. In conventional experiments, where one is concerned with the field scattered from the illuminated scattering volume, the first, second, third, and so forth scatterers are all close in the sense of Van Rijswijk and Smith. Thus, we shall take their results as further evidence that the independent-scatterer approximation is good and that the scattered light is Gaussian.

We proceed as before and consider the multiple-scattered field as a Born series of scattering events. We write for the correlation function of the multiple-scattered field [see Eq. (5), Ref 1.]

$$\langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle = \sum_{n=1}^{\infty} \langle \vec{E}_n^*(t) \cdot \vec{E}_n(0) \rangle + \sum_{i \neq j}^{\infty} \langle \vec{E}_i^*(t) \cdot \vec{E}_j(0) \rangle , \tag{1}$$

where $\vec{E}_i(t)$ is the ith-scattered field [see Eq. (4), Ref. 1].

We consider the cross term in Eq. (1) with $i > j$. $\vec{E}_j(0)$ represents scattering from j independent particles. If at a time t later, light is scattered from the same j particles, although not necessarily in the same order, the correlation of the two multiple-scattering events will be a function of t. However if $\vec{E}_i(t)$ represents these j events plus $i-j$ different events, the total correlation $\langle \vec{E}_i \vec{E}_j \rangle$ will be zero because these $i-j$ events are completely random. If we take $\vec{r}_i(t)$ as the position vector of the ith scatterer at time t and $\vec{k}_i$ as the wave vector of the ith scattering event, we may write

$$\langle \vec{E}_i^*(t) \cdot \vec{E}_j(0) \rangle \propto \langle \exp\{i\vec{k}_1 \cdot [\vec{r}_1(t) - \vec{r}_1(0)]\} \rangle \ldots \langle \exp\{i\vec{k}_j \cdot [\vec{r}_j(t) - \vec{r}_j(0)]\} \rangle \times \langle \exp[i\vec{k}_{j+1} \cdot \vec{r}_{j+1}(t)] \rangle \ldots \langle \exp[i\vec{k}_i \cdot \vec{r}_i(t)] \rangle . \tag{2}$$

This cross term is zero because the terms $\langle e^{i\vec{k}\cdot\vec{r}} \rangle = 0$.

If the additional $i-j$ events are from particles included in the first j particles, i.e., some particles scatter more than once in the sequence described by the cross term, then the correlation would not be zero. However, we feel the statistical weight of such terms will be much smaller than that of the $\langle \vec{E}_n^* \cdot \vec{E}_n \rangle$ terms and so we shall take them to be zero. We therefore eliminate the cross terms from Eq. (1) and have

$$\langle \vec{E}^*(t) \cdot \vec{E}(0) \rangle = \sum_{n=1}^{\infty} \langle \vec{E}_n^*(t) \cdot \vec{E}_n(0) \rangle , \tag{3}$$

which represents the sum of n-scattered fields.

B. Intensity

From Eq. (3) with $t=0$ we find the total multiple-scattered intensity to be

$$I = \sum_{n=1}^{\infty} I_n . \tag{4}$$

We stress that this is a sum over *all* orders of multiple scattering. To evaluate (4) we need to have a relation for the various orders of scattered intensity. Since the Born approximation is no longer valid for large amounts of scattering, another device is needed.

We shall use the fact that light scattering may be considered a random statistical process. This can be best illustrated by calculating the turbidity of a system by assuming it is a cumulative Poisson random process. To generalize this for our purposes, we assume the detected scattering volume and the illuminated volume are equal. We then assume that the probability of observing a photon after n scattering events is given by the Poisson distribution. Thus, the nth-order intensity is proportional to

$$I_n \propto P(n) = (\bar{n}^n/n!)e^{-\bar{n}}, \tag{5}$$

where $P(n)$ is the Poisson distribution with average $\bar{n}$. The average number of scattering events $\bar{n}$ can be found from a turbidity argument to be

$$\bar{n} = \sigma\rho x = x/l\ . \tag{6}$$

Here σ is the cross section of scattering for the particle and ρ is the particle number density. We will take x to be a distance parameter related to the mean size of the scattering volume, and l is the mean free path of the photon.

We wish to relate $\bar{n}$ to the depolarization ratio R of the scattered light. R has been used before to characterize the extent of multiple scattering.[7,10] We have

$$R = \frac{I_\perp}{I_\parallel} = \frac{\sum_{n=1}^{\infty} I_{n\perp}}{\sum_{n=1}^{\infty} I_{n\parallel}}\ . \tag{7}$$

Here $\perp$ and $\parallel$ denote depolarized and polarized, respectively, where we consider the standard geometry with incident beam polarized perpendicular to the scattering plane. Note that each order n has both a polarized and depolarized part, thus

$$I_n = I_{n\parallel} + I_{n\perp} \propto P(n)\ . \tag{8}$$

To solve Eq. (8) we require the depolarization ratio of the nth-order scattered light,

$$R_n = I_{n\perp}/I_{n\parallel}\ . \tag{9}$$

Solving Eqs. (8) and (9) for $I_{n\parallel}$ and $I_{n\perp}$ and substituting into (7) we have

$$R = R(\bar{n}) = \frac{\sum_{n=1}^{\infty} [R_n/(1+R_n)]P(n)}{\sum_{n=1}^{\infty} [1/(1+R_n)]P(n)}\ . \tag{10}$$

This expression gives R solely as a function of $\bar{n}$, the average number of scattering events.

To evaluate Eq. (10) we must know R_n for all n. Since there is no depolarized component for single scattering, $R_1 = 0$. We have found[1] for spherical symmetry and $r \ll \lambda$, that $R_2 = 0.125$ (for $r \sim \lambda$, R_2 decreases with increasing r/λ and becomes scattering-angle dependent[13]). A similar albeit tedious calculation gives $R_3 = 0.26$. R_n for $n > 3$ appears to be very difficult to calculate. For $n \gg 1$ we expect $R_n = 1$ because the polarizations will be completely randomized. We have evaluated Eq. (10) for $R_4 = 0.5$ and $R_n = 1.0$ for $n \geq 5$ and will use this in our analysis below. For $R_4 = 1.0$ the results are changed by 5%–10% as seen in Fig. 1 where we plot $\bar{n}$ vs R.

Equation (10) or Fig. 1 allows us to determine $\bar{n}$, the average number of scattering events, from

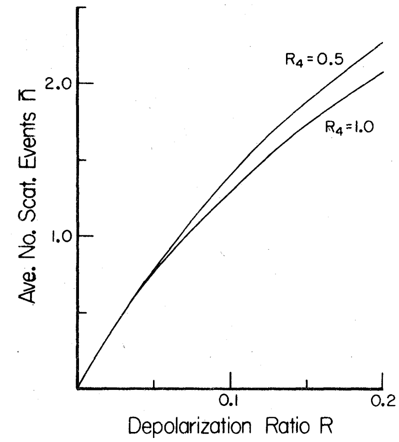

FIG. 1. Theoretical prediction of Eq. (10) for the average number of scattering events vs the experimental depolarization ratio.

the experimental depolarization ratio. Since $\bar{n}$ is related to the scattering cross section by Eq. (6), one may then determine the scattering cross section experimentally.

C. Linewidths

In this section we consider the linewidth, equal to the inverse correlation time, of the multiple-scattered light. To do so we consider our results for the double-scattered linewidth. We found for the spherical scattering geometry and for particles of radius $r \ll \lambda$ that the first cumulant of either the polarized or depolarized component of the double-scattered light was equal to twice the linewidth of the light single scattered at 90°.[1] This was a consequence of the assumption of two independent single-scattering events. One may easily show that the same result is obtained if one considers the double-scattered spectrum as the result of two single-scattering events each of which has an average or effective scattering angle of 90°. Thus, ignoring the nonexponentiality by setting the linewidth equal to the first cumulant, the double-scattering results may be expressed

$$\Gamma_2 = 2\Gamma_1(90°)\ . \tag{11}$$

It is now straightforward to consider the linewidth of the nth-order scattered light as due to n single-scattering events of average scattering angle 90°. Then,

$$\Gamma_n = n\Gamma_1(90°)\ , \tag{12}$$

where Γ_n is the nth-order linewidth, independent of scattering angle.

To find the effective linewidth of the total multiple-scattered field, we consider our Poisson random scattering process and Eq. (3). Equation (3) will be a sum of exponential correlation functions of linewidths Γ_n weighted by the Poisson distribution, $P(n)$. Such a sum will be nonexponential but we again consider only the first cumulant of the sum as the effective linewidth. The effective linewidths are then Poisson weighted averages which from Eqs. (8), (9), and (12) are

$$\Gamma_\perp = \Gamma_1(90^\circ)\frac{\sum_{n=1}^{\infty}[R_n/(1+R_n)]nP(n)}{\sum_{n=1}^{\infty}[R_n/(1+R_n)]P(n)} \tag{13a}$$

$$\Gamma_\parallel = \Gamma_1(90^\circ)\frac{\sum_{n=1}^{\infty}[1/(1+R_n)]nP(n)}{\sum_{n=1}^{\infty}[1/(1+R_n)]P(n)}\,. \tag{13b}$$

These linewidths for the full multiple-scattered field are independent of the scattering angle, represent the first cumulant of the nonexponential correlation function and most importantly are solely functions of $\bar{n}$ which can be determined from experimental depolarization ratio measurements. Plots of $\Gamma_\perp$ and $\Gamma_\parallel$ vs $\bar{n}$ normalized to $\Gamma_1(90^\circ)$ are given in Fig. 2 with the same R_n used in the intensity calculation. Use of $R_4=0.5$ or 1.0 seems to have little effect.

At two separate junctures in the above derivation we have approximated the correlation function as

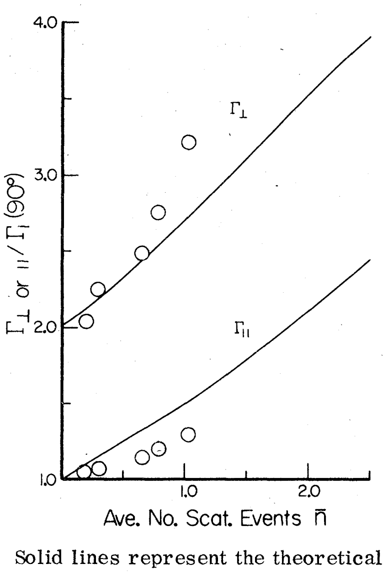

FIG. 2. Solid lines represent the theoretical results of Eqs. (13) for the ratio of the depolarized ($\perp$) or polarized ($\parallel$) linewidth to the linewidth for single scattering at a scattering angle of 90° vs the average number of scattering events $\bar{n}$. Circles represent linewidth data from a turbid system of Brownian particles where $\bar{n}$ was determined from the experimental depolarization ratio and Fig. 1.

an exponential with linewidth (inverse correlation time) equal to the first cumulant. Thus, our results of Eqs. (13) represent the first cumulant of the expectedly quite nonexponential correlation function of the multiple-scattered field. Unpublished results[13] indicate the double-scattered polarized correlation function is more nonexponential than the double-scattered depolarized correlation function. We might expect this trend to continue into all orders. In any event, accurate extraction of the first cumulant of the multiple-scattered correlation function from data on turbid systems might be difficult due to the possibly large nonexponentiality.

III. EXPERIMENT

We present here preliminary experimental results concerning the multiple-scattered depolarization ratio and linewidths. In the future we hope to systematize our scattering geometry and data analysis to obtain a cleaner experimental technique for these data. Our work here is meant only to suggest the validity of our theoretical results.

We suspended monodisperse samples of polystyrene spheres in distilled water at concentrations of 1.0×10^{11} to 5.76×10^{11} particles/cm^3. The radius of the particles was $r=0.055\pm0.001$ μm. The condition $r \ll \lambda$ holds for these particles as is verified by our double-scattering data.[1] We attempted to add ionic salts to reduce any possible Coulombic interactions which might affect our results.[14] These efforts always resulted in coagulation and so salts were not added.

The sample cell was a 0.8-cm-i.d. test tube. The vertically polarized beam of an argon-ion laser operating at $\lambda=5145$ Å was directed unfocused (visual diameter of approximately 3 mm) into the cell. Light scattered at 90° passed through a Glan-Thompson polarizer of extinction ratio 5×10^{-5} which selected the polarization of the scattered light. The light then passed through a 300-μm pinhole the effect of which was to give approximately one coherence area of light on the 0.1-in.-diam cathode of an ITT FW130 photomultiplier 1 m distant. The photon pulses were then detected and correlated and the first cumulants extracted as well as possible from the nonexponential spectra.

We stress that the beam is not focused, but spatial coherence on the cathode is obtained with the pinhole. Also, the illuminated volume defined by the laser beam is larger than the scattering volume defined by the pinhole and the cathode. The scattering volume is approximated by a cylinder 0.8 cm long and 600 μm diameter. We are not sure what effect this difference will have. Finally, the spherical scattering geometry[1] holds for this

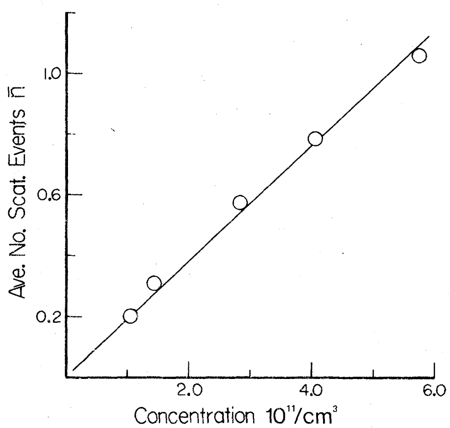

FIG. 3. Average number of scattering events $\bar{n}$ vs particle concentration. $\bar{n}$ was determined from depolarization ratio measurements and Fig. 1.

arrangement.

The depolarization ratios were used to determine $\bar{n}$ using Fig. 1. These values are then plotted against concentration in Fig. 3. The linearity of this plot is in keeping with Eq. (6) and the slope should be σx. Experimentally, Fig. 3 indicates $\sigma x = 1.93 \times 10^{-12}$ cm^3. The cross section σ can be evaluated from the results of electromagnetic theory and for our polystyrene particles $\sigma = 2.64 \times 10^{-12}$ cm^2 implying $x = 0.73$ cm for our experiment. This value, comparable to the dimensions of our illuminated volume, seems a bit large to describe the mean size of the scattering volume.

The linewidths are plotted as data points along with the theoretical predictions in Fig. 2. As before, $\bar{n}$ was determined from the experimental depolarization ratio and so there are no adjustable parameters. The theory and data appear to yield adequate agreement. The deviations of data and theory might be explained as due to Coulombic interactions tending to make the linewidth larger[14] or to the large nonexponentiality tending to make the linewidth appear smaller. This latter fact may well be the situation for the experimentally very nonexponential polarized correlation function.

IV. DISCUSSION

We have shown the polarized and depolarized scattered linewidths of the total multiple-scattered light are increasing functions of the average number of scattering events in the scattering process, $\bar{n}$. Since $\bar{n} = \rho x \sigma$, we predict a density dependence for these linewidths as observed by Colby *et al.*[2] and Kim *et al.*[3] We stress that the *double-scattered* linewidths are not functions of the density as suggested by Kim *et al.* In an effort to resolve this difference we consider their partitioned-cell experiment.

The partitioned-cell experiment of Kim *et al.* consisted of two cells side by side. One cell, the single-scattering cell (SSC), contained $r = 0.0455$-μm-diam particles at a concentration of 4.8×10^{10} particles/cm^3. The second, or double-scattering cell (DSC), contained the same particles at a concentration of 1.36×10^{12} particles/cm^3. The focused laser beam was incident upon the SSC and the depolarized scattered light from both cells was observed at 90°. When each compartment contained fluids (water) of viscosity 1.002 cP a linewidth of $\Gamma_\perp = 17\,930$ sec^{-1} was observed. However when the SSC contained a suspension with fluid viscosity of 1.83 cP the linewidth changed only slightly to $\Gamma_\perp = 17\,777$ sec^{-1}. Reversing this with fluid viscosity 1.836 cP in the DSC the linewidth fell to $\Gamma_\perp = 9875$ sec^{-1} which is to be expected because $\Gamma \propto \eta^{-1}$, η being the viscosity. They concluded that $\Gamma_\perp$ is not affected by the motion of the first scatterers in a double-scattering experiment.

To analyze this result, we first compare $\Gamma_\perp = 17\,930$ sec^{-1} to $\Gamma_1(90°)$. For their system we can calculate $\Gamma_1(90°) = 5600$ sec^{-1}. If we consider $\Gamma_\perp$ as due to the full multiple-scattered field, we can compare the ratio $\Gamma_\perp/\Gamma_1(90°)$ to Fig. 2 and determine $\bar{n} = 1.6$ for their experiment. We also consider $\bar{n} = \rho\sigma x$ with σ calculated from electromagnetic theory for their particles and x chosen arbitrarily to be our experimental $x = 0.73$ cm and find $\bar{n}_{SSC} = 0.06$ and $\bar{n}_{DSC} = 1.76$ corroborating the value implied by the linewidth data. The point of this exercise is to show that while there is essentially only single scattering in the SSC there is *multiple scattering*, not just double scattering, in the DSC.

We now consider the first cumulant value of the nth-order linewidth. Since the linewidth and diffusion constant are related by $\Gamma = Dk^2$, we have

$$\Gamma_n = \bar{k}^2 \sum_{i=1}^{n} D_i . \quad (14)$$

For $D_i = D$ for all i, Eq. (14) reduces to our result Eq. (12) with $\bar{k}$ the scattering wave vector at 90°. From Eqs. (8), (9), and (14), using the same reasoning which lead to Eqs. (13), the depolarized multiple-scattered linewidth is

$$\Gamma_\perp = \bar{k}^2 \frac{\sum_{n=1}^{\infty} [R_n/(1+R_n)]P(n) \sum_{i=1}^{n} D_i}{\sum_{n=1}^{\infty} [R_n/(1+R_n)]P(n)} . \quad (15)$$

Again, for $D_i = D$ for all i, Eq. (15) reduces to Eq. (13a). We have evaluated Eq. (15) with $D_1 = D/1.836$ and $D_i = D$ for $i \geq 2$ and $\bar{n} = 1.6$. This represents our theoretical partitioned-cell linewidth with higher viscosity in the SSC. We find $\Gamma_\perp(\eta_{SSC} = 1.836\text{ cP})/\Gamma_\perp(\eta_{SSC} = 1\text{ cP}) = 0.91$ compared to their experimental value of 0.99. Considering the difficulties in applying our argument to their unusual scattering geometry, we feel that this result indicates that Kim *et al.* have in fact observed multiple scattering due to *independent* scattering events.[15]

The relation between the depolarization ratio R and the average number of scattering events $\bar{n} = \rho\sigma x$ suggests the possibility of determining the cross section σ by measuring R. This has been considered by Reith and Swinney,[10] but only to second order. We hope that with experimentation a better characterization of the scattering volume size x may be achieved and thereby better define $\sigma = \bar{n}/\rho x$.

We also wish to point out that while our calculations have been for particles of size $r \ll \lambda$, it might also be extended to $r \sim \lambda$. To do so we would neglect any scattering-angle dependence of Γ_n for n large and redefine the average scattering angles to the forward direction with increasing r. This last point is suggested by the double-scattering data.[1]

V. CONCLUSION

We conclude that multiple scattering can be described as the result of a series of independent single-scattering events whose intensities at the detector are weighted by the Poisson distribution.

ACKNOWLEDGMENT

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[15] We point out that the theoretical particle concentration dependence of the linewidth in Ref. 3 is a result of their Eq. (3) that gives the average particle distance $\langle l \rangle$ as a function of the particle concentration. It seems to us, however, that whereas the ***nearest-neighbor*** distance decreases with increasing concentration, the ***average*** distance between particles is ***not*** a function of the particle concentration, but dependent only on the scattering volume size.