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Depolarized correlation function of light double scattered from a system of Brownian particles

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We consider the multiply scattered electric field from a system of noninteracting Brownian scatterers. We show that the lowest-order contribution to the depolarized correlation spectrum of the scattered light is due to double scattering. We find an expression in the far-field approximation for the electric-field correlation function double scattered from a system of pointlike particles. We show that while the correlation function is slightly nonexponential, the $t = 0$ slope of the correlation function is *independent* of scattering angle and equal to the single scattered correlation time corresponding to a scattering angle of 180°. We then generalize our result to include larger, Rayleigh-Debye particles of radius $l \lesssim \lambda$ where λ is the wavelength of the incident light. The results for larger particles are qualitatively similar to those for pointlike particles in that there is a lack of a large scattering-angle dependence in the correlation time of the double-scattered light, and the magnitude of the correlation time is slightly greater than the correlation time for single-scattered light at 180°. We then perform intensity autocorrelation experiments on two systems of polystyrene microspheres of radii $l = 0.055$ and 0.117 μm. We measure the depolarized scattered light correlation time and compare it to our theoretical results for double scattering. The agreement of theory and data is seen to be good. We discuss potential applications of this work to other phenomena.

I. INTRODUCTION

In recent years the technique of autocorrelation spectroscopy has expanded the use of laser light scattering into a wide variety of fields. Autocorrelation spectroscopy allows us to measure the temporal characteristics of system fluctuations that produce Rayleigh linewidths as small as a few hertz at optical frequencies. This has led to the wide use of correlation techniques to probe diffusion in liquids and biological systems and in the study of critical phenomena in liquids.[1]

In deriving the theoretical expression for the scattered light field correlation function which is the central quantity in correlation spectroscopy, one assumes that the scattered light is the result of only one scattering of the incident light from the fluctuations or the diffusing particles in the system. This single-scattering assumption is usually good for systems of small scattering cross section. However, for systems of large scattering cross section, such as a concentrated suspension of particles in a fluid or a fluid system near its critical point, this assumption may no longer be valid. This is because the probability that the light will scatter more than once on its way to the detector increases as the cross section for scattering goes up. Thus in order to understand the intensity and correlation function of the scattered light from dense systems, one must take into account the effects of multiple scattering.

Several groups have recently examined the effects of double scattering on the intensity of light scattered from fluids near the critical point. Oxtoby and Gelbart[2,3] show theoretically that double scattering is the major contribution to the depolarized scattered light near the critical point when $T - T_C \lesssim 1$ °C. Reith and Swinney[4] give experimental evidence to support this result. Oxtoby and Gelbart[3] and Bray and Chang[5] point out that one might infer an erroneously large value of the critical exponent η from intensity measurements near the critical point if the effects of multiple scattering are ignored. All this work has served to dramatize the fact that the effects of multiple scattering must be correctly accounted for if autocorrelation spectroscopy is to be a useful interpretive probe of fluid behavior very close to a critical point.

In other work Colby, Narducci, Bluemel, and Baer[6] performed systematic intensity and intensity correlation measurements on systems of highly concentrated polystyrene microspheres as a function of concentration and scattering angle. They found that the intensity of the scattered light became less and less a function of the scattering angle as the concentration increased; i.e., the Mie patterns characteristic of the scattering from individual microspheres tended to disappear. They also found that the correlation time of the scattered light decreased with increasing concentration. While they were unable to explain their data theoretically, they concluded that multiple scattering was responsible for these effects.

In this paper we propose a simple theory to treat the correlation function of double-scattered light. In particular, we concern ourselves with

double-scattered light from a system of Brownian particles. This problem has been considered before by Kelly.[7] However, his work does not agree with our results, because he failed to evaluate explicitly the Green's function resulting from the solution of the integral equation for the electric field [e.g., his Eq. (31)]. This Green's function contains the phase information of the light as it scatters from the first to the second scatterer. In our approach the Green's function is written explicitly from the start of our work in its exponential form as the leading coefficient of the electric dipole field propagator. By writing it explicitly, we are able to keep track of the phase of the light as it scatters from the first to the second scatterer, as well as the scattering from the second scatterer to the detector.

We will show that the lowest-order contribution to the depolarized scattered light is due to double-scattered light. We have measured the correlation function of the depolarized scattered light for two different-sized systems of Brownian particles.

We begin in Sec. II with the electric field propagation tensor to find the field scattered to any order. We then consider the correlation function of the scattered field and show that the double-scattered field correlation function is the lowest-order contributor to the depolarized correlation function. In Sec. III we derive the first-order (single-scattered) correlation function using our formalism. This has been done before, but we will find its development instructive when deriving the second-order correlation function. In Sec. IV we present our derivation of the double-scattered field correlation function. We make use of the far-field approximation and indicate how this may limit our theory. We present our results for a spherically symmetric scattering volume. We give expressions both for the case of particles with a radius much smaller than the wavelength of the incident light and for particles whose radius is of the same order of the wavelength of the incident light. In the latter case we make use of the Rayleigh-Debye theory for light scattering from dielectric spheres. We also discuss the intensity of the depolarized light and find agreement with prior work. In Sec. V we describe the data-taking procedures we used to determine the correlation function of the depolarized light. In particular, we discuss how we obtained an effectively spherical scattering geometry and the importance of proper polarization adjustment. We compare theory to experiment and find excellent agreement. Finally, in Sec. VI we discuss our results and consider their extension to other systems.

II. SCATTERED FIELD

To begin we consider the electric dipole field propagator,[7] $\vec{\vec{T}}(\vec{r}_{12})$, where

$$\vec{\vec{T}}(\vec{r}_{12}) = \frac{e^{ik|\vec{r}_1-\vec{r}_2|}}{|\vec{r}_1-\vec{r}_2|}\left[\left(1+\frac{i}{kr_{12}}-\frac{1}{k^2r_{12}^2}\right)\vec{\vec{I}} - \left(1+\frac{3i}{kr_{12}}-\frac{3}{k^2r_{12}^2}\right)\hat{r}_{12}\hat{r}_{12}\right], \tag{1}$$

with

$$\vec{r}_{12}=\vec{r}_1-\vec{r}_2, \quad \hat{r}_{12}=\vec{r}_{12}/|\vec{r}_{12}|.$$

Here $k=2\pi/\lambda$, λ being the wavelength of the radiation produced by the oscillating dipole, and $\vec{\vec{I}}$ is the unit tensor. The dipole field propagator is a result of electromagnetic theory and gives the field at point $\vec{r}_1$ due to an oscillating dipole at $\vec{r}_2$. Since an incident electromagnetic wave will induce dipoles in a medium, the dipole propagation tensor will describe the scattered field produced by these dipoles. If the electric polarization of a medium is taken to be the tensor $\vec{\vec{\alpha}}(\vec{r}, t)$, then the induced dipole due to an incident electric field is $\vec{\vec{\alpha}}\cdot\vec{E}$. The electric field at a point $\vec{r}_1$ and time t is then

$$\vec{E}(\vec{r}_1, t)=k^2\int_{\sigma(\vec{r}_1)}\vec{\vec{T}}(\vec{r}_{12})\cdot\vec{\vec{\alpha}}(\vec{r}_2, t)\cdot\vec{E}(\vec{r}_2, t)\,d^3r_2. \tag{2}$$

The integral is taken over the entire scattering volume except for a small volume element $\sigma(\vec{r}_1)$ centered at $\vec{r}_1$.

We solve Eq. (2) by iteration on the field:

$$\vec{E}(\vec{r}_1, t)=\vec{E}_0(\vec{r}_1, t)+\sum_{n=1}^{\infty}\vec{E}_n(\vec{r}_1, t), \tag{3}$$

$$\vec{E}_n(\vec{r}_1, t)=(k^{[1]})^2\int_{\sigma_1}d^3r_2\,\vec{\vec{T}}(\vec{r}_{12})\cdot\vec{\vec{\alpha}}(\vec{r}_2, t)\cdot(k^{[2]})^2\int_{\sigma_2}\cdots(k^{[n]})^2\int_{\sigma_n}d^3r_{n+1}\vec{\vec{T}}(\vec{r}_{n,n+1})\cdot\vec{\vec{\alpha}}(\vec{r}_{n+1}, t)\cdot\vec{E}_0(\vec{r}_{n+1}, t). \tag{4}$$

E_n represents an electric field that has been scattered n times, as shown by Eq. (4), and $k^{[n]}$ is the nth scattered wave vector.

In this paper we are concerned with the scattered field correlation function. Using Eq. (3) we find this correlation function to be of the form

$$\langle \vec{E}^*(\vec{r}_1, t)\cdot\vec{E}(\vec{r}_1, 0)\rangle = \sum_{n=1}^{\infty} \langle \vec{E}_n^*(\vec{r}_1, t)\cdot\vec{E}_n(\vec{r}_1, 0)\rangle + \sum_{i\neq j}^{\infty} \langle \vec{E}_i^*(\vec{r}_1, t)\cdot\vec{E}_j(\vec{r}_1, 0)\rangle , \tag{5}$$

where we have assumed the field average is stationary in time. The lowest-order term in Eq. (5) is the single-scattered correlation function $\langle \vec{E}_1^*(t)\cdot\vec{E}_1(0)\rangle$. The polarization of $\vec{E}_1(t)$ is parallel to the incident polarization and is the lowest-order contributor to the "polarized" scattered component. We will use the usual nomenclature, where "polarized" refers to that light scattered with polarization parallel to the incident-wave polarization; "depolarized" refers to light scattered with polarization perpendicular to the incident-wave polarization. The next-higher-order term in Eq. (5) is $\langle \vec{E}_1^*\cdot\vec{E}_2\rangle$. While $\vec{E}_2$ itself may have depolarized components, the scalar product with the polarized $\vec{E}_1$ demands that this term contribute only to the polarized spectrum.[8] Similar arguments can be made for any term of the form $\langle \vec{E}_1^*\cdot\vec{E}_m\rangle$. This leaves $\langle \vec{E}_2(t)^*\cdot\vec{E}_2(0)\rangle$ as the lowest-order depolarized term. In this paper we shall evaluate this term for the case of a medium with pointlike scatterers, and for the more realistic case of particles which are not necessarily pointlike (i.e., the radius need not be $\ll\lambda$), undergoing Brownian motion.

III. SINGLE SCATTERING

The properties of the first-order or single-scattered field, have been derived before[9] and the results are well known. We will solve Eqs. (3) and (4) to order $n=1$ and then determine the single-scattered field correlation function. This will help illuminate the procedure to be used when we consider the double-scattered problem.

Truncating Eq. (4) at $n=1$ we have

$$\vec{E}_1(\vec{r}_1, t) = k'^2 \int_{\sigma(\vec{r}_1)} d^3r_2\, \vec{T}(\vec{r}_{12})\cdot\vec{\alpha}(\vec{r}_2, t)\cdot\vec{E}_0(\vec{r}_2, t). \tag{6}$$

We write the incident electric field as a wave of wave vector $\vec{k}$ and frequency ω, with polarization $\hat{\epsilon}$,

$$\vec{E}_0(\vec{r}_2, t) = \hat{\epsilon}\mathcal{E}_0 e^{i\vec{k}\cdot\vec{r}_2 - i\omega t} \tag{7}$$

where $\mathcal{E}_0$ is the wave amplitude.

We will take the polarizability of the medium to be isotropic. The polarization tensor may then be written as the diad

$$\vec{\alpha}(\vec{r}, t) = a(\vec{r}, t)\hat{\alpha}\hat{\alpha}. \tag{8}$$

This isotropy implies that the induced moment will be parallel to the incident-field polarization; thus $\hat{\alpha}\cdot\hat{\epsilon}=1$. From Eqs. (6)–(8) the single-scattered field is

$$\vec{E}_1(\vec{r}_1, t) = \mathcal{E}_0 k'^2 e^{-i\omega t}\int d^3r_2\, a(\vec{r}_2, t)\cdot\vec{T}(\vec{r}_{12})\cdot\hat{\epsilon}\, e^{i\vec{k}\cdot\vec{r}_2}. \tag{9}$$

Since the observation point $\vec{r}_1$ is outside the scattering volume, we need no longer specify the integral in Eq. (9) to exclude the volume $\sigma(\vec{r}_1)$.

To proceed further we examine the field propagator $\vec{T}(\vec{r}_{12})$. In most scattering experiments the detector is many wavelengths distant from the scattering volume and this distance is much larger than the dimensions of the scattering volume. That is, $r_1 \gg 1/k$ and $r_1 \gg r_2$. These inequalities imply

$$|\vec{r}_1 - \vec{r}_2| \simeq r_1 - \vec{r}_2\cdot\hat{r}_1, \tag{10}$$

which to first order gives

$$|\vec{r}_1 - \vec{r}_2| \simeq r_1, \tag{11}$$

$$|\vec{r}_1 - \vec{r}_2|\, k \gg 1. \tag{12}$$

Equations (10)–(12) describe the *far-field approximation*[10] for a radiating dipole.

In applying the far-field approximation to the field-propagation tensor, we use Eq. (11) in the magnitude terms of the tensor, but we must use Eq. (10) in the phase term in order to evaluate the full effect of the scattered phase. In this approximation, for $\vec{k}' = k'\hat{r}_1$, Eq. (1) becomes

$$\vec{T}(\vec{r}_{12}) = (e^{ik'r_1}/r_1)\, e^{-i\vec{k}\cdot\vec{r}_2}(\vec{I} - \hat{r}_1\hat{r}_1). \tag{13}$$

Using Eq. (13) in Eq. (9) we find the single-scattered field to be

$$\vec{E}_1(\vec{r}_1, t) = \mathcal{E}_0 k'^2 \frac{e^{ik'r_1}}{r_1} e^{-i\omega t}[\hat{r}_1\times(\hat{\epsilon}\times\hat{r}_1)] \times \int d^3r_2\, a(\vec{r}_2, t)\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_2}. \tag{14}$$

We have used the identity $\vec{a}\times(\vec{b}\times\vec{c}) = \vec{a}\cdot\vec{c}\,\vec{b} - \vec{a}\cdot\vec{b}\,\vec{c}$.

Equation (14) is the result for the single-scattered field with the familiar $1/\lambda^2$ dependence; its strength dies off as $1/r$, and it has the proper dependence on polarization given by the vector products.

Now we consider the case of a system of par-

ticles with radius l much less than the wavelength of the incident electric field. Such a particle will scatter light isotropically in the plane perpendicular to the incident polarization. With such a system of scatterers the magnitude of the polarizability is

$$a(\vec{r},t)=\sigma\sum_{i=1}^{N}\delta[\vec{r}-\vec{r}_i(t)], \tag{15}$$

where σ is the electric field scattering cross section for one particle, and $\delta(\vec{r})$ is the Dirac δ function.

Substituting Eq. (15) into Eq. (14), we have

$$\vec{E}_1(\vec{r}_1,t)=\mathcal{E}_0k'^2\frac{e^{ik'r_1}}{r_1}\times e^{-i\omega t}\hat{r}_1\times(\hat{\epsilon}\times\hat{r}_1)\sigma\sum_{i=1}^{N}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_i(t)}, \tag{16}$$

so that the field correlation function is

$$\langle\vec{E}_1^*(\vec{r}_1,t)\cdot\vec{E}_1(\vec{r}_1,0)\rangle=\mathcal{E}_0^2k'^4\sigma^2r_1^{-2}\times\left\langle\sum_{i=1}^{N}e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}_i(t)}\sum_{j=1}^{N}e^{i(\vec{k}-\vec{k}')\cdot\vec{r}_j(0)}\right\rangle. \tag{17}$$

To evaluate Eq. (17), we assume there is no correlation between different particles. While there are systems in which correlations between different particles become important,[11] we will consider only systems which are dilute enough or for which the interactions are screened well enough so that these mutual correlations will not be important. In this case the ensemble average on the left-hand side of Eq. (17) is zero unless $i=j$. If $i=j$ all the terms in the sum are equal. Thus we may write

$$\langle\vec{E}_1^*(\vec{r}_1,t)\cdot\vec{E}_1(\vec{r}_1,0)\rangle=N\mathcal{E}_0^2k'^4\sigma^2r^{-2}\langle e^{i(\vec{k}-\vec{k}')\cdot[\vec{r}_2(0)-\vec{r}_2(t)]}\rangle. \tag{18}$$

This is the standard result for the correlation function of the single-scattered electric field. For the case of particles undergoing Brownian motion with a diffusion constant D, Eq. (18) gives

$$\langle\vec{E}_1^*(t)\cdot\vec{E}_1(0)\rangle=N\mathcal{E}_0^2k'^4\sigma^2r^{-2}e^{-D|\vec{k}-\vec{k}'|^2t}. \tag{19}$$

This result has been verified experimentally.[9]

IV. DOUBLE SCATTERING

A. Formalism

In this section we derive an expression for the correlation function of the double-scattered electric field. Our procedure will follow that used for the single-scattered field, as given above.

We start by evaluating Eq. (4) to second order,

$$\vec{E}_2(\vec{r}_1,t)=k'^2\int_{\sigma(\vec{r}_1)}d^3r_2\,\vec{\vec{T}}(\vec{r}_{12})\cdot\vec{\alpha}(\vec{r}_2,t)\cdot k''^2\times\int_{\sigma(\vec{r}_2)}d^3r_3\,\vec{\vec{T}}(\vec{r}_{23})\cdot\vec{\alpha}(\vec{r}_3,t)\cdot\vec{E}_0(\vec{r}_3,t), \tag{20}$$

where $\vec{k}''$ is the intermediate-scattering wave vector describing the scattering from the first to the second scatterer, and $\vec{k}'$ is the wave vector describing the scattering from the second scatterer to the detector. In the first integral we need not worry about the exclusion of the volume $\sigma(\vec{r}_1)$, because we take the observation point $\vec{r}_1$ to be outside the scattering volume. Furthermore, the excluded volume of the second integral $\sigma(\vec{r}_2)$ need not concern us if we consider double scattering from two different positions in space only. In the far-field approximation $\vec{\vec{T}}(\vec{r}_{12})$ in Eq. (20) takes the form given in Eq. (13) for the same reasons.

Now we must justify applying the far-field approximation to the tensor $\vec{\vec{T}}(\vec{r}_{23})$ which describes the scattering of the incident field from the first scatterer to the second scatterer. We make two assumptions: (i) $|\vec{r}_3-\vec{r}_2|\,k'\gg1$, which implies that the interparticle separation is, on the average, greater than the wavelength of the field and (ii) $r_2\gg r_3$. Assumption (i) depends upon the experimental situation, but is not difficult to satisfy in a real experiment. Assumption (ii) can be satisfied if we choose our origin arbitrarily close to the *first* scatterer at position $\vec{r}_3$. Thus r_3 can be made as small as we wish. Since we are deriving the time correlation function of the scattered field we require assumption (ii) to be satisfied for times of the order of the correlation time. For the case of a particle of radius 0.1 μm undergoing Brownian motion in water at 20 °C, r_3 may change by 0.03 μm in a correlation time. Using assumption (i), however, we see that assumption (ii) will still hold in general. Thus we may reasonably apply the far-field approximation given by assumptions (i) and (ii) to the tensor $\vec{\vec{T}}(\vec{r}_{23})$. Hence $\vec{\vec{T}}(\vec{r}_{23})$ will have the same form as $\vec{\vec{T}}(\vec{r}_{12})$ given in Eq. (13).

With an incident electric field given by Eq. (7) and an isotropic polarizability given by Eq. (8), the double-scattered field of Eq. (20) takes the form

$$\vec{E}_2(\vec{r}_1,t)=\mathcal{E}_0\frac{e^{ik'r_1}}{r_1}\,e^{-i\omega t}k'^2\int d^3r_2\,a(\vec{r}_2,t)e^{-i\vec{k}'\cdot\vec{r}_2}\,\frac{e^{ik''r_2}}{r_2}\,k''^2[\vec{I}-\hat{r}_1\hat{r}_1]$$
$$\cdot\int d^3r_3[\vec{I}-\hat{r}_2\hat{r}_2]\cdot\hat{\epsilon}e^{-i\vec{k}''\cdot\vec{r}_3}\,a(\vec{r}_3,t)e^{i\vec{k}\cdot\vec{r}_3}. \tag{21}$$

Here $\vec{k}$ is the incident wave vector.

We consider the term $e^{ik''r_2}$ in Eq. (21). Physically, we take $\vec{k}''$ to be the wave vector describing the scattering from the first to the second scatterer; thus $\vec{k}''$ is parallel to $\vec{r}_2-\vec{r}_3$. By assumption (ii) above, $r_2\gg r_3$; thus $\vec{r}_2-\vec{r}_3$ and $\vec{k}''$ are nearly parallel to $\vec{r}_2$, and thus $k''r_2\cong\vec{k}''\cdot\vec{r}_2$. With this adjustment Eq. (21) becomes

$$\vec{E}_2(\vec{r}_1,t)=\mathcal{E}_0\frac{e^{ik'r}}{r_1}e^{-i\omega t}k'^2k''^2[\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)]\int d^3r_2\,r_2^{-1}a(\vec{r}_2,t)e^{i(\vec{k}''-\vec{k}')\cdot\vec{r}_2}\int d^3r_3\,a(\vec{r}_3,t)e^{i(\vec{k}-\vec{k}'')\cdot\vec{r}_3}, \tag{22}$$

where $\hat{\epsilon}'$ is the polarization of the intermediate wave and is given by

$$\hat{\epsilon}'=\hat{r}_2\times(\hat{\epsilon}\times\hat{r}_2). \tag{23}$$

As might have been expected from the approximations we have made, Eq. (22) has the form of two completely independent scattering events in succession. Using physically intuitive arguments, we could have proposed Eq. (22) as the starting point of our theory. However, by proceeding as we have from the elementary electromagnetic theory, we are more aware of the approximations implicit in Eq. (22).

As we did in the case of single scattering, we examine the particular case of a system of pointlike particles. Using Eq. (15) in Eq. (22) we have

$$\vec{E}_2(\vec{r}_1,t)=\mathcal{E}_0\frac{e^{ik'r_1}}{r_1}e^{-i\omega t}k'^2k''^2\sigma^2[\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)]\sum_{i=1}^{N}\frac{1}{r_{2i}(t)}\,e^{i(\vec{k}''-\vec{k}')\cdot\vec{r}_{2i}(t)}\sum_{l=1}^{N}e^{i(\vec{k}-\vec{k}'')\cdot\vec{r}_{3l}(t)}. \tag{24}$$

The time correlation function of the double-scattered field is

$$\langle\vec{E}_2^{\,*}(\vec{r}_1,t)\cdot\vec{E}_2(\vec{r}_1,0)\rangle$$
$$=\frac{\mathcal{E}_0^2}{r_1^2}k'^4k''^4\sigma^4|\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)|^2$$
$$\times\left\langle\sum_{i,j=1}^{N}\frac{1}{r_{2i}(0)r_{2j}(t)}\exp\{i(\vec{k}''-\vec{k}')\cdot[\vec{r}_{2i}(0)-\vec{r}_{2i}(t)]\}\sum_{l,m=1}^{N}\exp\{i(\vec{k}-\vec{k}'')\cdot[\vec{r}_{3l}(0)-\vec{r}_{3m}(t)]\}\right\rangle. \tag{25}$$

We now make the assumption that there is no correlation between any two particles. This allows us to do two things to the expression in Eq. (25): First, the ensemble average of the product of the phase terms of the first and second scatterers becomes the product of the ensemble average of each term individually. Second, as in the single-scattering case the average is zero for each term unless $i=j$ or $l=m$ for the first or second scatterer, respectively, and the sums reduce to N times the argument of the sum. Thus for a noncorrelative system Eq. (25) becomes

$$\langle\vec{E}_2^{\,*}(\vec{r}_1,t)\cdot\vec{E}_2(\vec{r}_1,0)\rangle$$
$$=(\mathcal{E}_0^2/r_1^2)k'^4k''^4\sigma^4|\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)|^2N^2$$
$$\times(1/\langle r_2\rangle^2)\langle e^{i(\vec{k}''-\vec{k}')\cdot[\vec{r}(0)-\vec{r}(t)]}\rangle$$
$$\times\langle e^{i(\vec{k}-\vec{k}'')\cdot[\vec{r}(0)-\vec{r}(t)]}\rangle. \tag{26}$$

In Eq. (26) we have taken r_2 to be independent of the phases. We have also dropped the subscripts used to identify the first and second scatterers, since these were necessary only to keep the terms straight while making the averages above. Equation (26) is the general result we shall apply to the case of Brownian motion. For such a system each average in Eq. (26) yields the usual form for Brownian motion given in Eq. (19). For particles of diffusion constant D, we have

$$\langle\vec{E}_2^{\,*}(\vec{r}_1,t)\cdot\vec{E}_2(\vec{r}_1,0)\rangle$$
$$=(\mathcal{E}_0^2/r_1^2)k'^4k''^4\sigma^4|\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)|^2N^2$$
$$\times(1/\langle r_2\rangle^2)e^{-D|\vec{k}''-\vec{k}'|^2t}\,e^{-D|\vec{k}-\vec{k}''|^2t}. \tag{27}$$

The comments made after Eq. (22) apply here. Equation (27) has the form of two distinct and independent scattering events; each event modulates the incident wave and the resultant wave's correlation function is a product of the two individual correlation functions.

B. Integration over the intermediate scattering vector

Here we use the results in Eq. (27) to derive the correlation function that one would observe in a real experiment on a system of particles. To do this we must realize that while the detector may sit at a particular scattering angle relative to the incident beam, thus defining the final-scattered wave vector $\vec{k}'$, the intermediate-scattered wave vector $\vec{k}''$ may assume any direction in space. Thus to evaluate the correlation function seen in a real experiment we must integrate Eq. (27) over all possible directions of $\vec{k}''$. In doing this we assume spherical symmetry about the first scatterer. While this is not the most general situation, the experimental conditions can be adjusted so that this symmetry will be satisfied.

To begin we take the final-scattered wave vector to be in the scattering plane. The term "scattering plane" has the usual definition; it is the plane perpendicular to the incident polarization, the x-y plane in Fig. 1. The intermediate-scattering wave vector $\vec{k}''$ which is parallel to $\vec{r}_2$ is allowed to assume any direction.

From Fig. 1 we can write the following vectors in Cartesian coordinates:

$$\begin{aligned} &\hat{k} = -\hat{1}, \quad \hat{\epsilon} = \hat{3}, \\ &\hat{k}' = \hat{r}_1 = \hat{1}\cos\phi_1 + \hat{2}\sin\phi_1, \\ &\hat{k}'' = \hat{r}_2 = \hat{1}\sin\theta_2\cos\phi_2 + \hat{2}\sin\theta_2\sin\phi_2 + \hat{3}\cos\theta_2. \end{aligned} \tag{28}$$

In Eqs. (28), $\hat{1}$, $\hat{2}$, and $\hat{3}$ are the unit vectors in the x, y, and z directions, respectively.

It is now a simple matter to rewrite Eq. (27) in terms of θ_2, ϕ_1, and ϕ_2, assuming elastic scattering ($k = k' = k''$):

$$\begin{aligned} \langle \vec{E}_2^*(t)\cdot\vec{E}_2(0)\rangle = (\mathcal{E}_0^2/r_1^2)k^8\sigma^4 N^2(1/\langle r_2\rangle^2)\{(\sin^4\theta_2)_\parallel + [\cos^2\theta_2\sin^2(\phi_1-\phi_2)\sin^2\theta_2]_\perp\} \\ \times\exp(-Dk^2t\{4+2\sin\theta_2[\cos\phi_2 - \cos(\phi_2-\phi_1)]\}), \end{aligned} \tag{29}$$

where we have designated the polarized and depolarized components by $\parallel$ and $\perp$, respectively.

To find the average field correlation function, we integrate Eq. (29) over the volume of the sphere described by r_2, θ_2, and ϕ_2 and then normalize it with the same integral at $t = 0$. We were not able to perform the integral of Eq. (29) analytically. However, we can evaluate the slope of the average correlation function at $t = 0$. Since in essence we are summing exponentials, in general we expect a nonexponential spectrum. Nevertheless the $t = 0$ slope will give us a good idea of the behavior of the average double-scattered correlation function.[14]

The slope at $t = 0$ is given by

$$K_1 = -\lim_{t\to 0}\frac{d}{dt}\frac{\langle\langle \vec{E}_2^*(t)\cdot\vec{E}_2(0)\rangle\rangle_{av}}{\langle\langle \vec{E}_2^*(0)\cdot\vec{E}_2(0)\rangle\rangle_{av}}, \tag{30}$$

where K_1 is the first cumulant in the usual notation.[13] $\langle\ \rangle_{av}$ indicates the average over $\vec{r}_2$. Using Eqs. (29) and (30) and performing the proper integrals we find

$$(K_1)_{\parallel \text{ or } \perp} = 4Dk^2. \tag{31}$$

Equation (31) gives us the remarkable result that for either polarization, the *initial* slope of the double-scattered field correlation is *not* a function of the scattering angle (remember that $\vec{k}$ is the *incident* wave vector). Furthermore, the value of the initial slope is the same as that obtained for single scattering at a scattering angle of 180°. Intuitively we may picture the double-scattering process as two independent scattering events, each of which may involve scattering at an angle anywhere from 0° to 180°. Since the scattering is isotropic from pointlike particles, all angles are weighted equally, and so we might expect the average scattering angle for each event to be 90°. Two scatterings at 90° yield an *effective* 180°

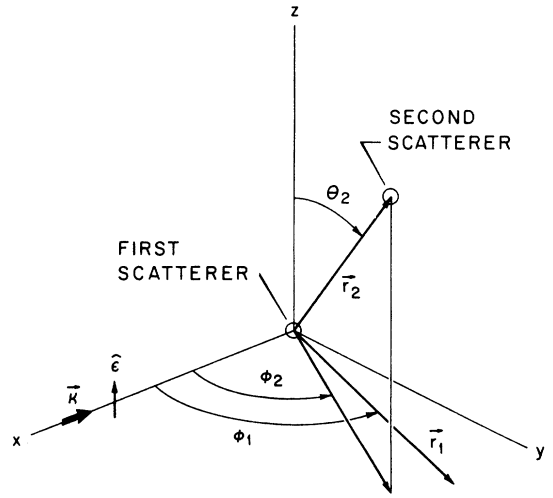

FIG. 1. Geometry for double scattering. Light is incident from the left-hand side along the x axis with polarization parallel to the z axis. Light is scattered from the first to the second scatterer along $\vec{r}_2$ and then from the second scatterer to the detector along $\vec{r}_1$ (under the far-field approximation). The experimental scattering angle is $\theta_{scat} = 180° - \phi_1$.

scattering process.

To get a more exact form of the total field correlation function at all times, we numerically integrated Eq. (29) over $\vec{r}_2$ and divided by the proper normalization factor, which was determined from a numerical integration of Eq. (29) with $t = 0$. The double numerical integration was performed with a simple program to compute the integral using trapezoid, midpoint, and Simpson methods. It was found for simple integrals of trigonometric functions which could be solved analytically that the midpoint method converged fastest to the correct value. Thus the midpoint method was used to evaluate the integrals. In Fig. 2 we present plots of the double-scattered field correlation function for the depolarized component. At $\theta_{\text{scat}} = 60°$ a cumulant analysis[13] gives a value of $K_2/K_1^2 = 0.07$ for the second cumulant. The results for the polarized component are similar, but we will not present them here. In our light-scattering experiment this component is effectively unobservable, since it always appears mixed in with the much more intense polarized single-scattered component. In Fig. 2 we have also

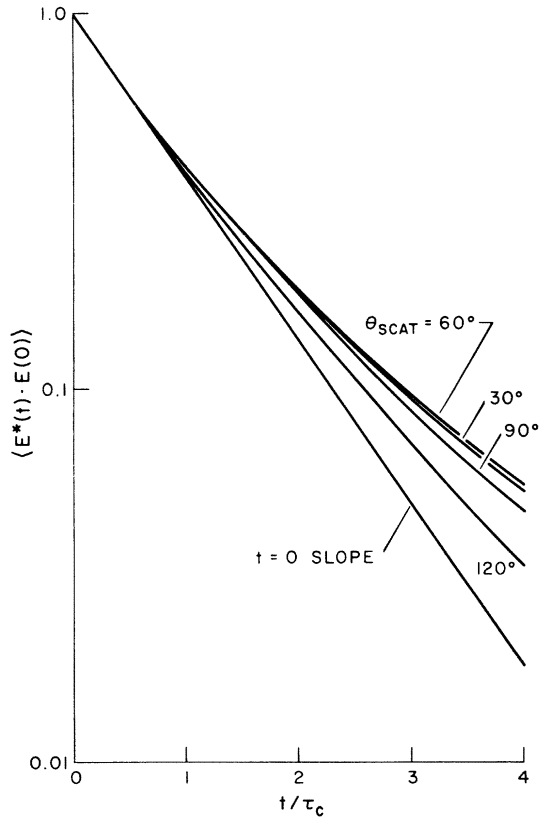

FIG. 2. Depolarized field correlation function due to double scattering from particles of radius $l \ll \lambda$. Note that all graphs have the same $t = 0$ slope.

plotted the straight line corresponding to the initial slope value given by Eq. (31). We see that this is a reasonable approximation to the correlation function for small times. While the nonexponentiality of the correlation function increases with decreasing scattering angle up to $\theta_{\text{scat}} \simeq 60°$ and then holds fairly constant, there is still a significant lack of scattering-angle dependence when compared to the single-scattered correlation function, where the slope increases as $\sin^2(\frac{1}{2}\theta_{\text{scat}})$.

C. Anisotropic scatterers

So far our results apply to the case of pointlike scatterers whose radius l is much less than the wavelength of the incident light ($l \ll \lambda$). As the size of the scatterer increases, the scattering from a given particle will become anisotropic, with more scattering in the forward direction. In the regime where $l \lesssim \lambda$, we expect the results given above will explain the double-scattered field correlation function qualitatively in that there will still be a lack of a major scattering-angle dependence and the correlation time $(1/K_1)$ will in general be shorter than that for single scattering. However, we must also expect that quantitatively the spectrum will be different.

To investigate the double-scattered spectrum of particles of radius $l \lesssim \lambda$, we shall apply the Rayleigh-Debye theory[12] to our formalism. The Rayleigh-Debye theory describes the scattering of electromagnetic radiation from dielectric spheres when the phase change of the radiation across the spheres is small. This condition is met when

$$2kl(m-1) \ll 1, \tag{32}$$

where $\vec{k}$ is the wave vector of the radiation and m is the relative index of refraction of the sphere; m is defined as the index of refraction of the sphere divided by the index of refraction of the medium. To be exact, we should use the full Mie scattering theory of electromagnetic wave scattering from dielectric spheres, but the formalism is too ponderous.

The scattering amplitude in the scattering plane for the Rayleigh-Debye theory is given by[12]

$$S(\beta) = (i/2\pi)k^2(m-1)l^3P(\beta), \tag{33}$$

where

$$P(\beta) = (3/u^3)[\sin u - u\cos u], \tag{34}$$

and where

$$u = 2kl\sin\tfrac{1}{2}\beta, \tag{35}$$

and β is the scattering angle.

To incorporate this into our theory, we use

$P(\beta)$ in Eq. (34) as an attenuation factor to be included in Eq. (24). Since there will be two scattering events, there will be two individual scattering angles, β_1 and β_2. They are the angles between $\vec{k}$ and $\vec{k}''$ and between $\vec{k}''$ and $\vec{k}'$, respectively, and are given by

$$\cos\beta_1 = \hat{k}\cdot\hat{k}''$$
$$\cos\beta_2 = \hat{k}''\cdot\hat{k}'. \tag{36}$$

From Eqs. (28) and the trigonometric identity for half angles we find

$$\sin\tfrac{1}{2}\beta_1 = [\tfrac{1}{2}(1+\sin\theta_2\cos\theta_2)]^{1/2}, \tag{37}$$

$$\sin\tfrac{1}{2}\beta_2 = \{\tfrac{1}{2}[1-\sin\theta_2\cos(\phi_2-\phi_1)]\}^{1/2}. \tag{38}$$

We are now ready to write the equation for the double-scattered field correlation function for Rayleigh-Debye scatterers undergoing Brownian motion. It will have the same form as Eq. (27) except that now we must include the factor given in Eq. (34) for each of the two scattering events. We have

$$\langle \vec{E}_2^*(t)\cdot\vec{E}_2(0)\rangle = (N^2A^2\mathcal{S}_0^2/r_1^2)k'^4k''^4\sigma^4\,|\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)|^2 \times (1/\langle r_2\rangle^2)e^{-D|\vec{k}''-\vec{k}'|^2t}\,e^{-D|\vec{k}-\vec{k}''|^2t}, \tag{39}$$

where the only difference between Eqs. (39) and (27) is the attenuation factor A^2, where

$$A = P(\beta_1)P(\beta_2). \tag{40}$$

We evaluated the initial slope, first cumulant, of the correlation function in Eq. (39) using Eq. (30), assuming elastic scattering. The resulting integrals are very complex and thus were performed numerically, as described above. The results of these calculations for various values of $2kl$ are given in Fig. 3, where we have plotted correlation time in units of $1/4Dk^2$ versus scattering angle. We point out that the correlation times at 180° for all values of $2kl$ are equal to the single-scattered correlation time at 180°. This property of double scattering was first pointed out by Ferrell.[15]

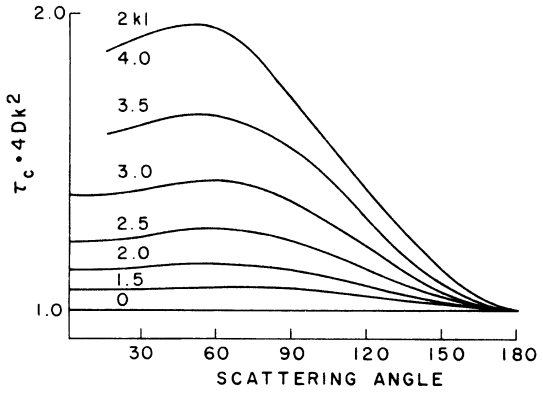

FIG. 3. General results for the depolarized spectrum due to double scattering from a system of Brownian particles.

D. Intensity

We can use our formalism to find the scattered intensity of the double-scattered light. The intensity is equal to the expression for the correlation function at $t=0$. For pointlike scatterers Eq. (19) gives us the single-scattered intensity as

$$I_1(\vec{r}_1) = (\mathcal{S}_0^2/r_1^2)k^4\sigma^2N. \tag{41}$$

Similarly, Eq. (27) at $t=0$ gives the double-scattered intensity for elastic scattering as

$$I_2(\vec{r}_1) = (\mathcal{S}_0^2/r_1^2)N^2k^8\sigma^4\,|\hat{r}_1\times(\hat{\epsilon}'\times\hat{r}_1)|^2\langle r_2\rangle^2. \tag{42}$$

The ratio of these quantities, with the density given by $\rho = N/V$, is

$$I_2/I_1 = \rho V k^4\sigma^2, \tag{43}$$

where we have left out the polarization terms and $1/\langle r_2\rangle^2$. This latter term should vary slowly with the scattering volume. Equation (43) is of the form given by others.[2,4] We see that the double-scattered component can be enhanced by increasing the density of the system, a fact we shall make use of later in Sec. V. We point out that for particles of radius $l \ll \lambda$ the cross section term goes as $\sigma \sim l^3$.

If we consider each polarization of the double-scattered light, we may find their relative intensities. Using Eq. (29) at $t=0$ and integrating over θ_2 and ϕ_2 for each component we find

$$I_{2\perp}/I_{2\parallel} = \tfrac{1}{8}. \tag{44}$$

Thus the depolarized component of the double-scattered light is only one-eighth as intense as the polarized part. Thus if one measures the ratio of the polarized to depolarized intensities in a scattering experiment, one must remember that some of the polarized component has been doubly scattered.

For the case of larger particles, $l \lesssim \lambda$, we may consider Eq. (39) at $t=0$ and perform the integrations over θ_2 and ϕ_2. We find that the double-scattered intensity is still peaked in the forward direction, but not so strongly as in the single-scattered case. Thus we can qualitatively say that the Mie pattern characteristic of microspheres is washed out in the depolarized component as found by Colby *et al.*[6]

V. EXPERIMENTAL

We have performed experiments to measure the depolarized correlation function of two systems of Brownian particles. Both systems were made up of polystyrene latex spheres, obtained from Dow Chemical Company, suspended in water. These spheres are very monodisperse in size. Thus there should be no nonexponentiality of the polarized correlation function[13] or scattering-angle-dependent diffusion constant[14] due to polydispersity. The smaller-sized sphere had a radius of 0.055 μm and is barely into the regime where one must consider the effects of anisotropic scattering as discussed above. The larger spheres had a radius of 0.117 μm. At this radius one must consider the depolarized correlation function in terms of the anisotropic Rayleigh-Debye scattering theory.

Since the depolarized to polarized scattered intensity ratio increases with concentration, as shown in Eq. (43), we worked with suspensions of high concentration. However, at large concentrations the polystyrene spheres, which are inherently charged, begin to interact. This violates our condition of noninteracting particles. To determine if a system of microspheres was interacting, we measured the correlation time of the polarized scattered light as a function of concentration. It is known[11] that the correlation time of the single-scattered polarized component of light scattered from a system of interacting Brownian particles decreases with increasing concentration. If a system was found to be interacting, we diluted it until no further concentration dependence was seen and the correlation time was the same as that measured in the very dilute limit. In this way we choose a concentration of 9×10^{-5} by volume for the $l=0.055$ μm system, and a concentration of 1.8×10^{-5} by volume for the $l=0.117$ μm system.

As both Bray and Chang[5] and Reith and Swinney[4] have shown, the measured intensity of the depolarized light is a function of the experimental scattering geometry. In deriving our results we have assumed a spherically symmetric distribution of second scatterers about a first scatterer. Equivalently, we could have considered a spherically symmetric distribution of first scatterers about the second scatterer. This latter situation can be satisfied experimentally if our detector looks at a small region near the center of the illuminated scattering volume. In this way we see second scatterers with a large, isotropic volume of first scatterers around them. We also considered the case where this spherical scattering symmetry breaks down.

In our experimental situation, as in most situations, the polarized component of the scattered light is many times larger than the depolarized component. Because of this, special care must be taken to eliminate all the polarized light when measurements on the depolarized light are being carried out. If there is strain in the sample cell some of the polarized component may be mixed in with the depolarized component, causing erroneous results. We examined our sample cell by placing it between crossed polarizers and found it to be free of strain. However, fingerprints and dust were evident on the wall of the cell. Thus one must take great care that the outside as well as the inside of the cell is clean and dust free in order to avoid mixing the depolarized and polarized components.

In our experimental setup, we directed the unfocused beam of an argon-ion laser operating at a wavelength of $\lambda=5145$ Å into our glass scattering cell. The beam diameter was ~5 mm and the scattering cell was a glass tube of 21 mm inside diameter. The unfocused beam provided a large scattering region in order to suit the conditions required by the assumption of spherical symmetry, as discussed above. Focusing of the beam by the glass cell caused no problems. Before entering the cell, the beam passed through a Glan-Thompson polarizing prism with an extinction ratio of 5×10^{-5}, giving the incident beam a vertical polarization. Light scattered in the horizontal plane passed immediately through a small aperture 1.3 mm in diameter and then through two more Glan-Thompson polarizers, each of which had an extinction ratio of 5×10^{-5}. These polarizers were adjustable so as to pass either the polarized or depolarized component of the scattered light. Two polarizers were used to ensure complete filtering of the unwanted component. The light was then collected by a lens of 37 mm focal length which focused the image of the 1.3-mm aperture onto a 300-μm-diam pinhole. The magnification of the aperture image by the lens was approximately 0.25. With this configuration we could pick out a small region in the center of the illuminated region. The 300-μm pinhole was 1 m from the cathode of an FW130 photomultiplier tube, thus projecting approximately one coherence area of scattered light on the cathode. Pulses from the photomultiplier tube were analyzed by our intensity autocorrelator to determine the correlation function of the scattered light. The correlation function was analyzed with an on-line Nova 800 computer to determine the correlation time using a fitting routine that weights the $t=0$ part of the spectrum heavily.[16]

Our calculations have been concerned with the

electric field correlation function of the scattered light. We measured the intensity correlation function of the scattered light in our experiments. These two correlation functions are related in a simple manner, by the Siegert relation, if the scattered electric field is Gaussian.[17] Since we are considering scattering from many different pairs of events, this Gaussian assumption should be satisfied for double scattering. Kelly[7] discusses this point and finds that the scattered field will be Gaussian for a large number of scatterers. Furthermore, Colby *et al.*[6] found experimentally that the light scattered from their dense systems was Gaussian. For these reasons we take our double-scattered field to be Gaussian.

Care had to be taken to adjust the polarizers to the correct polarization angle during depolarized spectrum measurements, or else erroneous results were obtained. Both the polarization of the incident beam and the detected light had to be adjusted to better than $\pm 0.3°$. Our procedure was to measure the count rate as a function of both the incident and the detection polarization angles to find the minimum in the count rate. This minimum in the count rate indicated that as much of the intense polarized component had been filtered out as possible. The minimum could be defined to better than $\pm 0.3°$. At a scattering angle of 30°, spectra run 1° away from the minimum were found to have correlation times 5% larger than spectra run at the minimum. This is because some of the polarized component which has a much larger correlation time than the depolarized component at a scattering angle of 30° was mixing in with the depolarized component. Indeed, it is conceivable that we were not always successful in removing all the polarized component with the polarizers, and some of our measured correlation times may be slightly large. However, we believe we were able to limit this error to $\leq 3\%$.

In Figs. 4 and 5 we plot the results of our experiments along with our theoretical predictions

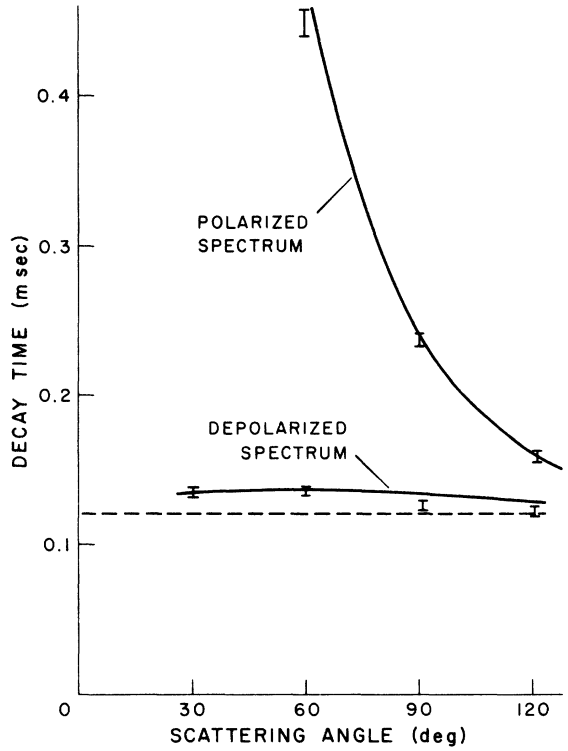

FIG. 4. Experimentally measured correlation time vs theory for both the polarized (single-scattered) and depolarized (double-scattered) light for the $l = 0.055$ μm system. The dashed line represents the theoretical prediction for light double scattered from particles of radius $l \ll \lambda$, Eq. (31). The lower solid line is the theoretical prediction for light scattered from particles of radius $l = 0.055$ μm using the Rayleigh-Debye modified theory, Eq. (39).

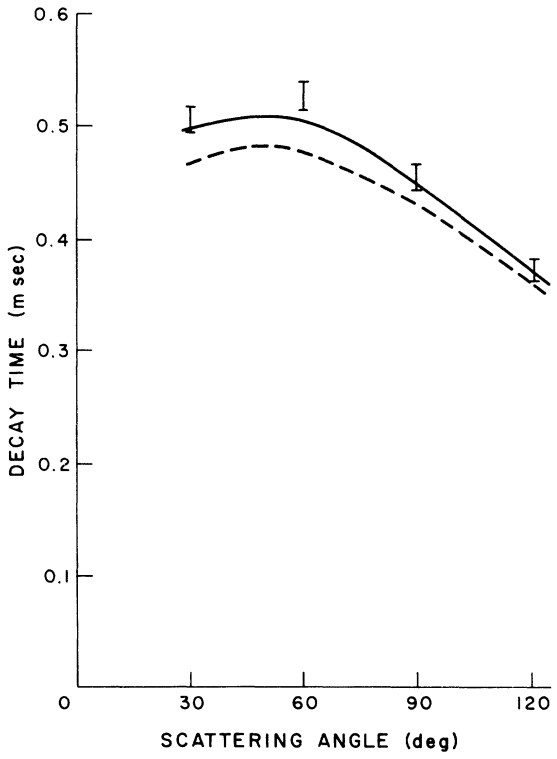

FIG. 5. Experimentally measured correlation time vs theory for the depolarized scattered light for the $l = 0.117$ μm system. The dashed line represents the prediction of the Rayleigh-Debye modified theory in Eq. (39) for particles of radius $l = 0.117$ μm. The solid line is the prediction of Eq. (39) for particles of radius $l = 0.123$ μm. The solid line is closest to what one would expect if the exact Mie theory were used.

as given by Eq. (39). The correlation times are normalized to 20 °C from our experimental condition of $T = 23.5 \pm 0.3$ °C, assuming a viscosity temperature dependence. Figure 4 shows our results for the $l = 0.55$ μm system. The upper curve shows the experimental results and the theoretical prediction for the polarized component. We see the characteristic $\sin^2(\frac{1}{2}\theta_{\text{scat}})$ dependence. The datum point for $\theta = 30°$ ($\tau_c = 1.59$ msec) runs off the graph on this scale and was not plotted. In marked contrast is the correlation-time behavior for the depolarized component plotted in the lower part of Fig. 4. Obviously the large scattering-angle dependence seen in the polarized component is gone in the depolarized component. The dashed line in Fig. 4 is the prediction of Eq. (31) for $l \ll \lambda$ and is seen to be inadequate to explain the data, being ~10% too low. The solid line nearest the depolarized data represents the results obtained from the numerical integration of Eq. (39), which takes into account the Rayleigh-Debye scattering from a particle of radius $l = 0.055$ μm. The agreement between theory and experiment is seen to be good.

Figure 5 presents our results for the system of $l = 0.117$ μm particles. The assumption of $l \ll \lambda$ would result in a predicted correlation time of $\tau = 0.257$ msec for the depolarized scattered light, by Eq. (31). This is obviously not the case and we must again use Eq. (39). Numerical integration of Eq. (39) gives the dashed line in Fig. 5. While the fit is much closer, it is still inadequate. We must remember, however, that the Rayleigh-Debye theory is only an approximation and it begins to lose validity when Eq. (32) is poorly satisfied. What is really needed is the exact Mie theory, but as mentioned earlier this would be very unwieldy. To get a better fit, we compared the predictions of the Rayleigh-Debye scattered intensity versus angle for various sized particles near $l = 0.117$ μm to the exact Mie theory for particles of radius $l = 0.117$ μm. These comparisons were made to fit the experimental conditions, where $m = 1.20$ for polystyrene in water, $\lambda = 5145$ Å, and the index of refraction of water is 1.33. It was found that the Rayleigh-Debye formula using a particle radius of $l = 0.123$ μm, agreed very well with the tabulated[18] Mie results for the true particle radius of $l = 0.117$ μm. Thus we rederived our theoretical prediction using Eq. (39) and a particle radius of $l = 0.123$ μm. We may consider this prediction to be the same as that which would be given by the exact Mie theory for a particle radius of $l = 0.117$ μm, the true particle radius. This result is the solid line in Fig. 5 and is seen to agree quite well with the data. We conclude that our theory is good for particles when the condition $l \ll \lambda$ is no longer satisfied, if the proper scattering function is known for the particle.

TABLE I. Effect of narrowing the incident beam on the measured correlation time of the depolarized light scattered from the $l = 0.117$ μm system. Beam diameters greater than 5 mm showed no change in τ_C.

θ_{scat} (deg.)	Beam diam (mm)	τ_C (msec)
60	5	0.524
	2.5	0.600
	1.6	0.650
90	5	0.447
	4	0.473
	1.6	0.505

We have also considered the situation when the assumption of a spherical scattering symmetry is invalid. Experimentally, this is equivalent to a narrowing of the incident beam. In Table I we give experimental data for the $l = 0.117$ μm system. It is seen that as one narrows the beam the correlation time of the depolarized light becomes longer. Theoretically, we realize that as the beam is narrowed many of the second scatterers viewed by the detector will not have first scatterers in the regions above and below them. This situation is approximated if, when we evaluate the correlation time from Eq. (39) using Eq. (30), instead of allowing θ_2 (Fig. 1) to range from 0° to 180° we allow it to range from α to $180° - \alpha$, letting α approach 90°. In this way we are flattening out the scattering volume. Performing the integrals, we find that the correlation times do indeed become longer for increasing α, giving curves similar to those in Fig. 3. As α approaches 90° the correlation time is ~23% longer at $\theta_{\text{scat}} = 90°$ for $2kl = 4.0$. Experimentally, α is not well defined and the method for nonspherical scattering symmetry given here can be considered only a first approximation to this very complex situation. Therefore we emphasize the convenience of the spherically symmetric expanded beam geometry to future experimenters.

We now consider the data of Colby *et al.*[6] They measured the correlation time of *all* the light scattered from their dense systems, not just the polarized or depolarized components separately. When the concentration of a system of particles is small we expect most of the scattered light to be single-scattered light and thus the correlation time to go as $\sin(\frac{1}{2}\theta_{\text{scat}})^{-2}$. This is what they find experimentally. As the particle concentration increases, the double-scattered contribution grows relative to the single-scattered contribution [see

Eq. (43)]. If the scattered light was dominated by this contribution, we have seen that we would expect no scattering-angle dependence and the value of the correlation time would be roughly equal to the value of the single-scattered correlation time at a scattering angle of 180°. (Actually, we would expect slightly larger correlation times than this value, since the particles used by Colby *et al.* had radii of the same order of magnitude as the wavelength of the light). For intermediate concentrations we would expect that a family of curves between these two extrema would result. This is indeed what was seen by Colby *et al.* in their Figures 7–9. We may even explain the nonexponentiality of the correlation function seen by Colby *et al.* in their Figures 12 and 13 as resulting from a superposition of the two different decays due to single and double scattering.

Perhaps the most remarkable characteristic of the depolarized scattered-light correlation time is its lack of a scattering-angle dependence compared to the polarized component. However, in both our experimental systems there is still some scattering-angle dependence. This is especially evident for the larger particles. It should be pointed out, however, that whereas for the polarized component we may speak of a k-dependent correlation time, implying that either θ_{scat} or the wavelength of the incident light may be changed to yield equivalent results, this is not the case for the depolarized component. For a change in the scattering angle, the depolarized component behaves as shown in Fig. 3: little dependence of τ_c on θ_{scat} and a broad maximum in τ_c at $\theta_{\text{scat}} \simeq 50°$. On the other hand, a change in wavelength would move the graph of τ_c vs θ_{scat} up and down for smaller or larger wavelengths, respectively. The point to be remembered is that one cannot expect changes in θ_{scat} or λ to yield equivalent results as in the case of the polarized scattered component.

VI. CONCLUSIONS

In this paper we have presented a formalism which enables us to find the correlation function of light doubly scattered from a system of particles undergoing Brownian motion. We have shown that this double-scattered light is the lowest-order contribution to the depolarized correlation function. In deriving our result we have made use of the far-field approximation. We have also assumed that there is no interaction between different particles. Our assumptions may be stated as follows: (i) The average spacing between individual particles is much greater than k^{-1}, where $\vec{k}$ is the incident wave vector. (ii) We assume statistical independence of all particles, i.e., we have no long-range interactions between particles in the system.

This work should prove useful for experimenters who may be considering the correlation function of light scattered from dense systems. Using the results given here one might take into account the effects of double scattering and thus arrive at the true single-scattered correlation function. However, the measurement of the depolarized correlation function may prove useful in its own right. For instance, if the assumption of no correlation between different particles is dropped, one might be able to measure the effects of the correlation between different particles on the depolarized spectrum. We have performed preliminary measurements on such interacting systems and the results are encouraging. Also, one might be able to explain the depolarized spectrum scattered from a system of fluids near the critical point. This would require the assumption of double scattering, which should be good when $T - T_c \leq 1$ °C, and could use the assumption of diffusing droplets as recently proposed to explain the single-scattered spectrum.[14,19] We are currently pursuing these problems in our laboratory.

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