

# Light Scattering in Colloidal Dispersions: Effects of Multiple Scattering\*

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We outline the derivation of expressions for higher-order scattered electric field strengths, including both multiple inter- and intraparticle scattering events, although only the former are of practical interest. Next an ensemble-averaging procedure for calculating the averages of second-order quantities is proposed and subsequently applied to derive equations for the average scattered intensity and the intensity autocorrelation function including second-order scattering. From these equations iterative schemes for correcting experimental data for double scattering are obtained. These iterative procedures are discussed and applied to a well-defined colloidal system. © 1985 Academic Press, Inc.

## 1. INTRODUCTION

The experimental study of interactions between colloidal particles by means of light scattering is hindered by the effect of multiple scattering. If the detected intensities are due to single scattering events only, then the interpretation of light scattering data is, at least in principle, straightforward. If these first-order intensities become large, relative to the incident intensity, double scattering events may become important. That is, the total scattered intensity includes, in addition to the first-order intensity, a so-called second-order intensity, due to successive scattering from two particles (or at two different points within a single particle). To be able to interpret these perturbed scattering data, it is necessary to correct for double, or even higher-order scattering events in order to obtain the first-order contribution.

The usual approach to the problem of multiple scattering in colloidal systems is essentially to solve the integral equation for the electric field strength as given by Oxtoby

and Gelbart (1) by iteration (2–5). The integral equation is an equation in the electric field strength as a function of position  $\mathbf{r}$  and time  $t$ . The corresponding integral kernel contains the dipole propagation tensor, which is too complicated to find any useful exact results (this is mainly due to the  $|\mathbf{r}|^{-1}$  dependence of the tensor). This forces one to make assumptions which often are not satisfied in practice, such as (a) the average interparticle distance is very large compared to the wavelength and (b) the particle size is very small compared to the wavelength. Thus an alternative approach should be found, not in  $\mathbf{r}$  space but for example in  $\mathbf{k}$  space via Fourier transformation. Indeed it is found that the Fourier transform of a “modified” dipole propagation tensor has a much simpler form than the original “modified” tensor (see Eqs. [8] and [11]).

A more extensive account of the subject treated in this paper can be found in a thesis of one of the authors (9).

We outline the derivation of expressions for the higher-order scattered electric field strengths, propose an ensemble-averaging procedure to obtain second-order averaged quantities, and derive equations for the average scattered intensity and the intensity autocorrelation function including second-

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order scattering events. From these equations iterative procedures are derived for correcting experimental data for double scattering in order to obtain the first-order contributions. The iterative schemes are applied to light-scattering data from a dispersion of silica particles in toluene.

## 2. SCATTERED ELECTRIC FIELD STRENGTHS (6)

Equations for  $n$ th-order scattered electric field strengths are derived. It is assumed that the assembly of Brownian particles is fixed in space, so they do not translate or rotate. This assumption involves two approximations. Retardation effects are neglected, and in the Maxwell equations the free current density is omitted. It is not difficult to confirm the validity of these approximations.

The Maxwell equations are the starting point of our discussion:

$$\nabla \Delta \mathbf{E}(\mathbf{r}, t) = -\frac{\partial}{\partial t} \mathbf{B}(\mathbf{r}, t) \quad [1a]$$

$$\nabla \Delta \mathbf{H}(\mathbf{r}, t) = \frac{\partial}{\partial t} \mathbf{D}(\mathbf{r}, t) \quad [1b]$$

where  $\mathbf{E}(\mathbf{r}, t)$ ,  $\mathbf{B}(\mathbf{r}, t)$ ,  $\mathbf{H}(\mathbf{r}, t)$ , and  $\mathbf{D}(\mathbf{r}, t)$  are the electric field strength, the magnetic induction, the magnetic field strength, and the dielectric displacement, respectively, all depending on the position  $\mathbf{r}$  and the time  $t$ . The materials in the scattering system are assumed to behave as linear dielectrics, with a magnetic susceptibility equal to that of vacuum,  $\mu_0$ :

$$\mathbf{D}(\mathbf{r}, t) = \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}, t) \quad [2a]$$

$$\mathbf{B}(\mathbf{r}, t) = \mu_0\mathbf{H}(\mathbf{r}, t). \quad [2b]$$

Here  $\epsilon(\mathbf{r})$  is the dielectric constant in the scattering system at  $\mathbf{r}$ . Furthermore it is assumed that the incident radiation is a monochromatic plane wave,

$$\mathbf{E}_0(\mathbf{r}, t) = \mathbf{E}_0 \exp\{i(\mathbf{k}_0, \mathbf{r}) - i\omega t\} \quad [3]$$

and that the scattering process is elastic. The scattered electric field strength is then of the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r}) \exp\{-i\omega t\}. \quad [4]$$

From Eqs. [1]–[4] one easily derives the following differential equation for the electric field strength:

$$\nabla(\nabla, \mathbf{E}(\mathbf{r})) - \nabla^2 \mathbf{E}(\mathbf{r}) = \mu_0 \epsilon(\mathbf{r}) \omega^2 \mathbf{E}(\mathbf{r}). \quad [5]$$

Here and in the following  $(\dots, \dots)$  denotes the  $\mathbb{R}^3$  inner product. Fourier transforming Eq. [5] with respect to  $\mathbf{r}$  yields

$$[k^2 - \mathbf{k}\mathbf{k} - \mu_0 \epsilon \omega^2] \mathbf{E}(\mathbf{k}) = \mu_0 \omega^2 \int (\epsilon(\mathbf{r}) - \epsilon) \mathbf{E}(\mathbf{r}) \exp(-i(\mathbf{k}, \mathbf{r})) d\mathbf{r} \quad [6]$$

where

$$\mathbf{E}(\mathbf{k}) = \int \mathbf{E}(\mathbf{r}) \exp\{-i(\mathbf{k}, \mathbf{r})\} d\mathbf{r} \quad [7]$$

and  $\epsilon$  is the dielectric constant of the solvent. Equation [6] is transformed into an integral equation in  $\mathbf{E}(\mathbf{k})$  inverting the tensor  $[k^2 - \mathbf{k}\mathbf{k} - \mu_0 \epsilon \omega^2]$  and expressing  $\mathbf{E}(\mathbf{r})$  on the right-hand side in terms of  $\mathbf{E}(\mathbf{k})$ . The inverse of the tensor does not exist in the points where  $|\mathbf{k}| = \pm \sqrt{\mu_0 \epsilon \omega^2} = \pm k_0$  ( $k_0$  is the magnitude of the wave vectors). This problem is solved by letting the solvent be slightly absorbent. Then  $\epsilon$  contains a small imaginary part  $i\alpha$ , and the inverse of the tensor exists for all (real)  $\mathbf{k}$ . In resulting equations the limit  $\alpha \downarrow 0$  will be taken. Actually this is a standard way in solving linear partial differential equations within the theory of distributions. This mathematical tool is given a physical interpretation here. Hence we write for the inverse (use  $k_0 = \sqrt{\mu_0 \epsilon \omega^2}$ ):

$$\mathbf{T}_\alpha(\mathbf{k}) = \frac{k_0^2 - \mathbf{k}\mathbf{k}}{k_0^2 [k^2 - (k_0 + i\alpha)^2]} \quad [8]$$

where  $\alpha$  is a small real number, and  $k_0$  is understood to be real. It is now possible to obtain the integral equation for the Fourier transform of the electric field strength  $\mathbf{E}(\mathbf{r})$

$$\begin{aligned} \mathbf{E}(\mathbf{k}) &= (2\pi)^3 \mathbf{E}_0 \delta(\mathbf{k} - \mathbf{k}_0) \\ &+ \frac{k_0^2}{(2\pi)^3} \mathbf{T}_\alpha(\mathbf{k}) \sum_j \int B_j(\mathbf{k}' - \mathbf{k}) \\ &\times \exp\{i(\mathbf{k}' - \mathbf{k}, \mathbf{r}_j)\} \mathbf{E}(\mathbf{k}') d\mathbf{k}' \quad [9] \end{aligned}$$

where the summation extends over all particles, and

$$\mathbf{B}_j(\mathbf{k}) = \int_{V_j} \frac{\Delta\epsilon_j(\mathbf{r})}{\epsilon} \exp\{i(\mathbf{k}, \mathbf{r})\} d\mathbf{r} \quad [10]$$

where the integration ranges over the volume  $V_j$  of particle  $j$ , with respect to a coordinate system with its origin at  $\mathbf{r}_j$ , the so-called position coordinate of particle  $j$ . In Eq. [10]  $\Delta\epsilon_j(\mathbf{r})$  is the difference in the dielectric constant of particle  $j$  and the solvent at  $\mathbf{r}$  with respect to the coordinate system with its origin at  $\mathbf{r}_j$ . If  $\Delta\epsilon_j(\mathbf{r})$  is small for all particles, Eq. [9] can be solved by iteration (formally applying a Neumann series expansion, i.e., the Banach fixed point theorem (10)). The second- and higher-order iterated terms in the thus obtained series solution contain integrals ranging over all values of the wave vectors. This does not reflect the elasticity of the scattering process. It should be possible to perform the integration over the magnitudes of the wave vectors. Indeed, using the asymptotic behavior and the symmetry properties of the integrands, noting that  $\mathbf{T}_\alpha(\mathbf{k})$  has two first-order poles at  $k = k_0 \pm i\alpha$  one can perform the integration over the magnitudes of the wave vectors by applying the residue theorem. As a final step in the derivation, the equations are Fourier inverted. The Fourier inversion can be performed first by substituting the definition [10] for  $B_{jn}(\mathbf{k}_{n-1} - \mathbf{k})$ , and using the relation

$$\tilde{\mathbf{T}}(\mathbf{r}) \equiv \lim_{\alpha \downarrow 0} \int d\mathbf{k} \mathbf{T}_\alpha(\mathbf{k}) \exp\{i(\mathbf{k}, \mathbf{r})\}$$

$$\begin{aligned} &= \lim_{\alpha \downarrow 0} \left( 1 + \frac{1}{k_0^2} \nabla \nabla \right) \\ &\quad \times \int d\mathbf{k} \frac{\exp\{i(\mathbf{k}, \mathbf{r})\}}{k^2 - (k_0 + i\alpha)^2} \\ &= 2\pi^2 \left[ 1 + \frac{i}{k_0 r} - \frac{1}{k_0^2 r^2} \right. \\ &\quad \left. - \left( 1 + \frac{3i}{k_0 r} - \frac{3}{k_0^2 r^2} \right) \frac{\mathbf{r}\mathbf{r}}{r^2} \right] \frac{\exp\{ik_0 r\}}{r}. \end{aligned} \quad [11]$$

Finally the far field approximation of this dipole propagation tensor is substituted,

$$\begin{aligned} \tilde{\mathbf{T}}(\mathbf{r}) &= 2\pi^2 \frac{\exp\{ik_0 r\}}{r} \\ &\quad \times \exp\{-i(\mathbf{k}_s, \mathbf{r}_n)\} \mathbf{T}(\mathbf{k}_s) \end{aligned} \quad [12]$$

where  $\mathbf{k}_s$  is the wave vector which is finally scattered toward the detector, and

$$\mathbf{T}(\mathbf{k}) \equiv 1 - \frac{\mathbf{k}\mathbf{k}}{k^2}. \quad [13]$$

The resulting equations where the limit  $\alpha \downarrow 0$  is taken are

$$\mathbf{E}(\mathbf{r}) = \sum_{n=1}^{\infty} \mathbf{E}_n(\mathbf{r}) \quad [14a]$$

with

$$\begin{aligned} \mathbf{E}_1(\mathbf{r}) &= \frac{2\pi^2 k_0^2}{(2\pi)^3} \frac{\exp\{ik_0 r\}}{r} \sum_j^{N_0} B_j(\mathbf{k}_0 - \mathbf{k}_s) \\ &\quad \times \exp\{i(\mathbf{k}_0 - \mathbf{k}_s, \mathbf{r}_j)\} \mathbf{T}(\mathbf{k}_s) \mathbf{E}_0 \end{aligned} \quad [14b]$$

and

$$\begin{aligned} \mathbf{E}_n(\mathbf{r}) &= 2\pi^2 k_0^2 \frac{(k_0 \pi i)^{n-1}}{(2\pi)^{3n}} \frac{\exp\{ik_0 r\}}{r} \sum_{j_1 j_2 j_3 \dots j_{n-2} j_{n-1} j_n}^{N_1 N_2 \dots N_{n-1} N_n} \oint dS_1 \oint dS_2 \dots \oint dS_{n-2} \oint dS_{n-1} \\ &\quad \times B_{j_1}(\mathbf{k}_0 - \mathbf{k}_1) B_{j_2}(\mathbf{k}_1 - \mathbf{k}_2) \dots B_{j_{n-1}}(\mathbf{k}_{n-2} - \mathbf{k}_{n-1}) B_{j_n}(\mathbf{k}_{n-1} - \mathbf{k}_s) \\ &\quad \times \exp\{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_{j_1})\} \exp\{i(\mathbf{k}_1 - \mathbf{k}_2, \mathbf{r}_{j_2})\} \dots \exp\{i(\mathbf{k}_{n-2} - \mathbf{k}_{n-1}, \mathbf{r}_{j_{n-1}})\} \\ &\quad \times \exp\{i(\mathbf{k}_{n-1} - \mathbf{k}_s, \mathbf{r}_{j_n})\} \times \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_{n-1}) \mathbf{T}(\mathbf{k}_{n-2}) \dots \mathbf{T}(\mathbf{k}_2) \mathbf{T}(\mathbf{k}_1) \mathbf{E}_0; \quad n \geq 2. \end{aligned} \quad [14c]$$

The integrations  $\oint dS_i$  ( $dS_i$  is an infinitesimal surface element) range over half-spherical surfaces in  $\mathbf{k}_i$  space with radius  $k_0$ , directed

along the vector  $\mathbf{r}_{j_{i+1}} - \mathbf{r}_{j_i}$  (see Fig. 1). Equation [14c] reflects the elasticity of the scattering

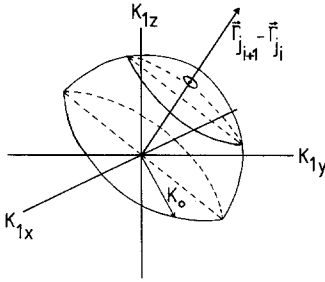


FIG. 1. The integration range in  $\int dS_i$  with the half-spherical surface oriented along the vector  $\mathbf{r}_{j_2} - \mathbf{r}_{j_1}$ . Note that  $dS_i = k_0^2 \sin \theta d\theta d\phi$  with  $\theta$  and  $\phi$  the spherical coordinates of  $\mathbf{k}_i$ .

process. Notice that in each term in the sum over  $j_1 \cdots j_n$  the surfaces generally have different orientations.  $N_1$  and  $N_2$  are the number of particles in that part of the scattering system where the incident intensity is not equal to zero, and in the part from which scattered radiation can be detected, respectively.  $N_0$  is the number of particles in the intersection of these two regions.  $N$  is the total number of particles in the scattering system. The definition of these numbers is depicted in Fig. 2. For obvious reasons  $\mathbf{E}_n(\mathbf{r})$  is interpreted as the  $n$ th-order scattered electric field strength.

What is the physical significance of the half-spherical surface integrals? Consider for example the second-order scattered electric field strength:

$$\begin{aligned} \mathbf{E}_2(\mathbf{r}) = & i \frac{2\pi^3 k_0^3}{(2\pi)^6} \frac{\exp\{ik_0 r\}}{r} \\ & \times \sum_{j_1 j_2}^{N_1 N_2} \int dS_1 B_{j_1}(\mathbf{k}_0 - \mathbf{k}_1) B_{j_2}(\mathbf{k}_1 - \mathbf{k}_s) \\ & \times \exp\{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_{j_1})\} \exp\{i(\mathbf{k}_1 - \mathbf{k}_s, \mathbf{r}_{j_2})\} \\ & \times \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_1) \mathbf{E}_0. \quad [15] \end{aligned}$$

Suppose  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|$  is large, that is, the particles  $j_1$  and  $j_2$  are far apart. The only values of  $\mathbf{k}_1$  that contribute to the integral in that case are those for which the phase  $i(\mathbf{k}_1, \mathbf{r}_{j_2} - \mathbf{r}_{j_1})$  is stationary (7). There is one such  $\mathbf{k}_1$ , namely  $\mathbf{k}_1 = k_0 \cdot (\mathbf{r}_{j_2} - \mathbf{r}_{j_1}) / |\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|$ , corresponding

to the scattering from particle  $j_1$  towards particle  $j_2$ . In this case  $E_2$  equals a product of  $E_1$ 's. This contribution behaves as  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|^{-1/2}$ . The contributions of  $\mathbf{k}_1$  values near the edge of the half-spherical surface behave as  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|^{-1}$ , and are important if  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|$  becomes somewhat smaller. Since the  $\mathbf{k}_1$  vectors on the edge are perpendicular to  $\mathbf{r}_{j_2} - \mathbf{r}_{j_1}$ , this shows that the physical interpretation of each *single*  $\mathbf{k}_1$  in the integrand in Eq. [15] as an intermediate scattered wave vector is somewhat oversimplified. Of course the interpretation of  $E_2$  as the *total* double scattering contribution stands. As the particles  $j_2$  and  $j_1$  approach each other, other  $\mathbf{k}_1$  values on the half-spherical surface contribute to the integral in Eq. [15] as well. Hence one might say that the half-spherical surface integrals take into account the fact that for the intermediate scattering events the full dipole propagation tensor is used in the derivation, and not some useful approximation. For example, using the far field approximation, one will find  $E_2$  to be equal to a product of  $E_1$ 's. Equation [15] is a generalization of equations obtained in this way.

Equation [14] does not include two or more successive scattering events within a single particle. It is understood that no adjacent indices in the multiple summation in Eq. [14] are equal. Whereas the interparticle multiple scattering contribution depends on the geometry of the scattering system, on the particle number density, and on single particle

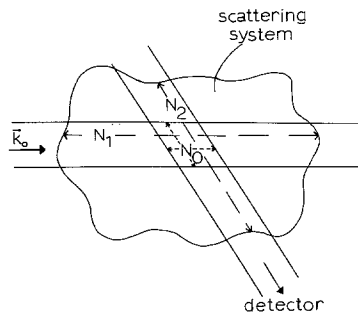


FIG. 2. The definition of the numbers  $N_0$ ,  $N_1$ , and  $N_2$ .

properties, the intraparticle contribution depends only on the single particle properties. It will be assumed that the difference in the dielectric constant of the particles and the solvent is small enough for all higher-order intraparticle scattering contributions to be neglected. Except in Section 3 where multiple intraparticle scattering is considered, only double scattering is discussed in the following, and consequently the only equations of further interest are Eqs. [14] for  $n = 1$  and  $n = 2$ .

3. MULTIPLE SCATTERING WITHIN SINGLE PARTICLES

Consider the one-particle problem. The integral equation [9] in this case is

$$\begin{aligned} \mathbf{E}(\mathbf{k}) &= (2\pi)^3 \mathbf{E}_0 \delta(\mathbf{k} - \mathbf{k}_0) \\ &+ \frac{k_0^2}{(2\pi)^3} \mathbf{T}_\alpha(\mathbf{k}) \int B(\mathbf{k}' - \mathbf{k}) \\ &\quad \times \exp\{i(\mathbf{k}' - \mathbf{k}, \mathbf{r}_0)\} \mathbf{E}(\mathbf{k}') d\mathbf{k}' \quad [16] \end{aligned}$$

where  $\mathbf{r}_0$  is the position coordinate of the particle. An iterated series expansion for  $\mathbf{E}(\mathbf{k})$  is obtained in the same way as for the multiparticle problem. Substituting in each term the definition of  $\mathbf{B}$  (Eq. [10]), and using Eq. [11] one obtains

$$\mathbf{E}(\mathbf{k}) = \sum_{n=1}^{\infty} \mathbf{E}_n(\mathbf{k}) \quad [16a]$$

with

$$\begin{aligned} \mathbf{E}_1(\mathbf{k}) &= k_0^2 \mathbf{T}_\alpha(\mathbf{k}) B(\mathbf{k}_0 - \mathbf{k}) \\ &\quad \times \exp\{i(\mathbf{k}_0 - \mathbf{k}, \mathbf{r}_0)\} \mathbf{E}_0 \quad [16b] \end{aligned}$$

and

$$\begin{aligned} \mathbf{E}_n(\mathbf{k}) &= \frac{k_0^{2n}}{(2\pi)^{3n-3}} \mathbf{T}_\alpha(\mathbf{k}) \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \\ &\quad \dots \int_V d\mathbf{r}_n \frac{\Delta\epsilon(\mathbf{r}_1)}{\epsilon} \frac{\Delta\epsilon(\mathbf{r}_2)}{\epsilon} \dots \frac{\Delta\epsilon(\mathbf{r}_n)}{\epsilon} \\ &\quad \times \exp\{i(\mathbf{k}_0, \mathbf{r}_1 + \mathbf{r}_0)\} \exp\{-i(\mathbf{k}, \mathbf{r}_n + \mathbf{r}_0)\} \\ &\quad \tilde{\mathbf{T}}(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \tilde{\mathbf{T}}(\mathbf{r}_2 - \mathbf{r}_1) \mathbf{E}_0; \quad n \geq 2. \quad [16c] \end{aligned}$$

Fourier inversion as in Section 2, again using the relations [11] and [12], gives

$$\mathbf{E}(\mathbf{r}) = \sum_{n=1}^{\infty} \mathbf{E}_n(\mathbf{r}) \quad [17a]$$

with

$$\begin{aligned} \mathbf{E}_1(\mathbf{r}) &= \frac{k_0^2}{4\pi} \frac{\exp\{ik_0 r\}}{r} \exp\{i(\mathbf{k}_0 - \mathbf{k}_s, \mathbf{r}_0)\} \\ &\quad \times B(\mathbf{k}_0 - \mathbf{k}_s) \mathbf{T}(\mathbf{k}_s) \mathbf{E}_0 \quad [17b] \end{aligned}$$

and

$$\begin{aligned} \mathbf{E}_n(\mathbf{r}) &= \frac{1}{4\pi} \frac{k_0^{2n}}{(2\pi)^{3n-3}} \frac{\exp\{ik_0 r\}}{r} \\ &\quad \times \exp\{i(\mathbf{k}_0 - \mathbf{k}_s, \mathbf{r}_0)\} \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \\ &\quad \dots \int_V d\mathbf{r}_n \frac{\Delta\epsilon(\mathbf{r}_1)}{\epsilon} \frac{\Delta\epsilon(\mathbf{r}_2)}{\epsilon} \dots \frac{\Delta\epsilon(\mathbf{r}_n)}{\epsilon} \\ &\quad \times \exp\{i(\mathbf{k}_0, \mathbf{r}_1)\} \exp\{-i(\mathbf{k}_s, \mathbf{r}_n)\} \\ &\quad \times \mathbf{T}(\mathbf{k}_s) \tilde{\mathbf{T}}(\mathbf{r}_n - \mathbf{r}_{n-1}) \dots \tilde{\mathbf{T}}(\mathbf{r}_2 - \mathbf{r}_1) \mathbf{E}_0; \\ &\quad n \geq 2. \quad [17c] \end{aligned}$$

Equations [17] are the equivalent of Eqs. [14] for the case of multiple scattering within a single particle. If the  $m$ th-order scattering tensor  $\mathbf{B}^{(m)}(\mathbf{k}_0, \mathbf{k}_s)$  is defined as

$$\begin{aligned} \mathbf{B}^{(m)}(\mathbf{k}_0, \mathbf{k}_s) &= \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 \dots \int_V d\mathbf{r}_m \frac{\Delta\epsilon(\mathbf{r}_1)}{\epsilon} \\ &\quad \times \frac{\Delta\epsilon(\mathbf{r}_2)}{\epsilon} \dots \frac{\Delta\epsilon(\mathbf{r}_m)}{\epsilon} \exp\{i(\mathbf{k}_0, \mathbf{r}_1)\} \\ &\quad \times \exp\{-i(\mathbf{k}_s, \mathbf{r}_m)\} \tilde{\mathbf{T}}(\mathbf{r}_m - \mathbf{r}_{m-1}) \\ &\quad \dots \tilde{\mathbf{T}}(\mathbf{r}_2 - \mathbf{r}_1); \quad n \geq 2 \quad [18] \end{aligned}$$

Eq. [17c] may be written more compactly as

$$\begin{aligned} \mathbf{E}_n(\mathbf{r}) &= \frac{1}{4\pi} \frac{k_0^{2n}}{(2\pi)^{3n-3}} \frac{\exp\{ik_0 r\}}{r} \exp\{i(\mathbf{k}_0 \\ &\quad - \mathbf{k}_s, \mathbf{r}_0)\} \mathbf{T}(\mathbf{k}_s) \mathbf{B}^{(n)}(\mathbf{k}_0, \mathbf{k}_s) \mathbf{E}_0. \quad [19] \end{aligned}$$

This equation should be compared to Eq. [17b], which is formally equivalent if for  $n = 1$ ,  $\mathbf{B}^{(n)}$  is defined as ( $\mathbf{I}$  is the identity)

$$\mathbf{B}^{(1)}(\mathbf{k}_0, \mathbf{k}_s) = \mathbf{I} B(\mathbf{k}_0 - \mathbf{k}_s). \quad [20]$$

A combination of inter- and intraparticle multiple scattering can be described without any difficulty, in the same way that Eqs. [14] and [17] are derived. The solution of the full multiple scattering problem including both multiple inter- and intraparticle scattering is obtained by replacing in Eqs. [14]  $B_{j_1} B_{j_2} \cdots B_{j_n} \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_{n-1}) \cdots \mathbf{T}(\mathbf{k}_2) \mathbf{T}(\mathbf{k}_1)$  by the ordered tensor product ( $a_m = [k_0^2 / (2\pi)^3]^{m-1}$ ):

$$\mathbf{T}(\mathbf{k}_s) \left[ \sum_{m=1}^{\infty} a_m \mathbf{B}_{j_n}^{(m)}(\mathbf{k}_s, \mathbf{k}_{n-1}) \right] \mathbf{T}(\mathbf{k}_{n-1}) \cdots \mathbf{T}(\mathbf{k}_1) \\ \times \left[ \sum_{m=1}^{\infty} a_m \mathbf{B}_{j_1}^{(m)}(\mathbf{k}_1, \mathbf{k}_0) \right].$$

As was mentioned before, in the following we will assume that differences in the dielectric constants of the Brownian particles and the solvent are small enough for intraparticle multiple scattering to be neglected.

#### 4. STATIC LIGHT SCATTERING

In Eq. [15] both the integration range (the direction of  $\mathbf{r}_{j_2} - \mathbf{r}_{j_1}$ ) and the integrand are stochastic variables. It is impossible to do the ensemble-averaging to obtain averaged scattered intensities, rigorously. If the scattering system has a center of symmetry, and the  $xy$  plane spanned by  $\mathbf{k}_0$  and  $\mathbf{k}_s$  ( $\mathbf{k}_0 \neq \pm \mathbf{k}_s$ ) is a plane of symmetry, one may argue that the averaging of the directions  $\mathbf{r}_{j_2} - \mathbf{r}_{j_1}$  will orientate the half-spherical surfaces along the positive (or negative)  $z$  axis (8). Then the averaging of the magnitudes  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|$  may be performed in the integrand. Remember that at least for spherical particles the probability function of  $\mathbf{r}_{j_2}$  and  $\mathbf{r}_{j_1}$  depends on  $|\mathbf{r}_{j_2} - \mathbf{r}_{j_1}|$  only. Furthermore,  $B_{j_i}$  is a function of the orientation of particle  $j_i$  only. For spherical particles then,  $B_{j_i}$  is not a stochastic variable, but some deterministic function of  $(\mathbf{k})$ . Hence we direct all surfaces in Eq. [15] along the positive  $z$  axis, treat  $B_{j_i}$  as given functions, and average the phase functions in the integrand with respect to  $\mathbf{r}_{j_2}$  and  $\mathbf{r}_{j_1}$ .

The ensemble-averaging procedure outlined above, neglecting third- and higher-

order scattering and assuming monodispersity, leads to

$$R = R_1 + R_2 \quad [21]$$

where  $R$  is the experimental Rayleigh ratio,  $R_1$  is the well-known first-order contribution,

$$R_1(|\mathbf{k}_0 - \mathbf{k}_s|, \mathbf{n}_0, \mathbf{n}_s) = \frac{4\pi^4 k_0^4}{(2\pi)^6} \rho v^2 P(|\mathbf{k}_0 - \mathbf{k}_s|) \\ \times S(|\mathbf{k}_0 - \mathbf{k}_s|)(\mathbf{T}(\mathbf{k}_s) \mathbf{n}_0, \mathbf{n}_s)^2, \quad [22]$$

where  $\mathbf{n}_0(\mathbf{n}_s)$  is the polarization of the incident (detected) radiation,  $P$  is the form factor defined as  $|B|^2/v^2$  ( $v$  being the volume of a particle),  $S$  is the structure factor, and

$$R_2(\mathbf{k}_0, \mathbf{k}_s, \mathbf{n}_0, \mathbf{n}_s) \\ = \frac{4\pi^6 k_0^6}{(2\pi)^{12}} \frac{1}{V_s} \sum_{j_1 j_2 j_3 j_4}^{N_1 N_2 N_1 N_2} \int dS_1 \int dS_2 \\ \times B(\mathbf{k}_0 - \mathbf{k}_1) B(\mathbf{k}_1 - \mathbf{k}_s) B(\mathbf{k}_0 - \mathbf{k}_2) \\ \times B(\mathbf{k}_2 - \mathbf{k}_s) \langle \cdots \rangle (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_1) \mathbf{n}_0) \\ \times (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_2) \mathbf{n}_0), \quad [23]$$

is the second-order contribution where  $V_s$  is the volume containing the  $N_0$  particles (see Fig. 2). The ensemble average  $\langle \cdots \rangle$  in Eq. [23] is given by

$$\langle \cdots \rangle \equiv \langle \exp\{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_{j_1})\} \\ \times \exp\{-i(\mathbf{k}_0 - \mathbf{k}_2, \mathbf{r}_{j_3})\} \\ \times \exp\{i(\mathbf{k}_1 - \mathbf{k}_s, \mathbf{r}_{j_2})\} \\ \times \exp\{-i(\mathbf{k}_2 - \mathbf{k}_s, \mathbf{r}_{j_4})\} \rangle. \quad [24]$$

This four-point average can be written as a product of two two-point averages if one assumes that  $N_0^2/N_1 N_2 \ll 1$ .<sup>2</sup> In that case the vast majority of the particles  $j_1$  and  $j_3$  (which are in the volume  $V_1$ , the illuminated volume; see Fig. 2) are statistically independent of the

<sup>2</sup> In practice this inequality is almost always satisfied. However, it may be replaced by the assumption that the range of interactions (static as well as dynamic) is very small compared to the dimensions of the scattering system, since in that case the vast majority of the particles  $j_1$  and  $j_3$  are independent during the total measuring time in an experiment.

particles  $j_2$  and  $j_4$  (which are in  $V_2$ , the detected volume), and  $\langle \dots \rangle$  may be approximated by

$$\begin{aligned} \langle \dots \rangle &= \langle \exp\{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_{j_1})\} \\ &\times \exp\{-i(\mathbf{k}_0 - \mathbf{k}_2, \mathbf{r}_{j_3})\} \rangle \\ &\times \langle \exp\{i(\mathbf{k}_1 - \mathbf{k}_s, \mathbf{r}_{j_2})\} \\ &\times \exp\{-i(\mathbf{k}_2 - \mathbf{k}_s, \mathbf{r}_{j_4})\} \rangle. \end{aligned} \quad [25]$$

Using the translational invariance of the probability density function of the position coordinates of two particles one finds

$$\begin{aligned} &\sum_{j_1 j_3}^{N_1 N_1} \langle \exp\{i(\mathbf{k}_0 - \mathbf{k}_1, \mathbf{r}_{j_1})\} \\ &\times \exp\{-i(\mathbf{k}_0 - \mathbf{k}_2, \mathbf{r}_{j_3})\} \rangle \\ &= \rho V_1 S(|\mathbf{k}_0 - \mathbf{k}_1|) \\ &\times \frac{\int_{V_1} \exp\{i(\mathbf{k}_2 - \mathbf{k}_1, \mathbf{r})\} d\mathbf{r}}{V_1}, \end{aligned} \quad [26a]$$

and

$$\begin{aligned} &\sum_{j_2 j_4}^{N_2 N_2} \langle \exp\{i(\mathbf{k}_1 - \mathbf{k}_s, \mathbf{r}_{j_2})\} \\ &\times \exp\{-i(\mathbf{k}_2 - \mathbf{k}_s, \mathbf{r}_{j_4})\} \rangle \\ &= \rho V_2 S(|\mathbf{k}_2 - \mathbf{k}_s|) \\ &\times \frac{\int_{V_2} \exp\{i(\mathbf{k}_1 - \mathbf{k}_2, \mathbf{r})\} d\mathbf{r}}{V_2}. \end{aligned} \quad [26b]$$

Notice that the right-hand sides of Eqs. [26] contain a factor which is very similar to the square root of the form factors of the (macroscopic) volumes  $V_1$  and  $V_2$ . If the wavelength is much smaller than the smallest dimension of  $V_1$  and  $V_2$ —in practice this is always the case—these form factors very rapidly drop to zero if  $|\mathbf{k}_1 - \mathbf{k}_2|$  is not equal to zero. Hence, in Eq. [23], after substitution of Eqs. [26],  $\mathbf{k}_2$  can be replaced by  $\mathbf{k}_1$  except in the form factors, and the integration over  $\mathbf{k}_2$  is performed only over the product of the form factors:

$$\begin{aligned} R_2(\mathbf{k}_0, \mathbf{k}_s, \mathbf{n}_0, \mathbf{n}_s) &= \frac{4\pi^6 k_0^6}{(2\pi)^{12}} \frac{V_1 V_2}{V_s} \\ &\times \int dS_1 [\rho v^2 P(|\mathbf{k}_0 - \mathbf{k}_1|) S(|\mathbf{k}_0 - \mathbf{k}_1|) \\ &\times S(|\mathbf{k}_0 - \mathbf{k}_1|) \rho v^2 P(|\mathbf{k}_1 - \mathbf{k}_s|) S(|\mathbf{k}_1 - \mathbf{k}_s|) \\ &\times S(|\mathbf{k}_1 - \mathbf{k}_s|) (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_1) \mathbf{n}_0)^2 G(\mathbf{k}_1)] \end{aligned} \quad [27]$$

where

$$\begin{aligned} G(\mathbf{k}_1) &\equiv \int dS_2 \frac{\int_{V_1} \exp\{i(\mathbf{k}_2 - \mathbf{k}_1, \mathbf{r})\} d\mathbf{r}}{V_1} \\ &\times \frac{\int_{V_2} \exp\{i(\mathbf{k}_1 - \mathbf{k}_2, \mathbf{r})\} d\mathbf{r}}{V_2} \end{aligned} \quad [28]$$

is a function completely determined by the geometry of the scattering system and the magnitude of the wave vectors. This function describes the interference of field strengths scattered from different points in  $V_1$  and  $V_2$ . Notice that the function varies with the scattering angle through its integration ranges  $V_1$  and  $V_2$ . It thus turns out that the geometry of the scattering system plays an important role as far as double scattering is concerned. Notice that with Eq. [22],  $R_2$  can be expressed in terms of  $R_1^{VV}$  (VV stands for vertically polarized incident and detected radiation)

$$\begin{aligned} R_2(\mathbf{k}_0, \mathbf{k}_s, \mathbf{n}_0, \mathbf{n}_s) &= \frac{1}{4\pi^2 k_0^2} \frac{V_1 V_2}{V_s} \\ &\times \int dS_1 R_1^{VV}(\mathbf{k}_0 - \mathbf{k}_1) R_1^{VV}(\mathbf{k}_1 - \mathbf{k}_s) \\ &\times (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s) \mathbf{T}(\mathbf{k}_1) \mathbf{n}_0)^2 G(\mathbf{k}_1). \end{aligned} \quad [29]$$

From this equation one can obtain an iterative correction procedure for double scattering; this procedure will be discussed shortly.

### 5. DYNAMIC LIGHT SCATTERING

From Eqs. [14] it can be seen that both  $\mathbf{E}_1$  and  $\mathbf{E}_2$  are Gaussian stochastic variables (8). Therefore the Siegert relation applies to both  $E_1$  and  $E_2$ :

$$\langle i_1(0)i_1(t) \rangle = \langle i_1 \rangle^2 + \frac{1}{4} \frac{\epsilon}{\mu_0} |\langle (\mathbf{E}_1(\mathbf{r}, 0), \mathbf{n}_s)(\mathbf{E}_1^*(\mathbf{r}, t), \mathbf{n}_s) \rangle|^2$$

and

$$\langle i_2(0)i_2(t) \rangle = \langle i_2 \rangle^2 + \frac{1}{4} \frac{\epsilon}{\mu_0} |\langle (\mathbf{E}_2(\mathbf{r}, 0), \mathbf{n}_s)(\mathbf{E}_2^*(\mathbf{r}, t), \mathbf{n}_s) \rangle|^2. \quad [30]$$

Here  $i(t)$  is the instantaneous scattered intensity. Due to the assumption  $N_0^2/N_1N_2 \ll 1$ , one can use approximate equations like  $\langle i_1(0)i_2(t) \rangle = \langle i_1 \rangle \langle i_2 \rangle$  and  $\langle E_1(0)E_2(t) \rangle = 0$  etc. After some algebra, using the fact that functions like  $(\int_V \exp\{i(\mathbf{k}, \mathbf{r})\} d\mathbf{r})/V$  are effectively zero for  $\mathbf{k} \neq \mathbf{0}$  if  $V$  is macroscopic, one then obtains

$$\begin{aligned} \langle i(0)i(t) \rangle &= \frac{1}{4} \frac{\epsilon}{\mu_0} \langle |\mathbf{E}_1(\mathbf{r}, 0) \\ &+ \mathbf{E}_2(\mathbf{r}, 0), \mathbf{n}_s|^2 |(\mathbf{E}_1(\mathbf{r}, t) + \mathbf{E}_2(\mathbf{r}, t), \mathbf{n}_s)|^2 \rangle \\ &= \langle i \rangle^2 + \frac{1}{4} \frac{\epsilon}{\mu_0} |\langle (\mathbf{E}_1(\mathbf{r}, 0), \mathbf{n}_s)(\mathbf{E}_1^*(\mathbf{r}, t), \mathbf{n}_s) \rangle \\ &+ \langle (\mathbf{E}_2(\mathbf{r}, 0), \mathbf{n}_s)(\mathbf{E}_2^*(\mathbf{r}, t), \mathbf{n}_s) \rangle|^2 \quad [31] \end{aligned}$$

where \* denotes complex conjugation. The ensemble averages can be calculated in the same way as for the static light scattering case. For the "normalized" intensity autocorrelation function defined as

$$\phi(t) = \frac{\langle i(0)i(t) \rangle - \langle i \rangle^2}{\langle i \rangle^2} \quad [32]$$

the relation

$$R\phi^{1/2}(t) = R_1\phi_1^{1/2}(t) + R_2\phi_2^{1/2}(t) \quad [33]$$

is found where  $\phi_1(\phi_2)$  is the autocorrelation function Eq. [32] with  $i_1(i_2)$  substituted for  $i$ . The term  $R_2\phi_2^{1/2}(t)$  gives the second-order contribution to the experimental quantity  $R\phi^{1/2}(t)$

$$\begin{aligned} R_2\phi_2^{1/2}(t) &= \frac{1}{4\pi^2 k_0^2} \frac{V_1 V_2}{V_s} \\ &\times \int dS_1 R_1^{VV}(\mathbf{k}_0 - \mathbf{k}_1) \phi_1^{VV/2}(\mathbf{k}_0 - \mathbf{k}_1, t) \end{aligned}$$

$$\begin{aligned} &\times R_1^{VV}(\mathbf{k}_1 - \mathbf{k}_s) \phi_1^{VV/2}(\mathbf{k}_1 - \mathbf{k}_s, t) \\ &\times (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s)\mathbf{T}(\mathbf{k}_1)\mathbf{n}_0)^2 G(\mathbf{k}_1) \quad [34] \end{aligned}$$

where  $\phi_1^{VV}$  is the first-order correlation function for vertically incident and detected radiation. For spherical particles one has

$$\phi_1^{VV}(\mathbf{k}, t) = \exp\{-2D(\mathbf{k})|\mathbf{k}|^2 t\} \quad [35]$$

where  $D(\mathbf{k})$  is the effective diffusion coefficient, and  $\mathbf{k} = \mathbf{k}_0 - \mathbf{k}_s$ . In Eq. [35] the  $\mathbf{k}$  dependence of  $\phi_1^{VV}$  is denoted explicitly. Notice that Eq. [34] is identical to Eq. [29], the static light scattering formula, except that  $R_1^{VV}$  is replaced by  $R_1^{VV} \phi_1^{VV/2}(t)$ .

## 6. CORRECTION FOR DOUBLE SCATTERING

Equations [29] and [34] may be written as

$$R = R_1 + T(R_1^{VV}) \quad [36a]$$

and

$$R\phi^{1/2}(t) = R_1\phi_1^{1/2}(t) + T(R_1^{VV} \phi_1^{VV/2}(t)). \quad [36b]$$

These equations define the nonlinear operator  $T$ :

$$\begin{aligned} Tf &= \frac{1}{4\pi^2 k_0^2} \frac{V_1 V_2}{V_s} \int dS_1 f(\mathbf{k}_0 - \mathbf{k}_1) f(\mathbf{k}_1 - \mathbf{k}_s) \\ &\times (\mathbf{n}_s, \mathbf{T}(\mathbf{k}_s)\mathbf{T}(\mathbf{k}_1)\mathbf{n}_0)^2 G(\mathbf{k}_1). \quad [37] \end{aligned}$$

In Eqs. [36] the quantities  $R$  and  $R\phi^{1/2}(t)$  are known functions, found from experiments. Consider VV experiments, in which the incident and detected radiation are vertically polarized. Equations [36] may then be considered as nonlinear Fredholm integral equations of the second kind in  $R_1^{VV}$  and  $\phi_1^{VV}(t)$ , respectively, if in Eq. [36b] we assume  $R_1^{VV}$  and  $R_2^{VV}$  to be known (to be obtained from Eq. [36a]). The integral equations can be solved by iteration if the operator norm of  $T$  is less than unity (10). This is the case if  $R_1^{VV}$  is small enough, depending on the geometry of the scattering system. The iterative schemes are

$$R_{1,r}^{VV} = R^{VV} - T(R_{1,r-1}^{VV}); \quad r \geq 1 \quad [38a]$$



and

$$\phi_{1,r}^{VV} = \left[ \left( 1 + \frac{R_2}{R_1} \right) \phi^{VV1/2} - \frac{1}{R_1} T(R_1 \phi_{1,r-1}^{VV1/2}) \right]^2; \quad r \geq 1 \quad [38b]$$

where for brevity we denoted  $R_1 \equiv R_1^{VV}$  and  $R_2 \equiv R_2^{VV}$  and omitted the time dependence of all  $\phi$ 's. In these schemes we defined  $R_{1,0}^{VV} \equiv R^{VV}$  and  $\phi_{1,0}^{VV} = \phi^{VV}$ . Hence as a first approximation the second-order contributions are calculated (numerically) by substituting the experimental VV data in Eq. [29] or Eq. [34] for the first-order function. Eqs. [38] give a first-order approximation for the first-order functions  $R_{1,1}^{VV}$  and  $\phi_{1,1}^{VV}$ . These functions are used in the same way to calculate a better approximation for the second-order quantities, etc. The solution for the first-order contribution is given by

$$R_1^{VV} = \lim_{r \rightarrow \infty} R_{1,r}^{VV} \quad [39a]$$

and

$$\phi_1^{VV} = \lim_{r \rightarrow \infty} \phi_{1,r}^{VV}. \quad [39b]$$

Of course in practice the iteration is stopped when successive differences between the iterated functions are (much) less than the estimated experimental errors. If the correction for double scattering is considerable (say  $R_2^{VV}/R_1^{VV} \geq 0.3$ ) one may apply the following iterative schemes instead of the schemes in Eqs. [38]:

$$R_{1,r}^{VV} = \frac{R^{VV} + R_{1,r-1}^{VV}}{2} - \frac{1}{2} T(R_{1,r-1}^{VV}); \quad r \geq 1 \quad [40a]$$

$$\phi_{1,r}^{VV}(t) = \left[ \frac{(1 + R_2/R_1) \phi^{VV1/2}(t) + \phi_{1,r-1}^{VV1/2}}{2} - \frac{1}{2R_1} T(R_1 \phi_{1,r-1}^{VV1/2}) \right]^2; \quad r \geq 1. \quad [40b]$$

For large corrections these schemes converge faster to the same limiting functions  $R_1^{VV}$  and

$\phi_1^{VV}$  (this follows from the uniqueness of the solution of Eqs. [36]).

7. EXPERIMENTAL

To apply the iterative correction procedures the geometry of the scattering system must be known, since the geometrical function, Eq. [28], is part of the kernel of the integral operator  $T$ , Eqs. [38]. We used 2-cm-diameter cylindrical cuvettes with cylindrical incident and detected beams of radiation, as schematically depicted in Fig. 3. To prevent large experimental errors in the geometry of the scattering system due to small misalignments, the radius of the incident beam is taken much larger than the radius of the detected beam. In determining the geometry one should take into account refraction at optical boundaries: the toluene bath (serving as a thermostat) and the cuvette. In the present case the radii of the incident and detected beams were 2.03 and 0.285 mm, respectively. Due to refraction of the beams at the boundary of the cuvette these radii depend inversely proportionally on the refractive index of the dispersion in the cuvette, which in the present case was 1.505. The integrals ranging over  $V_1$  and  $V_2$  occurring in the geometrical function can be evaluated explicitly (with respect to the coordinate system as depicted in Fig. 3):

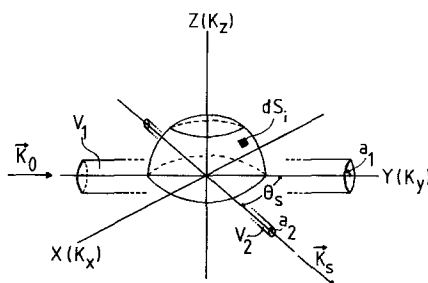


FIG. 3. The coordinate system with respect to which polarizations and integrations are defined.

$$G(\mathbf{k}_1) = \left(\frac{4}{\pi}\right)^2 \int dS_2 \frac{\sin[\frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_2 L]}{\frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_2 L} \frac{\sin[\frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_1 L \sin \theta_s + \frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_2 L \cos \theta_s]}{\frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_1 L \sin \theta_s + \frac{1}{2}(\mathbf{k}_2 - \mathbf{k}_1)_2 L \cos \theta_s} \\ \times f(\sqrt{|\mathbf{k}_2 - \mathbf{k}_1|^2 - (\mathbf{k}_2 - \mathbf{k}_1)_2^2} \cdot a_1) f(\sqrt{|\mathbf{k}_2 - \mathbf{k}_1|^2 - [(\mathbf{k}_2 - \mathbf{k}_1)_1 \sin \theta_s + (\mathbf{k}_2 - \mathbf{k}_1)_2 \cos \theta_s]^2} \cdot a_2) \quad [41]$$

where  $(\mathbf{k}_2 - \mathbf{k}_1)_\alpha$  is the  $\alpha$ th component of  $\mathbf{k}_2 - \mathbf{k}_1$  ( $\alpha = 1, 2$ , or  $3$ ), and

$$f(ka) = \frac{1}{4a^2} \int_0^{2\pi} d\phi \int_0^a d\rho \rho \exp\{ik\rho \cos \phi\} \\ = \frac{\pi J_1(ka)}{2ka}. \quad [42]$$

Here  $J_1$  is the first-order Bessel function,  $L$  is the diameter of the cuvette (2 cm),  $a_1$  and  $a_2$  are the radii of the incident beam (2.03 mm) and the detected beam (0.285 mm), respectively, and  $\theta_s$  is the scattering angle (the smallest angle between  $\mathbf{k}_0$  and  $\mathbf{k}_s$ ).

Static and dynamic experiments were performed on the same apparatus, using an argon laser (Spectra Physics Model 165) at 488-nm wavelength, and a Malvern correlator (Type K 7025).

To correct experimental Rayleigh ratios for attenuation (by multiplication with  $\exp\{\tau L\}$ ) we measured the turbidities  $\tau$  on a Bausch & Lomb Spectronic spectrometer.

The experiments were performed on a colloidal dispersion of silica particles with hydrodynamic radius  $39 \pm 3$  nm in toluene. The particles are  $\sim 10\%$  polydisperse in radius, as determined from electron micrographs. Furthermore, for the geometry used here,  $N_0^2/N_1 N_2 \approx 0.001$  (at  $90^\circ$  scattering angle). We expect the theory given in the previous sections to hold in this case.

### 7.1 Application of the Iterative Correction Procedures

It is found that the Rayleigh ratio  $R_2^{YV}$  (VV stands for vertically polarized incident and detected radiation) becomes small for large and small scattering angles. Therefore triple- and/or higher-order scattering events

may become important at these angles. As a consequence the iterative schemes should be applied in an intermediate scattering angle range, and in each iterative step results must be extrapolated towards the small and large angles. We found, depending somewhat on the amount of multiple scattering, that results should be extrapolated from the scattering angle range  $\sim (20^\circ, 160^\circ)$ . The extrapolations toward the small angles can be done by means of a Guinier plot:  $\ln R$  versus  $K^2 = |\mathbf{k}_0 - \mathbf{k}_s|^2$  is extrapolated linearly. The extrapolation toward the large angles is not difficult, since the  $K$  range corresponding to the angle range ( $160^\circ, 180^\circ$ ) is very small.

The results of the procedure for static light scattering for a number of concentrations (see Table I) are shown in Fig. 4. For sample 1, which is the largest concentration, the iterative scheme does converge, but yields values of  $R_2^{YV}$  which are larger than the corrected  $R_1^{YV}$  for most scattering angles. It is obvious that this sample shows too much multiple scattering to give any reliable cor-

TABLE I

The Concentrations, Turbidities, and Maximum Relative Corrections for Static Light Scattering Data for Samples 1-5

Sample	Concentration [g/cm <sup>3</sup> ]	Volume fraction <sup>a</sup>	Turbidity [cm <sup>-1</sup> ]	$(R_2^{YV}/R_1^{YV})_{\max}$
1	0.0275	0.016	1.01	>1
2	0.0169	0.010	0.62	0.43
3	0.0115	0.007	0.42	0.25
4	0.0084	0.005	0.31	0.10
5	0.0008	0.005	0.02	0.01

<sup>a</sup> Calculated from the weight concentration using 1.7 g/cm<sup>3</sup> for the particle mass density.

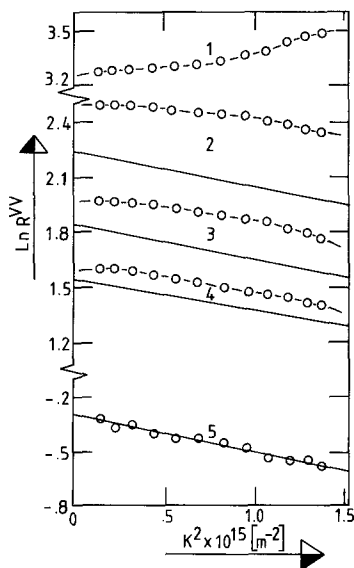


FIG. 4. The logarithm of VV Rayleigh ratios vs  $K^2 = |\mathbf{k}_0 - \mathbf{k}_s|^2$  for a number of concentrations.  $\circ$ , Experimental curves, —, double scattering corrected curves. The numbers refer to the concentrations as given in Table I. All Rayleigh ratios are corrected for attenuation. Rayleigh ratios are given in  $m^{-1}$ .

corrected Rayleigh ratios. For the remaining samples with lower concentrations and hence less multiple scattering, corrected results are reliable, and are given by the full curves in Fig. 4. After correction, straight Guinier plots are found, as expected. Furthermore, concentrations are low enough to neglect the effects of interaction between Brownian particles on the slopes of these plots, and the slopes of the corrected curves should be the same. Indeed within experimental error this was found to be the case. The corresponding double scattered Rayleigh ratios are plotted in Fig. 5, showing that these ratios are indeed small at small and large scattering angles.

Once the first-order Rayleigh ratios are known, depolarized Rayleigh ratios can be calculated (just change the polarizations  $n_0$  and  $n_s$  in Eqs. [22] and [29]), and compared directly with experimental data. An independent test of the iterative procedure involves

contrast variation experiments. For the results of such experiments we refer to Ref. (6). It is found that the agreement between experiment and theoretical calculations, and the results of the contrast variation experiments are very satisfactory.

Especially at small scattering angles, triple scattering shows up very clearly in the intensity autocorrelation function at short times, since the decay time of triply scattered intensities, at least at the smaller scattering angles, say  $\theta_s < 35^\circ$ , is very much smaller than the decay times for both doubly and singly scattered intensities. In the iterative schemes those times are considered for which the triply scattered intensities are decayed to zero;  $t > T$ . It is found that, depending slightly on the amount of multiple scattering, one should take  $\phi_1(T) \approx 0.7-0.9$ . Furthermore, for  $t > T$  the logarithm of the correlation functions could not be fitted with a second-order polynomial in  $t$  (the so-called second cumulant fit). Therefore we fitted the logarithm of the correlation function linearly in the time interval  $(T, T_0)$ , where  $\phi_1(T_0) \approx 0.4-0.6$ . Of course one could also do a linear fit in a time interval  $(T', T'_0)$  with say  $\phi_1(T') \approx 0.5$  and  $\phi_1(T'_0) \approx 0.2$ , and find different slopes, i.e., apparent diffusion coefficients. If, however, the iterative schemes are applied in the appropriate time intervals, the corrected results coincide, since the iterative

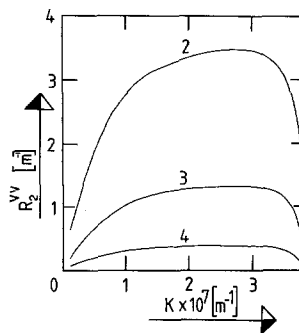


FIG. 5. The second-order VV Rayleigh ratios vs  $K = |\mathbf{k}_0 - \mathbf{k}_s|$ . The numbers refer to the concentrations as given in Table I.

schemes correct for these differences in slope caused by double scattering. We fitted the correlation function in a time interval with  $T$  chosen as small as possible, to prevent higher-order cumulants due to polydispersity from becoming important.

At large scattering angles the decay times of doubly and singly scattered intensities become equal, and one would expect the experimental ("apparent") diffusion coefficients to become equal to the first-order diffusion coefficient. This is indeed the case as can be seen from Fig. 6. Since the double scattering contribution to the scattered intensity is at its maximum at intermediate scattering angles, the apparent diffusion coefficient as a function of  $K = |\mathbf{k}_0 - \mathbf{k}_s|$  shows a maximum there. It is found that the corrected diffusion coefficients coincide with the "infinite diluted" experimental curve within experimental error (sample 5), as they should,

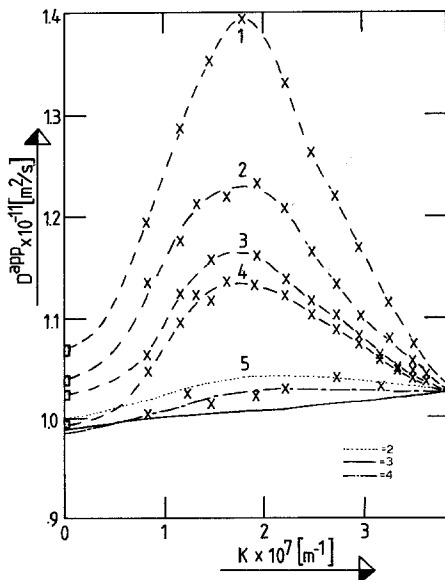


FIG. 6. Diffusion coefficients for a number of concentrations vs  $K = |\mathbf{k}_0 - \mathbf{k}_s|$ . The numbers refer to the concentrations as given in Table I. ( $\times$ ) Experimental curves. (---, —, - - -) curves for sample Nos. 2, 3, and 4, respectively, obtained after correction for double scattering. The points  $\square$  at  $K = 0$  are obtained by means of a linear extrapolation of  $D$  vs  $K^2$  for small  $K$ .

since interaction effects on the diffusion coefficient at these low concentrations are unimportant.

The iterative scheme may also be applied to correlation functions which have a form that differs from Eq. [35]. Instead of fitting in each iterative step in the case of a multi-parameter fit, a safer way to correct for double scattering is to apply the iterative scheme on the correlation function values  $\phi(K, t)$  themselves and fit only the resulting corrected correlation function.

As in the static light scattering case, depolarized correlation functions may be calculated from first-order results and directly compared to experimental functions, and contrast variation experiments may be performed to verify the theory. These experiments are described in Ref. (8). Results are very satisfactory, just as they were in the static light scattering case. An important result is that the decay time of second-order correlation functions changes only  $\sim 20\%$  over the scattering angle range  $\sim (20^\circ, 160^\circ)$ .

## 8. SUMMARY

We derived equations for the total scattered electric field strength from a system of Brownian particles fixed in space, assuming that

- (i) all materials in the scattering system are linear dielectrics with a magnetic susceptibility equal to that of free space,
- (ii) the scattering process is elastic, and the reaction of matter on the incident field strength is instantaneous,
- (iii) differences in the dielectric constants of the solvent and the Brownian particles are small.

In order to obtain useful equations for the average scattered intensity and the intensity autocorrelation function, it is furthermore assumed that

- (iv) intraparticle multiple scattering is unimportant.

(v) only second-order (and of course first-order) interparticle scattering is of importance,

(vi) the geometry of the scattering system satisfies certain conditions (two symmetry conditions and the condition that  $N_0^2/N_1N_2 \ll 1$ ).

Condition (vi) is necessary to obtain an ensemble-averaging procedure for second-order intensities and intensity correlation functions, and to be able to approximate a four-point ensemble average by a product of two two-point ensemble averages. This in turn yields equations which are useful for correcting iteratively data for double scattering. The iterative procedure is applied to a well-defined colloidal system, and the results are satisfactory. More extensive experiments are described in Refs. (6, 8, 9), which confirm the validity of the equations obtained here and

the iterative procedure to correct for double scattering.

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