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Multiple scattering of light from independent Brownian particles

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Using a perturbation method based on a multiple scattering expansion of Maxwell's equations, we have analyzed the effect of multiple scattering on the polarized and the depolarized field-correlation (FC) functions of light scattered from independent Brownian particles. The results of a complete second-order (CSO) calculation are presented. The expression obtained for the polarized FC function includes double scattering as well as turbidity corrections to the single scattering. Such turbidity corrections strongly influence the static and dynamic properties of the polarized FC function. The results of the CSO calculation reproduce quite well published experimental data on the angular and concentration behavior of the decay time of the polarized FC function. However, for the polarized intensity there is only qualitative agreement between theoretical and experimental values. The CSO analysis does not introduce turbidity corrections to double scattering and hence leads to the same expression for the depolarized FC function as does a pure, double-scattering calculation.

I. INTRODUCTION

Dynamic light scattering has become an important tool in the study of systems such as macromolecules in solution. In terms of the properties of the field-correlation (FC) function the analysis of macromolecular properties is rather straightforward as long as we have single scattering only. It is also generally accepted that an admixture of multiple scattering modifies the static and dynamic properties of the FC function, which may seriously hamper the interpretation.[1] The quantitative effect of multiple scattering has not been satisfactorily evaluated although some progress has been made during the last few years.

Analysis of multiple scattering from systems where the size of the macromolecules is comparable to the incident light was first performed by Kelly[2] and by Ivanov *et al.*[3] in 1973. Kelly considered only first-order corrections to the single scattering and found the dynamical properties of the FC function to remain essentially unchanged.

Ivanov *et al.*, in their analysis of double scattering from Brownian particles, concluded that the decay of the FC function is nearly exponential and faster than that of single scattering. The difference in the decay time τ_{FC} between the double and single scattering is more pronounced at small angles and vanishes in the backward direction.

In a recent experimental study Colby *et al.*[4] (hereafter referred to as paper I) measured FC functions for a system of Brownian particles and found that relative to single scattering, τ_{FC} for multiple scattering is shorter and has a more complicated angular dependence.

Quite recently Sorensen *et al.*[5] (hereafter referred to as paper II) extended the analysis of Kelly to include double scattering and obtained a good fit to their measurement of τ_{FC} for depolarized scattered light. Qualitatively, their results are in accordance with those of Ivanov *et al.*[3]

However, the second-order calculation by Ivanov *et al.*, and in paper II, is incomplete since contributions connected to turbidity corrections of single scattering are ignored. These contributions must be considered in discussing the effects of multiple scattering on the polarized FC function.

The purpose of the present paper is to present a complete-second-order (CSO) calculation of the FC function of the scattered field. We shall discuss the role played by the mixing of singly and triply scattered fields and by other scattered processes which have so far not been considered. We shall particularly concentrate on the effect of lowest-order contributions to multiple scattering on the polarized FC function.

The paper is organized as follows: In Sec. II we introduce a multiple-scattering expansion for the FC function. The analysis is based on a recursion formula for the nth-order scattered field derived from Maxwell's equations. In Sec. III we consider scattering from rigid macromolecules and discuss, quite generally, the kind of scattering processes that may occur in multiple scattering. In Sec. IV we derive CSO expressions for the polarized and depolarized FC functions for scattering on independent Brownian particles. These expressions are compared in Sec. V with those of the double-scattering approximation (paper II) and in Sec. VI with the experimental data given in paper I.

II. PERTURBATION EXPANSION OF THE FIELD-CORRELATION FUNCTION

We consider a stationary, plane-polarized, and monochromatic wave $\vec{E}_0(\vec{r},t)$:

$$\vec{E}_0(\vec{r},t)=E_0\hat{n}e^{i(\vec{k}_0\cdot\vec{r}-\omega_0 t)}\,, \tag{1}$$

incident on a solution of macromolecules. The total scattered field $\vec{E}_s(t)$ can be written

$$\vec{E}_s(t)=\sum_{n=1}^{\infty}\vec{E}_n(t)\,, \tag{2}$$

where $\vec{E}_n$ represents the nth-order multiply scattered field. The FC function for a stationary system is then[6]

$$\begin{aligned}G(t)&=\sum_{n=0}^{\infty}\sum_{m=1}^{n+1}G_{n+2-m,m}(t)\\&=\sum_{n=0}^{\infty}\sum_{m=1}^{n+1}\langle\vec{E}^*_{n+2-m}(t)\vec{E}_m(0)\rangle\,.\end{aligned} \tag{3}$$

As in single scattering, we seek an expression for $\vec{E}_n(t)$ in terms of the permittivity fluctuations of the scattering medium:

$$\epsilon(\vec{r},t)=\epsilon_m[1+\epsilon_1(\vec{r},t)]\,, \tag{4}$$

where ϵ_m is the average permittivity of the solvent and $\epsilon_1(\vec{r},t)$ the relative permittivity perturbation.

Introducing Eq. (4) in the Maxwell equations we obtain a hierarchy of equations, the nth order of which is[6]

$$\begin{aligned}&\nabla\times\vec{E}_n=-\mu\frac{\partial}{\partial t}\vec{H}_n\,,\\&\nabla\cdot\vec{E}_n=-\nabla\cdot(\epsilon_1\vec{E}_{n-1})\,,\\&\mu\nabla\cdot\vec{H}_n=0\,,\\&\nabla\times\vec{H}_n=\epsilon_m\frac{\partial}{\partial t}\vec{E}_n+\epsilon_m\frac{\partial}{\partial t}(\epsilon_1\vec{E}_{n-1})\,,\end{aligned} \tag{5}$$

where $\vec{E}_n$ is the nth-order scattered field resulting from the $(n-1)$th-order field scattered on the permittivity fluctuation, μ is the permeability, and $\vec{E}_{-1}\equiv 0$.

The incident field $\vec{E}_0$ is a solution of the zero-order equations of Eq. (4) with

$$k_0=\omega_0/c_m=(\mu\epsilon_m)^{1/2}\omega_0\,. \tag{6}$$

To solve Eq. (5) we introduce Hertz potentials and make the following six assumptions: (i) The detector is placed in a medium of the same refractive index as that of the scattering medium; (ii) the scattered light is detected at a point $\vec{R}$ in the far-field zone so that the detector only registers the one wave-vector component $\vec{k}_s=k_s\hat{R}$ of the scattered light; (iii) the scattering is nearly elastic e.g. $|\vec{k}_s|\approx k_0$; (iv) the time variations of the permittivity fluctuations are slow compared to ω_0^{-1} and to the time required for the field to propagate through the scattering medium; (v) the permittivity fluctuations are nonpropagating; (vi) the whole scattering volume V is illuminated by the incident light.

After Fourier transformation, we obtain the following expression for the multiply scattered field $\vec{E}_n$[6]:

$$\begin{aligned}\vec{E}_n(\vec{k}_s,t)=A_n e^{-i\omega_0 t}&\sum_{\vec{k}_{n-1}}\cdots\sum_{\vec{k}_1}f(\vec{k}_{n-1})\cdots\\&\times f(\vec{k}_1)\epsilon_1(\vec{q}_n,t)\cdots\\&\times\epsilon_1(\vec{q}_1,t)\overleftrightarrow{D}(\vec{k}_s)\cdot\overleftrightarrow{D}(\vec{k}_{n-1})\cdot\cdots\cdot\overleftrightarrow{D}(\vec{k}_1)\cdot\hat{n}\,.\end{aligned} \tag{7}$$

The corresponding equation for the singly scattered field $\vec{E}_1$ is

$$\vec{E}_1(\vec{k}_s,t)=A_1 e^{-i\omega_0 t}\epsilon_1(\vec{q},t)\overleftrightarrow{D}(\vec{k}_s)\cdot\hat{n}\,. \tag{8}$$

Here $\vec{q}_i$ is the momentum transfer in the ith scattering:

$$\vec{q}_i=\vec{k}_i-\vec{k}_{i-1}\,,\quad\vec{q}_n=\vec{k}_s-\vec{k}_{n-1}\,,\quad\text{and}\quad\vec{q}=\vec{k}_s-\vec{k}_0\,,$$

$$\overleftrightarrow{D}(\vec{k})=-\vec{k}\vec{k}/k_0^2+\overleftrightarrow{I}\,,$$

$\overleftrightarrow{I}$ being the unit tensor,

$$A_n=(k_0^2/4\pi)^n V(E_0/R)\exp(ik_0R)\,, \tag{9}$$

$$f(\vec{k})=\int_V d^3r\,|\vec{r}|^{-1}\exp[i(k_0|\vec{r}|+\vec{k}\cdot\vec{r})]\,. \tag{10}$$

To simplify, the integration in Eq. (10) is carried out over a sphere of radius L instead of the actual scattering volume V. This is similar to the spherical symmetry assumption used in paper II and leads to the following parametric form of $f(\vec{k})$:

$$f(\vec{k})=\begin{cases}2\pi iL/k & \text{for } |k_0-|\vec{k}||\le\pi/L\\0 & \text{otherwise}\,.\end{cases} \tag{11}$$

Some general features of multiple scattering, when these fluctuations are due to macromolecules only, are discussed in the next section.

III. MULTIPLE SCATTERING FROM RIGID MACROMOLECULES

Assuming identical macromolecules with no internal motion, there exists a simple relationship between $\epsilon_1(\vec{q},t)$ and the center-of-mass positions of the molecules leading to[6]

$$\prod_{l=1}^{n}\epsilon_1(\vec{q}_l,t)=(v_0\epsilon_r)^n\prod_{l=1}^{n}P(\vec{q}_l)\psi(\vec{q}_l,t)\,. \tag{12}$$

Here, v_0 is the volume of the macromolecule; $\epsilon_r=\epsilon_m^{-1}(\epsilon_p-\epsilon_m)$, where ϵ_p is the permittivity of the macromolecule; $P(\vec{q})$ is a scattering amplitude defined as

$$P(\vec{q})=v_0^{-1}\int_{v_0}d^3R\,e^{i\vec{q}\cdot\vec{R}}\,; \tag{13}$$

and $\psi(\vec{q},t)$ is the $\vec{q}$ component of the instantaneous macromolecular number density $\rho(\vec{r},t)$:

$$\rho(\vec{r},t)=\sum_{i=1}^{N}\delta(\vec{r}-\vec{r}_i(t))\,, \tag{14}$$

$$\psi(\vec{q},t)=V^{-1}\sum_{i=1}^{N}e^{-\vec{q}\cdot\vec{r}_i(t)}\,, \tag{15}$$

where N is the number of macromolecules within the scattering volume and δ the Dirac delta. Various processes occurring in multiple scattering are discussed in the Sec. III A and III B.

A. Inter- and intramolecular scattering

The product $\Pi_{l=1}^{n}\psi(\vec{q}_l,t)$ corresponding to the nth-order scattered field generally generates intramolecular as well as intermolecular multiple scattering. This is easily demonstrated by considering the product corresponding to two successive scatterings which, with the use of Eq. (15), can be written

$$\begin{aligned}\psi(\vec{q}_{l+1},t)\psi(\vec{q}_l,t)&\\ =V^{-2}\Big(&\sum_{i}\exp\{-i[\vec{q}_{l+1}+\vec{q}_l]\cdot\vec{r}_i(t)\}\\ &+\sum_{\substack{i,j\\ i\neq j}}\exp\{-i[\vec{q}_{l+1}\cdot\vec{r}_i(t)+\vec{q}_l\cdot\vec{r}_j(t)]\}\Big)\,. \end{aligned}\tag{16}$$

The first term on the right-hand side of Eq. (16) represents two scatterings within the same molecule, and the second term two successive single scatterings on different molecules.

With the multiple-scattering formalism, the scattering amplitude $P(\vec{q})$ as defined by Eq. (13) is an exact expression for the single-scattering contribution. In the following we shall neglect intramolecular scattering; thus the scattering amplitudes for the molecules are equivalent to those for small particles for which the Rayleigh-Debye approximation will hold.[7]

B. Higher-order dipole scattering

Just as in multiple scattering from fluids,[8] the incident field induces oscillating dipoles in a molecule. These dipoles radiate independently and the resulting secondary field in turn induces oscillating dipoles in another molecule. This is second-order dipole interaction. In general, higher-order multiply scattered fields can be due to higher-order dipole interaction involving (i) a pair of molecules, (ii) different molecules, or (iii) a combination of these interactions.

The relative contributions from interactions (i) and (ii) to triple scattering are expected to depend on the average macromolecular number density. In later calculations both contributions are included.

IV. SECOND-ORDER RESULTS FOR INDEPENDENT BROWNIAN PARTICLES

To second order in the multiple-scattering expansion, the FC function $G(\vec{k}_s,t)$ has the form

$$\begin{aligned}G(\vec{k}_s,t)=&G_{1,1}(\vec{k}_s,t)+G_{2,1}(\vec{k}_s,t)+G_{1,2}(\vec{k}_s,t)\\ &+G_{3,1}(\vec{k}_s,t)+G_{1,3}(\vec{k}_s,t)+G_{2,2}(\vec{k}_s,t)\,.\end{aligned}\tag{17}$$

For a specified scattering geometry, we shall in Sec. IV A and IV B evaluate Eq. (17) for a system of independent particles undergoing translatory Brownian motion.

A. Independent particles

Assuming independent particles, the N-particle distribution function factorizes into a product of one-particle functions, each of which has a contribution

$$\langle\psi(\vec{q},t)\rangle=\langle\psi^*(\vec{q},t)\rangle=\rho\delta_{\vec{q},0}\,, \tag{18a}$$

$$\langle\psi^*(\vec{q}_1,t)\psi(\vec{q}_2,t)\rangle=V^{-1}\rho g(\vec{q}_1,t)\delta_{\vec{q}_1\vec{q}_2}\,. \tag{18b}$$

Here

$$g(\vec{q},t)=e^{-Dq^2t}\,, \tag{18c}$$

where D is the diffusion constant and ρ the average particle number density.

Each one-particle contribution is real and since the assumption of spherical symmetry leads to a purely imaginary $f(\vec{k})$, all partial FC functions G_{lm} + c.c. involving an odd number of scatterings vanish. Hence the mixing of singly and doubly scattered fields in Eq. (17) does not give any contribution.

Momentum conservation is contained in the Kronecker δ's and energy conservation in the f factors. In the evaluation of all single particle contributions, terms occur which conserve momentum but violate (or nearly so) energy conservation and hence are omitted. An example of such a process occurring in the FC function for doubly scattered fields would be where the light is scattered from the first to the second particle at time $t=0$ and then from the second to the first at a later time t.

B. Scattering geometry and depolarization

As can be seen from Eq. (7), multiple scattering results in a depolarization of the scattered field. Assuming the incident field to be vertically polarized we separate the scattered field in a vertically and horizontally polarized component as shown in Fig. 1. The corresponding FC functions are denoted

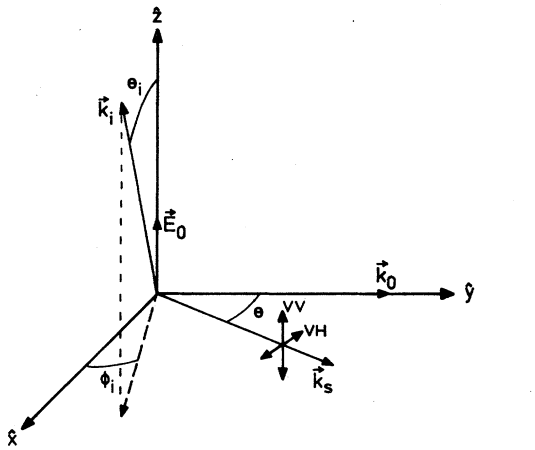

FIG. 1. Scattering geometry used in the calculation. The various symbols are self-explanatory.

$G_{VV}(\vec{k}_s, t)$ and $G_{VH}(\vec{k}_s, t)$ and are given by

$$\begin{aligned} G_{VV}(\vec{k}_s, t) = {} & G_{1,1}(\vec{k}_s, t) \\ & \times \Big(1 - 2\sigma L\rho \int d\Omega_{k_1} \sin^2\theta_1 P(\vec{k}_s, \vec{k}_1, \vec{k}_0) \\ & + \sigma L\rho \int d\Omega_{k_1} \sin^4\theta_1 P^2(\vec{k}_s, \vec{k}_1, \vec{k}_0) \\ & \times g(\vec{k}_s, \vec{k}_1, \vec{k}_0, t) - 2\sigma L^2\lambda^2\rho^2\Big) \end{aligned} \tag{19}$$

and

$$\begin{aligned} G_{VH}(\vec{k}_s, t) = {} & \tfrac{1}{4} G_{1,1}(\vec{k}_s, t)\sigma L\rho(\cos^4\theta + \sin^4\theta) \\ & \times \int d\Omega_{k_1} \sin^2 2\theta_1 \cos^2(\theta + \phi_1) P^2(\vec{k}_s, \vec{k}_1, \vec{k}_0) \\ & \times g(\vec{k}_s, \vec{k}_1, \vec{k}_0, t)\,. \end{aligned} \tag{20}$$

Here

$$P(\vec{k}_s, \vec{k}_1, \vec{k}_0) = \frac{P(\vec{k}_s - \vec{k}_1) P(\vec{k}_1 - \vec{k}_0)}{P(\vec{k}_s - \vec{k}_0)}\,, \tag{21}$$

$$g(\vec{k}_s, \vec{k}_1, \vec{k}_0, t) = \frac{g(\vec{k}_s - \vec{k}_1, t) g(\vec{k}_1 - \vec{k}_0, t)}{g(\vec{k}_s - \vec{k}_0, t)}\,, \tag{22}$$

$$G_{1,1}(\vec{k}_s, t) = \sigma P^2(\vec{q}) N(E_0^2/R^2) \exp[(i\omega_0 - Dq^2)t] \tag{23}$$

are the single-scattering FC function, and

$$\sigma = [(1/4\pi)\, k_0^2 \epsilon_r v_0]^2 \tag{24}$$

is a scattering cross section.

In Eqs. (19) and (20) we have made use of the fact that $|\vec{k}_i| \approx k_0$, so that

$$V^{-1} \sum_{\vec{k}_i} f(\vec{k}_i) \cdots = (2\pi)^{-3} \int d\Omega_{k_i} k_0^2 (\pi/L) f(\vec{k}_i) \cdots\,. \tag{25}$$

The four terms in the sum on the right-hand side of Eq. (19) represent, respectively, (a) single-single scattering, (b) triple-single scattering where one pair of particles is involved in the triply scattered field, (c) double-double scattering involving one pair of particles, and (d) triple-single scattering where three different particles are involved in the triply scattered field and double-double scattering on two particle pairs having one particle in common.

These results appear perhaps somewhat surprising since one might expect singly and triply scattered fields to be uncorrelated. Both these fields will in fact be correlated provided they are scattered on a common particle and the additional scattering of the triply scattered field has a vanishing phase. Similar arguments also apply to the more general case of correlations between singly and nth-order scattered fields.

It follows from the calculation that the terms (b) and (d) above have the single-scattering time dependence resulting in a modification of the amplitude of single-single scattering part of the FC function. Physically these terms correspond to first-order turbidity corrections of singly scattered light. Using a semiempirical method, such corrections have been applied by Bray and Chang.[9]

The term in (c) has a time dependence different from that of single scattering and corresponds to terms considered in the double-scattering approximation (cf. paper II).

Hence, the polarized FC function resulting from the CSO calculation Eq. (19) contains turbidity corrections of the singly scattered light as well as the contribution from doubly scattered light. The depolarized FC function Eq. (20) only contains the double-scattering contribution.

The dimensionless quantity $\sigma L\rho$ is roughly the fraction of the intensity due to single scattering. The perturbation expansion employed here requires $\sigma L\rho \ll 1$. The dimensionless quantity $\lambda^2 L\rho$ corresponds to the average number of particles as "seen by a photon" going through the scattering volume.

V. COMPARISON WITH THE DOUBLE-SCATTERING APPROXIMATION

The similarities and differences between the CSO and the double-scattering approximation treatments are most easily discussed in the Rayleigh approximation,[10] since then the various scattering amplitudes [cf. Eq. (13)] are equal to one and the integrals in Eqs. (19) and (20) can be solved exactly.

Both treatments lead to the same conclusions concerning the depolarized FC function G_{VH} which has been thoroughly discussed in paper II and shall, therefore, not be considered here.

The initial decay time τ_{VV} for the polarized FC function G_{VV} is given by the inverse first cumulant.[11] This can be calculated either by using the CSO expression for the polarized FC function Eq. (19) or by assuming the FC function to be simply the sum of singly and doubly scattered light and neglecting turbidity corrections. In both cases the angular dependence of τ_{VV} can be expressed as

$$\tau_{VV} = \tau_1\{1 - 8R[1 - \sin^{-2}(\theta/2)]\}^{-1}, \qquad (26)$$

where

$$\tau_1 = \{4Dk_0^2 \sin^2(\tfrac{1}{2}\theta)\}^{-1}$$

is the single-scattering decay time, θ the scattering angle, and R the ratio I_{VH}/I_{VV} at $\theta = \frac{1}{2}\pi$.

Although the two methods yield the same expression for τ_{VV}, they predict quite different density dependence of the ratio R and hence of τ_{VV}, as shall be discussed below.

The most striking difference between the two treatments appears in the expressions for the polarized intensity for which the CSO calculation gives

$$I_{VV} \propto \rho(1 - \tfrac{16}{5}\pi\sigma L\rho - 2\sigma^2\lambda^2\rho^2) \qquad (27)$$

and the double-scattering approximation

$$I_{VV} \propto \rho(1 + \tfrac{32}{15}\pi\sigma L\rho). \qquad (28)$$

According to Eq. (27), I_{VV} will decrease at the onset of multiple scattering, whereas Eq. (28) predicts an opposite effect. This difference is illustrated in Fig. 2 by the system in which light from a He-Ne laser is scattered from a water solution of polystyrene spheres of radius 50 nm.

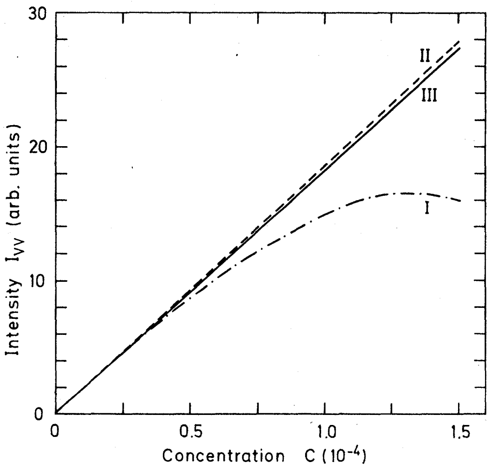

FIG. 2. Concentration dependence of the polarized scattered intensity I_{VV}. Curve I represents the CSO approximation, curve II the double-scattering approximation, and curve III the single-scattering approximation. The value for the parameter L [cf. Eqs. (27) and (28)] is 10^{-3} m.

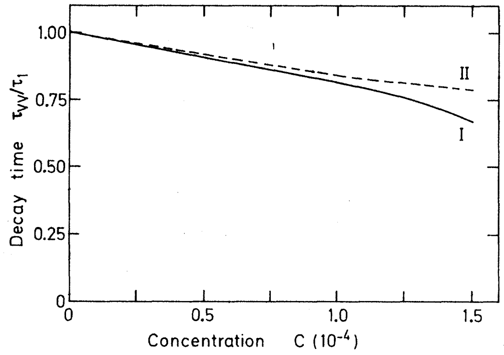

FIG. 3. Concentration dependence of the average initial decay time τ_{VV}. Curve I represents the CSO calculation and curve II the double-scattering approximation. The parameter $L = 10^{-3}$ m and the scattering angle $\theta = \frac{1}{6}\pi$.

The two treatments also give different predictions for the density variation of the ratio R, and hence of the decay time τ_{VV} [Eq. (26)]. In the low-density region, both predict τ_{VV} to decrease linearly with ρ. At higher densities the CSO calculation predicts a stronger than linear decrease of τ_{VV} with ρ, whereas the double-scattering approximation predicts τ_{VV} to fall off towards a density-independent value. This is demonstrated in Fig. 3 for the same system as in Fig. 2.

VI. COMPARISON WITH EXPERIMENTS

In the experiments reported in paper I, the polarized and depolarized components were not measured separately. However, in those experiments the results were not appreciably altered when polarizers were used to single out the polarized component. Hence we may apply the polarized correlation function G_{VV} in the comparison.

A more serious complication arises from the fact that relatively large polystyrene spheres (nominal diameters 312, 481, and 794 nm) were used for which the Rayleigh-Debye criterion is no longer fulfilled. We shall, therefore, restrict the comparison to the results of the smallest spheres. In the fit to the experimental data, we used the linear dimension L as an adjustable parameter. The results for $L = 0.8$ mm are shown in Figs. 4-6 and are discussed in the following.

In Fig. 4 is shown the variation of the intensity I_{VV} with concentration. The agreement between the experimental data and the theoretical curve is poor. However, this is not surprising since at a concentration $C = 2 \times 10^{-5}$ the experimental values already deviate more than 50% from those expected for single scattering.

The discrepancy between theoretical and experimental results is most likely due to the neglect of

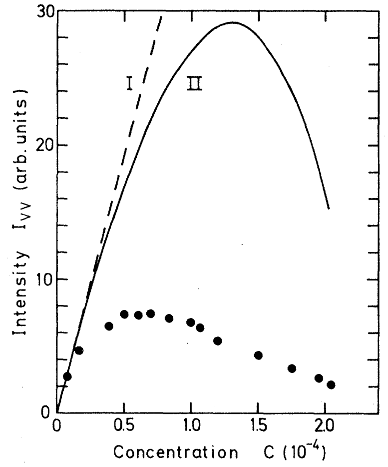

FIG. 4. Concentration dependence of the polarized scattered intensity. Curve I represents the single-scattering approximation, curve II the CSO approximation using $L = 8 \times 10^{-4}$ m. The points are experimental values taken from Colby *et al*. (Ref. 4).

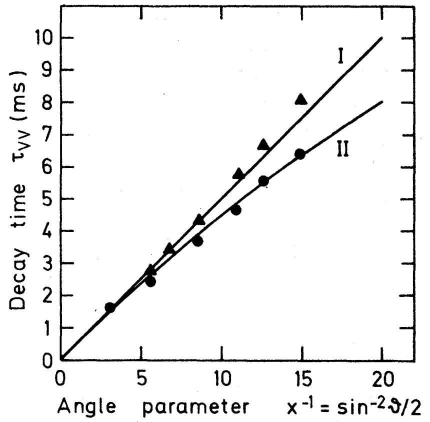

FIG. 6. Angular dependence of the average decay time τ_{VV}. The points are experimental values taken from Ref. 4. The curves represent results from the CSO calculations using $L = 8 \times 10^{-4}$. Curve I is with $C = 1 \times 10^{-6}$ and curve II with $C = 9 \times 10^{-4}$.

higher-order terms and in part to the breakdown of the Rayleigh-Debye approximation. Using a more realistic volume than the spherical one is not believed to alter the large discrepancy.

The use of the double-scattering approximation leads to an even larger discrepancy since it predicts that the intensity will increase beyond that expected for single scattering.

In Fig. 5 is shown the dependence of the decay time τ_{VV} concentration, and we see that the theoretical curve fits the experimental data fairly well up to a concentration of about $C = 1.5 \times 10^{-4}$. At higher concentrations the second-order calculation breaks down rapidly.

The agreement is also good for the angular dependence of the decay time τ_{VV} as shown in Fig. 6 for two concentrations. In curve II of Fig. 6, the concentration $C = 9 \times 10^{-5}$ has been used rather than $C = 5 \times 10^{-5}$ as given in paper I. This adjustment was motivated by the discrepancy between the experimental data for the concentration and angular dependences of the decay time (cf. Figs. 6 and 7 in paper I).

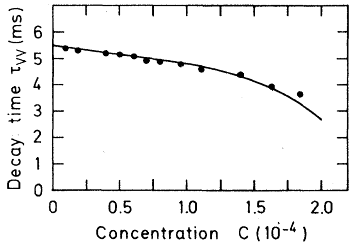

FIG. 5. Concentration dependence of the average initial decay time τ_{VV}. The points are values taken from Colby *et al*. (Ref. 4). The curve represents results from the CSO calculation using $L = 8 \times 10^{-4}$ m.

In the comparison of the experimental and calculated values for the decay time τ_{VV}, we arrive at the following two surprising results: (i) The CSO calculation is able to reproduce the experimental data even at concentrations where, according to the experimental intensity data, fields of higher-order multiplicity play an important role. (ii) Using the parameter value $L = 0.8$ mm resulting from the decay time fitting, the CSO calculation grossly underestimates the effect of multiple scattering even at low concentrations (cf. Fig. 4).

A possible explanation of these results is that the experiments may have been performed in a way which corresponds to a time integration of the FC function. Since the FC function consists of a sum of decaying exponentials, such an integration will reduce the contributions from the higher-order, rapidly decaying exponentials. Then the measured decay time τ_{VV} is well reproduced by the CSO approximation even in the presence of a high order of multiple scattering.

VII. SUMMARY

Introducing a few simplifications, we have performed a CSO calculation of the dynamic and static properties of the polarized and depolarized FC function of light scattered on independent Brownian particles.

The CSO calculation contains turbidity correction terms to single scattering as well as the term introduced in the double-scattering approximation by

Sorensen *et al.*[5] The analysis shows that inclusion of turbidity corrections is essential in treating the static properties of the polarized FC function. A CSO calculation does not introduce such corrections to double scattering, and hence predicts the same depolarized FC function as does the double-scattering approximation.

In the low-concentration region, the CSO calculations reproduce quite well the experimental data by Colby *et al.*[4] on the concentration and angular dependence of the decay time τ_{VV}. For the intensity I_{VV} the agreement is poor even at low concentrations, probably due to neglect of the higher-order terms.

Both the CSO treatment and the double-scattering approximation are first-order corrections to the single scattering. Since a further extension of the perturbation expansion is very difficult, there is a need for semiempirical treatment to describe the various properties of the FC functions when inclusion of fields of higher multiplicity is necessary.

To explore the regions of validity of the CSO theory and the double-scattering approximation, further experiments should be carried out with Brownian particles under conditions where the Rayleigh-Debye criterion is valid.

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