Multiple Light Scattering from Concentrated, Interacting Suspensions

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The effects of short-range interparticle correlations on the multiple scattering of light in colloidal suspensions are studied. Our measurements, and comparisons with theory, of the transport mean free path and the width of the coherent backscattering cone demonstrate the validity of the diffusion approximation of light in correlated suspensions. Dynamic multiple-light-scattering measurements allow determination of the short-time self-diffusion constant of the spheres. The data agree with hydrodynamic theory up to 45% volume fraction with no adjustable parameters.

Multiple scattering of classical waves such as light in disordered inhomogeneous media has become a subject of considerable interest in recent years.[1] Enhanced backscattering, analogous to the weak-localization phenomenon of electrons, can be well described in terms of a random walk of the light intensity[2,3] characterized only by the transport mean free path l^*. This analysis, known as diffusive transport theory, also provides a description of the temporal fluctuations of the backscattered light intensity for scatterers undergoing Brownian motion.[4-8] This allows determination of the short-time self-diffusion constant of the Brownian scatterers under conditions of very strong multiple scattering.

Previous experiments were performed on various suspensions consisting of different diameter spheres in a concentration range where strong multiple scattering occurred, but interparticle correlations were either small or neglected.[3,4,6,8,9] However, often when samples are concentrated enough to multiply scatter there also exist interparticle correlations. Here we examine whether in the presence of interparticle correlations the diffusion approximation of the transport of light is still valid and how l^* and the temporal fluctuations are modified. We report separate measurements of the transmitted intensity through a slab which is proportional to l^*, of the angular dependence of the coherent backscattering cone, and of the decay of the temporal autocorrelation function of the backscattered light intensity from large samples of colloidal suspensions. Concentrations ranged from 5% to 45% volume fraction, where the latter is near the liquid-to-crystal phase transition. Our measurements quantitatively agree with recent predictions of the effect of interparticle correlations on static[9] and dynamic[4-6] multiple scattering, thus enlarging the range of applications of this new technique.

For *noninteracting* scatterers the enhanced backscattering effect which arises from the constructive interference between time-reversed pairs of multiple-scattering paths has been well described within the diffusion approximation.[2,3] In the case of a semi-infinite sample with close to normal incidence of a plane wave of light, the coherent enhancement $\alpha(Q)$ of the copolarized scat-

tered intensity (albedo) decays linearly for small values of the scattering angle Θ measured from the backscattering direction,

$$\alpha(Q)/\alpha(0) = 1 - \delta Q l^* + \cdots . \tag{1}$$

The sum $Q = k_i + k_f$ of the incident (k_i) and emerging wave vector (k_f) becomes, as small angles, $Q = 2\pi\Theta/\lambda$, with Θ and the wavelength $\lambda = 2\pi/k_i$ both being measured outside the sample. δ is a numerical coefficient of order unity, the theoretical value of which somewhat depends on the choice of the boundary conditions.[2] $l^* = 1/\rho\sigma^*$ can be calculated from the transport cross section

$$\sigma^* = 1/\rho l^* = \int_0^{2nk_i} F(q)(1-\cos\theta)q\,dq , \tag{2}$$

$q = 4\pi n \sin(\theta/2)$ being the single-scattering wave vector, $F(q)$ the form factor, ρ the number density of the scatterers, and n the index of refraction of the solvent. Brownian motion of the scatterers results in temporal fluctuations of the intensity scattered into direction k_f. One obtains, in complete analogy to Eq. (1), that the initial decay for the autocorrelation function of the scattered field near backscattering is[4,7]

$$g_1(t) = G_1(t)/G_1(0) = 1 - \delta\sqrt{3t/2\tau} + \cdots , \tag{3}$$

where τ is the single-backscattering time, $\tau = 1/D_0 \times (2nk_i)^2$, with D_0 the Stokes-Einstein diffusion constant. The coefficient δ is the *same* as in Eq. (1) for copolarized detection and weak contributions of low-order scattering because the effects of polarization enter Eqs. (1) and (3) only through a normalization of $G_1(t)$ and $\alpha(Q)$ by the total incoherent intensity $G_1(0)$ and $\alpha(0)$.[1,5,6,9,10] The short-time behavior of $g_1(t)$ is dominated by contributions of long scattering paths which are completely depolarized and for which the diffusion approximation holds.[11] Note that recently described effects of internally reflected light at the interface will modify δ by the *same* amount in Eqs. (1) and (3).[12,13]

When *interparticle correlations are present,* extending over distances much smaller than l^*, the above description needs to be only slightly modified.[4-6] A correlated

domain of scatterers can be thought of as acting as a single effective scatterer with its angular-dependent scattering modified by the local structure factor $S(q)$. Then l^* in Eq. (2) has to be recalculated with $F(q)$ being replaced by $F(q)S(q)$. Introducing $l^{*'}$, the transport mean free path of the correlated scatterers, we have both

$$\frac{l^*}{l^{*'}} = \frac{\int_0^{2nk_i} q^2 F(q)S(q)q\,dq}{\int_0^{2nk_i} q^2 F(q)q\,dq}, \tag{4}$$

and

$$a(Q)/a(0) = 1 - \delta Q l^{*'} + \cdots . \tag{5}$$

In the static case, short-range interparticle correlations simply rescale l^*. However, because of the concentration dependence of $S(q)$, $l^{*'}$ is no longer proportional to $1/\rho$. In the case of dynamics one obtains[6]

$$G_1(t)/G_1(0) = 1 - \delta(3t/2\tau')^{1/2} + \cdots , \tag{6}$$

with the backscattering time τ' of the correlated system given by

$$\frac{\tau'}{\tau} = \frac{D_0}{D_s} \frac{\int_0^{2nk_i} q^2 F(q)S(q)q\,dq}{\int_0^{2nk_i} q^2 F(q)h(q)q\,dq} = \frac{D_0}{D_s}\mathcal{R} . \tag{7}$$

Hydrodynamic interparticle interactions are described by[14] $D(q) = D_s h(q)/S(q)$, with $h(q) = H(q)/H(\infty)$ and $D_s = D_0 H(\infty)$, the short-time self-diffusion constant. Note that Eqs. (4) and (7) are identical only without hydrodynamical corrections.

The simplest interacting colloidal system consists of hard spheres in a solvent and is the only case for which $h(q)$ has been calculated. To approximate such a system we used 0.46-μm-diam charged polystyrene spheres suspended in water to which salt was added to screen the electrostatic repulsion between particles. The suspension as purchased from Sigma was at a volume fraction (ϕ) of 10% and contained an unknown amount of salt and surfactant which stabilizes the suspension against aggregation. We concentrated the suspension by centrifugation and removal of the supernatant. The centrifuged pellet was irridescent, indicating that the spheres had formed a colloidal crystal. The crystal was diluted with 1 mM NaCl (screening length 0.01 μm) until the crystal melted as observed by the disappearance of the irridescence. This occurred at ϕ slightly greater than 45%. Since hard spheres melt at 50% $< \phi <$ 55% we feel that this system resembles hard spheres. The volume fractions were determined with an experimental accuracy of 5% by vacuum drying a known volume of the suspension and weighing the solids.

In transport theory, the transmission of light through a sample of thickeness L much greater than $l^{*'}$ is $3l^{*'}/5L$.[15] Previously[9] $l^{*'}$ was measured for a stock suspension ($l_s^{*'}$) of the same 0.46-μm-diam spheres used in this study to be $l_s^{*'} = 20 \pm 2$ μm, in agreement with the value calculated from Mie scattering theory using Eq. (4). Thus by measuring the ratio of the transmission

(T) through a sample of unknown $l^{*'}$ to the transmission through the stock suspension of spheres (T_s), the unknown $l^{*'}$ was determined from $T/T_s = l^{*'}/l_s^{*'}$. Samples placed in a 1-mm-thick by 10-mm-wide cuvette were illuminated with a 1-mm-diam Ar$^+$ laser beam ($\lambda = 514$ nm) and transmitted light was collected with a lens on a photomultiplier tube. The effects of internal reflection in transmission are expected to be small because of the transmission values of the samples ($< 2.5\%$).[13] We have checked this experimentally by partially index matching the sample-cell-to-air interface using a 15-cm cylindrical container filled with water. No differences in $l^{*'}$ with and without index matching were observed. In Fig. 1, $1/l^{*'}$ obtained as first described is plotted as a function of ϕ. It substantially deviates from being proportional to density at $\phi \geq 10\%$; at $\phi = 45\%$, $l^{*'}$ is about twice l^*.[16] For comparison we also plot $1/l^*$, as calculated[17] from the Mie form factor $F(q)$ and Eq. (2) (without correlations), and $1/l^{*'}$ of the correlated system by using Eq. (4) and an analytic expression[18] for the hard-core structure factor $S(q)$. There is less than a 5% difference between theory and experiment. *This indicates that the diffusion approximation is applicable in the case of short-range interparticle interactions.*

We next explore the angular dependence of the coherent backscattering albedo as a function of volume fraction. The experimental setup consisted of a 1-cm $\times$ 1-cm $\times$ 1.5-cm cuvette containing the sample to which the vertically polarized Ar$^+$ laser beam (diameter 8 mm) was incident several degrees off normal of the cell after passing through a wedge-shaped beam splitter. The scattered light repassed through the beam splitter and was focused with a 200-mm focal-length 35-mm camera lens onto a linear charge-coupled device placed at the focal distance of the lens and interfaced with a computer. The background, due to residual stray light,
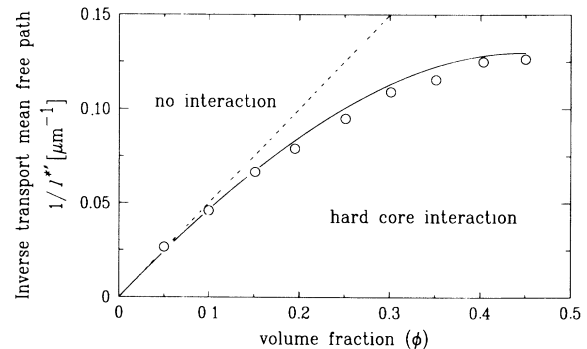

FIG. 1. The inverse of the transport mean free path of light ($1/l^{*'}$) for correlated 0.46-μm-diam polystyrene spheres as a function of volume fraction (ϕ). Data were obtained from the transmission of intensity through a 1-mm sample. The dashed line is calculated using Mie theory for the form factor (without interparticle correlations) and the solid line includes the calculated correction for correlations expressed by the Percus-Yevick structure factor.

513

measured without cuvette, was typically several percent of the signal and was subtracted from the data. In order to correct for the somewhat inhomogeneous response of our detection system we measured the angular dependence of the transmitted light through a 1-mm-thick cuvette filled with a colloid suspension of relatively high diffusive transmissivity by illumination from the backside. This provides a reference which is flat over the angles of interest. The corrected data were obtained by the following prescription: (data − background)/(reference − background).

To determine the incoherent wide-angle intensity, e.g., the base line of the cone, we first fitted the corrected data by the function $B + A \exp(-C|\Theta|)$. The corrected data were divided by B to normalize the base line and then 1 was subtracted to obtain the relative albedo of the cone. The amplitude A/B of the normalized cones was found to be independent of ϕ and equal to 0.59 ± 0.01. In the past, normalized amplitudes of up to 0.85 have been reported on similar samples, but using a different setup.[9] We believe that the incoherent background in our current setup has been increased due to light scattered out of the cone due to the lens system and beam splitter. This should not affect the width of the cone, but merely changes the base line and amplitude. In order to compare with Eq. (5), we fitted the relative albedo of the cone with the function $I(Q) = D - E\Theta + F\Theta^2$. The fit ranged over those values of Θ such that the relative albedo was greater than 0.5. For this central portion of the cone, at the most 10% of the intensity was present in the quadratic term F. In Fig. 2 we plot the initial slope of the cone, E/D, vs $2\pi l^{*\prime}/\lambda$, where $l^{*\prime}$ was obtained from the transmission data shown in Fig. 1. The initial decay of the cone is proportional to $l^{*\prime}$ and *thus the diffusion approximation for coherent backscattering is valid even in the presence of interparticle correlations.* Using the data of Fig. 2 and Eq. (5) we find $\delta = 1.62$
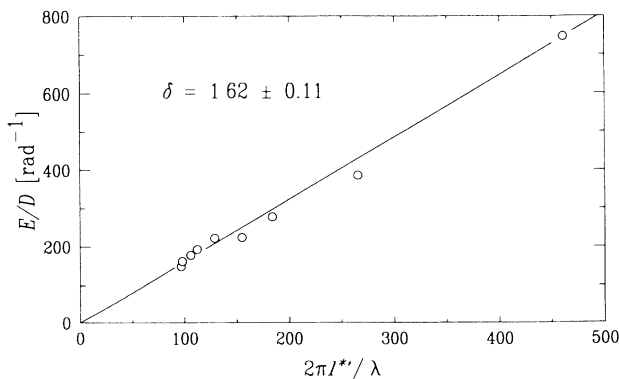
± 0.11. This is within the range of theoretical predictions for δ which lie between 1.5 and 2.5. Within the cited error, the value of δ was insensitive to the fitting interval.

Finally, we measured the intensity-intensity time autocorrelation function

$$g_2(t) = \langle I_0(0)I_0(t)/I_0(0)^2 \rangle \qquad (8)$$

in the same samples and sample cells at a scattering angle of 175° using a digital multibit correlator (ALV 3000). Since the scattered fields have a Gaussian distribution,[9] the normalized field autocorrelation function is $g_1(t)^2 = g_2(t) - 1$. In Fig. 3 we plot $\ln[g_1(t)]$ vs $\sqrt{t}$ with vertical incident and detected polarization for various volume fractions. All measurements were done at 20°C.

Equation (6) predicts that the initial decay of $g_1(t)$ is proportional to $\sqrt{t}$. However, the coherence length of our laser without an etalon (39 mm) causes a rounding off of $g_1(t)$ at short times because there is little contribution to the intensity fluctuations from scattering paths with length differences larger than the coherence length.[6] Through comparison of measurements taken with an etalon (2-m coherence length) and without, it has been demonstrated[6] that reliable estimates of the initial decay can be obtained by fitting data at longer times with the function

$$\ln[g_1(t)] = b - m\sqrt{t} + ct. \qquad (9)$$

Consequently, a fitting range between $t = 25$ and 225 μs was chosen because the analysis is neither affected by the short-time rounding nor by the long-time behavior where the diffusion approximation is no longer valid. This time
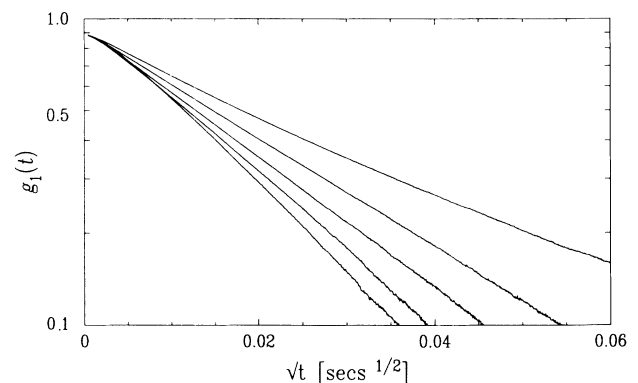
FIG. 2. The fitted initial decay of the coherent backscattered cone, E/D, as a function of $2\pi l^{*\prime}/\lambda$, where $l^{*\prime}$ was obtained from the transmission data shown in Fig. 1. A straight-line fit to the data demonstrates that the initial slope of the cone is proportional to $l^{*\prime}$.

FIG. 3. The time autocorrelation function $g_1(t)$ of the scattered field plotted logarithmically as a function of $\sqrt{t}$ for vertical incident and detected polarization. The volume fractions shown are 5%, 15%, 25%, 35%, and 45% with the dilute ones decaying the most rapidly. Notice that $g_1(t)$ is not exponential in $\sqrt{t}$. Its second cumulant (c/m^2) increases linearly with concentration, varying from −0.12 to 0.12 and changing sign at approximately $\phi = 25\%$.
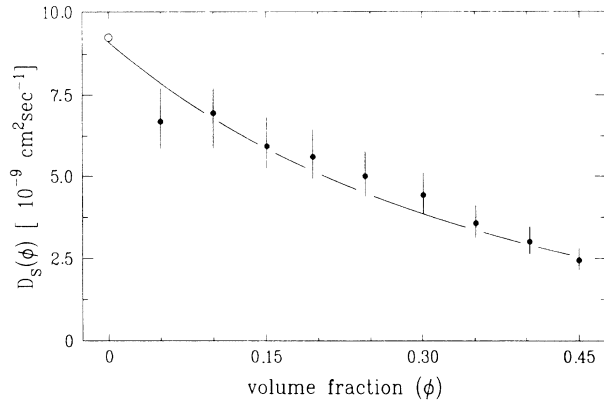
FIG. 4. The short-time self-diffusion constant D_s extracted using the data from Fig. 3 and Eq. (10) (solid circles). The error bars result from the uncertainty in the parameter δ. The solid line is a fit by $D_s = D_0 H(\infty)$ (Ref. 14) with D_0 the only fitting parameter. The open circle is an independent measure of D_0.

range also lies well above the time scale (~ 1 μs) for crossover from ballistic to diffusive particle motion discussed recently.[19] Equations (6) and (7) relate the short-time self-diffusion constant of colloidal particles to the initial slope of $g_1(t)$ as follows:

$$D_s(\phi) = \frac{m(\phi)^2}{6\delta^2 n^2 k_i^2} \mathcal{R}.$$ (10)

In Fig. 4 we plot $D_s(\phi)$ vs ϕ, where m is extracted from Fig. 3 using Eq. (9) and $\mathcal{R}$ is calculated from Eq. (7) using theoretical expressions for $S(q)$ (Ref. 18) and $H(q)$.[14,20] At high volume fractions $\mathcal{R}$ substantially differs from $l^*/l^{*\prime}$ indicating the importance of the q dependence of $h(q)$.[16] Using the index of refraction of water we have $(n k_i)^2 = 2.64 \times 10^{10}$ cm^{-2} and $\delta = 1.62 \pm 0.11$ as obtained above (Fig. 2). Note that the units of $D_s(\phi)$ are absolute and that there are *zero* free parameters. The solid line in Fig. 4 is a fit by a theoretical expression for the short-time self-diffusion constant of hard spheres[14] with the only parameter being D_0. The fit is quite close to the value $D_0 = (9.25 \pm 0.15) \times 10^{-9}$ cm^{2}s^{-1} which we have independently measured by dynamic single scattering in a dilute ($\phi = 10^{-5}$) suspension. This value is consistent with the manufacturers stated particle radius.

In this Letter, we show in a redundant way that the diffusion approximation for multiple light scattering can be extended to systems with interparticle correlations. The corresponding correction of the transport mean free path $l^{*\prime}$ was verified experimentally for the first time up to $\phi = 45\%$. The width of the coherent backscattering cone was observed to be inversely proportional to $l^{*\prime}$, in agreement with theory. Dynamic multiple-light-scattering data were analyzed using theories accounting for both the spatial correlations and hydrodynamic interactions. From these data the short-time self-diffusion con-

stant of concentrated interacting suspensions was extracted with zero free parameters and was found to agree closely with hydrodynamic theory. This suggests a general way to obtain the self-diffusion constant in multiply scattering media, provided $S(q)$ and $H(q)$ are known. At present this restricts this method to hard-sphere systems.

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