Assessment of $S(0,\phi)$ from multiply scattered light

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Two-wavelength measurements of isotropic scattering coefficient in concentrated, multiply scattering colloidal suspensions are used to extract $S(0,\phi)$ values, using a small wave number expansion of the interparticle structure factor, $S(q,\phi)$. Owing to the small particle size (150 nm) and near-infrared wavelengths (670–820 nm) used in this study, the approximation is reasonable and allows accurate estimation of $S(0,\phi)$. The estimated values of $S(0,\phi)$ agree well with that predicted using the Carnahan–Starling equation of state. © *1999 American Institute of Physics.* [S0021-9606(99)52044-8]

Equilibrium properties such as osmotic pressure and static structure factor of colloidal suspensions are of both practical and fundamental interest. Beyond the traditional areas of relevance which include ceramics, paints, coatings, food stuff, agricultural and pharmaceutical formulations, recent scientific interest in this particular class of soft materials stems from the possible novel applications of such materials, for example, in the synthesis of photonic band gap structure.[1]

The structure of colloidal suspensions is typically characterized by a radial distribution function, $g(r)$, or its Fourier transformed form, the static structure factor, $S(q,\phi)$. The static structure factor is usually measured experimentally using techniques that are based on radiative scatter from single colloidal particles, such as small angle scattering of neutrons,[2] x-rays,[3] light,[4] and turbidity.[5] These measurements are not applicable to cases of multiple scattering. A vast majority of typical colloidal suspensions however fall outside this narrow window. Suspensions such as white paint, milk, snow, clouds, etc., strongly scatter visible light and are good examples of this class of materials. At present, very few spectroscopic methods can successfully access the structure of such optically dense systems. Diffuse transmission spectroscopy,[6] which uses static transmission measurements, and diffusing wave spectroscopy,[7] which uses dynamical measurements of multiply scattered light, are two currently established methods to probe the structure of opaque colloidal solutions. While cross-correlation light scattering techniques[8] have been developed to characterize samples with high turbidity (transmission of ~1%), there remains the need for a simple optical means to interrogate structure in multiple scattering samples.

The purpose of this letter is to establish the use of frequency domain photon migration (FDPM) as a structural probe for optically opaque colloidal suspensions. Briefly, the technique involves launching intensity modulated, monochromatic light at modulation frequencies ranging from hundreds of kilohertz to hundreds of megahertz into a multiply scattering sample.[9] As it propagates through the medium, the photon density wave is phase shifted by an angle, θ_p, and its amplitude is attenuated by a factor, M, relative to the incident light (see Fig. 1). The propagation of a ''photon density wave'' within a random medium is influenced by its mean scattering and absorption lengths and can be accurately predicted by the diffusion approximation to the radiative transfer equation.[10] From appropriate solution of this optical diffusion equation, measurements of phase-shift and amplitude modulation attenuation are used to determine the absorption coefficient, μ_a, and the isotropic scattering coefficient, μ_s'. The advantages of using photon density waves are twofold. (i) Since the measurements involve propagation rather than the intensity of the detected light, they do not require an external calibration. (ii) Since the absorption and isotropic scattering coefficients are obtained as separate parameters rather than a single product (as determined by continuous wave or intensity based measurements), the technique provides a unique and accurate determination of the isotropic scattering coefficient.

In contrast to our previous work, where we carried out comparisons of the experimentally obtained $\mu_s'(\lambda)$ with model calculations,[9] in this Communication we present our attempt to recover the structure factor at zero wave vector, $S(0,\phi)$, information from dual-wavelength measurements of $\mu_s'(\lambda)$, without using any *a priori* model for $S(q,\phi)$.

For a monodisperse concentrated particulate system, the isotropic scattering coefficient can be predicted from knowledge of: (i) $F(n,x,\theta,\lambda)$, the particle form factor at wavelength, λ, of a particle of diameter x, having relative refractive index, n; (ii) ϕ, the volume fraction of particles; and (iii) $S(q,\phi)$, the static structure factor, where q is the wave vector, $q=(4\pi m/\lambda)\sin(\theta/2)$ (m is the refractive index of the medium; λ is the wavelength of light; and θ, the scattering angle) using the following relationship:[6,11]

$$\mu_s'(\lambda)=\left(\frac{12\phi}{x^3}\right)\left(\frac{\lambda}{2\pi m}\right)\int_0^{2\pi}F(n,x,\theta,\lambda)$$

$$\times S(q)(1-\cos\theta)\sin\theta\,d\theta. \qquad (1)$$

It should be emphasized, however, that Eq. (1) is an approximation which is valid strictly for a monodisperse system and is reasonable for a sample with a low degree of polydisper-

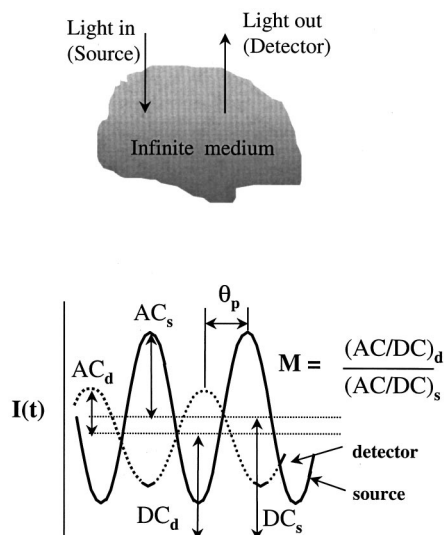[a]Author to whom all correspondence should be addressed; electronic mail: sevick@ecn.purdue.edu

FIG. 1. Diagram of the propagating photon density wave illustrating the phase shift and the amplitude modulation of a detected wave.
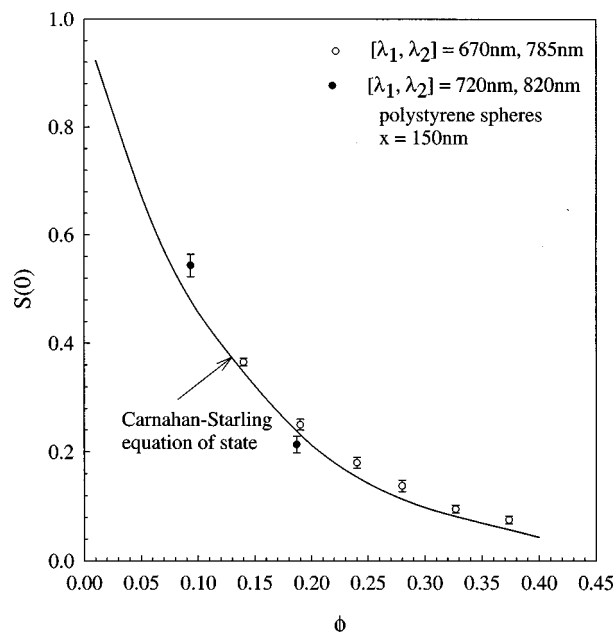

FIG. 2. Experimentally determined values of $S(0,\phi)$ vs latex volume fraction. The solid line is the theoretical prediction using the CS equation.

sity ($<\sim 10\%$). From Eq. (1) it can be seen that the term $S(q,\phi)$ is embedded within an integral and hence it is not possible obtain values of $S(q,\phi)$ directly from FDPM measurements without tedious and perhaps intractable solution to the Fredholm's integral equation. However, an average structure factor, $\langle S \rangle$ can be defined as

$$\langle S \rangle = \frac{\mu'_{s,\text{expt}}}{\mu'_{s,\text{Mie}}} = \frac{\int_0^\pi F(n,x,\theta,\lambda) S(q)(1-\cos\theta)\sin\theta\, d\theta}{\int_0^\pi F(n,x,\theta,\lambda)(1-\cos\theta)\sin\theta\, d\theta},$$
(2)

where $\mu'_{s,\text{expt}}$ is the scattering coefficient measured experimentally, and $\mu'_{s,\text{Mie}}$ is the calculated scattering coefficient using Mie theory. The scattering coefficient, $\mu'_{s,\text{Mie}}$, is computed using no particle interaction, which means $S(q,\phi) = 1$. The right-hand side of Eq. (2) can be easily calculated provided an analytic expression for predicting $S(q,\phi)$ is available. A rigorous inversion technique to obtain the full structure factor from multiple-wavelength measurements of $\mu'_s(\lambda)$ is nontrivial. Kaplan et al.[6] have carried out the inversion utilizing expansions of the structure factor using arbitrary basis functions. They obtained good qualitative agreement between the recovered and the actual experimental data near the first principal peak in $S(q,\phi)$.

However, if the value of the dimensionless wave vector (qx) is small, then $S(q,\phi)$ can be written as[12]

$$S(q,\phi) = S(0,\phi) + \alpha(\phi)x^2 q^2 + O(x^4 q^4).$$
(3)

This expression for $S(q,\phi)$ when substituted in Eq. (2) gives

$$\langle S \rangle \cong S(0,\phi) + \alpha(\phi)$$

$$\times \frac{\int_0^\pi F(n,x,\theta,\lambda)(x^2 q^2)(1-\cos\theta)\sin\theta\, d\theta}{\int_0^\pi F(n,x,\theta,\lambda)(1-\cos\theta)\sin\theta\, d\delta}.$$
(4)

Equation (4) has two unknown parameters $S(0,\phi)$ and $\alpha(\phi)$. From this equation the estimation of $S(0,\phi)$ and $\alpha(\phi)$ are carried out as follows. The angle averaged structure factor, $\langle S \rangle$, is experimentally measured at two different wavelengths. The integrals involving F on the right-hand side are then

calculated using Mie theory using known single-particle properties at the same two wavelengths. These data are then used to evaluate values of the parameters $S(0,\phi)$ and $\alpha(\phi)$. It is worthwhile to reiterate that the parameter values of $S(0,\phi)$ and $\alpha(\phi)$ are determined without an analytical model for $S(q,\phi)$. Consequently, information about the magnitude of $S(0,\phi)$ or the long-wavelength density fluctuation of a colloidal solution in thermal equilibrium, can be obtained from multiply scattered light. Isothermal osmotic compressibility (χ), for a monodisperse suspension, can then be determined as

$$S(0,\phi) = \left(\frac{6\phi}{\pi x^3}\right) kT\chi = \left(\frac{6}{\pi x^3}\right) kT \left(\frac{\partial \phi}{\partial \Pi}\right)_T,$$
(5)

where k is the Boltzmann, T the temperature, and Π the excess osmotic pressure.

We have used FDPM apparatus previously described[9] to measure isotropic scattering coefficients of aqueous dispersions of surfactant stabilized polystyrene spheres (PP788) supplied by Dow Chemicals, Midland, MI, with mean diameter of 150 nm (DLS) and polydispersity of $\sim 6.7\%$ (measured as standard deviation, S.D.). The ionic strength of all the suspensions were between 0.1 and 0.05 M. No evidence of flocculation due to attractive van der Waals interactions was noted. A 670 and a 785 nm laser diode or a Tsunami picosecond pulsed titanium sapphire (Ti:Sapph, Spectra Physics) laser operating at a repetition rate of 4 MHz were used as light sources. Details of the experimental setup and operation are available in our earlier publications.[9] The modulated or pulsed light was coupled to the colloidal solution using a 1000 μm optical fiber immersed into the solution. The scattered light propagated within the colloidal solution was collected using a second optical fiber located ~ 1 cm away from the source fiber. The collected light was analyzed for phase delay, θ_p, and amplitude attenuation, M, as a

FIG. 3. The relative percentage error (defined as $[(\langle S\rangle_{\text{exact}}-\langle S\rangle_{\text{approx}})\times 100/\langle S\rangle_{\text{exact}}]$) in $\langle S\rangle$ associated with using the approximate small "qx" form of $S(q,\phi)$ in place of the exact analytical form.
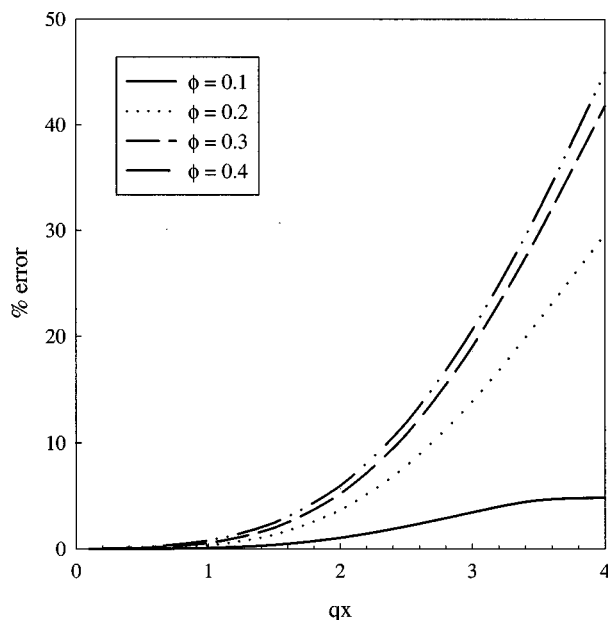

FIG. 4. The relative percentage error (defined as $[(\langle S\rangle_{\text{exact}}-\langle S\rangle_{\text{approx}})\times 100/\langle S\rangle_{\text{exact}}]$) shown for (a) 50 nm and (b) 150 nm particle as function of wavelength and the volume fraction of the latex.

function of modulation frequency of the laser diode or harmonic of the pulsed laser repetition rate, ω. A standard heterodyne technique was employed for signal detection which yielded a 100 Hz signal at the photomultiplier output from which the phase shift, θ_p, and modulation, M, were extracted.

FDPM measurements on the colloidal solution were conducted in 100 mL volumes. The value of the isotropic scattering and the absorption coefficients were extracted from the experimentally measured phase difference between two separate source detector pairs, $\Delta\theta_p^{\text{rel}}(\lambda,\omega)$. Owing to the large experimental volumes used, the analytical solution to the optical diffusion equation describing the propagation of light in an infinite medium can be used to evaluate μ_s' and μ_a from $\Delta\theta_{\text{rel}}(\lambda,\omega)$,[13]

$$\Delta\theta_p^{\text{rel}}(\lambda,\omega)=|r_{d1}-r_{d2}|\left\{\frac{3(\mu_s'+\mu_a)(\mu_a^2c^2+\omega^2)}{c}\right\}^{1/2}$$
$$\times\sin\left\{\frac{1}{2}\arctan\left(\frac{\omega}{\mu_a c}\right)\right\}, \qquad (6)$$

where r_{d1} and r_{d2} are the two detector positions; λ is the wavelength of light in vacuum, and c is the speed of light in the continuous medium. Equation (6) was fit to the experimental values of $\Delta\theta_p^{\text{rel}}(\lambda,\omega)$ to yield independent parameter estimates of the absorption coefficient, μ_a, and the isotropic scattering coefficient, $\mu_{s,\text{expt}}'$. The values of $\langle S\rangle$ were then obtained from Eq. (2) at two wavelengths and values of $S(0,\phi)$ as a function of volume fraction were subsequently determined using Eq. (4).

Figure 2 shows the typical $S(0,\phi)$ values derived from experimental FDPM measurements (symbols) as a function of particle volume fraction. The solid line provides predicted values of $S(0,\phi)$ from the semiempirical Carnahan–Starling
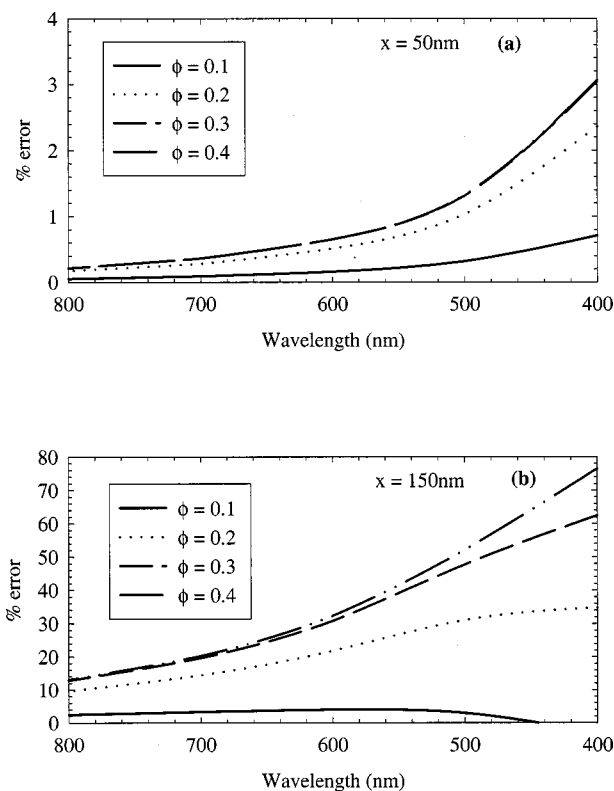
(CS) equation of state of hard spheres which describes $S(0,\phi)$ as a simple function of the volume fraction, ϕ, of the hard spheres:

$$S(0)=\frac{(1-\phi)^4}{(1+2\phi)^2-\phi^3(4-\phi)}. \qquad (7)$$

The excellent agreement between the CS equation of state and experimentally derived values of $S(0,\phi)$ may be expected. In our experiments the interparticle repulsion is screened to a very short range (less than ~5% of the particle diameter) and hence the polystyrene lattices closely resemble hard spheres. In addition, it is noteworthy that the influence of the polydispersity of our latex sample (S.D.=6.7%) seemingly does not influence our prediction of $S(0,\phi)$. This observation is in agreement with previous work by various researchers who show that polydispersity below 10% does not influence the structure factor significantly.[14,15]

However, the validity of this particular experimental approach to estimate $S(0,\phi)$ clearly depends on the accuracy of the small "qx" approximation. To better assess the limitation of this approximation, we evaluate the error of choosing the small "qx" approximation in monodisperse hard sphere systems, the analytical form of whose static structure factor has been derived using the Percus–Yevick (PY) approximation.[16,17] From the exact analytical form of $S(q)$, the coefficients $S(0,\phi)$ and $\alpha(\phi)$ can be calculated using series expansion. Thus, using the exact and approximate form of $S(q)$ for a hard sphere suspension the range of validity of the small "qx" assumption may be assessed readily.

From Fig. 3 it is evident that the approximation is satisfactory for values of $qx \leq 1$. Beyond this value, the error associated with the approximation increases with qx value and volume fraction.

Figure 4 shows the corresponding error (defined as $[(\langle S \rangle_{exact} - \langle S \rangle_{approx})/\langle S \rangle_{exact}]$) in the angle averaged structure factor $\langle S \rangle$, which is experimentally obtained. The results are presented as function of wavelength, particle size, and volume fraction. The trends are as expected, with the errors associated with the approximation increasing with increase in particle size and volume fraction for a given wavelength and with the decrease in wavelength for a given particle size and volume fraction. It can be seen that for sizes beyond ~ 150 nm, it becomes increasingly difficult to extract $S(0, \phi)$ from measurements in the visible wavelengths (400–800 nm) with sufficient accuracy. However, for the experimental wavelengths of 670 and 785 nm, used in this study, the error is less than 20%.

In summary, a simple dual wavelength FDPM measurement in an aqueous polystyrene latex suspension can be used to extract the value of $S(0, \phi)$ with reasonable accuracy. It should be emphasized that this particular approach allows one to probe the static structure of a colloidal suspension at a concentration regime where the conventional measurements of single particle radiative scattering techniques are not applicable. However, the use of small qx expansion of $S(q, \phi)$ to estimate $S(0, \phi)$ is reasonable only within the restrictive conditions posed, namely monodisperse spherical particles with qx values ranging between 0 and ~ 4. Thus, there is a narrow window in which the approximation is reasonable.

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