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Scatterer correlation effects on photon transport in dense random media

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Optically disordered systems where the number of scatterers per cubic wavelength exceeds unity typically exhibit mean-free-path lengths for photon transport longer than those predicted by the cross section given by Mie theory in the independent-scatterer approximation. The effects of spatial correlation among scatterers on photon transport are investigated in dense colloidal latex suspensions. Transport mean-free-path lengths obtained from time-resolved transmission of picosecond laser pulses, from suspensions successively diluted over two decades of scatterer density, are compared to conventional extinction lengths. Correlations introduced into the Mie formalism via a static structure factor based on a hard-core radial distribution function show good agreement with the experimental results.

I. INTRODUCTION

The possibility for study of localization effects in optically disordered systems has spurred a renewed interest in the study of light scattering from dense random media.[1] Strong photon localization may be observed in composite materials possessing sufficiently high density of scatterers with sufficiently high cross sections for scattering photons. Theoretical understanding of so-called classical wave localization, an analog to electron localization (but free of the complicating Coulomb interaction), has progressed dramatically.[1] A complete understanding of photon transport in such optically dense systems is desired as well for the extended states in the diffusive regime. Measurements of photon transport in a dense system of relatively weak scatterers are presented here to characterize better the effects of spatial correlations in dense (but not localizing) optically-disordered systems.

Photon transport in the diffusive regime can be characterized by the transport (or momentum-exchange) mean-free-path length,

$$\ell^* = (n\sigma^*)^{-1}, \tag{1}$$

where n is the number density of scatterers and

$$\sigma^* = \int \frac{d\sigma}{d\Omega}(1-\cos\theta)\, d\Omega. \tag{2}$$

$d\sigma/d\Omega$ is the differential Mie cross section for scattering into $d\Omega$ at an angle θ, derived from Maxwell's equations for an isolated uniform dielectric sphere.[2] Equation (1) is accurate only in the limit of dilute scatterer concentration, however. As n increases, spatial correlation among scatterers leads to phase correlation among scattered waves and weakens the effective cross section for scattering below that of an individual scatterer. Correlation effects may be introduced[3] by replacing σ^* with

$$\sigma_c^* = \int \frac{d\sigma}{d\Omega}\, S(\theta)\,(1-\cos\theta)\, d\Omega, \tag{3}$$

where $S(\theta)$ is the static structure factor obtained from an appropriate radial distribution function, $g(r)$, by

$$S(\mathbf{q}) = 1 + n\int [g(r)-1]\; e^{i\mathbf{q}\cdot\mathbf{r}}\; d^3\mathbf{r}. \tag{4}$$

$\mathbf{q}$ is the scattering vector of the elastically scattered photon of wave vector $\mathbf{k}$ and is related to the scattering angle by $q = 2k\sin(\theta/2)$.

II. OBSERVATIONS

A systematic study of photon transport in well characterized aqueous colloidal suspensions of monodisperse latex balls has been conducted over a range of densities spanning the dilute regime to the high-density regime, where correlations among particles become important. Photon-transport parameters were obtained for suspensions of 0.087, 0.135, and 0.198 μm diameter (d) latex balls with volume fractions f ranging from ~0.1% to 20%, obtained by successive dilution from the 10% stock suspension or by centrifuging.

Transport mean-free-path lengths, ℓ^*, were obtained using a time-resolved transmission technique optimized for fluid samples.[4] 10 psec pulses (λ_{vac}=0.5785 μm) from a synchronously pumped dye laser were injected into each sample through an optical fiber; transmitted pulses were detected with a biplanar phototube and a digital sampling oscilloscope for various values of effective sample thickness s, the distance between the launch point of the light (fiber tip) and the output window. Two parameters, the diffusion coefficient, $D = c\ell^*/3$, and an absorption parameter γ, as in $I(t) = e^{-\gamma t}\, I_D(t)$, were extracted from observed pulse shapes for all s by least-squares fitting of the solution of the diffusion equation with boundary conditions representing our experimental geometry.[4]

In addition, extinction mean-free-path lengths[5], ℓ, were obtained from the same samples for compari-

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son with ℓ^*. A computer-controlled variable-thickness cell was used in the usual extinction configuration to measure the relative intensity of transmitted unscattered light with variation of sample thickness x: $I = I_0 \exp(-x/\ell)$. Extinction data were obtained primarily with $\lambda_{\text{vac}}=0.5145\,\mu\text{m}$ from an argon ion laser because of its inherent stability and ease of operation; extinction measurements obtained using $\lambda_{\text{vac}} = 0.5785\,\mu\text{m}$ from the picosecond laser were observed to agree with the previous data after scaling for wavelength.

Observed values of ℓ^* and ℓ are shown in Fig. 1 over the accessible range of scatterer densities. To facilitate comparison of different ball sizes, dimensionless densities n' have been introduced as the number of scatterers per cubic wavelength, $n\lambda^3$, where $n = (6/\pi)\,f/d^3$ and λ is the wavelength *in water.* In all three samples, as the density is increased, departures from n^{-1} scaling of the mean-free-path lengths become apparent.

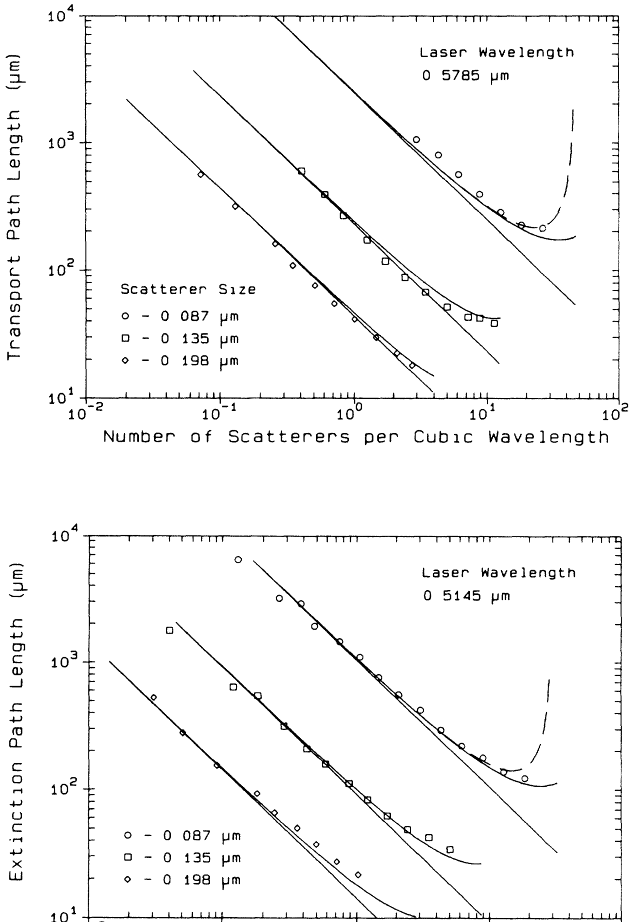

FIG. 1. Observed transport and extinction mean-free-path lengths. Departure from Mie theory without correlation correction (straight line) increases with increasing scatterer density. The correction from Percus-Yevick (PY) theory (solid curves) is compared to the hole-correction (HC) model (dashed curve) for the 0.087 μm scatterers.

III. DISCUSSION

The hole-correction model[6] provides the easiest introduction of particle correlations. Equation (4) can be evaluated analytically for the hole-correction distribution function given by $g(r) = 0,\ r < d$; $g(r) = 1,\ r \geq d$. Good agreement with our observations is obtained for the larger-diameter balls. Unfortunately the hole correction model begins to diverge for f higher than about 10% for the 0.087 μm balls, arising from physically inadmissible negative values calculated for $S(\theta)$ at small angles. The same limitation of the hole-correction model was previously noted in an analysis of extinction measurements from similarly dense systems.[6]

The Percus-Yevick $g(r)$ can be used to provide a better approximation.[3] An exact solution of the Percus-Yevick integral equation for $g(r)$ for hard spheres is available[7] and has been used here for evaluation of Eq. (4).[8] The resulting corrections are shown as the curved lines in Fig. 1 which increasingly deviate from the n^{-1} scaling as density is increased. Agreement is favorable with both transport and extinction observations.

The experimental data have been reduced by least-squares fitting of straight lines in the dilute limit, with slope of -1 representing n^{-1} scaling, thereby removing possible systematic errors such as incorrectly reported scatterer size. The observed high-density values are reported relative to these best-fit lines as correlation correction factors $\Gamma(n') = \ell_c/\ell$ and shown in Fig. 2 for comparison with theoretical values. *Correlation effects are capable of doubling observed mean-free-path lengths from the expected Mie-based lengths at the highest densities studied.*

Spatial correlation is observed to affect extinction more strongly than transport. The angular dependence of $S(\theta)$ is such that it deviates from unity mostly at small angles, deviating more strongly with increasing density. This angular dependence is somewhat similar to that of the factor $1 - \cos\theta$ already present in Eq. (2); each term serves to suppress the forward-scattering contribution to the overall cross section. Thus the correlation effect is correspondingly weaker for σ_c^* than σ_c.

For $n' < 1$ correlation effects on transport are relatively unimportant. Significant correction factors for extinction lengths can arise at lower values of n', however, especially for larger ball diameters. For a given actual density, say $f = 10\%$ (indicated by the arrows in Fig. 2), correlation effects are always stronger for smaller scatterers.

We have found that the following empirical expression can be used to represent the correction factors resulting from the Percus-Yevick model:

$$\Gamma(n') = \exp\left(B\,n' + C\,n'^2\right), \tag{5}$$

where the parameters B and C depend only on the size parameter d/λ as shown in Fig. 3. This form is rem-

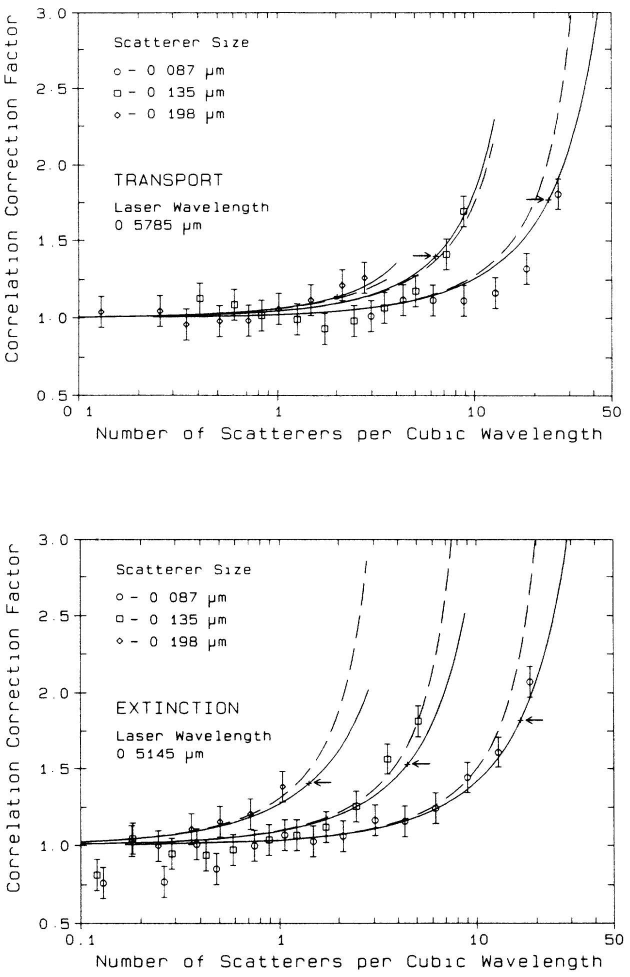

FIG. 2. Correlation correction factors. Departure from simple n^{-1} scaling of the path lengths is presented as the ratio of the observed to expected values, derived from best-fit n^{-1} scaling at low density. Percus-Yevick (solid curves) and hole-correction (dashed curves) factors are shown for comparison. The arrows indicate scatterer densities of 10%.

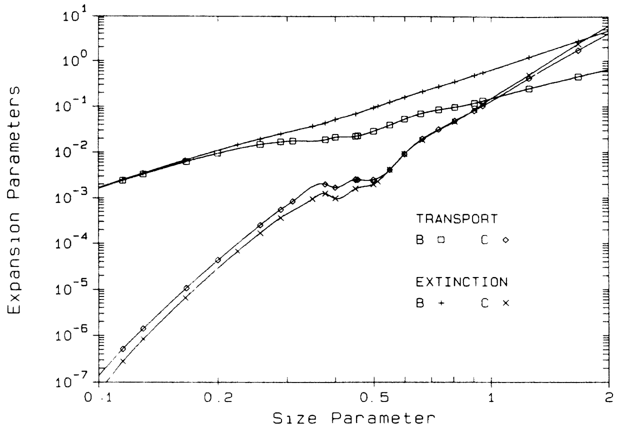

FIG. 3. Correlation expansion parameters. The correlation correction factor can be represented using the empirical expression in Eq. (5). The fitted parameters B (first order in n') and C (second order) depend only on the size parameter d/λ, where λ is the wavelength in the medium.

iniscent of a virial expansion and has been chosen for convenience in presenting a means of easily evaluating correlation corrections.[9] The error introduced by using this representation of Γ does not exceed 0.2% over the range shown in the figure for f up to 20%. The variation of the fitted parameters, in particular C, around a size parameter 0.4–0.6 corresponds to strong Mie resonances occurring at those values.

Previous studies[3,10] of coherent backscattering of light from colloidal latex suspensions have employed a comparison of observed backscattering widths with calculated ℓ^*. Correlation effects have been clearly observed in coherent backscattering at high densities[10] and have been included in the evaluation of transport calculations as described above.[3] We have shown by direct measurement of ℓ^* that this approach is indeed valid for these disordered systems. Clearly, correlation effects in photon transport cannot be ignored in the dense random systems currently being explored in localization studies, and in fact may tend to mask its observation.

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[1] For a review of recent work in this area see *Scattering and Localization of Classical Waves in Random Media*, edited by P. Sheng (World Scientific, Singapore, 1990).

[2] See, for example, C. F. Bohren and D. R. Huftman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983).

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[5] $\ell = (n\sigma)^{-1}$, where σ is given by Eq. (2) or (3) without the $1 - \cos\theta$ momentum-exchange factor.

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[9] The computer program used for direct evaluation of Γ will be provided on request for use by interested readers.

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