Multiple scattering efficiency and optical extinction

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In this investigation, scattering of laser light by polystyrene spheres has been examined. Our results demonstrate that certain multiple scattering data can be explained in terms of single scattering Mie theory. Multiple scattering can be interpreted as a succession of independent, single scattering events. Using this interpretation, we have derived an expression that yields the optimum particle size for maximum attenuation of laser light by particles suspended in a medium. The size is smaller than that predicted by the Mie theory alone. Results of this research have wide general application for all electromagnetic radiation and are particularly useful in determining optimum scattering materials and sizes for applications such as cavityless lasing, coherent backscatter, and localization of light.

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I. INTRODUCTION

Mie's theory [1] accurately describes electromagnetic radiation scattering when the particles are spherical, far apart and dilute. When the particle concentration is increased, multiple scattering occurs, which is governed by the radiative transport equation (RTE) [2,3]. If the concentration is very dense, photons undergo a random walk in the medium, which is known as optical diffusion. Optical diffusion is adequately described by the diffusion approximation to the RTE [4].

For most applications, light will be multiply scattered. Because the RTE is a nonseparable, integral-differential equation of first order for which a closed form solution does not exist, various approximations have been devised. We have coupled the solution of the simplest approximation to the RTE with certain Mie parameters. This analysis, along with the resulting light extinction measurements, shows that the size of particles that scatter light most efficiently is significantly smaller than that predicted using the Mie theory alone. The scattering efficiency calculated by our method accurately matches the experimental data over a wide range of particle sizes and optical thicknesses.

II. BACKGROUND

A useful parameter for describing light propagation in an attenuating medium is the *optical thickness* $\tau = z\xi$, where z is the optical path length and $\xi = a + s$ is the total attenuation arising from absorption and scattering. The steady-state solution to the RTE for a beam traveling in the z direction in a nonscattering, source-free medium is

$$L(z) = L(0)e^{-\tau}, \tag{1}$$

where $L(z)$ is the monochromatic radiance at position z [5]. Equation (1) is known variously as Bouguer, Lambert, or Beer's Law, or some hyphenated combination of these three. We shall refer to it as the BLB law. Strictly speaking, the BLB law is applicable only when scattering is negligible, because zero scattering is assumed in its derivation. However, the authors have previously shown that the BLB law can be used to analyze the total attenuation even when scattering is appreciable [6]. This extension is possible because an arbitrarily small solid angle subtended by the detector is equivalent to a very small scattering coefficient in the RTE. Experimentally, this condition is achieved by restricting the size of the input aperture to the detector.

The scattering strength of a single particle can be characterized by the light extinction Q, given by the Mie theory

$$Q = \sigma / \sigma_{\mathrm{geom}}, \tag{2}$$

where σ is the total cross section (scattering + absorption), and σ_{geom} is the geometric cross section of a spherical particle. The energy removed from a beam by a particle is proportional to Q, which is therefore a measure of the single scattering and absorbing efficiency of the particle. The attenuation of light for a suspension of particles can be related to the cross section by

$$\xi = \rho\sigma, \tag{3}$$

where ρ is the particle number density. By combining Eqs. (2) and (3) and using the definition for τ, we obtain

$$\tau = Qz\rho\sigma_{\mathrm{geom}}. \tag{4}$$

The extinction can therefore be determined from Eq. (4).

Measurements of the scattering extinction Q are limited to very dilute samples ($\tau \ll 1$) to insure single scattering events only. However, the scattering efficiency of a single particle is not necessarily the same as that for a dense ensemble of particles. To study the scattering properties of an ensemble of particles, we define a scattering efficiency for the ensemble using the relation in Eq. (4). We show that this method is valid for a wide range of optical thickness.

III. EXPERIMENT

We first designed an experiment to verify the coupling between the single scattering Mie parameter Q, and the multiple scattering parameter τ as given by Eq. (4). For this purpose, the transmission of an argon-ion laser beam (514.5 nm) through an aqueous suspension of polystyrene spheres at

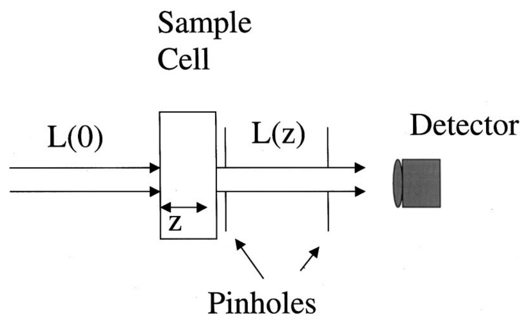

FIG. 1. Experimental setup for measuring optical thickness τ.

a fixed value of z (2.4 cm) was measured for a range of particle number densities. The optical thickness was obtained for each number density using Eq. (1). A schematic of the experimental setup is shown in Fig. 1. The pinholes serve to minimize the scattered light. Details of the experimental setup are given in Ref. [6]. The optical thickness was plotted as a function of $z\rho\sigma_{\mathrm{geom}}$, as shown for particle diameter $d=1.0$ μm in Fig. 2, where we intentionally extended the range of τ to show the limits of the transmission measurements. The linearity of the plot up to $\tau\cong 10$ shows that the forward scattered light does not affect the measurements in this range, justifying the use of Eq. (1). The extinction Q is determined from the slope of the line.

The extinction is a function of the size parameter x, where

$$x=\frac{\pi d}{\lambda}, \tag{5}$$

d is the particle diameter, and λ is the wavelength in the medium. The experiment was repeated for several particle diameters. Values of Q thus obtained are plotted in Fig. 3, as a function of size parameter, along with the values of Q computed numerically using the Mie theory. The measured results are in good agreement with the Mie theory, indicating that Q can be used to predict the multiple scattering parameter τ via Eq. (4), and vice versa.

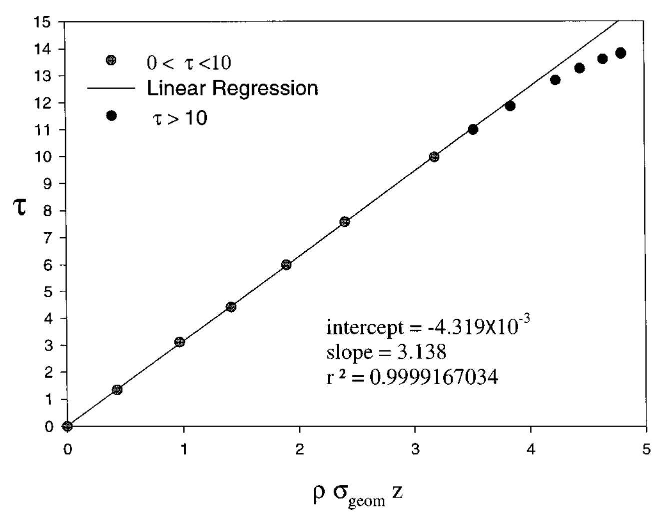

FIG. 2. Measured τ vs particle concentraiton for 1.0-μm spheres. The slope, intercept, and r-squared values are the result of the best linear fit for $0<\tau\leq 9.95$. The slope is the extinction $Q=3.135\pm 0.094$; $Q_{\mathrm{Mie}}=3.151$.

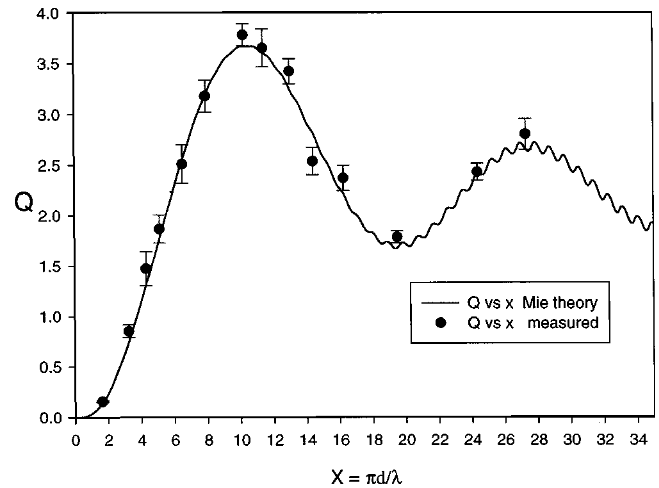

FIG. 3. Extinction Q vs size parameter x.

It should be noted that, in the visible spectrum, polystyrene absorption is zero. The attenuation is therefore due to scattering only. For single scattering $\tau<1$, for multiple scattering $1<\tau\lesssim 10$, and for diffusion $\tau\gtrsim 10$ [7]. The range of τ in our experiments was from zero up to $\tau\sim 10$. Our results can be accurately described by the Mie parameters, showing that the multiple scattering processes do not affect the measurement. Therefore the attenuation of light in the presence of multiple scattering can be understood in terms of the Mie theory.

IV. SCATTERING EFFICIENCY

While performing experiments similar to those described above, we observed an anomaly that could not be explained by the Mie extinction curve in Fig. 3. Namely, obtaining a fixed value of τ required a far smaller volume of spheres with size parameter 4.1 ($d=0.5$ μm) than spheres with size parameter 49 ($d=6$ μm). This result is contrary to the Mie theory in which a particle of diameter 6μm is much more efficient than a particle of diameter 0.5 μm in removing energy from a beam.

Consequently, we define the scattering efficiency of a particle suspension using the ratio of the volume occupied by the spheres to that of the sample volume. The most efficient scattering occurs when this volume ratio is a minimum for a given attenuation. This volume ratio is

$$R=\rho V_{\mathrm{sph}}, \tag{6}$$

where V_{sph} is the volume of a single sphere. By substituting for ρ from Eq. (4) and using the definition for the size parameter x from Eq. (5), we obtain

$$R=\frac{2\lambda\tau}{3\pi z}\frac{x}{Q}. \tag{7}$$

Equation (7) gives the volume fraction needed to obtain attenuation τ for a fixed particle size and optical path length. From the graphs of τ versus $z\rho\sigma_{\mathrm{geom}}$, we chose $\tau=8$, found the corresponding value of ρ, and calculated the experimental value of R from Eq. (6). Figure 4 shows these values plotted as a function of x, along with Eq. (7). Similar results

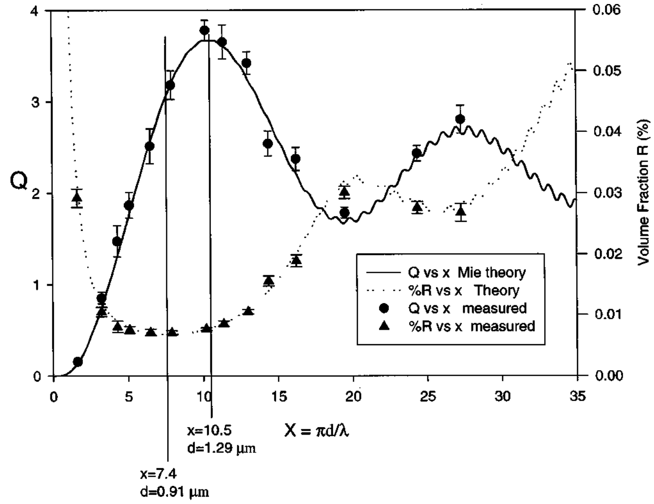

FIG. 4. Extinction Q vs size parameter x (left ordinate) and volume ratio R vs size parameter (right ordinate).

are obtained for other values of τ, as long as τ is restricted to the linear portion of the curve (<10). For comparision, the single particle scattering strength from the Mie theory of Fig. 3 is also shown. It is obvious that the most efficient scattering occurs at a smaller size parameter than that for the strongest scattering by a single particle. To achieve an optical thickness of 8, particles of size parameter $x=7.4$ ($d=0.91$ μm) are more efficient than those at $x=10.5$ ($d=1.29$ μm) predicted using the Mie theory.

Alternatively, Eq. (7) can be inverted to obtain the attenuation as a function of the volume fraction, i.e.,

$$\tau=\frac{3\pi zR}{2\lambda}\frac{Q}{x}. \tag{8}$$

In this case, the particle size that yields the most efficient scattering corresponds to the maximum of the function τ. The maximum of τ with R fixed corresponds to the minimum of R with τ fixed. A plot of τ as a function of x for fixed R using Eq. (8) is shown in Fig. 5, along with the experimental

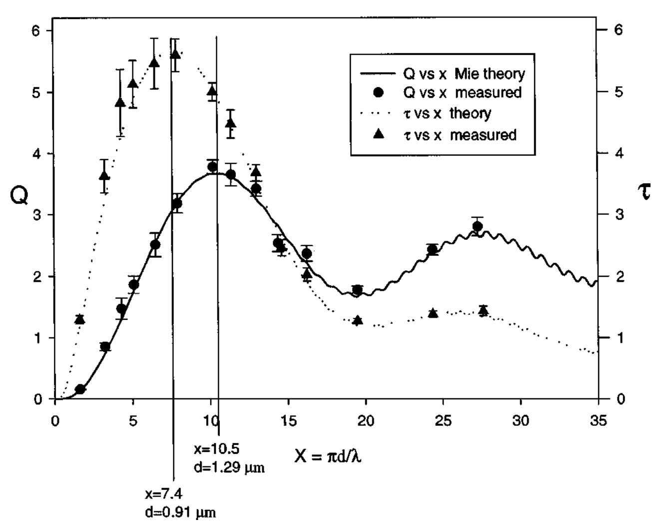

FIG. 5. Extinction Q vs size parameter x (left ordinate) and optical thickness τ vs size parameter (right ordinate).

TABLE I. Scattering parameters and particle size corresponding to $Q=2.72$.

x	d (μm)	R% ($\tau=8$)	τ ($R=0.01\%$)
6.85	0.84	0.0069	5.59
14.65	1.80	0.0147	2.60
27.85	3.43	0.0280	1.37

data. The plot of the scattering strength from the Mie theory in Fig. 3 is repeated for comparison.

To illustrate the importance of this result, we have compiled a list of values, shown in Table I, for x, d, R, and τ, for a fixed Q at $\lambda=514.5$ nm. If researchers were to use the Mie scattering extinction parameter to determine the most efficient scattering particle size for their application, they might conclude that particles of size parameter 27.85, 14.65, and 6.85 are equally efficient. Our data and analyses show this is not the case.

V. DISCUSSION

Examination of recently published reports indicates that this method may be applicable in achieving and optimizing localization of light. Researchers have been attempting to localize light for many years. Initial attempts were made using polystyrene spheres in water, resultling in only weak localization [8–11]. Using the reported values for particle size and wavelength, we have superimposed their values of x on our plot from Fig. 4 for polystyrene in water. The result is presented in Fig. 6. Wolf and Maret [8] found the best results for $x=3.74$, which is surprising because particles at $x=6.5$ are more efficient scatterers, both according to the Mie theory and our analysis. They attribute this to the increase in forward-scattered light for the larger particles, to which the theory is not applicable. Van Albada and Lagendijk [9] thought that the best scatterers would be those with a diameter comparable to the wavelength. Possibly they learned this

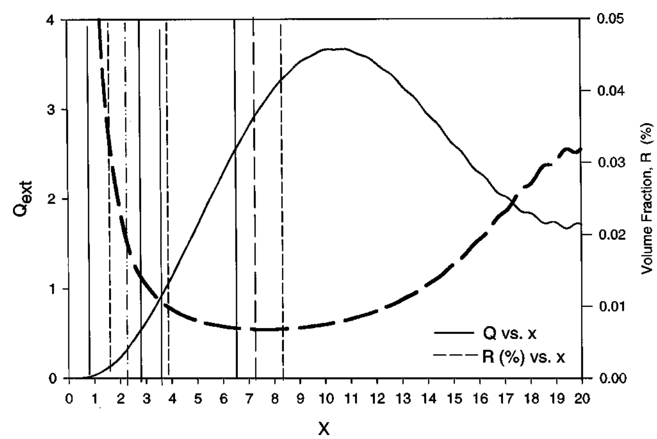

FIG. 6. Extinction and volume fraction (at $\tau=8$) vs size parameter for polystyrene in water. Weak localization has been reported for polystyrene in water at the indicated values of x. (— — —) van der Mark *et al.* [11], $x=1.74$, 3.91, and 8.4 though most data reported were for TiO_2 in methanol. (——) Wolf and Maret [8], $x=0.89$, 2.84, 3.74, and 6.50; most data were reported only for $x=3.74$. (— — —) Van Albada and Lagendijk [9], $x=7.2$. (— — —) Yoo *et al.* [10], $x=2.2$.

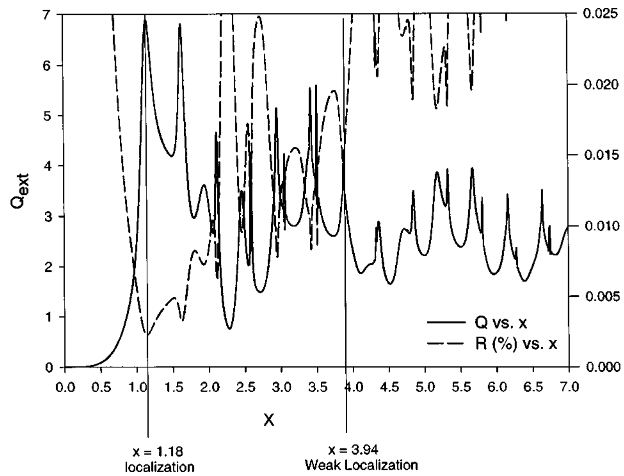

FIG. 7. Extinction and volume ratio (at $\tau=8$) vs size parameter for gallium arsenide in methanol. Wiersma *et al.* [13] report weak localization at $x=3.94$, and localization at $x=1.18$. The particle size for localization occurs at the global minimum for R.

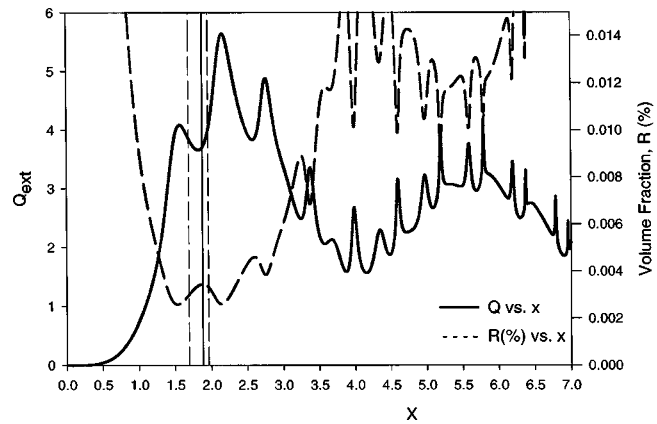

FIG. 8. Titanium dioxide in methanol. Extinction and volume fraction (at $\tau=8$) vs size parameter. Cavityless lasing was reported by Lawandy *et al.* [15] at $x=1.96$ for the pump and $x=1.69$ for the emission wavelengths. Weak localization was reported at $x=1.88$ by van der Mark *et al.* [11]. All of these occur near the global minimum in R.

from Anderson [12], who discussed, though qualitatively only, the importance of particle size with respect to wavelength and stressed the importance of a large mismatch between the refractive indices of the particles and the medium. Clearly, polystyrene in water does not scatter efficiently enough to induce localization. Increasing the density of particles will not help because the scattering events will no longer be independent and the scattered fields will interfere to enhance scattering in a preferred direction.

Higher refractive index dielectrics are needed for strong scattering. For example, weak localization has also been reported for titanium dioxide in methanol [11]. In 1997, localization was reported for gallium arsenide in methanol [13]. We calculated Q and R as functions of x for gallium arsenide in methanol, as shown in Fig. 7. The reported values of x for localization are superimposed on the plots. Weak localization was observed at $x=3.94$, and localization was reported at $x=1.18$. The global minimum for the volume fraction is at $x=1.14$. Comparison of the volume fraction at the global minimum for gallium arsenide (0.0023%) to that for polystyrene (0.017%) shows that gallium arsenide is a much better candidate for coherent backscattering. The global minimum is also pushed to smaller values of x for higher refractive indices, and smaller particles produce more uniform angular scattering. This analysis shows that a plot of R versus x for a candidate material and medium combination is essential to identify the optimum particle size for maximum scattering strength. Watson *et al.* [14] used an equivalent relation in comparing possible candidates, but this approach seems to have been largely ignored.

Another recent development that relies on efficient scattering is cavityless lasing. Lawandy *et al.* [15] reported linewidth collapse without a cavity when titanium dioxide particles were added to a laser dye and methanol solution. This has variously been explained as amplified spontaneous emission enhanced by diffusion of light in the gain medium [16,17], super-radiance [18], and feedback produced by scattering [19]. Regardless of the mechansim, the introduction of scatterers increases the effective path of photons in the pumped area, thereby increasing the absorption of the pump and the stimulated emission. We have plotted R veruss x for titanium dioxide in methanol, as shown in Fig. 8. The indicated values of x are for both the pump and the emission wavelengths reported for cavityless lasing. We have also indicated the value of x reported for weak localization. All three values are near the global minimum in R. The minimum value for R in this plot is 0.0026, which indicates that gallium arsenide is slightly more eficient than titanium dioxide. However, the curve for gallium arsenide is narrower near the minimum, which may be disadvantageous if the particle size distribution is large.

Our calculation for the scattering efficiency was extended to include a wide range of absorption and scattering coefficients, which are directly related to the imaginary and real refractive indices of the particles. Results of these calculations are shown in Fig. 9, where the global maximum of τ

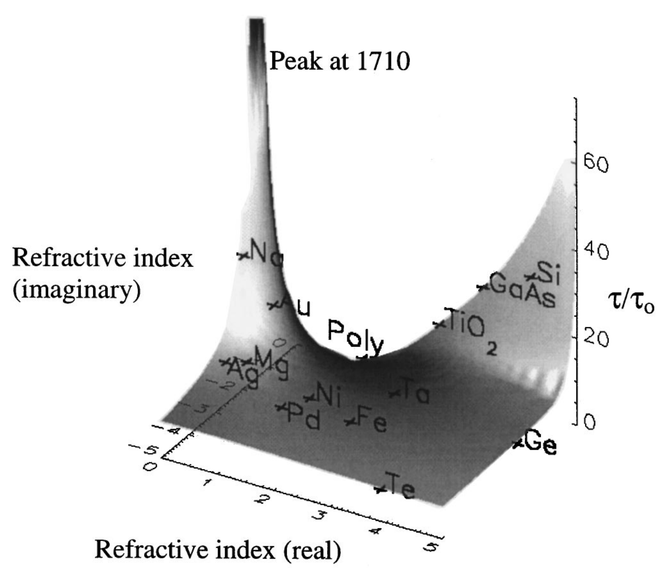

FIG. 9. Maximum scattering efficiency, normalized to polystyrene in water, as a function of real and imaginary refractive index. The refractive indices of various materials at $\lambda=514.5$ nm are overlaid on the plot.

versus x for each index ratio was plotted on the ordinate as a function of the refractive index ratio. The maximum of τ occurs at the value of x that implicitly gives the most efficient particle size for a given material (index ratio). The maximum of τ for each index ratio was normalized to τ_0, the maximum for polystyrene. This ratio yields the maximum efficiency of the material (not necessarily at the same x) relative to a baseline material (polystyrene). This plot can be used as a prescription for optimizing particle size and material type to maximize scattering and/or absorption for multiple scattering applications.

VI. CONCLUSIONS

The relationship of the multiple scattering optical thickness τ to the single scattering Mie extinction Q has been verified. Using polystyrene spheres in water, the scattering extinction of spherical particles has been measured. The results agree with theoretical prediction from the single scattering Mie theory. However, scattering extinction alone is not sufficient to explain the attenuation of light by a suspension of particles in a medium. This research identifies the scattering efficiency of an ensemble of particles as being a function of the single scattering parameter Q. The most efficient scattering is produced by particles of size smaller than that predicted by the Mie theory. As we have shown, although the BLB law is not valid for $\tau \gtrsim 10$, our analyses are also applicable to strongly scattering systems. This method of optimization is far superior to the conventional method of optimizing the Mie parameter Q.

ACKNOWLEDGMENTS

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