Multiple-scattering effects on static light-scattering optical structure factor measurements

Tahereh Mokhtari, Christopher M. Sorensen, and Amit Chakrabarti

We show that the extent and effect of multiple scattering on angularly resolved light-scattering intensity measurements, the optical structure factor, can be quantitatively described by a single parameter, the average number of scattering events along the scattering volume. This quantity is easily measured or calculated and hence provides a useful experimental indicator of multiple scattering, which is a hindrance to accurate structure factor measurements.

OCIS codes: 290.4210, 290.5820.

1. Introduction

Light-scattering measurements are important tools for the investigation and characterization of the structural and dynamic properties of polymer solutions, colloidal suspensions, aerosols, and gels. For simple interpretation of light-scattering experiments, it is important to have single scattering in which every photon reaching the detector has scattered only once. Therefore it is important to be aware of how multiple scattering can affect light-scattering measurements, how to detect it, and how one can possibly avoid it. Multiple scattering can become significant for systems with a strong refractive-index contrast, high volume fraction, or both. Previous work has shown that multiple scattering can affect scattering intensity measurements as the concentration of the dispersed particles in the solution increases for the same optical path length[1] (determined by either the thickness of the cell or the detector field of view) or the optical path length increases for the same particle concentration.[2]

The purpose of this short paper is to expose a simple, single parameter to quantitatively describe the extent of multiple scattering. This parameter, the average number of scattering events along the optical path length, is simply related to the transmittivity for systems with nonabsorbing particles. Hence it is easily measured in the laboratory. We demonstrate our ideas with angularly resolved scattering intensity measurements that, when plotted as a function of the scattering wave vector, yield the optical structure factor.[3]

2. Theory

When light passes through a medium, which is turbid due to the presence of particles, the transmitted intensity decreases exponentially with the propagation distance through the medium. This behavior, usually referred to as the Lambert–Beer law,[4] can be derived from two complimentary points of view that we will refer to as the extinction cross-section approach and the statistical approach. Below we use each to derive the Lambert–Beer law and then compare the results to find the photon mean free path in terms of the scattering cross section and the particle number density.

A. Extinction Cross-Section Approach

Envision a volume with differential thickness $\mathrm{d}x$ and area A and hence a volume $V = A\mathrm{d}x$. Include in this volume N particles with extinction cross section σ. Light incident on this volume, perpendicular to A, parallel to $\mathrm{d}x$, has intensity I. The length $\mathrm{d}x$ can be made small enough so that none of the particles fall in the extinction shadow of any other. Then the small amount of intensity lost as the light passes through this volume is

$$\mathrm{d}I = -I\frac{N\sigma}{A}. \tag{1}$$

Each side of Eq. (1) can be divided by $\mathrm{d}x$. On the right-hand side, use is made of $V = A\mathrm{d}x$ and the

The authors are with the Department of Physics, Kansas State University, Manhattan, Kansas 66506. The e-mail address for C. Sorensen is sor@phys.ksu.edu.

Received 24 June 2005; revised 28 August 2005; accepted 3 September 2005.

0003-6935/05/367858-04$15.00/0

particle number density $n = N/V$. The resulting differential equation yields

$$I(x) = I(0)\exp(-n\sigma x). \tag{2}$$

The simple derivation above does not include the wave nature of light. One can derive Eq. (2) starting directly from the Maxwell equations assuming that the spherically symmetric particles dispersed in the medium are independent scatterers and are made of an optically isotropic material.[5,6] Mishchenko *et al.* have presented a detailed analysis of the concept of the independent scatterers in their paper.[6] Independent scattering means that the scattered light by each particle is independent of the light scattered by all other particles in the system, and this is in accordance with having no coherent interference between the particles. To obtain this, the following assumptions should be satisfied.

(i) The distance from the observation point and the scatterer is much larger than any linear dimension of the scattering volume and the wavelength of the light.

(ii) Particle positions within the scattering volume are completely random during the time interval necessary to take a measurement.

(iii) The mean particle separation between the particles is at least several times larger than the radius of the particles. The linear dimension of the scattering volume is also much larger than the wavelength of the light.

(iv) The sum of the extinction cross sections of the particles filling the volume element is much smaller than the volume–element geometric cross section.

B. Statistical Approach

Consider a long right volume, e.g., a right cylinder, of length x and cross-sectional area A with a rate of photons per second, proportional to the light intensity $I(0)$, incident perpendicular to A. The medium inside the volume is turbid due to particles with an extinction cross section. At what rate, proportional to $I(x)$, do photons leave the other end of the volume?

We will make the assumption that the photons act like classical particles. We will also assume that the encounters of the photons with extincting particles in the volume are a Gaussian random process. For such a process we can envision photons encountering an extincting particle but then continuing on along the same path to possible encounters with other particles. Then the probability that a given photon has m encounters with extincting particles during its passage along the entire length x is given by the Poisson distribution:

$$P(s) = \exp(-\langle s\rangle)\frac{\langle s\rangle^{-s}}{s!}. \tag{3}$$

In Eq. (3) $\langle s\rangle$ is the average number of photon–particle encounters for an ensemble of photons. The average distance traveled between photon–particle encounters, i.e., the photon mean free path, is

$$l = x/\langle s\rangle. \tag{4}$$

In the real turbid medium situation only photons that have no encounters, i.e., $m = 0$, pass out of the far end of the volume. Thus by Eq. (3)

$$P(0) = \exp(-\langle s\rangle). \tag{5}$$

Then the light intensity passing through the volume, $I(x)$, is equal to this probability times the incident intensity, $I(0)$, to yield

$$I(x) = I(0)\exp(-\langle s\rangle). \tag{6}$$

Both approaches yield the Lambert–Beer law. Comparison connects the scattering variables to the statistical variables as

$$\langle s\rangle = n\sigma x, \tag{7}$$

$$l = (n\sigma)^{-1}. \tag{8}$$

3. Experimental Methods

The experiments were performed with aqueous dispersions of polystyrene latex spheres with a diameter of 9.6 μm (7.4% coefficient of variance), obtained from Interfacial Dynamics Corporation. The refractive index of polystyrene particles does not have an imaginary part in the visible spectral region. Therefore polystyrene particles are nonabsorbing, and the light extinction is due to scattering alone.

We used three cells with different optical path lengths. One cell was a quartz cuvette with an optical path length of 10 mm. The second and third cells were made of one O-ring sandwiched between two parallel quartz windows with a diameter of 23 mm. The cells seal the sample inside a metal sample holder with a hole centered on the quartz windows. The optical path lengths of the second and third cells were 4.8 and 2 mm.

The small-angle light-scattering (SALS) experiments[7] were performed with a vertically polarized argon-ion laser operating at a wavelength of $\lambda_0 = 488$ nm. The range of angles for the SALS experiments was $\theta = 0.9°–11.1°$ corresponding to wave vectors of $2.1 \times 10^3\ \mathrm{cm}^{-1} \leq q \leq 2.5 \times 10^4\ \mathrm{cm}^{-1}$, where

$$q = (4\pi/\lambda)\sin(\theta/2), \tag{9}$$

and λ is the wavelength of the light in the medium.

We prepared six aqueous dispersions of polystyrene microspheres with different volume fractions, each increasing by a factor of 2. The range of volume fractions was $5 \times 10^{-4} \leq f_v \leq 1.6 \times 10^{-2}$. The volume fraction is related to the particle number density n by $f_v = 4\pi R^3 n/3$ where R is the radius of the spherical particle. The colloidal suspensions were transferred

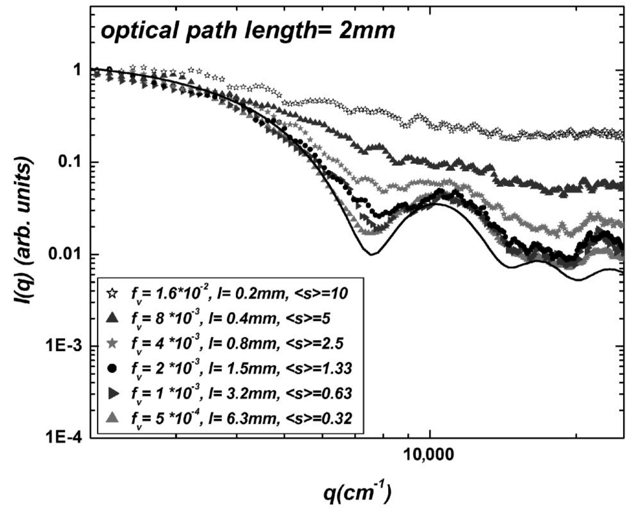

Fig. 1. Normalized light-scattering intensities (arbitrary units) plotted versus q at different volume fractions f_v. The solid curve is the Mie-scattering theory for the polystyrene 9.6 μm diameter spheres with a geometric size dispersion of 7.4%. The optical path length of the cell is 2 mm. The photon mean free path l and the average number of scattering events $\langle s \rangle$ are calculated for each concentration.

into each cell, and the scattered light intensity was measured versus the scattered angle. The background intensity was measured by filling the cell with distilled water before each set of runs. The background intensity was then subtracted from subsequent measurements of solutions. A photomultiplier was used to measure the incident light before and the transmitted light after it passed through the cell. These measurements were used to determine the transmittivity of the sample.

To find if the dispersed polystyrene particles at different volume fractions were independent scatterers, we checked the conditions required to have independent scattering mentioned previously [see conditions (i) through (iv) above]. The conditions were qualitatively satisfied. However, for our highest volume fraction the mean particle separation was almost six times larger than the particle size, which is right on the edge of having independent scatterers.

We remark that a small ratio of mean particle separation to size will likely cause multiple scattering to occur along with a loss of independent scattering. However, multiple scattering also occurs when this ratio is large, hence the scattering is independent, if the scattering volume is sufficiently large. It is this latter situation for which our results apply.

4. Results and Discussion

Figure 1 shows the experimental scattered intensities $I(q)$ versus q for the 2 mm optical path-length cell at different volume fractions. The Mie-scattering curve is plotted as the baseline. This curve was created by using the BHMIE code[8] integrated over a log-normal size distribution. The parameters needed to input the code were the most probable radius R of the

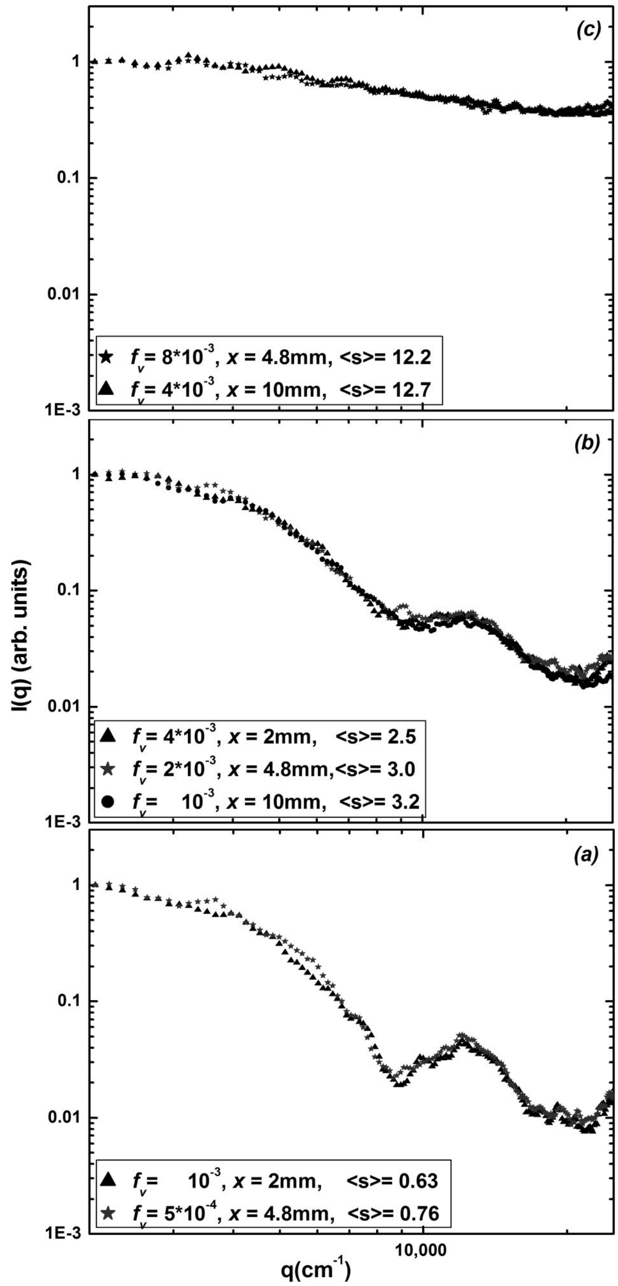

Fig. 2. Normalized light-scattering intensity (arbitrary units) plotted versus q for different average number of scattering events $\langle s \rangle$ of the photons with the 9.6 μm polystyrene particles. x is the optical path length of the cells. $\langle s \rangle$: (a) 0.7 ± 0.06, (b) 2.8 ± 0.4, (c) 12.4 ± 0.3.

polystyrene particles (4.8 μm) and 7.4% coefficient of variation of the radius, the relative refractive index of the particles ($m = 1.196$), and the wavelength of the light (488 nm). All curves are normalized to one on the intensity scale at $q = 2.1 \times 10^3$ cm^{-1}, our smallest experimental q value. In Fig. 1 we see that when the polystyrene solution is dilute, the scattered intensity is highly q (hence angle) dependent with the characteristic Mie ripples and mimics the theoretical calculation. As the volume fraction of the colloidal solution increases, the scattered intensity becomes more isotropic and loses its q dependence due to multiple-scattering effects.[1,2] The results were similar for the cells with 4.8 and 10 mm optical path lengths.

The photon mean free path for different volume fractions and the average number of scattering events $\langle s \rangle$ are also calculated and given in Fig. 1. This requires the total scattering cross section that can be obtained theoretically from BHMIE. The calculated optical cross section was $2.03\pi R^2$. Figure 1 shows that as the photon mean free path becomes smaller than the optical path length of the cell, or in other words the average number of scattering events $\langle s \rangle$ becomes larger, the multiple scattering becomes significant. Comparing the experimental results with the Mie curve suggests that, to have essentially only single scattering in an experiment, the photon mean free path should be of the order of the optical path length or larger. There is, of course, a practical upper limit for the photon mean free path because, when it is much greater than the path length, there would not be enough scattered light for the light-scattering measurements.

Both the theory and the results in Fig. 1 suggest that the simple fundamental parameter to describe the extent of multiple scattering is the ratio of the path length divided by the photon mean free path, i.e., the average number of scattering events $\langle s \rangle = x/l$. This is demonstrated in Figs. 2(a), 2(b), and 2(c) where the light-scattering data with similar $\langle s \rangle$ but different volume fractions and optical path lengths are plotted together ($\sim 0.7 \pm 0.06$, 2.8 ± 0.4, and 12.4 ± 0.3, respectively). The graphs are again normalized to one on the intensity scale at $q = 2.1 \times 10^3\ \mathrm{cm}^{-1}$. We see that the graphs with similar $\langle s \rangle$ overlap and show the same behavior. This supports our contention that the average number of scattering events is the universal parameter to describe the extent of multiple scattering. This extent can be quantified with the Poisson statistics of Eq. (4). For example, $P(2)/P(1) = \langle s \rangle/2$ would be the relative ratio of double scattering to single scattering.

Fortunately the value of $\langle s \rangle$ is simply obtained by either calculation or measurement. Measurement is particularly simple because by Eq. (7) one need measure only the relative amounts of incident and transmitted light, a ratio often called the transmittivity, to obtain $\langle s \rangle = \ln[I(0)/I(s)]$. We did this and found agreement between theory and experiment for $\langle s \rangle$ within $\sim 20\%$.

5. Conclusions

We have shown that the effect of multiple scattering on scattered intensity as a function of q (or θ) is described by a single parameter, $\langle s \rangle$, the average number of scattering events per photon along the length of the scattering volume. $\langle s \rangle$ is equal to the ratio of the photon mean free path to the scattering volume length and can be easily determined from a measurement of the transmittivity.

This work was supported in part by NASA grant NAG3-2360 and National Science Foundation grant CTS0403864.

References

1. C. Urban and P. J. Schurtenberger, "Characterization of turbid colloidal suspensions using light scattering techniques combined with cross-correlation methods," J. Colloid Interface Sci. **207,** 150–158 (1998).
2. M. Lattuada, H. Wu, and M. Morbidelli, "Estimate of fractal dimension of colloidal gels in the presence of multiple scattering," Phys. Rev. E **64,** 061404 (2001).
3. C. M. Sorensen, "Light scattering from fractal aggregates: a review," Aerosol Sci. Technol. **35,** 648–687 (2001).
4. G. S. Monk, *Light* (Dover, 1993).
5. M. I. Mishchenko, "Vector radiative transfer equation for arbitrarily shaped and arbitrarily oriented particles: a microphysical derivation from statistical electrodynamics," Appl. Opt. **41,** 7114–7134 (2002).
6. M. I. Mishchenko, J. W. Hovenier, and D. W. Machowski, "Single scattering by a small volume element," J. Opt. Soc. Am. A **21,** 71–87 (2004).
7. F. Ferri, "Use of charge coupled device camera for low-angle elastic light scattering," Rev. Sci. Instrum. **68,** 2265–2274 (1997).
8. C. E. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, 1983).