Surface Effects on the Coherent Reflection of Light from a Polydisperse Colloid

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Abstract

We consider the coherent reflection of light from a dilute polydisperse random system of particles. We focus our attention on the effects of the variation of the size distribution function induced near a flat solid interface. We also present a comparison of the theory with experimental results of the coherent reflectance of light in an internal reflection configuration.

Introduction

The coherent reflection and transmission of light in random systems of particles is potentially a useful tool to characterize highly scattering particles, colloids and composite materials. By coherent we mean the wave corresponding to the average electromagnetic field which is obtained by averaging over all possible configurations of the system (configurational average). The coherent transmission of electromagnetic waves through random systems of particles has been studied by several authors since long ago [1]. More recently, the coherent reflection of an electromagnetic wave from a half space of randomly located particles has been studied using a very intuitive approach [3], which turned out to be closely related to the so called effective-field approximation [4] and valid only for a dilute suspension of particles. We will call this approach the coherent-scattering model. For relatively dense systems a more elaborate procedure, called the quasi-crystalline approximation [2], has been also developed. This latter approximation is rather intensive numerically, and since we are exploring here the importance of surface effects on the reflectance, we will restrict ourselves to dilute colloidal systems where the inversion of experimental data can be easily done. We should also add that we have performed already experiments to test and to validate the coherent-scattering model finding that it can reproduce well the experimental data [5]. However, when dealing with polydisperse systems of particles in the presence of a flat interface between the matrix material and a homogeneous medium, the mere presence of the interface changes the density and size distribution over a region of the order of the width of the size distribution function. This region of variable density and size distribution may be called the surface region. In this paper we propose an iterative procedure to take into account in the reflectance calculations the presence of the surface region and compare its effects with the ones of a simpler approximation that we call the "sharp-surface" approximation. Finally, we also present a comparison between reflectance calculations using the coherent-scattering model and experimental data of light reflectance from a polydisperse colloidal suspension of latex particles, in an internal-reflection configuration.

Coherent Reflection Coefficient from a Polydisperse Random System of Particles with a Flat Matrix Interface

In Refs.[3,5] we obtained an approximate model for the coherent reflection coefficient from a half-space (r_{hs}) of identical spherical particles randomly located within a homogeneous boundless matrix with a real refractive index n_m. For polydisperse random systems of particles with the same refractive index n_p, we must average over the particle sizes. We get,

$$r_{hs} = \frac{\beta}{i(k_z^{eff} + k_z^m) + \alpha} \tag{1}$$

where

$$k_z^{eff} = \sqrt{(k_z^m)^2 - 2i\alpha k_z^m + \beta^2 - \alpha^2} \tag{2}$$

$$\alpha = -\frac{2\pi}{k_m^3}\int_0^\infty \rho(a)S_a(0)da \quad \text{and} \quad \beta = -\frac{2\pi}{k_m^3}\int_0^\infty \rho(a)S_{a,j}(\pi - 2\theta_m)da \tag{3}$$

Here $k_z^m = k_m \cos(\theta_m)$ is the z-component of the incident wavevector, $k_m = 2\pi n_m/\lambda$, θ_m is the angle of incidence, and $\rho(a)da$ is number density of particles with radii between a and $a + da$ and is given by $\rho_T n(a)$, where ρ_T is the total number density of particles and $n(a)$ is the dimensionless size distribution function. In the latter expressions, the functions S_a are the components of the amplitude scattering matrix of an isolated particle of radius a embedded within the matrix material, as defined in Ref. [6]. For the forward scattering amplitude we have $S_a(0) = S_{a,1}(\theta = 0) = S_{a,2}(\theta = 0)$; and for the scattering amplitude in the specular direction $S_{a,j}(\pi - 2\theta_m)$ we have that $j = 1$ or 2 for a TE or TM polarized incident wave, respectively. For a slab of the random system of particles of width L, the coherent reflection and transmission coefficients can be shown to be given by the well known formulas of continuum electromagnetics [3]. The expression in Eq. (1) is limited to dilute systems of particles but it is valid for all angles of incidence.

Assuming that $\rho(a)$ follows a log-normal distribution function, as it is usually the case,

$$\rho(a) = \frac{\rho_T}{a\sqrt{2\pi}\ln\sigma} \exp\left(-\frac{\ln^2(a/a_0)}{2\ln^2\sigma}\right) \tag{4}$$

where a_0 is the most probable radius, and σ is the width parameter of the distribution. In the experiments, however, the control is over the volume fraction occupied by the spheres. In this case, ρ_T in Eq. (4) is given by, $\rho_T = \left(3f/4\pi a_0^3\right) \exp[-\frac{1}{2}(3\ln\sigma)^2]$.

In actual experiments, light is incident on the system of particles from a medium different from that of the matrix. To model this situation we must introduce an additional interface in our model, namely that between the incident medium of real refractive index n_0 and the matrix. This can be done by using the well known three media reflection formula taking into account that the center of all particles must lie at least one radius away from the interface [3,5]. We must recall that the position of the particles is specified by the coordinates of their centers. However, when dealing with a polydisperse colloid, we have that the density and size distribution function must be different near the interface with respect to that of the bulk because smaller particles can approach closer the interface than larger ones. Assuming there is no correlation between spheres but there is an excluded-volume correlation between the spheres and the interface, we have,

$$\rho(a, z) = U(z - a)\rho(a) \tag{5}$$

where U is the unit step function, that is, $U(x) = 0$ if $x < 0$ and $U(x) = 1$ if $x > 0$.

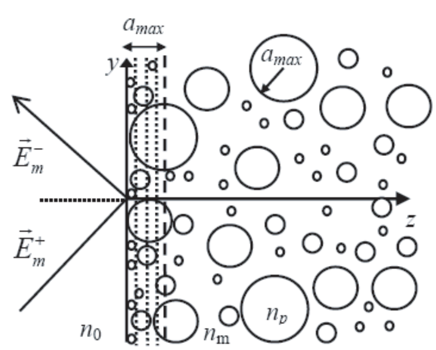

Figure 1: Illustration of the surface region and slab subdivision.

We may solve for the reflection coefficient of the random system of particles with a variable size distribution near the surface with an iterative procedure. First, let us consider a thin slab of particles from $z = 0$ to $z = \Delta z$ located at an infinitesimal distance, δ, in front of a uniform random half-space that occupies the space from $z = \Delta z + \delta$ to $z = \infty$. At this point we suppose there is no matrix interface. Let us consider that a linearly polarized plane wave, $\overrightarrow{E}_m^+ = E_0 \exp(i\overrightarrow{k}_+^m \cdot \overrightarrow{r})\hat{e}_m^+$, is incident at an angle θ_m. The reflected coherent wave can be expressed as $\overrightarrow{E}_m^- = r_1 E_0 \exp(i\overrightarrow{k}_-^m \cdot \overrightarrow{r})\hat{e}_m^-$ where r_1 is the coherent reflection coefficient of the random slab / half-space. The subscript '1' stands for slab 'one'. The coherent electric field at the gap in-between the slab and the uniform half-space consist of a right and a left propagating plane wave and is of the form,

$$\overrightarrow{E}_m^g = E_0 \left[A\exp(i\overrightarrow{k}_+^m \cdot \overrightarrow{r}) + B\exp(i\overrightarrow{k}_-^m \cdot \overrightarrow{r})\right]\hat{e} \tag{6}$$

where A and B are unknown complex coefficients. It is not difficult to show that the following relations hold,

$$A = t_l^{(1)} E_0 + B r_l^{(1)} \exp(-2ik_z^m \Delta z), \quad B = A r_0 \exp(2ik_z^m \Delta z), \quad r_1 E_0 = t_l^{(1)} B + r_l^{(1)} E_0 \tag{7}$$

where $r_l^{(1)}$ and $t_l^{(1)}$ are the coherent reflection and transmission coefficients of the slab of width Δz, $r_0 \equiv r_{hs}^{(0)}$ is the coherent reflection coefficient of the uniform half-space, and we let $\delta \rightarrow 0$. r_l and t_l are of the form [3],

$$r_l^{(1)} = \frac{r_{hs}^{(1)}[1-\exp(2ik_z^{eff(1)}\Delta z)]}{\left[1-\left(r_{hs}^{(1)}\right)^2 \exp(2ik_z^{eff(1)}\Delta z)\right]} \quad and \quad t_l^{(1)} = \frac{\left[1-\left(r_{hs}^{(1)}\right)^2\right] \exp\left[i\left(k_z^{eff(1)} - k_z^m\right)\Delta z\right]}{\left[1-\left(r_{hs}^{(1)}\right)^2 \exp(2ik_z^{eff(1)}\Delta z)\right]} \tag{8}$$

where $r_{hs}^{(1)}$ and $k_z^{eff(1)}$ are the coherent reflection coefficient of a uniform half-space and the z component of the effective propagation vector of a random system of particles of the same characteristics of the slab. Solving for r_1 from Eqs. (7) yields,

$$r_1 = \frac{\left(t_l^{(1)}\right)^2 r_0}{1 - r_l^{(1)} r_0} \exp(-2ik_z^m \Delta z) + r_l^{(1)} \tag{9}$$

We may add a second slab to the system and apply Eq. (9) again by changing on the right hand side $r_0 \rightarrow r_1$, $r_l^{(1)} \rightarrow r_l^{(2)}$, and $t_l^{(1)} \rightarrow t_l^{(2)}$, to obtain r_2 on the left hand side. We may repeat the procedure N times to model the surface region of the random system of particles. We can take N as large as necessary to model accurately a continuous size distribution function and denote the result as r_N. Now, we must introduce an incident medium different than the matrix of the actual random system. Then, one can show that the reflection coefficient r between the incident medium and the half-space matrix with randomly located colloidal particles, can be written as,

$$r(\theta_i) = \frac{r_m(\theta_i) + r_N(\theta_m)}{1 + r_m(\theta_i) r_N(\theta_m)} \tag{10}$$

where r_m is the Fresnel reflection coefficient of the incident medium - matrix interface, θ_i is the angle of incidence, and θ_m is given by Snell's law at the matrix interface: $\theta_m = \sin^{-1}[(n_m/n_0)\sin\theta_i]$. Note that r_N takes account of the effects of the surface region as it was described above. The iterative procedure proposed here to model the surface region makes the numerical evaluation of the reflection coefficient rather slow. It is of interest to see whether a simpler approximation, in which we evaluate the reflection coefficient of a polydisperse system of particles using Eqs. (1)-(4), but considering the system of particles as monodispersed, with a particle radius equal to the most probable radius a_0. In this case we may simply displace the uniform half-space of particles by $\Delta z = a_0$ and introduce the matrix interface at $z = 0$. The half space reflection coefficient acquires the phase factor $\exp(2ik_z^m a_0)$ and the compound reflection coefficient is given by Eq. (10) with r_N replaced by $r_{hs}^{(0)}(\theta_m)\exp(2ik_z^m a_0)$. We will refer to this approximation as the "sharp surface" (SS) approximation.

Numerical Results and Comparison with Experiment

We evaluate the coherent reflectance, $R = |r(\theta_i)|^2$, of a polydisperse half-space of particles with a matrix interface using the iterative procedure described above, as well as with the SS approximation. We compare the SS approximation with the iterative formulation in two examples assuming that the volume fraction of the particles, f, is small compared to one: (i) Highly scattering TiO_2 (rutile) particles assuming a refractive index of 2.8 and $a_0 = 112.5$ nm, and (ii) large latex-particles with $a_0 = 233.5$ nm and refractive index $n_p = 1.48$. Both examples were analyzed in an internal reflection configuration ($n_0 > n_m$) and around the critical angle of the incident-medium / matrix interface, where the contribution of the particles to the coherent reflectance is expected to be largest. For the TiO_2 particles, we found that the iterative method and the SS-approximation are very close to each other for σ less than about 1.25. For larger values of σ the difference starts to be noticeable and increases as σ increases. We found that using 10 slabs to model the surface region was sufficient for the iterative method to converge. In Fig. 2a we show plots of the reflectance of a TM polarized wave for $\sigma = 1.23$ and 1.6 for for TiO_2 particles. For the latex particles with $n_p = 1.48$, the difference was unnoticeable up to $\sigma = 2$; suggesting that the surface effects are stronger the more efficient the particles scatters light. In Fig. 2b we compare theory with and experimental data obtained by reflecting a laser beam ($\lambda = 633$ nm) from a glass-colloid interface around the critical angle. In this case the colloid was a polydisperse suspension of latex particles ($n_p = 1.48$) in water. The experimental setup and method are described elsewhere [5]. The particle size distribution was previously characterized by dynamic light scattering measurements, obtaining $a_0 \approx 233.5$ nm and $\sigma \approx 1.43$. In Fig. 2b we adjusted f and n_m to fit best the coherent-scattering model with the experimental data. The adjusted values are within the experimental uncertainty. We can appreciate that although the volume fraction of the particles in the colloid is rather large, the theory reproduces well the experimental data.

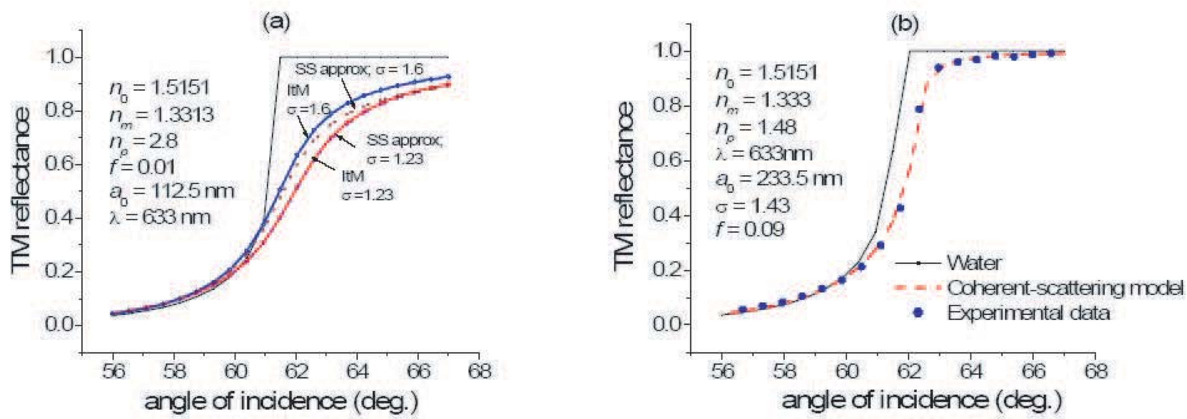

Figure 2: (a) The iterative method (ItM) versus the sharp surface (SS) approximation for TiO2 particles in water for two different values of . (b) Comparison of the coherent-scattering model with experimental data with latex particles in water. Parameters for each graph are shown in the inset.

Conclusion

When calculating the coherent reflectance of light from a dilute polydisperse colloid, if the width of the size distribution function is in the order of the wavelength of radiation or smaller, a "sharp surface" approximation using the most probable radius, is valid. We provide an example showing that the coherent-scattering model reproduces well the experimental results.

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