Optical Characterization of a Turbid Colloid by Light Reflection around the Critical Angle

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Abstract. We present a scattering theory model for the coherent reflectance of light from a turbid colloid in an internal reflection configuration. We compare with experimental measurements obtained with turbid suspensions of spherical latex particles and irregularly shaped TiO_2 particles. When the colloidal particles are not small compared to the wavelength of radiation, the reflectance curve as a function of the angle of incidence predicted by the scattering theory model, differs appreciably from that predicted by Fresnel's relations with an effective refractive index. Therefore, when the particles size is comparable or larger than the wavelength, one can not determine the effective refractive index in the usual way using a critical angle refractometer. We provide some insight to why Fresnel's relations do not work with turbid media.

INTRODUCTION

When light propagates through a random, turbid medium, its description is commonly divided into a coherent component and a diffuse one. The coherent component corresponds to the configurational average of the optical fields, whereas the diffuse component is related to the fluctuations about this average. A medium can be regarded as homogeneous when the power carried by the diffuse component is negligible, whereas a medium is considered turbid when the power carried by the diffuse component can be easily detected. In a homogenous medium, that is, when only the coherent component is important, one assigns a refractive index to the medium which corresponds to the ratio of the wavevector inside the medium to the wavenumber in vaccum. In this case the wavevector inside the medium actually corresponds to the effective wavevector of the coherent light, in general it is a complex vector, and its real and imaginary parts are the only observable components. Now, when light propagates within a turbid colloid made of particles which are not small compared to the wavelength of the incident radiation (large particles), the power carried by the diffuse component may be even larger than the one carried by the coherent component. Nevertheless, the coherent component still travels through the

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turbid medium with an effective wave vector, $\mathbf{k}^{eff}$ [1-8]. Therefore, one may still assign a refractive index to the turbid medium given by the ratio of the magnitudes of the real and imaginary parts of the effective wave vector to the wavenumber in vacuum, k_0; but, in this case one refers to an *effective refractive index*. The effective refractive index is generally a complex number even if the medium is not absorbing. In this case, the imaginary part of the effective refractive index comes only from the loss of power out of the coherent component which is transferred to the diffuse one. Although such a definition of an effective refractive index is a natural extension of the concept a refractive index of a homogeneous material, it has been noted by several authors that such an effective refractive index cannot be treated in the same way as the refractive index of a homogeneous material [1-3,6,8]. For instance, when light is transmitted through a slab of a turbid colloid made of large particles, the coherent wave suffers a phase lag according to the effective refractive index in the same way as if the light had traversed a slab of an equivalent homogeneous medium. Also, when a light beam is incident to a flat interface of a turbid colloid, the coherent component is transmitted and reflected. The transmitted beam refracts according to Snell's law and the effective refractive index [9]. However, the reflected and transmitted amplitudes do not obey the Fresnel relations with the effective refractive index [1,2]. Therefore, one can measure the effective refractive index of a turbid colloid from the phase lag or the refraction of the coherent wave in the usual way, as if one were dealing with an equivalent homogeneous medium. However, the measurement of the effective refractive index by light reflection cannot be done, in general, in the same way as for homogeneous media, because the Fresnel relations are no longer valid. The physical reason of why Fresnel relations are no longer valid for turbid media is an interesting and relevant question, essential to understand the validity and limitations of extending effective-medium theories to systems of large particles.

Now, when measuring the refractive index of liquids, it is common to use a critical-angle refractometer, also known as Abbe-type refractometers. Modern critical-angle refractometers are based on light reflection in an internal-reflection configuration. Critical-angle refractometers offer a high sensitivity, even though they are based on reflection measurements. The widespread use of critical-angle refractometers in the industry and research laboratories with all types of liquids, demands a thorough analysis of the errors and limitations of their use, in particular with colloids. G. H. Meeten and collaborators have studied experimentally the use of critical-angle refractometers with absorbing media and turbid colloids [10-13]. The errors incurred by an automatic critical-angle refractometer when used with absorbing media can be corrected in a simple way by considering the Fresnel relations with a complex index of refraction. However, in the case of turbid colloids it is not the case. G. H. Meeten and collaborators, have found experimentally that the effective refractive index of turbid colloids can be measured with a critical angle refractometer if the particles are not too large. However, when particles are large, there are inconsistencies that may lead to large errors.

In this work, we provide an alternative formula for the coherent reflection of light from a flat interface of a turbid medium consisting of a random suspension of large particles. We limit our analysis to the case of spherical particles, although extensions to randomly-oriented, non-spherical particles, are possible. We also provide some experimental results obtained by laser reflection from suspensions of latex and TiO_2 particles in water in an internal-reflection configuration. We compare them with the results of our alternative formula. Finally, we provide physical insight into why Fresnel relations are no longer valid when the particles in a turbid colloid are not small compared to the wavelength of incident radiation.

SCATTERING-THEORY MODEL

In a previous paper we have used electromagnetic-scattering theory to derive the half-space coherent reflection amplitude of a random system of spheres in the dilute limit [1]. In this derivation it is assumed that a collection of identical, non-magnetic spheres of refractive index n_p are embedded in a non-absorbing homogenous matrix of refractive index n_m, forming a *half-space* of particles within an otherwise homogeneous matrix (see Fig. 1). The z-axis is chosen perpendicular to the plane interface of the system and pointing towards the half-space of particles. The coherent reflection amplitude for an incident plane wave is given by,

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

where k^{eff} might be interpreted as playing the role of an *effective* propagation wavevector, whose z-component is given by

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

Here

$$\alpha = -\gamma \frac{k_m}{\cos\theta_m} S(0), \qquad \beta = -\gamma \frac{k_m}{\cos\theta_m} S_j(\pi - 2\theta_m) \tag{3}$$

where θ_m is the angle of incidence, $k_z^m = n_m k_0 \cos\theta_m$, k_0 is the wavenumber in vacuum,

$$\gamma = \frac{3}{2}\frac{f}{x_m^3}, \tag{4}$$

f is the volume fraction occupied by the particles, $x_m = n_m k_0$ is the size parameter in the matrix material, and the coefficients S_j denote the components of the scattering matrix of an isolated particle embedded within the matrix material. These coefficients can be calculated exactly using Mie theory. The scattering matrix relates the components of electric field of an incident plane wave with those of the scattered electric wave in the far-field region. That is,

$$\begin{pmatrix} \mathbf{E}^S_{far\parallel} \\ \mathbf{E}^S_{far\perp} \end{pmatrix} = \frac{\exp(ikr)}{-ikr} \begin{pmatrix} S_2(\theta) & S_4(\theta) \\ S_3(\theta) & S_1(\theta) \end{pmatrix} \begin{pmatrix} \mathbf{E}^i_{\parallel} \\ \mathbf{E}^i_{\perp} \end{pmatrix}, \tag{5}$$

where $\mathbf{E}_{\parallel}$ and $\mathbf{E}_{\perp}$ are the components of the electric field parallel and perpendicular to the plane of scattering, that is, the plane formed by the wave vector of the incident wave and the Poynting vector of the scattered waves. For spherical particles we have that $S_3 = S_4 = 0$ and $S(0) = S_1(\theta = 0) = S_2(\theta = 0)$. In Eq. (3) we have that $j = 1$ and $j = 2$

denote a TE and a TM polarized incident wave, respectively. Writing the reflection coefficient in full gives,

$$r_{hs} = \frac{\gamma S_j(\pi - 2\theta_m)/\cos\theta_m}{i\cos\theta_m + i\left\{\cos^2\theta_m + 2i\gamma S(0) - \left(\gamma^2/\cos^2\theta_m\right)\left[S(0)^2 - S_j(\pi-2\theta_m)^2\right]\right\}^{1/2} - \gamma S(0)/\cos\theta_m} \tag{6}$$

As discussed in Refs. [1,2] this expression is not equivalent to the reflection amplitude obtained by using Fresnel's relations with an effective index of refraction. In those references, the second order terms in γ were dropped in the denominator of the latter expression. For angles of incidence not too close to grazing these terms contribute negligibly to the reflection amplitude for systems with a low-density of particles. However, near grazing angles they may contribute more noticeably, as it will be explained below in relation to the internal-reflection configuration used in our measurements.

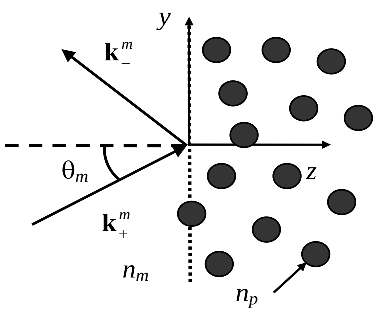

FIGURE 1. Schematic illustration of reflection of light from a half space of spherical particles. The dotted line represents the surface of the half-space; the particles' center lie to the right of it.

The Effective Refractive Index

The y-component of the effective wave vector, k_y^{eff}, must be equal to k_y^m [1,2], and the magnitude of the effective wave vector is given by, $(k^{eff})^2 = (k_y^{eff})^2 + (k_z^{eff})^2$. Then one could define an effective index of refraction through $k^{eff} \equiv n_{eff} k_0$ and get a closed expression for it, as

$$n_{eff} = \sqrt{n_m{}^2 - 2i\frac{\alpha k_z^m}{k_0^2} + \frac{\beta^2 - \alpha^2}{k_0^2}}, \tag{7}$$

We may note that β inside the square root in Eq. (7) is a function of the angle of incidence. However, for dilute systems at normal incidence, the second order terms inside the square root in Eq. (7) are in general negligible and we may simply drop them. Expanding the square root in powers of γ and dropping second order terms and higher, yields

$$n_{eff} \simeq n_m\left(1 - i\frac{k_z^m\alpha}{n_m^2 k_0^2}\right) = n_m\left[1 + i\gamma S(0)\right], \tag{8}$$

which is independent of the angle of incidence. This expression coincides with the one derived long time ago by van de Hulst [14] for the index of refraction of the *bulk* of a colloidal suspension. This expression is frequently referred to in the literature as van the Hulst's formula.

Nevertheless, numerical evaluation of Eq. (7) shows that the second order terms $(\beta^2 - \alpha^2)/k_0^2$ inside the square root may contribute significantly to n_{eff}, for large particles at large angles of incidence, even in case the density is low. But the effective refractive index with the inclusion of the second order terms depends now on the angle of incidence. If the system were boundless with uniformly distributed random inclusions, all directions should be equivalent, that is, the system must be isotropic, and the effective refractive index should not depend on the direction of propagation. In relation with this pretending inconsistency, please note that the expression given in Eq. (1) does not come from an effective-medium approach, it comes rather from the solution of multiple-scattering equations, where the expression for k_z^{eff} given in Eq. (2) can be regarded as an auxiliary function in the calculation and it is actually deprived of precise physical content. Therefore, the use of Eq. (6) in the interpretation of our experimental data does not imply the utilization of an effective-medium concept, and the inconsistency mentioned above appears when one tries to view the auxiliary function k_z^{eff} as the one corresponding to the propagation wavevector in a true effective- medium approach.

In order to clarify the source of these so called inconsistencies with the concepts related with an effective-medium approach, below we perform a thorough analysis of the electromagnetic response of a colloidal system and we conclude that for large inclusions this response is actually non-local, and that not recognizing this fact has been the main source of all problems related to the mishandling of effective-medium concepts in these kind of systems.

The Isotropic Effective-Medium Model

We will compare the results obtained from Eq. (6) with those coming from the simplest effective-medium approach which is the use of Fresnel relations for non-magnetic media with the effective refractive index given in Eq. (8), that is,

$$r_{iso}^{TE} = \frac{n_m \cos\theta_m - n_{eff}\sqrt{1-\left(n_m^2/n_{eff}^2\right)\sin^2\theta_m}}{n_m \cos\theta_m + n_{eff}\sqrt{1-\left(n_m^2/n_{eff}^2\right)\sin^2\theta_m}}, \tag{9a}$$

and

$$r_{iso}^{TM} = \frac{n_{eff} \cos\theta_m - n_m\sqrt{1-\left(n_m^2/n_{eff}^2\right)\sin^2\theta_m}}{n_{eff} \cos\theta_m + n_m\sqrt{1-\left(n_m^2/n_{eff}^2\right)\sin^2\theta_m}}. \tag{9b}$$

When the particles radii are very small compared to the incident wavelength, the particles scatter light isotropically. One can show that for dilute systems of particles, when these are small enough, Eq. (6) reduces to Eqs. (9a) and (9b) for j = 1 and 2, respectively [1]. However, for particles with radii not small compared to the wavelength, r_{hs} differs appreciably from r_{iso} for both polarizations [1,2]. We will refer to the approximations in Eqs. (9a) and (9b) as the isotropic effective- medium model.

The Coherent Reflection Coefficient in an Internal-Reflection Configuration

In an internal-reflection configuration we have an additional interface, namely, the incident-medium – matrix interface as shown in Fig. 2. Let us assume that the incidence medium is non-absorbing and has a refractive index, n_1. We denote by g the distance between the incidence-medium – matrix interface and the interface with the half-space of particles. We may regard the system as a three-media system, media 1 corresponds to the incidence medium, medium 2 corresponds to the matrix alone, and medium 3 is the composite medium made of particles embedded in the matrix. Then we can solve the reflection at the compound interface using the well known formula for reflection from a film on a substrate.

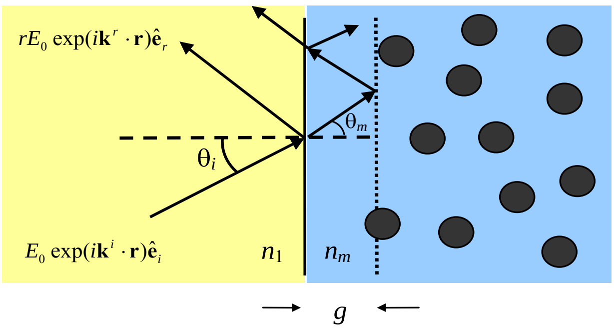

FIGURE 2. Geometry in the internal reflection configuration.

Note that the interface with the half-space of particles corresponds to a plane for which the centers of all particles lie to the right of it. Then a particle on the surface, that is, with its center on the surface, extends one radius, a, to the left of the interface. Therefore, the minimum possible value of g is one particle radius. If the particles do not interact with the surface so that the probability density of finding the center of any sphere is uniform throughout the half-space, including the region near the surface, we can assume that $g = a$. Therefore, the coherent reflection coefficient, r, from a random half-space of particles in an internal-reflection configurations is,

$$r = \frac{r_{12}^{Fresnel} + r_{hs}(\theta_m)\exp(2in_2k_0\cos\theta_m a)}{1 + r_{12}^{Fresnel} r_{hs}(\theta_m)\exp(2in_2k_0\cos\theta_m a)}, \quad (10)$$

where $r_{12}^{Fresnel}$ is the usual reflection coefficient at the 1-2 interface given by Fresnel's relations, and

$$\theta_m = \arcsin\left(\frac{n_1}{n_m}\sin\theta_i\right). \tag{11}$$

obeys Snell's law. Numerical evaluation of Eq. (10) shows that if the second order terms in the denominator of the expression of r_{hs} in Eq. (6) are dropped, the angle derivative of r becomes discontinuous at the critical angle of the interface between the incidence medium and the matrix alone, that is, at $\theta_i = \sin^{-1}(n_m/n_1)$, even in the presence of particles. The discontinuity increases as the particle radii increases. The discontinuity is non physical and indicates that these terms must be kept in our model for an internal-reflection configuration.

Here again we may compare our approach with the isotropic effective-medium model. In the latter case, one assumes that Fresnel's relations are valid for the interface between medium 1 and medium 3. Specifically, we write equations (9a) and (9b) but with n_m replaced by n_1. With regard to determining the effective refractive index with a modern critical angle refractometer, we have that errors may occur whenever the scattering theory model differs appreciably from the isotropic effective medium model.

The scattering-theory model was derived for a monodispersed system of spheres. The half-space reflection coefficient in Eq. (6) can be extended to polydispersed systems of spheres and non-spherical particles simply by replacing the quantities: $\gamma S(0)$ and $\gamma S_j(\pi - 2\theta_m)$ by their average with respect to particle size and orientation. When a matrix surface is introduced to the model, the size distribution and orientation density of probability function will be affected close to the surface. However, in dilute systems of particles these surface effects may be neglected.

EXPERIMENT

To test the validity of our model we will compare the results derived from it directly with experiment. In this section we compare our experimental internal-reflectance data from particles dispersed in water with both, the scattering-theory and the isotropic effective-medium models.

Our experimental setup is drawn in Fig. 3. It consists of a glass (BK7) dove prism mounted on top of a high precision goniometer. The dove prism geometry is appropriate to measure the reflectance about the critical angle of a glass-water interface, where the contribution of the particles is expected to be largest. A plastic ring was clamped between the base of the prism and a glass slab to form the sample container. We used a red laser diode of wavelength λ_0 = 0.633 μm. The index of refraction of the prism at this wavelength is n_1 = 1.5151. The reflectance curves were taken by rotating the goniometer in steps of one degree.

Initially, the container was filled with distilled water and the angle of incidence was fixed close to the critical angle. A reflectance curve with pure water was taken about the critical angle as a reference. Then, the water was replaced by the colloidal sample and a reflectance curve was taken over the same angular range. All reflectance curves were normalized with respect to the reflection signal just behind the critical angle with distilled water. The angle of incidence to the base of the prism, θ_i, was calculated using Snell's law of refraction at the entrance face of the prism. Corrections to the reflection signal at the different angles of incidence due to Fresnel reflection losses at the entrance and exit interfaces of the prism were done. Also, the contribution of diffuse light was checked to be negligible in all measurements.

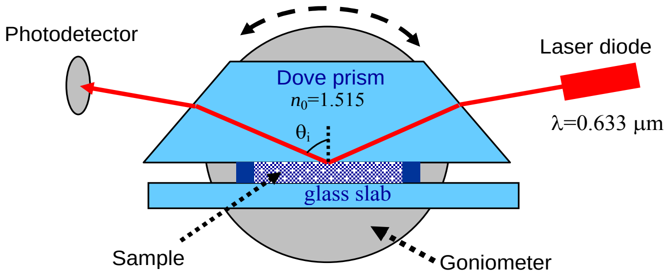

FIGURE 3. Schematic of the experimental setup.

We performed measurements with two types of particles: i) spherical latex particles with a nominal value of the refractive index of n_p = 1.47-1.48 and a mean radius of $\langle a \rangle$ = 234 nm; and ii) TiO_2 crystallites (Rutile) with a refractive index of $n_p \approx 2.8$ and a mean radius of $\langle a \rangle \approx 112.5$ nm. The particles size distribution for the latex was determined by dynamic light scattering using a commercial apparatus. The polydispersity was moderate in this case. The TiO_2 particles we used had been previously characterized [15] by electron microscopy. The size distribution followed a log-normal distribution with $\sigma \approx 1.33$. In the preparation of the samples with TiO_2 particles a surfactant was added in order to prevent (or reduce) the formation of aggregates.

Experimental reflectance data for latex particles and for two values of the filling fraction are shown in Fig. 4. Also shown in the figure are curves calculated with the scattering-theory model and the isotropic effective-medium model. To evaluate numerically both models we used Mie theory to calculate the scattering matrix elements. The values used for the theoretical curves were adjusted to fit best the experimental data. The parameters varied in the fitting procedure were a, n_p, n_m, and f. The values of a, n_p and n_m were restricted to be close to their nominal values of ~1.47-1.48, ~1.33, and 234 nm, respectively. Each parameter was adjusted individually by keeping the other parameters fixed close to its nominal value. The order in which the parameters were adjusted did not change appreciably the final result.

We can appreciate that the scattering theory model reproduces fairly well the experimental data. The particle size corresponds to the average particle size determined by dynamic light scattering. The adjusted values of the refractive index of the matrix, 1.3333 and 1.3355 for f = 5.7% and 8.7%, respectively, differ from that of pure water at the laser wavelength, that is, 1.33128. The reason is that some monomer was left dissolved in the water after the polymerization reaction by which the particles were formed. To test this hypothesis we filtered one of the samples and measured the refractive index of the remaining transparent liquid. We found that it was indeed larger than that of pure water by an amount close to the one used in the adjusted values. We also performed measurements of the beam attenuation due to scattering by transmission through a 1 mm thick glass container filled with diluted samples. In this case, the attenuation factor should be given by: $\exp[-2k_0\mathrm{Im}(n_{eff})]$, which is Lambert-Beer's law. The measured values of the beam attenuation were correctly reproduced, within the experimental uncertainty, by the factor $\exp[-2k_0\mathrm{Im}(n_{eff})]$ with n_{eff} calculated using the values of a, n_p, n_m obtained in Fig. 4, and a filling fraction, f, consistent with the value of f obtained in Fig. 4 reduced by the same factor by which the sample was diluted.

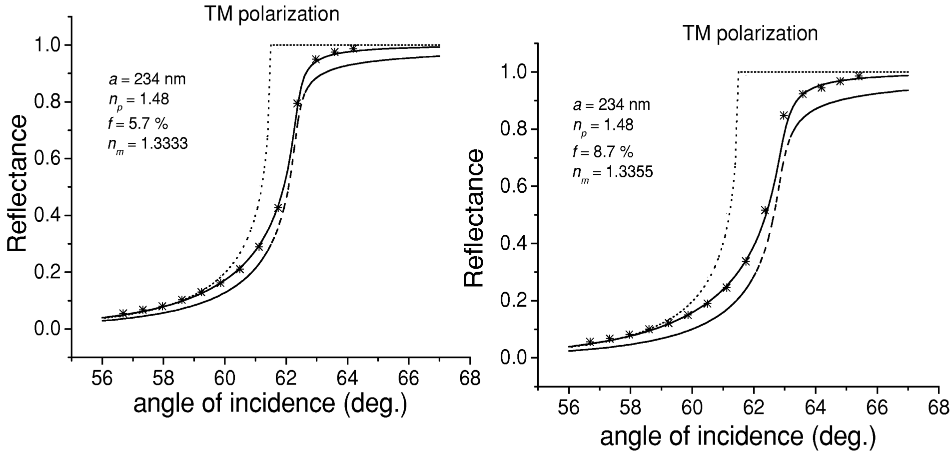

FIGURE 4. Reflectance data for TM polarized light with latex colloid (stars); scattering theory model (full line); reflectance with pure water (dotted line); isotropic effective-medium model (dashed line).

In Fig. 4 we also plot the reflectance curve predicted by the isotropic effective-medium model. Noticeable differences can be appreciated over the whole angular range shown. Attempts to adjust the effective medium model showed that it could not reproduce the experimental data. We performed an additional experiment with the latex particles at a filling fraction of $f = 14\%$. In this case neither model were able to reproduce the experimental data.

In Fig. 5 we show similar results for suspensions of TiO_2 particles in water. In this case the volume filling fraction was much lower since these particles disperse light more efficiently than the latex particles. The particle suspensions were prepared aiming to a somewhat larger value of the filling fraction. However, most probably not all of the particles could be dispersed. To compare with the scattering theory model and the isotropic effective approximation we assumed the particles were spherical. In this case we adjusted only three parameters, a, n_p, and f. The refractive index of the matrix was taken as that of pure water at the wavelength of the laser. We again see that the scattering theory model reproduces well the experimental data. The particle radius, a, was initially fixed close to the average particle radius determined by electron microscopy, $\langle a\rangle$. The adjusted value of a remained close to $\langle a\rangle$ and the refractive index of the particles agrees well with the refractive index of TiO_2 – Rutile.

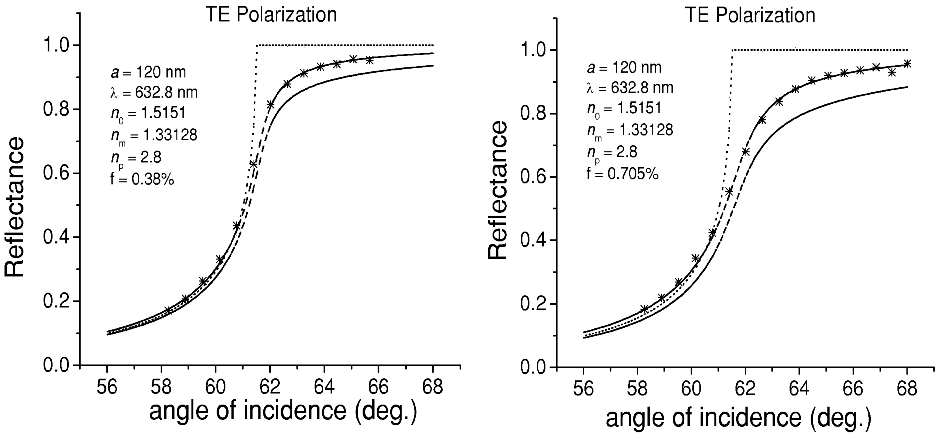

FIGURE 5. Reflectance data for TE polarized light with TiO_2 particle suspension (stars); scattering theory model (full line); reflectance with pure water (dotted line); isotropic effective medium model (dashed line).

The experimental results support the validity of the scattering-theory model and confirm that Fresnel relations are not satisfied with a turbid medium when the particles are not small compared to the wavelength. Nevertheless, the experiments also show that the high sensitivity to changes in the effective refractive index of the reflectance in an internal reflection configuration and about the critical angle is still there. This means that, in practice, it is still convenient to obtain reflectance curves about the critical angle; but, instead of obtaining the effective refractive index from the inflexion point of the reflectance curve based on the Fresnel relations, one should fit the scattering-theory model to the reflectance curve and obtain a, n_p, n_m, and f. Once knowing these values, if desired, one can calculate the effective refractive index using the van de Hulst formula Eq. (8).

NON-LOCAL EFFECTIVE RESPONSE

We may ask ourselves at this point, what is the physical reason why Fresnel relations are not valid at the interface of a turbid medium. To deal with this question we must take from the start an effective-medium approach and look into the nature of the effective-medium response of the system when particles are not small compared to the wavelength of radiation. We should recall that the effective medium refers only to the behavior of the coherent component of light. We start by writing the scattered field of an isolated particle illuminated by an arbitrary exciting field, $\mathbf{E}^{exc}$, in terms of the so called transition operator $\overline{\mathbf{T}}(\mathbf{r},\mathbf{r}')$ [3],

$$\mathbf{E}^{S}(\mathbf{r};\omega)=\int d^3r'\int d^3r''\overline{\mathbf{G}}\cdot(\mathbf{r},\mathbf{r}';\omega)\cdot\overline{\mathbf{T}}(\mathbf{r}',\mathbf{r}'';\omega)\cdot\mathbf{E}^{exc}(\mathbf{r}'';\omega)\,. \qquad (12)$$

where ω denotes the Fourier component in frequency space. We will assume, for simplicity in the presentation that the matrix is vacuum, thus here $\overline{\mathbf{G}}$ denotes the free

Green's function propagator. Also we will omit in the following the explicit dependence on ω unless it becomes necessary or illustrative.

Now, let us consider an ensemble of N particles illuminated by an incident wave, $\mathbf{E}^{inc}$. The incident wave is multiply scattered between the particles. Therefore, the exciting field to any specific particles is the incident wave plus the field radiated from all other N - 1 particles. It is possible to set up a system of N coupled equations relating the exciting field of each particle to the exciting field of all other particles plus the incident wave. Once solving for the exciting field for each particles one may calculate the total field as the incident field plus the field radiated by all the particles,

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}^{inc}(\mathbf{r}) + \sum_{p=1}^{N} \int d^3r' \int d^3r'' \overline{\mathbf{G}} \cdot (\mathbf{r}, \mathbf{r}') \cdot \overline{\mathbf{T}}(\mathbf{r}' - \mathbf{r}_p, \mathbf{r}'' - \mathbf{r}_p) \cdot \mathbf{E}_p^{exc}(\mathbf{r}'') \qquad (13)$$

where $\mathbf{r}_p$ is the position of the center of the p-th particle and $\mathbf{E}_p^{exc}$ is the field exciting the p-th particle. The sources of the scattered electric field are the induced currents within the particles. One could actually write the scattered field as,

$$\mathbf{E}^S(\mathbf{r}) = i\omega\mu_0 \int d^3r' \overline{\mathbf{G}} \cdot (\mathbf{r}, \mathbf{r}') \cdot \mathbf{J}_{ind}(\mathbf{r}'), \qquad (14)$$

and recognize that the induced current density is given by

$$\mathbf{J}_{ind}(\mathbf{r}) = \frac{1}{i\omega\mu_0} \sum_{p=1}^{N} \int d^3r'' \overline{\mathbf{T}}(\mathbf{r}' - \mathbf{r}_p, \mathbf{r}'' - \mathbf{r}_p) \cdot \mathbf{E}_p^{exc}(\mathbf{r}''). \qquad (15)$$

Now, let us look at the solution of this problem in the so called effective-field approximation [3]. In this case one assumes that the exciting field to each particle is equal to the average of the total field, that is,

$$\mathbf{E}^{exc}(\mathbf{r}) \simeq \langle \mathbf{E}(\mathbf{r}) \rangle . \qquad (16)$$

The average field, that is, the coherent wave, at any point in space is obtained by taking the configurational average of Eq. (13). Then, in the effective-field approximation, the coherent wave satisfies the following integral equation

$$\langle \mathbf{E}(\mathbf{r}) \rangle = \mathbf{E}^{inc}(\mathbf{r}) + \int d^3r' \int d^3r'' \overline{\mathbf{G}} \cdot (\mathbf{r}, \mathbf{r}') \cdot \left\langle \sum_{p=1}^{N} \overline{\mathbf{T}}(\mathbf{r}' - \mathbf{r}_p, \mathbf{r}'' - \mathbf{r}_p) \right\rangle \cdot \langle \mathbf{E}(\mathbf{r}'') \rangle, \qquad (17)$$

and the induced currents that give rise to the coherent scattered field are given by

$$\langle \mathbf{J}_{ind}(\mathbf{r}') \rangle = \frac{1}{i\omega\mu_0} \int d^3r'' \left\langle \sum_{p=1}^{N} \overline{\mathbf{T}}(\mathbf{r}' - \mathbf{r}_p, \mathbf{r}'' - \mathbf{r}_p) \right\rangle \cdot \langle \mathbf{E}(\mathbf{r}'') \rangle. \qquad (18)$$

If we now define a generalized average polarization field by,

$$\langle \mathbf{J}_{ind}(\mathbf{r}) \rangle = -i\omega \langle \mathbf{P}(\mathbf{r}) \rangle, \qquad (19)$$

we can identify an expression for the effective electric susceptibility for the coherent wave. We call this polarization field: "generalized", because its sources are all the induced currents, including those closed currents that might give rise to magnetic effects. The generalized polarization field is related to the average electric field through a generalized susceptibility kernel $\overline{\boldsymbol{\chi}}$. In this case we have a linear relation of the form,

$$\langle \mathbf{P}(\mathbf{r}') \rangle = \varepsilon_0 \int d^3r'' \overline{\boldsymbol{\chi}}(\mathbf{r}', \mathbf{r}'') \cdot \langle \mathbf{E}(\mathbf{r}'') \rangle, \qquad (20)$$

indicating that the generalized susceptibility is actually non-local. That is, the effective polarization vector at one point in space depends on the electric field at other points in space. We can identify the non-local generalized susceptibility as,

$$\overline{\boldsymbol{\chi}}(\mathbf{r}',\mathbf{r}'') = \frac{1}{i\omega\mu_0\varepsilon_0}\left\langle \sum_{p=1}^{N} \overline{\mathbf{T}}(\mathbf{r}'-\mathbf{r}_p, \mathbf{r}''-\mathbf{r}_p) \right\rangle. \tag{21}$$

If the spatial distribution of particles is, on the average, translationally invariant, we have that $\overline{\boldsymbol{\chi}}(\mathbf{r}',\mathbf{r}'') = \overline{\boldsymbol{\chi}}(\mathbf{r}'-\mathbf{r}'')$. Then transforming Eq. (20) to momentum space and writing back the dependence on frequency, one has

$$\langle \mathbf{P} \rangle(\mathbf{k},\omega) = \varepsilon_0 \overline{\boldsymbol{\chi}}(\mathbf{k},\omega)\cdot\langle \mathbf{E} \rangle(\mathbf{k},\omega). \tag{22}$$

This is the main result of this section: the effective response of a system of spheres is non-local and therefore it presents spatial dispersion. It can be seen that here the non-local length is the radius of the spheres. One can project the non-local generalized susceptibility $\overline{\boldsymbol{\chi}}(\mathbf{k},\omega)$ into a longitudinal and a transverse components and one can relate these components to the usual non-local dielectric $\varepsilon(k,\omega)$ and magnetic $\mu(k,\omega)$ responses. This implies that one must accept the appearance of an effective magnetic susceptibility, even if the components of the medium are non-magnetic.

Unfortunately, when one introduces an interface, the system is no longer translational invariant and one cannot use Eq. (22) directly. It has been shown before in problems related to non-local optics that when a system has a non-local response the regular boundary conditions used in continuum electrodynamics are insufficient, and one actually requires additional boundary conditions [16]; thus Fresnel's relations are no longer valid. This is the physical reason why the coherent wave does not satisfy anymore the Fresnel's relations at a plane interface with a suspension of particles when these are not small compared to the wavelength. In future publications we plan to provide a detail account of the non-local response of a system of spheres and investigate the magnetic effects.

CONCLUSIONS

Here we provide a scattering theory model for light reflection from a turbid colloid in an internal reflection configuration. We compare the results of our model with experimental measurements of the coherent reflectance of light from a turbid suspension of latex and TiO_2 particles in water, in an internal reflection configuration. We found that our model can reproduce the experimental data whereas an isotropic effective medium model based on the Fresnel relations with an effective refractive index cannot. Since the Fresnel relations are not valid for the coherent reflection of light from a plane the interface of a turbid colloid when particles are large we may conclude that it is not possible to determine the effective refractive index of a colloidal suspension of large particles by a critical angle refractometer. By large particles we mean particles which are not small compared to the wavelength of incident radiation. Nevertheless the high sensitivity of the reflectance about the critical angle of the incidence medium – matrix interface to variations of the effective refractive index is still there. Therefore, a possibly convenient method to characterize turbid colloids is by measuring the coherent reflectance versus angle of incidence about the critical angle but instead of calculating the refractive index from the inflexion point of the curve, as it is regularly done with homogeneous media, one should fit the scattering theory model to the experimental curve to obtain the particles size, their refractive index, and the density of particles. Then, if desired, one may calculate the effective refractive index. We also show that the effective electromagnetic response of an ensemble of particles is actually no-local. This is the physical reason why the Fresnel relations do not describe the coherent reflectance of a turbid colloid when the particles are large.

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