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Optical reflectance of a composite medium with a sparse concentration of large spherical inclusions

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We analyze the coherent reflection of a half-space of a composite material consisting of an homogeneous matrix with spherical inclusions. We pay attention to the case where the radius of the particles is comparable to the wavelength of the incident radiation. We consider a simple model for the interface of the composite and present numerical calculations to illustrate the contribution of the embedded particles to the optical reflectance and discuss surface effects.

1 Introduction

Composite and colloidal materials are becoming increasingly important in modern technology. These materials are designed and constructed to have physical properties that cannot be found in homogeneous materials. When two or more materials are mixed together at a micro- or nano-scale, the resulting composite has physical properties that are different from those of the constituent materials. In particular, their optical properties might be substantially different.

Here we will consider a simple type of composite which consists of discrete spherical inclusions embedded within an otherwise homogeneous matrix of a different material. When the size of the particles is small compared to the wavelength of the incident radiation, λ, one can use well-established approximations to calculate an effective index of refraction, such as the Maxwell Garnett or Bruggeman effective-medium theories [1, 2]. When the wavelength of light within the inclusions is no longer very large compared to the size of the particle, extended-effective medium theories are available [3]. Extended-medium theories include a dynamical correction to the calculation of the polarization and magnetization of the isolated particles providing effective optical coefficients, that is, an effective electrical permittivity and an effective magnetic permeability. Whenever these extended-effective-medium theories provide an adequate approximation to the effective optical coefficients, one may use them freely in the laws of continuous electrodynamics. In this case the effective-medium theory is called: unrestricted. For instance, one may use the Fresnel reflection coefficients with the resulting effective optical coefficients to calculate the reflection of a plane wave from a flat surface of the composite. However when the size of the particles is comparable to the wavelength of incident radiation, extended-effective-medium theories are

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no longer valid and it might not be possible to use, in the usual way, the effective-optical coefficients within the laws of continuous electrodynamics. In the case of large particles, one must solve the wave multiple-scattering problem and take configurational averages to calculate the macroscopic fields (also called average or coherent fields) and quantities such as their effective propagation wave vector or the reflection coefficient of a half space of the composite.

In previous works [4, 5] we have derived the reflection coefficient of the coherent field from a half-space with a plane interface of a sparse, random, uniformly-distributed ensemble of spherical particles in vacuum by two different procedures. In Ref. [4] we first calculate the average scattered field from an ensemble of particles located at random within a thin slab using the single scattering approximation. Then we took account of multiple scattering by modelling the half space as a semi-infinite pile of thin slabs to determine the propagation wave vector of the average wave travelling between the thin slabs, as well as the reflected average field. We found that in order to describe correctly the reflection of light from a half-space with effective optical properties, the effective medium should have besides an effective electric permittivity an effective magnetic permeability. Furthermore both of these effective optical coefficients turned out to depend on the polarization of the incident beam and on the angle of incidence. We reached the same conclusions and derive the same expressions for the optical effective coefficients in Ref. [5], where we start by setting up the multiple-scattering system of equations and solving for the average propagating and reflected fields using the effective-field approximation. Some examples were investigated numerically for particles in vacuum. One can show that when the radius of particles becomes smaller than the incident wavelength, the reflection coefficients found in Refs. [4, 5] reduce to the Fresnel reflection coefficients for an effective medium in which the effective magnetic permeability reduces to the one of vacuum. This means that in this limit the effective medium corresponding to a composite with nonmagnetic components is nonmagnetic, that is, it does not posses a dynamic effective magnetic response. Although this is true for small inclusions, what we have shown in Refs. [4, 5] is that this assessment is no longer true when the size of the inclusion is comparable to the wavelength of the incident radiation.

More accurate approximations to the effective propagation constant and half-space reflection coefficients from a random distribution of particles, based on multiple scattering theory and the so called quasi-crystalline approximation, have been put forth [6]. The quasi-crystalline approximation can be used to model dense ensembles of particles. However calculations with the quasi-crystalline approximation are quite more complicated. Our formulas are substantially simpler and allow us to investigate the main effects related to the coherent reflectance of a composite with spherical particles in a more transparent way, although we are limited to a low concentration of particles.

In this paper we use the previously derived formulas to analyze and discuss the reflectance from a half-space of a composite material consisting of a homogeneous matrix with a sparse, randomly-distributed ensemble of large spherical-particles, embedded within the matrix. First we review briefly the main results regarding the coherent reflectance of a half-space of a random ensemble of particles. Then we discuss the surface model for a composite material and then we present some numerical calculations of a system of particles with a high refractive index embedded within a polymeric-type matrix. Finally we present our conclusions.

2 Reflectance from a half-space of spherical particles

2.1 In vacuum

In previous works, we have derived the coherent reflection coefficients for a plane wave incident at oblique angles on a half space of a sparse concentration of identical spherical particles with refractive index n_p, embedded in vacuum. The reflection coefficient of the coherent wave can be written as

$$r_{hs} = \frac{-i\gamma S_m(\pi - 2\theta_i)}{\cos^2\theta_i + i\gamma S(0) + \sqrt{\cos^4\theta_i + 2i\gamma S(0)\cos^2\theta_i}}, \tag{1}$$

where θ_i is the angle of incidence, $S_m(\theta)$ are the elements of the 2×2 amplitude scattering matrix of an isolated particle [7], $m = 1$ for TE polarization, and $m = 2$ for TM polarization. $S(0) = S_1(0) = S_2(0)$ is the forward scattering amplitude, and

$$\gamma \equiv \frac{3f}{2x^3}, \tag{2}$$

where $f = \rho 4\pi a^3/3$ is the volume filling fraction of the spheres, ρ is the number density of spheres, a is the radius of the particles and $x = ka$ is the size parameter. This reflection coefficient is a good approximation for all angles of incidence but for a low density of particles (in the range of a few percent of volume fraction, depending on radius of the particles). The region of validity of this approximation in the space of variables (θ_i, f, n_p) is not well known to date, but a simple test to estimate the confidence of the approximation has been described in Ref. [4]. The effective index of refraction of the coherent wave travelling within the ensemble of particles was found to be, to lowest order in γ,

$$n_{\text{eff}} \approx 1 + i\gamma S(0), \tag{3}$$

which is the same expression as the one derived by van de Hulst, long time ago [8]. As mentioned above, we have also found that if one wants to interpret the ensemble of particles as a half-space of an effective (homogeneous) medium, then one is forced to accept an effective magnetic permeability in addition to an effective electric permittivity in order to reproduce Eq. (1) from the Fresnel reflection coefficients. These effective optical coefficients depend on both, the state of polarization, and the angle of incidence. Nevertheless, it is not necessary to interpret the ensemble of particles as an effective medium. One can always work directly with the expression for the reflection coefficient given by Eq. (1) and with the expression for the effective index of refraction given by Eq. (3).

2.2 In a matrix

The results obtained for the reflection coefficient of a half space of particles in vacuum can be easily extended to a half space of particles embedded in a boundless homogeneous matrix with optical coefficients ε_m and μ_m. We assume that both coefficients ε_m and μ_m are real, so that there is no absorption within the matrix. Then one can evaluate the scattering amplitudes for a particle considering that it is surrounded by a homogeneous medium. To recall this fact we will denote the scattering amplitude elements for particles embedded in a medium other than vacuum by $S'_m(\theta)$. We should also replace k for $n_m k$, with $n_m = \sqrt{\varepsilon_m \mu_m}$ in the expression for γ. Again we will use a prime to remind us about this fact. Then we have,

$$\gamma' \equiv \frac{3f}{2x'^3} = \frac{3f}{2(n_m ka)^3}. \tag{4}$$

Thus, the half space reflection coefficient for a plane wave traveling within the matrix and incident at an angle θ_m to a half space of particles embedded in the same matrix, is written as

$$r'_{hs} = \frac{-i\gamma' S'_m(\pi - 2\theta_i)}{\cos^2\theta_i + i\gamma' S'(0) + \sqrt{\cos^4\theta_i + 2i\gamma' S'(0)\cos^2\theta_i}}. \tag{5}$$

The effective index of refraction to first order in γ is,

$$n_{\text{eff}} \approx n_m[1 + i\gamma' S'(0)]. \tag{6}$$

3 Surface model for a half space of a composite material

If we consider the coherent reflection of a plane wave travelling in a homogeneous medium of refractive index n_0 that is incident at an angle θ_i on a half space of a composite material consisting of a homogeneous material with spherical inclusions, we must take care of modelling the surface carefully. We may

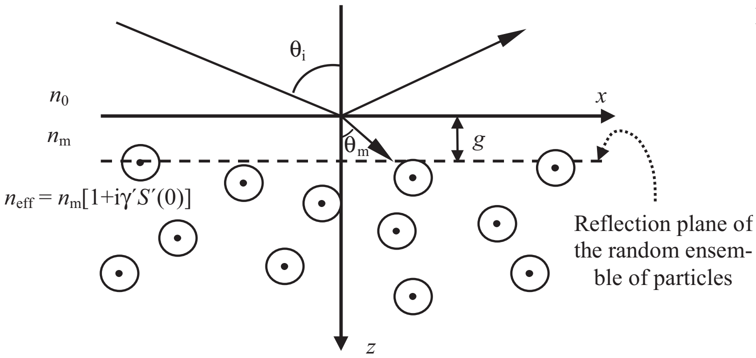

Fig. 1 Geometry of the problem.

have different situations. For instance, the particles may reach the surface of the homogeneous matrix and be partially outside the matrix, or the particles may be repelled from the surface leaving a slab of homogeneous matrix between the vacuum and the half space of the composite. Also, the surface of the matrix may have some roughness which will also affect the coherent reflection coefficient. All these effects may have a strong influence on the coherent reflectance from a composite that might be comparable or might be even larger than the contribution from the embedded particles. Therefore, in general, one must specify the surface conditions in order to have a reliable model for the coherent reflectance from a composite material.

Here we will assume that all the particles are completely embedded within the matrix. Thus, the minimum possible distance from the centre of the particles to the surface of the matrix is one particle radius. We will then model the system as a three-layered system as shown in Fig. 1. That is, we consider the composite material as a slab of homogeneous matrix of width g in contact with a half-space of homogeneous matrix with particles embedded in it. We must recall that the reflection coefficient of a half space of particles in Eq. (5) assumes that the centre of the particles are uniformly distributed on one side of a mathematical plane. This mathematical plane may be regarded as the reflection plane of the half space of particles, that is, as the surface of an effective homogeneous medium.

The relation between the angle of incidence to the composite, θ_i, and the angle of incidence to the half space of particles embedded in the matrix, θ_m, is given by Snell's law at the interface outside-medium/matrix, that is, $n_0 \sin \theta_i = n_m \sin \theta_m$. The coherent reflection coefficient from a half-space of the composite matrix material, r, is obtained by calculating the reflection from the system: outside-medium/homogeneous-matrix/composite-matrix. This corresponds to a thin slab of homogeneous matrix on a composite-matrix substrate. The reflection coefficient is

$$r = \frac{r_m + r'_{hs} \exp(2ikn_m \cos \theta_m \ g)}{1 + r_m r'_{hs} \exp(2ikn_m \cos \theta_m \ g)} \tag{7}$$

where r_m is the reflection coefficient of the outside-medium / homogeneous-matrix interface, and g is the width of the homogeneous-matrix slab (i.e., the distance to the reflection plane from the half space of particles). The latter equation may be modified without much difficulty to include, when important, the effect of roughness on the matrix interface by using a suitable model (see for example Ref. [9]), and g may be adjusted to accommodate on the boundary conditions some of the specific features of the density of particles. If the matrix interface is considered flat, then r_m is calculated with the Fresnel reflection coefficients. As already said, we will consider that the matrix has a real index of refraction and use Eq. (5) in Eq. (7). In general, when the particle radius is not small compared to the wavelength, the oscillating phase term: $\exp\left(2ikn_m \sqrt{n_m^2 - n_0^2 \sin^2 \theta_i} \ g\right)$, will have a noticeable effect and will be mixed with the behaviour of r'_{hs} which is mostly dependent on the particles properties.

In this paper we will consider only the case of external reflection, that is when $n_0 < n_m$. An example could be $n_0 = 1$ (air) and $n_m = 1.33-1.6$ (water, glass, or some kind of polymer). In this case, the refraction angle θ_m never approaches grazing, and r'_{hs} is always very small for a sparse concentration of particles. We will also restrict our analysis to the case of a non-magnetic matrix, that is, $\mu_m/\mu_0 = 1$. In this case, there is a Brewster's angle only for TM polarization. At an angle of incidence equal to Brewster's angle of the outside-medium/matrix interface we have that $r_m^{\mathrm{TM}} = 0$ and

$$r^{\mathrm{TM}} = r_{hs}'^{\mathrm{TM}} \exp\left(2ikn_m \cos\theta_m\, g\right).$$

The reflectance is given by $R = |r|^2$. Thus at the Brewster's angle of the matrix interface we have that $R^{\mathrm{TM}} = R_{hs}'^{\mathrm{TM}}$ is due to the presence of the particles alone. On the other hand, with the exception of angles near Brewster's angle, corresponding to the n_0/n_m interface in TM polarization, we can expand r as

$$r \simeq \left[r_m + r'_{hs} \exp\left(2ik\sqrt{n_m^2 - n_0^2 \sin^2\theta_i}\, g\right)\right]\left[1 - r_m r'_{hs} \exp\left(2ik\sqrt{n_m^2 - n_0^2 \sin^2\theta_i}\, g\right)\right]$$

$$\simeq r_m + (1 - r_m^2)\, r'_{hs} \exp\left(2ik\sqrt{n_m^2 - n_0^2 \sin^2\theta_i}\, g\right). \tag{8}$$

The reflectance is given by

$$R = R_m + (1 - r_m^2)^2\, R'_{hs} + 2r_m(1 - r_m^2)\, \mathrm{Re}\left[r'_{hs} \exp\left(2ik\sqrt{n_m^2 - n_0^2 \sin^2\theta_i}\, g\right)\right]. \tag{9}$$

For a composite with a sparse distribution of particles, $|r'_{hs}| \ll 1$, we may neglect the second term on the right hand side, which is proportional to $R'_{hs} = |r'_{hs}|^2$ and keep only the third term on the right hand side which is proportional to r'_{hs}. Thus, having the particles embedded in a matrix may yield a larger contribution to the coherent reflection from the particles than when the particles are in vacuum, because in the reflectance there is now a linear term in r'_{hs}, which for a dilute system is much larger than $|r'_{hs}|^2$. Now, for grazing incidence $r_m \to 1$, thus the factor, $(1 - r_m^2)$, that appears in the second and third terms on the right hand side of Eq. (9) goes to zero. Therefore, the relative importance of the contribution to the reflection from the particles decreases as the angle of incidence increases towards grazing incidence.

4 Numerical results

We will restrict our calculations to a specific system in which the particles are non-magnetic, with a real refractive index $n_p = 2.8$ and embedded in a homogeneous, non-magnetic ($\mu_m = 1$) matrix with a real refractive index $n_m = 1.45$. These values of refractive index are close to those in a typical white paint. We will also consider a volume filling fraction of spheres of $f = 0.1$. It is always interesting to compare our results with an heuristic model obtained by substituting the effective refractive index given by Eq. (6) in the Fresnel reflection coefficient and ignoring any possible magnetic effect. That is, by considering that the half space of particles behaves as an effective medium equivalent to an ordinary, homogeneous, non-magnetic, material where $\varepsilon_{\mathrm{eff}} = n_{\mathrm{eff}}^2$. We will refer to this heuristic approximation as the isotropic approximation. For a meaningful comparison, the isotropic model should also consider the surface model discussed above. Thus, the isotropic approximation consists of using Eq. (7) with r'_{hs} calculated with the Fresnel coefficients upon assuming $\varepsilon_{\mathrm{eff}} = n_{\mathrm{eff}}^2$. One can show that as the particle radius decreases, the isotropic approximation coincides with our reflection formula. Thus, the difference between our results and those of the isotropic approximation will give us an idea of the magnetic effects inherent to our approach.

4.1 Shift of Brewster's angle

First, let us consider the effect of the embedded particles on the value of the Brewster's angle of the composite material. In Fig. 2 we plot the reflectance for TM polarization versus the angle of incidence in the vicinity of Brewster's angle of the matrix interface for different particle radii. We assume that the particles can barely touch the matrix interface, that is we used $g = a$. We show the reflectance curves for the matrix alone and for the composite using our formulas and the isotropic approximation. We can ap-

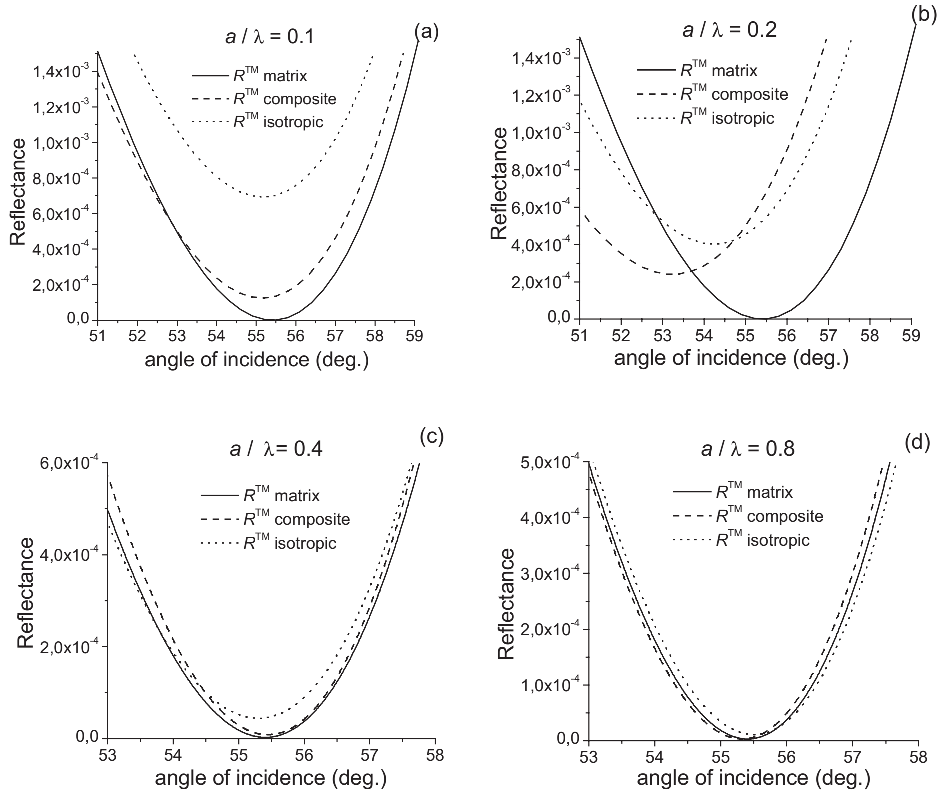

Fig. 2 TM reflectance versus angle of incidence about Brewster's angle of the matrix interface for different particle's radius, a) $a/\lambda = 0.1$, b) $a/\lambda = 0.2$, c) $a/\lambda = 0.4$, and d) $a/\lambda = 0.8$. The full curve is the reflectance for a homogeneous matrix, the dashed curve is the reflectance of the composite system for $g = a$, and the dotted line is for the isotropic model also with $g = a$.

preciate that the contribution of the particles shift the Brewster's angle from it's value for the matrix alone. The isotropic approximation predicts a different shift and overestimates the contribution of the particles to the reflectance. These plots also show that the contribution of the particles to the reflectance decreases as the particle radius increases, while keeping the filling fraction constant.

Surface roughness of the matrix interface would also result in a shift of the Brewster's angle [9]. Thus, if surface roughness is important, the shift of the Brewster's angle will have a contribution from both, the interface roughness and the embedded particles in the composite. Detailed modelling of the surface would be required in order to discern one effect from the other.

4.2 Contribution of the particles to the reflectance

In Fig. 3 we plot the fraction of the reflectance that is due to the presence of the particles as a function of the angle of incidence for two different values of the radius of the particles, $a/\lambda = 0.2$ and $a/\lambda = 0.4$, and for the case $g = a$. Fig. 3a is for TE polarization and Fig. 3b is for TM polarization. We can appreciate that the fraction of the reflectance due to the presence of the particles is larger for smaller angles of incidence. As already said, this fact can be understood from inspection of Eq. (9). In the graphs of Fig. 3 we also plot the curves predicted by the isotropic approximation and we can see that they are different in magnitude and even in sign for some angles of incidence. Thus, the isotropic approximation predicts already qualitatively erroneous results for particles as small as $a/\lambda = 0.2$. The plots in Fig. 3b reach a value of one at Brewster's angle of the matrix/air interface. This does not mean, however, that the contri-

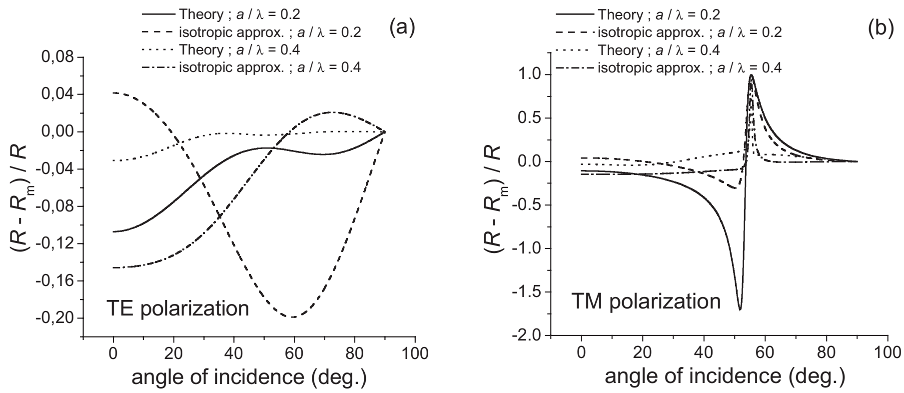

Fig. 3 Fraction of the reflectance due to the random ensemble of particles for two different particle radius, $a/\lambda = 0.2$ and $a/\lambda = 0.4$, a) for TE polarization and b) for TM polarization. All curves are for $g = a$.

bution to the reflectance coming from the particles is large, in fact, in the present example it is very small, as it can be seen in Fig. 2.

4.3 The surface parameter g

Now, we may inquire how strong is the effect of the surface features on the contribution of the particles to the reflectance. In Fig. 4 we plot the contribution of the particles to the total reflectance for three dif-

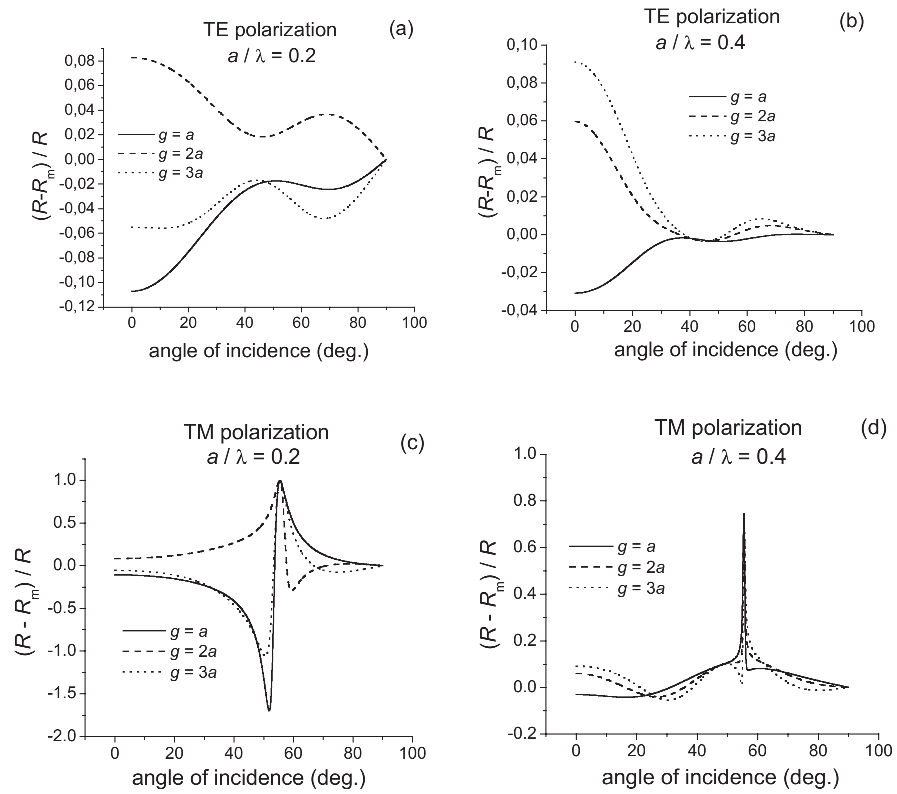

Fig. 4 Fraction of the reflectance due to the particles for different values of the g parameter, $g = a$, $2a$, and $3a$ and for two values of the particle's radius. a) $a/\lambda = 0.2$ and b) $a/\lambda = 0.4$ for TE polarization; c) $a/\lambda = 0.2$ and d) $a/\lambda = 0.4$ for TM polarization.

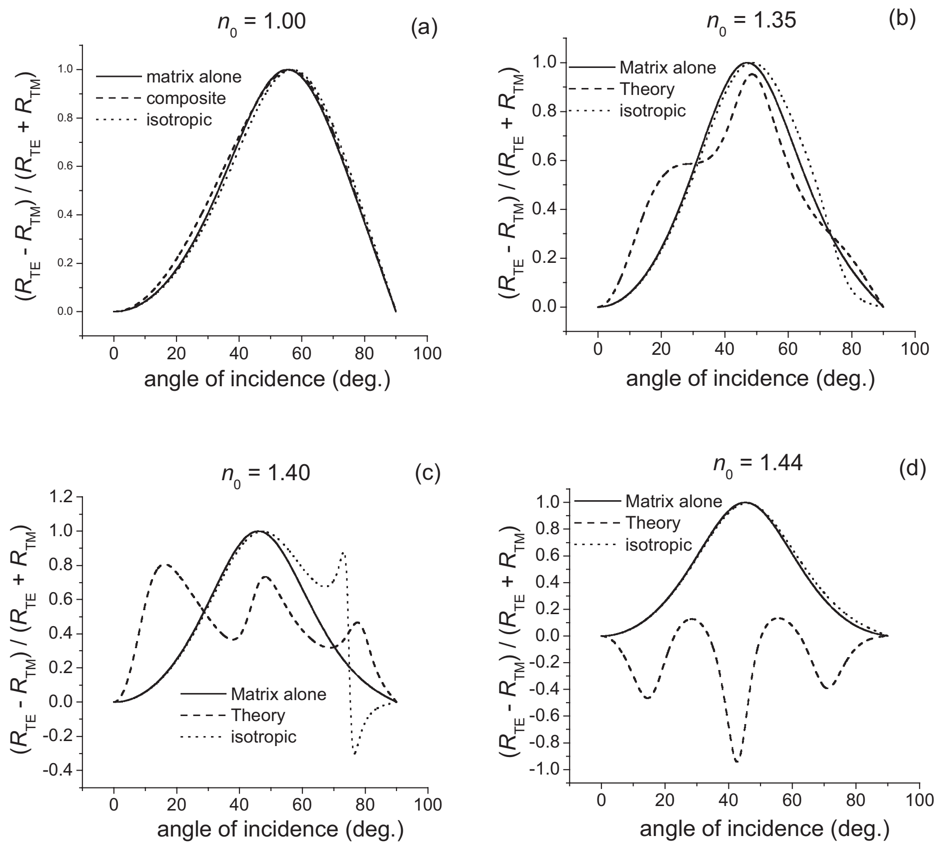

Fig. 5 Differential polarized reflectance $[(R_{TE} - R_{TM})/(R_{TE} + R_{TM})]$ for particles of radius $a/\lambda = 0.3$ and for different contrast between the outside medium and the matrix. a) $n_0 = 1.00$, b) $n_0 = 1.35$, c) $n_0 = 1.40$ and d) $n_0 = 1.44$. Curves were generated with $g = a$.

ferent values of g. The minimum value of g is a when one assumes that all particles are completely embedded within the matrix. However, due to surface conditions one may expect a transition region with lower or higher density of particles. Fig. 4 shows that the contribution of the particles to the reflectance changes significantly for most angles of incidence as g increases. This is an example of how the surface conditions affect the coherent reflectance in a composite.

4.4 Differential reflectance

One may be interested in obtaining information about the particles within the matrix from reflectance measurements. We have already shown in Ref. [5], that differential measurements of polarized reflectance, specifically $(R^{TE} - R^{TM})/(R^{TE} + R^{TM})$, of a half space of particles as a function of the angle of incidence can be qualitatively very different from measurements of half space of an ordinary homogeneous material. However, when the particles are embedded in a matrix, the contribution of the matrix interface to the differential measurements may be so large as to mask completely the effect of the particles on the differential measurements. This, of course, will be a function of the contrast between the external medium and the matrix. In Fig. 5 we plot the differential reflectance, $(R^{TE} - R^{TM})/(R^{TE} + R^{TM})$, versus the angle of incidence for different values of the refractive index of the external medium and for particles of radius $a/\lambda = 0.3$, and $g = a$. We also plot the curves for the isotropic approximation and for the matrix/air interface. For air as the external medium, $n_0 = 1$, the contribution of the particles is strongly masked by the matrix interface response. As the contrast of the external medium and the matrix is reduced, the differential curve for the composite material starts to differ strongly from that of the matrix alone. In Fig. 5c we see that, for a difference in refractive index between the matrix and the external medium of 0.1, the effect of the particles is already very noticeable and the differential curve of the composite material is qualitatively very different than that of the matrix alone. We can also see that the isotropic approximation differs qualitatively from the curve of the matrix alone. In the isotropic approximation this difference is due solely to the geometry of the surface model where we assume a slab of homogenous matrix of width $g = a$ between the matrix interface and the reflection plane of the particle ensemble. In Fig. 5d the difference between the refractive index of the external medium and that of the matrix is 0.01, and the effect of the matrix interface is now negligible on the differential measurement.

Figure 5 indicates that it may not be difficult to obtain information from the particles in a composite by matching the refractive index of the external medium to that of the matrix. In practice this should be possible by immersing the composite in a liquid mixture and adjusting its refractive index to be close to that of the matrix. Also, in this case the effect of surface roughness, if there is, will be reduced considerably.

5 Conclusions and discussion

We have analyzed the coherent reflectance of a composite material consisting of large spherical particles embedded in a homogeneous matrix. By coherent reflectance we mean the reflectance of the coherent or average field obtained from a configurational average, and by large particles we mean particles with radius comparable to the wavelength of radiation. In an experiment, the coherent reflectance would be measured as if one were dealing with an ordinary homogeneous material, that is, regarding the composite as an effective medium. In some cases, it may be necessary to subtract the contribution of the diffuse fields to the measurements.

In this paper we focused our attention on the surface model of a composite material. Physical restrictions in the surface region may have a strong influence on the coherent reflectance of a composite material. We considered a surface model in which the particles are completely surrounded by the matrix material. When the particles are located at random, except close to the surface, we can model the surface as slab of homogeneous matrix in-between the external medium and an effective medium consisting of the random ensemble of particles embedded in the matrix. The width of the slab should be specified based on a physical model of the interaction of the particles with the matrix interface.

In the graphs presented above, we assumed a flat matrix interface. In practice, when one deals with solid composites, the effect of the surface roughness may often be comparable or larger than the effect of the embedded particles. In our model of the surface of the composite, the surface roughness could be easily incorporated.

We showed that the presence of the embedded particles shifts the Brewster's angle from its value for the matrix/air interface. From this shift one cannot obtain the effective index of refraction in the usual way, that is, by assuming the isotropic approximation. Instead, one must compare the experimental data with the results of the reflection model presented here and the half-space reflection in Eq. (5). From this comparison one may obtain the values of the scattering matrix elements of the particles and the density of particles.

We showed that the width of the homogeneous layer on the surface model can have a strong influence on the contribution of the particles to the total reflectance of the composite. Although here we were limited to our specific surface model, the latter conclusion tells us that, in general, one must model with great care the surface of a composite in order to be able to relate reflectance measurements to the particles in the composite. Of course, as the contrast between refractive indexes of the external medium and the matrix material is lowered, the relative importance of the contribution of the particles to the reflectance increases and the surface model becomes less determinant. We found in our example, that a contrast in refractive index of about 0.1 is enough to unmask the contribution of the particles from the reflectance of the matrix interface in differential polarized reflectance measurements. This result indicates the possibility of performing experimental measurements of random ensemble of particles embedded in a solid matrix by roughly matching the refractive index of the external medium (e.g., with a liquid) with that of the matrix.

All calculations presented in this paper were for a volume filling fraction of 0.1. According to the confidence test suggested in Ref. [4], the plots presented in Sect. 4 may incur in relatively large errors for some angles of incidence and particle's radius. In the worst case, we expect the error to be of about 20% and only within limited intervals of the angle of incidence. Thus, the qualitative behaviour of the curves presented here is correct and the observations made from them are correct.

Finally, in some cases, one may need to consider the possibility of having particles partly embedded in the matrix and partly on the outside medium. One way of taking this possibility into account may be to consider the protruding particles on the surface as surface roughness. Nevertheless, experimental results on actual physical samples are very much needed.

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