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Overview of an effective-medium approach to the reflection and refraction of light at a turbid colloidal half-space

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It has been recently shown that the effective electromagnetic bulk response of a dilute colloidal system, composed by a large collection of identical big spheres, located at random, is spatially dispersive (non-local). Here, we extend this effective-medium approach to the calculation of the reflection and transmission amplitudes of the same system but with a flat interface. We use an integral-equation approach for the calculation of the average electric field. The integral equation is solved within the effective-field approximation, by proposing a plane-wave solution with effective parameters that are calculated by solving a set of consistency equations. We obtain explicit expressions for the transmission and reflection amplitudes as a function of the filling fraction, the radius of the inclusions and the angle of incidence. We show and discuss numerical results for a system of silver particles.

1 Introduction Colloids are usually defined as a system in which a dispersed phase is immersed within a homogeneous one. Typical examples of this kind of systems are: clouds, snow, milk, blood, paints, etc. The dispersed phase is usually referred to as colloidal particles or inclusions. Depending on the size a of the colloidal particles in relation to the wavelength λ of the incident radiation, the system looks either transparent whenever $a/\lambda \ll 1$ or it looks turbid whenever $a \approx \lambda$. Turbidity arises from the electromagnetic field scattered by the randomly located colloidal particles. In order to analyse the optical properties of a colloidal system it is convenient to split the total electromagnetic field within the system in two components: an average component, usually called the coherent beam, plus a fluctuating component, usually called diffuse field. While turbidity is associated to the diffuse field that travels in all different directions, the coherent beam, besides travelling along a definite direction, it is also refracted and reflected at a flat interface. Now, if one disregards the diffuse field, the coherent beam seems to behave as light does in homogeneous media, where a complex effective index of refraction could be defined, and we could regard this, as an optical property of a fictitious homogeneous medium known as: effective medium. The optical properties of the effective medium are given in terms of the optical and geometrical properties of the two colloidal phases as well as the statistical properties of the inclusions. The main advantage of an effective-medium approach is that having obtained the effective properties of the inhomogeneous system, one can use them in continuum electrodynamics as if the system were actually a homogeneous material. It has been recently shown [1] that although it is possible to construct an effective medium for the coherent beam in turbid colloids, this medium turns out to be *spatially dispersive*. This means that the effective electromagnetic response depends not only on the frequency ω of the exciting field but also on its wave vector $\boldsymbol{k}$. Nevertheless, it was also shown [1] how from the dispersion relation for the transverse modes, it was possible to derive a frequency-dependent effective index of refraction n_{eff} (ω). In previous works we studied the

reflection and refraction of light from a turbid colloidal half-space using a multiple-scattering approach [2–5] and looked at the repercussions on the properties of an underlying effective medium. In these latter works we already discussed the precautions that have to be taken for using an effective refractive index of a turbid colloidal system in continuum electrodynamics. For example, the use of $n_{\rm eff}(\omega)$ in Fresnel's relations to calculate the reflection amplitudes of the coherent beam from a flat interface may no longer be valid.

Here, we construct the theoretical framework to incorporate the presence of a flat interface in the spatially dispersive effective medium of the colloidal system, and show how to calculate correctly the transmission and reflected amplitudes of the coherent beam. Our approach is based on an integral-equation formulation and the construction of an effective electromagnetic response of the colloid that, due to the presence of the interface, is no longer translational invariant. We discuss also previous attempts to solve this problem as well as the inconsistencies found when trying to determine $n_{\rm eff}(\omega)$ using the conventional procedure followed in a reflection-based spectroscopy. Finally we comment on extensions of our approach and also on possible applications.

2 Review

2.1 Homogeneous material Here, we review the laws of refraction and reflection of light at a flat interface between vacuum and a homogeneous and isotropic material, in order to set a reference and to introduce notation. In this case, the dispersion relation of the electromagnetic modes in the system can be expressed as $k(\omega) = k_0 n(\omega)$ where $k_0 = \omega/c$, ω denotes the frequency of the incident radiation, c denotes the speed of light and k and n are the norm of the wavevector and the index of refraction in the homogeneous medium. In the presence of a flat interface Snell's law demands that the parallel component of the wavevector $k_{||} = k_0 \sin\theta_i$ should be continuous across the interface. Here θ_i is the angle of incidence. Therefore, in the presence of the interface, the dispersion relation becomes

$$k = \sqrt{k_{||}^2 + k_z^2} = k_0 n, \quad \text{or} \quad k_z = k_0\sqrt{n^2 - \sin^2\theta_i}, \tag{1}$$

where the Z-axis has been chosen perpendicular to the interface and directed towards the homogeneous material. In the presence of absorption, n is a complex quantity, thus $k_z = \mathrm{Re}\, k_z + i\,\mathrm{Im}\, k_z$ becomes also complex. This means that within the material the wave is inhomogeneous, that is, it propagates at an angle

$$\tan\theta_t = \frac{k_{||}}{\mathrm{Re}\, k_z}, \tag{2}$$

called angle of refraction (transmission), and its amplitude decays along the Z-axis with a penetration length equal to $1/\mathrm{Im}\ k_z$.

The reflection amplitudes of the electric field can be calculated using Fresnel's relations, which are given in terms of the electric permittivity ε and the magnetic permeability μ. They can be written, for s-polarization (E-field parallel to the Y-axis), as

$$r_s = \frac{E_r}{E_i} = \frac{k_{\rm iz} - \dfrac{\mu_0}{\mu_i}k_{\rm tz}}{k_{\rm iz} + \dfrac{\mu_0}{\mu_i}k_{\rm tz}}, \tag{3}$$

and for p-polarization (H-field parallel to the Y-axis), as

$$r_{\rm p} = \frac{E_r}{E_i} = \frac{k_{\rm iz} - \dfrac{\varepsilon_0}{\varepsilon}k_{\rm tz}}{k_{\rm iz} + \dfrac{\varepsilon_0}{\varepsilon}k_{\rm tz}}, \tag{4}$$

where the subindex i, r and t denote incident, reflected and transmitted, respectively, while $k_{\rm iz} = k_0\cos\theta_i$ and $k_{\rm tz}$ is given by Eq. (1). Here we use SI units, while ε_0 and μ_0 retain their usual meaning. Notice that in order to utilize Fresnel's relations the knowledge of the index of refraction $n = \sqrt{\varepsilon\mu/\varepsilon_0\mu_0}$ is not enough, it is also required to know ε and μ, separately; with exception of materials with no magnetic response ($\mu = \mu_0$) in which $n = \sqrt{\varepsilon/\varepsilon_0}$ would be certainly enough.

2.2 Previous attempts Probably the first attempt to obtain the effective index of refraction for the coherent beam in a dilute turbid colloid appeared in the book by van de Hulst [6] as early as 1957. The expression he obtained, using simple approximations in multiple-scattering theory and a model of randomly located, non-magnetic identical spheres, of radius a, in vacuum, can be written as

$$n_{\rm eff} = 1 + i\gamma S(0), \tag{5}$$

where $\gamma = 3f/2(k_0 a)^3$, f is the volume filling fraction of the inclusions and $S(0)$ is the diagonal component of the amplitude scattering matrix in the forward direction. Here, we follow the definition given in Ref. [7]. Now, it can be shown [5] that one cannot use naively this effective index of refraction in, for example, Fresnel's relations. Furthermore, if one uses Fresnel's relations to retrieve $n_{\rm eff}$ from measurements in conventional reflection-based refractometers, significant inconsistencies might be found [5]. The reason for this is that the effective index of refraction derived by van de Hulst corresponds to an effective medium that besides having a magnetic response it is also spatially dispersive (non-local), as we will see below.

2.3 Bulk non-local response It was recently shown [1], as it was mentioned above, that in a turbid colloid it is possible to construct an effective medium for the coherent beam, This effective medium turns out to be spatially dispersive, and for a model of randomly located identical spheres, explicit expressions for the bulk effective non-local *generalized* conductivity tensor $\overline{\overline{\sigma}}_{\rm eff}$ have been derived [1].

$\overline{\overline{\sigma}}_{\rm eff}$ is defined through

$$\langle \boldsymbol{J}\rangle(\boldsymbol{r},\omega) = \int \overline{\overline{\sigma}}_{\rm eff}(|\boldsymbol{r}-\boldsymbol{r}'|;\omega)\cdot\langle \boldsymbol{E}\rangle(\boldsymbol{r}';\omega), \tag{6}$$

where the brackets denote ensemble average over the random locations of the spheres, $\boldsymbol{J}$ is the *total* induced current density and $\boldsymbol{E}$ is the electric field. The frequency ω comes from a Fourier transform in time and the dependence on $|\boldsymbol{r}-\boldsymbol{r}'|$ indicates that the system is isotropic and translationally invariant and the non-local length is given by the size of the spheres. The name *generalized* indicates that the induced current density is not split in a polarization and magnetization components, here $\boldsymbol{J}$ includes both; it is the *total* induced current.

Since Eq. (6) is a convolution, after a Fourier transform in space one can write

$$\boldsymbol{J}(\boldsymbol{k},\omega) = \overline{\overline{\sigma}}_{\rm eff}(\boldsymbol{k},\omega)\cdot\boldsymbol{E}(\boldsymbol{k},\omega), \tag{7}$$

and one can readily see that the k-dependence (spatial dispersion) of $\overline{\overline{\sigma}}_{\rm eff}$ comes from the non-locality of the response. Due to the homogeneity and isotropy of the bulk system one can write the tensor

$$\overline{\overline{\sigma}}_{\rm eff}(\boldsymbol{k},\omega) = \sigma^{\rm L}_{\rm eff}(k,\omega)\hat{\boldsymbol{k}}\hat{\boldsymbol{k}} + \sigma^{\rm T}_{\rm eff}(k,\omega)(1-\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}), \tag{8}$$

in terms of only two scalar components $\sigma^{\rm L}_{\rm eff}$ and $\sigma^{\rm T}_{\rm eff}$ called the longitudinal and transverse components, respectively. It is possible to write $\sigma^{\rm L}_{\rm eff}(k,\omega)$ and $\sigma^{\rm T}_{\rm eff}(k,\omega)$ in terms of the more traditional $\varepsilon_{\rm eff}(k,\omega)$ and $\mu_{\rm eff}(k,\omega)$. In Ref. [1] explicit expressions for these four scalar quantities are derived as well as numerical results for a system of Ag and TiO_2 colloidal particles. It is interesting to point out that although the particles are non-magnetic, there is an effective magnetic response $\mu_{\rm eff}$ coming from the closed currents induced within the particles.

3 Formalism

3.1 Surface non-local response In this section we include the presence of the interface in the calculation of the generalized effective conductivity tensor. Since the system is no longer translationally invariant in the z-direction the bulk response is no longer adequate, due to the presence of a surface region whose size is of the order of the non-local length, that is, the size of the particles (see Fig. 1).

This means that $\overline{\overline{\sigma}}_{\rm eff}$ should depend now on z and z' separately, and can be written as $\overline{\overline{\sigma}}_{\rm eff}(\boldsymbol{k}_{||},z,z';\omega)$ where we have used a mixed Fourier representation taking account of translational invariance in the plane of the interface ($\boldsymbol{k}_{||}=\boldsymbol{k}_{||}{}'$). There have been, however, attempts to calculate the transmitted and reflected fields at a flat interface using the bulk response $\overline{\overline{\sigma}}_{\rm eff}(\boldsymbol{k},\omega)$, and one can recall the semi-classical infinite barrier model (SCIB) and the approach of the additional boundary conditions (ABC), used in non-local optics [8, 9], a couple decades ago. Nevertheless, all these previous attempts are valid only when the size of the surface region is much smaller than the wavelength of the incident radiation, which is not the case here.

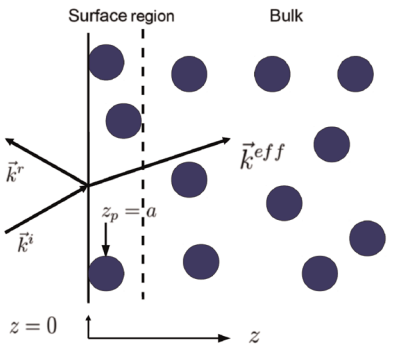

Figure 1 (online colour at: www.pss-b.com) Diagram of the reflection geometry. All particles are identical spheres of radius a, with their centers located at $z_p > a$. The fictitious flat surface is at $z = 0$ and $\boldsymbol{k}^i$, $\boldsymbol{k}^r$ are the wavevectors of the incident and reflected plane waves and. $\boldsymbol{k}^{\rm eff}$ is the effective wavevector in the bulk.

3.2 Isolated sphere Since our final objective is the calculation of the reflection and transmission amplitudes of the coherent beam in the independent-scattering approximation, for a dilute system of randomly located identical spheres, the main ingredient of this calculation is the full non-local *generalized* conductivity tensor of an isolated sphere $\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{r},\boldsymbol{r}')$. In the many-sphere system, this isolated sphere responds to the so-called exciting field $\boldsymbol{E}^{\rm exc}$, that is, the field coming from the external field plus the field scattered by all other spheres, thus one writes

$$\boldsymbol{J}^{\rm ind}(\boldsymbol{r};\omega) = \int_{\rm S} \overline{\overline{\sigma}}_{\rm s}(\boldsymbol{r},\boldsymbol{r}';\omega)\cdot\boldsymbol{E}^{\rm exc}(\boldsymbol{r}';\omega){\rm d}^3\boldsymbol{r}', \tag{9}$$

where $\boldsymbol{J}^{\rm ind}$ is the current density induced within the sphere and the integration is done over the volume of the sphere because $\overline{\overline{\sigma}}_{\rm s}$ vanishes whenever either $\boldsymbol{r}$ or $\boldsymbol{r}'$ lie outside the sphere.

The calculation of $\overline{\overline{\sigma}}_{\rm s}$ is performed by taking a Fourier transform in space of Eq. (9) and the exciting field as a single plane wave of unit amplitude, wavevector $\boldsymbol{k}$, frequency ω and polarization vector $\boldsymbol{e}_\beta$. Then, by writing $\boldsymbol{J}^{\rm ind} = \sum_\alpha J^{\rm ind}_\alpha \hat{\boldsymbol{e}}_\alpha$, and choosing three independent directions for the polarization vector $\hat{\boldsymbol{e}}_\alpha$, we have that all the components of $\overline{\overline{\sigma}}_{\rm s}$ are given by

$$\hat{\boldsymbol{e}}_\alpha\cdot\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k},\boldsymbol{k}';\omega)\cdot\hat{\boldsymbol{e}}_\beta = J^{\rm ind}_\alpha(\boldsymbol{k},\omega;\hat{\boldsymbol{e}}_\beta). \tag{10}$$

Thus the calculation of $\overline{\overline{\sigma}}_{\rm s}$ is reduced to the calculation of the currents induced within a sphere. Since the sphere responds locally to the interior fields, $\boldsymbol{J}^{\rm ind}$ will be given by

$$\begin{aligned}\boldsymbol{J}^{\rm ind}(\boldsymbol{r};\omega) = &-i\omega(\varepsilon_s-\varepsilon_0)E^{\rm int}(\boldsymbol{r};\omega)\\ &+\left(\frac{1}{\mu_0}-\frac{1}{\mu_s}\right)\nabla\times B^{\rm int}(\boldsymbol{r};\omega)\\ &-\left(\frac{1}{\mu_0}-\frac{1}{\mu_s}\right)\delta(r-a)\hat{\boldsymbol{e}}_r\times\boldsymbol{B}^{\rm int}(\boldsymbol{r};\omega),\end{aligned} \tag{11}$$

where the centre of the sphere is at the origin of the coordinate system, $\boldsymbol{E}^{\rm int}$ and $\boldsymbol{B}^{\rm int}$ are the electric and magnetic fields in the interior of the sphere ($r < a$) and, $\varepsilon_{\rm s}$ and $\mu_{\rm s}$ are their frequency-dependent *local* permittivity and permeability. Therefore, recognizing that the sphere responds *non-locally* to the exciting field while responds *locally* to the interior fields, the problem of calculating $\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k},\boldsymbol{k}';\omega)$ is reduced to the calculation of the interior fields, yielding a problem similar to Mie scattering. While in Mie scattering the incident plane wave is transverse and self-propagating, in our case $\boldsymbol{k}'$ and ω should be independent of each other thus this requires the presence of external currents. Following this procedure for different polarizations of the incident plane wave we have calculated the different components of $\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k},\boldsymbol{k}';\omega)$ for a system of Ag and TiO_2 in vacuum. The details of this complicated but important calculation will be reported elsewhere.

3.3 Relation with the single-scattering problem

Since the calculation of the interior fields within the isolated sphere is required for the calculation of the scattered field, there should be a relation between the generalized non-local conductivity tensor $\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k},\boldsymbol{k}';\omega)$and the scattering matrix. We can see this by first writing the scattered field at points in space outside the particle as

$$\boldsymbol{E}^{\rm S}(\boldsymbol{r}r) = \int \overline{\overline{G}}_0(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{J}^{\rm ind}(\boldsymbol{r}')\mathrm{d}^3\boldsymbol{r}', \tag{12}$$

where

$$\overline{\overline{G}}_0(\boldsymbol{r},\boldsymbol{r}') = \left(\overline{\overline{1}} + \frac{1}{k_0^2}\nabla\nabla\right)\frac{\mathrm{e}^{ik_0|\boldsymbol{r}-\boldsymbol{r}'|}}{4\pi|\boldsymbol{r}-\boldsymbol{r}'|}, \tag{13}$$

is the free Green's function dyadic. From here on we suppress in the notation the explicit dependence on ω, unless it leads to confusion. Then one substitutes the expression for $\boldsymbol{J}^{\rm ind}$ given by Eq. (9) into Eq. (12) taking $\boldsymbol{E}^{\rm exc}(\boldsymbol{r}') = \boldsymbol{E}_0^i\mathrm{e}^{i\boldsymbol{k}_i\cdot\boldsymbol{r}'}\hat{\boldsymbol{e}}^i$. Since the scattering matrix relates the scattered field in the far-field region with the incident field, we first perform a far-field expansion of the scattered field, and one gets

$$\boldsymbol{E}^S(\boldsymbol{r}) = i\omega\mu_0 E_0^i\frac{\mathrm{e}^{ik_0r}}{4\pi r}(\overline{\overline{1}} - \hat{\boldsymbol{k}}^s\hat{\boldsymbol{k}}^s)\cdot\overline{\overline{\sigma}}_s(\boldsymbol{k}^s,\boldsymbol{k}^i)\cdot\hat{\boldsymbol{e}}^i + O\left(\frac{1}{r^2}\right) + \ldots, \tag{14}$$

where $\boldsymbol{k}^s = k_0\hat{\boldsymbol{e}}_r$ and $\boldsymbol{k}^i = k_0\hat{\boldsymbol{k}}^i$ and $\hat{k}^s \equiv \boldsymbol{k}^s/k^s$ denotes unit vector. One can readily see that being $\overline{\overline{1}} - \hat{\boldsymbol{k}}^s\hat{\boldsymbol{k}}^s$ a transverse projector, the scattered far field is perpendicular to $\hat{\boldsymbol{k}}^s$ (transverse), thus the components of $(\overline{\overline{1}} - \hat{\boldsymbol{k}}^s\hat{\boldsymbol{k}}^s)\cdot\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k}^s,\boldsymbol{k}^i)$ can be directly related to the diagonal elements of the 2×2 scattering matrix for a sphere, whose definition is given through the following relation [7]

$$\begin{pmatrix} E_{||}^S \\ E_\perp^S \end{pmatrix} = \frac{\mathrm{e}^{ik_0r}}{-ik_0r}\begin{pmatrix} S_2(\theta) & 0 \\ 0 & S_1(\theta) \end{pmatrix}\begin{pmatrix} E_{||}^i \\ E_\perp^i \end{pmatrix}, \tag{15}$$

where the sub-indices $||$ and $\perp$mean parallel and perpendicular to the scattering plane, which is the plane that contains the vectors $\boldsymbol{k}^i$ and $\boldsymbol{k}^s$, θ is the angle between them. Thus comparing Eqs. (14) and (15), one gets the following relations between $\overline{\overline{\sigma}}_{\rm s}$ and $S_1(\theta)$, $S_2(\theta)$:

$$i\omega\mu_0(\overline{\overline{1}} - \hat{\boldsymbol{k}}^s\hat{\boldsymbol{k}}^s)\cdot\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k}^s,\boldsymbol{k}^i)\cdot\hat{\boldsymbol{e}}_\perp^i = \frac{4\pi}{-ik_0}S_1(\theta)\hat{\boldsymbol{e}}_\perp^S, \tag{16}$$

$$i\omega\mu_0(\overline{\overline{1}} - \hat{\boldsymbol{k}}^s\hat{\boldsymbol{k}}^s)\cdot\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{k}^s,\boldsymbol{k}^i)\cdot\hat{\boldsymbol{e}}_{||}^i = \frac{4\pi}{-ik_0}S_2(\theta)\hat{\boldsymbol{e}}_{||}^S. \tag{17}$$

These identities do not specify completely the dyadic $\overline{\overline{\sigma}}_{\rm s}$, and the other projections of $\overline{\overline{\sigma}}_{\rm s}$ that are used in the calculations below. However, these other projections have a small contribution compared to those from Eqs. (16) and (17). We use these identities whenever possible.

We should remark that we use the expressions above for the electric field in the far-field region only to establish, the identities given in Eqs. (16) and (17). However, our analysis on the reflection and refraction of light in turbid colloids does not require that the particles are located in the far-zone of each other. In many cases the particles will be, on the average, less than a wavelength apart from each other. The projections on the left hand side of Eqs. (16) and (17) arise from the averaging procedure, and not from a far-field requirement.

3.4 Integral equation for the mean field Here, we deal with the multiple-scattering problem, thus we will consider a collection of a large number N of identical spheres of radius a within a volume V, in the limit $N\to\infty$, $V\to\infty$ while $n_0 = N/V$ is kept finite. We start by deriving the equation obeyed by the total electric field

$$\boldsymbol{E}(\boldsymbol{r}) = \boldsymbol{E}^{\rm inc}(\boldsymbol{r}) + \boldsymbol{E}^{\rm ind}(\boldsymbol{r}), \tag{18}$$

where $\boldsymbol{E}^{\rm inc}$ is the incident or external field, while $\boldsymbol{E}^{\rm ind}$ is the field induced inside and outside of the particles, and it is given by Eq. (12) but for points outside and inside the particles. From now on the induced current density $\boldsymbol{J}^{\rm ind}$ will be the current density induced in all spheres. This is given by

$$\boldsymbol{J}^{\rm ind}(\boldsymbol{r}) = \sum\nolimits_p\int\overline{\overline{\sigma}}_{\rm s}(\boldsymbol{r}-\boldsymbol{r}_p;\boldsymbol{r}'-\boldsymbol{r}_p)\cdot\boldsymbol{E}^{{\rm exc},p}(\boldsymbol{r}')\mathrm{d}^3\boldsymbol{r}', \tag{19}$$

where the index p labels the spheres, $\boldsymbol{E}^{{\rm exc},p}$ is the field exciting the p-th sphere and $\boldsymbol{r}_p$ is the position vector of its centre. When one introduces this expression into Eq. (12) one obtains an equation for the scattered electric field $\boldsymbol{E}^S$ in term of the exciting field $\boldsymbol{E}^{{\rm exc},p}$ at all the particles. Since in the coherent beam the fluctuations of scattered field due to the random location of the spheres are smooth out by an adequate averaging procedure, such as an ensemble (configurational) average [11], we perform next

the ensemble average of the total electric field in the presence of the interface. For doing this:

(1) We build up the interface by assuming that the probability of finding the centre of a sphere within $\mathrm{d}^3 r$ is constant for $z > a$ and zero for $z < a$.
(2) We perform the following plane-wave expansion of $\overline{\overline{G}}_0$ that is more convenient for dealing with the flat-interface geometry [10]

$$\overline{\overline{G}}_0(\boldsymbol{r},\boldsymbol{r}') = -\frac{\hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z}{k_0^2}\delta(\boldsymbol{r}-\boldsymbol{r}') + \frac{i}{2}\int\frac{\mathrm{d}^2k_\parallel}{(2\pi)^2}\frac{1}{k_z^s}\left(\overline{\overline{1}} - \frac{\boldsymbol{k}_\pm\boldsymbol{k}_\pm}{k_0^2}\right)\mathrm{e}^{i\boldsymbol{k}_\pm(\boldsymbol{r}-\boldsymbol{r}')}, \tag{20}$$

where $\boldsymbol{k}_\pm = \boldsymbol{k}_\parallel \pm k_z^s\hat{\boldsymbol{e}}_z$ and $k_z^s = \sqrt{k_0^2 - k_\parallel^2}$. The choice $\pm$ is $+(-)$ for $z > z'$ ($z < z'$).

(3) We calculate the average field $\langle\boldsymbol{E}\rangle$ by taking an ensemble average over the random location of the spheres, and
(4) we take account of multiple scattering by approximating the exciting field at the every particle by the average field $\boldsymbol{E}^{\mathrm{exc},p} \approx \langle\boldsymbol{E}\rangle$. This approximation is known as the effective-field approximation (EFA), and is only valid for dilute systems.
(5) We take as an incident field a transverse plane wave of the form

$$\boldsymbol{E}^{\mathrm{inc}}(\boldsymbol{r}) = \hat{\boldsymbol{e}}^i E_0^i \mathrm{e}^{i\boldsymbol{k}_\parallel^i\cdot\boldsymbol{r}}\mathrm{e}^{ik_z^i z} \tag{21}$$

where $\boldsymbol{k}^i = (\boldsymbol{k}_\parallel^i, k_z^i)$ and $\hat{\mathbf{e}}^i \cdot \boldsymbol{k}^i = 0$.

Under these circumstances we obtain, for $z > 0$, the following integral equation for the average field:

$$\begin{aligned}\langle\boldsymbol{E}\rangle^+(z) &= \hat{\boldsymbol{e}}^i E_0^i \mathrm{e}^{ik_z^i z} \\ &+ i\omega\mu_0 n_0 \int\frac{\mathrm{d}k_z''}{2\pi}\left[-\frac{\hat{e}_z\hat{e}_z}{k_0^2}\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}_\parallel^i, k_z''; \boldsymbol{k}_\parallel^i, k_z'').\mathrm{e}^{ik_z''z}\right. \\ &+ \frac{1}{2k_z^i}(\overline{\overline{1}} - \hat{\boldsymbol{k}}^i\hat{\boldsymbol{k}}^i)\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^i, \boldsymbol{k}_\parallel^i + \hat{\boldsymbol{e}}_z k_z'')\frac{\mathrm{e}^{ik_z''z} - \mathrm{e}^{ik_z^i z}\mathrm{e}^{ia(k_z''-k_z^i)}}{k_z'' - k_z^i}, \\ &\left.- \frac{1}{2k_z^i}(\overline{\overline{1}} - \hat{\boldsymbol{k}}^r\hat{\boldsymbol{k}}^r)\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^r, \boldsymbol{k}_\parallel^i + \hat{\boldsymbol{e}}_z k_z'')\frac{\mathrm{e}^{ik_z''z}}{k_z'' + k_z^i}\right]\cdot\langle\boldsymbol{E}\rangle(k_z'')\end{aligned} \tag{22}$$

where $\boldsymbol{k}^i = (\boldsymbol{k}_\parallel^i, k_z^i)$, $\boldsymbol{k}^r = (\boldsymbol{k}_\parallel^i, -k_z^i)$, $k_z^i = \sqrt{k_0^2 - (k_\parallel^i)^2}$ (see Fig. 1) and $\langle\boldsymbol{E}\rangle(z)$ is defined through

$$\langle\boldsymbol{E}\rangle(\boldsymbol{r}_\parallel, z) = \mathrm{e}^{i(k_\parallel^i\cdot\boldsymbol{r}_\parallel)}\langle\boldsymbol{E}\rangle(z), \tag{23}$$

while

$$\langle\boldsymbol{E}\rangle(k_z) = \int_{-\infty}^{\infty}\mathrm{d}z\mathrm{e}^{-ik_z z}\langle\boldsymbol{E}\rangle(z) \tag{24}$$

is its Fourier transform. So the integral equation is given in terms of $\langle\boldsymbol{E}\rangle(z)$ and an integral over its Fourier transform. To solve this equation we propose the following ansatz

$$\langle\boldsymbol{E}\rangle(z) = \theta(z)tE_0^i\mathrm{e}^{ik_z^{\mathrm{eff}}}\hat{\boldsymbol{e}}^{\mathrm{eff}}, \tag{25}$$

where $\theta(z)$is the step function, thus

$$\langle\boldsymbol{E}\rangle(k_z) = tE_0^i\hat{\boldsymbol{e}}^{\mathrm{eff}}\frac{i}{k_z^{\mathrm{eff}} - k_z^i}. \tag{26}$$

Here, the transmission amplitude t, the effective z-component k_z^{eff} of an effective wave vector $\boldsymbol{k}^{\mathrm{eff}} = (\boldsymbol{k}_\parallel^i, k_z^{\mathrm{eff}})$ (see Fig. 1) and the polarization vector along $\hat{\boldsymbol{e}}^{\mathrm{eff}}$ are parameters to be determined by demanding consistency with the integral equation. Thus, by substituting Eqs. (25) and (26) into the integral equation, Eq. (22), we obtain two consistency relations:

$$\overline{\overline{M}}\cdot\hat{\boldsymbol{e}}^{\mathrm{eff}} = 0, \tag{27}$$

where

$$\begin{aligned}\overline{\overline{M}} \equiv \overline{\overline{1}} - \omega\mu_0 n_0\left[-\frac{\hat{\boldsymbol{e}}_z\hat{\boldsymbol{e}}_z}{k_0^2}\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^{\mathrm{eff}}, \boldsymbol{k}^{\mathrm{eff}}) + (\overline{\overline{1}} - \hat{\boldsymbol{k}}^i\hat{\boldsymbol{k}}^i)\right. \\ \left.\cdot\frac{\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^i, \boldsymbol{k}^{\mathrm{eff}})}{2k_z^i(k_z^{\mathrm{eff}} - k_z^i)} - (\overline{\overline{1}} - \hat{\boldsymbol{k}}^r\hat{\boldsymbol{k}}^r)\frac{\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^r, \boldsymbol{k}^{\mathrm{eff}})}{2k_z^i(k_z^{\mathrm{eff}} + k_z^i)}\right]\end{aligned} \tag{28}$$

and

$$\hat{\boldsymbol{e}}^i = i\omega\mu_0 n_0 t(\overline{\overline{1}} - \hat{\boldsymbol{k}}^i\hat{\boldsymbol{k}}^i)\cdot\frac{\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^i, \boldsymbol{k}^{\mathrm{eff}})}{2k_z^i(k_z^{\mathrm{eff}} - k_z^i)}\cdot\hat{\boldsymbol{e}}^{\mathrm{eff}}\mathrm{e}^{ia(k_z^{\mathrm{eff}} - k_z^i)}. \tag{29}$$

In the first consistency relation, the solution of Eq. (27) requires $\det\overline{\overline{M}} = 0$, and this condition yields the dispersion relation $k_z^{\mathrm{eff}}(\omega)$ of the electromagnetic modes in the presence of the interface [see Eq. (1) to compare with the local case]. The second consistency relation, Eq. (28), corresponds to the extinction of the incident wave (the Ewald–Oseen extinction theorem) and provides the value of the transmission coefficient t.

After having solved the dispersion relation for $k_z^{\mathrm{eff}}(\omega)$ and the transmission coefficient t, we go back to the integral equation and calculate the electric field for $z < 0$. We obtain that it has the form

$$\langle\boldsymbol{E}\rangle^-(\boldsymbol{r}_\parallel, z) = \mathrm{e}^{i\vec{k}_\parallel^i\cdot\vec{r}_\parallel}\langle\boldsymbol{E}\rangle^-(z), \tag{30}$$

where

$$\langle\boldsymbol{E}\rangle^-(z) = E_0^i\mathrm{e}^{ik_z^i z} + r_i\mathrm{e}^{2iak_z^i}E_0^i\mathrm{e}^{-ik_z^i z} \tag{31}$$

and

$$r_i = \frac{(\overline{\overline{1}} - \hat{\boldsymbol{k}}^r\hat{\boldsymbol{k}}^r)\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^r, \boldsymbol{k}^{\mathrm{eff}})\cdot\hat{\boldsymbol{e}}^{\mathrm{eff}}}{\hat{\boldsymbol{e}}^i\cdot\overline{\overline{\sigma}}_{\mathrm{s}}(\boldsymbol{k}^i, \boldsymbol{k}^{\mathrm{eff}})\cdot\hat{\boldsymbol{e}}^{\mathrm{eff}}}\frac{k_z^i - k_z^{\mathrm{eff}}}{k_z^i + k_z^{\mathrm{eff}}}. \tag{32}$$

where the subindex i denotes the dependence on the polarization ($\hat{e}^i$) of the incident wave.

Since the first term in the rhs of Eq. (31) corresponds to the incident wave, we can identify the second term in the rhs as the reflected field, and the factor r_i as the reflection amplitude. The constant phase multiplying r_i comes from our selection of origin.

4 Results

4.1 Light-cone approximation (LCA) The two main results of our work here are given by: (i) Eq. (27), whose solution yields the dispersion relation of the electromagnetic modes in the presence of the interface, and (ii) Eq. (32) that provides an explicit expression for the reflection amplitude of the coherent beam.

In this section we calculate the dispersion relation $k_z^{\rm eff}(\omega)$ and the reflection amplitude r within the LCA. This means that in Eqs. (27) and (32) one replaces $\overline{\overline{\sigma}}_s(\boldsymbol{k}^{\rm eff},\boldsymbol{k}^{\rm eff}) \approx \overline{\overline{\sigma}}_s(\boldsymbol{k}^i,\boldsymbol{k}^i)$, $\overline{\overline{\sigma}}_s(\boldsymbol{k}^i,\boldsymbol{k}^{\rm eff}) \approx \overline{\overline{\sigma}}_s(\boldsymbol{k}^i,\boldsymbol{k}^i)$ and $\overline{\overline{\sigma}}_s(\boldsymbol{k}^r,\boldsymbol{k}^{\rm eff}) \approx \overline{\overline{\sigma}}_s(\boldsymbol{k}^r,\boldsymbol{k}^i)$, sets $\hat{\boldsymbol{e}}^{\rm eff} = \hat{\boldsymbol{e}}^i$, then use expressions as the ones given in Eqs. (16) and (17) to relate these quantities to the scattering coefficients of the isolated particles, and finally use Eq. (27) to solve for $k_z^{\rm eff}(\omega)$. Now substitute $k_z^{\rm eff}(\omega)$ into Eq. (32) to calculate r_i. A detailed account of this calculation will be reported elsewhere. Following this procedure one gets for s and p polarization

$$r_s = \frac{S_1(\pi - 2\theta_i)}{S(0)} \frac{k_z^i - k_z^{\rm eff}}{k_z^i + k_z^{\rm eff}}, \tag{33}$$

$$r_p = \frac{S_2(\pi - 2\theta_i)}{S(0)} \frac{k_z^i - k_z^{\rm eff}}{k_z^i + k_z^{\rm eff}}. \tag{34}$$

We had obtained these reflection coefficients before, using the multiple-scattering approach [2, 3] (although they were expressed in a different way). One of the differences here is that the dispersion relation for $k_z^{\rm eff}$ contains additional terms other than the projections of the generalized conductivity tensor given in Eqs. (16) and (17). But, as already said these additional terms do not contribute appreciably in the dilute limit. Thus, the results obtained here within the LCA can be regarded as corrections to the multiple-scattering approach.

4.2 Refraction Here we show some results for the angle of refraction and the penetration depth as a function of the particle radius. In Figs. 2 and 3 we show a plot of the refraction angle and the penetration length, respectively, as a function of the radius of the spheres, calculated upon solving the dispersion relation within the LCA in both, p-and s-polarizations. One can see that these results and the ones predicted by the van de Hulst effective index of refraction are indistinguishable from each other. For moderate values of the volume filling fraction occupied by the particles, and large values of the angle of incidence, deviations are observed. However the effective-field approximation and the van de Hulst refractive index loose accuracy as the filling fraction occupied by the particles increases.

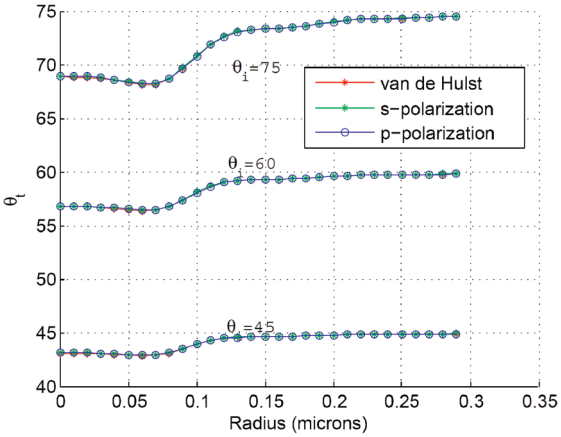

Figure 2 (online colour at: www.pss-b.com) Transmission angles calculated with the van de Hulst refractive index and with the solution of the null determinant of the matrix M for p-polarization and s-polarizations, as a function of the silver particles radius. Here $f = 0.02$, $\lambda = 0.63\,\mu$m and the electric permittivity of bulk silver $\varepsilon/\varepsilon_0 = -18.096 + i0.484$.

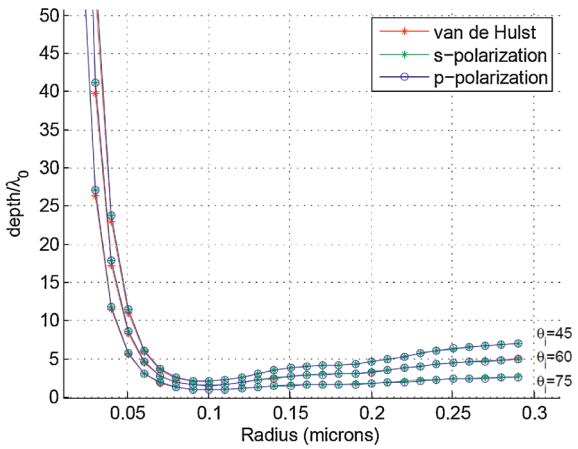

Figure 3 (online colour at: www.pss-b.com) Penetration length calculated with the van de Hulst refractive index and with the solution of the null determinant of the matrix M for p-polarization and s-polarizations, as a function of the silver particles radius. Here, $f = 0.02$, $\lambda = 0.63\,\mu$m and the electric permittivity of bulk silver $\varepsilon/\varepsilon_0 = -18.096 + i0.484$. We plot the penetration length predicted with the van de Hulst refractive index and the solution of the determinant of the matrix M for p-polarization and s-polarization.

On the other hand, the coherent description of the refraction of the coherent beam according to Snell's law and the van de Hulst complex effective refractive-index was already confirmed experimentally [4] for dilute colloids, showing that the van de Hulst refractive index is reliable for the interpretation of refraction results. This fact has been already exploited for retrieving particle properties from refraction experiments [12] and [13].

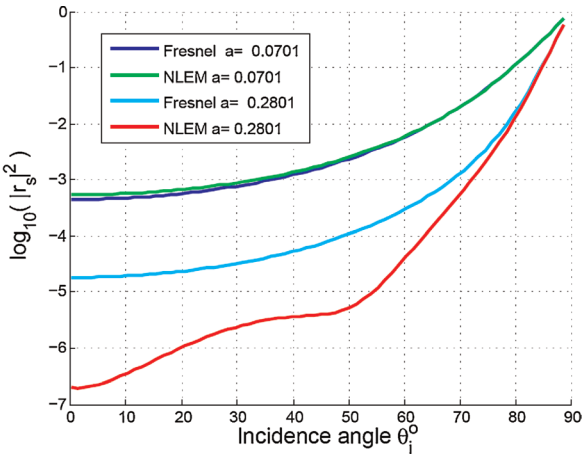

Figure 4 (online colour at: www.pss-b.com) Logarithm of the square amplitude of the reflection coefficient for *s*-polarization as a function of the angle of incidence for two particle radii: $a = 0.0701\ \mu$m and $a = 0.2801\ \mu$m. Here, $f = 0.02$, $\lambda = 0.63\ \mu$m and the electric permittivity of bulk silver $\varepsilon/\varepsilon_0 = -18.096 + i0.484$. For comparison we plot the predictions of the Fresnel's relations with the van de Hulst index of refraction and those of Eq. (33), labelled as non-local effective medium (NLEM).

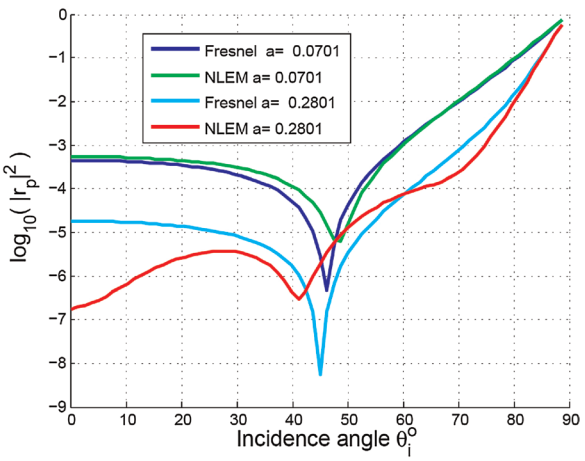

Figure 5 (online colour at: www.pss-b.com) Logarithm of the square amplitude of the reflection coefficient for *p*-polarization as a function of the angle of incidence for two particle radii: $a = 0.0701\ \mu$m and $a = 0.2801\ \mu$m. Here, $f = 0.02$, $\lambda = 0.63\ \mu$m and the electric permittivity of bulk silver $\varepsilon/\varepsilon_0 = -18.096 + i0.484$. For comparison we plot the predictions of the Fresnel's relations with the van de Hulst index of refraction and those of Eq. (34), labelled as non-local effective medium (NLEM).

4.2 Reflection In Fig. 4, the logarithm of the square of the reflection amplitude for the *s*-polarization is plotted as a function of the incidence angle for two particle radii. For comparison we plot the values predicted by the Fresnel formula, Eq. (3), using the van de Hulst's effective refractive index and the values obtained with Eq. (33). We can see that for the smaller particle size both results are basically the same, but for the larger particle radius there are appreciable differences. A similar result, using Eq. (34), is seen for *p*-polarization in Fig. 5. The dip seen in the plots for *p*-polarization corresponds to a Brewster-angle effect.

In general, for not very small particles, differences between the non-local effective medium theory and the Fresnel predictions are important. We can anticipate these differences from inspecting the corresponding formulas. In the non-local effective medium formula for the reflection coefficients, the scattering amplitude coefficients, S_1 or S_2 appear evaluated at the "specular direction" that is at $\pi - 2\theta_i$ whereas in the local Fresnel relationships with the van de Hulst effective refractive index involve only the forward scattering amplitude $S(0)$. However, for very small particles the coefficients S_1 or S_2 simplify and the reflection coefficient for the non-local theory approaches the Fresnel reflection coefficients as one may expect. Also, we may understand the failure of the Fresnel relationships recalling that the width of the surface region discussed in Section 3.1 increases as the particles' radius increases. Once this region has a width comparable to the wavelength of radiation we may no longer use the regular boundary conditions used in Continuum Electrodynamics of homogenous media, and thus we should not expect to obtain the Fresnel reflection coefficients.

5 Conclusions In this overview, we described the main steps to find a complete solution of the problem of light reflection and refraction by a half-space of randomly positioned spherical particles, in the effective-field approximation. It is shown that it is possible to state the problem using an effective medium approach, and solve it through the integral equation method. As a consequence, the need of boundary conditions is avoided, surpassing difficulties that appear when one has a non-local response of the effective medium. From the numerical results presented here we can see that the van de Hulst effective refractive index could be used safely to calculate the refraction angle and the penetration depth of the average wave, but not for the reflection coefficients. The integral-equation method yields the reflection formulas that must be used instead of the Fresnel's formulas in terms of the non-local generalized conductivity tensor of the sphere. The components of this simplify in the LCA (light cone approximation) and can be written in terms of the scattering amplitudes of an isolated sphere. Also, the integral-equation method provides the dispersion relation for an inhomogeneous half-space. The non-local effective medium approach used here, for the first time in a half-space of a turbid colloidal system, yields Eqs. (27)–(29) and (32) for the dispersion relation, the extinction theorem and the reflection coefficients. These new equations can be investigated beyond the light cone approximation, which is possibly the main contribution of this paper.

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