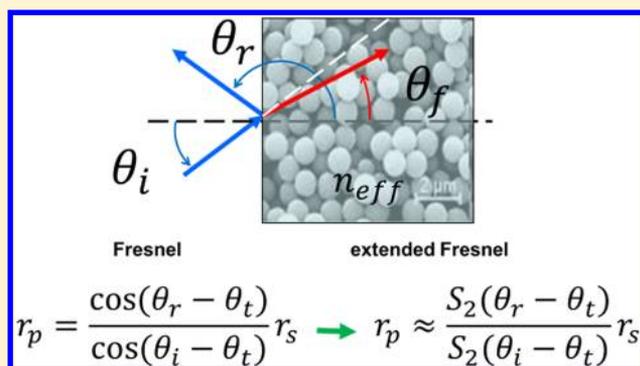Article

Extension of Fresnel's Formulas for Turbid Colloidal Suspensions: A Rigorous Treatment

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ABSTRACT: We provide new expressions for the reflection amplitudes of a half space of randomly located identical spherical particles that can be regarded as an extension of Fresnel's formulas when scattering is prominent. We derive them rigorously from Maxwell's equations by solving an integral equation for the electric field within the effective-field approximation. The integral equation is given in terms of the nonlocal conductivity tensor of an isolated sphere. Approximate expressions for the reflection amplitudes are also proposed and their accuracy is analyzed, first for the case of a self-sustained suspension of silver particles, and then for the more realistic situation of silver particles in water. In this latter case the integral equation is modified by introducing the half-space Green's function dyadic instead of the one in free-space, but the method of solution is analogous in both. This extension of Fresnel's formulas, together with the numerical comparison of the different approximations proposed here, is necessary for an accurate interpretation of reflection-spectroscopy measurements in dilute colloidal suspensions of practical interest. The connection between the nonlocal conductivity tensor and the **T**-matrix operator of scattering theory is also made manifest.

$$r_p = \frac{\cos(\theta_r - \theta_t)}{\cos(\theta_i - \theta_t)} r_s \quad \rightarrow \quad r_p \approx \frac{S_2(\theta_r - \theta_t)}{S_2(\theta_i - \theta_t)} r_s$$

INTRODUCTION

Light-reflection spectroscopy and angle-resolved reflectance, among other optical techniques, have become important and widespread tools for the characterization of a broad variety of materials.[1−3] The use of effective optical parameters has paved the way for the analysis of complex materials, particularly in suspensions and colloids. Nevertheless, when the size of the particles in the suspension is comparable to the wavelength of the exciting electromagnetic field, turbidity appears due to the scattering of light by the suspended particles. In this case, the definition of the effective optical parameters is not straightforward and sometimes it is not even possible. The usefulness of these effective parameters lies in the fact that, once they are determined, it is then possible to use them in the usual formulation of continuous electrodynamics as if they were parameters associated with common materials. A typical example is the effective refractive index, and one has to be aware, in first place, that due to the random location of the particles in the suspension, the scattered light has an average component (coherent beam) and a random component (diffuse field), and the effective refractive index is associated only to the behavior of the coherent beam. Furthermore, its imaginary part takes account of the attenuation of the coherent beam due to both absorption and scattering, and it can be used, for example, in Snell's law to determine the angle refraction at the flat interface of a suspension. Nevertheless, when one tries to use Fresnel's formulas to interpret reflection measurements in, e.g., standard critical-angle refractometers, inconsistencies might emerge.[4−7]

By extending the scope of what is known as effective-medium theory (EMT), it has been already shown[8] that the bulk effective electromagnetic response in turbid colloids is spatially dispersive (nonlocal), this means that it depends not only on the frequency of the external field but also on its wave vector. This means that Fresnel's formulas are no longer valid because they assume that the bulk electromagnetic response depends only on the frequency and it is not modified when an interface is introduced into the system; only then is the matching of boundary conditions for the electric and magnetic fields at the interface a valid procedure. Therefore, an accurate interpretation of optical spectroscopy in this type of system requires a new formulation. In its more general form, the problem could be posed as the calculation of the reflection amplitudes from a half-space of a bulk material with a spatially dispersive electromagnetic response. There have been attempts to solve this problem for systems with special features;[9−11] nevertheless, it is rather simple to show[12] that the bulk spatially dispersive response has to be modified to take account of the particular structure of the interface, and then a specific model for each system and each interface is necessarily required.

Here we choose, as a representative case, a system of randomly located identical spherical particles immersed within a nondissipative and homogeneous matrix constrained into a half-space, and we define the interface as a plane such that the probability of finding the center of randomly located colloidal particle on one side, is zero, whereas on the other side is constant. Then we calculate its electromagnetic response in the presence of the interface. In dilute systems this response is given in terms of the nonlocal conductivity tensor of an isolated sphere. By nonlocal conductivity we mean that the current induced by an exciting electromagnetic field at a given point within the sphere depends not only on the value of the field at that given point but also on the value of the field in its neighborhood. Here we approach the problem by solving the integral equation for the electromagnetic field in the effective-field approximation as in refs 8, 13, and 14. The final result is given in terms of the nonlocal conductivity tensor of an isolated sphere, providing explicit expressions for the reflection amplitudes that can be regarded as extensions of the Fresnel reflection coefficients. We call them "extensions" because Fresnel's formulas with an effective refractive index are recovered when scattering is negligible, that is, when the size of the particles is small in relation to the wavelength of the exciting electromagnetic field. The formulas we obtain are valid for dilute systems, and within this restriction the validity of rather simple expressions is also explored by performing a detailed numerical analysis for a system of general interes, such as silver particles in water.[15]

In this context our results could be important for solving, for example, the inconsistencies that prevail or appear when the effective index of refraction of a turbid colloid or suspension is determined by reflectivity measurements with modern critical-angle refractometers[5] and using naively Fresnel's formulas.[16] Our rigorous treatment of the problem could also help to understand the underlying physics. The need for an extension, or corrections, of the Fresnel's formulas for the optical characterization of turbid systems has been recently addressed in a rather heuristic way.[17,18]

An alternative approach to this same problem is to use multiple-scattering theory (MST) in terms of the **S** or **T** matrix of the isolated particles.[19] This approach has been applied successfully to problems of atmospheric physics,[19] where the matrix that supports the particles and the outside medium are the same (as in clouds). However, to our knowledge, a formal extension of MST to the case in which the matrix is a different material than the one outside (as in suspensions), has not yet been reported. Therefore, the expressions for the reflection amplitudes derived here fill this omission, at least for the dilute case where our theory is applicable. As a corollary of the present paper, we also show that our approach and MST are based, essentially, on the same integral equation after one identifies the nonlocal conductivity tensor of the isolated sphere as calculated in detail in ref 14 with its **T** matrix.

In this paper we first summarize the main results of the extended EMT for the bulk of turbid colloids. We use a wide definition of colloid as a two-phase system where a disperse phase is immersed within a homogeneous one. Then we introduce an interface between air and a half-space of self-sustained colloidal particles, through an integral equation for the average electric field. We solve this integral equation in the effective-field approximation and derive expressions for the reflection amplitudes of the coherent beam, together with different kinds of approximations that will facilitate its use in

practical situations. Then we address the more realistic situation of particles within a half-space of a nondissipative material matrix. In this case, the integral equation is modified by introducing the half-space Green's function dyadic instead of the one in free-space, and the we solve it in a similar way as in the free-standing case. Finally, we show numerical results for the full and approximate expressions with the purpose of setting the limits of validity of the approximate expressions, and we do this through a detailed analysis of the system of silver particles in water.

We have already reported, in a conference paper,[13] preliminary results of our approach to this problem. Here we include a full account of the theory in as much detail as possible, together with new analytical expressions for the reflection amplitudes, as well as an ample numerical analysis and a thorough discussion of our results.

FRESNEL'S REFLECTION AMPLITUDES

We start by recalling that in macroscopic electrodynamics of continuous media, in the absence of spatial dispersion (local optics), the reflection amplitudes for plane waves oscillating with a frequency ω, at a flat interface between nonmagnetic materials characterized with dielectric functions $\epsilon_i(\omega)$ and $\epsilon_f(\omega)$, are given by Fresnel's relations for nonmagnetic media. These relations for s- and p-polarization can be written as

$$r_s = \frac{k_z^i - k_z^f}{k_z^i + k_z^f} \tag{1}$$

$$r_p = \frac{\hat{k}^r \cdot \hat{k}^f}{\hat{k}^i \cdot \hat{k}^f}\left(\frac{k_z^i - k_z^f}{k_z^i + k_z^f}\right) \tag{2}$$

where $\vec{k}^i = \vec{k}_\parallel + k_z^i \hat{e}_z$, $\vec{k}^r - \vec{k}_\parallel - k_z^i \hat{e}_z$, and $\vec{k}^f = \vec{k}_\parallel + k_z^f \hat{e}_z$, are the incident, reflected, and transmitted wave vectors of the corresponding plane waves, the hat ^ denotes a unit vector and the sub index $\parallel$ denotes the component along the interface whereas the z axis is perpendicular to it and points toward the material with dielectric function ϵ_f. In s-polarization the electric field is along the x axis and in p-polarization it lies in the yz plane. Here it is assumed that ϵ_i is real and ϵ_f is, in general, complex, thus $k_\parallel^i = (\omega/c)\epsilon_i \sin \theta_i$ is also real, where θ_i denotes the angle of incidence. Finally, k_z^f and k_z^i are given by the dispersion relation of the transverse electromagnetic modes in each material at either side of the interface and given by $k_z^\alpha = [(\omega/c)^2 \epsilon_\alpha(\omega) - k_\parallel^i{}^2]^{1/2}$, where $\epsilon_\alpha(\omega)$ is the local electric permittivity of the material and $\alpha = i$ or f. It is also relevant to point out that in case of systems with very small colloidal particles (nonturbid colloids) that can be characterized with an effective index of refraction $n_{eff}(\omega)$, Fresnel's relations are also valid, the only thing to do is to replace $\epsilon_f(\omega)$ by $n_{eff}^2(\omega)$. Although this form of writing r_p (eq 2) is not the usual one written in textbooks, it is convenient here because it will be used later when we discuss the small-particle limit of our results.

THE BULK

Before turning to the problem of the calculation of the reflection amplitudes of a turbid colloidal system, we first summarize the results obtained in ref 8 for the effective electromagnetic response in the bulk. We start by considering the current density $\vec{J}^{ind}$ induced within an isolated, nonmagnetic sphere of radius a by an external electric field $\vec{E}^{ext}$ oscillating at

frequency ω. If the sphere is located with its center at the origin and is described by a local, in general, complex, dielectric response $\epsilon_s(\omega) \equiv \epsilon_0 + (i/\omega)\,\sigma_{loc}^s(\omega)$, where this relation defines $\sigma_{loc}^s(\omega)$ as the local, in general, complex, conductivity, then the current induced at any point $\vec{r}$ $(r < a)$ can be written as a local Ohm's law

$$\vec{J}^{\,int}(\vec{r};\omega) = \sigma_{loc}^s(\omega)\,\vec{E}^{\,int}(\vec{r};\omega) \tag{3}$$

where $\vec{E}^{\,int}$ is the internal field, that is, the sum of the external field plus the field generated by all the induced currents themselves. But one could also write this same induced current $\vec{J}^{\,ind}$ as the response not to the internal field $\vec{E}^{\,int}$, but to the external field $\vec{E}^{\,ext}$ exciting the sphere. In this case the response is nonlocal and can be written as

$$\vec{J}^{\,ind}(\vec{r};\omega) = \int_{V_S} \vec{\sigma}^s(\vec{r},\vec{r}';\omega)\cdot\vec{E}^{\,ext}(\vec{r}';\omega)\,d^3r' \tag{4}$$

where the integration volume V_S is the volume of the sphere. Because $\vec{E}^{\,ext}$ has no information at all about the presence of the sphere, it is the kernel $\vec{\sigma}(\vec{r},r';\omega)$ that takes account of all the geometric and electromagnetic properties of the sphere; and it is called the generalized nonlocal conductivity tensor. It is called *generalized* because the induced current $\vec{J}^{\,ind}$ is the *total* induced current; that is, it includes also those currents usually regarded as the source of the magnetic response of the sphere. It is also called nonlocal, because the value of the induced current at $\vec{r}$ depends on the value of the external electric field in the neighborhood of $\vec{r}$. The induced currents also generate an electromagnetic field outside the sphere that we will call the scattered field. In case the external field has no appreciable variations within the volume of the sphere (the sphere is small), one can take $\vec{E}^{\,ext}$, in eq 4, outside the integral, and the response becomes local again.

In the case of a boundless system composed of a great number of spheres, located randomly at fixed points in space, and in the presence of an external electric field oscillating at a frequency ω, the total induced current in the system will be the sum of the currents induced within each sphere. The field exciting each sphere (the exciting field) will be given by the external field plus the field scattered by all other spheres. Because this field is external to each sphere, the response of each sphere to its corresponding exciting field will be necessarily nonlocal, as in eq 4. Furthermore, the exciting field, as well as the currents induced within the spheres, have a stochastic nature due to the random location of the spheres; thus one can split both of them into two components, an average component plus a fluctuating one. The average is an average over space that smooths out the sharp variations of the field for lengths much less than the wavelength of the external field. Here we will perform this spatial average through a configuration (ensemble) average, although the precise choice of the averaging procedure will depend on the measuring device.

It is now right to ask whether it is possible to find a generalized *effective* conductivity tensor $\vec{\sigma}_{eff}$ that relates linearly the average induced current density in the colloidal system with the corresponding average of the electric field. It has been recently shown[8] that this is indeed possible, but because the response of each sphere to its corresponding exciting field is nonlocal, the effective response turns out to be also nonlocal. Because spatial nonlocality is equivalent to spatial dispersion in Fourier $\vec{k}$-space, one can write

$$\langle\vec{J}^{\,ind}\rangle(\vec{k},\omega) = \vec{\sigma}_{eff}(\vec{k},\omega)\cdot\langle\vec{E}\rangle(\vec{k},\omega) \tag{5}$$

where $\langle...\rangle$ denotes the average. It has been also shown[8] that in the effective-field approximation (EFA), valid for dilute systems, one simply gets

$$\vec{\sigma}_{eff}(\vec{k},\omega) = n_0\vec{\sigma}^s(\vec{k},\vec{k}'=\vec{k};\omega) \tag{6}$$

where n_0 is the number density of spheres,

$$\sigma^s(\vec{k},\vec{k}';\omega) = \int_{V_S} d^3r \int_{V_S} d^3r'\, e^{-i\vec{k}\cdot\vec{r}}\,\vec{\sigma}^s(\vec{r},\vec{r}';\omega)e^{i\vec{k}'\cdot\vec{r}'} \tag{7}$$

is the spatial Fourier transform of the generalized conductivity tensor $\vec{\sigma}(\vec{r},r';\omega)$ of an isolated sphere. Here one assumes that the colloidal system is, on the average, homogeneous and isotropic, and for this type of system the generalized *effective* conductivity tensor $\vec{\sigma}_{eff}$ can be written in terms of only two scalar quantities, that is,

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

where $\hat{k} \equiv \vec{k}/k$ denotes unit vector and the scalar functions σ_{eff}^L and σ_{eff}^T are called longitudinal and transverse components of $\vec{\sigma}_{eff}$ which can also be related to the more common effective electric permittivity $\epsilon_{eff}(k,\omega)$ and effective magnetic permeability $\mu_{eff}(k,\omega)$.[8]

One of the consequences of having a spatially dispersive response is that, besides the transverse electromagnetic modes, there are also longitudinal modes, as shown in detail in ref 8. Also, the dispersion relation of the transverse modes can be written as

$$k^2 = k_0^{\,2}\left(1 + \frac{i}{\omega}\sigma_{eff}^T(k,\omega)\right) \tag{9}$$

and can be used to define, properly, a frequency dependent effective index of refraction $n_{eff}(\omega)$ through $k^T(\omega) = k_0 n_{eff}(\omega)$, where $k^T(\omega)$ is the solution of eq 9. Here $k_0 = \omega/c$, where c is the speed of light in vacuum. It is also appropriate to point out that by taking in eq 9 $\sigma_{eff}^T(k,\omega) \approx \sigma_{eff}^T(k_0,\omega)$, the corresponding index of refraction can be written as[8]

$$n_{eff} = 1 + i\gamma S(0) \tag{10}$$

where $\gamma = (3/2)f/(k_0a)^3$, f is the volume filling fraction of the spheres and $S(0)$ is either one of the diagonal elements of the 2 × 2 scattering matrix in the forward direction (both elements are equal for forward scattering). This expression is exactly the same as the one proposed by van de Hulst long time ago,[20] but this derivation shows explicitly that it corresponds to a system with spatially dispersive effective response $\sigma_{eff}^T(k_0,\omega)$, and therefore, n_{eff} in eq 10 cannot be used, for example, in Fresnel's relations once the particles are not very small compared to the wavelength of the incident radiation.

Finally, it can be also shown[8] that in the long-wavelength limit $\sigma_{eff}^T(k{\to}0,\omega) = -i\omega\epsilon_0 n_0\alpha(\omega)$, where α denotes the polarizability of the isolated sphere. Thus, by using this limiting value in eq 9, one gets that in the low-density regime the effective index of refraction is given by

$$n_{eff}^{\,2} = 1 + n_0\alpha \tag{11}$$

as expected for a collection of spheres with polarizability α.

■ THE INTERFACE

The problem now is how to treat properly the presence of an interface in a system with a spatially dispersive electromagnetic

response, and how to calculate its reflection and transmission properties. First we recall that for common nonmagnetic homogeneous materials, characterized by a complex local electric permittivity, $\epsilon(\omega)$, the dispersion relation for transverse modes in the bulk, $k^2 = k_\parallel^2 + k_z^2 = (\omega/c)^2 \epsilon(\omega)$, is modified by the presence of a flat interface, because in this case $k_\parallel = k^i \sin \theta_i$ should be real, and only k_z is complex, and this gives rise to a new type of mode called inhomogeneous waves. Here k^i is the wave vector of the incident plane wave and θ_i is the angle of incidence. But when the electromagnetic response of the system is spatially dispersive, not only the presence of a flat interface requires $k_\parallel = k^i \sin \theta_i$ to be real but also the electromagnetic response in the presence of the interface is different from the one in the bulk. This is because the interface breaks up the translational invariance of the boundless system, thus the effective electromagnetic response depends now not on $\vec{r} - \vec{r}'$ but rather on $\vec{r}$ and $\vec{r}'$, separately, correspondingly in Fourier k-space it should depend on both $\vec{k}$ and $\vec{k}'$, separately; that is, one requires $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}, \vec{k}'; \omega)$ instead of the bulk response $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}, \omega)$. Nevertheless, because the translational invariance was broken only in the z-direction, and $k_\parallel = k'_\parallel = k^i \sin \theta_i$, what one actually requires is to determine $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}_\parallel, k_z; \vec{k}_\parallel, k'_z; \omega)$, which we succinctly write as $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}_\parallel, k_z; k'_z; \omega)$. One can interpret this by going back to r-space and finding from $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{r}_\parallel - \vec{r}'_\parallel; z, z'; \omega)$ that there is a region close to the interface, called the surface region, where the electromagnetic response differs from the one in the bulk. As a final comment we must point out that although the effective bulk response $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}; \omega)$ has a definite counterpart in macroscopic electrodynamics of continuous media, and more specifically in the field of nonlocal optics, $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}_\parallel, k_z; k'_z; \omega)$ has not.

Therefore, because the construction of $\overleftrightarrow{\sigma}_{\mathrm{eff}}(\vec{k}_\parallel, k_z; k'_z; \omega)$ would not yield any particular advantage because there is no macroscopic theory for this type of response, we will start by calculating directly, in the presence of a plane interface, the total induced current in the spheres in terms of the nonlocal conductivity of the isolated sphere. In this case, the total induced current $\vec{J}^{\mathrm{ind}}$ will be given by the sum of the current induced in each sphere when excited by $\vec{E}_{\mathrm{exc}}$, that is, by the external electric field plus the field scattered by all other spheres, and this scattered field depends obviously on the location of all other spheres in the half space (HS). Thus, one can write

$$\vec{J}^{\mathrm{ind}}(\vec{r};\omega) = \sum_{p=1}^{N} \int_{\mathbb{R}^3} \overleftrightarrow{\sigma}^s(\vec{r}-\vec{r}_p, \vec{r}'-\vec{r}_p; \omega) \cdot$$
$$\vec{E}_{\mathrm{exc}}(\vec{r}'; \vec{r}_1, \vec{r}_2, ..., \vec{r}_{p-1}, \vec{r}_{p+1}, ..., \vec{r}_N; \omega) \, \mathrm{d}^3 r' \quad (12)$$

where the integral over $\mathrm{d}^3 r'$ actually runs only over the volume of the spheres located within the HS, simply because $\overleftrightarrow{\sigma}^s$ vanishes whenever either $\vec{r}$ or $\vec{r}'$ lies outside the volume of the spheres. Now, with this induced current density we will construct an integral equation for the electric field, which after averaging together with some approximations, will serve to calculate the reflection amplitude of the coherent (average) beam.

■ THE INTEGRAL EQUATION

We start directly from Maxwell's equations for the electric field and write

$$\vec{E}(\vec{r};\omega) = \vec{E}_{\mathrm{inc}}(\vec{r};\omega) + i\omega\mu_0 \int_{\mathbb{R}^3} \mathrm{d}^3 r' \, \overleftrightarrow{G}_0(\vec{r}, \vec{r}'; \omega) \cdot \vec{J}^{\mathrm{ind}}(\vec{r}'; \omega) \quad (13)$$

where $\vec{E}_{\mathrm{inc}}$ is the incident (external) field,

$$\overleftrightarrow{G}_0(\vec{r}, \vec{r}'; \omega) = \left(\overleftrightarrow{1} + \frac{1}{k_0^2} \nabla\nabla \right) \frac{e^{ik_0|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|} \quad (14)$$

is the dyadic Green's function for empty space (free propagator), $k_0 = \omega/c$ and in the integral its principal value should be taken. If one now substitutes $\vec{J}^{\mathrm{ind}}$ given in eq 12 into eq 13, one uses the effective-field approximation (EFA), that is, one sets $\vec{E}_{\mathrm{exc}} \approx \langle \vec{E} \rangle$, and then takes the ensemble average of the resulting equation, one gets an integral equation for the average electric field $\langle \vec{E} \rangle$, which can be written as

$$\langle \vec{E} \rangle(\vec{r}) = \vec{E}_{\mathrm{inc}}(\vec{r}) + i\omega\mu_0 N \int_{z_p > a} \mathrm{d}^3 r_p \, f_1(\vec{r}_p)$$
$$\times \int_{\mathbb{R}^3} \mathrm{d}^3 r' \, \overleftrightarrow{G}_0(\vec{r}, \vec{r}') \cdot \int_{\mathbb{R}^3} \mathrm{d}^3 r'' \, \overleftrightarrow{\sigma}^s(\vec{r}'-\vec{r}_p, \vec{r}''-\vec{r}_p) \cdot \langle \vec{E} \rangle(\vec{r}'') \quad (15)$$

where $\vec{r}_p$ denotes the position of the spheres and we have simplified the notation by suppressing the explicit functional dependence on ω. Here, the averaging procedure introduces the quantity $f_1(\vec{r}_p) \, \mathrm{d}^3 r_p$, which is the probability to find the center of a sphere within $\mathrm{d}^3 r_p$. We will consider that the probability density $f_1(\vec{r}_p)$ is equal to $1/V$ for $z_p > a$, where V is the integration volume (Figure 1).
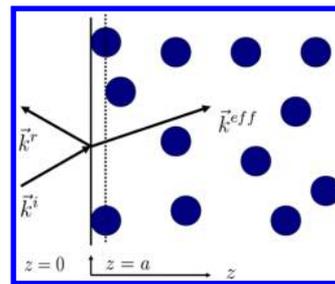

Figure 1. Schematic diagram of the colloidal system and coordinate system used in our analysis.

Thus, in the limit $V \to HS$, the quantity $N/V \to n_0$, where n_0 is the number of particles per unit volume, the so-called number density. In eq 15 the order of integration is important, because depending on the order taken it will yield two different results. On one hand, if the integration over $\mathrm{d}^3 r_p$ is performed first, it will correspond to taking first the average of the induced current and then calculating the field it generates; this procedure would try to preserve the quest for an effective response. On the other hand, if one leaves the integration over $\mathrm{d}^3 r_p$ until the end, it will correspond to calculating first the electric field generated by the whole induced current (average plus fluctuating) and performing the average of the field, afterward. Because the results of the two procedures are different, and we have checked that the second one (the one that accounts for the fluctuations of the induced current) yields better results, we will describe only this one, and later we will remark and comment about the final result of the first procedure. Finally, in the kernel of eq 15 the integral over $\mathrm{d}^3 r''$ runs only over the HS ($z'' > 0$), because $\overleftrightarrow{\sigma}^s$ is zero where there are no spheres; therefore, we find it convenient to leave the integration volume over all $\mathbb{R}^3$ but to take in the integral over

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d^3r'', $\langle \vec{E} \rangle (\vec{r}'')$ equal to zero outside the HS. Thus, it is convenient to split the average electric field as

$$\langle \vec{E} \rangle = \langle \vec{E} \rangle^- + \langle \vec{E} \rangle^+$$

where $\langle \vec{E} \rangle^- = \theta(-z)\langle \vec{E} \rangle$ and $\langle \vec{E} \rangle^+ = \theta(z)\langle \vec{E} \rangle$.

The integral equation (eq 15), although apparently complicated, has a plane wave solution when excited by an incident transverse plane wave. To see this, we first introduce a plane-wave representation for the dyadic Green's function, given by[29]

$$\vec{G}_0(\vec{r},\vec{r}') = -\frac{\hat{e}_z\hat{e}_z}{k_0^2}\delta(\vec{r}-\vec{r}')$$
$$+ \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{i}{2k_z}(\vec{I} - \hat{k}_\pm\hat{k}_\pm)e^{i\vec{k}_\parallel\cdot(\vec{r}_\parallel - \vec{r}_\parallel') + ik_z|z - z'|}\,dk_x\,dk_y$$

(16)

where $\hat{k}_+ = (k_x\hat{e}_x + k_y\hat{e}_y + k_z\hat{e}_z)/k_0$, if $z - z' > 0$, $\hat{k}_- = (k_x\hat{e}_x + k_y\hat{e}_y - k_z\hat{e}_z)/k_0$, if $z - z' < 0$, and $k_z = (k_0^2 - k_x^2 - k_y^2)^{1/2}$.

Because the presence of the interface breaks the translational invariance only in the z direction, it is also convenient to introduce a mixed Fourier representation for the electric field in the form $\vec{E}(\vec{k}_\parallel, z)$, and a full Fourier representation for $\vec{\sigma}^s(\vec{r},\vec{r}')$ in the form $\vec{\sigma}^s(\vec{k},\vec{k}') = \vec{\sigma}^s((\vec{k}_\parallel,\vec{k}_z),(\vec{k}_\parallel',\vec{k}_z')) \equiv \vec{\sigma}^s(\vec{k}_\parallel,\vec{k}_z,\vec{k}_z')$. After doing this in eq 15, and performing the necessary integrations, one is finally able to write the following.

For $z > 0$,

$$\langle \vec{E} \rangle^+(\vec{k}_\parallel, z) = \vec{E}_{inc}(\vec{k}_\parallel, z)$$
$$+ \frac{i\omega\mu_0 n_0}{2\pi}\int_{\mathbb{R}}dp_z''\,e^{ip_z''z}\left(-\frac{\hat{e}_z\hat{e}_z}{k_0^2}\cdot\vec{\sigma}^s(\vec{k}_\parallel;p_z'',p_z'')\right.$$
$$+ (\vec{I} - \hat{k}_+\hat{k}_+)\cdot\frac{\vec{\sigma}^s(\vec{k}_\parallel;k_z,p_z'')}{2k_z(p_z'' - k_z)}$$
$$\left.- (\vec{I} - \hat{k}_-\hat{k}_-)\cdot\frac{\vec{\sigma}^s(\vec{k}_\parallel;-k_z,p_z'')}{2k_z(p_z'' + k_z)}\right)\cdot\langle \vec{E} \rangle^+(\vec{k}_\parallel,p_z'')$$
$$- \frac{i\omega\mu_0 n_0}{2\pi}\frac{e^{ik_z z}}{2k_z}(\vec{I} - \hat{k}_+\hat{k}_+)\cdot$$
$$\int_{\mathbb{R}}dp_z''\,\frac{\vec{\sigma}^s(\vec{k}_\parallel,k_z,\vec{k}_\parallel,p_z'')}{p_z'' - k_z}\cdot\langle \vec{E} \rangle^+(\vec{k}_\parallel,p_z'')e^{ia(p_z'' - k_z)}$$

(17)

For $z < 0$, what is obtained is a relation for the electric field for $z < 0$ in terms of an integral over $\langle \vec{E} \rangle^+(\vec{k}_\parallel,p_z'')$ that is,

$$\langle \vec{E} \rangle^-(\vec{k}_\parallel, z) = \vec{E}_{inc}(\vec{k}_\parallel, z) - \frac{i\omega\mu_0 n_0}{2\pi}\frac{e^{-ik_z z}}{2k_z}(\vec{I} - \hat{k}_-\hat{k}_-)\cdot$$
$$\int_{\mathbb{R}}dp_z''\,\frac{\vec{\sigma}^s(\vec{k}_\parallel,-k_z,\vec{k}_\parallel,p_z'')}{p_z'' + k_z}\cdot\langle \vec{E} \rangle^+(\vec{k}_\parallel,p_z'')e^{ia(p_z'' + k_z)}$$

(18)

As mentioned above, this integral equation has a plane-wave solution when the system is excited by an incident transverse plane wave. Thus, we substitute in eq 17 a unit-amplitude incident plane wave of the form

$$\vec{E}_{inc}(\vec{k}_\parallel, z) = (2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)e^{ik_z^i z}\hat{e}^i$$

(19)

where $\hat{e}^i$ denotes its polarization and being transverse $\vec{k}_i\cdot\hat{e}^i = 0$. Then we propose as a solution of the integral equation, the following plane-wave *ansatz*

$$\langle \vec{E} \rangle^+(\vec{k}_\parallel, z) = (2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)t\theta(z)e^{ik_z^f z}\hat{e}^f$$

(20)

whose Fourier transform is

$$\langle \vec{E} \rangle^+(\vec{k}_\parallel, p_z'') = (2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)\frac{1}{i(p_z'' - k_z^f)}t\hat{e}^f$$

(21)

where t, k_z^f, and $\hat{e}^f$ denote amplitude, z-component of the wave vector, and polarization, respectively, of the plane-wave *ansatz* for the transmitted $(z > 0)$ electric field. These parameters are unknown and have to be determined by demanding consistency when eqs 19 and 21 are substituted into eq 17. Notice that one is assuming that the parallel component of the incident and transmitted wave vectors are equal: $k_\parallel^f = k_\parallel^i = k_0 \sin\theta_i$ (Snell's law).

The substitution mentioned above yields the next two consistency equations:

$$\hat{e}^f = i\omega\mu_0 n_0\left(-\frac{\hat{e}_z\hat{e}_z}{k_0^2}\cdot\vec{\sigma}^s(\vec{k}^f,\vec{k}^f) + (\vec{I} - \hat{k}^i\hat{k}^i)\cdot\frac{\vec{\sigma}^s(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)}\right.$$
$$\left.- (\vec{I} - \hat{k}^r\hat{k}^r)\cdot\frac{\vec{\sigma}^s(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)}\right)\cdot\hat{e}^f$$

(22)

and

$$\hat{e}^i = i\omega\mu_0 n_0\frac{1}{2k_z^i}(\vec{I} - \hat{k}^i\hat{k}^i)\cdot\frac{\vec{\sigma}^s(\vec{k}^i,\vec{k}^f)}{k_z^f - k_z^i}\cdot t\hat{e}^f e^{ia(k_z^f - k_z^i)}$$

(23)

where $\vec{k}^r = (\vec{k}_\parallel^i, -\vec{k}_z^i)$ and $\vec{k}^f = (\vec{k}_\parallel^i, \vec{k}_z^f)$ are the wave vectors of the reflected and transmitted waves. These consistency equations should determine t, k_z^f, and $\hat{e}^f$.

The first consistency equation (22), is a homogeneous equation that has a solution different from zero if and only if its determinant vanishes, that is,

$$\det\left[\vec{I} - i\omega\mu_0 n_0\left(-\frac{\hat{e}_z\hat{e}_z}{k_0^2}\cdot\vec{\sigma}^s(\vec{k}^f,\vec{k}^f) + (\vec{I} - \hat{k}^i\hat{k}^i)\cdot\right.\right.$$
$$\left.\left.\frac{\vec{\sigma}^s(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} - (\vec{I} - \hat{k}^r\hat{k}^r)\cdot\frac{\vec{\sigma}^s(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)}\right)\right] = 0$$

(24)

This is an implicit equation for $k_z^f(\omega)$ that has to be solved self-consistently, yielding the nonlocal dispersion relation of the "effective" wave-vector $\vec{k}^f(\omega) = (\vec{k}_\parallel^i(\omega), k_z^f(\omega))$ of the electromagnetic modes that are able to propagate in the system. Because $\vec{k}_\parallel^i$ is real and k_z^f is in general complex, these modes are similar in structure to the so-called inhomogeneous waves of continuous electrodynamics. It is called a nonlocal dispersion relation, because k_z^f also appears in the arguments of $\vec{\sigma}^s$, denoting the presence of spatial dispersion (nonlocality).

The second consistency relation (23) is analogous to the extinction theorem in continuous electrodynamics and can be solved for t after dot multiplying both sides of the equation by $\hat{e}^i$, yielding

$$t = \frac{2k_z^i}{i\omega\mu_0 n_0} \frac{k_z^f - k_z^i}{\hat{e}^i \cdot \vec{\sigma}^s(\vec{k}^i,\vec{k}^f) \cdot \hat{e}^f} e^{-ia(k_z^f - k_z^i)} \tag{25}$$

Now, one is able to calculate the electric field for $z < 0$, by substituting, first, eq 21 into eq 18, and then integrating over dp_z''. One gets

$$\langle\vec{E}\rangle^{(-)}(\vec{k}_\parallel,z) = \vec{E}_i(\vec{k}_\parallel,z) - i\omega\mu_0 n_0 \frac{e^{-ik_z^i z}}{2k_z^i}(\vec{I} - \hat{k}^r\hat{k}^r) \cdot$$

$$\frac{\vec{\sigma}^s(\vec{k}^r,\vec{k}^f)}{k_z^f + k_z^i} \cdot \hat{e}^f t e^{ia(k_z^f - k_z^i)} \tag{26}$$

where t is given by eq 25 that depends on the polarization $\hat{e}^i$ of the incident field. Because $\vec{E}_i(\vec{k}_\parallel,z)$ corresponds to the incident field for $z < 0$, one can identify the second term in eq 26 as the reflected electric field.

■ REFLECTION AMPLITUDES

By choosing in eq 26 $\hat{e}^i$ either perpendicular or parallel to the plane of incidence, we will obtain the reflection amplitudes for s- and p-polarization, respectively. The plane of incidence is the plane generated by $\vec{k}^i$ and a vector perpendicular to the interface. To write closed-form expressions for these reflection amplitudes, we will project $\vec{\sigma}^s(k,k')$, the nonlocal conductivity tensor of the isolated sphere, on a two definite vector basis. One basis is chosen with unitary vectors $\{\hat{e}_X, \hat{e}_Y, \hat{e}_Z\}$ lying along the coordinate axes XYZ chosen as follows: the Z axis along $\vec{k}$, the X axis along $\vec{k} \times \vec{k}'$, and Y axis along $\hat{e}_Z \times \hat{e}_X$ (Figure 2).
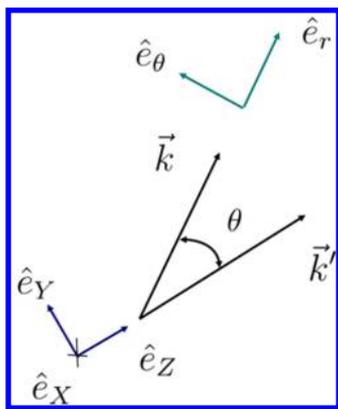
Figure 2. Unit vector basis used in our analysis. The Cartesian unit vectors are oriented as shown with the incident wave vector $\vec{k}'$, whereas the spherical-coordinates unit vectors refer to the scatter wave vector $\vec{k}$.

In the other vector basis $\{\hat{e}_X, \hat{e}_r, \hat{e}_\theta\}$, $\hat{e}_r$ lies along $\vec{k}$ and $\hat{e}_\theta$ lies along $\hat{e}_r \times \hat{e}_X$. By dot multiplying $\vec{\sigma}^s(k,k')$ on the left by $\{\hat{e}_X, \hat{e}_r, \hat{e}_\theta\}$ and on the right by $\{\hat{e}_X, \hat{e}_Y, \hat{e}_Z\}$, one obtains a (3×3) matrix representation of $\vec{\sigma}^s(k,k')$, and we denote, for example,

$$\sigma_{XX}^s = \hat{e}_X \cdot \vec{\sigma}^s \cdot \hat{e}_X$$

$$\sigma_{\theta Y}^s = \hat{e}_\theta \cdot \vec{\sigma}^s \cdot \hat{e}_Y$$

and

$$\sigma_{\theta Z}^s = \hat{e}_\theta \cdot \vec{\sigma}^s \cdot \hat{e}_Z \tag{27}$$

Therefore, using this matrix representation for $\vec{\sigma}^s$ and combining eqs 25 and 26, one can finally write the reflection amplitudes for s- and p-polarization, as

$$r_s = \frac{\sigma_{XX}^s(\vec{k}^r,\vec{k}^f)}{\sigma_{XX}^s(\vec{k}^i,\vec{k}^f)} \frac{k_z^i - k_z^f}{k_z^i + k_z^f} e^{i2ak_z^i} \tag{28}$$

and

$$r_p = \frac{\sigma_{\theta Y}^s(\vec{k}^r,\vec{k}^f) + s\sigma_{\theta Z}^s(\vec{k}^r,\vec{k}^f)}{\sigma_{\theta Y}^s(\vec{k}^i,\vec{k}^f) + s\sigma_{\theta Z}^s(\vec{k}^i,\vec{k}^f)} \frac{k_z^i - k_z^f}{k_z^i + k_z^f} e^{i2ak_z^i} \tag{29}$$

where $s = (\hat{e}^f \cdot \hat{k}^f)/(\hat{e}^f \cdot \hat{k}_\perp^f)$ is a geometrical factor and $\hat{k}_\perp^f$ is a unit vector along $\hat{k}_\perp^f \times \hat{e}_X$, and the phase factors arise from our choice of origin. These formulas are the main result of our work, they are valid in the dilute regime, and they give the reflection amplitudes in terms of components of the generalized nonlocal conductivity tensor of an isolated sphere: σ_{XX}^s, $\sigma_{\theta Y}^s$, and $\sigma_{\theta Z}^s$. Notice, however, that besides the explicit dependence on $\hat{k}_z^f$ and $\hat{e}^f$, the components of the conductivity tensor have to be evaluated at $(\vec{k}^r, \vec{k}^f)$ and $(\vec{k}^i, \vec{k}^f)$; thus it is required to solve first the dispersion relation for $\vec{k}^f(\omega)$ and use eq 22 to determine $\hat{e}^f$; then use k_z^f and $\hat{e}^f$ on the evaluation of eqs 28 and 29. It can also be shown that these expressions for r_s and r_p, in the limiting case of small spheres $k_0 a \ll 1$, turn into Fresnel's relations (eqs 1 and 2), as they should.

■ DISPERSION RELATION

As mentioned above, to calculate the reflection amplitudes using the expressions in eqs 28 and 29, one is required first to determine $\vec{k}^f = (\vec{k}_\parallel, \vec{k}_z^f)$ from the general expression for the dispersion relation given by eq 24. But before doing this, we will derive an approximate expression for $k_z^f(\omega)$ by considering that the conductivity tensor $\vec{\sigma}^s$ that appears in eq 24 with different arguments, has a bulk character, that is, $\vec{\sigma}^s(\vec{k}^r,\vec{k}^f) = \vec{\sigma}^s(\vec{k}^r,\vec{k}^f) = \vec{\sigma}^s(\vec{k}^f,\vec{k}^f)$. Then one uses the following identity

$$\frac{(\vec{I} - \hat{k}^i\hat{k}^i)}{2k_z^i(k_z^f - k_z^i)} - \frac{(\vec{I} - \hat{k}^r\hat{k}^r)}{2k_z^i(k_z^f + k_z^i)}$$

$$= \frac{1}{k_z^{f2} - k_z^{i2}}\left(\vec{I} - \frac{1}{k_0^2}\vec{k}^f\vec{k}^f\right) + \frac{\hat{e}_z\hat{e}_z}{k_0^2} \tag{30}$$

to write eq 24, as

$$\det\left[\vec{I} - i\omega\mu_0 n_0 \frac{1}{k_f^2 - k_0^2}\left(\vec{I} - \frac{1}{k_0^2}\vec{k}^f\vec{k}^f\right) \cdot \vec{\sigma}^s(\vec{k}^f,\vec{k}^f)\right] = 0 \tag{31}$$

We proceed to solve this equation by first choosing a vector basis $\{\hat{e}_X, \hat{k}_\perp^f, \hat{k}^f\}$ where $\hat{k}_\perp^f = \hat{k}^f \times \hat{e}_X$. In this basis

$$\vec{\sigma}^s(\vec{k}^f,\vec{k}^f) = \sigma^T(k^f)\hat{e}_X\hat{e}_X + \sigma^T(k^f)\hat{k}_\perp^f\hat{k}_\perp^f + \sigma^L(k^f)\hat{k}^f\hat{k}^f \tag{32}$$

becomes a diagonal dyadic that can be written in terms of its transverse σ^T and longitudinal σ^L components. By substituting eq 32 into eq 31, one obtains the equation for the dispersion relation as two independent equations, one for transverse modes

$$1 - i\omega\mu_0 n_0 \frac{\sigma^T(k^f)}{k_f^2 - k_0^2} = 0 \tag{33}$$

and the other for longitudinal modes

$$1 - i\omega\mu_0 n_0 \frac{1}{k_f^2 - k_0^2}\left(1 - \frac{k_f^2}{k_0^2}\right)\sigma^L(k^f) = 0 \tag{34}$$

For the transverse modes, one can further approximate in eq 33 $\sigma^T(k^f) \approx \sigma^T(k_0) = 4\pi S(0)/(-i k_0)$,[20] where $S(0)$ is either of the diagonal elements of the scattering matrix of the sphere, in the forward direction. The dispersion relation for transverse modes can then be written as

$$(k^f)^2 = k_0^{\,2}\left(1 + n_0 \frac{4\pi i}{k_0^{\,3}} S(0)\right) \tag{35}$$

which is known as the Foldy–Lax dispersion relation.[21] We now introduce the presence of the interface by demanding $\vec{k}_\parallel^f = \vec{k}_\parallel^i$, where $\vec{k}^i$ is the wave vector of the incident wave and one writes

$$k_z^f = \sqrt{k_z^{i\,2} + n_0 \frac{4\pi i}{k_0} S(0)} \tag{36}$$

Now we will show that the Foldy–Lax dispersion relation given in eq 36 is a rather good approximation to the full solution of eq 24. To solve eq 24, we first project the dyadic $\overleftrightarrow{\sigma}(\vec{k}^r, \vec{k}^f)$ into components by using the vector basis $\{\hat{e}_X, \hat{k}_\perp^f, \hat{k}^f\}$ to the right and $\{\hat{e}_X, \hat{k}_\perp^i, \hat{k}^i\}$ to the left and realizing that these vector basis sets correspond to $\{\hat{e}_X, \hat{e}_Y, \hat{e}_Z\}$ and $\{\hat{e}_X, \hat{e}_r, \hat{e}_\theta\}$ used above. Then one writes the vectors $\hat{k}_\perp^i$ and $\hat{k}^i$ in the basis $\{\hat{e}_X, \hat{k}_\perp^f, \hat{k}^f\}$ and by doing the corresponding operations with $\overleftrightarrow{\sigma}^s(\vec{k}^r, \vec{k}^f)$, one can finally write eq 24 as

$$\det \overleftrightarrow{M} = 0 \tag{37}$$

where the dyadic $\overleftrightarrow{M}$ in the basis $\{\hat{e}_X, \hat{k}_\perp^f, \hat{k}^f\}$ is displayed explicitly in Appendix A in terms of the components of $\overleftrightarrow{\sigma}$, σ_{XX}, $\sigma_{\theta Y}$, and $\sigma_{\theta Z}$ with arguments $(\vec{k}^i, \vec{k}^f)$ and $(\vec{k}^r, \vec{k}^f)$, and also in terms of $\overleftrightarrow{\sigma}^s(\vec{k}^f, \vec{k}^f)$ written in terms of its transverse $\sigma^T(k^f)$ and longitudinal $\sigma^L(k^f)$ components. Let us recall that $\vec{k}^r = (\vec{k}_\parallel^i, -k_z)$ and $\vec{k}^f = (\vec{k}_\parallel^i, k_z^f)$. The first thing one notices is that besides the diagonal components of $\overleftrightarrow{M}$, $\overleftrightarrow{M}$ has also nondiagonal components in $\hat{k}_\perp^f \hat{k}^f$ and $\hat{k}^f \hat{k}_\perp^f$. This means that the roots of $\det \overleftrightarrow{M} = 0$ will yield modes with a mixed transverse-longitudinal character. The roots of eq 37 were found numerically using an iteration procedure, whose starting value $k_z^{f[0]}$ was taken to be the Foldy–Lax expression, given in eq 36.

In Figures 3 and 4, we show the results for $\text{Re}(k_z^{f[i]})$ and $\text{Im}(k_z^{f[i]})$ up to 4 iterations, $i = 1, 2, 3, 4$, as a function of the volume filling fraction of the spheres, for spheres made of silver and radius $a = 0.1\ \mu m$, in a vacuum, and excited with an external field oscillating with a wavelength of 635 nm. One can immediately see in this case that, for filling fractions less than
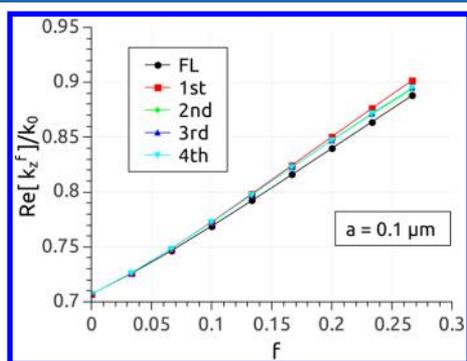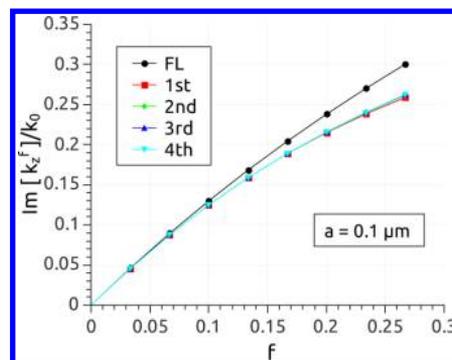
Figure 4. Imaginary part of wavenumber k_z^f as a function of the filling fraction obtained after 0, 1, 2, 3, and 4 iterations in the "exact" dispersion relation at a frequency of 0.63 μm for silver particles of radius $a = 0.10\ \mu m$.

about 6%, the dispersion relation given by the Foldy–Lax expression is an extremely good approximation. This iteration procedure was repeated (not shown here) for the same parameters, the same number of iterations, but with $a = 0.2\ \mu m$, and we observed that the convergence was even faster and the validity of the Foldy–Lax expression was good even at higher filling fractions, up to around 10%. This also shows that the dispersion relation in the bulk is not very sensitive to the effects introduced by the presence of the interface. We must add that in the numerical procedure of finding the roots of eq 37, we kept only one propagating solution, $\text{Re}(k_z^{f[i]}) > 0$ and $\text{Im}(k_z^{f[i]}) > 0$, whose rapid convergence meant that it was "close" to the Foldy–Lax solution; we did not explore for other roots that might also have yield information about the optical properties of the system. Actually, the fact that the real part of the z component of the "exact" effective wave vector bends away from the Foldy–Lax approximation means that the magnitude of the effective wave vector does not depend linearly on the volume fraction of the particles. This in turn reveals that dependent scattering effects are being taken into account by the exact solution to the dispersion relation.[22]

In relation to the polarization of the wave transmitted into the colloid, once the roots of eq 37 are found, one can determine the polarization $\hat{e}^f$ of the corresponding modes. It is clear that for s-polarization $\hat{e}^f = \hat{e}_x$ one has a pure transverse mode; but for p-polarization one finds

$$\hat{e}^f = \frac{1}{\sqrt{1 + s^2}}(\hat{k}_\perp^f + s\hat{k}^f) \tag{38}$$

where the factor $s = (\hat{e}^f \cdot \hat{k}^f)/(\hat{e}^f \cdot \hat{k}_\perp^f)$ is also displayed explicitly in Appendix A, and it is given in terms of the components of $\overleftrightarrow{\sigma}^s$, as well as the components of all the relevant wave vectors. One can see that this mode has a mixed transverse-longitudinal character; in case s is small, it will be mainly a transverse mode with a small longitudinal component; this seems to be the case, at least for the system of silver spheres explored in this work.

■ APPROXIMATIONS

Here we explore some plausible approximations to the expressions derived above (eqs 28 and 29) that will help us to have a further insight into their physical meaning and could be also useful in specific applications.

(i) Nonlongitudinal-Coupling Approximation (NLC). Let us recall that for an ("n the average") isotropic colloidal system, in the dilute regime, the bulk electromagnetic modes

Figure 3. Real part of wavenumber k_z^f as a function of the filling fraction obtained after 0, 1, 2, 3, and 4 iterations in the "exact" dispersion relation at a frequency of 0.63 μm for silver particles of radius $a = 0.1\ \mu m$.

are determined only by $\overleftrightarrow{\sigma}^s(\vec{k},\vec{k})$ see eq 6) and, as mentioned above, it can sustain modes with either transverse or longitudinal character.[8] Thus, the presence of the z component in $\sigma_{\theta z}$ and the geometric factor $s = (\hat{e}^f \cdot \hat{k}^f)/(\hat{e}^f \cdot \hat{k}^f_\perp)$ in the formula for r_p, can be understood as coming from the coupling through the interface of transverse and longitudinal bulk modes. Therefore, either to neglect $\sigma_{\theta z}$ or to take $s \approx 0$ in eq 29, will mean that the longitudinal character of the modes in the colloidal system is rather weak, and the transmitted wave will have, essentially, a transverse character. Therefore, within this approximation one writes

$$r_s = \frac{\sigma^s_{XX}(\vec{k}^r,\vec{k}^f)}{\sigma^s_{XX}(\vec{k}^i,\vec{k}^f)} \frac{k^i_z - k^f_z}{k^i_z + k^f_z} e^{i2ak^i_z} \tag{39}$$

$$r_p = \frac{\sigma^s_{\theta Y}(\vec{k}^r,\vec{k}^f)}{\sigma^s_{\theta Y}(\vec{k}^i,\vec{k}^f)} \frac{k^i_z - k^f_z}{k^i_z + k^f_z} e^{i2ak^i_z} \tag{40}$$

where $\vec{k}^f(\omega)$ has to be determined from the dispersion relation given in eq 24, with the same kind of approximations (no longitudinal coupling), although, as mentioned above, for low enough volume filling fractions of spheres, the dispersion relation given by the Foldy−Lax expression (eq 36) could be adequate to be used, not only in this derivation but also in the expressions derived below.

(ii) Light-Cone Approximation (LCA). The determination of the induced current density $\vec{J}^{ind}$ within the spheres generates an induced electric field, both inside and outside the spheres. The electric field outside is usually referred to as the scattered field $\vec{E}^s$, so there should be a relationship between the generalized conductivity tensor $\overleftrightarrow{\sigma}^s$ of the isolated sphere, and its scattering properties. To see this, we start by writing the scattered field of an isolated sphere as

$$\vec{E}^s(\vec{r}) = \int \overleftrightarrow{G}_0(\vec{r},\vec{r}') \cdot \vec{J}^{ind}(\vec{r}') \, d^3r' \tag{41}$$

where $\vec{r}$ lies outside the sphere. We then calculate the electric field in the far-field region ($r \gg 2\pi/k_0$) by expanding $\overleftrightarrow{G}_0$ to lowest order in $1/r$, introducing $\overleftrightarrow{\sigma}^s$ through eq 4, and exciting the sphere with an external transverse plane wave, given by $\vec{E}^{ext}(\vec{r}') = E^i_0 e^{i\vec{k}^i \cdot \vec{r}'} \hat{e}^i$. One gets

$$\vec{E}^s(\vec{r}) = i\omega\mu_0 E^i_0 \frac{e^{ik_0 r}}{4\pi r}(\overleftrightarrow{1} - \hat{k}^s\hat{k}^s) \cdot \overleftrightarrow{\sigma}^s(\vec{k}^s,\vec{k}^i) \cdot \hat{e}^i + O\left(\frac{1}{r^2}\right) \tag{42}$$

where $\vec{k}^s = k_0\hat{e}_r$, $\vec{k}^i = k_0\hat{k}^i$, and $\hat{k}^s = \vec{k}^s/k^s$. Here one can identify $\hat{k}^i$ as the wavevector of the incident wave whereas $\hat{k}^s$ corresponds to the direction of observation. One can immediately see that because $(\overleftrightarrow{1} - \hat{k}^s\hat{k}^s)$ is a transverse operator, the scattered field is perpendicular (transverse) to $\hat{k}^s$ and, therefore, the transverse components of $\overleftrightarrow{\sigma}$ can be identified with the diagonal components of the scattering matrix. Let us recall that the scattering matrix relates the transverse components of the scattered field with the corresponding ones of the incident field, and is defined as[23]

$$\begin{pmatrix} E^s_\parallel \\ E^s_\perp \end{pmatrix} = \frac{e^{ik_0 r}}{-ik_0 r} \begin{pmatrix} S_2(\theta) & 0 \\ 0 & S_1(\theta) \end{pmatrix} \begin{pmatrix} E^i_\parallel \\ E^i_\perp \end{pmatrix} \tag{43}$$

where the subindex $\parallel$ and $\perp$ denote parallel and perpendicular to the scattering plane, which is the plane spanned by the

vectors $\hat{k}^i$ and $\hat{k}^s$, and θ is the angle between them; also $S_1(0) = S_2(0) = S(0)$. If we now use eq 42 to calculate E^s_X for $\hat{e}^i = \hat{e}_X$, and E^s_θ for $\hat{e}^i = \hat{e}_Y$, and compare them with the relations between $E^s_\perp$ and $E^i_\perp$ and between $E^s_\parallel$ and $E^i_\parallel$, given in eq 43 we obtain

$$i\omega\mu_0 \frac{1}{4\pi}\sigma^s_{XX}(\vec{k}^s,\vec{k}^i) = \frac{1}{-ik_0}S_1(\theta) \tag{44}$$

$$i\omega\mu_0 \frac{1}{4\pi}\sigma^s_{\theta Y}(\vec{k}^s,\vec{k}^i) = \frac{1}{-ik_0}S_2(\theta) \tag{45}$$

Now we will use these relations to define what we call the light-cone approximation. Within this approximation one first assumes that the transmitted wave in the colloidal system is transverse $s \approx 0$, and also that $\sigma^s_{XX}(\vec{k}^r,\vec{k}^f) \approx \sigma^s_{XX}(\vec{k}^r,\vec{k}^i)$, and $\sigma^s_{XX}(\vec{k}^i,\vec{k}^f) \approx \sigma^s_{XX}(\vec{k}^i,\vec{k}^i)$ and that $\sigma^s_{\theta Y}(\vec{k}^r,\vec{k}^f) \approx \sigma^s_{\theta Y}(\vec{k}^r,\vec{k}^i)$ and $\sigma^s_{\theta Y}(\vec{k}^i,\vec{k}^f) \approx \sigma^s_{\theta Y}(\vec{k}^i,\vec{k}^i)$. These latter assumptions mean that in relation to the scattering process described by $\overleftrightarrow{\sigma}^s$, one assumes $\vec{k}^f \approx \vec{k}^i$, thus the exciting field is not the transmitted (refracted) field but it is rather the incident field with wave-vector $\vec{k}^i$ and magnitude k_0. Now, because the magnitude of the wave-vector $\vec{k}^i$, of the incident field, and of the scattered fields, either $\vec{k}^r$ or $\vec{k}^i$ (forward scattering), is the same and is equal to k_0, we say that they stay in the light cone and we call this approximation the light-cone approximation (LCA). Therefore, using the approximation of transversality mentioned above as well as the relations given in eqs 44 and 45, one can write the reflection amplitudes within the light-cone approximation as

$$r_s = \frac{S_1(\pi - 2\theta_i)}{S_1(0)}\left(\frac{k^i_z - k^f_z}{k^i_z + k^f_z}\right)e^{i2ak^i_z} \tag{46}$$

$$r_p = \frac{S_2(\pi - 2\theta_i)}{S_2(0)}\left(\frac{k^i_z - k^f_z}{k^i_z + k^f_z}\right)e^{i2ak^i_z} \tag{47}$$

where k^f_z has to be determined from the dispersion relation (eq 24). Nevertheless, this approximation suffers from an inconsistency problem; if one takes the small particle limit $ka \to 0$ one should get Fresnel's relations as given by eqs 1 and 2, and one does not. In this limit[23] $S_1(\theta) \to (3/2)a_1$ and $S_2(\theta) \to (3/2)a_1 \cos\theta$, where $a_1 = -i(2/3)(ka)^3(\epsilon_f - \epsilon_0)/(\epsilon_f + 2\epsilon_0)$. Therefore, one can readily see from eq 47 that although r_s tends to the correct limit, r_p is not, because

$$\lim_{ka\to 0} r_p^{LCA} = \frac{\hat{k}^r \cdot \hat{k}^i}{\hat{k}^i \cdot \hat{k}^i}\left(\frac{k^i_z - k^f_z}{k^i_z + k^f_z}\right) \neq \frac{\hat{k}^f \cdot \hat{k}^i}{\hat{k}^i \cdot \hat{k}^i}\left(\frac{k^i_z - k^f_z}{k^i_z + k^f_z}\right) \tag{48}$$

The reason is very clear: In the limit, $ka \to 0$, the difference between these two expressions is precisely in the first factor, the one that comes from the assumption $\vec{k}^f \approx \vec{k}^i$ in the scattering process. Because this replacement is the core of LCA, and it is preserved in the small particle limit, as explicitly shown in eq 48, one cannot expect to obtain the correct small particle limit.

(iii) Heuristic Approximation (HA). In trying to heal the inconsistency problem in LCA mentioned above, we have devised a similar approximation, with essentially the same assumptions as LCA, but with the correct small-particle limit. We simply assume that the effective wave vector of the plane wave that excites the sphere has magnitude k_0 but lies along the direction of the transmitted wave $\vec{k}^f$, whose direction can be obtained when one solves for k^f_z in the dispersion relation with an equivalent degree of approximation. Therefore, we simply change the angular arguments of the scattering matrix that

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appear in the expressions for r_s and r_p, by replacing $(\pi - 2\theta_i) \rightarrow \pi - (\theta_i + \theta_f)$ and $0 \rightarrow \theta_i - \theta_f$, where θ_f is the angle between the z axis and the wave-vector $\vec{k}^f$, in this way LCA is recovered by setting back $\theta_f = \theta_i$. We call this approximation the heuristic approximation, because it is not obtained from a rigorous mathematical derivation, but rather from an *ad hoc* modification for the correct fulfillment of a limiting value. We then write, in the heuristic approximation,

$$r_s = \frac{S_1(\pi - (\theta_i + \theta_f))}{S_1(\theta_i - \theta_f)} \frac{k_z^i - k_z^f}{k_z^i + k_z^f} e^{i2ak_z^i} \quad (49)$$

$$r_p = \frac{S_2(\pi - (\theta_i + \theta_f))}{S_2(\theta_i - \theta_f)} \frac{k_z^i - k_z^f}{k_z^i + k_z^f} e^{i2ak_z^i} \quad (50)$$

Note that here θ_f is in general complex because the transmitted wave is inhomogeneous and $\vec{k}^f$ is in general complex; nevertheless, these expressions will still remain valid in this case; the complex arguments of S_1 and S_2 can be evaluated by using, for example, $\cos(\pi - (\theta_i - \theta_f)) = \hat{k}^i \cdot \hat{k}^f$ and $\cos(\theta_i + \theta_f) = \hat{k}^i \cdot \hat{k}^f$. Again, the phase factors arise from our choice origin.

(iv) Fresnel Approximation (FA). The Fresnel approximation consists of assuming that the turbid colloid can be treated as a common material characterized with an effective index of refraction n_{eff}. In this respect, the reflection amplitudes will be given by Fresnel's relations, as given by eqs 1 and 2, using $k_z^f = k_0(n_{eff}^2 - \sin^2 \theta_i)^{1/2}$, where n_{eff} can be taken, for example, as the effective refractive index proposed by van de Hulst (eq 10) or the one derived from the Foldy–Lax dispersion relation. Although we have shown already that this procedure is not correct, here it will be used only for comparison purposes, and it will be regarded as a different approximation. Thus, in the Fresnel approximation we write again

$$r_s = \frac{k_z^i - k_z^f}{k_z^i + k_z^f} \quad (51)$$

$$r_p = \frac{\hat{k}^r \cdot \hat{k}^f}{\hat{k}^i \cdot \hat{k}^f} \left(\frac{k_z^i - k_z^f}{k_z^i + k_z^f} \right) \quad (52)$$

where k_z^f is determined by the dispersion relation and it will be, in general, complex.

As a final comment, we recall that in the process above of taking an ensemble average while solving the integral equation, we mentioned that an alternative procedure was first to average (integrate) over particle positions and then to calculate and solve the equation for the electric field. Well, if one follows that procedure in an analogous way as we have done it above, we end up with what we are calling here the Fresnel approximation.

Some of the approximations presented above do not require the calculation of the components of $\overleftrightarrow{\sigma}^s$, and for that reason they are very attractive. Thus, to check their accuracy, we will compare the numerical results obtained using the expressions corresponding to the different approximations, with the "exact" result given by eqs 28 and 29.

■ GENERALIZED NONLOCAL CONDUCTIVITY

We have derived above explicit expressions for the reflection amplitudes in the dilute regime (eqs 28 and 29), together with closed expressions for different kinds of approximations.

Therefore, to calculate them and to establish the accuracy of these approximations, one requires the tensor components of $\overleftrightarrow{\sigma}^s(\vec{k},\vec{k}')$, a calculation that will be displayed in this section. We start by recalling that, in real space, the generalized nonlocal conductivity tensor $\overleftrightarrow{\sigma}^s$ for an isolated sphere in vacuum, centered at the origin, obeys the following integral equation,[8]

$$\overleftrightarrow{\sigma}^s(\vec{r},\vec{r}';\omega) = \sigma_{loc}^s(\vec{r};\omega)[\delta(\vec{r} - \vec{r}')\overleftrightarrow{1}$$
$$+ i\omega\mu_0 \int_{V_s} G_0(\vec{r},\vec{r}'';\omega) \cdot \overleftrightarrow{\sigma}^s(\vec{r}'',\vec{r}'; \omega)\, d^3r''] \quad (53)$$

where

$$\sigma_{loc}^s(\vec{r};\omega) = \begin{cases} 0 & \text{if } r \notin V_s \\ \sigma_{loc}^s(\omega) & \text{if } r \in V_s \end{cases} \quad (54)$$

$\sigma_{loc}^s(\omega)$ is the local conductivity of the sphere defined in eq 3, and V_s is its volume. It was also pointed out in ref 8 that this integral equation is identical to the one obeyed by the transition operator $\overleftrightarrow{T}(\vec{r},\vec{r}')$ used in scattering theory (**T** matrix), when one identifies $\overleftrightarrow{T}(\vec{r},\vec{r}')$ with $i\omega\mu_0\overleftrightarrow{\sigma}^s(\vec{r},\vec{r}')$. Then it would be possible to use this integral equation to calculate $\overleftrightarrow{\sigma}^s(\vec{k},\vec{k}')$, as was already reported in refs 14 and 24. Here, we will use instead an alternative novel method grounded on the physical significance of eq 4, which will yield closed expressions for the components of $\overleftrightarrow{\sigma}^s$ through a Mie-type of scattering calculation.

We start by using eq 4 to calculate the current density induced within a sphere by the electric field of a plane wave of unit amplitude oscillating at frequency ω, with polarization along $\hat{e}_\beta$ and a wave-vector $\vec{k}'$. One readily writes

$$\vec{J}^{ind}(\vec{r};\vec{k}',\hat{e}_\beta;\omega) = \int_V \overleftrightarrow{\sigma}^s(\vec{r},\vec{r}';\omega) \cdot \hat{e}_\beta e^{i\vec{k}' \cdot \vec{r}'}\, d^3r' \quad (55)$$

If one now takes the k-Fourier transform of the above equation and then its α Cartesian component, one gets

$$J_\alpha^{ind}(\vec{k},\vec{k}';\hat{e}_\beta;\omega) = \hat{e}_\alpha \cdot \overleftrightarrow{\sigma}^s(\vec{k},\vec{k}';\omega) \cdot \hat{e}_\beta \equiv \sigma_{\alpha\beta}^s(\vec{k},\vec{k}';\omega) \quad (56)$$

where we have used the definition of the Fourier transform $\overleftrightarrow{\sigma}^s(\vec{k},\vec{k}';\omega)$ given in eq 7. Therefore, the physical interpretation of $\sigma_{\alpha\beta}^s(\vec{k},\vec{k}';\omega)$ is the α Cartesian component of the $\vec{k}$ Fourier transform of the current density induced within the sphere when excited by the electric field of a plane wave of unit amplitude oscillating with frequency ω, wave-vector $\vec{k}'$, and polarization along $\hat{e}_\beta$. But according to eq 3 the field inside the sphere, the internal field $\vec{E}^{int}$, is proportional to $\vec{J}^{ind}$, that is, $\vec{E}^{int} = (1/\sigma_{loc}^s)\vec{J}^{ind}$; therefore the problem is to calculate the electric field inside the sphere when excited by an incident plane wave. Because for a given oscillation frequency ω one requires the response of the system to any possible $\vec{k}'$, this problem is similar to the usual Mie-scattering problem with the difference that, here, the wave-vector $\vec{k}'$ of the incident plane wave has to be arbitrary, that is, independent of ω. In other words, the incident field is not a self-propagating wave, it is rather a plane wave with an arbitrary wave-vector $\vec{k}'$ and arbitrary polarization $\hat{e}_\beta$ that has to be generated, necessarily, by external currents. To generate this kind of plane waves traveling along the z-axis, the external currents should be given by

$$\vec{J}^{ext}(\vec{r};\vec{k}',\hat{e}_x;\omega) = \frac{1}{i\omega\mu_0}(k'^2 - k_0^2)e^{ik'z}\hat{e}_x \quad (57)$$

$$\vec{J}^{\text{ext}}(\vec{r};\vec{k}',\hat{e}_y;\omega) = \frac{1}{i\omega\mu_0}(k'^2 - k_0{}^2)e^{ik'z}\hat{e}_y \tag{58}$$

$$\vec{J}^{\text{ext}}(\vec{r};\vec{k}',\hat{e}_z;\omega) = -\frac{1}{i\omega\mu_0}k_0{}^2 e^{ik'z}\hat{e}_z \tag{59}$$

where $\vec{k}'$ and $\hat{e}_\beta$ ($\beta = x, y, z$) denote the wave vector and polarization of the plane waves generated by them. One can see that for $k' = k_0$ the incident plane wave with (transverse) polarization along $\hat{e}_x$ and $\hat{e}_y$ would be self-propagating in vacuum, thus there would be no need for external currents and $\vec{J}^{\text{ext}}(\vec{r};\vec{k}_0;\hat{e}_x;\omega) = \vec{J}^{\text{ext}}(\vec{r};\vec{k}_0;\hat{e}_y;\omega) = 0$. But a plane wave with polarization $\hat{e}_z$ is a longitudinal wave that cannot self-propagate in vacuum; thus, in this case it has to be generated by an external current and $\vec{J}^{\text{ext}}(\vec{r};\vec{k}';\hat{e}_z;\omega) \neq 0$, always.

Now, the calculation of the internal field in the presence of $\vec{J}^{\text{ext}}$ is performed in a similar way as in the (Mie) problem in which the incident plane wave is self-propagating. This means one expands all the fields, external and induced, in a vector-spherical-harmonics basis and the expansion coefficient are determined by the boundary conditions at infinity and at the surface of the sphere, including also the excitation by longitudinal plane waves. In Appendix B we display the results of this calculation and, choosing the vector basis $\{\hat{e}_X, \hat{e}_r, \hat{e}_\theta\}$ and $\{\hat{e}_X, \hat{e}_Y, \hat{e}_Z\}$ described above, we write the explicit expressions for the components σ^s_{XX}, $\sigma^s_{\theta Y}$, and $\sigma^s_{\theta z}$. Here one assumes that the material the sphere is made of, is completely described by a complex local conductivity σ^s_{loc}. The details of the calculation, as well as the case in which the sphere has a magnetic response, are reported in ref 14.

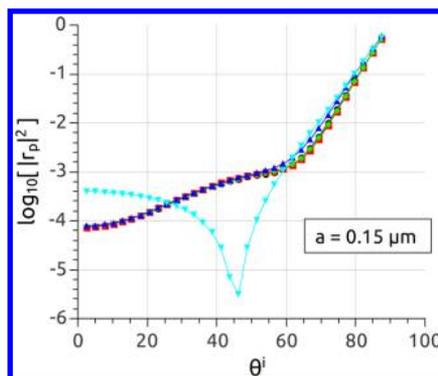## ■ REFLECTION AMPLITUDES: SILVER SPHERES/VACUUM

Here we calculate the absolute value of the reflection amplitudes using the expressions given in eqs 28 and 29, which we will call "exact", as well as the expressions for all the proposed approximations given by eq 39 and 40 called nonlongitudinal coupling (NLC), eq 47 called light-cone approximation (LCA), eq 50 called heuristic approximation (HA) and eq 52 called Fresnel approximation (FA). We will present numerical results for the case of free-standing spheres made of silver for different radii and different (volume) filling fractions. The sizes we consider in the examples below correspond to particles that absorb and scatter efficiently light at the chosen wavelength.[15] We will use in all these calculations the Foldy–Lax dispersion relation $k_z^{\text{f}}(\omega)$ given by eq 36, and as discussed above, it will be accurate enough in the limit of low-filling fractions (less than around 6%). This does not represent any additional limitation because at higher filling fractions the effective-field approximation itself will eventually cease to be valid.

In Figures 5−7 we show the case of a colloid of free-standing silver spheres, where the wavelength of the incident radiation is 0.630 μm and the filling fraction is 5%. At this wavelength the relative dielectric function of silver is $\epsilon_s/\epsilon_0 = -18.0958 + 0.484224i$, as taken from ref 25. The amplitudes of the reflection amplitudes for p-polarization were calculated as a function of the angle of incidence θ_i, for spheres with radii $a = 0.1, 0.15,$ and 0.2 μm, and for s-polarization for spheres with radii $a = 0.1$ and 0.2 μm in Figures 8 and 9.

We also display in Figure 10, as an illustration, the s-reflection amplitude of a colloid of free-standing TiO$_2$ spheres, as a function of the angle of incidence, log $|r_s(\theta_i)|^2$, using the
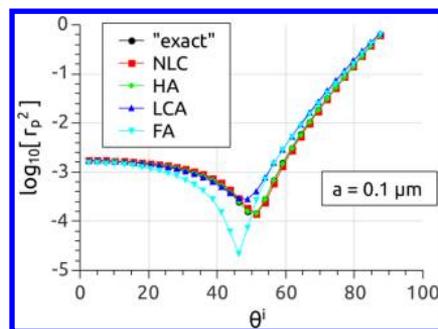
Figure 5. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of silver particles of radius $a = 0.10$ μm in vacuum at a frequency of 0.63 μm, for p-polarization and assuming $\epsilon_s/\epsilon_0 = 18.0958 + 0.484224i$, and a volume fraction of $f = 5\%$.
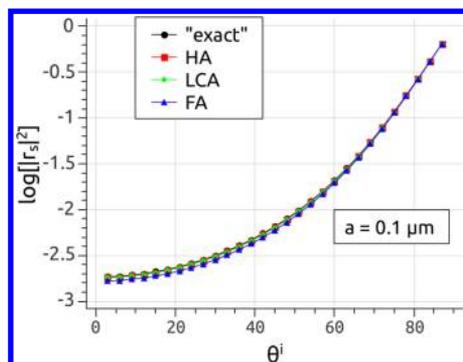

Figure 6. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of silver particles of radius $a = 0.15$ μm in vacuum at a frequency of 0.63 μm, for p-polarization and assuming $\epsilon_s/\epsilon_0 = 18.0958 + 0.484224i$, and a volume fraction of $f = 5\%$.
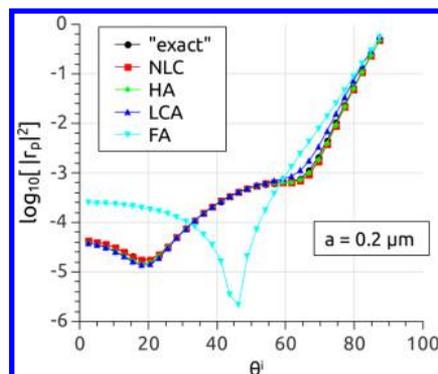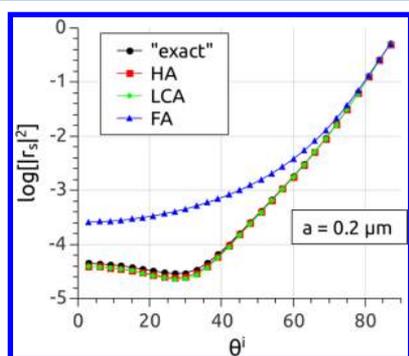

Figure 7. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of silver particles of radius $a = 0.20$ μm in vacuum at a frequency of 0.63 μm, for p-polarization and assuming $\epsilon_s/\epsilon_0 = 18.0958 + 0.484224i$ and a volume fraction of $f = 5\%$.

same parameters as before but for spheres of radius $a = 0.2$ μm and where the relative dielectric function of TiO corresponding to the incident wavelength of 0.630 μm is $\epsilon_s/\epsilon_0 = 2.84$.[26]

In Figure 5 we plot log$|r_p(\theta_i)|^2$ when the radius of the spheres is taken as 0.1 μm, and one can see that in Fresnel's approximation (FA), that is, when the colloid is characterized simply by a complex effective index of refraction, log$|r_p(\theta_i)|^2$ has the behavior typical of an absorbing material in continuum

Figure 8. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of silver particles of radius $a = 0.10$ μm in vacuum at a frequency of 0.63 μm, for s-polarization and assuming $\epsilon_s/\epsilon_0 = -18.0958 + 0.484224i$, and a volume fraction of $f = 5\%$.

Figure 9. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of silver particles of radius $a = 0.20$ μm in vacuum at a frequency of 0.63 μm, for s-polarization and assuming $\epsilon_s/\epsilon_0 = -18.0958 + 0.484224i$, and a volume fraction of $f = 5\%$.
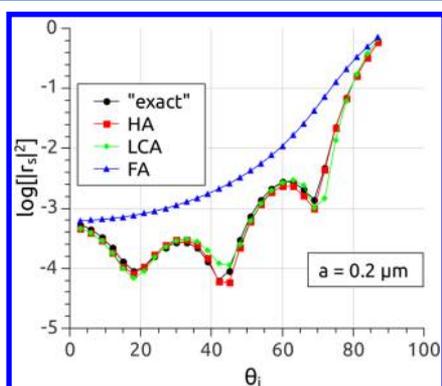
Figure 10. Logarithm of the amplitude square of the reflection coefficient as a function of the incidence angle for a colloidal system composed of titanium dioxide particles of radius $a = 0.20$ μm in vacuum at a frequency of 0.63 μm, for s-polarization and assuming $\epsilon_s/\epsilon_0 = 7.84$ and a volume fraction of $f = 5\%$.

electrodynamics, that is, it has a characteristic dip, reminiscence of the Brewster angle, and then it has a monotonic approach to the value 1 for $\theta_i = \pi/2$. Note here that all other approximations, except LCA, coincide among themselves and with the "exact" result but differ appreciably from FA, in particular in the region around the dip. This behavior remains when the radius of the spheres is increased to $a = 0.2$ μm, as seen in Figure 7, although in this case the difference between

the "exact" result and the FA is even more notorious. In the "exact" result the dip is not as acute as in FA and is shifted to smaller angles in relation to FA. Also the approach to the value $r_p = 1$ for $\theta_i = \pi/2$ is not as monotonic as in FA and it has a shoulder at angles of incidence where the FA has its dip. But what remains is that all other approximations, except the LCA, coincide to a quite reasonable degree of accuracy, among themselves and with the "exact" result. The behavior of the LCA is a bit different, and this difference might be a consequence of the inherent inconsistency of the LCA, in the sense that it does not have the correct small-particle limit. Therefore, one might conclude from looking at the plots shown in Figures 5−7 that at least for the parameters used in these calculations, the FA is by no means a good approximation, but the other approximations that can also be readily evaluated, like the heuristic approximation, are quite accurate. In Figure 8 we plot $\log|r_p(\theta_i)|^2$ for self-standing silver spheres with radii $a = 0.1$ μm using eqs 28, 47, 50, and 52, and one can see that the "exact" result and all other approximations, even the FA, lie very close to each other, in particular for θ_i larger and around 60°. Also, starting at $\theta_i = 0$, $\log|r_p(\theta_i)|^2$ has the characteristic slow monotonic increase toward the value 1 at $\theta_i = \pi/2$. But for $a = 0.2$ μm, this coincidence between FA, the other approximations and the "exact" result is no longer so, as shown in Figure 9. Here, although FA keeps the same overall behavior as in the case $a = 0.1$ μm, now the "exact" result and the other approximations (LCA and HA), although close to each other, differ distinctly from FA. First, the values of $\log|r_p(\theta_i)|^2$ for the "exact" result and the other approximations (LCA and HA), besides lying always below the ones of FA, they do not show a monotonic increase, they have rather a wide minimum, resembling more the behavior with θ_i of the absolute value of the reflection amplitude in p-polarization. Let us recall that in continuum electrodynamics, there is a Brewster angle for s-polarization in case the material has a magnetic response. Because for optical frequencies ordinary materials have no magnetic response, one does not expect a minimum in $\log|r_p(\theta_i)|^2$. Nevertheless, as was argued in ref 8, the bulk effective nonlocal response of a turbid colloid has an effective magnetic response at optical frequencies, due to the effect of the closed currents induced within the spheres. Therefore, the presence of the minimum in $\log|r_p(\theta_i)|^2$, in Figure 9, might be interpreted as a manifestation of that effective magnetic response, although in our formalism it comes from the angular dependence of the element S_1 of the scattering matrix of the isolated particles, as can be readily seen from eqs 47 and 50 corresponding to approximations LCA and HA, respectively. To make this more evident, we show in Figure 10 a plot of $\log|r_p(\theta_i)|^2$ for the case of self-standing spheres of TiO$_2$ of radius $a = 0.2$ μm, whose scattering matrix has a stronger angular dependence. One can see that, in this case, there is not just one minimum, but actually three minima.

It is evident that a system of self-standing spheres is not appropriate for the performance of accurate measurements. Thinking in a system like a colloidal suspension, one would require in the formalism the presence of a matrix occupying the half-space together with the spheres.

■ THE MATRIX

Here we extend the calculation of the reflection amplitudes discussed above, by considering the more realistic case when the spheres are not free-standing but they are instead immersed within a matrix made of a homogeneous material. The matrix

occupies the same half-space as the randomly located spheres, with a flat interface at $z = 0$, and is described by a real local dielectric function $\epsilon_1(\omega)$. But now, the currents $\vec{J}$ induced by the external field, in the presence of a matrix with a sharp interface, polarize the matrix by driving charges toward the interface, with the net result of leaving there induced surface-charge and surface-current densities. These are called "image charges" and "image currents" in analogy with the term used in the electrostatic case where this problem is solved through the method of images. To calculate the effect in the reflection amplitudes due to the "images", we proceed in exactly the same way as in the case of the self-standing spheres: we simply replace in the integral equation, eq 15, the free-space Green's function $\vec{G}_0$, by the half-space Green's function $\vec{G}_{HS}$. This Green's function was calculated from the expressions for the electric field produced by a point dipole in front of a material half-space, given in the so-called exact image theory.[27] One can show that $\vec{G}_{HS}$ can be written, for $z > 0$, as

$$\vec{G}_{HS}(\vec{r},\vec{r}') = \vec{G}_1(\vec{r},\vec{r}') + \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}d^2k_\parallel\, \vec{R}_I^+(\vec{k}_\parallel)\frac{i}{2k_z^1}e^{i\vec{k}_\parallel\cdot(\vec{r}_\parallel-\vec{r}_\parallel')}e^{ik_z^1(z+z')}$$

(60)

and for $z < 0$, as

$$\vec{G}_{HS}(\vec{r},\vec{r}') = \frac{1}{(2\pi)^2}\int_{\mathbb{R}^2}d^2k_\parallel\vec{R}_I^-(\vec{k}_\parallel)\frac{i}{2k_z^1}e^{i\vec{k}_\parallel\cdot(\vec{r}_\parallel-\vec{r}_\parallel')}e^{-ik_z^0z+ik_z^1z'}$$

(61)

where the first term $\vec{G}_1(\vec{r},\vec{r}')$ in eq 60, is the free propagator in the matrix, which has the same form as $\vec{G}_0$ in eq 14, but replacing $k_0 = \omega/c$ by $k_1 = \omega(\epsilon_1(\omega))^{1/2}/c$. The second term could be interpreted as an "image" term. Here we have defined

$$\vec{I}_\parallel = \hat{e}_x\hat{e}_x + \hat{e}_y\hat{e}_y$$

(62)

$$\vec{k}_\parallel = k_x\hat{e}_x + k_y\hat{e}_y$$

(63)

$$k_z^1 = \sqrt{k_1^2 - k_\parallel^2}$$

(64)

$$k_z^0 = \sqrt{k_0^2 - k_\parallel^2}$$

(65)

$$\vec{R}_I^+(\vec{k}_\parallel) = \frac{1}{k_1^2}\left(\vec{I}_\parallel - \frac{1}{k_z^1}\hat{e}_z\vec{k}_\parallel\right)\cdot\vec{R}(\vec{k}_\parallel)\cdot(k_1^2\vec{I}_\parallel - \vec{k}_\parallel\vec{k}_\parallel + k_z^1\vec{k}_\parallel\hat{e}_z)$$

(66)

$$\vec{R}_I^-(\vec{k}_\parallel) = \frac{1}{k_1^2}\left(\vec{I}_\parallel + \frac{1}{k_z^0}\hat{e}_z\vec{k}_\parallel\right)\cdot(\vec{I}_\parallel + \vec{R}(\vec{k}_\parallel))\cdot(k_1^2\vec{I}_\parallel - \vec{k}_\parallel\vec{k}_\parallel + k_z^1\vec{k}_\parallel\hat{e}_z)$$

(67)

$$\vec{R}(k_\parallel) = R_{10}^{TE}(k_\parallel)\vec{I}_\parallel - (R_{10}^{TE}(k_\parallel) + R_{10}^{TM}(k_\parallel))\frac{1}{k_\parallel^2}\vec{k}_\parallel\vec{k}_\parallel$$

(68)

$$R_{10}^{TE}(k_\parallel) = \frac{k_z^1 - k_z^0}{k_z^1 + k_z^0}$$

(69)

$$R_{10}^{TM}(k_\parallel) = \frac{\epsilon_0 k_z^1 - \epsilon_1 k_z^0}{\epsilon_0 k_z^1 + \epsilon_1 k_z^0}$$

(70)

These two last expressions (eqs 69 and 70) correspond to the Fresnel's reflection amplitudes for the air–matrix interface, where the superindex TM denotes p-polarization and TE denotes s-polarization.

Now, the integral equation for $z > 0$, analogous to eq 17, can be written as

$$\langle\vec{E}\rangle^+(\vec{k}_\parallel,z) = \vec{E}_i(\vec{k}_\parallel,z) + \langle\vec{E}\rangle_I^+(\vec{k}_\parallel,z) + \langle\vec{E}\rangle_{Img}^+(\vec{k}_\parallel,z) \quad (71)$$

where $\langle\vec{E}\rangle_I^+(\vec{k}_\parallel,z)$ is given by eq 17 with the replacement $k_0 \rightarrow k_1$ and

$$\langle\vec{E}\rangle_{Img}^+(\vec{k}_\parallel,z) = -i\omega\mu_0 n_0\vec{R}_I^+(\vec{k}_\parallel)\frac{e^{ik_z^1(z+a)}}{2k_z^1}\cdot$$
$$\frac{1}{2\pi}\int_{\mathbb{R}}dp_z\frac{\vec{\sigma}^s(\vec{k}_\parallel,-k_z^1,\vec{k}_\parallel,p_z)}{p_z + k_z^1}\cdot\langle\vec{E}\rangle^+(\vec{k}_\parallel,p_z)e^{iap_z}$$

(72)

For $z < 0$, we have the integral relation,

$$\langle\vec{E}\rangle^-(\vec{k}_\parallel,z) = \vec{E}_i(\vec{k}_\parallel,z) + \langle\vec{E}\rangle_I^-(\vec{k}_\parallel,z) + \langle\vec{E}\rangle_{Img}^-(\vec{k}_\parallel,z) \quad (73)$$

where $\langle\vec{E}\rangle_I^-(\vec{k}_\parallel,z)$ is given by eq 18 with the replacement $k_0 \rightarrow k_1$, and

$$\langle\vec{E}\rangle_{Img}^-(\vec{k}_\parallel,z) = -i\omega\mu_0 n_0\vec{R}_I^-(\vec{k}_\parallel)\frac{e^{-ik_z^0z+iak_z^1}}{2k_z^1}\cdot$$
$$\frac{1}{2\pi}\int_{\mathbb{R}}dp_z\frac{\vec{\sigma}^s(\vec{k}_\parallel,-k_z^1,\vec{k}_\parallel,p_z)}{p_z + k_z^1}\cdot\langle\vec{E}\rangle^+(\vec{k}_\parallel,p_z)e^{iap_z}$$

(74)

On one hand, in eq 71, the incident electric field will be taken as

$$\vec{E}_i(\vec{k}_\parallel,z) = t_F(2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)\hat{e}^t e^{ik_z^1z}\theta(z)$$

(75)

where t_F is the Fresnel's transmission coefficient of the air–matrix interface, and $\hat{e}^t$ is the polarization of the transmitted wave across this interface. On the other hand, in the integral relation in eq 73, for $z < 0$, the incident electric field has to take account also of the reflected field at the air–matrix interface, and will be given by

$$\vec{E}_i(\vec{k}_\parallel,z) = (2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)(\hat{e}^i e^{ik_z^0z} + r_F\hat{e}^r e^{-ik_z^0z})\theta(-z)$$

(76)

where $\hat{e}^i$ is the polarization of the incident field and r_F is the Fresnel's reflection coefficient of the air–matrix interface.

As solution of the integral equation we now propose the following *ansatz*:

$$\langle\vec{E}\rangle(\vec{k}_\parallel,p_z'') = (2\pi)^2\delta(\vec{k}_\parallel - \vec{k}_\parallel^i)\frac{1}{i(p_z'' - k_z^f)}t\hat{e}^f$$

(77)

where t and $\hat{e}^f$ are parameters that have to be determined by demanding consistency of eq 77 as solution of the integral equation (eq 71). When this is done, one obtains two consistency equations that are similar to the ones obtained in the free-standing case (eqs 24 and 25). One of them corresponds to the dispersion relation, and it turns out to be the same as eq 24 with the replacement of k_0 by k_1. The other one is analogous to eq 25 and can be written as

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$$t = t_{\mathrm{F}}\left[i\omega\mu_0 n_0 \frac{1}{2k_z^1}\hat{e}^{\,t}\cdot\left(\frac{(\vec{I}-\hat{k}^{\,i}\hat{k}^{\,i})}{k_z^{\mathrm{f}}-k_z^1}e^{ia(k_z^{\mathrm{f}}-k_z^1)} \right.\right.$$

$$\left.\left. + \frac{\vec{R}_{\mathrm{I}}^{\,+}(\vec{k}_{\|})}{k_z^{\mathrm{f}}+k_z^1}e^{ia(k_z^{\mathrm{f}}+k_z^1)} \right)\cdot\vec{\sigma}(\vec{k}^{\,\mathrm{f}},\vec{k}^{\,1})\cdot\hat{e}^{\,\mathrm{f}} \right]^{-1} \tag{78}$$

We now evaluate the expression for the average electric field $\langle\vec{E}\rangle(\vec{k}_{\|},z)$ for $z < 0$ (eq 73), by substituting, first, the *ansatz* (eq 77) into eq 74 for $\langle\vec{E}\rangle^-_{\mathrm{img}}$, and then substituting this expression for $\langle\vec{E}\rangle^-_{\mathrm{img}}$ into eq 73 together with the expression for the incident electric field $\vec{E}_{\mathrm{i}}$ given by eq 76. One gets

$$\langle\vec{E}\rangle^-(\vec{k}_{\|},z) = \vec{E}_{\mathrm{i}}(\vec{k}_{\|},z) + \langle\vec{E}\rangle^-_{\mathrm{I}}(\vec{k}_{\|},z) - i\omega\mu_0 n_0 \frac{e^{-ik_z^0 z}}{2k_z^1}\vec{R}_{\mathrm{I}}^-(\vec{k}_{\|}^{\,i})$$

$$\cdot\frac{\vec{\sigma}_{\mathrm{s}}(\vec{k}^{\,\mathrm{r}},\vec{k}^{\,\mathrm{f}})}{k_z^{\mathrm{f}}+k_z^1}\cdot t\hat{e}^{\,\mathrm{f}}e^{ia(k_z^1+k_z^{\mathrm{f}})}e^{i\vec{k}_{\|}^{\,i}\cdot\vec{r}_{\|}} \tag{79}$$

where t is given by eq 78. From this integral relation for $\langle\vec{E}\rangle^-(\vec{k}_{\|},z)$, after setting the polarization of the incident beam and after a bit of algebra,[14] one can extract closed-form expressions for the reflection amplitudes for s- and p-polarization, which one can write in a very attractive form, as

$$\underline{r}_{\mathrm{s}} = \frac{R_{01}^{\mathrm{TE}} + r_{\mathrm{cohs}}e^{i2ak_z^1}}{1 - R_{10}^{\mathrm{TE}}r_{\mathrm{cohs}}e^{i2ak_z^1}} \tag{80}$$

and

$$\underline{r}_{\mathrm{p}} = \frac{R_{01}^{\mathrm{TM}} + r_{\mathrm{cohp}}e^{i2ak_z^1}}{1 - R_{10}^{\mathrm{TM}}r_{\mathrm{cohp}}e^{i2ak_z^1}} \tag{81}$$

where the underline below the r denotes the total reflection amplitude in the presence of the matrix. It is interesting to note that these expressions for the reflection amplitudes have a structure very similar to the the ones used in continuum electrodynamics for the reflection amplitudes from a layer of finite width between two semi-infinite media.[28] Here the layer corresponds to a layer of width $2a$, bounded by the planes $z = 0$ and $z = 2a$, and with the dielectric response ϵ_1 of the matrix. We will call these expressions the three-media formulas, with medium 0 being the incidence medium ($z < 0$), medium 1 being the finite layer of the matrix material ($0 < z < a$), and medium 2 being the colloidal system. R_{01}^{TE} and R_{01}^{TM} are the Fresnel's reflection amplitudes for the *air–matrix* interface, whereas $r_{\mathrm{cohs}} = r_{\mathrm{s}}e^{-i2ak_z^1}$ and $r_{\mathrm{cohp}} = r_{\mathrm{p}}e^{-i2ak_z^1}$ and r_{s} and r_{p} are the reflection amplitudes for s- and p-polarization given by eqs 28 and 29 evaluated at k_1 instead of k_0. This means that medium 3 can be regarded as the matrix occupying the whole space while the centers of the spheres randomly located in the half-space $z > a$. Obviously, this interpretation cannot correspond to the actual geometry of the system, but what the expressions above (eqs 80 and 81) tell us is that one can imagine it in this way when calculating its reflection amplitudes. With this in mind, it is clear that the calculation of total reflection amplitudes for a half space of spherical particles immersed in a matrix ($\underline{r}_{\mathrm{s}}$ and $\underline{r}_{\mathrm{p}}$) is given only in terms of the reflection amplitudes between media 1 and 2 and between media 2 and 3. Let us add that one can also generate a series of approximations for $\underline{r}_{\mathrm{s}}$ and $\underline{r}_{\mathrm{p}}$, as the ones discussed above for the free-standing case, by inserting in eqs 80 and 81 the corresponding approximations for r_{cohs} and

r_{cohp}. We will call them with the same name, except for the one denoted as Fresnel approximation (FA), which we will call here Fresnel 3 media (F3M). In this approximation one regards the reflection amplitude between media 2 and 3 simply as the Fresnel reflection amplitude between the matrix and the colloid characterized with an effective index of refraction coming from, e.g., the Foldy–Lax dispersion relation for particles immersed within the matrix. We should also mention that one could have obtained this same approximation (F3M) by employing the alternative procedure discussed above while handling now the integral equation for the electric field (eq 71), consisting of averaging (integrate) first over particle positions, and performing later the other space integrals, which amounts to a different order of integration. Finally, we point out that the three-media formula rigorously derived here has been intuitively proposed earlier[5] for solving the same type of problem.

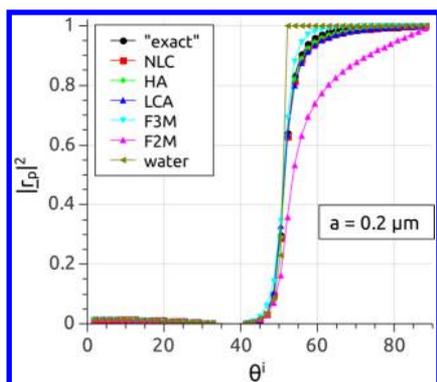## ■ REFLECTION AMPLITUDES: SILVER SPHERES/WATER

Here we perform a numerical evaluation of the reflection amplitudes for s- and p-polarization using the expressions given in eqs 80 and 81 for silver spheres in water bounded not by air, but by glass. We do this because we want to simulate an attractive experimental setup in which the colloidal suspension is set in contact with a prism with a high index of refraction, and light is introduced to the colloidal system through the prism. Because the index of refraction of the prism is higher than the one of water, there is a critical angle for total internal reflection even in the absence of the colloidal particles. As one adds the colloidal particles to the suspension, the sharp transition to total internal reflectance is smoothed out, and total reflectance is attained only up to $\theta_{\mathrm{i}} = \pi/2$. Nevertheless, although there is not a sharp transition to total reflectance, there are still strong variations of the reflectance with the angle of incidence, in a region of angles around the critical angle of the water–prism system, and experimentalists can take advantage of these strong variations to perform accurate measurements of the reflectance in this region. For this experimental setup, one has to be aware that in the formulas above for $\underline{r}_{\mathrm{s}}$ and $\underline{r}_{\mathrm{p}}$ one has to replace ϵ_0 (air) by ϵ_{P} (prism).

Here we evaluate eqs 80 and 81 by replacing r_{cohs} and r_{cohp} by $r_{\mathrm{cohs}} = r_{\mathrm{s}}e^{-i2ak_z^1}$ and $r_{\mathrm{cohp}} = r_{\mathrm{p}}e^{-i2ak_z^1}$ and taking r_{p} and r_{s} as given by expressions 28 and 29 but replacing k_0 by k_1; this evaluation will be called "exact". We also evaluate the approximations generated by using in eqs 80 and 81 the different approximate formulas for r_{cohs} and r_{cohp}, as discussed above, while preserving the same names: NLC (nonlongitudinal coupling), LCA (light-cone approximation), and HA (heuristic approximation), with the exception of the one labeled Fresnel approximation (FA), which in the present context will be called Fresnel 3 media (F3M) when the Fresnel approximation for r_{cohs} and r_{cohp} is used in eqs 80 and 81, and Fresnel 2 media (F2M) when the Fresnel relations given in eqs 69 and 70 are used for the prism-colloid interface, and the colloid being described by an effective index of refraction coming from the dispersion relation for k_z^1.

In Figures 11 and 12, we choose $\lambda_0 = 0.55\ \mu m$ and a filling fraction of $f = 0.05$, and plot the reflectance $|\underline{r}_{\mathrm{p}}|^2$ as a function of the angle of incidence θ_{i} for silver spheres of radius $a = 0.10\ \mu m$, in Figure 11, and radius $a = 0.20\ \mu m$, in Figure 12. For silver and water we use the values of the relative bulk dielectric functions corresponding to $\lambda_0 = 0.55\ \mu m$, as reported in refs 25 and 26, respectively, and for the prism we take $\epsilon_{\mathrm{P}}/\epsilon_0 = 2.9$.
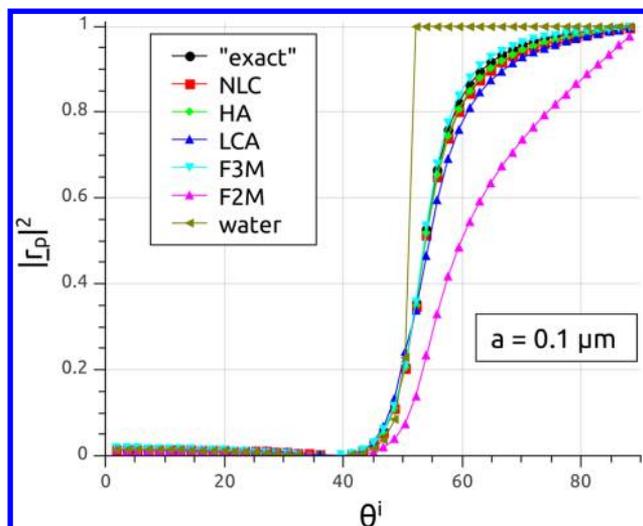
Figure 11. Absolute value square of the reflection amplitude as a function of the incidence angle for a colloidal system of silver spheres in water for a wavelength of 0.55 μm, a particle radius $a = 0.1$ μm, $\epsilon_s/\epsilon_0 = 13.09314 + 0.42564i$, f = 0.05, and p-polarization. The incident medium is glass (prism) with $\epsilon_P/\epsilon_0 = 2.9$.
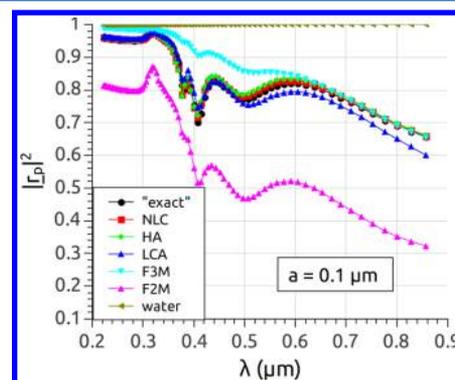

Figure 12. Absolute value square of the reflection amplitude as a function of the incidence angle for a colloidal system of silver spheres in water for a wavelength of 0.55 μm, a particle radius $a = 0.2$ μm, $\epsilon_s/\epsilon_0 = 13.09314 + 0.42564i$, f = 0.05, and p-polarization. The incident medium is glass (prism) with $\epsilon_P/\epsilon_0 = 2.9$.

Also, the value of k_z^1 was obtained from the dispersion relation. We use the Foldy−Lax expression (eq 36) for silver particles in water, which was checked to yield, for $f = 0.05$, an accurate solution of the general equation given by eq 37. One can see, in Figure 11, that the reflectance has a minimum related to the Brewster angle and then a sharp but smooth monotonic increase, with a "shoulder" when approaching the value 1 at $\theta_i = \pi/2$. For comparison we also plot the reflectance for the prism−water interface that displays a well-characterized sharp transition to total internal reflectance at the critical angle. In Figure 11 one can see that the results from the approximations denoted by NLC and the HA lie very close to the ones from the "exact" expression in the whole range of angles θ_i, whereas on one hand, the F2M is very much off in this same whole range, although the difference becomes even larger for angles θ_i after the minimum and up to $\theta_i = \pi/2$. On the other hand, the approximation denoted LCA represents a good approximation for θ_i before the minimum but starts to deviate from the "exact" results after the minimum, reaching deviations of about one or two percent for angles around $\theta_i \approx 60°$. Also, the

approximation denoted F3M although it has positive and negative deviations from the "exact" one at angles θ_i before the minimum, after the minimum it becomes a rather good approximation. In conclusion, one can ensure that in this case, an approximation that works quite well at all angles and that is, at the same time easy to calculate, is the HA. One can also see, in Figure 12, a similar behavior of $|r_p|^2$ for a system of silver spheres with the same parameters as before, but for spheres of a larger radius, that is, $a = 0.20$ μm. One observes that although the curves here follow the same trend as in Figure 11, the deviations are smaller. This might be due, for example, to specific Mie-type resonances in the scattering matrix for $\lambda_0 = 0.55$ μm and $a = 0.10$ μm, when looking at these results through HA. One also reaches similar conclusions looking at the reflectance in s-polarization, not shown here. In contrast to what happens in p-polarization, the behavior of the s-reflectance as a function of θ_i is rather monotonic with a "shoulder" before reaching the value 1 at $\theta_i = \pi/2$, and the minima that appear at small angles θ_i in the s-reflectance, for the case of self-standing silver spheres, not shown here.

It is clear that with this single example it is difficult to reach a general conclusion about the validity of the different approximations presented here, and the display of numerous examples might become rather cumbersome. Therefore, we proceed instead to generate a spectrum of the p-reflectance to check the validity of the approximations as a function of the incident wavelength. To do this, we choose first an angle of incidence close to the "shoulder", where the difference between the different calculations is larger, e.g., $\theta_i \approx 60°$. Then we choose a definite volume filling fraction, $f = 0.05$, and a definite radius of the spheres, $a = 0.10$ μm, to generate a spectrum by scanning the values of $|r_p|^2$ at different incident wavelengths. We display the results of this calculation in Figure 13 and then repeat the calculation in Figure 14 for $a = 0.20$ μm.

Figure 13. Spectrum of the absolute value square of the reflection amplitude for p-polarization, for silver particles immersed in water, with radius $a = 0.1$ μm, filling fraction f = 0.05, and an angle of incidence of 60°. The incident medium is glass (prism) with $\epsilon_P/\epsilon_0 = 2.9$.

In this way we are be able to spot the frequency region for which the differences between the "exact" result and the results corresponding to the different approximations become more evident. As one can see in these figures, this frequency region corresponds to $\lambda_0 \approx 0.50$ μm, but in general, the NLC, HA, and LCA are close to the exact solution in the whole range of wavelengths. In the case $a = 0.2$ μm, only the region of $\lambda > 0.55$ μm was displayed. This was done so because the iterative procedure employed to find the roots of the dispersion relation
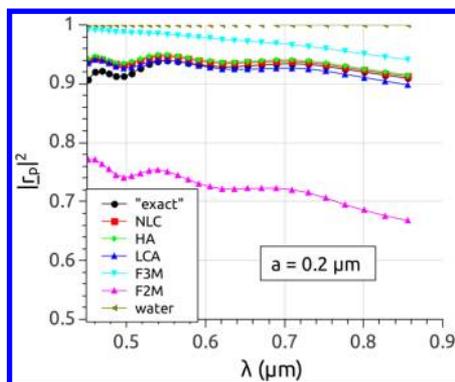
Figure 14. Spectrum of the absolute value square of the reflection amplitude for p-polarization, for silver particles immersed in water, with radius $a = 0.2$ μm, filling fraction f = 0.05, and an angle of incidence of $60°$. The incident medium is glass (prism) with $\epsilon_P/\epsilon_0 = 2.9$.

did not converge to a physical root at several wavelengths below $\lambda = 0.55$ μm. Possibly an alternative method for finding roots of nonlinear equations, must be employed for frequencies less than 0.55 μm.

CONCLUSIONS

As mentioned above, the relationship between the present approach and the results of multiple-scattering theory (MST) reported in refs 24 and 29 is the identification of the **T**-matrix operator used in MST with the generalized-nonlocal conductivity tensor used here. After this identification is made, the integral equations for the electric field in both approaches should be equivalent. Although in the present approach we solve this integral equation in the effective-field approximation, valid for dilute colloidal systems, in MST, more elaborated approximation schemes have been developed, which should be valid for denser colloidal systems. An example of these is the quasi-crystalline approximation.[19] Nevertheless, in most of the work done in MST the **T**-matrix operator is usually approximated and identified with the **S** matrix that describes the scattering of only transverse waves. The role played by the longitudinal modes, like the ones dealt in our approach, would require going beyond the **S** matrix by taking full account of the solution of the integral equation obeyed by the **T**-matrix operator. Here, instead of solving the corresponding integral equation obeyed by the generalized-nonlocal conductivity tensor, we took advantage of the physical interpretation of this conductivity tensor to calculate, in a rather simple way, closed expressions for all its components, including the coupling with the longitudinal modes. In our approach we obtain an equation for the dispersion relation in terms of the conductivity tensor evaluated within an effective medium where the incident wave and the waves scattered by the colloidal particles have wave vectors of different magnitudes and also different from the magnitude corresponding to the self-propagating modes in the matrix. In this way our approach incorporates dependent-scattering effects that are revealed by the prediction of a nonlinear dependence of the effective wavevector with the volume-density of particles. Furthermore, in the most widely known applications of MST[19] the randomly located colloidal particles are embedded in the same medium as the one outside, like in many applications to atmospheric problems. In contrast, we developed here a rigorous solution of the integral equation for the electric field that takes account of

the "image" currents induced by the half-space matrix where the particles are immersed, and that can be applied to problems of colloidal suspensions in contact with any material different than the matrix. This was done by using the half-space Green function in the integral equation for the average electric field and proving that the reflection amplitudes can be calculated using a formula which is equivalent to the classical three-media-reflection formula of continuum electrodynamics. This extension to the theory is crucial for modeling light reflection from colloidal suspensions (or composite materials) in most real situations encountered in the laboratory. In addition to the "exact" solution within the effective-field approximation we proposed several simpler approximations that could be used for analyzing practical applications. We explored the accuracy of these approximations by comparing the coherent reflectance predicted by them with that predicted by the "exact" solution. The examples chosen for illustrating the accuracy of different approximations corresponded to an exceptionally sensitive experimental setup, consisting of a suspension of particles in contact with a prism of higher index of refraction. We chose for our numerical examples water suspensions of silver particles that present strong resonant absorption at certain wavelengths while being good scatterers of visible light at other wavelengths.

APPENDIX A: DYADIC $\overset{\leftrightarrow}{M}$

Here we display the elements of the dyadic $\overset{\leftrightarrow}{M}$ that appears in eq 37, in the vector basis $\{\hat{e}_X, \hat{e}_L^f, \hat{e}^f\}$. In this basis $\overset{\leftrightarrow}{M}$ is written as

$$\overset{\leftrightarrow}{M} = \overset{\leftrightarrow}{I} - i\omega\mu_0 n_0 \left[\hat{e}_X\hat{e}_X \left(\frac{\sigma_{XX}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} - \frac{\sigma_{XX}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right) \right.$$
$$+ \hat{k}_\perp^f\hat{k}_\perp^f \left(-\frac{1}{k_0^2 k_f^2}k_\parallel^{i2}\sigma^T(k_f) + \beta^i\frac{\sigma_{\theta Y}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} - \beta^r\frac{\sigma_{\theta Y}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right)$$
$$+ \hat{k}_\perp^f\hat{k}^f \left(\frac{1}{k_0^2 k_f^2}k_\parallel^i k_z^f\sigma^L(k_f) + \beta^i\frac{\sigma_{\theta Z}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} - \beta^r\frac{\sigma_{\theta Z}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right)$$
$$+ \hat{k}^f\hat{k}_\perp^f \left(\frac{1}{k_0^2 k_f^2}k_\parallel^i k_z^f\sigma^T(k_f) - \gamma^i\frac{\sigma_{\theta Y}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} + \gamma^r\frac{\sigma_{\theta Y}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right)$$
$$+ \hat{k}^f\hat{k}^f \left(-\frac{1}{k_0^2 k_f^2}k_z^{f2}\sigma^L(k_f) - \gamma^i\frac{\sigma_{\theta Z}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} + \gamma^r\frac{\sigma_{\theta Z}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right)$$
$$+ \left. \hat{k}^f\hat{k}^f \left(-\frac{1}{k_0^2 k_f^2}k_z^{f2}\sigma^L(k_f) - \gamma^i\frac{\sigma_{\theta Z}(\vec{k}^i,\vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} + \gamma^r\frac{\sigma_{\theta Z}(\vec{k}^r,\vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right) \right]$$
$$(82)$$

where

$$\beta^i = \frac{k_\parallel^{i2} + k_z^f k_z^i}{k_0 k_f} \tag{83}$$

$$\beta^r = \frac{k_\parallel^{i2} - k_z^f k_z^i}{k_0 k_f} \tag{84}$$

$$\gamma^i = \frac{k_\parallel^i(k_z^f - k_z^i)}{k_0 k_f} \tag{85}$$

$$\gamma^r = \frac{k_\parallel^i(k_z^f + k_z^i)}{k_0 k_f} \tag{86}$$

and

$$k_f^2 = k_\parallel^{i\,2} + k_z^{f\,2} \tag{87}$$

Here we display also the expression for the factor $S = \hat{e}^f \cdot \hat{k}^f / \hat{e}^f \cdot \hat{k}_\perp^f$ that appears in eq 38, and write $s = a/b$, where

$$a = i\omega\mu_0 n_0 \left(\frac{1}{k_0^2 k_f^2} k_\parallel^i k_z^f \sigma^T(k_f) - \gamma^i \frac{\sigma_{\theta Y}(\vec{k}^i, \vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} \right.$$
$$\left. + \gamma^r \frac{\sigma_{\theta Y}(\vec{k}^r, \vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right) \tag{88}$$

$$b = 1 - i\omega\mu_0 n_0 \left(-\frac{1}{k_0^2 k_f^2} k_z^{f\,2} \sigma^L(k_f) - \gamma^i \frac{\sigma_{\theta Z}(\vec{k}^i, \vec{k}^f)}{2k_z^i(k_z^f - k_z^i)} \right.$$
$$\left. + \gamma^r \frac{\sigma_{\theta Z}(\vec{k}^r, \vec{k}^f)}{2k_z^i(k_z^f + k_z^i)} \right) \tag{89}$$

■ APPENDIX B: COMPONENTS $\sigma_{\alpha\beta}^s$

Here we write down the expressions for the components of the non-local conductivity tensor of the isolated sphere: $\sigma_{XX}^s(\vec{k}, \vec{k}')$, $\sigma_{\theta Y}^s(\vec{k}, \vec{k}')$, and $\sigma_{\theta Z}^s(\vec{k}, \vec{k}')$, for the case $\vec{k} = (\vec{k}_\parallel, k_z)$ and $\vec{k}' = (\vec{k}_\parallel, k_z')$. We denote $(\vec{k}, \vec{k}')$ as $(\vec{k}_\parallel; k_z, k_z')$, $k = |\vec{k}|$ and $k' = |\vec{k}'|$. Thus, we write

$$\sigma_{XX}^s(\vec{k}_\parallel; k_z, k_z') = 4\pi a^3 \sigma_{loc}^s \sum_{n=1}^{\infty} -\frac{2n+1}{n(n+1)}$$
$$\cdot \left(c_n(ka)\, I_{n,n}(k_s a, k'a, 2) \frac{d}{d\theta} P_n^1(\cos\theta) \right.$$
$$\left. + d_n(ka)\, J_2(n, k_s a, k'a) \frac{P_n^1(\cos\theta)}{\sin\theta} \right)$$
$$+ 4\pi a^3 \sigma_{loc}^s \frac{k^2 - k_0^2}{k^2 - k_s^2} \frac{j_1(a|k_z - k_z'|)}{a|k_z - k_z'|} \tag{90}$$

$$\sigma_{\theta Y}^s(\vec{k}_\parallel; k_z, k_z') = 4\pi a^3 \sigma_{loc}^s \sum_{n=1}^{\infty} -\frac{2n+1}{n(n+1)}$$
$$\cdot \left(c_n(ka)\, I_{n,n}(k_s a, k'a, 2) \frac{P_n^1(\cos\theta)}{\sin\theta} \right.$$
$$\left. + d_n(ka) J_2(n, k_s a, k'a) \frac{d}{d\theta} P_n^1(\cos\theta) \right)$$
$$+ 4\pi a^3 \sigma_{loc}^s \frac{k^2 - k_0^2}{k^2 - k_s^2} \frac{j_1(a|k_z - k_z'|)}{a|k_z - k_z'|} \cos\theta \tag{91}$$

$$\sigma_{\theta Z}^s(\vec{k}_\parallel; k_z, k_z') = 4\pi a^3 \sigma_{loc}^s \sum_{n=1}^{\infty} (2n+1) d_n^L(ka)\, J_2(n, k_s a, k'a)$$
$$\times \frac{d}{d\theta} P_n(\cos\theta) - 4\pi a^3 \sigma_{loc}^s \frac{\epsilon_0}{\epsilon_s} \frac{j_1(a|k_z - k_z'|)}{a|k_z - k_z'|} \sin\theta \tag{92}$$

where

$$k_z = \sqrt{k^2 - k_\parallel^2}$$

and

$$k_z' = \sqrt{k'^2 - k_\parallel^2} \tag{93}$$

$$k_s^2 = k_0^2 + i\omega\mu_0 \sigma_{loc}^s \tag{94}$$

and

$$k_0^2 = \frac{\omega^2}{c^2} \tag{95}$$

$$\cos\theta = \hat{k} \cdot \hat{k}' \equiv \frac{\vec{k} \cdot \vec{k}'}{kk'} \tag{96}$$

and

$$J_1(n, k_s a, k'a) = \frac{j_n(ak_s)}{ak_s} \frac{j_n(ak')}{ak'} \tag{97}$$

$$J_2(n, k_s a, k'a) = \frac{i}{k'a((k_s a)^2 - (k'a)^2)} \frac{a_n(k'a, k_s a)}{d_n(k'a, k_s a)} \tag{98}$$

$$I_{n,n}(x_1, x_2, 2)$$
$$= \frac{1}{x_1^2 - x_2^2} (x_2 j_n(x_1)\, j_{n-1}(x_2) - x_1 j_{n-1}(x_1)\, j_n(x_2)) \tag{99}$$

$$a_n^L(ka, k_0 a, k_s a) = \frac{k_s}{k_0} \frac{j_n(k_s a)}{h_n(k_0 a)} d_n^L(ka) \tag{100}$$

$$a_n^L(ka, k_0 a, k_s a) = \frac{\left(1 - \frac{\epsilon_0}{\epsilon_s}\right) \frac{j_n(ka)}{ka} h_n(k_0 a)}{J_n^*(k_s a)\, h_n(k_0 a) - \frac{k_s}{k_0} j_n(k_s a)\, H_n^*(k_0 a)} \tag{101}$$

$$a_n(ka, k_0 a, k_s a)$$
$$= \frac{(1-\alpha)J_n^*(ka)k j_n(k_s a) - (1-\alpha)k j_n(ka)\, J_n^*(k_s a)}{H_n^*(k_0 a)k j_n(k_s a) - k_0 h_n(k_0 a)\, J_n^*(k_s a)} \tag{102}$$

$$b_n(ka, k_0 a, k_s a)$$
$$= \frac{(1-\alpha)j_n(ka)k J_n^*(k_s a) - (1-\alpha)k J_n^*(ka)j_n(k_s a)}{h_n(k_0 a)k J_n^*(k_s a) - k_0 H_n^*(k_0 a)\, j_n(k_s a)} \tag{103}$$

$$c_n(ka, k_0 a, k_s a)$$
$$= \frac{h_n(k_0 a)(1-\alpha)k J_n^*(ka) - k_0 H_n^*(k_0 a)(1-\alpha)j_n(ka)}{h_n(k_0 a)k J_n^*(k_s a) - k_0 H_n^*(k_0 a)\, j_n(k_s a)} \tag{104}$$

$$d_n(ka, k_0 a, k_s a)$$
$$= \frac{H_n^*(k_0 a)(1-\alpha)k j_n(ka) - k_0 h_n(k_0 a)(1-\alpha)\, J_n^*(ka)}{H_n^*(k_0 a)k j_n(k_s a) - k_0 h_n(k_0 a)\, J_n^*(k_s a)} \tag{105}$$

$$J_n^*(\rho) = \frac{1}{\rho} \frac{d}{d\rho} (\rho j_n(\rho)) \tag{106}$$

$$H_n^*(\rho) = \frac{1}{\rho} \frac{d}{d\rho} (\rho h_n(\rho)) \tag{107}$$

$$\alpha = \frac{k^2 - k_0{}^2}{k^2 - k_s{}^2} \tag{108}$$

Here j_n and h_n are the spherical Bessel and spherical Hankel functions as defined by ref 30 and $\epsilon_s = \epsilon_0 + i\sigma_{loc}^s/\omega$.

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Notes
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