Rigorous theoretical framework for particle sizing in turbid colloids using light refraction

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Abstract: Using a non-local effective-medium approach, we analyze the refraction of light in a colloidal medium. We discuss the theoretical grounds and all the necessary precautions to design and perform experiments to measure the effective refractive index in dilute colloids. As an application, we show that it is possible to retrieve the size of small dielectric particles in a colloid by measuring the complex effective refractive index and the volume fraction occupied by the particles.

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1. Introduction

The optical properties of colloids have been a challenging area of research for many years providing also important applications [1-6]. In this paper we consider a colloid as a random system of particles embedded in a homogeneous matrix material. The appearance of a colloid can be turbid when the size of the particles composing the system is not very small compared to the wavelength. The existence of a diffuse field in a colloid, which manifests itself as turbidity, has been a source of confusion when referring to its effective optical parameters such as its effective refractive index. The concept of an effective refractive index of turbid colloids has actually remained rather vague. To develop a theory for the effective optical parameters of colloids one must first distinguish the presence of two types of fields: the coherent beam and the diffuse field. One must then recognize that the effective optical parameters should be associated only the coherent beam, which is actually defined as an average field, where the average is usually a configurational one taken over all possible random locations of the colloidal particles.

It has been shown by several authors [1-8] that the average electromagnetic field in a random colloidal medium propagates with an effective wave vector. From the effective wave vector, one may define an effective refractive index, appropriate to the coherent beam. Thus, when one refers to the refractive index of a turbid colloid, one actually refers to the effective refractive index that describes the optical behavior of the coherent beam. Very recently, we have established formally the nature of the electromagnetic response of the effective medium associated to the coherent beam in a colloid, and it turned out that its effective electric permittivity ε_{eff} and its effective magnetic permeability μ_{eff} are actually non-local with a non-local length given by the diameter of the colloidal particles. A non-local electromagnetic response is also known as spatially dispersive [9,10], and this means that ε_{eff} and μ_{eff} depend not only on the frequency but also on the wave vector of the electromagnetic fields propagating within the system. The non-local effective-medium approach for the electromagnetic response of a dilute colloid was developed in detail in Ref. [11]. In this reference, it was also shown that from the non-local dispersion relation for the transverse modes, one is able to obtain an effective refractive index that depends only on the frequency. However, when an effective refractive index derived from the dispersion relation of a system with a non-local response is naively used as the common refractive index in continuum electrodynamics, mistakes and misinterpretations might definitely occur. For instance, if one tries to measure the effective index of refraction of a colloidal system by measuring the reflectance in the usual internal-reflection set up, and then one uses Fresnel's relations to determine it, inconsistencies might be found as shown in Refs. [12,13].

Another important consequence of non-local optics is the possible excitation of propagating or evanescent longitudinal modes in the bulk or at an interface of the system. Although the presence of these modes might not modify the propagation of the transverse modes, it will definitely affect the value of the reflectance. However, the calculation of the reflection amplitudes of an electromagnetic wave from a non-local medium is still a topic of current research. Nevertheless, with proper precautions, one can determine the effective index of refraction of spatially dispersive systems using Snell's law, in the same way as one would deal with a usual local medium with a complex refractive index. In this way, one avoids the disputed use of Fresnel's reflection and transmission coefficients with an effective refractive index coming from a non-local dispersion relation. By refraction we mean, refraction in and out of the colloidal medium, as well as actual propagation of the refracted beam through the system.

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2. Non-local electromagnetic response of colloidal media

Here, we will present the main arguments that ascertain the non-locality of the electromagnetic response of colloidal media. For simplicity in the presentation, we will restrict our analysis only to mono-disperse colloids of randomly-positioned identical spherical particles of radius a, and refractive index n_p, suspended in vacuum. The fractional volume f occupied by the particles is assumed to be moderately small compared to one. We will assume an exp($-i\omega t$) time-dependence of fields and sources throughout this paper.

An effective-medium approach must provide constitutive relations among the average of the induced currents and charges and the average of the fields. In general, one must find a relation between the average induced current $\left\langle \vec{J}_{ind}(\vec{r}) \right\rangle$ and the average induced charge density $\left\langle \rho_{ind}(\vec{r}) \right\rangle$, with the average electric field $\left\langle \vec{E}(\vec{r}) \right\rangle$ and the average magnetic field $\left\langle \vec{B}(\vec{r}) \right\rangle$. If we consider that the particles forming the colloid of interest are nonmagnetic, one may find a direct relationship between the induced currents and the electric field within the particles. Then through an appropriate averaging procedure, one may determine a relation between the average current density in the system and the average electric field. This relationship defines what we call the electromagnetic response of the system.

Let us now consider a collection of N spheres in the presence of an external incident electric field. The induced current within a sphere centered at $\vec{r}_j$ may be written as [11],

$$\vec{J}_{ind,j}(\vec{r}) = \int \ddot{\sigma}_s^{NL}(\vec{r}-\vec{r}_j, \vec{r}\,'-\vec{r}_j) \cdot \vec{E}_{exc}(\vec{r}\,')d^3r' \tag{1}$$

where $\ddot{\sigma}_s^{NL}$ is the generalized non-local conductivity of an isolated particle and $\vec{E}_{exc}(\vec{r}\,')$ is the field exciting (incident to) the *j-th* particle, that is, the field scattered by all other particles plus the incident field. Here $\ddot{\sigma}_s^{NL}$ is called generalized because $\vec{J}_{ind,j}(\vec{r})$ is the total current density induced within the particle including the closed currents that are usually taken as responsible of the magnetic effects. It is also called non-local because it is not the response to the total field at $\vec{r}$ but a response to the exciting field external to the particle. Therefore all the information about the size and geometry of the sphere should be in the kernel $\ddot{\sigma}_s^{NL}$, and the integration should sample the external field not only at $\vec{r}$ but also in the space occupied by the particle. When $\vec{r}$ lies outside the particle, that is, when $\left|\vec{r}-\vec{r}_j\right| > a$, the integral in Eq. (1) should vanish because there are no induced currents in vacuum. One can also show that $\ddot{\sigma}_s^{NL}$ vanishes when $\left|\vec{r}'-\vec{r}_j\right| > a$. Here, we want to point out that $i\omega\mu_0\ddot{\sigma}_s^{NL}(\vec{r}-\vec{r}_j, \vec{r}'-\vec{r}_j)$ corresponds exactly to the T-matrix operator or transition operator used in scattering theory [6,7]. Therefore, using $\ddot{\sigma}_s^{NL}$ could also be called a T-matrix approach. As a final comment, we note that when the particles are small enough for the exciting field to not vary appreciably within the volume of the particle, one can take $\vec{E}_{exc}(\vec{r}') \approx \vec{E}_{exc}(\vec{r})$ out of the integral in Eq. (1), and write

$$\vec{J}_{ind,j}(\vec{r}) = \overleftrightarrow{\sigma}_s(\vec{r}) \cdot \vec{E}_{exc}(\vec{r}), \tag{2}$$

where in this local relationship

$$\ddot{\sigma}_s(r) = \int \ddot{\sigma}_s^{NL}(\vec{r}-\vec{r}_j, \vec{r}'-\vec{r}_j)d^3r' \tag{3}$$

corresponds to the usual local conductivity of the material the particles are made of.. Therefore non-local effects become important whenever the particles are big enough or are

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close enough for the exciting field to vary appreciably within them, and this is precisely the case in turbid colloids.

Now, the total current density induced in the system will be given by,

$$\vec{J}_{ind}(\vec{r}) = \sum_j \vec{J}_{ind,j}(\vec{r}) \,. \tag{4}$$

If we now perform a configurational average in order to calculate the average of the total induced current, and assume, at the same time, that one can approximate $\vec{E}_{exc}(\vec{r}) \cong \left\langle \vec{E}(\vec{r}) \right\rangle$, where the brackets denote configurational average, we obtain,

$$\left\langle \vec{J}_{ind}(\vec{r}) \right\rangle \cong \int \overleftrightarrow{\sigma}_{eff}(\vec{r},\vec{r}\,') \cdot \left\langle \vec{E} \right\rangle (\vec{r}\,') d^3 r' \tag{5}$$

where

$$\overleftrightarrow{\sigma}_{eff}(\vec{r},\vec{r}\,') = \rho_0 \int_V \overleftrightarrow{\sigma}_s^{NL}(\vec{r}-\vec{r}_j, \vec{r}\,'-\vec{r}_j) d^3 r_j \,. \tag{6}$$

Here ρ_0 is the number density N/V, V is the total volume and we have assumed a boundless system ($N \to \infty, V \to \infty, N/V$ finite) where the probability density $p(\vec{r}_j)$ to find the center of the j-th sphere in the volume V is considered uniform and equal to $d^3 r_j / V$. This approximation is known as the effective-field approximation, and is valid in the dilute regime.

If we now recall that $\overleftrightarrow{\sigma}_s^{NL}$ vanishes for either $\left|\vec{r}-\vec{r}_j\right| > a$ or $\left|\vec{r}'-\vec{r}_j\right| > a$, then, given $\vec{r}$ and $\vec{r}'$, the region of integration in the integral over r_j in Eq. (6) will be only the overlap region between two spheres of radius a, one centered at $\vec{r}$ and the other at $\vec{r}'$. Thus, if $\vec{r}$ and $\vec{r}'$ are farther apart from each other than $2a$, the kernel in Eq. (6) is zero for all $\vec{r}_j$ and the effective non-local conductivity vanishes. This can be expressed also by saying that the range of non-locality, or non-local length in $\overleftrightarrow{\sigma}_s^{NL}$, is $2a$. It is also easy to see that due to the symmetry of the sphere the integral over r_j will depend only on $\left|\vec{r}-\vec{r}\,'\right|$, that is,

$$\overleftrightarrow{\sigma}_{eff}(\vec{r},\vec{r}\,') = \overleftrightarrow{\sigma}_{eff}^{B}\left(\left|\vec{r}-\vec{r}\,'\right|\right) \tag{7}$$

where the superscript B denotes bulk. It is also relevant to point out that a spatial Fourier Transform of the effective conductivity $\overleftrightarrow{\sigma}_{eff}^{B}\left(\left|\vec{r}-\vec{r}\,'\right|\right)$ will yield $\overleftrightarrow{\sigma}_{eff}^{B}(k,\omega)$, which is in general a complex quantity. In particular, its imaginary part will be related not only to absorption processes but also to scattering, since the scattering processes take power out of the coherent beam into the diffuse beam. Furthermore, due to isotropy $\overleftrightarrow{\sigma}_{eff}^{B}(\vec{k},\omega)$ can de decomposed as

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

Where the two scalar functions $\sigma_{eff}^{B,L}(\vec{k},\omega)$ and $\sigma_{eff}^{B,T}(\vec{k},\omega)$ are the longitudinal and transverse projections, respectively, and $\hat{k} \equiv \vec{k}/k$. These projections also lead to the existence of longitudinal and transverse modes determined by the following dispersion relations:

$$1 + \frac{i}{\omega\varepsilon_0}\sigma_{eff}^{B,L}(\vec{k},\omega) = 0 \tag{9}$$

$$k^2 = \omega^2\varepsilon_0\mu_0 + i\omega\mu_0\sigma_{eff}^{B,T}(\vec{k},\omega) \,. \tag{10}$$

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We will denote by $k^L(\omega)$ the solution for the dispersion relation for the longitudinal modes and by $k^T(\omega)$ the corresponding one for the transverse modes. In this case one is able to define an effective index of refraction through

$$n_{eff}(\omega) = \frac{k^T(\omega)}{\omega\sqrt{\varepsilon_0\mu_0}}, \tag{11}$$

as it was shown in detail in Ref. [11]. Notice that although the dispersion relation might have a non-local character, the effective index of refraction depends only on the frequency.

Let us now consider a half-space geometry for the colloidal system, and assume that the probability density of finding the center of any particle in space, $p(\vec{r}_j)$, is uniformly distributed within the half-space $z > 0$. Thus, we have,

$$p(\vec{r}_j) = \begin{cases} \dfrac{d^3 r_j}{V} & \text{if} \quad z_j > 0 \\ 0 & \text{if} \quad z_j < 0. \end{cases} \tag{12}$$

We now recall that given $\vec{r}$ and $\vec{r}'$, the region of integration in the integral over r_j in Eq. (6) will be only the overlap region between two spheres of radius a, one centered at $\vec{r}$ and the other at $\vec{r}'$. Then by writing $\vec{r} = \left(\vec{r}_{\parallel}, z\right)$ and $\vec{r}' = \left(\vec{r}'_{\parallel}, z'\right)$ it is not difficult to see that in the half-space geometry, the non-local effective conductivity will be different for values of $-a < z < a$ than for values of $z > a$. Furthermore, it is also immediate that for $z > a$ the value of the integral in Eq. (6) is the same as in the boundless system, thus in this region the non-local effective conductivity has the bulk value. Therefore we will refer to points in space with values of $-a < z < a$ as the "surface region" and to points inside the half-space, but with values of z farther away than a, as the "bulk". This is illustrated in Fig. 1, where the surface region is drawn with a width 2a around the "probability interface" at $z = 0$. For points within the surface region, symmetry implies that the integral in Eq. (6) must depend on $\left|\vec{r}_{\parallel} - \vec{r}'_{\parallel}\right|$ and z, z' separately. Therefore, in the half-space geometry, we have,

$$\overleftrightarrow{\sigma}_{eff}(\vec{r}, \vec{r}') = \begin{cases} \overleftrightarrow{\sigma}^{B}_{eff}\left(\left|\vec{r} - \vec{r}'\right|\right) & \text{if} \quad z \in \text{ bulk} \\ \overleftrightarrow{\sigma}_{eff}\left(\left|\vec{r}_{\parallel} - \vec{r}'_{\parallel}\right|; z, z'\right) & \text{if} \quad z \in \text{ surface region} \\ 0 & \text{otherwise.} \end{cases} \tag{13}$$

It is clear that the existence of a surface region with an anisotropic response should be taken into account to calculate, for example, the reflection coefficient of the coherent beam at the interface. However, we do not need to have a detailed knowledge of the surface region to analyze the refraction of an incident beam into the bulk region. We only need to know that the surface region has a limited extent and ends where the bulk starts.

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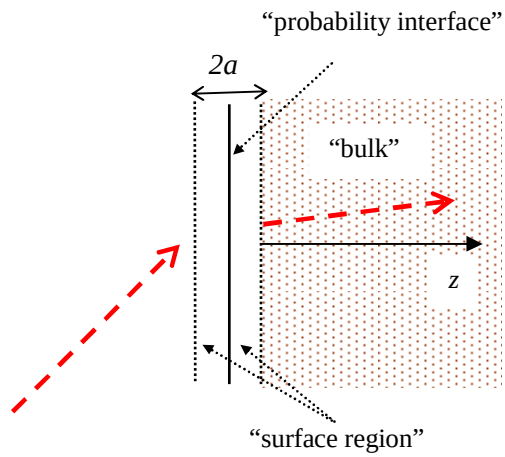

Fig. 1. Schematic illustrating the bulk and surface region in the effective medium of a half-space.

3. Refraction of the coherent beam into a non-local colloidal half-space

We will address the refraction of light in a colloidal half-space in the usual way but considering the non-local conductivity tensor described in the previous section, consisting of a bulk and a surface region. Solving a refraction problem corresponds to finding the direction of the effective wave-vector of the average propagating wave or waves excited in the bulk region by an incident plane wave. For this, we must solve the dispersion relation of refracted electromagnetic modes in the bulk region, and make sure that the appropriate boundary conditions can be satisfied at the boundaries of the surface region. Let us assume that a plane wave, given by $\vec{E}_{inc}(r) = E_{inc}\exp(i\vec{k}^i \cdot \vec{r})\hat{e}_i$, is incident into a half-space of a colloidal medium as shown in Fig. 1. First let us split the incident plane wave as

$$\vec{E}_{inc}(r) = E_{inc}\exp(i\vec{k}_{\|}^i \cdot \vec{r}_{\|})\exp(i\vec{k}_z^i z)\hat{e}_i\,, \tag{14}$$

where the subindex $\|$ denotes parallel to the interface of the colloidal system. Because of translational invariance in the *x*-*y* plane and the mere existence of boundary conditions at the boundaries of the surface region, the average electric field excited both within the surface region and within the bulk must take the form of a plane wave $\exp(i\vec{k}_{\|}^i \cdot \vec{r}_{\|})$ multiplied by a vector function of z. This statement is equivalent to Snell's law in local optics.

Therefore, the solutions of Maxwell's equations for the refracted field within the bulk have the form

$$\left\langle \vec{E} \right\rangle(r) = E_0\exp(i\vec{k}_{\|}^i \cdot \vec{r}_{\|})\exp\left(ik_z z\right)\hat{e} \tag{15}$$

where the effective wave vector $\vec{k} = \left(\vec{k}_{\|}^i, k_z\right)$ is given by the solution of the dispersion relations given in Eqs. (9) and (10). Furthermore, $\vec{k}$ is in general complex, and its real and imaginary parts are in general not parallel to each other (inhomogeneous waves). Since the spatial Fourier transform used to derive the dispersion relations given in Eqs. (9) and (10) assumed $\vec{k}$ as a real quantity, one might ask about its validity for complex $\vec{k}$. At this point one could take this extension simply as a formal analytic extension to the complex plane.

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Alternatively, since $\overleftrightarrow{\sigma}_{eff}^{B}(|\vec{r}-\vec{r}'|)$ vanishes for $|\vec{r}-\vec{r}'|>2a$, it can be seen immediately that the integral defining the spatial Fourier transform

$$\overleftrightarrow{\sigma}_{eff}^{B}(\vec{k},\omega)=\int\overleftrightarrow{\sigma}_{eff}^{B}(|\vec{r}-\vec{r}'|)\exp\left[-i\vec{k}\cdot(\vec{r}-\vec{r}')\right]d^3r' , \tag{16}$$

always exist even for complex wave vectors $\vec{k}$.

An important property to note here is that the integral in Eq. (16) must depend only on the square of the effective wave vector, that is on $k^2=\vec{k}\cdot\vec{k}=k_x^2+k_y^2+k_z^2$, which is in general a complex number, and should not be confused with the square magnitude. There is no restriction for k_x, k_y or k_z being real or complex independently and only the sum of their squares determines the integral in Eq. (16). Thus, from now on we can write $\overleftrightarrow{\sigma}_{eff}^{B}(\vec{k},\omega)=\overleftrightarrow{\sigma}_{eff}^{B}(k,\omega)$, where $k=\sqrt{\vec{k}\cdot\vec{k}}$ is a complex number and, as pointed out above, it is not the magnitude of the wave vector. This is valid whether the real and imaginary parts of the wave vector are parallel or not and means that $\overleftrightarrow{\sigma}_{eff}^{B}(k,\omega)$ will still be valid in general in the presence of losses coming from either dissipation or scattering and for homogeneous and inhomogeneous waves as well.

In conclusion, the refracted fields in the bulk region have the form given by Eq. (15), they might have a transverse and/or a longitudinal character and require the solution of the bulk dispersion relation given by Eqs. (9) and (10) and denoted by $k^T(\omega)$ and $k^L(\omega)$. In Ref. [11] one finds explicit expressions for $\sigma_{eff}^{B,T}(k,\omega)$ and $\sigma_{eff}^{B,L}(k,\omega)$ in the dilute regime, together with detailed numerical calculations for colloidal particles made of different materials in the optical-frequency window. In all these cases, we found that the dispersion relation for transverse modes, Eq. (10), has one fundamental solution that can be well approximated simply by using $k\approx k_0$ in $\sigma_{eff}^{T}(k,\omega)$ on the right hand side of Eq. (10). We refer to this approximation as the light-cone approximation and it was also shown that the effective index of refraction derived from this (non-local) approximation corresponds to the well known effective index of refraction derive by van de Hulst many years ago [14]. It was also pointed out that due to its non-local origin it has to be handled with care. Finally, the exact solution for $k^T(\omega)$ was also found in Ref. [11] by an iteration procedure starting with the light cone-approximation. Therefore, the z-component of the effective wave vector of the refracted field will be then given by

$$k_z(\omega)=\sqrt{k^T(\omega)-\vec{k}_{\parallel}^{\,i}\cdot\vec{k}_{\parallel}^{\,i}} \tag{17}$$

and using Eq. (11) one can write an equivalent relation as

$$k_z(\omega)=\sqrt{k_0^2 n_{eff}(\omega)-\vec{k}_{\parallel}^{\,i}\cdot\vec{k}_{\parallel}^{\,i}} \quad . \tag{18}$$

Also, it is possible to find additional solutions to the dispersion relations for transverse modes, as well as one or more solutions for longitudinal modes. However, we have found that at least for colloidal particles made of noble metals, latex and titanium dioxide, in the optical-frequency window, all these other modes that can actually exist in the bulk have a large imaginary component of the effective wave vector compared to that of the fundamental mode. Therefore, in a refraction experiment these other modes will decay much faster than the fundamental mode inside the bulk and will not interfere with the measurement of the refracted beam corresponding to the fundamental mode. However, these other modes may affect the transmittance of the fundamental mode into the bulk. In general, solving for the amplitude of the refracted fundamental mode will require a model for the surface region, in addition to taking into account all possible modes excited in the bulk.

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4. Colloids with a homogenous matrix medium different than vacuum

Let us now assume that the particles are embedded in a boundless homogeneous matrix that, for simplicity we assume as nonmagnetic, with an electric permittivity $\varepsilon_m(\omega)$. We can repeat the procedure outlined above in exactly the same way but with ε_0 for vacuum replaced by $\varepsilon_m(\omega)$ for the matrix. In this case, the effective non-local conductivity of an isolated particle corresponds to that of a particle embedded in the matrix, and the induced current within the particles is actually the current in excess to the current that would have been induced in the matrix in the absence of the particles. In this case, the dispersion relation for transverse modes is,

$$k^2 = \omega^2 \varepsilon_m \mu_0 + i\omega\mu_0 \sigma_{eff,m}^{B,T}(k,\omega)\,, \tag{19}$$

where $\sigma_{eff,m}^{B,T}$ is the transverse projection of the effective non-local bulk conductivity of an isolated particle embedded within the matrix, while

$$\sigma_{eff,m}^{B;L}(k,\omega) = i\omega\varepsilon_m(\omega)\,, \tag{20}$$

is the dispersion relation for longitudinal modes. Here $\sigma_{eff,m}^{B;L}$ is the longitudinal projection of the effective non-local bulk conductivity of an isolated particle embedded within in the matrix.

As already mentioned, the solution for the fundamental mode can be well approximated with the light-cone approximation in the dispersion relation for transverse modes. In this case, this approximation corresponds to replace k by k_m on the right hand side of Eq. (19). Now, following closely the procedure used in appendix D of Ref. [11], one can show that $\ddot{\sigma}_{eff,m}^{B,T}(k_m,\omega) = 4\pi\rho_0(\omega\varepsilon_m / k_m^3)S(0)$ where now S(0) corresponds to the diagonal element of the scattering matrix in the forward direction of an isolated particle embedded within the matrix (this same result was derived in Ref. [11] for particles in vacuum). Using $n_{eff}(\omega) = k^T(\omega)/k_0$, $k_m = n_m k_0$ and recalling that the refractive index of the matrix is $n_m = \sqrt{\varepsilon_m/\varepsilon_0}$ yields,

$$n_{eff}(\omega) = n_m(\omega)\sqrt{1 + 2i\frac{3f}{2x_m^3}S(0)} \approx n_m(\omega)\left[1 + i\frac{3}{2}\frac{f}{x_m^3}S(0) + \ldots\right] \tag{21}$$

where $x_m = k_m a$ is the size parameter in the matrix and we used $\rho_0 = 3f/4\pi a^3$, where f is the volume fraction occupied by the particles. Expanding the square root and keeping only the first two terms leads to the van de Hulst formula for the effective refractive index [14].

Finally, it is important to notice that although the van de Hulst expression is a good approximation to the solution of the non-local dispersion relation, an obvious improvement is to determine the effective index of refraction by solving the non-local dispersion relation with the exact expression for $\ddot{\sigma}_{eff,m}^{B,T}(k,\omega)$ (within the effective-field approximation) rather than using $\ddot{\sigma}_{eff,m}^{B,T}(k_m,\omega)$. As mentioned above, this solution can be obtained by an iteration procedure using the expressions for $\ddot{\sigma}_{eff,m}^{B,T}(k,\omega)$ given in Ref. [11].

5. Measurement of n_{eff}

At this point, we have made a rather complete analysis of the electromagnetic response of a turbid colloid, pointing out the non-local character of the transverse dispersion relation needed to define and determine properly the effective refractive index. With this in mind, in this

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section, we will analyze all the considerations that are necessary to measure accurately the effective index of refraction.

As shown in Eqs. (15) and (18), the effective wave vector of the refracted beam inside the bulk is calculated with the effective refractive index in the exact same way as in a usual homogeneous and local medium with a complex refractive index due to absorption. The main difference when dealing with a colloidal medium with an effective non-local electromagnetic response is the presence of the diffuse field, the presence of the surface regions and a transmission coefficient for this transverse mode into the bulk of the colloid that depends on the possible excitation of rapidly decaying modes within the surface region. However, the surface region is of limited extent dictated by the non-local length ($2a$ in the case of a mono-disperse colloid, as shown above). Additionally, one must recall that the effective refractive index is attached only to the behavior of the coherent or average field even if there is also a diffuse field which carries optical energy as well.

Therefore, devising a method to measure n_{eff} will simply require making sure that the effect of the surface regions is negligible, and that the measurement does not depend on the transmission or reflection coefficients of the refracted coherent beam in and out of the colloidal medium. Also, one must ensure that the diffuse field is not interfering with the measurement of only the average coherent component.

Usually, in dilute colloids, it is not difficult to subtract a possible spurious contribution of the diffuse field to the measurement of the coherent optical power carried by the average wave (coherent power). The diffuse field is spread smoothly over all scattering angles, whereas the coherent power can be restricted to a short range in scattering angles (in the order of $1\text{x}10^{-3}$ radians in the case of well collimated laser). Therefore, one may sample the diffuse power per unit area at scattering angles around the range of angles where the coherent power is concentrated. Then one may extrapolate the value of the contribution of the diffuse power when measuring the power density of the coherent wave and subtract it. In many cases, this correction will be negligible.

Making a measurement independent of the transmission coefficient of the average wave into a colloidal medium rules out reflectance techniques to measure the effective refractive index. Thus, one must look into interferometric or refraction methods. We can think of two ways of measuring a complex n_{eff} by transmitting a beam of light through a colloidal medium: i) in a slab geometry as illustrated in Fig. 2(a) or ii) in a prism geometry as illustrated in Fig. 2 (b). In the slab geometry one may obtain the real part of n_{eff} from the phase delay of the beam through the bulk region, and its imaginary part from its attenuation. To ensure that the effect of the surface regions on the phase delay measurement is negligible, as well as for making the measurement independent of the transmission coefficients at the interfaces of the colloidal slab, one can perform two measurements of the phase delay and of the attenuation of the coherent beam; a first measurement with a slab of width d_1 ($> 2a$) and a second one with a slab of width $d_2 > d_1$ but otherwise identical. Clearly, the difference in the measured phase delays corresponds to the phase delay of the coherent wave as it traverses a distance $d_2 - d_1$ in the bulk. On the other hand, the transmitted coherent power is proportional to the product of the transmittance factors at the interfaces times either $\exp[-2k_0\text{Im}(n_{eff})d_1]$ or $\exp[-2k_0\text{Im}(n_{eff})d_2]$. Being the transmittance factors at the interfaces equal in both cases, the ratio of the measured values of the transmitted coherent power is equal to $\exp[-2k_0\text{Im}(n_{eff})(d_2 - d_1)]$, and from this, we may obtain $\text{Im}(n_{eff})$ without knowing the transmittance factors of the interfaces.

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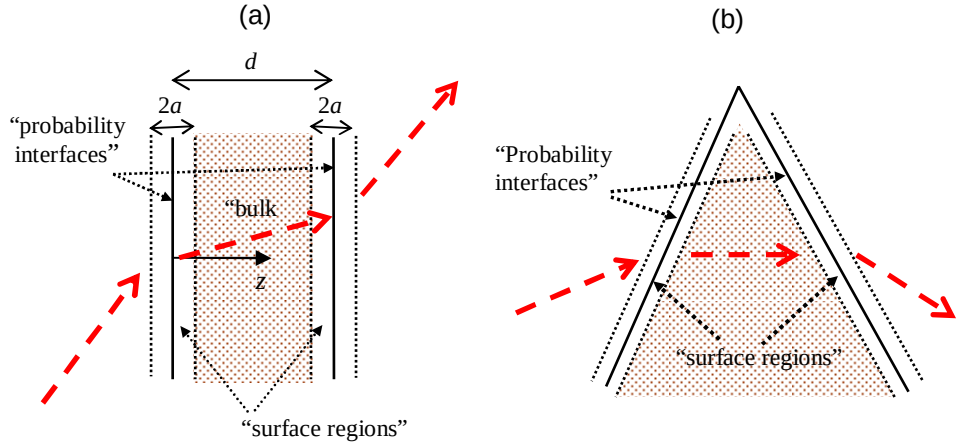

Fig. 2. Schematic illustration of refraction in (a) a colloidal slab and (b) a colloidal prism.

In the prism method, one measures the angle of refraction of the beam exiting the prism, and from this angle and the prism geometry, one infers the real part of the effective refractive index of the prism. This method has actually been tested by the authors in a previous publication [15] and referred to as the colloidal-prism method. However, at the time the exact non-local nature of the effective refractive index was not yet established. In the colloidal prism the coherent beam refracts according to Snell's law with the effective refractive index n_{eff}. Since n_{eff} is complex, the coherent wave inside the prism is an inhomogeneous wave, and Snell's law must be used in its generalized form for complex refractive indices. This is actually discussed in Ref. [15]. In the colloidal prism method, the surface regions have no effect on the measurement of the real part of n_{eff} as long as the beam cross section completely enters the bulk. This is perhaps a fundamental advantage of refraction measurements over interferometric ones in the case of non-local media. However, for the measurement of the attenuation of the coherent beam, necessary to derive the imaginary part of n_{eff}, one must also ensure here that the effects of the surface regions are negligible. As explained above, one could use the ratio between two measurements for two different distances traveled within the colloid to make the measurement independent of the transmittance factors at the interfaces of the colloidal medium. Also, the modeling and measurement of the beam's refraction must be performed with care when the wave attenuates as it traverses the prism, since this attenuation is not uniform through the beam's cross section, simply because different portion of the beam traverse different distances within the prism of the prism's shape. Nevertheless, this can be modeled using physical optics with a complex index of refraction with out much difficulty [15].

Clearly, in either the slab or the prism method, the distance traveled through the bulk can not be too long nor the colloid can be too turbid as not to transmit a measurable amount of coherent power. This means that in general one will be limited to measuring the effective refractive index of dilute colloids.

6. An application: Sizing small particles from measuring n_{eff}

Once the theoretical framework for understanding and measuring the effective refractive index of colloids is established, we can explore interesting applications. Particle sizing from optical properties has been investigated and used for many years. We can mention two techniques: angle-resolved scattering measurements and spectroturbidimetry. In the first

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technique, features from the scattering pattern of isolated particles (highly dilute limit) are measured and the particle size is inferred (see for example Refs. [16,17]). In spectroturbidimetry techniques (see for example Refs. [18-20]), a spectrum of the extinction coefficient is measured, and from it, the particle size distribution is obtained. In both these techniques the refractive index of the particles must be known and are limited to sufficiently large particles.

What we want to show is that by measuring not only the extinction coefficient, which is proportional to the imaginary part of the effective refractive index, but also the real part of the effective refractive index, we do not need to assume or guess the real refractive index of the particles, which is often not well known, and is an important source of errors. We have already made some measurements with latex particles in water [15] and found it was possible to determine the refractive index and size of the particles in that particular case. Here, we show that this method can actually be used for small particles as well as particles of moderate size. Furthermore, we provide a general picture of the inversion method and its limitations. By moderately sized particles we mean particles with a size parameter larger than one but not much larger.

Let us consider a monodisperse colloid of spherical particles of real refractive index dispersed in a matrix of real refractive index. Suppose we know, or have the means to measure, the volume fraction occupied by the particles f, and we measure both the real and imaginary parts of the effective refractive index. Then, using a model [e.g., Eq. (21)], it may be possible to retrieve the size of the particles and their refractive index. A graphical method can be used to obtain the inverse solution and explore the applicability and attainable sensitivity of the retrieval. Let us consider a system of spherical particles suspended in a matrix of refractive index of $n_m = 1.36$ and light of a wavelength in vacuum of $\lambda = 635$ nm. In Fig. 3(a), we plot the real part of the refractive index increment (that is, the contribution of the particles to the refractive index) normalized by the volume fraction, f, versus the imaginary part, also normalized by f. We plot curves for values of the refractive index of the particles of 1.45, 1.47, … 1.55. The symbols in each curve correspond to values of the particles radii from zero (points at the ordinate axis) to 1.5 μm at 30 nm steps. For simplicity, these plots were calculated using the van de Hulst effective refractive index of the system given by Eq. (21). Then, the measured values of $\mathrm{Re}(n_{eff} - n_m) / f$ and $\mathrm{Im}(n_{eff}) / f$ correspond to a point on the two-dimensional space of the graphs. By recognizing to which curve the experimental point belongs, we know the refractive index of the particles and by locating its position along this curve we obtain its radius. Figure 3(a) shows that inverting the refractive index and size of the particles from the measurement of $\mathrm{Re}(n_{eff} - n_m) / f$ and $\mathrm{Im}(n_{eff}) / f$ has a unique solution when the particle radius is in the interval from 0 to 1.5 μm. In Fig. 3(b), we plot the same curves but for particle's radii up to 50 nm at steps of 5 nm. In Figs. 4(a) and 4(b) we plot similar curves but for particles with a refractive index of 1.80, 1.85, 1.90, 1.95, and 2.0. In Fig. 4(a) the symbols are for particles of radius from 0 to 800 nm at steps of 10 nm. In Fig. 4(b) we plot this same graphs but for particle's radii from 0 to 50 nm at steps of 5 nm.

In both Figs. 3(b) and 4(b), we can appreciate clearly that the larger the refractive index of the particles, the better resolution will be possible in determining the particles radius because the points forming the curves are farther apart from each other. Also from these curves, we can see that in practice it should be relatively simple to size very small non-absorbing particles in the range of a few nanometers and a few tenths of nanometers. The limit in sizing very small, non-absorbing particles will come from our ability to measure $\mathrm{Im}(n_{eff}) / f$.

In Figs. 3(a) and 4(a) we can see that as the particles get very large, the curves get closer to each other, meaning that the resolution in determining a and n_p worsens. Actually, all curves will approach the origin and show oscillations as the particle radius increases as is clearly seen in Fig. 4(a). In this region the curves intersect each other and may intersect themselves. Therefore, in this region, it will not be possible to resolve the particle's radii and refractive index, showing that the present method is limited to moderate and small sized particles.

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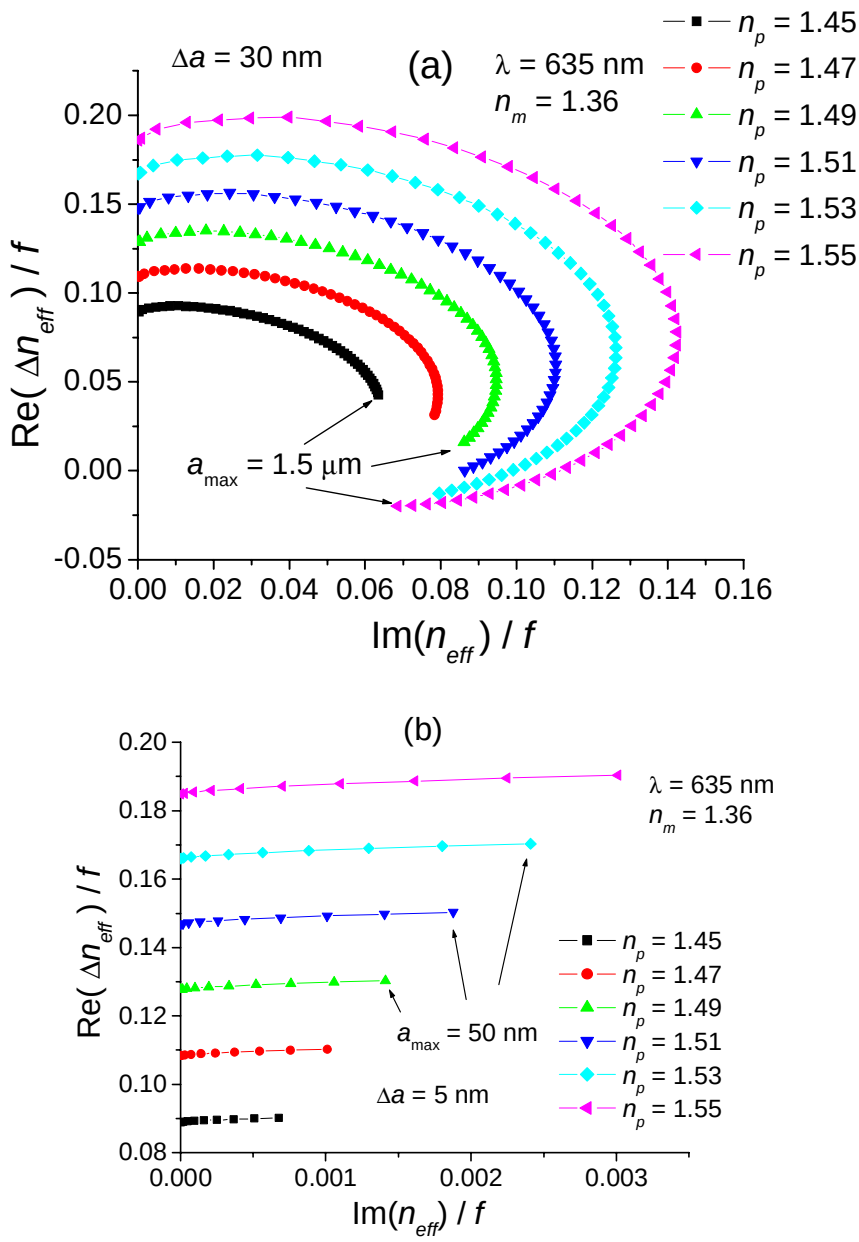

Fig. 3. Graphs of $\mathrm{Im}(n_{eff}) / f$ versus $\mathrm{Re}(n_{eff}) / f$ for a colloid with a matrix of refractive index n_m = 1.36 and particles of refractive index n_p = 1.45, 1.47, …1.55. The symbols in each plot in (a) are for a particles of radius a = 0, 30nm, 60nm, …1500 nm. In (b) are for a = 0, 5nm, 10nm, 15nm, …50nm.

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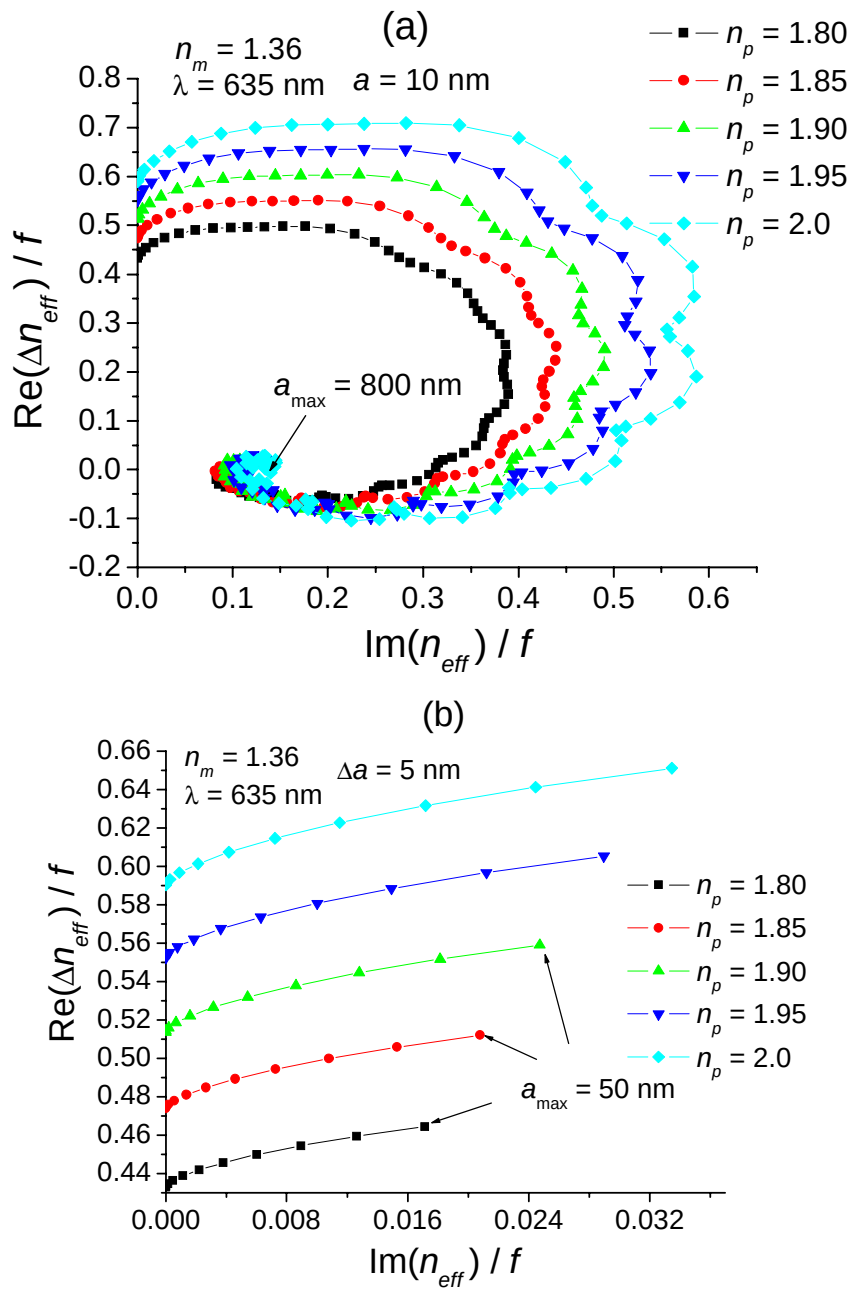

Fig. 4. Graphs of Im(n_{eff}) / f versus Re(n_{eff}) / f for a colloid with a matrix of refractive index n_m = 1.36 and particles of refractive index n_p = 1.80, 1.85, …2.0. The symbols in each plot in (a) are for a particles of radius a = 0, 10nm, 20nm, …800 nm. In (b) are for a = 0, 5nm, 10nm, 15nm, …50nm.

A rough and conservative estimate of the largest radius of the particles that can be characterized with the present method is when the curves turn around and head towards the origin. The turning point in each curve corresponds to when Im(n_{eff}) /f is maximum. In Fig. 5 we plot the particle's radii at which Im(n_{eff}) /f is maximum as a function of the refractive index of the particles, n_p. We can appreciate that the range in particle size for which the present

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method may be used decreases exponentially as the refractive index increases. For n_p = 2.0 the maximum particle size is about 176 nm.

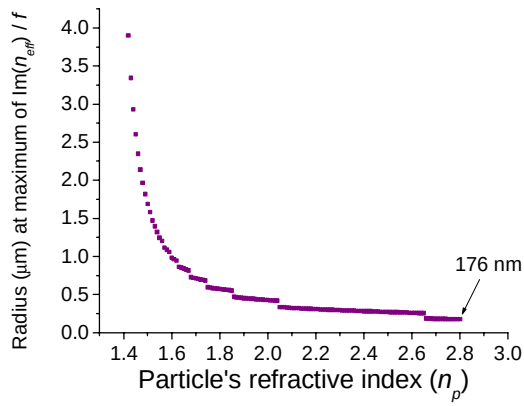

Fig. 5. Particle radius at which the imaginary part of the effective refractive is maximum as a function of the refractive index of the particles.

We must emphasize that the results presented here are for a monodisperse colloid of non-absorbing particles. If the particles absorb light, that is, their refractive index has an imaginary part, the curves may be affected and we may incur in an error. However, if the imaginary part of n_p is not too large the curves are nearly unaffected and we may still use the present method. To estimate the magnitude of the imaginary part of the particles' refractive index that may be tolerated by the present method we plot in Fig. 6(a) two curves for particles with n_p = 1.50 and 1.55 at steps of Δa = 80 nm, and we added the corresponding points for particles with an imaginary part of the refractive index of Im(n_p) = 1x10^{-3} and 1x10^{-2}. In Fig. 6(b) we do the same but for Re(n_p) = 1.80 and 1.90 and steps in a of 40nm. In Fig. 6 we can appreciate that the points for Im(n_p) = 1x10^{-3} (squares) are very close to those for Im(n_p) = 0 (circles), and the error we would incur if we ignored an imaginary part of n_p as large as 1x10^{-3} would be small (maximum error less than 5 nm in a and less than 0.001 in n_p).

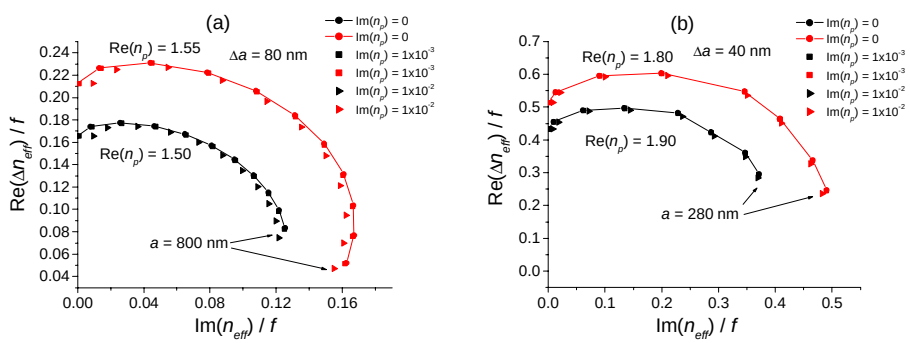

Fig. 6. Two curves for two different values of the particles' refractive index, (a) n_p = 1.50, 1.55 and (b) 1.80, 1.90 at steps of (a) Δa =80 nm and (b) Δa =80 nm. Points with the same value a and n_p but with an imaginary part added to n_p of Im(n_p) = 10^{-3} (squares) and Im(n_p) = 10^{-2} (triangles) are also plotted.

However, for Im(n_p) = 1x10^{-2} this error will not be small any more in this example and can be large in relative terms for small particles (up to 80 nm in a and about for n_p = 1.50). From inspection of Fig. 6(b) we see that the error in ignoring the imaginary part of n_p is less than in Fig. 6(a). Meaning that the method may tolerate larger values of Im(n_p) as the value of Re(n_p) increases. For practical purposes we may set a limit for the present method for particles with

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an imaginary part of their refractive index of $1x10^{-3}$. In most cases the experimental uncertainty will be larger than the error caused by assuming a real refractive index of the particles.

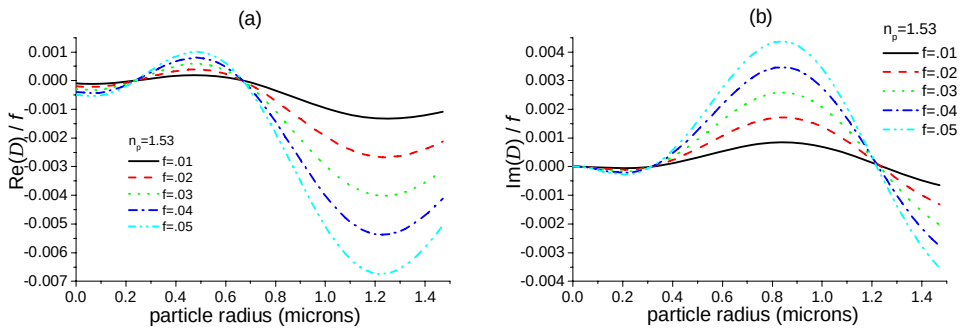

Fig. 7. Difference between the effective refractive index calculated by solving exactly the non-local dispersion equation for transverse modes [Eq. (19)] and that calculated with the van de Hulst expression [Eq. (21)] normalized by the particle's volume fraction f. The curves shown are for a volume fraction of f = 1%, 2%, 3%, 4% and 5% and a particles' refractive index of 1.53 immersed on a matrix of refractive index 1.36 and a vacuum wavelength of 635 nm.

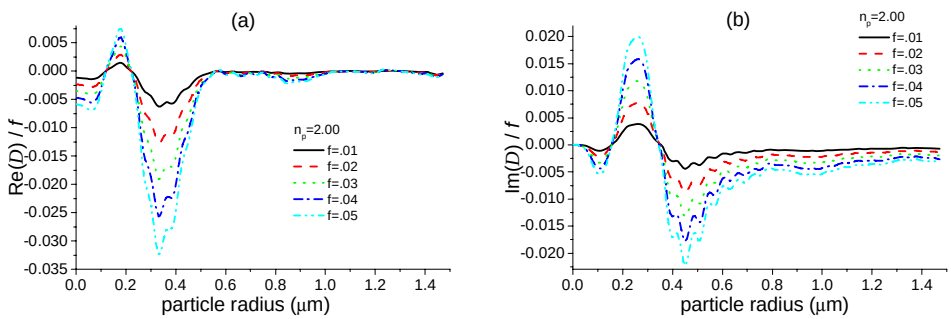

Fig. 8. Difference between the effective refractive index calculated by solving exactly the non-local dispersion equation for transverse modes [Eq. (19)] and that calculated with the van de Hulst expression [Eq. (21)] normalized by the particle's volume fraction *f*. The curves shown are for a volume fraction of *f* = 1%, 2%, 3%, 4% and 5% and a particles' refractive index of 2.00 immersed on a matrix of refractive index 1.36 and a vacuum wavelength of 635 nm.

As already mentioned, the calculations used to generate the plots in Figs. 3-6 were made with the van de Hulst expression for the effective refractive index, Eq. (21). This expression is in general a very good approximation to the exact solution of the non-local dispersion equation for transverse modes within the effective-field approximation, Eq. (19). Let us now define *D* as the difference between the exact solution to Eq. (19) and the van de Hulst formula in Eq. (21). In Figs. 7 and 8 we plot the real and imaginary parts of *D* normalized by the volume fraction occupied by the particles, *f*, as a function of the particles radius and for different values of *f* . To generate the plots in Figs. 7 and 8 we solved Eq. (19) iteratively using the expression for $\ddot{\sigma}_{eff,m}^{B,T}(k,\omega)$ derived in Ref. [11] but for particles embedded in a matrix with an electric permittivity $\varepsilon_m = (1.36)^2$. In Figs. 7 and 8 we assumed a vacuum wavelength of 635 nm and a refractive index of the particles of 1.53 and 2.00 respectively. We can appreciate in these graphs that the improvement of using the exact solution to Eq. (19) is in general modest for values of *f* below 5%. In Fig. 7 and for *f* = 5% the maximum difference in the real and imaginary parts of the calculated refractive index is about 0.007 and 0.004 respectively. In Fig. 8 the maximum differences are about 0.033 and 0.022 for the real and imaginary parts of *D* respectively. From Figs. 3 and 4 we can estimate that these differences would result in an error on the size determination of at most about 3%. For lower volume

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fractions these maximum differences are lower and the maximum error in determining the particle's size is about 1% for $f = 2\%$. Therefore, if a precision on the order of a few percent is required, it is in general safe to use the van de Hulst approximation to estimate the size and refractive index of particles from measurements of the effective refractive index.

7. Summary and conclusions

We have presented a rigorous theoretical framework for the definition and calculation of the effective refractive index of a dilute colloidal system, whether it is optically turbid or not. The effective refractive index comes from a non-local effective medium theory and is in general a complex number, even in the absence of optical absorption. The effective medium theory describes only the average or "coherent" wave and the non-local length is the diameter of the colloidal particles. We have restricted our analysis to monodisperse colloids of spherical particles.

The effective refractive index is associated with the fundamental solution to the non-local dispersion equation for transverse waves. The non-local nature of the average electromagnetic response of a colloidal system has important consequences that one must bear in mind when attempting to measure the effective refractive index. In particular, surface effects will in general invalidate the use of the usual Fresnel reflection coefficients for a flat interface. However, we showed that Snell's law in its generalized form for complex refractive indices can be used safely, in the usual way, with the effective refractive index. This clears two possible ways to measure the effective refractive index without significant complications coming from the non-local nature of the electromagnetic response: The real part of n_{eff} may be obtained either from the phase delay of the coherent wave as it traverse a known distance through the colloid or from refraction at an interface with the colloidal medium. The imaginary part may be obtained from the attenuation of the coherent wave. Approaches to deal with the interface effects were discussed.

Finally we illustrated the usefulness of measuring precisely the complex effective refractive index. In particular, we showed that from the measurement of the real and imaginary parts of the effective refractive index increment due to the colloidal particles and the volume fraction of the particles, it is possible to determine the size and refractive index of dielectric particles. This method is applicable particles with small and moderate size parameter. The maximum size parameter allowed for this method decreases as the refractive index increases. We also showed that for a precision of a few percent in the determination of the particle size in colloids with a volume fraction less than 5%, it is possible to use the so called van de Hulst formula for the effective refractive index to interpret the measurements. This is rather advantageous, since the valuation of the van de Hulst formula is relatively simple.

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