Recent Advances on the Effective Optical Properties of Turbid Colloids

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Abstract. We review the main concepts of the effective-medium approach for the calculation of the optical properties of colloidal systems composed by small colloidal particles and then pose the corresponding problem for turbid colloids, that is, systems with colloidal particles as big as the incident wavelength. Several attempts to properly define and to calculate the effective electromagnetic response of turbid colloidal systems are presented with special emphasis on its non-local (spatially dispersive) character and consequently on the problem of how to measure the corresponding effective index of refraction. For this purpose an alternative spectroscopy based on light refraction is proposed.

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INTRODUCTION

The calculation of the optical properties of inhomogeneous disordered systems poses an interesting challenge that has attracted the attention of many researchers who, by now, have developed a well-established field [1]. In this work we will consider colloidal systems that are simply defined as systems composed by a dispersed phase (colloidal particles) within a homogeneous one. Typical examples are milk, blood, paints, clouds, tissues as well as porous and polycrystalline materials, but here we will restrict ourselves to a simple model consisting of identical spheres located at random in vacuum. Extension to distributions of shapes and sizes, as well as the inclusion of a material matrix, as the homogeneous phase, might not be straightforward. Nevertheless, the main problems concerning the physics and the calculation of the effective electromagnetic response in this type of systems is already present in the random-sphere model. On addition we will be interested not only on the bulk properties of the system but also on the reflection and transmission of light in systems with a flat interface.

Different approaches have been developed over the years and we can identify as two main streams: (i) the use of multiple-scattering theory [2] and (ii) the approach usually known as effective-medium theory [3]. Here we will concentrate on the effective-medium approach but at the end we will try to show how it would be possible to find a connection between these two different kinds of theories.

The effective-medium approach has been very successful in dealing with systems in which the size of the colloidal particles is much smaller than the wavelength of the incident radiation. In this case it is possible to develop a theoretical framework very similar to the one commonly known as: macroscopic electrodynamics or continuum electrodynamics, in which one takes account of only the average (macroscopic) component of the electromagnetic field and neglects the fluctuations of the field due to the scattering of molecules, ions and electrons. For many years, this approach has been though to valid only when the power carried by the average field is much larger than the averaged power carried by the fluctuating field. The materials can then be characterized by continuous functions that describe the response of the system to an external electromagnetic field. When the external field is small in comparison to the molecular fields, the linear response is sufficient and for homogeneous (on the average) and isotropic materials only two frequency-dependent functions (optical parameters) are necessary: the electric

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permittivity, usually denoted by ε, and the magnetic susceptibility, usually denoted by μ, although it can be shown that this choice is not unique. The index of refraction n is given by $n=\sqrt{\varepsilon\mu/\varepsilon_0\mu_0}$, where we use the SI system of units and ε_0 and μ_0 have their usual meaning.

EFFECTIVE-MEDIUM THEORY FOR COLLOIDAL SYSTEMS

Considering now the case of colloidal media, when the size of the colloidal inclusions is much smaller than wavelength of the incident radiation, a similar approach can be developed by neglecting the fluctuating component of the electromagnetic field. In this case one usually refers to the average component of the electromagnetic field as the coherent wave. Then, the colloidal systems can be characterized by effective optical parameters and one refers to them as the effective permittivity ε_{eff}, the effective susceptibility μ_{eff} and the effective index of refraction n_{eff}. While in continuum electrodynamics of an ordinary material, like silver, the calculation of the macroscopic optical response (ε and μ) requires a quantum-mechanical treatment, in the calculation of the corresponding effective optical response (ε_{eff} and μ_{eff}) of a system of colloidal silver particles a quantum-mechanical treatment is not necessary, because each silver particle is regarded as "macroscopic" thus responding to the exciting field with essentially the ε and μ corresponding to bulk silver. Furthermore in the optical regime the magnetic response is so small that one usually takes $\mu\approx\mu_0$. Thus, the magnetic response of the materials involved is usually disregarded and one requires only one frequency-dependent optical parameter, which can be either ε or $n=\sqrt{\varepsilon/\varepsilon_0}$. The same happens in case of colloidal systems composed by small colloidal particles, and a typical example of a effective-medium approach in the case of identical colloidal spheres is the Maxwell-Garnett formula: $\varepsilon_{eff}/\varepsilon_0=(1+2f\tilde{\alpha})/(1-f\tilde{\alpha})$ where f is the volume filling fractioon of the spheres and $\tilde{\alpha}$ is proportional to the polarizability of the spheres. Further developments include extensions to adsorbed particles on a substrate and to colloidal particles of different shapes, sizes and different chirality. The treatment of the high-density regime has also required the inclusion of multipolar and correlation effects as well as the development of codes for numerical simulations [2]. Also, a rather formal mathematical treatment of this problem, known as homogenization theory, has been established.

The main advantage of an effective-medium approach is its immediate use in the continuum-electrodynamics formalism, having obtained a formula for the effective optical parameters, the inhomogeneous system can then be treated as an ordinary material. For example one could calculate the reflection amplitudes from a colloidal system with a flat interface simply using Fresnel´s formulas, or equivalently one could measure the effective index of refraction of a colloidal suspension by using the traditional Abbe refractometer that determines the refractive index through the use of Fresnel´s formulas close to the critical angle.

The problem now is to explore if it is possible to define effective optical parameters when the colloidal particles are not small, and hence, the scattering by the colloidal particles is strong ensuing the power carried by the fluctuating field (diffuse field) is not small in comparison with the power carried by the average field (coherent field). In such cases the system acquires a turbid appearance. This question becomes relevant when we ask ourselves: Can we use an Abbe refractometer to determine the effective index of refraction of milk or blood? and if we get a number, does it have a clear meaning?

Since the electromagnetic field can be split into a coherent plus a diffuse component, when one tries to to give an answer to the questions above, one first realizes that an effective medium will only make sense for the coherent beam, since it is the only beam that has a definite direction and the only one that can be reflected and refracted also with definite directions. Therefore, if one disregards the presence of the diffuse field and one considers only the coherent beam, then it is possible to think that its behavior could be described by an effective medium.

The first attempt to provide a formula for the effective index of refraction of a turbid colloid, composed by identical spheres of radius a randomly located in vacuum, was given by van de Hulst, and it reads

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

where $\gamma=3f/2(ka)^3$ and $S(0)$ is the scattering amplitude in the forward direction. Here $k=2\pi/\lambda$ is the wavevector of the incident radiation and λ its wavelength. Notice also that $S(0)$ is a complex quantity, thus even in the absence of absorption n_{eff} can have an imaginary part which can be interpreted as the decrease in intensity of the coherent field by conversion into the diffuse field, due to scattering.

The Non-local Electromagnetic Response

Recently we have shown that the electromagnetic response of a turbid colloidal system is actually non-local (spatially dispersive) [4], thus we have written

$$\left\langle \vec{J}_{ind} \right\rangle (\vec{k},\omega) = \bar{\bar{\sigma}}_{eff}(\vec{k},\omega)\cdot\left\langle \vec{E}\right\rangle(\vec{k},\omega) \qquad (2)$$

where $\left\langle \vec{J}_{ind} \right\rangle$ denotes the ensemble average of the total induced current density, $\left\langle \vec{E}\right\rangle$ the corresponding average of the electric field and the tensor $\bar{\bar{\sigma}}_{eff}$ the generalized effective conductivity. Here $\vec{k}$ denotes the wave vector and ω the frequency. By total we mean that in $\vec{J}_{ind}$ all induced currents are considered, even those which are commonly regarded as responsible of a magnetic response, and for this reason the effective conductivity is called generalized and its dependence on $\vec{k}$ denotes spatial dispersion, which in $\vec{r}$-space corresponds to a nonlocal response, that is,

$$\left\langle \vec{J}_{ind} \right\rangle (\vec{r},\omega) = \int \bar{\bar{\sigma}}_{eff}(\vec{r}-\vec{r}\,';\omega)\cdot\left\langle \vec{E}\right\rangle(\vec{r}\,';\omega) \qquad (3)$$

For a homogeneous (on the average) and isotropic system the tensor

$$\bar{\bar{\sigma}}_{eff}(\vec{k},\omega) = \sigma^{L}_{eff}(k,\omega)\hat{k}\hat{k} + \sigma^{T}_{eff}(k,\omega)(\bar{\bar{1}}-\hat{k}\hat{k}) \qquad (4)$$

can be written in terms of two scalar functions σ^{L}_{eff} and σ^{T}_{eff}, that are called longitudinal and transverse generalized effective conductivities, respectively, and they correspond to a splitting of the average induced current into longitudinal and transverse projections. But $\left\langle \vec{J}_{ind} \right\rangle$ can also be split into a polarization plus a magnetization current, that is,

$$\left\langle J_{ind} \right\rangle = \frac{\partial \vec{P}}{\partial t} + \nabla \times \vec{M} \qquad (5)$$

where $\vec{P}$ and $\vec{M}$ denote polarization and magnetization fields, respectively. These fields give rise to the traditional optical parameters ε and μ. Therefore, there should be a relationship between the two optical parameters σ^{L}_{eff} and σ^{T}_{eff} and ε and μ, where $\varepsilon(k,\omega)$ and $\mu(k,\omega)$ are now spatially dispersive. Explict expressions for $\varepsilon(k,\omega)$ and $\mu(k,\omega)$ were obtained [4] within the effective-field approximation, valid in the dilute regime. Besides the non-local nature of the electromagnetic response, these results show that there is a magnetic response $\mu_0/\mu(k,\omega)-1$ of the same order of magnitude as $\varepsilon(k,\omega)/\varepsilon_0 - 1$, both complex and proportional to the filling fraction of spheres. Having these expressions an effective index of refraction can be defined through the dispersion relation for the transverse modes

$$k = k_0\sqrt{\varepsilon^{T}(k,\omega)} \qquad (6)$$

by solving Eq. (5) for $k^{T}(\omega)$ and writing it as

$$k^{T}(\omega) = k_0 n_{eff}(\omega) \qquad (7)$$

where $k_0 = \omega / c$ and c denotes the speed of light. Another interesting fact is the appearance of longitudinal modes with a dispersion relation given by $\varepsilon^{L}(k,\omega)=0$. Nevertheless since the effective index of refraction comes from a non-local dispersion relation, it cannot be simply used in Fresnel's relations, and an alternative theory has to be developed if one requires measurements with a set up in which the reflection of light is involved, We are now working on the solution of this problem, and one of the main difficulties is to take account the region close to the surface where the electromagnetis response differs from the one in the bulk.

Refraction Spectroscopy

An alternative that can offer an unambiguous measurement of the effective index of refraction is the use of refraction, because Snell's law will overcome the problems related to the surface region, that is, the parallel component of the wave vector has to be continuous all over the surface region. Thus the measurement of the angle of refraction will be sufficient for the determination of the effective index of refraction. One must bear in mind, however, that the effective refractive index is in general complex and the measurements of the angle of refraction may not be straightforward. A detailed analysis of the optics involved in a particular setup is needed for a proper interpretation. Also, since the coherent light must be transmitted through the colloidal system, measurements of coherent refraction might be restricted to dilute colloidal solutions. Some advances have been made towards a refraction spectroscopy of the effective refractive index [5-6].

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