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A new approach for modeling composite materials

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ABSTRACT

The increasing use of composite materials is due to their ability to tailor materials for special purposes, with applications evolving day by day. This is why predicting the properties of these systems from their constituents, or phases, has become so important. However, assigning macroscopical optical properties for these materials from the bulk properties of their constituents is not a straightforward task.

In this research, we present a spectral analysis of three-dimensional random composite typical nanostructures using an Extension of the Discrete Dipole Approximation (E-DDA code), comparing different approaches and emphasizing the influences of optical properties of constituents and their concentration. In particular, we hypothesize a new approach that preserves the individual nature of the constituents introducing at the same time a variation in the optical properties of each discrete element that is driven by the surrounding medium. The results obtained with this new approach compare more favorably with the experiment than previous ones. We have also applied it to a non-conventional material composed of a metamaterial embedded in a dielectric matrix. Our version of the Discrete Dipole Approximation code, the EDDA code, has been formulated specifically to tackle this kind of problem, including materials with either magnetic and tensor properties.

1. Introduction

Research on metamaterial structures undergoes continuous progress due to their unique electromagnetic behavior and the associated application potential [1]. With constant advances in design approaches [2] and fabrication capabilities [3], metamaterial development appears to be restricted by the properties of naturally available materials used to build "à la carte" structures. In this sense, composite materials may assist with the tailoring of the optical properties of such sophisticated structures, for example considering a metamaterial structure embedded in a dielectric matrix.

Given that particle sizes larger than diameter ~ 3 nm (hundreds of atoms) become increasingly computationally demanding using exact techniques (like the Density Functional theory), it is necessary to model these composite materials using either effective medium theories (such as the Maxwell–Garnett formalism [4]) or approximative solutions based for example on finite element methods such as the Discrete Dipole Approximation (DDA) [5,6].

In any case, effective medium theories describe the effective dielectric function of complex systems through the dielectric function of its constituents and some additional parameter, like the filling fraction of each component [7]. Therefore, these theories can provide just an approximate description of the effective behavior of complex mixtures and it is questionable to what extent real random composites can be described by simple mixing formulae. Indeed, none of these approaches (effective medium theories or DDA) explicitly considers the distortion of the optical properties due to the embedding medium, acknowledging that a more advanced description is necessary for a correct prediction of the observed effective dielectric function and its consequences. This ends in a disagreement with experimental results [8], in spite of the fact that these theories are well accepted by the scientific community.

As a step towards a more advanced description, we have tried to devise expressions for effective optical properties taking into account the change in the local properties of each constituent due to the relative concentration in its surroundings. In other words, we propose a Combined Approach (CA) that considers the composite material to be made of discrete elements whose optical properties have been renormalized so that each constituent perceives the presence of the other according to its actual proportion in the composite.

In this work we present a spectral analysis of composite nanostructures using an Extension of the Discrete Dipole Approximation (E-DDA [6]), emphasizing the influences of optical properties of constituents and their concentration. We have performed simulations on typical shapes, like spheres and disks, both 3-D objects in which the discretization is followed by a random

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distribution of constituents when necessary. For the composition, we have used both noble and base metals as well as the case of a metamaterial embedded in a dielectric matrix.

The work is organized as follows: in Section 2, the theoretical background, on which our numerical method is based, is presented. In Section 3, the scattering geometry together with the material parameters are shown. Section 4 is devoted to the presentation and discussion of the main results obtained from our numerical model. Finally, in Section 5, the main conclusions of this research are summarized.

2. Theoretical background

2.1. E-DDA method

Our approach for modeling the optical response of random composite nanomaterials utilizes the recently developed E-DDA (Extended Discrete Dipole Approximation) methodology [6]. This extension of the Discrete Dipole Approximation (DDA, also known as coupled dipole method) has been devised to allow for the calculation of scattering objects with general (scalar or tensorial) electric and magnetic properties. The DDA itself as well as the E-DDA, relies on the same direct-space discretization scheme that is widely used to study the scattering of light by finite objects. Specifically, the assumptions of this methodology are:

- The volume of the object is considered as the union of non-overlapping, simple connected cells j of volume V_j ($j=1,\ldots,N$) with the total volume of the object given by $V=\sum_j V_j$.
- Each cell j is assumed homogeneous in its material properties and, because of its small size, the electric and magnetic fields are considered as constant throughout the volume V_j.

There are two criteria for validity of the DDA [5]: (1) $|n|kd\lesssim 1$ (so that the dipoles lattice spacing d is small as compared both with the wavelength within the material, $2\pi/(\Re\{n\}k)$, and with the attenuation length (or "skin depth"), $2\pi/(\Im\{n\}k)$, with $\Re\{n\}$ and $\Im\{n\}$ being the real and imaginary parts of the complex refractive index of the material and $k=\omega/c$) and (2) d must be small enough (N must be large enough) to describe the target shape with sufficient precision. It is important to note that the dipole spacing represents a discretization parameter both in the mathematical sense (elemental volume for the DDA) and in the physical one (maximum size for which an homogeneous composition is guaranteed).

In the E-DDA [6], both the electric and magnetic responses of the material are taken into account by considering the excitation of both an oscillating electric and magnetic point dipole located in the center of each cell. In addition, both the relative electric permittivity, $\overline{\overline{\varepsilon}}_r$, and the relative magnetic permeability, $\overline{\overline{\mu}}_r$, of the material, are 2nd order (or rank) tensors. Cells are built up from a simple cubic lattice. The induced electric dipole $\mathbf{P}_j$ under the action of a local electric field $\mathbf{E}_j$ is given by $\mathbf{P}_j=\varepsilon_0\varepsilon_m\overline{\overline{\alpha}}_j\mathbf{E}_j$, where ε_0 is the vacuum electric permittivity, ε_m is the relative electric permittivity of the surrounding (ambient) media, and $\overline{\overline{\alpha}}_j$ is the electric polarizability tensor. In the same way, the induced magnetic dipole $\mathbf{M}_j$ under the influence of a local magnetic field $\mathbf{H}_j$ is given by $\mathbf{M}_j=\overline{\overline{\chi}}_j\mathbf{H}_j$, where $\overline{\overline{\chi}}_j$ is the magnetic susceptibility tensor.

Both the electric ($\overline{\overline{\alpha}}_j$) and magnetic ($\overline{\overline{\chi}}_j$) polarizability tensors can be related to the relative optical properties ($\overline{\overline{\varepsilon}}_j$, $\overline{\overline{\mu}}_j$) through the well-known Clausius–Mossotti relation, exact for electrostatic (zero-frequency limit) polarizable point dipoles located on a cubic lattice (see e.g. [9–11, pp. 333–338]). At finite frequencies, a radiative correction needs to be added to take into account the phase lag between the incident light and the scattered light radiated by the dipole, due to absorption [12,13]

$$\overline{\overline{\alpha}}_j=\overline{\overline{\alpha}}_j^{\mathrm{CM}}\left(\overline{\overline{\mathbf{I}}}-\imath k^3\frac{\overline{\overline{\alpha}}_j^{\mathrm{CM}}}{6\pi}\right)^{-1} \tag{1}$$

$$\overline{\overline{\chi}}_j=\overline{\overline{\chi}}_j^{\mathrm{CM}}\left(\overline{\overline{\mathbf{I}}}-\imath k^3\frac{\overline{\overline{\chi}}_j^{\mathrm{CM}}}{6\pi}\right)^{-1} \tag{2}$$

where the superscript CM denotes the Clausius–Mossotti polarizabilities, $\overline{\overline{\mathbf{I}}}$ is the 3×3 identity matrix, and $k=2\pi/\lambda$.

As for extinction and absorption cross-sections, they have been implemented following [14]:

$$C_{\mathrm{ext}}=\frac{k}{\varepsilon_0\varepsilon_m|\mathbf{E}_0|^2}\sum_{j=1}^{N}\Im[\mathbf{P}_j\cdot(\mathbf{E}_j^{\mathrm{inc}})^*+\mu_0\mu_m(\mathbf{H}_j^{\mathrm{inc}})^*\cdot\mathbf{M}_j] \tag{3}$$

$$C_{\mathrm{abs}}=\frac{k}{\varepsilon_0\varepsilon_m|\mathbf{E}_0|^2}\sum_{j=1}^{N}\left\{\Im(\mathbf{E}_j^*\cdot\mathbf{P}_j)-\frac{k^3}{6\pi\varepsilon_0\varepsilon_m}|\mathbf{P}_j|^2+\mu_0\mu_m\left[\Im(\mathbf{H}_j^*\cdot\mathbf{M}_j)-\frac{k^3}{6\pi}|\mathbf{M}_j|^2\right]\right\} \tag{4}$$

The scattering cross-section can be readily obtained by the difference of the extinction and absorption cross-sections: $C_{\mathrm{sca}}=C_{\mathrm{ext}}-C_{\mathrm{abs}}$. Efficiencies may be obtained by simply dividing the corresponding cross-sections by the effective area πa_{eff}^2. The extinction efficiency Q_{ext} is the most experimentally accessible parameter, and we will use it in all cases except in those where a comparison with other results is required (where the authors use the absorption efficiency Q_{abs} instead).

2.2. Three models for the composite

2.2.1. Discrete Alloy (DA)

Direct application of the E-DDA to some given composite nanostructures (composed of more than one constituent) will provide the solution that we refer to as Discrete Alloy (DA). In this approach, each constituent preserves its bulk optical properties. The E-DDA formalism allows for considering different distributions of the constituents. Our choice consists of an uniform random distribution, where the optical properties of each dipole are assigned based on the filling fraction of each constituent.

2.2.2. Extended Maxwell–Garnett (EMG)

Effective medium theories define effective optical properties for a composite material in terms of the optical properties of its components and their geometrical arrangement [7,15]. The applicability of effective medium theories is restricted by the size of the structures composing the mixture: sufficiently large to preserve locally their own electromagnetic behavior and small enough for the composite to appear homogeneous compared to the wavelength of the interacting radiation. The simplest way to obtain the optical properties of a composite material is performing a Weighted Average (WA), by simply taking into account the relative concentration of each constituent

$$\varepsilon_{\mathrm{WA}}=f\cdot\varepsilon_1+(1-f)\cdot\varepsilon_2 \tag{5}$$

$$\mu_{\mathrm{WA}}=f\cdot\mu_1+(1-f)\cdot\mu_2 \tag{6}$$

where f is the filling fraction of material 1 in the composite. Over the last century, however, numerous effective medium theories have been proposed, being the Maxwell–Garnett expression one of the most successful to explain the effective behavior of a large number of composites. If the mixture consists of isolated and poorly interacting spherical inclusions (ε_i,μ_i) embedded in an