Describing the transition in the effective optical properties from 2D to 3D metamaterials: a simple extension of the Maxwell-Garnett rule

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Abstract
We propose and study a straightforward extension of the Maxwell-Garnett mixing rule, which makes it possible to encompass the effective properties of two-dimensional metamaterials, three-dimensional metamaterials and all intermediate situations. We apply this to the situation of a system of spherical resonators (gold nanoparticles) embedded in a host medium, in contact with a substrate. We study the continuous transition taking place from two-dimensional to fully three-dimensional effective properties, as a function of the system thickness. Our extension allows to study the effect of a depletion or accumulation of resonators near the substrate boundary, where surface effects due to image charges dominate. More generally, we are able to take into account any non-uniform distribution of resonators in the thickness and compute the outcome on the effective properties.

1. Introduction
One of the objectives in the study of optical metamaterials, is to build an artificial structure which behaves on the macroscopic scale as a medium with well-defined optical constants ε and µ. Many realizations of metamaterials are actually two-dimensional, with one layer of resonators, or only made of a small number of layers, and therefore dwell in an intermediate state between two-dimensional (2D) and three-dimensional (3D). One pending question is to predict when actual bulk values are reached as the thickness (number of layers) increases. In order to understand better how this dimensionality affects the macroscopic optical properties, it is necessary to study the transition from 2D to 3D explicitly. We propose a simple extension of the classical Maxwell-Garnett rule which makes it possible to describe this. We here focus on the case of plasmonic, spherical nanoparticles made of gold embedded in a dielectric matrix, although our approach could be easily adapted to other kind of resonating structures (other particle shapes, split rings, fishnets, ...).

2. Maxwell-Garnett in the 2D and 3D limits
The effective optical properties of an infinite, 3D dielectric matrix in which nanoparticles are dispersed with a low volume fraction, has traditionally been described using the Maxwell-Garnett mixing formula:

\[
\frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m} = \frac{1}{3\varepsilon_m} n\alpha_\infty,
\]

where \(\varepsilon_{\text{eff}}\) is the effective dielectric permittivity of the medium, \(\varepsilon_m\) that of the host matrix, \(n\) is the particle number density and \(\alpha_\infty\) is the classical polarizability for spheres in the quasi-static dipolar approximation: \(\alpha_\infty = 4\pi r^3 \varepsilon_m (\varepsilon - \varepsilon_m)/(\varepsilon + 2\varepsilon_m)\), with \(r\) the radius of the particle and \(\varepsilon\) the particle permittivity.
If, on the contrary, the system is so thin that there is only one layer of particles and this monolayer is physically supported by a substrate (which it has to be), then it is well-known that the polarizability of particles is modified due to the presence of an image dipole in the substrate. This gives rise to a polarizability tensor \( \alpha \) for the particle, with two different components, one parallel and the other perpendicular to the substrate, given in the dipolar approximation by [1, 2, 3]

\[
\alpha^\parallel(z) = \frac{\alpha_\infty}{1 + \alpha_\infty B(z)}, \quad \alpha^\perp(z) = \frac{\alpha_\infty}{1 + 2\alpha_\infty B(z)}, \quad B(z) = \frac{1}{32\pi\varepsilon_m(z + r)^3} \left( \varepsilon_m - \varepsilon_s \right) \varepsilon_m + \varepsilon_s, \tag{2}
\]

where \( z \) is the distance from the bottom of the particle to the substrate and \( \varepsilon_s \) is the substrate permittivity.

3. Extension of the Maxwell-Garnett rule

We now propose to blend these classical limiting cases (2D and 3D) together so as to provide a mixing rule able to treat continuously the transition between them, since intermediate situations are of high practical importance. As a first step, as illustrated in Fig. 1-(c), because the interaction with the substrate is fast-decreasing, we classify particles into two categories (species): either they are located on the substrate and hence interact with it (“surface” particles), with polarizability \( \alpha_s \), or they are farther away and do not interact with it (“bulk” particles), with polarizability \( \alpha_\infty \). To compute the effective optical properties of intermediate 2D/3D configuration, we then simply use a generalized Clausius-Mossotti formula adding the contribution of both species, which yields an anisotropic overall permittivity:

\[
\frac{\varepsilon^\parallel - \varepsilon_m}{\varepsilon^\parallel + 2\varepsilon_m} = \frac{1}{3\varepsilon_m} \left[ n_b \alpha_\infty + \frac{\rho}{D} \alpha^\parallel(z = 0) \right], \tag{3}
\]

with \( n_b \) the number of “bulk” particles per unit volume, \( \rho \) the number of “surface” particles per unit area, and \( D \) the film thickness.

It is naturally possible to refine this initial approach: rather than crudely using two types of particles, one can use a continuous description where all particles interact with the substrate with the polarizability \( \alpha(z) \) from Eq. 2. One can also take into account the effect of a varying particle density \( n(z) \) within the film thickness, by generalizing Eq. (3) as follows:

\[
\frac{\varepsilon^\parallel - \varepsilon_m}{\varepsilon^\parallel + 2\varepsilon_m} = \frac{1}{3\varepsilon_m} \int_0^D \frac{dn(z)}{dz} \alpha^\parallel(z) dz. \tag{4}
\]

4. Results

Using the two-species equation (3), we analyse how the effective optical properties are affected (i) by the system thickness \( D \) and (ii) by the density of “surface” particles \( \rho \) in contact with the substrate, or equivalently, by the corresponding substrate surface coverage calculated as \( \pi r^2 \rho \). The values of these parameters will determine whether we have a dominantly bulk (3D) or layer (2D) configuration, or a situation in between.

In Fig.1-(a) and (b) we plotted the real part of the refractive index \( n = \sqrt{\varepsilon_{\text{eff}}} \) as the sample thickness \( D \) is varied for a constant value of the substrate surface coverage (15.4%) and a constant total density of particles in the system \( n_b + \rho / D \). From these figures we see that for thin systems (20 nm), we have a strong anisotropy due to particle-substrate interaction (and also a redshift of the plasmon resonance due to the image dipoles in the substrate). When the sample thickness is increased, “bulk” particles start outnumbering “surface” ones, and both \( \text{Re}(n_\perp) \) and \( \text{Re}(n_\parallel) \) tend to the bulk value – which results in a decreasing anisotropy. This allows to estimate the thickness for which bulk values are reached within a given tolerance.

In Fig.1-(d), the film thickness \( D = 100 \) nm and total number of resonators are kept unchanged, but now the internal distribution of particles is being modified, by varying the surface coverage: when this increases, we see clearly that the plasmon response gets stronger.
Fig. 1: (a) $Re(n_\perp)$ and (b) $Re(n_\parallel)$ for different values of the sample thickness $D$ and fixed total particle density. The dashed line is the result for a 3D bulk, that is, without particle-substrate interaction. The surface coverage is kept constant at 15.4% (i.e., 500 particles/$\mu$m$^2$ with 14-nm particles). (c) A graphical representation of our film, where the green part represents the part in which the gold nanoparticles do not interact with the substrate and the red one where they do, in the simple two-species approach. (d) $Re(n_\perp)$ for different values of the surface coverage and fixed values of the film thickness ($D = 100$ nm) and total particle density.

5. Conclusion

We have shown how the Maxwell-Garnett mixing rule can very simply be extended in order to continuously predict the effective optical properties of systems from purely 2D up to fully 3D. We have only presented results for the particular case of a surface density and a volume density (two species); but using equation (4), we are also able to consider more realistic cases where the particles concentration profile is an arbitrary function of $z$. Moreover, multipolar interactions between the particles and the substrate, and/or the case of non-spherical particles [3, 4], can be accounted for by adapting Eq. 2. We finally emphasize that this extension of Maxwell-Garnett is nonetheless flawed since it does not correctly incorporate the boundary conditions at the substrate. We have extended our work and corrected Equation 3, showing that this indeed results in an increased substrate-induced anisotropy for the effective properties.

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References


