

# Mixtures and Composite Particles: Correspondence of Effective Description

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**Abstract**—This presentation focuses on the perfect analogy between the Maxwell Garnett mixing formula and the effective polarizability of a piecewise homogeneous dielectric sphere. Due to this correspondence, it is possible to transfer results between these domains, from extended mixtures to properties of single-particle scattering, and vice versa. As examples, we discuss the bounds for the effective parameters, dispersive character of mixtures, plasmonic cloaking, multiphase mixtures, and non-spherical extensions.

## I. INTRODUCTION

The effective permittivity of a mixture according to the Maxwell Garnett (MG) formula [1] is well known:

$$\varepsilon_{\text{MG}} = \varepsilon_e + 3\varepsilon_e p \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_i + 2\varepsilon_e - p(\varepsilon_i - \varepsilon_e)} \quad (1)$$

Here spherical inclusions with permittivity  $\varepsilon_i$  take a volume fraction  $p$  in a host medium with permittivity  $\varepsilon_e$ .<sup>1</sup> Despite its simplicity, the Maxwell Garnett formula has proven to be quite applicable for ordered mixtures for low or moderate inclusion loadings, even in the case of plasmonic mixtures [2].

From the scope of the present paper, it is particularly essential to note the interconnection between the MG formula and the Lorenz–Lorentz (Clausius–Mossotti) relation, which gives the effective permittivity as function of the normalized polarizability of the inclusion spheres

$$\frac{\varepsilon_{\text{MG}} - \varepsilon_e}{\varepsilon_{\text{MG}} + 2\varepsilon_e} = \frac{p\alpha}{3} \quad (2)$$

where the normalized polarizability of the inclusion spheres  $\alpha$  has the value  $3(\varepsilon_i - \varepsilon_e)/(\varepsilon_i + 2\varepsilon_e)$ .

As another avenue to effective description of mixed structures, instead of an extended mixture, one can also study the heterogeneity of a single composite particle. It is the aim of this presentation to point out the correspondence between the classical mixing formulas and effective dipole moment of a layered piecewise homogeneous dielectric sphere.

## II. HOMOGENIZATION BY EFFECTIVE POLARIZABILITY

Consider a composite sphere consisting of a spherical core (radius  $a$ , permittivity  $\varepsilon_2$ ) surrounded by a spherical coating

<sup>1</sup>All permittivities are relative (dimensionless).

(radius  $b$ , permittivity  $\varepsilon_1$ ), both isotropic. The normalized polarizability of such a sphere reads [3, Sec. 4.3]

$$\alpha_k = 3 \frac{(\varepsilon_1 - 1)(\varepsilon_2 + 2\varepsilon_1) + g(2\varepsilon_1 + 1)(\varepsilon_2 - \varepsilon_1)}{(\varepsilon_1 + 2)(\varepsilon_2 + 2\varepsilon_1) + 2g(\varepsilon_1 - 1)(\varepsilon_2 - \varepsilon_1)} \quad (3)$$

where  $g = (a/b)^3$  measures the relative fraction of the core.

This formula projects the three internal parameters of the particle into a single number, the polarizability. Given the deterministic structure of the sphere,  $\alpha$  is uniquely fixed by the internal structure, but not vice versa. There are several (infinite number of) possible spheres with the same polarizability. Of these, the simplest one is a homogeneous sphere.

Fig. 1 visualizes the idea of the present paper: not being interested in the internal structure of the composite sphere, we look for the effective permittivity for a homogeneous sphere that externally would look exactly like the original layered sphere (in a locally uniform static field). This leads us to the following relation

$$\varepsilon_{\text{eff}} = 1 + \frac{\alpha_k}{1 - \alpha_k/3} \quad (4)$$

where  $\varepsilon_{\text{eff}}$  is determined by (3).

Such a homogenization principle can also be called *internal homogenization* [4].

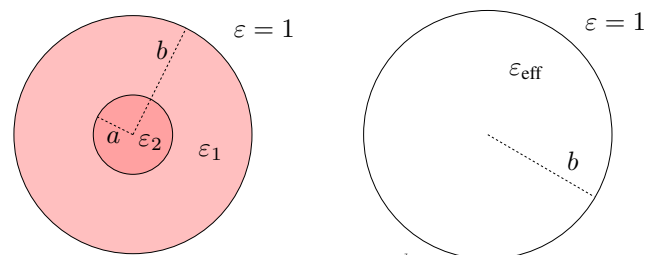


Fig. 1. Two-layer sphere and its homogenized version.

It does not require very much algebra to show that  $\varepsilon_{\text{eff}}$  in (4) and  $\varepsilon_{\text{MG}}$  in (1) are equal when the following conditions are met:

$$\varepsilon_1 = \varepsilon_e, \quad \varepsilon_2 = \varepsilon_i, \quad g = p \quad (5)$$

In other words, the permittivity that results from the effective-polarizability condition of a layered sphere is exactly the same as the Maxwell Garnett prediction when the core is treated as the inclusion and the surrounding shell as the host matrix!

### III. CONSEQUENCES

The exact correspondence between the homogenization of the layered sphere on one hand and Maxwell Garnett mixing rule on the other, provides us with the possibility to transfer the rich repertoire of results from either of these two domains to the other. Let us shortly discuss some of these.

#### A. Hashin–Shtrikman Bounds

A wide literature exists discussing the question about bounds for the effective material parameters of mixtures [5], [6], [7]. The Hashin–Shtrikman bounds for the effective permittivity of a statistically homogeneous and isotropic mixture are exactly the Maxwell Garnett formula and its inverse form (where the roles of the inclusion and the host phases are interchanged).

Let us interpret this fundamental result within the context of the polarizability of a composite sphere. We can then deduce the following optimization rule to build up the smallest possible dipole moment from a given amount of two materials with permittivity  $\varepsilon_1$  and  $\varepsilon_2$ : if  $\varepsilon_2 > \varepsilon_1$ , the minimum polarizability results from putting all material 2 to the center and material 1 form the outer layer around it. Likewise, the recipe for the “heaviest” sphere requires that material 2 forms the coating. All other possibilities of moulding the materials into a spherical form lead to dipole moments between these two values.

#### B. Dispersion Engineering

Dielectric materials are dispersive. Their permittivity is a function of frequency. When dispersive materials are combined with other materials, the mixture displays a new type of dispersion. It is known [3, Ch. 12], for example, that if in a mixture the inclusions obey Debye-type dispersion and the environment is dispersionless, the MG prediction for the effective permittivity is also Debye-type but the dispersive region is blue-shifted in frequency, sometimes quite strongly. As another example of dispersive heterogeneities, for a mixture where a non-dispersive insulating medium hosts conducting Drude-type inclusions, the effective behavior is a Lorentz dispersion with a resonance character.

Again, we can directly take these results into the analysis of the polarizability of the composite particle. For example, by enclosing a water droplet (which is a Debye dielectric) by a neutral dielectric spherical shell, the relaxation frequency of the particle can be controlled. Likewise, when a metallic sphere is surrounded by a dielectric layer, it attains a plasmonic resonance whose properties can be adjusted by the layer permittivity and thickness.

#### C. Cloaking Applications

The reverse route is also possible: transfer of results from composite inclusions into the domain of dielectric mixtures. One example is the problem of invisible inclusions. The polarizability of a layered sphere can be made zero by matching the permittivities and thicknesses of the layers using the condition (3) [8]. Of course, in this case, one of the permittivities has to

be less than unity, or even negative. Such a cloaking principle has been called *plasmonic cloaking* [9].

What does this mean in the domain of dielectric mixtures? The recipe that gives zero polarizability for a core-shell sphere can be directly taken for designing composite materials with unit permittivity. Obviously such media do not interact with the electric field, and hence would be very useful in various applications involving mechanical support structures of radiating or receiving antennas. In the composite, the less-than-unity dielectric can serve either as the matrix or the inclusion, just like in the case of the invisible layered sphere, either the core or shell can be plasmonic.

#### D. Multilayer Sphere

The concept of the effective permittivity of a layered sphere can be naturally extended to several spherical layers. The polarizability of an  $N$ -layer sphere  $\alpha_N$  can be written explicitly as a recursive extension of the two-layer result (3), see [10]. Using, e.g.  $\alpha_3$ , instead of  $\alpha_k = \alpha_2$  in (4) returns us the Maxwell Garnett prediction for the effective permittivity of a mixture where two-layer spheres work as inclusions in the environment that is of the material of the outermost layer.

However, the three-layer sphere does not correspond to a mixture where two separate phases  $\varepsilon_2$  and  $\varepsilon_3$  would be independently embedded in the host  $\varepsilon_1$  like in Fig. 2 (left panel). This raises the question about the partial homogenization of the inclusions: what would be the effective permittivity  $\varepsilon_{23}$  with which the phases 2 and 3 should be replaced so that the total mixture would have the same permittivity in both cases in the figure (right panel). In this case the phases 2 and 3 have fully symmetrical roles in the mixture whereas in the three-layer sphere the order of the layers has a crucial effect.

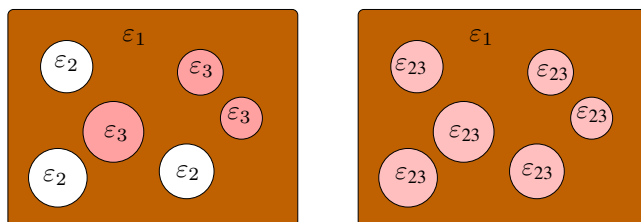


Fig. 2. Partial homogenization of a multiphase mixture.

Using the result for the multiphase mixture MG formula [3, Sec. 4.1] and balancing the effective permittivity with that of the two-phase MG result, the partial homogenization of Fig. 2 can be written as

$$\varepsilon_{23} = \frac{(\varepsilon_2+2)(\varepsilon_3+2)+2p_2(\varepsilon_2-1)(\varepsilon_3+2)+2p_3(\varepsilon_3-1)(\varepsilon_2+2)}{(\varepsilon_2+2)(\varepsilon_3+2)-p_2(\varepsilon_2-1)(\varepsilon_3+2)-p_3(\varepsilon_3-1)(\varepsilon_2+2)} \quad (6)$$

where  $p_2$  and  $p_3$  are the relative volumes of phases 2 and 3 from the volume occupied by them jointly. This form emphasizes the symmetrical role of the two phases with volume fractions  $p_2$  and  $p_3$  of the two phases. Note that  $p_3 = 1 - p_2$ .

The relation (6) can be forced into a Maxwell-Garnett-type form which hides the symmetry between phases 2 and 3:

$$\varepsilon_{23} = \varepsilon_2 + (\varepsilon_2 + 2)p_3 \frac{\varepsilon_3 - \varepsilon_2}{\varepsilon_3 + 2 - p_3(\varepsilon_3 - \varepsilon_2)} \quad (7)$$

Here, obviously  $p_3 = 0$  returns  $\varepsilon_{23} = \varepsilon_2$ , and in case  $p_3 = 1$  we have  $\varepsilon_{23} = \varepsilon_3$ .

### E. Non-Spherical Extension

Finally, let us study whether the homogenization correspondence which is in the focus of this paper can be generalized into a non-spherical geometry. As is known, the MG mixing rule can be extended into mixtures where the inclusions are ellipsoidal in form [3, Sec. 4.2]. Assuming that all ellipsoids are orientationally aligned, the mixture is anisotropic. Furthermore, the permittivity component along any of the axes of the ellipsoids reads

$$\varepsilon_{\text{eff},j} = \varepsilon_e + p\varepsilon_e \frac{\varepsilon_i - \varepsilon_e}{\varepsilon_e + (1-p)N_j(\varepsilon_i - \varepsilon_e)} \quad (8)$$

where  $N_j$  is the depolarization factor of the ellipsoid  $\varepsilon_i$  in the direction of the axis  $j$ . Note that  $N_j = 1/3$  returns (1).

The polarizability component  $\alpha_j$  of a homogeneous ellipsoid in free space reads

$$\alpha_j = \frac{\varepsilon_{\text{eff},j} - 1}{1 + N_j(\varepsilon_{\text{eff},j} - 1)} \quad (9)$$

Now, combining the MG result (8) for the effective permittivity with the polarizability (9) gives us the expression

$$\alpha_j = \frac{\varepsilon_e - 1 + \frac{p(\varepsilon_i - \varepsilon_e)(\varepsilon_e + N_j(1 - \varepsilon_e))}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}}{1 + N_j(\varepsilon_e - 1) + \frac{pN_j(1 - N_j)(\varepsilon_e - 1)(\varepsilon_i - \varepsilon_e)}{\varepsilon_e + N_j(\varepsilon_i - \varepsilon_e)}} \quad (10)$$

This result, however, does not exactly match the polarizability of a layered ellipsoid. The polarizability of a layered ellipsoid can be solved in closed form *provided that the ellipsoidal interfaces are confocal*. This means that the axis ratios do not remain the same for each layer. Then also the depolarization factors change.

For example, the two-layer ellipsoid result for the polarizability component in the direction  $j$  reads [11]

$$\alpha_j = \frac{\varepsilon_e - 1 + \frac{p(\varepsilon_i - \varepsilon_e)(\varepsilon_e + N_{je}(1 - \varepsilon_e))}{\varepsilon_e + N_{ji}(\varepsilon_i - \varepsilon_e)}}{1 + N_{je}(\varepsilon_e - 1) + \frac{pN_{je}(1 - N_{je})(\varepsilon_e - 1)(\varepsilon_i - \varepsilon_e)}{\varepsilon_e + N_{ji}(\varepsilon_i - \varepsilon_e)}} \quad (11)$$

where the depolarization factors  $N_{ji}$  and  $N_{je}$  are those (in direction  $j$ ) of the core inclusion and shell environment ellipsoids, respectively, and they are not equal.

Formulas (10) and (11) become equal in limiting cases: when the ellipsoid degenerates to a sphere, and also when the outer layer becomes thin. As an example, Fig. 3 shows the confocality requirement of an oblate ellipsoid (flattened sphere) when the whole ellipsoid has axial ratio 0.5 and the core volume is half of the total ellipsoid. In this case the depolarization factors in the direction of the axis of revolution (vertical, axial direction in the figure) are  $N_{je} = 0.527$  for the total ellipsoid and  $N_{ji} = 0.641$  for the core ellipsoid.

Fig. 4 displays the differences in the effective axial permittivity for the case when the core is of permittivity  $\varepsilon_i = 10$

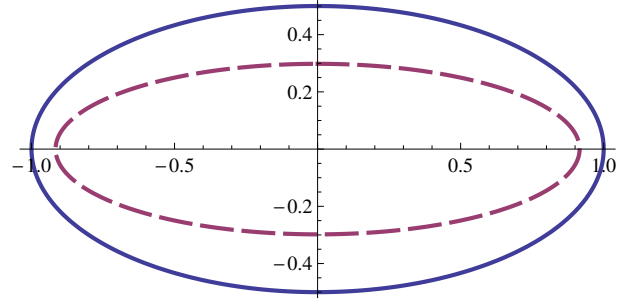


Fig. 3. Confocal oblate ellipsoids in the case when  $p = 0.5$  and the axis ratio of the environment ellipsoid is 1:2. Note the difference in axis ratios of the core and the shell which leads into non-equal depolarization factors for the two ellipsoids.

and the shell  $\varepsilon_e = 2$ . The effective axial permittivity of the composite ellipsoid is shown as function of the fractional volume of the core. The ellipsoid is oblate with the axis of revolution being one half of the equator axis like in Fig. 3. The figure shows that either for a small core ( $g \ll 1$ ), or for a thin shell ( $1 - g \ll 1$ ), the two predictions match.

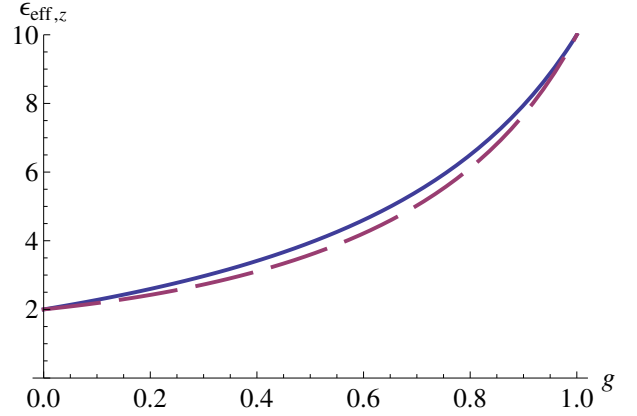


Fig. 4. The effective axial permittivity  $\varepsilon_{\text{eff},z}$  of a composite ellipsoid as a function of the core fraction. Permittivity of the core is 10 and that of the shell 2. The ellipsoid is oblate with axis ratio 1:2. Solid blue line: calculated from the MG-based formula (10); dashed red line: calculated from the layered-ellipsoid formula (11).

## IV. CONCLUSION

In this presentation, the exact correspondence between the classical Maxwell Garnett mixing formula for spherical inclusions on one hand and the homogenization condition for a composite sphere on the other was analyzed. In particular, it was applied for transfer of results between these two regimes. The agreement between the two formulas is particularly surprising due to the fact that the problem of a single-particle solution is an exact solution of a deterministic problem whereas the derivation of the Maxwell Garnett mixing rule relies on approximations for the interaction fields between neighboring particles in the mixture. For example, the polarizability formula (3) holds for any combination of parameters,

whereas the applicability of the MG formula (1) is limited to low or moderate volume fractions in practical applications.

Due to the long history of homogenization studies (the earliest ones heralding the Maxwell Garnett formula date from the 19th century), a wealth of theoretical results for mixtures exists in the literature and can be used for the understanding of the behavior of layered spheres, for example, bounds for the polarizability or dispersion behavior. These can be exploited for various purposes, like meteorological remote sensing of hydrometeors, or design of plasmonic nanoparticles for sensing applications.

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