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A tutorial on Maxwell Garnett approximation.

I. Introduction

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This tutorial is devoted to the Maxwell Garnett approximation and related theories. Topics covered in the first, introductory part of the tutorial include the Lorentz local-field correction, the Clausius-Mossotti relation and its role in the modern numerical technique known as the Discrete Dipole Approximation (DDA), the Maxwell Garnett mixing formula for isotropic and anisotropic media, multi-component mixtures and the Bruggeman mixing formula, and the concept of smooth field. © 2016 Optical Society of America

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1. INTRODUCTION

In 1904, Maxwell Garnett [1] has developed a simple but immensely successful *homogenization theory*. As any such theory, it aims to approximate a complex electromagnetic medium such a colloidal solution of gold micro-particles in water with a homogeneous *effective medium*. The Maxwell Garnett *mixing formula* gives the permittivity of this effective medium (or, simply, the effective permittivity) in terms of the permittivities of the individual constituents of the complex medium.

A closely related development is the Lorentz molecular theory of polarization. This theory considers a seemingly different physical system: a collection of point-like polarizable atoms or molecules in vacuum. The goal is however the same: compute the macroscopic dielectric permittivity of the medium made up by this collection of molecules. A key theoretical ingredient of the Lorentz theory is the so-called local-field correction, and this ingredient is also used in the Maxwell Garnett theory.

The two theories mentioned above seem to start from very different first principles. The Maxwell Garnett theory starts from the macroscopic Maxwell's equations, which are assumed to be valid on a fine scale inside the composite. The Lorentz theory does not assume that the macroscopic Maxwell's equations are valid locally. The molecules can not be characterized by macroscopic quantities such as permittivity, contrary to small inclusions in a composite. However, the Lorentz theory is still macroscopic in nature. It simply replaces the description of inclusions in terms of internal field and polarization by a cumulative characteristic called the polarizability. Within the approx-

imations used by both theories, the two approaches are mathematically equivalent.

An important point is that we should not confuse the theories of *homogenization* that operate with purely classical and macroscopic quantities with the theories that derive the macroscopic Maxwell's equations (and the relevant constitutive parameters) from microscopic first principles, which are in this case the microscopic Maxwell's equations and the quantum-mechanical laws of motion. Both the Maxwell Garnett and the Lorentz theories are of the first kind. An example of the second kind is the modern theory of polarization [2, 3], which computes the induced microscopic currents in a condensed medium (this quantity turns out to be fundamental) by using the density-functional theory (DFT).

This tutorial will consist of two parts. In the first, introductory part, we will discuss the Maxwell Garnett and Lorentz theories and the closely related Clausius-Mossotti relation from the same simple theoretical viewpoint. We will not attempt to give an accurate historical overview or to compile an exhaustive list of references. It would also be rather pointless to write down the widely known formulas and make several plots for model systems. Rather, we will discuss the fundamental underpinnings of these theories. In the second part, we will discuss several advanced topics that are rarely covered in the textbooks. We will also sketch a method for obtaining more general homogenization theories in which the Maxwell Garnett mixing formula serves as the zeroth-order approximation.

Over the past hundred years or so, the Maxwell Garnett approximation and its generalizations have been derived by many authors using different methods. It is unrealistic to cover all these approaches and theories in this tutorial. Therefore, we

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will make an unfortunate compromise and not discuss some important topics. One notable omission is that we will not discuss random media [4–6] in any detail, although the first part of the tutorial will apply equally to both random and deterministic (periodic) media. Another interesting development that we will not discuss is the so-called extended Maxwell Garnett theories [7–9] in which the inclusions are allowed to have both electric and magnetic dipole moments.

Gaussian system of units will be used throughout the tutorial.

2. LORENTZ LOCAL FIELD CORRECTION, CLAUSIUS-MOSSOTTI RELATION AND MAXWELL GARNETT MIXING FORMULA

The Maxwell Garnett mixing formula can be derived by different methods, some being more formal than the others. We will start by introducing the Lorentz local field correction and deriving the Clausius-Mossotti relation. The Maxwell Garnett mixing formula will follow from these results quite naturally. We emphasize however that this is not how the theory has progressed historically.

A. Average field of a dipole

The key mathematical observation that we will need is this: the integral over any finite sphere of the electric field created by a static point dipole \mathbf{d} located at the sphere's center is not zero but equal to $-(4\pi/3)\mathbf{d}$.

The above statement may appear counterintuitive to anyone who has seen the formula for the electric field of a dipole,

$$\mathbf{E}_d(\mathbf{r}) = \frac{3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{d}) - \mathbf{d}}{r^3}, \quad (1)$$

where $\hat{\mathbf{r}} = \mathbf{r}/r$ is the unit vector pointing in the direction of the radius-vector \mathbf{r} . Indeed, the angular average of the above expression is zero [10]. Nevertheless, the statement made above is correct. The reason is that the expression Eq. (1) is incomplete. We should have written

$$\mathbf{E}_d(\mathbf{r}) = \frac{3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{d}) - \mathbf{d}}{r^3} - \frac{4\pi}{3}\delta(\mathbf{r})\mathbf{d}, \quad (2)$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta-function.

The additional delta-term in Eq. (2) can be understood from many different points of view. Three explanations of varying degree of mathematical rigor are given below.

(i) A qualitative physical explanation can be obtained if we consider two point charges q/β and $-q/\beta$ separated by the distance βh where β is a dimensionless parameter. Now let β tend to zero. The dipole moment of the system is independent of β and has the magnitude $d = qh$. The field created by these two charges at distances $r \gg \beta h$ is indeed given by Eq. (1) where the direction of the dipole is along the axis connecting the two charges. But this expression does not describe the field in the gap. It is easy to see that this field scales as $-q/(\beta^3 h^2)$ while the volume of the region where this very strong field is supported scales as $\beta^3 h^3$. The spatial integral of the electric field is proportional to the product of these two factors, $-qh = -d$. Then $4\pi/3$ is just a numerical factor. \square

(ii) A more rigorous albeit not a very general proof can be obtained by considering a dielectric sphere of radius a and permittivity ϵ in a constant external electric field \mathbf{E}_{ext} . It is known

that the sphere will acquire a dipole moment $\mathbf{d} = \alpha \mathbf{E}_{\text{ext}}$ where the static polarizability α is given by the formula

$$\alpha = a^3 \frac{\epsilon - 1}{\epsilon + 2}. \quad (3)$$

This result can be obtained by solving the Laplace equation $\nabla \cdot \epsilon(\mathbf{r})\mathbf{E}(\mathbf{r}) = 0$ with appropriate boundary conditions at the sphere surface and at infinity. From this solution, we can also find that the electric field outside of the sphere is given by Eq. (1) (plus the external field, of course) while the field inside the sphere is constant and given by

$$\mathbf{E}_{\text{int}} = \frac{3}{\epsilon + 2} \mathbf{E}_{\text{ext}}. \quad (4)$$

The depolarizing field \mathbf{E}_{dep} is by definition the difference between the internal field (the total field existing inside the sphere) and the external (applied) field. By the superposition principle, $\mathbf{E}_{\text{int}} = \mathbf{E}_{\text{ext}} + \mathbf{E}_{\text{dep}}$. Thus, \mathbf{E}_{dep} is the field created by the charge induced on the sphere surface. By using Eq. (4), we find that

$$-\mathbf{E}_{\text{dep}} = \frac{\epsilon - 1}{\epsilon + 2} \mathbf{E}_{\text{ext}} = \frac{1}{a^3} \mathbf{d}. \quad (5)$$

Integrating over the volume of the sphere, we obtain

$$\int_{r < a} \mathbf{E}_{\text{dep}} d^3 r = -\frac{4\pi}{3} \mathbf{d}. \quad (6)$$

We can write more generally for any $R \geq a$,

$$\int_{r < R} (\mathbf{E} - \mathbf{E}_{\text{ext}}) d^3 r = \int_{r < R} \mathbf{E}_d d^3 r = -\frac{4\pi}{3} \mathbf{d}. \quad (7)$$

The expression in the right-hand side of Eq. (7) is the pre-factor in front of the delta-function in Eq. (2). \square

(iii) The most general derivation of the singular term in Eq. (2) can be obtained by computing the static Green's tensor for the electric field,

$$G(\mathbf{r}, \mathbf{r}') = -\nabla_{\mathbf{r}} \otimes \nabla_{\mathbf{r}'} \frac{1}{|\mathbf{r} - \mathbf{r}'|}. \quad (8)$$

Here the symbol \otimes denotes tensor product. For example, $(\mathbf{a} \otimes \mathbf{b})\mathbf{c} = \mathbf{a}(\mathbf{b} \cdot \mathbf{c})$, $(\mathbf{a} \otimes \mathbf{b})_{\alpha\beta} = a_\alpha b_\beta$, etc. The singularity originates from the double differentiation of the non-analytical term $|\mathbf{r} - \mathbf{r}'|$. This can be easily understood if we recall that in one dimension

$$\frac{\partial^2 |x - x'|}{\partial x \partial x'} = \delta(x - x').$$

The actual evaluation of the right-hand side of Eq. (8) is straightforward but lengthy, and we leave it for an exercise. If we perform the differentiation accurately and then set $\mathbf{r}' = 0$, we will find that $G(\mathbf{r}, 0)\mathbf{d}$ is identical to the right-hand side of Eq. (2). \square

Now, the key approximation of the Lorentz molecular theory of polarization, as well as that of the Maxwell Garnett theory of composites, is that the regular part in the right-hand side of Eq. (2) averages to zero and, therefore, it can be ignored whereas the singular part does not average to zero and should be retained. We will now proceed with applying this idea to a physical problem.

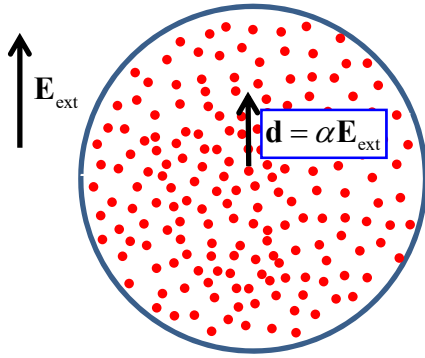


Fig. 1. (color online) A collection of dipoles in external field. The particles are distributed inside a spherical volume either randomly (as shown) or periodically. It is assumed however that the macroscopic density of particles is constant inside the sphere and equal to $v^{-1} = N/V$. Here v is the specific volume per one particle.

B. Lorentz local field correction

Consider some spatial region \mathbb{V} of volume V containing $N \gg 1$ small particles of polarizability α each. We can refer to the particles as to “molecules”. The only important physical property of a molecule is that it has a linear polarizability. The specific volume per one molecule is $v = V/N$. We will further assume that \mathbb{V} is connected and sufficiently “simple”. For example, we can consider a plane-parallel layer or a sphere. In these two cases, the macroscopic electric field inside the medium is constant, which is important for the arguments presented below. The system under consideration is schematically illustrated in Fig. 1.

Let us now place the whole system in a constant external electric field \mathbf{E}_{ext} . We will neglect the electromagnetic interaction of all the dipoles since we have decided to neglect the regular part of the dipole field in Eq. (2). Again, the assumption that we use is that this field is unimportant because it averages to zero when summed over all dipoles. In this case, each dipole “feels” the external field \mathbf{E}_{ext} and therefore it acquires the dipole moment $\mathbf{d} = \alpha \mathbf{E}_{\text{ext}}$. The total dipole moment of the object is

$$\mathbf{d}_{\text{tot}} = N\mathbf{d} = N\alpha\mathbf{E}_{\text{ext}}. \quad (9)$$

On the other hand, if we assign the sample some macroscopic permittivity ϵ and polarization $\mathbf{P} = [(\epsilon - 1)/4\pi]\mathbf{E}$, then the total dipole moment is given by

$$\mathbf{d}_{\text{tot}} = V\mathbf{P} = V\frac{\epsilon - 1}{4\pi}\mathbf{E}. \quad (10)$$

In the above expression, \mathbf{E} is the macroscopic electric field inside the medium, which is, of course, different from the applied field \mathbf{E}_{ext} . To find the relation between the two fields, we can use the superposition principle and write

$$\mathbf{E} = \mathbf{E}_{\text{ext}} + \left\langle \sum_n \mathbf{E}_n(\mathbf{r}) \right\rangle, \quad \mathbf{r} \in \mathbb{V}. \quad (11)$$

Here $\mathbf{E}_n(\mathbf{r})$ is the field produced by the n -th dipole and $\langle \dots \rangle$ denotes averaging over the volume of the sample. Of course, the individual fields $\mathbf{E}_n(\mathbf{r})$ will fluctuate and so will the sum of all these contributions, $\sum_n \mathbf{E}_n(\mathbf{r})$. The averaging in the right-hand side of Eq. (11) has been introduced since we believe that

the macroscopic electric field is a suitably defined average of the fast-fluctuating “microscopic” field.

We now compute the averages in Eq. (11) as follows:

$$\langle \mathbf{E}_n(\mathbf{r}) \rangle = \frac{1}{V} \int_{\mathbb{V}} \mathbf{E}_d(\mathbf{r} - \mathbf{r}_n) d^3r \approx -\frac{4\pi}{3} \frac{\mathbf{d}}{V}, \quad (12)$$

where \mathbf{r}_n is the location of the n -th dipole and $\mathbf{E}_d(\mathbf{r})$ is given by Eq. (2). In performing the integration, we have disregarded the regular part of the dipole field and, therefore, the second equality above is approximate. We now substitute Eq. (12) into Eq. (11) and obtain the following result:

$$\begin{aligned} \mathbf{E} &= \mathbf{E}_{\text{ext}} + \sum_n \langle \mathbf{E}_n \rangle = \mathbf{E}_{\text{ext}} - N \frac{4\pi}{3} \frac{\mathbf{d}}{V} \\ &= \left(1 - \frac{4\pi}{3} \frac{\alpha}{v} \right) \mathbf{E}_{\text{ext}}. \end{aligned} \quad (13)$$

In the above chain of equalities, we have used $\mathbf{d} = \alpha \mathbf{E}_{\text{ext}}$ and $V/N = v$.

All that is left to do now is substitute Eq. (13) into Eq. (10) and use the condition that Eq. (9) and Eq. (10) must yield the same total dipole moment of the sample. Equating the right-hand sides of these two equations and dividing by the total volume V results in the equation

$$\frac{\alpha}{v} = \frac{\epsilon - 1}{4\pi} \left(1 - \frac{4\pi}{3} \frac{\alpha}{v} \right). \quad (14)$$

We now solve this equation for ϵ and obtain

$$\epsilon = 1 + \frac{4\pi(\alpha/v)}{1 - (4\pi/3)(\alpha/v)} = \frac{1 + (8\pi/3)(\alpha/v)}{1 - (4\pi/3)(\alpha/v)}. \quad (15)$$

This is the Lorentz formula for the permittivity of a non-polar molecular gas. The denominator in Eq. (15) accounts for the famous local field correction. The external field \mathbf{E}_{ext} is frequently called the local field and denoted by \mathbf{E}_L . Equation Eq. (13) gives us the linear relation between the local field and the average macroscopic field.

If we did not know about the local field correction, we could have written naively $\epsilon = 1 + 4\pi(\alpha/v)$. Of course, in dilute gases, the denominator in Eq. (15) is not much different from unity. To first order in α/v , the above (incorrect) formula and Eq. (15) are identical. The differences show up only to second order in α/v . The significance of higher-order terms in the expansion of ϵ in powers of α/v and the applicability range of the Lorentz formula can be evaluated only by constructing a more rigorous theory from which Eq. (15) is obtained as a limit. Here we can mention that, in the case of dilute gases, the local field correction plays a more important role in nonlinear optics, where field fluctuations can be enhanced by the nonlinearities. Also, in some applications of the theory involving linear optics of condensed matter (with ϵ substantially different from unity), the exact form of the denominator in Eq. (15) turns out to be important. An example will be given in Sec. C below.

It is interesting to note that we have derived the local field correction without the usual trick of defining the Lorentz sphere and assuming that the medium outside of this sphere is truly continuous, etc. The approaches are however mathematically equivalent if we get to the bottom of what is going on in the Lorentz molecular theory of polarization. The derivation shown above illustrates one important but frequently overlooked fact, namely, that the mathematical nature of the approximation made by the Lorentz theory is very simple: it is

to disregard the regular part of the expression Eq. (2). One can state the approximation mathematically by writing $\mathbf{E}_d(\mathbf{r}) = -(4\pi/3)\delta(\mathbf{r})\mathbf{d}$ instead of Eq. (2). No other approximation or assumption is needed.

C. Clausius-Mossotti relation

Instead of expressing ϵ in terms of α/v , we can express α/v in terms of ϵ . Physically, the question that one might ask is this. Let us assume that we know ϵ of some medium (say, it was measured) and know that it is describable by the Lorentz formula. Then what is the value of α/v for the molecules that make up this medium? The answer can be easily found from Eq. (14) and it reads

$$\frac{\alpha}{v} = \frac{3}{4\pi} \frac{\epsilon - 1}{\epsilon + 2}. \quad (16)$$

This equation is known as the Clausius-Mossotti relation.

It may seem that Eq. (16) does not contain any new information compared to Eq. (15). Mathematically this is indeed so because one equation follows from the other. However, in 1973, Purcell and Pennypacker have proposed a numerical method for solving boundary-value electromagnetic problems for macroscopic particles of arbitrary shape [11] that is based on a somewhat nontrivial application of the Clausius-Mossotti relation.

The main idea of this method is as follows. We know that Eq. (16) is an approximation. However, we expect Eq. (16) to become accurate in the limit $a/h \rightarrow 0$, where $h = v^{1/3}$ is the characteristic inter-particle distance and a is the characteristic size of the particles. Physically, this limit is not interesting because it leads to the trivial results $\alpha/v \rightarrow 0$ and $\epsilon \rightarrow 1$. But this is true for *physical* particles. What if we consider *hypothetical* point-like particles and assign to them the polarizabilities that follow from Eq. (16) with some experimental value of ϵ ? It turns out that an array of such hypothetical point dipoles arranged on a cubic lattice and constrained to the overall shape of the sample mimics the electromagnetic response of the latter with arbitrarily good precision as long as the macroscopic field in the sample does not vary significantly on the scale of h (so h should be sufficiently small). We, therefore, can replace the actual sample by an array of N point dipoles. The electromagnetic problem is then reduced to solving N linear *coupled-dipole equations* and the corresponding method is known as the discrete dipole approximation (DDA) [12].

One important feature of DDA is that, for the purpose of solving the coupled-dipole equations, one should not disregard the regular part of the formula Eq. (2). This is in spite of the fact that we have used this assumption to arrive at Eq. (16) in the first place! This might seem confusing, but there is really no contradiction because DDA can be derived from more general considerations than what was used above. Originally, it was derived by discretizing the macroscopic Maxwell's equations written in the integral form [11]. The reason why the regular part of Eq. (2) must be retained in the coupled-dipole equations is because we are interested in samples of arbitrary shape and the regular part of Eq. (2) does not really average out to zero in this case. Moreover, we can apply DDA beyond the static limit, where no such cancellation takes place in principle. However, the Clausius-Mossotti relation must be modified beyond the static limit to take account for the radiative correction and other corrections associated with the finite frequency [13] – otherwise, the method will violate energy conservation and can produce other abnormalities.

We note however that, if we attempt to apply the DDA to the static problem of a dielectric sphere in a constant external field, we will obtain the correct result from the DDA either with or without account for the point-dipole interaction. In other words, if we represent a dielectric sphere of radius R and permittivity ϵ by a large number N of point dipoles with the same polarizability determined by Eq. (16) and uniformly distributed inside the sphere, subject all these dipoles to the external field and solve the arising coupled-dipole equations, we will recover the correct result for the total dipole moment of the large sphere. We can obtain this result without accounting for the interaction of the point dipoles. This can be shown by observing that the polarizability of the large sphere, α_{tot} , is equal to $N\alpha$, where α is given by Eq. (16). Alternatively, we can solve the coupled-dipole equations with the full account of the dipole-dipole interaction on a supercomputer and – quite amazingly – we will obtain the same result. This is so because the regular parts of the dipole fields, indeed, cancel out in this particular geometry (as long as $N \rightarrow \infty$, of course). This simple observation underscores the very deep theoretical insight of the Lorentz and Maxwell Garnett theories.

We also note that, in the context of the DDA, the Lorentz local-field correction is really important. Previously we have remarked that this correction is not very important for dilute gases. But if we started from the “naive” formula $\epsilon = 1 + 4\pi(\alpha/v)$, we would have gotten an incorrect Clausius-Mossotti relation of the form $\alpha/v = (\epsilon - 1)/4\pi$ and, with this definition, DDA would definitely not work even in the simplest geometries.

To conclude this subsection, we would like to emphasize one important but frequently overlooked point regarding the DDA. Namely, the point dipoles used in the DDA do not correspond to any physical particles. Their normalized polarizabilities α/v are computed from the actual ϵ of material, which can be significantly different from unity. Yet the size of these dipoles is assumed to be vanishingly small. In this respect, DDA is very different from the Foldy-Lax approximation [14, 15], which is known in the physics literature as, simply, the *dipole approximation* (DA) and which describes the electromagnetic interaction of sufficiently small *physical* particles via dipole radiation fields. The coupled-dipole equations are, however, formally the same in both DA and DDA.

D. Maxwell Garnett mixing formula

We are now ready to derive the Maxwell Garnett mixing formula. We will start with the simple case of small spherical particles in vacuum. This case is conceptually very close to the Lorentz molecular theory of polarization. Of course, the latter operates with “molecules”, but the only important physical characteristic of a molecule is its polarizability, α . A small inclusions in a composite can also be characterized by its polarizability. Therefore, the two models are almost identical.

Consider spherical particles of radius a and permittivity ϵ , which are distributed in vacuum either on a lattice or randomly but uniformly on average. The specific volume per one particle is v and the volume fraction of inclusions is $f = (4\pi/3)(a^3/v)$. The effective permittivity of such medium can be computed by applying Eq. (15) directly. The only thing that we will do is substitute the appropriate expression for α , which in the case

considered is given by Eq. (3). We then have

$$\epsilon_{\text{MG}} = \frac{1 + 2f \frac{\epsilon - 1}{\epsilon + 2}}{1 - f \frac{\epsilon - 1}{\epsilon + 2}} = \frac{1 + \frac{1 + 2f}{3}(\epsilon - 1)}{1 + \frac{1 - f}{3}(\epsilon - 1)}. \quad (17)$$

This is the Maxwell Garnett mixing formula (hence the subscript MG) for small inclusions in vacuum. We emphasize that, unlike in the Lorentz theory of polarization, ϵ_{MG} is the effective permittivity of a composite, not the usual permittivity of a natural material.

Next, we remove the assumption that the background medium is vacuum, which is not realistic for composites. Let the host medium have the permittivity ϵ_h and the inclusions have the permittivity ϵ_i . The volume fraction of inclusions is still equal to f . We can obtain the required generalization by making the substitutions $\epsilon_{\text{MG}} \rightarrow \epsilon_{\text{MG}}/\epsilon_h$ and $\epsilon \rightarrow \epsilon_i/\epsilon_h$, which yields

$$\epsilon_{\text{MG}} = \epsilon_h \frac{1 + 2f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}}{1 - f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}} = \epsilon_h \frac{1 + \frac{1 + 2f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h}}{1 + \frac{1 - f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h}}. \quad (18)$$

We will now justify this result mathematically by tracing the steps that were made to derive Eq. (17) and making appropriate modifications.

We first note that the expression Eq. (2) for a dipole embedded in an infinite host medium [16] should be modified as

$$\mathbf{E}_{\mathbf{d}}(\mathbf{r}) = \frac{1}{\epsilon_h} \left[\frac{3\hat{\mathbf{r}}(\hat{\mathbf{r}} \cdot \mathbf{d}) - \mathbf{d}}{r^3} - \frac{4\pi}{3} \delta(\mathbf{r}) \mathbf{d} \right], \quad (19)$$

This can be shown by using the equation $\nabla \cdot \mathbf{D} = \epsilon_h \nabla \cdot \mathbf{E} = 4\pi\rho$, where ρ is the density of the electric charge making up the dipole. However, this argument may not be very convincing because it is not clear what is the exact nature of the charge ρ and how it follows from the constitutive relations in the medium. Therefore, we will now consider the argument (ii) given in Sec. A and adjust it to the case of a spherical inclusion of permittivity ϵ_i in a host medium of permittivity ϵ_h . The polarization field in this medium can be decomposed into two contributions, $\mathbf{P} = \mathbf{P}_h + \mathbf{P}_i$, where

$$\mathbf{P}_h(\mathbf{r}) = \frac{\epsilon_h - 1}{4\pi} \mathbf{E}(\mathbf{r}), \quad \mathbf{P}_i(\mathbf{r}) = \frac{\epsilon(\mathbf{r}) - \epsilon_h}{4\pi} \mathbf{E}(\mathbf{r}). \quad (20)$$

Obviously, $\mathbf{P}_i(\mathbf{r})$ is identically zero in the host medium while $\mathbf{P}_h(\mathbf{r})$ can be nonzero anywhere. The polarization $\mathbf{P}_i(\mathbf{r})$ is the *secondary source* of the scattered field. To see that this is the case, we can start from the equation $\nabla \cdot \epsilon(\mathbf{r}) \mathbf{E}(\mathbf{r}) = 0$ and write

$$\nabla \cdot \epsilon_h \mathbf{E}(\mathbf{r}) = -\nabla \cdot [\epsilon(\mathbf{r}) - \epsilon_h] \mathbf{E}(\mathbf{r}) = 4\pi\rho_i(\mathbf{r}), \quad (21)$$

where $\rho_i = -\nabla \cdot \mathbf{P}_i$. Therefore, the relevant dipole moment of a spherical inclusion of radius a is $\mathbf{d} = \int_{r < a} \mathbf{P}_i d^3r$. The corresponding polarizability is given by

$$\alpha = a^3 \epsilon_h \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} \quad [\text{compare to Eq. (3)}]. \quad (22)$$

The depolarizing field inside the inclusion is

$$-\mathbf{E}_{\text{dep}} = \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} \mathbf{E}_{\text{ext}} = \frac{\mathbf{d}}{\epsilon_h a^3} \quad [\text{compare to Eq. (5)}]. \quad (23)$$

We thus find that the generalization of Eq. (7) in a medium with a non-vacuum host is

$$\int_{r < R} (\mathbf{E} - \mathbf{E}_{\text{ext}}) d^3r = \int_{r < R} \mathbf{E}_{\mathbf{d}} d^3r = -\frac{4\pi}{3\epsilon_h} \mathbf{d}. \quad (24)$$

Correspondingly, the formula relating the external and the average fields now reads

$$\mathbf{E} = \left(1 - \frac{4\pi}{3\epsilon_h} \frac{\alpha}{v} \right) \mathbf{E}_{\text{ext}}, \quad (25)$$

where α is given by Eq. (22). We now consider a spatial region \mathbb{V} that contains many inclusions and compute its total dipole moment by two formulas: $\mathbf{d}_{\text{tot}} = N\alpha \mathbf{E}_{\text{ext}}$ and $\mathbf{d}_{\text{tot}} = V[(\epsilon_{\text{MG}} - \epsilon_h)/4\pi] \mathbf{E}$. Equating the right-hand sides of these two expressions and substituting \mathbf{E} in terms of \mathbf{E}_{ext} from Eq. (25), we obtain the result

$$\epsilon_{\text{MG}} = \epsilon_h + \frac{4\pi(\alpha/v)}{1 - (4\pi/3\epsilon_h)(\alpha/v)}. \quad (26)$$

Substituting α from Eq. (22) and using $4\pi a^3/3v = f$, we obtain Eq. (18). As expected, one power of ϵ_h cancels in the denominator of the second term in the right-hand side of Eq. (26), but not in its numerator. \square

Finally, we make one conceptually important step, which will allow us to apply the Maxwell Garnett mixing formula to a much wider class of composites. Equation Eq. (17) was derived under the assumption that the inclusions are spherical. But Eq. (18) does not contain any information about the inclusions shape. It only contains the permittivities of the host and the inclusions and the volume fraction of the latter. We therefore make the conjecture that Eq. (17) is a valid approximation for inclusions of any shape as long as the medium is spatially-uniform and isotropic on average. Making this conjecture now require some leap of faith, but a more solid justification will be given in the second part of this tutorial.

3. VARIOUS FORMS AND GENERALIZATIONS OF THE MAXWELL GARNETT MIXING FORMULA

A. Anisotropic particles

So far, we have considered only isotropic composites. By isotropy we mean here that all directions in space are equivalent. But what if this is not so? Equation Eq. (17) can not account for anisotropy. However, it is easy to derive a generalization of Eq. (17) that can. To this end, we will use ellipsoidal inclusions.

Consider the case when all inclusions are identical and similarly-oriented ellipsoids with the semiaxes a_1, a_2, a_3 that are parallel to the axes X, Y and Z of a Cartesian frame. The polarizability of all ellipsoids is in this case a tensor $\hat{\alpha}$ whose principal values α_p are given by

$$\alpha_p = \frac{a_1 a_2 a_3}{3} \frac{\epsilon_h (\epsilon_i - \epsilon_h)}{\epsilon_h + \nu_p (\epsilon_i - \epsilon_h)}, \quad p = 1, 2, 3. \quad (27)$$

Here ν_p are the depolarization factors. Analytical formulas for ν_p are given, for example, in [17]. The Maxwell Garnett permittivity of the composite is then also a tensor and its principal values are obtained by a straightforward generalization of Eq. (26):

$$(\epsilon_{\text{MG}})_p = \epsilon_h + \frac{4\pi(\alpha_p/v)}{1 - (4\pi/3\epsilon_h)(\alpha_p/v)}. \quad (28)$$

Substituting Eq. (27) into Eq. (28) we obtain

$$(\epsilon_{\text{MG}})_p = \epsilon_h \frac{1 + \frac{3v_p + 2f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h}}{1 + \frac{3v_p - f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h}}. \quad (29)$$

In the case of spherical inclusions, $v_1 = v_2 = v_3 = 1/3$ and we recover the expression Eq. (18). If the inclusions are prolate spheroids resembling long thin needles ($a_1 = a_2 \ll a_3$), we have $v_1 = v_2 = 1/2$ and $v_3 = 0$. If the inclusions are oblate spheroids resembling thin pancakes ($a_1 = a_2 \gg a_3$), then $v_1 = v_2 = 0$ and $v_3 = 1$.

An interesting result is obtained if $3v_p = f$. This combination of parameters is achievable if $f \ll 1$ by using prolate or oblate spheroids with sufficiently small aspect ratios. If the above equality holds for polarization p , then we obtain $(\epsilon_{\text{MG}})_p = \epsilon_i$ independently of ϵ_h .

B. Multi-component mixtures and the Bruggeman mixing formula

Equation Eq. (18) can be rewritten in the following form:

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}. \quad (30)$$

Let us now assume that the medium contains inclusions made of different materials with permittivities ϵ_n ($n = 1, 2, \dots, N$). Then Eq. (30) is generalized as

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = \sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_h}{\epsilon_n + 2\epsilon_h}, \quad (31)$$

where f_n is the volume fraction of n -th component. This result can be obtained by applying the arguments of Sec. 2 to each component separately.

We now notice that the parameters of the inclusions (ϵ_n and f_n) enter Eq. (31) symmetrically, but the parameters of the host, ϵ_h and $f_h = 1 - \sum_n f_n$, do not. That is, Eq. (31) is invariant under the permutation

$$\epsilon_n \longleftrightarrow \epsilon_m \text{ and } f_n \longleftrightarrow f_m, \quad 1 \leq n, m \leq N. \quad (32)$$

However, Eq. (31) is not invariant under the permutation

$$\epsilon_n \longleftrightarrow \epsilon_h \text{ and } f_n \longleftrightarrow f_h, \quad 1 \leq n \leq N. \quad (33)$$

In other words, the parameters of the host enter Eq. (31) not in the same way as the parameters of the inclusions. It is usually stated that the Maxwell Garnett mixing formula is not symmetric.

But there is no reason to apply different rules to different medium components unless we know something about their shape or the volume fraction of the “host” is much larger than that of the “inclusions”. At this point, we do not assume anything about the geometry of inclusions (see the last paragraph of Sec. D). Moreover, even if we knew the exact geometry of the composite, we would not know how to use it – the Maxwell Garnett approximation does not provide any adjustable parameters to account for changes in geometry that keep the volume fractions fixed. Therefore, the only reason why we can distinguish the “host” and the “inclusions” is because the volume fraction of the former is much larger than that of the latter. As a result, the Maxwell Garnett theory is obviously inapplicable when the volume fractions of all components are comparable.

In contrast, the Bruggeman mixing formula [18], which we will now derive, is symmetric with respect to all medium components and does not treat any one of them differently. Therefore, it can be applied, at least formally, to composites with arbitrary volume fractions without causing obvious contradictions. This does not mean that the Bruggeman mixing formula is always “correct”. However, one can hope that it can yield meaningful corrections to Eq. (31) under the conditions when the volume fraction of inclusions is not very small. We will now sketch the main logical steps leading to the derivation of the Bruggeman mixing formula, although these arguments involve a lot of hand-waving.

First, let us formally apply Eq. (31) to the following physical situation. Let the medium be composed of N kinds of inclusions with the permittivities ϵ_n and volume fractions f_n such that $\sum_n f_n = 1$. In this case, the volume fraction of the host is zero. One can say that the host is not physically present. However, its permittivity still enters Eq. (31).

We know already that Eq. (31) is inapplicable to this physical situation, but we can look at the problem at hand from a slightly different angle. Assume that we have a composite consisting of N components occupying a large spatial region \mathbb{V} such as the sphere shown in Fig. 1 and, on top of that, let \mathbb{V} be embedded in an infinite host medium [16] of permittivity ϵ_h . Then we can *formally* apply the Maxwell Garnett mixing formula to the composite inside \mathbb{V} even though we have doubts regarding the validity of the respective formulas. Still, the effective permittivity of the composite inside \mathbb{V} can not possibly depend on ϵ_h since this composite simply does not contain any host material. How can these statements be reconciled?

Bruggeman’s solution this dilemma is the following. Let us formally apply Eq. (31) to the physical situation described above and find the value of ϵ_h for which ϵ_{MG} would be equal to ϵ_h . The particular value of ϵ_h determined in this manner is the Bruggeman effective permittivity, which we denote by ϵ_{BG} . It is easy to see that ϵ_{BG} satisfies the equation

$$\sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_{\text{BG}}}{\epsilon_n + 2\epsilon_{\text{BG}}} = 0 \quad \text{where} \quad \sum_{n=1}^N f_n = 1. \quad (34)$$

We can see that Eq. (34) possesses some nice mathematical properties. In particular, if $f_n = 1$, then $\epsilon_{\text{BG}} = \epsilon_n$. If $f_n = 0$, ϵ_{BG} does not depend on ϵ_n .

Physically, the Bruggeman equation can be understood as follows. We take the spatial region \mathbb{V} filled with the composite consisting of all N components and place it in a homogeneous infinite medium with the permittivity ϵ_h . The Bruggeman effective permittivity ϵ_{BG} is the special value of ϵ_h for which the dipole moment of \mathbb{V} is zero. We note that the dipole moment of \mathbb{V} is computed approximately, using the assumption of non-interacting “elementary dipoles” inside \mathbb{V} . Also, the dipole moment is defined with respect of the homogeneous background, i.e., $\mathbf{d}_{\text{tot}} = \int_{\mathbb{V}} [(\epsilon(\mathbf{r}) - \epsilon_h)/4\pi] \mathbf{E}(\mathbf{r}) d^3r$ [see the discussion after equation Eq. (20)]. Thus, Eq. (34) can be understood as the condition that \mathbb{V} blends with the background and does not cause a macroscopic perturbation of a constant applied field.

We now discuss briefly the mathematical properties of the Bruggeman mixing formula. By multiplying Eq. (34) by $\prod_{n=1}^N (\epsilon_n + 2\epsilon_{\text{BG}})$, we obtain a polynomial equation of order N with respect to ϵ_{BG} . The polynomial has N (possibly, degenerate) roots, some of which can be spurious. If we knew the analytical form of all roots, we would discard the solutions that do not satisfy the condition $\epsilon_{\text{BG}} = \epsilon_n$ if $f_n = 1$. However, if the

order of the polynomial is large and the roots are known only numerically, the problem of sorting out the spurious solutions can become nontrivial.

Consider the exactly-solvable case of a two-component mixture with $f_1 = f$ and $f_2 = 1 - f$. The two solutions are in this case

$$\epsilon_{\text{BG}} = \frac{1}{4} \left[b \pm \sqrt{8\epsilon_1\epsilon_2 + b^2} \right], \quad (35)$$

where

$$b = (3f - 1)\epsilon_1 + (2 - 3f)\epsilon_2 \quad (36)$$

and the square root branch is defined by the condition $0 \leq \arg(\sqrt{z}) < \pi$. It can be verified that the solution Eq. (35) with the plus sign satisfies the above condition (and also yields ϵ_{BG} with a non-negative imaginary part) while the one with the minus sign does not. Therefore, the latter should be discarded.

The Bruggeman and the Maxwell Garnett mixing formulas coincide to first order in f , but the second-order terms are different. Thus, for the two-component mixture considered above, the expansions near $f = 0$ are of the form

$$\frac{\epsilon_{\text{MG}}}{\epsilon_2} = 1 + 3 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} f + 3 \frac{(\epsilon_1 - \epsilon_2)^2}{(\epsilon_1 + 2\epsilon_2)^2} f^2 + \dots \quad (37a)$$

$$\frac{\epsilon_{\text{BG}}}{\epsilon_2} = 1 + 3 \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} f + 9\epsilon_1 \frac{(\epsilon_1 - \epsilon_2)^2}{(\epsilon_1 + 2\epsilon_2)^3} f^2 + \dots \quad (37b)$$

We finally note that one of the presumed advantages of the Bruggeman mixing formula is that it is symmetric. However, there is no physical requirement that the exact effective permittivity of a composite has this property. Imagine a composite consisting of spherical inclusions of permittivity ϵ_1 in a homogeneous host of permittivity ϵ_2 . Let the spheres be arranged on a cubic lattice and have the radius adjusted so that the volume fraction of the inclusions is exactly 1/2. The spheres would be almost but not quite touching. It is clear that, if we interchange the permittivities of the components but keep the geometry unchanged, the effective permittivity of the composite will change. For examples, if spheres are conducting and the host dielectric, then the composite is not conducting as a whole. If we now make the host conducting and the spheres dielectric, then the composite would become conducting. However, the Bruggeman mixing formula predicts the same effective permittivity in both cases. This example shows that the symmetry requirement is not fundamental since it disregards the geometry of the composite. Due to this reason, the Bruggeman mixing formula should be applied with care and, in fact, it can fail quite dramatically.

C. Maxwell Garnett formula and the smooth field

Let us assume that a certain field $\mathbf{S}(\mathbf{r})$ changes very slowly on the scale of the medium heterogeneities. Then, for any rapidly-varying function $F(\mathbf{r})$, we can write

$$\langle \mathbf{S}(\mathbf{r})F(\mathbf{r}) \rangle = \langle \mathbf{S}(\mathbf{r}) \rangle \langle F(\mathbf{r}) \rangle, \quad (38)$$

where $\langle \dots \rangle$ denotes averaging taken over a sufficiently small volume that still contains many heterogeneities. We will call the fields possessing the above property *smooth*.

To see how this concept can be useful, consider some well-known results for one-dimensional periodic (say, in the direction Z) media [19]. The medium can be homogenized, that is,

described by an effective permittivity tensor $\hat{\epsilon}_{\text{eff}}$ whose two different principal values, $\epsilon_{\text{eff}}^{\parallel}$ and $\epsilon_{\text{eff}}^{\perp}$ correspond to the polarizations parallel (along X or Y axes) and perpendicular (along Z) to the layers. The results established in [19] is $\epsilon_{\text{eff}}^{\parallel} = \langle \epsilon(z) \rangle$ and $\epsilon_{\text{eff}}^{\perp} = \langle \epsilon^{-1}(z) \rangle^{-1}$. These two results can be obtained without any complicated mathematics by applying the concept of the smooth field. To this end, we recall that, at sharp interfaces, the tangential component of the electric field \mathbf{E} and the normal component of the displacement \mathbf{D} are continuous.

In the case of parallel polarization, the electric field \mathbf{E} is tangential and continuous at the surfaces where different layers touch. Therefore, $\mathbf{E}(z)$ is in this case smooth. Consequently, we can write

$$\langle \mathbf{D}(z) \rangle = \langle \epsilon(z)\mathbf{E}(z) \rangle = \langle \epsilon(z) \rangle \langle \mathbf{E}(z) \rangle. \quad (39)$$

We also can say that $\langle \mathbf{D} \rangle = \hat{\epsilon}_{\text{eff}} \langle \mathbf{E} \rangle$. Comparing this to Eq. (39), we conclude that $\epsilon_{\text{eff}}^{\parallel} = \langle \epsilon(z) \rangle$.

For the perpendicular polarization, both the electric field and the displacement are perpendicular to the layers. The electric field jumps at the surfaces of discontinuity and, therefore, it is not smooth. But the displacement is smooth. Correspondingly, we can write

$$\langle \mathbf{E}(z) \rangle = \langle \epsilon^{-1}(z)\mathbf{D}(z) \rangle = \langle \epsilon^{-1}(z) \rangle \langle \mathbf{D}(z) \rangle. \quad (40)$$

From this, we immediately find that $\epsilon_{\text{eff}}^{\perp} = \langle \epsilon^{-1} \rangle^{-1}$.

So in the one-dimensional case considered above, either the electric field or the displacement are smooth, depending on the polarization. In the more general 3D case, we do not have such a nice property. However, let us conjecture that, to some approximation, the linear combination of the form $\mathbf{S}(\mathbf{r}) = p\mathbf{E}(\mathbf{r}) + (1-p)\mathbf{D}(\mathbf{r}) = [p + (1-p)\epsilon(\mathbf{r})]\mathbf{E}(\mathbf{r})$, where p is a mixing parameter, is smooth for any polarization of the electric field. Application of Eq. (38) results in the following equalities:

$$\langle \mathbf{E} \rangle = \langle \mathbf{S} \rangle \langle [p + (1-p)\epsilon]^{-1} \rangle, \quad (41a)$$

$$\langle \mathbf{D} \rangle = \langle \mathbf{S} \rangle \langle \epsilon [p + (1-p)\epsilon]^{-1} \rangle. \quad (41b)$$

Comparing these two expressions and assuming that the medium is isotropic (which we already did when we introduced the polarization-independent ansatz for $\mathbf{S}(\mathbf{r})$), we find that the effective permittivity is given by

$$\epsilon_{\text{eff}} = \frac{\langle \epsilon [p + (1-p)\epsilon]^{-1} \rangle}{\langle [p + (1-p)\epsilon]^{-1} \rangle}. \quad (42)$$

The above equation is, in fact, the Maxwell Garnett mixing formula, if we only adjust the parameter p correctly. To see that this is the case, let us rewrite Eq. (18) in the following rarely-used form:

$$\epsilon_{\text{MG}} = \frac{\langle \epsilon(\epsilon + 2\epsilon_h)^{-1} \rangle}{\langle (\epsilon + 2\epsilon_h)^{-1} \rangle}. \quad (43)$$

Here we assume that $\epsilon(\mathbf{r})$ is equal to ϵ_i with the probability f and to ϵ_h with the probability $1 - f$ and the averages are computed accordingly. Therefore, (42) and (43) coincide if we take $p = 2\epsilon_h / (1 + 2\epsilon_h)$.

Thus, the Maxwell Garnett approximation is equivalent to assuming that the field $\mathbf{S}(\mathbf{r}) = [(\epsilon(\mathbf{r}) + 2\epsilon_h) / (1 + 2\epsilon_h)]\mathbf{E}(\mathbf{r})$ is

smooth. The mixing parameter p depends explicitly on the permittivity of the host because the Maxwell Garnett mixing formula is not symmetric.

It is not easy to find the smooth field for the Bruggeman approximation. The linear ansatz used above will not work; a more general nonlinear functional of the fields must be considered.

4. SUMMARY AND OUTLOOK

The above sections cover the material that one encounters in standard textbooks. The tutorial could end here. However, we can not help noticing that the arguments we have presented are not complete and not mathematically rigorous. There are several topics that we need to discuss if we want to gain a deeper understanding of the homogenization theories in general and of the Maxwell Garnett mixing formula in particular.

First, the standard expositions of the Maxwell Garnett mixing formula and of the Lorentz molecular theory of polarization rely heavily on the assumption that polarization field $\mathbf{P}(\mathbf{r}) = [(\epsilon(\mathbf{r}) - 1)/4\pi]\mathbf{E}(\mathbf{r})$ is the dipole moment per unit volume. But this interpretation is neither necessary for defining the constitutive parameters of the macroscopic Maxwell's equations nor, generally, correct. We've been careful to operate only with *total* dipole moments of macroscopic objects. Still, this point requires some additional discussion.

Second, the Lorentz local-field correction relies on integrating the electric field of a dipole over spheres of finite radius. It is assumed that, since the integral is zero for any finite radius R , the integral over the whole space is converging. But this statement is mathematically incorrect. The integral of the electric field of a static dipole taken over the whole space does not converge to any result. Therefore, if we deform the spherical surface that bounds the integration domain to some other shape, we would obtain an arbitrary integration result.

Third, we have worked exclusively within statics. But the theory is almost always applied to high frequencies. In this case, equation Eq. (2) is not applicable; a more general formula must be used. Incidentally, the integral of the field of an oscillating dipole diverges even stronger than that of a static dipole. It is also not correct to use the purely static expression for the polarizabilities at finite frequencies.

The above topics will be addresses in the second part of this tutorial.

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