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Vadim Markel

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Introduction to Maxwell Garnett approximation: tutorial

VADIM A. MARKEL *

Aix-Marseille Université, CNRS, Centrale Marseille, Institut Fresnel UMR 7249, 13013 Marseille, France

vmarkel@fresnel.fr

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This tutorial is devoted to the Maxwell Garnett approximation and related theories. Topics covered in this 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 equation, the concept of smooth field, and Wiener and Bergman-Milton bounds. © 2016

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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 as 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 and volume fractions 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 the internal field and polarization by a cumulative characteristic called the polarizability. Within the approximations 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 then 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 will make an unfortunate compromise and not discuss some important topics. One notable omission is that we will not dis-

*On leave from the Department of Radiology, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA; vmarkel@mail.med.upenn.edu

cuss 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,

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

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 (1) is incomplete. We should have written

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

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

The additional delta-term in (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. This set-up is illustrated in Fig. 1. 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 (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

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

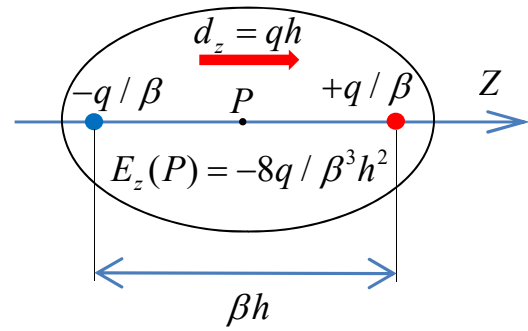


Fig. 1. (color online) Illustration of the set-up used in the derivation (i) of the equation (2). The dipole moment of the system of two charges in the Z -direction is $d_z = qh$. The electric field in the mid-point P is $E_z(P) = -8q/\beta^3 h^2$. The oval shows the region of space where the strong field is supported; its volume scales as $\beta^3 h^3$. Note that rigorous integration of the electric field of a truly point charge is not possible due to a divergence. In this figure, the charges are shown to be of finite size. In this case, a small spherical region around each charge gives a zero contribution to the integral.

This result can be obtained by solving the Laplace equation with the appropriate boundary conditions at the sphere surface and at infinity. From this solution, we can find that the electric field outside of the sphere is given by (1) (plus the external field, of course) while the field inside 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 (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 $R \geq a$,

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

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

(iii) The most general derivation of the singular term in (2) can be obtained by computing the static Green's tensor for the electric field [11],

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

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, $\frac{\partial^2 |x - x'|}{\partial x \partial x'} = \delta(x - x')$. Evaluation of the right-hand side

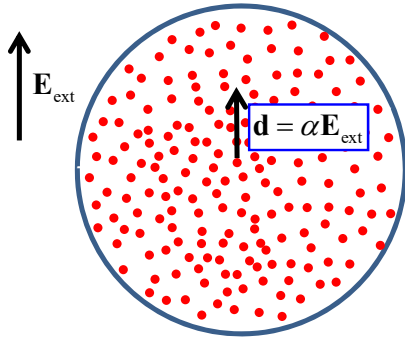


Fig. 2. (color online) A collection of dipoles in an external field. The particles are distributed inside a spherical volume either randomly (as shown) or periodically. It is assumed, however, that the macroscopic density of particles is constant inside the sphere and equal to $v^{-1} = N/V$. Here v is the specific volume per one particle.

of (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 (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 (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.

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. 2.

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 (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 (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 (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 (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 (12) into (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 (13) into (10) and use the condition that (9) and (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 (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 . Eq. (13) is 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 (15) is not much different from unity. To first order in α/v , the above (incorrect) formula and (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 (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 (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 (2). One can state the approximation mathematically by writing $\mathbf{E}_d(\mathbf{r}) = -(4\pi/3)\delta(\mathbf{r})\mathbf{d}$ instead of (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 (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 (16) does not contain any new information compared to (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 [12] that is based on a somewhat non-trivial application of the Clausius-Mossotti relation.

The main idea of this method is as follows. We know that (16) is an approximation. However, we expect (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 polarizability that follows from (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) [13].

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 expression (2). This is in spite of the fact that we have used this assumption to arrive at (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 [12]. The reason why the regular part of (2) must be retained in the coupled-dipole equations is because we are interested in samples of arbitrary shape and the regular part

of (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. Of course, the expression for the dipole field (2) and the Clausius-Mossotti relation (16) must be modified beyond the static limit to take into account the effects of retardation, the radiative correction to the polarizability, and other corrections associated with the finite frequency [14] – otherwise, the method will violate energy conservation and can produce other abnormalities.

We note, however, that, if we attempt to apply DDA to the static problem of a dielectric sphere in a constant external field, we will obtain the correct result from 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 equivalent point dipoles uniformly distributed inside the sphere and characterized by the polarizability (16), subject all these dipoles to an 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 (16). Alternatively, we can solve the coupled-dipole equations with the full account of 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 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 the incorrect “Clausius-Mossotti” relation of the form $\alpha/v = (\epsilon - 1)/4\pi$ and, with this definition of α/v , DDA would definitely not work even in the simplest geometries.

To conclude the discussion of DDA, we would like to emphasize one important but frequently overlooked fact. Namely, the point dipoles used in 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 [15, 16], 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 the dipole radiation fields. The coupled-dipole equations are, however, formally the same in both DA and DDA.

The Clausius-Mossotti relation and the associated coupled-dipole equation (this time, applied to physical molecules) have also been used to study the fascinating phenomenon of ferroelectricity (spontaneous polarization) of nanocrystals [17], the surface effects in organic molecular films [18], and many other phenomena wherein the dipole interaction of molecules or particles captures the essential physics.

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 inclusion 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 (15) directly. The only thing that we will do is substitute the appropriate expression for α , which in the case considered is given by (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

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

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

We first note that the expression (2) for a dipole embedded in an infinite host medium [19] 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

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

where $\rho_i = -\nabla \cdot \mathbf{P}_i$ (note that the total induced charge is $\rho = \rho_i + \rho_h$, $\rho_h = -\nabla \cdot \mathbf{P}_h$). 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 α and the depolarizing field inside the inclusion \mathbf{E}_{dep} can be found by solving the Laplace equation for a sphere embedded in an infinite host, and are given by

$$\alpha = a^3 \epsilon_h \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} \quad [\text{compare to (3)}], \quad (21a)$$

$$-\mathbf{E}_{\text{dep}} = \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} \mathbf{E}_{\text{ext}} = \frac{\mathbf{d}}{\epsilon_h a^3} \quad [\text{compare to (5)}]. \quad (21b)$$

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

$$\int_{r < R} (\mathbf{E} - \mathbf{E}_{\text{ext}}) d^3r = \int_{r < R} \mathbf{E}_{\mathbf{d}} d^3r = -\frac{4\pi}{3\epsilon_h} \mathbf{d}. \quad (22)$$

Correspondingly, the formula relating the external and the average fields (Lorentz local field correction) now reads

$$\mathbf{E} = \left(1 - \frac{4\pi}{3\epsilon_h} \alpha \right) \mathbf{E}_{\text{ext}}, \quad (23)$$

where α is given by (21a). We now consider a spatial region 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 (23), we obtain the result

$$\epsilon_{\text{MG}} = \epsilon_h + \frac{4\pi(\alpha/v)}{1 - (4\pi/3\epsilon_h)(\alpha/v)}. \quad (24)$$

Substituting α from (21a) and using $4\pi a^3/3v = f$, we obtain (18). As expected, one power of ϵ_h cancels in the denominator of the second term in the right-hand side of (24), 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 (18) was derived under the assumption that the inclusions are spherical. But (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 (18) 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 requires some leap of faith, but a more solid justification will be given in the second part of this tutorial.

3. MULTI-COMPONENT MIXTURES AND THE BRUGGEMAN MIXING FORMULA

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

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = f \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h}. \quad (25)$$

Let us now assume that the medium contains inclusions made of different materials with permittivities ϵ_n ($n = 1, 2, \dots, N$). Then (25) is generalized as

$$\frac{\epsilon_{\text{MG}} - \epsilon_h}{\epsilon_{\text{MG}} + 2\epsilon_h} = \sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_h}{\epsilon_n + 2\epsilon_h}, \quad (26)$$

where f_n is the volume fraction of the 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 the equation (26) symmetrically, but the parameters of the host, ϵ_h and $f_h = 1 - \sum_n f_n$, do not. That is, (26) is invariant under the permutation

$$\epsilon_n \longleftrightarrow \epsilon_m \text{ and } f_n \longleftrightarrow f_m, \quad 1 \leq n, m \leq N. \quad (27)$$

However, (26) is not invariant under the permutation

$$\epsilon_n \longleftrightarrow \epsilon_h \text{ and } f_n \longleftrightarrow f_h, \quad 1 \leq n \leq N. \quad (28)$$

In other words, the parameters of the host enter (26) 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 if 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. 2D). Moreover, even if we knew the exact geometry of the composite, we would not know how to use it – the Maxwell Garnett mixing formula 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 [20], 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 (26) 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 the mixing formula (26) 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 (26).

We know already that (26) 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. 2 and, on top of that, let \mathbb{V} be embedded in an infinite host medium [19] 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 to this dilemma is the following. Let us formally apply (26) 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

$$\sum_{n=1}^N f_n \frac{\epsilon_n - \epsilon_{\text{BG}}}{\epsilon_n + 2\epsilon_{\text{BG}}} = 0 \quad \text{where} \quad \sum_{n=1}^N f_n = 1. \quad (29)$$

We can see that (29) possesses some nice mathematical properties. In particular, if $f_n = 1$, then $\epsilon_{\text{BG}} = \epsilon_n$. If $f_n = 0$, then 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 to 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 (20)]. Thus, (29) 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 equation. Multiplying (29) 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. But for each set of parameters, only one of these roots is the physical solution; the rest are spurious. If the roots are known analytically, one can find the physical solution by applying the condition $\epsilon_{\text{BG}}|_{f_n=1} = \epsilon_n$ and also by requiring that ϵ_{BG} be a continuous and smooth function of f_1, \dots, f_N [21]. However, if N is sufficiently large, the roots are not known analytically. In this case, the problem of sorting the solutions can be solved numerically by considering the so-called Wiener bounds [22] (defined in Sec. 6 below).

Consider the exactly-solvable case of a two-component mixture. The two solutions are in this case

$$\epsilon_{\text{BG}} = \frac{b \pm \sqrt{8\epsilon_1\epsilon_2 + b^2}}{4}, \quad b = (2f_1 - f_2)\epsilon_1 + (2f_2 - f_1)\epsilon_2, \quad (30)$$

and the square root branch is defined by the condition $0 \leq \arg(\sqrt{z}) < \pi$. It can be verified that the solution (30) with the plus sign satisfies $\epsilon_{\text{BG}}|_{f_n=1} = \epsilon_n$ and also yields $\text{Im}(\epsilon_{\text{BG}}) \geq 0$, whereas the one with the minus sign does not. Therefore, the latter should be discarded. The solution (30) with the “+” is a continuous and smooth function of the volume fractions as long as we use the square root branch defined above and $f_1 + f_2 = 1$.

If we take $\epsilon_1 = \epsilon_h$, $\epsilon_2 = \epsilon_i$, $f_2 = f$, then the Bruggeman and the Maxwell Garnett mixing formulas coincide to first order in f , but the second-order terms are different. The expansions near $f = 0$ are of the form

$$\frac{\epsilon_{\text{MG}}}{\epsilon_h} = 1 + 3 \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} f + 3 \frac{(\epsilon_i - \epsilon_h)^2}{(\epsilon_i + 2\epsilon_h)^2} f^2 + \dots \quad (31a)$$

$$\frac{\epsilon_{\text{BG}}}{\epsilon_h} = 1 + 3 \frac{\epsilon_i - \epsilon_h}{\epsilon_i + 2\epsilon_h} f + 9\epsilon_i \frac{(\epsilon_i - \epsilon_h)^2}{(\epsilon_i + 2\epsilon_h)^3} f^2 + \dots \quad (31b)$$

Of course, we would also get a similar coincidence of expansions to first order in f if we take $\epsilon_2 = \epsilon_h$, $\epsilon_1 = \epsilon_i$ and $f_1 = f$.

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.

4. ANISOTROPIC COMPOSITES

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? The Maxwell Garnett mixing formula (18) can not account for anisotropy. To derive a generalization of (18) that can, we will consider inclusions in the form of uniformly-distributed and similarly-oriented ellipsoids.

Consider first an assembly of $N \gg 1$ small noninteracting spherical inclusions of the permittivity ϵ_i that fill uniformly a large spherical region of radius R . Everything is embedded in a host medium of permittivity ϵ_h . The polarizability α of each inclusion is given by (21a). The total polarizability of these particles is $\alpha_{\text{tot}} = N\alpha$ (since the particles are assumed to be not interacting). We now assign the effective permittivity ϵ_{MG} to the large sphere and require that the latter has the same polarizability α_{tot} as the collection of small inclusions. This condition results in equation (25), which is mathematically equivalent to (18). So the procedure just described is one of the many ways (and, perhaps, the simplest) to derive the isotropic Maxwell Garnett mixing formula.

Now let all inclusions be identical and similarly-oriented ellipsoids with the semiaxes a_x, a_y, a_z that are parallel to the X, Y and Z axes of a Cartesian frame. It can be found by solving the Laplace equation [23] that the static polarizability of an ellipsoidal inclusion is a tensor $\hat{\alpha}$ whose principal values α_p are given by

$$\alpha_p = \frac{a_x a_y a_z}{3} \frac{\epsilon_h (\epsilon_i - \epsilon_h)}{\epsilon_h + v_p (\epsilon_i - \epsilon_h)}, \quad p = x, y, z. \quad (32)$$

Here the numbers v_p ($0 < v_p < 1$, $v_x + v_y + v_z = 1$) are the ellipsoid depolarization factors. Analytical formulas for v_p are given in [23]. For spheres ($a_p = a$), we have $v_p = 1/3$ for all p , so that (32) is reduced to (21a). For prolate spheroids resembling long thin needles ($a_x = a_y \ll a_z$), we have $v_x = v_y \rightarrow 1/2$ and $v_z \rightarrow 0$. For oblate spheroids resembling thin pancakes ($a_x = a_y \gg a_z$), $v_x = v_y \rightarrow 0$ and $v_z \rightarrow 1$.

Let the ellipsoidal inclusions fill uniformly a large ellipsoid of a similar shape, that is, with the semiaxes R_x, R_y, R_z such that $a_p/a_{p'} = R_p/R_{p'}$ and $R_p \gg a_p$. As was done above, we assign the large ellipsoid an effective permittivity $\hat{\epsilon}_{\text{MG}}$ and require that its polarizability $\hat{\alpha}_{\text{tot}}$ be equal to $N\hat{\alpha}$, where $\hat{\alpha}$ is given

by (32). Of course, different directions in space in the composite are no longer equivalent and we expect $\hat{\epsilon}_{\text{MG}}$ to be tensorial; this is why we have used the overhead hat symbol in this notation. The mathematical consideration is, however, rather simple because, as follows from the symmetry, $\hat{\epsilon}_{\text{MG}}$ is diagonal in the reference frame considered. We denote the principal values (diagonal elements) of $\hat{\epsilon}_{\text{MG}}$ by $(\epsilon_{\text{MG}})_p$. In the geometry considered, all tensors $\hat{\alpha}$, $\hat{\alpha}_{\text{tot}}$, $\hat{\epsilon}_{\text{MG}}$ and $\hat{\nu}$ (the depolarization tensor) are diagonal in the same axes and, therefore, commute.

The principal values of $\hat{\alpha}_{\text{tot}}$ are given by an expression that is very similar to (32), except that a_p must be substituted by R_p and ϵ_i must be substituted by $(\epsilon_{\text{MG}})_p$. We then write $\hat{\alpha}_{\text{tot}} = N\hat{\alpha}$ and, accounting for the fact that $N a_x a_y a_z = f R_x R_y R_z$, obtain the following equation:

$$\frac{(\epsilon_{\text{MG}})_p - \epsilon_h}{\epsilon_h + v_p [(\epsilon_{\text{MG}})_p - \epsilon_h]} = f \frac{\epsilon_i - \epsilon_h}{\epsilon_h + v_p (\epsilon_i - \epsilon_h)}. \quad (33)$$

This is a generalization of (25) to the case of ellipsoids. We now solve (33) for $(\epsilon_{\text{MG}})_p$ and obtain the conventional anisotropic Maxwell Garnett mixing formula, viz,

$$\begin{aligned} (\epsilon_{\text{MG}})_p &= \epsilon_h \frac{1 + (1 - v_p) f \frac{\epsilon_i - \epsilon_h}{\epsilon_h + v_p (\epsilon_i - \epsilon_h)}}{1 - v_p f \frac{\epsilon_i - \epsilon_h}{\epsilon_h + v_p (\epsilon_i - \epsilon_h)}} \\ &= \epsilon_h \frac{\epsilon_h + [v_p (1 - f) + f] (\epsilon_i - \epsilon_h)}{\epsilon_h + v_p (1 - f) (\epsilon_i - \epsilon_h)}. \end{aligned} \quad (34)$$

It can be seen that (34) reduces to (18) if $v_p = 1/3$. In addition, (34) has the following nice properties. If $v_p = 0$, (34) yields $(\epsilon_{\text{MG}})_p = f\epsilon_i + (1 - f)\epsilon_h = \langle \epsilon(\mathbf{r}) \rangle$. If $v_p = 1$, (34) yields $(\epsilon_{\text{MG}})_p^{-1} = f\epsilon_i^{-1} + (1 - f)\epsilon_h^{-1} = \langle \epsilon^{-1}(\mathbf{r}) \rangle$. We will see in Sec. 5 below that these results are exact.

It should be noted that equation (34) implies that the Lorentz local field correction is not the same as given by (23). Indeed, we can use equation (34) to compute the macroscopic electric field \mathbf{E} inside the large “homogenized” ellipsoid subjected to an external field \mathbf{E}_{ext} . We will then find that

$$\mathbf{E} = \left(1 - \hat{\nu} \frac{4\pi}{\epsilon_h} \frac{\hat{\alpha}}{v} \right) \mathbf{E}_{\text{ext}}. \quad (35)$$

Here $\hat{\nu} = \text{diag}(v_x, v_y, v_z)$ is the depolarization tensor. The difference between (35) and (23) is not just that in the former expression $\hat{\alpha}$ is tensorial and in the latter it is scalar (this would have been easy to anticipate); the substantial difference is that the expression (35) has the factor of $\hat{\nu}$ instead of $1/3$.

The above modification of the Lorentz local field correction can be easily understood if we recall that the property (22) of the electric field produced by a dipole only holds if the integration is extended over a sphere. However, we have derived (34) from the assumption that an assembly of many small ellipsoids mimic the electromagnetic response of a large “homogenized” ellipsoid of a similar shape. In this case, in order to compute the relation between the external and the macroscopic field in the effective medium, we must compute the respective integral over an elliptical region \mathbb{E} rather than over a sphere. If we place the dipole \mathbf{d} in the center of \mathbb{E} , we will obtain

$$\int_{\mathbb{E}} (\mathbf{E} - \mathbf{E}_{\text{ext}}) d^3 r = \int_{\mathbb{E}} \mathbf{E}_d d^3 r = -\hat{\nu} \frac{4\pi}{\epsilon_h} \mathbf{d}. \quad (36)$$

In fact, equation (36) can be viewed as a definition of the depolarization tensor $\hat{\nu}$.

Thus, the specific form (34) of the anisotropic Maxwell Garnett mixing formula was obtained because of the requirement that the collection of small ellipsoidal inclusions mimic the electromagnetic response of the large homogeneous ellipsoid of the same shape. But what if the large object is not an ellipsoid or an ellipsoid of a different shape? It turns out that the shape of the “homogenized” object influences the resulting Maxwell Garnett mixing formula, but the differences are second order in f .

Indeed, we can pose the problem as follows: let $N \gg 1$ small, noninteracting ellipsoidal inclusions with the depolarization factors ν_p and polarizability $\hat{\alpha}$ (32) fill uniformly a large sphere of radius $R \gg a_x, a_y, a_z$; find the effective permittivity of the sphere $\hat{\epsilon}'_{\text{MG}}$ for which its polarizability $\hat{\alpha}_{\text{tot}}$ is equal to $N\hat{\alpha}$. The problem can be easily solved with the result

$$\begin{aligned} (\hat{\epsilon}'_{\text{MG}})_p &= \epsilon_h \frac{1 + \frac{2f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h + \nu_p(\epsilon_i - \epsilon_h)}}{1 - \frac{f}{3} \frac{\epsilon_i - \epsilon_h}{\epsilon_h + \nu_p(\epsilon_i - \epsilon_h)}} \\ &= \epsilon_h \frac{\epsilon_h + (\nu_p + 2f/3)(\epsilon_i - \epsilon_h)}{\epsilon_h + (\nu_p - f/3)(\epsilon_i - \epsilon_h)}. \end{aligned} \quad (37)$$

We have used the prime in $\hat{\epsilon}'_{\text{MG}}$ to indicate that (37) is not the same expression as (34); note also that the effective permittivity $\hat{\epsilon}'_{\text{MG}}$ is tensorial even though the overall shape of the sample is a sphere. As one could have expected, the expression (37) corresponds to the Lorentz local field correction (23), which is applicable to spherical regions.

As mentioned above, $\hat{\epsilon}_{\text{MG}}$ (34) and $\hat{\epsilon}'_{\text{MG}}$ (37) coincide to first order in f . We can write

$$\hat{\epsilon}_{\text{MG}}, \hat{\epsilon}'_{\text{MG}} = \epsilon_h \left(1 + f \frac{\epsilon_i - \epsilon_h}{\epsilon_h + \nu_p(\epsilon_i - \epsilon_h)} \right) + O(f^2). \quad (38)$$

As a matter of fact, expression (37) is just one of the family of approximations in which the factors $2f/3$ and $f/3$ in the numerator and denominator of the first expression in (37) are replaced by $(1 - n_p)f$ and $n_p f$, where n_p are the depolarization factors for the large ellipsoid. The conventional expression (34) is obtained if we take $n_p = \nu_p$; expression (37) is obtained if we take $n_p = 1/3$. All these approximations are equivalent to first order in f .

Can we tell which of the two mixing formulas (34) and (37) is more accurate? The answer to this question is not straightforward. The effects that are quadratic in f also arise due to the electromagnetic interaction of particles, and this interaction is not taken into account in the Maxwell Garnett approximation. Besides, the composite geometry can be more general than isolated ellipsoidal inclusions, in which case the depolarization factors ν_p are not strictly defined and must be understood in a generalized sense as some numerical measures of anisotropy. If inclusions are similar isolated particles, we can use (36) to define the depolarization coefficients for any shape; however, this definition is rather formal because the solution to the Laplace equation is expressed in terms of *just three* coefficients ν_p only in the case of ellipsoids (an infinite sequence of similar coefficients can be introduced for more general particles).

Still, the traditional formula (34) has nice mathematical properties and one can hope that, in many cases, it will be more accurate than (37). We have already seen that it yields exact results in the two limiting cases of ellipsoids with $\nu_p = 0$ and $\nu_p = 1$. This is the consequence of using similar shapes for the large sample and the inclusions. Indeed, in the limit when, say,

$\nu_x = \nu_y \rightarrow 1/2$ and $\nu_z \rightarrow 0$, the inclusions become infinite circular cylinders. The large sample also becomes an infinite cylinder containing many cylindrical inclusions of much smaller radius (the axes of all cylinders are parallel). Of course, it is not possible to pack infinite cylinders into any finite sphere.

We can say that the limit when $\nu_x = \nu_y = 0$ and $\nu_z = 1$ corresponds to the one-dimensional geometry (a layered plane-parallel medium) and the limit $\nu_x + \nu_y = 1$ and $\nu_z = 0$ corresponds to the two-dimensional geometry (infinitely long parallel fibers of elliptical cross section). In these two cases, the overall shape of the sample should be selected accordingly: a plane-parallel layer or an infinite elliptical fiber. Spherical overall shape of the sample is not compatible with the one-dimensional or two-dimensional geometries. Therefore, (34) captures these cases better than (37).

Additional nice features of (34) include the following. First, we will show in Sec. 5 that (34) can be derived by applying the simple concept of the *smooth field*. Second, because (34) has the correct limits when $\nu_p \rightarrow 0$ and $\nu_p \rightarrow 1$, the numerical values of $(\hat{\epsilon}_{\text{MG}})_p$ produced by (34) always stay inside and sample completely the so-called Wiener bounds, which are discussed in more detail in Sec. 6 below.

We finally note that the Bruggeman equation can also be generalized to the case of anisotropic inclusions by writing [24]

$$\sum_{n=1}^N f_n \frac{\epsilon_n - (\hat{\epsilon}_{\text{BG}})_p}{(\hat{\epsilon}_{\text{BG}})_p + \nu_{np}[\epsilon_n - (\hat{\epsilon}_{\text{BG}})_p]} = 0. \quad (39)$$

Here ν_{np} is the depolarization coefficient for the n -th inclusion and p -th principal axis. The notable difference between the equation (39) and the equation given in [24] is that the depolarization coefficients in (39) depend on n . In [24] and elsewhere in the literature, it is usually assumed that these coefficients are the same for all medium components. While this assumption can be appropriate in some special cases, it is difficult to justify in general. Moreover, it is not obvious that the tensor $\hat{\epsilon}_{\text{BG}}$ is diagonalizable in the same axes as the tensors $\hat{\nu}_n$. Due to this uncertainty, we will not consider the anisotropic extensions of the Bruggeman's theory in detail.

5. MAXWELL GARNETT MIXING 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

$$\langle \mathbf{S}(\mathbf{r})F(\mathbf{r}) \rangle = \langle \mathbf{S}(\mathbf{r}) \rangle \langle F(\mathbf{r}) \rangle, \quad (40)$$

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 the well-known example of a one-dimensional, periodic (say, in the Z direction) medium of period h . The medium can be homogenized, that is, described by an effective permittivity tensor $\hat{\epsilon}_{\text{eff}}$ whose principal values, $(\epsilon_{\text{eff}})_x = (\epsilon_{\text{eff}})_y$ and $(\epsilon_{\text{eff}})_z$, correspond to the polarizations parallel (along X or Y axes) and perpendicular to the layers (along Z), and are given by

$$(\epsilon_{\text{eff}})_{x,y} = \langle \epsilon(z) \rangle = \sum_{n=1}^N f_n \epsilon_n, \quad (41a)$$

$$(\epsilon_{\text{eff}})_z = \langle \epsilon^{-1}(z) \rangle^{-1} = \left[\sum_{n=1}^N \frac{f_n}{\epsilon_n} \right]^{-1}. \quad (41b)$$

Here the subscript in $(\epsilon_{\text{eff}})_{x,y}$ indicates that the result applies to either X or Y polarization and we have assumed that each elementary cell of the structure consists of N layers of the widths $f_n h$ and permittivities ϵ_n , where $\sum_n f_n = 1$. The result (41) has been known for a long time in statics. At finite frequencies, it has been established in [25] by taking the limit $h \rightarrow 0$ while keeping all other parameters, including the frequency, fixed (in this work, Rytov has considered a more general problem of layered media with nontrivial electric and magnetic properties).

Direct derivation of (41) at finite frequencies along the lines of Ref. [25] requires some fairly lengthy calculations. However, this result can be established without any complicated mathematics, albeit not as rigorously, by applying the concept of 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 X or Y polarizations, the electric field \mathbf{E} is tangential at all surfaces of discontinuity. Therefore, $E_{x,y}(z)$ is in this case smooth [26] while $E_z = 0$. Consequently, we can write

$$\langle D_{x,y}(z) \rangle = \langle \epsilon(z) E_{x,y}(z) \rangle = \langle \epsilon(z) \rangle \langle E_{x,y}(z) \rangle. \quad (42)$$

On the other hand, we expect that $\langle D_{x,y} \rangle = \langle \hat{\epsilon}_{\text{eff}} \rangle_{x,y} \langle E_{x,y} \rangle$. Comparing this to (42), we arrive at (41a).

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

$$\langle E_z(z) \rangle = \langle \epsilon^{-1}(z) D_z(z) \rangle = \langle \epsilon^{-1}(z) \rangle \langle D_z(z) \rangle. \quad (43)$$

Combining $\langle D_z \rangle = \langle \hat{\epsilon}_{\text{eff}} \rangle_z \langle E_z \rangle$ and (43), we immediately arrive at (41b).

Alternatively, the two expressions in (41) can be obtained as the limits $\nu_p \rightarrow 0$ and $\nu_p \rightarrow 1$ of the anisotropic Maxwell Garnett mixing formula (34). Since (41) is an exact result, (34) is also exact in these two limiting cases.

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, for the external field applied along the axis p ($= x, y, z$) and to some approximation, the linear combination of the form $S_p(\mathbf{r}) = \beta_p E_p(\mathbf{r}) + (1 - \beta_p) D_p(\mathbf{r}) = [\beta_p + (1 - \beta_p)\epsilon(\mathbf{r})] E_p(\mathbf{r})$ is smooth. Here β_p is a mixing parameter. Application of (40) results in the following equalities:

$$\langle E_p(\mathbf{r}) \rangle = \langle S_p(\mathbf{r}) \rangle \langle [\beta_p + (1 - \beta_p)\epsilon(\mathbf{r})]^{-1} \rangle, \quad (44a)$$

$$\langle D_p(\mathbf{r}) \rangle = \langle S_p(\mathbf{r}) \rangle \langle \epsilon(\mathbf{r}) [\beta_p + (1 - \beta_p)\epsilon(\mathbf{r})]^{-1} \rangle. \quad (44b)$$

Comparing these two expressions, we find that the effective permittivity is given by

$$(\epsilon_{\text{eff}})_p = \frac{\langle \epsilon(\mathbf{r}) [\epsilon(\mathbf{r}) + \beta_p / (1 - \beta_p)]^{-1} \rangle}{\langle [\epsilon(\mathbf{r}) + \beta_p / (1 - \beta_p)]^{-1} \rangle}. \quad (45)$$

The above equation is, in fact, the anisotropic Maxwell Garnett mixing formula (34), if we only adjust the parameter β_p correctly. To see that this is the case, let us rewrite (34) in the following rarely-used form:

$$(\epsilon_{\text{MG}})_p = \frac{\langle \epsilon(\mathbf{r}) [\epsilon(\mathbf{r}) + (1/\nu_p - 1)\epsilon_h]^{-1} \rangle}{\langle [\epsilon(\mathbf{r}) + (1/\nu_p - 1)\epsilon_h]^{-1} \rangle}. \quad (46)$$

Here $\epsilon(\mathbf{r})$ is equal to ϵ_i with the probability f and to ϵ_h with the probability $1 - f$ and the averages are computed accordingly. Expressions (45) and (46) coincide if we take

$$\beta_p = \frac{(1 - \nu_p)\epsilon_h}{\nu_p + (1 - \nu_p)\epsilon_h}. \quad (47)$$

The mixing parameter β_p depends explicitly on ϵ_h because the Maxwell Garnett mixing formula is not symmetric.

Thus, the anisotropic Maxwell Garnett approximation (34) is equivalent to assuming that, for p -th polarization, the field $[(1 - \nu_p)\epsilon_h + \nu_p\epsilon(\mathbf{r})]E_p(\mathbf{r})$ is smooth. Therefore, (34) can be derived quite generally by applying the concept of the smooth field. The depolarization factors ν_p are obtained in this case as adjustable parameters characterizing the composite anisotropy and not necessarily related to ellipsoids.

The alternative mixing formula (37) can not be transformed to a weighted average $\langle \epsilon(\mathbf{r}) F_p(\mathbf{r}) \rangle / \langle F_p(\mathbf{r}) \rangle$, of which (45) and (46) are special cases. Therefore, it is not possible to derive (37) by introducing a smooth field of the general form $F_p[\epsilon(\mathbf{r})]E_p(\mathbf{r})$, at least not without explicitly solving the Laplace equation in the actual composite. Finding the smooth field for the Bruggeman equation is also problematic.

6. WIENER AND BERGMAN-MILTON BOUNDS

The discussion of the smooth field in the previous section is closely related to the so-called Wiener bounds on the “correct” effective permittivity $\hat{\epsilon}_{\text{eff}}$ of a composite medium. Of course, introduction of bounds is possible only if $\hat{\epsilon}_{\text{eff}}$ can be rigorously and uniquely defined. We will see in the second part of this tutorial that this is, indeed, the case, at least for periodic composites in the limit $h \rightarrow 0$, h being the period of the lattice. Maxwell Garnett and Bruggeman mixing formulas give some relatively simple approximations to ϵ_{eff} , but precise computation of the latter quantity can be complicated. Wiener bounds and their various generalizations can be useful for localization of ϵ_{eff} or determining whether a given approximation is reasonable. For example, the Wiener bounds have been used to identify the physical root of the Bruggeman equation (29) for a multi-component mixture [22].

In 1912, Wiener has introduced the following inequality for the principal values $(\epsilon_{\text{eff}})_p$ of the effective permittivity tensor of a multi-component mixture of substances whose individual permittivities ϵ_n are purely real and positive [27]:

$$\langle \epsilon^{-1} \rangle^{-1} \leq (\epsilon_{\text{eff}})_p \leq \langle \epsilon \rangle, \quad \text{if } \epsilon_n > 0. \quad (48)$$

It can be seen that the Wiener bounds depend on the set of $\{\epsilon_n, f_n\}$ but not on the exact geometry of the mixture. The lower and upper bounds in (48) are given by the expressions (41).

The Wiener inequality is not the only result of this kind. We can also write $\min_n(\epsilon_n) \leq (\epsilon_{\text{eff}})_p \leq \max_n(\epsilon_n)$; sharper estimates can be obtained if additional information is available about the composite [28]. However, all these inequalities are inapplicable to complex permittivities that are commonly encountered at optical frequencies. This fact generates uncertainty, especially when metal-dielectric composites are considered. A powerful result that generalizes the Wiener inequality to complex permittivities was obtained in 1980 by Bergman [29] and Milton [30]. We will state this result for the case of a two component mixture with the constituent permittivities ϵ_1 and ϵ_2 .

Consider the complex ϵ -plane and mark the two points ϵ_1 and ϵ_2 . Then draw two lines connecting these points: one a

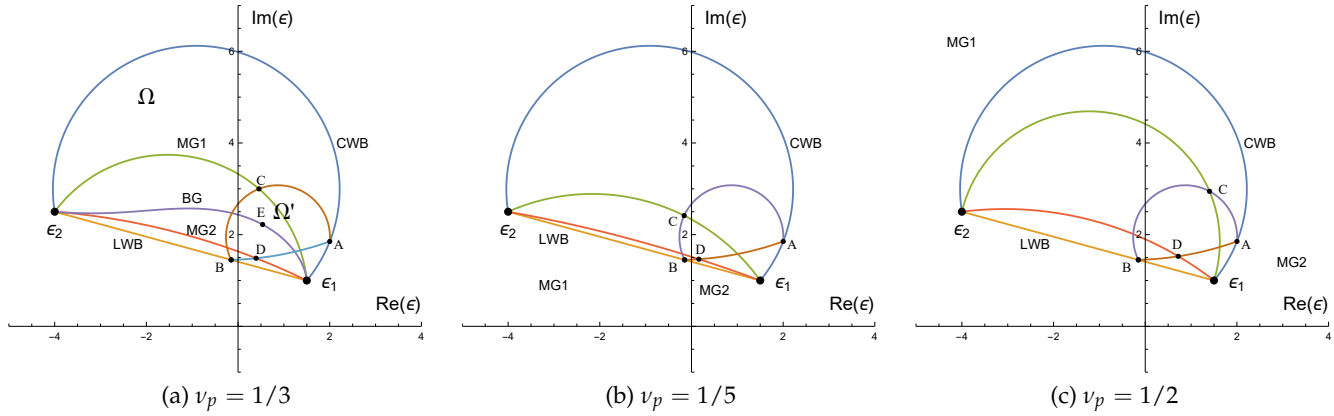


Fig. 3. (color online) Illustration of the Wiener and Bergman-Milton bounds for a two-component mixture with $\epsilon_1 = 1.5 + 1.0i$ and $\epsilon_2 = -4.0 + 2.5i$. Curves MG1, MG2 and BG are parametric plots of the complex functions $(\epsilon_{MG})_p$ [formula (34)] and ϵ_{BG} [formula (30)] as functions of f for $0 \leq f \leq 1$ and three different values of ν_p , as labeled. Arcs ACB and ADB are parametric plots of $(\epsilon_{MG})_p$ as a function of ν_p for fixed f and different choice of the host medium (hence two different arcs). Notations: LWB - linear Wiener bound; CWB - circular Wiener bound; MG1 - Maxwell Garnett mixing formula in which $\epsilon_h = \epsilon_1, \epsilon_i = \epsilon_2$ and $f = f_2$; MG2 - same but for $\epsilon_h = \epsilon_2, \epsilon_i = \epsilon_1$ and $f = f_1$, BG - symmetric Bruggeman mixing formula; A, B, C, D, E mark the points on CWB, LWB, MG1, MG2, BG curves for which $f_1 = 0.7$ and $f_2 = 0.3$. Point E and curve BG are shown in Panel (a) only. Only the curves MG1 and MG2 depend on ν_p . The region Ω (delineated by LWB and CWB) is the locus of all points $(\epsilon_{eff})_p$ that are attainable for the two-component mixture regardless of f_1 and f_2 ; Ω' (between the two arcs ACB and ADB) is the locus of all points that are attainable for this mixture and $f_1 = 0.7, f_2 = 0.3$.

straight line and another a circle that crosses ϵ_1, ϵ_2 and the origin (three points define a circle). We only need a part of this circle - the arc that does not contain the origin. The two lines can be obtained by plotting parametrically the complex functions $\eta(f) = f\epsilon_1 + (1-f)\epsilon_2$ and $\zeta(f) = [f/\epsilon_1 + (1-f)/\epsilon_2]^{-1}$ for $0 \leq f \leq 1$ and are marked in Fig. 3 as LWB (linear Wiener bound) and CWB (circular Wiener bound).

The closed area Ω (we follow the notations of Milton [30]) between the lines LWB and CWB is the locus of all complex points $(\epsilon_{eff})_p$ that can be obtained in the two-component mixture. We can say that Ω is *accessible*. This means that, for any point $\zeta \in \Omega$, there exists a composite with $(\epsilon_{eff})_p = \zeta$. The boundary of Ω is also accessible, as was demonstrated with the example of one-dimensional medium in Sec. 5. However, all points outside Ω are not accessible - they do not correspond to $(\epsilon_{eff})_p$ of any two-component mixture with the fixed constituent permittivities ϵ_1 and ϵ_2 .

We do not give a mathematical proof of these properties of Ω but we can make them plausible. Let us start with a one-dimensional, periodic in the Z direction, two-component layered medium with some volume fractions f_1 and f_2 . The principal value $(\epsilon_{eff})_z$ for this geometry will correspond to a point A on the line CWB and the principal values $(\epsilon_{eff})_x = (\epsilon_{eff})_y$ will correspond to a point B on LWB. The points A and B are shown in Fig. 3 for $f_1 = 0.7$ and $f_2 = 0.3$. We will then continuously deform the composite while keeping the volume fractions fixed until we end up with a medium that is identical to the original one except that it is rotated by 90° in the XZ plane. In the end state, $(\epsilon_{eff})_x$ will correspond to the point A and $(\epsilon_{eff})_y = (\epsilon_{eff})_z$ will correspond to the Point B. The intermediate states of this transformation will generate two continuous trajectories [the loci of the points $(\epsilon_{eff})_x$ and $(\epsilon_{eff})_z$] that connect A and B and one closed loop starting and terminating at B [the loci of the points $(\epsilon_{eff})_y$]. Two such curves that connect A and B (the arcs ACB and ADB) are also shown in Fig. 3.

Now, let us scan f_1 and f_2 from $f_1 = 1, f_2 = 0$ to $f_1 = 0, f_2 =$

1. The points A and B will slide on the lines CWB and LWB from ϵ_1 to ϵ_2 , and the continuous curves that connect them will fill the region Ω completely while none of these curves will cross the boundary of Ω . On the other hand, while deforming the composite between the states A and B, we can arrive at a composite of an arbitrary three-dimensional geometry modulo the given volume fractions. Thus, for a two component medium with arbitrary volume fractions, we can state that (i) $(\epsilon_{eff})_p \in \Omega$ and (ii) if $\zeta \in \Omega$, then there exists a composite with $(\epsilon_{eff})_p = \zeta$.

We now discuss the various curves shown in Fig. 3 in more detail.

The curves marked as MG1, MG2 display the results computed by the Maxwell Garnett mixing formula (34) with various values of ν_p , as labeled. MG1 is obtained by assuming that $\epsilon_h = \epsilon_1, \epsilon_i = \epsilon_2, f = f_2$. We then take the expression (34) and plot $(\epsilon_{MG})_p$ parametrically as a function of f for $0 \leq f \leq 1$ for three different values of ν_p . MG2 is obtained in a similar fashion but using $\epsilon_h = \epsilon_2, \epsilon_i = \epsilon_1, f = f_1$.

Notice that, at each of the three values of ν_p used, the curves MG1 and MG2 do not coincide because (34) is not “symmetric” in the sense of (28). For this reason, MG1 and MG2 can not be accurate *simultaneously* anywhere except in the close vicinities of ϵ_1 and ϵ_2 . Since there is no reason to prefer MG1 over MG2 or vice versa (unless f_1 or f_2 are small), MG1 and MG2 can not be accurate *in general*, that is for any composite that is somehow compatible with the parameters of the mixing formula. This point should be clear already from the fact that composites that are not made of ellipsoids are not characterizable mathematically by *just three* depolarization factors ν_p .

However, in the limits $\nu_p \rightarrow 0$ and $\nu_p \rightarrow 1$, MG1 and MG2 coincide with each other and with either LWB or CWB. In these limits MG1 and MG2 are exact.

In Panel (a), we also plot the curve BG computed according to (30) with the “+” sign. This BG curve follows closely MG1 in the vicinity of ϵ_1 and MG2 in the vicinity of ϵ_2 . This result is expected since the Maxwell Garnett and Bruggeman approxima-

tions coincide to first order in f : see (31) and recall that $f = f_2$ for MG1 and $f = f_1$ for MG2.

The two arcs ACB and ADB that connect the points A and B are defined by the following conditions: if continued to full circles, ACB will cross ϵ_1 and ADB will cross ϵ_2 . The arcs can also be obtained by plotting $(\epsilon_{\text{MG}})_p$ as given by (34) parametrically as a function of ν_p for fixed f_1 and f_2 . To plot the arc ACB, we set $\epsilon_h = \epsilon_1$, $\epsilon_i = \epsilon_2$ and $f = f_2$ in (34), just as was done in order to compute the curve MG1. However, instead of fixing ν_p and varying f , we now fix $f = 0.3$ and vary ν_p from 0 to 1. Similarly, the arc ADB is obtained by setting $\epsilon_h = \epsilon_2$, $\epsilon_i = \epsilon_1$, $f = f_1$ and varying ν_p in the same interval.

The region delineated by the arcs ACB and ADB is denoted by Ω' . It is important for the following reason. Above, we have defined the region Ω , which is the locus of all points $(\epsilon_{\text{eff}})_p$ for the two-component mixture regardless of the volume fractions. If we fix the latter to f_1 and f_2 , the region of allowed $(\epsilon_{\text{eff}})_p$ can be further narrowed. It is shown in Refs. [29, 30] that this region is precisely Ω' . Note that the Maxwell Garnett approximation (34) with the same f_1 and f_2 yields the results on the boundary of Ω' . Conversely, any point on the boundary of Ω' corresponds to (34) with some ν_p . The isotropic Bruggeman's solution is safely inside Ω' - see point E in Panel (a).

Just like Ω , the region Ω' is also accessible. This means that each point inside Ω' corresponds to a certain composite with given ϵ_1 , ϵ_2 , f_1 and f_2 . However, it is not obvious how the boundaries of Ω' can be accessed. Above, we have seen that the boundaries of Ω are accessed by the solutions to the homogenization problem in a very simple one-dimensional geometry wherein the smooth field \mathbf{S} can be easily (and precisely) defined. The same is true for Ω' . It can be shown [29] that the geometry for which the boundary of Ω' is accessed is an assembly of coated ellipsoids that are closely packed to fill the entire space. This is possible if we take an infinite sequence of such ellipsoids of ever decreasing size. Note that all major axes of the ellipsoids should be parallel, the core and the shell of each ellipsoid should be confocal, and the volume fractions of the ϵ_1 and ϵ_2 substances comprising each ellipsoid should be fixed to f_1 and f_2 . The arrangement in which ϵ_1 is the core and ϵ_2 is the shell will give one circular boundary of Ω' and the arrangement in which ϵ_2 is in the core and ϵ_1 is in the shell will give another boundary.

Of course, the above arrangement is a purely mathematical construct, it is not realizable in practice. However, it is interesting to note that the Maxwell Garnett mixing formula (34) turns out to be exact in this strange geometry. In the special case when the ellipsoids are spheres, the isotropic Maxwell Garnett formula (18) is exact. This isotropic, arbitrarily dense packaging of coated spheres of progressively reduced radiuses was considered by Hashing and Shtrikman [28] in 1962.

We can now see why the anisotropic Maxwell Garnett mixing formula (34) is special. First, it samples the region Ω completely. In other words, any two-component mixture with ϵ_1 and ϵ_2 -type constituents has the effective permittivity principal values $(\epsilon_{\text{eff}})_p$ that are equal to a value $(\epsilon_{\text{MG}})_p$ produced by (34) with the same ϵ_1 and ϵ_2 (but perhaps with different volume fractions). Second, (34) is restricted to Ω . In other words, any value $(\epsilon_{\text{MG}})_p$ produced by (34) is equal to $(\epsilon_{\text{eff}})_p$ of some composite with the same ϵ_1 and ϵ_2 (but perhaps with different volume fractions).

To conclude the discussion of bounds, we note that Refs. [29, 30] contain an even stronger result. If, in addition to ϵ_1 , ϵ_2 , f_1 , f_2 , it is also known that the composite is isotropic on average, then

the allowed region for ϵ_{eff} (now a scalar) is further reduced to $\Omega'' \subset \Omega' \subset \Omega$. Here Ω'' is delineated by yet another pair of circular arcs that connect the points C and D and, if continued to circles, also cross the points A and B. These arcs are not shown in Fig. 3.

7. SCALING LAWS

Maxwell Garnett and Bruggeman theories give some approximations to the effective permittivity of a composite $\hat{\epsilon}_{\text{eff}}$. Wiener and Bergman-Milton bounds discussed in the previous section do not provide approximations or define $\hat{\epsilon}_{\text{eff}}$ precisely but rather restrict it to a certain region in the complex plane. However, the very possibility to derive approximations or to place bounds on $\hat{\epsilon}_{\text{eff}}$ relies on the availability of an unambiguous definition of this quantity. We will sketch an approach to defining and computing $\hat{\epsilon}_{\text{eff}}$ in the second part of this tutorial. Now we note that this definition is expected to satisfy the following two scaling laws [9].

The first law is invariance under coordinate rescaling $\mathbf{r} \rightarrow \beta \mathbf{r}$, where $\beta > 0$ is an arbitrary real constant. In other words, the result should not depend on the physical size of the heterogeneities. Of course, one can not expect a given theory to be valid when the heterogeneity size is larger than the wavelength. Therefore, the above statement is not about the physical applicability of a given theory. Rather, it is about the mathematical properties of the theory itself. We can say that any standard theory is obtained in the limit $h \rightarrow 0$, where h is the characteristic size of the heterogeneity, say, the lattice period. The result of taking this limit is, obviously, independent of h .

The second law is the law of unaltered ratios: if every ϵ_n of a composite medium is scaled as $\epsilon_n \rightarrow \beta \epsilon_n$, then the effective permittivity (as computed by this theory) should scale similarly, viz, $\hat{\epsilon}_{\text{eff}} \rightarrow \beta \hat{\epsilon}_{\text{eff}}$.

Theories (either exact or approximate) that satisfy the above two laws can be referred to as *standard*. It is easy to see that the Maxwell Garnett and the Bruggeman theories are standard. On the other hand, the so-called *extended* homogenization theories that consider magnetic and higher-order multipole moments of the inclusions do not generally satisfy the scaling laws.

8. SUMMARY AND OUTLOOK

The sections 2,3,4, we have covered the material that one encounters in standard textbooks. Sections 5,6,7 contain somewhat less standard but, still, mathematically simple material. The tutorial could end here. However, we can not help noticing that the arguments we have presented are not complete and not always 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. The physical picture based on the polarization being the density of dipole moment is in many cases adequate, but in some other cases it can fail. 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 or ellipsoids of finite radius. It can be assumed naively that, since the integral is convergent for some finite integration regions, it also converges over the whole space. But this assumption 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 arbitrarily deform the surface that bounds the integration domain, we would obtain an arbitrary integration result. In fact, we have already seen that this result depends on whether the surface is spherical or ellipsoidal. This dependence, in turn, affects the Lorentz local field correction. Consequently, developing a more rigorous mathematical formalism that does not depend on evaluation of divergent integrals is desirable.

Third, we have worked mostly within statics. We did discuss finite frequencies in the sections devoted to smooth field and Wiener and Bergman-Milton bounds, but not in any substantial detail. However, the theory of homogenization is almost always applied at high frequencies. In this case, equation (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 addressed in the second part of this tutorial.

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