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Effective-medium theory for weakly nonlinear composites

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We propose an approximate general method for calculating the effective dielectric function of a random composite in which there is a weakly nonlinear relation between electric displacement and electric field of the form $\mathbf{D}=\epsilon\mathbf{E}+\chi|\mathbf{E}|^2\mathbf{E}$, where ϵ and χ are position dependent. In a two-phase composite, to first order in the nonlinear coefficients χ_1 and χ_2, the effective nonlinear dielectric susceptibility is found to be $\chi_e=\sum_{i=1,2}(\chi_i/p_i)(\partial\epsilon_e/\partial\epsilon_i)_0|\partial\epsilon_e/\partial\epsilon_i|_0$, where $\epsilon_e^{(0)}$ is the effective dielectric constant in the linear limit ($\chi_i=0, i=1,2$) and ϵ_i and p_i are the dielectric function and volume fraction of the ith component. The approximation is applied to a calculation of χ_e in the Maxwell-Garnett approximation (MGA) and the effective-medium approximation. For low concentrations of nonlinear inclusions in a linear host medium, our MGA reduces to the results of Stroud and Hui. An exact calculation of χ_e is carried out for the Hashin-Shtrikman microgeometry and compared to our MG approximation.

I. INTRODUCTION

There are many phenomena in composite media in which nonlinearity plays an important role. Among these are dielectric breakdown in metal-insulator composites and the nonlinear optical susceptibility of composite media. In this paper we will be concerned with determining the effective nonlinear dielectric susceptibility of a two-phase, weakly nonlinear, inhomogeneous composite.

For linear composites, the effective dielectric ϵ_e is a function of the geometry of the composite, and the volume fraction and the physical properties of each component. There have been numerous approximations developed to calculate ϵ_e in the linear regime. Two of the most widely used methods are the Maxwell-Garnett approximation[1] (MGA) and the effective-medium approximation[2] (EMA). Both methods involve an approximation which results in a uniform field inside one or more of the pure components.

In a nonlinear composite, unlike a linear one, the dielectric function depends on the applied electric field. If the applied electric field is sufficiently low, however, the relevant nonlinear effective susceptibilities can be obtained by a perturbation approach. This perturbation approach can be used to give an *exact* expression for the nonlinear susceptibility in terms of the electric field distribution in the related *linear* medium.[3] Recently, Stroud and Hui[3] have used this result in the low-concentration limit to obtain an exact expression for the cubic nonlinear susceptibility of a composite medium in the limit of a small concentration of nonlinear inclusions in a linear host.

In this paper, we derive a more general type of approximation for the nonlinear susceptibility—one which is not limited to a system of dilute nonlinear inclusions in a linear host. The resulting approximation for nonlinear media is similar in spirit to the well-known effective-medium approximation[2] for linear composite media. Besides this generalization, we also present an *exact* calculation of the nonlinear susceptibility for a composite that has the special geometry first discussed by Hashin and Shtrikman.[4]

The remainder of the paper is organized as follows. In Sec. II, we present our general method of approximation, and apply it to obtain a number of specific results. Section III describes an exact calculation of the nonlinear susceptibilities for the Hashin-Shtrikman microgeometry and compares this result with the Maxwell-Garnett approximation. A brief discussion and summary follows in Sec. IV.

II. GENERAL APPROXIMATION METHOD AND ITS APPLICATIONS

We consider a two-component composite in which each component is described by a weakly cubic nonlinear relation between the electric displacement $\mathbf{D}$ and electric field

$\mathbf{E}$ of the form

$$\mathbf{D}_i = \epsilon_i^{(0)}\mathbf{E}_i + \chi_i |\mathbf{E}|^2 \mathbf{E} . \quad (1)$$

Such an expansion will always be possible provided that $\chi_i |\mathbf{E}|^2 \ll \epsilon_i^{(0)}$ $(i,1,2)$. The term quadratic in electric field will vanish unless the constituents lack inversion symmetry. The space-averaged fields and displacements $\langle \mathbf{E} \rangle$ and $\langle \mathbf{D} \rangle$ are related by an equation of the same form:

$$\langle \mathbf{D} \rangle = \epsilon_e \langle \mathbf{E} \rangle + \chi_e |\langle \mathbf{E} \rangle|^2 \langle \mathbf{E} \rangle . \quad (2)$$

Our goal is to find approximations for χ_e.

Now in a binary composite, the linear effective dielectric function can always be written in the form

$$\epsilon_e^{(0)} = F(\epsilon_1^{(0)}, \epsilon_2^{(0)}, p_1) , \quad (3)$$

where p_1 is the volume fraction of the ϵ_1 component, and F is some function which will, in general, depend on the geometry of the composite. In order to obtain our approximation for χ_e, we initially assume that only component 1 is nonlinear, so that $\epsilon_2 = \epsilon_2^{(0)}$. We then invoke an approximate nonlinear form of Eq. (3):

$$\epsilon_e = F(\epsilon_1, \epsilon_2, p_1) . \quad (4)$$

Here $\epsilon_i = \epsilon_i^0 + \chi_i \langle |\mathbf{E}_i|^2 \rangle$ and $\langle |\mathbf{E}_i|^2 \rangle$ is the mean square of the electric field in the ith component in the linear limit. Equation (4) is strictly valid only if ϵ_1 and ϵ_2 are constant in each component. Thus, our use of Eq. (4) here involves making the approximation that the field $\mathbf{E}$ is uniform in the nonlinear component. This assumption is consistent with the spirit of linear effective-medium approximations.

Next, we expand the function F in a Taylor series about the linear $\epsilon_e^{(0)}$, to obtain

$$\epsilon_e \approx F(\epsilon_1^{(0)}, \epsilon_2, p_1) + F'(\epsilon_1^{(0)}, \epsilon_2^{(0)}, p_1) \chi_1 \langle |E_1|^2 \rangle , \quad (5)$$

where χ_1 is the nonlinear coefficient of the component 1 and $F' = \partial F / \partial \epsilon_1$. Now this partial derivative can be expressed *exactly* in terms of the average squared electric field in component 1 in the *linear* limit; the relation is[5]

$$p_1 \langle |\mathbf{E}_1|^2 \rangle / E_0^2 = (\partial \epsilon_e / \partial \epsilon_1)_{(0)} \equiv F'(\epsilon_1^{(0)}, \epsilon_2^{(0)}, p_1) , \quad (6)$$

where E_0 is the external field. Therefore, we have

$$\epsilon_e = \epsilon_e^{(0)} + \frac{\chi_1}{p_1} F' |F'| E_0^2 , \quad (7)$$

and by the definition of the effective nonlinear coefficient χ_e, we obtain

$$\chi_e = \frac{\chi_1}{p_1} \left(\frac{\partial \epsilon_e}{\partial \epsilon_1} \right)_0 \left| \frac{\partial \epsilon_e}{\partial \epsilon_1} \right|_0 . \quad (8)$$

These considerations are easily generalized to the case where both components are nonlinear. In this instance, we simply expand Eq. (1) around both $\epsilon_1^{(0)}$ and $\epsilon_2^{(0)}$, so that

$$\epsilon_e = \epsilon_e^{(0)} + \frac{\chi_1}{p_1} F_1' |F_1'| E_0^2 + \frac{\chi_2}{p_2} F_2' |F_2'| E_0^2 , \quad (9)$$

where $F_i' = (\partial \epsilon_e / \partial \epsilon_i)$ $(i=1,2)$. We now find that χ_e is given by

$$\chi_e = \frac{\chi_1}{p_1} F_1' |F_1'| + \frac{\chi_1}{p_2} F_2' |F_2'| . \quad (10)$$

Equation (10) is our principal result. It is based on the assumption that the fluctuations $\langle |E_i|^4 \rangle - \langle |E_i|^2 \rangle^2$ within the ith component are small, compared to $\langle |E_i|^4 \rangle$ itself. This approximation will be most accurate in geometries, such as the Hashin-Shtrikman geometry discussed below, for which the electric field is nearly uniform within the nonlinear component, and less accurate when these fluctuations are large, such as near a percolation threshold. To illustrate its predictions, we proceed to apply this general formula to various binary composites with different geometric configurations and different densities of inclusions.

A. Low-density limit

We first consider a linear host containing a very small volume fraction of nonlinear inclusions. In this case, we recover the known results of the low-density theory.[3] The argument is the following: in the low-density regime, the effective dielectric function of such a composite in the linear limit is

$$\epsilon_e^{(0)} = \epsilon_2 + 3\epsilon_2 p_1 \frac{\epsilon_1^{(0)} - \epsilon_2}{\epsilon_1^{(0)} + 2\epsilon_2} , \quad (11)$$

where ϵ_2 is the host material and ϵ_1 the nonlinear inclusion. $\partial \epsilon_e^{(0)} / \partial \epsilon_1^{(0)}$ is then

$$\left(\frac{\partial \epsilon_e}{\partial \epsilon_1} \right)_0 = p_1 \left(\frac{3\epsilon_2}{\epsilon_1^{(0)} + 2\epsilon_2} \right)^2 . \quad (12)$$

Substituting Eq. (12) into Eq. (8), we obtain

$$\chi_e = \chi_1 p_1 \left(\frac{3\epsilon_2}{\epsilon_1^{(0)} + 2\epsilon_2} \right)^2 \left| \left(\frac{3\epsilon_2}{\epsilon_1^{(0)} + 2\epsilon_2} \right)^2 \right| . \quad (13)$$

This is the same as the result of Stroud and Hui.[3]

B. Maxwell-Garnett approximation

Next, we obtain χ_e for a composition which in the linear regime is described by the Maxwell-Garnett approximation. As is well known, the MG approximation is most appropriate for a composite in which one of the constituents plays the role of a host medium and the other acts as an inclusion. If medium 2 is then host, then the MG approximation takes the form[6]

$$\frac{\epsilon_e^{(0)}}{\epsilon_2^{(0)}} = \frac{\epsilon_1^{(0)}(1+2p_1) + 2\epsilon_2^{(0)}(1-p_1)}{\epsilon_1^{(0)}(1-p_1) + \epsilon_2^{(0)}(2+p_1)} . \quad (14)$$

From this we obtain

$$F_1' = \left.\frac{\partial\epsilon_e}{\partial\epsilon_1}\right|_0 = \frac{9p_1\epsilon_2^{(0)2}}{[\epsilon_2^{(0)}(2+p_1)+\epsilon_1^{(0)}(1-p_1)]^2}\,, \tag{15}$$

and

$$F_2' \equiv \left.\frac{\partial\epsilon_e}{\partial\epsilon_2}\right|_0 = p_2\frac{2\epsilon_2^{(0)2}p_1 - 4\epsilon_1^{(0)}\epsilon_2^{(0)}p_1 + 2\epsilon_1^{(0)2}p_1 + 4\epsilon_2^{(0)2} + 4\epsilon_1^{(0)2} + \epsilon_2^{(0)} + \epsilon_1^{(0)2}}{[\epsilon_2^{(0)}(2+p_1)+\epsilon_1^{(0)}(1-p_1)]^2}\,. \tag{16}$$

From these two formulas, we can calculate χ_e using Eq. (10).

C. Exactly solvable microgeometry: Parallel cylinders and slabs

There exist a number of special microgeometries for which $\epsilon_e^{(0)}$ can be calculated exactly. The first of these is the case where the components are arranged in the form of (not necessarily circular) cylinders parallel to the external field. Another soluble geometry is one in which the constituents are arranged in the form of flat slabs perpendicular to the applied field. The effective dielectric constant takes the form

$$\epsilon_e^{(0)} = p_1\epsilon_1^{(0)} + p_2\epsilon_2^{(0)} \tag{17}$$

for parallel cylinders and

$$\epsilon_e^{(0)} = 1\Bigg/\left(\frac{p_1}{\epsilon_1^{(0)}} + \frac{p_2}{\epsilon_2^{(0)}}\right) \tag{18}$$

for parallel slabs. These results are analogous to the effective capacitance for capacitors in parallel and in series.

Using Eq. (10), we obtain for the effective nonlinear dielectric susceptibility

$$\chi_e = p_1\chi_1 + p_2\chi_2 \tag{19}$$

for parallel cylinders and

$$\chi_e = \frac{\chi_1 p_1}{[p_1 + (\epsilon_1^{(0)}p_2/\epsilon_2^{(0)})]^4} + \frac{\chi_2 p_2}{[p_2 + (\epsilon_2^{(0)}p_1/\epsilon_1^{(0)})]^4} \tag{20}$$

for parallel slabs. Both of these results are exact for a weakly nonlinear medium, since the local field is in fact uniform in each component in these two cases, even if the components are weakly nonlinear. [The local field may be uniform in these geometries even if the components are strongly nonlinear, but in such cases the results (19) and (20) will no longer apply.]

D. Effective-medium approximation

In the effective-medium approximation[2,6] (EMA), the effective dielectric function $\epsilon_e^{(0)}$ is one of the solutions of the quadratic equation

$$p_1\frac{\epsilon_1^{(0)}-\epsilon_e^{(0)}}{\epsilon_e^{(0)}+g(\epsilon_1^{(0)}-\epsilon_e^{(0)})} + (1-p_1)\frac{\epsilon_2^{(0)}-\epsilon_e^{(0)}}{\epsilon_e^{(0)}+g(\epsilon_2^{(0)}-\epsilon_e^{(0)})} = 0\,. \tag{21}$$

Here g is a geometric factor related to the depolarization factor of the inclusions and dependent on their shape. For a three-dimensional composite with compact, roughly spherical inclusions, $g=\frac{1}{3}$, while for a two-dimensional composite with circular inclusions, $g=\frac{1}{2}$. If $\epsilon_1^{(0)}$ and $\epsilon_2^{(0)}$ are real and positive, then the physically relevant solution is the positive one.

The required derivatives F_1' and F_2' can readily be computed from this equation, with the results

$$\begin{aligned} F_1' = \frac{1}{2(g-1)}\Big[&[2(\epsilon_1^{(0)}-\epsilon_2^{(0)})p_1^2 + 2(\epsilon_2^{(0)}-2\epsilon_1^{(0)}g)p_1 + 2(\epsilon_1^{(0)}-\epsilon_2^{(0)})g^2 \\ &+2\epsilon_2^{(0)}g]/(2\{(\epsilon_2^{(0)}-\epsilon_1^{(0)})^2p_1^2 + [2(\epsilon_2^{(0)2}-\epsilon_1^{(0)2})g - 2\epsilon_2^{(0)2} + 2\epsilon_1^{(0)}\epsilon_2^{(0)}]p_1 \\ &+(\epsilon_2^{(0)}-\epsilon_1^{(0)})^2g^2 + 2\epsilon_2^{(0)}(\epsilon_1^{(0)}-\epsilon_2^{(0)})g + \epsilon_2^{(0)2}\}^{1/2}) - p_1 + g\Big]\,, \end{aligned} \tag{22}$$

and

$$\begin{aligned} F_2' = \frac{1}{2(g-1)}\Big[&[2(\epsilon_2^{(0)}-\epsilon_1^{(0)})p_1^2 + 2(2\epsilon_2^{(0)}g - 2\epsilon_2^{(0)} + \epsilon_1^{(0)})p_1 + 2(\epsilon_2^{(0)}-\epsilon_1^{(0)})g^2 + 2(\epsilon_1^{(0)}-2\epsilon_2^{(0)})g + 2\epsilon_2^{(0)}] \\ &\times(2\{(\epsilon_2^{(0)}-\epsilon_1^{(0)})^2p_1^2 + [2(\epsilon_2^{(0)2}-\epsilon_1^{(0)2})g - 2\epsilon_2^{(0)2} + 2\epsilon_1^{(0)}\epsilon_2^{(0)}]p_1 \\ &+(\epsilon_2^{(0)}-\epsilon_1^{(0)})^2g^2 + 2\epsilon_2^{(0)}(\epsilon_1^{(0)}-\epsilon_2^{(0)})g + \epsilon_2^{(0)2}\}^{1/2})^{-1} + p_1 + g - 1\Big]\,. \end{aligned} \tag{23}$$

Given these formulas for F_1' and F_2', one can readily calculate the effective dielectric nonlinear susceptibility χ_e using

Eq. (10). The resulting expression for χ_e exhibits interesting behavior, especially near the percolation threshold, which will be discussed elsewhere.

III. EXACT RESULTS FOR THE HASHIN-SHTRIKMAN MICROGEOMETRY

In the Hashin-Shtrikman microgeometry,[4] the entire binary composite is composed of coated spheres with a core made of one component ϵ_1 and a concentric spherical shell made of the other component ϵ_2 [see Fig. 1(a)]. These composite spheres must come in a variety of sizes in order to fill up the entire volume, but all must have the same ratio of core volume to shell volume. It is easy to show[4] that for this microgeometry the bulk effective linear dielectric constant $\epsilon_e^{(0)}$ is exactly equal to the MG result. Furthermore, in the linear limit it is possible to evaluate the local electric field $\mathbf{E}(\mathbf{r})$ exactly within both the cores (where it is uniform but different from the average field E_0) and the shells [where it is not uniform; see Fig. 1(b)]. Given these fields, we can exactly evaluate the nonlinear susceptibility χ_e from the expression[3]

$$\chi_e = \frac{1}{V}\int dV \chi(\mathbf{r})(E/E_0)^4 . \tag{24}$$

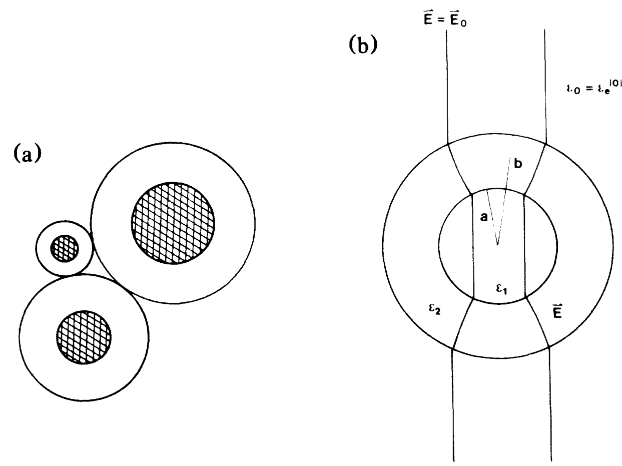

FIG. 1. (a) Schematic representation of the Hashin-Shtrikman microgeometry. The cores are described by ϵ_1,χ_1; the shells by ϵ_2,χ_2. The ratio of core-to-shell volume is the same for each composite sphere, and equal to the ratio of volume fractions $p_1/(1-p_1)$. (b) Schematic showing the solution for the local electric field in the Hashin-Shtrikman microgeometry. The field $\mathbf{E}$ remains undistorted and equal to the applied field $\mathbf{E}_0$ outside the inclusion, is uniform but $\neq\mathbf{E}_0$ in the core, and has a dipolar form in the shell.

The result is

$$\chi_e = \chi_1 p_1 \left(\frac{3\epsilon_2^{(0)}}{(1-p_2)\epsilon_1^{(0)}+(2+p_1)\epsilon_2^{(00)}} \right)^4 + \frac{\chi_2(1-p_1)}{[(1-p_1)\epsilon_1^{(0)}+(2+p_1)\epsilon_2^{(0)}]^4}$$
$$\times [(\epsilon_1^{(0)}+2\epsilon_2^{(0)})^4 + \tfrac{36}{5} p_1 \epsilon_1^{(0)2}(\epsilon_1^{(0)}+2\epsilon_2^{(0)})^2 - \tfrac{8}{5} p_1(1+p_1)\epsilon_1^{(0)3}(\epsilon_1^{(0)}+2\epsilon_2^{(0)}) + \tfrac{8}{5} p_1(1+p_1+p_1^2)\epsilon_1^{(0)4}] . \tag{25}$$

Comparing this to the MG result found earlier, and given implicitly by Eqs. (14)–(16), we can show that the coefficient of χ_1 is the same, but that of χ_2 is different. This difference has a simple explanation: The MGA for χ_e is based on the assumption that $\mathbf{E}$ is uniform in each component, while in the Hashin-Shtrikman geometry $\mathbf{E}$ is uniform within the cores but not the shells of the composite spheres.

IV. DISCUSSION AND CONCLUSIONS

We have presented a simple approximation for the nonlinear susceptibility χ_e of a weakly nonlinear dielectric composite. The approximation consists of assuming that the field is uniform in each of the nonlinear components. Given this approximation, we have easily obtained expressions for χ_e based on the MG and EM approximations for a linear dielectric composite. We have also calculated χ_e exactly for several simple, solvable microgeometries.

Our results are applicable not only to nonlinear media but also to $1/f$ noise or resistance fluctuations in composite conductors. The connection arises because the mean-square resistance fluctuations are given by an expression similar to Eq. (24).[3,7,8] Our EMA result thus provides an approximate calculation for the noise power spectrum. The result proves to differ from that of Ref. 7. In particular, our result exhibits no divergence of the relative noise at the EMA percolation threshold. A detailed comparative discussion of the various types of effective-medium approximations that can be developed for this problem will be given elsewhere.[8]

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