Nonlinear susceptibility of composite optical materials in the Maxwell Garnett model

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(Received 11 December 1991)

Within the context of the Maxwell Garnett model, we calculate the nonlinear susceptibility of a composite optical material comprised of spherical inclusion particles contained within a host material. We allow both constituents to respond nonlinearly and to exhibit linear absorption. Our treatment takes complete account of the tensor nature of the nonlinear interaction, under the assumption that each constituent is isotropic and that the composite is macroscopically isotropic. The theory predicts that there are circumstances under which the composite material can possess a nonlinear susceptibility that is larger than that of either of its constituents. It also predicts that, for the case in which the host material responds nonlinearly, the tensor properties of the nonlinear susceptibility of the composite can be very different from those of the host material.

PACS number(s): 42.65.An, 42.70.Nq

I. INTRODUCTION

Approaches to the development of optical systems with desirable nonlinear optical properties, such as large nonlinearities and fast responses, generally follow one of three routes. The first is that of *molecular engineering*, where one attempts to find, or to design at the molecular level, materials with intrinsic nonlinear optical properties of interest. The second is that of *propagation design*, where the geometry of the system results in light propagation which enhances the effect of the nonlinearities. Here the optical fiber is a prime example [1]; diffraction-free propagation over long distances leads to the dramatic importance of nonlinear effects, despite the small intrinsic nonlinearities of optical glass. Quasi-phase-matching in second-harmonic generation structures [2] is another example.

A third approach is based on *materials architecture*. Here different materials are combined to form a composite optical material [3]. Such a medium is comprised of a mixture of two or more components that differ in general with respect to both their linear and nonlinear optical characteristics, yet is homogeneous on a distance scale of the order of the optical wavelength. Hence the propagation of light can be described by means of suitably defined effective linear and nonlinear optical susceptibilities. Multiple quantum wells and superlattices fall into this category, although these structures are small enough that bulk properties cannot be ascribed to their components. Other examples are the metal colloids [4] and semiconductor-doped glasses [5] studied experimentally and theoretically by, e.g., Flytzanis and co-workers, where large enhancements (up to 10^4) in the value of the nonlinear susceptibility were reported [4], albeit with concomitantly enhanced absorption. In such simpler—and in principle easier to manufacture—composite materials, it is often a good first approximation to treat the linear- and nonlinear-response coefficients of the constituent materials to be the bulk response coefficients, or to be those coefficients modified slightly to describe, e.g., the change in transport properties due to the small size of the inclusion particles.

The earliest theory to deal with the *linear* optical properties of such composites is due to Maxwell Garnett. In his work [6], the composite material is assumed to be comprised of spherical inclusion particles embedded in a host material, both of which are assumed to be isotropic and to respond linearly to the incident light. Agarwal and Dutta Gupta [7] and Haus *et al.* [8] have presented theoretical studies of composite nonlinear optical materials based on the Maxwell Garnett model with a nonlinear response in the inclusion material, but curiously enough a full generalization of the Maxwell Garnett model to predict the first nonlinear correction to the effective-medium dielectric constant has not yet been developed. This we do here. We allow either or both components to possess a third-order nonlinear optical response, which for isotropic materials can be characterized by two parameters usually denoted A and B, and in terms of those parameters and the dielectric constants of the constituent materials we derive expressions for the parameters A and B of the effective medium. The results of our calculation are completely consistent with previous studies [4,7,8] but generalize those earlier results considerably in that we allow the possibility of nonlinearity in both host and inclusion, and that we explicitly treat the tensor nature of the nonlinear susceptibility. The theory predicts that there are circumstances under which the composite material can possess a nonlinear susceptibility larger than that of its constituents. And for a nonlinear host material, we find that the tensor properties of the nonlinear susceptibility of the composite can be considerably different than those of the pure host material.

The paper is organized as follows. In Sec. II we present the model of the composite material topology and the basic equations that govern the electromagnetic fields in it. In Sec. III we give a heuristic derivation of the relation between the mesoscopic and macroscopic electric fields, an argument that in essence goes back to Lorentz [9]; a more rigorous derivation of essentially the same result is presented in Appendix A. This relation is used in Sec. IV to derive the well-known Maxwell Garnett result for the effective-medium dielectric constant; in the course of this determination some results crucial for later sections are presented. In Sec. V we consider the case of nonlinearity in the inclusion material, and in Sec. VI that of nonlinearity in the host material; some geometrical formulas required in Sec. VI are derived in Appendix B. Example results for composite nonlinear susceptibilities are given in Secs. V and VI; we summarize our results and consider the case of nonlinearity in both the host and inclusion materials in Sec. VII.

Aside from any possible applications, investigations such as ours are of interest because they begin to address the fundamental question: How are the nonlinear optical properties of a composite material related to those of its constituents? The general answer to this question certainly depends on the topology of the composite. Here, in generalizing the Maxwell Garnet model to nonlinear response, we consider only the simplest possible topology. The answer for a topology of a composite material consisting of two or more interdispersed components, the topology that in linear response is considered in the theory of Bruggeman [10], can be expected to be rather different. We plan to turn to that topology in a future publication.

II. THE MODEL AND BASIC EQUATIONS

We assume a composite topology where small particles, which we call *inclusions*, are distributed in a *host* medium. As an approximation, the inclusions are assumed to be spheres of radius a. We define the characteristic distance between inclusion particles to be b, and we assume that

$$a \ll b \ll \lambda , \tag{2.1}$$

where λ is the wavelength of light in vacuum at frequencies of interest (see Fig. 1). Denoting the electric- and magnetic-field vectors by $\mathbf{e}(\mathbf{r},t)$ and $\mathbf{b}(\mathbf{r},t)$, respectively, we write the Maxwell equations in the form

$$\begin{aligned}
&\nabla\cdot\mathbf{e}(\mathbf{r},t) = -4\pi\nabla\cdot\mathbf{p}(\mathbf{r},t) , \\
&\nabla\cdot\mathbf{b}(\mathbf{r},t) = 0 , \\
&\nabla\times\mathbf{e}(\mathbf{r},t) + \frac{1}{c}\frac{\partial}{\partial t}\mathbf{b}(\mathbf{r},t) = \mathbf{0} , \\
&\nabla\times\mathbf{b}(\mathbf{r},t) - \frac{1}{c}\frac{\partial}{\partial t}\mathbf{e}(\mathbf{r},t) = \frac{4\pi}{c}\frac{\partial}{\partial t}\mathbf{p}(\mathbf{r},t) ,
\end{aligned} \tag{2.2}$$

where $\mathbf{p}(\mathbf{r},t)$ is the dipole moment per unit volume, and where magnetic effects are assumed to be negligible. We seek stationary solutions of these equations of the form

$$\mathbf{e}(\mathbf{r},t) = \mathbf{e}(\mathbf{r})e^{-i\omega t} + \text{c.c.} \tag{2.3}$$

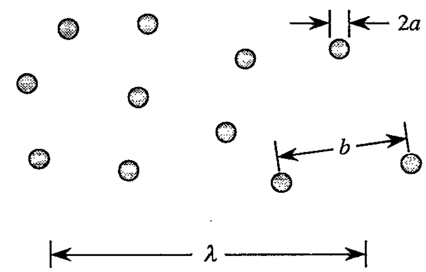

FIG. 1. The composite topology.

We describe the dielectric response of the material system by means of the relation

$$\mathbf{p}(\mathbf{r}) = \chi(\mathbf{r})\mathbf{e}(\mathbf{r}) + \mathbf{p}^{\mathrm{NL}}(\mathbf{r}) , \tag{2.4}$$

where

$$\chi(\mathbf{r}) = \begin{cases} \chi^i & \text{if } \mathbf{r} \text{ designates a point within an inclusion} \\ \chi^h & \text{if } \mathbf{r} \text{ designates a point within the host} \end{cases} \tag{2.5}$$

is the spatially varying linear susceptibility, and where $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$ is the nonlinear polarization, to which we turn in detail in Sec. V. If we define

$$\mathbf{p}'(\mathbf{r}) \equiv \begin{cases} (\chi^i - \chi^h)\mathbf{e}(\mathbf{r}) & \text{if } \mathbf{r} \text{ designates a point within an inclusion} \\ \mathbf{0} & \text{if } \mathbf{r} \text{ designates a point within the host ,} \end{cases} \tag{2.6}$$

and combine Eqs. (2.2)–(2.6), the Maxwell equations (2.2) become

$$\begin{aligned}
&\nabla\cdot[\epsilon^h\mathbf{e}(\mathbf{r})] = -4\pi\nabla\cdot\mathbf{p}^s(\mathbf{r}) , \\
&\nabla\cdot\mathbf{b}(\mathbf{r}) = 0 , \\
&\nabla\times\mathbf{e}(\mathbf{r}) - i\tilde{\omega}\mathbf{b}(\mathbf{r}) = \mathbf{0} , \\
&\nabla\times\mathbf{b}(\mathbf{r}) + i\tilde{\omega}\epsilon^h\mathbf{e}(\mathbf{r}) = -4\pi i\tilde{\omega}\mathbf{p}^s(\mathbf{r}) ,
\end{aligned} \tag{2.7}$$

with $\tilde{\omega} \equiv \omega/c$, where the inclusion and host linear dielectric constants are given by

$$\epsilon^{i,h} = 1 + 4\pi\chi^{i,h} , \tag{2.8}$$

and where we have introduced the "source" polarization

$$\mathbf{p}^s(\mathbf{r}) \equiv \mathbf{p}'(\mathbf{r}) + \mathbf{p}^{\mathrm{NL}}(\mathbf{r}) . \tag{2.9}$$

We have used lowercase letters ($\mathbf{e}$, $\mathbf{b}$, etc.) for the electromagnetic fields appearing in these equations because, although we have adopted a macroscopic description of each constituent of the composite, we next introduce a "more macroscopic" description which we obtain by averaging the fields over a volume that contains many inclusions. We perform this average through the use of a smoothly varying weighting function $\Delta(\mathbf{r}) = \Delta(r)$, where $r = |\mathbf{r}|$. The volume integral of $\Delta(\mathbf{r})$ is normalized to unity,

$$\int \Delta(\mathbf{r}-\mathbf{r}')d\mathbf{r}' = 1 , \tag{2.10}$$

and it has a range R satisfying the inequalities

$$b \ll R \ll \lambda . \tag{2.11}$$

The averaged fields are then defined by

$$\mathbf{E}(\mathbf{r})=\int \Delta(\mathbf{r}-\mathbf{r}')\mathbf{e}(\mathbf{r}')d\mathbf{r}' ,$$
$$\mathbf{P}(\mathbf{r})=\int \Delta(\mathbf{r}-\mathbf{r}')\mathbf{p}(\mathbf{r}')d\mathbf{r}' , \qquad (2.12)$$
$$\mathbf{P}^{\mathrm{NL}}(\mathbf{r})=\int \Delta(\mathbf{r}-\mathbf{r}')\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')d\mathbf{r}' .$$

etc., where the integrals are to be performed over all space. It is easily confirmed that this averaging procedure commutes with differentiation, e.g.,

$$\frac{\partial \mathbf{E}(\mathbf{r})}{\partial x}=\int \frac{\partial \Delta(\mathbf{r}-\mathbf{r}')}{\partial x}\mathbf{e}(\mathbf{r}')d\mathbf{r}'$$
$$=-\int \frac{\partial \Delta(\mathbf{r}-\mathbf{r}')}{\partial x'}\mathbf{e}(\mathbf{r}')d\mathbf{r}'$$
$$=\int \Delta(\mathbf{r}-\mathbf{r}')\frac{\partial \mathbf{e}(\mathbf{r}')}{\partial x'}d\mathbf{r}' , \qquad (2.13)$$

where the third of Eqs. (2.13) follows from the second by a partial integration and the assumption that $\Delta(\mathbf{r}-\mathbf{r}')\rightarrow 0$ as $|\mathbf{r}-\mathbf{r}'|\rightarrow\infty$. By performing an average of the Maxwell equations (2.7), we thus find that

$$\nabla\cdot[\epsilon^h \mathbf{E}(\mathbf{r})]=-4\pi\nabla\cdot\mathbf{P}^s(\mathbf{r}) ,$$
$$\nabla\cdot\mathbf{B}(\mathbf{r})=0 ,$$
$$\nabla\times\mathbf{E}(\mathbf{r})-i\varpi\mathbf{B}(\mathbf{r})=\mathbf{0} , \qquad (2.14)$$
$$\nabla\times\mathbf{B}(\mathbf{r})+i\varpi\epsilon^h\mathbf{E}(\mathbf{r})=-4\pi i\varpi\mathbf{P}^s(\mathbf{r}) ,$$

where

$$\mathbf{P}^s(\mathbf{r})\equiv\mathbf{P}'(\mathbf{r})+\mathbf{P}^{\mathrm{NL}}(\mathbf{r}) . \qquad (2.15)$$

Our goal is to find a constitutive relation between $\mathbf{P}^s(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$. Since the range R of $\Delta(\mathbf{r})$ is very much larger than the characteristic separation b of the inclusions, we expect that the resulting linear and nonlinear susceptibilities will be spatially uniform; however, since $R \ll \lambda$, these averaged fields can be used to describe the propagation of light through the medium. The resulting susceptibilities thus characterize an "effective medium" that describes the optical properties of the composite material, and we refer to the averaged fields $\mathbf{E}(\mathbf{r})$, $\mathbf{B}(\mathbf{r})$, etc. as "macroscopic fields." We refer to the fields $\mathbf{e}(\mathbf{r})$ and $\mathbf{b}(\mathbf{r})$ as "mesoscopic fields," since they contain more spatial information than the macroscopic fields, but yet are themselves averages of the microscopic electric and magnetic fields, which vary greatly over interatomic distances.

III. MESOSCOPIC AND MACROSCOPIC FIELDS: A SIMPLE PHYSICAL ARGUMENT

Since the mesoscopic polarization $\mathbf{p}(\mathbf{r})$ is a known function of the mesoscopic electric field $\mathbf{e}(\mathbf{r})$ [see Eqs. (2.4)–(2.6) and Sec. V], an important step in deriving a constitutive relation between $\mathbf{P}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ is in relating $\mathbf{e}(\mathbf{r})$ to $\mathbf{E}(\mathbf{r})$. For then $\mathbf{p}(\mathbf{r})$ can be related to $\mathbf{E}(\mathbf{r})$, and the spatial average of $\mathbf{p}(\mathbf{r})$ will give $\mathbf{P}(\mathbf{r})$ in term of $\mathbf{E}(\mathbf{r})$.

It turns out that one can derive a relation between $\mathbf{e}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ that is both rigorous and useful. That relation is derived in Appendix A, and is used in Secs. IV, V, and VI to derive the constitutive relation of the composite medium. In this section we present a simple physical argument that leads to essentially the same result as that derived in Appendix A. This simple physical argument, which follows the original argument of Lorentz [9], is somewhat heuristic; but we give it here for the benefit of the reader not interested in all the mathematical details, and to show why the rigorous result derived in Appendix A is physically reasonable.

We wish to relate $\mathbf{e}(\mathbf{r})$, which is given by the particular solution of the mesoscopic Maxwell equations (2.7) plus a homogeneous solution, to $\mathbf{E}(\mathbf{r})$, which is given by the particular solution of the macroscopic Maxwell equations (2.14) plus a homogeneous solution of those equations. We surround the point $\mathbf{r}$ by a sphere of radius R centered at $\mathbf{r}$ (see Fig. 2), and we write

$$\mathbf{e}(\mathbf{r})=\mathbf{e}^0(\mathbf{r})+\mathbf{e}^{\mathrm{in}}(\mathbf{r})+\mathbf{e}^{\mathrm{out}}(\mathbf{r}) ,$$
$$\mathbf{E}(\mathbf{r})=\mathbf{E}^0(\mathbf{r})+\mathbf{E}^{\mathrm{in}}(\mathbf{r})+\mathbf{E}^{\mathrm{out}}(\mathbf{r}) , \qquad (3.1)$$

where $\mathbf{e}^0(\mathbf{r})$ and $\mathbf{E}^0(\mathbf{r})$ are the above-mentioned homogeneous solutions. We define $\mathbf{e}^{\mathrm{in}}(\mathbf{r})$ to be the contribution to $\mathbf{e}(\mathbf{r})$ from $\mathbf{p}^s(\mathbf{r}')$ taken at points $\mathbf{r}'$ within the sphere, and $\mathbf{e}^{\mathrm{out}}(\mathbf{r})$ to be the contribution from points $\mathbf{r}'$ outside the sphere. Likewise, $\mathbf{E}^{\mathrm{in}}(\mathbf{r})$ and $\mathbf{E}^{\mathrm{out}}(\mathbf{r})$ contain, respectively, the contributions to $\mathbf{E}(\mathbf{r})$ from $\mathbf{P}^s(\mathbf{r}')$ taken at points $\mathbf{r}'$ inside and outside the sphere. Now, since $\mathbf{E}^0(\mathbf{r})$ is the spatial average of $\mathbf{e}^0(\mathbf{r})$ over a distance of the order of R, and $\mathbf{e}^0(\mathbf{r})$ varies only over distances of order λ, which is very much greater than R, we may take $\mathbf{e}^0(\mathbf{r})\simeq\mathbf{E}^0(\mathbf{r})$. Further, since we have assumed that $R \gg b$, the precise locations of the inclusions outside the sphere are unimportant in determining $\mathbf{e}^{\mathrm{out}}(\mathbf{r})$, and to good approximation we may take $\mathbf{e}^{\mathrm{out}}(\mathbf{r})\simeq\mathbf{E}^{\mathrm{out}}(\mathbf{r})$. Then, combining Eqs. (3.1), we have

$$\mathbf{e}(\mathbf{r})-\mathbf{E}(\mathbf{r})=\mathbf{e}^{\mathrm{in}}(\mathbf{r})-\mathbf{E}^{\mathrm{in}}(\mathbf{r}) . \qquad (3.2)$$

Next, since $R \ll \lambda$, we can use the laws of electrostatics (the $\varpi\rightarrow 0$ limit of the Maxwell equations) in estimating both $\mathbf{e}^{\mathrm{in}}(\mathbf{r})$ and $\mathbf{E}^{\mathrm{in}}(\mathbf{r})$. For the latter, we can also assume that $\mathbf{P}^s(\mathbf{r})$ is effectively uniform over the sphere, and so Eqs. (2.14) in the electrostatic limit immediately yield [11]

$$\mathbf{E}^{\mathrm{in}}(\mathbf{r})=-\frac{4\pi}{3\epsilon^h}\mathbf{P}^s(\mathbf{r}) . \qquad (3.3)$$

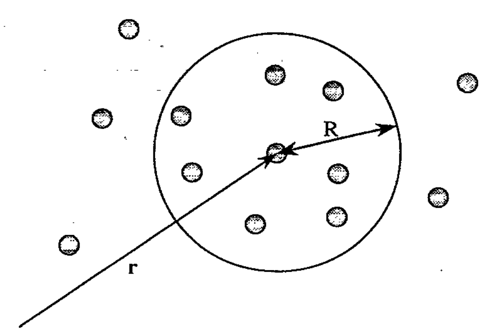

FIG. 2. A sphere of radius R is centered on the point $\mathbf{r}$, which may lie either in an inclusion (as illustrated) or in the host medium.

We find $\mathbf{e}^{\text{in}}(\mathbf{r})$ by solving Eqs. (2.7) in the electrostatic limit, and then restricting the source term $\mathbf{p}^s(\mathbf{r}')$ that appears in the solution to points $\mathbf{r}'$ within the sphere ($|\mathbf{r}-\mathbf{r}'|<R$). The result is [12]

$$\mathbf{e}^{\text{in}}(\mathbf{r})=\int_{\eta\le|\mathbf{r}-\mathbf{r}'|\le R}\overleftrightarrow{\mathbf{T}}(\mathbf{r}-\mathbf{r}')\cdot p^s(\mathbf{r}')d\mathbf{r}'-\frac{4\pi}{3\epsilon^h}\mathbf{p}^s(\mathbf{r}) , \tag{3.4}$$

where the radius η of the region excluded from the integration is allowed to go to zero after the integral in Eq. (3.4) is performed. This integral involves the static dipole-dipole coupling tensor for a medium of dielectric constant ϵ^h, which is given by

$$\overleftrightarrow{\mathbf{T}}(\mathbf{r})\equiv\frac{3\hat{\mathbf{r}}\hat{\mathbf{r}}-\overleftrightarrow{\mathbf{U}}}{\epsilon^h r^3} , \tag{3.5}$$

where $\hat{\mathbf{r}}=\mathbf{r}/r$ and $\overleftrightarrow{\mathbf{U}}=\hat{\mathbf{x}}\hat{\mathbf{x}}+\hat{\mathbf{y}}\hat{\mathbf{y}}+\hat{\mathbf{z}}\hat{\mathbf{z}}$. Defining

$$\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})=\begin{cases}\overleftrightarrow{\mathbf{T}}(\mathbf{r}), & r>\eta\\ 0, & r<\eta\end{cases} \tag{3.6}$$

and a cutoff function

$$c'(\mathbf{r})=\begin{cases}1, & r<R\\ 0, & r>R ,\end{cases} \tag{3.7}$$

we can combine Eqs. (3.2), (3.3), and (3.4) to give

$$\mathbf{e}(\mathbf{r})=\mathbf{E}(\mathbf{r})+\frac{4\pi}{3\epsilon^h}\mathbf{P}^s(\mathbf{r})+\int\overleftrightarrow{\mathbf{T}}^0(\mathbf{r}-\mathbf{r}')c'(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^s(\mathbf{r}')d\mathbf{r}' -\frac{4\pi}{3\epsilon^h}\mathbf{p}^s(\mathbf{r}) . \tag{3.8}$$

This equation is the central result of this section. It shows how the difference between $\mathbf{e}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ depends only on $\mathbf{p}^s(\mathbf{r}')$ at points $\mathbf{r}'$ within a distance $R\ll\lambda$ of $\mathbf{r}$ [cf. Eq. (3.2)]. This result is crucial in deriving, to good approximation, a local relation between $\mathbf{P}^s(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ (Secs. IV–VI below). Our derivation of Eq. (3.8) is not rigorous, but the essential physics of Eq. (3.8) is correct; the rigorous derivation of a more exact relation is given in Appendix A. In the next section we state that more exact relation, and return to the formal development of our theory.

IV. THE MAXWELL GARNETT EQUATIONS

In this section we derive the Maxwell Garnett equations, which provide a good approximate description of the linear optical properties of a composite medium of our assumed topology. This result is of course well known [6], but we recover it here both to illustrate our approach and to illustrate the nature of the approximations involved. In addition, we obtain some results that are needed for the calculation of the nonlinear optical response that is presented in the following sections.

In both this section and the next, we use the rigorous form of Eq. (3.8), as derived in Appendix A. There, using only the mesoscopic Maxwell equations (2.7), the macroscopic Maxwell equations (2.14), and the definitions [see Eq. (2.12)] of macroscopic fields in terms of mesoscopic fields, we find an exact relation (A43) between $\mathbf{e}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ for a $\Delta(r)$ characterized by *any* range R. For $R\ll\lambda$, that result reduces to

$$\mathbf{e}(\mathbf{r})=\mathbf{E}^c(\mathbf{r})-\frac{4\pi}{3\epsilon^h}\mathbf{p}^s(\mathbf{r})+\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^s(\mathbf{r}')d\mathbf{r}' , \tag{4.1}$$

where

$$\mathbf{E}^c(\mathbf{r})=\mathbf{E}(\mathbf{r})+\frac{4\pi}{3\epsilon^h}\mathbf{P}^s(\mathbf{r}) \tag{4.2}$$

is the so-called "cavity field" [the $\mathbf{E}(\mathbf{r})-\mathbf{E}^{\text{in}}(\mathbf{r})$ of Sec. III]. Here

$$\overleftrightarrow{\mathbf{T}}^c(\mathbf{r})=\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})c(\mathbf{r}) \tag{4.3}$$

is the product of $\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})$ [Eq. (3.6)] and a cutoff function $c(r)$ [$c(0)=1$, $c(r)\to 0$ as $r\to\infty$]. The function $c(r)$ is not the simple cutoff function $c'(r)$ that appeared in Sec. III [Eq. (3.7)], but is given by Eq. (A60); nonetheless, $c(r)$ has a range on the order of R.

We next note three useful results that follow from the properties of the static dipole tensor:

$$\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}-\mathbf{r}')d\mathbf{r}'=0 , \tag{4.4a}$$

$$\int_{\substack{\text{sphere,}\\ \mathbf{r}\in\text{sphere}}}\overleftrightarrow{\mathbf{T}}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}'=0 , \tag{4.4b}$$

$$\int_{\substack{\text{sphere,}\\ \mathbf{r}'\notin\text{sphere}}}\overleftrightarrow{\mathbf{T}}^0(\mathbf{r}-\mathbf{r}')d\mathbf{r}=\frac{4\pi}{3}a^3\overleftrightarrow{\mathbf{T}}(\mathbf{r}_0-\mathbf{r}') . \tag{4.4c}$$

In the first equation, the range of integration is over all space and the result follows from the fact that $c(r)$ depends only on $r=|\mathbf{r}|$, and that the integral of $\overleftrightarrow{\mathbf{T}}^0(\mathbf{r})$ over solid angle, for fixed r, vanishes. In the second two equations, the range of integration is the interior of a sphere of radius a; in Eq. (4.4b) $\mathbf{r}$ is any point within the sphere, while in Eq. (4.4c) $\mathbf{r}'$ is a point outside the sphere and $\mathbf{r}_0$ the position of the center of the sphere. Equations (4.4b) and (4.4c) may be derived, e.g., by using the fact that $\overleftrightarrow{\mathbf{T}}(\mathbf{r})=\epsilon_h^{-1}\nabla\nabla r^{-1}$, and using Gauss's theorem.

We now return to a consideration of the polarization of the medium. From Eq. (2.6) we have

$$4\pi\mathbf{p}'(\mathbf{r}'')=(\epsilon^i-\epsilon^h)\Theta^i(\mathbf{r}'')\mathbf{e}(\mathbf{r}'') , \tag{4.5}$$

where we have used Eq. (2.8) and where we define $\Theta^i(\mathbf{r}'')=1$ if the point $\mathbf{r}''$ is in an inclusion and $\Theta^i(\mathbf{r}'')=0$ if $\mathbf{r}''$ is in the host. Next, we use Eq. (4.1) and neglect any nonlinear behavior [$\mathbf{p}^{\text{NL}}(\mathbf{r})=0$]; then $\mathbf{p}^s(\mathbf{r})=\mathbf{p}'(\mathbf{r})$ [Eq. (2.9)], and Eq. (4.5) yields

$$\begin{aligned}4\pi\mathbf{p}'(\mathbf{r}'')&=(\epsilon^i-\epsilon^h)\Theta^i(\mathbf{r}'')\left[\mathbf{E}^c(\mathbf{r}'')-\frac{4\pi}{3\epsilon^h}\mathbf{p}'(\mathbf{r}'')+\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}''-\mathbf{r}')\cdot\mathbf{p}'(\mathbf{r}')d\mathbf{r}'\right]\\&=3\epsilon^h\beta\Theta^i(\mathbf{r}'')\left[\mathbf{E}^c(\mathbf{r}'')+\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}''-\mathbf{r}')\cdot\mathbf{p}'(\mathbf{r}')d\mathbf{r}'\right] ,\end{aligned} \tag{4.6}$$

where we have put

$$\beta \equiv \frac{\epsilon^i - \epsilon^h}{\epsilon^i + 2\epsilon^h} . \tag{4.7}$$

We now wish to use Eq. (4.6) in the expression for $\mathbf{P}'$ [see Eq. (2.12)],

$$\mathbf{P}'(\mathbf{r}) = \int \Delta(\mathbf{r}-\mathbf{r}'')\mathbf{p}'(\mathbf{r}'')d\mathbf{r}'' , \tag{4.8}$$

for which we need $\mathbf{p}'(\mathbf{r}'')$ at points $\mathbf{r}''$ within approximately R of $\mathbf{r}$. We next introduce the standard approximations that are made in deriving the Maxwell Garnett equation. The crucial ansatz is that, at points $\mathbf{r}''$ within R of $\mathbf{r}$, $\mathbf{p}'(\mathbf{r}'')$ within the inclusions can be approximated in Eq. (4.8) by a uniform value that we call $\wp(\mathbf{r})$. That is, $\mathbf{p}'(\mathbf{r}'')$ in Eq. (4.8) can be replaced by $\wp(\mathbf{r})\Theta^i(\mathbf{r}'')$, and we find

$$\mathbf{P}'(\mathbf{r}) = f\wp(\mathbf{r}) , \tag{4.9}$$

where

$$f = \int \Delta(\mathbf{r}-\mathbf{r}'')\Theta^i(\mathbf{r}'')d\mathbf{r}'' \tag{4.10}$$

is the macroscopic fill fraction of inclusions, here for simplicity assumed to be essentially uniform throughout the medium. To find an expression for $\wp(\mathbf{r})$, we return to Eq. (4.6).

Look first at the term involving $\overleftrightarrow{\mathbf{T}}^c$: For a point $\mathbf{r}''$ in a given inclusion, the integral over points $\mathbf{r}'$ in the same inclusion will give zero by virtue of Eq. (4.4b), the assumption of a mesoscopically uniform $\wp(\mathbf{r})$, and the fact that $c(\mathbf{r}''-\mathbf{r}')$ is essentially uniform over an inclusion. Now consider the integral over points $\mathbf{r}'$ in different inclusions. Since the range R of $c(\mathbf{r}''-\mathbf{r}')$ satisfies $R \gg b$, there are many neighboring inclusions involved. If these inclusions are randomly distributed with respect to the first inclusion, we expect on average no contribution from the integral, by virtue of the assumption of a mesoscopically uniform $\wp(\mathbf{r})$ and Eq. (4.4a). Neglecting the corrections that could result from any correlations in the positions of the inclusions, we set the total contribution from the integral involving $\overleftrightarrow{\mathbf{T}}^c$ equal to zero.

Next, note that in Eq. (4.6) $\mathbf{E}^c(\mathbf{r}'')$ is already a macroscopic field, obtained from the spatial average over a range R of the mesoscopic field $\mathbf{e}(\mathbf{r})+4\pi\mathbf{p}'(\mathbf{r})/3\epsilon^h$. Thus, its variation over distances of order R can be expected to be small, and we can set $\mathbf{E}^c(\mathbf{r}'') \simeq \mathbf{E}^c(\mathbf{r})$ in Eq. (4.6) for points $\mathbf{r}''$ within R of $\mathbf{r}$. It is then clear that the mesoscopically uniform polarization $\wp(\mathbf{r})$ appearing in Eq. (4.9) should be taken as

$$4\pi\wp(\mathbf{r}) = 3\epsilon^h\beta\mathbf{E}^c(\mathbf{r}) . \tag{4.11}$$

Using Eq. (4.11) in (4.9), and recalling that here

$$\mathbf{E}^c(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + \frac{4\pi}{3\epsilon^h}\mathbf{P}'(\mathbf{r}) \tag{4.12}$$

[Eq. (4.2) with $\mathbf{P}^{NL}=\mathbf{0}$], we find that

$$4\pi\mathbf{P}'(\mathbf{r}) = 3\epsilon^h\beta f(1-\beta f)^{-1}\mathbf{E}(\mathbf{r}) . \tag{4.13}$$

Finally, using Eq. (2.6) in Eq. (2.4) we have, neglecting nonlinear effects,

$$\mathbf{p}(\mathbf{r}) = \chi^h\mathbf{e}(\mathbf{r}) + \mathbf{p}'(\mathbf{r}) ,$$
$$\mathbf{P}(\mathbf{r}) = \chi^h\mathbf{E}(\mathbf{r}) + \mathbf{P}'(\mathbf{r}) , \tag{4.14}$$

where the second of Eqs. (4.14) comes from spatial averaging the first. The total displacement $\mathbf{D}(\mathbf{r})$ is thus given by

$$\mathbf{D}(\mathbf{r}) = \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r}) = \epsilon^h\mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}'(\mathbf{r}) \equiv \epsilon\mathbf{E}(\mathbf{r}) , \tag{4.15}$$

where the last of Eqs. (4.15) defines the effective-medium dielectric constant ϵ. Using Eq. (4.13), we find that ϵ satisfies

$$\frac{\epsilon-\epsilon^h}{\epsilon+2\epsilon^h} = \beta f , \tag{4.16}$$

which is the usual Maxwell Garnett result.

We close this section by deducing some relations that will prove useful in the following section. Using Eqs. (4.13) and (4.16) in Eq. (4.12) we find that

$$\mathbf{E}^c(\mathbf{r}) = \frac{\epsilon+2\epsilon^h}{3\epsilon^h}\mathbf{E}(\mathbf{r}) . \tag{4.17}$$

Next, we combine Eqs. (4.5), (4.11), and (4.17) to determine the mesoscopic electric field $\mathbf{e}(\mathbf{r})$ inside an inclusion; the result is

$$\mathbf{e}(\mathbf{r}) = \frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\mathbf{E}(\mathbf{r}) \tag{4.18}$$

if $\mathbf{r}$ lies in an inclusion. The mesoscopic field $e(\mathbf{r})$ at points outside an inclusion is given below in Eq. (6.4). Finally, the dipole moment $\boldsymbol{\mu}$ of an inclusion associated with the polarization $\wp(\mathbf{r})$ of Eq. (4.11) is given by

$$\boldsymbol{\mu} \equiv \frac{4\pi}{3}a^3\wp(\mathbf{r}) = a^3\epsilon^h\beta\mathbf{E}^c(\mathbf{r}) . \tag{4.19}$$

V. NONLINEARITY IN THE INCLUSIONS

We now turn to the nonlinear problem, where $\mathbf{p}^{NL}(\mathbf{r}) \neq \mathbf{0}$. Combining Eqs. (2.4) and (2.6), we find that the total mesoscopic polarization can be expressed as

$$\mathbf{p}(\mathbf{r}) = \chi^h\mathbf{e}(\mathbf{r}) + \mathbf{p}'(\mathbf{r}) + \mathbf{p}^{NL}(\mathbf{r}) \tag{5.1}$$

[cf. Eq. (4.14)]. Spatial averaging of this result gives

$$\mathbf{P}(\mathbf{r}) = \chi^h\mathbf{E}(\mathbf{r}) + \mathbf{P}'(\mathbf{r}) + \mathbf{P}^{NL}(\mathbf{r}) , \tag{5.2}$$

and introducing the definition of $\mathbf{D}(\mathbf{r})$ we have

$$\mathbf{D}(\mathbf{r}) \equiv \mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}(\mathbf{r})$$
$$= \epsilon^h\mathbf{E}(\mathbf{r}) + 4\pi\mathbf{P}'(\mathbf{r}) + 4\pi\mathbf{P}^{NL}(\mathbf{r}) . \tag{5.3}$$

For a medium that is weakly nonlinear, we expect that, when $\mathbf{P}'(\mathbf{r})$ and $\mathbf{P}^{NL}(\mathbf{r})$ are written to third order in the electric-field strength $\mathbf{E}(\mathbf{r})$, we will have a relation of the form

$$\mathbf{D}(\mathbf{r}) = \epsilon\mathbf{E}(\mathbf{r}) + 4\pi A[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}^*(\mathbf{r})]\mathbf{E}(\mathbf{r})$$
$$+ 2\pi B[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})]\mathbf{E}^*(\mathbf{r}) , \tag{5.4}$$

where the tensor nature of the third-order terms in Eq. (5.4) follows from symmetry arguments if we assume that, at the macroscopic level, the medium is isotropic [13]. We neglect nonlinear processes such as third-harmonic generation, and concern ourselves only with the nonlinear modification of the propagation of light at its incident frequency. The two parameters A and B are in general independent, although for electronic nonlinearities we must have $A-B\to 0$ as $\omega\to 0$. The determination of A and B in terms of the corresponding nonlinear coefficients of the host and inclusions is the problem to which we now turn.

In the present section, we treat the problem in which only the inclusion material responds nonlinearly to the optical field. Assuming for simplicity that the inclusion material is itself isotropic and uniform, we then have a nonlinear polarization of the form

$$\mathbf{p}^{\mathrm{NL}}(\mathbf{r})=\Theta^i(\mathbf{r})\mathbf{p}^{\mathrm{NL},i}(\mathbf{r}) , \tag{5.5}$$

where

$$\mathbf{p}^{\mathrm{NL},i}(\mathbf{r})= A^i[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}^*(\mathbf{r})]\mathbf{e}(\mathbf{r})+\tfrac{1}{2}B^i[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}(\mathbf{r})]\mathbf{e}^*(\mathbf{r}) , \tag{5.6}$$

and where A^i and B^i are the nonlinear coefficients of the inclusion material. Since we are looking only for the lowest-order macroscopic nonlinearity [Eq. (5.4)], it suffices to estimate $\mathbf{e}(\mathbf{r})$ in Eq. (5.6) from the results of a calculation that neglects the nonlinearity itself. That is, we use Eq. (4.18) in Eq. (5.6) to obtain

$$\mathbf{p}^{\mathrm{NL},i}(\mathbf{r})=\left|\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right]\times\{A^i[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}^*(\mathbf{r})]\mathbf{E}(\mathbf{r})+\tfrac{1}{2}B^i[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})]\mathbf{E}^*(\mathbf{r})\} . \tag{5.7}$$

Next, we average Eq. (5.5) [cf. Eqs. (2.12) and (5.7)] to find $\mathbf{P}^{\mathrm{NL}}(\mathbf{r})$. Using the fact that $\mathbf{E}(\mathbf{r})$ can be assumed to vary little over a range R, and using expression (4.10) for f, we find that

$$\mathbf{P}^{\mathrm{NL}}(\mathbf{r})=f\left|\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right]\times\{A^i[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}^*(\mathbf{r})]\mathbf{E}(\mathbf{r})+\tfrac{1}{2}B^i[\mathbf{E}(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})]\mathbf{E}^*(\mathbf{r})\} . \tag{5.8}$$

Referring back to Eqs. (5.2)–(5.4), we see that, in order to determine $\mathbf{D}(\mathbf{r})$ and subsequently to find expressions for A and B, our remaining task is to find $\mathbf{P}'(\mathbf{r})$. This result cannot be taken simply from the linear calculation of Sec. IV, because $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$ makes a contribution to $\mathbf{e}(\mathbf{r})$ and thus to $\mathbf{p}'(\mathbf{r})$ to lowest nonvanishing order in the nonlinearity. From Eq. (4.5), we have

$$4\pi\mathbf{p}'(\mathbf{r}'')=(\epsilon^i-\epsilon^h)\Theta^i(\mathbf{r}'')\mathbf{e}(\mathbf{r}'') , \tag{5.9}$$

but we must now use the full set of Eqs. (4.1) and (4.2), with $\mathbf{p}^s(\mathbf{r}'')=\mathbf{p}'(\mathbf{r})+\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$, $\mathbf{P}^s(\mathbf{r})=\mathbf{P}'(\mathbf{r})+\mathbf{P}^{\mathrm{NL}}(\mathbf{r})$. Equation (5.9) thereby becomes

$$\begin{aligned}4\pi\mathbf{p}'(\mathbf{r}'')&=(\epsilon^i-\epsilon^h)\Theta^i(\mathbf{r}'')\left[\mathbf{E}^c(\mathbf{r}'')-\frac{4\pi}{3\epsilon^h}\mathbf{p}'(\mathbf{r}'')-\frac{4\pi}{3\epsilon^h}\mathbf{p}^{\mathrm{NL},i}(\mathbf{r}'')+\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}''-\mathbf{r}')\cdot[\mathbf{p}'(\mathbf{r}')+\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')]d\mathbf{r}'\right]\\&=3\epsilon^h\beta\Theta^i(\mathbf{r}'')\left[\overleftrightarrow{\mathbf{E}}^c(\mathbf{r}'')-\frac{4\pi}{3\epsilon^h}\mathbf{p}^{\mathrm{NL},i}(\mathbf{r}'')+\int\overleftrightarrow{\mathbf{T}}^c(\mathbf{r}''-\mathbf{r}')\cdot[\mathbf{p}'(\mathbf{r}')+\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')]d\mathbf{r}'\right] ,\end{aligned} \tag{5.10}$$

where β is given by Eq. (4.7), and where the cavity field now contains a nonlinear contribution and is given by

$$\mathbf{E}^c(\mathbf{r})=\mathbf{E}(\mathbf{r})+\frac{4\pi}{3\epsilon^h}\mathbf{P}'(\mathbf{r})+\frac{4\pi}{3\epsilon^h}\mathbf{P}^{\mathrm{NL}}(\mathbf{r}) . \tag{5.11}$$

However, we can still argue, much as we did after Eq. (4.8), that $\mathbf{p}'(\mathbf{r}'')$ can be approximated within the inclusion by a mesoscopically uniform value, to be denoted by $\not{\!\mathbf{p}}(\mathbf{r})$, at points $\mathbf{r}''$ within R of $\mathbf{r}$; then, as in Sec. IV,

$$\mathbf{P}'(\mathbf{r})=f\not{\!\mathbf{p}}(\mathbf{r}) . \tag{5.12}$$

Note that, from Eq. (5.7) and the fact that $\mathbf{E}(\mathbf{r})$ varies little over a range of R, $\mathbf{p}^{\mathrm{NL},i}(\mathbf{r}'')$ has also been taken to be uniform in this sense, $\mathbf{p}^{\mathrm{NL},i}(\mathbf{r}'')=\Theta^i(\mathbf{r}'')\not{\!\mathbf{p}}^{\mathrm{NL}}(\mathbf{r})$. Following the arguments given after Eq. (4.8), we see that again we may neglect contributions from the integral involving $\overleftrightarrow{\mathbf{T}}^c$, and we find [instead of Eqs. (4.11) and (4.12)] that

$$4\pi\not{\!\mathbf{p}}(\mathbf{r})=3\epsilon^h\beta\left[\mathbf{E}^c(\mathbf{r})-\frac{4\pi}{3\epsilon^h}\not{\!\mathbf{p}}^{\mathrm{NL}}(\mathbf{r})\right] , \tag{5.13}$$

where $\mathbf{E}^c(\mathbf{r})$ is given by Eq. (5.11). Combining Eqs. (5.7) and (5.8) and (5.11)–(5.13), we can solve for $\mathbf{P}'(\mathbf{r})$; in fact, it is clear from Eq. (5.3) that we need the sum of $\mathbf{P}'(\mathbf{r})$ and $\mathbf{P}^{\mathrm{NL}}(\mathbf{r})$, for which we find

$$\mathbf{P}'(\mathbf{r})+\mathbf{P}^{\mathrm{NL}}(\mathbf{r})=\frac{\epsilon-\epsilon^h}{4\pi}\mathbf{E}(\mathbf{r})+\left[\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right]\mathbf{P}^{\mathrm{NL}}(\mathbf{r}) , \tag{5.14}$$

where $\mathbf{P}^{\mathrm{NL}}(\mathbf{r})$ is given by Eq. (5.8) and ϵ is given by Eq. (4.16) [14]. Using Eqs. (5.8) and (5.14) in Eq. (5.3) and comparing with Eq. (5.4), we identify

$$\begin{aligned}A&=f\left|\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right]^2A^i ,\\B&=f\left|\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{\epsilon^i+2\epsilon^h}\right]^2B^i\end{aligned} \tag{5.15}$$

as the nonlinear coefficients of the effective medium. Note that the "local-field correction factor," in this case

$(\epsilon+2\epsilon^h)/(\epsilon^i+2\epsilon^h)$, appears in fourth order [15] in Eqs. (5.15); three powers enter because the nonlinearity is cubic in the field [Eqs. (5.6) and (5.8)], while the fourth appears because the material also responds linearly to the field generated by the nonlinear polarization [Eqs. (5.13) and (5.14)] [16].

The results given by Eqs. (5.15) are illustrated graphically in Fig. 3. Here the vertical axis can be taken to represent either the nonlinear coefficient A of the composite normalized to the nonlinear coefficient A^i of the inclusion material or the value of B for the composite normalized to the nonlinear coefficient B^i of the inclusion material. The horizontal axis gives the fill fraction f of the nonlinear material. For illustrative purposes we have plotted these curves over the entire range $0 \leq f \leq 1$, even though interinclusion correlations not included in this theory can in general be expected to modify significantly the results if we do not have $f \ll 1$. For the case in which the linear dielectric constants of the host and inclusion materials are equal, we see that the nonlinear coefficients of the composite are simply equal to those of the inclusion multiplied by the fill fraction f. More generally, we see that the nonlinearity of the composite material increases with f at a rate that is either more or less rapid than linear, depending upon the ratio of the linear dielectric constants. This result makes sense in that for an inhomogeneous material of our assumed topology the electric field will tend to become concentrated in regions of lower dielectric constant. For $\epsilon^i < \epsilon^h$, the electric field within the nonlinear component (the inclusion material) will be larger than the spatially averaged electric field, thus enhancing the effective nonlinearity of the composite material.

Note also that Eqs. (5.15) predict that, for the case in which only the inclusion material is nonlinear, the ratio of nonlinear coefficient A/B for the composite is equal to the ratio A^i/B^i of the inclusion material. In the next section, we shall see that in the opposite limiting case in which only the host is nonlinear, the ratio A/B for the composite is not necessarily equal to the ratio A^h/B^h for the host.

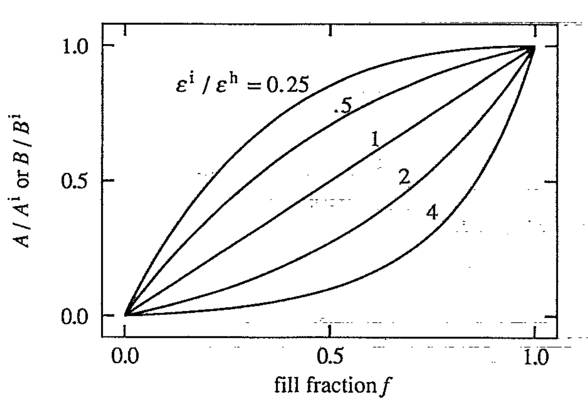

FIG. 3. Variation of the nonlinear coefficients A and B of a composite optical material with the fill fraction f for several different values of the ratios of linear permeabilities.

VI. NONLINEARITY IN THE HOST

We now consider the more complicated situation in which the host material is nonlinear with response coefficients A^h and B^h, but the inclusion material is linear. Equations (5.1)–(5.4) are then still valid, but instead of Eqs. (5.5) and (5.6) we have

$$\mathbf{p}^{\mathrm{NL}}(\mathbf{r})=\Theta^h(\mathbf{r})\mathbf{p}^{\mathrm{NL},h}(\mathbf{r}) , \tag{6.1}$$

where $\Theta^h(\mathbf{r})=1$ if the point $\mathbf{r}$ is in the host material and 0 if $\mathbf{r}$ is in an inclusion, and where

$$\mathbf{p}^{\mathrm{NL},h}(\mathbf{r})= A^h[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}^*(\mathbf{r})]\mathbf{e}(\mathbf{r})+\tfrac{1}{2}B^h[\mathbf{e}(\mathbf{r})\cdot\mathbf{e}(\mathbf{r})]\mathbf{e}^*(\mathbf{r}) . \tag{6.2}$$

As in Sec. V, it suffices to estimate $\mathbf{e}(\mathbf{r})$ in Eq. (6.2) from the results of a calculation (Sec. IV) performed neglecting the nonlinearity itself. In the linear limit $\mathbf{p}^s(\mathbf{r})=\mathbf{p}'(\mathbf{r})$, where $\mathbf{p}'(\mathbf{r})$ vanishes within the host material, so for use in Eq. (6.2) the field $\mathbf{e}(\mathbf{r})$ of Eq. (4.1) reduces to

$$\mathbf{e}(\mathbf{r})=\mathbf{E}^c(\mathbf{r})+\int \overleftrightarrow{\mathbf{T}}^c(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}'(\mathbf{r}')d\mathbf{r}' . \tag{6.3}$$

Now consider a particular inclusion, centered for simplicity at the origin. In its neighborhood a nonlinear polarization will be induced according to Eqs. (6.1)–(6.3). In evaluating the contribution from the $\overleftrightarrow{\mathbf{T}}^c$ term in Eq. (6.3), we may neglect the contributions from all the other inclusions except the one at the origin, following the arguments given in the paragraph following Eq. (4.10). So outside our particular inclusion we have

$$\mathbf{e}(\mathbf{r})=[\overleftrightarrow{\mathbf{U}}+a^3\beta\epsilon^h\overleftrightarrow{\mathbf{T}}(\mathbf{r})]\cdot\mathbf{E}^c , \tag{6.4}$$

where we have used Eq. (4.19) for the (linear) dipole moment of the inclusion, and Eq. (4.4c) for the integral over the inclusion. We have assumed we are at distances $r<b\ll R$ from our particular inclusion, so $\overleftrightarrow{\mathbf{T}}^c$ has been approximated as $\overleftrightarrow{\mathbf{T}}^0$; we shall see shortly that it is only at such distances that we get a significant contribution from the $\overleftrightarrow{\mathbf{T}}$ term in Eq. (6.4) to Eq. (6.2). The fact that $r\ll R$ has allowed us to treat $\mathbf{E}^c(\mathbf{r})$ as essentially uniform, $\mathbf{E}^c\equiv\mathbf{E}^c(\mathbf{r}=0)$.

Writing the Cartesian components of Eq. (6.4) as

$$e_i(\mathbf{r})=(\delta_{ij}+r^{-3}a^3\beta t_{ij})E_j^c , \tag{6.5}$$

where repeated indices are to be summed over, and where

$$t_{ij}\equiv(3n_in_j-\delta_{ij}) , \tag{6.6}$$

with $\mathbf{n}\equiv\mathbf{r}/r$, we can use Eqs. (6.2) and (6.5) in Eq. (6.1) to determine $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$ in the neighborhood of our particular inclusion. We find

$$\mathbf{p}^{\mathrm{NL}}(\mathbf{r})=\mathbf{p}^{\mathrm{NL}u}(\mathbf{r})+\mathbf{p}^{\mathrm{NL}d}(\mathbf{r}) , \tag{6.7}$$

where

$$\mathbf{p}^{\mathrm{NL}u}(\mathbf{r})=A^h(\mathbf{E}^c\cdot\mathbf{E}^{c*})\mathbf{E}^c+\tfrac{1}{2}B^h(\mathbf{E}^c\cdot\mathbf{E}^c)\mathbf{E}^{c*} , \tag{6.8}$$

and

$$p_m^{\mathrm{NL}d}(\mathbf{r})= A^hD_{mljk}^{\beta\beta\beta^*}(\mathbf{r})E_l^cE_j^cE_k^{c*} + \tfrac{1}{2}B^hD_{mljk}^{\beta^*\beta\beta}(\mathbf{r})E_l^{c*}E_j^cE_k^c , \tag{6.9}$$

where $D^{\beta\beta\beta^*}_{mljk}$ and $D^{\beta^*\beta\beta}_{mljk}$ are specified by Eq. (B11) of Appendix B, and the discussion following Eq. (B12). Note that $\mathbf{p}^{\mathrm{NL}u}(\mathbf{r})$ is uniform in the neighborhood of our particular inclusion, while $\mathbf{p}^{\mathrm{NL}d}(\mathbf{r})$ is a nonlinear polarization that "dresses" the inclusion, and is nonzero only close to it. Of course, there are terms in $\mathbf{p}^{\mathrm{NL}d}(\mathbf{r})$ that cancel $\mathbf{p}^{\mathrm{NL}u}(\mathbf{r})$ when $\mathbf{r}$ is inside the inclusion [see Eq. (B11) of Appendix B], since $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$ is zero there. Now we put Eq. (6.7) into the third of Eq. (2.12) to determine $\mathbf{P}^{\mathrm{NL}}(\mathbf{r})$. We treat $\mathbf{E}^c$ as uniform over the range R of $\Delta(\mathbf{r})$ [recall the discussion preceding Eq. (4.11)]; adding up the contributions from the D terms inclusion by inclusion, and neglecting the variation of Δ over the range of the D's, we find that

$$P^{\mathrm{NL}}_m = A^h(\mathbf{E}^c\cdot\mathbf{E}^{c*})E^c_m + \tfrac{1}{2}B^h(\mathbf{E}^c\cdot\mathbf{E}^c)E^{c*}_m + A^h\mathcal{N}\left[\int D^{\beta\beta\beta^*}_{mljk}(\mathbf{r}')d\mathbf{r}'\right]E^c_lE^c_jE^{c*}_k + \tfrac{1}{2}B^h\mathcal{N}\left[\int D^{\beta^*\beta\beta}_{mljk}(\mathbf{r}')d\mathbf{r}'\right]E^{c*}_lE^c_jE^c_k\ , \qquad (6.10)$$

where $\mathcal{N}\equiv f/(4\pi a^3/3)$ is the number of inclusions per unit volume. The integrals in Eq. (6.10) receive contributions only from terms in the D's that drop off as r^{-6} and r^{-9} for $r>a$; the integrals are evaluated in Appendix B and are given by Eqs. (B14). Substituting those expressions into Eq. (6.10), and using Eq. (4.17) for $\mathbf{E}^c$, we find that

$$\mathbf{P}^{\mathrm{NL}} = (\mathbf{E}\cdot\mathbf{E}^*)\mathbf{E}[A^h(1-f)+fA^h(\tfrac{11}{5}|\beta|^2+\tfrac{1}{5}\beta^2+\tfrac{1}{10}\beta|\beta|^2)+fB^h(\tfrac{12}{5}|\beta|^2+\tfrac{3}{5}\beta|\beta|^2)]\left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]$$
$$+(\mathbf{E}\cdot\mathbf{E})\mathbf{E}^*[B^h(1-f)+fB^h(2\beta^2-\tfrac{4}{5}|\beta|^2-\tfrac{1}{5}\beta|\beta|^2)+fA^h(\tfrac{3}{5}\beta^2+\tfrac{3}{5}|\beta|^2+\tfrac{3}{10}\beta|\beta|^2)]\left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]\ , \qquad (6.11)$$

where β is given by Eq. (4.7) and ϵ by Eq. (4.16). The terms $A^h(1-f)$ and $B^h(1-f)$ describe the nonlinear polarization that would result if all of the host material [fill fraction $(1-f)$] responded nonlinearly only to the cavity field; the other terms result from the "dressings of nonlinear polarization" induced above and beyond this in the neighborhood of each inclusion by its own dipole field.

To complete our expression (5.3) for the displacement field $\mathbf{D}(\mathbf{r})$, and subsequently to identify the effective-medium nonlinear-response coefficients A and B [Eq.(5.4)], we must now find $\mathbf{P}'(\mathbf{r})$. Since $\mathbf{p}'(\mathbf{r})$ is nonzero only in the inclusions [see Eq.(2.6)], we return to the consideration of one particular inclusion as discussed at the start of this section. For points $\mathbf{r}$ at $r<a$ we have

$$\mathbf{p}'(\mathbf{r}) = \frac{\epsilon^i-\epsilon^h}{4\pi}\left[\mathbf{E}^c - \frac{4\pi}{3\epsilon^h}\mathbf{p}'(\mathbf{r}) + \int \overleftrightarrow{\mathbf{T}}^c(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^s(\mathbf{r}')d\mathbf{r}'\right]\ , \qquad (6.12)$$

where we have used Eqs. (2.6), (2.8), and (4.1), as well as the fact that $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})=\mathbf{0}$ inside the inclusion; $\mathbf{E}^c$ of course is given by [see Eq. (4.2)]

$$\mathbf{E}^c = \mathbf{E} + \frac{4\pi}{3\epsilon^h}\mathbf{P}' + \frac{4\pi}{3\epsilon^h}\mathbf{P}^{\mathrm{NL}}\ , \qquad (6.13)$$

where we again neglect the variation of $\mathbf{E}^c$ over our particular inclusion. The integral in Eq. (6.12) involves $\mathbf{p}^s(\mathbf{r}) = \mathbf{p}^{\mathrm{NL}}(\mathbf{r}) + \mathbf{p}'(\mathbf{r})$. Following the arguments given after Eq. (4.10), the contribution from $\mathbf{p}'(\mathbf{r})$ is negligible and, arguing similarly with $\mathbf{p}^{\mathrm{NL}}(\mathbf{r})$ we can neglect the contributions from the dressings of nonlinear polarizations [see the discussion after Eq. (6.11)] surrounding all inclusions other than the particular one under consideration. That is, the $\mathbf{p}^s(\mathbf{r}')$ in Eq. (6.12) can be replaced by the $\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')$ given by Eq. (6.7). Doing this, and integrating Eq. (6.12) over our particular inclusion, we find

$$\boldsymbol{\mu}' = \frac{a^3}{3}(\epsilon^i-\epsilon^h)\left[\mathbf{E}^c - \frac{\boldsymbol{\mu}'}{a^3\epsilon^h} + \mathcal{E}\right]\ , \qquad (6.14)$$

where

$$\boldsymbol{\mu}' \equiv \int_{\mathrm{sphere}} \mathbf{p}'(\mathbf{r})d\mathbf{r} \qquad (6.15)$$

is the dipole moment associated with the $\mathbf{p}'(\mathbf{r})$ of our particular inclusion, and where

$$\mathcal{E} \equiv \int \overleftrightarrow{\mathbf{T}}(\mathbf{r}')\cdot\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')d\mathbf{r}'\ , \qquad (6.16)$$

with $\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')$ given by Eq. (6.7). In arriving at Eqs. (6.14) and (6.16) we have omitted the cutoff function $c(r)$ from $\overleftrightarrow{\mathbf{T}}^c$. For $\mathbf{p}^{\mathrm{NL}u}$ it is not needed, as long as we integrate Eq. (6.16) over solid angle first, since $\mathbf{p}^{\mathrm{NL}u}$ is uniform; and $\mathbf{p}^{\mathrm{NL}d}$ is confined to the neighborhood of the inclusion, so a cutoff function of range $R \gg b$ is not required. In arriving at the form of Eq. (6.16) we have also been able to use Eq. (4.4c), since $\mathbf{p}^{\mathrm{NL}}(\mathbf{r}')$ vanishes for points $\mathbf{r}'$ in the inclusion; note also that $\overleftrightarrow{\mathbf{T}}(-\mathbf{r}') = \overleftrightarrow{\mathbf{T}}(\mathbf{r}')$. As usual, we have neglected the variation of macroscopic fields over distances on the order of $a \ll R$. Putting Eqs. (3.5) and (6.7) in Eq. (6.16) we may evaluate $\mathcal{E}$; we find

$$\epsilon^h\mathcal{E}_p/4\pi = A^h\left[\int B^{\beta\beta\beta^*}_{pljk}(\mathbf{r}')d\mathbf{r}'\right]E_lE_jE^*_k \times\left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right] + \tfrac{1}{2}B^h\left[\int B^{\beta^*\beta\beta}_{pljk}(\mathbf{r}')d\mathbf{r}'\right]E^*_lE_jE_k \times\left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2\left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]\ , \qquad (6.17)$$

where the definitions of the integrals appearing in Eq. (6.17) are given in Appendix B; the values of the integrals are also worked out there [Eq. (B13)]. With these results, we find

$$\epsilon^h \mathcal{E}/4\pi = (\mathbf{E}\cdot\mathbf{E}^*)\mathbf{E}\{ A^h[\tfrac{2}{3}\beta+\tfrac{1}{15}(\beta+\beta^*)+\tfrac{1}{30}(\beta^2+2|\beta|^2)+\tfrac{7}{15}\beta|\beta|^2] + \tfrac{1}{2}B^h[\tfrac{4}{5}\beta+\tfrac{1}{5}(\beta^2+2|\beta|^2)+\tfrac{2}{15}\beta|\beta|^2]\} \left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2 \left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]$$
$$+(\mathbf{E}\cdot\mathbf{E})\mathbf{E}^*\{ A^h[\tfrac{1}{5}(\beta+\beta^*)+\tfrac{1}{10}(\beta^2+2|\beta|^2)+\tfrac{1}{15}\beta|\beta|^2] + \tfrac{1}{2}B^h[\tfrac{2}{3}\beta^*-\tfrac{4}{15}\beta-\tfrac{1}{15}(\beta^2+2|\beta|^2)+\tfrac{2}{5}\beta|\beta|^2]\} \left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2 \left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right] . \quad (6.18)$$

We now determine $\mathbf{P}'(\mathbf{r})$ by averaging $\mathbf{p}'(\mathbf{r})$. Neglecting the variation of $\Delta(\mathbf{r})$ over distances on the order a, we find that the integral (2.12) reduces to essentially a sum of the dipole moments $\boldsymbol{\mu}'$. Using Eq. (6.14) and neglecting as usual the variation of macroscopic fields over distances of the order of R, we find

$$4\pi\mathbf{P}'(\mathbf{r}) = 3\epsilon^h\beta f[\mathbf{E}^c(\mathbf{r})+\mathcal{E}(\mathbf{r})] \quad (6.19)$$

[contrast with Eq. (4.11)], where now $\mathcal{E}(\mathbf{r})$ is given as a function of $\mathbf{r}$ by Eq. (6.18). Putting Eq. (6.13) into Eq. (6.19) we find that we may write

$$\mathbf{P}'(\mathbf{r})+\mathbf{P}^{\mathrm{NL}}(\mathbf{r}) = \frac{\epsilon-\epsilon^h}{4\pi}\mathbf{E}(\mathbf{r}) + \frac{\epsilon+2\epsilon^h}{3\epsilon^h}\mathbf{P}^{\mathrm{NL}}(\mathbf{r}) + \frac{\epsilon+2\epsilon^h}{4\pi}\beta f\mathcal{E}(\mathbf{r}) , \quad (6.20)$$

where ϵ is given by Eq. (4.16), and we have used Eq. (4.7) for β; using Eq. (6.20) in Eq. (5.3) we can then write

$$\mathbf{D}(\mathbf{r}) = \epsilon\mathbf{E}(\mathbf{r}) + \mathbf{D}^{\mathrm{NL}}(\mathbf{r}) , \quad (6.21)$$

where

$$\mathbf{D}^{\mathrm{NL}}(\mathbf{r}) = \frac{\epsilon+2\epsilon^h}{3\epsilon^h}[4\pi\mathbf{P}^{\mathrm{NL}}(\mathbf{r})] + (\epsilon+2\epsilon^h)\beta f\mathcal{E}(\mathbf{r}) . \quad (6.22)$$

Substituting Eqs. (6.11) and (6.18) into (6.22) and comparing with Eq. (5.4), we may identify the nonlinear-response coefficients of the effective medium. We find

$$A = \left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2 \left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]^2 [(1-f)A^h + f(\tfrac{7}{5}\beta^2|\beta|^2+\tfrac{3}{10}\beta|\beta|^2+\tfrac{1}{10}\beta^3+\tfrac{12}{5}|\beta|^2+\tfrac{12}{5}\beta^2)A^h + f(\tfrac{2}{5}\beta^2|\beta|^2+\tfrac{9}{5}\beta|\beta|^2+\tfrac{3}{5}\beta^3+\tfrac{12}{5}|\beta|^2+\tfrac{12}{5}\beta^2)\tfrac{1}{2}B^h] ,$$
$$B = \left|\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right|^2 \left[\frac{\epsilon+2\epsilon^h}{3\epsilon^h}\right]^2 [(1-f)B^h + f(\tfrac{6}{5}\beta^2|\beta|^2-\tfrac{3}{5}\beta|\beta|^2-\tfrac{1}{5}\beta^3+\tfrac{6}{5}|\beta|^2+\tfrac{6}{5}\beta^2)B^h + f(\tfrac{1}{5}\beta^2|\beta|^2+\tfrac{9}{10}\beta|\beta|^2+\tfrac{3}{10}\beta^3+\tfrac{6}{5}|\beta|^2+\tfrac{6}{5}\beta^2)2A^h] . \quad (6.23)$$

As in the results of Sec. V, there are four "local-field correction factors" which appear in the expressions above. They are different here than in Sec. V, of course, because they apply to the local field in the *host* [see Eq. (4.17)] rather than in the *inclusion* [see Eq. (4.18)]. Beyond that, the results for the nonlinearity in the host are much more complicated because, as is clear from comparing the derivations in Secs. V and VI, the mesoscopic fields are much more complicated in the host. In particular, while if the nonlinearity is in the inclusions we have $A/B = A^i/B^i$, we do not have $A/B = A^h/B^h$ if the nonlinearity is in the host. Some of the predictions of Eqs. (6.23) are shown in Figs. 4 and 5.

In Fig. 4 we plot the enhancement in the quantity $A+\frac{1}{2}B$ [i.e., we plot $(A+\frac{1}{2}B)/(A^h+\frac{1}{2}B^h)$] as a function of the fill fraction f of inclusion material for several values of the ratio ϵ^i/ϵ^h of linear dielectric constants. We have chosen to plot the quantity $A+\frac{1}{2}B$ because it is proportional to the nonlinear refractive index "experienced" by linear polarized light; as mentioned above, in

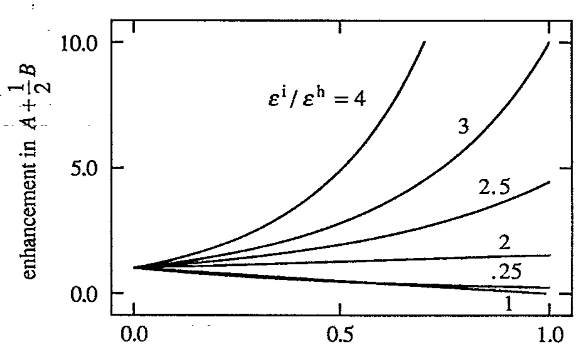

FIG. 4. Enhancement in $A+\frac{1}{2}B$ vs the fill fraction f of inclusion material for several values of the ratio ϵ^i/ϵ^h of linear susceptibilities, for the case in which the host material responds nonlinearly and the inclusion material responds linearly.

general the enhancement in A is different from the enhancement in B. Moreover, as can be verified by careful examination of Eqs. (6.23), the enhancement in $A+\frac{1}{2}B$ for a given value of f does not depend upon the ratio B^h/A^h of nonlinear coefficients of the host material; conversely, the enhancement in A or B separately does depend on the ratio B^h/A^h. For the case in which the inclusion and host have the same value of the dielectric constant, we see that $A+\frac{1}{2}B$ decreases linearly to zero as f increases from zero to one. The origin of this behavior is simply that the amount of nonlinear material decreases as the fraction of inclusion material increases. Nonetheless, for ϵ^i/ϵ^h greater than approximately 2 we find that the quantity $A+\frac{1}{2}B$ increases as the fill fraction of (linear) inclusion material increases. This effect occurs because the presence of the inclusion material modifies the electric-field distribution within the composite material in such a manner that the spatially averaged cube of the electric field within the host material is significantly increased.

Some of the tensor properties of the nonlinear response of the composite material are shown in Fig. 5. In each graph, the ratio B/A for the composite is plotted as a function of the fill fraction f for several values of the ratio ϵ^i/ϵ^h of linear dielectric constants. Parts (a), (b), and (c) of the figure refer, respectively, to the cases $B^h=0$, $B^h/A^h=1$, and $B^h/A^h=6$, and correspond physically to a nonlinear response dominated by electrostriction ($B^h=0$), electronic response in the low-frequency limit ($B^h/A^h=1$), and molecular orientation ($B^h/A^h=6$). From part (a) we see that, even when B^h vanishes, the composite can possess nonlinear coefficients A and B that are comparable in size. From part (b) we see that, for the special case $B^h/A^h=1$, the ratio of nonlinear coefficients of the composite is equal to that of the host for any value of f.

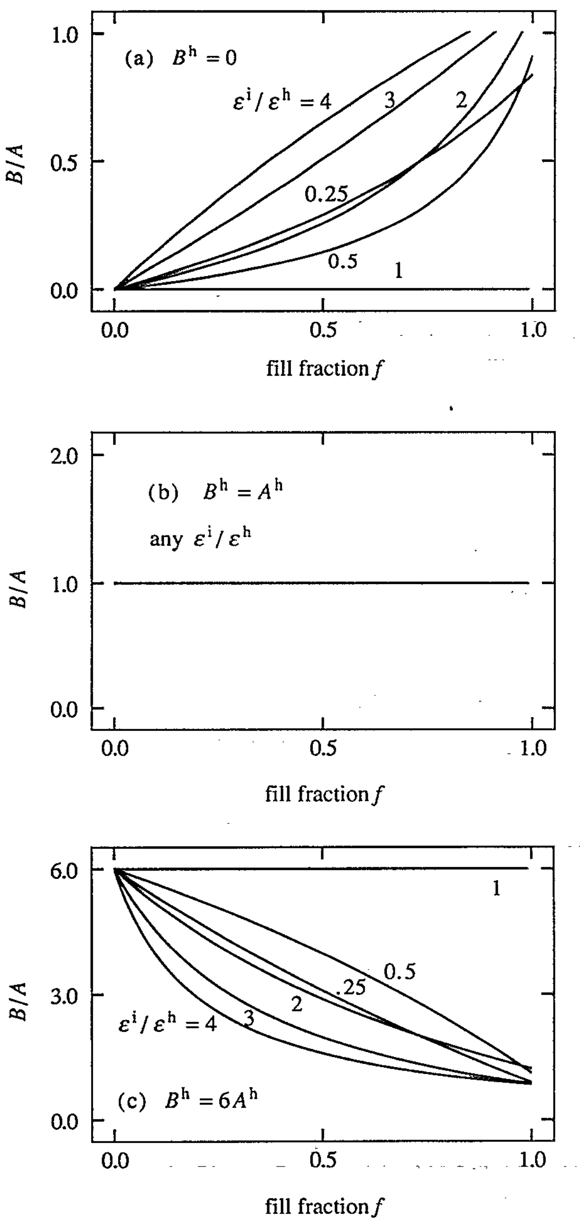

FIG. 5. Ratio B/A of nonlinear coefficients of the composite material vs the fill fraction f of inclusion material for several values of the ratio ϵ^i/ϵ^h of linear susceptibilities, for the case in which the inclusion material responds linearly and in which the host material responds nonlinearly with (a) $B^h=0$, (b) $B^h=A^h$, and (c) $B^h=6A^h$.

VII. SUMMARY

In summary, we have generalized the Maxwell Garnett theory of the optical response of composite materials by allowing either or both constituents of the material to possess a third-order nonlinear susceptibility. Equations (5.15) and (6.23), respectively, give the key results of our calculation for cases in which only the inclusion material and in which only the host material is nonlinear. It is easy to show that, if both components respond nonlinearly, the effective values of A and B are obtained by summing the two contributions given by Eqs. (5.15) and (6.23). In these equations, A and B are defined by Eq. (5.4), A^i and B^i by Eq. (5.6), A^h and B^h by Eq. (6.2), ϵ by Eq. (4.16), and β by Eq. (4.7). Our treatment takes full account of the tensor nature of the nonlinear interaction under the assumptions that each component is optically isotropic and that the composite is macroscopically isotropic. For the case in which only the inclusion material is nonlinear, our results are consistent with those of previous workers [4,7,8]. For the case in which the host material is nonlinear, the nonlinear susceptibilities A and B for the composite can be considerably larger than those of the host material itself; moreover, the ratio B/A for the composite can be very different from that of the host. We note that in all of the examples presented we have assumed that both constituents are lossless and thus that the parameters ϵ^i, ϵ^h, A^i, B^i, A^h, and B^h are all real. Nonetheless, the formulas presented here are correct even in the more general case where those parameters are complex.

ACKNOWLEDGMENTS

The authors gratefully acknowledge discussions of the contents of this paper with J. J. Maki and M. S. Malcuit.

APPENDIX A

In this appendix we derive a relation between the electric field $\mathbf{e}(\mathbf{r})$ satisfying the Maxwell equations

$$\begin{aligned}
&\nabla\cdot[\epsilon\mathbf{e}(\mathbf{r})]=-4\pi\nabla\cdot\mathbf{p}(\mathbf{r})\ ,\\
&\nabla\cdot\mathbf{b}(\mathbf{r})=0\ ,\\
&\nabla\times\mathbf{e}(\mathbf{r})-i\tilde{\omega}\mathbf{b}(\mathbf{r})=\mathbf{0}\ ,\\
&\nabla\times\mathbf{b}(\mathbf{r})+i\tilde{\omega}\epsilon\mathbf{e}(\mathbf{r})=-4\pi i\tilde{\omega}\mathbf{p}(\mathbf{r})\ ,
\end{aligned}\tag{A1}$$

and its macroscopic average $\mathbf{E}(\mathbf{r})$,

$$\mathbf{E}(\mathbf{r})=\int\Delta(\mathbf{r}-\mathbf{r}')\mathbf{e}(\mathbf{r}')d\mathbf{r}'\ .\tag{A2}$$

Equations (A1) are identical to Eqs. (2.7), with ϵ^h and $\mathbf{p}^s(\mathbf{r})$ replaced by ϵ and $\mathbf{p}(\mathbf{r})$, respectively, to simplify the notation; ϵ is taken to be uniform and, as before, $\tilde{\omega}\equiv\omega/c$. For most of this appendix [up to and including Eq. (A43)] we need assume only that $\Delta(\mathbf{r})$ is a spherically symmetric function, $\Delta(\mathbf{r})=\Delta(r)$, where $r=|\mathbf{r}|$, which vanishes sufficiently rapidly as $r\to\infty$.

A relation similar to the one we find here was considered earlier [14], where we took $\epsilon=1$ and assumed that $\mathbf{p}(\mathbf{r})$ was a sum of Dirac δ functions. Here we are interested in $\epsilon\neq1$, and in a $\mathbf{p}(\mathbf{r})$ that is continuous except for stepwise discontinuities at the surfaces of our inclusions; in the usual way $\mathbf{p}(\mathbf{r})$ is assumed to vanish as $r\to\infty$, and we are interested in solutions of Eqs. (A1) for which the particular component satisfies the usual outgoing radiation condition [17].

We begin with two forms of the solution to Eqs. (A1). The first is obtained by noting that those equations can be written as

$$\begin{aligned}
&\nabla\cdot[\epsilon\mathbf{e}(\mathbf{r})]=-4\pi\nabla\cdot\mathbf{p}(\mathbf{r})\ ,\\
&\nabla\cdot[\sqrt{\epsilon}\mathbf{b}(\mathbf{r})]=0\ ,\\
&\nabla\times[\epsilon\mathbf{e}(\mathbf{r})]-ik[\sqrt{\epsilon}\mathbf{b}(\mathbf{r})]=\mathbf{0}\ ,\\
&\nabla\times[\sqrt{\epsilon}\mathbf{b}(\mathbf{r})]+ik[\epsilon\mathbf{e}(\mathbf{r})]=-4\pi ik\mathbf{p}(\mathbf{r})\ ,
\end{aligned}\tag{A3}$$

where $k\equiv\sqrt{\epsilon}\tilde{\omega}$ is taken to have $\operatorname{Im}k\geq0$, $\operatorname{Re}k>0$ if $\operatorname{Im}k=0$. Thus the solutions for $\epsilon\mathbf{e}(\mathbf{r})$, $\sqrt{\epsilon}\mathbf{b}(\mathbf{r})$ may be recovered, upon replacement of $\tilde{\omega}$ by k, from the solutions in the $\epsilon=1$ limit. The latter solutions are well known [18], and so we identify from the solution to Eq. (A1) for $\mathbf{e}(\mathbf{r})$ as

$$\mathbf{e}(\mathbf{r})=\lim_{\eta\to0}\int_{\eta(\mathbf{r})}\overleftrightarrow{\mathbf{F}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}(\mathbf{r}')d\mathbf{r}'-\frac{4\pi}{3\epsilon}\mathbf{p}(\mathbf{r})\ ,\tag{A4}$$

with

$$\overleftrightarrow{\mathbf{F}}(\mathbf{r})\equiv\epsilon^{-1}(\nabla\nabla+\overleftrightarrow{\mathbf{U}}k^2)\frac{e^{ikr}}{r}\ ,\tag{A5}$$

where $\overleftrightarrow{\mathbf{U}}$ is the unit dyadic; in component form,

$$F_{ij}(\mathbf{r})=\epsilon^{-1}\left[\frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j}+\delta_{ij}k^2\right]\frac{e^{ikr}}{r}\ ,\tag{A6}$$

where the subscripts label Cartesian components. The notation in Eq. (A4) indicates that a small sphere of radius η, centered at $\mathbf{r}'=\mathbf{r}$, is to be excluded from the $\mathbf{r}'$ integration, and then at the end of the calculation the radius η of the excluded sphere is to be allowed to approach zero. This "excluded sphere" is necessary to make Eq. (A4) unambiguous [19], since $\overleftrightarrow{\mathbf{F}}(\mathbf{r})$ diverges (as r^{-3}) as $r\to0$. A convenient shorthand is to rewrite Eq. (A4) as

$$\mathbf{e}(\mathbf{r})=\int\overleftrightarrow{\mathbf{F}}{}^0(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}(\mathbf{r}')d\mathbf{r}'-\frac{4\pi}{3\epsilon}\mathbf{p}(\mathbf{r})\ ,\tag{A7}$$

where

$$\overleftrightarrow{\mathbf{F}}{}^0(\mathbf{r})=\begin{cases}\overleftrightarrow{\mathbf{F}}(\mathbf{r}), & r>\eta\\ 0, & r<\eta\ ,\end{cases}$$

$$\eta\to0 \text{ after evaluating the integral}\ .\tag{A8}$$

The expression (A4) or (A7) is valid at all points $\mathbf{r}$ except those (a set of measure zero) where $\mathbf{p}(\mathbf{r})$ is changing discontinuously; at such points $\mathbf{e}(\mathbf{r})$ is itself varying discontinuously in a steplike manner, as described by Eq. (A4) or (A7) as $\mathbf{r}$ moves from one side of the surface to the other. Finally, we note that we have omitted any homogeneous solution of Eqs. (A1) in writing down Eq. (A4). We continue to omit such homogeneous solutions until later in this appendix [see Eq. (A44)].

A second form of the particular solution to Eq. (A1) may be obtained by taking the curl of the third of those equations, using the identity curl curl=grad div$-\nabla^2$, and the first of Eqs. (A1) to find

$$(\nabla^2+k^2)\mathbf{e}(\mathbf{r})=-4\pi\mathbf{q}(\mathbf{r})\ ,\tag{A9}$$

where

$$\mathbf{q}(\mathbf{r})=\tilde{\omega}^2\mathbf{p}(\mathbf{r})+\epsilon^{-1}\nabla[\nabla\cdot\mathbf{p}(\mathbf{r})]\ .\tag{A10}$$

The particular solution to Eq. (A9) is well known [20],

$$\mathbf{e}(\mathbf{r})=\int\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\mathbf{q}(\mathbf{r}')d\mathbf{r}'\ .\tag{A11}$$

Strictly speaking, an excluded sphere centered at $\mathbf{r}'=\mathbf{r}$ should be specified in Eq. (A11), since the Green function $|\mathbf{r}-\mathbf{r}'|^{-1}\exp(ik|\mathbf{r}-\mathbf{r}'|)$ is undefined as $r'\to r$ [16]. But because the divergence is in practice masked by the volume element $d\mathbf{r}'$, the omission of the excluded volume here usually does not lead to difficulties. We proceed now by using Eq. (A11) to find an expression for $\mathbf{E}(\mathbf{r})$.

Using Eq. (A11) in Eq. (A2), we find

$$\mathbf{E}(\mathbf{r})=\int I(k;\mathbf{r}-\mathbf{r}')\mathbf{q}(\mathbf{r}')d\mathbf{r}'\ ,\tag{A12}$$

where

$$I(k;\mathbf{r})=\int\Delta(\mathbf{r}')\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'\ .\tag{A13}$$

Using the Green's-function expansion [21]

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}=4\pi ik\sum_{l,m}j_l(kr_<)h_l^{(1)}(kr_>)Y_{lm}^*(\Theta',\phi')Y_{lm}(\Theta,\phi)\ ,\tag{A14}$$

where $r_<$ and $r_>$ are, respectively, the lesser and greater of r and r', the Y_{lm} are the spherical harmonics, and j_l

and $h_l^{(l)}$ are, respectively, the lth-order spherical Bessel and Hankel functions of the first kind, we find

$$I(k;\mathbf{r})=4\pi ik\, h_0^{(1)}(kr)\int_{r'=0}^{r}\Delta(r')j_0(kr')(r')^2dr' + 4\pi ik\, j_0(kr)\int_{r'=r}^{\infty}\Delta(r')h_0^{(1)}(kr')(r')^2dr' , \tag{A15}$$

which shows that $I(k;\mathbf{r})$ depends only on k and $r=|\mathbf{r}|$. Writing the first integral as the difference between an integral over all r' and one between r and ∞, we use $h_0^{(1)}=(ikr)^{-1}\exp(ikr)$ to find

$$I(k;\mathbf{r})=\bar{\Delta}(k)\frac{e^{ikr}}{r}+\tilde{I}(k;\mathbf{r}) , \tag{A16}$$

where

$$\bar{\Delta}(k)=4\pi\int_0^\infty r^2\Delta(r)j_0(kr)dr=\int\Delta(r)e^{ik\hat{\mathbf{n}}\cdot\mathbf{r}}d\mathbf{r} , \tag{A17}$$

with $\hat{\mathbf{n}}$ a unit vector in an arbitrary direction, and

$$\begin{aligned}\tilde{I}(k;\mathbf{r})&= 4\pi ik\, j_0(kr)\int_{r'=r}^{\infty}\Delta(r')h_0^{(1)}(kr')(r')^2dr' - 4\pi ik\, h_0^{(1)}(kr)\int_{r'=r}^{\infty}\Delta(r')j_0(kr')(r')^2dr'\\ &=k[n_0(kr)\Delta_1(k;r)-j_0(kr)\Delta_2(k;r)] ,\end{aligned} \tag{A18}$$

where

$$\begin{aligned}\Delta_1(k;r)&\equiv 4\pi\int_{r'=r}^{\infty}\Delta(r')j_0(kr')(r')^2dr' ,\\ \Delta_2(k;r)&\equiv 4\pi\int_{r'=r}^{\infty}\Delta(r')n_0(kr')(r')^2dr' .\end{aligned} \tag{A19}$$

The second form of Eq. (A18) is obtained by using $h_0^{(1)}(x)=j_0(x)+in_0(x)$, where $n_0(x)$ is the zeroth-order spherical Bessel function of the second kind; it demonstrates that $\tilde{I}(k;r)$ is purely real.

Inserting Eq. (A16) into Eq. (A12), we find that

$$\mathbf{E}(\mathbf{r})=\bar{\Delta}(k)\int\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\mathbf{q}(\mathbf{r}')d\mathbf{r}'+\int\tilde{I}(k;\mathbf{r}-\mathbf{r}')\mathbf{q}(\mathbf{r}')d\mathbf{r}' . \tag{A20}$$

It is now convenient, for a given field point $\mathbf{r}$, to write

$$\mathbf{p}(\mathbf{r}')=\mathbf{p}^>(\mathbf{r}')+\mathbf{p}^<(\mathbf{r}') , \tag{A21}$$

where

$$\mathbf{p}^>(\mathbf{r}')=\begin{cases}\mathbf{p}(\mathbf{r}') & \text{if } |\mathbf{r}-\mathbf{r}'|>\eta\\ 0 & \text{if } |\mathbf{r}-\mathbf{r}'|<\eta ,\end{cases} \tag{A22}$$

and where for the moment η is an arbitrary positive number. We then put

$$\begin{aligned}\mathbf{q}^>(\mathbf{r}')&=\varpi^2\mathbf{p}^>(\mathbf{r}')+\epsilon^{-1}\nabla'[\nabla'\cdot\mathbf{p}^>(\mathbf{r}')] ,\\ \mathbf{e}^>(\mathbf{r})&=\int\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\mathbf{q}^>(\mathbf{r}')d\mathbf{r}' ,\\ \mathbf{E}^>(\mathbf{r})&=\bar{\Delta}(k)\int\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}\mathbf{q}^>(\mathbf{r}')d\mathbf{r}' + \int\tilde{I}(k;\mathbf{r}-\mathbf{r}')\mathbf{q}^>(\mathbf{r}')d\mathbf{r}' ,\end{aligned} \tag{A23}$$

and likewise for $\mathbf{q}^<(\mathbf{r}')$, $\mathbf{e}^<(\mathbf{r})$, and $\mathbf{E}^<(\mathbf{r})$; here $\nabla'\equiv\partial/\partial\mathbf{r}'$. Note that $\mathbf{q}^<(\mathbf{r}')$ and $\mathbf{q}^>(\mathbf{r}')$ are both singular at $|\mathbf{r}-\mathbf{r}'|=\eta$, although their sum is not. Nonetheless, since $\mathbf{p}^>(\mathbf{r}')$ vanishes at $\mathbf{r}'=\mathbf{r}$, we may insert the first of Eqs. (A23) into the first integral in the third of Eqs. (A23) and perform two partial integrations. The result is

$$\mathbf{E}^>(\mathbf{r})=\bar{\Delta}(k)\int\overleftrightarrow{\mathbf{F}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^>(\mathbf{r}')d\mathbf{r}'+\mathbf{E}^{(1)}(\mathbf{r})+\mathbf{E}^{(2)}(\mathbf{r}) , \tag{A24}$$

where

$$\begin{aligned}\mathbf{E}^{(1)}(\mathbf{r})&=\epsilon^{-1}\int\tilde{I}(k;\mathbf{r}-\mathbf{r}')\nabla'[\nabla'\cdot\mathbf{p}^>(\mathbf{r}')]d\mathbf{r}' ,\\ \mathbf{E}^{(2)}(\mathbf{r})&=\varpi^2\int\tilde{I}(k;\mathbf{r}-\mathbf{r}')\mathbf{p}^>(\mathbf{r}')d\mathbf{r}' ,\end{aligned} \tag{A25}$$

and the $\overleftrightarrow{\mathbf{F}}$ in Eq. (A24) is given by Eq. (A5). We next partially integrate the expression for $\mathbf{E}^{(1)}(\mathbf{r})$ twice, again using the fact that $\mathbf{p}^>(\mathbf{r}')$, and $\nabla'\cdot\mathbf{p}^>(\mathbf{r}')$, vanish at $\mathbf{r}'=\mathbf{r}$. The first partial integration yields

$$\mathbf{E}^{(1)}(\mathbf{r})=\epsilon^{-1}\int\nabla\tilde{I}(k;\mathbf{r}-\mathbf{r}')[\nabla'\cdot\mathbf{p}^>(\mathbf{r}')]d\mathbf{r}' , \tag{A26}$$

using $\nabla'\tilde{I}(k;\mathbf{r}-\mathbf{r}')=-\nabla\tilde{I}(k;\mathbf{r}-\mathbf{r}')$. From Eq. (A18) we find

$$\nabla\tilde{I}(k;\mathbf{r})=\hat{\mathbf{r}}\frac{\partial\tilde{I}(k;r)}{\partial r}=\hat{\mathbf{r}}f(k;r)\equiv\mathbf{V}(k;\mathbf{r}) , \tag{A27}$$

where

$$f(k;\mathbf{r})=k^2[n_0'(kr)\Delta_1(kr)-j_0'(kr)\Delta_2(kr)] , \tag{A28}$$

with $n_0'(x)\equiv dn_0(x)/dx$ and $j_0'\equiv dj_0(x)/dx$, and where we have used

$$\begin{aligned}\frac{\partial\Delta_1(k;r)}{\partial r}&=-4\pi r^2\Delta(r)j_0(kr) ,\\ \frac{\partial\Delta_2(k;r)}{\partial r}&=-4\pi r^2\Delta(r)n_0(kr)\end{aligned} \tag{A29}$$

[see Eqs. (A19)]. The second partial integration gives

$$\mathbf{E}^{(1)}(\mathbf{r})=\epsilon^{-1}\int[\mathbf{p}^>(\mathbf{r}')\cdot\nabla]\mathbf{V}(k;\mathbf{r}-\mathbf{r}')d\mathbf{r}' . \tag{A30}$$

To evaluate this expression we need the components

$$\begin{aligned}\frac{\partial V_i(k;\mathbf{r})}{\partial x_j}&=\frac{\partial}{\partial x_j}\left[\frac{x_i}{r}f(k;r)\right]\\ &=\left[\frac{\delta_{ij}}{r}-\frac{x_ix_j}{r^3}\right]f(k;r)+\frac{x_ix_j}{r^2}\frac{\partial f(k;r)}{\partial r} .\end{aligned} \tag{A31}$$

We find

$$\frac{\partial f(k;r)}{\partial r}=g(k;r)-4\pi\Delta(r) , \tag{A32}$$

where

$$g(k;r)=k^3[n_0''(kr)\Delta_1(k;r)-j_0''(kr)\Delta_2(k;r)] , \tag{A33}$$

with $n_0''(x)=dn_0'(x)/dx$, etc.; we have used Eq. (A28) and the Wronskian relation $j_0(x)n_0'(x)-j_0'(x)n_0(x)=x^{-2}$. Using Eq. (A32) in Eq. (A31) we write

$$\frac{\partial V_i(k;\mathbf{r})}{\partial x_j}=-\frac{4\pi}{3}\delta_{ij}\Delta(r)+K_{ij}(k;\mathbf{r}) , \quad \text{(A34)}$$

where

$$K_{ij}(k;\mathbf{r})=\delta_{ij}\left[\frac{f(k;r)}{r}+\frac{4\pi}{3}\Delta(r)\right]+\frac{x_ix_j}{r^2}\left[g(k;r)-\frac{f(k;r)}{r}-4\pi\Delta(r)\right] , \quad \text{(A35)}$$

and so

$$\mathbf{E}^{(1)}(\mathbf{r})=-\frac{4\pi}{3\epsilon}\mathbf{P}^{>}(\mathbf{r})+\epsilon^{-1}\int\overleftrightarrow{\mathbf{K}}(k;\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^{>}(\mathbf{r}')d\mathbf{r}' , \quad \text{(A36)}$$

where

$$\mathbf{P}^{>}(\mathbf{r})=\int\Delta(\mathbf{r}-\mathbf{r}')\mathbf{p}^{>}(\mathbf{r}')d\mathbf{r}' . \quad \text{(A37)}$$

Using Eq. (A35) in Eq. (A24) along with the second of Eqs. (A25), we find

$$\mathbf{E}^{>}(\mathbf{r})=\overline{\Delta}(k)\int\overleftrightarrow{\mathbf{F}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^{>}(\mathbf{r}')d\mathbf{r}'-\frac{4\pi}{3\epsilon}\mathbf{P}^{>}(\mathbf{r})-\int\overleftrightarrow{\mathbf{N}}(k;\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^{>}(\mathbf{r}')d\mathbf{r}' , \quad \text{(A38)}$$

where

$$\overleftrightarrow{\mathbf{N}}(k;\mathbf{r})\equiv-\epsilon^{-1}\overleftrightarrow{\mathbf{K}}(k;\mathbf{r})-\tilde{\omega}^2\overleftrightarrow{\mathbf{U}}\mathcal{I}(k;\mathbf{r}) . \quad \text{(A39)}$$

Finally using Eqs. (A18) and (A35) in Eq. (A39) we can write

$$\overleftrightarrow{\mathbf{N}}(k;\mathbf{r})=\overleftrightarrow{\mathbf{N}}^{(1)}(k;\mathbf{r})+\overleftrightarrow{\mathbf{N}}^{(2)}(k;\mathbf{r}) , \quad \text{(A40)}$$

where

$$\overleftrightarrow{\mathbf{N}}^{(1)}(k;\mathbf{r})=-\epsilon^{-1}\overleftrightarrow{\mathbf{U}}\left[\frac{k^2n_0'(kr)\Delta_1(k;r)}{r}+\frac{4\pi}{3}\Delta(r)+k^3n_0(kr)\Delta_1(k;r)\right]+\epsilon^{-1}\hat{\mathbf{r}}\hat{\mathbf{r}}\left[\frac{k^2n_0'(kr)\Delta_1(k;r)}{r}+4\pi\Delta(r)-k^3n_0''(kr)\Delta_1(k;r)\right] , \quad \text{(A41)}$$

$$\overleftrightarrow{\mathbf{N}}^{(2)}(k;\mathbf{r})=\epsilon^{-1}\overleftrightarrow{\mathbf{U}}\left[\frac{k^2j_0'(kr)\Delta_2(k;r)}{r}+k^3j_0(kr)\Delta_2(k;r)\right]-\epsilon^{-1}\hat{\mathbf{r}}\hat{\mathbf{r}}\left[\frac{k^2j_0'(kr)\Delta_2(k;r)}{r}-k^3j_0''(kr)\Delta_2(k;r)\right] .$$

We now return to Eq. (A22) and consider the effect of taking the limit $\eta\to 0$. For certain fields this must be done with some care. For example, it is *not* true that $\mathbf{e}^{<}(\mathbf{r})\to 0$ as $\eta\to 0$, because the field inside a polarized sphere centered at $\mathbf{r}$ will not vanish even as the radius of that sphere becomes vanishingly small. However, it is true that $\mathbf{E}^{<}(\mathbf{r})\to 0$ as $\eta\to 0$, since the fraction due to the sphere of the volume over which $\mathbf{e}^{<}(\mathbf{r})$ is integrated to yield $\mathbf{E}^{<}(\mathbf{r})$ vanishes as $\eta\to 0$, and of course the field outside the small sphere of polarization, but due to it, vanishes as $\eta\to 0$; thus as $\eta\to 0$ we have $\mathbf{E}^{>}(\mathbf{r})\to\mathbf{E}(\mathbf{r})$. We also have $\mathbf{P}^{>}(\mathbf{r})\to\mathbf{P}(\mathbf{r})$ as $\eta\to 0$, and

$$\lim_{\eta\to 0}\int\overleftrightarrow{\mathbf{F}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}^{>}(\mathbf{r}')d\mathbf{r}'=\mathbf{e}(\mathbf{r})+\frac{4\pi}{3\epsilon}\mathbf{p}(\mathbf{r}) , \quad \text{(A42)}$$

which follows from Eq. (A4). So in the limit $\eta\to 0$, Eq. (A38) yields

$$\mathbf{E}(\mathbf{r})+\frac{4\pi}{3\epsilon}\mathbf{P}(\mathbf{r})=\overline{\Delta}(k)\left[\mathbf{e}(\mathbf{r})+\frac{4\pi}{3\epsilon}\mathbf{p}(\mathbf{r})\right]-\int\overleftrightarrow{\mathbf{N}}^{0}(k;\mathbf{r}-\mathbf{r}')\cdot\mathbf{p}(\mathbf{r}')d\mathbf{r}' , \quad \text{(A43)}$$

where, following the convention of Eqs. (A7) and (A8), we have put

$$\overleftrightarrow{\mathbf{N}}^{0}(k;\mathbf{r})=\begin{cases}\overleftrightarrow{\mathbf{N}}(k;\mathbf{r}), & r>\eta\\ 0, & r<\eta ,\end{cases}$$

$\eta\to 0$ after evaluating the integral . (A44)

Now recall that in writing Eqs. (A4), (A7), and (A11) we have neglected a homogeneous solution of Eqs. (A1). Such a homogeneous solution $\mathbf{e}^0(\mathbf{r})$ satisfies

$$(\nabla^2+k^2)\mathbf{e}^0(\mathbf{r})=\mathbf{0} \quad \text{(A45)}$$

[cf. Eq. (A9)], and will lead to a contribution $\mathbf{E}^0(\mathbf{r})$,

$$\mathbf{E}^0(\mathbf{r})=\int\Delta(\mathbf{r}-\mathbf{r}')\mathbf{e}^0(\mathbf{r}')d\mathbf{r}' , \quad \text{(A46)}$$

to the macroscopic field. From Eq. (A45) we see that $\mathbf{e}^0(\mathbf{r})$ will be a sum (or integral) of fields of the form $\exp(ik\hat{\mathbf{n}}\cdot\mathbf{r})$, where $\hat{\mathbf{n}}$ is an arbitrary unit vector; so from Eqs. (A17) and (A46) we see that

$$\mathbf{E}^0(\mathbf{r})=\overline{\Delta}(k)\mathbf{e}^0(\mathbf{r}) . \quad \text{(A47)}$$

Thus, even if the total $\mathbf{E}(\mathbf{r})$ includes $\mathbf{E}^0(\mathbf{r})$, and the total $\mathbf{e}(\mathbf{r})$ includes $\mathbf{e}^0(\mathbf{r})$, Eq. (A43) will still hold.

The result (A43) of our manipulation is an exact result. It follows directly from the Maxwell Eqs. (A1), the condition of outgoing radiation implicit in the solutions (A4) and (A11), and the fact that the averaging function $\Delta(\mathbf{r})$ has spherical symmetry, $\Delta(\mathbf{r})=\Delta(r)$. We now approximate Eq. (A43) using the assumption that the range R of $\Delta(r)$ satisfies $kR\ll 1$. Since $\Delta_1(k;r)$ and $\Delta_2(k;r)$ will also have a range on the order of R, $\overleftrightarrow{\mathbf{N}}(k;\mathbf{r})$ will as well [see Eqs. (A40) and (A41)]. We can recover an approximation for $\overleftrightarrow{\mathbf{N}}(k;\mathbf{r})$ in the limit $kR\ll 1$ by expanding $j_0(kr)=(kr)^{-1}\sin(kr)$ and $n_0(kr)=-(kr)^{-1}\cos(kr)$ in powers of kr to obtain asymptotic series approximations for $\Delta_1(k;r)$ and then using those in Eq. (A41). For $\Delta_1(k;r)$ we find

$$\Delta_1(k;r)\sim\Delta_1(r)-\tfrac{1}{6}(kR)^2\Delta_1^{\mathrm{II}}(r)+\dots , \quad \text{(A48)}$$

where

$$\Delta_1(r)=4\pi\int_r^\infty (r')^2\Delta(r')dr' ,$$
$$\Delta_1^{\rm II}(r)=4\pi\int_r^\infty (r')^2\Delta(r')\left[\frac{r'}{R}\right]^2 dr' , \qquad (A49)$$

and, putting $\Delta_3(k;r)\equiv kr\Delta_2(k;r)$, we find

$$\Delta_3(k;r)\sim\Delta_3(r)-\tfrac{1}{2}(kR)^2\Delta_3^{\rm II}(r)+\dots , \qquad (A50)$$

where

$$\Delta_3(r)=-4\pi\int_r^\infty (r')^2\Delta(r')\left[\frac{r}{r'}\right]dr' ,$$
$$\Delta_3^{\rm II}(r)=-4\pi\int_r^\infty (r')^2\Delta(r')\left[\frac{r}{r'}\right]\left[\frac{r'}{R}\right]^2 dr' . \qquad (A51)$$

Using Eqs. (A48) and (A50) in Eqs. (A41), and expanding the spherical Bessel functions and their derivatives for small kr, we find

$$\overleftrightarrow{\rm N}^{(1)}(k;{\bf r})\sim\overleftrightarrow{\rm N}^{(1)}({\bf r})+(kR)^2\overleftrightarrow{\rm N}^{(1){\rm II}}({\bf r})+\dots , \qquad (A52)$$

where

$$\overleftrightarrow{\rm N}^{(1)}({\bf r})=\frac{3\hat{\bf r}\hat{\bf r}-\overleftrightarrow{\rm U}}{\epsilon r^3}\left[\Delta_1(r)+\frac{4\pi}{3}r^3\Delta(r)\right] ,$$
$$\overleftrightarrow{\rm N}^{(1){\rm II}}({\bf r})=\frac{\hat{\bf r}\hat{\bf r}}{\epsilon r^3}\left[\frac{1}{2}\left[\frac{r}{R}\right]^2\Delta_1(r)-\frac{1}{2}\Delta_1^{\rm II}(r)\right]$$
$$+\frac{\overleftrightarrow{\rm U}}{\epsilon r^3}\left[\frac{1}{2}\left[\frac{r}{R}\right]^2\Delta_1(r)+\frac{1}{6}\Delta_1^{\rm II}(r)\right] , \qquad (A53)$$

and

$$\overleftrightarrow{\rm N}^{2}(k;{\bf r})\sim\overleftrightarrow{\rm N}^{(2)}({\bf r})+(kR)^2\overleftrightarrow{\rm N}^{(2){\rm II}}({\bf r})+\dots , \qquad (A54)$$

where

$$\overleftrightarrow{\rm N}^{(2)}({\bf r})=0 ,$$
$$\overleftrightarrow{\rm N}^{(2){\rm II}}({\bf r})=\frac{\overleftrightarrow{\rm U}}{\epsilon r^3}\left[\frac{2}{3}\left[\frac{r}{R}\right]^2\Delta_3^{\rm II}(r)\right] . \qquad (A55)$$

We are interested only in the lowest order in kR, so we take $\overleftrightarrow{\rm N}(k;{\bf r})\to\overleftrightarrow{\rm N}^{(1)}({\bf r})$. Consistent with this we take (now assuming that $\Delta({\bf r})$ is normalized to unity [Eq. (2.10)]), $\overline{\Delta}(k)\to 1$. Our exact result (A43) then simplifies to the approximate expression

$${\bf e}({\bf r})={\bf E}^c({\bf r})-\frac{4\pi}{3\epsilon}{\bf p}({\bf r})+\int\overleftrightarrow{\rm T}^c({\bf r}\to{\bf r}')\cdot p({\bf r}')d{\bf r}' , \qquad (A56)$$

where

$${\bf E}^c({\bf r})\equiv{\bf E}({\bf r})+\frac{4\pi}{3\epsilon}{\bf P}({\bf r}) \qquad (A57)$$

is the "cavity field" that is introduced immediately in more heuristic derivations (see Sec. II), and

$${\bf T}^c({\bf r})=\overleftrightarrow{\rm T}^0({\bf r})c(r) , \qquad (A58)$$

where

$$\overleftrightarrow{\rm T}^0({\bf r})=\begin{cases}\dfrac{3\hat{\bf r}\hat{\bf r}-\overleftrightarrow{\rm U}}{\epsilon r^3}, & r>\eta\\ 0, & r<\eta ,\end{cases}$$

$\eta\to 0$ after evaluating the integral (A59)

is the static dipole-dipole coupling tensor in a background medium of dielectric constant ϵ, cut off for $r<\eta$ at the origin, and

$$c(r)=\Delta_1(r)+\frac{4\pi}{3}r^3\Delta(r) \qquad (A60)$$

is a function that cuts off at large r, $c(0)=1$, $c(r)\to 0$, as $r\to\infty$, with a range on the order of R.

APPENDIX B

In this appendix we state some geometrical formulas that are useful in calculating the nonlinear response of the host material in the neighborhood of an inclusion (see Sec. VI). Defining

$${\bf r}=x\hat{\bf x}+y\hat{\bf y}+z\hat{\bf z} ,$$
$$\hat{\bf n}\equiv{\bf r}/r=\hat{\bf x}\sin\theta\cos\phi+\hat{\bf y}\sin\theta\sin\phi+\hat{\bf z}\cos\theta , \qquad (B1)$$

where $r=|{\bf r}|$ and (θ,ϕ) are the usual angular spherical coordinates, we denote the Cartesian components of $\hat{\bf n}$ by n_i:

$$n_1=\sin\theta\cos\phi,\quad n_2=\sin\theta\sin\phi,\quad n_3=\cos\theta . \qquad (B2)$$

For any quantity $q=q(\theta,\phi)$, we define

$$\overline{q}\equiv\frac{1}{4\pi}\int q(\theta,\phi)d\Omega , \qquad (B3)$$

where $d\Omega=\sin\theta d\theta\, d\phi$ is an element of solid angle. It is then easy to verify that

$$\overline{n_i}=0 ,$$
$$\overline{n_in_j}=\tfrac{1}{3}\delta_{ij} ,$$
$$\overline{n_in_jn_k}=0 ,$$
$$\overline{n_in_jn_kn_l}=\tfrac{1}{15}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) , \qquad (B4)$$

where δ_{ij} is the Kronecker δ ($\delta_{ij}=1$ if $i=j$, $\delta_{ij}=0$ otherwise). All of the results of this appendix are based on Eqs. (B4). For example, putting [cf. Eq. (6.6)]

$$t_{ij}\equiv 3n_in_j-\delta_{ij} ,$$
$$s_{ij}\equiv t_{ik}t_{kj}=3n_in_j+\delta_{ij} , \qquad (B5)$$

where throughout this appendix repeated indices are summed over, we easily find

$$\overline{t_{ij}}=0 ,$$
$$\overline{s_{ij}}=2\delta_{ij} ,$$
$$\overline{t_{ml}t_{jk}}=\overline{t_{ml}s_{jk}}=\tfrac{3}{5}(\delta_{mj}\delta_{lk}+\delta_{mk}\delta_{lj})-\tfrac{2}{5}\delta_{ml}\delta_{jk} ,$$
$$\overline{s_{ml}s_{jk}}=\tfrac{18}{5}\delta_{ml}\delta_{jk}+\tfrac{3}{5}(\delta_{mj}\delta_{lk}+\delta_{mk}\delta_{lj}) , \qquad (B6)$$

which are used in deriving the results below.

We first define some auxiliary quantities that are useful in intermediate steps of the calculations:

$$C_{mljk}^{\alpha\beta\gamma} \equiv (\delta_{ml}+\sigma^{\alpha}t_{ml})(\delta_{ij}+\sigma^{\beta}t_{ij})(\delta_{ik}+\sigma^{\gamma}t_{ik}) ,$$
$$\sigma^{\alpha} \equiv r^{-3}a^{3}\alpha , \tag{B7}$$

where the Greek indices label a set of parameters α that are independent of r, θ, and ϕ; a is also a constant. Further, we define

$$A_{pljk}^{\alpha\beta\gamma}=r^{-3}t_{pm}C_{mljk}^{\alpha\beta\gamma} ,$$
$$F_{mljk}^{\alpha\beta\gamma}=C_{mljk}^{\alpha\beta\gamma}-\delta_{ml}\delta_{jk} . \tag{B8}$$

We can then easily determine that

$$\int_a^{\infty} r^2\overline{A_{pljk}^{\alpha\beta\gamma}}dr=\delta_{pl}\delta_{jk}[\tfrac{2}{3}\alpha-\tfrac{2}{15}(\beta+\gamma)-\tfrac{1}{15}(\alpha\beta+\alpha\gamma+\beta\gamma)+\tfrac{2}{5}\alpha\beta\gamma]$$
$$+(\delta_{pj}\delta_{lk}+\delta_{pk}\delta_{lj})[\tfrac{1}{5}(\beta+\gamma)+\tfrac{1}{10}(\alpha\beta+\alpha\gamma+\beta\gamma)+\tfrac{1}{15}\alpha\beta\gamma] , \tag{B9}$$

and

$$\int_a^{\infty} r^2\overline{F_{mljk}^{\alpha\beta\gamma}}dr=\tfrac{1}{3}a^3\delta_{ml}\delta_{jk}[2\beta\gamma-\tfrac{2}{5}(\alpha\beta+\alpha\gamma)-\tfrac{1}{5}\alpha\beta\gamma]$$
$$+\tfrac{1}{3}a^3(\delta_{mj}\delta_{lk}+\delta_{mk}\delta_{lj})$$
$$\times[\tfrac{3}{5}(\alpha\beta+\alpha\gamma)+\tfrac{3}{10}\alpha\beta\gamma] . \tag{B10}$$

Now our quantities of interest are

$$B_{pljk}^{\alpha\beta\gamma}\equiv\frac{1}{4\pi}A_{pljk}^{\alpha\beta\gamma}\Theta(r-a) ,$$
$$D_{mljk}^{\alpha\beta\gamma}\equiv-\delta_{ml}\delta_{jk}+C_{mljk}^{\alpha\beta\gamma}\Theta(r-a)$$
$$=-\delta_{ml}\delta_{jk}\Theta(a-r)+F_{mljk}^{\alpha\beta\gamma}\Theta(r-a) , \tag{B11}$$

where $\Theta(x)=0$ and 1 for $x<0$ and $x>0$, respectively. In particular, we seek

$$\int B_{pljk}^{\alpha\beta\gamma}d\mathbf{r}=\int_a^{\infty} r^2\overline{A_{mljk}^{\alpha\beta\gamma}}dr ,$$
$$\int D_{mljk}^{\alpha\beta\gamma}d\mathbf{r}=-\frac{4\pi}{3}a^3\delta_{ml}\delta_{jk}+4\pi\int_a^{\infty} r^2\overline{F_{mljk}^{\alpha\beta\gamma}}dr , \tag{B12}$$

where as usual $d\mathbf{r}=r^2dr\,d\Omega$. Using the results [(B9) and (B10)], the integrals of B and D in Eq. (B12) can be easily found. We require two particular cases for the choices of α, β, and γ. In the first we want $\alpha=\beta$, $\gamma=\beta^*$; these terms we denote by $B_{pljk}^{\beta\beta\beta^*}$ and $D_{mljk}^{\beta\beta\beta^*}$. In the second we want $\gamma=\beta$, $\alpha=\beta^*$; these terms we denote by $B_{pljk}^{\beta^*\beta\beta}$ and $D_{mljk}^{\beta^*\beta\beta}$. Collecting contributions, we find

$$\int B_{pljk}^{\beta\beta\beta^*}d\mathbf{r}=\delta_{pl}\delta_{jk}[\tfrac{2}{3}\beta-\tfrac{2}{15}(\beta+\beta^*)-\tfrac{1}{15}(\beta^2+2|\beta|^2)+\tfrac{2}{5}\beta|\beta|^2]+(\delta_{pj}\delta_{lk}+\delta_{pk}\delta_{lj})[\tfrac{1}{5}(\beta+\beta^*)+\tfrac{1}{10}(\beta^2+2|\beta|^2)+\tfrac{1}{15}\beta|\beta|^2] ,$$
$$\int B_{pljk}^{\beta^*\beta\beta}d\mathbf{r}=\delta_{pl}\delta_{jk}[\tfrac{2}{3}\beta^*-\tfrac{4}{15}\beta-\tfrac{1}{15}(\beta^2+2|\beta|^2)+\tfrac{2}{5}\beta|\beta|^2]+(\delta_{pj}\delta_{lk}+\delta_{pk}\delta_{lj})[\tfrac{2}{5}\beta+\tfrac{1}{10}(\beta^2+2|\beta|^2)+\tfrac{1}{15}\beta|\beta|^2] , \tag{B13}$$

and

$$\int D_{mljk}^{\beta\beta\beta^*}d\mathbf{r}=\frac{4\pi}{3}a^3\delta_{ml}\delta_{jk}[-1+2|\beta|^2-\tfrac{2}{5}(\beta^2+|\beta|^2)-\tfrac{1}{5}\beta|\beta|^2]+\frac{4\pi}{3}a^3(\delta_{mj}\delta_{lk}+\delta_{mk}\delta_{lj})[\tfrac{3}{5}(\beta^2+|\beta|^2)+\tfrac{3}{10}\beta|\beta|^2] ,$$
$$\int D_{mljk}^{\beta^*\beta\beta}d\mathbf{r}=\frac{4\pi}{3}a^3\delta_{ml}\delta_{jk}[-1+2\beta^2-\tfrac{4}{5}|\beta|^2-\tfrac{1}{5}\beta|\beta|^2]+\frac{4\pi}{3}a^3(\delta_{mj}\delta_{lk}+\delta_{mk}\delta_{lj})[\tfrac{6}{5}|\beta|^2+\tfrac{3}{10}\beta|\beta|^2] . \tag{B14}$$

These results are used in Sec. VI.

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