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Effective dielectric response of nonlinear composites

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A perturbative approach is developed to compute the local field for the case of a nonlinear inclusion embedded in a nonlinear host. The result is applied to nonlinear composites. General formulas for calculating the effective nonlinear susceptibility up to the case of fifth-order nonlinearity are given. The formulation is applied to problems in two dimensions (2D) and in three dimensions (3D). For 2D problems, the cases of cylindrical inclusions and concentric cylindrical inclusions are studied. By invoking an exact mapping, the problem of the concentric cylinder can be mapped onto the problem of an elliptic cylinder. A general expression of the effective nonlinear susceptibility for a dilute composite of randomly oriented elliptic cylinders embedded in a linear host is derived. For 3D problems, the cases of spherical inclusions and coated spherical inclusion are studied. General expressions for the effective nonlinear susceptibility are given in the dilute limit up to the case of fifth-order nonlinearity. For composites consisting of spherical inclusions coated by a nonlinear material and embedded in linear host, it is possible to enhance the nonlinear response of the composite by tuning material parameters such as the linear dielectric constants of the host, coating and core materials, and by adjusting the thickness of the coating.

I. INTRODUCTION

The physics of nonlinear composite systems has attracted much interest in the past few years.[1-4] A typical system is that of a composite material in which a material with nonlinear dielectric response is randomly embedded in a host medium which can be either linear or nonlinear. Such systems may be of practical importance in designing new nonlinear optical materials, because one can tune the nonlinear response by controlling parameters such as the volume fraction of the constituents. It has been suggested that the strong local field effects, such as the large local field at the surface plasmon resonance frequency of a metallic sphere, may lead to enhanced nonlinear response in a random mixture. Although most previous studies have concentrated on spherical inclusions, the effects of nonspherical shape of the inclusions have also been examined.[5,6]

In a recent paper, a systematic perturbation expansion method was developed and employed to solve electrostatic boundary-value problems of weakly nonlinear media.[7] The treatment is also applicable to nonlinearities at finite frequencies. Following Ref. 7, we assume that in some regions of the nonlinear composite media, the displacement $\mathbf{D}$ is related to the local electric field $\mathbf{E}$ by a nonlinear equation. Here we extend the assumption slightly to include the fifth-order nonlinearity:

$$\mathbf{D}=\epsilon\mathbf{E}+\chi|\mathbf{E}|^2\mathbf{E}+\eta|\mathbf{E}|^4\mathbf{E} \ , \tag{1}$$

where ϵ is the dielectric constant and χ and η are the nonlinear susceptibilities of the medium. We denote ϵ_m, χ_m, and η_m as the coefficients in the host and ϵ_i, χ_i, and η_i as those in the inclusion. These coefficients will, in general, differ from the inclusion to the host. In what follows, we use the index $m\,(i)$ for the host (inclusion) materials. Although in this work attention is focused on the case of nonlinear dielectric media at zero frequency, our results are applicable to other problems described by formally identical equations.[1-6]

For electrostatic problems, the electric field $\mathbf{E}$ satisfies

$$\nabla\times\mathbf{E}=0 \ . \tag{2}$$

From Eq. (2) there exists a potential φ such that

$$\mathbf{E}=-\nabla\varphi \ . \tag{3}$$

The displacement $\mathbf{D}$ obeys the Maxwell's equation in the absence of free charges

$$\nabla\cdot\mathbf{D}=0 \ . \tag{4}$$

The boundary conditions for the continuity of the potential φ and the displacement $\mathbf{D}$ must be applied on the surfaces of inclusions:

$$\varphi^m=\varphi^i \text{ on } \partial\Omega_i \ , \tag{5}$$

$$\hat{\mathbf{n}}\cdot\mathbf{D}^m=\hat{\mathbf{n}}\cdot\mathbf{D}^i \text{ on } \partial\Omega_i \text{ (from } \nabla\cdot\mathbf{D}=0) \ , \tag{6}$$

where the superscripts m and i denote, respectively, the quantities in the host region and in the inclusion region and $\partial\Omega_i$ denotes the surface of the inclusion.

The object of the present investigation is threefold. In a previous paper,[7] we developed a perturbation expansion method to solve the boundary-value problem of nonlinear media. We computed the electrostatic potential to second order in the expansion parameter. From this potential, the effective conductivity was computed in the limit of low inclusion concentration. Since both the local field $\mathbf{E}$ and the displacement $\mathbf{D}$ are obtained as power series in the expansion parameter, we can take one step forward to calculate the electrostatic energy density, again as a perturbation expansion. From that we derive alternative formula for the effective susceptibility. Secondly, we also extend the treatment of Ref. 1 to include the fifth-order nonlinearity. Lastly, we extend the calculations to deal with more complicated geometry—elliptic cylinders and concentric spheres.

The plan of the paper is as follows. In Sec. II, we briefly review the perturbation approach to the nonlinear problem, and derive general expressions for the nonlinear susceptibilities in an inhomogeneous medium including terms up to the case of fifth-order nonlinearity. As examples of two-dimensional problems, we study the case of concentric cylinders embedded in a host in Sec. III. It turns out that the concentric cylinder problem can be mapped onto the problem of elliptic cylinders. An expression for the effective nonlinear susceptibility of randomly oriented elliptic cylinders in a linear host medium is derived. In Sec. IV, we study the case of spherical inclusions and give expressions for the effective nonlinear susceptibilities up to the case of fifth-order nonlinearity. Section V contains a discussion of the case of concentric spheres. It is shown that if the coating material is nonlinear, it is possible to enhance the nonlinear response of a random mixture by suitably choosing the linear dielectric constants of the core, coating, and host materials so that the local field in the coating region is large. We summarize our results in Sec. VI.

II. PERTURBATION EXPANSION METHOD

In Ref. 7, the perturbation expansion method was developed to solve nonlinear electrostatic problems. The method is valid if the nonlinearities are small. Here we slightly extend the treatment to include the fifth-order term. The region of convergence can be estimated from Eq. (1). We require $|\mathbf{D}_{\rm nonlinear}|<|\mathbf{D}_{\rm linear}|$ which gives $\chi|\mathbf{E}|^2/\epsilon<1$ and $\eta|\mathbf{E}|^4/\epsilon<1$. We introduce here a dimensionless parameter λ to expand the potentials and electric fields. The expansions (in λ) for the electrostatic potential read

$$\varphi^i=\varphi_0^i+\lambda\varphi_1^i+\lambda^2\varphi_2^i+\cdots \quad \text{in } \Omega_i \;, \tag{7}$$

$$\varphi^m=\varphi_0^m+\lambda\varphi_1^m+\lambda^2\varphi_2^m+\cdots \quad \text{in } \Omega_m \;, \tag{8}$$

where Ω_i and Ω_m denote inclusion and host regions. We write the electric field as an expansion in λ

$$\mathbf{E}^\alpha=\mathbf{E}_0^\alpha+\lambda\mathbf{E}_1^\alpha+\lambda^2\mathbf{E}_2^\alpha+\cdots \quad \text{in } \Omega_\alpha,\;\; \alpha=m,i \;. \tag{9}$$

Now define the quantity

$$\begin{aligned} G^\alpha&=|\mathbf{E}^\alpha|^2=(\nabla\varphi^\alpha)\cdot(\nabla\varphi^\alpha)\\ &=G_0^\alpha+\lambda G_1^\alpha+\lambda^2G_2^\alpha+\cdots,\quad \alpha=m,i \;, \end{aligned}\tag{10}$$

where

$$G_0^\alpha=(\nabla\varphi_0^\alpha)^2 \;,$$

$$G_1^\alpha=2(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_1^\alpha) \;,$$

$$G_2^\alpha=(\nabla\varphi_1^\alpha)^2+2(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_2^\alpha) \;.$$

Then the expansion for the displacement in each region is given by

$$\mathbf{D}^\alpha=\mathbf{D}_0^\alpha+\lambda\mathbf{D}_1^\alpha+\lambda^2\mathbf{D}_2^\alpha+\cdots \;, \tag{11}$$

where

$$\mathbf{D}_0^\alpha=-\epsilon_\alpha\nabla\varphi_0^\alpha \;,$$

$$\mathbf{D}_1^\alpha=-\epsilon_\alpha\nabla\varphi_1^\alpha-\beta_\alpha G_0^\alpha\nabla\varphi_0^\alpha \;,$$

$$\mathbf{D}_2^\alpha=-\epsilon_\alpha\nabla\varphi_2^\alpha-\beta_\alpha(G_1^\alpha\nabla\varphi_0^\alpha+G_0^\alpha\nabla\varphi_1^\alpha)-\gamma_\alpha(G_0^\alpha)^2\nabla\varphi_0^\alpha \;,$$

where $\beta_\alpha=\chi_\alpha/\lambda$, $\gamma_\alpha=\eta_\alpha/\lambda^2$, and $\alpha=m,i$.

In Ref. 7, we took the divergence of Eq. (11) to obtain a hierarchy of Poisson equations for the potential. The zeroth-order potential satisfies the Laplace equation $\nabla^2\varphi_0^\alpha=0$, which together with the boundary conditions, form a standard textbook problem of a linear inclusion embedded in a linear host subject to an applied far field; they can be readily solved for simple geometries. The first-order potential satisfies a more complicated Poisson equation

$$\nabla^2\varphi_1^\alpha=-\frac{\beta_\alpha}{\epsilon_\alpha}\nabla\varphi_0^\alpha\cdot\nabla G_0^\alpha \;,$$

the solution of which depends only on the zeroth-order potential. Details of the solution can be found in Ref. 7. In the present work, we attempt an alternative approach to compute the effective dielectric constant. As the electric field $\mathbf{E}(\mathbf{x})$ and the displacement $\mathbf{D}(\mathbf{x})$ are written as perturbation expansions, we can take one step forward to compute the electrostatic energy per unit volume, $w(\mathbf{x})=\mathbf{D}(\mathbf{x})\cdot\mathbf{E}(\mathbf{x})$. We find

$$w^\alpha=\mathbf{D}^\alpha\cdot\mathbf{E}^\alpha=w_0^\alpha+\lambda w_1^\alpha+\lambda^2w_2^\alpha+\cdots \;, \tag{12}$$

where

$$w_0^\alpha=\epsilon_\alpha G_0^\alpha \;,$$

$$w_1^\alpha=\epsilon_\alpha G_1^\alpha+\beta_\alpha(G_0^\alpha)^2 \;,$$

$$w_2^\alpha=\epsilon_\alpha G_2^\alpha+2\beta_\alpha G_0^\alpha G_1^\alpha+\gamma_\alpha(G_0^\alpha)^3 \;.$$

From this we suggest a possible definition of the effective dielectric constant by relating the total electrostatic energy to the effective coefficients. Consider a homogeneous medium of coefficients ϵ_e, χ_e, $\eta_e,\ldots$, the total electrostatic energy is

$$\int_V \mathbf{D}(\mathbf{x})\cdot\mathbf{E}(\mathbf{x})d^3x=V\left[\epsilon_e\bar{\mathbf{E}}^2+\chi_e\bar{\mathbf{E}}^4+\eta_e\bar{\mathbf{E}}^6+\cdots\right] , \tag{13}$$

where $\bar{\mathbf{E}}=(1/V)\int_V\mathbf{E}(\mathbf{x})d^3x$ is the space averaged electric field. We thus identify (with $\lambda=1$) to zeroth order

$$\begin{aligned} \epsilon_e&=\frac{1}{V\bar{\mathbf{E}}^2}\int_V\epsilon_\alpha G_0^\alpha d^3x\\ &=\frac{1}{VE_0^2}\int_V\epsilon(\mathbf{x})|\nabla\varphi_0(\mathbf{x})|^2d^3x \;. \end{aligned}\tag{14}$$

To first order, we have

$$\chi_e = \frac{1}{V\bar{\mathbf{E}}^4}\int_V [\epsilon_\alpha G_1^\alpha + \chi_\alpha (G_0^\alpha)^2] d^3x \ .$$

Since $G_1^\alpha = 2\nabla\varphi_0^\alpha \cdot \nabla\varphi_1^\alpha$ and $\nabla^2\varphi_0^\alpha = 0$, one can show that the first term vanishes. We find

$$\chi_e = \frac{1}{VE_0^4}\int_V \chi(\mathbf{x}) |\nabla\varphi_0(\mathbf{x})|^4 d^3x \ , \tag{15}$$

a result which coincides with Refs. 1 and 3. It is remarkable to note that the computation of ϵ_e and χ_e depends on the zeroth-order solution $\varphi_0(\mathbf{x})$ only. This offers us a simple formula for calculating the effective nonlinear susceptibilities of more complicated geometries. To second order,

$$\eta_e = \frac{1}{V\bar{\mathbf{E}}^6}\int_V [\epsilon_\alpha G_2^\alpha + 2\chi_\alpha G_0^\alpha G_1^\alpha + \eta_\alpha (G_0^\alpha)^3] d^3x \ .$$

Again using $G_2^\alpha = (\nabla\varphi_1^\alpha)^2 + 2\nabla\varphi_0^\alpha \cdot \nabla\varphi_2^\alpha$ and $\nabla^2\varphi_0^\alpha = 0$, we find

$$\eta_e = \frac{1}{VE_0^6}\int_V [\epsilon(\mathbf{x})|\nabla\varphi_1(\mathbf{x})|^2 + 4\chi(\mathbf{x})|\nabla\varphi_0(\mathbf{x})|^2 \times \nabla\varphi_0(\mathbf{x})\cdot\nabla\varphi_1(\mathbf{x}) + \eta(\mathbf{x})|\nabla\varphi_0(\mathbf{x})|^6] d^3x \ , \tag{16}$$

which is a new result. Note that the computation of η_e depends on the first- as well as the zeroth-order solutions. We also note that η_e can be nonzero even if $\eta(\mathbf{x})$ is identically zero everywhere in the inhomogeneous medium. Equations (14)–(16) are applicable to nonlinearities at finite frequencies by taking complex $\epsilon(\mathbf{x})$, $\chi(\mathbf{x})$, and $\eta(\mathbf{x})$. We consider below several important examples to illustrate the use of the formulas in actual computations of the effective susceptibilities.

III. DIELECTRIC CYLINDERS IN UNIFORM FIELD

A. Concentric cylinders

As a simple example in two dimensions, let us consider the field for an infinite dielectric cylinder of dielectric constant ϵ_c and radius ρ_1, surrounded by a *nonlinear* dielectric layer of ϵ_s and χ_s and radius ρ_2, and embedded in a host of ϵ_m with its axis set perpendicular to a uniform far field E_0. The calculation of the zeroth-order potential is a standard problem in the literature.[8] We want to solve $\nabla^2\varphi_0^c = 0$ in Ω_c, $\nabla^2\varphi_0^s = 0$ in Ω_s, and $\nabla^2\varphi_0^m = 0$ in Ω_m subject to the boundary conditions Eqs. (5) and (6). The solution is well known[9]:

$$\varphi_0^c = -c_1 E_0 r\cos\theta, \quad r < \rho_1 \ , \tag{17a}$$

$$\varphi_0^s = -E_0(fr - gr^{-1})\cos\theta, \quad \rho_1 < r < \rho_2 \ , \tag{17b}$$

$$\varphi_0^m = -E_0(r - dr^{-1})\cos\theta, \quad r > \rho_2 \ . \tag{17c}$$

The coefficients c_1, d, f, and g can be determined from the boundary conditions. We find

$$f = \frac{2\epsilon_m z}{(\epsilon_s - \epsilon_m)x + (\epsilon_s + \epsilon_m)z} \ , \tag{18}$$

where $x = (\epsilon_c - \epsilon_s)/(\epsilon_c + \epsilon_s)$ is a dipolar factor relating the core and shell materials and $z = (\rho_2/\rho_1)^2$ is a factor related to the thickness of the shell material. We also find that $g = x\rho_1^2 f$, $c_1 = (1-x)f$, and

$$d = \frac{z\rho_1^2[(\epsilon_s + \epsilon_m)x + (\epsilon_s - \epsilon_m)z]}{(\epsilon_s - \epsilon_m)x + (\epsilon_s + \epsilon_m)z} \ .$$

When $\rho_2 \to \rho_1$, i.e., $z \to 1$, which corresponds to the case of no coating material, we recover the case of a dielectric cylinder of radius ρ_1 and dielectric constant ϵ_c embedded in a host of ϵ_m. One can show that the coefficient d becomes $\rho_1^2(\epsilon_c - \epsilon_m)/(\epsilon_c + \epsilon_m)$. By using the zeroth-order potential, we can calculate the effective susceptibilities. Let us use Eq. (15) to calculate χ_e:

$$\chi_e = \frac{1}{VE_0^4}\int_0^{2\pi} d\theta \left[\chi_s \int_{\rho_1}^{\rho_2} r|\nabla\varphi_0^s|^4 dr\right] = p\chi_s f^4 \left[\frac{-3 + 12x^2 + x^4}{3} - \frac{x^4}{3z^3} - \frac{4x^2}{z} + z\right] , \tag{19}$$

where again $x = (\epsilon_c - \epsilon_s)/(\epsilon_c + \epsilon_s)$, $z = (\rho_2/\rho_1)^2$, and $p\,(=\Omega_s/V)$ is the volume fraction of the shell. We shall discuss the enhancement of local field when we come to the more realistic case of concentric spheres.

B. Elliptic cylinders

By using the results of concentric cylinders, one can transform them into those of elliptic cylinders.[8] Consider an infinite elliptic cylinder of major axis m and minor axis n, and of dielectric constant ϵ_i and nonlinear susceptibility χ_i, embedded in a linear host of ϵ_m. The equation for the elliptic boundary can be written as

$$\frac{x_1^2}{m^2} + \frac{x_2^2}{n^2} = 1 \ .$$

Let $a^2 = m^2 - n^2$ and $b^2 = (m+n)/(m-n)$. By using complex variables $\zeta = x_1 + ix_2$, we perform the transformation[8] $\zeta = a(\zeta_1 + \zeta_1^{-1})/2$ or

$$\zeta_1 = a^{-1}[\zeta + (\zeta^2 - a^2)^{1/2}] \ . \tag{20}$$

The equation shows that at large distance from the origin, $\zeta \to a\zeta_1/2$ so that a uniform field $\varphi'(\zeta_1) = -aE_0\zeta_1/2$ transforms into *a uniform field* $\varphi(\zeta) = -E_0\zeta$ in the corresponding region. On the other hand, the elliptic boundary is transformed into a circle of radius $b > 1$, and the origin $\zeta = 0$ is transformed into a unit circle $\zeta_1 = 1$ on which $\varphi' = 0$. Thus the results of the concentric cylinder can be mapped directly onto those of the elliptic cylinder by using the complex transformation Eq. (20). For far field not parallel to either of the axes, it is clear that the desired field can be obtained by superimposing a vertical field (along x_2) of strength $E_0\sin\phi$ on a horizontal one (along x_1) of $E_0\cos\phi$, where ϕ is the angle between the direction of field with the major axis. We therefore find the field inside the elliptic inclusion

$$\mathbf{E}^i = E_0(m+n)\left[\frac{\hat{\mathbf{x}}_1\cos\phi}{m + (\epsilon_i/\epsilon_m)n} + \frac{\hat{\mathbf{x}}_2\sin\phi}{(\epsilon_i/\epsilon_m)m + n}\right] ,$$

where $\hat{\mathbf{x}}_1$ and $\hat{\mathbf{x}}_2$ are unit vectors along the major and minor axes, respectively. Note the field is *still* uniform. We can compute the effective nonlinear susceptibility for a *dilute* composite of nonlinear elliptic inclusions of concentration p quite straightforwardly:

$$\chi_e = p\chi_i (m+n)^4 \left[\left[\frac{\cos\phi}{m+(\epsilon_i/\epsilon_m)n} \right]^2 + \left[\frac{\sin\phi}{(\epsilon_i/\epsilon_m)m+n} \right]^2 \right]^2 . \tag{21}$$

In general, there may be a distribution of the angle ϕ in a composite. If so, an angular average over ϕ is needed to obtain the effective nonlinear susceptibility. For totally randomly oriented elliptic inclusions, the angular average can be easily performed to give

$$\chi_e = \frac{3}{8} p\chi_i (m+n)^4 \left\{ \left[m + \left[\frac{\epsilon_i}{\epsilon_m} \right] n \right]^{-4} + \left[\left[\frac{\epsilon_i}{\epsilon_m} \right] m + n \right]^{-4} + \frac{2}{3} \left[m + \left[\frac{\epsilon_i}{\epsilon_m} \right] n \right]^{-2} \times \left[\left[\frac{\epsilon_i}{\epsilon_m} \right] m + n \right]^{-2} \right\} . \tag{22}$$

The above formula represents a generalization of the result in dilute limit[1] to the elliptic case. Similar considerations for nonspherical inclusions in three-dimensional problems have been worked out.[5,6] In this case there exists no mapping relating the problems of concentric spheres and nonspherical inclusion.

IV. SPHERICAL INCLUSIONS

Next, we consider a simple example of a spherical inclusion of radius ρ embedded in a host, subject to a uniform external field $\mathbf{E} = E_0\hat{\mathbf{z}}$ applied along the z direction. The region $r < \rho$ is filled with a spherical inclusion of dielectric constant ϵ_i and nonlinear susceptibilities χ_i and η_i while the region $r > \rho$ is filled with a host medium of ϵ_m, χ_m, and η_m.

We want to solve $\nabla^2\varphi_0^m = 0$ in Ω_m and $\nabla^2\varphi_0^i = 0$ in Ω_i subject to the boundary condition Eqs. (5) and (6). The solution is well known[8]:

$$\varphi_0^m = -E_0(r - br^{-2})\cos\theta , \tag{23a}$$

$$\varphi_0^i = -cE_0 r\cos\theta , \tag{23b}$$

where $b = (\epsilon_i - \epsilon_m)\rho^3/(\epsilon_i + 2\epsilon_m)$, $c = 3\epsilon_m/(\epsilon_i + 2\epsilon_m)$.

By using the zeroth-order potential, we can calculate the effective susceptibilities of a dilute composite. For instance, we can calculate ϵ_e from Eq. (14). However, as pointed out by Bergman,[4] if the host has a large but finite volume $V = 4\pi R^3/3$, then there will be two types of corrections. These are small corrections of order R^{-3} and large corrections of order unity which appear near the surface of the sample.

$$\epsilon_e = \frac{1}{VE_0^2} \int_0^\pi 2\pi \sin\theta \, d\theta \left[\epsilon_i \int_0^\rho r^2 |\nabla\varphi_0^i|^2 dr + \epsilon_m \int_\rho^R r^2 |\nabla\varphi_0^m|^2 dr \right] + \frac{2\epsilon_m b\Omega_i}{V} ,$$

where the last term is the surface contribution and Ω_i is the volume of the inclusion. One finds, in the dilute limit,

$$\epsilon_e = \epsilon_m + \frac{3p\epsilon_m(\epsilon_i - \epsilon_m)}{\epsilon_i + 2\epsilon_m} , \tag{24}$$

where $p = \Omega_i/V$ is the volume fraction. Similarly, we can calculate χ_e from Eq. (15) by using the zeroth-order potential. Again there is a surface term $4\chi_m b\Omega_i/V$. We find

$$\chi_e = \chi_m + p\chi_m \left[-1 + 4b_0 + \frac{36b_0^2}{5} + \frac{8b_0^3}{5} + \frac{8b_0^4}{5} \right] + p\chi_i c^4 , \tag{25}$$

where

$$b_0 = b\rho^{-3} = (\epsilon_i - \epsilon_m)/(\epsilon_i + 2\epsilon_m)$$

is a factor related to the induced dipole moment due to the applied far field. Equation (25) has previously been obtained by Bergman.[4]

It is instructive to obtain the higher-order nonlinear susceptibility η_e by using the zeroth-order potential. This occurs when $\chi_m = \chi_i = 0$ and corresponds to the case of embedding inclusions of response $\mathbf{D} = \epsilon_i\mathbf{E} + \eta_i|\mathbf{E}|^4\mathbf{E}$ in a host medium characterized by $\mathbf{D} = \epsilon_m\mathbf{E} + \eta_m|\mathbf{E}|^4\mathbf{E}$. By using the last term of Eq. (16), we obtain (with the addition of a surface term $6\eta_m b\Omega_i/V$)

$$\eta_e = \eta_m + p\eta_m \left[-1 + 6b_0 + \frac{78b_0^2}{5} + \frac{232b_0^3}{35} + \frac{456b_0^4}{35} + \frac{192b_0^5}{35} + \frac{464b_0^6}{175} \right] + p\eta_i c^6 . \tag{26}$$

The general nonlinear problem of a nonlinear spherical inclusion embedded in a host requires much labor.[10] Interested readers are referred to Ref. 10.

In order to have some estimate of the contribution to the higher-order susceptibility due to the first-order potential, let us consider the case of a nonlinear inclusion of ϵ_i, χ_i, and η_i embedded in a *linear* host of ϵ_m. In this case $\chi_m = \eta_m = 0$ and the electrostatic potential can be solved exactly. The potential in the inclusion can be written as

$$\varphi^i = -Cr\cos\theta , \tag{27}$$

where C is a constant coefficient. Equation (27) implies that the electric field is uniform inside the inclusion, i.e., $|\nabla\varphi^i| = C$. Hence φ^i satisfies the nonlinear field equation.

The potential φ^m for the host is

$$\varphi^m = -(E_0 r - B r^{-2})\cos\theta \ , \tag{28}$$

which automatically satisfies the boundary condition at infinity. The constants B and C can be determined from boundary conditions, and we obtain

$$\chi_i C^3 + \eta_i C^5 + (\epsilon_i + 2\epsilon_m)C = 3\epsilon_m E_0 \ .$$

We find the perturbation expansion for the coefficient $C(=|\nabla\varphi^i|)$

$$C = cE_0 - \left[\frac{\chi_i}{\epsilon}\right] c^3 E_0^3 + \left[3\left[\frac{\chi_i}{\epsilon}\right]^2 - \left[\frac{\eta_i}{\epsilon}\right]\right] c^5 E_0^5 + \cdots \ , \tag{29}$$

where $\epsilon = \epsilon_i + 2\epsilon_m$. Thus, a nonzero χ_i gives corrections to the local field of the form E_0^3, E_0^5, and so on. We also find that $B = (E_0 - C)\rho^3$.

For the case of a nonlinear inclusion in a linear host, the first-order potential is therefore given by

$$\varphi_1^m = \frac{c^3 E_0^3 \rho^3 \chi_i \cos\theta}{(\epsilon_i + 2\epsilon_m) r^2} \ , \tag{30a}$$

$$\varphi_1^i = \frac{c^3 E_0^3 \chi_i r \cos\theta}{\epsilon_i + 2\epsilon_m} \ . \tag{30b}$$

By using Eq. (16) together with the expressions for the first-order potential, one can calculate η_e for a dilute composite. The result is

$$\eta_e = p\eta_i c^6 - \frac{3p\chi_i^2 c^6}{\epsilon_i + 2\epsilon_m} \ . \tag{31}$$

The last term in Eq. (31) gives the contribution to η_e due to corrections of local field in the sphere as a result of a nonzero χ_i.

V. CONCENTRIC SPHERES

Here we consider a more complicated geometry of concentric spheres.[11–14] The region $r < \rho_1$ is filled with a linear core of dielectric constant ϵ_c and the region $\rho_1 < r < \rho_2$ is filled with a *nonlinear* shell of ϵ_s, χ_s while the region $r > \rho_2$ is filled with a linear host of ϵ_m. The aim here is to calculate the effective nonlinear susceptibility χ_e. The calculation of the zeroth order potential is similar to that of Sec. III. We find

$$\varphi_0^c = -c_1 E_0 r \cos\theta, \quad r < \rho_1 \ , \tag{32a}$$

$$\varphi_0^s = -E_0(fr - gr^{-2})\cos\theta, \quad \rho_1 < r < \rho_2 \ , \tag{32b}$$

$$\varphi_0^m = -E_0(r - dr^{-2})\cos\theta, \quad r > \rho_2 \ . \tag{32c}$$

The coefficients c_1, d, f, and g are determined by the boundary conditions. We shall give the expressions for f and g only, as the calculation of χ_e only involves integration over the shell [see Eq. (15)]. The local field strength *f in the shell* has a form similar to Eq. (18), and is given by

$$f = \frac{3\epsilon_m z}{2(\epsilon_s - \epsilon_m)x + (\epsilon_s + 2\epsilon_m)z} \ , \tag{33}$$

where $x = (\epsilon_c - \epsilon_s)/(\epsilon_c + 2\epsilon_s)$ is a dipolar factor relating the core and shell materials, and $z = (\rho_2/\rho_1)^3$ is a factor related to the thickness of the shell material. We also find that $g = x\rho_1^3 f$. From Eq. (33), one can see that an enhancement of the local field occurs for $\epsilon_m > \epsilon_s$. In Fig. 1, we plot the factor f against z for different values of $\epsilon_m > \epsilon_s$ at $x = 0.7$. Large enhancement occurs for large values of the ratio ϵ_m/ϵ_s, and f decreases as the thickness increases for all cases. The dipolar factor g has similar behavior, as it is linearly related to f.

By using the zeroth-order potential, we can calculate the effective susceptibility. Using Eq. (15),

$$\chi_e = \frac{1}{VE_0^4}\int_0^\pi 2\pi \sin\theta\, d\theta \left[\chi_s \int_{\rho_1}^{\rho_2} r^2 |\nabla\varphi_0^s|^4 dr\right] = p\chi_s f^4 \left[\frac{-5 + 36x^2 + 8x^3 + 8x^4}{5} - \frac{8x^4}{5z^3} - \frac{8x^3}{5z^2} - \frac{36x^2}{5z} + z\right] \ , \tag{34}$$

where again $x = (\epsilon_c - \epsilon_s)/(\epsilon_c + 2\epsilon_s)$, $z = (\rho_2/\rho_1)^3$, and $p = \Omega_s/V$ is the volume fraction of the shells. It is instructive to obtain the small x and small $(z-1)$ series expansions for the expression in the bracket of χ_e. Let us define

$$S = \frac{-5 + 36x^2 + 8x^3 + 8x^4}{5} - \frac{8x^4}{5z^3} - \frac{8x^3}{5z^2} - \frac{36x^2}{5z} + z \ .$$

Near $x = 0$, we find a small x expansion of the form

$$S = (z-1) + \frac{36}{5}\left[1 - \frac{1}{z}\right]x^2 + \mathcal{O}(x)^3 \ ,$$

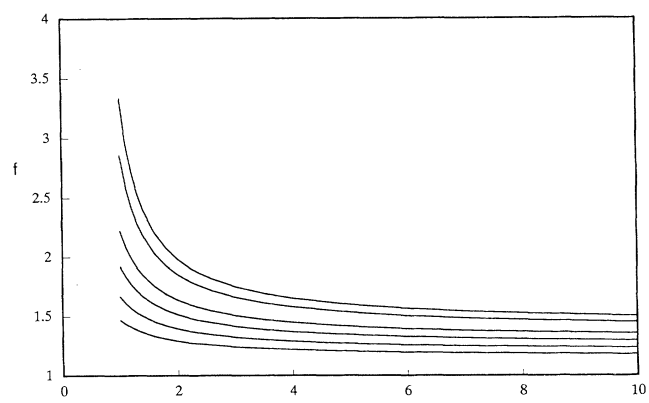

FIG. 1. The factor f, which is proportional to the local field (see text) in the shell, plotted against the thickness parameter z for various values of ϵ_m/ϵ_s at the dipolar factor $x = 0.7$. From top to bottom in order of decreasing ϵ_m to ϵ_s ratio: $\epsilon_m/\epsilon_s = 8$, $\frac{16}{3}$, $\frac{16}{5}$, $\frac{5}{2}$, 2, and $\frac{5}{3}$.

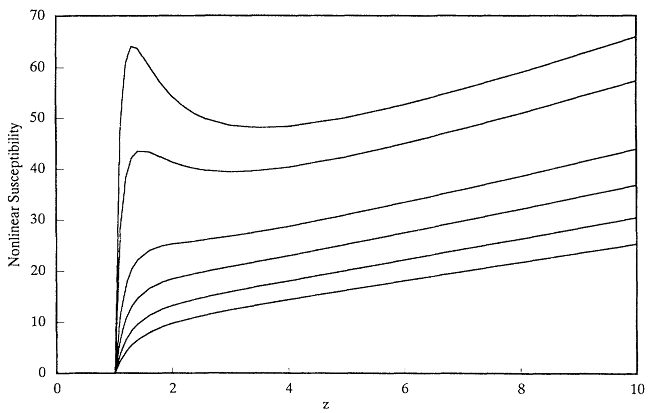

FIG. 2. The reduced nonlinear susceptibility $\chi_e/(p\chi_s)$ plotted against z for various values of ϵ_m/ϵ_s at $x=0.7$. We use the same values of ϵ_m/ϵ_s as in Fig. 1.

which is quadratic near $x=0$. This expression implies that the dielectric response has a minimum for the case when the dielectric constants of the core and the shell are equal. Near $z=1$, i.e., for a thin layer of nonlinear coating material, we find

$$S=\frac{5+36x^2+16x^3+24x^4}{5}(z-1)+\tfrac{12}{5}x^2(3+2x+4x^2)(z-1)^2+\mathcal{O}(z-1)^3 . \qquad (35)$$

From these series expansions, we can see that $S=0$ at $z=1$, which corresponds to the case of no nonlinear coating material, and S increases as z increases. For example, if $\epsilon_c=8\epsilon_s$ and $\rho_2/\rho_1=1.3$, we have $x=0.7$ and $z\approx 2$ so that $S\approx 3.5$. This enhancement factor is further increased by the factor f^4, where f is given by Eq. (33). By tuning the ratio ϵ_m/ϵ_s, the factor f can itself be enhanced.

In Fig. 2, we plot the product f^4S, which is proportional to $\chi_e/(p\chi_s)$, for different values of $\epsilon_m>\epsilon_s$ at $x=0.7$. One can see clearly that there exists a maximum in the effective nonlinear susceptibility. Thus by suitably choosing the material properties, it is possible to design a coated inclusion in which the local field in the nonlinear coating material is strong and in turn, the nonlinear response is enhanced. The criterion is that the coating should be thin, with dielectric constant $\epsilon_s<\epsilon_m$ and with a large χ_s.

We note that our results can be readily generalized to the case of finite frequencies by using a frequency dependent $\epsilon(\omega)$. In this case, the interesting possibility arises that the local field in the coating may be enhanced at some particular frequencies due to collective excitations. Application of the present formulation to composites at finite frequencies will be presented in a future publication.

The computation of the first-order potential of the concentric sphere case is more difficult but similar to the uncoated sphere case. We find

$$\varphi_1^s=-\left[\left[f_1^{(1)}r+g_1^{(1)}r^{-2}+\frac{\beta_s}{\epsilon_s}H_1^{(1)}(r)\right]P_1(\cos\theta)+\left[f_1^{(3)}r^3+g_1^{(3)}r^{-4}+\frac{\beta_s}{\epsilon_s}H_1^{(3)}(r)\right]\times P_3(\cos\theta)\right]E_0^3 , \qquad (36)$$

where

$$H_1^{(1)}(r)=\tfrac{8}{5}fg^2r^{-5}+\tfrac{2}{3}g^3r^{-8} ,$$

$$H_1^{(3)}(r)=-\tfrac{6}{5}f^2gr^{-2}+\tfrac{12}{5}fg^2r^{-5}+\tfrac{3}{11}g^3r^{-8}$$

are polynomials of order 8; $P_1(\cos\theta)$ and $P_3(\cos\theta)$ are Legendre polynomials of order 1 and 3, respectively. The coefficients $f_1^{(1)}$, $g_1^{(1)}$, $f_1^{(3)}$, and $g_1^{(3)}$ can be determined from the boundary conditions at ρ_1 and ρ_2.

VI. CONCLUSION

In conclusion, we have developed perturbation expansions to compute the effective dielectric response of nonlinear composites, and have used this formalism to treat several problems. General expressions are given for the effective linear dielectric function, and for the effective nonlinear susceptibilities. In particular, we have extended previous treatments to include fifth-order nonlinearities. Our expressions are applicable to the general case when the dielectric functions and nonlinear susceptibilities are complex. For problems in 2D, we studied the cases of cylinders and concentric cylinders embedded in a host medium. Using an exact mapping, the case of concentric cylinder can be mapped onto the case of elliptic cylinders. Expressions for the effective nonlinear susceptibility in the dilute limit for cylindrical and elliptic inclusions are given. In 3D, we studied both uncoated spherical inclusions and spherical inclusions coated with a layer of nonlinear material. We derive general expressions for the nonlinear susceptibility in terms of the linear dielectric constants of the core, coating, and host materials and the thickness of the coating. By suitably adjusting these parameters, it may be possible to enhance the nonlinear response of a composite consisting of inclusions with thin nonlinear coating embedded in a linear host medium. Applications of the present formulation to realistic composites is now under way and results will be reported in the future.

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