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Effective conductivity of nonlinear composites of spherical particles: A perturbation approach

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The perturbation expansion method is employed to compute the effective nonlinear conductivity of a random composite material characterized by a weakly nonlinear relation between the current density **J** and the electric field **E** of the form $\mathbf{J}=\sigma\mathbf{E}+\chi|\mathbf{E}|^2\mathbf{E}$, where σ and χ take on different values in the inclusion and in the host. We develop perturbation expansions to obtain analytic formulas of the potential to arbitrary order in χ. As an example, we apply the method to deal with a spherical inclusion in a host, both of either linear or nonlinear **J**-**E** relations, and obtain the potential to second order in χ. For low inclusion concentrations, we derive the effective conductivity to the first, the third, and the fifth order.

I. INTRODUCTION

There are many electrical-transport phenomena in solids in which nonlinearity plays an important role.[1–6] A typical example consists of studying a nonlinear composite medium in which an inclusion with nonlinear current-field (**J**-**E**) characteristics is randomly embedded in a host with either linear or nonlinear **J**-**E** response. Recently the macroscopic properties of nonlinear composites have attracted much interest.[3–6] Zeng *et al.*[6] proposed an approximate general method for calculating the effective nonlinear dielectric function of a random composite in which one or more of the components has a weakly nonlinear relation between the electric displacement and the external applied electric field.

In a recent paper, a perturbation expansion method was employed to solve electrostatic boundary-value problems of weakly nonlinear media,[7] in which it is assumed that in some regions of the nonlinear composite media the current density **J** is related to the local electric field **E** by the nonlinear equation (i.e., of cubic nonlinearity)

$$\mathbf{J}=\sigma\mathbf{E}+\chi|\mathbf{E}|^2\mathbf{E}\ , \tag{1}$$

where σ and χ are the first and third conductivity coefficients of the medium. In what follows, we use the index m (i) for the host (inclusion) material. Both σ and χ will in general take on different values (i.e., σ_i,χ_i in the inclusion and σ_m,χ_m in the host). In Ref. 7, we have developed the perturbation expansion method to solve the electrostatic boundary-value problem of a cylindrical inclusion embedded in a host medium. Here we want to extend the method to a more realistic system of spherical inclusions.

The above equation must be supplemented by the usual electrostatic equations, namely,

$$\nabla\cdot\mathbf{J}=0\ , \tag{2}$$

and

$$\nabla\times\mathbf{E}=0\ . \tag{3}$$

From Eq. (3), there exists a potential φ such that

$$\mathbf{E}=-\nabla\varphi\ . \tag{4}$$

The boundary conditions for the continuity of the potential φ and the current density **J** must be applied on the surfaces of inclusions:

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

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

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

The organization of the paper is as follows. In Sec. II, we follow Ref. 7 to review the perturbation expansions for the nonlinear field equations and the boundary conditions for the purpose of establishing notations. Section III deals with a simple three-dimensional example of a spherical inclusion. We discuss the general case of a nonlinear spherical inclusion embedded in a nonlinear host. We derive the analytic expansions for the potential of the inclusion in the presence of a uniform external electric field. In Sec. IV, we generalize the method of Landau and Lifshitz to calculate the effective conductivity of nonlinear composite media which is valid for a low inclusion concentration. We illustrate the method by considering several important cases.

II. PERTURBATION EXPANSION METHOD

The perturbation expansion method was originally developed for solving nonlinear harmonic-oscillator problems.[8] Here the method is extended to solve more complicated electrostatic problems, which is valid if the nonlinearities are small. Although the choice of the expansion parameter χ is merely arbitrary, it is reasonable to choose $\chi \geq \chi_m, \chi_i$. The region of convergence can be estimated from Eq. (1). We require $|\mathbf{J}_{\rm nonlinear}| < |\mathbf{J}_{\rm linear}|$, which gives $\chi|\mathbf{E}|^2/\sigma < 1$. The expansions (in χ) for the electrostatic potential read

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

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

Again, superscripts i and m denote, respectively, the quantities in the inclusion (Ω_i) and in the host regions (Ω_m). As Eq. (1) contains the factor $|\mathbf{E}|^2$, it is convenient to define the quantity

$$G^\alpha = |\mathbf{E}^\alpha|^2 = (\nabla\varphi^\alpha)\cdot(\nabla\varphi^\alpha), \quad \alpha = m, i . \tag{9}$$

Taking the gradient of Eqs. (7) and (8), we may also write the electric field as an expansion in χ:

$$\mathbf{E}^\alpha = \mathbf{E}_0^\alpha + \chi\mathbf{E}_1^\alpha + \chi^2\mathbf{E}_2^\alpha + \cdots \quad \text{in } \Omega_\alpha, \quad \alpha = m, i . \tag{10}$$

We write G^α as an expansion in χ:

$$\begin{aligned} G^\alpha &= G_0^\alpha + \chi G_1^\alpha + \chi^2 G_2^\alpha + \cdots \\ &= (\nabla\varphi_0^\alpha)^2 + 2\chi(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_1^\alpha) \\ &\quad + \chi^2[(\nabla\varphi_1^\alpha)^2 + 2(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_2^\alpha)] + \cdots . \end{aligned} \tag{11}$$

Thus the coefficients G_j^α are given by

$$G_0^\alpha = (\nabla\varphi_0^\alpha)^2 , \tag{12a}$$

$$G_1^\alpha = 2(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_1^\alpha) , \tag{12b}$$

$$G_2^\alpha = (\nabla\varphi_1^\alpha)^2 + 2(\nabla\varphi_0^\alpha)\cdot(\nabla\varphi_2^\alpha) . \tag{12c}$$

The expansion for the current density in each region is given by

$$\begin{aligned} \mathbf{J}^\alpha &= -\sigma_\alpha\nabla\varphi_0^\alpha - \chi[\sigma_\alpha\nabla\varphi_1^\alpha + \beta_\alpha G_0^\alpha\nabla\varphi_0^\alpha] \\ &\quad - \chi^2[\sigma_\alpha\nabla\varphi_2^\alpha + \beta_\alpha(G_1^\alpha\nabla\varphi_0^\alpha + G_0^\alpha\nabla\varphi_1^\alpha)] + \cdots \\ &= \mathbf{J}_0^\alpha + \chi\mathbf{J}_1^\alpha + \chi^2\mathbf{J}_2^\alpha + \cdots , \end{aligned} \tag{13}$$

where

$$\beta_\alpha = \frac{\chi_\alpha}{\chi} \quad (\alpha = m, i) \tag{14}$$

is the ratio of χ_α to the expansion parameter χ. The coefficients $\mathbf{J}_j^\alpha$ are given by

$$\mathbf{J}_0^\alpha = -\sigma_\alpha\nabla\varphi_0^\alpha , \tag{15a}$$

$$\mathbf{J}_1^\alpha = -\sigma_\alpha\nabla\varphi_1^\alpha - \beta_\alpha G_0^\alpha\nabla\varphi_0^\alpha , \tag{15b}$$

$$\mathbf{J}_2^\alpha = -\sigma_\alpha\nabla\varphi_2^\alpha - \beta_\alpha(G_1^\alpha\nabla\varphi_0^\alpha + G_0^\alpha\nabla\varphi_1^\alpha) . \tag{15c}$$

For electrostatic problems, the electric field $\mathbf{E}$ and the current density $\mathbf{J}$ must satisfy Eqs. (2) and (3). Substituting Eq. (15) into Eq. (2), we obtain the perturbation expansions in each region:

$$\sigma_\alpha\nabla^2\varphi_0^\alpha = 0 , \tag{16a}$$

$$\sigma_\alpha\nabla^2\varphi_1^\alpha + \beta_\alpha(\nabla\varphi_0^\alpha\cdot\nabla G_0^\alpha + G_0^\alpha\nabla^2\varphi_0^\alpha) = 0 , \tag{16b}$$

$$\begin{aligned} &\sigma_\alpha\nabla^2\varphi_2^\alpha + \beta_\alpha(\nabla\varphi_1^\alpha\cdot\nabla G_0^\alpha + \nabla\varphi_0^\alpha\cdot\nabla G_1^\alpha + G_1^\alpha\nabla^2\varphi_0^\alpha \\ &\qquad + G_0^\alpha\nabla^2\varphi_1^\alpha) = 0, \quad \alpha = m, i . \end{aligned} \tag{16c}$$

At the boundary, the continuity of φ and $\mathbf{J}$ must be satisfied. Substituting Eqs. (7) and (8) into Eq. (5), we obtain the boundary condition for φ_j^α:

$$\varphi_j^m = \varphi_j^i \quad \text{on } \partial\Omega_i, \quad j = 0, 1, 2, \cdots . \tag{17}$$

Similiarly, using Eq. (6), we have the following boundary condition for $\mathbf{J}_j^\alpha$:

$$\hat{\mathbf{n}}\cdot\mathbf{J}_j^m = \hat{\mathbf{n}}\cdot\mathbf{J}_j^i \quad \text{on } \partial\Omega_i, \quad j = 0, 1, 2, \cdots . \tag{18}$$

Equations (15)–(18) summarize the necessary ingredients for solving nonlinear electrostatic boundary-value problems using the perturbation expansion method. In addition, we require the electrostatic potential to yield a uniform field at infinity. The basic perturbation method is nearly the same as that in Ref. 7, but the present work has several new applications such as application to spherical (rather than cylindrical) inclusions. We shall discuss below a simple three-dimensional example to illustrate the use of the present method.

III. BOUNDARY-VALUE PROBLEMS OF A SPHERICAL INCLUSION

We consider the simple case of a spherical inclusion of radius ρ embedded in a host, subject to a uniform external electric field $\mathbf{E}_0 = \hat{\mathbf{z}}E_0$. We discuss the general case of a nonlinear spherical inclusion in a nonlinear host. For convenience in the present study, we write the corresponding boundary conditions in spherical coordinates. On the spherical surface of radius ρ, we have, up to second order in χ,

$$\sigma_m\nabla_r\varphi_0^m|_\rho = \sigma_i\nabla_r\varphi_0^i|_\rho , \tag{19a}$$

$$\sigma_m\nabla_r\varphi_1^m + \beta_m G_0^m\nabla_r\varphi_0^m|_\rho = \sigma_i\nabla_r\varphi_1^i + \beta_i G_0^i\nabla_r\varphi_0^i|_\rho , \tag{19b}$$

$$\begin{aligned} &\sigma_m\nabla_r\varphi_2^m + \beta_m(G_1^m\nabla_r\varphi_0^m + G_0^m\nabla_r\varphi_1^m)|_\rho \\ &\qquad = \sigma_i\nabla_r\varphi_2^i + \beta_i(G_1^i\nabla_r\varphi_0^i + G_0^i\nabla_r\varphi_1^i)|_\rho . \end{aligned} \tag{19c}$$

We require the solutions of the potential to be nonsingular at the origin, and the electric field at infinity to coincide with the external applied field. For the zeroth order, we want to solve using Eq. (16a),

$$\nabla^2\varphi_0^m = 0 \quad \text{in } \Omega_m$$

and

$$\nabla^2\varphi_0^i=0 \quad \text{in } \Omega_i ,$$

subject to the boundary conditions at $r=\rho$ [Eqs. (17) and (19a)],

$$\varphi_0^m|_\rho=\varphi_0^i|_\rho$$

and

$$\sigma_m\nabla_r\varphi_0^m|_\rho=\sigma_i\nabla_r\varphi_0^i|_\rho ,$$

where ρ is the radius of the spherical inclusion. This forms a standard textbook problem. We include the solution here for completeness. The general solution is given by[9]

$$\varphi_0^\alpha(r,\theta)=\sum_{l=1}^{\infty}(\mathcal{A}_l^\alpha r^l+\mathcal{B}_l^\alpha r^{-(l+1)})P_l(\cos\theta) , \quad \alpha=m,i , \tag{20}$$

where $P_l(\cos\theta)$ is the Legendre polynomial of order l; $\mathcal{A}_l^\alpha,\mathcal{B}_l^\alpha$ are constant coefficients. In order to satisfy the boundary condition at infinity ($r\to\infty$), we must have $\mathcal{A}_1^m=-E_0$ and $\mathcal{A}_l^m=0$ for all $l>1$. On the other hand, if the potential φ is nonsingular at the origin ($r=0$), we must have $\mathcal{B}_l^i=0$ for all l. Matching boundary conditions at $r=\rho$ gives

$$\varphi_0^m=-E_0(r-br^{-2})P_1(\cos\theta) , \tag{21a}$$

$$\varphi_0^i=-cE_0rP_1(\cos\theta) , \tag{21b}$$

where $P_1(\cos\theta)=\cos\theta$ is the Legendre polynomial of order $l=1$. The coefficients b and c are given by

$$b=\rho^3(\sigma_i-\sigma_m)/(\sigma_i+2\sigma_m)$$

and

$$c=3\sigma_m/(\sigma_i+2\sigma_m) .$$

To first order, using Eq. (16b), we have

$$\sigma_m\nabla^2\varphi_1^m=-\beta_m(\nabla\varphi_0^m\cdot\nabla G_0^m+G_0^m\nabla^2\varphi_0^m) \quad \text{in } \Omega_m . \tag{22}$$

Since the zeroth-order solution gives a uniform electric field inside the sphere, $\nabla G_0^i=0$. We have

$$\nabla^2\varphi_1^i=0 \quad \text{in } \Omega_i . \tag{23}$$

Equation (22) in the host is a nonhomogeneous linear differential equation; the homogeneous solution is known. For the particular solution, we need to compute the right-hand side of Eq. (22). We omit the lengthy derivations and give the results.

$$(\nabla\varphi_0^m\cdot\nabla G_0^m+G_0^m\nabla^2\varphi_0^m)$$
$$=12[(\tfrac{12}{5}b^2r^{-7}+3b^3r^{-10})P_1(\cos\theta)+(br^{-4}+\tfrac{8}{5}b^2r^{-7}+b^3r^{-10})P_3(\cos\theta)]E_0^3 ,$$

where $P_3(\cos\theta)=\frac{1}{2}(5\cos^3\theta-3\cos\theta)$ is the Legendre polynomial of order $l=3$. The particular solution of φ_1^m can be obtained:

$$\overline{\varphi}_1^m=-\frac{\beta_m}{\sigma_m}[(\tfrac{8}{5}b^2r^{-5}+\tfrac{2}{3}b^3r^{-8})P_1(\cos\theta)+(-\tfrac{6}{5}br^{-2}+\tfrac{12}{5}b^2r^{-5}+\tfrac{3}{11}b^3r^{-8})P_3(\cos\theta)]E_0^3 .$$

Combining with the homogeneous solution [Eq. (20)], the general solution of φ_1^m is given by

$$\varphi_1^m=-\left[\left[b_1^{(1)}r^{-2}+\frac{\beta_m}{\sigma_m}f_1^{(1)}(r^{-1})\right]P_1(\cos\theta)+\left[b_1^{(3)}r^{-4}+\frac{\beta_m}{\sigma_m}f_1^{(3)}(r^{-1})\right]P_3(\cos\theta)\right]E_0^3 , \tag{24}$$

where $f_1^{(1)}(y)=\frac{8}{5}b^2y^5+\frac{2}{3}b^3y^8$ and $f_1^{(3)}(y)=-\frac{6}{5}by^2+\frac{12}{5}b^2y^5+\frac{3}{11}b^3y^8$ are polynomials of order y^8. The general solution of φ_1^i inside the sphere is given by

$$\varphi_1^i=-[c_1^{(1)}rP_1(\cos\theta)+c_1^{(3)}r^3P_3(\cos\theta)]E_0^3 . \tag{25}$$

The coefficients $b_1^{(1)}$, $b_1^{(3)}$, $c_1^{(1)}$, and $c_1^{(3)}$ are determined by the boundary conditions. From $(\partial/\partial z)\varphi^m(\infty)=-E_0$ and $(\partial/\partial z)\varphi_0^m(\infty)=-E_0$, we obtain

$$\frac{\partial}{\partial z}\varphi_j^m(\infty)=0, \quad j=1,2,3\cdots . \tag{26}$$

That is, the electrostatic potential is required to yield a uniform field at infinity. We note that Eq. (24) satisfies condition (26). The boundary conditions at $r=\rho$ are

$$\varphi_1^m|_\rho=\varphi_1^i|_\rho ,$$

and

$$\sigma_m\nabla_r\varphi_1^m+\beta_mG_0^m\nabla_r\varphi_0^m|_\rho=\sigma_i\nabla_r\varphi_1^i+\beta_iG_0^i\nabla_r\varphi_0^i|_\rho .$$

The coefficients are given by

$$b_1^{(1)}=\rho^3(\sigma_iA_1^{(1)}+B_1^{(1)})/(\sigma_i+2\sigma_m) ,$$

$$c_1^{(1)}=(B_1^{(1)}-2\sigma_mA_1^{(1)})/(\sigma_i+2\sigma_m) ,$$

$$b_1^{(3)}=\rho^5(3\sigma_iA_1^{(3)}+B_1^{(3)})/(3\sigma_i+4\sigma_m) ,$$

$$c_1^{(3)}=\rho^{-2}(B_1^{(3)}-4\sigma_mA_1^{(3)})/(3\sigma_i+4\sigma_m) ,$$

where

$$A_1^{(1)}=-\frac{\beta_m}{\sigma_m}\rho^{-1}f_1^{(1)}(\rho^{-1}) .$$

$$A_1^{(3)}=-\frac{\beta_m}{\sigma_m}\rho^{-1}f_1^{(3)}(\rho^{-1}) ,$$

$$B_1^{(1)}=-\beta_m\rho^{-2}[f_1^{(1)}(\rho^{-1})]' +\beta_m(1+2b_0)(1+\tfrac{8}{5}b_0+\tfrac{14}{5}b_0^2)-\beta_i c^3 ,$$

$$B_1^{(3)}=-\beta_m\rho^{-2}[f_1^{(3)}(\rho^{-1})]'+\tfrac{6}{5}\beta_m b_0(1+2b_0)(2+b_0) ,$$

where $b_0=b\rho^{-3}=(\sigma_i-\sigma_m)/(\sigma_i+2\sigma_m)$ is a factor related to the induced dipole moment of a linear spherical inclusion subject to an applied far field, which vanishes when both media have the same linear part of conductivity; $[f_1^{(l)}(\rho^{-1})]'$ denotes the derivative of $f_1^{(l)}(y)$ with respect to y evaluated at $y=\rho^{-1}$. We observe that the constants $A_1^{(l)}$ and $B_1^{(l)}$ depend on the zeroth-order solution only. We shall see below that in fact $A_j^{(l)}$ and $B_j^{(l)}$ depend on solutions of order j-1 and lower.

To second order, we want to solve the equations

$$\sigma_m\nabla^2\varphi_2^m=-\beta_m(\nabla\varphi_1^m\cdot\nabla G_0^m+\nabla\varphi_0^m\cdot\nabla G_1^m +G_0^m\nabla^2\varphi_1^m) \text{ in } \Omega_m ,$$

and

$$\sigma_i\nabla^2\varphi_2^i=-\beta_i(\nabla\varphi_0^i\cdot\nabla G_1^i) \text{ in } \Omega_i ,$$

again owing to $\nabla G_0^i=0$. The above equations are subject to the boundary conditions at $r=\rho$:

$$\varphi_2^m|_\rho=\varphi_2^i|_\rho ,$$

$$\sigma_m\nabla_r\varphi_2^m+\beta_m(G_1^m\nabla_r\varphi_0^m+G_0^m\nabla_r\varphi_1^m)|_\rho =\sigma_i\nabla_r\varphi_2^i+\beta_i(G_1^i\nabla_r\varphi_0^i+G_0^i\nabla_r\varphi_1^i)|_\rho .$$

The general solution of φ_2^m is given by

$$\varphi_2^m=-\left[\left[b_2^{(1)}r^{-2}+\frac{\beta_m}{\sigma_m}f_2^{(1)}(r^{-1})\right]P_1(\cos\theta)+\left[b_2^{(3)}r^{-4}+\frac{\beta_m}{\sigma_m}f_2^{(3)}(r^{-1})\right]P_3(\cos\theta) +\left[b_2^{(5)}r^{-6}+\frac{\beta_m}{\sigma_m}f_2^{(5)}(r^{-1})\right]P_5(\cos\theta)\right]E_0^5 , \tag{27}$$

where $f_2^{(l)}(y)$ are polynomials of order y^{14}. The general solution of φ_2^i is given by

$$\varphi_2^i=-\left[\left[c_2^{(1)}r-\frac{6\beta_i c^2 c_1^{(3)}}{5\sigma_i}r^3\right]P_1(\cos\theta)+c_2^{(3)}r^3P_3(\cos\theta)+c_2^{(5)}r^5P_5(\cos\theta)\right]E_0^5 . \tag{28}$$

The coefficients $b_2^{(1)}$, $b_2^{(3)}$, $b_2^{(5)}$, $c_2^{(1)}$, $c_2^{(3)}$, and $c_2^{(5)}$ can be determined from the boundary conditions. We find

$$b_2^{(1)}=\rho^3(\sigma_i A_2^{(1)}+B_2^{(1)})/(\sigma_i+2\sigma_m) ,$$

$$c_2^{(1)}=(B_2^{(1)}-2\sigma_m A_2^{(1)})/(\sigma_i+2\sigma_m) ,$$

$$b_2^{(3)}=\rho^5(3\sigma_i A_2^{(3)}+B_2^{(3)})/(3\sigma_i+4\sigma_m) ,$$

$$c_2^{(3)}=\rho^{-2}(B_2^{(3)}-4\sigma_m A_2^{(3)})/(3\sigma_i+4\sigma_m) ,$$

$$b_2^{(5)}=\rho^7(5\sigma_i A_2^{(5)}+B_2^{(5)})/(5\sigma_i+6\sigma_m) ,$$

$$c_2^{(5)}=\rho^{-4}(B_2^{(5)}-6\sigma_m A_2^{(5)})/(5\sigma_i+6\sigma_m) ,$$

where $A_2^{(l)}$ and $B_2^{(l)}$ depend on constants of the first- and zeroth-order solution only. We learn through the calculations that higher-order terms of the potential can be solved by the same procedure. However, analytic formulas of the potential corresponding to the zeroth, first, and second orders of χ are sufficient from the viewpoint of practical applications and for the main purposes of our present work. The calculations also reveal some regularities in the formulas: The jth terms of χ, φ_j^m, and φ_j^i are proportional to E_0^{2j+1}, which contain the terms with $P_{2j+1}(\cos\theta)$. Based on the calculations, we observe that the general solutions of the potential are of the form

$$\varphi_j^m(r,\theta)=-E_0^{2j+1}\sum_{l=1,3,5,\cdots}^{2j+1}\left[b_j^{(l)}r^{-(l+1)}+\frac{\beta_m}{\sigma_m}f_j^{(l)}(r^{-1})\right]P_l(\cos\theta),\quad j=1,2,3,\ldots, \tag{29}$$

where $f_j^{(l)}(y)$ is a polynomial of order y^{6j+2}.

$$\varphi_j^i(r,\theta)=-E_0^{2j+1}\sum_{l=1,3,5,\cdots}^{2j+1}\left[c_j^{(l)}r^l+\frac{\beta_i}{\sigma_i}g_j^{(l)}(r)\right]P_l(\cos\theta) ,\quad j=1,2,3,\ldots, \tag{30}$$

where $g_j^{(l)}(y)$ are polynomials of order significantly lower than those of $f_j^{(l)}(y)$ due to $\nabla G_0^i=0$, i.e., the uniform zeroth-order solution in the spherical case. Note that the sums are over odd values of l only. Moreover, the particular solutions of φ_j^m and φ_j^i vanish, respectively, whenever χ_m and χ_i are equal to zero.

IV. EFFECTIVE CONDUCTIVITY AT LOW INCLUSION CONCENTRATION

In the present work, the local electric field is obtained in terms of the external uniform field by the perturbation expansion method, which should be valid in the limit of small nonlinearities. The present method offers us the opportunity to discuss the macroscopic behaviors of nonlinear composite media. For example, we can extend slightly the method of Landau and Lifshitz[10] to deal with nonlinear composite media, which is valid for low inclusion concentration.

$$\begin{aligned}\frac{1}{V}\int_{\Omega_i}&[(\sigma_i-\sigma_m)\mathbf{E}+(\chi_i-\chi_m)|\mathbf{E}|^2\mathbf{E}\\ &+(\eta_i-\eta_m)|\mathbf{E}|^4\mathbf{E}+\cdots]dV\\ &=(\sigma_e-\sigma_m)\overline{\mathbf{E}}+(\chi_e-\chi_m)|\overline{\mathbf{E}}|^2\overline{\mathbf{E}}\\ &+(\eta_e-\eta_m)|\overline{\mathbf{E}}|^4\overline{\mathbf{E}}+\cdots ,\end{aligned} \tag{31}$$

where $\overline{\mathbf{E}}$ denotes the average electric field and η_m is the fifth-order coefficient of conductivity. The present method also reveals the important fact that if two composite media have the *same* microstructure and have the *same* linear part of the conductivity both for the inclusion and the host, then they should have the *same* linear part of the effective conductivity. Let us consider a composite of spherical inclusions of density p_i. We illustrate the method by considering several important cases.

A. A linear spherical inclusion in a linear host

In this case, we have $\chi_m=\chi_i=0$. Only the zeroth-order solution survives. The local electric field is simply given by $\mathbf{E}^i=\hat{\mathbf{z}}cE_0$, which is uniform. Substituting it into Eq. (31), we obtain

$$\sigma_e=\sigma_m+3\sigma_m p_i\frac{\sigma_i-\sigma_m}{\sigma_i+2\sigma_m} , \tag{32}$$

where p_i is the concentration of the inclusions.

B. A nonlinear spherical inclusion in a nonlinear host

In this case we may choose $\chi=\chi_m$ so that $\beta_m=1$. To compute the local electric field, one can show that it is sufficient to consider the field along the z direction ($\theta=0$). Retaining the first, third, and fifth powers of E_0, one finds

$$\begin{aligned}E_z^i&=cE_0+\chi_m(c_1^{(1)}+3c_1^{(3)}z^2)E_0^3\\ &+\chi_m^2\left[c_2^{(1)}+3\left[c_2^{(3)}-\frac{6\beta_i c^2c_1^{(3)}}{5\sigma_i}\right]z^2+5c_2^{(5)}z^4\right]E_0^5 ,\\ |\mathbf{E}^i|^2E_z^i&=c^3E_0^3+3\chi_m c^2(c_1^{(1)}+3c_2^{(3)}z^2)E_0^5 .\end{aligned}$$

It is reasonable to assume that there are many inclusions of approximately the same radius in a composite medium. Therefore we have, for n inclusions,

$$\frac{1}{V}\int_{\Omega_i}r^2d^3x\approx p_i^{5/3}(V/n)^{2/3} ,$$

which vanishes as n tends to infinity. Substituting them into Eq. (31), we derive the third- and fifth-order coefficients of the conductivity. The third-order coefficient of the effective conductivity is

$$\chi_e=\chi_m+p_i[(\sigma_i-\sigma_m)\chi_m c_1^{(1)}+(\chi_i-\chi_m)c^3] , \tag{33}$$

while the fifth-order coefficient is of the form

$$\eta_e=\chi_m p_i[(\sigma_i-\sigma_m)\chi_m c_2^{(1)}+3(\chi_i-\chi_m)c^2c_1^{(1)}] . \tag{34}$$

When $\chi_i=0$, i.e., we have a linear spherical inclusion in a nonlinear host. The third and fifth coefficients are, respectively,

$$\begin{aligned}\chi_e&=\chi_m+\chi_m p_i[(\sigma_i-\sigma_m)c_1^{(1)}-c^3] ,\\ \eta_e&=\chi_m^2p_i[(\sigma_i-\sigma_m)c_2^{(1)}-3c^2c_1^{(1)}] .\end{aligned}$$

C. A nonlinear spherical inclusion in a linear host

Here $\chi_m=0$ and we may take $\chi=\chi_i$ so that $\beta_i=1$. In this case we can solve the problem exactly. The potential for the host is

$$\varphi^m=-(E_0r-Br^{-2})\cos\theta , \tag{35}$$

which automatically satisfies the boundary condition at infinity. It is easy to show that

$$\varphi^i=-Cr\cos\theta \tag{36}$$

satisfies the nonlinear field equation. The constants B and C can be determined from the boundary conditions. We have

$$\begin{aligned}&B\rho^{-2}+C\rho=E_0\rho ,\\ &2\sigma_m B\rho^{-3}-\sigma_i C-\chi_i C^3=-\sigma_m E_0 .\end{aligned}$$

Eliminating B, we obtain the equation for C:

$$\chi_i C^3+\sigma C=3\sigma_m E_0 ,$$

where $\sigma=\sigma_i+2\sigma_m$. We therefore conclude that the results for the electrostatic potential are essentially the same as those of a linear composite. They differ only by the integration constants. The solution for C can be obtained by iteration starting with $C=3\sigma_m E_0/\sigma=cE_0$, which holds when $\chi_i=0$. We find

$$\begin{aligned}C=cE_0&-\left[\frac{\chi_i}{\sigma}\right]c^3E_0^3+3\left[\frac{\chi_i}{\sigma}\right]^2c^5E_0^5\\ &-12\left[\frac{\chi_i}{\sigma}\right]^3c^7E_0^7+\cdots ;\end{aligned} \tag{37}$$

again $\sigma=\sigma_i+2\sigma_m$. We also find that $B=(E_0-C)\rho^3$, which reduces to bE_0 when $\chi_i=0$. Using the expansion for C for computing the local field and substituting it into

Eq. (31), we find the third-order coefficient of the effective conductivity

$$\chi_e = \chi_i p_i c^4 \ , \tag{38}$$

which coincides with the result of Zeng *et al.*[6] Stroud and Hui[5] made basically the same assumptions for a spherical inclusion in the nonlinear problem; they found a result [Eq. (3.2) in Ref. 5] identical to Eq. (38). Their result is valid to the first order in χ only, while we have gone further to the second order. The fifth-order coefficient is found to be

$$\eta_e = -3\chi_i \left[\frac{\chi_i}{\sigma} \right] p_i c^6 \ . \tag{39}$$

D. Nonlinear spherical problem with the same linear conductivity

Here we consider a special case in which the inclusion and the host medium have the *same* linear conductivity, i.e., $\sigma_i = \sigma_m = \Sigma$. In this case, the zeroth-order problem becomes that of a homogeneous medium and $\varphi_0^m = \varphi_0^i = -E_0 r \cos\theta$. Then $b=0$, $c=1$, and $b_0=0$. We can let $\chi=1$. From Eqs. (24) and (25), we find the first-order potential

$$\varphi_1^m = -\frac{E_0^3 \rho^3}{3\Sigma}(\chi_m - \chi_i) r^{-2} P_1(\cos\theta) \tag{40}$$

and

$$\varphi_1^i = -\frac{E_0^3}{3\Sigma}(\chi_m - \chi_i) r P_1(\cos\theta) \ . \tag{41}$$

Note the effect of $\chi_m \neq \chi_i$ alone is similar to that of $\sigma_m \neq \sigma_i$ in the linear case. The results [Eqs. (40 and (41)] can be used to obtain the effective nonlinear conductivity for the case of a composite in which the components differ only by their nonlinear susceptibilities. However, one can employ the effective-medium approximation. Consider a spherical inclusion with linear conductivity Σ and nonlinear susceptibility χ_α $(\alpha = m, i)$ embedded in a host medium of nonlinear conductivity χ_e. To first order in χ_α, the electric potential inside the sphere is

$$\varphi^\alpha = \varphi_0^\alpha - \frac{E_0^3}{3\Sigma}(\chi_e - \chi_\alpha) r P_1(\cos\theta) \ . \tag{42}$$

Let p_i be the volume fraction of material i in the composite. The effective-medium approximation amounts to the condition that the volume average of the second term in Eq. (42), which corresponds to the extra term in the electric field inside the sphere due to χ_α, vanishes. Up to the first order in χ, we have

$$p_i(\chi_e - \chi_i) + (1-p_i)(\chi_e - \chi_m) = 0 \ , \tag{43}$$

which gives

$$\chi_e = p_i \chi_i + (1-p_i)\chi_m \ , \tag{44}$$

a result which coincides with Eq. (33) when $\sigma_i = \sigma_m$. Equation (44) implies that when the inclusion and the host medium have the *same* linear conductivity, the effective nonlinear susceptibility of a random mixture is simply the *volume average* of the nonlinear susceptibilities of the constituents.

V. CONCLUSION

The perturbation expansion method is often applied to evolution behaviors of nonlinear ordinary differential systems (for example, the anharmonic oscillator). In this work, we extend this method to solve the nonlinear partial differential equations pertaining to the electrostatic boundary-value problem. We give a formalism of the perturbation expansion method which is suitable to deal with field equations and boundary conditions of the nonlinear composite media in the limit of small nonlinearities. As an example, we apply the perturbation expansion method to compute the potential in nonlinear composite media of spherical particles and obtain analytic formulas of the potential to the zeroth, first, and second order in the expansion parameter. The method can also be used to derive analytic formulas for higher-order terms of the potential.

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