Nonlinear alternating current responses of graded materials

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When a composite of nonlinear particles suspended in a host medium is subjected to a sinusoidal electric field, the electrical response in the composite will generally consist of alternating current (ac) fields at frequencies of higher-order harmonics. The situation becomes more interesting when the suspended particles are graded, with a spatial variation in the dielectric properties. The local electric field inside the graded particles can be calculated by the differential effective dipole approximation, which agrees very well with a first-principles approach. In this work, a nonlinear differential effective dipole approximation and a perturbation expansion method have been employed to investigate the effect of gradation on the nonlinear ac responses of these composites. The results showed that the fundamental and third-harmonic ac responses are sensitive to the dielectric-constant and/or nonlinear-susceptibility gradation profiles within the particles. Thus, by measuring the ac responses of the graded composites, it is possible to perform a real-time monitoring of the fabrication process of the gradation profiles within the graded particles.

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I. INTRODUCTION

Graded materials with spatial gradients in their structure [1] are abundant in Nature, and have received much attention as one of the advanced inhomogeneous composite materials in diverse engineering applications [2]. These materials can be made to realize quite different, and thus, to some extent, more useful and interesting, physical properties from the homogeneous materials. For graded materials, the traditional theories [3] for homogeneous materials do not work any longer. Recently, we presented a first-principles approach [4,5] and a differential effective dipole approximation [6,7], to investigate the dielectric properties of the graded materials. To our interest, the two methods have been demonstrated to be in excellent agreement with each other [4]. In the case of graded materials, the problem will become more complicated by the presence of nonlinearity inside them. Fortunately, for deriving the equivalent nonlinear susceptibility of graded particles, we have succeeded in putting forth a nonlinear differential effective dipole approximation (NDEDA) [8]. As expected, this NDEDA has also been demonstrated to be in excellent agreement with a first-principles approach [8].

In addition, the finite-frequency response of nonlinear composite materials has attracted much attention both in research and industrial applications during the last two decades [9]. When a composite with linear/nonlinear particles embedded in a linear/nonlinear host medium is subjected to a sinusoidal electric field, the electrical response in the composite will generally consist of alternating current (ac) fields at frequencies of higher-order harmonics [10–14]. In fact, a convenient method of probing the nonlinear characteristics of the composite is to measure the harmonics of the nonlinear polarization under the application of a sinusoidal electric field [15]. The strength of the nonlinear polarization should be reflected in the magnitude of the harmonics. For the purpose of extracting such harmonics, the perturbation expansion [12–14] and self-consistent methods [13,16] can be used.

In this work, based on the NDEDA, we shall investigate the effect of gradation (inhomogeneity) inside the particles (inclusions) on the ac responses of the graded composite by making use of a perturbation expansion method [17]. Here, the composite under consideration is composed of linear/nonlinear graded particles which are randomly embedded in a linear/nonlinear host medium in the dilute limit. To this end, it is shown that the fundamental and third-order harmonic ac responses are sensitive to the dielectric-constant (or nonlinear-susceptibility) gradation profile within the particle. Thus, by measuring the ac responses of the graded composites, it is possible to perform a real-time monitoring of the fabrication process of the gradation profiles within graded particles.

This paper is organized as follows. In Sec. II, we shall present the formalism, which is followed by the numerical results in Sec. III. In Sec. IV, the discussion and conclusion will be given.

II. FORMALISM

Let us consider nonlinear graded spherical particles with radius a and dielectric gradation profile $\tilde{\epsilon}_1(r)=\epsilon_1(r)+\chi_1(r)E_1^2$ inside it, being embedded in a nonlinear host medium of dielectric constant $\tilde{\epsilon}_2=\epsilon_2+\chi_2 E_2^2$, in the presence of a uniform external electric field E_0 along the z axis. Here $\epsilon_1(r)$ or ϵ_2 [$\chi_1(r)$ or χ_2] denotes the corresponding linear dielectric constant (nonlinear susceptibility), E_1 and E_2 stand for the local electric field inside the particles and the host medium, respectively. Note that both gradation profiles $\epsilon_1(r)$ and $\chi_1(r)$ are radial functions where $r<a$.

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Throughout the paper, we shall focus on the case of weak nonlinearity only (that is, $\chi_1(r)E_1{}^2 \ll \epsilon_1(r)$ and $\chi_2 E_2{}^2 \ll \epsilon_2$), as well as the low concentration limit.

A. Comparison between a differential effective dipole approximation and a first-principles approach

Recently, we put forth a DEDA (differential effective dipole approximation) [6,7] for calculating the equivalent dielectric constant $\overline{\epsilon}_1(r)$ [8] of the spherical graded particle of radius r. This DEDA receives the form

$$\frac{d\overline{\epsilon}_1(r)}{dr} = \frac{[\epsilon_1(r) - \overline{\epsilon}_1(r)][\overline{\epsilon}_1(r) + 2\epsilon_1(r)]}{r\epsilon_1(r)}. \quad (1)$$

Note that Eq. (1) is just the Tartar formula, derived for assemblages of spheres with varying radial and tangential conductivities [1]. In the original derivation of the Tartar formula [1], Tartar considered anisotropic spherical graded particles where the conductivity in the radial direction (thus called "radial conductivity") is different from that in the tangential direction (thus called "tangential conductivity"). It is worth noting that, in treating the composite of interest, the calculation of conductivities is mathematically the same as that of dielectric constants. So far, the equivalent $\overline{\epsilon}_1(r = a)$ for the whole graded particle can be calculated, at least numerically, by solving the differential equation [Eq. (1)], as long as $\epsilon_1(r)$ (the dielectric-constant gradation profile) is given. Once $\overline{\epsilon}_1(r = a)$ is determined, we can readily take one step forward to obtain the volume average of the linear local electric field inside the particles as

$$\langle \mathbf{E}_1{}^{(\mathrm{lin})} \rangle = \frac{3\epsilon_2}{\overline{\epsilon}_1(r=a) + 2\epsilon_2}\mathbf{E}_0, \quad (2)$$

where $\langle \cdots \rangle$ denotes the volume average. Hence, the DEDA [Eq. (1)] offers a convenient way to obtain the local electric field [Eq. (2)]. It is worth remarking that the DEDA [Eq. (1)] is valid for arbitrary gradation profiles.

To show the correctness of Eq. (2), we shall alternatively present a first-principles approach for calculating the local electric field inside the particle. For this purpose, let us take the power-law gradation profile [$\epsilon(r) = A(r/a)^n$] as a model. For this profile, the potential within the graded particle can be given by solving the electrostatic equation, $\boldsymbol{\nabla} \cdot [\epsilon_1(r)\boldsymbol{\nabla}\Phi] = 0$ [4],

$$\Phi_1(r) = -\eta_1 E_0 r^s \cos\theta, \quad r < a, \quad (3)$$

where the coefficient η_1 is determined by performing appropriate boundary conditions,

$$\eta_1 = \frac{3a^{1-s}\epsilon_2}{sA + 2\epsilon_2},$$

and $s = [\sqrt{9 + 2n + n^2} - (1+n)]/2$. Based on the relation between the linear local electric field and the potential [$\mathbf{E}_1{}^{(\mathrm{lin})}(r) = -\boldsymbol{\nabla}\Phi_1(r)$], we have

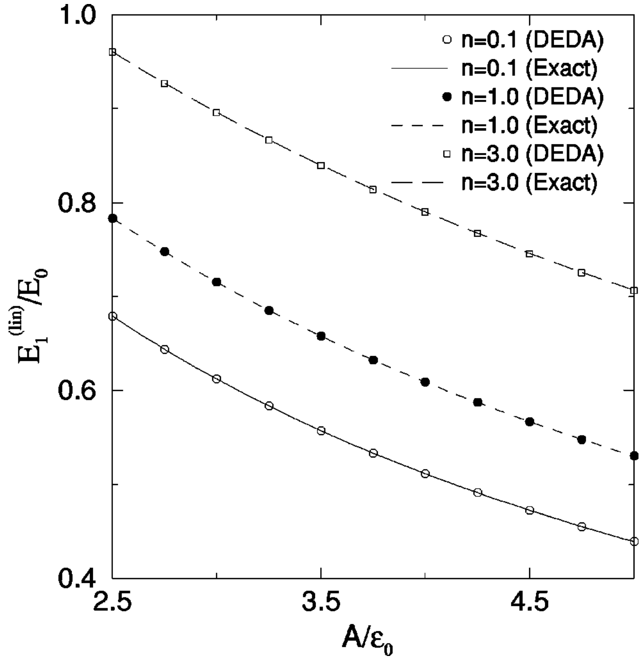

FIG. 1. For a power-law gradation profile $\epsilon_1(r) = A(r/a)^n$: a comparison between the approximate result [obtained from the DEDA, Eq. (2)] and the exact solution [predicted by a first-principles approach, Eq. (5)], for the linear electric field $E_1{}^{(\mathrm{lin})}$ plotted as a function of A for various n. Parameters: $\chi_1(0) = 0.1\epsilon_0$, $D = 0.1\epsilon_0$, and $\chi_2 = 0$.

$$\mathbf{E}_1{}^{(\mathrm{lin})}(r) = \eta_1 E_0 r^{s-1}\{[(s-1)\cos\theta\sin\theta\cos\phi]\hat{\mathbf{x}} + [(s-1) \times \cos\theta\sin\theta\sin\phi]\hat{\mathbf{y}} + [(s-1)\cos^2\theta + 1]\hat{\mathbf{z}}\}, \quad (4)$$

where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are the unit vectors along x, y, and z axes, respectively. So far, it is straightforward to obtain the volume average of the local electric field inside the particles,

$$\langle \mathbf{E}_1{}^{(\mathrm{lin})} \rangle = \frac{1}{V}\int_V \mathbf{E}_1{}^{(\mathrm{lin})}(r)\,dV, \quad (5)$$

where V is the volume of the spherical particles.

In Fig. 1, we shall numerically compare Eq. (2) (local field predicted by the DEDA) with Eq. (5) (local field obtained from the first-principles approach).

B. Nonlinear polarization and its higher harmonics

1. Nonlinear differential effective dipole approximation

In a recent work [8], we have established a NDEDA by deriving a differential equation for the equivalent nonlinear susceptibility $\overline{\chi}_1(r)$, namely,

$$\frac{d\overline{\chi}_1(r)}{dr} = \overline{\chi}_1(r)\left[\frac{4d\overline{\epsilon}_1(r)/dr}{2\epsilon_2 + \overline{\epsilon}_1(r)}\right] + \overline{\chi}_1(r)\frac{8y-3}{r} + \frac{3\chi_1(r)}{5r}\left(\frac{\overline{\epsilon}_1(r) + 2\epsilon_1(r)}{3\epsilon_1(r)}\right)^4 \times (5 + 36x^2 + 16x^3 + 24x^4), \quad (6)$$

where

$$x=\frac{\overline{\epsilon_1}(r)-\epsilon_1(r)}{\overline{\epsilon_1}(r)+2\epsilon_1(r)} \quad \text{and} \quad y=\frac{[\epsilon_1(r)-\epsilon_2][\overline{\epsilon_1}(r)-\epsilon_1(r)]}{\epsilon_1(r)[\overline{\epsilon_1}(r)+2\epsilon_2]}.$$

Similarly, $\overline{\chi_1}(r=a)$ can be obtained, at least numerically, by solving Eq. (6), once the initial conditions, namely, $\epsilon_1(r=0)$ and $\chi_1(r=0)$ are given.

In what follows, we can investigate the nonlinear ac response of the graded spherical particle by seeing it as a homogeneous particle having the constitutive relation between the displacement and the local electric field [18],

$$\mathbf{D}_1=\overline{\epsilon_1}(r=a)\mathbf{E}_1+\overline{\chi_1}(r=a)E_1{}^2\mathbf{E}_1\equiv\tilde{\overline{\epsilon_1}}(r=a)\mathbf{E}_1,$$

where $\overline{\epsilon_1}(r=a)$ and $\overline{\chi_1}(r=a)$ are determined by Eqs. (1) and (6), respectively. For the sake of convenience, we shall represent $\overline{\epsilon_1}(r=a)$ by $\overline{\epsilon_1}$, $\tilde{\overline{\epsilon_1}}(r=a)$ by $\tilde{\overline{\epsilon_1}}$ as well as $\overline{\chi_1}(r=a)$ by $\overline{\chi_1}$, if there are no special instructions.

2. Nonlinear ac responses

If we apply a sinusoidal electric field like

$$E_0(t)=E_0\sin(\omega t), \tag{7}$$

the local electric field $\sqrt{\langle E_1{}^2\rangle}$ and the induced dipole moment

$$\tilde{p}=\tilde{\epsilon}_e a^3\frac{\tilde{\overline{\epsilon_1}}-\tilde{\epsilon}_2}{\tilde{\overline{\epsilon_1}}+2\tilde{\epsilon}_2}E_0 \tag{8}$$

will depend on time sinusoidally, too. Here the effective dielectric constant of the system ($\tilde{\epsilon}_e$) is given by the following dilute-limit expression:

$$\tilde{\epsilon}_e=\tilde{\epsilon}_2+3\tilde{\epsilon}_2 f\frac{\tilde{\overline{\epsilon_1}}-\tilde{\epsilon}_2}{\tilde{\overline{\epsilon_1}}+2\tilde{\epsilon}_2}, \tag{9}$$

where f is the volume fraction of the particles. By virtue of the inversion symmetry, the local electric field is a superposition of odd-order harmonics such that

$$\sqrt{\langle E_1{}^2\rangle}=E_\omega\sin(\omega t)+E_{3\omega}\sin(3\omega t)+\cdots. \tag{10}$$

Similarly, the induced dipole moment contains harmonics like

$$\tilde{p}=p_\omega\sin(\omega t)+p_{3\omega}\sin(3\omega t)+\cdots. \tag{11}$$

These harmonics coefficients can be extracted from the time dependence of the solution of $\sqrt{\langle E_1{}^2\rangle}$ and $\tilde{p}$.

3. Analytic solutions for the nonlinear ac responses

In what follows, we will perform a perturbation expansion method to extract the third harmonics of the local electric field and the induced dipole moment. It is known that the perturbation expansion method is applicable to weak nonlinearity only, limited by the convergence of the series expansion.

Let us start from the dilute-limit expression for the effective linear dielectric constant (ϵ_e) of the system of interest, namely, Eq. (9), where $\overline{\chi_1}=\chi_2=0$.

Next, we obtain the linear local electric fields $\langle E_1{}^2\rangle$ and $\langle E_2{}^2\rangle$, respectively:

$$\langle E_1{}^2\rangle=\frac{E_0{}^2}{f}\frac{\partial\epsilon_e}{\partial\overline{\epsilon_1}}\equiv F(\overline{\epsilon_1},\epsilon_2,f,E_0), \tag{12}$$

$$\langle E_2{}^2\rangle=\frac{E_0{}^2}{1-f}\frac{\partial\epsilon_e}{\partial\epsilon_2}\equiv G(\overline{\epsilon_1},\epsilon_2,f,E_0). \tag{13}$$

In view of the existence of nonlinearity inside the two components, we readily obtain the following local electric fields for the nonlinear particle and host, respectively:

$$\langle E_1{}^2\rangle=F(\tilde{\overline{\epsilon_1}},\tilde{\epsilon}_2,f,E_0), \tag{14}$$

$$\langle E_2{}^2\rangle=G(\tilde{\overline{\epsilon_1}},\tilde{\epsilon}_2,f,E_0). \tag{15}$$

For the below series expansions, we will take $\tilde{\overline{\epsilon_1}}=\overline{\epsilon_1}+\overline{\chi_1}E_1{}^2\approx\overline{\epsilon_1}+\overline{\chi_1}\langle E_1{}^2\rangle$ and $\tilde{\epsilon}_2=\epsilon_2+\chi_2E_2{}^2\approx\epsilon_2+\chi_2\langle E_2{}^2\rangle$, in Eqs. (14) and (15), where $\langle\cdots\rangle$ denotes the volume average of $\cdots$. Let us expand the local electric field $\langle E_1{}^2\rangle$ and $\langle E_2{}^2\rangle$ into a Taylor expansion, taking $\overline{\chi_1}\langle E_1{}^2\rangle$ and $\chi_2\langle E_2{}^2\rangle$ as the perturbative quantities:

$$\langle E_1{}^2\rangle=F(\overline{\epsilon_1},\epsilon_2,f,E_0)+\frac{\partial}{\partial\tilde{\overline{\epsilon_1}}}F(\tilde{\overline{\epsilon_1}},\epsilon_2,f,E_0)|_{\tilde{\overline{\epsilon_1}}=\overline{\epsilon_1}}\overline{\chi_1}\langle E_1{}^2\rangle$$
$$+\frac{\partial}{\partial\tilde{\epsilon}_2}F(\overline{\epsilon_1},\tilde{\epsilon}_2,f,E_0)|_{\tilde{\epsilon}_2=\epsilon_2}\chi_2\langle E_2{}^2\rangle+\cdots, \tag{16}$$

$$\langle E_2{}^2\rangle=G(\overline{\epsilon_1},\epsilon_2,f,E_0)+\frac{\partial}{\partial\tilde{\overline{\epsilon_1}}}G(\tilde{\overline{\epsilon_1}},\epsilon_2,f,E_0)|_{\tilde{\overline{\epsilon_1}}=\overline{\epsilon_1}}\overline{\chi_1}\langle E_1{}^2\rangle$$
$$+\frac{\partial}{\partial\tilde{\epsilon}_2}G(\overline{\epsilon_1},\tilde{\epsilon}_2,f,E_0)|_{\tilde{\epsilon}_2=\epsilon_2}\chi_2\langle E_2{}^2\rangle+\cdots. \tag{17}$$

Keeping the lowest orders of $\overline{\chi_1}\langle E_1{}^2\rangle$, we can rewrite Eq. (16) as

$$\langle E_1{}^2\rangle=h_1E_0{}^2+(h_2+h_3)E_0{}^4, \tag{18}$$

where

$$h_1=\frac{9\epsilon_2{}^2}{(\overline{\epsilon_1}+2\epsilon_2)^2},\quad h_2=-\frac{162\epsilon_2{}^4\overline{\chi_1}}{(\overline{\epsilon_1}+2\epsilon_2)^5},$$

$$h_3=\frac{18\overline{\epsilon_1}\epsilon_2\chi_2[(1+3f)\overline{\epsilon_1}^2+(4-6f)\overline{\epsilon_1}\epsilon_2+(4-6f)\epsilon_2{}^2]}{(1-p)(\overline{\epsilon_1}+2\epsilon_2)^5}.$$

Because of the time dependence of the electric field [Eq. (7)], we can take one step forward to obtain the local electric field in terms of the harmonics (E_ω and $E_{3\omega}$),

$$\sqrt{\langle E_1{}^2\rangle}=E_\omega\sin(\omega t)+E_{3\omega}\sin(3\omega t), \tag{19}$$

where

$$E_\omega=\sqrt{h_1}E_0+\frac{3}{8}\frac{h_2+h_3}{\sqrt{h_1}}E_0{}^3, \tag{20}$$

$$E_{3\omega}=-\frac{1}{8}\frac{h_2+h_3}{\sqrt{h_1}}E_0{}^3. \tag{21}$$

Similarly, based on Eq. (8), we obtain the induced dipole moment in terms of the harmonics (p_ω and $p_{3\omega}$),

$$\tilde{p}/a^3=(p_\omega/a^3)\sin(\omega t)+(p_{3\omega}/a^3)\sin(3\omega t), \tag{22}$$

where

$$p_\omega/a^3=k_1E_0+\frac{3}{4}(k_2+k_3)E_0{}^3, \tag{23}$$

$$p_{3\omega}/a^3=-\frac{1}{4}(k_2+k_3)E_0{}^3, \tag{24}$$

with

$$k_1=\epsilon_e\frac{\overline{\epsilon_1}-\epsilon_2}{\overline{\epsilon_1}+2\epsilon_2},\quad k_2=\frac{3\epsilon_2{}^2h_1\overline{\chi_1}[\overline{\epsilon_1}+6f\overline{\epsilon_1}+(2-6f)\epsilon_2]}{(\overline{\epsilon_1}+2\epsilon_2)^3},$$

$$k_3=\frac{j_1\chi_2[(1+3f)\overline{\epsilon_1}^3-18f\overline{\epsilon_1}^2\epsilon_2-3(2-3f)\overline{\epsilon_1}\epsilon_2{}^2-2(2-3f)\epsilon_2{}^3]}{(\overline{\epsilon_1}+2\epsilon_2)^3}.$$

In the above derivation, we have used an identity $\sin^3(\omega t)=(3/4)\sin(\omega t)-(1/4)\sin(3\omega t)$.

III. NUMERICAL RESULTS

For numerical calculations, we take $\chi_1(r)=\chi_1(0)+D(r/a)$, and other parameters: volume fraction $f=0.09$, external field strength $E_0=1$, linear part of host dielectric constant $\epsilon_2=1$.

The validation of using the DEDA is shown in Fig. 1. In this figure, we investigate the linear local electric field by using a power-law gradation profile inside the particles, in an attempt to compare the DEDA with the first-principles approach. As expected, an excellent agreement is demonstrated between the DEDA [Eq. (2)] and the first-principles approach [Eq. (5)]. In addition, it is worth noting that, for a linear gradation profile within the graded particles, the first-principles approach holds as well [4], and the excellent agreement between the two methods can also be found [4] (figure not shown here).

Next, we discuss a power-law gradation profile [$\epsilon_1(r)=A(r/a)^n$]; see Fig. 2. In this figure, the harmonics of local electric field and the induced dipole moment are investigated as a function of A for various n. In this case, increasing A (or decreasing n) leads to increasing $\tilde{\epsilon}_1$ (namely, the equivalent dielectric constant of the graded particle under consideration) and in turn yields a decreasing local electric field inside the particle. Thus, either an increase in A or a decrease in n leads to the weakening third-order harmonics ($E_{3\omega}$ and $p_{3\omega}$), as displayed in Fig. 2.

The x axes of Figs. 3 and 4 represent the slope (C) of a linear gradation profile. It is because during the fabrication of graded spherical particles by using diffusion, the dielectric constant at the center $\epsilon_1(0)$ may vary slightly while that at the grain boundary can change substantially.

For a linear gradation profile [$\epsilon_1(r)=\epsilon_1(0)+C(r/a)$], Fig. 3 shows the harmonics as a function of C for various

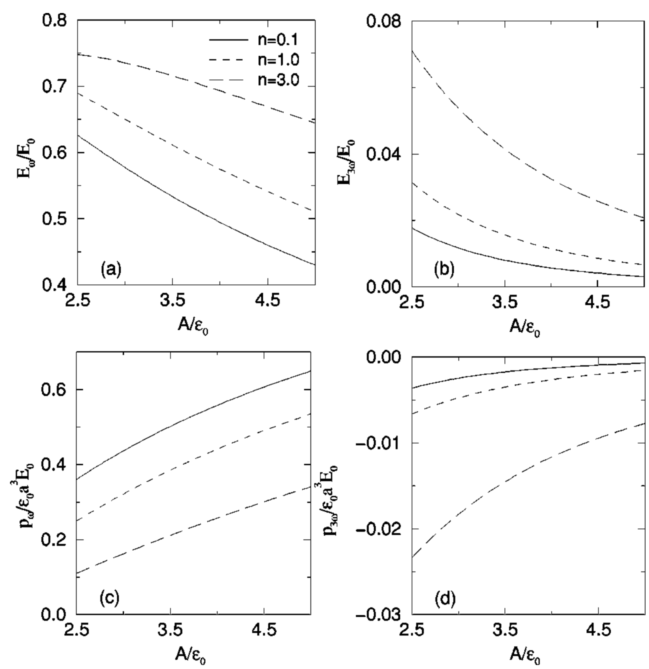

FIG. 2. For a power-law gradation profile $\epsilon_1(r)=A(r/a)^n$: (a) fundamental and (b) third harmonics of the local electric field and (c) fundamental and (d) third harmonics of the induced dipole moment, plotted as a function of A, for various n. Parameters: $\chi_1(0)=0.1\epsilon_0$, $D=0.1\epsilon_0$, and $\chi_2=0$.

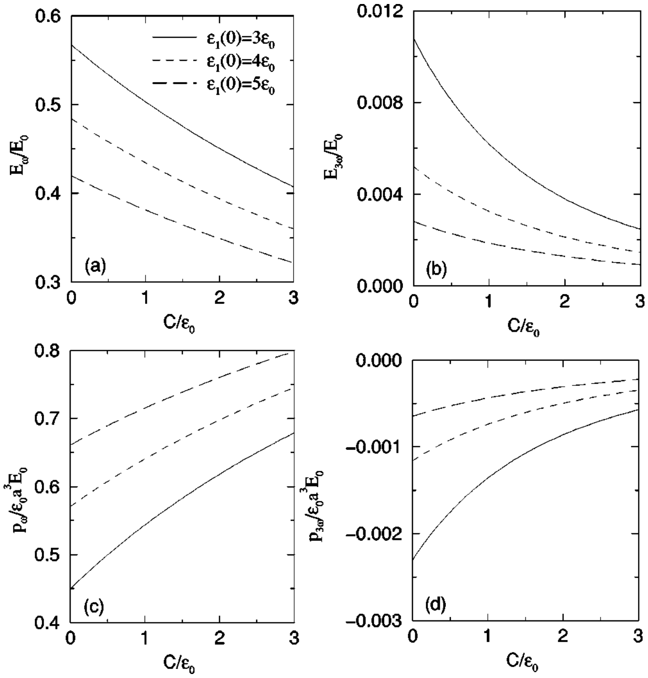

FIG. 3. For the linear gradation profile $\epsilon_1(r)=\epsilon_1(0)+C(r/a)$: (a) fundamental and (b) third harmonics of the local electric field and (c) fundamental and (d) third harmonics of the induced dipole moment, plotted as a function of C, for various $\epsilon_1(0)$. Parameters: $\chi_1(0)=0.1\epsilon_0$, $D=0.1\epsilon_0$, and $\chi_2=0$.

$\epsilon_1(0)$. In this case, increasing C or $\epsilon_1(0)$ yields an increasing $\tilde{\epsilon}_1$, and hence one obtains the decreasing local electric field. As a result, the larger C or $\epsilon_1(0)$ leads to the weaker third-order harmonics ($E_{3\omega}$ and $p_{3\omega}$); see Fig. 3.

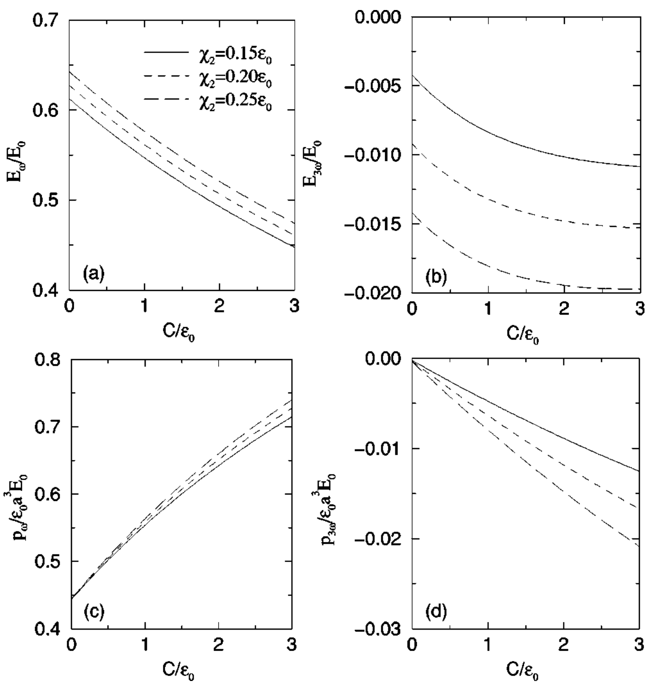

FIG. 4. Same as Fig. 3, but for various χ_2. Parameters: $\chi_1(0)=0$, $D=0$, and $\epsilon_1(0)=3\epsilon_0$.

Figure 4 displays the effect of χ_2 on the harmonics, for a linear gradation profile $[\epsilon_1(r)=\epsilon_1(0)+C(r/a)]$. Here, increasing χ_2 leads to an increase of the local electric field inside the graded particle of interest. Therefore, the third-order harmonics ($E_{3\omega}$ and $p_{3\omega}$) increase for increasing χ_2.

As mentioned above, as A and C increase, the equivalent dielectric constant of the particle should be increased accordingly, which in turn yields a decreasing local electric field, and hence, in Figs. 2–4, E_ω decreases for increasing A or C. On the other hand, it is found that, in Figs. 2–4, p_ω increases for increasing A or C which is, in fact, due to the increasing effective dielectric constant $\tilde{\epsilon}_e$ [refer to Eq. (8)]. Similarly, this analysis works fairly well for understanding the effects of n and $\epsilon_1(0)$ on E_ω and p_ω, as displayed in Figs. 2 and 3. However, increasing χ_2 can increase not only the local electric field inside the particles, but also the effective dielectric constant $\tilde{\epsilon}_e$, and hence we observe increasing E_ω and p_ω, as shown in Fig. 4.

In addition, we also discuss the effect of nonlinear-susceptibility gradation profiles (no figures shown here). For a linear gradation profile $\chi_1(r)=\chi_1(0)+D(r/a)$, as $\chi_1(0)$ (or D) increases, the third harmonics of both the electric field and the induced dipole moment increases accordingly. On the other hand, for a power-law gradation profile $\chi_1(r)=B(r/a)^m$, increasing B (or decreasing m) leads to increasing third harmonics. To understand such results, we can again resort to the above analysis on the effect of the relevant parameters on the local field as well as the effective dielectric constant.

IV. DISCUSSION AND CONCLUSION

Here some comments are in order. We have investigated the nonlinear ac responses of the graded material where linear/nonlinear graded particles are randomly embedded in a linear/nonlinear host medium in the dilute limit. In fact, the nonlinear differential effective dipole approximation (NDEDA) is valid for arbitrary gradation profiles. In particular, based on the first-principles approach, the exact solution is obtainable, not only for power-law profiles (see Sec. II A), but also for linear profiles (refer to Ref. [4]).

In this work, the dielectric constant and nonlinear susceptibility of the graded particles under consideration are real, frequency independent, and vary only in the radial direction. We can extend our results to complex, frequency-dependent susceptibilities. In fact, the NDEDA [8] was originally derived for treating complex frequency-dependent susceptibilities. By using the original NDEDA, the complex frequency-dependent susceptibilities can be studied. That allows us to extend the present work to include an intrinsic dielectric dispersion in the graded particles.

As an extension, it is of particular interest to see what happens to the nonlinear ac responses of graded particles in anisotropic structures, like field-induced electrorheological fluids. In doing so, we can make use of the anisotropic Maxwell-Garnett approximation [13], which allows us to calculate the effective dielectric constant, both parallel and perpendicular to the anisotropic axis. For details, please refer to Ref. [13].

To sum up, based on our recently established NDEDA, we have investigated the nonlinear ac responses of a composite with linear/nonlinear graded spherical particles embedded in a linear/nonlinear host medium, and found the fundamental and third harmonic ac responses are sensitive to the dielectric-constant (or nonlinear-susceptibility) gradation profile within the particles. Again, for extracting the linear local electric field, the DEDA agrees very well with the first-principles approach. In experiments, the graded particles can be made by using the method of diffusion. During the fabrication process, one can measure the nonlinear ac response of the graded particles, so that one can monitor the gradation profiles *in situ*.

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[1] G. W. Milton, *The Theory of Composites* (Cambridge University Press, Cambridge, 2002), Chap. 7.
[2] See, for example, *Proceedings of the First International Symposium on Functionally Graded Materials*, edited by M. Yamanouchi, M. Koizumi, T. Hirai, and I. Shioda (Functionally Gradient Materials Forum amd The Society of Non-traditional Technology, Tokyo, 1990).
[3] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).
[4] L. Dong, G.Q. Gu, and K.W. Yu, Phys. Rev. B **67**, 224205 (2003).
[5] G. Q. Gu and K. W. Yu, J. Appl. Phys. **94**, 3376 (2003).
[6] K.W. Yu, G.Q. Gu, and J.P. Huang, e-print, cond-mat/0211532.
[7] J.P. Huang, K.W. Yu, G.Q. Gu, and M. Karttunen, Phys. Rev. E **67**, 051405 (2003).
[8] L. Gao, J.P. Huang, and K.W. Yu, Phys. Rev. B **69**, 075105 (2004).
[9] D.J. Bergman and D. Stroud, Solid State Phys. **46**, 147 (1992).
[10] O. Levy, D.J. Bergman, and D. Stroud, Phys. Rev. E **52**, 3184 (1995).
[11] P.M. Hui, P.C. Cheung, and D. Stroud, J. Appl. Phys. **84**, 3451 (1998).
[12] G.Q. Gu, P.M. Hui, and K.W. Yu, Physica B **279**, 62 (2000).
[13] J.P. Huang, J.T.K. Wan, C.K. Lo, and K.W. Yu, Phys. Rev. E **64**, 061505(R) (2001).
[14] J.P. Huang, L. Gao, and K.W. Yu, J. Appl. Phys. **93**, 2871 (2003).
[15] D.J. Klingenberg, MRS Bull. **23**, 30 (1998).
[16] J.T.K. Wan, G.Q. Gu, and K.W. Yu, Phys. Rev. E **63**, 052501 (2001).
[17] G.Q. Gu and K.W. Yu, Phys. Rev. B **46**, 4502 (1992).
[18] D. Stroud and P.M. Hui, Phys. Rev. B **37**, 8719 (1988).