# Harmonic generation, induced nonlinearity, and optical bistability in nonlinear composites

Ohad Levy* and David J. Bergman
*School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel*

David G. Stroud
*Department of Physics, Ohio State University, Columbus, Ohio 43210*
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We investigate the dielectric response of composite materials containing a quadratically nonlinear component. The bulk effective second order nonlinearity coefficients of a few simple microgeometries are calculated, and found to diverge in the vicinity of a quasistatic resonance of the composite. It is shown that second and third harmonic generation can be much enhanced in such composites, compared to bulk samples of the nonlinear component. An induced cubic nonlinearity (ICN), which also diverges near a resonance, is generated in the composite, even though none of its components possess it intrinsically. This ICN may be much larger than the effective nonlinearity of a composite with the same microgeometry and a cubic nonlinear component. Finally, such composites are shown to exhibit optical bistability. Such bistability is shown to be theoretically possible far away from a quasistatic resonance, even when all the components have real, positive dielectric constants. This is in contrast to bistability in composites containing a cubic nonlinear component, in which at least one metallic component and a close approach to a resonance are needed. However, tuning to the vicinity of a resonance is still needed in order to obtain bistability at reasonable levels of the applied field. Thresholds in the order of $10^4$ W/cm$^2$ are predicted for a particular layered microgeometry with three components.

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## I. INTRODUCTION

The optical properties of composite materials have been the subject of numerous studies during the last two decades [1]. In recent years there has been a growing interest in the properties of nonlinear composites. Because of their potential uses in optical devices, the most commonly considered materials are made of nonlinear particles embedded in a linear host [1–5]. The nonlinearities of such materials may be strongly enhanced relative to bulk samples of the same materials [5–8], and intrinsic bistability may arise in them under certain conditions [9–17]. These effects are the results of a possibly great enhancement of the electric field within the particles. This enhancement can be produced by an appropriate ratio of the host-to-particle complex dielectric permittivity and by a modification of the field inside a given particle by neighboring particles. The quasistatic resonance (sometimes called the surface plasmon resonance) is an extreme manifestation of this so-called local field effect.

The nonlinearity considered in previous studies is usually cubic and weak, i.e., the dielectric function of the nonlinear component is of the general form $\epsilon(E) = \epsilon + \chi|E|^2$, where $E$ is the local electric field, $\epsilon$ is the linear dielectric constant, $\chi$ is the cubic nonlinear susceptibility, and $\chi|E|^2 \ll \epsilon$. This type of nonlinearity is the leading weakly nonlinear term in the dielectric response of materials that have inversion symmetry. The electric field applied to such a system is usually assumed to be monochromatic. The nonlinear term in this case depends only on the intensity of the local electric field and not on the field vector itself. Therefore no higher harmonics are generated and all the fields in the system are of the same frequency as the applied field.

In this paper, we consider composite materials in which the nonlinear component is not inversion symmetric. The first nonlinear term in the dielectric function is then linear in the field $\epsilon(E) = \epsilon + dE$, where $d$ is the quadratic nonlinear susceptibility. The explicit dependence on the electric field vector gives rise to harmonic components of the polarization in the nonlinear particles and to harmonic local fields in the composite. These fields must be taken into account when calculating the bulk effective dielectric response of the composite.

We will examine the consequences of this effect in a few simple microgeometries. We find that the bulk effective quadratic nonlinearity of the composite can be much enhanced compared to that of the nonlinear component and that the generation of harmonic fields can become much stronger. This opens up the possibility of using such a composite as the active material in improved second harmonic generation devices. Intrinsic optical bistability also appears in these composites, but under conditions that differ from those previously found for composites of cubic nonlinear components [9–17]. Of special interest is the possibility of bistable behavior far from a quasistatic resonance and in composites with purely dielectric components only. This possibility stands in contrast to cubic nonlinear materials, where a necessary condition for bistability is at least one component with a dielectric con-

*Present address: Courant Institute of Mathematical Sciences, New York University, New York, NY 10012.

 

stant having a negative real part and a small imaginary part.

The rest of the paper is organized as follows. In Sec. II we develop the theory of second order nonlinearity in a composite medium. We treat a composite made of spherical nonlinear inclusions randomly dispersed in a linear host and two examples of layered microgeometries. In Sec. III we discuss the harmonic generation processes in such composites. The bulk effective coefficients of both second harmonic generation (SHG) and third harmonic generation (THG) are calculated and shown to be enhanced in the vicinity of a quasistatic resonance. In Sec. IV, we examine the bulk effective response at the fundamental frequency. We consider both the phenomenon of induced cubic nonlinearity (ICN) and the electro-optic effect, which is the change in the dielectric coefficient of a material induced by the presence of a static electric field. It is shown that the induced cubic nonlinearity may be much larger than in composites of the same microgeometries having a nonlinear component with an intrinsic cubic nonlinearity. In Sec. V we discuss the phenomenon of intrinsic optical bistability. It is shown that, although theoretically possible in purely dielectric systems, bistability is not practically achievable because of the enormous electric field required. In the vicinity of a resonance, however, we find threshold field intensities of the order of $10^4$ W/cm$^2$ for a layered three-component microgeometry. Finally, a short discussion and conclusions are given in Sec. VI.

## II. THE THEORY AND ITS APPLICATION TO THREE SIMPLE MICROGEOMETRIES

The study of nonlinear composites is difficult, because the usual mathematical methods developed for linear composites are inapplicable. The analysis is thus limited to dilute composites of spheroidal inclusions (which may be multicoated with a nonlinear core) and to layered composites, in which the field inside the nonlinear component is uniform. In this section we will consider three such examples. In all cases, we will assume that the quasistatic limit is valid, i.e., $\nabla \times E = 0$, where $E$ is the local electric field. This assumption is generally adequate provided that the grain sizes are all small in comparison to both the wavelength of the electromagnetic field in the surrounding medium, and the skin depth of the electromagnetic fields in the grains, so that electromagnetic scattering and phase matching effects can be neglected. These propagation effects need to be taken into account in the usual way when analyzing the performance of optical devices in which the active nonlinear element is a composite material, but they need not be taken into account when calculating the bulk effective properties of the composite material as such.

### A. Parallel slabs microstructure

We begin by considering a system in which the nonlinear component $\epsilon_a(E)$ and the linear component $\epsilon_b$ form a layered structure of parallel slabs. The nonlinear component is assumed to have only lowest order nonlinearities, i.e., those quadratic in the local electric field. We consider the case in which the applied field is perpendicular to the slabs. In this example both fields $E$ and $D$ are then perpendicular to the slabs and are uniform in each component. (The case where these fields are parallel to the slabs is less interesting because the local electric field is then uniform.) Because the applied and interior fields are therefore in the same direction, we need not carry along the vector notation, and can denote the fields as complex scalars (thus retaining information about relative phases).

The applied electric field can be represented by a Fourier series in time

$$E_0(t) = \sum_{n=-\infty}^{\infty} E_{0,n\omega} \exp(-in\omega t) \tag{2.1}$$

where, in general, $E_{0,-n\omega} = E^*_{0,n\omega}$. In most cases, we will consider a monochromatic applied field of frequency $\omega$ (all coefficients vanish except $n = 1$ or $-1$). The nonlinear component will generate local fields at all the harmonic frequencies. Thus the interior field in component $a$ will be represented by

$$E_a(t) = \sum_{n=-\infty}^{\infty} E_{a,n\omega} \exp(-in\omega t). \tag{2.2}$$

The constitutive relation in component $b$ is linear and may be written

$$D_{b,n\omega} = \epsilon_{b,n\omega} E_{b,n\omega}. \tag{2.3}$$

In component $a$, we have, in general,

$$D_{a,m\omega} = \epsilon_{a,m\omega} E_{a,m\omega} + \sum_{n=-\infty}^{\infty} d_{(m+n)\omega,-n\omega} E_{a,(m+n)\omega} E_{a,-n\omega} + \cdots \tag{2.4}$$

where the omitted terms are of third and higher order in $E_a$. The coefficients $d_{\omega,\omega'}$ denote the second order susceptibilities of material $a$.

The volume averaged, or externally applied, electric field is in this case

$$\langle E \rangle = E_0 = p_a E_a + p_b E_b, \tag{2.5}$$

where $p_a$ and $p_b$ are the volume fractions of the components $a$ and $b$, respectively, and $E_a$ and $E_b$ are the local fields in the two components. The volume averaged displacement field is

$$\langle D \rangle = D_0 = \epsilon_a(E_a) E_a = \epsilon_b E_b, \tag{2.6}$$

where we used the continuity condition on the normal component of $D$. The local field $E_a$ is determined by

$$[p_a \epsilon_b + p_b \epsilon_a(E_a)] E_a = \epsilon_b E_0, \tag{2.7}$$

where $E_0$ and $E_a$ are time dependent fields. When (2.1) and (2.2) are used to represent those fields each of the frequency components of (2.7) can be considered separately. This leads to an infinite sequence of nonlinear equations among the Fourier expansion coefficients. We will assume a monochromatic applied field that has only an $\omega$ component. All the other fields, including $D_0$, have static and harmonic components in addition to the fundamental component. In order to simplify the discussion we only include terms up to third order in the nonlinearity coefficients $d$ and discard all terms of higher order. This is a kind of perturbation expansion, valid if the nonlinearity is not too strong. It does not rule out the possibility of multiple solutions and bistable behavior.

Under these assumptions, at the fundamental frequency $\omega$ we have

$$(p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}+2p_bd_{0,\omega}E_{a,0})\,E_{a,\omega} +2p_bd_{2\omega,-\omega}E_{a,2\omega}E^*_{a,\omega}=\epsilon_{b,\omega}E_{0,\omega}. \quad (2.8)$$

At the same time the zero frequency equation takes the form

$$(p_a\epsilon_{b,0}+p_b\epsilon_{a,0})\,E_{a,0}+2p_b[d_{\omega,-\omega}\,|E_{a,\omega}|^2 +d_{2\omega,-2\omega}\,|E_{a,2\omega}|^2]=0, \quad (2.9)$$

while that for the second harmonic $2\omega$ is

$$(p_a\epsilon_{b,2\omega}+p_b\epsilon_{a,2\omega}+2p_bd_{0,2\omega}E_{a,0})\,E_{a,2\omega} +2p_bd_{3\omega,-\omega}E_{a,3\omega}E^*_{a,\omega}+p_bd_{\omega,\omega}E^2_{a,\omega}=0, \quad (2.10)$$

and that for the third harmonic $3\omega$ is

$$(p_a\epsilon_{b,3\omega}+p_b\epsilon_{a,3\omega})\,E_{a,3\omega}+2p_bd_{2\omega,\omega}E_{a,2\omega}E_{a,\omega}=0. \quad (2.11)$$

Since the contributions of higher harmonic components of $E_a(t)$ to these equations are of higher order in $d$, they are neglected in this calculation.

Solving Eq. (2.11) for $E_{a,3\omega}$ we get

$$E_{a,3\omega}=-\frac{2p_bd_{2\omega,\omega}E_{a,2\omega}E_{a,\omega}}{p_a\epsilon_{b,3\omega}+p_b\epsilon_{a,3\omega}}. \quad (2.12)$$

Substituting this in (2.10) and solving for $E_{a,2\omega}$ we find

$$E_{a,2\omega}=-\frac{p_bd_{\omega,\omega}E^2_{a,\omega}}{p_a\epsilon_{b,2\omega}+p_b\epsilon_{a,2\omega}+2p_bd_{0,2\omega}E_{a,0}-\frac{4p_b^2d_{2\omega,\omega}d_{3\omega,-\omega}|E_{a,\omega}|^2}{p_a\epsilon_{b,3\omega}+p_b\epsilon_{a,3\omega}}}. \quad (2.13)$$

Substituting this and the solution of (2.9) for $E_{a,0}$ in (2.8), and keeping only terms up to third order in $d$, we find

$$\left(p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}-p_b\chi\,|E_{a,\omega}|^2\right)E_{a,\omega}=\epsilon_{b,\omega}E_{0,\omega}, \quad (2.14)$$

where

$$\chi\equiv\frac{4p_bd_{0,\omega}d_{\omega,-\omega}}{p_a\epsilon_{b,0}+p_b\epsilon_{a,0}}+\frac{2p_bd_{\omega,\omega}d_{2\omega,-\omega}}{p_a\epsilon_{b,2\omega}+p_b\epsilon_{a,2\omega}}. \quad (2.15)$$

If both sides of (2.14) are multiplied by their complex conjugates, one obtains a cubic equation for $|E_{a,\omega}|^2$ in which all coefficients are real. This can be written in a simplified form if we define

$$t\equiv\frac{p_b\,|\chi|\,|E_{a,\omega}|^2}{|p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}|}, \quad (2.16)$$

$$\mu\equiv\frac{\mathrm{Re}\left(\frac{p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}}{\chi}\right)}{\left|\frac{p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}}{\chi}\right|}, \quad (2.17)$$

$$\alpha\equiv\frac{p_b\,|\chi|\,|\epsilon_{b,\omega}E_{0,\omega}|^2}{|p_a\epsilon_{b,\omega}+p_b\epsilon_{a,\omega}|^3}. \quad (2.18)$$

We thus get the simple cubic equation

$$f(t)\equiv t^3-2\mu t^2+t=\alpha. \quad (2.19)$$

Obviously, any real, positive solution for $t$ leads to a single, generally complex, solution for $E_{a,\omega}$ [see (2.14)]. The function $f(t)$, for three different values of $\mu$ is shown in Fig. 1.

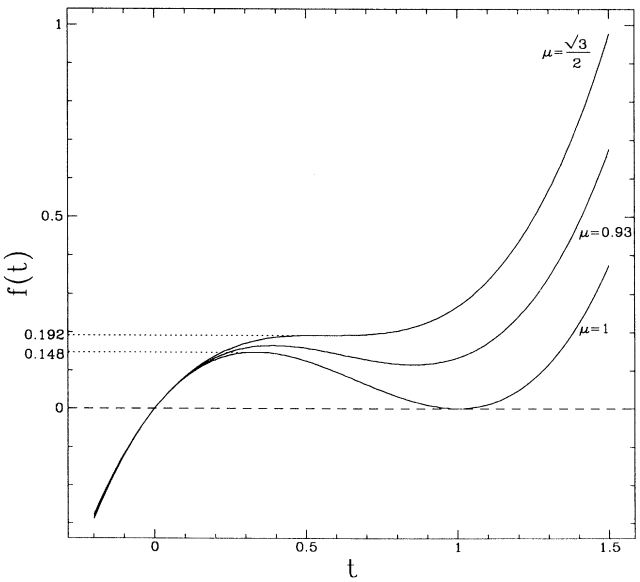


FIG. 1. The cubic function $f(t)$ at different values of $\mu$. $\mu=1$ ($\mu=\sqrt{3}/2$) is the largest (smallest) value for which bistability is possible. The threshold values of $\alpha$ in these extremal cases are indicated.

### B. Low density of spherical inclusions

In this case we consider a random assemblage of nonlinear spheres $\epsilon_a(E)$ embedded in a linear host $\epsilon_b$. Again the inclusions are assumed to have only lowest order nonlinearities, i.e., those quadratic in the local electric field. We assume that the spheres are not too densely packed, so that, applying a uniform field $E_0$ on the system, the field locally applied to each sphere $E_{ex}$ is also uniform, and is equal to the Lorentz local field. This is the well-known Clausius-Mossotti approximation, in which only dipolar interactions among the inclusions are taken into account. It is widely used for calculating the properties of linear composites [1]. It can be extended to this nonlinear case because, even then, the field inside each spherical inclusion is uniform when a uniform electric field is applied to it. In this approximation the interior and exterior electric fields are both uniform and are connected by

$$D_{a,n\omega} + 2\epsilon_{b,n\omega} E_{a,n\omega} = 3\epsilon_{b,n\omega} E_{ex,n\omega}. \tag{2.20}$$

This follows from the electrostatic boundary conditions on $D$ and $E$ at the sphere surface [18]. In this case, even when the applied field $E_0(t)$ is monochromatic, the local exterior field felt by a single sphere $E_{ex}(t)$ will include higher harmonics. This is taken into account when we Fourier analyze Eq. (2.20). At the fundamental frequency $\omega$ we have

$$[\epsilon_{a,\omega} + 2\epsilon_{b,\omega} + 2d_{0\omega}E_{a,0}]\,E_{a,\omega} + 2d_{2\omega,-\omega}E_{a,2\omega}E^*_{a,\omega} = 3\epsilon_{b,\omega}E_{ex,\omega}, \tag{2.21}$$

at $\omega = 0$ we have

$$[\epsilon_{a,0} + 2\epsilon_{b,0}]\,E_{a,0} + 2d_{\omega,-\omega}|E_{a,\omega}|^2 + 2d_{2\omega,-2\omega}|E_{a,2\omega}|^2 = 3\epsilon_{b,0}E_{ex,0}, \tag{2.22}$$

at $2\omega$ we have

$$[\epsilon_{a,2\omega} + 2\epsilon_{b,2\omega} + 2d_{0,2\omega}E_{a,0}]\,E_{a,2\omega} + 2d_{3\omega,-\omega}E_{a,3\omega}E^*_{a,\omega} + d_{\omega,\omega}E^2_{a,\omega} = 3\epsilon_{b,2\omega}E_{ex,2\omega}, \tag{2.23}$$

and at $3\omega$ we have

$$[\epsilon_{a,3\omega} + 2\epsilon_{b,3\omega}]\,E_{a,3\omega} + 2d_{2\omega,\omega}E_{a,2\omega}E_{a,\omega} = 3\epsilon_{b,3\omega}E_{ex,3\omega}. \tag{2.24}$$

The exterior field is

$$E_{ex} = E_0 + \frac{4\pi}{3\epsilon_b}\langle P\rangle, \tag{2.25}$$

where $\langle P\rangle$ is the volume averaged polarization of the spherical inclusions. This polarization is given by the volume fraction of the spheres multiplied by their dipolar moments

$$\langle P\rangle = \frac{p_a}{4\pi}\left[D_a(t) - \epsilon_b E_a(t)\right]. \tag{2.26}$$

Substituting the different frequency components of $E_{ex}$ into Eqs. (2.21)–(2.24) we find, at the fundamental frequency

$$[(\epsilon_{a,\omega} - \epsilon_{b,\omega} + 2d_{0\omega}E_{a,0})\,p_b + 3\epsilon_{b,\omega}]\,E_{a,\omega} + 2p_b d_{2\omega,-\omega}E_{a,2\omega}E^*_{a,\omega} = 3\epsilon_{b,\omega}E_{0,\omega}, \tag{2.27}$$

at $\omega = 0$

$$[(\epsilon_{a,0} - 2\epsilon_{b,0})\,p_b + 3\epsilon_{b,0}]\,E_{a,0} + 2p_b d_{\omega,-\omega}|E_{a,\omega}|^2 + 2p_b d_{2\omega,-2\omega}|E_{a,2\omega}|^2 = 0, \tag{2.28}$$

at $2\omega$

$$[(\epsilon_{a,2\omega} - \epsilon_{b,2\omega} + 2d_{0,2\omega}E_{a,0})\,p_b + 3\epsilon_{b,2\omega}]\,E_{a,2\omega} + 2p_b d_{3\omega,-\omega}E_{a,3\omega}E^*_{a,\omega} + p_b d_{\omega,\omega}E^2_{a,\omega} = 0, \tag{2.29}$$

and at $3\omega$

$$[(\epsilon_{a,3\omega} - \epsilon_{b,3\omega})\,p_b + 3\epsilon_{b,3\omega}]\,E_{a,3\omega} + 2p_b d_{2\omega,\omega}E_{a,2\omega}E_{a,\omega} = 0. \tag{2.30}$$

Here the applied electric field is assumed to be uniform and monochromatic with frequency $\omega$. $\omega$ is assumed small enough such that the quasistatic approximation applies even at $3\omega$. As in the previous example we have discarded all terms of fourth order and higher in $d$.

These equations can be solved, in the same way as in the previous example, to give

$$E_{a,3\omega} = -\frac{2p_b d_{2\omega,\omega}E_{a,2\omega}E_{a,\omega}}{(\epsilon_{a,3\omega} - \epsilon_{b,3\omega})\,p_b + 3\epsilon_{b,3\omega}}, \tag{2.31}$$

$$E_{a,2\omega} = -\frac{p_b d_{\omega,\omega}E^2_{a,\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega} + 2d_{0,2\omega}E_{a,0})\,p_b + 3\epsilon_{b,2\omega} - \frac{4p_b^2 d_{2\omega,\omega}d_{3\omega,-\omega}|E_{a,\omega}|^2}{(\epsilon_{a,3\omega} - \epsilon_{b,3\omega})p_b + 3\epsilon_{b,3\omega}}}, \tag{2.32}$$

and

$$\left[(\epsilon_{a,\omega} - \epsilon_{b,\omega})\,p_b + 3\epsilon_{b,\omega} - p_b\chi|E_{a,\omega}|^2\right]E_{a,\omega} = 3\epsilon_{b,\omega}E_{0,\omega}, \tag{2.33}$$

where

$$\chi \equiv \frac{4p_b d_{0,\omega}d_{\omega,-\omega}}{(\epsilon_{a,0} - \epsilon_{b,0})\,p_b + 3\epsilon_{b,0}} + \frac{2p_b d_{\omega,\omega}d_{2\omega,-\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega})\,p_b + 3\epsilon_{b,2\omega}}. \tag{2.34}$$

There is only one difference between Eqs. (2.31)–(2.34) and their analogs in the previous example, Eqs. (2.12)–(2.15): the denominators contain the expression for the quasistatic resonance of the composite. This parameter is microgeometry dependent: the factor $p_a\epsilon_b+p_b\epsilon_a$ in the parallel slabs microgeometry changes to $(\epsilon_a-\epsilon_b)\,p_b+3\epsilon_b$ in the case of dilute spheres. The vanishing of this denominator at a specific frequency implies that the system is exactly at the quasistatic resonance for that frequency. The corresponding frequency component of the field inside the nonlinear material is enhanced in the vicinity of such a resonance. These quasistatic resonances can only be approached if one of the components is a true dielectric, with $\epsilon$ that is positive and approximately real, while another has an $\epsilon$ with a negative real part and a small imaginary part in the relevant frequency range (usually, this implies a metallic component). The existence of sharp resonances in the dielectric response of composite materials is generally limited to periodic microgeometries and to dilute mixtures of identical inclusions [1].

As in Sec. II A, Eq. (2.33) can also be simplified by multiplying both sides by their complex conjugates and defining

$$t \equiv \frac{p_b\,|\chi|\,|E_{a,\omega}|^2}{|(\epsilon_{a,\omega}-\epsilon_{b,\omega})\,p_b+3\epsilon_{b,\omega}|}, \tag{2.35}$$

$$\mu \equiv \frac{\mathrm{Re}\left(\frac{(\epsilon_{a,\omega}-\epsilon_{b,\omega})p_b+3\epsilon_{b,\omega}}{\chi}\right)}{\left|\frac{(\epsilon_{a,\omega}-\epsilon_{b,\omega})p_b+3\epsilon_{b,\omega}}{\chi}\right|}, \tag{2.36}$$

$$\alpha \equiv \frac{p_b\,|\chi|\,|3\epsilon_{b,\omega}E_{0,\omega}|^2}{|(\epsilon_{a,\omega}-\epsilon_{b,\omega})\,p_b+3\epsilon_{b,\omega}|^3}. \tag{2.37}$$

We then get again the simple cubic equation (2.19).

### C. Three-component parallel slabs microstructure

Next we consider a composite made of parallel layers of two kinds. One is made of a linear dielectric of dielectric constant $\epsilon_d$, while the other is itself a two-component composite of cylinders, perpendicular to the plane of the layer, composed of another linear material $\epsilon_m$ and a nonlinear dielectric $\epsilon_{nl}(E)$ (see Fig. 2). The dielectric function of the composite layers is

$$\epsilon_c(E) = f_m\epsilon_m + f_{nl}\epsilon_{nl}(E) \tag{2.38}$$

where $f_{nl}$ is the volume fraction of the nonlinear component in the layer and $f_m = 1-f_{nl}$ is the volume fraction of the linear component in that layer. The electric field in the composite layers $E_c$ is uniform and is given by

$$[(1-p_d)\,\epsilon_d + p_d\epsilon_c(E_c)]\,E_c = \epsilon_d E_0, \tag{2.39}$$

where $p_d$ is the volume fraction of the dielectric layers in the composite and $E_0$ is a uniform electric field applied perpendicular to the layers. This relation is similar to (2.7) and can be analyzed in the same way. Assuming

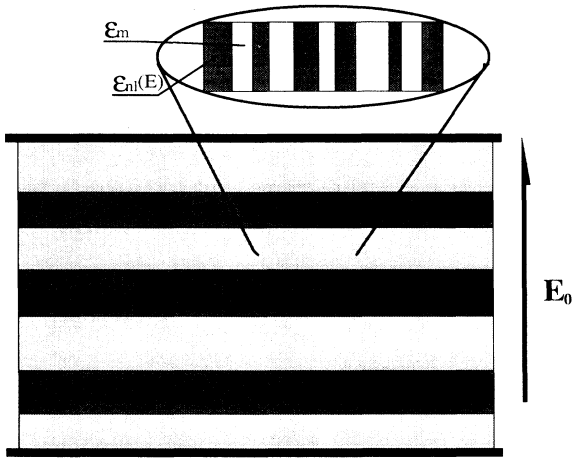


FIG. 2. A three-component microgeometry of dielectric and composite parallel slabs. The two-component layers contain the nonlinear material $\epsilon_{nl}(E) = \epsilon_{nl} + dE$.

$E_0$ to be monochromatic of frequency $\omega$, we get again several equations for the different frequency components of (2.39). The $\omega$ component leads to

$$[(1-p_d)\,\epsilon_{d,\omega} + p_d\epsilon_{c,\omega} + 2p_d f_{nl} d_{0,\omega}E_{c,0}]\,E_{c,\omega} + 2p_d f_{nl} d_{2\omega,-\omega}E_{a,2\omega}E^*_{a,\omega} = \epsilon_{d,\omega}E_{0,\omega} \tag{2.40}$$

where $\epsilon_c$ is the linear part of $\epsilon_c(E)$. This equation is similar in form to (2.8): The only difference is in the location of the quasistatic resonance, which is now determined by $(1-p_d)\,\epsilon_{d,\omega}+p_d\epsilon_{c,\omega}=0$. The zero frequency component of (2.39) leads to

$$[(1-p_d)\,\epsilon_{d,0} + p_d\epsilon_{c,0}]\,E_{c,0} + 2p_d f_{nl}\left[d_{\omega,-\omega}\,|E_{c,\omega}|^2 + d_{2\omega,-2\omega}\,|E_{c,2\omega}|^2\right] = 0, \tag{2.41}$$

while the $2\omega$ component leads to

$$[(1-p_d)\,\epsilon_{d,2\omega} + p_d\,(\epsilon_{c,2\omega} + 2f_{nl}d_{0,2\omega}E_{c,0})]\,E_{c,2\omega} + p_d f_{nl}\left[2d_{3\omega,-\omega}E_{c,3\omega}E^*_{c,\omega} + d_{\omega,\omega}E^2_{c,\omega}\right] = 0, \tag{2.42}$$

and the $3\omega$ component leads to

$$[(1-p_d)\,\epsilon_{d,3\omega} + p_d\epsilon_{c,3\omega}]\,E_{c,3\omega} + 2p_d f_{nl} d_{2\omega,\omega}E_{c,2\omega}E_{c,\omega} = 0. \tag{2.43}$$

Solving as in the two previous subsections, we find

$$E_{c,3\omega} = -\frac{2p_d f_{nl} d_{2\omega,\omega}E_{c,2\omega}E_{c,\omega}}{(1-p_d)\,\epsilon_{d,3\omega} + p_d\epsilon_{c,3\omega}}, \tag{2.44}$$

which corresponds to (2.12) and (2.31) in the previous examples. Substituting this in (2.42) we get

$$E_{a,2\omega} = -\frac{p_d f_{nl} d_{\omega,\omega} E_{c,\omega}^2}{(1-p_d)\,\epsilon_{d,2\omega} + p_d \epsilon_{c,2\omega} + 2p_d f_{nl} d_{0,2\omega} E_{c,0} - \frac{4p_d^2 f_{nl}^2 d_{2\omega,\omega} d_{3\omega,-\omega} |E_{c,\omega}|^2}{(1-p_d)\epsilon_{d,3\omega} + p_d \epsilon_{c,3\omega}}}, \tag{2.45}$$

which corresponds to (2.13) and (2.32) in the previous examples. Substituting (2.41) and (2.45) in (2.40), keeping only terms up to third order in $d$, we find

$$\left[(1-p_d)\,\epsilon_{d,\omega} + p_d \epsilon_{c,\omega} - p_d \chi |E_{c,\omega}|^2\right] E_{c,\omega} = \epsilon_{d,\omega} E_{0,\omega}, \tag{2.46}$$

where

$$\chi \equiv \frac{4p_d f_{nl}^2 d_{0,\omega} d_{\omega,-\omega}}{(1-p_d)\,\epsilon_{d,0} + p_d \epsilon_{c,0}} + \frac{2p_d f_{nl}^2 d_{\omega,\omega} d_{2\omega,-\omega}}{(1-p_d)\,\epsilon_{d,2\omega} + p_d \epsilon_{c,2\omega}}. \tag{2.47}$$

As in the previous examples, when both sides of (2.46) are multiplied by their complex conjugates, one obtains a cubic equation for $|E_{c,\omega}|^2$ in which all coefficients are real, and which can be written in the simplified form of (2.19) if we define

$$t \equiv \frac{p_d |\chi|\, |E_{c,\omega}|^2}{|(1-p_d)\,\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}|}, \tag{2.48}$$

$$\mu \equiv \frac{\mathrm{Re}\left(\frac{(1-p_d)\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}}{\chi}\right)}{\left|\frac{(1-p_d)\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}}{\chi}\right|}, \tag{2.49}$$

$$\alpha \equiv \frac{p_d |\chi|\, |\epsilon_{d,\omega} E_{0,\omega}|^2}{|(1-p_d)\,\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}|^3}. \tag{2.50}$$

To summarize this section, we have shown that the different frequency components of the local fields inside a quadratically nonlinear composite subject to a uniform monochromatic external field can be calculated up to third harmonic using a perturbation type calculation. The main results of this calculation are that each of these local field components is enhanced in the vicinity of a quasistatic resonance of the composite at the appropriate frequency and that the fundamental frequency component of the local field is related to the applied field by a simple cubic equation. These results are used in the following sections to calculate the bulk effective optical response of such composites at the different harmonic frequencies.

## III. GENERATION OF SECOND AND THIRD HARMONICS

In this section we calculate the bulk effective susceptibilities $d_{\omega,\omega}^{(e)}$, for second harmonic generation and $d_{\omega,\omega,\omega}^{(e)}$, for third harmonic generation, in the composite microgeometries discussed above. The bulk effective susceptibility $d_{\omega,\omega}^{(e)}$ may be defined, as is usual in composite media, by relating the volume averages of the $2\omega$ component of $D$ and the $\omega$ component of $E$

$$D_{0,2\omega} \equiv d_{\omega,\omega}^{(e)} E_{0,\omega}^2 + \cdots . \tag{3.1}$$

In the two-component parallel slabs microgeometry of Sec. II A, the volume averaged second harmonic (SH) component of $D$ is

$$D_{0,2\omega} = \epsilon_{a,2\omega} E_{a,2\omega} + d_{\omega,\omega} E_{a,\omega}^2 + 2d_{3\omega,-\omega} E_{a,3\omega} E_{a,\omega}^*. \tag{3.2}$$

On substituting the zero order solution for $E_{a,\omega}$ from (2.14), $E_{a,2\omega}$ from (2.13), and $E_{a,3\omega}$ from (2.12) we find

$$d_{\omega,\omega}^{(e)} = p_a d_{\omega,\omega} \left(\frac{\epsilon_{b,2\omega}}{p_a \epsilon_{b,2\omega} + p_b \epsilon_{a,2\omega}}\right) \left(\frac{\epsilon_{b,\omega}}{p_a \epsilon_{b,\omega} + p_b \epsilon_{a,\omega}}\right)^2. \tag{3.3}$$

We can use the same approach for the two other microgeometries discussed in Sec. II. For the dilute assemblage of spheres of Sec. II B we find

$$d_{\omega,\omega}^{(e)} = p_a d_{\omega,\omega} \left(\frac{3\epsilon_{b,2\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega})\, p_b + 3\epsilon_{b,2\omega}}\right) \times \left(\frac{3\epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega})\, p_b + 3\epsilon_{b,\omega}}\right)^2, \tag{3.4}$$

while for the three-component layered microgeometry of Sec. II C we find

$$d_{\omega,\omega}^{(e)} = (1-p_d)\, f_{nl} d_{\omega,\omega} \left(\frac{\epsilon_{d,2\omega}}{(1-p_d)\,\epsilon_{d,2\omega} + p_d \epsilon_{c,2\omega}}\right) \times \left(\frac{\epsilon_{d,\omega}}{(1-p_d)\,\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}}\right)^2. \tag{3.5}$$

These results constitute an extension of the perturbation method of Ref. [6] to the case where the applied field and the induced polarization can have different frequencies. Note that the only difference among the three results is in the location of the microgeometry dependent quasistatic resonances which appear in the denominators. The bulk effective SH coefficient $d_{\omega,\omega}^{(e)}$ has a second order divergence whenever the composite medium has a quasistatic resonance at the fundamental frequency. In addition to this, $d_{\omega,\omega}^{(e)}$ also has a first order divergence at the $2\omega$ quasistatic resonance of the composite medium. The two resonances appear together because of the mixing between the SH component and the fundamental frequency component of the local field. This divergence is weaker than that of the bulk effective Kerr coefficient (i.e., the third order nonlinearity coefficient) of composites with cubic nonlinear components, where a fourth order divergence is obtained [6].

As noted in Sec. II these quasistatic resonances can

only be approached in periodic composites or in dilute mixtures of identical inclusions where one of the components is a dielectric, with real and positive $\epsilon$, while the other has an $\epsilon$ with a negative real part and a small imaginary part in the relevant frequency range [1]. Usually, this will be a metal. Therefore metal-dielectric composites are the most likely composites in which to observe the enhancement of $d^{(e)}_{\omega,\omega}$ (and of other coefficients discussed below) associated with such resonances.

The bulk effective THG coefficient $d^{(e)}_{\omega,\omega,\omega}$ can be calculated in a similar way. It is defined by

$$D_{0,3\omega} \equiv d^{(e)}_{\omega,\omega,\omega} E^3_{0,\omega} + \cdots . \tag{3.6}$$

The volume averaged third harmonic (TH) component of $D$ in the two-component parallel slabs microgeometry is

$$D_{0,3\omega} = \epsilon_{a,3\omega} E_{a,3\omega} + d_{2\omega,\omega} E_{a,2\omega} E_{a,\omega}. \tag{3.7}$$

On substituting the appropriate expressions for $E_{a,\omega}$, $E_{a,2\omega}$, and $E_{a,3\omega}$, we find

$$d^{(e)}_{\omega,\omega,\omega} = -\frac{p_a p_b d_{\omega,\omega} d_{2\omega,\omega}}{p_a \epsilon_{b,2\omega} + p_b \epsilon_{a,2\omega}} \left( \frac{\epsilon_{b,3\omega}}{p_a \epsilon_{b,3\omega} + p_b \epsilon_{a,3\omega}} \right) \times \left( \frac{\epsilon_{b,\omega}}{p_a \epsilon_{b,\omega} + p_b \epsilon_{a,\omega}} \right)^3 . \tag{3.8}$$

The results for the two other cases we considered are

$$d^{(e)}_{\omega,\omega,\omega} = -\frac{p_a p_b d_{\omega,\omega} d_{2\omega,\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega}) p_b + 3\epsilon_{b,2\omega}} \times \left( \frac{3\epsilon_{b,3\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega}) p_b + 3\epsilon_{b,2\omega}} \right) \times \left( \frac{3\epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega}) p_b + 3\epsilon_{b,\omega}} \right)^3 \tag{3.9}$$

for the dilute assemblage of spheres, and

$$d^{(e)}_{\omega,\omega,\omega} = -\frac{2p_d (1-p_d) f^2_{nl} d_{\omega,\omega} d_{2\omega,\omega}}{(1-p_d)\epsilon_{d,2\omega} + p_d \epsilon_{c,2\omega}} \times \left( \frac{\epsilon_{d,3\omega}}{(1-p_d)\epsilon_{d,3\omega} + p_d \epsilon_{c,3\omega}} \right) \times \left( \frac{\epsilon_{d,\omega}}{(1-p_d)\epsilon_{d,\omega} + p_d \epsilon_{c,\omega}} \right)^3 \tag{3.10}$$

for the three-component layered microgeometry. Again, the only differences among these results are in the locations of the quasistatic resonances which appear as denominators. They depend on the details of the microgeometry and vanish at the appropriate quasistatic resonances. We can see that $d^{(e)}_{\omega,\omega,\omega}$ has a third order divergence at the fundamental frequency quasistatic resonance and two first order divergences at the $2\omega$ and $3\omega$ resonances. The mixing of the three different frequency components of the local field gives rise to the appearance of all the corresponding resonances. The divergences are reflected in the amplitude of the TH signal which is enhanced in the vicinity of each of these resonances.

## IV. INDUCED CUBIC NONLINEARITY AND THE ELECTRO-OPTIC EFFECT

In all of the examples of Sec. II, the dielectric response of the composite at the fundamental frequency $\omega$ includes a cubic nonlinear term. In the spherical inclusions microgeometry, this nonlinearity clearly appears in Eq. (2.33). This expression has the same form as the equation describing a suspension of spherical inclusions with dielectric function $\epsilon_a(E) = \epsilon_a + \chi_I |E|^2$. The intrinsic cubic nonlinearity coefficient $\chi_I$ of the spheres in this example would be equal to $-\chi$ of Eq. (2.34). The same effect occurs in the two-component and three-component parallel slabs microgeometries, where the corresponding expressions for the cubic nonlinearity coefficient $-\chi$ are (2.15) and (2.47), respectively. This cubic nonlinearity is not an intrinsic property of any of the nonlinear components of these composites. It results from the mixing of the $\omega$ and $2\omega$ components of the electric field in those components. We will call this phenomenon *induced cubic nonlinearity* (ICN).

To determine the effect of ICN on the bulk effective behavior of the composite at the fundamental frequency, we relate the volume averaged $\omega$ components of $D$ and $E$ by

$$\langle D_\omega \rangle = \epsilon^{(e)}_\omega E_{0,\omega} + \chi^{(e)} |E_{0,\omega}|^2 E_{0,\omega} + \cdots , \tag{4.1}$$

where $\epsilon^{(e)}_\omega$ is the bulk effective dielectric constant of the composite and $\chi^{(e)}$ is the bulk effective cubic nonlinearity coefficient. Carrying out this calculation for the dilute spheres case we find

$$\epsilon^{(e)}_\omega = \epsilon_{b,\omega} + 3p_a \epsilon_{b,\omega} \frac{\epsilon_{a,\omega} - \epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega}) p_b + 3\epsilon_{b,\omega}}. \tag{4.2}$$

This is the well-known Clausius-Mossotti result for a linear composite. $\chi^{(e)}$ is then

$$\chi^{(e)} = -p_a \chi \left( \frac{3\epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega}) p_b + 3\epsilon_{b,\omega}} \right)^2 \times \left| \frac{3\epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega}) p_b + 3\epsilon_{b,\omega}} \right|^2 , \tag{4.3}$$

where $\chi$ is given by (2.15). There is a fourth order divergence of the effective ICN coefficient at the quasistatic resonance at frequency $\omega$.

A different discussion of induced higher order nonlinearity in a composite medium has been given recently [19]. However, besides being limited to a dilute composite, that discussion also does not take into account the frequency spectrum of **E** and **D**. It is therefore not directly applicable to the case where the intrinsic nonlinearity of the components is quadratic in nature. Nevertheless, the enhancement factors, which appear in (4.3) and become large in the vicinity of the appropriate quasistatic resonance, are similar in form to those that were found in Ref. [19].

Let us now consider composites in which one of the components is metallic. When *either* component is

metallic, its zero frequency dielectric coefficient is infinite, the static component of all the local fields vanishes, and many of our expressions simplify. The ICN coefficients become

$$\chi = \frac{2p_b d_{\omega,\omega} d_{2\omega,\omega}}{(\epsilon_{a,2\omega} - \epsilon_{b,2\omega})\, p_b + 3\epsilon_{b,2\omega}} \tag{4.4}$$

in the dilute spheres microgeometry;

$$\chi = \frac{2p_b d_{\omega,\omega} d_{2\omega,\omega}}{p_a \epsilon_{b,2\omega} + p_b \epsilon_{a,2\omega}} \tag{4.5}$$

in the two-component parallel slabs microgeometry; and

$$\chi = \frac{2p_d f_{nl}^2 d_{\omega,\omega} d_{2\omega,\omega}}{(1-p_d)\, \epsilon_{d,2\omega} + p_d \epsilon_{c,2\omega}} \tag{4.6}$$

in the three-component layered microgeometry.

In all three cases, the coefficient $\chi$ of the ICN has two interesting general properties. First, it can be either positive or negative, depending on the sign of the denominator—i.e., on whether the system is above or below its $2\omega$ resonance. By contrast, the cubic nonlinear coefficients of pure materials and the bulk effective Kerr coefficients of composites of such materials, are usually positive. Secondly, the magnitude of $\chi$ can be varied by changing the volume fractions of the components. In particular, $\chi$ diverges in the vicinity of the quasistatic resonance at the SH frequency. This causes a first order divergence of $\chi^{(e)}$ at that resonance. By contrast, the cubic nonlinear behavior in composites of the *same microgeometry* but *third order* nonlinear components has only a fourth order divergence at the fundamental frequency resonance [6,7]. Because of this difference the ICN may be as important as the intrinsic cubic nonlinearity in some materials. The ICN is maximized by the closest possible approach to the resonance at the SH frequency, and thus requires that the components' dielectric constants at $2\omega$, rather than $\omega$, have a minimal imaginary part.

As an example, in the two-component parallel slabs microgeometry we choose the nonlinear component to be purely dielectric and its volume fraction to be $p_a = 0.1$. The linear component is chosen to be metallic with a real part of the dielectric constant that satisfies the resonance condition $\mathrm{Re}(p_a\epsilon_{b,2\omega} + p_b\epsilon_{a,2\omega}) = 0$ and an imaginary part equal to 0.2 (which is the minimal value in metals, obtained for Ag in the optical range [20]). A typical value for nonresonant second order susceptibility in pure materials is $d = 5 \times 10^{-8}$ esu [21]. Substituting these values in (4.5) we find $\chi = 2.25 \times 10^{-13}$ esu. This result is approximately two orders of magnitude larger than the typical nonresonant third order susceptibility of pure materials $\chi = 3 \times 10^{-15}$ esu [21]. It should also be noted that $\chi^{(e)}$ will be negative in this case.

Finally, we use the same approach to obtain the bulk effective electro-optic coefficient for the composites discussed in Sec. II. In this case, besides a monochromatic field of frequency $\omega$, we assume that there is also a static (zero frequency) field applied to the sample. The only change in Sec. II is that now the right-hand side of the zero frequency equations (2.9), (2.28), and (2.41) is taken to be nonzero. The volume averaged $D$ field at the fundamental frequency will now have an additional term of the form $d_{0,\omega}^{(e)} E_{0,0} E_{0,\omega}$, where $d_{0,\omega}^{(e)}$ is the bulk effective electro-optic coefficient of the composite. For the dilute spheres microgeometry we obtain

$$d_{0,\omega}^{(e)} = 2p_a d_{0,\omega} \left( \frac{3\epsilon_{b,0}}{(\epsilon_{a,0} - \epsilon_{b,0})\, p_b + 3\epsilon_{b,0}} \right) \times \left( \frac{3\epsilon_{b,\omega}}{(\epsilon_{a,\omega} - \epsilon_{b,\omega})\, p_b + 3\epsilon_{b,\omega}} \right)^2 . \tag{4.7}$$

Once again, we see the characteristic form of the enhancement factor [as in the expression (3.4) for $d_{\omega,\omega}^{(e)}$], which is expected on the basis of the perturbation theory described in Ref. [6], and the second order divergence near the surface plasmon resonance of the spherical inclusions at the fundamental frequency. Similar results are obtained for the two other microgeometries. The only difference is again in the locations of the quasistatic resonances in the denominators.

## V. INTRINSIC OPTICAL BISTABILITY

In Sec. II it was found that the $\omega$ component of the uniform electric field inside the nonlinear component, for every microgeometry we considered, can be calculated from the simple cubic equation (2.19). Any real positive solution of that equation leads to a possible solution for that local field. The equation always has at least one such solution. Bistability arises when it has (two) more such solutions. In order for that to happen, $\mu$ and $\alpha$ must satisfy the following conditions:

$$\mu \geq \frac{\sqrt{3}}{2}, \tag{5.1}$$

$$\frac{2}{27}\left[ -\left(8\mu^2 - 9\right)\mu - \left(4\mu^2 - 3\right)^{\frac{3}{2}} \right] < \alpha < \frac{2}{27}\left[ -\left(8\mu^2 - 9\right)\mu + \left(4\mu^2 - 3\right)^{\frac{3}{2}} \right]. \tag{5.2}$$

In addition to these conditions, it should be noted that the maximum possible value of $\mu$ is 1. In that case, the above calculated range of values of $\alpha$ becomes maximal, $0 < \alpha < 4/27 \cong 0.148$. This defines the range of the applied field $E_{0,\omega}$ in which there is more than one real solution to Eq. (2.19), for the case where all the components are purely dielectric (i.e., all $\epsilon$'s are real and positive and consequently $\mu = 1$). The possibility of having bistability in this geometry contrasts with the conditions for intrinsic bistability in composites made of cubic nonlinear components, where bistability cannot occur in purely dielectric composites [1,9–17]. In the present case, as $\mu$ decreases, the limiting values of $\alpha$ approach each other, the range of applied fields in which bistability can occur shrinks, until at $\mu = \sqrt{3}/2$ it becomes a single value corresponding to $\alpha = 3\sqrt{3}/27 \cong 0.192$, and bistability is lost. These two extreme cases of $f(t)$, as well as one

intermediate case, are shown in Fig. 1.

Figure 1 suggests that, in order for bistability to appear when $\mu \approx 1$, $\alpha$ should be increased above its upper limit value of 0.148, so that the solution for $t$ is forced into the upper branch of the curve. For other values of $\alpha$, the solution could stay on the lower branch while the applied field, and hence $\alpha$, is increased, thus avoiding bistable behavior.

The threshold external field required for bistability is determined by the microgeometry. For the spherical inclusions microgeometry, we find from the definition of $\alpha$ (2.37) that this threshold is given by

$$E^2_{0,\omega,th} = \frac{4}{27}\frac{|(\epsilon_{a,\omega} - \epsilon_{b,\omega})\, p_b + 3\epsilon_{b,\omega}|^3}{2p_b\,|\chi|\,|3\epsilon_{b,\omega}|^2}. \tag{5.3}$$

To get a minimal threshold we have to choose $\chi$ as large as possible. The largest values reported for the second order nonlinearity coefficient in the literature are of the order of $d = 10^{-5}$ esu [for Te along the (1,1,1) axis] [22].

If the composite is purely dielectric then the numerator of (5.3) and the denominator terms of $\chi$ are of order 1 and the threshold field is $E^2_{0,\omega,th} \approx 7.4 \times 10^8$ esu. The incident energy flux required to produce bistable behavior is therefore

$$I_{th} = \frac{c}{4\pi}E^2_{0,\omega,th} \approx 1.8 \times 10^{11}\ \frac{\mathrm{W}}{\mathrm{cm}^2}. \tag{5.4}$$

This extremely high value makes the observation of bistable behavior in purely dielectric composites impractical. One expects that, as $E_{a,\omega}$ increases monotonically with the applied field $E_{0,\omega}$, the volume averaged SH displacement field $D_{0,2\omega}$ will also do so.

To force bistability, the right hand side of Eq. (5.3) must be lowered to reasonable values. This can be done by using nondielectric components, decreasing $\mu$, and approaching a quasistatic resonance. To achieve this, at least one of the components must be metallic. In this case $\chi$ is given by the simplified expression (4.4) and the threshold field is approximately

$$E^2_{0,\omega,th} = \frac{4}{27}\frac{|(\epsilon_{a,2\omega} - \epsilon_{b,2\omega})\, p_b + 3\epsilon_{b,2\omega}|\,|(\epsilon_{a,\omega} - \epsilon_{b,\omega})\, p_b + 3\epsilon_{b,\omega}|^3}{2p_b^2 d_{\omega,\omega} d_{2\omega,-\omega}\,|3\epsilon_{b,\omega}|^2}. \tag{5.5}$$

The closer the composite to its resonance, the lower the threshold field. This decrease is limited by the lower limit of $\mu$ and by the imaginary parts of the dielectric constants of the components. We already discussed this problem in Sec. IV. Here again we choose, as an example, a purely dielectric nonlinear component and a metallic linear component with a real part of the dielectric constant that satisfies the resonance condition $\mathrm{Re}[(\epsilon_{a,\omega} - \epsilon_{b,\omega})\, p_b + 3\epsilon_{b,\omega}] = 0$ and an imaginary part equal to 0.2. Assuming $d = 10^{-5}$ esu and a typical value $|\epsilon_{b,\omega}| = 2$ in a very dilute mixture $p_b \approx 1$, we find $E^2_{0,\omega,th} \approx 10^6$ esu. The threshold intensity is thus

$$I_{th} \approx 3 \times 10^8\ \frac{\mathrm{W}}{\mathrm{cm}^2}. \tag{5.6}$$

This value is three orders of magnitude lower than that obtained for the purely dielectric case but it is still very large. However, this threshold can be lowered further by using other microgeometries, in which the electric field in the nonlinear component is more effectively enhanced near a resonance. The parallel slabs microgeometry is such an example. The $\mu = 1$ threshold field in this case is given by

$$E^2_{0,\omega,th} = \frac{4}{27}\frac{|p_b\epsilon_{a,2\omega} + p_a\epsilon_{b,2\omega}|\,|p_b\epsilon_{a,\omega} + p_a\epsilon_{b,\omega}|^3}{2p_b^2 d_{\omega,\omega} d_{2\omega,-\omega}\,|\epsilon_{b,\omega}|^2}. \tag{5.7}$$

Choosing $p_b = 0.9$ and the values cited above for $|\epsilon_{b,\omega}|$, $d$, and the imaginary part of $\epsilon_{b,\omega}$, we find near the resonance at the fundamental frequency $E^2_{0,\omega,th} \approx 10^3$ esu. The threshold intensity in this case is

$$I_{th} \approx 3.5 \times 10^5\ \frac{\mathrm{W}}{\mathrm{cm}^2}, \tag{5.8}$$

which is three orders of magnitude less than in the spherical inclusions microgeometry but is still rather large.

A better result can be obtained in the three-component layered microgeometry where $\epsilon_m$ is the metallic component. The threshold field for such a composite is

$$E^2_{0,\omega,th} = \frac{4}{27}\frac{|(1-p_d)\,\epsilon_{d,2\omega} + p_d\epsilon_{c,2\omega}|\,|(1-p_d)\,\epsilon_{d,\omega} + p_d\epsilon_{c,\omega}|^3}{2p_d^2 f_{nl}^2 d_{\omega,\omega} d_{2\omega,-\omega}\,|\epsilon_{d,\omega}|^2}. \tag{5.9}$$

Choosing, for example, $p_d = 0.1$, $f_m = 0.1$, $|\epsilon_{d,\omega}| = 2$ and the above values for $d$ and the imaginary part of $\epsilon_{m,\omega}$, we find $E^2_{0,\omega,th} \approx 200$ esu, which gives for the threshold intensity

$$I_{th} \approx 5 \times 10^4\ \frac{\mathrm{W}}{\mathrm{cm}^2}. \tag{5.10}$$

The lower threshold here is a result of the great enhance-

ment of the electric field in the composite layers near the resonance. An advantage of this microgeometry over two-component composites is that this enhancement is achieved in the nonlinear component with a relatively low concentration of metal. It is, in fact, equivalent to using the metal as the nonlinear component in a two-component composite but with a nonlinearity coefficient several orders of magnitude larger than in ordinary metals. Using three components also allows greater flexibility in choosing the materials and the tuning conditions for achieving resonance. We note also that the same kind of result would have been obtained if the $\epsilon_d$ component were chosen to be the same as $\epsilon_{nl}$. This emphasizes the point that it is the special microstructure which is largely responsible for lowering the threshold.

## VI. DISCUSSION AND CONCLUSIONS

We have presented results for the behavior of composite materials containing second order nonlinear components. It was shown that such materials can have enhanced second order nonlinear susceptibilities. This enhancement is closely related to the existence of sharp quasistatic resonances in the dielectric response of the composite material and is similar in nature to that found in previous studies for the third order nonlinear susceptibilities. A major difference which appears in the case discussed here is that higher harmonic fields are generated which have an important effect upon the dielectric response of the composite even at the fundamental frequency. The response of the composite at the harmonic frequencies may include a significant enhancement of the SHG and THG processes. Therefore such composites might be a much better choice for use in SHG devices than their pure nonlinear components. At the fundamental frequency, these fields give rise to an ICN with a magnitude and sign that are both strongly microgeometry dependent. The effective coefficient of this ICN is also enhanced in the vicinity of a quasistatic resonance. It may be larger than those of cubic nonlinear composites with the same microgeometry.

As pointed out in the Introduction, the appearance of optical bistability in metal-dielectric composites made of cubic nonlinear components has been predicted and discussed in a number of previous articles. Here we demonstrate this possibility in composites made of quadratic nonlinear components. Such materials are interesting because optical bistability can occur in them even when all the components are purely dielectric. It is no longer necessary that the composite include a metallic component and lie close to a quasistatic resonance, as with cubic nonlinear components. Nevertheless, it should be noted that metal-dielectric composites with cubic nonlinear components may well be more promising for achieving bistability, since they require lower threshold field intensities. In some such three-component cubic nonlinear composites threshold intensities of only a few $W/cm^2$ are needed [15,17], as compared to minimal values of the order of $10^4$ $W/cm^2$ in the examples described in this paper. Possibly other geometries not discussed here, such as suspensions of metal spheres coated with a SHG material, may prove to be still more promising.

We showed in this paper that the nonlinear bulk effective optical properties of composite materials may be much stronger then those of their pure nonlinear components. Such a composite may thus be a better material for use in nonlinear optical devices. The quasistatic calculation of these bulk effective properties is based on the assumption that the characteristic scale of the microscopic inhomogeneities inside the composite is much smaller than the wavelength of the local electric fields. Incorporating such a composite as the active element in an optical device would give rise to the usual propagation and phase matching effects which depend on the macroscopic shape of the element and the anisotropy of its structure. The quasistatic approximation does not apply to these macroscopic effects and they thus should be taken into account by the usual methods when analyzing the performance of such a device.

The results presented in Secs. III–V show that the layered microgeometries are by far the best choices for further study. This is due to the greater enhancement of the electric field in the nonlinear component which they can produce near a resonance. The enhancement obtained in the dilute inclusions type of composite is much smaller and thus causes smaller nonlinear effects. The layered composites should also be easier to fabricate and their anisotropic structure would be easier to match with the anisotropic crystal structure of all real materials that have a quadratic nonlinearity.

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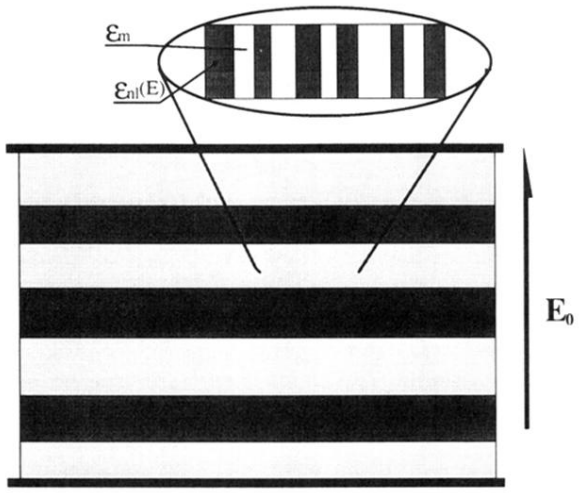


FIG. 2. A three-component microgeometry of dielectric and composite parallel slabs. The two-component layers contain the nonlinear material $\epsilon_{nl}(E) = \epsilon_{nl} + dE$.