Theory of second harmonic generation in composites of nonlinear dielectrics

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We consider the effective nonlinear susceptibility tensor $\mathbf{d}(-2\omega;\omega,\omega)$ for second harmonic generation in a nonlinear composite medium. We derive a simple expression for this susceptibility in terms of the position-dependent tensor $\mathbf{d}$, and three factors that describe the local field enhancement in a corresponding linear medium. The resulting expression can be used to calculate the local-field enhancement of $\mathbf{d}$ in many geometries. In the dilute limit, the general expression reduces to a result previously derived. © *1997 American Institute of Physics.*
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INTRODUCTION

The nonlinear response of composite materials has been of much recent interest,[1–3] in part because it may exhibit critical behavior near a percolation threshold,[4,5] and also because, at finite frequencies, it may be strongly enhanced by local field effects.[5–9] A number of theories has been developed specifically for *weakly nonlinear* materials[2–11], especially the Kerr effect, i.e., the cubic nonlinear susceptibility. These theories allow composite Kerr susceptibility to be calculated in terms of the component Kerr coefficients and local field enhancement factors which involve only the related *linear* composites.

In this Paper, we derive a similar expression for the susceptibility for second harmonic generation (SHG) in a nonlinear composite. This susceptibility is qualitatively different from the Kerr coefficient, because it intrinsically involves two different frequencies. Our SHG expression, like the earlier one for the Kerr coefficient, involves the nonlinear susceptibilities of the constituents and also local field enhancements which depend only on the properties of the related *linear* random composites. In the dilute limit, our result reduces to an earlier expression found by Levy *et al.*,[12] but our result is quite general and applicable to a wide range of geometries, as well as being amenable to various approximations. Finally, since our result refers to a coefficient involving more than one frequency, it may be a useful prototype for developing expressions for other such coefficients, such as those that describe frequency addition or subtraction.

FORMALISM AND RESULTS

We consider a macroscopically inhomogeneous medium, of volume V enclosed by a surface S, consisting of two types of materials, a and b, with different macroscopic **D**-**E** relations. If we include only quadratic nonlinearities, then the general form of this relationship *at zero frequency* would be

$$D_i=\epsilon E_i+\sum_{jk} d_{ijk}E_jE_j\,, i=x,y,z, \tag{1}$$

where D_i (E_i) is the ith component of the displacement (electric) field $\mathbf{D}$ ($\mathbf{E}$). The linear dielectric constant $\epsilon(\mathbf{x})$ would take on the values ϵ^a (ϵ^b) for $\mathbf{x}$ in regions occupied by material a (b). Similarly, the second-order nonlinear susceptibility tensor d_{ijk} takes the form d_{ijk}^a or d_{ijk}^b for $\mathbf{x}$ in regions occupied by material a or b. The finite frequency generalization of Eq. (1) is described below.

The displacement $\mathbf{D}$ at each point $\mathbf{x}$ in V satisfies Gauss's law with no free charges, i.e., $\nabla\cdot\mathbf{D}=0$. We will also assume that the quasistatic limit is valid, so that the electric field satisfies $\nabla\times\mathbf{E}=0$, and

$$\mathbf{E}(\mathbf{x})=-\nabla\Phi(\mathbf{x}), \tag{2}$$

where Φ is a scalar potential. On any interface between a and b materials, Φ and the normal component of $\mathbf{D}$ are continuous, i.e.,

$$\Phi^a=\Phi^b,\ \hat{n}\cdot\mathbf{D}^a=\hat{n}\cdot\mathbf{D}^b \text{ on } \partial\Omega, \tag{3}$$

where the superscripts a and b label the two regions separated by the interface $\partial\Omega$.

To work at finite frequencies, we assume that a monochromatic external applied field of the form

$$\mathbf{E}_0(t)=\mathbf{E}_{0,\omega}e^{-i\omega t}+c.c. \tag{4}$$

Such a field can be achieved by imposing on S a boundary condition $\Phi_0(\mathbf{x})=-\mathbf{E}_{0,\omega}\cdot\mathbf{x}e^{-i\omega t}+c.c.$ for $\mathbf{x}$ on the surface S.

Given this applied field, the potential within V, in general, has the form

$$\Phi(\mathbf{x})=\sum_{n=-\infty}^{\infty}\phi_n(\mathbf{x})e^{-in\omega t}, \tag{5}$$

since the nonlinearity of the components inside the composite will generate local potentials and fields at all harmonic frequencies. Here, the subscript n labels the different harmonics of the fundamental frequency ω. The local field in components a and b can be expressed as

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$$\mathbf{E}^{\alpha}(\mathbf{x},t) = -\sum_{n=-\infty}^{\infty} \nabla \phi_n^{\alpha}(\mathbf{x}) e^{-in\omega t} \equiv \sum_{n=-\infty}^{\infty} \mathbf{E}_{n\omega}^{\alpha}(\mathbf{x}) e^{-in\omega t}, \tag{6}$$

where the superscript α ($\alpha = a,b$) explicitly labels the fields for $\mathbf{x}$ in region α. Similarly, the Cartesian components of the displacement $\mathbf{D}$ at $\mathbf{x}$ are given by an appropriate generalization of Eq. (1) which includes the higher harmonics generated by the nonlinear relation between $\mathbf{D}$ and $\mathbf{E}$:

$$D_i^{\alpha} = \sum_{n=-\infty}^{\infty} (D_{n\omega}^{\alpha})_i e^{-in\omega t}, \tag{7}$$

with

$$(D_{n\omega}^{\alpha})_i = -\epsilon_{n\omega}^{\alpha} (\nabla \phi_n^{\alpha}(\mathbf{x}))_i + \sum_{jk} \sum_{m=-\infty}^{\infty} (d_{ijk}^{\alpha})^{(n-m,m)} \times (\nabla \phi_{n-m}^{\alpha})_j (\nabla \phi_m^{\alpha})_k . \tag{8}$$

Here the subscript in $\epsilon_{n\omega}^{\alpha}$ indicates the frequency dependence of the linear dielectric constant, while the superscripts in $(d_{ijk}^{\alpha})^{(n-m,m)}$ keep track of the different Fourier components involved in the frequency sum.

The problem of finding $\mathbf{D}$ and $\mathbf{E}$ everywhere inside V can thus be divided into an infinite number of coupled problems corresponding to the different Fourier components $\exp(-in\omega t)$. The condition that the displacement be divergence free implies that for $\mathbf{x}$ belonging to region α we must have

$$\nabla \cdot \mathbf{D}_{n\omega}^{\alpha} = 0 \text{ for } \alpha = a,b, \text{ all } n. \tag{9}$$

With the help of Eq. (8), Eq. (9) becomes

$$-\epsilon_{n\omega}^{\alpha} \nabla^2 \phi_n^{\alpha}(\mathbf{x}) + \sum_{ijk} \sum_{m=-\infty}^{\infty} (d_{ijk}^{\alpha})^{(n-m,m)} \frac{\partial}{\partial x_i} \left(\frac{\partial}{\partial x_j} \phi_{n-m}^{\alpha} \right) \times \left(\frac{\partial}{\partial x_k} \phi_m^{\alpha} \right) = 0 \quad (\alpha = a,b, \text{ all } n). \tag{10}$$

Eq. (10) is the generalization of Laplace's equation $\nabla^2 \phi(\mathbf{x}) = 0$ which includes the possibility of harmonic generation due to the presence of nonlinear materials. From Eq. (3) the boundary conditions for each Fourier component become

$$\phi_n^a = \phi_n^b, \hat{n} \cdot \mathbf{D}_{n\omega}^a = \hat{n} \cdot \mathbf{D}_{n\omega}^b, \quad \text{on } \partial\Omega, \text{ all } n. \tag{11}$$

Eq. (10) for the Fourier components of the potential, together with the boundary conditions given by Eq. (11) on $\partial\Omega$ and the externally imposed applied field, mathematically define the problem of composites containing materials with quadratically nonlinear susceptibilities, including all effects of harmonic generation and bistability.

The coupled set of Eqs. (10) is, in general, difficult to solve. In weakly nonlinear composites, however, this set of equations may reasonably be truncated to include only a few lowest harmonics. The neglected higher harmonics then involve higher powers of the nonlinear susceptibility. Even these truncated equations can be solved exactly in only a few cases, such as layered structures and dilute composites of spherical nonlinear inclusions in a linear host.[12]

To define the effective response for second harmonic generation in an inhomogeneous medium, we assume that the composite behaves as a homogeneous medium with effective parameters. We consider a homogeneous medium with effective linear dielectric constant $\epsilon^{(e)}$, which may be frequency dependent, and effective nonlinear susceptibility $d_{ijk}^{(e)}$, subjected to the same boundary conditions given by Eq. (4). The volume-averaged ith component of the (2ω) harmonic of the displacement $D_{2\omega}^{(u)}$ in such a uniform media is

$$\frac{1}{V} \int (D_{2\omega}^{(u)})_i d^3x = \frac{1}{V} \int \epsilon_{2\omega}^{(e)} (E_2)_i d^3x + \sum_{jk} \sum_{m=-\infty}^{\infty} (d_{ijk}^{(e)})^{(2-m,m)} \frac{1}{V} \times \int (E_{2-m})_j (E_m)_k d^3x. \tag{12}$$

Since the medium is homogeneous, the field inside it is uniform and equal to $\mathbf{E}_{0,\omega} e^{-i\omega t} + c.c.$ It follows immediately that the first term on the right side of Eq. (12) vanishes, and only the $m=1$ term survives in the summation. In particular, if we choose a coordinate system such that $\mathbf{E}_{0,\omega} \| \hat{z}$, then

$$\frac{1}{V} \int (D_{2\omega}^{(u)})_i d^3x = (d_{izz}^{(e)})^{(1,1)} (E_{0,\omega})_z^2 . \tag{13}$$

Thus the effective nonlinear susceptibility for SHG can be defined through the volume average $\langle \cdots \rangle$ of $D_{2\omega}(\mathbf{x})$ in an *inhomogeneous* medium:

$$(d_{izz}^{(e)})^{(1,1)} = \frac{1}{V(E_{0,\omega})_z^2} \int (D_{2\omega}(\mathbf{x}))_i d^3x \equiv \frac{1}{(E_{0,\omega})_z^2} \langle (D_{2\omega}(\mathbf{x}))_i \rangle. \tag{14}$$

This general relationship between the effective SHG susceptibility and the spatial average of $\mathbf{D}_{2\omega}(\mathbf{x})$ forms the basis for developing approximations for a weakly nonlinear composite. (Note that the quantity we call $d^{(e)(1,1)}$ is usually called $d^{(e)}(-2\omega;\omega,\omega)$ in standard textbooks in nonlinear optics,[13] with the frequencies involved in the process explicitly stated.) In what follows, we express the effective SHG susceptibility in terms of electric fields for certain equivalent *linear* problems.

It follows from Eq. (8) that, to first order in $(d_{ijk}^{\alpha})^{(1,1)}$,

$$D_{2\omega,i} = \epsilon_{2\omega}^{\alpha} E_{2\omega,i} + \sum_{jk} (d_{ijk}^{\alpha})^{(1,1)} E_{\omega,j} E_{\omega,k} , \tag{15}$$

where $\epsilon_{2\omega}^{\alpha}$ is the position-dependent linear dielectric function at frequency 2ω. The spatial average of the first term in Eq. (15) can be written as

$$\langle \epsilon_{2\omega} E_{2\omega,i} \rangle = \langle \delta\epsilon_{2\omega} E_{2\omega,i} \rangle, \tag{16}$$

where $\delta\epsilon_{2\omega}(\mathbf{x}) = \epsilon_{2\omega}(\mathbf{x}) - \epsilon_{2\omega}^e$, $\epsilon_{2\omega}^e$ being the effective linear dielectric function at frequency 2ω. Here we have used $\langle E_{2\omega,i} \rangle = 0$, which follows since this average equals the applied field at frequency 2ω, which is zero.

Using $\nabla \cdot \mathbf{D}_{2\omega} = 0$ and Eqs. (15) and (16), we have

$$-\nabla\cdot(\epsilon^e_{2\omega}\mathbf{E}_{2\omega})=\nabla\cdot(\delta\epsilon_{2\omega}\mathbf{E}_{2\omega}+\mathbf{d}\mathbf{E}_\omega\mathbf{E}_\omega), \tag{17}$$

where $\mathbf{d}$ is a shorthand for the tensor d_{ijk}. Since $\mathbf{E}_{2\omega}=-\nabla\phi_{2\omega}(\mathbf{x})$, it follows that

$$\phi_{2\omega}(\mathbf{x})=-\int G_{2\omega}(\mathbf{x},\mathbf{x}')\nabla'\cdot(\delta\epsilon_{2\omega}(\mathbf{x}')\mathbf{E}_{2\omega}(\mathbf{x}') +\mathbf{d}(\mathbf{x}')\mathbf{E}_\omega(\mathbf{x}')\mathbf{E}_\omega(\mathbf{x}'))d^3x'. \tag{18}$$

Here $G_{2\omega}(\mathbf{x},\mathbf{x}')$ is an electrostatic Green's function satisfying[7,14]

$$\epsilon^e_{2\omega}\nabla^2G_{2\omega}(\mathbf{x},\mathbf{x}')=-\delta(\mathbf{x}-\mathbf{x}') \tag{19}$$

in volume V with the boundary condition $G(\mathbf{x},\mathbf{x}')=0$ for $\mathbf{x}'$ on the surface S.

Integrating the right-hand side of Eq. (18) by parts, and taking the negative gradient of both sides, we obtain an integral equation for the Fourier components of $\mathbf{E}$:

$$\mathbf{E}_{2\omega}(\mathbf{x})=\int \mathscr{G}_{2\omega}(\mathbf{x},\mathbf{x}')(\delta\epsilon_{2\omega}(\mathbf{x}')\mathbf{E}_{2\omega}(\mathbf{x}') +\mathbf{d}(\mathbf{x}')\mathbf{E}_\omega(\mathbf{x}')\mathbf{E}_\omega(\mathbf{x}'))d^3x'. \tag{20}$$

Here $\mathscr{G}$ is a matrix Green's function defined in dyadic notation by

$$\mathscr{G}=\nabla'\nabla'G. \tag{21}$$

Eq. (20) can be regarded as the position representation of the equation

$$\mathbf{E}_{2\omega}=\mathscr{G}_{2\omega}(\delta\epsilon_{2\omega}\mathbf{E}_{2\omega}+\mathbf{d}\mathbf{E}_\omega\mathbf{E}_\omega). \tag{22}$$

This relation can also be viewed as a condensed operator notation, in that the right-hand side involves not only a matrix multiplication but also an integration over $\mathbf{x}'$. Eq. (22) may be solved formally for $\mathbf{E}_{2\omega}$ giving

$$\mathbf{E}_{2\omega}=(\mathbf{1}-\mathscr{G}_{2\omega}\delta\epsilon_{2\omega})^{-1}\mathscr{G}_{2\omega}\mathbf{d}\mathbf{E}_\omega\mathbf{E}_\omega. \tag{23}$$

Using Eqs. (16) and (23), the entire quantity in Eq. (15) of which we need the spatial average may be written as

$$\delta\epsilon_{2\omega}\mathbf{E}_{2\omega}+\mathbf{d}\mathbf{E}_\omega\mathbf{E}_\omega=(\mathbf{1}-\delta\epsilon_{2\omega}\mathscr{G}_{2\omega})^{-1}\mathbf{d}\mathbf{E}_\omega\mathbf{E}_\omega. \tag{24}$$

In order to get the effective SHG tensor, we now write $\mathbf{E}_\omega(\mathbf{x})$ as the solution of an integral equation analogous to Eq. (20):[7,14]

$$\mathbf{E}_\omega(\mathbf{x})=\mathbf{E}_{0,\omega}+\int \mathscr{G}_\omega(\mathbf{x},\mathbf{x}')\delta\epsilon_\omega(\mathbf{x}')\mathbf{E}_\omega(\mathbf{x}')d^3x'. \tag{25}$$

This may again be solved formally for $\mathbf{E}_\omega$ to yield

$$\mathbf{E}_\omega=(\mathbf{1}-\mathscr{G}_\omega\delta\epsilon_\omega)^{-1}\mathbf{E}_{0,\omega}, \tag{26}$$

where $\mathbf{E}_{0,\omega}$ is the applied field at frequency ω.

Reverting back explicitly to component notation, we write the spatial average of $D_{2\omega,i}$ as

$$\langle D_{2\omega,i}\rangle=\langle[(\mathbf{1}-\delta\epsilon_{2\omega}\mathscr{G}_{2\omega})^{-1}]_{i\ell}d_{\ell mn} \times[(\mathbf{1}-\mathscr{G}_\omega\delta\epsilon_\omega)^{-1}]_{mj} \times[(\mathbf{1}-\mathscr{G}_\omega\delta\epsilon_\omega)^{-1}]_{nk}\rangle E_{0,\omega,j}E_{0,\omega,k}, \tag{27}$$

where an integration over $\mathbf{x}'$ and a summation over repeated indices are implied. From this equation, we can finally deduce an explicit expression for the effective SHG susceptibility. Our result is more concisely expressed by introducing the operators

$$\mathscr{K}=(\mathbf{1}-\delta\epsilon\mathscr{G})^{-1} \tag{28}$$

and

$$\mathscr{K}^T=(\mathbf{1}-\mathscr{G}\delta\epsilon)^{-1}, \tag{29}$$

each specified at a particular frequency. Then it follows from Eq. (14) that

$$d^{(e)(1,1)}_{ijk}=\langle\mathscr{K}_{2\omega;i\ell}d_{\ell mn}\mathscr{K}^T_{\omega,mj}\mathscr{K}^T_{\omega,nk}\rangle. \tag{30}$$

Eq. (30) is the central result of the present work. It gives a general expression for the effective susceptibility for SHG in a random composite, in terms of certain enhancement factors which are expressed as the tensors $\mathscr{K}$ and $\mathscr{K}^T$.

Finally, we express Eq. (30) in terms of quantities that can be calculated explicitly. From Eq. (26), we have

$$\mathscr{K}^T_{\omega,mj}(\mathbf{x})=\frac{1}{E_{0,\omega,j}}E_{\omega,m}(\mathbf{x}), \tag{31}$$

with a similar expression for $\mathscr{K}^T_{\omega,nk}(\mathbf{x})$. That is, this quantity is the induced mth Cartesian component of electric field at position $\mathbf{x}$ and frequency ω when a field $E_{0,\omega}$ is applied in the jth direction at the same frequency in the *linear* random medium. Similarly

$$\mathscr{K}_{2\omega,i\ell}(\mathbf{x})=\frac{1}{E_{0,2\omega,i}}E_{2\omega,\ell}(\mathbf{x}), \tag{32}$$

using the same notation, and we are here referring to the same *linear* random medium at frequency 2ω.

DISCUSSION

Eqs. (30)–(32) represent an explicit and general prescription for calculating the effective second-harmonic susceptibility. The expression involves knowledge of (i) the second-harmonic susceptibility of each component of the random composite and (ii) the fields in the related *linear* random medium at frequencies ω and 2ω. The SHG susceptibilities of the components can have arbitrary tensorial symmetry.

Our principal result, Eq. (30), while fully general, cannot be evaluated exactly for most random composites. However, in some special cases, an exact result is possible. On such case is a system consisting of a volume fraction p ($p\ll 1$) of spheres with linear dielectric function ϵ^a and SHG susceptibility $d^{a(1,1)}_{ijk}$ randomly embedded in a linear host medium with dielectric function ϵ^b. In this case the interaction between the spheres can be ignored, and the spheres treated independently. Then $\mathscr{K}^T_{\omega,mj}$ is simply the well-known local field factor given by $3\epsilon^b_\omega\delta_{mj}/(\epsilon^a_\omega+2\epsilon^b_\omega)$. A similar expression holds for $\mathscr{K}_{2\omega}$. Hence, the effective SHG susceptibility is

$$d^{(e)(1,1)}_{ijk}=pd^{a(1,1)}_{ijk}\left(\frac{3\epsilon^b_{2\omega}}{\epsilon^a_{2\omega}+2\epsilon^b_{2\omega}}\right)\left(\frac{3\epsilon^b_\omega}{\epsilon^a_\omega+2\epsilon^b_\omega}\right)^2. \tag{33}$$

A similar expression has previously been obtained by Levy *et al.*[12] for this dilute limit. It is gratifying that this expression emerges as a special case of our general result.

In a nondilute composite in which the components do not necessarily have spherical shapes, various approximations are necessary to evaluate the general expression. Nonetheless, the general expression, since it only involves properties of the *linear* medium (at two different frequencies) and the nonlinear susceptibilities of the components, should be treatable by a range of analytical approximations, or possibly by numerical techniques.

In summary, we have developed a general expression for the second harmonic susceptibility of a random composite medium, in the limit of weak nonlinearity. The resulting form expresses this susceptibility in terms of the SHG susceptibilities of the individual composites and the *linear* properties of the composite at two different frequencies. Our result reduces to previous forms in the dilute limit, but is considerably more general. It should therefore be useful in estimating the (possibly large) enhancement of SHG susceptibilities in random composites arising from local field effects.

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