

Theory of third harmonic generation in random composites of nonlinear dielectrics

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We consider the effective nonlinear susceptibility tensor χ for third harmonic generation (THG) in a nonlinear composite medium in which the components may have nonvanishing second- and third-order nonlinear susceptibilities. We derive an expression for this susceptibility in terms of the positional-dependent second- and third-order susceptibilities within the composite, as well as several factors which describe the local field effect in a corresponding linear medium. We consider both the THG due to the presence of THG susceptibility in the components, and the induced THG due to the presence of second-order nonlinear susceptibilities in the components. The resulting expression can be used to calculate both local field and percolation effects on χ in a wide range of geometries. The general expression reduces to a simple result in the dilute limit, which is similar to that previously derived. An effective medium approximation, which is applicable to the whole range of concentration, is proposed for both the effective second and third harmonic susceptibilities. Results obtained from the general expression and the effective medium approximation are found to be in good agreement with those obtained by numerical simulations for a model system of nonlinear composites consisting of a nonlinear metallic component and a linear insulating component.

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I. INTRODUCTION

There has recently been considerable interest in the nonlinear response of composite materials.¹⁻³ This interest has arisen for several reasons. The nonlinear response, like its linear counterpart, may have critical properties near a percolation threshold.^{4,5} At finite frequencies, the nonlinear susceptibilities are believed to be strongly enhanced by local field effects.⁵⁻⁹ The local field and percolation effects lead to highly nontrivial and interesting behavior in the effective nonlinear response. In particular, the enhanced nonlinear optical response in composites may be useful for designing novel switching devices for use in photonics and real-time coherent optical signal processors.

A number of authors have developed theories applicable specifically to *weakly nonlinear* materials.²⁻¹³ Stroud and Hui⁵ derived a general expression for the effective Kerr susceptibility in terms of the local electric field distribution in *linear* composites with the same microgeometry but with the nonlinear response of the components turned off. Such an expression forms the basis for the development of various theories and approximations for the calculation of cubic nonlinear susceptibility. In particular, these approaches allow one to estimate the cubic nonlinear response (i.e., the Kerr susceptibility) in terms of the Kerr coefficients of the individual components and a local field enhancement factor for dilute concentrations of nonlinear components in a linear host. Effective medium-type approximations applicable for the whole range of concentrations have also been developed

based on the general expression. Such approximations are useful in studying the local field and percolation effects. Experimentally, enhanced nonlinear optical response has been observed in composites consisting of alternating layers of titanium dioxide and a conjugated polymer,¹⁴ and in Au:SiO₂ composite films near the percolation threshold.¹⁵

Recently, Hui, and Stroud¹⁶ derived a similar expression for the effective 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. The SHG expression, like the earlier one for the Kerr coefficient, involves the nonlinear susceptibilities of the individual constituents, and local field factors which depend on the properties of the related *linear* random composites. The effective SHG susceptibility $d_{ijk}^{(e)(1,1)}$, where the superscripts indicate the mixing of two waves at frequency ω , is given in terms of the SHG susceptibilities d_{ijk} of the components as a volume average over the composite

$$d_{ijk}^{(e)(1,1)} = \langle \mathcal{H}_{2\omega;i} \mathcal{H}_{\omega,mn}^T \mathcal{H}_{\omega,mj}^T \mathcal{H}_{\omega,nk}^T \rangle, \quad (1)$$

where $\mathcal{H}(x)$ and $\mathcal{H}^T(x)$ are matrices related to the induced electric field at position x in the related linear random medium when an external field is applied, and the frequency subscript in \mathcal{H} and \mathcal{H}^T indicates the frequency of the induced and applied fields. Levy *et al.*¹⁷ considered SHG and induced third harmonic generation (THG) in composites with specific geometries, namely dilute spherical nonlinear inclusions in a linear host, and multilayer structures. In the dilute limit, the above expression reduces to an earlier expression

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found in Ref. 17, but Eq. (1) is quite general and applicable to a wide range of geometries, as well as amenable to various approximations.

Since second- and third-order nonlinear effects are the dominant nonlinear optical response in materials, it is desirable to derive a general expression for the effective THG susceptibility in random composite materials. In this article, we derive an expression similar to Eq. (1) for the THG susceptibility in a nonlinear composite. This problem is more complicated than the SHG susceptibility in that two effects have to be considered. There is an induced THG due to the presence of second-order nonlinear response in the components. In addition, THG may also result from the intrinsic THG susceptibilities of the components in the composite. Our result is general and forms the basis for developing approximations and numerical methods for studying THG in random composites. Furthermore, 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 which describe frequency addition or subtraction.

In the remainder of this article, we first describe the equations for calculating the THG coefficient in a random, weakly nonlinear composite, and then use this general formalism to obtain the desired expression for the THG coefficient. As an illustration, we apply the results to the case of a dilute concentration of nonlinear components in a linear host. For general range of concentrations, we propose an effective medium approximation (EMA) for both the SHG and THG susceptibilities in nonlinear composites, and thus provide a simple way to study both the local field enhancement and percolation effects in SHG and THG in composites. To establish the validity of our results, we compare the results obtained from the general expressions and the EMA to those obtained by direct simulations for a two-dimensional (2D) model system consisting of a nonlinear metallic component and a linear insulating component. Results from the different methods are found to agree well.

II. FORMALISM AND RESULTS

A. Basic equations; The effective third harmonic susceptibility

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 \mathbf{D} - \mathbf{E} relations. If we include both quadratic and cubic nonlinearities, then the general form of this relationship at zero frequency would be

$$D_i = \epsilon E_i + \sum_{jk} d_{ijk} E_j E_k + \sum_{ijkl} \chi_{ijkl} E_j E_k E_l, \quad i = x, y, z, \quad (2)$$

where D_i (E_i) is the i th component of the displacement (electric) field \mathbf{D} (\mathbf{E}). The linear dielectric constant $\epsilon(x)$, which is taken to be a scalar for simplicity, would take on the values ϵ^a (ϵ^b) for \mathbf{x} in regions occupied by material a (b). Similarly, the second-order (third-order) nonlinear susceptibility d_{ijk} (χ_{ijkl}), which is in general a rank-3 (rank-4) tensor, takes the form d_{ijk}^a (χ_{ijkl}^a) and d_{ijk}^b (χ_{ijkl}^b) for \mathbf{x} in regions occupied by

material a and material b , respectively. At finite frequencies, Eq. (2) must be generalized in a way which connects different frequencies, as described below. While the intrinsic cubic nonlinearities of the components will certainly lead to an effective cubic nonlinearity in the composite, the quadratic nonlinear term would also lead to an induced cubic nonlinear response.

The displacement \mathbf{D} at each point \mathbf{x} in V satisfies Gauss's law with no free charges, i.e., $\nabla \cdot \mathbf{D} = 0$. In what follows, we make the additional assumption that the quasi-static limit is valid, so that the electric field in V satisfies $\nabla \times \mathbf{E} = 0$. Hence, a scalar potential $\Phi(x)$ can be defined through the relation

$$\mathbf{E}(x) = -\nabla \Phi(x). \quad (3)$$

The boundary conditions are that on any interface between regions of a and b materials, the potential Φ and the normal component of the displacement \mathbf{D} are continuous, i.e.,

$$\Phi^a = \Phi^b \quad \text{on } \partial\Omega \quad (4)$$

and

$$\hat{n} \cdot \mathbf{D}^a = \hat{n} \cdot \mathbf{D}^b \quad \text{on } \partial\Omega, \quad (5)$$

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

We now wish to consider the behavior of this composite medium at finite frequencies, with the specific goal of obtaining a form for the effective third-order susceptibility of the composite. To accomplish this, we assume that a monochromatic external field of the form

$$\mathbf{E}_0(t) = \mathbf{E}_{0,\omega} e^{-i\omega t} + \text{c.c.} \quad (6)$$

is applied to the system. Such a field can be achieved by imposing on the surface S a boundary condition

$$\Phi_0(\mathbf{x}) = -\mathbf{E}_{0,\omega} \cdot \mathbf{x} e^{-i\omega t} + \text{c.c.} \quad \text{for } \mathbf{x} \text{ on } S. \quad (7)$$

Given this applied field, the potential at \mathbf{x} within volume V , in general, has the form

$$\Phi(\mathbf{x}) = \sum_{n=-\infty}^{\infty} \phi_n(\mathbf{x}) e^{-in\omega t} \quad (8)$$

since the nonlinear character of the components inside the composite will generate local potential and fields at all the harmonic frequencies. Here, the subscript n in the Fourier component $\phi_n(\mathbf{x})$ labels the different harmonics of the fundamental frequency ω . The local field in components a and b can be expressed as

$$\mathbf{E}^\alpha(\mathbf{x}, t) = - \sum_{n=-\infty}^{\infty} \nabla \phi_n^\alpha(\mathbf{x}) e^{-in\omega t} \equiv \sum_{n=-\infty}^{\infty} \mathbf{E}_{n\omega}^\alpha(\mathbf{x}) e^{-in\omega t}, \quad (9)$$

where we have added a superscript α ($\alpha = a, b$) to explicitly label 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. (2) which includes the higher harmonics generated by the nonlinear relation between \mathbf{D} and \mathbf{E}

$$D_i^\alpha = \sum_{n=-\infty}^{\infty} (D_{n\omega}^\alpha)_i e^{-in\omega t} \tag{10}$$

with

$$\begin{aligned} (D_{n\omega}^\alpha)_i = & -\epsilon_{n\omega}^\alpha [\nabla \phi_n^\alpha(\mathbf{x})]_i + \sum_{jk} \sum_{m=-\infty}^{\infty} (d_{ijk}^\alpha)^{(n-m,m)} \\ & \times (\nabla \phi_{n-m}^\alpha)_j (\nabla \phi_m^\alpha)_k \\ & - \sum_{jkl} \sum_{p,q=-\infty}^{\infty} (\chi_{ijkl}^\alpha)^{(n-p-q,p,q)} \\ & \times (\nabla \phi_{n-p-q}^\alpha)_j (\nabla \phi_p^\alpha)_k (\nabla \phi_q^\alpha)_l. \end{aligned} \tag{11}$$

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

The problem of solving \mathbf{D} and \mathbf{E} everywhere inside the volume 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 is divergence free implies that for \mathbf{x} belonging to region α we must have

$$\nabla \cdot \mathbf{D}_{n\omega}^\alpha = 0 \text{ for } \alpha = a, b, \text{ all } n. \tag{12}$$

With the help of Eq. (11), Eq. (12) becomes

$$\begin{aligned} -\epsilon_{n\omega}^\alpha \nabla^2 \phi_n^\alpha(\mathbf{x}) + \sum_{ijk} \sum_{m=-\infty}^{\infty} (d_{ijk}^\alpha)^{(n-m,m)} \frac{\partial}{\partial x_i} \left[\left(\frac{\partial}{\partial x_j} \phi_{n-m}^\alpha \right) \right. \\ \left. \times \left(\frac{\partial}{\partial x_k} \phi_m^\alpha \right) \right] - \sum_{ijkl} \sum_{p,q=-\infty}^{\infty} (\chi_{ijkl}^\alpha)^{(n-p-q,p,q)} \\ \times \frac{\partial}{\partial x_i} \left[\left(\frac{\partial}{\partial x_j} \phi_{n-p-q}^\alpha \right) \left(\frac{\partial}{\partial x_k} \phi_p^\alpha \right) \left(\frac{\partial}{\partial x_l} \phi_q^\alpha \right) \right] = 0, \\ (\alpha = a, b, \text{ all } n). \end{aligned} \tag{13}$$

Equation (13) 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 Eqs. (4) and (5), the boundary conditions for each Fourier component become

$$\phi_n^a = \phi_n^b, \text{ on } \partial\Omega, \text{ all } n \tag{14}$$

and

$$\hat{n} \cdot \mathbf{D}_{n\omega}^a = \hat{n} \cdot \mathbf{D}_{n\omega}^b, \text{ on } \partial\Omega, \text{ all } n. \tag{15}$$

Equation (13) for the Fourier components of the potential, together with the boundary conditions given by Eqs. (14) and (15) on $\partial\Omega$ and the externally imposed applied field, mathematically define the problem of composites containing materials with quadratically and cubically nonlinear susceptibilities, including all effects of harmonic generation and bistability.

In general, the coupled set of Eqs. (13) is difficult to solve. In the case of weakly nonlinear composites, however, it is a reasonable approximation to truncate this set of equations to include only the few lowest harmonics. The neglected higher harmonics then involve higher orders in the

nonlinear susceptibilities. 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.¹⁷

To define the effective response of an inhomogeneous medium, one assumes that the medium behaves as a homogeneous medium with effective parameters. In the present work, we aim at defining the effective nonlinear susceptibility for third harmonic generation. To that end, we consider a homogeneous medium with an effective linear dielectric constant $\epsilon^{(e)}$ (which may be frequency dependent), as well as effective second- and third-order nonlinear susceptibilities $d_{ijk}^{(e)}$ and $\chi_{ijkl}^{(e)}$, subject to the same boundary conditions (6) and (7). The volume-averaged i th component of the (3 ω) harmonic of the displacement $D_{3\omega}^{(u)}$ in such a uniform media is

$$\begin{aligned} \frac{1}{V} \int (D_{3\omega}^{(u)})_i d^3x \\ = \frac{1}{V} \int \epsilon_{3\omega}^{(e)} (E_3)_i d^3x + \sum_{jk} \sum_{m=-\infty}^{\infty} (d_{ijk}^{(e)})^{(3-m,m)} \\ \times \frac{1}{V} \int (E_{3-m})_j (E_m)_k d^3x \\ + \sum_{jkl} \sum_{p,q=-\infty}^{\infty} (\chi_{ijkl}^{(e)})^{(3-p-q)} \\ \times \frac{1}{V} \int (E_{3-p-q})_j (E_p)_k (E_q)_l d^3x. \end{aligned} \tag{16}$$

Since the medium is homogeneous, the field inside the medium is uniform and equal to $\mathbf{E}_{0,\omega} e^{-i\omega t} + \text{c.c.}$ It follows immediately that the first and second terms on the right hand side of Eq. (16) vanish, and only the $p = q = 1$ term survives in the summations in the third term. In particular, if we choose a coordinate system such that the applied field $\mathbf{E}_{0,\omega}$ is along the \hat{z} direction, then

$$\frac{1}{V} \int (D_{3\omega}^{(u)})_i d^3x = (\chi_{izzz}^{(e)})^{(1,1,1)} (E_{0,\omega})_z^3. \tag{17}$$

Thus the effective nonlinear susceptibility for (THG) can be defined through the volume average $\langle \dots \rangle$ of $\mathbf{D}_{3\omega}(\mathbf{x})$ in an inhomogeneous medium

$$\begin{aligned} (\chi_{izzz}^{(e)})^{(1,1,1)} &= \frac{1}{(E_{0,\omega})_z^3 V} \int [D_{3\omega}(\mathbf{x})]_i d^3x \\ &\equiv \frac{1}{(E_{0,\omega})_z^3} \langle [D_{3\omega}(\mathbf{x})]_i \rangle. \end{aligned} \tag{18}$$

This general relationship between the effective THG susceptibility and the spatial average of $\mathbf{D}_{3\omega}(\mathbf{x})$ forms the basis for developing approximations. In what follows, we provide an explicit expression for the effective THG susceptibility in terms of electric fields for certain equivalent linear problems. This expression is valid to first order in the THG susceptibilities and second order in the quadratic nonlinear susceptibilities of the constituents. It should be noted that (apart from a constant) the quantity we call $\chi^{(e)(1,1,1)}$ is usu-

ally written as $\chi^{(e)}(-3\omega; \omega, \omega, \omega)$ in standard textbooks in nonlinear optics,¹⁸ with the frequencies involved in the process explicitly stated.

B. Explicit form for $\chi_{ijkl}^{(e)(1,1,1)}$

We now derive an explicit form for $\chi_{ijkl}^{(e)(1,1,1)}$ for a weakly nonlinear composite medium. It follows from Eq. (11) that

$$\begin{aligned}
 D_{3\omega,i} &= \epsilon_{3\omega}^\alpha E_{3\omega,i} + \sum_{jk} [(d_{ijk}^\alpha)^{(2,1)} E_{2\omega,j} E_{\omega,k} \\
 &\quad + (d_{ijk}^\alpha)^{(1,2)} E_{\omega,j} E_{2\omega,k}] \\
 &\quad + \sum_{jkl} (\chi_{ijkl}^\alpha)^{(1,1,1)} E_{\omega,j} E_{\omega,k} E_{\omega,l} \\
 &= \epsilon_{3\omega}^\alpha E_{3\omega,i} + \sum_{jk} 2(d_{ijk}^\alpha)^{(2,1)} E_{2\omega,j} E_{\omega,k} \\
 &\quad + \sum_{jkl} (\chi_{ijkl}^\alpha)^{(1,1,1)} E_{\omega,j} E_{\omega,k} E_{\omega,l}, \tag{19}
 \end{aligned}$$

where $\epsilon_{3\omega}^\alpha$ is the position-dependent linear dielectric function at frequency 3ω , and the permutational symmetry of the second-order susceptibility $d_{ijk}[-(\omega_1 + \omega_2); \omega_1, \omega_2]$ has been used. In Eq. (19), we have kept those terms either linear in χ_{ijkl} or quadratic in d_{ijk} .

The spatial average of the first term in Eq. (19) can be written as

$$\langle \epsilon_{3\omega}^\alpha E_{3\omega,i} \rangle = \langle \delta\epsilon_{3\omega} E_{3\omega,i} \rangle, \tag{20}$$

where $\delta\epsilon_{3\omega}(\mathbf{x}) = \epsilon_{3\omega}(\mathbf{x}) - \epsilon_{3\omega}^e$, $\epsilon_{3\omega}^e$ being the effective linear dielectric function at frequency 3ω . Here we have used $\langle E_{3\omega,i} \rangle = 0$, which follows since this average equals the applied field at frequency 3ω , which is zero.

Using $\nabla \cdot \mathbf{D}_{3\omega} = 0$ and Eqs. (19) and (20), we have

$$-\nabla \cdot (\epsilon_{3\omega}^e \mathbf{E}_{3\omega}) = \nabla \cdot (\delta\epsilon_{3\omega} \mathbf{E}_{3\omega} + 2\mathbf{d}^{(2,1)} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega), \tag{21}$$

where \mathbf{d} is shorthand for the tensor d_{ijk} and χ is shorthand for the tensor χ_{ijkl} . Since $\mathbf{E}_{3\omega} = -\nabla \Phi_{3\omega}(\mathbf{x})$, it follows that

$$\begin{aligned}
 \Phi_{3\omega}(\mathbf{x}) &= - \int G_{3\omega}(\mathbf{x}, \mathbf{x}') \nabla' \cdot [\delta\epsilon_{3\omega}(\mathbf{x}') \mathbf{E}_{3\omega}(\mathbf{x}') \\
 &\quad + 2\mathbf{d}^{(2,1)}(\mathbf{x}') \mathbf{E}_{2\omega}(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}') \\
 &\quad + \chi \mathbf{E}_\omega(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}')] d^3 x'. \tag{22}
 \end{aligned}$$

Here $G_{3\omega}(\mathbf{x}, \mathbf{x}')$ is an electrostatic Green's function satisfying^{7,19}

$$\epsilon_{3\omega}^e \nabla^2 G_{3\omega}(\mathbf{x}, \mathbf{x}') = -\delta(\mathbf{x} - \mathbf{x}') \tag{23}$$

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. (22) by parts, and taking the negative gradient of both sides, we obtain an integral equation explicitly for the Fourier components of \mathbf{E}

$$\begin{aligned}
 \mathbf{E}_{3\omega}(x) &= \int \mathcal{G}_{3\omega}(\mathbf{x}, \mathbf{x}') [\delta\epsilon_{3\omega}(\mathbf{x}') \mathbf{E}_{3\omega}(\mathbf{x}') + 2\mathbf{d}^{(2,1)}(\mathbf{x}') \\
 &\quad \times \mathbf{E}_{2\omega}(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}') + \chi(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}') \\
 &\quad \times \mathbf{E}_\omega(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}')] d^3 x'. \tag{24}
 \end{aligned}$$

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

$$\mathcal{G} = \nabla' \nabla' G. \tag{25}$$

Equation (24) can be regarded as the position representation of the equation

$$\mathbf{E}_{3\omega} = \mathcal{G}_{3\omega} (\delta\epsilon_{3\omega} \mathbf{E}_{3\omega} + 2\mathbf{d}^{(2,1)} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega). \tag{26}$$

This relation can also be viewed as a condensed operation notation, in that the right hand side involves not only a matrix multiplication but also an integration over \mathbf{x}' . Equation (26) may be solved formally for $\mathbf{E}_{3\omega}$ giving

$$\mathbf{E}_{3\omega} = (1 - \mathcal{G}_{3\omega} \delta\epsilon_{3\omega})^{-1} \mathcal{G}_{3\omega} (2\mathbf{d}^{(2,1)} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega). \tag{27}$$

Hence, the entire quantity in Eq. (19) of which we need the spatial average may be written as

$$\begin{aligned}
 \delta\epsilon_{3\omega} \mathbf{E}_{3\omega} + 2\mathbf{d}^{(2,1)} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega \\
 &= [\delta\epsilon_{3\omega} (\mathbf{1} - \mathcal{G}_{3\omega} \delta\epsilon_{3\omega})^{-1} \mathcal{G}_{3\omega} + \mathbf{1}] \\
 &\quad \times (2\mathbf{d}^{(2,1)} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega) \\
 &= (\mathbf{1} - \delta\epsilon_{3\omega} \mathcal{G}_{3\omega})^{-1} (2\mathbf{d} \mathbf{E}_{2\omega} \mathbf{E}_\omega + \chi \mathbf{E}_\omega \mathbf{E}_\omega \mathbf{E}_\omega). \tag{28}
 \end{aligned}$$

In order to get the effective THG tensor, we need an expression for $\mathbf{E}_{2\omega}$. If we keep only terms to lowest order in χ , we find that the 2ω component of the electric field comes from the second harmonic generation via the effect of $\mathbf{d}^{(1,1)}$. Using $\nabla \cdot \mathbf{D}_{2\omega} = 0$ and carrying out a similar analysis as above for the 2ω component, we obtain¹⁶

$$\mathbf{E}_{2\omega} = (\mathbf{1} - \mathcal{G}_{2\omega} \delta\epsilon_{2\omega})^{-1} \mathcal{G}_{2\omega} \mathbf{d}^{(1,1)} \mathbf{E}_\omega \mathbf{E}_\omega. \tag{29}$$

The field $\mathbf{E}_\omega(x)$ can similarly be written as the solution of an integral equation analogous to Eq. (24)^{7,19}

$$\mathbf{E}_\omega(\mathbf{x}) = \mathbf{E}_{0,\omega} + \int \mathcal{G}_\omega(\mathbf{x}, \mathbf{x}') \delta\epsilon_\omega(\mathbf{x}') \mathbf{E}_\omega(\mathbf{x}') d^3 x'. \tag{30}$$

This may again be solved formally for \mathbf{E}_ω to yield

$$\mathbf{E}_\omega = (\mathbf{1} - \mathcal{G}_\omega \delta\epsilon_\omega)^{-1} \mathbf{E}_{0,\omega}, \tag{31}$$

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

Substituting \mathbf{E}_ω into Eqs. (28) and (29) and reverting back explicitly to component notation, we write the spatial average of $D_{3\omega,i}$ as

$$\begin{aligned}
 \langle D_{3\omega,i} \rangle &= \langle [(\mathbf{1} - \delta\epsilon_{3\omega} \mathcal{G}_{3\omega})^{-1}]_{im} (2d_{mnp}^{(2,1)} \\
 &\quad \times [(\mathbf{1} - \mathcal{G}_{2\omega} \delta\epsilon_{2\omega})^{-1}]_{nq} \mathcal{G}_{2\omega,qr} d_{rst}^{(1,1)} + \chi_{mstip}^{(1,1,1)}) \\
 &\quad \times [(\mathbf{1} - \mathcal{G}_\omega \delta\epsilon_\omega)^{-1}]_{sj} [(\mathbf{1} - \mathcal{G}_\omega \delta\epsilon_\omega)^{-1}]_{tk} \\
 &\quad \times [(\mathbf{1} - \mathcal{G}_\omega \delta\epsilon_\omega)^{-1}]_{pl} \rangle E_{0,\omega,j} E_{0,\omega,k} E_{0,\omega,l}, \tag{32}
 \end{aligned}$$

where an integration over \mathbf{x}' is implied and repeated indices are summed over. An average over \mathbf{x} is also implied in the volume average. From this equation, we can finally deduce

an explicit expression for the effective THG susceptibility. Our result is more concisely expressed by introducing the operators

$$\mathcal{H} = (\mathbf{1} - \delta\epsilon\mathcal{F})^{-1} \tag{33}$$

and

$$\mathcal{H}^T = (\mathbf{1} - \mathcal{F}\delta\epsilon)^{-1} \tag{34}$$

each specified at a particular frequency. Then it follows from Eq. (18) that we simply have

$$\begin{aligned} \chi_{ijkl}^{(e)(1,1,1)} = & \langle \mathcal{H}_{3\omega;im} (2d_{mnp}^{(2,1)} \mathcal{H}_{2\omega,nq}^T \mathcal{F}_{2\omega,qr} d_{rst}^{(1,1)} \\ & + \chi_{mstp}^{(1,1,1)}) \mathcal{H}_{\omega,sj}^T \mathcal{H}_{\omega,tk}^T \mathcal{H}_{\omega,pl}^T \rangle. \end{aligned} \tag{35}$$

Equation (35) is the main result of the present work. It gives a general expression for the effective susceptibility for THG in a random composite, in terms of certain enhancement factors which are expressed as the tensors \mathcal{H} and \mathcal{H}^T . There are two contributions to the effective THG coefficient. The term involving the factors of the second-order susceptibilities $d^{(2,1)}$ and $d^{(1,1)}$ corresponds to the effect of first forming a 2ω component and then combining the 2ω component with a ω component to give a 3ω component. The other term, which involves the third-order susceptibilities $\chi^{(1,1,1)}$, represents the effect arising from the intrinsic third harmonic susceptibilities of the constituents.

Finally, we wish to express the result (35) in terms of quantities which can be calculated explicitly. From Eq. (31), we have

$$\mathcal{H}_{\omega,mj}^T(\mathbf{x}) = \frac{1}{E_{0,\omega,j}} E_{\omega,m}(\mathbf{x}) \tag{36}$$

with a similar expression for $\mathcal{H}_{\omega,nk}^T(\mathbf{x})$. That is, this quantity is the induced m th Cartesian component of electric field at position \mathbf{x} and frequency ω when a field $E_{0,\omega}$ is applied in the j th direction at the same frequency in the *linear* random medium. Similarly, at frequency 2ω (3ω)

$$\mathcal{H}_{2\omega(3\omega),il}(\mathbf{x}) = \frac{1}{E_{0,2\omega(3\omega),i}} E_{2\omega(3\omega),l}(\mathbf{x}) \tag{37}$$

using the same notation, and we are here dealing with the same *linear* random medium at frequency 2ω (3ω).

Equations (35)–(37) represent a completely explicit and general prescription for calculating the effective third harmonic susceptibility. The expression involves (i) a knowledge of the second- and third-order nonlinear susceptibilities of each component of the random composite; and (ii) the fields in the related *linear* random medium at frequencies ω , 2ω and 3ω . The nonlinear susceptibilities of the components can have any arbitrary tensorial symmetry.

III. APPLICATIONS

A. Dilute limit

Our principal result, Eq. (35), is fully general. However, it cannot be evaluated exactly for most random composites and hence various approximations are needed. In some special cases, an exact result is possible. One such case is a system consisting of a volume fraction p ($p \ll 1$) of spheres

with linear dielectric function ϵ^a and nonlinear susceptibilities d_{ijk}^a and χ_{ijkl}^a 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 can be treated independently. Then $\mathcal{H}_{\omega,mj}^T$ is simply the well-known local field factor given by $3\epsilon_{\omega}^b \delta_{mj} / (\epsilon_{\omega}^a + 2\epsilon_{\omega}^b)$. Similar expressions hold for $\mathcal{H}_{2\omega}$ and $\mathcal{H}_{3\omega}$. Hence, the effective THG susceptibility is

$$\begin{aligned} \chi_{ijkl}^{(e)(1,1,1)} = & p \left(\frac{3\epsilon_{3\omega}^b}{\epsilon_{3\omega}^a + 2\epsilon_{3\omega}^b} \right) \left(\frac{3\epsilon_{\omega}^b}{\epsilon_{\omega}^a + 2\epsilon_{\omega}^b} \right)^3 \\ & \times \left(\chi_{ijkl}^{a(1,1,1)} - \frac{2d_{inl}^{a(1,2)} d_{njk}^{a(1,1)}}{\epsilon_{2\omega}^a + 2\epsilon_{2\omega}^b} \right). \end{aligned} \tag{38}$$

A similar expression has previously been obtained by Levy *et al.*¹⁷ for this dilute limit. It is evident from Eq. (38) that enhancement in the THG may be produced by local field effects, especially at the surface plasmon resonance frequency. Recent studies have shown that anisotropy in a random system may be useful in separating the resonance frequencies corresponding to this enhancement effect from those corresponding to absorption. Our general result, Eq. (35), is a good starting point for carrying out similar investigations for THG in random composites with anisotropy.

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

B. Voltage summation method

In particular, one can perform numerical calculations on random resistor networks at different frequencies and carry out the averages in Eq. (35) explicitly. Since the averages involve summations over products of voltage differences between neighboring nodes in a random *linear* resistor network, the method is termed the voltage summation method (VSM). It should be pointed out that this approach is simply Eq. (35) stated in the context of discrete resistor networks.

To illustrate the basic idea, we consider a 2D realization of the random system. The system is modeled as two types of bonds randomly placed on a 2D square lattice. There is a concentration p of nonlinear bonds and a concentration $1 - p$ of linear bonds. The generalization to the case of a mixture of two or more types of nonlinear bonds in the system is straightforward. For simplicity we consider the case in which the lowest order nonlinear response in the nonlinear component is cubic. In this case, the first term in Eq. (35), which represents the induced THG, vanishes. For this model, the nonlinear bonds are characterized by the linear conductance g_a and nonlinear susceptibility χ_a , the latter representing the response to three voltages at frequency ω . The linear com-

ponent is characterized by a conductance g_b . To model a mixture of metallic and insulating components, we take g_a and g_b to be of the forms

$$g_a(\omega) = \frac{1 + i\omega RC - \omega^2 LC}{R + i\omega L} \quad (39)$$

and

$$g_b = i\omega C. \quad (40)$$

The nonlinear susceptibility χ_a is assumed to be independent of frequency. This choice of g_a and g_b has been widely used in studying the frequency response in random composites,²⁰ because the ratio g_a/g_b has the same form as the Drude dielectric function of a metal with the plasma frequency $\omega_p = \sqrt{1/LC}$ and relaxation time $\tau = L/R$. Equation (35) suggests that the effective THG susceptibility can be obtained by finding the voltages at the nodes of the random network in the presence of an applied voltage V_0 across the network at two different frequencies ω and 3ω in the *absence* of χ_a , i.e., in the corresponding *linear* random resistor network problem with the nonlinear term χ_a turned off. We can then use standard methods, such as solving Kirchhoff's Law self-consistently by the relaxation method, or inverting a complex matrix, to solve for the voltages at the nodes. The latter method has the advantage that one can avoid both critical slowing down in the vicinity of the percolation threshold and convergence problems at resonant frequencies. After one solves for the voltages in the *linear* network at two frequencies, the effective THG susceptibility χ_{eff}/χ_a can be obtained numerically via the second term on the right hand side of Eq. (35); this term involves an average over the product of voltage differences across the nonlinear bonds at ω and at 3ω .

Figure 1 shows the real and imaginary parts of the effective THG coefficient χ_{eff}/χ_a as a function of frequency for five different values of concentration, as calculated using the VSM and the present model for the dielectric functions. The parameters are chosen to be $C=1$, $L=1$, and $R=0.1$. The dashed lines are the results of the voltage summation method. The data are obtained on 30×30 lattices with data averaged over ten different configurations for each value of ω and p .

To establish the validity of the VSM, we have also performed direct numerical simulations on random nonlinear networks retaining the nonlinear terms. Kirchhoff's Law is solved for the voltage at each node. Although the applied voltage imposed on the nonlinear network consists only of a component at frequency ω , the voltage at each node inside the network has components at frequencies ω and 3ω . Thus, solving Kirchhoff's Law amounts to simultaneously solving the two equations $\sum I^{(\omega)} = 0$ and $\sum I^{(3\omega)} = 0$ at each node. (The summations are carried out over all the bonds connected to the node under consideration). The two equations at each node must be solved self-consistently for the voltages at frequencies ω and 3ω ; the effective THG can be extracted from these solutions. Note that this approach requires a more complicated calculation than the VSM in that there are two equations to solve at each node, each of which has nonlinear terms. On the positive side, this method basically solves the nonlinear network problem exactly.

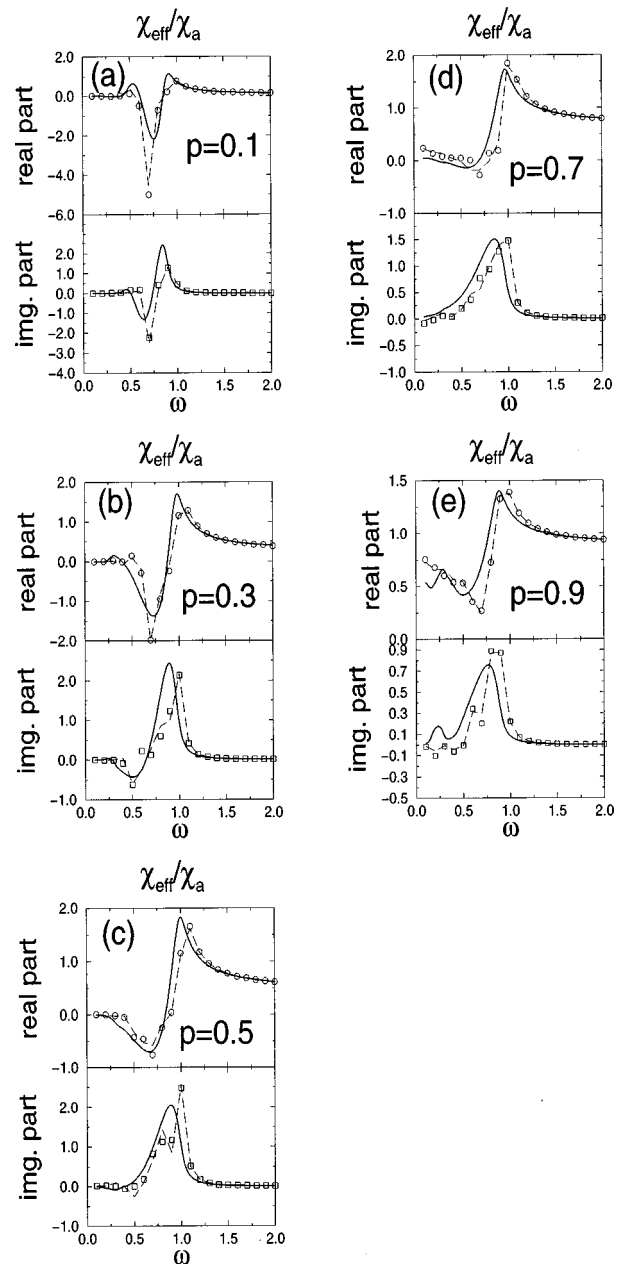


FIG. 1. The real and imaginary parts of the effective THG in a two-dimensional system consisting of a nonlinear metallic component and a linear insulating component as described in the text, plotted as a function of frequency for five different values of concentration p of the metallic component: (a) $p=0.1$, (b) 0.3, (c) 0.5, (d) 0.7, and (e) 0.9. The dashed lines are results obtained by the voltage summation method [essentially Eq. (35)]. The symbols are results from direct numerical simulations on random nonlinear networks. The solid lines are results of the effective medium approximation.

We have performed direct simulations of this kind on the 2D system previously discussed; our results are shown in Fig. 1 together with those obtained by the VSM. It is obvious that the VSM, which is a numerical realization of our general expression Eq. (35), gives results in good agreement with direct simulations. For $p=0.1$, which represents a low-concentration case, one clearly sees the so-called surface plasmon resonance, which occurs at $\omega/\omega_p = 1/\sqrt{2}$ in 2D. As the metallic concentration increases, the peak is broadened

and the metallic behavior dominates for p larger than the percolation threshold, which is $1/2$ in 2D square lattices.

Our numerical examples indicate that the VSM is a systematic and reliable way to study the effective nonlinear response. Since the VSM involves only calculations on linear random networks, convergence of the voltages at the nodes can be easily achieved. Given the good agreement with results from direct simulations, the method should be very useful in the design of novel composites aiming at providing specific THG and other nonlinear optical properties.

C. Effective medium approximation

Besides numerical investigations, it is desirable to have a simple analytical approximation that captures the essential features at least qualitatively. One such approximation in random composites is the effective medium approximation (EMA). A natural effective medium approximation for $\mathbf{d}^{(e)(1,1)}$ and $\chi^{(e)(1,1,1)}$ immediately suggests itself. Namely, we calculate the electric fields within each (assumed spherical) particle as if that particle is embedded in an effective medium with dielectric constant ϵ^e . The result for $\mathbf{d}^{(e)(1,1)}$ in this approximation, which follows from Eq. (1), is

$$\mathbf{d}^{(e)(1,1)} = \sum_{\alpha} p_{\alpha} \mathbf{d}^{\alpha} \left(\frac{3\epsilon_{2\omega}^e}{\epsilon_{2\omega}^{\alpha} + 2\epsilon_{2\omega}^e} \right) \left(\frac{3\epsilon_{\omega}^e}{\epsilon_{\omega}^{\alpha} + 2\epsilon_{\omega}^e} \right)^2. \quad (41)$$

Here p_{α} is the volume fraction of the α th component in the random composites, and \mathbf{d}^{α} is the value of \mathbf{d} in the α th component. The effective dielectric constant ϵ^e can be computed from the usual linear effective medium approximation via¹⁻³

$$\sum_{\alpha} p_{\alpha} \frac{\epsilon^{\alpha} - \epsilon^e}{\epsilon^{\alpha} + 2\epsilon^e} = 0. \quad (42)$$

Similarly, for a random composite consisting of a concentration p of nonlinear component with coefficients d_{ijk}^a and χ_{ijkl}^a of concentration p combined with linear components of concentration $1 - p$, we have

$$\chi_{ijkl}^{(e)(1,1,1)} = p \left(\frac{3\epsilon_{3\omega}^e}{\epsilon_{3\omega}^a + 2\epsilon_{3\omega}^e} \right) \left(\frac{3\epsilon_{\omega}^e}{\epsilon_{\omega}^a + 2\epsilon_{\omega}^e} \right)^3 \times \left(\chi_{ijkl}^{a(1,1,1)} - \frac{2d_{inl}^{a(1,2)} d_{njk}^{a(1,1)}}{\epsilon_{2\omega}^a + 2\epsilon_{2\omega}^e} \right) \quad (43)$$

with ϵ^e determined by the linear effective medium approximation given by Eq. (42). While the local field factors are explicit in our proposed EMA, percolation effects are also included through the linear EMA, since Eq. (42) is, perhaps, the simplest approximation in which percolation effects are taken into account.

For nonlinear components with vanishing SHG coefficients, the second term in Eq. (43) vanishes. The approximation can then be applied to the same 2D system studied via the VSM and by direct simulations in the previous subsection. In Fig. 1, the solid lines give the EMA results. It is clear that EMA captures the correct qualitative features of the effective THG, including the resonance peaks and the concentration dependence. It should be appreciated that, while the VSM gives better agreement when compared with direct

simulation data than the EMA, the EMA involves solving only the two equations Eqs. (42) and (43). The merit of EMA, as in other useful approximations, is that it gives a simple and direct way to estimate the effective THG susceptibility *without* performing any numerical calculations on either linear or nonlinear random networks.

IV. SUMMARY

In summary, we have developed a general expression for the third harmonic susceptibility of a random composite medium, in the limit of weak nonlinearity. The resulting form expresses this susceptibility in terms of the second-order and THG susceptibilities of the individual components, and the *linear* properties of the composite at three different frequencies. As an application of our general formula, an expression for the effective response in the dilute limit is obtained. Our results should therefore be useful in estimating the enhancement of THG susceptibilities in random composites arising from local field effects. They should also be a good starting point for developing approximations and numerical methods for studying the effective nonlinear response of a composite. To establish the validity of our general expression, we convert this expression into a voltage summation method for calculating the effective THG susceptibility in discrete random nonlinear resistor networks. The network method involves only calculations on random linear resistor networks at different frequencies. The results for this numerical method are in good agreement with those obtained by direct simulations on random nonlinear resistor networks. Finally, we have proposed an effective medium approximation for both the effective SHG and THG susceptibilities. The EMA is found to give results in good qualitative agreement with our simulation data. This simple approximation should therefore be useful in studying the influence of percolation on the effective nonlinear response in random composites.

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