Nonlinear susceptibilities of granular matter

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We discuss the nonlinear behavior of a random composite material in which current density and electric field are related by $\mathbf{J} = \sigma \mathbf{E} + a |\mathbf{E}|^2 \mathbf{E}$, with σ and a position dependent. To first order in the nonlinear coefficient a, the effective nonlinear conductivity of the composite material is shown to be expressible as $a_e = \langle a | \mathbf{E} | ^4 \rangle / E_0^4$, where E_0 is the magnitude of the applied field, the angular brackets denote a volume average, and E is the electric field in the *linear* limit (a = 0). To the same order, the coefficient a_e is also shown to be related to the mean-square conductivity fluctuation in an analogous problem in which the composite is linear but the conductivity fluctuates: The connection is $\lambda a_e = V(\delta \sigma_{\rm rms})^2$, where V is the volume, $\delta \sigma_{\rm rms}$ is the rms conductivity fluctuation, and λ is a constant with dimensions of energy. In the low-concentration regime ($p \ll 1$, where p is the concentration of nonlinear material), an expression for a_e is derived which is exact to first order in p. The ratio a_e/σ_e^2 (where σ_e is the conductivity of the composite) is shown to diverge near the percolation threshold for both a metal-insulator composite and a normal-metal-perfect-conductor composite; the power law characterizing the divergence is estimated. The results are generalized to nonlinear dielectric response at finite frequencies. At low concentrations, the cubic nonlinear dielectric susceptibility is found to be $\chi_e = p\chi_i | 3\epsilon_h / (\epsilon_i + 2\epsilon_h) |^2 [3\epsilon_h / (\epsilon_i + 2\epsilon_h)]^2$ (plus terms of higher order in χ_i), where p is the volume fraction of inclusion, ϵ_i and ϵ_h are the dielectric constants of the nonlinear inclusion and of the host, and χ_i is the nonlinear electric susceptibility of the inclusion. This expression becomes very large near a Maxwell-Garnett resonance, in analogy with similar local-field effects in surface-enhanced Raman scattering.

I. INTRODUCTION

There are many electrical-transport phenomena in solids in which the current density is not linear in the applied electric field. At zero frequency, such nonlinearities play a role in such diverse effects as dielectric breakdown, the burning out of fuses, and the field dependence seen in hopping conductivity in heavily doped semiconductors. At finite frequencies, the nonlinear dependence of displacement current on electric field in some materials is the basis of nonlinear optical phenomena.

In this paper we consider some aspects of nonlinear behavior in granular materials and other composites. Nonlinearities may be enhanced in such materials, particularly near a so-called percolation threshold at which one component of the composite just forms an infinite connected path. Recent measurements and calculations have estimated the enhancement of these nonlinearities in metal-insulator composites.¹⁻¹² At finite frequency, little work has been carried out near the percolation threshold. Some evidence, such as measurements on CdS "quantum dots" and related materials¹³ embedded in an insulating host, suggests that dilute suspensions of small particles may have enhanced nonlinear susceptibilities at special frequencies.

Our particular goal in this paper is to derive several general results applicable to cubic nonlinearities. These are the leading nonlinear terms in homogeneous materials with inversions symmetry. We derive a general expression for the effective cubic susceptibility of a composite material, in terms of the electric field distribution in the related *linear* material. This expression is exact through *first* order in the nonlinear susceptibility. We also prove an interesting connection between the effective nonlinear susceptibility and the mean-square resistance fluctuations in a related linear material. Such a connection has previously been proven by Aharony¹⁴ for a special case, but our result is considerably more general. Finally, we use our general formulation to obtain an exact expression for the nonlinear susceptibility at small concentrations of impurities, once again through first order in the nonlinear susceptibilities of the constituents.

Granular materials are of interest because they may have large nonlinear susceptibilities at zero or at finite frequencies. We briefly consider two circumstances in which this may occur: near a percolation threshold, and at frequencies near the "Maxwell-Garnett" or surfaceplasmon resonance. We analyze these cases using exact inequalities, previous results from the study of conductivity fluctuations in granular matter, and a lowconcentration approximation.

The remainder of this paper describes these results in more detail. In Sec. II we present exact results for the cubic nonlinear susceptibilities of granular systems. Several specific examples are then discussed in Sec. III. A brief discussion follows in Sec. IV.

II. FORMALISM

We wish to calculate the effective linear and nonlinear susceptibilities of a medium which is both inhomogeneous and nonlinear. The goal is to know the nonlinear sus-

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ceptibility of the composite material, given the linear and nonlinear susceptibilities of the host and the inclusions. In this section we will prove several general results about these nonlinear susceptibilities.

We consider the case of nonlinear conductor at zero frequency. This example will serve as a paradigm for nonlinear susceptibilities of all kinds. We assume that the current density J is related to the local electric field E by the nonlinear equation

$$\mathbf{J}(\mathbf{x}) = \sigma(\mathbf{x})\mathbf{E}(\mathbf{x}) + a(\mathbf{x}) |\mathbf{E}(\mathbf{x})|^2 \mathbf{E}(\mathbf{x}) , \qquad (2.1)$$

where $\sigma(\mathbf{x})$ and $a(\mathbf{x})$ are the linear and nonlinear conductivities of the medium. Since the medium is inhomogeneous as well as nonlinear, both σ and a depend on position. In writing Eq. (2.1) we have assumed that all components in the inhomogeneous medium have inversion symmetry. This implies that the leading nonlinear term is of *third* order in the electric field.

Equation (2.1) must be supplemented by the usual electrostatic equations, namely

$$\nabla \cdot \mathbf{J} = 0 , \qquad (2.2)$$

 $\nabla \times \mathbf{E} = \mathbf{0} , \qquad (2.3)$

and appropriate boundary conditions (specified below). The set of equations (2.1)-(2.3), plus the boundary conditions, constitute a boundary-value problem for J and E which can be solved, in principle, given the geometry of the inhomogeneous medium. Equation (2.3) implies that the electric field can be expressed as the gradient of a potential,

$$\mathbf{E} = -\nabla\phi \quad . \tag{2.4}$$

Note that Eqs. (2.2)-(2.4) are applicable not only to inhomogeneous conductors, but also to other nonlinear problems described by formally identical equations. An important example is a nonlinear dielectric, in which the electric displacement **D** is the divergence-free field, related to **E** by a linear dielectric constant and a nonlinear susceptibility. This case is discussed further below.

It is convenient to choose boundary conditions such that the inhomogeneous conductor is represented as a region of volume V, surrounded by surface S. The boundary condition is

$$\phi = -\mathbf{E}_0 \cdot \mathbf{x} \quad \text{on } S \quad , \tag{2.5}$$

which, if the medium within V were uniform, would give rise to a uniform electric field \mathbf{E}_0 everywhere within V. Even in an *inhomogeneous* conductor, with these boundary conditions, the space-averaged electric field within Vstill equals \mathbf{E}_0 :

$$\langle \mathbf{E} \rangle = V^{-1} \int \mathbf{E}(\mathbf{x}) d^3 x = \mathbf{E}_0 . \qquad (2.6)$$

The effective transport coefficients of the composite can be defined in several ways. For example, the spaceaveraged current density, $\langle \mathbf{J} \rangle$, is related to the spaceaveraged electric field, $\langle \mathbf{E} \rangle (=\mathbf{E}_0)$, by a nonlinear equation of the form

$$\langle \mathbf{J} \rangle = \sigma_e \mathbf{E}_0 + a_e | \mathbf{E}_0 |^2 \mathbf{E}_0 . \qquad (2.7)$$

The coefficients σ_e and a_e in (2.7) may be defined as the effective linear and nonlinear conductivities of the composite medium. Another possible definition is to relate the total power dissipated, $W = \int \mathbf{J} \cdot \mathbf{E} d^3 x$, to the effective coefficients by the equation

$$W = \int \mathbf{J} \cdot \mathbf{E} \, d^3 x = V(\sigma_e \mid \mathbf{E}_0 \mid^2 + a_e \mid \mathbf{E}_0 \mid^4) \,. \tag{2.8}$$

It is shown in the Appendix that definitions (2.7) and (2.8) are equivalent. We may thus choose whichever is the more convenient for any given calculation.

We next prove an important exact connection between the effective nonlinear conductivity a_e and resistance fluctuations in a *linear* composite. The latter quantity has been discussed extensively in a number of experimental and theoretical papers.^{15–23} A connection between noise and the fourth moment of the current distribution has been drawn,²⁰ but the connection to nonlinearity has not yet been made explicitly, except in a particular lattice model.¹⁴ The proof to be presented here is quite general, independent of the details of the composite morphology. The identification is exact, however, only to *first* order in the nonlinear conductivity $a(\mathbf{x})$.

The proof is most easily accomplished starting from definition (2.8) for the effective transport coefficients. We write the power dissipated as

$$W = \int [\sigma(\mathbf{x})\mathbf{E} \cdot \mathbf{E} \, d^3 x + a(\mathbf{x}) | \mathbf{E} |^4] d^3 x = W_2 + W_4 .$$
(2.9)

We now evaluate this expression through *first* order in $a(\mathbf{x})$. The second term on the right-hand side may be written, to first order in $a(\mathbf{x})$,

$$W_4 = V \langle a(\mathbf{x}) | \mathbf{E} | ^4 \rangle_{\text{lin}} = (W_4)_{\text{lin}},$$
 (2.10)

where the subscript means that the electric field is to be taken from the solution to the *linear* problem $[a(\mathbf{x})=0]$. Since $a(\mathbf{x})$ is finite, $\mathbf{E}(\mathbf{x})$ will differ from $\mathbf{E}_{\text{lin}}(\mathbf{x})$, the electric field which would exist if $a(\mathbf{x})$ were identically zero. The difference will be of first order in $a(\mathbf{x})$, and hence will have only a second-order effect on W_4 .

Likewise, in W_2 we write

$$W_2 = \int \sigma(\mathbf{x}) |\mathbf{E}_{\text{lin}}(\mathbf{x}) + \delta \mathbf{E}(\mathbf{x})]|^2 d^3 \mathbf{x}$$

= $(W_2)_{\text{lin}} + \delta W_2$, (2.11)

where \mathbf{E}_{lin} is defined above, and $\delta \mathbf{E}(\mathbf{x})$ is the extra electric field that is induced by a nonzero $a(\mathbf{x})$. To first order in $a(\mathbf{x})$, the change in W_2 due to the nonlinearity vanishes,

$$\delta W_2 = 2 \int \sigma(\mathbf{x}) \mathbf{E}_{\text{lin}}(\mathbf{x}) \cdot \delta \mathbf{E}(\mathbf{x}) d^3 \mathbf{x} = 0 . \qquad (2.12)$$

This is a special case of Tellegen's theorem.²⁴ Thus, through first order in a(x), the effective coefficients σ_e and a_e are entirely determined by the behavior of the electric field in the linear problem:

$$V\sigma_e \mid \mathbf{E}_0 \mid^2 = \int \sigma(\mathbf{x}) \mid \mathbf{E}_{\text{lin}}(\mathbf{x}) \mid^2 d^3 x \quad , \qquad (2.13)$$

$$Va_e | \mathbf{E}_0 |^4 = \int a(\mathbf{x}) | \mathbf{E}_{\text{lin}}(\mathbf{x}) |^4 d^3 x$$
 (2.14)

We next show that the nonlinear effective conductivity a_e can be obtained from the resistance fluctuations in a *linear* composite. The resistance fluctuation problem is defined using the same geometry as in the nonlinear problem, and with the same boundary conditions on the potential. We assume that there is a linear relation between current density J' and electric field E',

$$\mathbf{J}'(\mathbf{x}) = \sigma'(\mathbf{x})\mathbf{E}'(\mathbf{x}) , \qquad (2.15)$$

and that the conductivity $\sigma'(\mathbf{x})$ is drawn from an ensemble with a mean value $\sigma(\mathbf{x})$ and a fluctuation of $\delta\sigma(\mathbf{x})$:

$$\sigma'(\mathbf{x}) = \sigma(\mathbf{x}) + \delta\sigma(\mathbf{x}) . \qquad (2.16)$$

The mean value $\sigma(\mathbf{x})$ is the same conductivity that enters the nonlinear problem described above. The fluctuating part of the conductivity is assumed to be drawn from a statistical ensemble, with zero ensemble average at each point \mathbf{x} , and with correlation functions obeying the relation

$$\langle \delta \sigma(\mathbf{x}) \delta \sigma(\mathbf{x}') \rangle_{av} = \lambda a(\mathbf{x}) \delta(\mathbf{x} - \mathbf{x}')$$
 (2.17)

In Eq. (2.17) the notation $\langle \rangle_{av}$ means an ensemble average (to be distinguished from the spatial averages which are denoted by unsubscripted angular brackets), $\delta(\mathbf{x} - \mathbf{x}')$ is a three-dimensional Dirac δ function, λ is a constant with dimensions of energy, and $a(\mathbf{x})$ is the nonlinear susceptibility defined in Eq. (2.1).

The effective conductivity of this network is denoted σ'_{e} and is defined by the relation

$$\langle \mathbf{J}' \rangle = \sigma'_{e} \mathbf{E}_{0} , \qquad (2.18)$$

where $\langle \rangle$ denotes a volume average for one member of the ensemble. Since $\sigma'(\mathbf{x})$ is fluctuating, the effective con-

ductivity of the composite is also fluctuating. We can define an ensemble average and root-mean-square fluctuation by the relations

$$\sigma_e = \langle \sigma'_e \rangle_{\rm av} , \qquad (2.19)$$

$$\delta \sigma_e = [\langle (\sigma'_e - \sigma_e)^2 \rangle_{\rm av}]^{1/2} . \qquad (2.20)$$

We shall show that the nonlinear effective conductivity a_e can be determined from σ_e and $\delta\sigma_e$. Consider the relation

$$V\sigma'_{e} |\mathbf{E}_{0}|^{2} = \int \mathbf{J}' \cdot \mathbf{E}' d^{3}x , \qquad (2.21)$$

where J' and E' denote the current density and field in a particular member of the ensemble of conductors with conductivity $\sigma'(\mathbf{x}) = \sigma(\mathbf{x}) + \delta\sigma(\mathbf{x})$. To first order in $\delta\sigma(\mathbf{x})$, the right-hand side of (2.21) is

$$\int \mathbf{J}' \cdot \mathbf{E}' \, d^3 x = \int \mathbf{J} \cdot \mathbf{E}_{\text{lin}} d^3 x$$

+ $\int \delta \sigma(\mathbf{x}) \mathbf{E}_{\text{lin}}(\mathbf{x}) \cdot \mathbf{E}_{\text{lin}}(\mathbf{x}) d^3 x$
+ $2 \int \sigma(\mathbf{x}) \mathbf{E}_{\text{lin}}(\mathbf{x}) \cdot \delta \mathbf{E}(\mathbf{x}) d^3 x$. (2.22)

Here, $\sigma(\mathbf{x})$ is the ensemble-averaged conductivity at point \mathbf{x} , $\mathbf{E}_{\text{lin}}(\mathbf{x})$ is the corresponding electric field which would exist if the conductivity were $\sigma(\mathbf{x})$, and $\mathbf{J}(\mathbf{x}) = \sigma(\mathbf{x}) \mathbf{E}_{\text{lin}}(\mathbf{x})$. The last term in (2.22) can be shown to vanish, which is a special case of Cohn's theorem.²⁴

Combining (2.21) and (2.22), we see that

$$V(\sigma'_e - \sigma_e) | \mathbf{E}_0 |^2 = \int \delta \sigma(\mathbf{x}) | \mathbf{E}_{\text{lin}}(\mathbf{x}) |^2 d^3 x , \quad (2.23)$$

Upon squaring this equation and taking the ensemble average, we obtain

$$V^{2}(\delta\sigma_{e})^{2} |\mathbf{E}_{0}|^{4} = \int \int \langle \delta\sigma(\mathbf{x})\delta\sigma(\mathbf{x}') \rangle_{av} |\mathbf{E}_{lin}(\mathbf{x})|^{2} |\mathbf{E}_{lin}(\mathbf{x}')|^{2} d^{3}x d^{3}x' = \lambda \int a(\mathbf{x}) |\mathbf{E}_{lin}(\mathbf{x})|^{4} d^{3}x , \qquad (2.24)$$

where the electric field $\mathbf{E}_{lin}(\mathbf{x})$ appearing on the righthand side of Eq. (2.26) is the field which would exist if the conductivity were $\sigma(\mathbf{x})$. Since the right-hand side is also the integral which determines a_e in the nonlinear problem [see Eq. (2.14)], we get

$$V(\delta\sigma_e)^2 = \lambda a_e \quad , \tag{2.25}$$

which proves that the nonlinear effective conductivity is proportional to the mean-square conductivity fluctuations in an analogous linear problem. [This equivalence holds only if the noise has the special property (2.17).]

III. ILLUSTRATION

A. Dilute limit

An important special case of a nonlinear medium is the dilute limit, in which a small amount of nonlinear medium is embedded in a linear material. When both materials are linear, the low-concentration limit is well known. We will derive the generalization of this approximation for the nonlinear case. The result follows immediately from Eq. (2.10). If we have a concentration p (by volume) of nonlinear material 2, embedded in medium 1, then the effective nonlinear conductivity is

$$a_e = pa_2 \langle |\mathbf{E}_{\text{lin}}|^4 \rangle_2 / |\mathbf{E}_0|^4 , \qquad (3.1)$$

where a_2 is the nonlinear conductivity of medium 2 and $\langle \rangle_2$ denotes the average value in medium 2. This result is valid to first order in a_2 . If material 2 exists in the form of spheres, then to lowest order in *p* it is sufficient to calculate the field within the spheres as if the outer material were uniformly of type 1. This assumption gives, for a_e ,

$$a_e = pa_2 [3\sigma_1 / (\sigma_2 + 2\sigma_1)]^4 . \tag{3.2}$$

This is to be combined with the standard result for σ_e , in the limit $p \ll 1$,

$$\sigma_e = \sigma_1 [1 + 3p(\sigma_2 - \sigma_1) / (\sigma_2 + 2\sigma_1)] . \tag{3.3}$$

Because of result (2.25) proved in the preceding section, Eq. (3.2) also gives the conductivity noise induced when a fluctuating conductivity is introduced into a previously linear medium. The translation to the noise problem is straightforward. Medium 1 is assumed to be linear, with nonfluctuating conductivity σ_1 . Medium 2 has a conductivity consisting of a nonfluctuating part σ_2 plus a fluctuating part $\delta \sigma_2$ with zero mean and correlation function

$$\langle \delta \sigma_2(\mathbf{x}) \delta \sigma_2(\mathbf{x}') \rangle = \lambda a_2 \delta(\mathbf{x} - \mathbf{x}')$$

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The composite medium has effective conductivity σ and rms fluctuation in conductivity $\delta \sigma_e$; σ_e is given in the dilute limit by Eq. (3.3), while $\delta \sigma_e$ is obtained from (3.2) by multiplying by $\sqrt{\lambda/V}$.

B. Percolation threshold

In the study of composite media, an important special composition is the percolation threshold, at which one or another of the two components first forms a connected path across the sample. Many properties of composites (conductivity, for example) are known to behave in singular fashion near the percolation threshold.^{25,26} We now show that the nonlinear conductivity a_e also behaves singularly near this threshold, by exploiting the connection between nonlinearity and noise.

We consider first a mixture of conductor, conductivity σ_1 and nonlinear conductivity a_1 , present in volume fraction p, and insulator, with $\sigma_2 = a_2 = 0$. Near $p = p_c$, the volume fraction at which the metallic component first forms an infinite connected cluster, $\sigma_e \sim \sigma_1 (p - p_c)^t$, and we write $a_e/\sigma_e^2 \sim (p-p_c)^{-\kappa}$. We can estimate κ from previous work on the analogous *noise* problem, as well as the percolation problem. $^{27-30}$ The results are summarized in Table I for various models of lattice and continuum percolation. The details of the models are described in the table caption and in the references cited. In all cases studied, for both two and three dimensions, the rel-

ative strength of the nonlinearity, as described by the ratio a_e/σ_e^2 , diverges near $p = p_c$. As shown earlier, this ratio also governs the ratio of conductivity fluctuations to conductivity in a noisy system near percolation, from which we have deduced many of the results in the table.

Table I also shows analogous results for a mixture of normal metal and perfect conductor. In this case, the normal metal, present in volume fraction p_1 , has linear conductivity σ_1 and nonlinear conductivity a_1 , as before. The perfect conductor has infinite linear conductivity. The percolation threshold p_c in this case denotes the volume fraction of medium 1 at which the perfect conductor forms a connected path and shorts out the resistance. Near but below p_c , σ_e is large and finite, varying as $\sigma_e \sim \sigma_1 (p_c - p)^{-s}$, while the ratio $a_e / \sigma_e^2 \sim (a_1 / \sigma_1^2) (p_c - p)^{-\kappa'}$. Values of s and κ' are quoted in Table I, which also indicates the source of these values for various models. Once again the dimensionless ratio describing the strength of the nonlinearity (or of the noise, in the analogous fluctuation problem), a_e/σ_e^2 , diverges near p_c in both two and three dimensions.

We now prove an inequality which shows, quite generally, that the strength of the nonlinearity diverges near percolation for both cases just discussed. Consider first the composite of normal metal and insulator. The coefficients a_e and σ_e may be written (again through first order in a_1)

$$a_e = pa_1 \langle |\mathbf{E}_{\text{lin}}|^4 \rangle_{\text{met}} / |\mathbf{E}_0|^4 , \qquad (3.4)$$

$$\sigma_e = p \sigma_1 \langle |\mathbf{E}_{\text{lin}}|^2 \rangle_{\text{met}}^2 / |\mathbf{E}_0|^4 , \qquad (3.5)$$

where $\langle \rangle_{\text{met}}$ means that the average is to be taken over the metallic portion of the composite. Since

$$\langle |E_{\text{lin}}|^4 \rangle_{\text{met}} > \langle |E_{\text{lin}}|^2 \rangle_{\text{met}}^2 ,$$
 (3.6)

it follows that

$$a_e / \sigma_e^2 > a_1 / \sigma_1^2 , \qquad (3.7)$$

or, if it is assumed that a_e/σ_e^2 varies near $p=p_c$ as

TABLE I. Values of the percolation exponents t, s, and κ for various models of composites in two and three dimensions (2D, 3D). The exponents t, s, κ , and κ' are defined in the text. The names "lattice model" and "Swiss cheese" refer to particular models of percolating systems defined in Halperin et al. (footnote b below). The values κ_l and κ_u are lower and upper bounds to κ obtained in Refs. 16 and 17; κ'_l and κ'_u are lower and upper bounds on κ' from Ref. 17.

Structure	t	S	κι	ĸu	к	κ'_l	κ'u	к'
2D lattice model	1.29 ^a	1.29 ^a	1.07 ^{e, f}	1.37 ^{e, f}	1.12 ^e	1.07 ^f	1.37 ^f	1.34 ⁱ
2D Swiss cheese ^b	1.29 ^b				3.16 ^{g, h}			
BD lattice model	2.0 ^c	0.95 ^d	1.53 ^{e, f}	1.60 ^{e, f}	2.33 ^j	0.38 ^f	1.02 ^f	0.66 ⁱ
BD Swiss cheese ^b	2.5 ^b				5.14 ^{g, h}			

^aReferences 12, 28, and 29.

^bB. I. Halperin, S. Feng, and P. N. Sen, Phys. Rev. Lett. 54, 2391 (1985).

^cReference 28.

^dHeermann and Stauffer, Ref. 30.

^eReference 16.

^fReference 17.

^gR. Rammal, Phys. Rev. Lett. 55, 1428 (1985).

^hTremblay et al., Ref. 27.

ⁱP. M. Hui and D. Stroud, Ref. 22.

^JReference 15.

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$$(p-p_c)^{-\kappa}$$
, that
 $\kappa > 0$, (3.8)

where κ is defined the same way as in Table I. Since (3.8) is a strict inequality (the equality sign is not allowed for any except a δ -function distribution of field strength), the exponent κ is positive definite and the relative noise strictly diverges near p_c . A similar argument can be used to derive the same inequality for a composite of normal metal and perfect conductor.

C. Nonlinear optical properties

These results can also be mapped onto nonlinearities at finite frequencies. In this case, both conductor and insulator are best described by complex dielectric functions rather than conductivities. The imaginary part of the dielectric functions are related to the ac conductivities.³¹ The formal mapping of our previous results is straightforward. We consider a two-component composite, the *i*th component being described by a nonlinear relation between electric displacement **D** and electric field **E** of the form

$$\mathbf{D} = \boldsymbol{\epsilon}_i \mathbf{E} + \boldsymbol{\chi}_i \mid \mathbf{E} \mid^2 \mathbf{E} . \tag{3.9}$$

As in the static case, the lowest-order nonlinear susceptibility, for a material with inversion symmetry, is the cubic term.³² In principle, however, the nonlinear susceptibility χ_i , like ϵ_i , is complex and frequency dependent. The quantities in Eq. (3.9) are, in general, complex. The physical fields, denoted \mathbf{E}_{phys} and \mathbf{D}_{phys} , are, of course, real and are related to E and D by

$$\mathbf{E}_{\text{phys}} = \operatorname{Re}(\mathbf{E}e^{-i\omega t}) , \qquad (3.10)$$
$$\mathbf{D}_{\text{phys}} = \operatorname{Re}(\mathbf{D}e^{-i\omega t}) .$$

Besides the cubic term included in (3.9), there is also a frequency-tripling term, cubic in the applied field, which leads to a polarization at frequency 3ω [all the terms included in (3.9) are at frequency ω].³² We have not considered this term although it, too, may be enhanced in a composite medium.

If the eddy currents can be neglected, as will usually be the case when the particle dimensions are small compared to a wavelength of radiation, then the electric field in (3.9) is curl-free, satisfying $\nabla \times \mathbf{E} = \mathbf{0}$, while the displacement field is divergenceless, $\nabla \cdot \mathbf{D} = 0$. The equations describing **D** and **E** in the inhomogeneous medium are thus formally identical to those for **J** and **E** at zero frequencies, and we can carry over many previous results for nonlinear *conductivities* to nonlinear *susceptibilities*. One small but significant change appears in Eqs. (2.7) and (2.8). The equations analogous to these are

$$\langle \mathbf{D} \rangle = \epsilon_e \mathbf{E}_0 + \chi_e | \mathbf{E}_0 |^2 \mathbf{E}_0 , \qquad (3.11)$$

$$W = \int \mathbf{D} \cdot \mathbf{E} \, d^3 x = V(\epsilon_e \mid \mathbf{E}_0 \mid^2 + \chi_e \mid \mathbf{E}_0 \mid^4) \,. \quad (3.12)$$

In Eq. (3.12) the second factor in the integrated is **E** and not **E**^{*}, as might have been expected; otherwise, one could not carry out the necessary integrations by parts to prove (3.11) and (3.12) equivalent. Arguments analogous to those which lead to Eq. (2.14) give the following general expression for the nonlinear effective susceptibility:

$$V\chi_e \mid \mathbf{E}_0 \mid {}^4 = \int \chi(\mathbf{x}) \mid \mathbf{E}_{\text{lin}}(\mathbf{x}) \mid {}^2 \mathbf{E}_{\text{lin}}(\mathbf{x}) \cdot \mathbf{E}_{\text{lin}}(\mathbf{x}) d^3 x \quad .$$
(3.13)

In particular, when a small concentration of spheres of nonlinear material is included in a linear host, the effective nonlinear susceptibility is

$$\chi_e = p \chi_1 | 3\epsilon_2 / (\epsilon_1 + 2\epsilon_2) |^2 [3\epsilon_2 / (\epsilon_1 + 2\epsilon_2)]^2 , \quad (3.14)$$

where χ_1 is the nonlinear susceptibility of material 1, present in volume fraction $p \ll 1$, and ϵ_1 and ϵ_2 are the linear dielectric functions of material 1 and host material 2. Once again, this result is valid to first order in χ_1 . Except for the absolute-value signs, our result is the same as that obtained in Ref. 33 by a different argument. If one follows the argument in the latter reference, taking into account the absolute-value signs appearing in Eq. (3.9), one correctly obtains Eq. (3.14).

An interesting new feature is present in Eq. (3.14) which is lacking at zero frequency. Namely, one gets a vast enhancement of nonlinearity at frequencies such that $\epsilon_1 + 2\epsilon_2 \sim 0$, a situation which cannot occur in the static limit. But at finite frequencies, this is the condition for the occurrence of a surface-plasmon resonance, i.e., a resonant mode of the charge in the small particle. This results is potentially of great practical importance in developing materials of large nonlinear susceptibilities, but has received to date only a little discussion in the literature.^{13,33–35} The enhancement seen in Eq. (3.14) is reminiscent of a similar enhancement seen in Raman scattering from small particles ("surface-enhanced Raman scattering") and arises from the same reason: a great increase in electric field near or within a small particle at certain characteristic frequencies.³⁶

IV. DISCUSSION

The results we have presented here show that, not surprisingly, nonlinearities can be strongly enhanced in composite media. A number of previous papers¹⁻¹² have also reached this conclusion in particular cases. The present results offer a rather general formulation of the problem, and show that this enhancement exists in a wide variety of cases.

Particularly promising for further work are nonlinearoptical effects in composites. We have considered here only one effect of this kind: cubic nonlinearity in which the induced polarization is at the same frequency as the incident field. There are many other effects to be considered. Two examples are frequency doubling or tripling, and nonlinear effects arising from simultaneous application of a dc and an ac electric field. There are indications that some of these other effects may also be strongly enhanced in small particle composites.³³⁻³⁵ If so, these materials may well be useful for a variety of nonlinear-optical applications. The cubic nonlinearities discussed here are themselves of much potential interest for various combinations of real materials. We plan to investigate these and other cases in future work. This work was supported by the National Science Foundation through Grant No. DMR-84-14257. Useful conversations with Professor D. J. Bergman are gratefully acknowledged.

APPENDIX: PROOF OF EQUIVALENCE OF EQS. (2.7) AND (2.8)

One possible definition of the effective linear conductivity σ_e and effective nonlinear conductivity a_e is to write the integrated power dissipated as

$$W = \int \mathbf{J} \cdot \mathbf{E} \, d^3 x = V(\sigma_e \mid E_0^2 \mid +a_e \mid \mathbf{E}_0 \mid^4) \,. \tag{A1}$$

To relate this form to our other definition, Eq. (2.7), we write W as

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$$W = -\int \mathbf{J} \cdot \nabla \phi \, d^3 x$$

= $-\int \nabla \cdot (\mathbf{J}\phi) d^3 x$
= $-\int \mathbf{\hat{n}} \cdot \mathbf{J}\phi \, d^2 x$
= $-\int_S \mathbf{\hat{n}} \cdot \mathbf{J}\phi_0 d^2 x$
= $V \langle \mathbf{J} \rangle \cdot \mathbf{E}_0$. (A2)

Equating (A1) and (A2), and noting that these are both valid for any choice of \mathbf{E}_0 , we equate the coefficients of \mathbf{E}_0 to obtain

$$\langle \mathbf{J} \rangle = \sigma_e \mathbf{E}_0 + a_e | \mathbf{E}_0 |^2 \mathbf{E}_0 ,$$
 (A3)

which is our other equivalent defining equation, Eq. (2.7), for σ_e and a_e .

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