

Second-harmonic generation for a dilute suspension of coated particlesP. M. Hui,¹ C. Xu,^{1,2} and D. Stroud³¹*Department of Physics, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong*²*Department of Physics, Suzhou University, Suzhou 215006, People's Republic of China*³*Department of Physics, The Ohio State University, Columbus, Ohio 43210-1106, USA*

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We derive an expression for the effective second-harmonic coefficient of a dilute suspension of coated spherical particles. It is assumed that the coating material, but not the core or the host, has a nonlinear susceptibility for second-harmonic generation (SHG). The resulting compact expression shows the various factors affecting the effective SHG coefficient. The effective SHG per unit volume of nonlinear coating material is found to be greatly enhanced at certain frequencies, corresponding to the surface-plasmon resonance of the coated particles. Similar expression is also derived for a dilute suspension of coated discs. For coating materials with third-harmonic (THG) coefficient, results for the effective THG coefficients are given for the cases of coated particles and coated discs.

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I. INTRODUCTION

With the advancements in nanotechnology, it has become possible to fabricate nanoparticles of various kinds with specific geometries. For years, random or ordered composite materials consisting of two or more materials with different physical properties have been studied intensively, with the aim of tuning the effective physical properties of the composite by properly choosing the constituent materials, the structure of the composite, and/or the volume fraction of each of the constituents. Ordered composites, for example, have led to the development of semiconductor heterostructures and devices, and photonic band-gap materials. Composites consisting of small particles of one material randomly embedded in a host medium also show interesting behavior.¹ The percolation effect that occurs as the volume fraction of one component increases leads to a qualitative change in the physical response of a random composite. In the dilute concentration limit, various physical responses are affected by local-field effects due to the inhomogeneous nature of the system.

Of particular interest is the optical response of nanoparticles and nanoparticles with specially designed geometry.²⁻⁵ For example, using a nanoshell geometry on particles, it has been found that the effective Raman scattering can be enhanced by as much as 10^6 .⁶ The surface-plasmon resonance is found to be shifted in nanoparticles coated with gold.⁷ The optical properties of nanoparticles may also be affected by quantum size effects.⁸ In general, it is expected that the local-field effects play a significant role in the nonlinear response in composites consisting of small particles as the response depends on high powers of the field.⁹ Greatly enhanced nonlinear response in composite systems, when coupled with a fast response time, could lead to applications in the design of switching devices and optical communication systems. An excellent review on the nonlinear optical properties of random media has been given by Shalaev.¹⁰ An up-to-date account on problems related to computational electromagnetics in dielectric heterostructures has recently been given by Brosseau and Beroual.¹¹ The current status on research on

the properties of nanostructured random media is best reflected in the recent compilation by Shalaev.¹²

A number of theories has been developed for weakly nonlinear composites,^{10,13-19} with the focus mainly on third-order nonlinear susceptibility such as the Kerr effect. In previous works,^{20,21} we derived general expressions for nonlinear susceptibility for the second-harmonic generation (SHG) and third-harmonic generation (THG) in random composites. The authors also developed simple approximation for the dilute concentration limit and effective-medium type approximation for arbitrary concentrations. With recent advancements in the fabrication of coated particles and with possible enhanced local-field effect in mind, we study SHG in a dilute suspension of coated spheres. Specifically, we assume that only the coating material has a nonvanishing SHG coefficient. The core and the host medium are linear in nature. We derive an expression for the effective SHG coefficient per unit volume of nonlinear material in the system. It is found that with modest choice of material parameters, the SHG coefficient can be greatly enhanced at certain frequencies. We also study the two-dimensional (2D) version of the problem, i.e., the SHG coefficient in a 2D dilute suspension of coated discs in a linear host, and similar enhancement is found. When the coated material has a nonvanishing THG coefficient, we give the resulting expression for the effective THG coefficient per unit volume of nonlinear material in both 3D and 2D random composites.

The plan of the paper is as follows. In Sec. II, we derive the effective SHG coefficient in a dilute suspension of coated spheres in a linear host. We illustrate the possible enhancement effect by considering a model system of particles with a metallic core and coated by a nonlinear material. In Sec. III, we give the corresponding results for a 2D dilute suspension of coated discs. Results for the effective THG coefficient in both 3D and 2D cases are given in Sec. IV, together with a summary.

II. FORMALISM

We consider the effective susceptibility for second-harmonic generation (SHG) of a dilute suspension of *coated*

particles embedded in a linear host in both 3D and 2D. In 3D, the system consists of coated spheres; while in 2D, the system consists of coated cylinders with aligned axes (or coated discs). The spheres (cylinders) are supposed to have inner radius r_1 and outer radius r_2 . The core medium is supposed to have (possibly complex) dielectric constant ϵ_1 , the coating has dielectric constant ϵ_2 , and the host has dielectric constant ϵ_3 . In addition, the coating, but neither the host nor the core, has a nonlinear susceptibility for second-harmonic generation. This susceptibility is, in general, a tensor of rank three²² and is denoted by $d_{ijk}(-2\omega; \omega, \omega)$ or $d_{ijk}(\omega, \omega)$, with each of the subscripts running over the three Cartesian indices. Note that the elements of d may be complex. The total volume fraction of coating material in the composite is f , and $f \ll 1$ is assumed.

Hui and Stroud²⁰ have derived a general expression for the *effective* nonlinear SHG susceptibility $d_{ijk}^e(-2\omega; \omega, \omega)$ of a composite, under the assumption that the nonlinearity is weak. When applied to the system considered here, the result may be written in the form

$$d_{ijk}^e = f d_{\ell mn} \langle K_{i\ell}(2\omega) K_{mj}(\omega) K_{nk}(\omega) \rangle. \quad (1)$$

Here

$$K_{nk}(\mathbf{x}, \omega) = \frac{E_n(\mathbf{x}, \omega)}{E_{0,k}(\omega)} \quad (2)$$

is the possible local-field enhancement factor giving the n -th component of the local electric field at position \mathbf{x} and frequency ω when the applied field E_0 is in the k th direction at frequency ω . $\langle \dots \rangle$ denotes an average over the volume of the *nonlinear shell* and the average is to be calculated in the *linear* limit. We use the convention that repeated indices are summed over.

Equations (1) and (2), as well as all the results below, are also obtained in the quasistatic approximation, according to which the local electric field may be written as the negative gradient of a scalar potential. This approximation is most accurate when the particle radii are small compared to both the wavelength of light in the medium and the skin depth of metallic particles. The quasistatic approximation neglects such effects as radiative losses, which may become important at shorter wavelengths; it also omits diffuse scattering, as discussed further in the last section of the paper.

We consider the 3D case of coated spheres in a linear host. In the dilute concentration limit where the interaction between particles can be neglected, the electric field in the coated shell can be calculated using standard electrostatics.²³ The electric field in the spherical shell \mathbf{E}_s , where the subscript denotes the spherical shell with the coating medium, in the presence of an external field $E_0 \hat{z}$ is related to the electric potential via

$$\mathbf{E}_s = -\nabla \Phi_s \quad (3)$$

with

$$\Phi_s(r, \theta) = -\mathcal{E}_s r \cos \theta + \frac{p_s \cos \theta}{r^2}, \quad (4)$$

where

$$\mathcal{E}_s = \Gamma_s E_0, \quad (5)$$

$$p_s = \lambda_s r_1^3 \Gamma_s E_0. \quad (6)$$

Here Γ_s and λ_s are given by

$$\Gamma_s = \frac{3\epsilon_3}{\epsilon_2 + 2\epsilon_3 + 2(\epsilon_2 - \epsilon_3)\lambda_s/\mu_s}, \quad (7)$$

$$\lambda_s = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2}, \quad (8)$$

where μ_s is related to the ratio of the outer to inner radii

$$\mu_s = (r_2/r_1)^3. \quad (9)$$

The electric field in the coating medium can then be explicitly evaluated with the result

$$\mathbf{E}_s = \mathcal{E}_s \hat{z} + \frac{3(xz\hat{x} + yz\hat{y} + z^2\hat{z}) - r^2\hat{z}}{r^5} p_s, \quad (10)$$

where r is the distance from the center of the sphere to the point under consideration inside the spherical shell. Note that p_s has dimensions of a dipole moment, and it is the dipole moment of the coated particle in the linear limit. Comparing with results of a single dielectric sphere in a host, the coated sphere behaves as a sphere with an effective dielectric constant $\tilde{\epsilon}_s$ of the form

$$\tilde{\epsilon}_s = \frac{1 + 2\lambda_s/\mu_s}{1 - \lambda_s/\mu_s} \epsilon_2, \quad (11)$$

with λ_s and μ_s given by Eqs. (8) and (9). It can be immediately seen from Eq. (11) that the surface-plasmon resonance of a coated particle can be tuned^{5,7} by the material parameters λ_s and the geometrical parameter μ_s of the particle.

To proceed and for the purpose of illustrating the possible enhancement in SHG, we will make the assumption that of the possible components of d in the shell, only d_{iii} are non-zero and that these are all equal, i.e., $d_{iii} = d(-2\omega; \omega, \omega) \equiv d_{\omega, \omega}$ ($i = x, y, \text{ or } z$). Depending on the symmetry of the nonlinear materials concerned, d_{ijk} would have vanishing components for certain combinations of the indices. For example, one may also have $d_{ijk} \neq 0$ only for $i \neq j \neq k$. Our calculations can also be carried out for the latter case. Using Eq. (1) in the dilute concentration limit gives

$$d_{\omega, \omega}^e = f d_{\omega, \omega} \sum_{i=x,y,z} \langle K_{zi}(2\omega) K_{iz}^2(\omega) \rangle_{shell}, \quad (12)$$

where we have denoted the surviving SHG coefficient d_{zzz}^e by $d_{\omega, \omega}^e$ for simplicity. The brackets $\langle \dots \rangle_{shell}$ denote the average of the enclosed quantity over the volume of the spherical shell, and f is the volume fraction of coating material in the system.

It is easily shown that only the $i = z$ term in the above sum contributes, when a suitable angular average is carried out over the volume of the shell. In order to evaluate that re-

maining term in Eq. (12), we need to calculate the average over the shell volume of the quantity

$$\left[\mathcal{E}_s(2\omega) + \frac{3z^2 - r^2}{r^5} p_s(2\omega) \right] \left[\mathcal{E}_s(\omega) + \frac{3z^2 - r^2}{r^5} p_s(\omega) \right]^2, \quad (13)$$

where we have indicated the frequency at which the field and the dipole moment are to be evaluated explicitly. Defining $B_s = (3z^2 - r^2)/r^5$, the average is easily evaluated by noting that

$$\begin{aligned} \langle B_s \rangle_{shell} &= 0, \\ \langle B_s^2 \rangle_{shell} &\equiv S_2 = \frac{1}{v_{shell}} \left(\frac{1}{r_1^3} - \frac{1}{r_2^3} \right) \frac{16\pi}{15}, \\ \langle B_s^3 \rangle_{shell} &\equiv S_3 = \frac{1}{v_{shell}} \left(\frac{1}{r_1^6} - \frac{1}{r_2^6} \right) \frac{32\pi}{105}. \end{aligned} \quad (14)$$

Here $v_{shell} = (4\pi/3)(b^3 - a^3)$ is the volume of the spherical shell. Carrying out the average of expression (13), the effective SHG susceptibility is then given in terms of these quantities by

$$\begin{aligned} \frac{d_{\omega,\omega}^e}{fd_{\omega,\omega}} &= \frac{1}{E_0(2\omega)E_0^2(\omega)} (\mathcal{E}_s(2\omega)\mathcal{E}_s^2(\omega) + S_2[\mathcal{E}_s(2\omega)p_s^2(\omega) \\ &+ 2\mathcal{E}_s(\omega)p_s(2\omega)p_s(\omega)] + S_3p_s(2\omega)p_s^2(\omega)). \end{aligned} \quad (15)$$

Equation (15) is the main result of this section. The left-hand side of Eq. (15) gives the effective SHG susceptibility of the composite *per unit volume* of the nonlinear coating material normalized by the SHG susceptibility of the coating material. Here $p_s(\omega)$ and $p_s(2\omega)$ are the dipole moments that would be induced in a *linear* particle when an electric field is applied at frequencies ω or 2ω .

The magnitude of the right-hand side of Eq. (15) thus gives the possible enhancement in the effective SHG coefficient due to the geometry of the particles (coated particles) and the host medium through the factor Γ_s . As a model system, we consider spherical particles in which the inner core is a Drude metal, which has a dielectric constant of the form

$$\epsilon_\omega = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \quad (16)$$

with ω_p being the plasma frequency and τ the relaxation time. We take $\omega_p = 2.28 \times 10^{16} \text{ s}^{-1}$ and $\tau = 6.9 \times 10^{-15} \text{ s}$, numbers that correspond to bulk aluminum. Note that $\omega_p \tau \sim 100\text{--}200$ are typical of metals. The nonlinear shell is assumed to have a frequency-independent dielectric constant $\epsilon_2 = 2.52$, while the host medium also has a frequency-independent dielectric constant $\epsilon_3 = 1.76$. These numbers are typical of nonconducting materials. Figure 1 shows the real and imaginary parts of $d_{\omega,\omega}^e/(fd_{\omega,\omega})$ for this model system as a function of frequency ω/ω_p and for different ratios of outer to inner radii. We note that an enhancement factor of

nonlinear shell and metal core (3D)

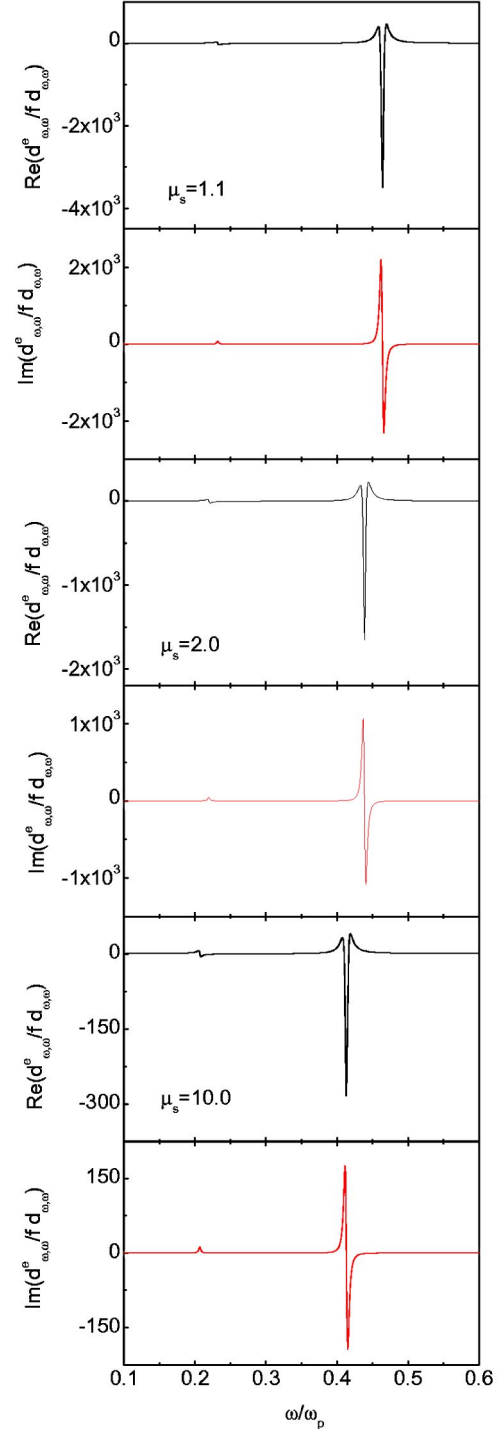


FIG. 1. The real and imaginary parts of the effective SHG coefficient $d_{\omega,\omega}^e/(fd_{\omega,\omega})$ per unit volume of nonlinear coating material as a function of frequency ω/ω_p for a dilute suspension of particles with metallic core coated with a nonlinear material. Results for three different ratios of the outer to inner radii μ_s of the particles are shown.

the order of 10^3 can be achieved at suitable frequencies. At certain resonance frequency of the coated particle, the local-field in the shell region is sufficiently large to drive a much enhanced SHG susceptibility. This frequency corresponds to

the surface-plasmon resonance of the coated particle, the value of which depends on the core material, the coating material, and the host medium. The frequency can also be tuned by properly selecting the material parameters and/or by tuning the ratio of the outer to inner radii. We see in Fig. 1 that as the ratio increases, the resonance shifts to lower frequency. We also note that higher enhancement per unit volume of nonlinear coating material is achieved for thinner coating. Therefore, one would expect a dilute suspension of spherical particles coated with a thin layer of nonlinear materials will give the largest enhancement per unit volume of nonlinear material.

III. 2D CASE: COATED CYLINDERS

A two-dimensional random composites on the x - y plane, for example, can be considered as a random dispersion of cylindrical particles in a host medium, with the axes of cylinders aligned in the same direction perpendicular to the plane. A cross section of the system consists of circular discs embedded in the host. A calculation of the electric field \mathbf{E}_c in the coated shell of a cylinder in the presence of an applied field $E_0\hat{x}$ can be carried out in a way similar to the 3D case using standard electrostatics. Instead of Eq. (10) in 3D, we have for the 2D case

$$\mathbf{E}_c = \mathcal{E}_c \hat{x} + \frac{2(x^2\hat{x} + xy\hat{y}) - r^2\hat{x}}{r^4} p_c, \quad (17)$$

where r is the distance from the center of a disc (or cylinder) to the position under consideration inside the coating shell. Here,

$$E_c = \Gamma_c E_0, \quad (18)$$

$$p_c = \lambda_c r_1^2 \Gamma_c E_0, \quad (19)$$

$$\Gamma_c = \frac{2\epsilon_3}{\epsilon_2 + \epsilon_3 + (\epsilon_2 - \epsilon_3)\lambda_c/\mu_c}, \quad (20)$$

$$\lambda_c = \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + \epsilon_2}, \quad (21)$$

$$\mu_c = \left(\frac{r_2}{r_1}\right)^2, \quad (22)$$

and the subscript c is used to indicate that the case of coated cylinders or discs is being considered. Comparing with results of a single dielectric circular disc in a host, a coated disc behaves as a disc with an effective dielectric constant $\tilde{\epsilon}_c$ of the form

$$\tilde{\epsilon}_c = \frac{1 + \lambda_c/\mu_c}{1 - \lambda_c/\mu_c} \epsilon_2, \quad (23)$$

with λ_c and μ_c given by Eqs. (21) and (22).

To obtain an expression for 2D similar to Eq. (15), we make the same assumption for the SHG coefficient of the coating material. This leads to an expression similar to Eq.

(12) for the effective SHG susceptibility, except that we need to evaluate the average over the shell *area* of the quantity

$$\left[\mathcal{E}_c(2\omega) + \frac{2x^2 - r^2}{r^4} p_c(2\omega) \right] \left[\mathcal{E}_c(\omega) + \frac{2x^2 - r^2}{r^4} p_c(\omega) \right]^2, \quad (24)$$

instead of the expression (13) in 3D. Defining $B_c = (2x^2 - r^2)/r^4$, the average is easily evaluated by noting that

$$\langle B_c \rangle_{shell} = 0,$$

$$\langle B_c^2 \rangle_{shell} \equiv \tilde{S}_2 = \frac{1}{a_{shell}} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2} \right) \frac{\pi}{2},$$

$$\langle B_c^3 \rangle_{shell} = 0. \quad (25)$$

Here a_{shell} is the area of the circular shell (ring) of coating. The effective SHG susceptibility is then found to be

$$\frac{d_{\omega,\omega}^e}{fd_{\omega,\omega}} = \frac{1}{E_{0,2\omega} E_{0,\omega}^2} [\mathcal{E}_c(2\omega) \mathcal{E}_c^2(\omega) + \tilde{S}_2 (\mathcal{E}_c(2\omega) p_c^2(\omega) + 2\mathcal{E}_c(\omega) p_c(2\omega) p_c^2(\omega))]. \quad (26)$$

Equation (26) is the result in 2D, analogous to Eq. (15) in 3D. It gives the effective SHG susceptibility *per unit area* of nonlinear coating medium normalized to the SHG susceptibility of the coating medium in a 2D dilute suspension of coated discs in a linear host.

Figure 2 shows $d_{\omega,\omega}^e/(fd_{\omega,\omega})$ as a function of frequency in the 2D case, for the same model system considered in the preceding section. The features are similar to those in the 3D case. The enhancement factor tends to be larger in 2D than in 3D for the same set of model parameters. For discs coated with thin layer of nonlinear material, the SHG response per unit area of nonlinear material can be driven by the local field to achieve an enhancement of 10^3 , for modest choice of material parameters.

IV. DISCUSSION

It is straightforward to generalize the formalism to THG.²¹ For coating nonlinear material in which the leading nonlinear response is THG with the THG coefficient denoted by $\chi_{\omega,\omega,\omega}$, we can again use the local electric field at the shell region to drive an enhanced THG response per unit volume of nonlinear material in a dilute suspension. The derivation is similar to that in Sec. II, although somewhat tedious. The result is

$$\begin{aligned} \frac{\chi_{\omega,\omega,\omega}^e}{f\chi_{\omega,\omega,\omega}} &= \frac{1}{E_0(3\omega)E_0^3(\omega)} [\mathcal{E}_s(3\omega)\mathcal{E}_s^3(\omega) \\ &+ 3S_2\mathcal{E}_s(\omega)p_s(\omega)(\mathcal{E}_s(\omega)p_s(3\omega) + \mathcal{E}_s(3\omega)p_s(\omega)) \\ &+ S_3p_s^2(\omega)(3\mathcal{E}_s(\omega)p_s(3\omega) + \mathcal{E}_s(3\omega)p_s(\omega)) \\ &+ S_4p_s(3\omega)p_s^3(\omega)], \end{aligned} \quad (27)$$

nonlinear shell and metal core (2D)

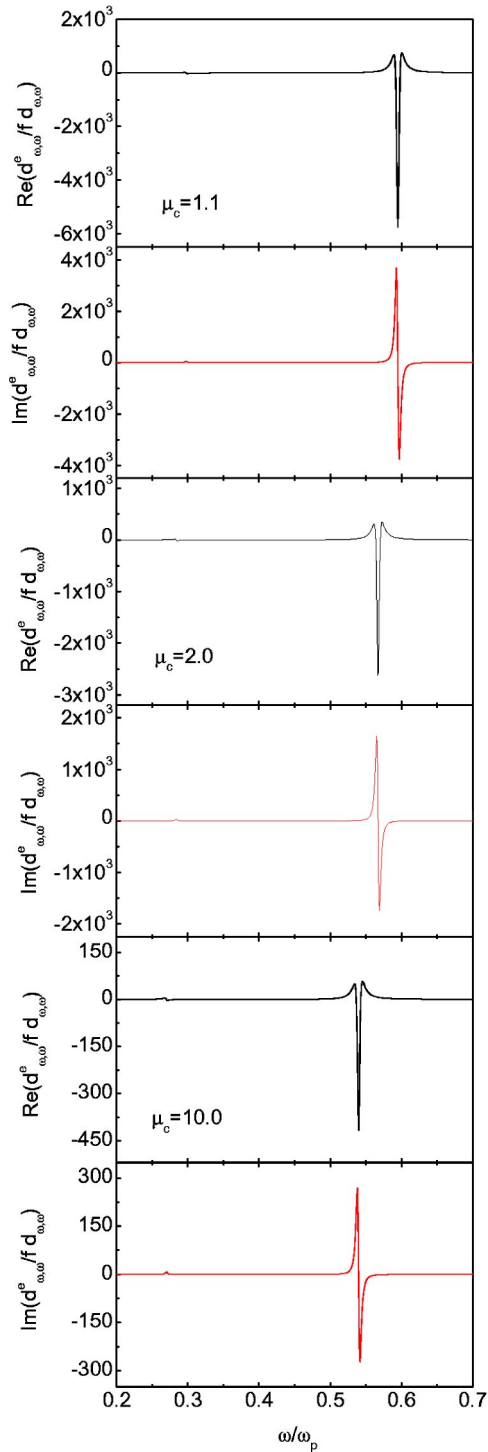


FIG. 2. The real and imaginary parts of the effective SHG coefficient $d_{\omega,\omega,\omega}^e/(fd_{\omega,\omega,\omega})$ per unit area of nonlinear coating material as a function of frequency ω/ω_p for a dilute suspension of discs with metallic core coated with a nonlinear material in a 2D system. Results for three different ratios of the outer to inner radii μ_c of the discs are shown.

nonlinear shell and metal core (3D)

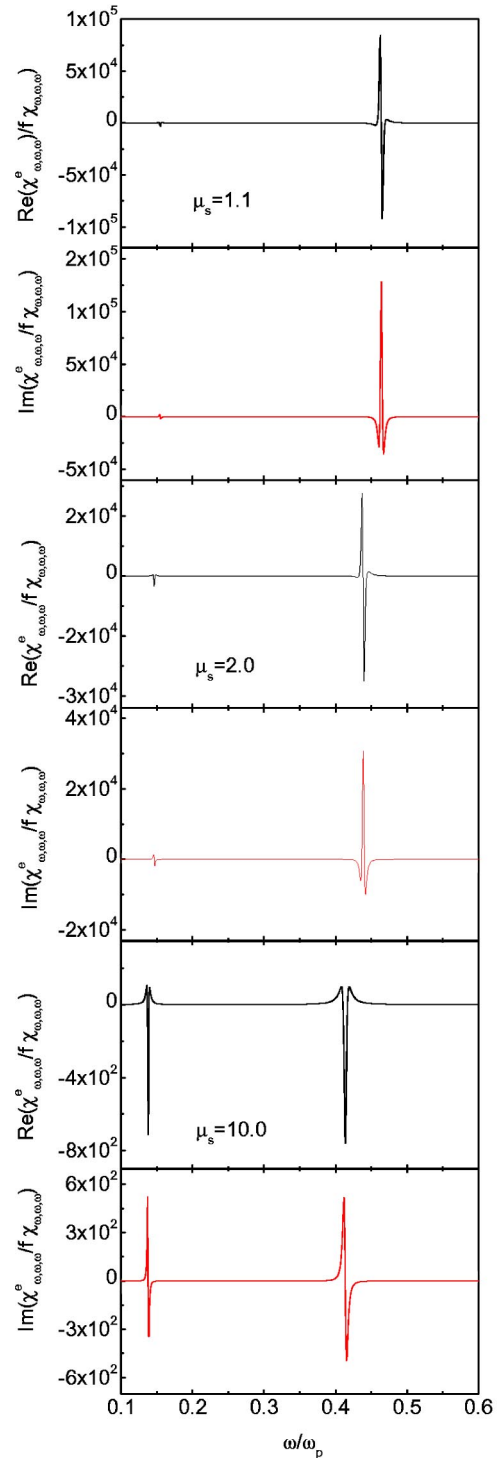


FIG. 3. The real and imaginary parts of the effective THG coefficient $\chi_{\omega,\omega,\omega}^e/(f\chi_{\omega,\omega,\omega,\omega,\omega})$ per unit volume of nonlinear coating material as a function of frequency ω/ω_p for a dilute suspension of particles with metallic core coated with a nonlinear material. Results for three different ratios of the outer to inner radii μ_s of the particles are shown.

where

$$S_4 = \langle B_s^4 \rangle = \frac{1}{v_{shell}} \left(\frac{1}{r_1^9} - \frac{1}{r_2^9} \right) \frac{64\pi}{105} \quad (28)$$

for a dilute suspension of coated spherical particles.

In the 2D case of coated discs of nonlinear THG coating material, the result is

$$\begin{aligned} \frac{\chi_{\omega,\omega,\omega}^e}{f\chi_{\omega,\omega,\omega}} = & \frac{1}{E_0(3\omega)E_0^3(\omega)} [\mathcal{E}_c(3\omega)\mathcal{E}_c^3(\omega) \\ & + 3\tilde{S}_2\mathcal{E}_c(\omega)p_c(\omega)(\mathcal{E}_c(\omega)p_c(3\omega) + \mathcal{E}_c(3\omega)p_c(\omega)) \\ & + \tilde{S}_4p_c(3\omega)p_c^3(\omega)], \end{aligned} \quad (29)$$

where

$$\tilde{S}_4 = \langle B_c^4 \rangle = \frac{1}{a_{shell}} \left(\frac{1}{r_1^6} - \frac{1}{r_2^6} \right) \frac{\pi}{8}. \quad (30)$$

To illustrate the enhancement in THG susceptibility, we use the same choice of material parameters as our model system and calculate the enhancement factor corresponding to Eq. (27) for spherical particles. Results are shown in Fig. 3. Since the THG is driven by higher power of the local-field, the enhancement factor is found to be of the order of 10^5 at resonance frequency, for our choice of parameters.

Note that, when we calculate the effective SHG and THG susceptibilities in the present work, we do so by treating the medium as effectively *homogeneous*, with effective properties. Thus, our calculation would lead to a collimated beam of harmonic emission when this effective medium is used in an SHG experiment. Besides this collimated emission, some diffuse scattering at the second-harmonic frequency is also expected, because of the inhomogeneity of the medium. Indeed, such diffuse SHG scattering has been observed in a recent experiment, carried out near the percolation threshold of a random metal-insulator composite,²⁴ in addition to the collimated beam described here. This diffusive scattering should have an intensity varying as a power of the particle radius. The present approach would need to be extended to include such diffuse scattering.

Finally, we briefly comment on the validity of the low-concentration approximation used to obtain Eqs. (15), (16), (27), and (29). These equations are obtained by calculating the fields and displacement vectors as if the coated particles feel a *uniform* applied field. In actuality, the local-field should include the dipole fields produced by the other particles. These fields may start to become significant when the dipole field due to one particle, calculated at the position of a neighboring particle, becomes comparable to the applied electric field. Although this condition may be satisfied near resonance even for $f \ll 1$, the large enhancements we find may still persist at higher f , because the interaction fields, even though they can be substantial, may approximately cancel out if the environment of a particle can be approximated as isotropic. The local-field factors at higher concentrations can be estimated using such methods as the Maxwell-Garnett or effective-medium approximations.

Our results for SHG [Eqs. (15) and (26)] and THG [Eqs. (27) and (29)] are applicable to other possible structures of coated particles, as long as the composite is in the dilute concentration limit and SHG originates from the coating material. One could use a dielectric core and a metallic shell with a nonvanishing SHG coefficient.²⁵ In general, careful choices can be made so that the local electric field in the coating region is enhanced. This enhanced local-field can then be used to drive the SHG response. In addition, it is possible to tune the local-field by tuning the core size and the shell thickness. For composites of higher concentrations, the Maxwell-Garnett approximation and the effective-medium approximation can be invoked in estimating the local-field factors. In higher concentrations, percolation effects can also lead to possible enhancement in SHG and other nonlinear response.

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