Nonlinear response of composite materials containing coated spheres: Giant enhancement due to the particle structure and distribution

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We derive the exact third-order polarizability of a nonlinear coated sphere. We then study the effective third-order nonlinear susceptibility $\chi_e^{(3)}$ (Kerr coefficient) of a composite containing such coated spheres, including the interparticle interactions within mean-field theory. We show that the coated particle structure can significantly enhance the nonlinear response of a particle near resonance. Furthermore, we show that the interparticle interaction can further increase or decrease the nonlinear resonance peak by more than one order of magnitude, depending on the particle concentration, distribution, and structure, while shifting the resonance frequencies. Therefore, the spectrum of $\chi_e^{(3)}$ can be sensitively tuned by varying a concentration-distribution parameter. [S0163-1829(97)06438-2]

I. INTRODUCTION

Virtually any dielectric material will exhibit some nonlinear behavior when a sufficiently strong electric field is applied. The nonlinear part of the response at optical frequencies has proved to be essential in optical communication and laser technologies. Since the invention of the laser, nonlinear optics has thus developed into an important and independent field of research. Materials with a large nonlinear optical response have been developed and found numerous applications in optical switching, photoelastic, and phase-conjugate devices.[1,2]

In most applications, it is crucial that a large nonlinear response occurs in a desired frequency range. The nonlinear optical response of a material is determined by both its intrinsic properties and the electric-field distribution in the system. Correspondingly, in order to obtain a large nonlinear response, one may attempt to directly engineer a material with a large intrinsic nonlinear optical response in the desired frequency range. Alternatively, one may design a composite material with an appropriate linear response such that the resulting optical field is more concentrated in the nonlinear component, or the component with the largest nonlinear response. Recently, using such a local-field effect, Fisher *et al.*[3] have succeeded in producing a composite of alternating layers of titanium dioxide and a nonlinear polymer, such that the effective third-order nonlinear susceptibility $\chi_e^{(3)}$ is enhanced by about 35%. Similar enhancements have also been obtained in granular composite systems of uniform spheres[4] and coated spheres.[5] Various calculations for systems with uniform and coated spheres[6] have previously indicated that a strong enhancement of the nonlinear response is quite possible. However, the exact nonlinear polarizability of coated spheres and their interparticle interactions have not been previously obtained.

In this paper, we derive the exact first-order (linear) and third-order (nonlinear) polarizabilities of coated spheres. We then determine their interparticle interactions in mean-field theory. Both have dramatic effects on the nonlinear response. Namely, the coated structure can enhance the nonlinear response by several orders of magnitude, while the interparticle interactions can further modify the nonlinear resonance peak of the isolated particles by more than one order of magnitude, while shifting the resonance frequency. The precise effect is determined by the concentration and the distribution of the particles, combined with their structure. We consider the general case of a coated sphere of core radius a and outer radius b, where both the core (1) and the coating (2) materials can be nonlinear, and are described by a response

$$\mathbf{D}_i=\epsilon_i\mathbf{E}+\chi_i^{(3)}|\mathbf{E}|^2\mathbf{E}, \quad (i=1,2). \tag{1}$$

Such particles are then embedded in a linear host medium with a dielectric function ϵ_3. As customary, we consider the long-wavelength limit, so that the problem can be treated quasistatically. In this paper, we consider a simple anisotropic pair distribution, with azimuthal and reflection symmetry in the z direction, assumed parallel to the applied electric field $\mathbf{E}_0$. That is

$$n(\mathbf{r})=\begin{cases}0, & r<2b,\\ N[h_1(r)+h_2(r)P_2(\cos\theta)], & r\geqslant 2b,\end{cases} \tag{2}$$

where N is the average number density of the particles, $P_2(\cos\theta)$ is the second-order Legendre polynomial, and $h_1(r)$ and $h_2(r)$ are arbitrary functions of the radial distance, satisfying the conditions

$$h_1(r\geqslant R_0)=1, \quad h_2(r\geqslant R_0)=0, \tag{3}$$

outside the correlation range R_0. Thus, Eq. (2) defines an $L=1$ pair distribution.[7]

The nonlinear response of a composite system containing particles of arbitrary structure can be determined exactly, including fully the multipolar interactions among the particles.[8] That requires in the first place the determination of polarization coefficients which describe the complete linear and nonlinear response of the isolated particles, depending on their structure. Secondly, it requires knowledge of the system microscopic configuration. For disordered systems, in the mean-field approximation, it has been shown that the

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effective third-order susceptibility for an $L=1$ pair distribution is given by [cf. Eq. (30) in Ref. 8]

$$\chi_e^{(3)}=\frac{\epsilon_3}{2}\left(\frac{4\pi}{3}\right)N\frac{\langle \nu_{10}^{101010}\rangle}{[1-(4\pi/3)N(1+K_1^1)\langle\lambda_{10}^{10}\rangle]^4}. \tag{4}$$

Out of all the first-order (linear) and third-order (nonlinear) polarization coefficients of the (identical) particles, $\lambda_{lm}^{l_1m_1}$ and $\nu_{lm}^{l_1m_1l_2m_2l_3m_3}$, Eq. (4) requires knowledge of only the $l=1,m=0$ polarizabilities, and their averages over orientations, denoted by $\langle\rangle$. Furthermore, Eq. (4) requires knowledge of

$$K_1^1=\frac{3}{2\pi N}\sqrt{\frac{4\pi}{5}}\int_{r\leqslant R_0}n(\mathbf{r})\frac{Y_{20}^*(\mathbf{r})}{r^3}d^3\mathbf{r}=\frac{6}{5}\int_{2b}^{R_0}\frac{h_2(r)}{r}dr, \tag{5}$$

which is a dimensionless parameter describing the $L=1$ pair distribution [cf. Eq. (21) of Ref. 7]. In particular, $K_1^1=0$ corresponds to an isotropic distribution. In general, $K_1^1<0$ represents a ''prolate'' distribution, where there is less chance of finding a particle in the z direction than in a transverse direction. The opposite case $K_1^1>0$ corresponds to an ''oblate'' distribution. We have previously considered specifically a model of ellipsoidal inclusions,[7] where K_1^1 ranges from -1 to 2. We emphasize that although only the dipolar polarizabilities appear in Eq. (4), that is *not* the result of making the dipole approximation. Rather, the theory includes all orders of multipoles. However, within mean-field theory and for $L=1$ pair distributions, the higher multipoles do not produce any contribution to the effective dielectric function.[7]

II. BOUNDARY-VALUE PROBLEM FOR λ_{10}^{10} AND ν_{10}^{101010}

In order to determine the first-order and third-order polarizabilities λ_{10}^{10} and ν_{10}^{101010}, needed in Eq. (4), for the coated particles considered in this paper, we have to immerse a single particle in a uniform external field E_0, and find the induced dipole moment up to the third-order in E_0. This poses the following boundary-value problem (derived from $\nabla\cdot\mathbf{D}=0$):

$$\epsilon\nabla^2U+\chi^{(3)}[(\nabla|U|^2)\cdot\nabla U+|\nabla U|^2\nabla^2U]=0,$$

$$U=-\sqrt{\frac{4\pi}{3}}E_0rY_{1,0}(\mathbf{r}),\quad b\ll r,$$

$$U|_{a-0}=U|_{a+0},$$

$$\epsilon_1\frac{\partial U}{\partial r}\bigg|_{a-0}+\chi_1^{(3)}|\nabla U|^2\frac{\partial U}{\partial r}\bigg|_{a-0}=\epsilon_2\frac{\partial U}{\partial r}\bigg|_{a+0}+\chi_2^{(3)}|\nabla U|^2\frac{\partial U}{\partial r}\bigg|_{a+0}, \tag{6}$$

$$U|_{b-0}=U|_{b+0},$$

$$\epsilon_2\frac{\partial U}{\partial r}\bigg|_{b-0}+\chi_2^{(3)}|\nabla U|^2\frac{\partial U}{\partial r}\bigg|_{b-0}=\epsilon_3\frac{\partial U}{\partial r}\bigg|_{b+0}.$$

The solution is not trivial, hence, we outline it in adequate detail.

We begin by expanding the total potential U as

$$U=u^{(1)}E_0+u^{(3)}E_0^3+O^*(E_0^5). \tag{7}$$

In Eq. (7), only odd orders of E_0 appear, due to the reflection symmetry in $z\to -z$. Substituting Eq. (7) into Eq. (6) and comparing terms of the same power in E_0, we obtain the boundary-value problems for $u^{(1)}$:

$$\nabla^2u^{(1)}=0,$$

$$u^{(1)}|_{a-0}=u^{(1)}|_{a+0},\quad \epsilon_1\frac{\partial u^{(1)}}{\partial r}\bigg|_{a-0}=\epsilon_2\frac{\partial u^{(1)}}{\partial r}_{a+0},$$

$$u^{(1)}|_{b-0}=u^{(1)}|_{b+0},\quad \epsilon_2\frac{\partial u^{(1)}}{\partial r}\bigg|_{b-0}=\epsilon_3\frac{\partial u^{(1)}}{\partial r}_{b+0},$$

$$u^{(1)}=-\sqrt{\frac{4\pi}{3}}rY_{1,0}(\mathbf{r}),\quad b\ll r; \tag{8}$$

and for $u^{(3)}$:

$$\nabla^2u^{(3)}=-\frac{\chi^{(3)}}{\epsilon}\nabla u^{(1)}\cdot\nabla|\nabla u^{(1)}|^2,$$

$$u^{(3)}|_{a-0}=u^{(3)}|_{a+0},$$

$$\epsilon_1\frac{\partial u^{(3)}}{\partial r}\bigg|_{a-0}+\chi_1^{(3)}|\nabla u^{(1)}|^2\frac{\partial u^{(1)}}{\partial r}_{a-0}=\epsilon_2\frac{\partial u^{(3)}}{\partial r}\bigg|_{a+0}+\chi_2^{(3)}|\nabla u^{(1)}|^2\frac{\partial u^{(1)}}{\partial r}\bigg|_{a+0},$$

$$u^{(3)}|_{b-0}=u^{(3)}|_{b+0},$$

$$\epsilon_2\frac{\partial u^{(3)}}{\partial r}\bigg|_{b-0}+\chi_2^{(3)}|\nabla u^{(1)}|^2\frac{\partial u^{(1)}}{\partial r}\bigg|_{b-0}=\epsilon_3\frac{\partial u^{(3)}}{\partial r}\bigg|_{b+0}. \tag{9}$$

From Eq. (8), we obtain

$$u^{(1)}=\begin{cases}-ArY_{10}(\mathbf{r}), & r\leqslant a,\\ \left[-Br+\dfrac{C}{r^2}\right]Y_{1,0}(\mathbf{r}), & a\leqslant r\leqslant b,\\ -\sqrt{\dfrac{4\pi}{3}}rY_{1,0}(\mathbf{r})+\left(\dfrac{4\pi}{3}\right)\dfrac{q_{10}^{(1)}}{r^2}Y_{1,0}(\mathbf{r}), & r\geqslant b,\end{cases} \tag{10}$$

where

$$A=6\sqrt{3\pi}\epsilon_2\epsilon_3b^3/\Delta,$$

$$B=2\sqrt{3\pi}(\epsilon_1+2\epsilon_2)\epsilon_3b^3/\Delta,$$

$$C=2\sqrt{3\pi}(\epsilon_1-\epsilon_2)\epsilon_3a^3b^3/\Delta,$$

$$q_{10}^{(1)}=\sqrt{\frac{3}{4\pi}}[(\epsilon_1-\epsilon_2)(2\epsilon_2+\epsilon_3)a^3+(\epsilon_1+2\epsilon_2)(\epsilon_2-\epsilon_3)b^3]b^3/\Delta, \qquad (11)$$

with

$$\Delta=2(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_3)a^3+(\epsilon_1+2\epsilon_2)(\epsilon_2+2\epsilon_3)b^3. \qquad (12)$$

From Eq. (10), we obtain

$$\nabla u^{(1)}\cdot\nabla|\nabla u^{(1)}|^2=\begin{cases}0, & r\leqslant a,\\ \frac{27}{5\pi}\left(\frac{4BC^2}{r^7}+\frac{5C^3}{r^{10}}\right)Y_{1,0}(\mathbf{r})+\frac{9\sqrt{21}}{35\pi}\left(\frac{5B^2C}{r^4}+\frac{8BC^2}{r^3}+\frac{5C^3}{r^{10}}\right)Y_{3,0}(\mathbf{r}), & a\leqslant r\leqslant b.\end{cases} \qquad (13)$$

Therefore, only in the region $a\leqslant r\leqslant b$, the differential equation for $u^{(3)}$ is not homogeneous. Using Eq. (13), we obtain a particular solution of Eq. (9), namely

$$u_p^{(3)}=-\frac{\chi_2^{(3)}}{\epsilon_2}[\sigma_1(r)Y_{1,0}(\mathbf{r})+\sigma_3(r)Y_{3,0}(\mathbf{r})], \quad a\leqslant r\leqslant b, \qquad (14)$$

where

$$\sigma_1(r)=\frac{1}{10\pi}\left(\frac{12BC^2}{r^5}+\frac{5C^3}{r^8}\right),$$

$$\sigma_3(r)=\frac{9\sqrt{21}}{35\pi}\left(-\frac{12B^2C}{2r^2}+\frac{BC^2}{r^5}+\frac{5C^3}{44r^8}\right). \qquad (15)$$

Superposing to that a general solution of the homogeneous equation $\nabla^2u^{(3)}=0$, we obtain the complete solution:

$$u^{(3)}=\begin{cases}D_1rY_{1,0}(\mathbf{r})+D_3r^3Y_{3,0}(\mathbf{r}), & r\leqslant a,\\ \left[F_1r+\frac{G_1}{r^2}-\frac{\chi_2^{(3)}}{\epsilon_2}\sigma_1(r)\right]Y_{1,0}(\mathbf{r})+\left[F_3r^3+\frac{G_3}{r^4}-\frac{\chi_2^{(3)}}{\epsilon_2}\sigma_3(r)\right]Y_{3,0}(\mathbf{r}), & a\leqslant r\leqslant b,\\ \left(\frac{4\pi}{3}\right)\frac{q_{10}^{(3)}}{r^2}Y_{1,0}(\mathbf{r})+\left(\frac{4\pi}{5}\right)\frac{q_{30}^{(3)}}{r^4}Y_{3,0}(\mathbf{r}), & b\leqslant r.\end{cases} \qquad (16)$$

From Eq. (10), we also obtain

$$|\nabla u^{(1)}|^2\frac{\partial u^{(1)}}{\partial r}=\begin{cases}-\frac{3}{4\pi}A^3Y_{1,0}(\mathbf{r}), & r\leqslant a,\\ -\beta_1(r)Y_{1,0}(\mathbf{r})-\beta_3(r)Y_{3,0}(\mathbf{r}), & a\leqslant r\leqslant b,\end{cases} \qquad (17)$$

where

$$\beta_1(r)=\frac{3}{20\pi}\left(5B^3+18\frac{B^2C}{r^3}+30\frac{BC^2}{r^6}+28\frac{C^3}{r^9}\right),$$

$$\beta_3(r)=\frac{9\sqrt{21}}{70\pi}\left(2\frac{B^2C}{r^3}+5\frac{BC^2}{r^6}+2\frac{C^3}{r^9}\right). \qquad (18)$$

Substituting Eqs. (16)–(18) into the boundary conditions in Eq. (9), and comparing the coefficients of $Y_{1,0}(\mathbf{r})$, we obtain

$$aD_1-aF_1-\frac{1}{a^2}G_1=-\frac{\chi_2^{(3)}}{\epsilon_2}\sigma_1(a),$$

$$\epsilon_1D_1-\epsilon_2F_1+\frac{2\epsilon_2}{a^3}G_1=\frac{3}{4\pi}\chi_1^{(3)}A^3-\chi_2^{(3)}\left.\frac{d\sigma_1(r)}{dr}\right|_a-\chi_2^{(3)}\beta_1(a),$$

$$bF_1+\frac{1}{b^2}G_1-\left(\frac{4\pi}{3}\right)\frac{1}{b^2}q_{10}^{(1)}=\frac{\chi_2^{(3)}}{\epsilon_2}\sigma_1(b),$$

$$\epsilon_2F_1-\frac{2\epsilon_2}{b^3}G_1+\left(\frac{4\pi}{3}\right)\frac{2\epsilon_3}{b^3}q_{10}^{(1)}=\chi_2^{(3)}\left.\frac{d\sigma_1(r)}{dr}\right|_b+\chi_2^{(3)}\beta_1(b). \qquad (19)$$

From Eq. (19), we then obtain

$$q_{10}^{(3)}=\left(\frac{3}{4\pi}\right)^2\frac{\chi_1^{(3)}}{\Delta}3\epsilon_2\epsilon_3^3a^3b^3A^3+\left(\frac{3}{4\pi}\right)\frac{\chi_2^{(3)}}{\Delta}b^3\Bigg\{3a^3\left[\epsilon_1\frac{\sigma_1(a)}{a}-\epsilon_2\left.\frac{d\sigma_1(r)}{dr}\right|_a-\epsilon_2\beta_1(a)\right]-[2(\epsilon_1-\epsilon_2)a^3+(\epsilon_1+2\epsilon_2)b^3]\frac{\sigma_1(b)}{b}-[(\epsilon_1-\epsilon_2)a^3-(\epsilon_1+2\epsilon_2)b^3]\left[\left.\frac{d\sigma_1(r)}{dr}\right|_b+\beta_1(b)\right]\Bigg\}. \qquad (20)$$

Explicitly,

$$q_{10}^{(3)}=\sqrt{\frac{3}{4\pi}}\frac{(3\epsilon_3 b)^3}{\Delta^4}\Big\{\chi_1^{(3)}(3\epsilon_2)^4a^3b^9-\frac{1}{5}\chi_2^{(3)}[8(\epsilon_1-\epsilon_2)^4a^{12}+8(\epsilon_1-\epsilon_2)^3(\epsilon_1+2\epsilon_2)a^9b^3+36(\epsilon_1-\epsilon_2)^2(\epsilon_1+2\epsilon_2)^2a^6b^6$$
$$-(47\epsilon_1^4-8\epsilon_1^3\epsilon_2-204\epsilon_1^2\epsilon_2^2-296\epsilon_1\epsilon_2^3+56\epsilon_2^4)a^3b^9-5(\epsilon_1+2\epsilon_2)^4b^{12}]\Big\}. \tag{21}$$

Then, the induced dipole moment on the coated sphere is given by

$$q_{10}=q_{10}^{(1)}E_0+q_{10}^{(3)}E_0^3+O^*(E_0^5), \tag{22}$$

and the first-order[9] and third-order polarizabilities are, respectively,

$$\lambda_{10}^{10}\equiv\sqrt{\frac{4\pi}{3}}\frac{\partial q_{10}}{\partial E_0}\bigg|_{E_0=0}=\frac{(\epsilon_1-\epsilon_2)(2\epsilon_2+\epsilon_3)(a/b)^3+(\epsilon_1+2\epsilon_2)(\epsilon_2-\epsilon_3)}{2(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_3)(a/b)^3+(\epsilon_1+2\epsilon_2)(\epsilon_2+2\epsilon_3)}b^3\equiv\alpha b^3, \tag{23}$$

$$\nu_{10}^{101010}\equiv\sqrt{\frac{4\pi}{3}}\frac{\partial^3 q_{10}}{\partial E_0^3}\bigg|_{E_0=0}=\frac{2}{\epsilon_3}\left[\frac{3\epsilon_3}{2(\epsilon_1-\epsilon_2)(\epsilon_2-\epsilon_3)(a/b)^3+(\epsilon_1+2\epsilon_2)(\epsilon_2+2\epsilon_3)}\right]^4\Big\{\chi_1^{(3)}(3\epsilon_2)^4(a/b)^3+\frac{1}{5}\chi_2^{(3)}[5(\epsilon_1+2\epsilon_2)^4$$
$$+(47\epsilon_1^4-8\epsilon_1^3\epsilon_2-204\epsilon_1^2\epsilon_2^2-296\epsilon_1\epsilon_2^3+56\epsilon_2^4)(a/b)^3-36(\epsilon_1-\epsilon_2)^2(\epsilon_1+2\epsilon_2)^2(a/b)^6-8(\epsilon_1-\epsilon_2)^3(\epsilon_1+2\epsilon_2)(a/b)^9$$
$$-8(\epsilon_1-\epsilon_2)^4(a/b)^{12}]\Big\}b^3$$
$$\equiv\frac{2}{\epsilon_3}\kappa b^3. \tag{24}$$

These are exact results. The third-order polarizability (24) has not been previously obtained. One can easily verify that, for $b\rightarrow a$, Eqs. (23) and (24) reduce to those for uniform spheres that have been previously obtained [cf. Eqs. (35) and (36) of Ref. 8]:

$$\lambda_{10}^{10}=\frac{\epsilon_1-\epsilon_3}{\epsilon_1+2\epsilon_3}a^3,\quad \nu_{10}^{101010}=2\frac{\chi_1^{(3)}}{\epsilon_3}\left(\frac{3\epsilon_3}{\epsilon_1+2\epsilon_3}\right)^4a^3. \tag{25}$$

These results can also be obtained by taking the limits $\epsilon_2\rightarrow\epsilon_1$ and $\chi_2^{(3)}\rightarrow\chi_1^{(3)}$ in Eqs. (23) and (24).

III. GIANT ENHANCEMENT OF THE EFFECTIVE KERR COEFFICIENT

Now, substituting Eqs. (23) and (24) into Eq. (4), one obtains the effective third-order nonlinear susceptibility (Kerr coefficient)

$$\chi_e^{(3)}=v\frac{\kappa}{(1-F\alpha)^4}, \tag{26}$$

where $v=(4\pi/3)Nb^3$ is the particle volume fraction, and $F=v(1+K_1^1)$ is a crucial concentration-distribution parameter. In the low concentration limit, $\chi_e^{(3)}\approx v\kappa$, and there is a significant enhancement at the linear coated-sphere resonance frequency ω_r, where the denominators of both α and κ in Eqs. (23) and (24) reach a minimum in magnitude. However, the interparticle interaction, namely, the factor $1/[1-F\alpha]^4$, modifies both the resonance peak and the resonance frequency of $\chi_e^{(3)}$. The following examples will show that such a modification can be quite significant, even at moderate particle concentrations. We consider coated spheres with only one nonlinear component, which is either in the coating or in the core. We compute the effective Kerr coefficient normalized by both the volume fraction and the Kerr coefficient of the nonlinear component of the particles. This normalized quantity depends only on the concentration-distribution parameter F, and represents the enhancement of the Kerr coefficient. We use various values of F between 0.15 and 0.75. These values of F correspond, for example, to a volume fraction $v=0.3$, with K_1^1 varying between -0.5 and 1.5. The effect of the interparticle interaction is shown by comparison with the results in the low-concentration limit, where $F=v=0$.

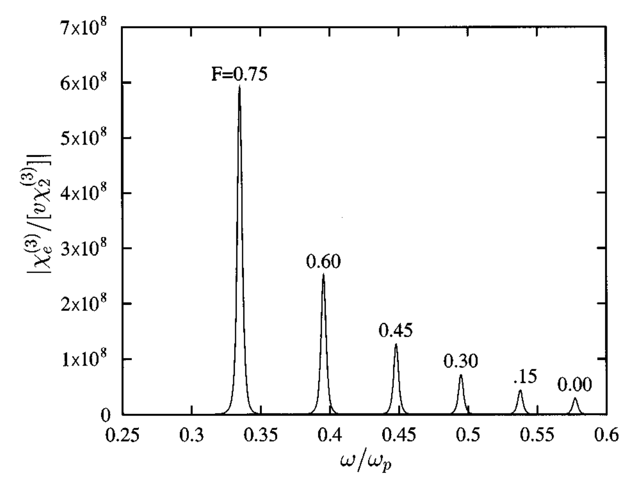

FIG. 1. Spectrum of the normalized $\chi_e^{(3)}$ for various values of the concentration-distribution parameter F. The particles have an Al core and a nonlinear dielectric coating shell with $\epsilon_2=1.0$, and $a/b=0.96$.

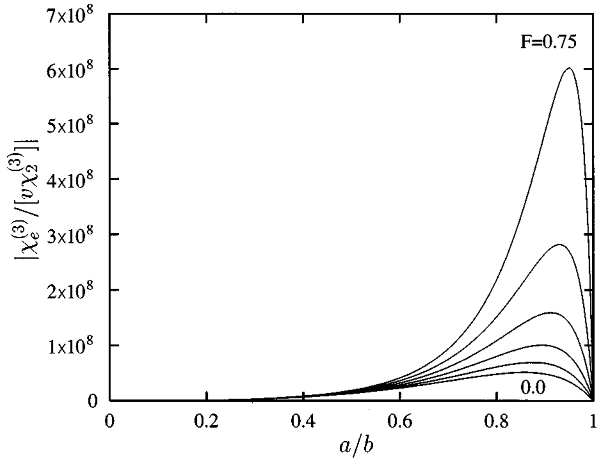

FIG. 2. Peak value of the normalized $\chi_e^{(3)}$ for the system of Fig. 1, with varying a/b.

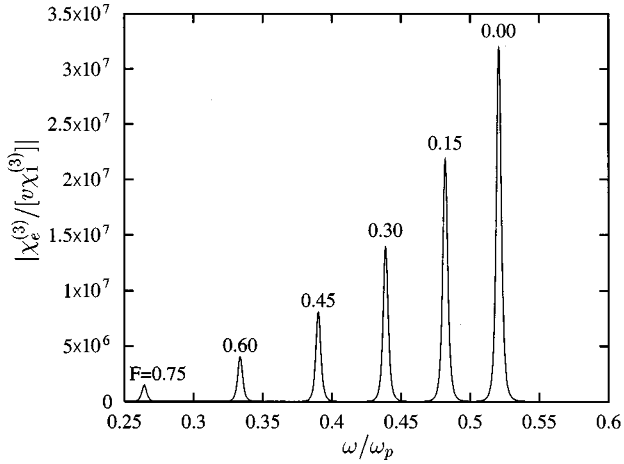

FIG. 4. Same as Fig. 1, but for particles having a nonlinear core and an Al coating shell.

In a first example, we consider particles with a metal core of radius a and a nonlinear coating of outer radius b. For the metal response, we assume the (linear) Drude model

$$\epsilon = 1 - \frac{\omega_p^2}{\omega(\omega + j\gamma)}, \tag{27}$$

where ω_p and γ are the plasma frequency and the damping coefficient, respectively. We use the parameters for Al: $\omega_p = 2.28\times 10^{16}\ \mathrm{s}^{-1}$ and $\gamma = 1.45\times 10^{14}\ \mathrm{s}^{-1}$. For simplicity, we assume that the linear part of the dielectric function of the coating material and that of the host medium are $\epsilon_2 = \epsilon_3 = 1.0$. On the other hand, we must point out that the values of ϵ_2 and ϵ_3 significantly affect the results in general (the larger ϵ_3/ϵ_2, the larger the enhancement). Figure 1 shows the spectrum of the normalized Kerr coefficient for $a/b = 0.96$. In this case, the enhancement due to the particle structure ($F=0$) is about 3×10^7, at the resonance frequency $\omega_r = 0.577\omega_p$. This is due to the fact that, at ω_r, the linear core repels the field into the nonlinear coating. The interparticle interaction, working constructively with the particle structure, further concentrates the field into the nonlinear coating. At $F=0.75$, the interparticle interaction enhances the peak by a factor of 20, and shifts it by $\Delta\omega = 0.24\omega_p$ to a lower frequency. In this case, an oblate distribution ($F > 0.3$) enhances the nonlinear response, and shifts the resonance peak to lower frequencies, compared with the spherical distribution ($F = v = 0.3$), whereas a prolate distribution ($F < 0.3$) does the opposite.

The effect of the interparticle interactions and that of the particle structure are in fact interdependent. To provide a complete picture, we show the peak values and the resonance frequencies of the normalized Kerr coefficient as functions of a/b in Figs. 2 and 3. In particular, Fig. 2 shows that the most significant enhancement occurs for very thin nonlinear coatings. Figure 3 shows that the frequency shift is most significant the thinner the nonlinear coating. Lacking interparticle interactions or anisotropic particle distributions, previous theories have not predicted the corresponding enhancement and shift of the nonlinear resonance peak. The second effect, namely, the frequency shift, is perhaps the most significant for practical applications, because it allows one to adjust a giant nonlinear response to the desired frequency.

As a second example, we exchange the core and coating materials, showing the results in Figs. 4–6. The enhancement due to the particle structure is of the same order of magni-

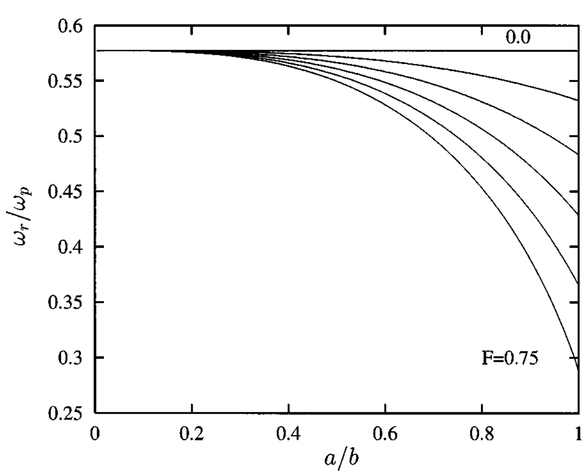

FIG. 3. Resonance frequency of the normalized $\chi_e^{(3)}$ for the system of Fig. 1, with varying a/b.

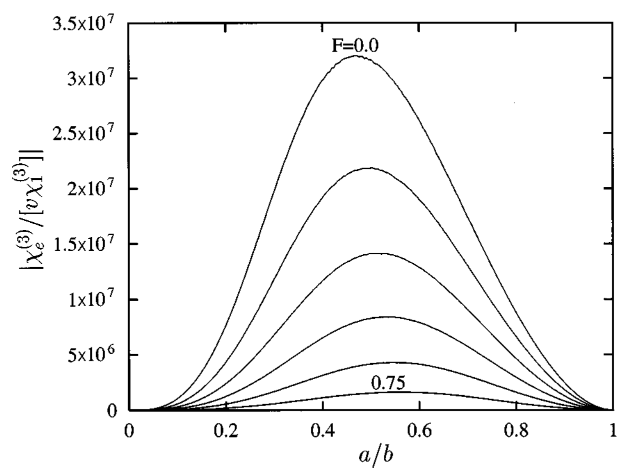

FIG. 5. Same as Fig. 2, but for particles having a nonlinear core and an Al coating shell.

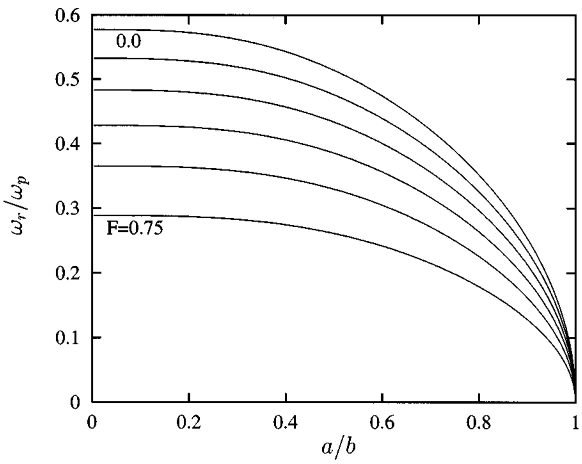

FIG. 6. Same as Fig. 3, but for particles having a nonlinear core and an Al coating shell.

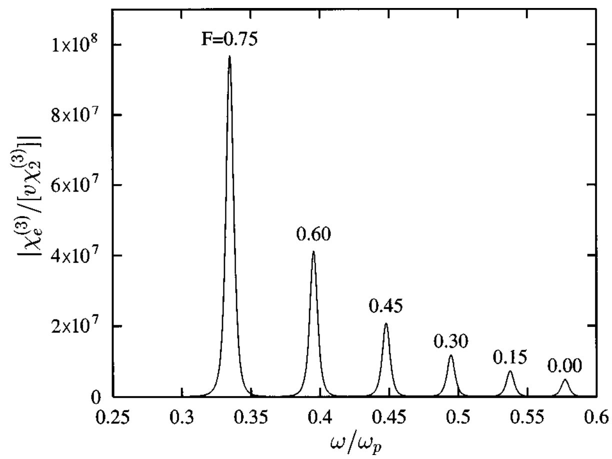

FIG. 8. Same as Fig. 1, but for particles having a Na core.

tude as in the previous example. However, in this case the interparticle interaction works destructively and *reduces* the resonance peak of isolated particles ($F=0$), while still shifting the resonance peak to lower frequencies. For $a/b=0.48$, the reduction is about 21 times. Also oppositely to the previous example, in this case an oblate distribution ($F>0.3$) *reduces* the nonlinear response, while still shifting the resonance peak to lower frequencies, compared with the spherical distribution ($F=v=0.3$), whereas a prolate distribution ($F<0.3$) does the opposite. These features are similar to those in uniform spheres.[8] We have equally computed cases using Au, Na, Ag, Cu as the linear component, and found the same general features. Here, we show in Figs. 7 and 8 the results for Au and Na cores as further examples.

The examples that we have provided have been selected for the purpose of illustration. In practice, there are of course many other factors, such as mechanical, thermal, chemical, and loss properties, that must be taken into consideration in the design and operation of actual components. In particular, one must consider that near the peak of $|\chi_e^{(3)}|$ the absorption is also typically large. This leads to various figures of merit that have been introduced to estimate the performance of specific systems.[10] For the purpose of a general illustration, we may consider a typical figure of merit, defined as

$$W=\frac{n_e^{(2)}I}{\alpha_e\lambda_0}, \tag{28}$$

where $n_e^{(2)}I$, I, α_e, and λ_0 represent the effective nonlinear refractive index, the intensity of light in the medium, the effective absorption coefficient, and the wavelength in vacuum, respectively. Figure 9 shows this figure of merit, normalized by $n_2^{(2)}I$ of the coating material, for particles with an Al core. Despite the absorption, the normalized figure of merit remains strongly enhanced at resonance, up to a value of 15 440 for $F=0.75$. In such case, the $W>1$ condition (required, for example, for optical switching) can be attained if only $n_2^{(2)}I>6.5\times 10^{-5}$, which is easily satisfied by ordinary nonlinear materials even at quite low laser intensities. In this example, the interparticle interaction enhances the figure of merit by as much as 8.8 times.

It is interesting to note that a nonlinear intermolecular enhancement has also been found in two-level quantum systems with nearest-neighbor dipole-dipole interactions.[11,12] However, both the physics and the theoretical treatment involved in such systems differ from ours, and the enhancements found there are also much smaller.

IV. CONCLUSIONS

In summary, coating particles can drastically enhance the nonlinear response at the resonance frequencies of the linear

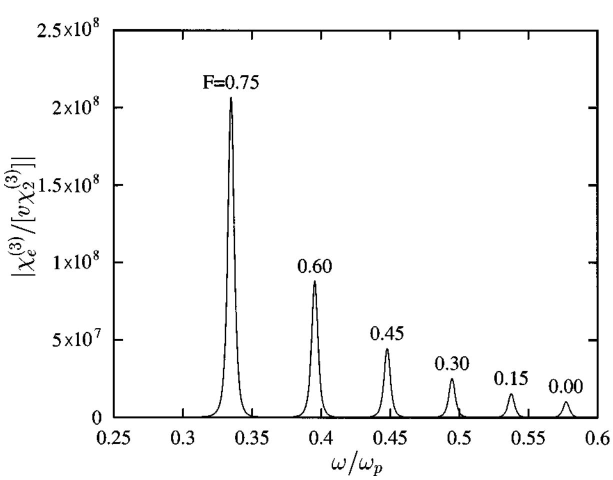

FIG. 7. Same as Fig. 1, but for particles having a Au core.

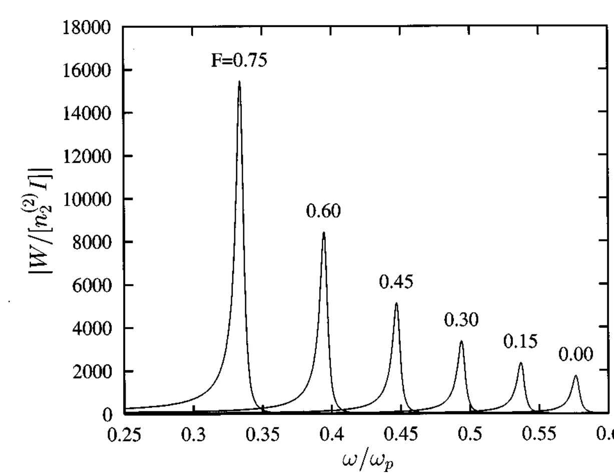

FIG. 9. Normalized figure of merit for the system of Fig. 1.

component, whether the nonlinear component is used as the coating shell or the particle core. Several metals and even insulators can be used as the linear component for the enhancement. The interparticle interaction, which is determined by the particle distribution, further affects the overall response of the composite system. Since the interparticle interaction is always present (not just for certain combinations of materials, coated structures, and at some frequencies near the resonance), the theoretical understanding of this effect is crucial to correctly predict the response. In particular, the interparticle interaction can be exploited to enhance and, more importantly, shift the overall spectrum of $\chi_e^{(3)}$, by appropriately selecting a concentration-distribution parameter. To achieve an optimal enhancement, both the effects of the particle structure and the interparticle interactions must be considered. This opens the way to a combination of truly predictive theoretical calculations and experimental design, capable of producing and controlling giant nonlinear responses, and especially to tune them to frequency ranges of interest in technological applications.

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