Fourier approach to the electric field and the nonlinear susceptibility for a periodic composite

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By using series expressions of space-dependent electrical field in a periodic composite, which are obtained by a simple Fourier approach, the frequency dependence of the effective third-order nonlinear susceptibility χ_e of the metal-insulator composites with simple cubic arrays of coated spheres has been exactly calculated. The results show that the frequency-dependent nonlinear response of the composites has two sharp peaks when the metal phase forms a shell structure. The strengths of the peaks are very sensitive to the relaxation time of the metal. The dependences of both the shapes and strengths of the peaks on the radii of the cores of the coated spheres are also studied. [S0163-1829(98)01642-7]

The nonlinear susceptibilities of composite materials may be strongly enhanced relative to bulk samples of the same materials.[1] Such an enhancement can be attributed to purely classical effect,[2,3] namely, the electric field within the particles is greatly increased at optical frequencies because the composite is inhomogeneous.[3] In the past 10 years, a variety of approaches have been proposed to this problem.[1–10] In this Brief Report, we present our exact calculations of the frequency-dependent cubic nonlinear susceptibility of periodic composite. Our calculations are based on a general expression of χ_e for a composite material, which has been obtained by Stroud and Hui:[2]

$$\chi_e=\sum_i p_i\chi_i\langle(\mathbf{E}\cdot\mathbf{E}^*)(\mathbf{E}\cdot\mathbf{E})\rangle_{i,\mathrm{lin}}/\mathbf{E}_0^4, \tag{1}$$

where χ_i and p_i are the cubic nonlinear susceptibility and volume fraction of the ith component, $\mathbf{E}_0$ is the applied electric field, $\langle\ \rangle_{i,\mathrm{lin}}$ denotes a volume average over the volume of the ith component in the linear limit where $\chi_i=0$. We first calculate the space-dependent electrical field $\mathbf{E}(\mathbf{r})$ in a composite, then exactly evaluate χ_e from using Eq. (1). In this work, we only consider the simplest case, that is, a periodic composite consists of two kinds of isotropic components and the composite has cubic symmetry. The procedure presented in the following can be easily extended to more general cases.

The method used for calculating the electrical field in this work has close relation to the well-known Bergman-Milton theory of the effective dielectric function $\varepsilon_{\mathrm{eff}}$ of the composite[1,11] and the Fourier approaches to the $\varepsilon_{\mathrm{eff}}$ of the periodic composite.[12–15]

In a periodic composite, the space-dependent electrical field can be expressed as

$$\mathbf{E}(\mathbf{r})=\sum_{\mathbf{k}} \mathbf{E}_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}),$$

where $\mathbf{k}$ is the reciprocal vector of the periodic structure. By substituting the expression of the Fourier coefficients of the electrical field $\mathbf{E}_{\mathbf{k}}$ presented in Ref. 12 into the above equation, we obtain a series expression of $\mathbf{E}(\mathbf{r})$:

$$\mathbf{E}(\mathbf{r})=E_0\left\{\hat{\mathbf{e}}+\sum_{l=1}^{\infty}(1/w)^l\mathbf{C}_l(\mathbf{r})\right\},$$
$$w=\frac{p_1\varepsilon_1+p_2\varepsilon_2}{\varepsilon_2-\varepsilon_1}, \tag{2}$$

where ε_i is the dielectric constant of the ith component. $E_0=|\langle\mathbf{E}\rangle|$ is the module of the volume average of the electric field, $\hat{\mathbf{e}}$ is the unit vector in the direction of $\langle\mathbf{E}\rangle$. We assume that the composite is the filler of a parallel plate, for this condition, $\langle\mathbf{E}\rangle$ is equivalent to the applied electrical field $\mathbf{E}_0$, and $\hat{\mathbf{e}}$ is in the direction of the applied field. In addition,

$$\mathbf{C}_l(\mathbf{r})=\sum_{\mathbf{k}_1}{}'\cdots\sum_{\mathbf{k}_l}{}'\hat{\mathbf{k}}_1\exp(i\mathbf{k}_1\cdot\mathbf{r})(\hat{\mathbf{k}}_1\cdot\hat{\mathbf{k}}_2)\,\theta(\mathbf{k}_1-\mathbf{k}_2)\cdots\times(\hat{\mathbf{k}}_{l-1}\cdot\hat{\mathbf{k}}_l)\,\theta(\mathbf{k}_{l-1}-\mathbf{k}_l)(\hat{\mathbf{k}}_l\cdot\hat{\mathbf{e}})\,\theta(\mathbf{k}_l),\tag{3}$$

where "$\Sigma'_{\mathbf{k}_l}$" means that the summation is over $\mathbf{k}_l$ excluding the cases for $\mathbf{k}_l=0$ and $\mathbf{k}_l=\mathbf{k}_{l-1}$, $\hat{\mathbf{k}}$ is the unit vector in the $\mathbf{k}$ direction. $\theta(\mathbf{k})$ is the Fourier coefficient of the indicator function of the first component:[15]

$$\theta(\mathbf{k})=\frac{1}{V}\int_{V_1}\exp(-i\mathbf{k}\cdot\mathbf{r})d\mathbf{r},\tag{4}$$

where $V=a^3$ is the volume of the unit cell, a is the linear size of the cell. V_1 is the volume of the first component in a unit cell.

Another useful expression of $\mathbf{E}(\mathbf{r})$, whose form is analogous to that of the expression of ε_{eff} for periodic composite obtained by Bergman and Dunn[15] is

$$\mathbf{E}(\mathbf{r})=\sum_{\mathbf{k}}\mathbf{E}_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})=E_0\left\{\hat{\mathbf{e}}+\sum_{l=1}^{\infty}(1/s)^l\mathbf{C}_l^F(\mathbf{r})\right\},\quad s=\frac{\varepsilon_2}{\varepsilon_2-\varepsilon_1}.\tag{5}$$

The expression of $\mathbf{C}_i^F(\mathbf{r})$ is slightly different from Eq. (3). Whereas the terms for $\mathbf{k}_l=\mathbf{k}_{l-1}$ are excluded in $\mathbf{C}_l(\mathbf{r})$, these terms are included in the summation in $\mathbf{C}_l^F(\mathbf{r})$. The relation between $\mathbf{C}_l(\mathbf{r})$ and $\mathbf{C}_l^F(\mathbf{r})$ is

$$\mathbf{C}_l^F(\mathbf{r})=\sum_{q=0}^{l-1}c_{l-1}^q p_1^q\mathbf{C}_{l-q}(\mathbf{r}),\quad c_l^q=\frac{l!}{q!(l-q)!}.\tag{6}$$

An alternative and very useful approach to the calculation of $\mathbf{E}(\mathbf{r})$ is to calculate $\mathbf{D}(\mathbf{r})$ first, then calculate $\mathbf{E}(\mathbf{r})$ from using the relation

$$\mathbf{E}(\mathbf{r})=\frac{1}{\varepsilon(\mathbf{r})}\mathbf{D}(\mathbf{r}).\tag{7}$$

$\mathbf{D}(\mathbf{r})$ is expressed as

$$\mathbf{D}(\mathbf{r})=D_0\left(\hat{\mathbf{d}}+\sum_{l=1}^{\infty}(1/u)^l\mathbf{C}_l^D(\mathbf{r})\right),\quad u=\frac{p_2\varepsilon_1+p_1\varepsilon_2}{\varepsilon_1-\varepsilon_2}.\tag{8}$$

Or

$$\mathbf{D}(\mathbf{r})=D_0\left(\hat{\mathbf{d}}+\sum_{l=1}^{\infty}(1/t)^n\mathbf{C}_l^H(\mathbf{r})\right),\quad t=\frac{\varepsilon_1}{\varepsilon_1-\varepsilon_2},\tag{9}$$

where $D_0\hat{\mathbf{d}}=\langle\mathbf{D}(\mathbf{r})\rangle$, $\hat{\mathbf{d}}$ is the unit vector in the direction of $\langle\mathbf{D}(\mathbf{r})\rangle$. In addition,

$$\mathbf{C}_l^D(\mathbf{r})=\sum_{\mathbf{k}_1}{}'\cdots\sum_{\mathbf{k}_l}{}'[\hat{\mathbf{e}}_{\mathbf{k}_{1x}}\exp(i\mathbf{k}_1\cdot\mathbf{r})\,\hat{\mathbf{e}}_{\mathbf{k}_{1y}}\exp(i\mathbf{k}_1\cdot\mathbf{r})]\,\theta(\mathbf{k}_1)\begin{pmatrix}\hat{\mathbf{e}}_{\mathbf{k}_{1x}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{2x}} & \hat{\mathbf{e}}_{\mathbf{k}_{1x}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{2y}}\\ \hat{\mathbf{e}}_{\mathbf{k}_{1y}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{2x}} & \hat{\mathbf{e}}_{\mathbf{k}_{1y}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{2y}}\end{pmatrix}\theta(\mathbf{k}_1-\mathbf{k}_2)\cdots\times\begin{pmatrix}\hat{\mathbf{e}}_{\mathbf{k}_{(l-1)x}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{lx}} & \hat{\mathbf{e}}_{\mathbf{k}_{(l-1)x}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{ly}}\\ \hat{\mathbf{e}}_{\mathbf{k}_{(l-1)y}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{lx}} & \hat{\mathbf{e}}_{\mathbf{k}_{(l-1)y}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{ly}}\end{pmatrix}\theta(\mathbf{k}_{l-1}-\mathbf{k}_l)\begin{pmatrix}\hat{\mathbf{d}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{lx}}\\ \hat{\mathbf{d}}\cdot\hat{\mathbf{e}}_{\mathbf{k}_{ly}}\end{pmatrix}\theta(\mathbf{k}_l),\tag{10}$$

where $\hat{\mathbf{e}}_{\mathbf{k}_x},\hat{\mathbf{e}}_{\mathbf{k}_y}$ are unit vectors, $\hat{\mathbf{e}}_{\mathbf{k}_x},\hat{\mathbf{e}}_{\mathbf{k}_y}$, and $\hat{\mathbf{k}}$ form an orthogonal triad. Equations (8)–(10) are obtained by using a procedure analogous to that used in the derivation of Eqs. (2)–(5).

The relation between $\mathbf{C}_l^D(\mathbf{r})$ and $\mathbf{C}_l^H(\mathbf{r})$ is similar to that between $\mathbf{C}_l(\mathbf{r})$ and $\mathbf{C}_l^F(\mathbf{r})$, that is, the terms for $\mathbf{k}_l=\mathbf{k}_{l-1}$ are included in the summation in $\mathbf{C}_l^H(\mathbf{r})$, whereas these terms are excluded in $\mathbf{C}_l^D(\mathbf{r})$. We also have

$$\mathbf{C}_l^H(\mathbf{r})=\sum_{q=0}^{l=1}c_{l-1}^q p_1^q\mathbf{C}_l^D(\mathbf{r}).$$

Composites made of coated spheres or of coated cylinders are of particular interest.[5–7,16–18] In this paper, we consider a composite composed of coated spheres, each of them with a core made of linear insulator and a concentric spherical shell made of nonlinear metal. The insulator has frequency-independent dielectric constant $\varepsilon_2=1$. The nonlinear metal has a Drude dielectric function:

$$\varepsilon_{1l}=1-\frac{\omega_p^2\tau^2}{1+\omega^2\tau^2}+i\,\frac{\omega_p^2\tau}{\omega(1+\omega^2\tau^2)},$$

where ω_p denotes the plasmon frequency, τ is a characteristic relaxation time. The third-order nonlinear susceptibility of the metal is taken as a unit. We further assume that the host and the core are composed of same material and the coated spheres are embedded in the host with three-dimensional simple-cubic structure. For this system the $\theta(\mathbf{k})$ can be expressed as

$$\theta(\mathbf{k})=\theta^0(\mathbf{k},R_1)-\theta^0(\mathbf{k},R_2),\tag{11}$$

$$\theta^0(\mathbf{k},R_\alpha)=3p(\alpha)\,\frac{1}{X_\alpha^3}(\sin X_\alpha-X_\alpha\cos X_\alpha),\tag{12}$$

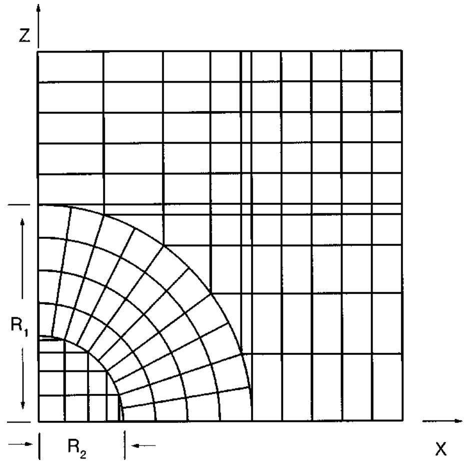

FIG. 1. Schematic drawing of the mesh used in the calculation.

where $\mathbf{k}=(2\pi/a)(n_x,n_y,n_z)$, n_x,n_y,n_z=integers, R_1 and R_2 are the outer and inner radii of the shells. $p(\alpha)=4\pi R_\alpha^3/3V$, $X_\alpha=kR_\alpha$ ($\alpha=1,2$), k is the modular of $\mathbf{k}$.

First, $\mathbf{E}(\mathbf{r})$ [or $\mathbf{D}(\mathbf{r})$] is calculated. Because of the similarity between the expressions of $\mathbf{E}(\mathbf{r})$ [or $\mathbf{D}(\mathbf{r})$] obtained in this work and that of $\varepsilon_{\mathrm{eff}}$ presented in Ref. 15, a procedure analo gous to that used in Ref. 15 for the calculation of $\varepsilon_{\mathrm{eff}}$ is used in this work. The expansion coefficients of series (2), (5), (8), and (9) are calculated for a reciprocal lattice of size N, that is, the truncated lattice involving all $\mathbf{k}$ vectors with n_x, n_y, and n_z running from $-N$ to $+N$ in all directions; then $\mathbf{E}(\mathbf{r})$ or $\mathbf{D}(\mathbf{r})$ is calculated by using Padé analysis[19] using L terms of one of these series. In the calculation, the symmetry is imposed to reduce the volume used in the calculation to $\frac{1}{16}$ of the unit-cell volume. A mesh is generated and is schematically shown in Fig. 1. The electrical field at the center of each division of the mesh is calculated. In this work, meshes with different numbers of calculated points ranging from 2300 to 3400 in the $\frac{1}{16}$ unit cell are adopted.

By substituting $\mathbf{E}(\mathbf{r})$ obtained in Eq. (1), the cubic nonlinear susceptibility $\chi_e(\omega)$ of the composite is calculated. The results, which are obtained from using series (8) for $N=30$ and $L=18$ are present in Figs. 2 and 3.

Figure 2 shows the real part of the effective nonlinear susceptibility of the composite Re(χ_e) as a function of frequency for several values of R_2/R_{2c} ranging from 0 up to 1, with the volume fraction of metal $p_{\mathrm{metal}}[=p(1)-p(2)]$ and relaxation time of the metal fixed ($p_{\mathrm{metal}}=0.1$, $\omega_p\tau=10$), where R_{2c} is a particular value of the inner radii of the shells at which the metal phase forms an infinite cluster in the composite. When $R_2=0$, i.e., the shape of the metal is spheres, not shells, there is one enhancement peak in the $\chi_e(\omega)$ curve that occurs at $\omega\approx0.6\omega_p$, the frequency determined approximately by the plasmon resonance condition for an uncoated sphere[4] [see Fig. 2(a)]. When the metal phase

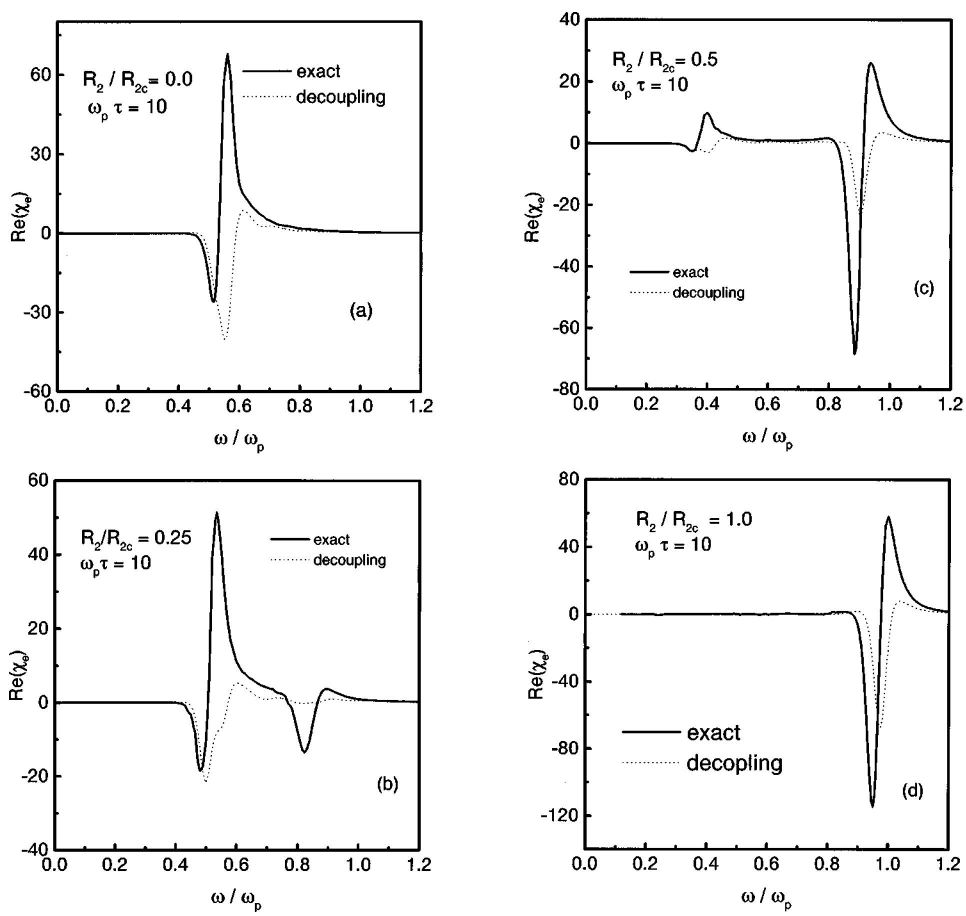

FIG. 2. Re(χ_e) vs ω for several values of R_2/R_{2c}. (R_2/R_{2c}=0.0, 0.25, 0.5, 1.0.) The volume fraction of the metal is 0.1, the relaxation time of the metal is $\omega_p\tau=10$. The solid lines are the exact results, the dotted lines are the results calculated from using the decoupling approximation.

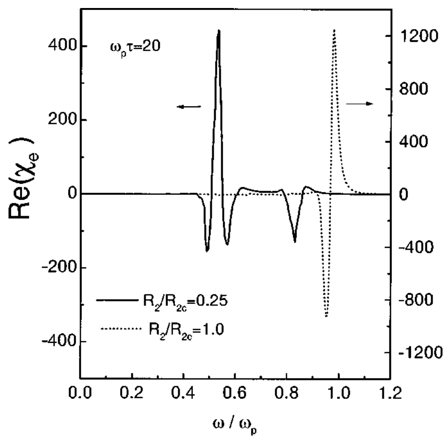

FIG. 3. Re(χ_e) vs ω with $\omega_p\tau=20$, $p_{\text{metal}}=0.1$, and $R_2/R_{2c}=0.25,1$. The solid line is the result for $R_2/R_{2c}=0.25$, the dotted line is the result for $R_2/R_{2c}=1$.

forms the shell structure, there are two enhancement peaks in each $\chi_e(\omega)$ curve. The first one still appears at $\omega\approx 0.6\omega_p$, the second one appears at $\omega\approx 0.9\omega_p$, the frequency determined approximately by that of the coated sphere[4] [see Figs. 2(b) and 2(c)]. Whereas the height of the second peak increases with an increase of R_2, the first one decreases with an increase of R_2 and disappears when $R_2/R_{2c}\geqslant 0.75$. In Fig. 2(d), we present the Re(χ_e)$-\omega$ curve for $R_2/R_{2c}=1.0$. The shapes of the Re(χ_e)$-\omega$ curve for $R_2/R_{2c}=0.75$ and that for $R_2/R_{2c}=1.0$ are the same. The height of the enhancement peaks for $R_2/R_{2c}=0.75$ is about 10% lower than that for $R_2/R_{2c}=1.0$.

We have also calculated the cubic nonlinear susceptibility $\chi_e(\omega)$ by using the decoupling approximation[3]

$$\chi_e=\sum_i \frac{\chi_i}{p_i}\left|\frac{\partial\varepsilon_{\text{eff}}}{\partial\varepsilon_i}\right|\frac{\partial\varepsilon_{\text{eff}}}{\partial\varepsilon_i},$$

$$\varepsilon_{\text{eff}}=\frac{\langle\varepsilon(\mathbf{r})E(\mathbf{r})\rangle}{\langle E(\mathbf{r})\rangle}.$$

for the same composites. The results are also shown in Fig. 2. We can see that the Re[$\chi_e(\omega)$]$-\omega$ curves obtained from using the two approaches present analogous features, but the peaks calculated by using decoupling approximation are lower than the corresponding ones calculated exactly.

Our calculations show that the enhancement of χ_e sensitively depends on the relaxation time τ of the metal. The results of Re[$\chi_e(\omega)$] for $p_{\text{metal}}=0.1$, $\omega_p\tau=20$, and $R_2/R_{2c}=0.25$, 1 are presented in Fig. 3. Comparing Fig. 3 to Figs. 2(b) and 2(c), we can see that when $\omega_p\tau$ changes from 10 to 20, the shape of the first enhancement peaks changes, but that for the second enhancement peaks remains unchanged. We can also see that with an increase of $\omega_p\tau$ the heights of the peaks increases. It shows that an extremely large enhancement of the nonlinear susceptibility can be obtained for the composites that contain very small quantities of nonlinear material if the shell structure of the nonlinear material forms.

In brief summary, we have proposed a Fourier approach to calculate the electric field in periodic composites. This method is simple and straightforward, and valid to any periodic microgeometry. In the series expressions of $\mathbf{E}(\mathbf{r})$, $\mathbf{r}$ appears only in the last fold of each term of the summations. If the calculated point increases by one time, the calculating work only increases a little. For the two-compounds composite, the effect of the geometric structure and the effect of the electric properties on the local field can be dealt with separately. Where the frequency-dependent properties are concerned, the geometric part need not be calculated repeatedly.

As an application of this method, the frequency dependence of bulk effective third-order nonlinear response of simple cubic arrays of nonlinear coated spheres embedded in a linear host has been calculated. The calculation is based on the Stroud-Hui expression of the bulk effective third-order susceptibility of a composite,[2] and the results are exact.

Our method can be generated to the multicomponent periodic composites. However, in the general cases, when the number of the components is greater than 2, the geometric information cannot be separated from the material information.

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