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T-matrix approach to the nonlinear susceptibilities of heterogeneous media

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The nonlinear susceptibilities of a heterogeneous medium are calculated by using a generalization of the standard T-matrix approach. Results for the susceptibilities for degenerate and nondegenerate four-wave mixing and nonlinear absorption are obtained. These are evaluated explicitly for a medium with nonlinear spherical grains. The role of various resonances in the generation of the signals is discussed. In the special cases of low concentration of inhomogeneities, present results agree with those of Flytzanis and co-workers [Opt. Lett. **9**, 344 (1984); **10**, 511 (1985); J. Opt. Soc. Am. B **4**, 5 (1987)].

I. INTRODUCTION

The linear optics of the heterogeneous media is reasonably well understood.[1-5] One has a variety of methods to calculate the effective dielectric function using different approximate schemes. For the small volume fraction $f\,(<0.1)$ of the inhomogeneities, the Maxwell-Garnett formula and the coherent-potential approximation[2,5] are very often used. The nonlinear-optical properties of the heterogeneous media have become important in connection with metal colloids and semiconductor crystallites.[6-13] Flytzanis and co-workers[6-8] have carried out a series of investigations on nonlinear mixing signals produced by a colloidal medium. They have also developed a phenomenological approach to calculate the effective third-order nonlinearity $\bar{\chi}^{(3)}$ of such a medium. However, no general methods exist for the evaluation of the effective nonlinearities of heterogeneous media in a systematic way.

In this paper we describe a T-matrix approach for the calculation of the third- and fifth-order nonlinearities of a heterogeneous medium. In Sec. II we present the general formulation. In Sec. III we present the explicit forms of $\bar{\chi}^{(3)}$ and $\bar{\chi}^{(5)}$ for a medium with nonlinear spherical grains. Each grain is assumed to be a Kerr-like medium. In Sec. IV we discuss the effect of the cooperative resonances[14] on the four-wave-mixing signal. We show the dependence of the cooperative resonances on the volume fraction. In the limit of very small volume fraction, the cooperative resonances go over to the usual shape resonances and our formula for effective $\bar{\chi}^{(3)}$ reduces to the phenomenological result of Flytzanis *et al.* In Sec. V we study the reflection characteristics[15,16] at a nonlinear colloid interface. Finally, in Sec. VI we calculate the effective nonlinearities for nondegenerate four-wave mixing; we give explicit results for a medium with spherical grains.

II. T-MATRIX APPROACH FOR EFFECTIVE NONLINEAR SUSCEPTIBILITIES

In this section we develop the T-matrix formalism for a nonlinear heterogeneous medium. We restrict ourselves only to the case of odd-order nonlinearities up to fifth order. We make a quasistatic approximation, i.e., we assume that the linear dimensions of the inhomogeneities are much smaller compared to the wavelength of the incident radiation. For simplicity, we take the linear dielectric function and the higher-order nonlinear susceptibilities of the constituent media to be scalars. We adopt the method of Gubernatis[2] to obtain the effective third- and fifth-order nonlinear susceptibilities.

Let the nonlinear medium be characterized by a dielectric function

$$\epsilon=\epsilon_0+\delta\epsilon_M \;, \tag{2.1}$$

where ϵ_0 is the spatially invariant (homogeneous) part and $\delta\epsilon_M$ is the nonhomogeneous part with field-independent as well as field-dependent parts

$$\delta\epsilon_M=\delta\epsilon+4\pi\chi^{(3)}|\mathbf{E}|^2+4\pi\chi^{(5)}|\mathbf{E}|^4 \;. \tag{2.2}$$

In Eq. (2.2) $\delta\epsilon$ is the linear part, $\chi^{(3)}$ and $\chi^{(5)}$ are the third- and fifth-order nonlinearity coefficients, respectively. We treat $\delta\epsilon_M$ as a perturbation to ϵ_0 and solve the Maxwell equation

$$\nabla\cdot\mathbf{D}=0, \quad \mathbf{D}=\epsilon\mathbf{E} \tag{2.3}$$

where $\mathbf{D}$ is the displacement vector and $\mathbf{E}$ is the electric field. If $\overleftrightarrow{G}(r,r')$ is the Green's function satisfying the equation

$$\nabla\cdot\epsilon_0\overleftrightarrow{G}=\delta(\mathbf{r}-\mathbf{r}')\overleftrightarrow{I} \;, \tag{2.4}$$

then the solution of Eq. (2.3) can be expressed as

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_0+\int d\mathbf{r}'[\delta\epsilon_M(\mathbf{r}')\mathbf{E}(\mathbf{r}')\cdot\nabla']\overleftrightarrow{G}(\mathbf{r},\mathbf{r}') \;. \tag{2.5}$$

In Eq. (2.5) $\mathbf{E}_0$ is the solution of the homogeneous equation

$$\nabla\cdot\epsilon_0\mathbf{E}_0=0 \;. \tag{2.6}$$

Following Gubernatis, Eq. (2.5) can be rewritten in a compact form

$$\mathbf{E}=\mathbf{E}_0+G\delta\epsilon_M\mathbf{E} \;. \tag{2.7}$$

Substituting Eq. (2.2) in Eq. (2.7), we obtain

$$\mathbf{E}=\mathbf{E}_0+G\delta\epsilon\mathbf{E}+4\pi G\chi^{(3)}|\mathbf{E}|^2\mathbf{E}+4\pi G\chi^{(5)}|\mathbf{E}|^4\mathbf{E} . \quad (2.8)$$

The integral equation (2.8) has a solution which can be obtained iteratively. We write the solution in the form

$$\mathbf{E}=\mathbf{E}_0+GT^{(1)}\mathbf{E}_0+4\pi GT^{(3)}|\mathbf{E}_0|^2\mathbf{E}_0+4\pi GT^{(5)}|\mathbf{E}_0|^4\mathbf{E}_0 . \quad (2.9)$$

The T matrices ($T^{(1)},T^{(3)},T^{(5)}$) can be expressed in terms of the integral operator G and the medium characteristics $\delta\epsilon$, $\chi^{(3)}$, and $\chi^{(5)}$, e.g.,

$$T^{(1)}=\delta\epsilon(I-G\delta\epsilon)^{-1} , \quad (2.10)$$

$$T^{(3)}=\chi^{(3)}(I+GT^{(1)})^2(|I+GT^{(1)}|^2) . \quad (2.11)$$

It will be shown later that for actual calculations, one does not need the explicit forms of the T matrices. Only the averages of the T matrices are needed. Keeping in mind the expression for $\delta\epsilon_M$ given by Eq. (2.2), we compare Eq. (2.7) with Eq. (2.9) to obtain

$$\delta\epsilon\mathbf{E}=T^{(1)}\mathbf{E}_0 , \quad (2.12)$$

$$\chi^{(3)}|\mathbf{E}|^2\mathbf{E}=T^{(3)}|\mathbf{E}_0|^2\mathbf{E}_0 , \quad (2.13)$$

$$\chi^{(5)}|\mathbf{E}|^4\mathbf{E}=T^{(5)}|\mathbf{E}_0|^4\mathbf{E}_0 . \quad (2.14)$$

Equations (2.12)–(2.14) enable us to rewrite the second equation of Eq. (2.3) as

$$\mathbf{D}=\epsilon_0\mathbf{E}+T^{(1)}\mathbf{E}_0+4\pi T^{(3)}|\mathbf{E}_0|^2\mathbf{E}_0+4\pi T^{(5)}|\mathbf{E}_0|^4\mathbf{E}_0 . \quad (2.15)$$

In what follows we perform an ensemble averaging (denoted by angular brackets) of Eqs. (2.9) and (2.15) to obtain the relations

$$\langle\mathbf{E}\rangle=(1+\langle GT^{(1)}\rangle)\mathbf{E}_0+4\pi\langle GT^{(3)}\rangle|\mathbf{E}_0|^2\mathbf{E}_0+4\pi\langle GT^{(5)}\rangle|\mathbf{E}_0|^4\mathbf{E}_0 , \quad (2.16)$$

$$\langle\mathbf{D}\rangle=\epsilon_0\langle\mathbf{E}\rangle+\langle T^{(1)}\rangle\mathbf{E}_0+4\pi\langle T^{(3)}\rangle|\mathbf{E}_0|^2\mathbf{E}_0+4\pi\langle T^{(5)}\rangle|\mathbf{E}_0|^4\mathbf{E}_0 . \quad (2.17)$$

Note that Eqs. (2.16) and (2.17) hold only up to the fifth order. Introducing the effective linear dielectric function ($\bar{\epsilon}$) and effective third- and fifth-order nonlinear susceptibilities $\bar{\chi}^{(3)}$ and $\bar{\chi}^{(5)}$, we can write the average displacement vector as

$$\langle\mathbf{D}\rangle=\bar{\epsilon}\langle E\rangle+4\pi\bar{\chi}^{(3)}|\langle\mathbf{E}\rangle|^2\langle\mathbf{E}\rangle+4\pi\bar{\chi}^{(5)}|\langle\mathbf{E}\rangle|^4\langle\mathbf{E}\rangle+\cdots . \quad (2.18)$$

Substituting Eq. (2.16) into Eqs. (2.17) and (2.18), we obtain two different forms for the mean displacement

$$\langle\mathbf{D}\rangle=[\epsilon_0(1+\langle GT^{(1)}\rangle)+\langle T^{(1)}\rangle]\mathbf{E}_0+4\pi(\epsilon_0\langle GT^{(3)}\rangle+\langle T^{(3)}\rangle)|\mathbf{E}_0|^2\mathbf{E}_0+4\pi(\epsilon_0\langle GT^{(5)}\rangle+\langle T^{(5)}\rangle)|\mathbf{E}_0|^4\mathbf{E}_0 , \quad (2.19)$$

$$\begin{aligned}\langle\mathbf{D}\rangle=\bar{\epsilon}(1+\langle GT^{(1)}\rangle)\mathbf{E}_0&+4\pi[(\bar{\epsilon}\langle GT^{(3)}\rangle)+\bar{\chi}^{(3)}|1+\langle GT^{(1)}\rangle|^2(1+\langle GT^{(1)}\rangle)]|\mathbf{E}_0|^2\mathbf{E}_0\\&+4\pi\{\bar{\epsilon}\langle GT^{(5)}\rangle+4\pi\bar{\chi}^{(3)}[2\langle GT^{(3)}\rangle|1+\langle GT^{(1)}\rangle|^2+\langle GT^{(3)}\rangle^*(1+\langle GT^{(1)}\rangle)^2]\\&\quad+\bar{\chi}^{(5)}|1+\langle GT^{(1)}\rangle|^4(1+\langle GT^{(1)}\rangle)\}|\mathbf{E}_0|^4\mathbf{E}_0 . \end{aligned} \quad (2.20)$$

A comparison of Eqs. (2.19) and (2.20) yields the following expressions for $\bar{\epsilon}$, $\bar{\chi}^{(3)}$, and $\bar{\chi}^{(5)}$:

$$\bar{\epsilon}=\epsilon_0+\frac{\langle T^{(1)}\rangle}{1+\langle GT^{(1)}\rangle} , \quad (2.21)$$

$$\bar{\chi}^{(3)}=[(1+\langle GT^{(1)}\rangle)|1+\langle GT^{(1)}\rangle|^2]^{-1}\times[\langle T^{(3)}\rangle-(\bar{\epsilon}-\epsilon_0)\langle GT^{(3)}\rangle] , \quad (2.22)$$

$$\begin{aligned}\bar{\chi}^{(5)}=[(1+\langle GT^{(1)}\rangle)|1+\langle GT^{(1)}\rangle|^4]^{-1}&\times\{\langle T^{(5)}\rangle-(\bar{\epsilon}-\epsilon_0)\langle GT^{(5)}\rangle\\&-4\pi\bar{\chi}^{(3)}[2\langle GT^{(3)}\rangle|1+\langle GT^{(1)}\rangle|^2\\&+\langle GT^{(3)}\rangle^*(1+\langle GT^{(1)}\rangle)^2]\} .\end{aligned} \quad (2.23)$$

Note that a substitution of Eq. (2.21) in Eq. (2.22), and Eqs. (2.21) and (2.22) in Eq. (2.23) gives the explicit expressions for the effective third- and fifth-order nonlinear susceptibilities $\bar{\chi}^{(3)}$ and $\bar{\chi}^{(5)}$, respectively. For example, for $\bar{\chi}^{(3)}$ we obtain

$$\bar{\chi}^{(3)}=\frac{\langle T^{(3)}\rangle(1+\langle GT^{(1)}\rangle)-\langle T^{(1)}\rangle\langle GT^{(3)}\rangle}{(1+\langle GT^{(1)}\rangle)^2|1+\langle GT^{(1)}\rangle|^2} . \quad (2.24)$$

It can be clearly seen from Eq. (2.24) that the resonant character of the effective third-order nonlinear susceptibility will be given by the zeros of $(1+\langle GT^{(1)}\rangle)$. Note further that the zeros of the denominator in Eq. (2.24) have a multiplicity of 4. Hence the electromagnetic resonance contribution to the third-order nonlinear phenomena will be rather strong. Moreover, the average value

$\langle GT^{(1)}\rangle$ is sensitive to the volume fraction. As a consequence, the location of these new resonances will depend on the values of the volume fraction.

III. EFFECTIVE NONLINEAR SUSCEPTIBILITIES FOR A HETEROGENEOUS MEDIUM WITH SPHERICAL GRAINS

In order to have a better understanding of the results cited in Sec. II, we consider a simple model heterogeneous medium. Let the medium consist of nonlinear spherical grains embedded in a linear dielectric with dielectric constant ϵ_0. Let the grains be characterized by the nonlinear dielectric function

$$\epsilon(\omega)=\epsilon_1(\omega)+\epsilon_2|\mathbf{E}|^2 , \tag{3.1}$$

where ϵ_1 is the linear part and ϵ_2 is the nonlinearity constant. Note that we are assuming that the grains have cubic nonlinearity. A cubic nonlinearity in the constituent medium can also lead to higher-order nonlinearities so far as the macroscopic properties of the composite medium are concerned.

For a sphere the applied field $\mathbf{E}_0$ and the Maxwell field $\mathbf{E}$ are related by the expression

$$\mathbf{E}=\frac{3\epsilon_0}{\epsilon(\omega)+2\epsilon_0}\mathbf{E}_0 . \tag{3.2}$$

Using Eq. (3.1), Eq. (3.2) can be written as

$$\mathbf{E}=\frac{3\epsilon_0}{\epsilon_1+2\epsilon_0}\mathbf{E}_0-\frac{\epsilon_2}{\epsilon_1+2\epsilon_0}|\mathbf{E}|^2\mathbf{E} . \tag{3.3}$$

Making use of iterations, Eq. (3.3) can be expressed as

$$\mathbf{E}=\mathbf{E}_0x-\frac{\epsilon_2}{3\epsilon_0}x^2|x|^2|\mathbf{E}_0|^2\mathbf{E}_0 +\frac{\epsilon_2}{3\epsilon_0}x^2|x|^4B|\mathbf{E}_0|^4\mathbf{E}_0 . \tag{3.4}$$

where x and B are defined by

$$x=\frac{3\epsilon_0}{\epsilon_1+2\epsilon_0},\quad B=2\left[\frac{\epsilon_2x}{3\epsilon_0}\right]+\left[\frac{\epsilon_2x}{3\epsilon_0}\right]^* . \tag{3.5}$$

A comparison of Eq. (3.4) with Eq. (2.16) yields

$$1+\langle GT^{(1)}\rangle=x , \tag{3.6}$$

$$4\pi\langle GT^{(3)}\rangle=-\frac{\epsilon_2}{3\epsilon_0}|x|^2x^2 , \tag{3.7}$$

$$4\pi\langle GT^{(5)}\rangle=\frac{\epsilon_2}{3\epsilon_0}x^2|x|^4B . \tag{3.8}$$

Substituting Eq. (3.4) in Eq. (2.4), the following equation can be obtained:

$$\mathbf{D}=\epsilon_1x\mathbf{E}_0+\epsilon_2\left[1-\frac{\epsilon_1x}{3\epsilon_0}\right]x|x|^2|\mathbf{E}_0|^2\mathbf{E}_0 -\epsilon_2\left[1-\frac{\epsilon_1x}{3\epsilon_0}\right]Bx|x|^4|\mathbf{E}_0|^4\mathbf{E}_0 . \tag{3.9}$$

Comparing Eq. (3.9) with Eq. (2.19) we obtain

$$\langle T^{(1)}\rangle=(\epsilon_1-\epsilon_0)x , \tag{3.10}$$

$$4\pi\langle T^{(3)}\rangle=\epsilon_2x^2|x|^2 , \tag{3.11}$$

$$4\pi\langle T^{(5)}\rangle=-\epsilon_2x^2|x|^4B . \tag{3.12}$$

The results given by Eqs. (3.6)–(3.8) and Eqs. (3.10)–(3.12) hold well for a single nonlinear sphere, where averaging of Eqs. (3.4) and (3.9) was performed in a trivial manner. These results can be generalized to the case of a colloidal medium if we neglect such features as size dispersion, correlation effects, etc., i.e., we assume that the T matrix for composite medium can be written as the sum of the T matrices of the individual grains. We have thus generalized the Maxwell-Garnett approximation to nonlinear medium. If f is the volume fraction of the grains in the composite medium, Eqs. (3.6)–(3.8) and Eqs. (3.10)–(3.12) are modified as follows:

$$\langle GT^{(1)}\rangle=f(x-1) , \tag{3.13}$$

$$4\pi\langle GT^{(3)}\rangle=-f\left[\frac{\epsilon_2}{3\epsilon_0}\right]|x|^2x^2 , \tag{3.14}$$

$$4\pi\langle GT^{(5)}\rangle=f\left[\frac{\epsilon_2}{3\epsilon_0}\right]|x|^4x^2B , \tag{3.15}$$

$$\langle T^{(1)}\rangle=f(\epsilon_1-\epsilon_0)x , \tag{3.16}$$

$$4\pi\langle T^{(3)}\rangle=f\epsilon_2x^2|x|^2 , \tag{3.17}$$

$$4\pi\langle T^{(5)}\rangle=-f\epsilon_2x^2|x|^4B . \tag{3.18}$$

Thus we obtain the T matrices from the studies of the macroscopic Maxwell equation for a Kerr medium. Next, we derive the explicit expressions for the effective linear dielectric function as well as effective nonlinear susceptibilities. Substituting Eqs. (3.13)–(3.18) in Eqs. (2.21)–(2.23) we obtain

$$\bar{\epsilon}=\epsilon_0+\frac{f(\epsilon_1-\epsilon_0)x}{1+f(x-1)}=\epsilon_0+f(\epsilon_1-\epsilon_0)/P , \tag{3.19}$$

$$\bar{\chi}^{(3)}=\frac{\epsilon_2}{4\pi}f\frac{|x|^2x^2}{|1+f(x-1)|^2[1+f(x-1)]^2}=(\epsilon_2f)/(4\pi|P|^2P^2) , \tag{3.20}$$

$$\bar{\chi}^{(5)}=(\epsilon_2f)\left\{-B+f\left[2\left[\frac{\epsilon_2x}{3\epsilon_0P}\right]+\left[\frac{\epsilon_2x}{3\epsilon_0P}\right]^*\right]\right\}\Big/(4\pi|P|^4P^2) . \tag{3.21}$$

In Eqs. (3.20) and (3.21) we have used the following definition:

$$P=\frac{1}{x}[1+f(x-1)] . \qquad (3.22)$$

We notice that Eq. (3.19) gives the standard Maxwell-Garnett result. From Eq. (2.20) it is clear that the limit of $4\pi\bar{\chi}^{(3)}$ as $f\rightarrow 1$ is ϵ_2. This implies that the effective third-order susceptibility coincides with the nonlinearity coefficient ϵ_2 when the whole space is filled by the nonlinear medium. On the other hand, $f\rightarrow 0$ implies that the space is filled by the linear medium only. Hence the effective nonlinear susceptibilities vanish. A very interesting feature which emerges from Eq. (3.21) is that the effective fifth-order susceptibility is nonzero though the grains possess a nonlinearity of only third order. In fact, a third-order nonlinearity of the grains can lead to all higher odd-order nonlinearities in the macroscopic behavior of the composite medium. If ϵ_2 is real then $\bar{\chi}^{(5)}$ is proportional to ϵ_2^2. In the limit $f\rightarrow 1$, $P\rightarrow 1$ and Eq. (3.21) yields $\bar{\chi}^{(5)}=0$ because the whole space is filled by a cubic nonlinear medium.

In this section we have written the T matrix for a composite system as the sum of T matrices corresponding to the individual grains. One can, in principle, also investigate the effective nonlinear susceptibilities in the coherent potential approximation. There are various ways in which this approximation can be improved upon and the effects of correlations, etc., can be included. Sheng's[17] approach, for example, treats the pair correlations between nearest neighbors by using cluster approximation. Another possible approach for somewhat higher f values would be to generalize Bruggeman's[18] approach to nonlinear media.

IV. RESONANT CHARACTER OF THE NONLINEAR SIGNALS GENERATED BY HETEROGENEOUS MEDIA

In this section we restrict ourselves to the discussion of the resonances in the effective linear dielectric function and effective third-order susceptibility for a composite medium having spherical grains. The resonances in the linear effective medium are well understood. They have been studied[14,19,20] in connection with the anomalous absorption behavior of colloids and very thin metal films. The predominant feature which appears in the optical properties of metal colloids or very thin granular metal films can be attributed to the excitation of collective oscillations of the conduction electrons by the electric field of the incident light waves. Indeed, from Eq. (3.19) we notice that the resonances in $\bar{\epsilon}$ are determined by the zeros of the function $P=[1+f(x-1)]/x$, which can be rewritten as follows:

$$P=\frac{D+f(N-D)}{N} , \qquad (4.1)$$

where

$$N=3\epsilon_0 ,$$

$$D=\epsilon_1+2\epsilon_0 .$$

Thus, the resonances will be given by the zeros of $D+f(N-D)$ and their location will depend on the values of ϵ_0, ϵ_1, and f. In the small f limit the resonances are characterized by the zeros of $D(=\epsilon_1+2\epsilon_0)$. For metallic grains, when $\text{Re}(\epsilon_1)$ can be negative, D can have complex zeros depending on the dispersive properties of the grain material. Physically this implies that localized plasmons can be excited in the grains. Because of the excitation of the localized plasmons there can be significant enhancement of the local fields (recall that in the lowest order $\mathbf{E}=\mathbf{E}_0 x$). Thus, to summarize, the cooperative resonances given by the zeros of $D+f(N-D)$ (which are sensitive to the value of f) in the small f limit reduce to the standard shape resonances given by the zeros of D and the resonances are associated with significant local-field enhancement.

The role of local-field enhancement can be even more significant in case of third- and higher-order nonlinear processes. This is because of the fact that the zeros of $D+f(N-D)$ are of multiplicity 4 for $\bar{\chi}^{(3)}$ [see Eq. (3.20)] and of multiplicity 6 for $\bar{\chi}^{(5)}$ [see Eq. (3.21)]. The local-field-enhanced third-order nonlinear process like phase conjugation in heterogeneous media was studied experimentally by Flytzanis and co-workers. They showed that at resonance a metal dielectric composite medium with volume fraction of metallic grains as little as 10^{-4} can show a nonlinearity comparable to that of CS_2. For theoretical calculations they used the phenomenological formula which in our notation reads

$$\bar{\chi}^{(3)}\simeq f\frac{\epsilon_2}{4\pi}|x|^2x^2 . \qquad (4.2)$$

Note that Eq. (4.2) is identical to our result given by Eq. (3.20) in the small f limit. Obviously Eq. (4.2) does not reflect the dependence of the resonance positions on the value of f. In fact, the resonances shift towards larger wavelengths as the value of f is increased. The amount of the shift can be easily calculated if we assume a free-electron model for the grain material, i.e., we assume that

$$\text{Re}\epsilon(\lambda)=1-\frac{\lambda^2}{\lambda_p^2} , \qquad (4.3)$$

where λ_p is the plasma frequency. The location of the resonance is then characterized by the equation

$$1-\frac{\lambda^2}{\lambda_p^2}+\left[\frac{2+f}{1-f}\right]\epsilon_0=0 , \qquad (4.4)$$

and the amount of shift is given by the relation

$$\Delta\lambda=\lambda_p\left[\sqrt{3}-\left[1+\frac{2+f}{1-f}\right]^{1/2}\right] . \qquad (4.5)$$

It is clear from Eq. (4.5) that the shift is positive (for $f<1$) and, for example, for $\epsilon_0=1$, $f=0.1$ it is approximately equal to 5%.

In order to have a better understanding, we study the real ($\bar{\epsilon}'$) and imaginary ($\bar{\epsilon}''$) parts of the effective linear dielectric function $\bar{\epsilon}(=\bar{\epsilon}'+i\bar{\epsilon}'')$ as a function of wavelength λ for $\epsilon_0=1$. We also study $|\bar{\chi}^{(3)}|^2$ which reflects the intensity of the nonlinear signal generated by the heterogeneous medium and $\mathrm{Im}(\bar{\chi}^{(3)})$ which characterizes the change in the absorption in the medium. We have taken the complex values of the bulk dielectric function $\epsilon_1(\lambda)$ for silver (we have used silver as the grain material) from the work of Johnson and Christy.[21] The results for $\bar{\epsilon}'(\lambda)$ and $\bar{\epsilon}''(\lambda)$ are shown in Fig. 1. The graphs of $|4\pi\bar{\chi}^{(3)}/\epsilon_2|^2$ and $\mathrm{Im}(4\pi\bar{\chi}^{(3)}/\epsilon_2)$ as functions of λ are plotted in Figs. 2(a) and 2(b), respectively. Different curves in Fig. 1 correspond to three different values of f, namely, $f=0.1, 0.08, 0.06$. In Figs. 2(a) and 2(b) we have used the following values of f; namely, $f=0.1, 10^{-2}, 10^{-6}$. It is clear from Fig. 1 that with an increase in f the resonance gets red shifted. The resonance also becomes more prominent as f increases, i.e., the total absorption in the medium increases. Besides, for larger values of f there is a wavelength region where $\bar{\epsilon}'(\lambda)<0$. The linear effective medium behaves like a metal in this region. With a decrease in the value of f this region shrinks and ultimately vanishes, thereby meaning that the macroscopic behavior of the heterogeneous medium is close to that of a dielectric. Nevertheless, the cooperative resonances given by the zeros of $D+f(N-D)$ remain intact even in this case. The location of the resonances in $|4\pi\bar{\chi}^{(3)}/\epsilon_2|^2$ is analogous [see Fig. 2(a)] to that discussed above. For very small f, $D+f(N-D)\sim D$, the resonance is basically the shape resonance and occurs near $\lambda=3550$ Å. With an increase in f the resonance shifts towards larger values of λ. The shift is significant in the range of f from 0.01 to 0.1. For example, for $f=0.1$ the shift is about 2%. The deviation from the calculated value (5%) is due to the fact that free-electron model is not a good approximation for the metal in the wavelength range under consideration. We did not perform calculations for values of f larger than 0.1 since for such values correlation effects have to be taken into account. One more feature that can be noted from Fig. 2(a) is that the nonlinear signal intensity is proportional to f^2 and hence increases drastically with an increase in f [note the logarithmic scale in Fig. 2(a)]. The imaginary part of $4\pi\bar{\chi}^{(3)}/\epsilon_2$ proportional to the nonlinear absorption is plotted as function of λ in Fig. 2(b)

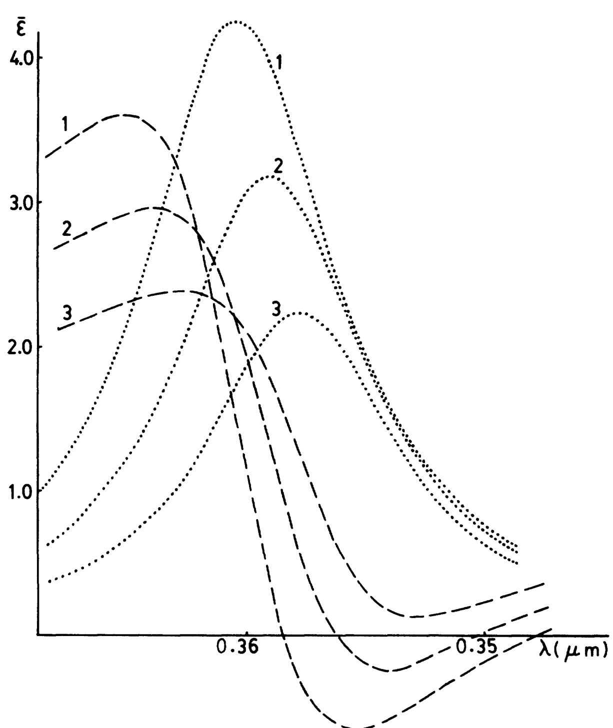

FIG. 1. Wavelength (μm) dependence of the real (dashed) and imaginary (dotted) parts of the effective dielectric function $\bar{\epsilon}$. Curves 1, 2, and 3 correspond to $f=0.1$, 0.08, and 0.06, respectively.

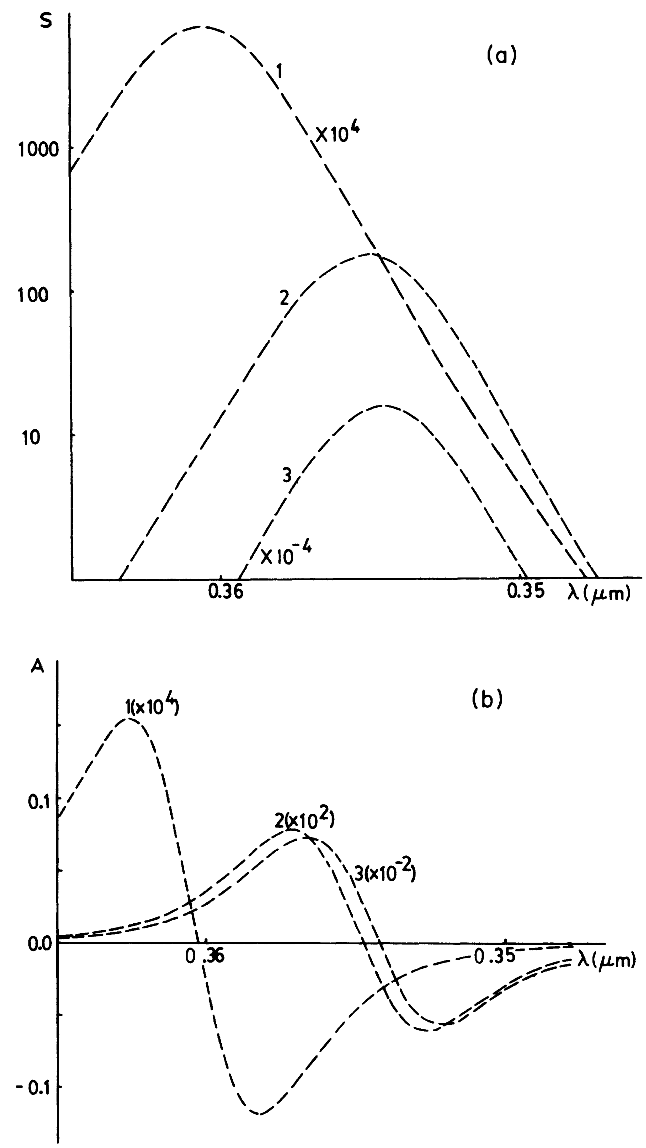

FIG. 2. (a) Four-wave-mixing signal $S\sim|4\pi\bar{\chi}^{(3)}/\epsilon_2|$ as a function of wavelength λ (μm). Curves 1, 2, and 3 correspond to the values of $f=0.1$, 10^{-2}, and 10^{-6}, respectively. (b) Nonlinear absorption $A\sim\mathrm{Im}(4\pi\bar{\chi}^{(3)}/\epsilon_2)$ as a function of wavelength λ (μm). Curves 1, 2, and 3 correspond to $f=0.1$, 10^{-2}, and 10^{-6}, respectively.

for three different values of f, namely, $f=0.1, 10^{-2}, 10^{-6}$. It is clear from Fig. 2(b) that the nonlinear contribution to the absorption of the medium is with different signs depending on the wavelength. For example, for $f=0.1$ nonlinearity of the effective medium decreases (increases) the total absorption if $\lambda < 3603$ Å ($\lambda > 3603$ Å).

V. REFLECTION FROM A DIELECTRIC-NONLINEAR COLLOID INTERFACE: NUMERICAL RESULTS

We consider a semiinfinite nonlinear heterogeneous medium bounded by a linear dielectric with dielectric constant ϵ_i. The nonlinear heterogeneous medium consists of metallic grains embedded in a dielectric with dielectric function ϵ_0. The macroscopic properties of such nonlinear medium are characterized by the effective linear dielectric function given by Eq. (3.19) and effective cubic nonlinearity given by Eq. (3.20) (we consider a nonlinearity only up to third order). Let the half-space $z>0$ be occupied by the nonlinear medium and let the dielectric occupy the other half-space $z<0$. Let a transverse electric (TE)-polarized plane monochromatic wave be incident normally on the interface from the linear medium side. For the half-space $z>0$ the wave equation for the nonzero component of the electric field $E_x^>$ can be written as

$$\frac{d^2E_x^>}{dz^2}+k_0^2(\bar{\epsilon}_1+\bar{\epsilon}_2|E_x^>|^2)E_x^>=0 , \tag{5.1}$$

where $\bar{\epsilon}_1=\bar{\epsilon}$ and $\bar{\epsilon}_2=4\pi\bar{\chi}_3$. It is clear from Eqs. (3.19) and (3.20) that for metallic grains or for lossy media the effective linear and nonlinear susceptibilities are complex, i.e.,

$$\bar{\epsilon}_1=\bar{\epsilon}'_1+i\bar{\epsilon}''_1 , \tag{5.2}$$

$$\bar{\epsilon}_2=\bar{\epsilon}'_2+i\bar{\epsilon}''_2 . \tag{5.3}$$

Because of the complex character of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, the solution of Eq. (5.1) is not trivial. In what follows, we let

$$E_x^> =\tilde{E}(z)e^{ik_0\sqrt{\bar{\epsilon}'_1}z} , \tag{5.4}$$

with $k_0=\omega/c$ and make the slowly varying envelope approximation. Then the equation for $\tilde{E}(z)$ can be written as follows:

$$2ik_0\sqrt{\bar{\epsilon}'_1}\frac{d\tilde{E}}{dz}+k_0^2(i\bar{\epsilon}''_1+\bar{\epsilon}_2|\tilde{E}|^2)\tilde{E}=0 . \tag{5.5}$$

Introducing the real amplitude A and phase φ of $\tilde{E}(z)$ as

$$\tilde{E}(z)=A(z)e^{i\varphi(z)} , \tag{5.6}$$

Eq. (5.5) can be decomposed into a set of two coupled equations:

$$\frac{dA}{dz}+\frac{k_0\bar{\epsilon}''_1}{2\sqrt{\bar{\epsilon}'_1}}\left[1+\frac{\bar{\epsilon}''_2}{\bar{\epsilon}''_1}A^2\right]A=0 , \tag{5.7}$$

$$\frac{d\varphi}{dz}=\frac{k_0\bar{\epsilon}'_2}{2\sqrt{\bar{\epsilon}'_1}}A^2 . \tag{5.8}$$

The solution of Eqs. (5.7) and (5.8) can be written as

$$A(z)=\frac{A_0e^{-\alpha z}}{[1+\beta A_0^2(1-e^{-2\alpha z})]^{1/2}} , \tag{5.9}$$

$$\varphi(z)=\varphi_0+\frac{\gamma}{2\alpha\beta}\ln[1+\beta A_0^2(1-e^{-2\alpha z})] , \tag{5.10}$$

where

$$\gamma=\frac{k_0\bar{\epsilon}'_2}{2\sqrt{\bar{\epsilon}'_1}},\quad \beta=\frac{\bar{\epsilon}''_2}{\bar{\epsilon}''_1},\quad \alpha=\frac{k_0\bar{\epsilon}''_1}{2\sqrt{\bar{\epsilon}'_1}} , \tag{5.11}$$

and A_0 is the amplitude and φ_0 is the phase at $z=0$. Using Maxwell's equation and Eq. (5.5), the tangential component of the magnetic field H_y can be expressed as

$$H_y^> = \left[\sqrt{\bar{\epsilon}'_1}\left[1+\frac{i\bar{\epsilon}''_1}{2\bar{\epsilon}'_1}\right]+\frac{\bar{\epsilon}_2}{2\sqrt{\bar{\epsilon}'_1}}A^2\right]Ae^{i\varphi} . \tag{5.12}$$

If $\bar{\epsilon}''_1 \ll \bar{\epsilon}'_1$, then Eq. (5.12) can be rewritten in the form

$$H_y^> \simeq \sqrt{\bar{\epsilon}_1}\left[1+\frac{\bar{\epsilon}_2}{2\sqrt{\bar{\epsilon}_1\bar{\epsilon}'_1}}A^2\right]Ae^{i\varphi} . \tag{5.13}$$

For the half-space $z<0$, the field components E_x and H_y can be written as

$$E_x^< = A_{i+}e^{ik_0\sqrt{\epsilon_i}z}+A_{i-}e^{-ik_0\sqrt{\epsilon_i}z} , \tag{5.14}$$

$$H_y^< =\sqrt{\epsilon_i}(A_{i+}e^{ik_0\sqrt{\epsilon_i}z}-A_{i-}e^{-ik_0\sqrt{\epsilon_i}z}) . \tag{5.15}$$

Using the continuity of the tangential components of **E** and **H** across $z=0$, we obtain

$$A_{i+}+A_{i-}=A_0e^{i\varphi_0} , \tag{5.16}$$

$$\sqrt{\epsilon_i}(A_{i+}-A_{i-})=\left[\bar{\epsilon}_1\left[1+\frac{\bar{\epsilon}_2A_0^2}{\sqrt{\bar{\epsilon}_1\bar{\epsilon}'_1}}\right]\right]^{1/2}A_0e^{i\varphi_0} . \tag{5.17}$$

On solving Eqs. (5.16) and (5.17), we obtain the reflectivity R and the intensity of the incident field I_i as functions of the intensity A_0^2 in the medium:

$$R=\left|\frac{A_{i-}}{A_{i+}}\right|^2=\left|\frac{1-\left[\frac{\bar{\epsilon}_1}{\epsilon_i}\left[1+\frac{\bar{D}I_0}{\sqrt{\bar{\epsilon}_1\bar{\epsilon}'_1}}\right]\right]^{1/2}}{1+\left[\frac{\bar{\epsilon}_1}{\epsilon_i}\left[1+\frac{\bar{D}I_0}{\sqrt{\bar{\epsilon}_1\bar{\epsilon}'_1}}\right]\right]^{1/2}}\right|^2 , \tag{5.18}$$

$$I_i=\epsilon_2|A_{i+}|^2=\frac{I_0}{4}\left|1+\left[\frac{\bar{\epsilon}_1}{\epsilon_i}\left[1+\frac{\bar{D}I_0}{\sqrt{\bar{\epsilon}_1\bar{\epsilon}'_1}}\right]\right]\right|^2 . \tag{5.19}$$

The parameters I_0 and $\bar{D}$ are defined by

$$I_0=\epsilon_2A_0^2,\quad \bar{D}=f/(P^2|P|^2) . \tag{5.20}$$

In what follows, we calculate R numerically using Eq.

(5.18) with Eq. (5.20) for the following set of parameter values: $\epsilon_0=\epsilon_i=1$, $f=0.1,0.08,0.06$. We normalize all intensities in terms of ϵ_2, i.e., we set $\epsilon_2=1$. We investigate the reflection characteristics in the wavelength range from 3450 to 3700 Å.

We study the wavelength dependence of the normal incident reflection coefficient for a linear ($\epsilon_2=0$) semiinfinite heterogeneous medium. The results are shown in Fig. 3, where we have plotted R as a function of wavelength λ for three different values of volume fraction, namely, $f=0.1,0.08,0.06$. It is clear from Fig. 3 that the shift in the resonance in R is analogous to that for $\bar{\epsilon}$ and $\bar{\chi}^{(3)}$. Note further that the maxima of R correspond to the region where $\bar{\epsilon}'_1$ is minimum.

Next, we study the power dependence of the reflection produced by a nonlinear heterogeneous medium. Using Eqs. (5.18) and (5.19) we calculate R as a function of I_i treating I_0 as the parameter. We have varied the parameter I_0 in a range so that

$$\left| \frac{\bar{D} I_0}{\sqrt{\bar{\epsilon}_1 \bar{\epsilon}'_1}} \right| \ll 1 . \tag{5.21}$$

The inequality reflects the validity of the slowly varying envelope approximation. In the range of intensities given by Eq. (5.21) the numerical results show that the system exhibits only power saturation. Moreover, this power saturation is different for different wavelengths. For example, for $f=0.1$ and for wavelengths greater that 3603 Å R increases as the input power is increased, whereas, for lower wavelengths the behavior is just the opposite. For $\lambda > 3603$ Å total absorption in the nonlinear medium

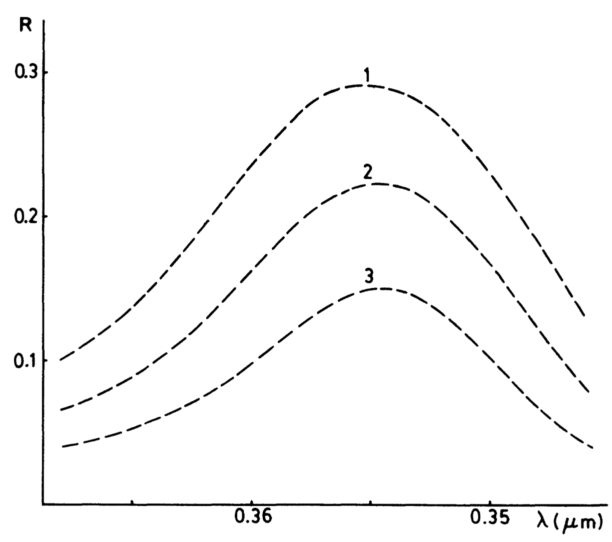

FIG. 3. Normal incidence reflection coefficient R as a function of the wavelength λ (μm) for $\epsilon_0=1=\epsilon_i$. Curves 1, 2, and 3 correspond to $f=0.1$, 0.08, and 0.06, respectively.

[see Fig. 2(b)] is increased and this leads to an increase in the value of the reflection coefficient.[22]

VI. NONDEGENERATE FOUR-WAVE MIXING IN A HETEROGENEOUS MEDIUM

In this section we develop the theory for the effective third-order susceptibility $\bar{\chi}^{(3)}(\omega_1,\omega_1,-\omega_2)$ for nondegenerate four-wave mixing involving light fields at the frequencies ω_1, ω_2, and $\omega_s(=2\omega_1-\omega_2)$. The average electric field amplitudes at the frequencies ω_1, ω_2, and ω_s can be written as

$$\langle \mathbf{E}_j(\omega_j) \rangle = \langle \mathbf{E}_j^L \rangle + \langle \mathbf{E}_j^{\mathrm{NL}} \rangle , \quad j=1,2,s \tag{6.1}$$

where $\langle \mathbf{E}_j^L \rangle$ and $\langle \mathbf{E}_j^{\mathrm{NL}} \rangle$ for $j=1,2,s$ are given by [see Eq. (2.16)]

$$\langle \mathbf{E}_j^L \rangle = \mathbf{E}_{j0}(1+\langle G T_j^{(1)} \rangle), \quad j=1,2,s \tag{6.2}$$

and

$$\begin{aligned} \langle \mathbf{E}_1^{\mathrm{NL}} \rangle = 4\pi(& \langle G T_{111}^{(3)} \rangle \,|\mathbf{E}_{10}|^2 \mathbf{E}_{10} + \langle G T_{122}^{(3)} \rangle \,|\mathbf{E}_{20}|^2 \mathbf{E}_{10} \\ & + \langle G T_{1ss}^{(3)} \rangle \,|\mathbf{E}_{s0}|^2 \mathbf{E}_{10} \\ & + \langle G T_{s21}^{(3)} \rangle \mathbf{E}_{s0} \mathbf{E}_{20} \mathbf{E}_{10}^{*}) , \end{aligned} \tag{6.3}$$

$$\begin{aligned} \langle \mathbf{E}_2^{\mathrm{NL}} \rangle = 4\pi(& \langle G T_{222}^{(3)} \rangle \,|\mathbf{E}_{20}|^2 \mathbf{E}_{20} + \langle G T_{211}^{(3)} \rangle \,|\mathbf{E}_{10}|^2 \mathbf{E}_{20} \\ & + \langle G T_{2ss}^{(3)} \rangle \,|\mathbf{E}_{s0}|^2 \mathbf{E}_{20} \\ & + \langle G T_{11s}^{(3)} \rangle \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{s0}^{*}) , \end{aligned} \tag{6.4}$$

$$\begin{aligned} \langle \mathbf{E}_s^{\mathrm{NL}} \rangle = 4\pi(& \langle G T_{sss}^{(3)} \rangle \,|\mathbf{E}_{s0}|^2 \mathbf{E}_{s0} + \langle G T_{s11}^{(3)} \rangle \,|\mathbf{E}_{10}|^2 \mathbf{E}_{s0} \\ & + \langle G T_{s22}^{(3)} \rangle \,|\mathbf{E}_{20}|^2 \mathbf{E}_{s0} \\ & + \langle G T_{112}^{(3)} \rangle \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^{*}) . \end{aligned} \tag{6.5}$$

In Eqs. (6.2)–(6.5), $\mathbf{E}_{j0}$ is the macroscopic field with frequency ω_j, $T_j^{(1)}$ is the linear T matrix at frequency ω_j:

$$T_j^{(1)} = T^{(1)}(\omega_j) , \tag{6.6}$$

$T_{ijk}^{(3)}$ are the third-order T matrices which have been introduced in a manner analogous to the one in Eq. (2.9),

$$T_{ijk}^{(3)} = T^{(3)}(\omega_i,\omega_j,-\omega_k), \quad i,j,k=1,2,s . \tag{6.7}$$

It is obvious from Eqs. (6.1)–(6.5) that $\langle \mathbf{E}_j^L \rangle$ ($\langle \mathbf{E}_j^{\mathrm{NL}} \rangle$) represents the linear (nonlinear) part of $\langle \mathbf{E}_j \rangle$, i.e., it arises from the linear (nonlinear) susceptibility of the medium.

The average value of the electric displacement vector $\mathbf{D}_s$ at frequency ω_s can also be decomposed into the linear and nonlinear parts and can be written as.

$$\langle \mathbf{D}_s \rangle = \langle \mathbf{D}_s^L \rangle + \langle \mathbf{D}_s^{\mathrm{NL}} \rangle , \tag{6.8}$$

with [see Eq. (2.19)]

$$\langle \mathbf{D}_s^L \rangle = [\langle T_s^{(1)} \rangle + \epsilon_0 (1 + \langle G T_s^{(1)} \rangle)] \mathbf{E}_{s0} \tag{6.9}$$

and

$$\begin{aligned} \langle \mathbf{D}_s^{\mathrm{NL}} \rangle = 4\pi [& (\epsilon_0 \langle G T_{sss}^{(3)} \rangle + \langle T_{sss}^{(3)} \rangle) \, | \mathbf{E}_{s0} |^2 \mathbf{E}_{s0} \\ & + (\epsilon_0 \langle G T_{s11}^{(3)} \rangle + \langle T_{s11}^{(3)} \rangle) \, | \mathbf{E}_{10} |^2 \mathbf{E}_{s0} \\ & + (\epsilon_0 \langle G T_{s22}^{(3)} \rangle + \langle T_{s22}^{(3)} \rangle) \, | \mathbf{E}_{20} |^2 \mathbf{E}_{s0} \\ & + (\epsilon_0 \langle G T_{112}^{(3)} \rangle + \langle T_{112}^{(3)} \rangle) \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^*] . \end{aligned} \tag{6.10}$$

In deriving Eqs. (6.9) and (6.10), Eqs. (6.1)–(6.5) were used. Introducing the effective linear dielectric function $\bar{\epsilon}_s$ and effective nonlinear susceptibilities $\bar{\chi}_{ijk}^{(3)}$, $\langle \mathbf{D}_s^L \rangle$, and $\langle \mathbf{D}_s^{\mathrm{NL}} \rangle$ can be written as [see Eq. (2.20)].

$$\langle \mathbf{D}_s^L \rangle = \bar{\epsilon}_s (1 + \langle G T_s^{(1)} \rangle) \mathbf{E}_{s0} , \tag{6.11}$$

$$\begin{aligned} \langle \mathbf{D}_s^{\mathrm{NL}} \rangle = 4\pi \{ & [\bar{\epsilon}_s \langle G T_{sss}^{(3)} \rangle + \bar{\chi}_{sss}^{(3)} \, | 1 + \langle G T \rangle_s^{(1)} \rangle |^2 (1 + \langle G T_s^{(1)} \rangle)] \, | \mathbf{E}_{s0} |^2 \mathbf{E}_{s0} \\ & + [\bar{\epsilon}_s \langle G T_{s11}^{(3)} \rangle + \bar{\chi}_{s11}^{(3)} \, | 1 + \langle G T_1^{(1)} \rangle |^2 (1 + \langle G T_s^{(1)} \rangle)] \, | \mathbf{E}_{10} |^2 \mathbf{E}_{s0} \\ & + [\bar{\epsilon}_s \langle G T_{s22}^{(3)} \rangle + \bar{\chi}_{s22}^{(3)} \, | 1 + \langle G T_2^{(1)} \rangle |^2 (1 + \langle G T_s^{(1)} \rangle)] \, | \mathbf{E}_{20} |^2 \mathbf{E}_{s0} \\ & + [\bar{\epsilon}_s \langle G T_{112}^{(3)} \rangle + \bar{\chi}_{112}^{(3)} (1 + \langle G T_1^{(1)} \rangle)^2 (1 + \langle G T_2^{(1)} \rangle)^*] \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^* \} . \end{aligned} \tag{6.12}$$

Comparing Eq. (6.9) with Eq. (6.11), we obtain the expression for linear effective dielectric function at frequency $\bar{\epsilon}_s$, which coincides with Eq. (2.21). A comparison of Eqs. (6.10) and (6.12) yields the following:

$$\bar{\chi}_{sss}^{(3)} = \frac{\langle T_{sss}^{(3)} \rangle - (\bar{\epsilon}_s - \epsilon_0) \langle G T_{sss}^{(3)} \rangle}{(1 + \langle G T_s^{(1)} \rangle) \, | 1 + \langle G T_s^{(3)} \rangle |^2} , \tag{6.13}$$

$$\bar{\chi}_{sjj}^{(3)} = \frac{\langle T_{sjj}^{(3)} \rangle - (\bar{\epsilon}_s - \epsilon_0) \langle G T_{sjj}^{(3)} \rangle}{(1 + \langle G T_s^{(1)} \rangle) \, | 1 + \langle G T_j^{(1)} \rangle |^2} , \quad j = 1,2, \quad j = 1,2 \tag{6.14}$$

$$\bar{\chi}_{112}^{(3)} = \frac{\langle T_{112}^{(3)} \rangle - (\bar{\epsilon}_s - \epsilon_0) \langle G T_{112}^{(3)} \rangle}{(1 + \langle G T_1^{(1)} \rangle)^2 (1 + \langle G T_2^{(1)} \rangle)^*} . \tag{6.15}$$

These susceptibilities $\bar{\chi}_{sss}^{(3)}$ and $\bar{\chi}_{sjj}^{(3)}$ describe, respectively, the nonlinear absorption of the wave at ω_s in presence of the field at ω_s or the field ω_j. The susceptibility $\bar{\chi}_{112}^{(3)}$ describes the nondegenerate four-wave mixing. In the limit of degenerate four-wave mixing the result (6.15) reduces to the result (2.22).

In what follows, we present the explicit results, for example, for $\bar{\chi}_{112}^{(3)}$ for spherical grains embedded in a linear dielectric. For a single sphere the nonlinear polarization at frequency $\omega_s (= 2\omega_1 - \omega_2)$ can be expressed as

$$\mathbf{P}^{\mathrm{NL}} = \chi_{112}^{(3)} \mathbf{E}_1 \mathbf{E}_1 \mathbf{E}_2^* . \tag{6.16}$$

Substituting the expressions for $\mathbf{E}_1$ and $\mathbf{E}_2$ of the type given by Eq. (3.4) and retaining terms up to third order, Eq. (6.16) can be rewritten as

$$\mathbf{P}^{\mathrm{NL}} = \chi_{112}^{(3)} x_1^2 x_2^* \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^* , \tag{6.17}$$

where

$$x_j = \frac{3\epsilon_0}{\epsilon(\omega_j) + 2\epsilon_0} , \quad j = 1,2,s . \tag{6.18}$$

It should be kept in mind that $\mathbf{P}^{\mathrm{NL}}$ as given by Eq. (6.17) is uniform but it need not have same components in all the directions. The electric field inside the spherical grain can be calculated by solving the Laplace equation with proper boundary conditions incorporating the effects of the nonlinear polarization given by Eq. (6.17). The calculations show that

$$\mathbf{E}_s^{\mathrm{NL}} = -\frac{4\pi}{\epsilon + 2\epsilon_0} \mathbf{P}_{\mathrm{NL}} . \tag{6.19}$$

Substitution of Eq. (6.17) in Eq. (6.19) yields

$$\mathbf{E}_s^{\mathrm{NL}} = -\frac{4\pi}{3\epsilon_0} \chi_{112}^{(3)} x_s x_1^2 x_2^* \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^* . \tag{6.20}$$

Comparing Eq. (6.20) with Eq. (6.5), we obtain

$$\langle G T_{112}^{(3)} \rangle = -\frac{1}{3\epsilon_0} \chi_{112}^{(3)} x_s x_1^2 x_2^* . \tag{6.21}$$

The electric displacement at ω_s can be written as

$$\mathbf{D}_s^{\mathrm{NL}} = \epsilon_0 \langle \mathbf{E}_s^{\mathrm{NL}} \rangle + 4\pi \langle T_{112}^{(3)} \rangle \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^* . \tag{6.22}$$

Substituting Eq. (6.20) in Eq. (6.22) we obtain

$$\mathbf{D}_s^{\mathrm{NL}} = 4\pi \left[\epsilon_0 \left[-\frac{1}{3\epsilon_0} \chi_{112}^{(3)} x_s x_1^2 x_2^* \right] + \langle T_{112}^{(3)} \rangle \right] \mathbf{E}_{10} \mathbf{E}_{10} \mathbf{E}_{20}^* . \tag{6.23}$$

$\mathbf{D}_s^{\mathrm{NL}}$ can also be expressed as

$$\mathbf{D}_s^{\mathrm{NL}} = \epsilon \mathbf{E}_s^{\mathrm{NL}} + 4\pi \mathbf{P}^{\mathrm{NL}} . \tag{6.24}$$

Eqs. (6.17) and (6.20), when substituted in Eq. (6.24), yield

$$\mathbf{D}_s^{\mathrm{NL}}=4\pi\chi_{112}^{(3)}x_1^2x_2^*\left[1-\frac{\epsilon(\omega_s)}{\epsilon(\omega_s)+2\epsilon_0}\right]\mathbf{E}_{10}\mathbf{E}_{10}\mathbf{E}_{20}^* . \quad (6.25)$$

A comparison of Eqs. (6.23) and (6.25) yields the explicit expression for $\langle T_{112}^{(3)}\rangle$

$$\langle T_{112}^{(3)}\rangle=\chi_{112}^{(3)}x_s x_1^2 x_2^* . \quad (6.26)$$

For a heterogeneous medium with volume fraction f of the spherical grains the averaged T matrices in the Maxwell-Garnett approximation can be written as follows:

$$\langle T_j^{(1)}\rangle=f(\epsilon(\omega_j)-\epsilon_0)x_j , \quad (6.27)$$

$$\langle GT_j^{(1)}\rangle=f(x_j-1) , \quad (6.28)$$

$$\langle T_{112}^{(3)}\rangle=\chi_{112}^{(3)}f x_s x_1^2 x_2^* , \quad (6.29)$$

$$\langle GT_{112}^{(3)}\rangle=-\frac{1}{3\epsilon_0}f x_s x_1^2 x_2^* . \quad (6.30)$$

Note that in case of degenerate four-wave mixing ($\omega_1=\omega_2=\omega_s$) the expressions for $\langle T_{112}^{(3)}\rangle$ and $\langle GT_{112}^{(3)}\rangle$ reduce to the form given by Eqs. (3.11) and (3.7) since $\epsilon_2=4\pi\chi^{(3)}$. Substituting Eqs. (6.27)–(6.30) in Eq. (6.15), we obtain the expression for the effective nonlinear susceptibility $\bar{\chi}_{112}^{(3)}$

$$\bar{\chi}_{112}^{(3)}=\chi_{112}^{(3)}f \times\frac{x_s x_1^2 x_2^*}{[1+f(x_s-1)][1+f(x_1-1)]^2[1+f(x_2-1)]^*} . \quad (6.31)$$

A similar calculation shows that $\bar{\chi}_{211}^{(3)}$ can be expressed by the relation

$$\bar{\chi}_{211}^{(3)}=\chi_{211}^{(3)}f\frac{|x_1|^2x_2^2}{|1+f(x_1-1)|^2[1+f(x_2-1)]^2} . \quad (6.32)$$

It is clear from Eq. (6.31) that the resonances in $\bar{\chi}_{112}^{(3)}$ are given by the zeros of $[D_j+f(N_j-D_j)]$ $(j=1,2,s)$ [see Eq. (4.1) and subsequent discussions in Sec. IV]. Moreover, the zeros of $[D_j+f(N_j-D_j)]$ for $j=2,s$ are simple, whereas that for $j=1$ is of multiplicity 2. This implies that the resonances given by the zeros of $[D_1+f(N_1-D_1)]$ will be stronger compared to the other two. Note further that in a real experimental situation when, for example, ω_1 is fixed and ω_2 is scanned $\bar{\chi}_{112}^{(3)}$, shows a double hump due to the zeros of $D_j+f(N_j-D_j), j=2,s$. Besides, the number of resonance peaks will depend also on the number of zeros of $[D_j+f(N_j-D_j)]$ for fixed j when $\epsilon(\omega)$ has several poles. This is the case in certain semiconductors. The phase conjugate signals generated by such a medium can be obtained using the usual propagation equations[23] and the expressions like (6.31) and (6.32) for $\bar{\chi}_{112}^{(3)}, \bar{\chi}_{211}^{(3)}$.

Thus, to summarize, we have presented a T-matrix approach for calculating the effective medium parameters (linear dielectric function, third- and higher-order nonlinear susceptibilities) for a nonlinear heterogeneous medium in the quasistatic approximation. We have applied the theory to obtain the explicit expressions for the effective dielectric function and third- and higher-order nonlinear susceptibilities for a colloidal medium consisting of nonlinear spherical grains embedded in a linear dielectric. We have shown the existence of strong new resonances in the nonlinear susceptibilities. We found that a third-order nonlinearity in the bulk constituent medium can lead to higher-order nonlinear susceptibilities in the effective medium. In the small volume fraction limit our theory leads to the phenomenological result of Flytzanis *et al.* We discussed the resonances in the nonlinear signals generated by such media. As an application of the theory we obtained the power dependence of the reflection coefficient in the range of powers where the slowly varying envelope approximation holds good. We obtained different power saturation of the reflection coefficient depending on the incident light wavelength. We further developed the T-matrix expressions for various nonlinear susceptibilities for a nondegenerate four-wave-mixing process. We obtained the effective four-wave-mixing susceptibility $\bar{\chi}_{112}^{(3)}$ for a heterogeneous medium consisting of nonlinear spherical grains[24] embedded in a linear dielectric.

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[22]Because of the limitation (5.21), we cannot reach the bistable region for such systems. The behavior in the bistable region has been studied using numerical simulations (Refs. 15 and 16).

[23]See, for example, D. M. Pepper and A. Yariv, in *Optical Phase Conjugation,* edited by R. A. Fisher (Academic, New York, 1983), p. 41.

[24]In the present work we have evaluated effective susceptibilities by ignoring retardation effects. The retardation effects can be included in the framework of, say, Refs. 3 and 4. Such effects would enable one to understand the dependence of χ's on the size of the grains. It may also be noted that the spatial dispersion (Ref. 5) of the grains also makes susceptibilites depend on the size.