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2000 J. Phys.: Condens. Matter 12 6825

(http://iopscience.iop.org/0953-8984/12/30/311)

J. Phys.: Condens. Matter **12** (2000) 6825–6836. Printed in the UK PII: S0953-8984(00)12404-X

Effective non-linear optical properties of metal–dielectric composites of spheroidal particles

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Received 8 March 2000, in final form 30 June 2000

Abstract. Non-linear optical properties of randomly oriented non-linear spheroidal metal particles in a dielectric host are investigated. Two different Maxwell-Garnett-type approximations are derived based on whether a self-consistency condition on the net polarization is invoked. These two methods lead to quite different spectral density functions. Moreover, we show that the shape of particles has a large influence on the spectral function through the depolarization effects and thereby has a pronounced effect on the optical absorption and non-linear optical susceptibility. We suggest that the self-consistent formalism can be used for large volume fractions, as mutual interaction between different polarizations is included in the theory.

1. Introduction

Non-linear optical properties of granular composite materials have attracted much attention in recent years because of their potential applications in physics and engineering [1, 2]. A typical system is composed of non-linear metal particles, randomly embedded in a linear (or non-linear) dielectric host. Such a composite system is a candidate for the role of enhancing the optical non-linearity through the local field effects and/or surface plasmon resonances. These enhancement mechanisms are sensitive to the composite microstructure.

In a recent work [3], we proposed the use of a structurally anisotropic composite to enhance the optical non-linearity. The results show that such an anisotropy can separate the absorption peak from the non-linearity enhancement peak and thus further enhance the figure of merit. Anisotropy is clearly a phenomenon common in most materials and it can be an intrinsic material property or can be induced by the application of fields. In real applications, the shape of granular inclusions may deviate from a spherical shape during fabrication. Moreover, the optical non-linearity can be enhanced by using non-spherical (e.g., spheroidal) inclusions [4].

In this work, we consider a system in which spheroidal metal particles are randomly embedded in a dielectric host in an attempt to investigate how a non-spherical particle shape can affect the effective non-linear response. In references [4] and [5], the effective non-linear susceptibility was derived for composites of spheroidal particles in the dilute limit. For simplicity, we assume that the spheroidal inclusions possess an isotropic dielectric function but with the uniaxial axis lying along the z-axis. Each spheroidal particle is described by two depolarization factors, which we denote by L_{xy} and L_z, satisfying the sum rule $L_z + 2L_{xy} = 1$. Since the inclusions are randomly oriented (corresponding to a uniform distribution of spheroids over the entire solid angles), the effective response is still isotropic.

0953-8984/00/306825+12$30.00

For other distributions, such as a random orientation in a plane, an anisotropic dielectric tensor is needed [6]. We will adopt two different models to investigate the effects of the particle shape dependence of the linear and non-linear optical properties of composite media.

We use the spectral representation [7, 8], which is a mathematically rigorous formal expression for the effective linear dielectric constant ϵ_e. It offers the advantage of a separation of material parameters from the geometric information, which is characterized by the spectral density function $m(s')$. With $m(s')$ given, we will not only study the influence of particle shape on the linear optical properties, but we will also calculate the non-linear optical susceptibility [3, 11].

This paper is organized as follows. In the next section, we formulate the linear and non-linear response with the use of the spectral representation. In sections 3 and 4, we derive the effective linear response ϵ_e first without self-consistency and then by a self-consistent theory. We then calculate the spectral density function $m(s')$ both numerically and analytically as a function of the depolarization factor and volume fractions. In section 5, the linear and non-linear optical properties such as optical absorption and the enhancement of optical non-linearity are investigated. This is followed by a summary of our results in section 6.

2. Formulation of effective linear and non-linear response under spectral representation

Let us consider a non-linear composite system, in which spheroidal metal particles with volume fraction f are randomly embedded in an isotropic dielectric host. The local constitutive $\boldsymbol{D}$–$\boldsymbol{E}$ relation of components is given by $\boldsymbol{D} = \epsilon_i \boldsymbol{E} + \chi_i |\boldsymbol{E}|^2 \boldsymbol{E}$, where ϵ_i and χ_i are the (scalar) dielectric constant and the third-order non-linear susceptibility of the components. The uniaxial axis of the spheroidal particles is assumed to be randomly oriented in space. Such spheroidal particles are described by the depolarization factors L_z and L_{xy}, which are positive and satisfy the sum rule $L_z + 2L_{xy} = 1$. For spherical particles, $L_z = L_{xy} = 1/3$, while for cylindrical ones, $L_z = 0$ and $L_{xy} = 1/2$. In general, L_z is strongly shape dependent and is given by [12–14]

$$L_z = \frac{1}{1-r^2} + \frac{r}{(r^2-1)^{3/2}} \ln(r + \sqrt{r^2-1}) \tag{1}$$

for prolate spheroids with an aspect ratio $r = c/a > 1$ while

$$L_z = \frac{1}{1-r^2} + \frac{r}{(1-r^2)^{3/2}} \arccos r \tag{2}$$

for oblate spheroids with $r = c/a < 1$, where a $(=b)$, c are the semi-axes of a spheroid along the Cartesian axes. With a given aspect ratio r, one can determine uniquely a depolarization factor L_z. Thus, in subsequent calculations, we shall use L_z to characterize the shape of the spheroidal particles.

We restrict our discussion to the quasi-static approximation, i.e., $d/\lambda \ll 1$, where d is the characteristic size of the particle and λ is the wavelength of the incident light. In the quasi-static approximation, the composite media can be regarded as an effective homogeneous medium, with an effective linear dielectric function ϵ_e and effective non-linear susceptibility χ_e, defined by [5]

$$\boldsymbol{D} = \epsilon_e \boldsymbol{E}_0 + \chi_e |\boldsymbol{E}_0|^2 \boldsymbol{E}_0 \tag{3}$$

where $\boldsymbol{E}_0 \equiv \langle \boldsymbol{E} \rangle$ is the spatial averaged electric field. Our aim here is to calculate the effective linear and non-linear response for non-linear spheroidal particles randomly embedded in a linear or non-linear host.

For two-component composites, it has proved convenient to adopt the spectral representation of the effective linear response [7, 8]: let $v = 1 - \epsilon_1/\epsilon_2$, $w = 1 - \epsilon_e/\epsilon_2$, and $s = 1/v$; we find

$$w(s) = \int_0^1 \frac{m(s')}{s - s'}\,\mathrm{d}s' \tag{4}$$

where $m(s')$ is the spectral density function, which is obtained through a limiting process:

$$m(s') = \lim_{\eta \to 0^+} -\frac{1}{\pi}\,\mathrm{Im}[w(s' + \mathrm{i}\eta)]. \tag{5}$$

Once $m(s')$ is given, the effective linear dielectric constant and the non-linear optical susceptibility can be obtained with the knowledge of the material parameter s. For the effective linear response ϵ_e, we have

$$\epsilon_e = \epsilon_2\left[1 - \int \frac{m(s')}{s - s'}\,\mathrm{d}s'\right] \tag{6}$$

while for the effective non-linear susceptibility χ_e, we evaluate in the mean-field approximation, i.e.,

$$\chi_e = \sum_i \frac{f_i \chi_i \langle |\boldsymbol{E}|^2 \boldsymbol{E}^2 \rangle_{lin,i}}{E_0^4} \approx \sum_i \frac{f_i \chi_i \langle |\boldsymbol{E}|^2 \rangle_{lin,i} \langle \boldsymbol{E}^2 \rangle_{lin,i}}{E_0^4} \tag{7}$$

where f_i equals f (or $1 - f$) for $i = 1$ (or 2), and the subscript means that the electric field is to be taken from the solution to the corresponding linear problem. We have adopted the decoupling approximation in the above equation, which works well when the field within the metal particles is fairly uniform but may become inaccurate when the variation of the field inside them is large. Such an approximation yields a lower bound for the accurate result [3]. The local field averages in equation (7) are given by [3, 9–11]

$$\begin{aligned} f\langle \boldsymbol{E}^2 \rangle_{lin,1} &= \int_0^1 \mathrm{d}s'\, \frac{s^2 m(s')}{(s - s')^2} E_0^2 \\ (1 - f)\langle \boldsymbol{E}^2 \rangle_{lin,2} &= \left[1 - \int_0^1 \mathrm{d}s'\, \frac{(s^2 - s')m(s')}{(s - s')^2}\right] E_0^2 \end{aligned} \tag{8}$$

and

$$\begin{aligned} f\langle |\boldsymbol{E}|^2 \rangle_{lin,1} &= \int_0^1 \mathrm{d}s'\, \frac{|s|^2 m(s')}{|s - s'|^2} E_0^2 \\ (1 - f)\langle |\boldsymbol{E}|^2 \rangle_{lin,2} &= \left[1 - \int_0^1 \mathrm{d}s'\, \frac{(|s|^2 - s')m(s')}{|s - s'|^2}\right] E_0^2. \end{aligned} \tag{9}$$

Thus we have formulated the spectral representation for calculating the effective linear and non-linear optical properties. In the next two sections, we will derive the spectral density by two different methods.

3. Maxwell-Garnett-type approximation (MGA1)

We start out by averaging the electric field in the spheroidal inclusions:

$$\langle \boldsymbol{E}_1 \rangle = \frac{1}{3}\left[\frac{\epsilon_2}{L_z\epsilon_1 + (1 - L_z)\epsilon_2} + \frac{2\epsilon_2}{L_{xy}\epsilon_1 + (1 - L_{xy})\epsilon_2}\right]\langle \boldsymbol{E} \rangle \tag{10}$$

where $\langle \boldsymbol{E} \rangle$ is the average field of the whole system, which is just the applied field $\boldsymbol{E}_0$ under appropriate boundary conditions. For a non-dilute mixture of spheroidal inclusions, randomly

dispersed in a dielectric host, $\langle \boldsymbol{E} \rangle$ should be replaced by the Lorentz local field $\langle \boldsymbol{E}_L \rangle$, which includes the contribution from the dipole moments of all other inclusions. The expression for the spatial average of the electric field is thus

$$\langle \boldsymbol{E} \rangle = \boldsymbol{E}_0 = f\langle \boldsymbol{E}_1 \rangle + (1-f)\langle \boldsymbol{E}_L \rangle. \tag{11}$$

On the other hand, we average the dielectric displacement $\langle \boldsymbol{D} \rangle$ over the whole volume of the composite and get

$$\langle \boldsymbol{D} \rangle = f\epsilon_1\langle \boldsymbol{E}_1 \rangle + (1-f)\epsilon_2\langle \boldsymbol{E}_L \rangle. \tag{12}$$

According to the definition of the effective dielectric constant ϵ_e, we have

$$\epsilon_e = \frac{\langle \boldsymbol{D} \rangle}{\langle \boldsymbol{E} \rangle} = \frac{\langle \boldsymbol{D} \rangle}{\boldsymbol{E}_0} = \frac{f\epsilon_1\langle \boldsymbol{E}_1 \rangle + (1-f)\epsilon_2\langle \boldsymbol{E}_L \rangle}{f\langle \boldsymbol{E}_1 \rangle + (1-f)\langle \boldsymbol{E}_L \rangle}. \tag{13}$$

Substituting equations (11), (12) into equation (13), we have

$$\epsilon_e = \epsilon_2 \frac{3 + f[\beta_z(1-L_z) + 2\beta_{xy}(1-L_{xy})]}{3 - f(\beta_z L_z + 2L_{xy}\beta_{xy}]} \tag{14}$$

where $\beta_i = (\epsilon_1 - \epsilon_2)/[\epsilon_2 + L_i(\epsilon_1 - \epsilon_2)]$ $(i = z, xy)$.

We should remark that the above formalism has been found with the T-matrix method [13]. In this way, the randomly oriented spheroidal particle is replaced by an effective spherical particle and hence the mutual interaction between different polarizations is explicitly neglected in the calculation of the Lorentz local electric field. As pointed out by Nan *et al* [13], the derivation takes on the first-order approximation of the T-matrix and ignores the mutual interaction between different polarizations, and thus it can only be valid for small volume fractions. In fact, the case for volume fractions larger than 0.5 is unattainable for a suspension of hard spheroids.

In the dilute limit, equation (14) reduces to

$$\epsilon_e = \epsilon_2 \left\{ 1 + \frac{f}{3}\left[\frac{\epsilon_1 - \epsilon_2}{\epsilon_2 + L_z(\epsilon_1 - \epsilon_2)} + 2\frac{\epsilon_1 - \epsilon_2}{\epsilon_2 + L_{xy}(\epsilon_1 - \epsilon_2)} \right] \right\} \tag{15}$$

which was already reported in references [4] and [5].

From equation (14), the function $w(s)$ is found to be

$$w(s) = \frac{F_1}{s - s_1} + \frac{F_2}{s - s_2} \tag{16}$$

where the poles s_1 and s_2 are located at

$$\begin{aligned} s_1 &= \frac{1}{12}[3 - 2f + 3L_z + \sqrt{(2f - 3 - 3L_z)^2 - 72(1-f)(1-L_z)L_z}] \\ s_2 &= \frac{1}{12}[3 - 2f + 3L_z - \sqrt{(2f - 3 - 3L_z)^2 - 72(1-f)(1-L_z)L_z}] \end{aligned} \tag{17}$$

and F_1, F_2 are the residues of these poles:

$$F_1 = \frac{f}{6}\frac{1 + 3L_z - 6s_1}{s_2 - s_1} \qquad F_2 = \frac{f}{6}\frac{1 + 3L_z - 6s_2}{s_1 - s_2}. \tag{18}$$

Thus the spectral density function can be written as a sum of two delta functions:

$$m(s') = F_1\delta(s' - s_1) + F_2\delta(s' - s_2). \tag{19}$$

In figure 1, we plot the poles s_1, s_2 together with the residues F_1 and F_2 against the depolarization factor L_z for several volume fractions $f = 0.1$, $f = 1/3$ and $f = 0.5$. We see that s_1 (s_2) decreases (increases) firstly for prolate spheroids ($L_z < 1/3$) and reaches a minimum (maximum) for spherical particles ($L_z = 1/3$) and it then increases (decreases) with

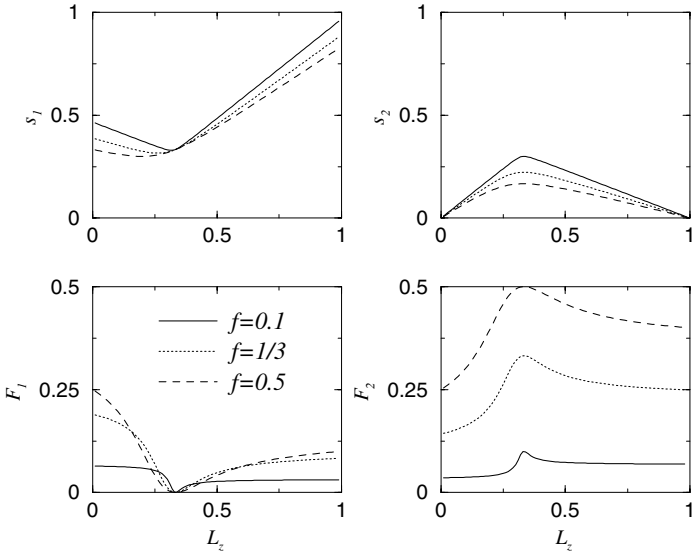


Figure 1. The poles (s_1, s_2) and residues (F_1, F_2) of the spectral density for MGA1 plotted against L_z for different values of volume fractions $f = 0.1, 1/3$ and 0.5.

the further increase of L_z, but these poles decrease when the volume fraction increases except for the case of $L = 1/3$. On the other hand, the residues F_1, F_2 also exhibit a non-monotonic behaviour with the increase of L_z. That is, F_1 decreases to zero at $L_z = 1/3$ and then increases, while F_2 increases and reaches the maximum value f at $L_z = 1/3$. We also find that F_2 is monotonically increasing as f increases, but F_1 takes on a more complex behaviour with f. We remark that when the inclusions are spherical in shape, we will still get two poles s_1 and s_2. However, the residue of the first pole is zero; the spectral function is still a single delta function, as expected. When the shape of the inclusions is far from being spherical, we obtain two poles with non-zero residues leading to two surface plasmon resonance frequencies, reflected in the optical absorption spectrum.

4. Maxwell-Garnett-type approximation based on the self-consistent condition of zero net polarization (MGA2)

In this section, we generalize our cellular model [15] to study the system in which the spheroidal metal inclusions are dispersed in a dielectric host medium. To formulate the cellular model, we construct the Wigner–Seitz cell of each microspheroid and replace the composite by a fictitious homogeneous medium of a dielectric constant ϵ_m, except for one of the cells. The cell is then replaced by a spheroidal core of dielectric constant ϵ_1, coated by a spheroidal shell of ϵ_2. The core and the shell are confocal and have the same aspect ratio, characterized by $r = b_c c_c = b_s/c_s$, where the subscripts c and s mean core and shell.

The effective linear dielectric constant ϵ_e is given by the dilute-limit expression:

$$\epsilon_e = \epsilon_m + p\epsilon_m[b_z(\epsilon_1, \epsilon_2, \epsilon_m, y) + 2b_{xy}(\epsilon_1, \epsilon_2, \epsilon_m, y)] \tag{20}$$

where p is an infinitesimal volume fraction and $y \equiv (a_c^2 c_c)/a_s^2 c_s$ is the volume ratio of the core to the whole coated spheroid. b_z is the dipole factor for a single-coated spheroidal inclusion

along the z-axis [16]:

$$b_z = \frac{1}{3}\frac{(\epsilon_2-\epsilon_m)[\epsilon_2+L_z(\epsilon_1-\epsilon_2)]+(\epsilon_1-\epsilon_2)y[\epsilon_2+L_z(\epsilon_m-\epsilon_2)]}{(\epsilon_2-\epsilon_1)(\epsilon_m-\epsilon_2)yL_z(1-L_z)+[\epsilon_2+(\epsilon_1-\epsilon_2)L_z][\epsilon_m+(\epsilon_2-\epsilon_m)L_z]} \tag{21}$$

where $y \equiv (a_c^2 c_c)/a_s^2 c_s$ is the volume ratio of the core to the whole coated spheroid. The effective dielectric constant ϵ_e can be obtained self-consistently with equation (20) and equation (21), if we identify y with f and ϵ_m with ϵ_e; then equation (20) becomes a self-consistent equation, which readily implies that

$$b_z + 2b_{xy} = 0 \tag{22}$$

where b_{xy} can be obtained by replacing the subscript b with xy in equation (21). In the above equation, the mutual interaction between different polarizations is taken into account in a self-consistent way and equation (22) can thus be used for large volume fractions.

From equations (21) and (22), the function $w(s)$ is therefore

$$\begin{aligned} w(s) = \frac{1}{5-3L_z}\Bigg\{3 &+ \frac{3f(1-L_z)}{2[s-(1-f)(1-L_z)/2]} + \frac{f(1-3L_z)}{2[s-L_z(1-f)]} \\ &+ \frac{6}{(1-3L_z)(1-f)}\left[\frac{1}{s-L_z(1-f)} - \frac{1}{s-(1-L_z)(1-f)/2}\right] \\ &\times \sqrt{(s-x_{1-})(s-x_{1+})(s-x_{2-})(s-x_{2+})}\Bigg\}. \end{aligned} \tag{23}$$

The branch should be chosen so that the phase of $s - x_{i\pm}$ $(i = 1, 2)$ is restricted to within $(0, 2\pi)$. Here x_{1-}, x_{1+}, x_{2-} and x_{2+} are solutions of the following equation:

$$144x^4 + C_3x^3 + C_2x^2 + C_1x + C_0 = 0 \tag{24}$$

with

$$C_0 = (L_z-1)(1-f)^2[9L_z^3(4-4f+9f^2) - 9L_z^2(4+7f^2) - fL_z(28+17f) - f^2] \tag{25}$$

$$C_1 = 4(1-f)[9L_z^3(2-3f+f^2) + 9L_z^2(3-f)f + L_z(7f^2-18-25f) - 7f(1+f)] \tag{26}$$

$$C_2 = 36L_z^2(4f-f^2-3) + 72L_z(3-2f-f^2) + 36 + 128f - 20f^2 \tag{27}$$

$$C_3 = 144[L_z(f-1) - 1 - f]. \tag{28}$$

Then the spectral density $m(s')$ is found analytically to be

$$\begin{aligned} m(s') = \frac{1}{5-3L_z}\Bigg\{&3f(1-L_z)\delta\left[s' - \frac{(1-L_z)(1-f)}{2}\right] \\ &+ f(1-3L_z)\theta(1-3L_z)\delta[s'-L_z(1-f)] \\ &+ \frac{6}{\pi|(1-3L_z)|(1-f)}\left|\frac{1}{s'-L_z(1-f)} - \frac{1}{s'-(1-L_z)(1-f)/2}\right| \\ &\times \sqrt{(s'-x_{1-})(s'-x_{1+})(s'-x_{2-})(s'-x_{2+})} \\ &\times [\theta(s'-x_{1-}) - \theta(s'-x_{1+}) + \theta(s'-x_{2-}) - \theta(s'-x_{2+})]\Bigg\}. \end{aligned} \tag{29}$$

We also calculate $m(s')$ numerically from equation (22). We put $s = s' + \mathrm{i}\eta$ and choose the real part at one thousand equally spaced values across the interval $0 < s' < 1$ and the imaginary part η at some positive value such as 0.001. The actual value of η is indeed unimportant. We find that the result is acceptable by checking the sum rule

$$\int_0^1 m(s')\,\mathrm{d}s' = f. \tag{30}$$

In figure 2, we plot the spectral density $m(s')$ against s' for several values of $L_z = 0.05$, $1/3$, 0.5, 0.75 and for the volume fractions $f = 0.1$, 0.3, 0.5, 0.7.

We find that, for prolate spheroids ($L_z < 1/3$), the spectral density exhibits two peaks centred around $s_1 = (1 - L_z)(1 - f)/2$ and $s_2 = L_z(1 - f)$, values that are similar to, but numerically different from, those of MGA1. For $L_z = 1/3$, i.e., the particles are spherical in shape, we obtain the well known MGA spectral density $m(s') = f\delta[s' - (1 - f)/3]$ with the pole $s_1 = (1 - f)/3$ and the residue $F = f$. In the figure, a single peak is shown. For a further increase in L_z, there exists only one peak and the location of the peak shifts to small s'. Quite different from that of MGA1, the spectral density of MGA2 contains two continuous spectra. This can be understood on the basis of the fact that the mutual interaction between different polarizations is taken into account through the self-consistent solution. For a small volume fraction, the continuous spectrum sharpens, while when f gradually increases, the interaction among inclusions becomes strong; it results in a broad spectrum.

As we have obtained the spectral density by two methods, we can readily investigate the effective linear dielectric constant and the third-order non-linear susceptibility.

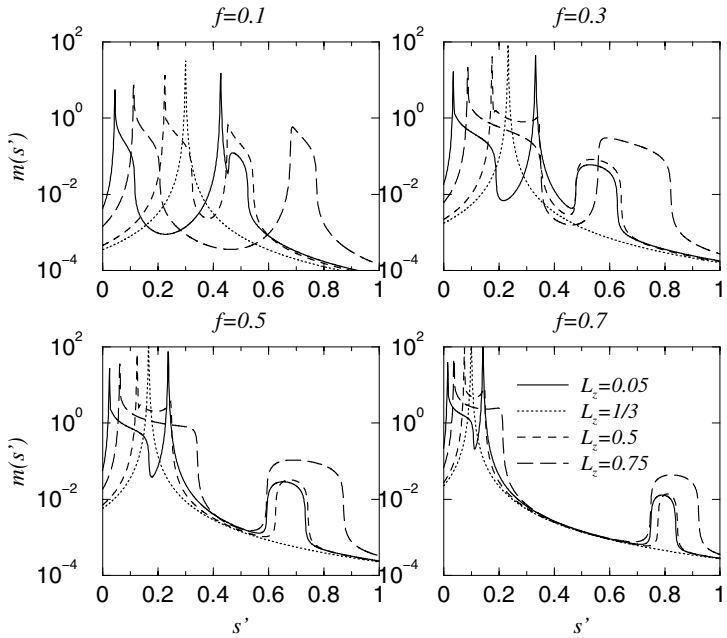


Figure 2. The spectral density $m(s')$ for MGA2 against s' for various $f = 0.1$, 0.3, 0.5, 0.7 and $L_z = 0.05$, $1/3$, 0.5 and 0.75.

5. Shape dependence of the linear absorption and the enhancement of optical non-linearity

We are now in a position to study the dependence of the linear absorption $\mathrm{Im}(\epsilon_e)$ and the third-order non-linear susceptibility χ_e on the depolarization factor L_z. In model calculations, we adopt the Drude model for the dielectric function of metal nanoparticles:

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + \mathrm{i}\gamma)} \tag{31}$$

where ω_p is the plasmon frequency and γ is the damping constant. We choose $\gamma = 0.01\omega_p$, which is typical of a good bulk metal, and $\epsilon_2 = 1.77$, which is the dielectric constant of water. In general, the third-order non-linearity of metal particles is several orders of magnitude larger than that of a dielectric matrix and the matrix contribution to the effective non-linear susceptibility is small. Thus we assume that the metal component can be taken to be non-linear, while the host medium is linear.

In figure 3, the linear absorption spectrum $\mathrm{Im}(\epsilon_e)$ is plotted against frequency ω for various L_z and f, both for (a) MGA1 and (b) MGA2. As is evident from the results, the absorption spectrum $\mathrm{Im}(\epsilon_e)$ exhibits a behaviour similar to that of the spectral density. The result from MGA1 shows a large linear absorption at the two resonant frequencies for spheroidal particles, which is related to the surface plasmon resonance of the metal particles. These frequencies depend strongly on the depolarization factor but weakly on the volume fractions, especially for needlelike ($L \to 0$) and platelike ($L \to 1$) particles.

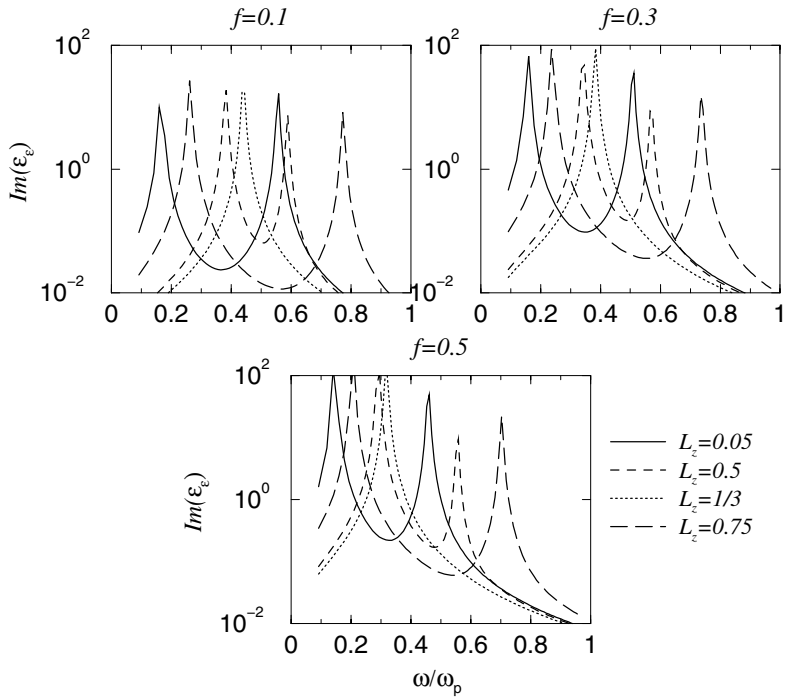
However, for MGA2, in addition to one (or two) surface plasmon resonant frequencies for oblate (or prolate) spheroidal particles, we also observe two absorption bands, which are absent in the results from MGA1. With increasing volume fraction, when the interaction between particles becomes stronger, broad absorption bands in the regions $0.2 < \omega/\omega_p < 0.4$ and $0.7 < \omega/\omega_p < 0.9$ are observed. For a small volume fraction (such as $f = 0.1$), the two approximations yield almost identical results. In fact, in the dilute limit, the self-consistent solution of equation (22) still reduces to the dilute-limit expressions (equation (15)), because in this limit, the interaction between particles can be neglected. From the figure, we clearly see that the particle shape (parametrized by the depolarization factor) plays an important role in determining the optical absorption including its resonant frequencies (or resonant bands) and magnitudes.

Moreover, we concentrate on the effect of the depolarization factor on the enhancement of optical non-linearity $|\chi_e|/\chi_1$, as shown in figure 4, both for MGA1 and MGA2. For MGA1, the optical non-linearity is found to be greatly enhanced at the two surface plasmon resonant frequencies. Such a behaviour has been reported experimentally [4] and it occurs at the same frequency as that of the linear absorption. However, the enhancement of non-linearity is more pronounced than that of linear absorption. For MGA2, the optical non-linearity can be enhanced not only in one resonant frequency but also within a certain band as a result of the mutual interaction between different polarizations. Concomitantly, MGA1 and MGA2 yield similar enhancement of non-linearity at low volume fractions such as $f = 0.1$.

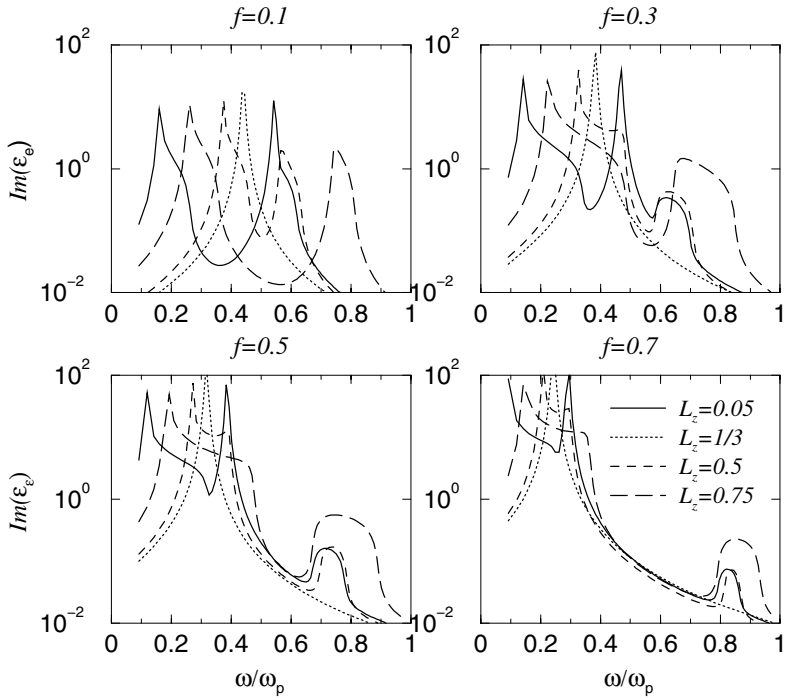
From the above study, we conclude that the linear absorption and even the effective non-linear optical susceptibility are strongly dependent on the depolarization factor. Our results suggest that it may be possible to tune the frequency range of enhancement of non-linearity by controlling the particle shape.

6. Discussion and conclusions

In this work, we have investigated the effects of the depolarization factor (and thus the shape of the granular component) on the non-linear optical properties of a suspension of spheroidal metal particles randomly embedded in a dielectric host. Maxwell-Garnett-type approximations have been derived which reduce to the standard MGA approximation in the limit of spherical particles. We show that the spectral density and the optical properties depend strongly on the depolarization factor. As we include the mutual interaction between different polarizations in the self-consistent calculation, the absorption and optical enhancement spectra become broad continuous functions. This demonstrates that the non-self-consistent theory (MGA1) can only be suitable for low volume fractions. For larger volume fractions the

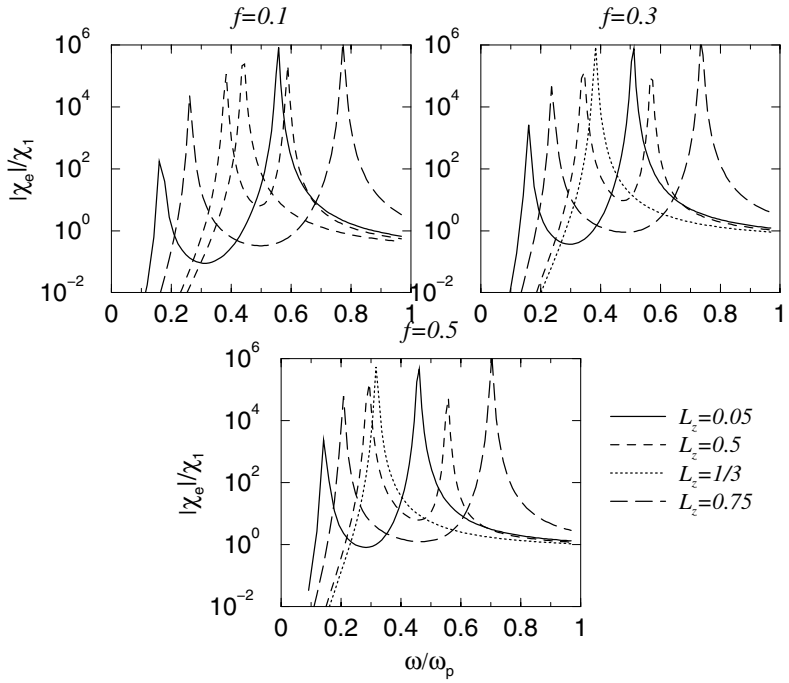


(a)

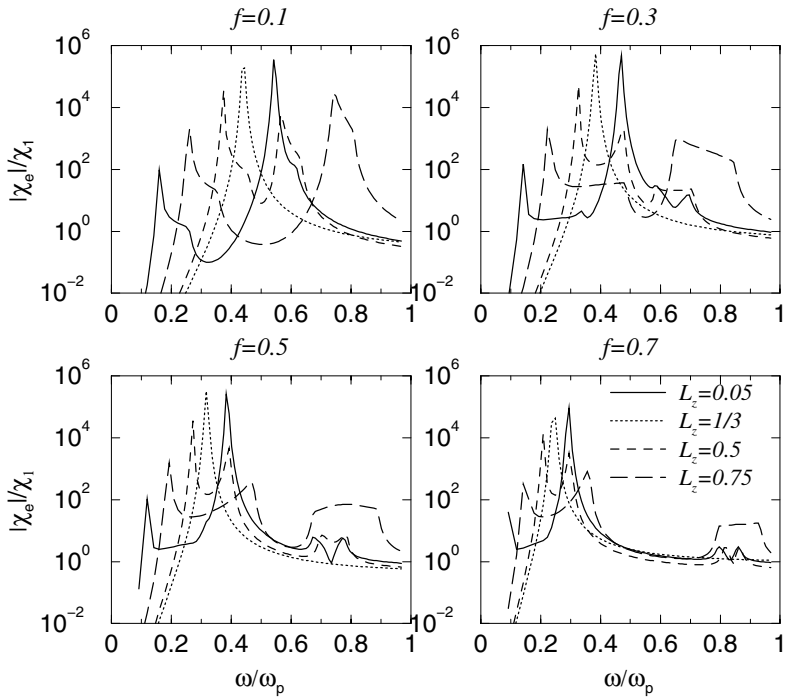


(b)

Figure 3. The linear absorption $\mathrm{Im}(\epsilon_e)$ against the frequency ω for (a) MGA1 and (b) MGA2. The values of the physical parameters are the same as those of figure 2.



(a)



(b)

Figure 4. Similar to figure 3, but for the enhancement of the third-order non-linear susceptibility $|\chi_e|/\chi_1$ against ω for (a) MGA1 and (b) MGA2.

mutual interaction between different polarizations becomes strong and we cannot neglect it any longer.

Here, we would like to add a few comments regarding our results. Our results can not only help obtain a large enhancement of non-linear optical response, but also they help attain the maximum response in any desired frequency regime by adjusting the shape of metal particles. However, a large enhancement of non-linearity is always accompanied by a large absorption, which hinders practical applications. In this respect, we may manipulate composite microstructure, such as by the use of correlated [17] and anisotropic [18] microstructure, to achieve a large enhancement of optical non-linearity and a concomitant suppression of optical absorption.

In this work, we assume that all the metal particles have the same shape and depolarization factor. According to the analysis of the absorption coefficient and conjugate reflectivity in related experiments, it has been shown that the particles can have a distribution of shapes. Our model can easily be generalized to a distribution of shapes by including a distribution of depolarization factors. So far, we have considered the Maxwell-Garnett-type models, which means that two constituents are asymmetric (i.e., distinct inclusion particles are embedded in a host material). For a symmetric microstructure (i.e., two interdispersed components are randomly distributed), we should apply the Bruggeman-type approximation [19] for the spheroidal inclusion case.

Our calculation may have relevance to a recent optical non-linearity enhancement experiment on Au:TiO_2 composites, in which the Au particles are non-spherical in shape in samples as prepared in the fabrication process and a large enhancement was reported for the annealed samples [20]. For these samples, there is no strong evidence of any clustering/correlation in the microstructure and the cellular model is expected to be good. Our calculation reveals that the optical properties are highly sensitive to the particle shape and thus allows an extra freedom of adjusting the magnitude of the enhancement and the frequency where the enhancement occurs.

Acknowledgments

This work was supported by the Research Grants Council of the Hong Kong SAR Government under project CUHK 4290/98P. Two of us (LG and ZYL) acknowledge the National Science Foundation of China for financial support under Grant No 19774042.

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