Effects of the dispersion of sizes in the dielectric response of composites

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We extend the method of the renormalized polarizability in the Maxwell Garnett theory recently developed in order to obtain a dielectric function of composite systems consisting of a host matrix with inclusions of small metallic spheres of two different sizes. We introduce two renormalized polarizabilities, one for each size, and we obtain the result that they obey two coupled quadratic equations. We obtain three peaks in the imaginary part of the dielectric function and we identify its physical origin.

I. INTRODUCTION

The optical properties of composites made of metallic inclusions, whose size is much smaller than the wavelength of light, embedded in a homogeneous material continues to be a current topic of actual research.[1-5] The interest in this problem remains because the agreement between theory and experiment is still far from being satisfactory as well as for the potential application of these materials in solar energy conversion systems.[6] After the pioneering work of Maxwell Garnett[7] (MGT), new effective-medium theories[5,8-26] have been formulated in order to incorporate different types of effects which were not considered in this earlier approach. Being MGT, a self-consistent mean-field theory, the main improvement has been the inclusion of the dipolar fluctuations[5,8-17] (or multiple-scattering) and higher-order multipole interactions.[8,12,13,15,17] The distribution of sizes and shapes of the inclusions has also been considered at different levels of approximation.[8,11,19-26] There have been several attempts in order to deal with a distribution of sizes together with the dipolar fluctuations.[8,11,24-26] One of them[11] is based on the lattice-gas coherent-potential approximation (LG-CPA) and considers spheres of two different radii. In others[8,24] the disorder is introduced by constructing a cubic crystal in which the unit cell contains spheres whose radii and location are generated at random. Field distribution functions[24] and cluster expansions[25] have also been used.

Although there have been efforts[1,4] to construct samples with spheres of highly uniform radius the effect of the size distribution upon the results of identical spheres is still unresolved. In this paper, we extend a recently developed effective-medium theory[5] made for an ensemble of identical spheres to the case of spheres of two different radii. In this theory[5] the effect of the dipolar fluctuations is contained in a single parameter which plays the role of a renormalized polarizability. In Sec. II we develop the formalism in which we introduce two different renormalized polarizabilities in order to take into account the coupling of the dipolar fluctuations of each type of sphere. We find that they obey two coupled quadratic algebraic equations. In Sec. III, we apply our theory to the case of Drude spheres embedded in gelatin. We present results for different ratios of the spheres radii as well as for different ratios of their volume fraction. Section IV is devoted to conclusions.

II. THEORY

Let us consider a homogeneous and isotropic ensemble with $N_a+N_A=N\gg 1$ spheres made of the same material with dielectric function ϵ_s but of two different sizes; N_a with radius a and N_A with radius A, located at random positions $\{\mathbf{R}_i\}$ and $\{\mathbf{R}_I\}$, respectively. The spheres are embedded in a host homogeneous medium with dielectric function ϵ_h and they find themselves in the presence of an external electric field E^{ex} of frequency ω and wavelength much greater than the radius of either sphere and the typical separation between them. The induced dipole moments $\mathbf{p}_i$ and $\mathbf{p}_I$ associated to each sphere are given by

$$\mathbf{p}_\beta(\omega)=\alpha_\beta(\omega)\left[\mathbf{E}^0+\sum_i \overleftrightarrow{\mathbf{t}}_{\beta i}\cdot\mathbf{p}_i(\omega)+\sum_I \overleftrightarrow{\mathbf{t}}_{\beta I}\cdot\mathbf{p}_I(\omega)\right], \tag{1a}$$

where i (I) runs over the spheres of radius a (A) and the Greek subindices run over both i and I,

$$\overleftrightarrow{\mathbf{t}}_{\alpha\beta} \equiv \nabla_\alpha \nabla_\beta (1/R_{\alpha\beta}) \tag{1b}$$

is the dipole-dipole interaction tensor in the quasistatic limit and $R_{\alpha\beta} \equiv |\mathbf{R}_\alpha - \mathbf{R}_\beta|$. Here $\mathbf{E}_0$ is the electric field induced in the host medium in the absence of the spheres and

$$\alpha_\beta = a_\beta^3 (\epsilon_s - \epsilon_h)/(\epsilon_s + 2\epsilon_h) , \tag{1c}$$

where $a_\beta = a$ (A) for $\beta = i$ (I), is the effective polarizability of an isolated sphere embedded in the host medium.

The macroscopic or effective dielectric response $\epsilon_M(\omega)$ of the system can be obtained through Eq. (6) of Ref. 5, that is,

$$\frac{\epsilon_h}{\epsilon_M} = 1 - 4\pi\epsilon_h \chi^{\mathrm{ex},l}(q \to 0, \omega) , \tag{2a}$$

where $\chi^{\mathrm{ex},l}$ is the longitudinal projection of the external susceptibility defined by

$$n\langle \mathbf{p} \rangle (\mathbf{q},\omega) = \overleftrightarrow{\chi}^{\mathrm{ex}}(\mathbf{q},\omega) \cdot \mathbf{E}^{\mathrm{ex}}(q,\omega) , \tag{2b}$$

where $\mathbf{q}$ is the wave vector, n is the total number density of spheres and $n\langle \mathbf{p} \rangle (\mathbf{q},\omega)$ is the Fourier transform of the average polarization field given by $\langle \sum_\beta \mathbf{p}_\beta \delta(\mathbf{r} - \mathbf{R}_\beta) \rangle$. Here $\mathbf{r}$ is the position, $\langle \cdots \rangle$ means ensemble average, and the superscript l indicates longitudinal projection.

Now $\chi^{\mathrm{ex},l}$ is calculated[5] by exciting the system with a longitudinal external field $\mathbf{E}^{\mathrm{ex}} = \hat{\mathbf{q}} E^{\mathrm{ex}}$, thus Eq. (1) becomes

$$\mathbf{P}_\beta = \alpha_\beta \left[\hat{\mathbf{q}} E^{\mathrm{ex}}/\epsilon_h + \sum_i \overleftrightarrow{\mathbf{T}}_{\beta i} \cdot \mathbf{P}_i + \sum_I \overleftrightarrow{\mathbf{T}}_{\beta I} \cdot \mathbf{P}_I \right] , \tag{3a}$$

where $\hat{\mathbf{q}} = \mathbf{q}/q$,

$$\mathbf{P}_\beta \equiv \mathbf{p}_\beta e^{-i\mathbf{q}\cdot\mathbf{R}_\beta} , \tag{3b}$$

$$\overleftrightarrow{\mathbf{T}}_{\alpha\beta} \equiv \overleftrightarrow{\mathbf{t}}_{\alpha\beta} e^{-i\mathbf{q}\cdot(\mathbf{R}_\alpha - \mathbf{R}_\beta)} , \tag{3c}$$

and we omit in the notation the explicit dependence on q and ω.

We follow the same procedure of Ref. 5 but now we define two renormalized polarizabilities, α_a^* and α_A^*, through the equation

$$\mathbf{P}_\beta = \alpha_\beta^* \left[\hat{\mathbf{q}} E^{\mathrm{ex}}/\epsilon_h + \sum_i \overleftrightarrow{\mathbf{T}}_{\beta i} \cdot \langle \mathbf{P}_a \rangle + \sum_I \overleftrightarrow{\mathbf{T}}_{\beta I} \cdot \langle \mathbf{P}_A \rangle \right] . \tag{4}$$

where $\alpha_\beta^* = \alpha_a^*$ (α_A^*) for $\beta = i$ (I) and $\langle \mathbf{P}_a \rangle$ $(\langle \mathbf{P}_A \rangle)$ is the average dipole moment of the spheres of radius a (A) which is independent of position due to the translational invariance of the ensemble.

Taking ensemble average and longitudinal projection of Eq. (4) we obtain

$$\langle P_\beta \rangle^l = \frac{\alpha_\beta^*}{1 + 2f\tilde{\alpha}_{\mathrm{av}}^*} (E^{\mathrm{ex}}/\epsilon_h) , \tag{5a}$$

where

$$f\tilde{\alpha}_{\mathrm{av}}^* \equiv f_a \tilde{\alpha}_a^* + f_A \tilde{\alpha}_A^* , \tag{5b}$$

$\langle P_\beta \rangle^l = \langle P_a \rangle^l$ $(\langle P_A \rangle^l)$ for $\beta = i$ (I), f_a (f_A) is the volume fraction of spheres of radius a (A), $f = f_a + f_A$ is the total volume fraction, and $\tilde{\alpha}_\beta^* \equiv \alpha_\beta^*/a_\beta^3$. Since $N\langle \mathbf{P} \rangle = N_a \langle \mathbf{P}_a \rangle + N_A \langle \mathbf{P}_A \rangle$, Eqs. (5) and (2) yield, finally,

$$\frac{\epsilon_M - \epsilon_h}{\epsilon_M + 2\epsilon_h} = f\tilde{\alpha}_{\mathrm{av}}^* , \tag{6}$$

which is identical to Eq. (15) of Ref. 5 but with $\tilde{\alpha}_{\mathrm{av}}^*$ instead of $\tilde{\alpha}^*$. This means that in the case of spheres of different sizes the renormalized polarizability should be replaced by its average. The Maxwell Garnett theory is recovered by substituting $f\tilde{\alpha}_{\mathrm{av}}^*$ by $f\tilde{\alpha}_{\mathrm{av}} = f_a \tilde{\alpha}_a + f_A \tilde{\alpha}_A$. But since $\tilde{\alpha}_\beta \equiv \alpha_\beta / a_\beta^3 = (\epsilon_s - \epsilon_h)/(\epsilon_s + 2\epsilon_h)$ is independent of the size of the spheres then $\tilde{\alpha}_{\mathrm{av}} = \tilde{\alpha}$ and one concludes that MGT is insensitive to the particle size distribution.

In order to calculate α_β^* we follow Ref. 5, that is we impose a self-consistency condition by substituting Eq. (4) into the right-hand side (rhs) of Eq. (3a). Then we take ensemble average and longitudinal projection of the resulting equations. Afterwards we use Eq. (5) and we assume that the three-particle distribution function $\rho_{\alpha\beta\gamma}^{(3)}$ between particles of radius a_α, a_β, a_γ, can be written as a product of two-particle distribution functions, that is,

$$\rho_{\alpha\beta\gamma}^{(3)}(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3) = \rho_{\alpha\beta}^{(2)}(R_{12}) \rho_{\beta\gamma}^{(2)}(R_{23}) . \tag{7}$$

The validity of this approximation was discussed in Ref. 5. Finally after some algebra we obtain the following two coupled quadratic equations:

$$\frac{\tilde{\alpha}_\beta^*}{\tilde{\alpha}} = 1 + \tfrac{1}{4} f_{\beta\beta} (\alpha_\beta^*)^2 + \tfrac{1}{4} f_{\bar{\beta}\beta} \tilde{\alpha}_{\bar{\beta}}^* \alpha_\beta^* , \tag{8a}$$

where

$$f_{\beta\beta} \equiv 3f \int_0^\infty \frac{\rho_{\beta\beta}^{(2)}(2a_\beta x)}{x^4} dx , \tag{8b}$$

$$f_{\bar{\beta}\beta} \equiv \frac{24}{(1+\gamma_{\bar{\beta}})^3} f_{\bar{\beta}} \int_0^\infty \frac{\rho_{\bar{\beta}\beta}^{(2)}(a_{\bar{\beta}} + a_\beta)x}{x^4} dx , \tag{8c}$$

and

$$\gamma_{\bar{\beta}} = a_{\bar{\beta}} / a_\beta . \tag{8d}$$

Here the subindex β $(\bar{\beta})$ runs over the subindices a, A (A, a), and $\rho_{\beta\beta}^{(2)}(R)$ $[\rho_{\bar{\beta}\beta}^{(2)}(R)]$ is the probability density of finding a particle of radius a_β at a distance R from a particle of radius a_β $[a_{\bar{\beta}}]$. The normalization of $\rho_{\alpha\beta}^{(2)}(R)$ is

$$\frac{1}{V} \int \rho_{\alpha\beta}^{(2)}(R) d^3R = 1 . \tag{8e}$$

In order to proceed further we assume that $\rho_{\beta\beta}^{(2)}$ and $\rho_{\bar{\beta}\beta}^{(2)}$ are simply given by the hole correction (HC), that is,

$$\rho_{\beta\beta}^{(2)}(R) = \Theta(R - 2a_\beta) , \tag{9a}$$

$$\rho_{\bar{\beta}\beta}^{(2)}(R) = \Theta(R - (a_{\bar{\beta}} + a_\beta)) , \tag{9b}$$

where Θ is the unit step function. In a more realistic situation $\rho_{\beta\beta}^{(2)}$ and $\rho_{\bar{\beta}\beta}^{(2)}$ should be determined directly from the samples.

Substituting Eq. (9) into Eq. (8) we obtain

$$\tfrac{1}{4} f_a \tilde{\alpha}(\tilde{\alpha}_a^*)^2 - \left[1 - f_A \frac{2}{(1+\gamma_A)^3}\tilde{\alpha}_A^*\right]\tilde{\alpha}_a^* + \tilde{\alpha} = 0 \;, \qquad (10a)$$

$$\tfrac{1}{4} f_A \tilde{\alpha}(\tilde{\alpha}_A^*)^2 - \left[1 - f_a \frac{2}{(1+\gamma_a)^3}\tilde{\alpha}_a^*\right]\tilde{\alpha}_A^* + \tilde{\alpha} = 0 \;, \qquad (10b)$$

where $\gamma_A \equiv A/a = 1/\gamma_a$. Setting $\gamma_A = 1$, using Eq. (1c) and $f = f_a + f_A$, one recovers Eq. (22a) of Ref. 5 which describes a system of identical spheres.

The decoupling of these two quadratic equations [Eq. (10)] leads to a quartic equation for $\tilde{\alpha}_a^*$ (or $\tilde{\alpha}_A^*$) which has four roots. To each root of $\tilde{\alpha}_a^*$ there is a corresponding one of $\tilde{\alpha}_A^*$ thus a value of $\tilde{\alpha}_{\rm av}^*$ [Eq. (5)] and of ϵ_M [Eq. (6)]. From these four roots we choose the solution such that $\tilde{\alpha}_{\rm av}^*$ approaches that corresponding to the case of identical spheres

$$\frac{\tilde{\alpha}^*}{2} = \frac{1 - \sqrt{1 - f_e \tilde{\alpha}^2}}{f_e} \qquad (11)$$

continuously when $\gamma_A \to 1$.

III. RESULTS AND DISCUSSION

Equation (10) was solved and the theory was applied to a system of Drude spheres embedded in gelatin. We took $\epsilon_h = 2.37$,

$$\epsilon_s(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} \;, \qquad (12)$$

and $\omega_p \tau = 92$. Here ω_p is the plasma frequencies and τ is the relaxation time. In Figs. 1 and 2 we show the results for $\mathrm{Im}\epsilon_M$ as a function of ω/ω_p for $f = 0.3$, different values of γ_A and $f_a = 0.2$ and 0.28, respectively. The case $\gamma_A = 1$ corresponds to a system of identical spheres and it was analyzed in Ref. 5. We can see in Fig. 1 that with increasing γ_A, besides the main low-frequency peak, two more peaks develop. For a larger f_a one can see, in Fig. 2 ($f_a = 0.28$), that the middle peak becomes the main peak as γ_A increases. In both cases the peak in the middle does not change its position as a function of γ_A.

As was already discussed in Ref. 5 the structure of $\mathrm{Im}\epsilon_M(\omega)$ is related to the absorption of the system by the excitation of its long-wavelength (optically active) electromagnetic modes. While in the Maxwell Garnett Theory (MGT) there is only one optically active mode due to the absence of dipolar fluctuations, in our theory these fluctuations are taken into account through α_β^* and we obtain a collection of optically active modes in a continuous finite-frequency region. For the case of identical spheres[5] ($\gamma_A = 1$) there is a single peak in $\mathrm{Im}\epsilon_M(\omega)$ which is asymmetric, wider and redshifted with respect to the MGT peak. We recollect here that the width of the MGT peak comes solely from the relaxation time τ in Eq. (12); as $\tau \to \infty$ the peak becomes a δ function. In our theory even for $\tau \to \infty$ the peak retains a finite width. For $\gamma_A > 1$ there are three peaks in $\mathrm{Im}\epsilon_M(\omega)$ which become more prominent as γ_A increases. They are related to three groups of modes which are more clearly distinguishable when $\gamma_A \gg 1$. But in a system of spheres of two very different sizes ($\gamma_A \gg 1$) the electric field produced by the big spheres varies slowly in the scale of the

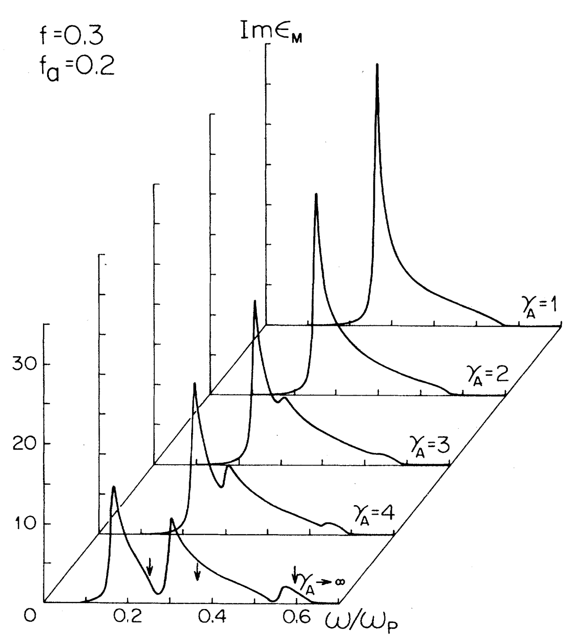

FIG. 1. Imaginary part of the macroscopic dielectric response of a composite as a function of the frequency. The composite is made up of Drude spheres with $\omega_p \tau = 92$ embedded in gelatin with $\epsilon_h = 2.37$. The filling fraction is $f = 0.3$, of which $f_a = 0.2$ corresponds to small spheres and the rest to large spheres. Results are presented for several ratios γ_A of the sphere's radii. The positions of the three peaks predicted by MGT2 are indicated by arrows.

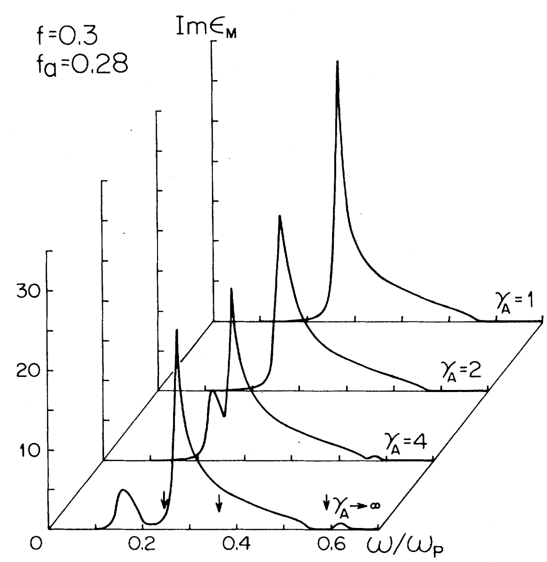

FIG. 2. Imaginary part of the macroscopic dielectric response as a function of frequency for the same parameters as in Fig. 1 but with $f_a = 0.28$.

small spheres. Therefore one can consider that the big spheres (A) are embedded in a homogeneous medium made of the small spheres (a) with an effective dielectric function $\epsilon_M^{(1)}$. This latter function can be calculated using an effective-medium theory and then iterating one calculates the effective dielectric function $\epsilon_M^{(2)}$ of the system of big spheres embedded in $\epsilon_M^{(1)}$.

In order to identify the physical origin of the resonances we choose for this iterative process the simplest effective-medium theory. This is MGT which by neglecting the dipolar fluctuations reduces drastically the number of modes. In MGT this process leads to the following relations, which we call MGT2:

$$\frac{\epsilon_M^{(1)}}{\epsilon_h}=\frac{1+2f_a\tilde{\alpha}}{1-f_a\tilde{\alpha}} \tag{13a}$$

and

$$\epsilon_M^{(2)}=\left[\frac{1+2f_A\tilde{\alpha}_1}{1-f_A\tilde{\alpha}_1}\right]\epsilon_M^{(1)}\ , \tag{13b}$$

where $\tilde{\alpha}_1=(\epsilon_s-\epsilon_M^{(1)})/(\epsilon_s+2\epsilon_M^{(1)})$.

In Fig. 3 we show the results of this iteration for $\mathrm{Im}\epsilon_M^{(2)}(\omega)$ using the same parameters as in Figs. 1 and 2 for $f_a=0.2$, 0.25, and 0.28. Obviously here $\epsilon_M^{(2)}$ does not depend on γ_A but only on the volume fractions f_a and f_A. One can see three well-defined peaks which correspond to the three modes associated to a system of spheres (A) embedded in a dispersive medium characterized by $\epsilon_M^{(1)}(\omega)$. Their width comes solely from a finite τ in Eq. (12). It can also be checked that the position of the central peak corresponds to the resonance of $\epsilon_M^{(1)}$ which describes a system of identical spheres with volume fraction f_a. This follows directly from the fact that $\epsilon_M^{(1)}$ factors out in the rhs of Eq. (13b). In Figs. 1 and 2 we also show with arrows the positions of the peaks of MGT2.

The dipolar fluctuations can be incorporated through a simple extension of MGT2. This consists of iterating the theory of the renormalized polarizability[5] as we did with MGT. This means that first we calculate α^* for the small spheres embedded in a host medium by using Eq. (11), and we obtain $\epsilon_M^{(1)}$ using Eq. (15) of Ref. 5. Then we iterate the process to get the macroscopic response $\epsilon_M^{(2)}$ of a system of large spheres embedded in an effective medium with dielectric response $\epsilon_M^{(1)}$. We call this process α^*2. In Fig. 4 we show $\mathrm{Im}\epsilon_M^{(2)}(\omega)$ using the same parameters as in Figs. 1 and 2 for $f_a=0.2$, 0.25, and 0.28. It can be seen that $\mathrm{Im}\epsilon_M^{(2)}(\omega)$ also has three characteristic peaks shifted with respect to the three peaks of MGT2 whose positions, for $f_a=0.2$, are indicated by arrows. Thus the three groups of resonances which appear for $\gamma_A\neq1$ and in MGT2 remain in α^*2 even in the presence of dipolar fluctuations. We identify the physical origin of the central peak as the resonance of the effective medium of the small spheres within the dispersionless host and that of the remaining two peaks as the collective modes of the large spheres within the dispersive medium $\epsilon_M^{(1)}(\omega)$.

In Figs. 1 and 2 we also show the results obtained from Eq. (10) in the limit $\gamma_A\to\infty$. This limit is taken by keeping f_a, f_A, and a finite while $A\to\infty$. In this case Eq. (10a) decouples from Eq. (10b) and it becomes the equation that describes a system of identical spheres with volume fraction f_a, which yields the central peak in Figs. 1 and 2 ($\gamma_A\to\infty$). In our theory the peaks in $\mathrm{Im}\epsilon_M(\omega)$

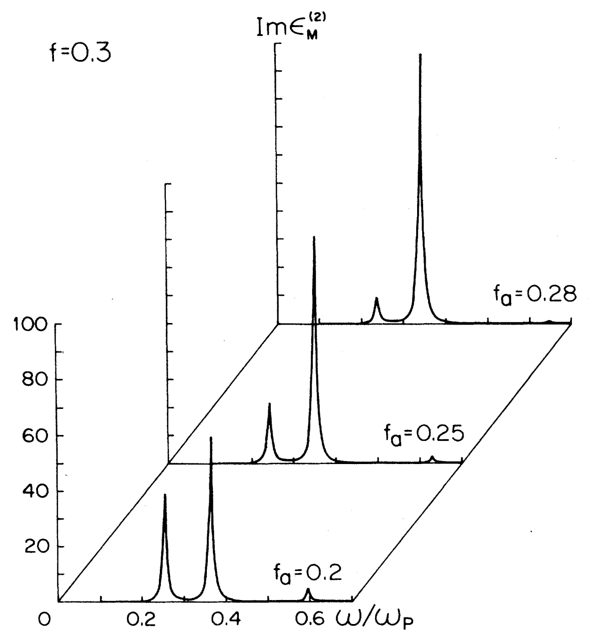

FIG. 3. Imaginary part of the macroscopic dielectric response as a function of frequency, calculated within MGT2 for a total filling fraction $f=0.3$ and different filling fractions f_a for the small spheres.

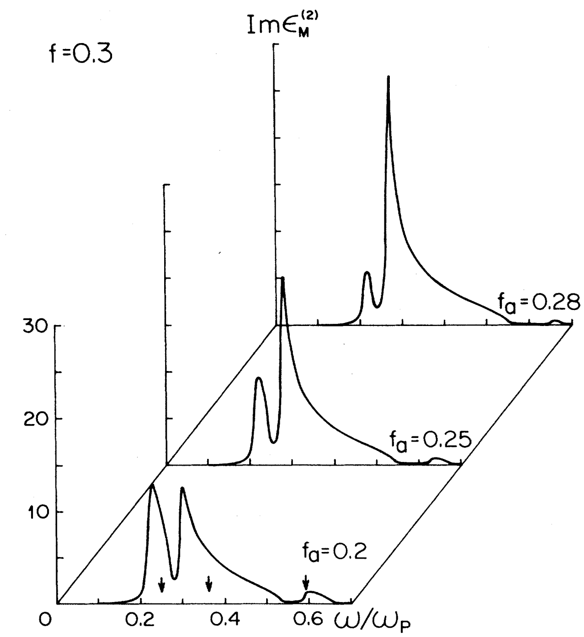

FIG. 4. Imaginary part of the macroscopic dielectric response as a function of frequency calculated within α^*2. The parameters are as in Fig. 3 and the positions of the MGT2 peaks are indicated by arrows.

for $\gamma_A \to \infty$ are asymmetric, wider, and shifted with respect to the ones in MGT2 due to the generation of new modes caused by the dipolar fluctuations. One also notes that as γ_A decreases the position of the central peak does not move appreciably. It can also be seen that the position of the peaks in α^*2 (Fig. 4) do not agree with the ones of $\gamma_A \to \infty$ (Figs. 1 and 2). In α^*2 the red shift of the low-energy peak is not as large as in $\gamma_A \to \infty$ and the high-energy peak in α^*2 is blue shifted with respect to the corresponding one in $\gamma_A \to \infty$.

Actually, within the quasistatic approximation, the limit $\gamma_A \to \infty$ is not strictly allowed because when the radius of the spheres becomes of the order of magnitude of the wavelength of light retardation effects—not considered here—will be important. But even within the quasistatic limit one expects the dipolar approximation to breakdown when $\gamma_A \gg 1$ for the following reason: The dipolar field produced by a small sphere induces both dipole and quadrupole moments in a nearby large sphere. The ratio of the quadrupole field to the dipole field acting back on the small sphere goes as $(A/R)^2$ where R is the distance between the two centers. Assuming now that the edge-to-edge mean separation between the big and small spheres is approximately the same as the one between two small spheres the condition $(A/R)^2 \ll 1$ leads to $\gamma_A^2/(2F+\gamma_A-1)^2 \ll 1$, where $F^3=(1-f_A)/f_a$. This sets an upper limit for γ_A for big enough f_a. For example, for $f_a=0.28$ and $f_A=0.02$, this means that $1/(1+2/\gamma_A)^2 \ll 1$ and γ_A cannot go beyond, say, 1.5 for a 20% accuracy. Therefore this explains the discrepancy between the present theory and α^*2, which becomes a better approximation when γ_A is large enough.

On the other hand for $\gamma_A \gtrsim 1$ only one of the three resonances is distinguishable. This is the case treated by Liebsch and Villaseñor[11] using LG-CPA. We have calculated $\text{Im}\epsilon_M$ with the same parameters they used in their work and our results do not agree with theirs. While we only obtain a very slight red shift of the main peak for $\gamma_A \gtrsim 1$, they obtain a blue shift and some additional broadening. Furthermore we recall that in our approach there is a dependence on the two-particle distribution functions while LG-CPA relies on a cubic lattice. In our case the introduction of a different choice of two-particle distribution functions will give rise to quantitative differences although not to qualitative changes.

IV. CONCLUSIONS

We have extended the effective-medium theory of the renormalized polarizability[5] formulated for a system of identical spheres to the case of spheres of two different sizes, by introducing two different renormalized polarizabilities, one for each type of sphere. We obtain that they obey two coupled quadratic equations whose coefficients depend on functionals of three different two-particle distribution functions. We chose the hole correction for all three, and we obtained that in this system there are three main groups of resonances which appear as three definite peaks in $\text{Im}\epsilon_M(\omega)$. These peaks become more clearly distinguishable as the ratio γ_A of the radii of the two spheres increases. We identify these resonances in the limit $\gamma_A \gg 1$ by comparing our results with a double iteration of MGT which we called MGT2. In MGT2 one considers, in the absence of dipolar fluctuations, that the big spheres are embedded in an effective dispersive medium composed by the small spheres with effective response $\epsilon_M^{(1)}(\omega)$. This system has only three resonant modes. Our results for $\gamma_A \gg 1$ show also these three peaks but broader, asymmetric, and shifted with respect to the corresponding ones in MGT2 since in the presence of dipolar fluctuations the optically active modes span a finite frequency range near the peaks of MGT2. Then we set up limits for the validity of the dipolar approximation used in our theory, and we found that for a given volume fraction of the small spheres the quadrupole effects become more important as γ_A increases. The upper limit for γ_A increases as f_a decreases. Nevertheless we find a better limit for $\gamma_A \gg 1$ and $f_a \gg f_A$ by a double iteration of the theory of the renormalized polarizability.[5] We show that in this case there are also three main groups of resonances whose line shape is broader and shifted with respect to the ones of MGT2. Although our results depend on functionals of the two-particle distribution functions and we have chosen the hole correction for all of them, we do not expect qualitative changes to our results by choosing other functional forms. The specific form of these distribution functions will depend on the sample preparation process and experimental work in these systems will be extremely helpful. One can infer from our work that the existence of more sphere sizes will lead to a larger number of resonances in $\text{Im}\epsilon_M$. In the case of continuous distribution this will give a close superposition of resonances which will show up as a broader peak.

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[1]W. J. Kaiser, E. M. Logothetis, and L. E. Wenger, J. Phys. C **18**, L837 (1985); Solid State Commun. **58**, 83 (1986).

[2]J. Perrin, B. Despax, and E. Kay, Phys. Rev. B **32**, 719 (1985).

[3]T. Yamaguchi, M. Sakai, and N. Saito, Phys. Rev. B **32**, 2126 (1985).

[4]S. I. Lee, T. W. Noh, J. R. Gaines, Y. H. Ko, and E. R. Kreidler, Phys. Rev. B **37**, 2918 (1988); T. W. Noh, Y. Song, S. I. Lee, J. R. Gaines, H. D. Purk, and E. R. Kreidler, *ibid.* **33**, 3793 (1986).

[5]R. G. Barrera, G. Monsivais, and W. L. Mochán, Phys. Rev. B

38, 5371 (1988).

[6]See, for example, A. J. Sievers, in *Solar Energy Conversion: Topics in Applied Physics,* edited by B. O. Seraphin (Springer-Verlag, Berlin, 1979) Vol. 31, p. 57; H. G. Graighead, R. Bartynski, R. A. Buhrman, L. Wojcik, and A. J. Sievers, Sol. Energy Mater. **1**, 105 (1979).

[7]J. C. Maxwell Garnett, Philos. Trans. R. Soc. Ser. A **203**, 385 (1904); **203**, 237 (1906).

[8]W. Lamb, D. M. Wood, and N. W. Aschcroft, Phys. Rev. B **21**, 2248 (1980).

[9]P. Sheng, Phys. Rev. Lett. **45**, 60 (1980); Phys. Rev. B **22**, 6364 (1980); Opt. Laser Technol. **13**, 253 (1981).

[10]B. N. J. Persson and A. Liebsch, Solid State Commun. **44**, 1637 (1982); J. Phys. C **16**, 5375 (1983).

[11]A. Liebsch and P. Villaseñor-González, Phys. Rev. B **29**, 6907 (1984).

[12]D. J. Bergman, J. Phys. C **12**, 4947 (1979); Phys. Rev. B **19**, 2359; Phys. Rep. **43**, 377 (1978).

[13]J. M. Gerardy and M. Ausloss, Phys. Rev. B **22**, 4950 (1980); Surf. Sci. **106**, 319 (1981); Phys. Rev. B **25**, 4204 (1982).

[14]A. Bittar, S. Berthier, and J. Lafait, J. Phys. (Paris) **45**, 623 (1984).

[15]B. U. Felderhof, G. W. Ford, and E. G. D. Cohen, J. Stat. Phys. **28**, 649 (1982); **28**, 135 (1982).

[16]M. Gómez, L. Fonseca, G. Rodríguez, A. Velázquez, and L. Cruz, Phys. Rev. B **32**, 3429 (1985).

[17]V. A. Davis and L. Schwartz, Phys. Rev. B **33**, 6627 (1986); **31**, 5155 (1985).

[18]G. S. Agarwal and R. Ingura, Phys. Rev. B **30**, 6108 (1984).

[19]R. W. Cohen, G. D. Cody, M. D. Coutts, and B. Abeles, Phys. Rev. B **8**, 3689 (1973).

[20]D. Stroud, Phys. Rev. B **12**, 3368 (1975).

[21]P'Oneil and A. Ignatiev, Phys. Rev. B **18**, 6540 (1978).

[22]R. J. Warmack and S. L. Humphrey, Phys. Rev. B **34**, 2246 (1986); **29**, 2926 (1984).

[23]S. W. Kennerly, J. W. Little, R. J. Warmack, and T. L. Ferrell, Phys. Rev. B **29**, 2926 (1984).

[24]J. M. Gerardy and M. Ausloos, Phys. Rev. B **26**, 4703 (1982).

[25]B. U. Felderhof and R. B. Jones, Z. Phys. B **62**, 231 (1986); **62**, 225 (1986); **62**, 215 (1986); **62**, 43 (1985).

[26]Y. Kantor and D. J. Bergman, J. Phys. C **15**, 2033 (1982).