Correlation and multipolar effects in the dielectric response of particulate matter: An iterative mean-field theory

F. Claro
Facultad de Física, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago 22, Chile

R. Rojas
Departamento de Física, Universidad Federico Santa María, Casilla 110-V, Valparaíso, Chile
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A systematic approach for treating correlations and multipolar effects in particulate matter is proposed. The method consists of an iterative extension of the Maxwell-Garnett (MG) mean-field approach. The first iterate beyond MG that involves up to three-particle correlations is solved fully to all multipolar orders using Kirkwood's superposition approximation and yields a simple improved formula for the composite dielectric constant at low filling. We find that at 5% filling resonances that originate in multipolar couplings carry about 6% of the total strength. Our results reproduce accurately low-density measurements on pure argon.

I. INTRODUCTION

The Maxwell-Garnett (MG) formula is the standard expression used to obtain the dielectric response of a dilute ensemble of inclusions in a matrix in the long-wavelength limit.[1,2] Its justification rests on two basic assumptions. One is that excitations of dipolar character only are important. The other is that space correlations between such excitations may be ignored. The validity of these assumptions has been questioned extensively in the past especially when the formula is applied to a not so dilute sample.[3–8] The strength of multipolar contributions to the local field where each particle sits is not negligible when the inclusions are close, and the induced multipoles become important. Also, in a disordered sample the local field differs from site to site, a fact that the MG formula ignores.

We here present a simple scheme that allows for systematic corrections to the MG formula, where both multipolar effects and space correlations are included. The novelty of our approach is that it retains the central mean-field concept that characterizes the MG solution. To introduce the basic idea, consider a random distribution of N identical inclusions of dipole polarizability α_1 and volume v_0 embedded in a matrix of dielectric constant ϵ_0 and total volume V placed in an external uniform electric field $\mathbf{E}_0$. For simplicity, assume the sample to be a thin slab and the applied field to point in the direction perpendicular to the parallel faces of the slab, which we call the z direction. The excitations in a given particle are coupled to all other inclusions through the local field it experiences. In the dipole approximation the moment in the ith inclusion is given by

$$\mathbf{p}_i=\alpha_1\left[\mathbf{E}+\sum_j \mathsf{t}_{ij}\cdot\mathbf{p}_j\right] . \tag{1}$$

The quantity in parentheses is the local field. $\mathbf{E}$ is the average field in the matrix in the absence of inclusions while the sum represents the contribution from all the other inclusions, with t_{ij} a tensor of purely geometric character. Equation (1) represents a set of $3N$ linear equations whose exact solution is known in principle but remains impractical to compute when N is large, save for highly symmetrical arrays.[9] The MG approximation for a random distribution of inclusions is to replace each dipole $\mathbf{p}_j$ in the right of Eq. (1) by the average value over sites $\langle\mathbf{p}\rangle=p\hat{z}$, and thereafter take the same average of the entire Eq. (1). The resulting equation may be easily solved for $p=\alpha_{\text{eff}}E$, where α_{eff} is the effective polarizability of a particle in the presence of the others. One gets for the inverse of this quantity

$$\frac{1}{\alpha_{\text{eff}}}=\frac{1}{\alpha_1}+\frac{8\pi}{3v_0}f , \tag{2}$$

where $f=Nv_0/V$ is the filling fraction of the inclusions. We have used the expression for the average dipole coupling[10]

$$\left\langle\sum_j \mathsf{t}_{ij}\right\rangle_{zz}=-\frac{8\pi}{3v_0}f . \tag{3}$$

Equation (2) gives the response of an inclusion in the standard MG theory. As we shall see in Sec. II, a fully multipolar treatment yields no corrections to Eq. (2) in this approximation. Our theory extends the basic MG approach just described, applying it to iterates of the multipolar version of Eq. (1). As the iteration proceeds, higher and higher correlation orders are included and multipole coupling becomes important from the first-order correction onwards. While MG is recognized as valid at low densities, our iterates represent improved versions of the same MG approach and may be viewed as approximations reliable at progressively higher densities.

In Sec. II we develop our extension of the MG scheme to cover correlations and multipolar excitations, and present a full solution up to three-particle correlations.

In Sec. III this solution is analyzed in the spectral representation and in Sec. IV we present our discussion.

II. EXTENDED MAXWELL-GARNETT THEORY

A fully multipolar version of Eq. (1) may be written in a spherical-harmonic basis $Y_l^m(\hat{r})$. Calling q_{lmi} the multipole moment of order l,m excited at site i it reads[9]

$$q_{lmi}=\sqrt{3/4\pi}\alpha_{10i}\delta_{l,1}\delta_{m,0}E+\sum_{l'm'j}B_{lmi}^{l'm'j}q_{l'm'j}\ , \tag{4}$$

where

$$B_{lmi}^{l'm'j}=\alpha_{lmi}b_{lm}^{l'm'}\frac{Y_{l+l'}^{*m-m'}(\hat{r}_{ij})}{r_{ij}^{l+l'+1}}\ , \tag{5}$$

$$b_{lm}^{l'm'}=(-1)^{l'+m'+1}\left[\frac{4\pi(2l+1)}{(2l'+1)(2l+2l'+1)}\frac{(l+l'+m-m')!(l+l'-m+m')!}{(l+m)!(l-m)!(l'+m')!(l'-m')!}\right]^{1/2}. \tag{6}$$

Here α_{lmi} is the polarizability of the inclusion at site i in the presence of the dielectric matrix, and $\mathbf{r}_{ij}=\mathbf{r}_j-\mathbf{r}_i=r_{ij}\hat{r}_{ij}$.

An iterative solution of Eq. (4) may be obtained by successive substitution of itself into the right-hand side of the equation. The average dipole polarization may then be expressed in terms of the average of all powers of the coupling (5). In practice however, only a few terms in the expansion may be calculated, by diagrammatic or other methods,[11,12] and their relative significance to the exact solution is unclear. We propose instead to stop the iteration process after n steps and thereafter use the MG decoupling scheme described in Sec. I. This defines an nth-order approximation that introduces corrections to the MG formula in a systematic way keeping the basic and very successful physical idea that underlies this formula.

We shall first show that the zeroth-order approximation yields exactly the dipolar MG formula since higher multipole couplings do not contribute to the MG local field. For simplicity we assume in what follows the particles to be identical and spherically symmetric, so that $\alpha_{lmi}=\alpha_l$. In the zeroth order of the theory outlined above the moments in the right-hand side of Eq. (4) are directly replaced by an average $\langle q_{lm}\rangle$ and thereafter an average is taken of the resulting expression. This yields for the average dipole moment $p=(4\pi/3)^{1/2}\langle q_{10}\rangle$ in our slab geometry

$$p=\frac{1}{1+\frac{8\pi}{3}\frac{\alpha_1}{v_0}f}\left[\alpha_1E+\left[\frac{4\pi}{3}\right]^{1/2}\sum_{lmj}{}'\langle B_{10i}^{lmj}\rangle\langle q_{lm}\rangle\right]. \tag{7}$$

The first term is the standard dipolar MG result Eq. (2) while the second represents corrections due to higher multipoles. The prime in the sum means that $l>1$. Averages are to be taken over sites i or, equivalently, over a statistical ensemble of configurations characterized by a distribution function $\rho(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_N)$ for the N identical inclusions in the sample. The sum over sites j in Eq. (7) includes two-particle couplings and its average may be expressed in the form

$$\left\langle\sum_j B_{10i}^{lmj}\right\rangle=(N-1)\alpha_1b_{10}^{lm}\times\int\int\frac{Y_{l+1}^{*-m}(\hat{r}_{12})}{r_{12}^{l+2}}\rho_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2\ , \tag{8}$$

where the p-particle distribution $\rho_p(\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_p)$ is defined as the integral of the distribution ρ over the positions of $N-p$ particles. In a homogeneous sample $\rho_2=\rho(r_{12})$ so one of the integrals in (8) simply yields a factor V. The orthogonality of spherical harmonics makes the remaining integral over angles vanish. Thus the last term in (7) is zero and there are no multipolar corrections to the MG formula within the standard theory.

To go beyond MG we iterate Eq. (4) once and obtain

$$q_{lmi}=\sqrt{3/4\pi}\left[\alpha_{10i}\delta_{l,1}\delta_{m,0}+\sum_j\alpha_{10j}B_{lmi}^{10j}\right]E+\sum_{\substack{l'm'j\\l''m''k}}B_{lmi}^{l'm'j}B_{l'm'j}^{l''m''k}q_{l''m''k}\ . \tag{9}$$

We replace as before in the right-hand side the moments by their average and then take an overall average, thus completing the steps that define the first-order approximation in our theory. For identical and spherically symmetric particles we obtain

$$p=\frac{\left[1-\frac{8\pi}{3}\frac{\alpha_1}{v_0}f\right]\alpha_1E+\left[\frac{4\pi}{3}\right]^{1/2}\sum_{l'm'}\sum_{l'',m''}{}'\langle\sum_{jk}B_{10i}^{l'm'j}B_{l'm'j}^{l'',m''k}\rangle\langle q_{l''m''}\rangle}{1-\sum_{l'm'}\langle\sum_{jk}B_{10i}^{l'm'j}B_{l'm'j}^{10k}\rangle}\ , \tag{10}$$

where the average needed now is

$$\left\langle \sum_{jk} B_{10i}^{l'm'j} B_{l'm'j}^{l''m''k} \right\rangle = (N-1)\int\int B_{101}^{l'm'2} B_{l'm'2}^{l''m''1} \rho_2(\mathbf{r}_1,\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + (N-1)(N-2)\int\int\int B_{101}^{l'm'2} B_{l'm'2}^{l''m''3} \rho_3(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \ . \tag{11}$$

Using translational invariance and the properties of spherical harmonics we obtain for the first integral in the right-hand side, using (5) and (6),

$$\frac{4\pi}{2l'+3}[(l'+1)^2 - m'^2]\alpha_1\alpha_{l'} V \int_0^\infty dr \frac{\rho_2(r)}{r^{2l'+2}} \delta_{l'',1}\delta_{m'',0} \ . \tag{12}$$

The second term in Eq. (11) is more difficult to evaluate since it involves the coupling of three particles: the multipole at site 3 excites a multipole at site 2 which in turn contributes to the dipole excitation at site 1. For the three-particle distribution function we use the superposition approximation[13]

$$\rho_3(1,2,3) = V^3 \rho_2(1,2)\rho_2(2,3)\rho_2(3,1) \ . \tag{13}$$

For brevity of notation we use here and in what follows the particle label to denote its position vector. The integral of interest has the form

$$I = V^3 \int\int\int B_{101}^{l'm'2} B_{l'm'2}^{l''m''3} \rho_2(1,2)\rho_2(2,3) \times \rho_2(3,1) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \ .$$

Adding and subtracting $1/V^2$ from the last factor in the integrand we split I in two separate integrals:

$$I = I_1 - I_2 \ ,$$

$$I_1 = V\int d\mathbf{r}_2 B_{101}^{l'm'2} \rho_2(1,2) V \int d\mathbf{r}_3 B_{l'm'2}^{l''m''3} \rho_2(2,3) \ ,$$

$$I_2 = V\int d\mathbf{r}_1 \int d\mathbf{r}_2 B_{101}^{l'm'2} \rho_2(1,2) \times \int d\mathbf{r}_3 B_{l'm'2}^{l''m''3} \rho_2(2,3)[1 - V^2\rho_2(1,3)] \ .$$

I_1 is just the product of two integrals whose form was already discussed in connection with (7), and has the value, using Eq. (3),

$$I_1 = \left[\frac{8\pi}{3} \frac{\alpha_1}{V} \right]^2 \delta_{l',1}\delta_{m',0}\delta_{l'',1}\delta_{m'',0} \ .$$

The integral over $\mathbf{r}_3$ in I_2 has its main contribution coming from a small volume v centered at $\mathbf{r}_1$ since the bracket in the integrand approaches zero about a diameter away from the center of the inclusion at such location. An approximate value is obtained replacing this integral by $v\rho_2(2,1)B_{l'm'2}^{l''m''1}$, where the effective volume v is defined by

$$v\rho_2(2,1) = \int d\mathbf{r}_3 \rho_2(2,3)[1 - V^2\rho_2(1,3)] \ . \tag{14}$$

The replacement is exact for a dilute hard-spheres system [$\rho_2(ax) = \Theta(x-2)/V^2$, with $x = r_{12}/a$ and Θ the unit-step function], and $r_{12} > 4a$. Then the integral involves the average over a spherical volume, of the potential due to a multipole outside such volume, and this equals the potential at the center of the sphere. Then $v = 8v_0$. For $2a < r_{12} < 4a$ the replacement is an approximation even for hard spheres. In the latter case we get, from (14), $5.5v_0 < v = x(3 - x^2/16)v_0 < 8v_0$. This yields

$$I_2 = V^2 \int d\mathbf{r}_{12} B_{101}^{l'm'2} B_{l'm'2}^{l''m''1} v\rho_2^2(r_{12}) = 4\pi \frac{(l'+1)^2 - m'^2}{2l'+3} \alpha_1\alpha_{l'} V^2 \int_0^\infty dr\, v \frac{\rho_2^2(r)}{r^{2l'+2}} \delta_{l'',1}\delta_{m'',0} \ . \tag{15}$$

From the above results we obtain, after some algebra,

$$\sum_{m'} \left\langle \sum_{jk} B_{10i}^{l'm'j} B_{l'm'j}^{l''m''k} \right\rangle = f\beta_1\beta_{l'} \left[4f\delta_{l'1} + \frac{l'+1}{2^{2l'+1}+1} H_{l'} \right] \delta_{ll',1}\delta_{m'',0} \ . \tag{16}$$

The quantity $\beta_l = \alpha_l / a^{2l+1}$ is a dimensionless polarizability, defined in terms of the particle radius $a = (3v_0/4\pi)^{1/3}$, and

$$H_l = (2l+1)2^{2l+1} \int_0^\infty \left[1 - fg(x)\frac{v}{v_0} \right] \frac{g(x)}{x^{2l+2}} dx \ , \tag{17}$$

where $g(x) = V^2\rho_2(ax)$ is the usual pair correlation function, a function of f in general. Equation (16) represents the average dipolar excitation produced by the multipoles l'', m'' through the intermediacy of the multipoles l', m'. Because of the Kronecker δ functions the only nonzero couplings are dipole to dipole. Thus the triple sum in Eq. (10) makes no contribution to the average dipole moment. For a dilute hard-spheres system, we obtain from (17) ($l > 1$)

$$H_l = 1 - \frac{f}{2^{2l}} \left[\frac{2l+1}{l(l-1)} [2l(11 \times 2^{2l-3} - 1) - 3(2^{2l} - 1)] + 4 \right] \ , \tag{18}$$

$$H_1 = 1 - \frac{f}{4}(31 - 6\ln 2) \ .$$

The integral I_2 also appears in other treatments of correlations.[13–15] A different method of evaluation has been given, which starts by taking a directional average of the couplings and thereafter uses Fourier transforms.[15] For a dilute hard-spheres system this method yields qualitatively similar results to our Eq. (18) (see Appendix). We have also evaluated Eq. (17) using a virial expansion[16] as well as the Percus-Yevick pair correlation function for the hard-sphere model[17] and have in all cases ob-

tained similar results.

Substituting (16) in Eq. (10), we get for the effective inclusion polarizability

$$\frac{1}{\alpha_{\text{eff}}}=\frac{1}{\alpha_1}+\frac{8\pi}{3v_0}f-\frac{4\pi f}{3v_0}Q\ , \tag{19}$$

$$Q=\frac{\sum_{l=1}^{\infty}\frac{l+1}{2^{2l+1}+1}H_l\beta_l}{1-\frac{8\pi}{3v_0}f\alpha_1}\ . \tag{20}$$

Equation (19) is our final result for the first iterate correction to the MG formula. The first two terms are just the MG result Eq. (2) while the last term is the fully multipolar correction due to three-particle correlations. Note that the strength of these correlations at each multipole order is proportional to the quantities H_l defined above. We remark the simplicity of this result. Higher-order approximations may be obtained by iterating further Eq. (3) over itself and then proceeding with averages in the manner illustrated in the first two orders of approximation treated above. Averages, however, become more and more difficult to compute as four- and more-particle correlations are included, and at present we have not gone beyond first order.

Equation (19) gives the effective inclusion polarizability in terms of which the average dielectric constant $\bar{\epsilon}$ of the composite medium may be expressed. The total polarization in the sample is the sum of two contributions: that of the inclusions and that of the dielectric matrix. Using the fact that in a thin-slab placed in a perpendicular field the displacement vector is the field due solely to the fixed external charges, the ensuing identity $1-1/\bar{\epsilon}=(1-1/\epsilon_0)+4\pi N\alpha_{\text{eff}}/V\epsilon_0$ yields

$$\bar{\epsilon}=\frac{\epsilon_0}{1-\frac{4\pi f}{v_0}\alpha_{\text{eff}}}\ . \tag{21}$$

We remark that α_{eff} is defined as the effective response of the inclusion to the average field E that would exist in the dielectric matrix in the absence of any inclusions, and equals the field E_0 due to the fixed external charges only if the dielectric constant of the matrix $\epsilon_0=1$. With the aid of Eqs. (19) and (21) one gets the relation

$$\frac{\bar{\epsilon}+2\epsilon_0}{\bar{\epsilon}-\epsilon_0}=\frac{1}{f\beta_1}-Q\ , \tag{22}$$

which is of the Clausius-Mossotti form, with the correction term Q given by (20).

III. SPECTRAL REPRESENTATION

A convenient way to exhibit the structure present in the dielectric function Eq. (21) is through its spectral representation. It is defined by the expression[18,19]

$$\frac{\bar{\epsilon}}{\epsilon_0}=1+f\int_0^1\frac{G(n')}{(\epsilon/\epsilon_0-1)^{-1}+n'}dn'\ . \tag{23}$$

Here ϵ is the complex dielectric constant of the inclusions. The spectral density $G(n)$ is a real, positive definite quantity that measures the strength of the mode of depolarization factor n. The structure in this function determines the structure in the optical-absorption coefficient, for instance. It is a function of geometry only and obeys the sum rules

$$\int_0^1 G(n')dn'=1\ , \tag{24}$$

$$\int_0^1 n'G(n')dn'=\frac{1-f}{3}\ . \tag{25}$$

Letting $\epsilon=1-(n+is)^{-1}$, Eq. (23) may be inverted to get

$$G(n)=\frac{1}{\pi f}\lim_{s\to 0}\text{Im}\frac{\bar{\epsilon}(-n-is)}{\epsilon_0}\ . \tag{26}$$

Knowledge of $\bar{\epsilon}$ in terms of ϵ then allows one to get the spectral density.

In the standard MG approximation one easily finds from Eqs. (2), (21), and (26), $G(n)=\delta(n-(1-f)/3)$. There is a single mode of weight one at $n=(1-f)/3$. Our first iterate solution Eq. (19) yields a spectral density with a more complex structure. The simplest expression is obtained in the dipole ($l=1$, only) approximation. From Eqs. (19) and (23) we get, in the dilute limit for hard spheres $[g_0(x)=\Theta(x-2)]$,

$$G(n)=\frac{1}{2}\left[\left[1-\frac{1}{z}\right]\delta\left[n-\frac{1}{3}+\frac{f}{2}+\frac{fz}{6}\right]\right]+\frac{1}{2}\left[\left[1+\frac{1}{z}\right]\delta\left[n-\frac{1}{3}+\frac{f}{2}-\frac{fz}{6}\right]\right]\ , \tag{27}$$

where $z=(1+8H_1/9f)^{1/2}$. There are two modes of different strength. Figure 1 shows the position of the modes [Fig. 1(a)] and strengths [Fig. 1(b)] for H_1 as given in Eq. (18). The dashed line is the (single mode) MG result, which also follows the average depolarization factor given by Eq. (25). The labels $(-)$ and $(+)$ represent the first and second terms in Eq. (27), respectively. Note that at filling $f_c=0.149$ the $(+)$ mode joins the MG solution, reaching strength one. At the same filling the $(-)$ mode reaches zero strength. At higher fillings the solution gives unphysical results. This is a feature common to other approximate theories, only that the value of f_c obtained in each theory is different.[20] We believe that it arises from the approximations made in the computation of I_2. In particular, we have found our results to be quite sensitive to the value of this integral. In Sec. II we showed replacement (14) to be exact for $x=r_{12}/a>4$, and only approximate in the other relevant interval $2<x<4$. If in this latter interval we set $v(x)=\gamma x(3-x^2/16)+8(1-\gamma)$ for the effective volume, the parameter γ may be used conveniently to modify the value of I_2. The function $v(x)$ and its derivative are continuous at $x=4$. For $\gamma=1$ one obtains the form derived in Sec. II. Decreasing γ moves the critical filling to higher values without altering the shape of the curves in Fig. 1. For instance, setting $\gamma=0.674$ yields $f_c=\pi/6$, the filling fraction at which spheres in a cubic lattice touch. Thus a decrease of γ from a value of one to this latter value, which changes the area under the curve $v(x)$

by just 4% without altering its form, increases the value of f_c by a factor larger than 3. This illustrates the sensitivity of results at moderate- and high-filling fractions to how the integral I_2 is evaluated.

Carrying multipoles higher than the dipole makes the structure in $G(n)$ richer. The modes in our dilute hard-spheres model may be obtained from the zeros of the function

$$P(x)=x-f-\frac{fx}{x-2f}\sum_{l=1}^{L}\frac{l+1}{2^{2l+1}+1}\frac{H_l}{1+(c_l/3)(x-1)}\ , \tag{28}$$

where $x=1-3n$ is the unknown, $c_l=(2l+1)/l$, and L is the highest multipole order considered. Once a solution is known, its strength is given, as obtained from (26), by

$$w=\left[2+\frac{f}{1-3n-2f}\times\left[1+\frac{1}{3}\sum_{l=1}^{L}\frac{l+1}{2^{2l+1}+1}\frac{(c_l-3)H_l}{(c_l n-1)^2}\right]\right]^{-1}. \tag{29}$$

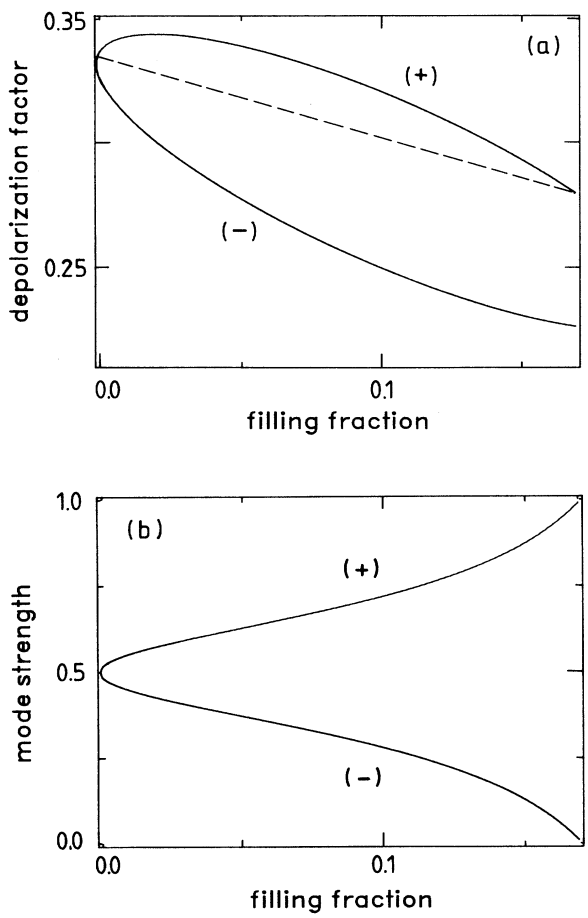

FIG. 1. Position (a) and strength (b) of resonant modes in the dipole approximation. The dashed line represents the MG approximation. For curve labels see text.

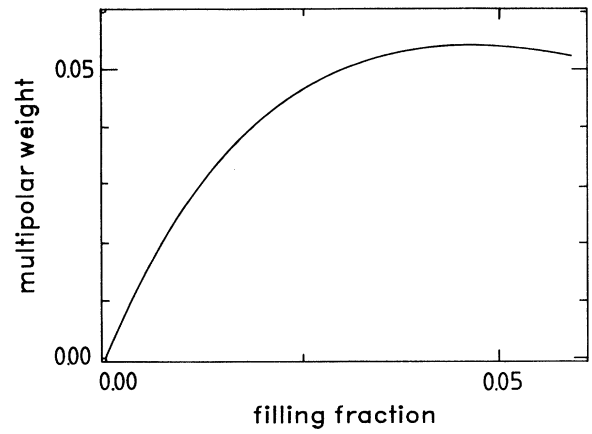

FIG. 2. Weight of resonances introduced by multipolar couplings ($l \geq 2$), not included in Fig. 1.

The function (28) is a polynomial of order $L+1$ and has as many zeros. The spectral density associated with the first iterate Eq. (19) consists therefore of $L+1$ δ functions that represent the resonances of the system. We have calculated these resonances in the range $0<f<f_c$ using Eq. (18), and found them to be a sequence where the first two are those given in Fig. 1(a) slightly displaced, while the rest are distributed at higher values of n, making the overall spectrum wider. However, the weights of the latter, though not negligible, are small at the filling fractions considered. This was to be expected since, as is known, higher multipoles become relevant when the distance between particles is less than three-particle radii[21] and this is the average distance in a sample with $f=0.155$. Figure 2 shows the total weight of the new resonances, those not included in Fig. 1(b), as a function of filling fraction. As the figure shows, the influence of high multipoles is less than 6% in the low-filling range we display. At higher fillings multipolar excitations should

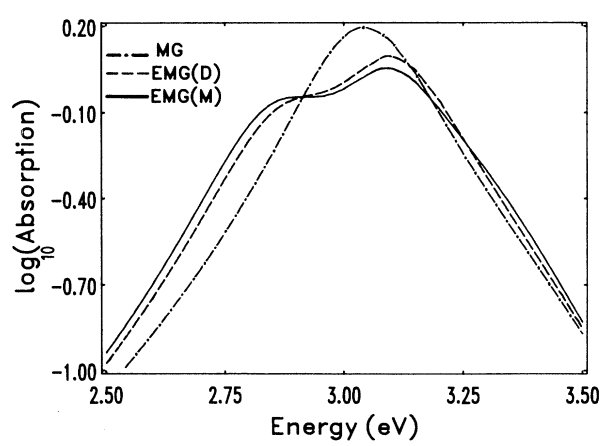

FIG. 3. Absorption spectrum for silver particles in gelatin at filling $f=0.05$. Curves are for the extended Maxwell-Garnett first iterate solution in the dipole (D) and multipole (M) approximations, and for the Maxwell-Garnett (MG) solution.

become more important, yet our results show a decrease in their weight. As discussed earlier, the results are influenced by the approximations made when deriving Eq. (18), and the anomaly may be healed by using a value of γ smaller than one. Based on Figs. (1) and (2) we believe Eq. (19) to be accurate below $f \sim 0.05$.

Figure 3 (dashed line) shows the resonance region obtained using Eqs. (18), (23), and (27) for silver spheres embedded in gelatin[22] at 5% filling, in the dipole ($l=1$ only) approximation. The difference with the MG solution (chain-dashed line) is small due to the small filling fraction, but not negligible. Notice that two peaks are visible and that the resonance region is broader than that given by the MG formula, in agreement with experiment.[23] The multipolar result (solid line) gives a still wider absorption region.

IV. CONCLUSION

We have proposed an iterative scheme that defines successive corrections to the Maxwell-Garnett formula. Our theory is different from previous ones in that we keep the essential mean-field approach that characterizes this latter expression. The standard way of correcting the MG formula is to iterate Eq. (1) many times and keep terms up to some power of the polarizability, usually the second power.[24] In this latter approach to first order in the polarizability one gets, for the effective inclusion polarizability,

$$\alpha_{\text{eff}} = \left[1+\alpha_1\left\langle \sum_j t_{ij} \right\rangle\right]\alpha_1 , \tag{30}$$

which agrees with the MG result (2) only to first order in the filling fraction f. Although this is precisely the order up to which the MG formula is believed to be exact, its results are usually accepted at higher values of f since, save for the width of the Mie resonance, they follow the qualitative features of experiment.[25] As we have shown, our theory improves precisely upon the width of the absorption peak. Also, our theory includes an arbitrary order of multipolar excitations, which as we show give a non-negligible contribution to absorption even at low values of f. We have discussed the first iterate correction only. Higher iterates involve correlations of four- and more-particle correlation functions, which we have not attempted to evaluate. Their effect on the response of the system is currently under study and will be reported elsewhere. Accurate formulas for high-filling fractions would require knowledge of such iterates.

Experiments with argon gas have found an increase in the Clausius-Mossotti (CM) expression $C(f)=v_0(\bar{\epsilon}-1)/f(\bar{\epsilon}+2)$ with density, followed by a decrease.[26,27] In order to check our theory we have calculated this quantity using our Eqs. (18), (20), and (22), keeping up to quadrupolar terms since the highest-pole polarizability we found in the literature for argon was the quadrupole. We use the polarizabilities $\alpha_1 = 1.494$ Å^3 and $\alpha_2 = 1.957$ Å^5 obtained by Lahiri and Mukherji,[28] and the radius $a = 1.54$ Å listed in the Campbell periodic table.[29] Figure 4 shows our results (solid line) together with the experimental results of Refs. 25 (circles) and 26 (squares). The agreement is remarkable in the range shown. While

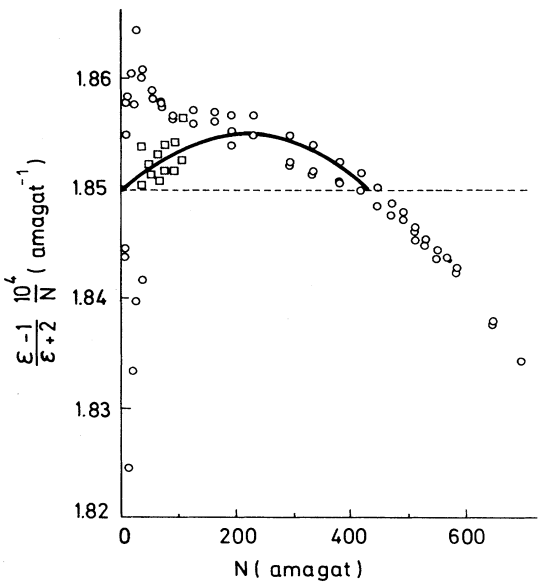

FIG. 4. Clausius-Mossotti expression as a function of density for pure argon. Circles and squares are experimental results from Refs. 26 and 27, respectively. The solid line is our first iterate result keeping up to quadrupolar terms. The horizontal (dashed) line represents the Maxwell-Garnett approximation.

at low density we regard our theory as accurate, at higher densities the agreement with experiment could be fortuitous. In fact the density at which the curve crosses the CM value in Fig. 4 is sensitive to both the values of the polarizabilities and the atomic radius taken in the definition of the filling fraction f. Values found in the literature for the polarizability show discrepancies and the atomic radius is not a well-defined quantity. It is also possible that the actual shape of the experimental curve for argon may be affected by a decrease in the polarizability with density, an effect we have not taken into account.[30,31]

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APPENDIX

Following Felderhof[15] we obtain for a dilute hard-spheres system

$$H_l = 1 - \frac{2l+1}{2^{l-1}} f \sum_{h=0}^{l} C(k,l) F(l-2k) ,$$

where $C(0,l)=C(l,l)=1$ and, for other values of k, $C(k,l)=(2k-1)!!(2l-2k-1)!!/k!(l-k)!$. Also,

$$F(s)=\tfrac{3}{16}(\delta_{s,\pm 2}+2\delta_{s,\pm 1})+\frac{4+2u-\sqrt{3}w}{2(4-s^2)}(1-\delta_{s,\pm 2})-\frac{2-u-\sqrt{3}w}{2(s^2-1)}(1-\delta_{s,\pm 1})-2\frac{2(-1)^s-u+2\sqrt{3}w}{4s^2-1},$$

with $u=\cos(\pi s/3)$ and $w=s\sin(\pi s/3)$.

[1]For a review see, for example, R. Landauer, in *Electrical Transport and Optical Properties of Inhomogeneous Media,* edited by J. C. Garland and D. B. Tanner (AIP, New York, 1978), p. 2.

[2]D. G. Stroud and P. M. Hui, in *Physics and Chemistry of Small Clusters,* edited by P. Jena, B. K. Rao, and S. N. Khanna (Plenum, New York, 1987), p. 547.

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

[4]A. Liebsch and P. Villasenor, Phys. Rev. B **29**, 6907 (1984).

[5]W. L. Mochan and R. G. Barrera, Phys. Rev. B **32**, 4984 (1985); **32**, 4989 (1985).

[6]B. U. Felderhof and R. B. Jones, Z. Phys. B **52**, 43 (1985); **52**, 215 (1985); Phys. Rev. B **39**, 5669 (1989).

[7]V. A. Davis and L. Schwartz, Phys. Rev. B **31**, 5155 (1985).

[8]M. Gomez, L. Fonseca, G. Rodriguez, A. Velasquez, and L. Cruz, Phys. Rev. B **32**, 3429 (1985).

[9]F. Claro, Phys. Rev. B **30**, 4989 (1984); **35**, 406 (1987).

[10]This average depends on the sample geometry and the value here is appropriate for a thin slab only. The numerical factor equals $4\pi/3$ for a thin slab with an in-plane field and zero for a spherical sample. See C. J. F. Bottcher, *Theory of Electric Polarization* (Elsevier, Amsterdam, 1973), paragraph 37.

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

[12]R. Barrera, Guillermo Monsivais, W. Luis Mochan, and E. Anda, Phys. Rev. B **39**, 9998 (1989).

[13]J. G. Kirkwood, J. Chem. Phys. **4**, 592 (1936).

[14]J. Yvon, *Recherches sur la Théorie Cinétique des Liquids* (Hermann, Paris, 1937).

[15]B. U. Felderhof, J. Phys. C **15**, 3943 (1982); **15**, 3953 (1982).

[16]B. R. A. Nijboer and L. Van Hove, Phys. Rev. **85**, 777 (1952).

[17]W. R. Smith and D. Henderson, Mol. Phys. **19**, 411 (1970).

[18]R. Fuchs, Phys. Rev. B **11**, 1732 (1975); in *Electrical Transport and Optical Properties of Inhomogeneous Media,* Ref. 1, p. 276.

[19]D. J. Bergman, Phys. Rep. **43**, 377 (1978).

[20]G. Stell and G. S. Rushbrooke, Chem. Phys. Lett. **52**, 1344 (1984).

[21]F. Claro, Phys. Rev. B **25**, 7875 (1982); Solid State Commun. **49**, 229 (1984).

[22]For the dielectric constant of silver we used the bulk data as given in *Physics Data: Optical Constant of Metals,* edited by J. H. Weaver, C. Krafka, D. W. Lynch, and E. E. Koch (Fachinformations-zentrum, Karlsruhe, 1981), Part II, pp. 46 and 47. For gelatin we took $\epsilon_0=2.37$.

[23]U. Kreibig and L. Genzel, Surf. Sci. **156**, 678 (1985).

[24]For a discussion of various approximations, see the article by J. E. Gubernatis, in *Electrical Transport and Optical Properties of Inhomogeneous Media,* Ref. 1, p. 84. See also Ref. 10.

[25]W. P. Halperin, Rev. Mod. Phys. **58**, 533 (1986).

[26]A. Michels, C. A. ten Seldam, and S. D. J. Overdijk, Physica **17**, 781 (1951).

[27]G. J. Oudemans, Ph.D. thesis, University of Amsterdam, 1967 (unpublished).

[28]J. Lahiri and A. Mukherji, Phys. Rev. **155**, 24 (1967).

[29]M. Clyde Day, Jr. and Joel Selbin, *Theoretical Inorganic Chemistry* (Reinhold, New York, 1962), p. 98.

[30]E. F. O'Brien, V. P. Gutschik, V. McKoy, and J. P. McTague, Phys. Rev. A **8**, 690 (1973).

[31]G. Senatore and K. R. Subbaswamy, Phys. Rev. B **34**, 5754 (1986).