The Optical Response of Composites at Low Filling Fractions: A New Diagrammatic Summation

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Abstract. We extend a previously developed diagrammatic formalism for the calculation of the effective dielectric response of composites, prepared as a collection of small spherical inclusions embedded in an otherwise homogeneous matrix. This is done within the long wavelength, dipolar approximation for a low filling fraction of spheres. We propose a new diagrammatic approximation and we compare our results with recently reported numerical simulations.

I. Introduction

The electromagnetic response of composite media has attracted the attention of many investigators since the pioneering work of JC Maxwell more than a century ago. In his Treatise[1], JC Maxwell poses the problem, and advances an approximate solution, of calculating the effective dc conductivity of a conductor with a well-defined volume fraction of small insulating inclusions. The main difficulty in this problem is to find a proper way of averaging the fields and currents generated by the presence of the inclusions. Furthermore, as the volume fraction of the inclusions increases, the system goes through a metal-insulator transition which nowdays is being treated with percolation theory[2]. A well documented review of the historical development of this problem can be found in the work of Landauer[3]. Here we will be interested not in the dc response but rather in the electromagnetic response of the composite at finite frequencies. We will consider an homogeneous matrix filled with identical spherical inclusions with radius much less than the wavelength of the electromagnetic radiation. The effective dielectric response of this system, as a function of frequency and filling fraction, was first calculated, within the mean field approximation (MFA), by JC Maxwell Garnett[4] as early as 1904. His result becomes completely equivalent to the Clausius-Mossotti or Lorentz-Lorenz relation[5], which links the dielectric response of a fluid with the polarizability and density of its molecules, if the molecules are regarded as polarizable spheres embedded in vacuum.

In the MFA one assumes that in the presence of a long-wavelength external electric field all the spheres acquire exactly the same induced dipole moment which is taken equal to the average dipole moment and is calculated self-consistently. Therefore any improvement upon MFA has to include, in some way or another, the effect of the fluctuations around the average of the induced dipole moments. If the spheres were arranged in a periodic lattice, then every sphere would have exactly the same surroundings and all of them would acquire, in the long wavelength limits, the same induced dipole moment: there would be no fluctuations. In this case, the MFA yields an exact result[5] and we conclude that it is the disorder in the location of the spheres the source of the dipolar fluctuations.

The problem of considering the effects of disorder and consequently the effects of dipolar fluctuations in the dielectric response of a composite has also a long history. There have been many diffe-

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rent types of approaches to this problem: density expansions[6], linked cluster expansions[7], perturbation expansions[8], integral equations[9], multiple-scattering methods[10], intuitive arguments[11,12], diagrammatic theories[13], location of bounds[14], numerical simulations[15,16], etc. In order to decide the benefits of each of these approaches, one has to compare their results with the experimental ones. Due to the fact that the experiments performed up to now. do not resemble properly the models used in the theoretical work, the comparison between theory and experiment has been a painful process. The preparation of homogeneous and isotropic samples, with a well-defined filling fraction of identical spheres with radius in the nanometer range, has not been an easy task. Problems like particle clustering, a distribution of shapes and sizes, and an anomalous high density of dislocations in the small particles have obscured a clear interpretation of the effects of disorder in the optical experiments. On the other hand, as pointed out by several authors,[9,12] beyond MFA the effective dielectric response of a composite depends not only on the filling fraction of the spheres but also on the structure of their two-and three-particle distribution functions. In other words, different types of disorder will lead to different results. Now, since most of the experimentalist do not report the actual distribution functions of the inclusions in their samples, this yields to another source of confusion; this might explain some of the discrepancies[17] found in experiments performed in differently prepared samples.

In this work, we reformulate a diagrammatic approach reported earlier,[13] for the calculation of the effective dielectric response of a composite prepared as mixture of identical spheres embedded in an otherwise homogeneous matrix. This formalism is valid in the low-density regime where all the m-th particle distribution functions of the spheres can be approximated by unsymmetrized products of two-particle distribution functions. After setting up the formalism, we extend a previously performed diagrammatic summation[13] by including an infinite set of diagrams which should be important at low densities. Then we compare our results with the only "experiments" that, we believe, will give the fairest possible comparison: the numerical simulations recently performed by Cichocki and Felderhof[16] for a collection of Drude spheres within the dipolar approximation. The structure of the paper is as follows: in section II we develop the theoretical framework and section III is devoted to results, comments and conclusions.

II. Formalism

Lets consider an homogeneous and isotropic ensemble of $N \gg 1$ spheres of radius a and dielectric function ϵ_m embedded in a host medium with dielectric function ϵ_h. The system is in the presence of a space- and time-dependent external electric field which oscillates with frequency ω and wave-vector $\mathbf{q}$. Furthermore, we assume that $qa \ll 1$ thus the induced interaction between the spheres can be taken in the quasi-static limit. The local electric field induces an effective dipole $\mathbf{p}_i$ on the i-th sphere given by

$$\mathbf{p}_i(\omega) = \alpha(\omega)[\mathbf{E}_i^{\circ} + \sum_j \overleftrightarrow{\mathbf{t}}_{ij} \cdot \mathbf{p}_j(\omega)], \tag{1}$$

where $\mathbf{E}_i^{\circ}$ is the electric field induced in the medium at $\mathbf{R}_i$ in the absence of the spheres, $\alpha(\omega) = a^3[\epsilon_m(\omega) - \epsilon_h(\omega)]/[\epsilon_m(\omega) + 2\epsilon_h(\omega)]$ is the effective polarizability of an isolated sphere in the medium and

$$\overleftrightarrow{\mathbf{t}}_{ij} = (1 - \delta_{ij})\nabla_i\nabla_j(1/R_{ij}) \tag{2}$$

is the dipole-dipole interaction tensor in the quasi-static limit. Here $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$ and δ_{ij} is the Kronecker delta.

The polarization is then defined as the average dipole moment per unit volume and it can be related to the effective dielectric response ϵ_{eff} of the system through[12]

$$\frac{\epsilon_h(\omega)}{\epsilon_{eff}(\omega)} = 1 - 4\pi\epsilon_h(\omega)\chi^{ex,\ell}(q \to 0, \omega), \tag{3a}$$

where $\overleftrightarrow{\chi}^{ex}(\mathbf{q},\omega)$ is the external susceptibility defined by

$$n < \mathbf{p} > (\mathbf{q},\omega) = \overleftrightarrow{\chi}^{ex}(\mathbf{q},\omega) \cdot \mathbf{E}^{ex}(\mathbf{q},\omega), \tag{3b}$$

and the superscript ℓ denotes longitudinal projection. Here $\mathbf{E}^{ex}(\mathbf{q},\omega)$ and $n < \mathbf{p} > (\mathbf{q},\omega)$ are the Fourier transforms of the external field and the average polarization field, respectively, n is the number density of spheres and $<>$ means ensemble average. The appearance of the longitudinal projection, is only a matter of convenience which takes advantage of the fact that the $q \to 0$ limit of either the longitudinal or transverse response coincide. The limiting process ($q \to 0$) is necessary in order to get around the evaluation of a few non-convergent integrals.[12]

We consider that the system is excited by a longitudinal external field of the form $\mathbf{E}^{ex} = \hat{q}E^{ex}e^{i(\mathbf{q}\cdot\mathbf{r}-\omega t)}$ and we rewrite Eq. (1) as

$$\mathbf{P}_i = \alpha(\mathbf{E}_L + \sum_j \Delta \overleftrightarrow{\mathbf{T}}_j \cdot \mathbf{P}_j), \tag{4}$$

where $\mathbf{E}_L = \hat{q}E^{ex}/\epsilon_h + N < \overleftrightarrow{\mathbf{T}} > \cdot < \mathbf{P} >$ is the Lorentz field. Here

$$\mathbf{P}_i = \mathbf{p}_i e^{-\mathbf{q}\cdot\mathbf{R}_i} \qquad \text{and} \qquad \overleftrightarrow{\mathbf{T}}_{ij} = \overleftrightarrow{\mathbf{t}}_{ij} e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)} \tag{5}$$

are so defined in order to get rid of trivial exponential factors, and N is the total number of spheres.

The formal solution of Eq. (4) is

$$\mathbf{P}_i = \alpha \sum_j (\overleftrightarrow{\mathbf{V}}^{-1})_{ij} \cdot \mathbf{E}_L, \tag{6a}$$

where

$$\overleftrightarrow{\mathbf{V}}_{ij} = \mathbf{1}\delta_{ij} - \alpha \Delta \mathbf{T}_{ij} \tag{6b}$$

and $\mathbf{1}$ is the unit matrix. We now define the Lorentz susceptibility as

$$n < \mathbf{P} > (q,\omega) = \overleftrightarrow{\chi}^{L}(q,\omega) \cdot \mathbf{E}^{L}(q,\omega), \tag{7}$$

and it can be easily shown that the effective dielectric response ϵ_{eff} is given by

$$\epsilon_{eff} = \frac{1 + 2f\hat{\alpha}^*}{1 - f\hat{\alpha}^*}, \tag{8a}$$

where $f = n4\pi a^3/3$ is the volume fraction of spheres, $\hat{\alpha}^* = \alpha^*/a^3$ and

$$n\alpha^* = \chi_L^{\ell}(q \to 0,\omega) = lim_{q\to 0} < \sum_j (\overleftrightarrow{\mathbf{V}}^{-1})_{ij}^{\ell} > . \tag{8b}$$

Eq. (8a) is an exact equation and it has the same functional form as the Maxwell Garnett formula[4] (or Clausius-Mossotti relation[5]), except that the bare polarizability α is replaced by a dressed polarizability α^* which is proportional to the dipolar response of the sphere to the Lorentz field rather than to the local field.

According to Eq. (8b) the calculation of α^* requires the evaluation of the ensemble average of the inverse of matrix $\overleftrightarrow{\mathbf{V}}_{ij}$, defined in Eq. (6b), which in the thermodynamic limit becomes an infinite matrix with stochastic elements. This is obviously a complicated problem. We perform instead a series representation of the inverse of $\overleftrightarrow{\mathbf{V}}_{ij}$ in powers of $\alpha\Delta\overleftrightarrow{\mathbf{T}}_{ij}$, that is

$$\sum_j (\overleftrightarrow{\mathbf{V}}^{-1})_{ij} = 1 + \alpha \sum_j \Delta \overleftrightarrow{\mathbf{T}}_{ij} + \alpha^2 \sum_{jk} \Delta \overleftrightarrow{\mathbf{T}}_{ik} \cdot \Delta \overleftrightarrow{\mathbf{T}}_{kj} + ..., \tag{9}$$

we then take an ensemble average assuming that in the low-density regime the s-particle distribution function can be factored as unsymmetrized sequential products of two-particle distribution functions, that is

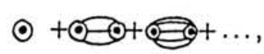
$$\rho^{(s)}(\mathbf{R}_1,\ldots,\mathbf{R}_s) = \prod_{\substack{ij \\ (j=i+1)}} \rho^{(2)}(R_{ij}). \tag{10}$$

The end result is a series representation of α^* which can cast in a diagrammatic form as

$\xi \equiv \frac{\alpha^*}{\alpha} =$  (11)

where each diagram in this series is irreducible; this means that it cannot be split into two independent diagrams by cutting a single line. The precise definition of each diagram is given in Ref. 13; here we will only say that in order to draw a diagram one cannot lift the pencil from the paper, that each line carries a factor α, each black dot carries a factor n, the other factor is an integral over the coordinates of the particles depicted by black dots, being the white dot the reference sphere. The integrand contains the longitudinal projection of the scalar product of r tensors T_{ij} and the s-particle distribution functions where r is the total number of lines and s is the total number of dots (blacks and white).

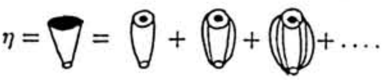
In this work we propose the following diagrammatic approximation:

$\xi =$  (12a)

where

$\Delta =$  (12b)

and

$\eta =$  (12c)

This is an extension of the renormalized polarizability theory (RPT) developed in Ref. 13, which only considered

$\xi = \Delta$ and $\eta =$  . (13)

Here we are including diagrams that, we believe, should be important in the low-density regime because they take full account of the interaction between only two renormalized dots. For example, if we replace the renormalized dots by unrenormalized ones, we then recover the two-particle-linked-cluster-expansion results of Felderhof, Ford and Cohen[18].

The solution of the system of diagrammatic equations given by Eq. (12) yields to

$$\xi = \Delta + \frac{1}{3} f \hat{\alpha} \Delta^2 log(\frac{64 - \hat{\alpha}^2\Delta^2}{64 - 4\hat{\alpha}^2\Delta^2}) \tag{14a}$$

and

$$\Delta^{-1} = 1 - \frac{1}{3} f \hat{\alpha}\sqrt{\Delta} log \frac{(4+\hat{\alpha}\sqrt{\Delta})(8+\hat{\alpha}\sqrt{\Delta})}{(4-\hat{\alpha}\sqrt{\Delta})(8-\hat{\alpha}\sqrt{\Delta})}, \tag{14b}$$

which have to be solved self-consistently. Here $\hat{\alpha} \equiv \alpha/a^3$.

III. Results and Discussion

We present our results in terms of the Bergman's spectral representation of the effective dielectric function. It has been shown[19] that ϵ_{eff} can be written as

$$\epsilon_{eff} = 1 - f \int_{o}^{1} \frac{g(u)}{t-u} du, \tag{15a}$$

where

$$t = \frac{1}{1 - \epsilon_m/\epsilon_h} \quad . \tag{15b}$$

The spectral representation is a normal-mode representation in a normal-mode variable u, where the frequency of the modes is determined by the pole location ($t = u$) and $g(u)$ is their strength. The main advantage of this representation is that $g(u)$ does not depend on the physical nature of the elements which constitute the composite but only the geometrical location of the spheres.

In Fig. 1 we show the spectral function $g(u)$, as a function of u, for volume fractions of 0.1, 0.2 and 0.3, calculated with Eq. (14) (solid line), with RPT as defined in Eq. (13) (broken line) and the "experimental" results of Cichocki and Felderhof[16] (dotted line). For the two-particle distribution function, here we used a simple step function $\theta(R_{12} - 2a)$ which should be valid in the low density regime. We can see that for $f = 0.1$ we obtain an excellent agreement with "experiment" and the difference between these new results and RPT clearly demonstrates the importance of the additional class of diagrams contained in the present approximation. For $f = 0.2$ the agreement between theory and experiment is not so good and our new results lie now something in between the "experiment" and RPT. Finally for $f = 0.3$ our new results resemble very much RPT but the agreement with experiment is far from being good. Therefore, for such high filling fractions the effect of the additional class of diagrams is indeed negligible. These corroborates our earlier assertion about the importance of this class of diagrams in the low-density regime. The disagreement between theory and "experiment", at higher

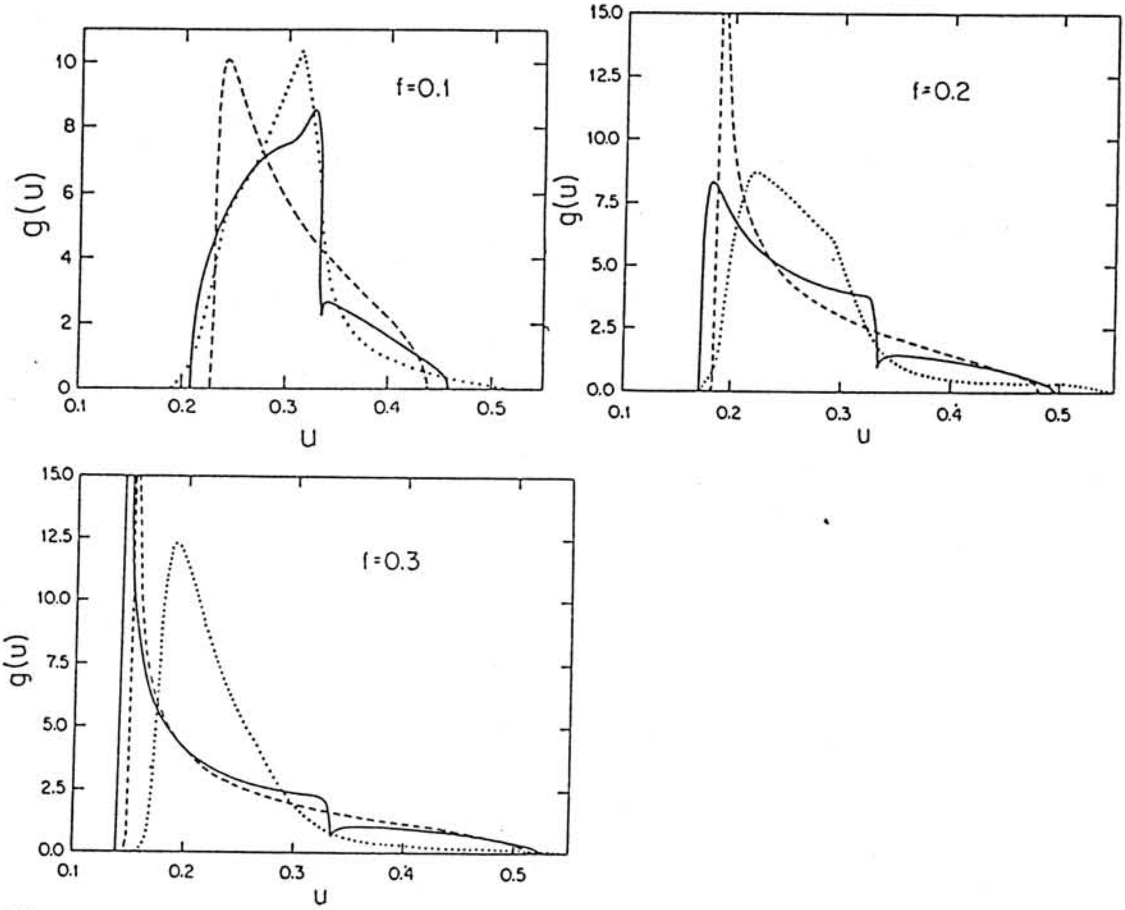


Fig 1. The spectral function $g(u)$ as a function of u for volume fractions of 0.1, 0.2 and 0.3, calculated with Eq. (14) (solid line), with RPT as defined in Eq. (13) (broken line) and the "experimental" results of Cichocki and Felderhof (dotted line).

volume fractions, can be explained by noticing that in this regime the factorization of the distribution functions, as given by Eq. (10), is no longer valid. Also, at high filling fractions, $\rho^{(2)}(R_{12})$ is not a simple step function any more and better approximations, something like Percus-Yevick[20], should be used. Work along these lines is now in progress and it will be reported elsewhere.

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