Effective Dielectric Response of Composites: A New Diagrammatic Approach

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INTRODUCTION

The interest in the dielectric response of composites has been renewed by the application of a wide variety of mathematical techniques borrowed from other fields of physics. The use of these materials as selective absorbers in solar energy devices [1] and the study of fluids in rocks and porous materials for oil exploration [2], has also contributed to the revival of the actual research in composites. It has been recognized that the topology of the composite plays a crucial role in the response of the system to an external perturbation [3]. Here we treat the dielectric response of a system composed by spherical inclusions located at random in an otherwise homogeneous matrix. Although the problem was posed more than a century ago [4] only until recently, theories beyond the mean field approximation started to be developed. Multiple scattering theory [5], cluster expansions [6], lattice gas models [7], numerical simulations [8], homogenization theory [9], renormalization [10] and diagrammatic techniques [11] have been the main ingredients of the recently developed theories. Comparison with experiment has been troublesome because the experiments have been done in samples with a poorly characterized microstructure. Also, the generalization of the theories applicable to models which described better the actual experimental conditions, is not straightforward. This situation requires theoretical work in two different directions. First, the development of a theory which retains the main aspects of the problem but that is simple enough to be extendable to more complicated situations *i.e.* spheres with a given distribution of radii, the inclusion of multipolar interactions, the effects of clustering and dimensionality and systems of particles with different shapes. On the other hand, it is also necessary to develop, even in the simplest model, a systematic approach which allows to make

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an adequate comparison of the different types of calculations and which generates a scheme for obtaining better and better approximations. Here we will present a new diagrammatic approach for the calculation of the effective dielectric response of a composite which encompasses, in a certain way, both of these directions. It can also be viewed as a reformulation of the diagrammatic approach developed in Ref. 11

Formalism

Lets consider an homogeneous an isotropic ensemble of $N \gg 1$ identical spheres, with radius a_o and dielectric functions ϵ_s, located at random positions $\{\mathbf{R}_i\}$ within a homogeneous matrix with dielectric function ϵ_h. The system is in the presence of a position dependent external field $\mathbf{E}^{ex}(\mathbf{r},\omega)$ oscillating at frequency ω and with wavelength much larger than a_o and the typical separation between spheres. The dipolar moment $\mathbf{p}_i$ induced at the i-th sphere is then given by

$$\mathbf{p}_i = \alpha[\mathbf{E}_o(\mathbf{R}_i) + \sum \overleftrightarrow{\mathbf{t}}_{ij} \cdot \mathbf{p}_j] \tag{1a}$$

where $\mathbf{E}_o$ is the electric field in the absence of the spheres,

$$\alpha = a_o^3(\epsilon_s - \epsilon_h)/(\epsilon_s + 2\epsilon_h) \tag{1b}$$

is the effective polarizability of each sphere,

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

is the dipole-dipole interaction tensor in the quasi-static approximation and we omit the explicit dependence on ω.

The induced average polarization per unit volume (polarization field)

$$\langle \sum_i \mathbf{p}_i\delta(\mathbf{r} - \mathbf{R}_i)\rangle \equiv n\mathbf{p}(\mathbf{r}) \tag{2}$$

is related to the macroscopic (or effective) dielectric response of the system ϵ_M by [10]

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

or by

$$\frac{\epsilon_M(\omega)}{\epsilon_h(\omega)} = 1 + 4\pi\chi^{ex,t}(\mathbf{q} \to 0, \omega) \tag{4}$$

where n is the number density of spheres, $\langle ... \rangle$ means ensemble average and $\overleftrightarrow{\chi}^{ex}(q, \omega)$ is the Fourier transform of the external susceptibility, defined through

$$n\mathbf{p}(\mathbf{q}, \omega) = \overleftrightarrow{\chi}^{ex}(\mathbf{q}, \omega) \cdot \mathbf{E}^{ex}(\mathbf{q}, \omega). \tag{5}$$

Here $\mathbf{p}(\mathbf{q})$ is the spatial Fourier transform of $\mathbf{p}(\mathbf{r})$ and the superscripts ℓ and t mean longitudinal and transverse projections, respectively. We have used the fact that the $\mathbf{q} \to 0$ limit of ϵ_M^ℓ and ϵ_M^t of a system which is homogeneous, isotropic and invariant under inversions, are identical.

For the purpose of calculation we choose Eq. (3). Furthermore, since there is no macroscopic coupling between transverse and longitudinal fields, due to the symmetry properties of the ensemble, it is sufficient to consider only a single Fourier longitudinal component of the external field, that is

$$\mathbf{E}^{ex}(\mathbf{r}) = \hat{\mathbf{q}} E^{ex} e^{i\mathbf{q}\cdot\mathbf{r}}, \tag{6}$$

where $\mathbf{q}$ is the wavevector, $\hat{\mathbf{q}} = \mathbf{q}/q$ and the explicit dependence on ω has been omitted. Then by substituting Eq. (6) into Eq. (1a) one obtains

$$\mathbf{P}_i(\mathbf{q}) = \alpha[\hat{\mathbf{q}} E^{ex}/\epsilon_h + \sum_j \overleftrightarrow{\mathbf{T}}_{ij}(\mathbf{q}) \cdot \mathbf{P}_j(\mathbf{q})] \tag{7a}$$

where

$$\mathbf{P}_i(\mathbf{q}) = \mathbf{p}_i e^{-i\mathbf{q}\cdot\mathbf{R}_i}, \tag{7b}$$

$$\overleftrightarrow{\mathbf{T}}_{ij}(\mathbf{q}) = \overleftrightarrow{\mathbf{t}}_{ij} e^{-i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_j)}, \tag{7c}$$

have been defined only in order to remove the trivial exponential factors. The Fourier transform of the polarization field is given by

$$\mathbf{p}(\mathbf{q}) = \langle \mathbf{P}_i(q) \rangle \equiv \langle \mathbf{P} \rangle \tag{8}$$

where we have assumed that the volume and ensemble averages are identical. Also, the ensemble average of $\mathbf{P}_i$ is independent of i due to the translational symmetry of the ensemble.

We now add and substract in the rhs of Eq. (7a) the term

$$\sum_j \overleftrightarrow{\mathbf{T}}_{ij} \cdot \langle \mathbf{P}_j \rangle \equiv N\langle \mathbf{T} \rangle \cdot \langle \mathbf{P} \rangle \text{and write}$$

$$\mathbf{P}_i = \alpha[\mathbf{E}_L + \sum_j \Delta \overleftrightarrow{\mathbf{T}}_{ij} \cdot \mathbf{P}_j], \tag{9a}$$

where

$$\mathbf{E}_L \equiv \hat{\mathbf{q}} E^{ex}/\epsilon_h + N \langle \mathbf{T} \rangle \cdot \langle \mathbf{P} \rangle \tag{9b}$$

is called the Lorentz field,

$$\Delta \overleftrightarrow{\mathbf{T}}_{ij} \equiv \overleftrightarrow{\mathbf{T}}_{ij} - \langle \overleftrightarrow{\mathbf{T}} \rangle, \tag{9c}$$

the relation $\langle \overleftrightarrow{\mathbf{T}} \rangle = (1/N) \sum_j \overleftrightarrow{\mathbf{T}}_{ij}$ has been used and the explicit dependence of **q** has been omitted. Here N is the total number of spheres.

The formal solution of Eq. (7) is immediately given by

$$\mathbf{P}_i = \alpha \sum_j (\overleftrightarrow{\mathbf{V}}^{-1})_{ij} \cdot \mathbf{E}^L, \tag{10a}$$

where $(\overleftrightarrow{\mathbf{V}}^{-1})_{ij}$ is the ij-th element of the inverse operator $\overleftrightarrow{\mathbf{V}}$, whose elements are defined by

$$\overleftrightarrow{\mathbf{V}}_{ij} = \overleftrightarrow{\mathbf{1}} \delta_{ij} - \alpha \Delta \overleftrightarrow{\mathbf{T}}_{ij}. \tag{10b}$$

We now take ensemble average and longitudinal projection of Eq. (10a) in order to obtain

$$n \langle P \rangle^{\ell} = n\alpha \langle \sum_j (V^{-1})^{\ell}_{ij} \rangle E^{\ell}_L \equiv \chi^{L,\ell} E^{\ell}_L, \tag{11}$$

where $\overleftrightarrow{\chi}^L$ is called the Lorentz susceptibility. It can be shown [10] that

$$\overleftrightarrow{\mathbf{E}}_L = \hat{\mathbf{q}}(E^{ex}/\epsilon_h - \frac{8\pi}{3} n \langle \mathbf{P} \rangle), \tag{12}$$

and using this result it can be easily proved that

$$\chi^{ex,\ell}(\mathbf{q},\omega) = \frac{\chi^{L,\ell}(\mathbf{q},\omega)}{1 + \frac{8\pi}{3}\chi^{L,\ell}(\mathbf{q},\omega)}. \tag{13}$$

We define a renormalized polarizability α^* as

$$n\alpha^*(\omega) \equiv \chi^{L,\ell}(\mathbf{q} \to 0, \omega) \tag{14}$$

and substituting Eqs. (13) and (14) into Eq. (3) we finally get

$$\frac{\epsilon_M - \epsilon_h}{\epsilon_M + 2\epsilon_h} = f\hat{\alpha}^*, \tag{15}$$

where $\hat{\alpha}^* \equiv \hat{\alpha}/a_o^3$ and $f \equiv n4\pi a_o^3/3$ is the volume fraction occupied by the spheres. We want to emphasize that Eq. (15) is an it exact expression. It has the same functional form as the Maxwell-Garnett mean field approximation (MGT) [12] but with a renormalized polarizability $\hat{\alpha}^*$ instead of the bare polarizability $\hat{\alpha} \equiv \alpha/a_o^3$.

We now use Eq. (11) and a series representation of its inverse in order to write

$$\sum_j (\overleftrightarrow{\mathbf{V}}^{-1})_{ij} = \overleftrightarrow{\mathbf{1}} + \alpha \sum_j \Delta \overleftrightarrow{\mathbf{T}}_{ij} + \alpha^2 \sum_{jk} \Delta \overleftrightarrow{\mathbf{T}}_{ik} \cdot \Delta \overleftrightarrow{\mathbf{T}}_{kj} + ... \tag{16}$$

Then we take the longitudinal projection and the ensemble average of Eq. (16) using the following simplifying assumption

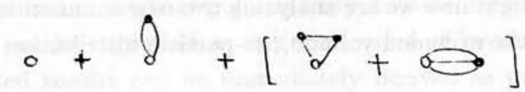
$$\rho^{(m)}(\mathbf{R}_1, ..., \mathbf{R}_m) = \Pi_{i,j}\rho^{(2)}(R_{ij}), \tag{17}$$

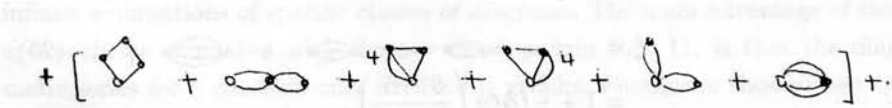
where $\rho^{(m)}$ is the m-particle distribution function as defined in Ref. 11 and the product is over all the open sequential pairs. The result can be expressed in the language of diagrams through the definitions introduced in Ref. 11, *i.e.*

$$\equiv \lim_{\mathbf{q}\to 0} \int \hat{\mathbf{q}} \cdot \overleftrightarrow{\mathbf{T}}_{12} \cdot \overleftrightarrow{\mathbf{T}}_{21} \cdot \hat{q}\rho^{(2)}(R_{12}) d^3R_2. \tag{18}$$

We obtain

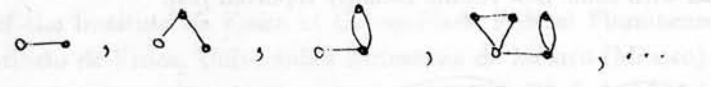
$$\xi \equiv \frac{\alpha^*}{\alpha} = \sum_r \sum_s L(r,s) =$$





(19)

where $L(r,s)$ are the sum of all renormalized graphs. That is all graphs with r lines and s black dots which can be drawn using the same rules given in Ref. 11 but omitting all graphs that can be disjoint into two separate graphs by cutting a single line between two dots. For example, the following graphs are omitted in $L(r,s)$:



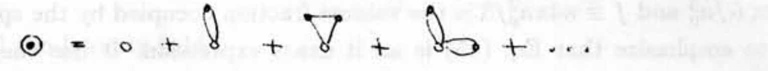
(20)

Lets recall that each graph is proportional to $\hat{\alpha}^r f^s$, thus the graphs in square brackets in Eq. (1a) correspond to an expansion in powers of $\hat{\alpha}$.

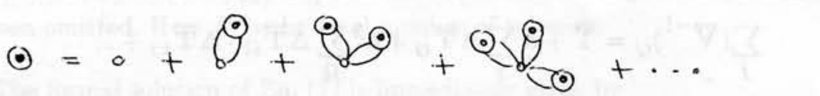
If now we take

(i) $\xi = \circ \equiv 1$ (21)

we recover MGT.

(ii) $\xi =$  (22)

that is the sum of all simply-connected rings, we recover the results of Ref. 11. We recollect that a cruder approximation can be constructed by taking ξ as the solution of

 (23)

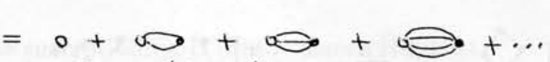
which yields $\hat{\alpha}^*$ in a simple analytical form [11]

$$\frac{\hat{\alpha}^*}{2} = 1 - \frac{\sqrt{1 - f_e \hat{\alpha}^2}}{f_e \hat{\alpha}} \tag{24}$$

This approximation has also an intuitive interpretation [10] which allows a straightforward generalization to system of spheres with a given distribution of radii [13] an also to more complicated systems.

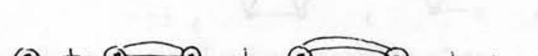
Right now we are analyzing two new summations of specific classes of diagrams using the excluded volume two-particle distribution function:

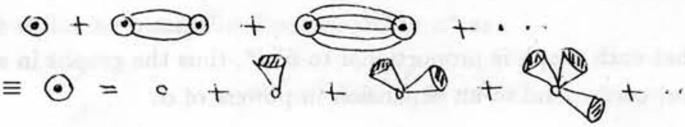
(i)

$\xi =$  (25)

$$= 1 + \frac{2}{3} f \hat{\alpha} \ell n \left(\frac{8 + \hat{\alpha}}{8 - 2\hat{\alpha}} \right).$$

This expression can be considered a low density approximation because it takes the lowest number of black dots (one) for a given number of lines. It also agrees with Eq. (18) of Ref. 11 where a similar summation was also performed, and it should be now compared with some new results recently reported [14].

(ii) $\xi =$  (26a)

$\Delta \equiv$  (26b)

 (26c)

which leads to

$$\xi = \Delta + \frac{1}{3} f \hat{\alpha} \Delta^2 \left[\ell n \frac{64 - \hat{\alpha}^2 \Delta^2}{64 - 4\hat{\alpha}^2 \Delta^2} \right] \tag{27a}$$

where Δ is the self-consistent solution of the following equation:

$$\Delta = \left[1 - \frac{1}{3} f \hat{\alpha} \sqrt{\Delta} \ell n \frac{(4 + \hat{\alpha}\sqrt{\Delta})(8 + \hat{\alpha}\sqrt{\Delta})}{(4 - \hat{\alpha}\sqrt{\Delta})(8 - \hat{\alpha}\sqrt{\Delta})} \right]^{-1} \tag{27b}$$

If we now compare Eq. (26) with Eqs. (25) and (27) of Ref. 11, we can see that Eq. (31) of this same reference is obtained by taking $\xi = \Delta$. This approximation can be considered to be valid in the intermediate density regime, because the graphs included in Eq. (26b) have more black dots, for a given number of lines, than other possible graphs. Since in [Eq. (26)] we are also considering graphs of the type shown in Eq. (25), we expect that this new approximation should be good for densities in the whole range, from low to intermediate. The numerical results as well as the discussion of this new approximations will be reported elsewhere.

In conclusion, we have developed a new diagrammatic approach for the calculation of the effective dielectric response ϵ_M of a system of identical spheres embedded in a homogeneous matrix (within the dipolar long-wavelength approximation). We obtain an expression for ϵ_M which has the same analytical form as MGT but with a renormalized polarizability $\hat{\alpha}^*$ instead of the bare polarizability $\hat{\alpha}$. We showed that this renormalized polarizability can be expressed as an infinite sum of irreducible diagrams and previously reported results can be immediately derived as partial infinite summations of specific classes of diagrams. The main advantage of this new approach, as compared with the one developed in Ref. 11, is that the diagrammatic series for ξ contains only irreducible graphs. Finally we showed two specific ways of carrying out new type of summations applicable for low and intermediate concentrations.

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