DIELECTRIC RESPONSE OF A CHAIN OF DISORDERED POLARIZABLE SPHERES: NUMERICAL SIMULATION AND THEORY

PEDRO VILLASEÑOR-GONZALEZ[†], CECILIA NOGUEZ*[‡] AND RUBEN G. BARRERA[‡]

† Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, México.
* Facultad de Ciencias, Universidad Nacional Autónoma de México, 01000 México D.F., México.
‡ Instituto de Física, Universidad Nacional Autónoma de México, Apdo. Postal 20-364, 01000 México D.F., México.

ABSTRACT

We applied to a one-dimensional system (1D) a recently developed diagrammatic formalism, in order to calculate the effective dielectric response of a chain of polarizable spheres embedded in an homogeneous host. The effective response is calculated within the dipolar, quasi-static approximation, through the summation of selected classes of diagrams. We compared our results with a numerical simulation, where the position of each sphere was generated at random and the induced dipole moment of each sphere was calculated by solving a set of linear equations through matrix inversion and using periodic boundary conditions.

INTRODUCTION

The optical properties of a composite systems are determined through the knowledge of its dielectric response. Here we are interested in composites with a separate-grain topology and the simplest and most recurrent [1] 3D system is the one containing a homogeneous matrix within identical spherical inclusions. A pioneering work towards the calculation of the effective dielectric response of this system was done at the beginning of this century by JC Maxwell Garnett [2]. In his work he assumed that (i) only the dipolar moment is induced at each sphere (dipolar-approximation) and that (ii) the local field is the same in all the spheres and equal to its average (mean-field-approximation). The objective of actual theories is to improve the mean-field-approximation, thus we are interested in taking into account the fluctuations of the local field and exploring their effects on the effective dielectric response. One source of these fluctuations is the disorder in the position of the spheres and its mathematical treatment has been the main subject of recently developed theories. An ample variety of procedures like multiple scattering [3], cluster expansions [4], numerical simulations [5], renormalization [6], diagrammatic techniques [7,8], etc., have been devised in order to calculate the effective dielectric response of a disordered system.

On the other hand, the comparision with experiment has been a painful task because the samples used by the experimentalist do not resemble properly the models used in the theoretical work. Problems like clustering and distributions of shapes and sizes of the inclusions make the interpretation of the absorption spectra more difficult. Moreover until recently, the experimentalists have not been aware of the need to report more information about microstructure of their samples. Therefore, the only fair test of the present theories is the comparision of their results with recently reported numerical simulations; as was done in Ref. [8].

In general, one-dimensional (1D) systems have been simpler to solve than those in 3D. Moreover, the random 1D chain has been a classic test for models in different fields of theoretical physics. Nevertheless, our main interest in dealing here with a 1D chain is to suppress a strong assumption used in the diagrammatic approach of Ref. [8] about the unsymmetrized factorization of the m−particle distribution function, in order to test the validity of the summation of the different classes of diagrams.

FORMALISM

We consider a linear chain of length L of $N \gg 1$ identical spheres located at random positions $\{\vec{R}_i\}$. Each sphere has a radius a and dielectric function ϵ_s. The chain

is within a homogeneous host medium with dielectric constant ϵ_h. We excite the system with an external electric field $\vec{E}^{ex}(\omega)$ oscillating with frequency ω and wavelength much larger than a and the typical separation between the spheres. Under this conditions, the interaction between the spheres can be taken in the quasi-static limit. In the dipolar approximation, the local field induces an effective dipole moment given by

$$\vec{p}_i(\omega) = \alpha(\omega)\Big[\vec{E}_i^0 + \sum_j \overleftrightarrow{t}_{ij} \cdot \vec{p}_j\Big], \tag{1}$$

where $\alpha(\omega) = a^3(\epsilon_s(\omega) - \epsilon_h(\omega))/(\epsilon_s(\omega) + 2\epsilon_h(\omega))$ is the polarizability of an isolated sphere, $\vec{E}_i^0 = \vec{E}_i^{ex}/\epsilon_h$ is the electric field induced in the medium at $\vec{R}_i$ in the absence of the spheres and $\overleftrightarrow{t}_{ij} = (1 - \delta_{ij})\vec{\nabla}_i\vec{\nabla}_j(1/R_{ij})$ is the dipole-dipole interaction tensor. The macroscopic external susceptibility is defined by $n < P >\equiv \overleftrightarrow{\chi}_{ex} \cdot \vec{E}_{ex}$, where $< P >$ is the average dipole moment and n is the number density. Following the same approach as in Ref. [8] the components of the effective macroscopic susceptibility along its principal axis is given by

$$\chi_{ex}^{\gamma\gamma} = \frac{1}{\pi}\frac{8f\hat{\alpha}\xi^\gamma}{8 - f\hat{\alpha}\xi^\gamma} \tag{2}$$

where, γ denotes the principal axis along the longitudinal and the transversal directions with respect to the chain axis, $f = 2Na/L$ is the filling fraction, $\hat{\alpha} = \alpha/a^3$,

$$\xi^\gamma \equiv \langle \sum_j (V^{-1})_{ij}^\gamma \rangle, \tag{3}$$

$< \cdots >$ means ensemble average. Here

$$\overleftrightarrow{V}_{ij} \equiv \delta_{ij} - \alpha\Delta\overleftrightarrow{t}_{ij} \tag{4}$$

and $\Delta\overleftrightarrow{t}_{ij} = \overleftrightarrow{t}_{ij} - \langle\overleftrightarrow{t}\rangle$. We use Eq. (4) and a series representation of its inverse, in order to write

$$\sum_j (V^{-1})_{ij}^\gamma = 1 + \alpha\sum_j \Delta t_{ij}^\gamma + \alpha^2\sum_{jk} \Delta t_{ij}^\gamma \cdot \Delta t_{jk}^\gamma + \cdots . \tag{5}$$

In order to take the ensemble average of Eq. (5) we require the knowledge of all the m-particle distribution function $\rho^{(m)}$ [7]. Since in 1D $\rho^{(m)}$ can be expressed as an unsymmetrized sequential products $\rho^{(2)}$'s [9], i.e. $\rho^{(3)}(\vec{R}_1, \vec{R}_2, \vec{R}_3) = \rho^{(2)}(R_{12})\rho^{(2)}(R_{23})$ the ensemble average of Eq. (5) can be written as an infinite sum which can be expressed in the language of diagrams through the followings definitions:

$$\circ \quad \equiv 1 \tag{6a}$$

$$\wedge \equiv \alpha^2\frac{N^2}{L^2}\int t_{12}^\gamma t_{23}^\gamma \rho^{(2)}(R_{12})\rho^{(2)}(R_{23})dR_2 dR_3, \tag{6b}$$

$$\multimap \equiv \alpha^2\frac{N}{L}\int t_{12}^\gamma t_{21}^\gamma \rho^{(2)}(R_{12})dR_2, \tag{6c}$$

We obtain

$$\xi^\gamma = \sum_r \sum_s L(r,s) \equiv \circ + \multimap + \Big[\nabla + \multimap\Big] + \Big[\Diamond + \nabla \\ + \nabla_2 + \nabla_4 + \infty + \multimap + \multimap\Big] + \cdots \tag{7}$$

where $L(r, s)$ are the sum of all graphs with r lines and s black dots which can be drawn using the same rules given in Ref. [7]. Each diagram cannot be split into two independent diagrams by cutting a single line. One might interpret each diagram as the contribution to the polarization of a series of elementary processes in which αt_{ij}^{γ} propagates the polarization from sphere i to sphere j. Since a diagram with r lines and s black dots is proportional to $\hat{\alpha}^r f^s$, its relative importance in the series can be estimated among the realtive magnitude of this factor. For example, in the low (high)-density regime the most important diagrams will be those with the smallest (largest) number of dots for a given number of lines.

While in 3D the unsymmetrized factorization of $\rho^{(m)}$ restricts the theory to the low-density regime, here in 1D there is no such restriction and the only remaining test is our ability to choose and sum the appropiate class of diagrams. If we take $\xi^{\gamma} = o = 1$ we recover the mean-field-approximation for this 1D system. Therefore the inclusion of any other class of diagrams, will take account of the dipolar fluctuations in an approximate way. Here we choose and sum the following diagrams

$$\xi^{\gamma} = \odot \; + \; \text{⬡} \; + \; \text{⬡} \; + \; \cdots \tag{8a}$$

where

$$\odot \equiv \Delta^{\gamma} = \; o \; + \; \text{▽} \; + \; \text{◁} \; + \; \text{◁} \; + \; \cdots \tag{8b}$$

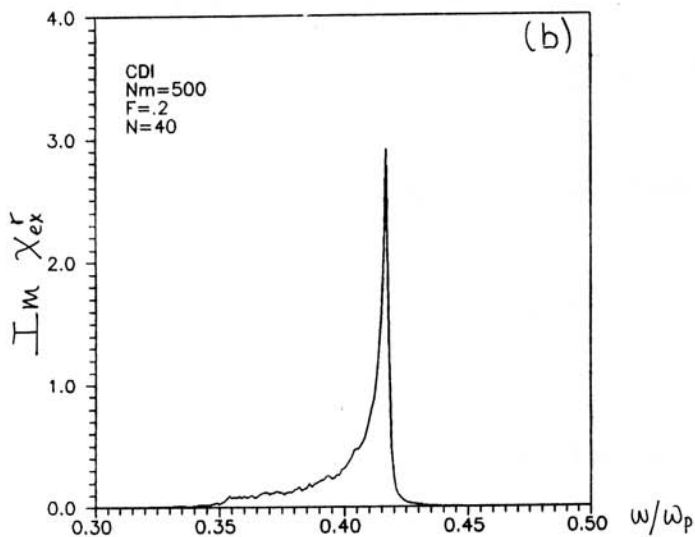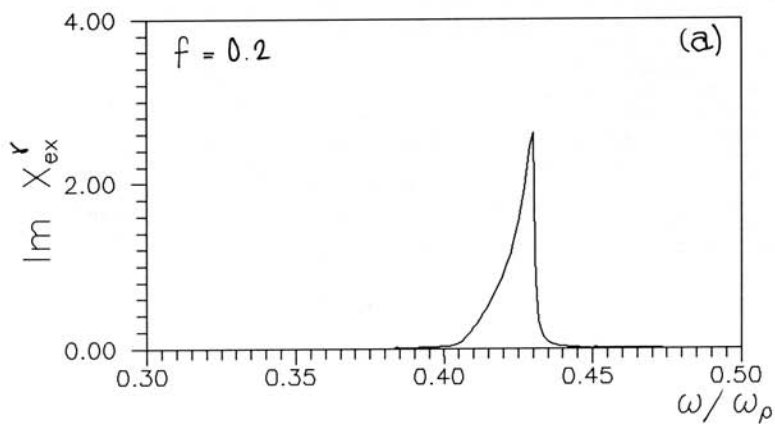$$\text{▽} \equiv \eta^{\gamma} = \; \text{◗} \tag{8c}$$

Using the exclude volume two-particle distribution function, we can rewrite Eq. (8) as

$$\xi^{\gamma} = \Delta^{\gamma} \left[1 - \frac{fb}{12} \left(\frac{3b^2}{4} + \frac{1}{2} \ln \frac{(b^2 - 4)^2}{(4 + 2b + b^2)(4 - 2b + b^2)} - \sqrt{3} \tan^{-1} \frac{\sqrt{3}b^2}{b^2 + 8} \right) \right] \tag{9}$$

where $b^3 = \hat{a}\Delta^{\gamma}$ and Δ^{γ} is the solution of

$$(\Delta^{\gamma})^2 - \Delta^{\gamma} + 1 = 0. \tag{10}$$

In Fig. (1) we show $Im\chi_{ex}^{\gamma}$ as function of $\tilde{\omega}$ for a Drude spheres with $\omega_p \tau = 800$, $\epsilon_h = 2.37$ and $f = 0.2$ for (a) theoretical results and (b) numerical simulation.

Figure 1 $Im\chi^{\gamma}_{ex}$ as function of $\tilde{\omega}$ for $f = 0.2$, (a) we used Eq. (9) with the approximation of Eq.(10) and (b) we used the result of the numerical simulation.

NUMERICAL SIMULATION

We generate the position of each sphere along the chain with a particular type of disorder. Then we calculate the induced dipole moment from Eq. (1) solving a set of linear equations through matrix inversion. In order to remove effects due to lenght of the chain, we consider periodic boundary conditions by closing the chain to itself.

(i) We consider an ordered distribution, i.e., the separation between the spheres is the same and the induced average polarization per unit volume is calculated, given by

$$\chi_{ez}^{\gamma} = \frac{f}{2\pi} \frac{\langle P^{\gamma} \rangle}{E_0^{\gamma}} \tag{11}$$

and we take the average of the induced dipole moment of the spheres. In Fig. (2) we show $Im\chi_{ez}^{\gamma}$ as function of $\tilde{\omega} = \omega/\omega_p$ for Drude spheres with $\omega_p\tau = 800$ embedded in gelatin ($\epsilon_h = 2.37$), $N = 40$, different filling fractions and γ in the longitudinal direction. In this Fig. we can see a red-shift of the peaks of absortion with respect to the one for $f = 0.2$ as has been obtained from mean-field-approximation theories of 3D systems .
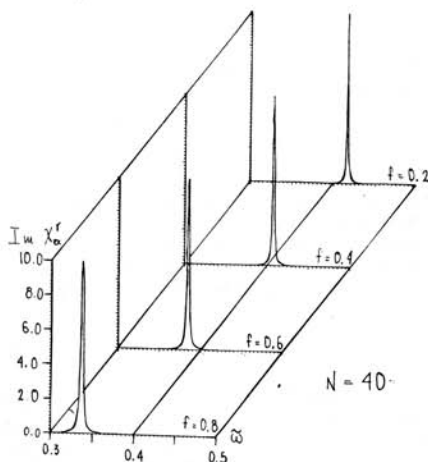
Figure 2 $Im\chi_{ez}^{\gamma}$ as function of $\tilde{\omega}$ for $f = 0.2, 0.4, 0.6$ and 0.8 and γ in the longitudinal direction.

(ii) We consider a disordered distribution where the position of each sphere is generated as follows: we locate a sphere at each end of the chain and define $N - 2$ equidistant sites along the chain. The next sphere is random located between the first sphere and the first site, if there is overlaping between the spheres we discard the sphere and take another with random position, too. We do that until we will have the desired filling fraction. Then, we solve the set of linear equations for this configuration and calculate the average of the induced polarization per unit volume. We take the ensemble average of Nm configurations, in order to obtain the susceptibility from Eq. (11). In Fig. (3) we show $Im\chi_{ez}^{\gamma}$ as function of $\tilde{\omega}$ for the same Drude spheres, $\epsilon_h = 2.37$, $f = 0.3$ and γ in the longitudinal direction, where $N = 40$ and $Nm = 1, 5,$ and 3000. From this Fig. we can see a principal peak and secondary peaks, when Nm increases the peaks disappear.
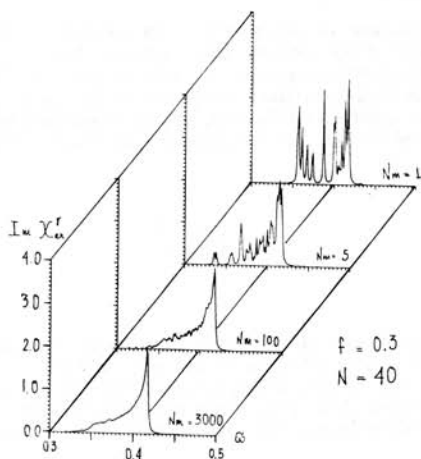
Figure 3 $Im\chi^{ex}$ as function of $\tilde{\omega}$ for $f = 0.3$ and $Nm = 1$, 5, 100 and 3000 and γ in the longitudinal direction.

CONCLUSIONS

We obtained the effective dielectric response of a chain of polarizable spheres embedded in a homogeneous matrix within the dipolar approximation by the summation of a selected class of diagrams. We found agreement between the theoretical results and the numerical simulation in the low-density regime. We expect that by carrying out new type of summations, we will be able to extend the agreement to higher-densities.

REFERENCES

1. See for example: "Electrical Transport and Optical Properties of Inhomogeneous Media", AIP Conference Proceedings, Eds. J.C. Gerland and D.B. Tanner (American Institute of Physics, New York 1978); "Electrodynamics of Interfaces and Composite Systems", Advanced Series in Surface Science, **Vol.** 4, Eds. R.G. Barrera and W.L. Mochán (World Scientific, Singapore, 1988); **ETOPIM 2**, Proceedings of the Second International Conference on Electrical Transport and Optical Properties of Inhomogeneous Media, Eds. J. Lafait and D.B. Tanner (North Holland, Amsterdam, 1989).
2. J.C. Maxwell Garnett, *Philos. Trans. R. Soc. London* **302**, 385 (1904).
3. L. Tsang and J.A. Kong, *J. Appl. Phys.* **53**, 7162 (1982).
4. B.U. Felderhof and R.B. Jones, *Z. Phys.* **B 62**, 43 (1985); **62** 215 (1986); **62**, 225 (1986).
5. S. Kumar and R.I. Cukier, *J. Phys. Chem.* **93**, 4334 (1989); B. Cichocki and B.U. Felderhof. *J. Chem. Phys.* **90**, 4960 (1989).
6. R.G. Barrera, G. Monsivais and W.L. Mochán, *Phys. Rev.* **B 38**, 5371 (1988).
7. R.G. Barrera, G. Monsivais, W.L. Mochán and E. Anda, *Phys. Rev.* **B 39** 9998 (1989).
8. R.G. Barrera, C. Noguez and E.V. Anda, (to be published by *J. Chem. Phys.*, January 1992.)
9. See for exemple, A. Robledo and J.S. Rowlinson, *Molec. Phys.* **58**, 711 (1986) and references therein.