Statistically correlated polarization fields and optical properties of a composite medium

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A definition of the effective dielectric constant incorporates correlation effects between fields scattered by particles supposed to be distributed randomly in the matrix. The *radius* distribution of the particles is taken into account. The *field* distribution function necessary for a correct averaging procedure is derived explicitly.

In order to *describe the electrical and optical properties of aggregated* systems such as those found in "composite" materials, one needs a theory of the *effective dielectric constant* (EDC).[1]

Two-groups of "theories" are usually considered. One is the *Maxwell-Garnett theory* (MGT) (preferred for describing the optical properties of granular systems), the other is usually called the *effective-medium theory* (EMT) (and is more often used in the study of percolation). It will appear that it is important to stress that the usual MGT and EMT or extensions are based on a *single-site approximation* and neglect correlation between polarization fields. An exact solution of Maxwell's equations for aggregates incidentally takes into account such effects. Furthermore, if the correct weight factor for averaging the fields is used (rather than the usual "concentration" dependence), the EDC will be of much greater value. We will see that we obtain a very tractable formula (requiring only a few seconds of numerical work on our IBM 370/158).

Extending the Clippe-Evrard-Lucas (CEL) theory for ionic powders[2] we have included all high-order polar interactions between (spherical) particles as well as retardation, and thus presented an N-site single-cluster MGT.[3–5] Nevertheless, for the sake of brevity and clarity here only the dipolar fields will be used, while retardation effects are not taken into account, i.e., we present the long-wavelength limit of a general statistical theory. Our results are in much better agreement with experimental data.[6]

After having solved Maxwell's equations "exactly," one has to define an EDC in terms of an average over all *field configurations.* This requires the nontrivial task of obtaining the probability function for the fields in a random medium. A second average must be made, but is generally omitted, i.e., because the particles inserted in the composite have irregular sizes, one has to average over their size distribution as well. This will also be done here; such a distribution is the log-normal distribution,[7]

$$f(R)=\frac{1}{(2\pi)^{1/2}}\frac{1}{R\sigma}\exp\left[-\frac{1}{2}\left(\frac{\ln(R/R_0)}{\sigma}\right)^2\right] ,$$

where σ is a measure of the width of the distribution while R_0 is a radius of particles *(thus supposed to be spherical)* such that 50% of them have a radius R less than R_0. Typical values of $\sigma_{\mathrm{LN}}\equiv e^{\sigma}$ are between 1.1 and 1.5 and R_0 is of the order of 500–1000 nm.

Beside the spherical hypothesis ($H0$), three physical hypotheses are needed in order to render our treatment as analytical as possible. ($H1$) We suppose that due to the randomness in the distribution of particles the system can be described as an *average medium* in which the electrical field (hence the polarization field) is weakly varying. ($H2$) The position of the particles in space is supposed to be normally distributed (as in the Gaussian broadening model of Fuchs[7]). ($H3$) The topology of the *a priori* large cluster of spheres is arbitrary but they are considered to be embedded in a large sphere (of radius a) outside of which *the* MGT *applies, and hence outside of which the EDC has the MGT form.*

Therefore ($H1$) and ($H3$) indicate that our theory will interpolate between the EMT and the MGT by taking into account clustering effects, while ($H2$) is primarily needed below to obtain an analytical form for the field-distribution function. From ($H1$) and ($H2$), it results also that the "small parameter" is the density gradient.

We expand the various fields outside and inside each spherical particle and outside the large sphere in terms of spherical wave-vector functions.[3,5,8] After applying the usual boundary conditions at the surface of each sphere the expansion coefficients $b_{nm}(j)$ describing the fields outside the particle (j) are solutions of a linear matricial equation

$$b_{nm}(j)+\Delta_n(j)\sum_{i\neq j}\sum_{q,p} b_{qp}(i)\langle X_{qp}(i)|H_{nm}(j)\rangle=-d_{nm}\Delta_n(j) \ , \tag{1}$$

where $\Delta_n(j)$ is the 2^n polar susceptibility of the (j) particle, e.g., for a homogeneous spherical particle of radius R it reads

$$\Delta_n(j)=n(\epsilon_j-\epsilon_M)R^{2n+1}/(n\epsilon_j+(n+1)\epsilon_M) \ ,$$

where ϵ_j and ϵ_M are the dielectric constants of the particle at "site" j and that of the matrix (M). The indices n and q refer to the field polar order, while m and p, respectively, span the space of usual polarization indices with values, respectively, between $[-n,+n]$ and $[-q,+q]$. The coefficient d_{nm} describes the external field, while the interaction matrix elements $\langle X(i)|H(j)\rangle$ between the N spheres are extensively given in Ref. 5.

Here we neglect all terms with n or $q \geqslant 1$. This has been proved acceptable if the density of particles is not too high, or if the particles are not in close contact.[4]

In such a case, the matrix elements are explicitly given by

$$\langle X_{1p}(i)|H_{1m}(j)\rangle=-2a_{ij}^{-3}\exp[i(p-m)\beta_{ij}]\sum_{l=-1}^{+1}\frac{(-)^l}{(1+l)!(1-l)!}O(1,p,l,\alpha_{ij})O(1,m,l,\alpha_{ij}) \ ,$$

where $(a_{ij},\alpha_{ij},\beta_{ij})$ are the spherical coordinates of the center of particle j in a reference frame centered on particle i, and $O(n,m,l,\alpha)$ is the "Jeffreys coefficient" relating spherical harmonics in different reference frames.[3,9]

Mathematically, $(H1)$ means that we can write $b_{1m}(j)/\Delta_1(j)\equiv B_m$, i.e., B_m is a constant for all j; this is obviously true in the absence of interactions between particles or for spheres regularly distributed on a lattice.[10] Defining

$$G_{pm}(j)\equiv\sum_{i\neq j}\Delta_1(i)\langle X_{1p}(i)|H_{1m}(j)\rangle$$

and supposing that the external field is uniformly applied in the z direction between the parallel plates of an infinite condensor we are led to conserve only the $m=0$ term in the above equations.

The solution of Eq. (1) is obviously (dropping here the index j)

$$b_{10}=-d_{10}\Delta_1(1+G_{00})^{-1} \ , \tag{2}$$

since $G_{pm}=0$ if $p\neq m$. Notice that $d_{10}^2=4\pi/3$.

An algebraic calculation of G_{00} allows one to recover the MGT and, hence, the Clausius-Mossoti relation for the EDC.[1] We define the "field fluctuation" G as $G=G_{00}-G_{MG}$, and search for the field distribution function of G in order to average b_{10} in Eq. (2). Because G is in general a complex function, one must look for a two variable distribution function $W(G',G'')$ with $G\equiv G'+iG''$. Furthermore the terms G' and G'' are not statistically independent.

Let us write[11]

$$W(G',G'')=\frac{1}{4\pi^2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}dt\,du\,A(t,u)\times\exp[-i(tG'+uG'')] \tag{3}$$

and calculate the characteristic function $A(t,u)$. Because of $(H2)$, $A(t,u)$ is the product of the characteristic functions of the distribution of each term in the dipolar sum, i.e.,

$$A(t,u)=A(0,0)\times\left\{\left\langle\int_{\mathcal{V}}\exp[i(tg'+ug'')]dv\right\rangle_R\right\}^{N-1} \ , \tag{4}$$

where the brackets $\langle\cdots\rangle_R$ denote an average with respect to $f(R)$, while the volume of integration $\mathcal{V}$ is that outside a sphere (of radius r_m) containing only one particle but inside the large sphere defined in $(H3)$, and

$$g'\equiv\Delta_1'(R)\langle X_{10}(\vec{r})|H_{10}(0)\rangle$$

and similarly for g''. Let a and N tend to infinity such that $N-1=\lambda(4\pi a^3/3)$. One obtains $A(t,u)=\exp[-C(t,u)]$ with

$$C(t,u)=\left\langle\int_{\mathcal{V}}\{1-\exp[i(tg'+ug'')]\}dv\right\rangle_R \ . \tag{5}$$

Expanding the exponential in Eq. (5) up to the quadratic term leads after some algebra to

$$W(G',G'')=\frac{1}{2\pi\sigma'\sigma''}\frac{1}{(1-\rho^2)^{1/2}}\exp\left(-\frac{1}{2}\frac{(G'/\sigma')^2+(G''/\sigma'')^2-2\rho G'G''/\sigma'\sigma''}{1-\rho^2}\right) \ , \tag{6}$$

with $(\sigma')^2 = \frac{4}{5}\frac{4}{3}\pi\lambda\ \langle \Delta_1'^2/r_m^3 \rangle_R$ and similarly for σ'', while

$$\rho = \langle \Delta_1' \Delta_1'' \rangle_R / (\langle \Delta_1'^2 \rangle_R \langle \Delta_1''^2 \rangle_R) \ .$$

When $\rho = \pm 1$ (i.e., in the case of homogeneous spheres) our solution is formally similar to that of Fuchs[7] when $f(R)$ is a delta function.

An EDC can now be defined preferably *in terms of electrostatic energy stored (or lost) U rather than fields.*[12] The variation of U due to the presence of spheres is from a "microscopic" viewpoint

$$\Delta U = \frac{1}{2}\epsilon_M \sum_{j=1}^{N} \int_{v_j} \left(1 - \frac{\epsilon_j^*}{\epsilon_M} \right) \vec{E}_0 \cdot \vec{E}_j^* \, dv \ ,$$

but is also given by

$$\Delta U = \frac{1}{2}\epsilon_M (1 - \epsilon_M/\epsilon_{\rm eff}) |\vec{E}_0|^2 \ ,$$

which thus defines $\epsilon_{\rm eff}$. The latter equation is so written because it is obviously imposed that the sources of the $\vec{D}$ field remain constant both in the "effective" and '"microscopic" cases (we suppose that ϵ_M is real). Hence,[13] one obtains a very tractable analytical formula, i.e.,

$$\epsilon_{\rm eff} = \epsilon_M (1 + \sqrt{12\pi}\lambda \langle \langle b_{10} \rangle_R \rangle)^{-1} \ , \tag{7}$$

from which one can calculate typical quantities. We have chosen cases as those discussed by Lamb *et al.*,[15] i.e., spherical metallic inclusions in a dielectric matrix. For a delta-function distribution of sphere radii it is observed that the position of the maximum in $\epsilon''_{\rm eff}$ corresponding to the peak in the usual absorption coefficient $A(\omega) = 2\epsilon''(\omega)/n(\omega)c$ occurs much below the Fröhlich mode ω_s, and the shift of the peak is toward lower frequencies as a function of filling, as seen in usual experiments.[1,6] On Fig. 1 we reproduce the reflectivity (at $\omega = \omega_p/5$) as a function of the filling factor f as obtained in Ref. 15 for EMT or MGT; it is seen that taking into account correlation between fields in the case of *equal size* particles ($\sigma_{\rm LN} = 1$) already modifies the value of the reflectivity (at $f \neq 0$). The size effect is even more drastic ($\sigma_{\rm LN} = 1.2$ and 1.4 curves).

The reflectivity as a function of frequency is seen on Fig. 2 where different filling factors and size distributions are considered. The dashed line indicates the position of the expected reflectivity peak at the Fröhlich mode when the spheres are noninteracting.

An interesting result is seen on this figure. As here, the reflectivity spectra are experimentally found to be asymmetrical: a sharp rise at low frequency is followed by a smoother decrease at high frequency.[6] Except for fits introducing "depolarization" factors,[7,14,15] only an averaging procedure explicitly taking into account the field distribution probably leads to such an agreement with experimental results. We conjecture that high-order polar interaction terms

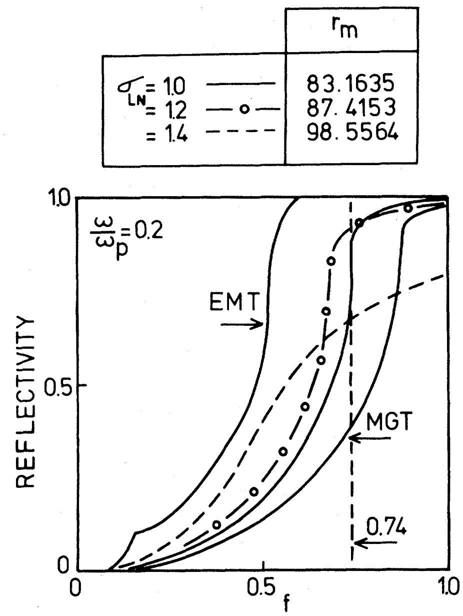

FIG. 1. Reflectivity for a metal-insulator composite at a frequency $\omega = 0.2\omega_p$ as obtained from various approximations (EMT, MGT) with input data as in Ref. 15, or taking into account correlation effects, and various size distributions of the particles.

will, among other things, shift the peak position.[4]

Having shown the positive aspects of the theory, let us comment on the "negative ones." (1) The theory has been worked out for spherical particles made of the same material. (2) As the MGT, our theory suffers from not indicating any percolation threshold. (3) The theory is applicable to random systems in absence of any anisotropic short-range order due to ($H1$,$H2$). If a chainlike distribution is

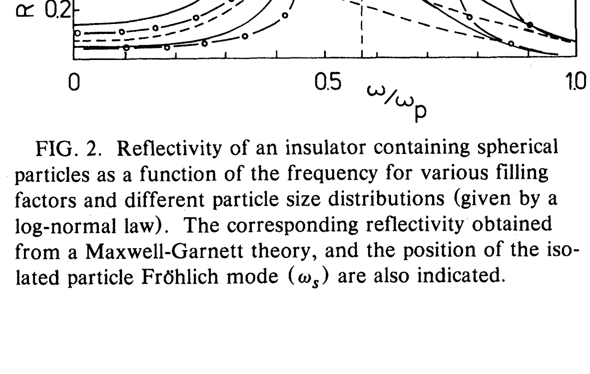

FIG. 2. Reflectivity of an insulator containing spherical particles as a function of the frequency for various filling factors and different particle size distributions (given by a log-normal law). The corresponding reflectivity obtained from a Maxwell-Garnett theory, and the position of the isolated particle Fröhlich mode (ω_s) are also indicated.

present, the experimental spectra show a two-peak structure at much lower and higher frequencies.[6,14] This shows that $(H2)$ plays an important role in the shape of the spectrum and might have to be modified with respect to specific experimental investigations when anisotropic distributions are present. (4) At large σ_{LN}, hence when large spheres are present, $(H2)$ becomes obviously very unrealistic, and the neglect of position correlations is quite incorrect. One could show that the validity of our theory is limited at the (nevertheless, very reasonable) value $\sigma_{LN} \simeq 1.4$.

Formal extensions of this work are obvious and seem reasonably realizable.

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[12]See also, D. Bergman in Ref. 1, p. 46.

[13]The filling factor is entering Eq. (13) through the definition $f = \frac{4}{3}\lambda r_m^3$, where r_m (as in Ref. 7) is a "cutoff radius" measuring a mean spherical sphere, and depends here on the radius distribution function $f(R)$. Notice that σ' and σ'' are also functions of f.

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