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Effective dielectric properties of composite materials in the surface layer

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In the framework of the mean-field picture, an expression for the effective dielectric permittivity of an inhomogeneous medium near a flat interface with another dielectric is derived as a function of the distance from the boundary. The obtained formula should be considered as a counterpart of the standard Maxwell-Garnett one, but in the vicinity of a flat boundary. Possibilities of a more precise derivation using already established methods for bulk systems are briefly discussed as well.

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The history of the problem about effective dielectric properties of inhomogeneous media goes back to the classical works of Maxwell,[1] Garnett,[2] Wagner,[3] and others. But despite the rich history, this problem still attracts considerable attention resulting in a number of publications during the last decade.[4–9] Of course, the main point of all recent works is the consideration of multiparticle effects that become very important for relatively high concentrations. The proposed methods range from consistently analytical[5,7,10–12] or of more empirical nature[13,14] to numerically driven calculations.[9] Evidently, this interest is strongly stimulated by possible experimental applications allowing to gain information about microstructure of composites based on the analysis of their dielectric properties:[15–17] characteristics such as size of inclusions are not present in the simple Maxwell-Garnett formula.[2]

Another problem, strongly connected with the mentioned one but received much less attention, arises if one considers effective dielectric function of a composite material *near* an interface with a homogeneous medium. In this case, the interface plays the role of an effective mirror allowing us to employ the already developed methods. Here we will show that, for instance, repolarization technique[8] can be easily adopted for this purpose. The same should be possible for all methods based on the mean-field approach[10–12] as well as more sophisticated or numerical procedures.[4,9,18,19] On the other hand, even the simplest approximation in this problem will contain information about the size of inclusions, possibly proposing an alternative for the experimental measurements for revealing geometrical properties of the dissolved component.

The above stated problem is also related to a so-called "imperfect interface" problem,[20] an excellent review of which can be found in Ref. 21.

In this work we will use an expression for the dielectric permittivity of a composite material as a function of "elementary" polarizabilities of the inclusions. Thereafter, a formula for the one-particle polarizability near the interface will be derived by means of the method described in Ref. 8.

Let us start from a general expression for the *macroscopically* defined (i.e., on the scale strongly exceeding the size of inclusions) electric field $\vec{E}_M$ and displacement $\vec{D}_M$,[22]

$$\vec{D}_M=\overleftrightarrow{\epsilon}\vec{E}_M; \tag{1}$$

which, in fact, is to be considered as a definition of the dielectric permittivity tensor $\overleftrightarrow{\epsilon}$ if $\vec{D}_M$ and $\vec{E}_M$ are independently calculated. If a macroscopic sample of the dielectric material is placed into an external field $\vec{E}_0$, then all polarization effects are described[22] by the polarization vector $\vec{P}(\vec{r})$, so that

$$\vec{E}_M=\vec{E}_0+\nabla_{\vec{r}}\left(\nabla_{\vec{r}}\int_V \frac{\vec{P}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}dV'\right),$$

$$\vec{D}_M=\vec{E}_M+4\pi\vec{P}, \tag{2}$$

where $\nabla_{\vec{r}}$ means differentiation upon $\vec{r}$, and the integration is conducted over the entire volume of the sample. The polarization vector $\vec{P}$ in its turn is usually expressed in terms of the polarizability tensor $\overleftrightarrow{A}$ as

$$\vec{P}=\overleftrightarrow{A}\vec{E}_0. \tag{3}$$

Tensor $\overleftrightarrow{A}$ describes dielectric properties of the sample and, in particular, the permittivity $\overleftrightarrow{\epsilon}$. In the case of an inhomogeneous medium, $\overleftrightarrow{A}$ has to be determined on the mesoscopic scale, i.e., strongly exceeding the size of the inclusions but small enough to define the spatial dependence $\overleftrightarrow{A}(\vec{r})$.

Due to the presence of a flat surface (interface), it is natural to write the polarizability $\overleftrightarrow{A}$ in the form

$$\overleftrightarrow{A}=A_{\parallel}\vec{n}\vec{n}+A_{\perp}(\overleftrightarrow{I}-\vec{n}\vec{n}), \tag{4}$$

where $\vec{n}$ is a unit vector perpendicular to the interface and $\overleftrightarrow{I}$ is a unit 3×3 tensor; here $\vec{n}\vec{n}$ means tensor product.

For simplicity, we will assume that the sample is "homogeneous in average," implying that the volume fraction f of the dielectric inclusions (permittivity ϵ_2) immersed into the matrix (permittivity ϵ_1) is constant. Both the matrix and inclusions are uncharged.

It is convenient to represent the flat interface as one between a large sphere of the radius $\mathcal{R}$ (containing the material) and its homogeneous dielectric surrounding. Assuming this spherical symmetry, we conclude that $A_{\parallel}$ and $A_{\perp}$ depend only on the distance from the center of the sphere [Fig. 1] (or, equivalently, from the surface in the limit $\mathcal{R}\rightarrow\infty$), so that it is possible to integrate out space angles in Eq. (2), which yields

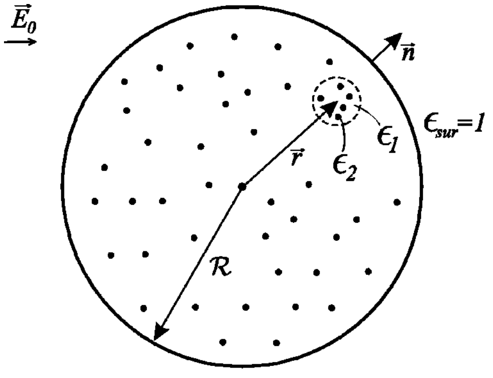

FIG. 1. Dielectric inhomogeneous sphere surrounded by homogeneous dielectric medium.

$$\vec{E}_M=\vec{E}_0-\frac{4\pi}{3}f_1(r)\vec{E}_0-\frac{4\pi}{3}f_2(r)(\vec{E}_0\cdot\vec{n})\vec{n}, \tag{5}$$

where $r=|\vec{r}|$ and

$$f_1(r)=\frac{1}{r^3}\int_0^r r'^2dr'[A_\parallel(r')+2A_\perp(r')]$$

$$+2\int_r^{\mathcal{R}}\frac{1}{r'}dr'[A_\parallel(r')-A_\perp(r')],$$

$$f_2(r)=\frac{3}{r^3}\int_0^r r'^2dr'[A_\parallel(r')+2A_\perp(r')]-3A_\parallel(r). \tag{6}$$

As a result, the permittivity tensor $\overleftrightarrow{\epsilon}$ defined by Eq. (1) takes the form

$$\overleftrightarrow{\epsilon}=\epsilon_\parallel\vec{n}\vec{n}+\epsilon_\perp(\overleftrightarrow{I}-\vec{n}\vec{n}), \tag{7}$$

with components $\epsilon_\parallel$ and $\epsilon_\perp$ determined as

$$\left(\frac{\epsilon_\perp}{\epsilon_1}-1\right)\quad\left(1-\frac{4\pi}{3}f_1\right)=4\pi A_\perp,$$

$$\left(\frac{\epsilon_\parallel}{\epsilon_1}-1\right)\quad\left(1-\frac{4\pi}{3}(f_1+f_2)\right)=4\pi A_\parallel. \tag{8}$$

Here and throughout the paper we use dielectric permittivity relative to the homogeneous dielectric (on the right-hand side in Fig. 2).

Now the problem is evaluated to the one of finding the polarization tensor $\overleftrightarrow{A}$, which is related to the set of *irreducible k*-particle polarizabilities $\overleftrightarrow{\alpha}^{(k)}$ as

$$\overleftrightarrow{A}=\frac{f}{v}[\overleftrightarrow{\alpha}^{(1)}+\overleftrightarrow{\alpha}^{(2)}+\cdots]. \tag{9}$$

Here we also assume all inclusions to be identical spheres of radius a ($v=4\pi a^3/3$). The assumption about the spherical shape will be used further during $\overleftrightarrow{\alpha}^{(1)}$ calculation, whereas one about monodispersity is *not* of crucial importance: size distribution effects will be discussed later. Furthermore, we will restrict ourselves to the one-particle irreducible polarizability $\overleftrightarrow{\alpha}^{(1)}$ only to show transparently the analogy between one-particle problem in the presence of the interface and the two-particle one in the bulk. In other words it means that only the terms linear upon volume fraction f of inclusions will be taken into account corresponding to *low* concentration regime. This approximation is probably not sufficient for practical purposes, but will transparently show the essence of the method discussed.

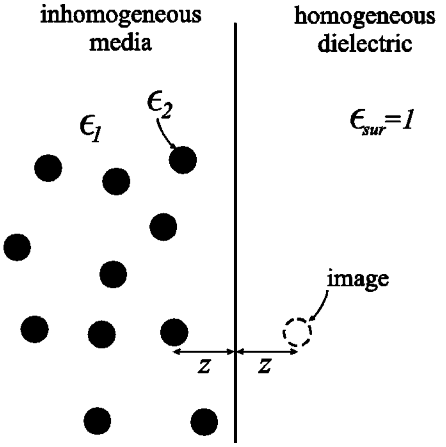

FIG. 2. Spherical inclusion in the surface layer and its electrostatic image.

Following the same logic as before, $\overleftrightarrow{\alpha}^{(1)}$ is divided into two independent parts $\alpha_\parallel$ and $\alpha_\perp$. The longitudinal component $\alpha_\parallel$ is a polarizability of a single particle in the field $\vec{E}_0\|\vec{n}$. However, due to the presence of the interface, the particle's electrostatic image also has to be taken into account; implying that effectively a two-particle problem should be solved. Of course, the same is true for all $\overleftrightarrow{\alpha}^{(k)}$ where effectively $2k$ particles are involved.

Proceeding in the quantitative way, we consider a particle at the distance $z>a$ from the interface. Knowing that it generates an electrostatic image, we make use of the two-particle repolarization technique developed in Ref. 8. Its essence is in the iterative procedure where the repolarization operator $\hat{\mathcal{P}}$ can be introduced, so that the field generated by the first particle (which has multipole moments $F_n^{(1)}$, $n=1,\ldots,\infty$) induces moments $F_n^{(2)}$ on the second one, and is represented as

$$F_k^{(2)}=\sum_n \mathcal{P}_{kn}F_n^{(1)}. \tag{10}$$

This treatment can be generalized for the present case. As it is well known,[22] the multipole moments of the electrostatic image are connected to the original point particle ones (i.e., no polarization of spheres is taken into account yet) by a simple rule

$$F_n^{(i)}=\frac{\epsilon_1-1}{\epsilon_1+1}F_n^{(p)}, \tag{11}$$

where (i) refers to the image and (p) to the particle. Therefore, due to presence of the image, the particle effectively "polarizes itself" so that its multipole moments on the sth step of the iteration is connected with the previous one by

$$F_k^{(p),s}=F_k^{(p),s-1}+\sum_n \mathcal{P}_{kn}F_n^{(p),s-1}, \tag{12}$$

where, for instance, the longitudinal component of $\hat{\mathcal{P}}$ has the implicit form

$$\mathcal{P}_{\|kn}=\frac{(-1)^n(n+k)!}{n!k!}\sqrt{\frac{2n+1}{2k+1}}\frac{a^{2k+1}}{\epsilon_1(2z)^{n+k+1}}\frac{\epsilon_1-1}{\epsilon_1+1}\kappa(k). \tag{13}$$

Here $\kappa(k)=(\epsilon_1-\epsilon_2)k/[\epsilon_1(k+1)+\epsilon_2 k]$. "Longitudinal" refers to polarization in the external field $\vec{E}_0\|\vec{n}$, i.e., perpendicular to the surface.

To start the iteration procedure, one also needs the initial set of moments, i.e., induced by polarization in the electrostatic uniform filed $\vec{E}_0$: dipole moment $F_1^{(p)}=-\sqrt{\pi/3}a^3E_0\kappa(1)$ and the others, $F_i^{(p)}=0$ $(i>1)$. Repeating the iteration one gets an asymptotical result for the polarizability $\alpha_\|$, which is extracted from the formulas as a proportionality coefficient between the dipole moment of the particle $F_1^{(p)}=\Sigma_s F_1^{(p),s}$ and the external field E_0. Due to the iterative nature of the method, the result for $\alpha_\|$ has the following form:

$$\alpha_\|=-a^3\kappa(1)-2\kappa^2(1)\beta\frac{a^6}{(2z)^3}+\sum_{s=2}^{\infty}\alpha_\|^{(s)},$$

$$\alpha_\|^{(s)}=\sum_{n_1,\ldots,n_{s-1}=1}^{\infty}C^\|_{n_1,\ldots,n_{s-1}}\kappa^2(1)\times\kappa(n_1)\cdots\kappa(n_{s-1})\beta^s a^3\left(\frac{a}{2z}\right)^{2(n_1+\cdots+n_{s-1})+s+2},$$

$$C^\|_{n_1,\ldots,n_s}=(-1)^{n_1+\cdots+n_s+1}\times\frac{(n_1+1)(n_1+n_2)!\cdots(n_{s-1}+n_s)!(n_s+1)}{n_1!(n_2!)^2\cdots(n_{s-1}!)^2n_s!}. \tag{14}$$

Here $\beta=(\epsilon_1-1)/[\epsilon_1(\epsilon_1+1)]$.

Using exactly the same approach, the transversal part of the operator $\hat{\mathcal{P}}$ is obtained, yielding

$$\alpha_\perp=-a^3\kappa(1)-\kappa^2(1)\beta\frac{a^6}{(2z)^3}-2\kappa^3(1)\beta^2\frac{a^9}{(2z)^6}+\cdots. \tag{15}$$

At this point using Eqs. (14), (8), and (9), one is able to express the dielectric permittivity $\vec{\vec{\epsilon}}$ as a function of the distance from the surface. So far we have taken into account the inclusions effects that are only linear upon concentration, although in the framework of this restriction no additional assumptions were made.

To avoid bulky formulas, we present $\vec{\vec{\epsilon}}$ in the implicit form with accuracy only up to a^3/z^3. Higher accuracy can be easily achieved using higher-order terms from Eqs. (14) and (15),

$$\epsilon_x=\epsilon_1\left[1+\frac{3(\epsilon_2-\epsilon_1)}{\epsilon_2+2\epsilon_1}f\right]-\frac{3c_x}{8}f\frac{\epsilon_1-1}{\epsilon_1+1}\frac{(\epsilon_2-\epsilon_1)^2}{(\epsilon_2+2\epsilon_1)^2}\frac{a^3}{z^3}+\cdots, \tag{16}$$

where $x=(\|,\perp)$ and $c_\|=2$, $c_\perp=1$.

The bulk value of the dielectric permittivity $(z\to\infty)$ coincides with the classical Maxwell-Garnett formula.[2] In contrast to the bulk part, the surface terms contain implicitly the size of the inclusions—this outcome is obvious because a is the only parameter of the length dimension and has to be used to "measure" the distance from the interface.

Let us now discuss the validity region of the obtained expression (16). As it was pointed out above, only linear upon concentration effects were considered, so that $O(f^2)$ terms are not present. At the same time, the first of those terms (which were not taken into account in the present work) are proportional to f^2 (particle-particle, image-image interactions) or f^2a^3/z^3 (particle image of another particle interaction). This implies that the condition

$$f\ll\frac{a^3}{z^3}<1$$

is to be satisfied. In other words, an average interparticle distance should exceed an average distance between a particle and the interface in the region of applicability of Eq. (16). There are two possibilities when the above condition breakes. First of all, this happens in the case of relatively high concentrations $(f\lesssim 1)$, which is far from the scope of the paper. Also, distances z of the order of $a/f^{1/3}$ are not covered by Eq. (16). They correspond to the region where the surface terms in $\vec{\vec{\alpha}}^{(1)}$ and bulk ones in $\vec{\vec{\alpha}}^{(2)}$ are of the same order. The latter in this case can be accounted by the methods of Refs. 4 and 6 and others. However, we need to point out that, nevertheless, the first nontrivial surface contribution is already included in Eq. (16).

Expression (16) can be consistently applied in the case $\epsilon_1\neq 1$ because an assumption about sharp interface was put in the very basis (11) of the calculation. Qualitatively different situation $\epsilon_1=1$, where the interface is not as well defined as before, should be considered separately. We just note that in order to obtain the "surface effects" terms for such a "smooth" interface, one has to take into account the spatial dependence of the volume fraction of inclusions $f(z)$ in the vicinity of the border.

Here we have considered a monodisperse material. But a generalization taking into account size polydispersity can be easily done by producing averaging of expressions (14) with a given size distribution function. This yields a trivial result in the present approach because only one-particle polarizabilities were taken into account.[23] Of course, some real systems exhibit a broad inclusions' size distribution, so that the polydispersity effects will be present due to multiparticle polarization and possibly exceed the surface contribution (although they remain spatially *independent*). Probably, this problem can be approximately solved by substitution of the polarizabilities $(\epsilon_2 - \epsilon_1)/(\epsilon_2 + 2\epsilon_1)$ in Eq. (16) by their renormalized counterparts (see, e.g., the method proposed in Ref. 4) that take into account interparticle polarizations.

From an experimental point of view, boundary effects become extremely important in experiments with thin films. Interfacial effects evidently have to be considered if, for instance, the dielectric spectroscopy method is applied to such a confined system. Indeed, even Eq. (16) shows that the corresponding terms cannot be neglected in this case.

An application of only one possible method[8] for accounting multiparticle effects in the ''surface layer problem'' was discussed. However, using the presented idea, a lot of well-developed techniques (including exact analytical methods; see, e.g., Refs. 10 and 5, and references therein) previously applied to the bulk systems can be used in the problem of obtaining effective dielectric properties of the inhomogeneous material near the interface. In this sense, the presented result (16) is the simplest one, which considers interfacial effects, and can be viewed as a generalization of the Maxwell-Garnett formula.

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