F I Z I K A V O L U M E 10 S U P P L E M E N T 2, 1978
Proceedings of the VI Yugoslav Symposium of the Physics of Condensed Matter, Kruševac, September, 18-22, 1978

OPTICAL PROPERTIES OF COMPOSITE MEDIA

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We present some theoretical results concerning the dielectric and optical properties of media which are composed of two materials, intermixed in such a way that the medium as a whole is homogeneous on a macroscopic scale. The electrostatic theory we use sets a lower limit to the wavelength of light to which the theory is applicable. The theory can be applied to experimental systems such as colloidal particles[1], discontinuous metallic films[2], rough surfaces of metals, powders of ionic crystals, etc. We assume that the constituents can be described by local, isotropic and size-independent dielectric functions. The "inner" material with the dielectric function ε_i occupies a volume V_i (which may consist of a number of separate grains), which is of a finite extent, and the rest of the space V_e is occupied by the "external" material ε_e. We want to find the effective polarizability $\bar{\alpha}$ or the polarizability per unit volume $\bar{\chi}$ of the composite medium.

We introduce the scalar potential ϕ by $\vec{E}=-\nabla\phi$. We denote $g(\vec{r},\vec{r}')=|\vec{r}-\vec{r}'|^{-1}$, and define the quantity μ by:

$$\mu = \frac{\varepsilon_i+\varepsilon_e}{\varepsilon_i-\varepsilon_e}$$

The potential ϕ satisfies the integral equation[3]

$$\phi(\vec{r}) = \frac{2\varepsilon_e}{\varepsilon_i+\varepsilon_e}\,\phi_o(\vec{r}) + \frac{1}{2\pi\mu}\int_S \frac{\partial}{\partial n_i'}\, g(\vec{r},\vec{r}')\phi(\vec{r}')\,dS' \,.$$

The integration is performed over all interfaces, and n_i' denotes the distance into V_i along a normal at the point $\vec{r}'$ of the interface. The field ϕ_o depends upon boundary conditions.

In the case of no external field, $\phi_o=0$, a set of eigenfunctions $\phi_q(\vec{r})$ can be found. The corresponding eigenvalues

μ_q are real, and $|\mu_q| \leq 1$ [3]. The kernel of the integral equation is not symmetrical and the eigenfunctions are not mutually orthogonal. However, it can be shown that they are orthogonal to the functions

$$\Phi_q(\vec{r}) = \frac{\partial}{\partial n_i'} \phi_q(\vec{r}) \ .$$

Now we specify that the external field described by ϕ_o is a constant electric field $\vec{E}_o$, and look for the induced dipole moment in a sphere S_1 which completely encloses the component V_i:

$$\vec{p} = \int_{V_1} d\vec{r}\ \chi(\vec{r})\ \vec{E}(\vec{r}) \ ,$$

where $\chi(\vec{r})=(\varepsilon-1)/4\pi$ equals either χ_e or χ_i. It follows[3]:

$$p_k = V_1 \sum_{j=1}^{3} E_{oj}\left[\chi_e \delta_{kj} + f\alpha_{kj}\right],$$

where f is the filling factor $f=V_i/V_1$, and k,j denote Cartesian components. The first term in the square brackets is the isotropic polarizability of the pure "external" material, and the second term is the change of polarizability due to the presence of the "inner" material. Introducing the function

$$C_{kj}(\mu') = \frac{1}{2\pi V_i} \sum_q \frac{p_{qk}\, P_{qj}^*}{\mu - \mu_q} \ ,$$

where

$$p_{qk} = \int_S x_k\ \Phi_q(\vec{r})\ dS \ ,$$

we find[3,4]:

$$\alpha_{kj}(\mu(\omega)) = \frac{1}{2\pi} \int_{-1}^{1} \frac{C_{kj}(\mu')}{\mu - \mu(\omega)}\, d\mu' \ .$$

The following sum rules hold:

$$2\pi \int_{-1}^{1} d\mu\ C_{kj}(\mu) = \delta_{kj} \ ,$$

$$2\pi \sum_k \int_{-1}^{1} \mu\ d\mu\ C_{kk}(\mu) = 1, \qquad k=1,2,3.$$

In the complex μ plane, the polarizability α has a cut from

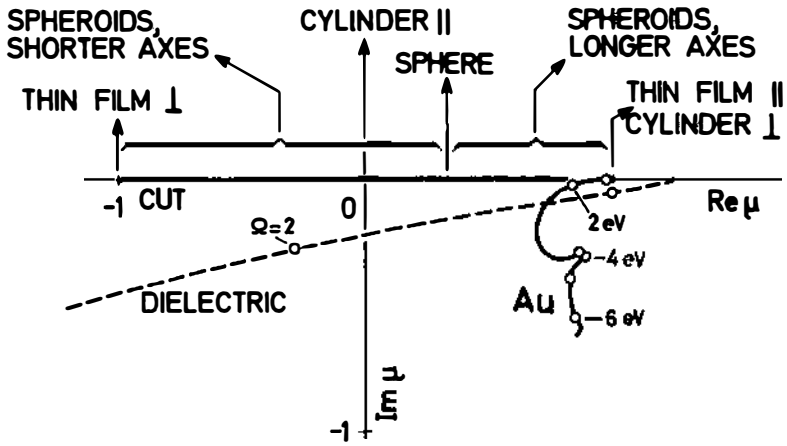

Fig. 1. The complex μ plane with the curves μ(ω), ω>0, for a model dielectric function of ionic crystals and for gold. The position of the peaks of the function C(μ) on the interval [-1,1] for various bodies with second-order surfaces is also indicated.

μ=-1 to μ=+1, and is analytical elsewhere. In the complex ω plane, the analytical properties of α are determined by the mapping μ(ω). In Fig. 1 the mapping of the positive real ω axis is shown for the model dielectric function of ionic crystals:

$$\varepsilon = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1-\Omega^2-i\gamma\Omega} ,$$

(where $\Omega=\omega/\omega_T$), with constant damping γ, and for the experimental dielectric function of gold[5]. The curve of gold departs rapidly from the real μ axis, because of the influence of interband transitions. For more free-electron-like metals the curve follows the real axis from below for a much larger interval.

Explicit calculation of eigenmodes for various boundary interfaces is difficult, and can be performed only numerically even for single particles of a general shape[6,7]. Only for second-order surfaces (sphere, cylinder, spheroids, etc.) does the function C consist of a single delta-peak for each symmetry direction. In Fig. 1 the position of these peaks is also shown; this gives a good indication of the shape of the function C for more complex geometries.

The coefficient of the absorption of light is proportional

to ω Im $\alpha(\omega)$ [4]. If the curve $\mu(\omega)$ is near the real axis, the absorption coefficient $a(\omega)$ depends directly upon the magnitude of the function $C(\mu)$ at the nearest point on the cut [4], i.e. the sample geometry markedly affects the light absorption. If the curve $\mu(\omega)$ is far from the real axis, the absorption coefficient depends little upon the function C. In the case of gold, this means that at long wavelengths the absorption depends much more upon the structure of the sample than at short wavelengths.

The approximations most widely used in treating composite media are discussed in Ref. 4. The theory presented here enables one to gain a deep insight into the problem within the framework of non-retarded (electrostatic) theory, and to compare the advantages of various approximate approaches.

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