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Electromagnetic Response of Interacting System of Metallic Particles

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A theoretical approach is formulated for the calculation of the macroscopic dielectric response of a random system of metallic spheres embedded in an uniform dielectric medium. The appreciable deviations from the Maxwell-Garnett formula are found. It is noted that with the metal volume fraction increase the role of pair multipole interactions between inclusions becomes significant. The frequency dependence of the imaginary part of the effective dielectric function of the system is calculated with account of the dipole-dipole interaction between particles which consist of two different kinds.

1. Introduction

The calculation of frequency-dependent dielectric function of a composite presents an old though still unsolved problem [1-3]. There have been many different approaches [4-13] to its solution, but there is still no the theory that could provide complete quantitative agreement with the corresponding experimental measurements. We study suspension of metallic spheres randomly distributed in an insulating matrix. The effective dielectric function $\tilde{\varepsilon}$ of such system is given by the Maxwell-Garnett formula (MG) [1] under small concentration of inclusions. In present work, we propose the generalization of method of the paper [8] to the case of the composite containing spherical metallic inclusions of different sizes. We take into account only the pair multipole interaction between inclusions (the first correction to the MG approximation). An observed sharp absorption maximum can be attributed to surface plasma modes of individual pair of spheres. A general expression of $\tilde{\varepsilon}$ and its imaginary part as functions of parameters of the composite containing inclusions of the same metal particles but with two different sizes is considered in Section 2 using this method. In Section 3 the brief discussion of the results is given.

1. The dielectric function of a composite

We consider a system that consists of the uniform dielectric matrix with embedded in it spherical particles of different kinds (noted below by indices $a, b, \ldots$). The matrix dielectric permittivity is ε_0, and the particles dielectric constants are $\varepsilon_a, \varepsilon_b, \ldots$, respectively. Let the number of spheres of kind a be N_a, $b - N_b, \ldots$. The total number of particles is $N = \sum_\alpha N_\alpha$. The system is located in the external field proportional to $e^{-i\omega t}$ with a wavelength $\lambda = 2\pi c/\omega$ which is large compared to the sphere radius and the mean distance between particles; $n_a = N_a/V$, $n_b = N_b/V$, ... are the concentrations of particles of the kinds $a, b, \ldots$

Generalizing the method of cluster expansion [8-11] to our case we can obtain the following relation for the effective dielectric permittivity of a system [14]:

$$\frac{\tilde{\varepsilon}+2\varepsilon_0}{\tilde{\varepsilon}-\varepsilon_0} = \frac{1}{\frac{4\pi}{3}\sum_\alpha n_\alpha \alpha_\alpha} - \frac{\sum_{a,b} n_a n_b \int_0^\infty R^2 \,\mathrm{d}R\, \Phi_{ab}(R)\left[\beta^{\parallel}_{ab}(R) + 2\beta^{\perp}_{ab}(R)\right]}{\left(\sum_\alpha n_\alpha \alpha_\alpha\right)^2}, \quad (1)$$

$\alpha_a = \frac{\varepsilon_a - \varepsilon_0}{\varepsilon_a + 2\varepsilon_0} r_a^3$ is the common dipole polarizability of a single particle of a kind a; $\Phi_{ab}(R)$ is the two-particle distribution function of particles in the matrix, r_a is a radius of particle a, $R = \left|\vec{R}_a - \vec{R}_b\right|$, $\vec{R}_a$ and $\vec{R}_b$ are the origins of spheres a and b, respectively, $\beta^{\parallel,\perp}$ are the longitudinal and transverse parts of two-particle polarizability. Formula (1) is a generalization of relation (5.8) of the paper [11] to the case of system with inclusions of different kind. Taking into account only the pair dipole-dipole interaction between particles, we have [14-16]:

$$\beta_{ab}^{\parallel} = X_{10}^{(a)}(R) - \alpha_a - 2\frac{\alpha_a \alpha_b}{R^3},$$

$$\beta_{ab}^{\perp} = X_{11}^{(a)}(R) - \alpha_a + \frac{\alpha_a \alpha_b}{R^3};$$

$$X_{10}^{(a)} = \alpha_a \frac{1 + 2\alpha_b R^{-3}}{1 - 4\alpha_a \alpha_b R^{-6}}, \quad X_{11}^{(a)} = \alpha_a \frac{1 - \alpha_b R^{-3}}{1 - \alpha_a \alpha_b R^{-6}} \tag{2}$$

It should be noted that the developed method allows generalization to the case of the higher pair multipole interactions [17] as well as to the case of multiparticle interactions. The convergence of the integral in Eq. (1) in the limit $N \to \infty$, $V \to \infty$, $N/V = \text{const}$ was discussed in [8-11] in details. Using an elementary approximation for the two-particle distribution function $\Phi_{ab}(R)$:

$$\Phi(R) = \begin{cases} 1 & R > r_a + r_b \\ 0 & R < r_a + r_b \end{cases} \tag{3}$$

and restricting ourselves with the case of two kinds of particles of different radii when $n_a = n_b = n_0$;

$$\varepsilon_a = \varepsilon_b = \varepsilon; \quad B_a = B_b = B = \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0}; \quad \Delta_{ab} = \Delta = \frac{r_b}{r_a} < 1,$$

from Eqs. (1-3) we get

$$\tilde{\varepsilon} = \varepsilon_0 \left[1 + \frac{3 f_0 \left(1 + \Delta^3\right)}{B^{-1} - f_0\left(1 + \Delta^3\right) - \frac{2}{3} f_0 D} \right] \tag{4}$$

where

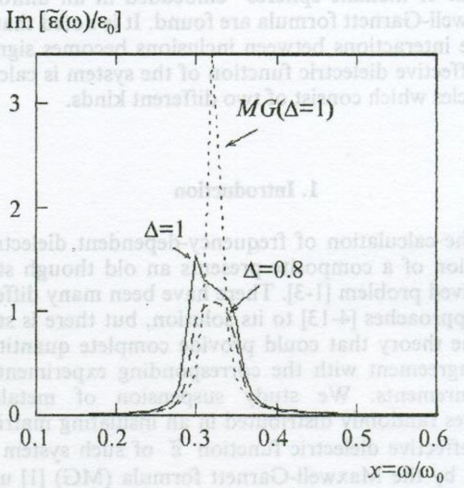
$$D = \left(\frac{1 + \Delta^6}{1 + \Delta^3} \right) \ln \frac{8 + B}{8 - 2B} + \frac{\Delta^3}{2(1 + \Delta^3)} \left(L_+ - L_- \right), \tag{5}$$

$$L_{\pm} = \left(\Delta^{3/4} \pm \Delta^{-3/4} \right)^2 \ln \frac{(1+\Delta)^3 \pm B\Delta^{3/2}}{(1+\Delta)^3 \mp 2B\Delta^{3/2}}$$

and $f_0 = \frac{4\pi}{3} R^3 n_0$ is the filling factor of inclusions.

Using this formula, we have carried out the numerical calculation of the frequency dependence of the imaginary part of $\tilde{\varepsilon}$ under various parameters of the composite (See a Figure) consisting of a glass matrix with embedded silver inclusions. The dielectric function $\varepsilon(\omega)$ of the metallic spheres is given by the Drude model [3]

$$\varepsilon(\omega) = \varepsilon'_\infty + i\varepsilon''_\infty - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \tag{6}$$



Plot of the imaginary part of $\tilde{\varepsilon}(\omega)/\varepsilon_0$ depending on $x = \omega/\omega_p$ and parameter Δ for silver spheres in a glass at volume fraction $f_0 = 0.04$; MG – Maxwell-Garnett approximation at $\Delta = 1$

with $\varepsilon'_\infty = 4.5$, $\varepsilon''_\infty = 0.16$, $\omega_p = 1.46 \cdot 10^{16}\ s^{-1}$, $\gamma = 1.68 \cdot 10^{14}\ s^{-1}$ for silver spheres. It should be noted that from Eqs. (2) in a particular case $\Delta = 1$ $\varepsilon''_\infty = 0$ and $\gamma = 0$, we obtain the frequencies of dipole surface plasmons for the particles, all of the same size [18-19]:

$$\omega_\parallel^2 = \omega_s^2 \frac{1 - 2\rho^3}{1 - 2\rho^3 B(\infty)}, \quad \omega_\perp^2 = \omega_s^2 \frac{1 + \rho^3}{1 + \rho^3 B(\infty)}, \tag{7}$$

$$B(\infty) = \frac{\varepsilon'_\infty - \varepsilon_0}{\varepsilon'_\infty + 2\varepsilon_0}$$

where $\rho = \frac{r}{R}$, and $\omega_s = \frac{\omega_p}{\sqrt{\varepsilon'_\infty + 2\varepsilon_0}}$ is a surface plasmon frequency of a separate particle.

2. Discussion of received results

Here we briefly discuss the obtained results. First, hold the case $\Delta = 1$. Then from Eqs. (4)-(5) it follows, that $\tilde{\varepsilon}$ can be found from the relation

$$\tilde{\varepsilon} = \varepsilon_0 \left(1 + \frac{3fB}{1 - fB - \frac{2}{3} fB \ln \frac{8+B}{8-2B}} \right), \qquad (8)$$

at $f = 2f_0$, which comes to the MG approximation when the term with logarithm in the denominator of Eq. (8) is neglected. It was analyzed in details in paper [14]. This term is associated with the pair dipole-dipole interaction (PDDI) between inclusions. The account of PDDI results in appearance of bounded absorption frequency band instead of a single frequency ω_s in the system. Really, at $\Delta = 1$ and $\varepsilon''_\infty \to 0$, $\gamma \to 0$ from Eq. (7) follows that each particle can absorb at two ($\omega_{\|}$ and $\omega_{\perp}$) frequencies, which values essentially depend on a distance R between a fixed particle and any other particle of the system. So, at $R \to \infty$, $\omega_{\|} = \omega_{\perp} = \omega_s$ and at $R = 2R_0$ (the minimal distance between particles) these frequencies are given by expressions

$$\overline{\omega}_{\|}^2 = \frac{\omega_p^2}{\varepsilon'_\infty + 3\varepsilon_0}; \quad \overline{\omega}_{\perp}^2 = \frac{\omega_p^2}{\varepsilon'_\infty + \frac{5}{3}\varepsilon_0}. \qquad (9)$$

Actually, this frequencies $\omega_{\|}$ and $\omega_{\perp}$ define the merges of continuous spectrum of absorption. The spectral dependence of $\tilde{\varepsilon}(\omega)$ of composite is obtained after averaging over the all possible positions of the particle pair in the matrix. It should be noted that in the metallic composite at $f \sim 0.1$ and more, the fine structure of the spectrum can be observed [4,14] if only PDDI is taken into account. The account of higher pair interactions between inclusions (quadrupole $l = l' = 2$, octupole $l = l' = 3$, etc.) can be made within the frameworks of our theory and would result in some partial smoothing of the frequency dependencies of $\operatorname{Im} \tilde{\varepsilon}(\omega)$ [17]. The similar effects can be caused also by other reasons – by many particles interactions, by the effect of clustering of particles, etc.

In case $r_b \ll r_a$ $(\Delta \to 0)$ the $\tilde{\varepsilon}$ value can be found from Eq. (8) at $f = f_0$ i. e. the contribution of particles with small radius (r_b) into value of $\tilde{\varepsilon}$ is negligibly small. The intermediate case is shown in the Figure where from it follows that account of simplest size distribution turns to smoothing fine structure in the frequency dependency of $\operatorname{Im} \tilde{\varepsilon}(\omega)$.

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Электромагнитный отклик системы взаимодействующих частиц

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Предложен теоретический подход к вычислению эффективной диэлектрической проницаемости системы, состоящей из двух сортов металлических сфер разного радиуса, случайно расположенных в диэлектрической среде. Изучены отклонения от формулы Максвелла-Гарнетта. Показано, что с увеличением объемной фракции частиц в системе становятся существенными эффекты мультипольного взаимодействия между частицами. С учетом диполь-дипольного взаимодействия рассмотрено поведение частотной зависимости мнимой части эффективной диэлектрической проницаемости системы.

Електромагнітний відгук системи взаємодіючих металічних частинок

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Запропоновано теоретичний підхід до обчислення ефективної діелектричної проникності системи, яка складається з двох видів металічних сфер різних радіусів, випадково розташованих в діелектричному середовищі. Вивчено відхилення від формули Максвелла-Гарнетта. Показано, що із збільшенням об'ємної фракції частинок в системі стають істотними ефекти мультипольної взаємодії між частинками. З урахуванням диполь-дипольної взаємодії розглянуто поведінку частотної залежності уявної частини ефективної діелектричної проникності системи.