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Electrodynamic Calculation of Effective Electromagnetic Parameters of a Dielectric Medium with Metallic Nanoparticles of a Given Size

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Abstract—The frequency dependence of the effective complex permittivity and effective complex permeability of a heterostructure based on a dielectric medium containing metallic nanoparticles of spherical shape is calculated by an original method. In contrast to the Bruggeman [21] and the Maxwell Garnett [17] approaches, which use the quasi-static approximation in calculations, a nonuniform distribution of electromagnetic fields inside metallic particles is calculated, which allows the analysis of the electromagnetic parameters of the heterostructure not only as a function of frequency but also as a function of the nanoparticle size. It is shown that the plasmon resonant frequency decreases with increasing both the size and the concentration of particles in the heterostructure. It is also shown that a dielectric medium containing nonmagnetic metallic nanoparticles exhibits diamagnetic properties. In this case, the position of the maximum on the frequency dependence of the imaginary part of the magnetic susceptibility coincides with the relaxation frequency of charge carriers. The calculated spectra of the real and imaginary components of the permittivity of the heterostructure with a size of metallic particles less than 10 nm are in good agreement with Bruggeman calculations; however, the agreement with Maxwell Garnett calculations is observed only at nanoparticle concentrations lower than 10^{-6}.

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1. INTRODUCTION

Modern technologies allow not only the fabrication of metallic nanoparticles of spherical shape with a size of from a few to hundreds of nanometers but also to produce, on the basis of these nanoparticles, aqueous suspensions of various concentrations, which are used, in particular, in medicine [1–3]. Metallic nanoparticles are also used to enhance the electromagnetic field near long molecular chains of dyes, which gives rise to local bistability in the vicinity of a particle [4]. It is well known that metallic nanoparticles exhibit plasmon resonances with frequencies in the optical range [5, 6]. That is why heterostructures based on a dielectric medium containing metallic nanoparticles, including aqueous suspensions, are colored, the color depending on the size of nanoparticles [7]. Since plasmon resonances in particles should manifest themselves in the frequency dependence of the electromagnetic parameters of heterostructures, the problem of calculating the effective permittivity and permeability of these structures is of great topical interest.

It is well known that, under an incident plane electromagnetic wave, forced electromagnetic oscillations in any inhomogeneous body of spherical shape represent a superposition of electric and magnetic multipole oscillations of orders from the first to infinity. The components of the electric and magnetic fields of such oscillations are described by spherical functions [8–10]. It is also known that the resonances of electric and magnetic multipole oscillations in dielectric spheres are observed at frequencies at which the size of a sphere is commensurate to the wavelength of the electromagnetic wave in the dielectric material. However, for multipole electric oscillations in metallic nanoparticles, which are often called plasmon oscillations, there are observed resonant excitations (plasmons) at frequencies at which the wavelength λ_m in the material is much greater than the particle radius a [6]. Plasmons of different multipolarity affect the character of electromagnetic wave scattering by metallic nanoparticles embedded in a dielectric matrix [11].

The resonant frequencies ω_n of multipole electric oscillations are given by the equations

$$(n+1)\varepsilon_d + n\varepsilon_m(\omega) = 0. \tag{1}$$

These equations are obtained from the condition of vanishing of the denominators of the electric field amplitudes [8–10] as $a \to 0$. Here ε_d is the relative permittivity of the surrounding medium, and $\varepsilon_m(\omega)$ is the relative complex permittivity of the nanoparticle material, which is expressed by the following formula within a modified Drude model [12]:

$$\varepsilon_m(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma}, \quad (2)$$

where ε_∞ is the optical permittivity of the metal, ω_p is the frequency of plasma oscillations in the metal, and γ is the relaxation frequency of charge carriers. It was assumed when deriving this formula that harmonic oscillations are described by the factor $\exp(-i\omega t)$. Formulas (1) and (2) imply that the resonant frequencies ω_n and the quality factors Q_n of multipole electric oscillations are expressed by the following formulas for $2\pi a \ll \lambda_m$:

$$\omega_n = \sqrt{\frac{\omega_p^2}{(1+n^{-1})\varepsilon_d + \varepsilon_\infty} - \left(\frac{\gamma}{2}\right)^2}. \quad (3)$$

$$Q_n = \sqrt{\frac{\omega_p^2\gamma^{-2}}{(1+n^{-1})\varepsilon_d + \varepsilon_\infty} - \frac{1}{4}}. \quad (4)$$

Plasmon oscillations with $n = 1$, i.e., electric dipole oscillations, have the greatest amplitude. The amplitudes of other (quadrupole, octupole, etc.) plasmon oscillations rapidly decrease both with increasing their order n and with decreasing particle radius a.

Note that forced magnetic multipole oscillations in spherical metallic nanoparticles have no resonances in the optical range because the real part of the denominators of their amplitudes does not vanish for $a < \lambda_m$ [13]. However, in the presence of a dc magnetic field, a magnetic dipole resonance is observed together with the electric dipole resonance [14].

It is known from experiments [5, 7, 8] that the frequency ω_1 of plasmon oscillations of a metallic nanoparticle starts to slowly decrease with increasing particle radius a; but this occurs only when the radius a exceeds a certain value on the order of 5 nm. In [5], the authors attributed this phenomenon to the presence of several damping mechanisms of plasmons, using the quasi-static approximation. In another paper [15], the dependence of the resonant frequency of plasmon oscillations on the size of a metallic nanoparticle was attributed to quantum size-dependent effects, also in the quasi-static approximation. However, as shown in [6], the dependence of the resonant frequencies of multipole plasmon oscillations on the particles size can be obtained by the electrodynamic calculation of the electromagnetic field distribution inside a particle; i.e., one can give up using the quasi-static approximation, in which it is assumed that the local high-frequency properties of the nanoparticle material are uniform over the whole volume of the particle and coincide with the local properties of the bulk material.

Most authors also apply the electric dipole quasi-static approximation to calculate the effective complex permittivity ε_{eff} of a dielectric medium containing metallic nanoparticles. Therefore, the formulas obtained by these authors do not contain the radius a of metallic nanoparticles and, hence, do not describe the effect of the nanoparticle size on the frequency dispersion of ε_{eff} near the plasmon resonant frequency ω_1. Among these formulas are the Maxwell–Wagner formula [16]

$$\varepsilon_{\text{eff}} = \varepsilon_d\left[1 + 3c_m\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \Big/ \left(1 - c_m\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}\right)\right] \quad (5)$$

and the Maxwell Garnett formula [12, 17–20], identical to it, which is especially frequently cited by researchers, as well as the Bruggeman formula [20, 21]

$$\begin{gathered}\varepsilon_{\text{eff}} = \frac{H_B + \sqrt{H_B^2 + 8\varepsilon_m\varepsilon_d}}{4}, \\ H_B = (2 - 3c_m)\varepsilon_d - (1 - 3c_m)\varepsilon_m.\end{gathered} \quad (6)$$

Here, c_m stands for the volume concentration of metallic nanoparticles in the dielectric medium.

Formula (5) is obtained in the approximation of low concentration c_m of metallic nanoparticles in a heterostructure, when the interaction between particles can be neglected. In formula (6), the interaction between nanoparticles is taken into account only in the mean-field approximation. The values of ε_{eff} calculated by these two formulas coincide only for very low concentrations ($c_m < 1 \times 10^{-6}$); however, these values strongly differ already for $c_m = 1 \times 10^{-5}$. It follows from both formulas that the resonant frequency ω_1 of dipole plasmon oscillations is expressed by formula (3) with $n = 1$.

In [22], the authors compared the existing variants of the refinement of Maxwell Garnett's theory to take into account the effect of the nanoparticle size on $\varepsilon_{\text{eff}}(\omega)$. In one of the variants [13], it was suggested that the static electric polarizability of a nanoparticle should be replaced by the electrodynamic polarizability, which is described by formulas of the Mie theory [8–10]. A similar approach was used in [23] when deriving a formula for calculating the effective permeability μ_{eff} of a heterostructure.

In [24], to take into account the dependence of the effective permeability on the particle size, the authors used the formalism of integral equations and Green's functions. However, such a formalism assumes that the electric field inside a nanoparticle is uniform, which is a rough approximation, although it is also used in [25, 26].

Thus, the known formulas for calculating the effective complex permittivity, which allow one to take into account the dependence of ε_{eff} on the radius a of metallic nanoparticles in a heterostructure, have been obtained on the basis of the Maxwell Garnett approach. However, a considerable discrepancy between the results of calculation of ε_{eff} by the quasi-static formulas of Maxwell Garnett and Bruggeman even at low concentration of nanoparticles in a heterostructure ($c_m = 1 \times 10^{-5}$) shows that too rough approximations have been made when deriving these formulas.

The investigations carried out in the present work have been motivated by the necessity to develop a model and perform a calculation of a heterostructure consisting of a dielectric matrix with metallic nanoparticles for a more accurate description of the dielectric properties of the object compared with the Maxwell Garnett and Bruggeman models. The amplitudes of electromagnetic fields in the model are assumed to be nonuniform in the volume of a particle, which is absolutely correct from the physical viewpoint under conditions of plasmon excitations in metallic particles. In other words, particles of infinitesimally small sizes are replaced by particles with real dimensions. The interaction between particles is taken into account within the Bruggeman approach. As a result, we obtain formulas for calculating the effective complex permittivity, as well as the effective permeability of a heterostructure. This allows us to analyze the electromagnetic parameters of the medium as a function of frequency, the size of nanoparticles, and their concentration in the heterostructure. The correctness of the approach is proved, in particular, by a significant reduction in the frequency of a plasmon resonance with increasing size of metallic particles, which was observed experimentally in aqueous suspensions of silver nanoparticles [5, 7].

2. COMPARISON OF THE MAXWELL GARNETT AND BRUGGEMAN APPROACHES IN CALCULATING THE EFFECTIVE PARAMETERS OF HETEROSTRUCTURES

The Maxwell Garnet approach is based on the approximate formula

$$\varepsilon_{\text{eff}} = \varepsilon_d + \frac{P}{\varepsilon_0 E}, \qquad (7)$$

where ε_0 is the absolute permittivity of vacuum, ε_{eff} is the relative effective permittivity of a heterostructure with nanoparticles, ε_d is the relative permittivity of the heterostructure matrix, and P is the dielectric polarization of metallic nanoparticles under an electromagnetic field with electric field amplitude E. This approach implicitly assumes that formula (7) follows from the well-known formula

$$D \equiv \varepsilon_0 E + P = \varepsilon_0 \varepsilon_d E,$$

which is used to describe the dielectric properties of only continuous homogeneous media, in which no multipole, except for dipole, oscillations can be excited. This means that this approach basically does not allow the description of higher order multipole excitations in metallic particles, which are well observed experimentally.

Moreover, a serious flaw in the Maxwell Garnett approach is that the dipole moments of real spherical metallic particles of radius a are replaced in calculation by equivalent moments of dipoles placed at the centers of the particles reduced to a point size ($a = 0$). Under such replacement, the real electric field in a nanoparticle has a singularity. However, this singularity of the field is not taken into account, and it is assumed that the field inside a particle is the same as in the surrounding matrix. As a result, the depolarization field inside a particle is ruled out, and, therefore, the contribution of metallic particles to the effective permittivity of the heterostructure is overestimated.

The Bruggeman approach is based on a rigorous formula that reflects the continuity of the electric induction flux:

$$\Delta\Phi \equiv \iint \varepsilon_r(\mathbf{r}) E_n(\mathbf{r}) ds - \varepsilon_{\text{eff}} \iint E_0 ds = 0, \qquad (8)$$

where $\Delta\Phi$ is the jump of the electric induction flux on the integration surface; $E_n(\mathbf{r})$ is the component of the microscopic electric field normal to the integration surface; $\varepsilon_r(\mathbf{r})$ is the local relative permittivity of the heterostructure that takes the values ε_m inside a chosen metallic nanoparticle, ε_d inside a chosen dielectric particle, and ε_{eff} outside the chosen particle; and $\mathbf{E}_0$ is the macroscopic electric field of the wave that is orthogonal to the integration surface. This formula is obtained by integrating the Maxwell equation

$$\operatorname{div}(\varepsilon_r \mathbf{E}) = 0 \qquad (9)$$

over any surface orthogonal to the microscopic field $\mathbf{E}_0$. It is obvious that this surface is the averaging surface of the microscopic field. Since the heterostructure is assumed to be macroscopically homogeneous, the location of the averaging surface for the microscopic field can be chosen arbitrarily. Obviously, the concept of effective permittivity ε_{eff} makes sense only when the transverse dimensions of the surface are greater than the transverse size of a nanoparticle but much less than the wavelength in the heterostructure.

Note that, in the Bruggeman approach, only one nanoparticle is considered explicitly; however, its interaction with other nanoparticles is still taken into account, but only in the mean-field approximation in the heterostructure, which is characterized by the parameter ε_{eff}.

Thus, in calculating the effective complex permittivity of a dielectric medium with metallic nanoparticles, the Bruggeman approach is more rigorous than the Maxwell Garnett approach.

3. CALCULATION OF EFFECTIVE ELECTROMAGNETIC PARAMETERS OF A DIELECTRIC MEDIUM WITH METALLIC NANOPARTICLES

We will assume that the heterostructure is a medium consisting of dielectric and metallic nanoballs. We represent the integral jump in the electric induction flux $\Delta\Phi$ on the integration surface, which is calculated by formula (8), as a sum of jumps from single nanoparticles in the averaged medium:

$$\Delta\Phi = n_m\Delta\Phi_m + n_d\Delta\Phi_d, \qquad (10)$$

where n_m and n_d are the numbers of metallic and dielectric nanoparticles, respectively, in the integration area and $\Delta\Phi_m$ and $\Delta\Phi_d$ are the contributions of these separate particles in the homogeneous medium with ε_{eff} and μ_{eff} to the integral jump.

We start the calculation with the jump of $\Delta\Phi_m$. To this end, we consider the propagation of a plane electromagnetic wave in a homogeneous medium containing a single spherical metallic nanoparticle. Suppose that the macroscopic field components of the wave are expressed by the formulas

$$\begin{aligned} E_x(z) &= E_0\exp(ik_{\text{eff}}z), \\ H_y(z) &= H_0\exp(ik_{\text{eff}}z), \end{aligned} \qquad (11)$$

where the amplitudes of the electric and magnetic fields are related by the formula $E_0 = Z_{\text{eff}}H_0$ and the wave number k_{eff} and the characteristic impedance Z_{eff} are defined by the formulas

$$\begin{aligned} k_{\text{eff}} &= \sqrt{\varepsilon_{\text{eff}}\mu_{\text{eff}}}\,\frac{\omega}{c}, \\ Z_{\text{eff}} &= Z_0\sqrt{\frac{\mu_{\text{eff}}}{\varepsilon_{\text{eff}}}}, \quad Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}. \end{aligned} \qquad (12)$$

Let us single out a single particle in the heterostructure and place the origin of coordinates at its center. Consider a microscopic electromagnetic field inside and near this nanoparticle. Outside the particle, the field is a superposition of the field of the incident wave given by formulas (11) and the field of the reflected wave. Inside the particle, this field is characterized by the field of the transmitted wave. As is known [9], the field components of the reflected wave are expressed by

$$\begin{aligned} \mathbf{E}^r &= E_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}(A_n^r\mathbf{m}^r_{o1n} - iB_n^r\mathbf{n}^r_{e1n}), \\ \mathbf{H}^r &= E_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}(-iA_n^r\mathbf{n}^r_{o1n} - B_n^r\mathbf{m}^r_{e1n}), \end{aligned} \qquad (13)$$

where the vector functions $\mathbf{m}^r_{o1n}(r, \theta, \varphi)$, $\mathbf{n}^r_{o1n}(r, \theta, \varphi)$, $\mathbf{m}^r_{e1n}(r, \theta, \varphi)$, and $\mathbf{n}^r_{e1n}(r, \theta, \varphi)$ are defined in the spherical system of coordinates by the formulas

$$\begin{aligned} \mathbf{m}^r_{\substack{o\\e}1n} &= \substack{\cos\\ -\sin}\,\varphi h_n^{(1)}(k_{\text{eff}}r)\frac{P_n^1(\cos\theta)}{\sin\theta}\mathbf{i}_\theta \\ &\quad - \substack{\sin\\ \cos}\,\varphi h_n^{(1)}(k_{\text{eff}}r)\frac{dP_n^1(\cos\theta)}{d\theta}\mathbf{i}_\varphi, \\ \mathbf{n}^r_{\substack{o\\e}1n} &= \substack{\sin\\ \cos}\,\varphi n(n+1)\frac{h_n^{(1)}(k_{\text{eff}}r)}{k_{\text{eff}}r} \\ &\quad \times P_n^1(\cos\theta)\mathbf{i}_r + \substack{\sin\\ \cos}\,\varphi\frac{[k_{\text{eff}}rh_n^{(1)}(k_{\text{eff}}r)]'}{k_{\text{eff}}r} \\ &\quad \times\frac{dP_n^1(\cos\theta)}{d\theta}\mathbf{i}_\theta + \substack{\cos\\ -\sin}\,\varphi \\ &\quad \times\frac{[k_{\text{eff}}rh_n^{(1)}(k_{\text{eff}}r)]'}{k_{\text{eff}}r}\frac{P_n^1(\cos\theta)}{\sin\theta}\mathbf{i}_\varphi, \end{aligned} \qquad (14)$$

and the coefficients A_n^r and B_n^r, which are the amplitudes of magnetic and electric multipole excitations of the nth order, respectively, are defined by the formulas

$$\begin{aligned} A_n^r &= -\frac{\mu_m j_n(k_m a)[k_{\text{eff}}a j_n(k_{\text{eff}}a)]' - \mu_{\text{eff}} j_n(k_{\text{eff}}a)[k_m a j_n(k_m a)]'}{\mu_m j_n(k_m a)[k_{\text{eff}}a h_n^{(1)}(k_{\text{eff}}a)]' - \mu_{\text{eff}} h_n^{(1)}(k_{\text{eff}}a)[k_m a j_n(k_m a)]'}, \\ B_n^r &= -\frac{\varepsilon_m j_n(k_m a)[k_{\text{eff}}a j_n(k_{\text{eff}}a)]' - \varepsilon_{\text{eff}} j_n(k_{\text{eff}}a)[k_m a j_n(k_m a)]'}{\varepsilon_m j_n(k_m a)[k_{\text{eff}}a h_n^{(1)}(k_{\text{eff}}a)]' - \varepsilon_{\text{eff}} h_n^{(1)}(k_{\text{eff}}a)[k_m a j_n(k_m a)]'}. \end{aligned} \qquad (15)$$

Here $j_n(x)$ and $h_n^{(1)}(x)$ are spherical Bessel functions whose order n coincides with the order of the multipole excitation, $P_n^m(x)$ is the associated Legendre function of the first kind, μ_m and μ_{eff} are relative permeability of the metal of the nanoparticle and the relative effective permeability of the heterostructure, respectively, and the wave number for the metal of the nanoparticle is defined by the formula

$$k_m = \sqrt{\varepsilon_m\mu_m}\,\omega/c. \qquad (16)$$

The prime over the square bracket indicates differentiation with respect to $k_m a$ or $k_{\text{eff}}a$, depending on the content of the bracket.

The field components of the wave transmitted into the nanoparticle are expressed as

$$\mathbf{E}^t = E_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}(A_n^t\mathbf{m}_{o1n}^t - iB_n^t\mathbf{n}_{e1n}^t),$$
$$\mathbf{H}^t = \frac{Z_{\mathrm{eff}}}{Z_m}H_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}(-iA_n^t\mathbf{n}_{o1n}^t - B_n^t\mathbf{m}_{e1n}^t), \tag{17}$$

where Z_m is the characteristic impedance of the metallic medium of the nanoparticle,

$$Z_m = Z_0\sqrt{\mu_m/\varepsilon_m}, \tag{18}$$

the vector functions $\mathbf{m}_{o1n}^t(r, \theta, \varphi)$, $\mathbf{n}_{o1n}^t(r, \theta, \varphi)$, $\mathbf{m}_{e1n}^t(r, \theta, \varphi)$, and $\mathbf{n}_{e1n}^t(r, \theta, \varphi)$ are defined by the formulas

$$\mathbf{m}^t_{\substack{o\\e}1n} = \genfrac{}{}{0pt}{}{\cos}{-\sin}\varphi j_n(k_mr)\frac{P_n^1(\cos\theta)}{\sin\theta}\mathbf{i}_0$$
$$+\genfrac{}{}{0pt}{}{-\sin}{-\cos}\varphi j_n(k_mr)\frac{dP_n^1(\cos\theta)}{d\theta}\mathbf{i}_\varphi,$$

$$\mathbf{n}^t_{\substack{o\\e}1n} = \genfrac{}{}{0pt}{}{\sin}{\cos}\varphi n(n+1)\frac{j_n(k_mr)}{k_mr}$$
$$\times P_n^1(\cos\theta)\mathbf{i}_r + \genfrac{}{}{0pt}{}{\sin}{\cos}\varphi\frac{[k_mrj_n(k_mr)]'}{k_mr} \tag{19}$$
$$\times\frac{dP_n^1(\cos\theta)}{d\theta}\mathbf{i}_0 + \genfrac{}{}{0pt}{}{\cos}{-\sin}\varphi\frac{[k_mrj_n(k_mr)]'}{k_mr}\frac{P_n^1(\cos\theta)}{\sin\theta}\mathbf{i}_\varphi,$$

and the amplitudes are given by

$$A_n^t = \frac{\mu_m j_n(k_{\mathrm{eff}}a)[k_{\mathrm{eff}}ah_n^{(1)}(k_{\mathrm{eff}}a)]' - \mu_m h_n^{(1)}(k_{\mathrm{eff}}a)[k_{\mathrm{eff}}aj_n(k_{\mathrm{eff}}a)]'}{\mu_m j_n(k_ma)[k_{\mathrm{eff}}ah_n^{(1)}(k_{\mathrm{eff}}a)]' - \mu_{\mathrm{eff}}h_n^{(1)}(k_{\mathrm{eff}}a)[k_maj_n(k_ma)]'},$$
$$B_n^t = \frac{\varepsilon_m j_n(k_{\mathrm{eff}}a)[k_{\mathrm{eff}}ah_n^{(1)}(k_{\mathrm{eff}}a)]' - \varepsilon_m h_n^{(1)}(k_{\mathrm{eff}}a)[k_{\mathrm{eff}}aj_n(k_{\mathrm{eff}}a)]'}{\varepsilon_m j_n(k_ma)[k_{\mathrm{eff}}ah_n^{(1)}(k_{\mathrm{eff}}a)]' - \varepsilon_{\mathrm{eff}}h_n^{(1)}(k_{\mathrm{eff}}a)[k_maj_n(k_ma)]'}\frac{Z_m}{Z_{\mathrm{eff}}}. \tag{20}$$

Consider in greater detail the electromagnetic field in two orthogonal planes that pass through the center of the nanoparticle and are orthogonal to the vectors $\mathbf{E}_0$ and $\mathbf{H}_0$ of the incident wave. Note that the only unit vector $\mathbf{i}_\varphi$ of the spherical system of coordinates is orthogonal to these planes. From formulas (13) and (17) we obtain orthogonal field components in Cartesian coordinates:

$$E_x^r = E_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}\left(A_n^rh_n^{(1)}(k_{\mathrm{eff}}r)\frac{dP_n^1(\cos\theta)}{d\theta}\right.$$
$$\left.- iB_n^r\frac{[k_{\mathrm{eff}}rh_n^{(1)}(k_{\mathrm{eff}}r)]'}{k_{\mathrm{eff}}r}\frac{P_n^1(\cos\theta)}{\sin\theta}\right), \tag{21}$$
$$H_y^r = H_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}\left(-iA_n^r\frac{[k_{\mathrm{eff}}rh_n^{(1)}(k_{\mathrm{eff}}r)]'}{k_{\mathrm{eff}}r}\right.$$
$$\left.\times\frac{P_n^1(\cos\theta)}{\sin\theta} + B_n^rh_n^{(1)}(k_{\mathrm{eff}}r)\frac{dP_n^1(\cos\theta)}{d\theta}\right),$$

and

$$E_x^t = E_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}\left(A_n^tj_n(k_mr)\frac{dP_n^1(\cos\theta)}{d\theta}\right.$$
$$\left.- iB_n^t\frac{[k_mrj_n(k_mr)]'}{k_mr}\frac{P_n^1(\cos\theta)}{\sin\theta}\right),$$
$$H_y^t = \frac{Z_{\mathrm{eff}}}{Z_m}H_0\sum_{n=1}^{\infty} i^n\frac{2n+1}{n(n+1)}\left(-iA_n^t\frac{[k_mrj_n(k_mr)]'}{k_mr}\right. \tag{22}$$
$$\left.\times\frac{P_n^1(\cos\theta)}{\sin\theta} + B_n^tj_n(k_mr)\frac{dP_n^1(\cos\theta)}{d\theta}\right).$$

According to formulas (8) and (10), the jump $\Delta\Phi_m$ is expressed by the following formula in spherical coordinates:

$$\Delta\Phi_m = 2\int_{\theta=0}^{\pi}\int_{r=0}^{a}(\varepsilon_mE_x^t - \varepsilon_{\mathrm{eff}}E_0)rdrd\theta$$
$$+ 2\varepsilon_{\mathrm{eff}}\int_{\theta=0}^{\pi}\int_{r=0}^{R}E_x^rrdrd\theta, \tag{23}$$

where R is the radius of the domain in the plane $x = 0$ over which the microscopic field is averaged.

Before substituting formulas (21) and (22) into Eq. (23) and integrating it, we first integrate the components E_x^r and E_x^t only with respect to the angle θ; after that, the contribution of some part of multipole excitations in the integrals vanishes, and the expressions obtained are simplified:

$$\begin{aligned}\int\limits_{\theta=0}^{\pi} E_x^r d\theta = E_0 \sum_{n=1,3,5,\ldots}^{\infty} i^{n-1}\frac{2n+1}{n(n+1)} \\ \times B_n^r \frac{[k_{\text{eff}} r h_n^{(1)}(k_{\text{eff}} r)]'}{k_{\text{eff}} r} \int\limits_{\theta=0}^{\pi} \frac{dP_n(\cos\theta)}{d\cos\theta} d\theta,\end{aligned} \tag{24}$$

$$\begin{aligned}\int\limits_{\theta=0}^{\pi} E_x^t d\theta = E_0 \sum_{n=1,3,5,\ldots}^{\infty} i^{n-1}\frac{2n+1}{n(n+1)} \\ \times B_n^t \frac{[k_m r j_n(k_m r)]'}{k_m r} \int\limits_{\theta=0}^{\pi} \frac{dP_n(\cos\theta)}{d\cos\theta} d\theta.\end{aligned} \tag{25}$$

We can see that the sums in these integrals contain the contributions of electric multipole excitations only of odd orders, i.e., the electric dipole excitations ($n = 1$), electric octupole excitation ($n = 3$), etc.

Since the amplitudes of multipole excitations B_n^r and B_n^t rapidly decay with increasing order n, to simplify further calculations, we will take into account only dipole excitations. We will also assume that the size of the domain of radius R over which the microscopic field is averaged is much less than the wavelength, i.e., $|k_{\text{eff}}R| \ll 1$. This inequality is a natural condition that justifies the use of the effective electromagnetic parameters of the heterostructure when describing dynamic processes in it. It allows one to keep only the leading terms in the coefficients B_1^r and B_1^t and in the function $[k_{\text{eff}} r h_n^{(1)}(k_{\text{eff}} r)]'$. We will describe the microscopic field inside the metallic nanoparticle without the quasi-static approximation, i.e., we will impose no additional inequality on $|k_m a|$ except for the natural inequality $a < R$.

After substituting the simplified expressions (24) and (25), formula (23) is rewritten as

$$\Delta\Phi_m = \frac{a^3}{R^3}\frac{\varepsilon_m J(\varepsilon_m a) - \varepsilon_{\text{eff}}}{\varepsilon_m J(k_m a) + 2\varepsilon_{\text{eff}}} 2\pi R^2 \varepsilon_{\text{eff}} E_0, \tag{26}$$

where the function $J(x)$ is defined by the formula

$$J(x) = 2\frac{1 - x\cot x}{x^2 + x\cot x - 1}. \tag{27}$$

In a similar way we can calculate the contribution of a single dielectric nanoparticle of arbitrarily small radius b to the jump $\Delta\Phi_d$. This contribution is expressed by a similar formula

$$\Delta\Phi_d = \frac{b^3}{R^3}\frac{\varepsilon_d J(k_d b) - \varepsilon_{\text{eff}}}{\varepsilon_d J(k_d b) + \varepsilon_{\text{eff}}} 2\pi R^2 \varepsilon_{\text{eff}} E_0. \tag{28}$$

Substituting expressions (26), (28), and (10) into Eq. (8), we obtain the sought equation for calculating the effective permittivity of the heterostructure:

$$c_m \frac{\varepsilon_m J(k_m a) - \varepsilon_{\text{eff}}}{\varepsilon_m J(k_m a) + 2\varepsilon_{\text{eff}}} + c_d \frac{\varepsilon_d - \varepsilon_{\text{eff}}}{\varepsilon_d + 2\varepsilon_{\text{eff}}} = 0, \tag{29}$$

where the coefficients of the relative volume concentration of metal and dielectric are given by the formulas $c_m = n_m a^3/R^3$ and $c_d = n_d b^3/R^3$ and are related by the condition $c_m + c_d = 1$. These formulas take into account that, for $|x| \ll 1$, the function $J(x)$ is a constant equal to one.

As a result, from expression (29) we obtain an equation that is quadratic in the sought quantity ε_{eff} and therefore has two solutions:

$$\varepsilon_{\text{eff}} = \frac{H_\varepsilon \pm \sqrt{H_\varepsilon^2 + 8\varepsilon_m\varepsilon_d J(k_m a)}}{4}, \tag{30}$$

where

$$H_\varepsilon = (2 - 3c_m)\varepsilon_d - (1 - 3c_m)\varepsilon_m J(k_m a).$$

Note that, for $|k_m a| \ll 1$, formula (30) exactly coincides with the well-known Bruggeman formula (6) if we consider only the solution with plus sign.

In the monograph [12], as well as in [27], the authors suggest leaving only the plus sign at the square root when choosing a solution to the Bruggeman equation. However, since the permittivity ε_m of metallic particles is complex, this choice of the solution for the effective permittivity ε_{eff} is not always correct.

Indeed, as is known, the positive sign of the imaginary part of ε_{eff} indicates the presence of dielectric or ohmic loss in the medium, which determines the attenuation of the electromagnetic wave, while the negative sign contradicts physics: it implies the amplification of the electromagnetic wave, i.e., the generation of energy in the structure. Therefore, the sign at the square root should be chosen so that the imaginary part of ε_{eff} always remains positive. The correct choice of the sign for the solution to Eq. (29) is guaranteed automatically if we rewrite formula (30) as

$$\varepsilon_{\text{eff}} = \frac{H_\varepsilon + i\sqrt{-H_\varepsilon^2 - 8\varepsilon_m\varepsilon_d J(k_m a)}}{4}. \tag{31}$$

It is important that the sign of $\text{Re}\,\varepsilon_{\text{eff}}$ may be any.

Performing similar calculations for the magnetic fields $\mathbf{H}^r$ and $\mathbf{H}^t$ defined by formulas (13) and (17), we can calculate the effective permeability of a dielectric medium containing metallic nanoparticles. In this case, it is easy to show that only magnetic multipole oscillations of odd order contribute to μ_{eff}. However, for simplicity, we will take into account only magnetic dipole oscillations. As a result, we obtain a formula for calculating the effective relative permeability of a dielectric medium with metallic nanoparticles:

$$\mu_{\text{eff}} = \frac{H_\mu + i\sqrt{-H_\mu^2 - 8\mu_m\mu_d J(k_m a)}}{4}, \tag{32}$$

where

$$H_\mu = (2 - 3c_m)\mu_d - (1 - 3c_m)\mu_m J(k_m a). \tag{33}$$

For $\mu_m = \mu_d$ and $|k_m a| \ll 1$, formula (32) is simplified to

$$\mu_{\text{eff}} = \mu_d\left(1 + \frac{c_m}{10}\frac{\omega^2}{c^2}a^2\varepsilon_m\right). \tag{34}$$

Note that the effective permeability μ_{eff} of the heterostructure is different from unity even for $\mu_m = \mu_d = 1$ if $k_m a \neq 0$, which was pointed out earlier in [28].

The calculation performed shows that electric multipole oscillations of any order in nanoparticles do not contribute to the effective permeability of the heterostructure, just as magnetic multipole oscillations of any order do not contribute to the effective permittivity of the medium.

4. RESULTS OF INVESTIGATIONS AND THEIR ANALYSIS

We pointed out that the difference between the formulas obtained in the present study and the Maxwell Garnett and Bruggeman formulas consists in that our formulas show the dependence of the effective electromagnetic parameters of a heterostructure on the size of nanoparticles contained in the matrix. It is also important to note that, for a nanoparticle radius of $a <$ 5 nm and a concentration of $c_m < 10^{-6}$, the frequency dependences of the components of the effective complex permittivity $\varepsilon_{\text{eff}} = \varepsilon' + i\varepsilon''$ constructed by the Maxwell Garnett and Bruggeman formulas and our formulas are almost indistinguishable. However, for a concentration of $c_m > 10^{-5}$, the functions $\varepsilon'(f)$ and $\varepsilon''(f)$ constructed by the Maxwell Garnett formula significantly differ from the corresponding functions constructed by the Bruggeman and our formulas.

Figure 1 demonstrates the frequency dependences of the effective complex permittivity components of an aqueous suspension of silver particles with concentration of $c_m = 10^{-3}$, calculated by formula (31) for several values of the particle radius, as well as the frequency dependence calculated by the Maxwell Garnett (5) and Bruggeman (6) formulas. In these calculations, the permittivity ε_m of metallic particles is determined by formula (2). In this case, the values of the parameters entering this formula are borrowed from [6]: the plasma frequency $\omega_p/2\pi$ = 1600 THz, the relaxation frequency of charge carriers $\gamma/2\pi$ = 20 THz, and the optical permittivity of the metal $\varepsilon_\infty = 1$. According to the data from [29], the permittivity of water (the dielectric matrix of the heterostructure under investigation) is $\varepsilon_d = 1.788$. All these parameters are used in our further investigations.

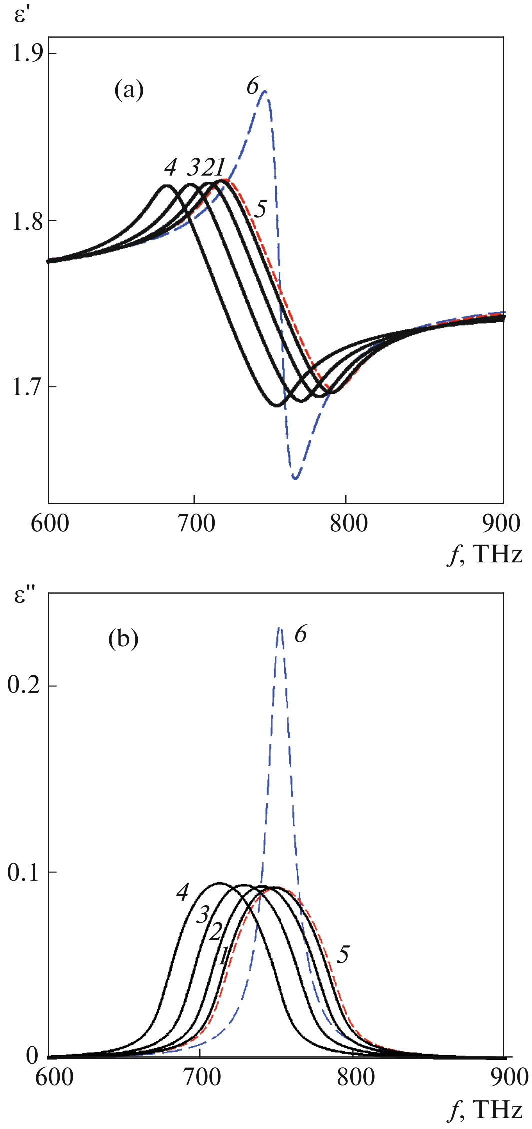

Fig. 1. (Color online) Frequency dependence of the (a) real and (b) imaginary parts of the effective permittivity of the aqueous suspension of silver nanoparticles with concentration $c_m = 1 \times 10^{-3}$ calculated by formula (31) for a = 10 (*1*), 20 (*2*), 30 (*3*), and 40 nm (*4*); (*5*) calculation by the Bruggeman formula, and (*6*) calculation by the Maxwell Garnett formula.

The functions in Fig. 1 are plotted in a narrow frequency range near the resonant frequency f_1 of dipole ($n = 1$) oscillations of particles. One can see that the resonance curves calculated by the Maxwell Garnett and Bruggeman formulas differ significantly. In particular, the maxima of the imaginary components ε_1'' of permittivities, which characterize the absorption in the heterostructure, and the widths Δf_1 of the reso-

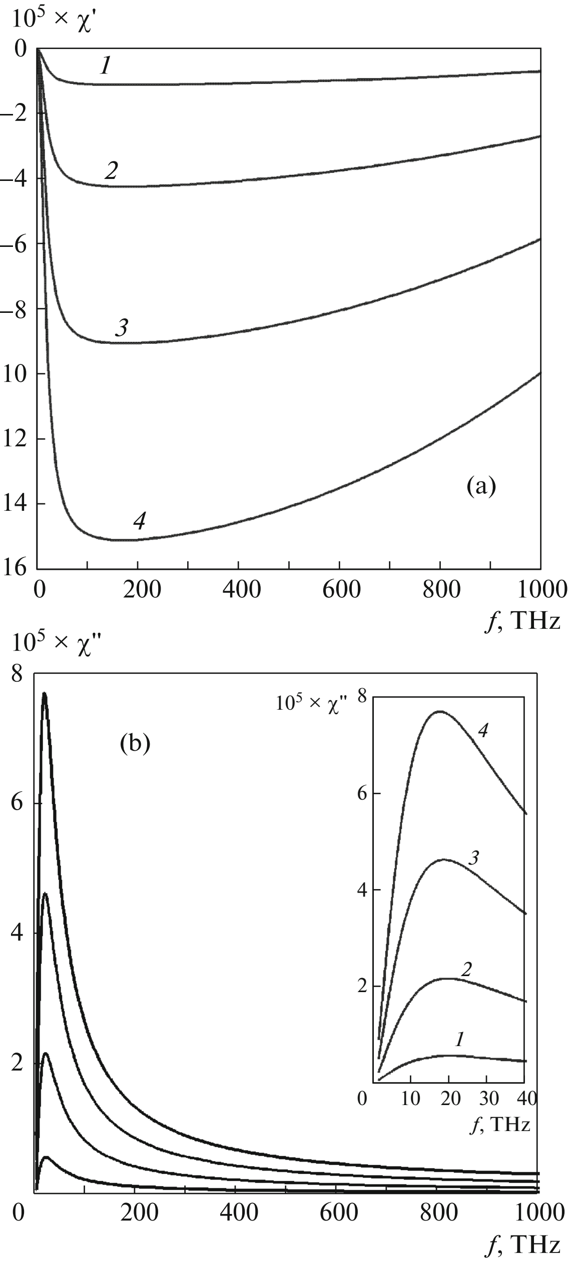

Fig. 2. (Color online) Frequency dependences of the (a) real and (b) imaginary parts of the effective relative magnetic susceptibility of the aqueous suspension of silver nanoparticles with concentration $c_m = 1 \times 10^{-3}$ calculated by formula (32) for particle radius $a = 10$ (*1*), 20 (*2*), 30 (*3*), and 40 nm (*4*).

nance lines measured at half-maximum level differ by a factor of more than two, although the resonant frequencies f_1 coincide. The diagrams in Fig. 1 constructed by our formula (31), in contrast to the Maxwell Garnett and Bruggeman formulas, show a significant decrease in the plasma resonant frequency f_1 with increasing size of metallic nanoparticles $a >$ 10 nm. However, for $a < 5$ nm, the resonance curves calculated by formula (31) are almost indistinguishable from the analogous curves calculated by the Bruggeman formula (6).

It is obvious that if a heterostructure does not contain magnetic particles, its effective permeability μ_{eff} is close to unity. Therefore, it is more convenient to describe the magnetic properties of the aqueous suspension of silver by the effective relative magnetic susceptibility $\chi_{\text{eff}} = \mu_{\text{eff}} - 1$. Figure 2 plots the diagrams of $\chi_{\text{eff}} = \chi' + i\chi''$ calculated by formula (32) in a wide range of frequencies for several sizes of silver nanoparticles with a concentration of $c_m = 1 \times 10^{-3}$ in the suspension. Here it is assumed that $\mu_m = \mu_d = 1$.

Note that the real part of the magnetic susceptibility $\chi'(f)$ of the heterostructure does not show a magnetic dipole resonance in the frequency range considered, because the frequency of this resonance, in contrast to that of the electric dipole resonance, is much higher than the frequency range. However, the function $\chi''(f)$ exhibits a pronounced maximum in the far infrared region, whose frequency $f_{\max}$, according to investigations, is virtually independent of the size of particles in the suspension when their radius $a <$ 30 nm. The inset in Fig. 2 demonstrates a fragment of the region of maximum of $\chi''(f)$ in which it is clearly seen that $f_{\max} \approx 20$ THz; however, one should note that the maximum frequency monotonically decreases with increasing size of nanoparticles.

To explain the nature of the nonresonant maximum on the frequency dependence of the imaginary component of the magnetic susceptibility of the suspension, we substitute the complex permittivity $\varepsilon_m(\omega)$ of the nanoparticle material (see formula (2)) into formula (34), rightly assuming that the particle size in the chosen frequency range is much less than the wavelength, $|k_m a| \ll 1$. Then we single out the imaginary part in the expression obtained:

$$\chi'' = \frac{c_m \gamma}{10} \frac{\omega_p^2}{c^2} a^2 \frac{\omega^2}{\omega^2 + \gamma^2}. \tag{35}$$

We can see that the maximum of the imaginary part of the effective magnetic susceptibility is exactly at the relaxation frequency $\omega_{\max} = \gamma$ of charge carriers. This fact shows that the relaxation frequency of charge carriers in the heterostructure can be determined experimentally. To this end, one should only measure the frequency of maximum attenuation of electromagnetic waves, which obviously coincides with the maximum frequency of the function $\chi''(f)$.

Figure 2 also shows that the real part of χ' is always negative. This means that heterostructures containing nonmagnetic metallic particles in a dielectric matrix exhibit the properties of diamagnetics with effective magnetic susceptibility on the order of 10^{-5} for the concentration and size of nanoparticles considered. However, as the radius a of nanoparticles and their volume concentration c_m in the heterostructure increase, the effective magnetic susceptibility χ_{eff} can increase in absolute value by orders of magnitude. For example, for a = 100 nm and c_m = 0.1, the imaginary component of the susceptibility measured at the relaxation frequency of charge carriers ($\gamma/2\pi$ = 20 THz) increases to $\chi'' = 2.2 \times 10^{-2}$, and the real component at its minimum frequency $f_{\min}$ = 153 THz increases to $\chi' = -5.4 \times 10^{-2}$. Note that, in the static limit, χ_{eff} vanishes, which is clearly seen in Fig. 2.

Figure 3 presents the frequency dependences of the effective complex permittivity ε_{eff} calculated for a concentration of silver particles in an aqueous suspension of $c_m = 1 \times 10^{-2}$ for several sizes of nanoparticles (curves *1*–*3*). The comparison of the diagrams in Figs. 1 and 3 shows that a ten times increase in the concentration c_m leads to an order of magnitude increase in the maximum of the imaginary component of the effective permittivity ε_1'' calculated by the Maxwell Garnett formula. However, a similar quantity calculated by the Bruggeman formula increases only by a factor of 3.5. In this case, the difference between these two maximum values of ε_1'' increases from a factor of two (for $c_m = 1 \times 10^{-3}$) to seven (for $c_m = 1 \times 10^{-2}$).

Figure 4 demonstrates the resonant frequency f_1, as well as the maximum (resonant) value of the imaginary component of the effective permittivity ε_1'', as a function of the radius a of silver nanoparticles, which are computed by formula (31) for several concentrations c_m (curves *1*–*3*). In this figure, the straight curves *4* and *5* represent the values of the corresponding parameters calculated by the Bruggeman formulas only for two values of concentration in order not to overload the figure, and the straight curves *6* and *7* represent the values calculated by the Maxwell Garnett formulas, which are derived under the assumption of infinitely small particles.

We can see that the resonant frequencies calculated by the Bruggeman formula and by formula (31) well coincide for any particle concentrations in the suspension, but only for very small particle sizes. The resonant frequency calculated by the Maxwell Garnett formula agrees with these calculations also for very small nanoparticle sizes, but for very low concentrations c_m in the suspension. As should be expected, the resonant frequency f_1 calculated by formula (31) decreases not only with increasing radius a but also with increasing concentration of particles in the suspension. In this case, the resonant value ε_1'' of the imaginary part of the permittivity weakly increases with increasing radius a but rapidly increases with increasing concentration of particles in the suspension. For a nanoparticle concentration of c_m = 0.1 in the suspension, the maximum value of the permittivity calculated by the Maxwell Garnett formula is too large, ε_1'' = 23.86; therefore, it is not shown in Fig. 4b.

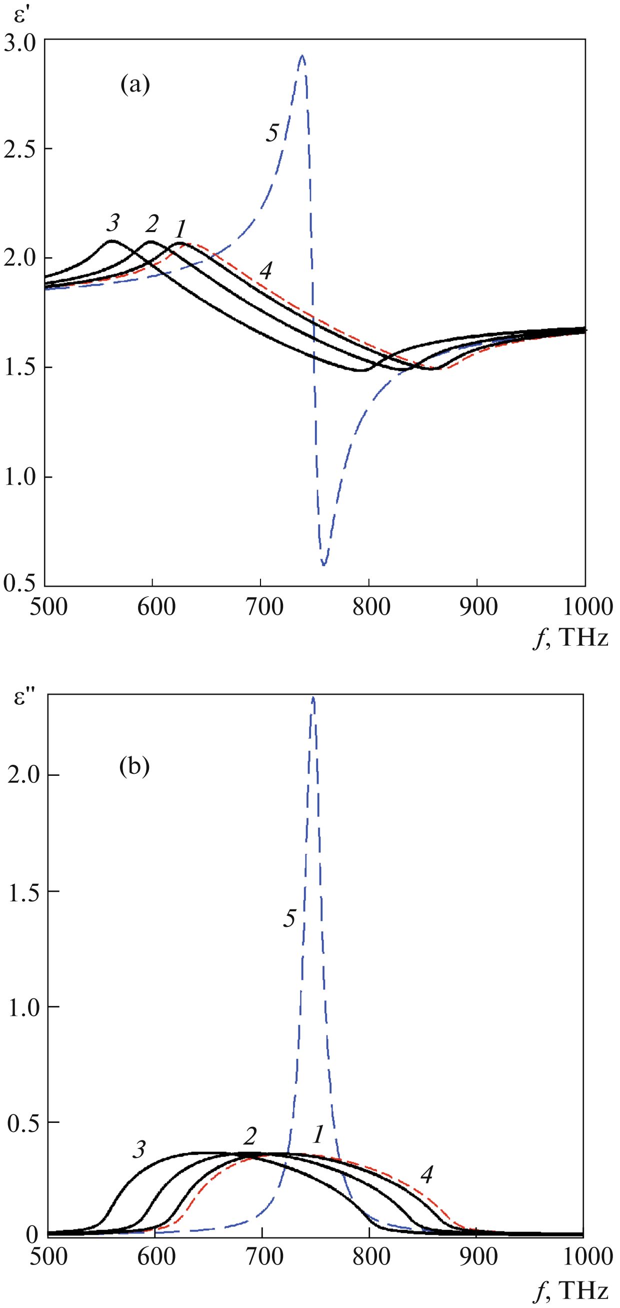

Fig. 3. (Color online) Frequency dependence of the (a) real and (b) imaginary parts of the effective permittivity of the aqueous suspension of silver nanoparticles with $c_m = 1 \times 10^{-2}$, calculated by formula (31) for a = 20 (*1*), 40 (*2*), and 60 nm (*3*); (*4*) calculation by the Bruggeman formulas, and (*5*) calculation by the Maxwell Garnett formula.

The overstated value of the effective permittivity, which is obtained when calculating by the Maxwell Garnett formula and increases with increasing concentration of particles in the heterostructure, is explained as follows. First, when calculating the

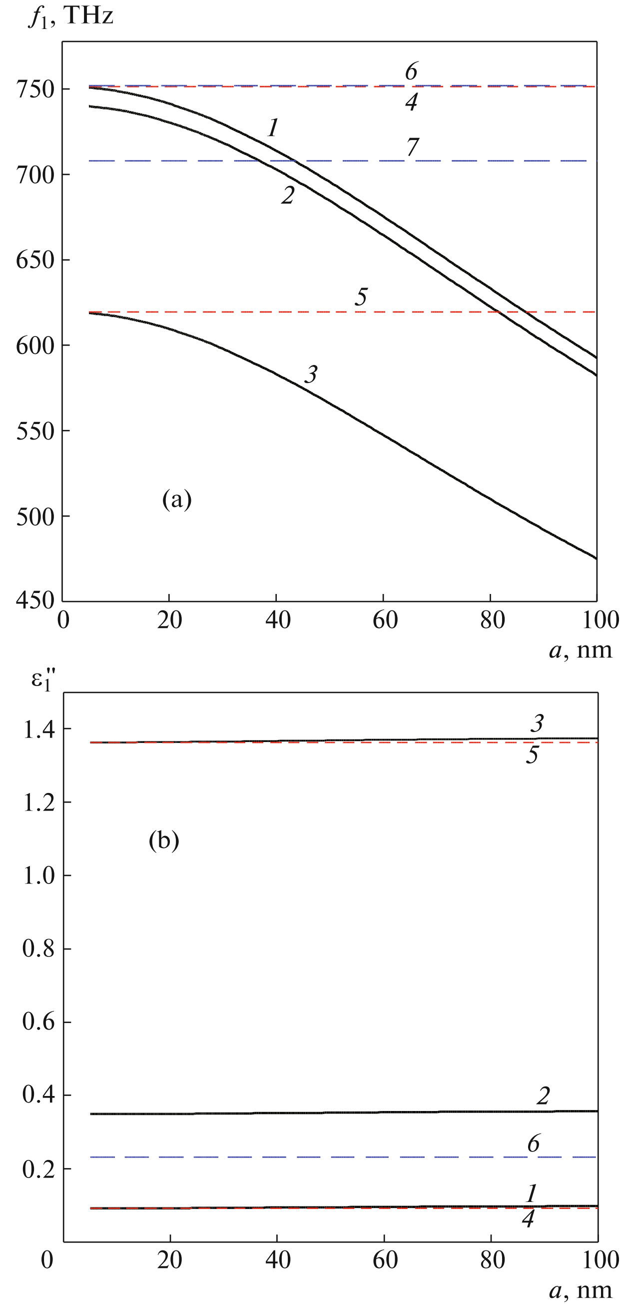

Fig. 4. (Color online) (a) Resonant frequency f_1 and (b) resonant value of the imaginary part of the effective permittivity ε_1'' as a function of the radius of silver nanoparticles, calculated by formula (31) for c_m = (*1*) 0.001, (*2*) 0.01, (*3*) 0.1, as well as by the Bruggeman formula for c_m = (*4*) 0.001 and (*5*) 0.1 and by the Maxwell Garnett formula for (*6*, *7*) $c_m = 0.001$.

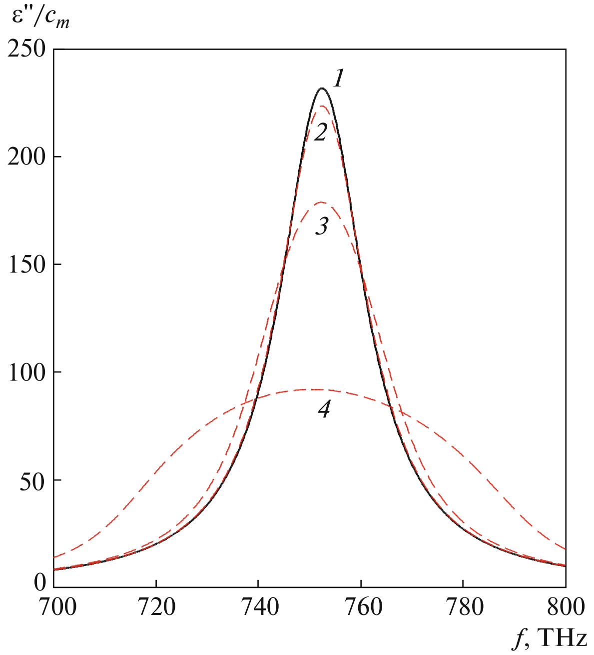

Fig. 5. (Color online) Frequency dependences of the imaginary part of the effective permittivity of the aqueous suspension of silver nanoparticles, calculated by the Maxwell Garnett formula for (*1*) $c_m = 1 \times 10^{-5}$–1×10^{-3} and by the Bruggerman formula for c_m = (*2*) 1×10^{-5}, (*3*) 1×10^{-4}, and (*4*) 1×10^{-3}.

dielectric polarization P of metallic nanoparticles (see formula (7)), the quasi-static Maxwell Garnett approach uses a model in which a real particle of given size possessing a dipole moment is replaced by a point particle with the same dipole moment. In this case, the electric field inside the particle is assumed to be the same as the field in the surrounding dielectric matrix, i.e., the depolarization field inside the particle is neglected. Second, the Maxwell Garnet approach does not take into account the interaction of particles.

Obviously, such rough approximations can be justified only for very low concentrations of particles in the heterostructure. Investigations have shown that, already for $c_m > 10^{-6}$, such approximations give an appreciable error, which rapidly increases with increasing c_m.

This fact is confirmed by the frequency dependence diagrams $\varepsilon''(f)$ constructed in Fig. 5 for several concentrations c_m by the Maxwell Garnett formula (curve *1*) and by the Bruggeman formula (curves *2*–*4*). For clarity, all the curves are normalized by the corresponding concentration c_m. Note that the diagrams constructed by the Maxwell Garnett formula for concentrations of $c_m = 1 \times 10^{-5}$, 1×10^{-4}, and 1×10^{-3} are shown by the same curve *1* because they are virtually indistinguishable.

In the quasi-static Bruggeman approach, the field inside a particle is assumed to be uniform under the assumption that the particle size is much less than the wavelength; however, the depolarization field is taken into account. Obviously, such an approximation also

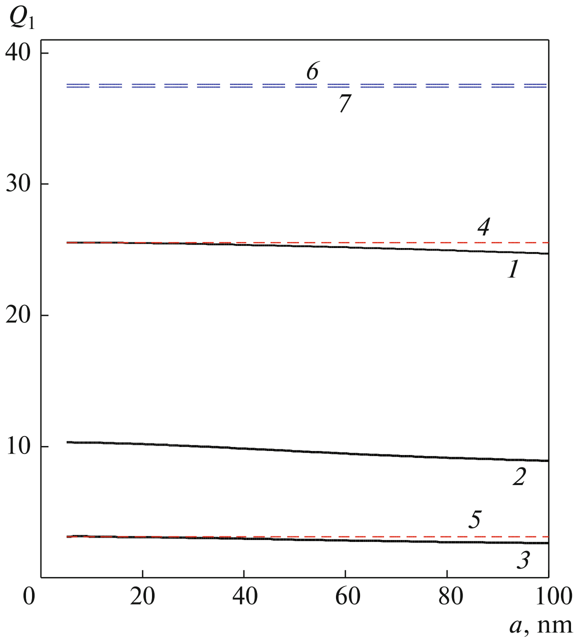

Fig. 6. (Color online) Quality factor of the electric dipole plasmon resonance in the aqueous suspension of silver nanoparticles as a function of their radius, calculated in this work for c_m = (*1*) 0.0001, (*2*) 0.001, and (*3*) 0.01, as well as by the Bruggerman formula for c_m = (*4*) 0.0001 and (*5*) 0.01 and by the Maxwell Garnett formula for c_m = (*6*) 0.0001 and (*7*) 0.01.

requires that the particle size should be small. As already pointed out, the advantage of the Bruggeman model is that it takes into account the interaction between a singled-out particle and other nanoparticles of the heterostructure in the mean-field approximation. The interaction of particles results in the strong broadening of the resonance curve $\varepsilon''(f)$ with increasing concentration c_m in the heterostructure (see Fig. 5). An important characteristic of any resonance is its quality factor, which can be calculated by the conventional formula $Q_1 = f_1/\Delta f_1$.

The solid lines *1*–*3* in Fig. 6 represent the quality factor Q_1 of the electric dipole plasmon resonance calculated by our formula as a function of the radius a of silver particles in aqueous suspensions with various concentrations of nanoparticles. One can see that the quality factor slowly decreases with increasing particle radius; however, it decreases much faster with increasing concentration of nanoparticles in the suspension. For two values of nanoparticle concentration in the suspension, Fig. 6 also shows the values of Q_1 obtained by the Bruggeman formula (lines *4* and *5*) and by the Maxwell Garnett formula (lines *6* and *7*). One can see that, for small particle sizes, the quality factor of the electric dipole plasmon resonance according to Bruggeman well coincides with our calculation. However, the quality factor Q_1 obtained by the Maxwell Garnett formula, first, is significantly overstated and, second, is almost independent of the concentration of nanoparticles in the suspension.

5. CONCLUSIONS

The presented electrodynamic calculation of the frequency dependence of the effective complex permittivity and the effective complex permeability of a heterostructure consisting of a dielectric matrix containing metallic nanoparticles of spherical shape takes into account the size of nanoparticles. In contrast to the Bruggeman and Maxwell Garnett approaches, which use the quasi-static approximation in which the particles size is assumed to be much less than the wavelength in the metal, we have calculated the nonuniform distribution of electromagnetic fields inside metallic nanoparticles. We have established that electric multipole oscillations of any order in nanoparticles do not contribute to the effective permeability of the heterostructure, just as magnetic multipole oscillations do not contribute to the effective permittivity of the medium. In this case, only electric multipole excitations of odd orders, i.e., dipole, octupole, etc., excitations can contribute to the effective permittivity ε_{eff}, just as only magnetic multipole excitations of odd orders can contribute to the effective permeability μ_{eff}.

We have shown that the frequency of the electric dipole plasmon resonance decreases both with increasing size of particles and with increasing their concentration in the heterostructure. These facts are confirmed by experimental investigations of aqueous suspensions of metallic nanoparticles [5, 7]. We have also shown that the dielectric medium containing nonmagnetic metallic nanoparticles exhibits diamagnetic properties, which suggests that experimental investigations should be carried out in this direction. An important result of the study is the established fact that the frequency of the maximum on the frequency dependence of the imaginary part of the magnetic susceptibility coincides with the relaxation frequency of charge carriers. This fact makes it possible the experimental measurement of the relaxation frequency by the frequency of maximum absorption of electromagnetic radiation by the heterostructure under the excitation of magnetic dipole oscillations in it.

The calculated spectra of the real and imaginary components of the permittivity of the heterostructure with a size of metallic particles less than 10 nm well agrees with the Bruggeman calculations; however, the agreement with the Maxwell Garnett calculations is observed only for very low concentrations of nanoparticles less than 10^{-6}. This is attributed to too rough approximations used in the Maxwell Garnett approach; in particular, this approach does not take into account the interaction between the particles of the heterostructure, which is taken into account in the Bruggeman approach in the mean-field approximation. Moreover, the Maxwell Garnett approach does not take into account the depolarization field, because a particle of finite size is replaced by a point dipole in this approach. Nevertheless, many authors use the Maxwell Garnett approach [15, 30] and his formula in their investigations even for high concentrations of particles in a heterostructure up to $c_m = 0.2$ [31].

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