A GENERALIZATION OF THE MIE THEORY FOR A SPHERE WITH SPATIALLY DISPERSIVE PERMITTIVITY

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The Mie theory is generalized to the case of a sphere with spatially dispersive permittivity with regard for longitudinal electromagnetic waves and transverse ones with a single-valued dependence of the wavenumber on the frequency. The generalized Mie coefficients are determined with the help of the method of additional boundary conditions using the condition of electron opacity of the surface. The theory is applicable for the modeling of optical processes involving metals, does not require to simplify the dependence of the permittivity on the light frequency and wavenumber, and does not apply the electrostatic approximation. A relative error of this approximation in calculating the extinction cross-section of a 10 nm-radius silver sphere is shown to exceed 50% in a wide frequency interval.

Optical processes involving metal nanoparticles attracted attention of investigators in the past and are studied till now. An important role in these processes can be played by the spatial dispersion of the permittivity ε, i.e., by the dependence of ε not only on the angular frequency of light ω, but also on the wave vector $\mathbf{k}$ [1–14]. The theories allowing for $\varepsilon(\omega, \mathbf{k})$ are called non-local. In particular, the non-local theory of the electromagnetic response of a small sphere [1, 2] was constructed with the use of the notion of effective permittivity (EP). The EP concept was applied to the modeling of the fluorescence and the decay of excited molecules in a neighborhood of metal nanospheres [3–6], surface-enhanced Raman scattering [7–9], optical response of composite materials [10] and metal nanoshells [11], electromagnetic coupling between an atomic-microscope probe and a substrate [12, 13], and van der Waals interaction between a molecule and a spherical cavity in a metal [14]. However, the effective permittivity is expressed through an integral that can be analytically calculated only for certain idealized functions $\varepsilon(\omega, k)$. That is why works [3–7, 10, 11, 14] used the Drude dielectric function modified with regard for the spatial dispersion. As will be shown below, this function provides no accurate description of metal properties. In addition, the EP model employs the electrostatic approximation, whose error is also found in this study.

A powerful technique of simulating the optical processes involving spherical particles is the Lorenz–Mie theory (see [15–18] or the site www.scattport.org with available classical works by Lorenz, Love, Mie, and Debye). When studying the properties of a plasma sphere, the authors of independent studies [19,20] took non-local effects into account and extended the Mie theory. They noted a possibility of the excitation of synchronous longitudinal oscillations of the electromagnetic field and the charge in plasma – plasma oscillations [15]. In [19, 20], the generalized Mie coefficients were determined for the scattered electromagnetic field and the field inside a sphere with regard for plasma oscillations. Based on these formulas, work [20] predicted the existence of additional resonances in spectra of the extinction cross-section with frequencies exceeding the plasma one. Using the electrostatic approximation and the hydrodynamic plasma model, the frequencies and the widths of these resonances were determined.

Among the pioneer studies taking the spatial dispersion of ε into account, we mention work [21]. Its aim was to investigate the thermal emission of a radially inhomogeneous plasma sphere considered as an assembly of homogeneous layers. The theory used the hydrody-

namic model of the motion of plasma electrons and the Lorenz model [15] to take the polarization of a molecular subsystem into account. The sphere was surrounded by a medium with $\varepsilon \neq 1$. The model [21] predicted the excitation of longitudinal (plasma) oscillations of the electromagnetic field. For the determination of the amplitudes of vector spherical harmonics in layers of the sphere, the additional boundary conditions of the continuity of the radial component of the hydrodynamic electron velocity and the electromagnetic pressure at the boundaries of inner layers, as well as the condition of zero hydrodynamic electron velocity on the sphere surface, were used. Thus, the theoretical model [21] adequately involves the peculiarities of plasma formations of the ionosphere and the properties of metallic [15] and stratified metal-dielectric spheres [22]. While studying the thermal emission, the authors of work [21] solved a number of other important problems, in particular, they found the electromagnetic field created by a point electric dipole. Thereby, they actually derived the Green tensor of the electromagnetic field for a multilayer sphere with regard for non-local effects. The obtained characteristics of the electromagnetic field play a key role in the theory of spontaneous phototransitions of atoms and molecules in a vicinity of conducting bodies and (or) those absorbing electromagnetic radiation [22–24]. Commenting their calculations, the authors of work [21] have extended the Lorenz–Mie theory of the diffraction of a plane electromagnetic wave to the case of a multilayer sphere with regard for the excitation of longitudinal electromagnetic waves. Such a generalization is of great importance even if neglecting the dependence of ε on k [25].

It is worth noting that the first studies [19, 20], as well as other extensions of the Lorenz–Mie theory [26, 29] applied the continuity condition for the normal component of the electric field strength $\mathbf{e}_r \cdot \mathbf{E}$ on the sphere surface ($r = a$). This condition follows from a more general constraint imposed on the current density, $\mathbf{e}_r \cdot \mathbf{j}(r = a) = 0$, and is satisfied if a rarefied plasma or a simple metal is located in a medium with $\varepsilon = 1$. However, the use of the continuity condition $\mathbf{e}_r \cdot \mathbf{E}$ can lead to invalid conclusions for real metals.

The continuity condition $\mathbf{e}_r \cdot \mathbf{E}$ can be regarded as an additional boundary condition (ABC). The ABC method in crystal optics was studied by Pekar [30, 31] in details. According to review [32], the Pekar ABC (the condition of zero exciton part of the polarization vector of a medium on the sphere surface) provided a better agreement with experimental data than other ABCs. The Pekar conditions allowed one to derive the generalized Mie coefficients [27] and to construct the electrodynamic theory of a spatially dispersive medium with a spherical inclusion [28]. The generalization of the Mie theory proposed in [27] used two roots k_1^{T} and k_2^{T} of the dispersion equation for transverse waves

$$k^2 - (\omega/c)^2\, \varepsilon^{\mathrm{T}}(\omega,\, k) = 0, \tag{1}$$

where c is the velocity of light in vacuum. However, as will be shown below, Eq.(1) sometimes has only one real root. In this case, the use of the theory proposed in [27] yields results contradicting research data.

The given work proposes a new version of the Mie theory that can be applied when longitudinal electromagnetic waves and transverse waves with the single-valued dependence $k^{\mathrm{T}}(\omega)$ propagate in a sphere. In Section 2, a formula for the generalized Mie coefficients is obtained with the use of the condition of electron opacity of the particle surface. The proposed theory allows one to use the realistic permittivities of metals or dielectrics. In Section 3, we determine the error of the electrostatic approximation in the optics of metal nanoparticles. Sections 4 and 5 compare various versions of the Mie theory and the EP concept. In particular, Section 5 indicates the importance of taking the interband transitions in metals into account.

1. Electromagnetic Waves in a Medium with Spatially Dispersive Permittivity

First, we compare the characteristics of electromagnetic waves in media with and without spatial dispersion of the permittivity. We will consider media with diagonal permittivity tensors and equal diagonal elements ε. If the spatial dispersion is absent, then all electromagnetic waves are transverse and have the wavenumber

$$k_0^{\mathrm{T}} = (\omega/c)\,\sqrt{\varepsilon(\omega)}. \tag{2}$$

Hereinafter, the time dependence of the electric and magnetic field vectors is described by the factor $\exp(-\imath\,\omega\, t)$.

If ε depends on k, then Eq. (1) can have two solutions: k_1^{T} and k_2^{T}. In addition, the longitudinal electromagnetic waves with the wavenumber k^{L} determined by the equation

$$\varepsilon^{\mathrm{L}}(\omega,\, k) = 0 \tag{3}$$

also can propagate in the medium.

The hydrodynamic model of electrons in metals yields the following permittivities [29, 33, 34]:

$$\varepsilon^{\mathrm{T}}(\omega) = \varepsilon_{\mathrm{g}} + \varepsilon_{\mathrm{h}}(\omega,\, 0), \quad \varepsilon^{\mathrm{L}}(\omega,\, k) = \varepsilon_{\mathrm{g}} + \varepsilon_{\mathrm{h}}(\omega,\, k), \tag{4}$$

where $\varepsilon_{\rm g}$ is the part of the permittivity independent of plasma oscillations. For simple metals, we obtain $\varepsilon_{\rm g} = 1$,

$$\varepsilon_{\rm h}(\omega,\, k) = \frac{-\,\omega_{\rm p}^2}{\omega^2 + i\Gamma\omega - (\beta k)^2}, \tag{5}$$

where $\omega_{\rm p}$ and Γ are the plasma frequency and the damping constant, respectively, $\beta = \sqrt{3/5}\, v_{\rm F}$, $v_{\rm F}$ is the Fermi velocity of electrons in a metal. The phenomenological parameter Γ for a metal sphere is introduced as follows [15]:

$$\Gamma = \Gamma_{\rm b} + A\, v_{\rm F}/a, \tag{6}$$

where a is the sphere radius. For a silver nanosphere in vacuum, $A = 0.25$ [35].

Realistic models of metals use values of $\varepsilon_{\rm g}$ different from 1 in formulas (4), (8). The permittivity $\varepsilon_{\rm g} \neq 1$ is related to the existence of interband transitions in metals [15, 24]. According to [36], we have for silver: $\omega_{\rm p} = 9.17$ eV, $\Gamma_{\rm b} = 0.021$ eV,

$$\varepsilon_{\rm g} = 1 + \frac{2.2\,\omega_{\rm ib}^2}{\omega_{\rm ib}^2 - \omega^2 - \imath\,\Gamma_{\rm ib}\,\omega}, \tag{7}$$

where $\omega_{\rm ib} = 5.27$ eV, and $\Gamma_{\rm ib} = 1.14$ eV. Here, the frequencies in energy units represent the products of the angular frequencies measured in $\rm s^{-1}$ by $\hbar = h/(2\pi)$, where h is the Planck constant.

Formula (4) for $\varepsilon^{\rm T}$ does not suppose the spatial dispersion for transverse waves in metals. However, works [1–8, 11, 12, 14] used the single permittivity for longitudinal and transverse waves:

$$\varepsilon(\omega,\, k) = \varepsilon_{\rm g} + \varepsilon_{\rm h}(\omega,\, k). \tag{8}$$

If relation (8) is used to simulate metal properties, there appears the problem of determination of true and fictitious roots of the dispersion equation (1). In contrast to the true root of the dispersion equation, the fictitious one predicts the existence of waves absent in nature. The appearance of fictitious roots was explained in [31] by the example of solving the approximate algebraic equation

$$0.1 = \ln(1+x) \simeq x - \frac{1}{2}x^2. \tag{9}$$

One of the roots of the approximate equation $x_1 = 0.1056$ is close to that of the accurate one $x_0 = 0.1052$. The other root $x_2 = 1.8944$ differs from the accurate value x_0 by an order of magnitude, whereas $\ln(1+x_2) \simeq 1.06 >> 0.1$. The root x_2 is fictitious.

Let us compare the roots of Eq.(1) with permittivities (4) and (8), by calculating them for the typical parameters $\omega = 3.5$ eV, $a = 10$ nm, and those given above for Ag [36]. The real and imaginary parts of $k_1^{\rm T}$ (one of the roots obtained for (8)) and $k_0^{\rm T}$ of Eq.2) that follows from (1) and (4) coincide to within four significant figures. Respectively, the permittivity $\varepsilon_1^{\rm T} = -2.171 + \imath\, 1.035$ is close to $\varepsilon_0^{\rm T} = -2.170 + \imath\, 1.035$. On the contrary, the other root considerably differs from $k_0^{\rm T}$. The real part of $k_2^{\rm T}$ exceeds $\mathrm{Re}\, k_0^{\rm T}$ by a factor of 814 and $\varepsilon_2^{\rm T} = 7.75 \times 10^4 + \imath\, 972$. The latter estimate testifies to the fact that the real part of the permittivity of silver in the visible spectral region is positive but not negative; moreover, it exceeds the permittivity of diamond by more than four orders of magnitude. The discrepancy of this prediction with research data can be explained in two ways: 1) the permittivity $\varepsilon^{\rm T}$ does not depend on k as is supposed by the first formula (4); in this case, the wavenumber of transverse waves is determined by Eq.(2); 2) the root $k_2^{\rm T}$ of Eq.(1) with the permittivity of a noble metal (8) is fictitious.

The theory developed in the following section uses one parameter of transverse waves — $k^{\rm T}$. It can be equal to $k_0^{\rm T}$ if applying Eqs.(4) or $k_1^{\rm T} \simeq k_0^{\rm T}$ if using Eq. (8).

2. Generalization of the Mie Theory

The Lorenz–Mie theory determines the electromagnetic fields inside and outside a sphere with are excited by an incident plane electromagnetic wave. In order to solve the problem, the electric field vector of the plane wave is expanded in terms of vector spherical harmonics [15, 16, 32, 37]:

$$\mathbf{E} = E_0 e^{-\imath\,\omega\, t}\, \hat{\Xi}_l\, (\mathbf{M}_{{\rm o}1l}^{(1)} - \imath\, \mathbf{N}_{{\rm e}1l}^{(1)}), \tag{10}$$

where the symbol $\hat{\Xi}_l$ means $\displaystyle\sum_{l=1}^{\infty} \imath^l\, \frac{2\,l+1}{l\,(l+1)}$,

$$\begin{aligned} \mathbf{M}_{\sigma\, m\, l}^{(1)\atop(3)} &= \nabla \times [\mathbf{r}\, \frac{j_l}{h_l}(kr)\, Y_{\sigma\, m\, l}(\theta,\, \phi)], \quad \mathbf{N} = \frac{1}{k}\nabla \times \mathbf{M}, \\ \mathbf{L}_{\sigma\, m\, l} &= \frac{1}{k}\nabla [\, \frac{j_l}{h_l}(kr)\, Y_{\sigma\, m\, l}(\theta,\, \phi)], \end{aligned} \tag{11}$$

the upper indices (1) and (3) indicate the use of the spherical Bessel function j_l and the first-order spherical Hankel function h_l, respectively,

$$Y_{{e\atop o}\, m\, l}(\theta,\, \phi) = P_l^m(\cos\theta)\, {\cos \atop \sin}(m\phi), \tag{12}$$

where P_l^m are the associated Legendre functions.

The vector wave functions M, N, and L form the fundamental system of solutions of the wave equation

$$\nabla \times \nabla \times \mathbf{F} - k^2\, \mathbf{F} = 0, \tag{13}$$

to which the Maxwell equations for a monochromatic field is reduced [15, 16, 37]. In Eq. (13), **F** can stand for either the electric or magnetic field. The incident wave (10) creates a reflected field and a field in the sphere. Applying the indicated fundamental system of solutions, these electric fields can be put down in the form

$$\mathbf{E}^{\mathrm{R}} = E_0 e^{-\imath\,\omega\,t}\,\hat{\Xi}_l\,(a_l\,\mathbf{M}^{(3)}_{\mathrm{o}1l} - \imath\,b_l\,\mathbf{N}^{(3)}_{\mathrm{e}1l}), \tag{14}$$

$$\mathbf{E}^{\mathrm{T}} = E_0 e^{-\imath\,\omega\,t}\,\hat{\Xi}_l\,(a_l^{\mathrm{T}}\,\mathbf{M}^{(1)}_{\mathrm{o}1l} - \imath\,b_l^{\mathrm{T}}\,\mathbf{N}^{(1)}_{\mathrm{e}1l} + b_l^{\mathrm{L}}\,\mathbf{L}_{\mathrm{e}1l}). \tag{15}$$

The same way as the incident wave (10), field (14) is a function of $k_\mu = (\omega/c)\,\sqrt{\varepsilon_\mu}$, where ε_μ is the permittivity of a medium surrounding the sphere. (That is why expansions of 10) and (14) do not contain the functions **L**). In what follows, the products of the wavenumbers by a will be denoted as $x = k_\mu\,a$, $z = k^{\mathrm{T}}\,a$, and $z^{\mathrm{L}} = k^{\mathrm{L}}\,a$.

Five relative amplitudes a_l, b_l, a_l^{T}, b_l^{T}, and b_l^{L} must be found from the boundary conditions on the sphere surface. The continuity conditions of the tangential components of the electric and magnetic fields allow one to determine only four amplitudes (for each l). In order to calculate all amplitudes, one should use an additional boundary condition. This work proposes to use the condition of the surface opacity for electrons of a metal particle as an ABC:

$$(\mathbf{j}\,\mathbf{n})\,|_{\mathbf{r}\in S} = 0. \tag{16}$$

Here, **j** stands for the current density induced by the action of the electromagnetic field on electrons of the conduction band, and **n** is the normal vector to the surface S restricting the electron motion. The vector of electric displacement **D** is connected with **E** and **j** by the relation

$$\mathbf{D} = \mathbf{E} + 4\pi\,\left(\mathbf{P}_0 + \frac{\imath}{\omega}\,\mathbf{j}\right), \tag{17}$$

where $\mathbf{P}_0$ is a part of the polarization vector of the medium independent of **j**. Using the notation $\mathbf{P}_{\mathrm{ex}} = \dfrac{\imath}{\omega}\,\mathbf{j}$, condition (16) can be rewritten in a more general form [1]:

$$(\mathbf{P}_{\mathrm{ex}}\,\mathbf{n})\,|_{\mathbf{r}\in S} = 0, \tag{18}$$

where $\mathbf{P}_{\mathrm{ex}}$ is the "exciton" part of the polarization vector of a medium. In our problem,

$$\mathbf{P}_{\mathrm{ex}} \propto \hat{\Xi}_l\,\left[\imath\,b_l^{\mathrm{T}}(\varepsilon_{\mathrm{g}} - \varepsilon_1^{\mathrm{T}})\,\mathbf{N}^{(1)}_{\mathrm{e}1l} + b_l^{\mathrm{L}}\varepsilon_{\mathrm{h}}(\omega,\,k^{\mathrm{L}})\,\mathbf{L}_{\mathrm{e}1l}\right]. \tag{19}$$

For a simple metal ($\mathbf{P}_0 = 0$) in air ($\varepsilon_\mu = 1$), Eq. (18) can be formulated as the continuity condition of the normal component of **E**. This ABC was used in the previous studies [1, 26, 29, 34, 38].

Equation (18) with term (19) determines the relation between the coefficients b_l^{L} and b_l^{T},

$$-\,b_l^{\mathrm{L}} = b_l^{\mathrm{T}}\,\frac{\varepsilon_1^{\mathrm{T}} - \varepsilon_{\mathrm{g}}}{\varepsilon_{\mathrm{g}}}\,l\,(l+1)\,\frac{j_l(z)}{z\,j_l'(z^{\mathrm{L}})}. \tag{20}$$

The relative amplitudes a_l and b_l in formula (14) represent the Mie coefficients for transverse electric (TE_l) and magnetic (TM_l) waves, respectively. If there exists only one true wavenumber $k^{\mathrm{T}}(\omega)$, then the formula for a_l coincides with that in the classical Mie theory,

$$a_l = -\,\frac{j_l(x)\,\psi_l'(z) - j_l(z)\,\psi_l'(x)}{h_l(x)\,\psi_l'(z) - j_l(z)\,\zeta_l'(x)}, \tag{21}$$

where $\psi_l(z) = z\,j_l(z)$, $\zeta_l(x) = x\,h_l(x)$. The modified coefficient b_l can be presented in the form

$$b_l = -\,\frac{(1+\delta_l)\,x\,\psi_l(x)\,\psi_l'(z) - z\,\psi_l(z)\,\psi_l'(x)}{(1+\delta_l)\,x\,\zeta_l(x)\,\psi_l'(z) - z\,\psi_l(z)\,\zeta_l'(x)}, \tag{22}$$

where

$$\delta_l = \frac{\varepsilon_1^{\mathrm{T}} - \varepsilon_{\mathrm{g}}}{\varepsilon_{\mathrm{g}}}\,\frac{l\,(l+1)\,j_l(z)\,j_l(z^{\mathrm{L}})}{\psi_l'(z)\,z^{\mathrm{L}}\,j_l'(z^{\mathrm{L}})}. \tag{23}$$

In some cases, formulas (21) and (22) represent published data. At $\varepsilon_{\mathrm{g}} = \varepsilon_\mu$, a coincidence with the results of work [26] is achieved. If $\varepsilon_{\mathrm{g}} = 1$, we obtain the Mie coefficients from work [29]. Finally, the formula for the classical coefficient b_l follows from Eq.(22) at $\beta k = 0$, which yields $\delta_l = 0$.

Formulas (21), (22), and (14) provide a complete description of the scattered field. In particular, an important characteristic of light scattering and absorption is the extinction cross-section normalized to the geometrical cross-section of the sphere $\pi\,a^2$,

$$Q_{\mathrm{ext}} = \frac{2}{x^2}\,\sum_{l=1}^{\infty}(2l+1)\,\mathrm{Re}\,(-\,a_l - b_l). \tag{24}$$

3. Electrostatic Approximation in the Optics of Metal Nanoparticles

The electrostatic approximation in the optics of metal nanoparticles is applied if the dimensions of particles are much smaller than the light wavelength λ. In this case, the time derivatives in the wave equations are omitted. Respectively, when simulating the properties of spheres, the Riccati–Bessel functions ψ_l and the Riccati–Hankel

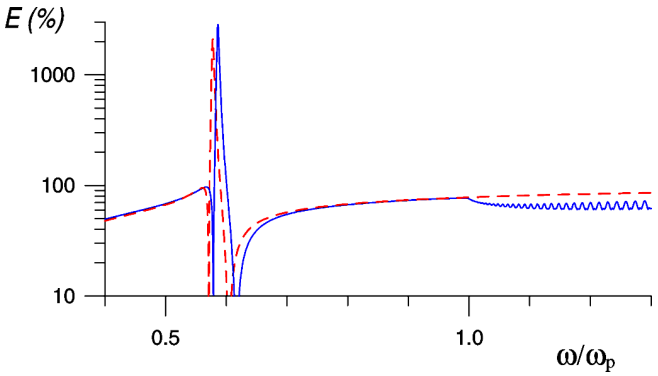

Fig. 1. Relative error (31) of the electrostatic approximation found within classical electrodynamics (dashed curve) and non-local theory. Solid curve demonstrates the error of calculating the real part of the coefficient b_1 by formulas (29) with effective permittivity (33). The sphere radius is 10 nm, calculations are performed for $\varepsilon_{\rm g} = 1$ and parameters of silver taken from [5, 6, 11]

ones $\zeta_l = \psi_l + \imath\,\chi_l$ are replaced by their approximate values according to the formulas

$$\psi_l(z) \simeq \frac{z^{l+1}}{(2\,l+1)!!}, \quad \chi_l(z) \simeq \frac{(2\,l-1)!!}{z^l}, \quad |z| \ll 1. \quad (25)$$

The use of formulas (25) for calculating coefficients (21) and (22) yields $a_l \simeq 0$ and the approximate value of the coefficient b_l:

$$\tilde{b}_l \simeq \imath\,\Delta_l - \Delta_l^2, \quad (26)$$

where

$$\Delta_l = \frac{(l+1)\,(\varepsilon-1)\,x^{2l+1}}{(2\,l-1)!!\,(2\,l+1)!!\,(l\,\varepsilon+l+1)}. \quad (27)$$

Here, $\varepsilon = \varepsilon^{\rm T}/\varepsilon_\mu$ is the relative permittivity of the sphere.

The quantity Δ_l is proportional to the multipole polarization of a small sphere

$$\alpha_l = \frac{l\,\varepsilon - l}{l\,\varepsilon + l + 1}\,a^{2l+1}. \quad (28)$$

In particular, the coefficient $\tilde{b}_1$ can be expressed in terms of the electric dipole polarization of the sphere α_1:

$$\tilde{b}_1 = \imath\,\frac{2}{3}\,k_\mu^3\,\alpha_1, \quad \alpha_1 = \frac{\varepsilon-1}{\varepsilon+2}\,a^3. \quad (29)$$

It is worth noting that the error of the electrostatic approximation can be large even at $a \ll \lambda$. It is due to the inaccurate calculation of the differences in the denominators of the Mie coefficients. In particular, the quantity $\varepsilon + 2$ in the denominator of the formula for the electric dipole polarization α_1 is the approximate value of the difference

$$z\,\frac{\psi_l'(z)}{\psi(z)} - \varepsilon\,x\,\frac{\chi_l'(x)}{\chi(x)} = A - B + C. \quad (30)$$

Here, $A = l + 1 \simeq z\,\dfrac{\psi_l'(z)}{\psi(z)}$, $B = -\varepsilon\,l \simeq \varepsilon\,x\,\dfrac{\chi_l'(z)}{\chi(z)}$, $C = z\,\dfrac{\psi_l'(z)}{\psi(z)} - \varepsilon\,x\,\dfrac{\chi_l'(x)}{\chi(x)} - A + B$, $l = 1$. Moreover, $|A| \gg |C|$ and $|B| \gg |C|$. Thus, according to the logic of the electrostatic approximation, $A - B + C \simeq A - B$ even at $A - B \simeq 0$. In fact, in the region of the Fröhlich resonance, where the value of (30) is close to zero, the following inequality can be satisfied: $|C| \gg |A - B|$. In this case, approximations (25) will be too rough. Let us check this statement by numerical estimates.

The calculations performed in [5, 6, 11] were based on the electrostatic approximation and permittivity (8) with the parameters of silver: $\varepsilon_{\rm g} = 1$, $\omega_{\rm p} = 1.36 \times 10^{16}$ s^{-1}, $\Gamma = \Gamma_{\rm b} + A\,v_{\rm F}/a$, $\Gamma_{\rm b} = 2.56 \times 10^{13}$ s^{-1}, $A = 0.25$, and $v_{\rm F} = 1.40 \times 10^6$ m s^{-1}. For a silver sphere with the given $\varepsilon(\omega, 0)$ and the radius $a = 10$ nm, we obtain that $|C| > |A - B|$ for all frequencies $\omega \le 0.8\,\omega_{\rm p}$. At the Fröhlich frequency $\omega = \omega_{\rm p}/\sqrt{3}$ (for $a \ll \lambda = 240$ nm), we derive $|C| = 128\,|A - B|$, which conflicts with the assumption of electrostatics $|C| \ll |A - B|$.

The experimentally measured quantity is the extinction cross-section $Q_{\rm ext}$. At $x \ll 1$, the value of $Q_{\rm ext}$ depends significantly on the real part of the coefficient b_1 [see formulas (24), (26), and (27)]. Thus, the relative error of the electrostatic approximation can be determined as

$$E = \left|\frac{{\rm Re}\,(b_1 - \tilde{b}_1)}{{\rm Re}\,b_1}\right| \times 100\%. \quad (31)$$

The results of calculating the quantity E are presented in Fig. 1. They show that the relative error of the electrostatic approximation is worse than 50% almost in the whole frequency range and exceeds 2000% at some frequencies in the region of the Fröhlich resonance. This error appears due to the use of approximate formulas (25). Taking the spatial dispersion of ε into account (for example with the help of the EP concept), it is impossible to improve the value of E.

4. Concept of Effective Permittivity

Let us compare the proposed model with the only nonlocal theory known in metal optics, namely the concept of effective permittivity. The EP model is based upon

the electrostatic approximation and the ABC method. The use of these approximations in [1, 2] allowed the authors to find the formula for the l-th order polarizability of a small sphere in air in the form (28) but with ε replaced by the effective permittivity $\epsilon_l = \epsilon_l(\omega, a)$,

$$\epsilon_l(\omega, r) = \left[\frac{2}{\pi}(2l+1)\, a \int\limits_0^\infty \frac{j_l(kr)\, j_l(ka)}{\varepsilon(\omega, k)}\, dk\right]^{-1}. \qquad (32)$$

In some cases, the quantity ϵ_l can be calculated analytically. In particular, for permittivity (8), we obtain

$$\frac{\varepsilon_{\rm loc}}{\epsilon_l} = 1 + (\frac{\varepsilon_{\rm loc}}{\varepsilon_{\rm g}} - 1)\,(2l+1)\, I_{l+1/2}(u) K_{l+1/2}(u), \qquad (33)$$

where $\varepsilon_{\rm loc} = \varepsilon(\omega, 0)$, I_ν, K_ν are the modified Bessel functions, $u = (a/\beta)\,(\omega_{\rm p}^2/\varepsilon_{\rm g} - \omega^2 - i\,\omega\,\Gamma)^{1/2}$.

As one can see from Fig. 1, a significant disadvantage of the EP concept is its construction on the basis of the electrostatic approximation. At the same time, this theory is "sensitive" to effects related to the spatial dispersion of the permittivity. The result of replacing $\epsilon(\omega)$ by the effective permittivity $\epsilon_l(\omega, a)$ determined by Eq.(32) is illustrated in Fig. 2. This figure shows cross-section (24) calculated according to the classical formula for b_l [(22) with $\delta_l = 0$], but using ϵ_l. The dependence $Q_{\rm ext}(\omega)$ derived in this way is compared to the results of calculations performed according to formulas (21)–(24) and the result of classical local electrodynamics. Two dependences $Q_{\rm ext}(\omega)$ obtained with regard for the spatial dispersion of ε almost do not differ in Fig. 2 – the respective lines actually coincide.

The both non-local models predict the existence of additional resonances in the extinction spectrum at $\omega > \omega_{\rm p}$. Their appearance looks somewhat mysterious if restricting oneself to electrostatics and neglecting the excitation of waves of various types. However, the additional maxima in the cross-section of light extinction by metal nanospheres were predicted in [26] and can be simply explained within the generalized Mie theory. Above the plasma frequency, the attenuation of longitudinal waves is not too large. Thus, there appear the additional energy sinks, and the light absorption intensifies. The inset in Fig. 2 demonstrates that, indeed, the additional maxima of $Q_{\rm ext}$ correlate with the maxima of the absolute ratio $\left|b_1^{\rm L}/b_1^{\rm T}\right|$ determined by formula (20).

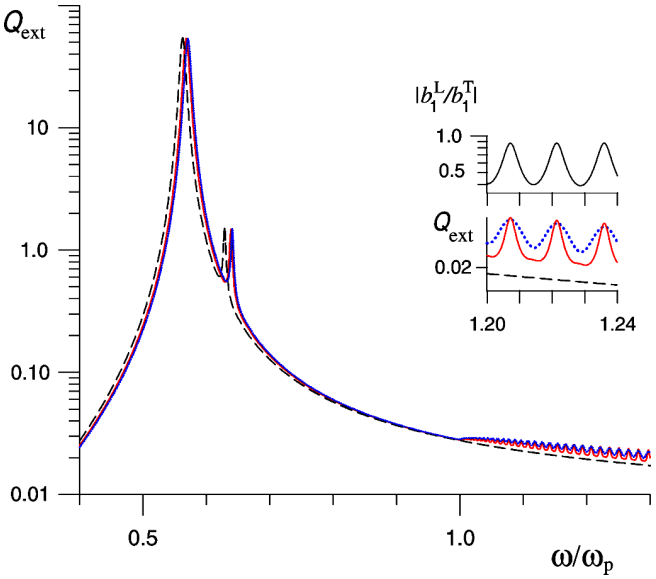

Fig. 2. Normalized extinction cross-section obtained for a silver sphere with the help of different versions of the Mie theory – classical one (dashed line), the model proposed in this work (solid one), and the classical one with the use of effective permittivity (33) (dotted line). The inset shows the enlarged part of the graph and the absolute value of the ratio $b_1^{\rm L}/b_1^{\rm T}$. The parameters of a silver nanosphere are the same as those used in the calculations represented in Fig. 1

5. Light Extinction by a Silver Nanosphere

If $\varepsilon_{\rm g} = 1$, then the absolute maximum of $Q_{\rm ext}$ known as the Fröhlich resonance is attained at $\omega/\omega_{\rm p} \simeq 1/\sqrt{3} \simeq 0.577$ (see Fig. 2). The corresponding value of $\omega \simeq 5.1$ eV significantly contradicts the research data. In experiment [39], silver particles with diameters ranging from 2 to 150 nm were formed due to the homogeneous nucleation in the flux of a mixture of a noble gas with silver vapors. The resonance in the light scattering spectrum was observed at 367 ± 5 nm ($\omega \simeq 3.38$ eV). The main contribution to the spectrum was made by silver particles with diameters in the interval 40–60 nm. In [35], Ag clusters with diameters of 2–4 nm formed a sharp peak in the light absorption spectra with a maximum at $\omega = 3.65$ eV. During the display of 80-nm silver spheres against the dark background [40], the intensity spectrum of scattered light had a maximum at $\omega = 2.9$ eV.

The theory agrees with the experimental data if $\varepsilon_{\rm g} \neq 1$. For example, formula (7) and Ag parameters from [36] allow one to calculate the spectra presented in Fig. 3. Comparing Figs. 2 and 3, one can see that the application of the simplified Drude model overestimates the peak value of $Q_{\rm ext}$ by a factor of 30. According to Fig. 3, there are no considerable differences between the generalized and classical Mie theories. At the same time, the classical Lorenz–Mie theory agrees well with experimen-

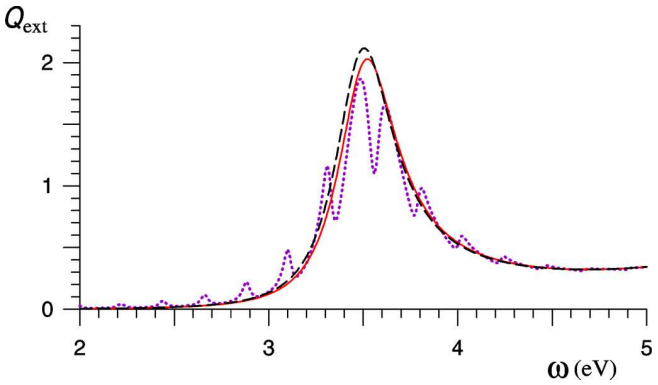

Fig. 3. Normalized extinction cross-section of a realistic silver sphere found with the help of the classical (dashed line) and the proposed generalized (solid curve) Mie theories. The sphere radius is 10 nm, the parameters of Ag are taken from [36]. The dotted line shows the prognosis of the Mie theory from [27]

tal data [15] (though with the use of the phenomenological parameter A in formula (6) [15, 36, 41]).

The developed theory uses only one root $k_1^{\mathrm{T}}(\omega) \simeq k_0^{\mathrm{T}}(\omega)$ of Eq.(1) with permittivity (8), whereas the root $k_2^{\mathrm{T}}(\omega)$ is discarded. One may assume that the additional transverse waves with wave vectors $k_2^{\mathrm{T}}(\omega)$ really exist in metals, but have low amplitudes. In this case, formulas of [27] should be applied. The respective result is depicted in Fig. 3 by a dotted line. It is seen that the non-local model [27] predicts anomalous oscillations of $Q_{\mathrm{ext}}(\omega)$, and the spectrum of $Q_{\mathrm{ext}}(\omega)$ has a double maximum with a gap in the region of the Fröhlich resonance. No spectral peculiarities of this kind were observed experimentally. They are due to the interference of transverse waves with true and fictitious wavenumbers. Thus, the theory proposed in [27] turns out to be inapplicable for simulating the properties of metal particles.

Theoretical work [34] was devoted to the study of light scattering by dimers of silver nanospheres with equal radii of 5 and 50 nm. One of the main conclusions made there was that about a failure of the classical Mie theory and the necessity of taking longitudinal electromagnetic waves in a metal into account. Calculations performed in [34] employed the theory of light scattering by clusters of metal spheres described in [38] that, in turn, used the non-local version of the Mie theory proposed in [26]. The latter theory differs from the proposed here only in the choice of the ABC as a continuity condition of the normal component of the electric field. Respectively, formulas [26] for the generalized Mie coefficient can be applied only in the case where metal spheres have an idealized permittivity with $\varepsilon_{\mathrm{g}} = 1$ and are located in air [34]. In practice, however, the role of the permittivity $\varepsilon_{\mathrm{g}} \neq 1$ in the light scattering can appear more important than that of the dependence of ε on k.

6. Conclusions

The work extends the Lorenz–Mie theory by considering the longitudinal electromagnetic waves that can exist in a sphere due to the spatially dispersive permittivity. The model is applicable if the transverse electromagnetic waves in a sphere have a single-valued frequency dependence of the wavenumber. The theory uses the condition of the surface opacity for electrons of the metal particle. It can be put down as the condition of of vanishing the normal component of the exciton part of the polarization vector on the surface of a medium with spatially dispersive permittivity. Similar ABC was used in the alternative approach proposed in works [1, 2] developing the concept of the effective permittivity of a small sphere. In contrast to [1, 2], the proposed model does not apply the electrostatic approximation. According to the numerical estimates performed with the use of the literature data for a 10 nm-radius silver sphere, the relative error of this approximation near the plasmon resonance can exceed 2000%. In addition, the proposed theory requires no simplification of the dependence of the permittivity on the light frequency and the wavenumber.

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УЗАГАЛЬНЕННЯ ТЕОРІЇ
МІ ДЛЯ КУЛІ З ПРОСТОРОВОЮ
ДИСПЕРСІЄЮ ДІЕЛЕКТРИЧНОЇ ПРОНИКНОСТІ

В.В. Дацюк

Р е з ю м е

Теорію Мі узагальнено на випадок кулі з просторовою дисперсією діелектричної проникності, враховуючи існування поздовжніх електромагнітних хвиль та поперечних хвиль з однозначною залежністю хвильового числа від частоти. Узагальнені коефіцієнти Мі визначено методом додаткових межових умов, використовуючи умову непрозорості поверхні для електронів. Теорія застосовна для моделювання оптичних процесів за участі металів і не потребує спрощення залежності діелектричної проникності від частоти і хвильового числа світла. Модель не використовує електростатичне наближення. Показано, що відносна помилка цього наближення при обчисленні перериза екстинкції світла срібною кулею радіуса 10 нм у широкому інтервалі частот перевищує 50%.