

DEPENDENCE OF LIGHT SCATTERING CROSS-SECTION BY METAL NANOPARTICLES ON THEIR SHAPE

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A theory of light scattering by ellipsoidal metal nanoparticles, the size of which is smaller than the free electron path length in those nanoparticles and much smaller than the light wavelength, has been developed. Effects of nanoparticle shape on both the frequencies and the band half-widths of plasmon resonances have been taken into account. The tensor character of the optical conductivity, which is typical of ellipsoidal metal nanoparticles with such dimensions, has been considered for the first time in the framework of the light scattering problem. The obtained formula for the scattering cross-section demonstrates a substantial influence of the nanoparticle shape on the frequency and polarization dependences of scattered light.

1. Introduction

The classical results obtained by Rayleigh in 1871 started many theoretical and experimental works devoted to the phenomenon of light scattering by small particles, the dimensions of which are considerably smaller than the length of a scattered wave. A review of basic results obtained in this direction can be found in recently published monographies [1, 2] and the references therein. According to the Rayleigh theory, the cross-section of light scattering by a spherical particle at a far distance from it is proportional to $\omega^4 |\alpha(\omega)|^2$, where ω is the light frequency, and $\alpha(\omega)$ is the particle polarizability. In metallic nanoparticles, the frequency dependence of the polarizability is mainly governed by plasma resonances. A spherical particle is known to have one such resonance, a spheroidal one (an ellipsoid of revolution) is characterized by two resonances, whereas an ellipsoidal particle with three different curvature radii possesses three plasma resonances. If the nanoparticle shape deviates from the sphere, the particle polarizability is no more a scalar, but a tensor quantity. The general form for the polarization of an ellipsoidal metallic nanoparticle induced by an electromagnetic wave, the length of which considerably exceeds the particle dimensions, is given in work [1]. The polarizability tensor can be used to express the cross-sections of light absorption and scattering by metallic nanoparticles.

In theoretical works dealing with the phenomenon of light scattering by metallic nanoparticles, the latter are characterized by such parameters as their size, shape, and dielectric permittivity $\epsilon(\omega)$. As a rule, the dependence $\epsilon(\omega)$ is taken from the Drude–Sommerfeld model [1],

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \nu^2} + i\frac{\nu}{\omega} \frac{\omega_p^2}{\omega^2 + \nu^2}, \quad (1)$$

where ω is the light frequency, ν^{-1} is the relaxation time of the electron subsystem,

$$\omega_p = \left(\frac{4\pi e^2}{m} n \right)^{1/2}, \quad (2)$$

is the plasma (bulk) frequency, e the electron charge, m the electron mass, and n the electron concentration.

When being applied to metallic clusters, formula (1) is often corrected. First, the unity on its right-hand side is often substituted by ϵ_0 , a number, which should approximately take into account the contribution of the ionic subsystem to $\epsilon(\omega)$. This number is different for different metals [3].

Second, when the size of a spherical metallic particle becomes smaller than the electron mean free path, the formal substitution

$$\nu \rightarrow \frac{3}{4} \frac{v_F}{R}, \quad (3)$$

where v_F is the Fermi velocity, and R is the particle radius (or, in a more general form [4],

$$\nu \rightarrow \nu + A \frac{v_F}{R},$$

where A is a certain number (an effective parameter)) should be made in Eq. (1). Substitution (3) for spherical nanoparticles can be rigorously substantiated in the limiting cases of high and low frequencies (in comparison with the collision frequency) [5, 6]. However, a question arises: What should be done in the cases where the particle is asymmetric, and its size in one or all directions

is smaller than the mean free path of electrons? The answer becomes clear, if one recalls that the imaginary part of the dielectric permittivity, $\epsilon''(\omega)$, in Eq. (1) is responsible for dissipation processes. In particular, if the particle size is larger than the electron mean free path, we have [7]

$$\epsilon''(\omega) = \frac{4\pi}{\omega} \sigma(\omega), \quad (4)$$

where $\sigma(\omega)$ is the optical (high-frequency) conductivity.

As was shown in work [5], if the metallic particle shape is asymmetric, and if its dimension, at least in one direction, is smaller than the mean free path of electron, the optical conductivity transforms from a scalar into a tensor. The diagonal components of this tensor determine the half-widths of plasma resonances. This work aimed at studying the influence of the light-scattering particle shape on the scattering processes by taking into account not only the corresponding dependence of plasma resonance frequencies (it was already done earlier), but also their half-widths. Since the half-widths determine the heights of corresponding plasma peaks, the influence of the particle shape on these half-widths can substantially modify the frequency dependence of the light scattering cross-section by asymmetric metallic nanoparticles.

2. Formulation of the Problem

Let us consider the problem, proceeding from the general case where the metallic particle has an ellipsoidal shape with three curvature radii (R_x, R_y, R_z) . At a certain stage, which will be indicated below, in order to carry out analytical calculations to the end, we confine the consideration to the spheroidal particle shape, i.e. we adopt that $R_x = R_y \equiv R_\perp$ and $R_z = R_\parallel$. The choice of this shape for the particle is beneficial, because the analytical results obtained here can be applied to a wide spectrum of nanoparticle shapes (from disk- to rod-like ones) by a formal deformation of curvature radii. Hence, let an ellipsoidal metallic nanoparticle be located in the field of an electromagnetic wave

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{-i(\omega t - \mathbf{k} \mathbf{r})}, \quad (5)$$

where \mathbf{E}_0 is the electric field amplitude of the wave, ω its frequency, \mathbf{k} the wave vector, \mathbf{r} the coordinate vector, and t the time. Field (5) induces an internal electric field in the metallic particle, which is spatially uniform in the dipole approximation, i.e. at $kR \ll 1$, where $R = \max(R_x, R_y, R_z)$, and equals [7]

$$E_{\text{in}}^j e^{-i\omega t} = \frac{E_0^j e^{-i\omega t}}{1 + L_j(\epsilon - 1)}, \quad (6)$$

where L is the depolarization factor.

The internal field \mathbf{E}_{in} induces a high-frequency current in the particle, and the dissipation is related just to this circumstance. To determine the form of the high-frequency current and, hence, the optical conductivity of the metallic nanoparticle, it is necessary to find the distribution function of electrons over their velocities. More precisely, it is necessary to find an addend to the Fermi distribution function, which is associated with the action of the local field (6).

In the linear approximation, the distribution function looks like

$$f(\mathbf{r}, \mathbf{v}, t) = f_0(\varepsilon) + f_1(\mathbf{r}, \mathbf{v}) e^{-i\omega t}, \quad (7)$$

where $f_0(\varepsilon)$ is the Fermi distribution function of electrons over the energy ε . For $f_1(\mathbf{r}, \mathbf{v})$, we obtain the kinetic equation

$$(\nu - i\omega) f_1(\mathbf{r}, \mathbf{v}) + \mathbf{v} \frac{\partial f_1(\mathbf{r}, \mathbf{v})}{\partial \mathbf{r}} + e\mathbf{E}_{\text{in}} \mathbf{v} \frac{\partial f_0}{\partial \varepsilon} = 0. \quad (8)$$

Besides Eq. (8), the function $f_1(\mathbf{r}, \mathbf{v})$ must satisfy boundary conditions that determine the character of the electron scattering at the surface of a metallic particle. As such, similarly to what was done in the majority of works on this topic, we adopt the conditions corresponding to the diffuse character of the scattering, i.e.,

$$f_1(\mathbf{r}, \mathbf{v})|_s = 0, \quad \text{at } v_n < 0, \quad (9)$$

where v_n is the velocity component normal to the surface.

It is worth noting that Eq. (8) does not involve the action of a vortex electric field associated with the magnetic component of an external electromagnetic wave. This field is responsible for the so-called magnetic absorption [5]. In the range of plasma resonance frequencies, this mechanism of absorption (or scattering) gives a relatively small contribution [5, 8]. In the case of an ellipsoidal nanoparticle, the boundary conditions (9) depend on the angles, and this circumstance creates additional difficulties in solving Eq. (8). These difficulties can be avoided, if we pass to a deformed system of co-ordinates in Eqs. (8) and (9) such that the ellipsoidal form transforms into the spherical one. The same deformation should be carried out for the space of velocities. The relations between the deformed (primed) co-ordinates and undeformed ones look like

$$\begin{aligned} x'_i &= \gamma_i x_i, & v'_i &= \gamma_i v_i; & \gamma_i &= \frac{R}{R_i}, \\ R &= (R_x R_y R_z)^{1/3}. \end{aligned} \quad (10)$$

For brevity, we used the notation x'_i , where $i = 1, 2, 3$, instead of x, y, z , and a similar notation for the velocities. Note that deformation (10) keeps the particle volume constant. This feature will enable us to distinguish below between the effects induced by the nanoparticle shape and its volume.

In the deformed coordinate system, Eq. (8) and the boundary condition (9) read

$$(\nu - i\omega) f_1(\mathbf{r}', \mathbf{v}') + \mathbf{v}' \frac{\partial f_1(\mathbf{r}', \mathbf{v}')}{\partial \mathbf{r}'} + e \mathbf{E}_{\text{in}} \mathbf{v}' \frac{\partial f_0}{\partial \varepsilon} = 0, \quad (11)$$

$$f_1(\mathbf{r}', \mathbf{v}')|_{r'=R} = 0 \quad \text{at} \quad \mathbf{r}' \mathbf{v}' < 0. \quad (12)$$

Equation ((11) with the boundary conditions (12) is easily solved within the method of characteristics [5, 9] to give the solution

$$f_1(\mathbf{r}', \mathbf{v}) = -e \mathbf{E}_{\text{in}} \mathbf{v} \frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \frac{1 - e^{-(\nu - i\omega) t_0(\mathbf{r}', \mathbf{v}')}}{\nu - i\omega}, \quad (13)$$

where the characteristic $t_0(\mathbf{r}', \mathbf{v}')$ looks like

$$t_0(\mathbf{r}', \mathbf{v}') = \frac{1}{v'^2} \left\{ \mathbf{r}' \mathbf{v}' + \sqrt{(R^2 - r'^2)v'^2 + (\mathbf{r}' \mathbf{v}')^2} \right\}. \quad (14)$$

Function (13) can be used to determine the density of a high-frequency current in the metallic nanoparticle,

$$\mathbf{I}(\mathbf{r}, \omega) = 2e \left(\frac{m}{2\pi \hbar} \right)^3 \iiint \mathbf{v} f_1(\mathbf{r}, \mathbf{v}) d^3v. \quad (15)$$

Introducing the tensor of complex conductivity $\sigma_{\alpha\beta}^c(\mathbf{r}, \omega)$ according to the relation

$$I_\alpha(\mathbf{r}, \omega) = \sum_{\beta=1}^3 \sigma_{\alpha\beta}^c(\mathbf{r}, \omega) E_{\text{in}}^\beta, \quad (16)$$

and using formulas (13) and (15), we obtain the following expression for the components of this tensor:

$$\begin{aligned} \sigma_{\alpha\beta}^c(\mathbf{r}, \omega) &= 2e \left(\frac{m}{2\pi \hbar} \right)^3 \times \\ &\times \iiint v_\alpha \left\{ -e v_\beta \frac{\partial f_0}{\partial \varepsilon} \frac{1 - e^{-(\nu - i\omega) t_0(\mathbf{r}', \mathbf{v}')}}{\nu - i\omega} \right\} d^3v. \end{aligned} \quad (17)$$

Here, it is worth emphasizing that, although the field E_{in} in ellipsoidal particles does not depend on coordinates in the dipole approximation, the distribution function $f_1(\mathbf{r}, \mathbf{v})$ does owing to the boundary condition (12),

and so do the current density $I(\mathbf{r}, \omega)$ and the complex conductivity $\sigma_{\alpha\beta}^c(\mathbf{r}, \omega)$. However, the physical meaning can be attributed, as a rule, to the quantities averaged over the nanoparticle volume. In particular, in the case of the monochromatic wave (5), the energy absorbed by a metallic nanoparticle per unit time is

$$\begin{aligned} w &= \frac{1}{2} \text{Re} \int d\mathbf{r} \{ \mathbf{I}(\mathbf{r}', \omega) \mathbf{E}_{\text{in}}^* \} = \\ &= \frac{V}{2} \sum_{\alpha, \beta=1}^3 \text{Re} \langle \sigma_{\alpha\beta}^c(\omega) \rangle E_{\text{in}}^\alpha (E_{\text{in}}^\beta)^*, \end{aligned} \quad (18)$$

where

$$\langle \sigma_{\alpha\beta}^c(\omega) \rangle = \frac{1}{V} \int d\mathbf{r}' \sigma_{\alpha\beta}^c(\mathbf{r}', \omega) \quad (19)$$

are the components of the complex conductivity tensor averaged over the nanoparticle volume V .

There exists a well-known relation for the components of the dielectric permittivity tensor [10],

$$\epsilon_{\alpha\beta}(\mathbf{r}, \omega) = \delta_{\alpha\beta} + i \frac{4\pi}{\omega} \sigma_{\alpha\beta}^c(\mathbf{r}, \omega). \quad (20)$$

The influence of the surface on the conductivity phenomenon is described in Eq. (17) by the characteristic $t_0(\mathbf{r}', \mathbf{v}')$. As is seen from Eq. (14), $t_0 \sim R/v_F$ by the order of magnitude. This means that t_0^{-1} by its order of magnitude corresponds to the transit frequency of an electron that moves between the walls, $t_0^{-1} \sim v_F/R$. Therefore, the inequality $\nu t_0 \gg 1$ would mean that the frequency of collisions in the bulk, ν , is much higher than the frequency of electron collisions with the surface. In this case, formally putting $\nu \rightarrow \infty$ and $\partial f_0/\partial \varepsilon \sim -\delta(\varepsilon - \varepsilon_F)$ in Eq. (17), we obtain

$$\sigma_{\alpha\beta}(\omega) = \frac{1}{4\pi} \frac{\omega_p^2}{\nu - i\omega} \delta_{\alpha\beta}. \quad (21)$$

This formula demonstrates that the conductivity remains a scalar quantity in this case and does not depend on coordinates. Substituting Eq. (21) into Eq. (20), we obtain an expression for the dielectric permittivity in form (1).

In the general case of an ellipsoid-shaped metallic nanoparticle, the dimensions of which are smaller than the mean free path of an electron, when the scattering of electrons by the surface plays a considerable role, the optical conductivity (17) has a tensor character. As a result, the complex dielectric permittivity of a nanoparticle also transforms into a tensor. In this case, the relation between the internal field \mathbf{E}_{in} and the electric field

of an external electromagnetic wave, \mathbf{E}_0 , must be corrected. Instead of formula (6), the new relation looks like

$$E_{\text{in}}^j e^{-i\omega t} = \frac{E_0^\beta e^{-i\omega t}}{1 + L_\beta (\epsilon_{\beta\beta}(\omega) - 1)} \quad (22)$$

in the coordinate system of principal ellipsoid axes, where $\epsilon_{\beta\beta}(\omega)$ is the diagonal component of the dielectric permittivity tensor (along the β -axis, $\epsilon_{\beta\beta}(\omega) \equiv \langle \epsilon_{\beta\beta}(\omega) \rangle$).

3. Polarizability Tensor

The electric dipole moment induced in a metallic nanoparticle by an electromagnetic wave field is expressed in terms of the high-frequency current $\mathbf{I}(\mathbf{r}, t)$ as follows:

$$\frac{\partial}{\partial t} \mathbf{d}(t) = \int_V d\mathbf{r} \mathbf{I}(\mathbf{r}', t). \quad (23)$$

Applying the Fourier transformation and using Eq. (16), we obtain

$$d_\alpha(\omega) = \frac{iV}{\omega} \sum_{\beta=1}^3 \langle \sigma_{\alpha\beta}^c(\omega) \rangle E_{\text{in}}^\beta. \quad (24)$$

The polarizability tensor is introduced by the relation

$$d_\beta(\omega) = \sum_{\beta'=1}^3 \alpha_{\beta\beta'}(\omega) E_0^{\beta'}. \quad (25)$$

Comparing expressions (24) and (25) with each other and using Eq. (22), we obtain

$$\alpha_{\beta\beta}(\omega) = \frac{iV}{\omega} \frac{\langle \sigma_{\beta\beta}^c(\omega) \rangle}{1 + L_\beta (\epsilon_{\beta\beta}(\omega) - 1)}. \quad (26)$$

Now, averaging relation (20) over the particle volume and substituting the result into Eq. (26), we obtain

$$\alpha_{\beta\beta}(\omega) = \frac{V}{4\pi} \frac{\epsilon_{\beta\beta}(\omega) - 1}{1 + L_\beta (\epsilon_{\beta\beta}(\omega) - 1)}. \quad (27)$$

It is evident that, having determined the components of the complex conductivity tensor from Eq. (17) and using Eqs. (20) and (27), we can easily obtain the polarizability tensor of a metallic nanoparticle. According to Eq. (17), the averaged components of the complex conductivity tensor look like

$$\langle \sigma_{\alpha\beta}^c \rangle = \left(\frac{m}{2\pi\hbar} \right)^3 \frac{2e^2}{\nu - i\omega} \int \frac{d^3r'}{V} \times$$

$$\times \int d^3v v_\alpha v_\beta \delta(\varepsilon - \varepsilon_F) \left\{ 1 - e^{-(\nu - i\omega)t_0(\mathbf{r}', \mathbf{v}')} \right\}. \quad (28)$$

By applying the formula (see details in works [6, 9])

$$\int \frac{d^3r'}{V} \left\{ 1 - e^{-(\nu - i\omega)t_0(\mathbf{r}', \mathbf{v}')} \right\} = \frac{3}{4} \left\{ \frac{4}{3} - \frac{2}{q} + \frac{4}{q^3} - \frac{4}{q^2} \left(1 + \frac{1}{q} \right) e^{-q} \right\} \equiv \frac{3}{4} \Psi(q),$$

where $q = \frac{2}{v'}(\nu - i\omega)$, the components of the conductivity tensor (28) can be expressed in the form

$$\langle \sigma_{\alpha\beta}^c(\omega) \rangle = \frac{3}{2} \left(\frac{m}{2\pi\hbar} \right)^3 \frac{e^2}{\nu - i\omega} \times \int \frac{d^3r'}{V} \int d^3v \delta(\varepsilon - \varepsilon_F) v_\alpha v_\beta \Psi(q). \quad (29)$$

Formula (29) for the averaged components of the complex conductivity tensor, as well as all the previous formulas, was derived in the general case of ellipsoid-shaped nanoparticle with three different curvature radii (R_x, R_y, R_z). Further calculations of the angular integrals in formula (29) become complicated, because, in accordance with Eq. (10), the magnitude of deformed velocity vector, v' , in the expression $q = q(v')$ is angle-dependent. This dependence looks much simpler in the case of ellipsoid-of-revolution geometry where $R_x = R_y = R_\perp$ and $R_z = R_\parallel$. In this case (see formula (10)),

$$v' = R \left\{ \frac{\sin^2 \theta}{R_\perp^2} + \frac{\cos^2 \theta}{R_\parallel^2} \right\}^{1/2} v, \quad (30)$$

where θ is the angle between the vector \mathbf{v} and the ellipsoid rotation axis. Further calculations of the quantity $\langle \sigma_{\alpha\beta}^c(\omega) \rangle$ by formula (29) do not make difficulty (see work [5]).

Formulas (29), (27), and (20) demonstrate that only the components

$$\alpha_{xx} = \alpha_{yy} \equiv \alpha_\parallel, \quad \alpha_{zz} = \alpha_\perp \quad (31)$$

of the polarizability tensor are different from zero for a spheroidal metallic nanoparticle. In accordance with Eq. (21), we obtain

$$\alpha_{\perp, \parallel}(\omega) = \frac{V}{4\pi} \frac{\epsilon_{\perp, \parallel}(\omega) - 1}{1 + L_{\perp, \parallel}(\epsilon_{\perp, \parallel}(\omega) - 1)}. \quad (32)$$

For $\epsilon_{\perp,\parallel}(\omega)$, using Eqs. (29) and (20), we obtain

$$\epsilon_{\perp,\parallel}(\omega) = 1 - \frac{\omega_p^2}{\omega^2} + i \frac{4\pi}{\omega} \sigma_{\perp,\parallel}(\omega), \quad (33)$$

where the notation

$$\sigma_{\perp}(\omega) = \text{Re} \langle \sigma_{xx}^c(\omega) \rangle = \text{Re} \langle \sigma_{yy}^c(\omega) \rangle;$$

$$\sigma_{\parallel}(\omega) = \text{Re} \langle \sigma_{zz}^c(\omega) \rangle \quad (34)$$

was introduced.

We are interested in the light scattering by small particles in the visible range of frequencies. Therefore, while deriving expressions (33), (20), and (29), we neglected small corrections proportional to the ratio between the frequency of collisions and the light frequency. In the same approximation, from Eq. (29), we obtain that, for the size of nanoparticles smaller than the mean free path of an electron [5],

$$\sigma_{\perp}(\omega) = \frac{9}{16} \frac{n e^2 v_F}{m \omega^2} \left\{ \begin{array}{l} \frac{3\pi}{8R_{\perp}}, \text{ for } R_{\perp} \ll R_{\parallel} \\ \frac{1}{2R_{\parallel}}, \text{ for } R_{\perp} \gg R_{\parallel} \end{array} \right\}, \quad (35)$$

$$\sigma_{\parallel}(\omega) = \frac{9}{16} \frac{n e^2 v_F}{m \omega^2} \left\{ \begin{array}{l} \frac{\pi}{4R_{\perp}}, \text{ for } R_{\perp} \ll R_{\parallel} \\ \frac{1}{R_{\parallel}}, \text{ for } R_{\perp} \gg R_{\parallel} \end{array} \right\}. \quad (36)$$

In addition, if $R_{\perp} = R_{\parallel} = R$,

$$\sigma_{\perp}(\omega) = \sigma_{\parallel}(\omega) = \frac{3}{4} \frac{n e^2 v_F}{m \omega^2 R}. \quad (37)$$

Hence, formulas (32), (33), and (35)–(37) completely determine the dependences of the components of the polarizability tensor for a particle on its shape. We recall once more that although the particle is considered to be spheroidal, the relation between the curvature radii R_{\perp} and R_{\parallel} can be arbitrary (for the fixed particle volume, see Eq. (10)). Exact expressions for $\sigma_{\perp,\parallel}(\omega)$ at arbitrary R_{\perp} and R_{\parallel} are given in works [5, 11].

4. Light Scattering Cross-Section by Metallic Nanoparticles

The electric component (5) of an electromagnetic wave induces a dipole moment in a metallic nanoparticle, which generates, in turn, a scattered wave. In addition to the electric dipole moment, a magnetic dipole moment can also be generated, but by a magnetic component of the wave. The reasons of why the latter moment is not considered in this work were presented above. Let us

examine the scattered wave at far distances from the particle (in comparison with the wavelength). In this region, it can be considered as transverse. The electric component of the scattered wave will be denoted as \mathbf{E}' , and the magnetic one as \mathbf{H}' , with $E' = H'$. The intensity of radiation emitted by the electric dipole into the solid angle $d\Omega$ at a distance R_0 and averaged over the period looks like [7]

$$dI_s = \frac{c}{8\pi} |\mathbf{E}' \times \mathbf{H}'| R_0^2 d\Omega = \frac{c}{8\pi} |\mathbf{H}'|^2 R_0^2 d\Omega, \quad (38)$$

where c is the light speed. For the emission by the electric dipole, we have [7]

$$\mathbf{H}' = \frac{\omega^2}{c^2 R_0} \mathbf{n}_0 \times \mathbf{d}(\omega), \quad (39)$$

where \mathbf{n}_0 is a unit vector, which defines the observation direction. Therefore, for the scattering cross-section, we obtain the expression

$$d\Sigma = dI_s / \frac{c}{8\pi} |\mathbf{H}'|^2. \quad (40)$$

The angular dependence of the light intensity scattered by a spheroidal particle is also determined by two more unit vectors, besides the unit vector \mathbf{n} introduced above. Namely, these are \mathbf{p}_0 , a unit vector that describes the polarization of the output light flux, and \mathbf{q}_0 , a unit vector that describes the orientation of the spheroid symmetry axis (see the Figure). As is seen from Eqs. (31) and (25), in the coordinate system connected with the principal spheroid axis, we have

$$\mathbf{d}(\omega) = \alpha_{\perp}(\omega) \mathbf{E}_0^{\perp} + \alpha_{\parallel}(\omega) \mathbf{E}_0^{\parallel}, \quad (41)$$

where

$$\mathbf{E}^{\parallel} = (\mathbf{q}_0 \mathbf{E}_0) \mathbf{q}_0; \quad \mathbf{E}_0^{\perp} = \mathbf{E}_0 - (\mathbf{q}_0 \mathbf{E}_0) \mathbf{q}_0. \quad (42)$$

Hence, the dipole moment of a spheroidal particle is a sum of two mutually perpendicular moments. Using Eqs. (39) and (41), we obtain

$$\begin{aligned} |\mathbf{H}'|^2 &= \frac{\omega^4}{c^4 R_0^2} \left\{ |\alpha_{\perp}(\omega)|^2 (\mathbf{n}_0 \times \mathbf{E}_0^{\perp})^2 + \right. \\ &+ |\alpha_{\parallel}(\omega)|^2 (\mathbf{n}_0 \times \mathbf{E}_0^{\parallel})^2 + (\alpha_{\perp}(\omega) \alpha_{\parallel}^*(\omega) + \alpha_{\perp}^*(\omega) \alpha_{\parallel}(\omega)) \times \\ &\left. \times (\mathbf{n}_0 \times \mathbf{E}_0^{\perp}) (\mathbf{n}_0 \times \mathbf{E}_0^{\parallel}) \right\}. \quad (43) \end{aligned}$$

Substituting Eq. (43) into Eq. (38) and applying Eqs. (40) and (42), we obtain the following expression for the scattering cross-section:

$$d\Sigma = \frac{\omega^4}{c^4} \left\{ |\alpha_{\perp}(\omega)|^2 [\mathbf{n}_0 \times (\mathbf{p}_0 - (\mathbf{q}_0 \mathbf{p}_0) \mathbf{q}_0)]^2 + |\alpha_{\parallel}(\omega)|^2 (\mathbf{n}_0 \times \mathbf{q}_0)^2 (\mathbf{q}_0 \mathbf{p}_0)^2 + 2\text{Re} \alpha_{\perp}(\omega) \times \alpha_{\parallel}^*(\omega) [\mathbf{n}_0 \times (\mathbf{p}_0 - (\mathbf{q}_0 \mathbf{p}_0) \mathbf{q}_0)] (\mathbf{n}_0 \times \mathbf{q}_0)(\mathbf{q}_0 \mathbf{p}_0) \right\} d\Omega. \quad (44)$$

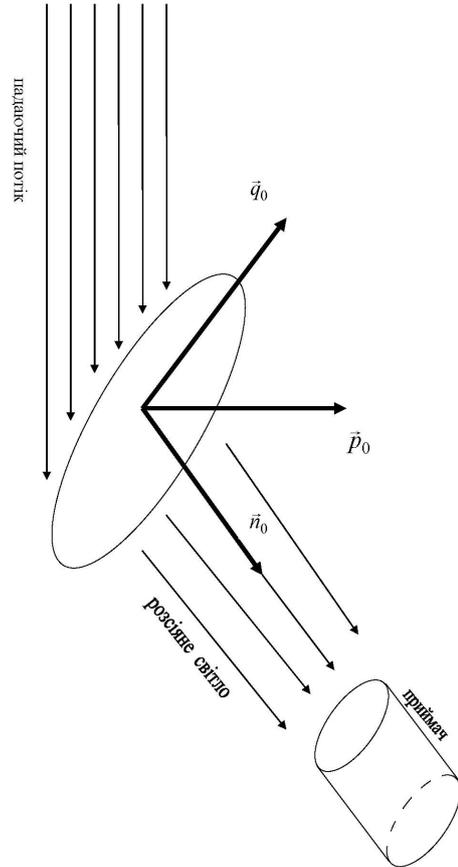
It is not difficult to verify that, in the case of a spherical particle ($\alpha_{\perp} = \alpha_{\parallel} = \alpha$), all terms in Eq. (44), which contain the unit vector \mathbf{q}_0 , mutually compensate one another, so that we obtain the well-known expression for a spherical particle:

$$d\Sigma = \frac{\omega^4}{c^4} |\alpha(\omega)|^2 (\mathbf{n}_0 \times \mathbf{p}_0)^2 d\Omega = \frac{\omega^4}{c^4} |\alpha(\omega)|^2 \sin^2 \nu' d\Omega, \quad (45)$$

where ν' is the angle between the unit vector \mathbf{n}_0 and the electric field \mathbf{E}_0 .

In the literature, the concept of specific polarizability is often used to focus on the role of a particle volume in the scattering. Therefore, we emphasize that the issue in this work in accordance with Eq. (32) concerns the polarizability of the whole particle.

Hence, we have analyzed the simplest case and obtained expression (44) for the light scattering cross-section by a spheroidal metallic particle. In order to avoid any misunderstanding, let us recall once more that the general expressions for the cross-sections of light absorption and dispersion written down in terms of diagonal elements of the polarizability tensor of an ellipsoidal metallic particle can be found, e.g., in monograph [1], together with expressions for the corresponding averaged quantities derived in the case of the chaotic orientation of identical ellipsoidal particles. However, in the cited work, as well as in other works dealing with this problem (see also review [12]), its authors used an expression for the dielectric permittivity function, which corresponded to the Drude–Sommerfeld model, i.e. expression (1). As was already emphasized above, the Drude–Sommerfeld model should be somewhat modified, if the nanoparticle size becomes smaller than the electron mean free path [11]. The essence of this modification becomes clear, if



Schematic diagram of light scattering (depicted is only a part of the light flux directed toward a receiver)

we take expressions (32) and (33) into account. In particular, we obtain

$$|\alpha_{\perp, \parallel}(\omega)|^2 = \left(\frac{V}{4\pi} \right)^2 \times \frac{\omega_p^4 + (4\pi\sigma_{\perp, \parallel}(\omega)\omega)^2}{(\omega^2 - \omega_{\perp, \parallel}^2)^2 + (4\pi L_{\perp, \parallel}\sigma_{\perp, \parallel}(\omega)\omega)^2}, \quad (46)$$

where the frequencies

$$\omega_{\perp, \parallel} \equiv \sqrt{L_{\perp, \parallel}} \omega_p \quad (47)$$

correspond to plasma resonances in spheroidal metallic particles. The addend in the numerator can be neglected in comparison with ω_p^4 in the visible range of frequencies. Formula (46) demonstrates that the diagonal components of the polarizability tensor have sharp peaks at plasma resonance frequencies. The half-widths of those peaks are governed by the diagonal elements of the optical conductivity tensor $\sigma_{\perp, \parallel}(\omega)$. In particular, according

to expression (46), the ratio between the heights of those peaks is

$$|\alpha_{\perp}(\omega)|_{\omega=\omega_{\perp}}^2 / |\alpha_{\parallel}(\omega)|_{\omega=\omega_{\parallel}}^2 \approx \left\{ \frac{L_{\parallel} \sigma_{\parallel}(\omega_{\parallel}) \omega_{\parallel}}{L_{\perp} \sigma_{\perp}(\omega_{\perp}) \omega_{\perp}} \right\}^2. \quad (48)$$

The dependence of expressions (46) and (48) on the particle shape is grounded on the same dependences of both the depolarization coefficients L_{\perp} and L_{\parallel} , and the components of the optical conductivity tensor $\sigma_{\perp}(\omega)$ and $\sigma_{\parallel}(\omega)$. As for the size dependences for the components of the optical conductivity tensor of a spheroidal metallic particle, they are given by formulas (35)–(37) in various limiting cases. The general expressions for those components are presented in our works [5, 6, 11].

The depolarization coefficients have very simple forms in the case of an ellipsoid of revolution [7], namely,

$$L_x = L_y \equiv L_{\perp} = \frac{1}{2}(1 - L_{\parallel}), \quad (49)$$

$$L_z \equiv L_{\parallel} = \left\{ \begin{array}{ll} \frac{1-e_p^2}{2e_p^3} \left(\ln \frac{1+e_p}{1-e_p} - 2e_p \right), & R_{\perp} < R_{\parallel} \\ \frac{1+e_p^2}{e_p^3} (e_p - \arctan e_p), & R_{\perp} > R_{\parallel} \end{array} \right\}, \quad (50)$$

where

$$e_p^2 \equiv |1 - R_{\perp}^2/R_{\parallel}^2|.$$

One can easily see that expression (37) for the high-frequency conductivity in the spherical case ($R_{\perp} = R_{\parallel} = R$) can be obtained from Eq. (1), if one takes Eq. (4) and substitution (3) into account. Recall that this substitution is widely used in the literature, if the nanoparticle size is smaller than the mean free path of an electron. However, an attempt to use substitution (3) with an intermediate R -value between the minimum and the maximum of nanoparticle dimensions does not bring about a desirable result in the asymmetric case ($R_{\perp} \neq R_{\parallel}$). As one can see from Eqs. (48) and (35)–(37), the use of this approximation and the actual components of the conductivity tensor (35) and (36) gives rise to a difference by several times between the heights of plasma peaks. For instance, in the case of an oblate spheroid ($R_{\perp} \gg R_{\parallel}$), the corresponding results differ by a factor of four. Hence, the calculation of the nanoparticle shape influence on the half-widths of plasma resonances in the framework of the light scattering problem is essentially important, being not reducible to small corrections to the results known for a spherical particle.

Above, we have shortly analyzed the influence of the nanoparticle shape on the processes of light scattering taking the expression for $|\alpha_{\perp, \parallel}(\omega)|^2$, which enters into formula (44) for the scattering cross-section, as an example. Besides $|\alpha_{\perp, \parallel}(\omega)|^2$, this formula also includes the expression $\text{Re}(\alpha_{\perp}(\omega) \alpha_{\parallel}^*(\omega))$, which also depends on the particle shape. However, its sensitivity to the shape of a scattering particle is a little lower, so we will not dwell on it.

5. Conclusion

In this work, an analytical expression was obtained for the cross-section of light scattering by a metallic particle of spheroidal shape. The expression involves not only the influence of the particle shape on the plasma resonance frequencies (which has already been taken into consideration earlier), but also the influence of this shape on the half-widths of the plasma resonances. If the nanoparticle dimensions are smaller than the mean free path of an electron, the electron conductivity of an asymmetric particle becomes a tensor quantity, and the diagonal elements of this tensor together with the depolarization coefficients determine the half-widths of the plasma resonances. In their turn, the plasma resonances and their half-widths govern the intensity of light scattering in the frequency range close to the resonances. It was shown that the results obtained for the cross-section of light scattering by an anisotropic metallic nanoparticle considering and not considering the influence of the nanoparticle shape on the half-widths of the plasma resonances can differ by several times.

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ЗАЛЕЖНІСТЬ ПЕРЕРІЗУ РОЗСІЯННЯ СВІТЛА МЕТАЛЕВИМИ НАНОЧАСТИНКАМИ ВІД ЇХ ФОРМИ

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Резюме

Розвинуто теорію розсіяння світла еліпсоїдальними металевими наночастинками, розміри яких менші за довжину вільного пробігу електрона у частинці, а також значно менші за довжину електромагнітної хвилі. Враховано вплив форми наночастинки як на частоти плазмових резонансів, так і на їх півширини. У задачі розсіяння світла вперше враховано тензорний характер оптичної провідності, що наявний у випадку таких розмірів еліпсоподібних металевих наночастинок. За допомогою отриманого виразу для поперечника розсіяння проілюстровано істотний вплив форми частинки на частотні і поляризаційні залежності розсіяного світла.