Hetero- and low-dimensional structures

Width of the surface plasmon resonance line in spherical metal nanoparticles

A.A. Biliuk, O.Yu. Semchuk, O.O. Havryliuk

O. Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine
17, General Naumov str., 03164 Kyiv, Ukraine
E-mail: philosoph.tb@gmail.com

Abstract. In recent years, there has been increasing interest in the study of the optical properties of metallic nanostructures. This interest is primarily related to the practical application of such nanostructures in quantum optical computers, micro- and nanosensors. These applications are based on the fundamental optical effect of excitation of surface plasmons. Surface plasmons are electromagnetic excitations of electron plasma of metals at the metal-dielectric interface, which are accompanied by fluctuations in the surface charge density. The consequence of this phenomenon is surface plasmon resonance (SPR) – an increase in the energy absorption cross-section of a metal nanoparticle as the incident light frequency (laser irradiation) approaches to the frequency of the nanoparticle SPR. The SPR frequency for metallic nanoparticles in a dielectric matrix ε_m is found. Light-excited plasmon vibrations of conduction electrons in metallic nanoparticles located in a dielectric matrix will eventually attenuate due to various relaxation processes, in particular due to interaction of the conduction electrons with the crystal lattice (electron-phonon interaction) or due to electron-electron interaction at the surface of the nanoparticles, when the average free electron path in the nanoparticles exceeds its size. It defines the natural width of SPR line. It has been shown that oscillations of the SPR line width can be observed in metallic nanoparticles with a change in the dielectric constant of the medium in which they are. The oscillations are well expressed in nanoparticles with smaller radii and disappear for nanoparticles of larger radii. The magnitude of these oscillations increases with decreasing the nanoparticle radius and increases markedly with increasing the dielectric constant of the environment.

Keywords: metal nanoparticles, conduction electrons, surface plasmons, plasmon frequency, surface plasmon resonance line width, dielectric medium, dielectric constant.

1. Introduction

The optical spectra of metallic nanoparticles are characterized by the presence in the visible light range of a pronounced resonance band called the surface plasmon resonance (SPR) band. This phenomenon – appearance of local surface modes of oscillations inherent to free electrons at the surface of the metal nanoparticles – is of interest from both theoretical and practical points of view. The presence of enhancement of local fields in metal nanoparticles caused by SPR can significantly increase the efficiency of solar cells, create a new elemental base for the means of information transmitting and processing [1]. In addition, this resonance interaction is accompanied by a number of nonlinear optical effects, such as increased light absorption efficiency, enhance-ment of luminescence, Raman scattering as well as others that have been successfully used to enhance the resolution of microscopes [2], precision drug trans-portation and treatment of tumor diseases [3]. It is known that location of the SPR band is significantly influenced by the shape of nanoparticles and dielectric properties of the environment (dielectric matrix) [4]. These properties of metal nanoparticles can be used to improve the sensitivity of chemical and biological sensors [5]. Plasma structures are used to improve the efficiency of thin-film solar cells – placement of metallic nanoparticles onto the surface, inside or between photosensitive layers of solar cells (SC). [6]. In these structures, metal (plasmon) nanoparticles can primarily act as additional scattering elements for the long-wave component of sunlight illuminating SC. In particular, in the presence of a

reflecting rear metal contact, the light reflected in the SC surface direction will be partially redirected by the metal nanoparticles back to the semiconductor. Thus, the incident light will at least once more pass through the SC material, thereby increasing the length of its optical path and increasing the likelihood of increasing light absorption by the light-sensitive semiconductor layer of SC. Also, to improve the efficiency of energy conversion in solar cells, a layer of organic PEDOT polymer, which contains metal nanoparticles, namely gold and silver, is used [7, 8]. In addition, to increase the efficiency of thin-film SC, the effect of resonant excitation of plasmon modes in metal nanoparticles enclosed in a semiconductor matrix can be used. Then, the metal nanoparticles (5…20 nm in size) will serve as effective "antennas" for the incident light. Localized plasmonic modes will appear on the surface of the metal nanoparticles, due to the energy of which additional generation of electron-hole pairs in the semiconductor will occur, and thus the solar cell efficiency will increase.

In this paper, the effect of the dielectric medium on the width of the SPR line in metallic spherical nanoparticles contained in a dielectric matrix has been studied. It is shown that oscillations of the width of the SPR line can be observed in metallic nanoparticles with a change in the dielectric constant of the medium in which they are.

2. Theoretical part

The absorption and scattering spectra of metallic nanoparticles are characterized by the resonance bands that are absent in bulk materials. The nature of these bands is related to the collective behavior of the conduction electrons of metallic nanoparticles in the light (laser) wave field. In the electron gas of metals, like to that in plasma, collective vibrations – plasmons – can be excited. The plasma (plasmon) frequency (*i.e.*, the frequency of the bulk plasma oscillations) $\omega_p = \sqrt{4\pi n e^2 / m}$ (*e* – electron charge, *n* – concentration of electrons in a metal nanoparticle, *m* – effective electron mass) is one of the most important characteristics of metal in general and metal nanoparticles in particular. For most metals, its order value 10^{15} s^{-1}, that is, it coincides with the frequencies of free electromagnetic waves in the ultraviolet range. In addition, appearance of the so-called surface plasmons is possible in metallic nanoparticles. The surface plasmons in metallic nanoparticles are called collective electron density fluctuations at the boundary of the metal nanoparticle. Excitation of surface plasmons by light (laser radiation) is as follows. The electric field of the light (laser) wave shifts the cloud of free electrons and creates uncompensated charges around the surface of the nanoparticle (Fig. 1) and causes coherent oscillations of the electron cloud near the equilibrium position due to the returning forces of uncompensated charges on the surface.
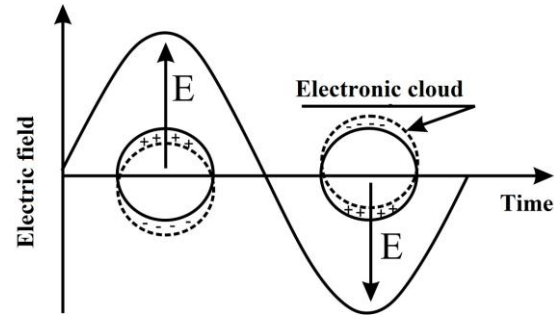

Fig. 1. Schematic representation of localized plasmonic oscillations in a metal nanoparticle arising under the influence of laser radiation.

The optical resonance associated with these oscillations is called localized surface plasmon resonance. In general, the natural frequency of these oscillations does not coincide with the frequency of the incident electromagnetic (laser) wave and is defined by many factors, including the concentration and effective mass of the conduction electrons, the shape, structure and size of the nanoparticles, the interparticle interaction and the influence of the environment. However, for an elementary description of the optics of nanoparticles with SPR, a combination of ordinary dipole approximation and Drude theory is sufficient for the dielectric function of a metal. The essence of SPR is that the cross-section of light absorption by a metal nanoparticle resonantly increases as the frequency of the external field (laser wave) approaches to the frequency of plasmon localized in the metal nanoparticle. That is, the localized plasmon behaves like a regular oscillator in relation to the response to external perturbation.

Let us now analyze absorption of laser radiation in metal nanoparticles at the frequencies close to SPR. Consider nanoparticles, which linear dimensions are much smaller than the wavelength of laser radiation λ. In this case, the metal nanoparticle is in spatially homogeneous, but oscillating electric $\vec{E} = \vec{E}_0 \exp\left[i\left\{\vec{k}\vec{r} - \omega t\right\}\right]$ and magnetic $\vec{H} = \vec{H}_0 \exp\left[i\left\{\vec{k}\vec{r} - \omega t\right\}\right]$ fields in time. The electric field of laser wave induces a local potential electric field $\vec{E}_l$, inside the metal nanoparticle, which in turn causes an electric current $\vec{j}_e$. The magnetic field of laser wave induces a vortex electric field $\vec{E}_{vr}$ in the nanoparticles, which leads to the emergence of eddy electric current $\vec{j}_{vr}$ (Foucault current). Therefore, the total energy of electromagnetic (laser) wave *W* absorbed by the metal nanoparticle will be equal [9]:

$$W = W_e + W_m = \frac{1}{2}\,\mathrm{Re}\int_v \left(\vec{J}_e \vec{E}_l^* + \vec{J}_{vr}\vec{E}_{vr}^*\right)d\vec{r}, \qquad (1)$$

where *V* is the volume of nanoparticles.

The first term corresponds to the electric absorption and the second one to the magnetic absorption. Thus, to determine the total energy absorbed by a metal nanoparticle, it is necessary to know the potential $\vec{E}_l$ and eddy electric fields $\vec{E}_{vr}$ inside the particle, and the corresponding currents $\vec{j}_e$ and $\vec{j}_{vr}$. Therefore, the processes of absorption of light (laser radiation) by metal nanoparticles need to take into account both electrical and magnetic absorption. In what follows, we will only consider the case where electrical absorption is prevailing. In addition, we assume that the size of the metal nanoparticle is much smaller than the average free electron path l_e. In this case, the collision of the conduction electrons with the surface of the metal nanoparticle becomes the most influential relaxation process and therefore other relaxation processes, such as diffusion scattering of electrons by the surface of the nanoparticle, can be neglected.
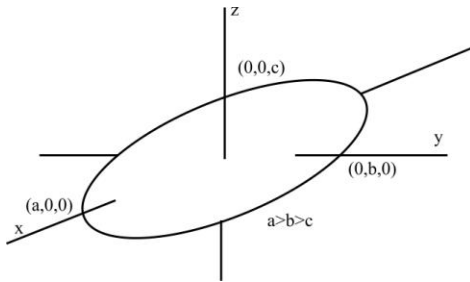

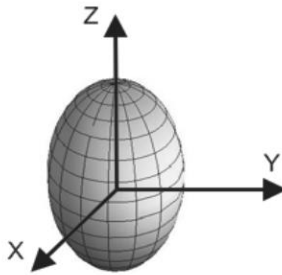**Fig. 2.** Schematic representation of the ellipsoidal nanoparticle.
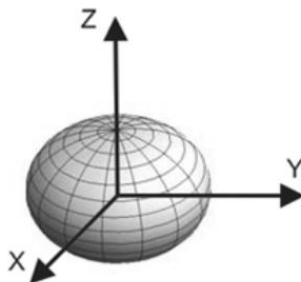

Fig. 3. Elongated spheroid ($a > b = c$).

Fig. 4. Flattened spheroid ($a = b > c$).

The absorption of light (laser radiation) by a metal nanoparticle also depends essentially on its shape. The most widespread model of nanoparticle shape is a three-axis ellipsoid $a > b > c$ (Fig. 2).

From the viewpoint of practical application, nanoparticles in the form of elongated or flattened spheroids – which are formed by the rotation of an ellipse around a short or long axis – are of greatest interest. Figs 2 and 3 schematically illustrate these two types of rotational ellipsoids.

In the case of an elongated spheroid (Fig. 3), its two small half-axes are equal to each other ($b = c$), whereas in the case of a flattened spheroid (Fig. 4) its two large half-axes are equal ($a = b$).

If you introduce the designation $R_\parallel$ for the large half-axis, and $R_\perp$ for the small half-axis of ellipsoid, then in the case of elongated spheroid $R_\parallel = a > R_\perp = b = c$, and the flattened $R_\parallel = c < R_\perp = a = b$.

Analytical expressions for the longitudinal geometric factor $L_\parallel = L_z$ of elongated ($R_\parallel > R_\perp$) and flattened ($R_\parallel < R_\perp$) spheroids with the eccentricity e_p are as follows [9]:

$$L_\parallel = L_z = \begin{cases} \dfrac{e_p^2 - 1}{2e_p^2}\left[\ln\left(\dfrac{1+e_p}{1-e_p}\right) - 2e_p\right] \\[2mm] \text{elongated spheroid}, R_\parallel > R_\perp, e_p^2 = 1 - \dfrac{R_\perp^2}{R_\parallel^2}; \\[4mm] \dfrac{\sqrt{1-e_p^2}}{2e_p^3}\left[\dfrac{\pi}{2} - \text{arctg}\left(\dfrac{\sqrt{1-e_p^2}}{e_p}\right)\right] - \dfrac{1-e_p^2}{2e_p} \\[2mm] \text{flattened spheroid}, R_\parallel < R_\perp, e_p^2 = 1 - \dfrac{R_\parallel^2}{R_\perp^2}. \end{cases}$$

$$(2)$$

The longitudinal $L_\parallel$ and transverse $L_\perp$ geometric factors for spheroids satisfy the relation $L_\parallel + 2L_\perp = 1$ (for the case of a sphere $L_\parallel = L_\perp = 1/3$).

Fig. 5 shows the longitudinal geometric factors $L_\parallel = L_z$ for the elongated and flattened spheroids calculated using the formula (2). From Fig. 5, in particular, it is seen that the shape of the flattened spheroid changes from a disk ($e_s = 1$) to a ball ($e_s = 0$), and an elongated spheroid from a needle ($e_s = 1$) to a ball ($e_s = 0$).

Now let's consider how the environment affects the surface plasmon resonance frequency. Suppose that a metal nanoparticle of an ellipsoidal shape (for simplicity, spheroidal) with the dielectric function $\varepsilon(\omega)$ is in a medium with the dielectric constant ε_m. For simplicity, we assume that Re $\varepsilon_m \equiv \varepsilon_m$ (*i.e.*, the real part of the dielectric constant inherent to environment is independent of frequency), and its imaginary part is zero Im $= \varepsilon_m$. In this case, the relationship between the inner
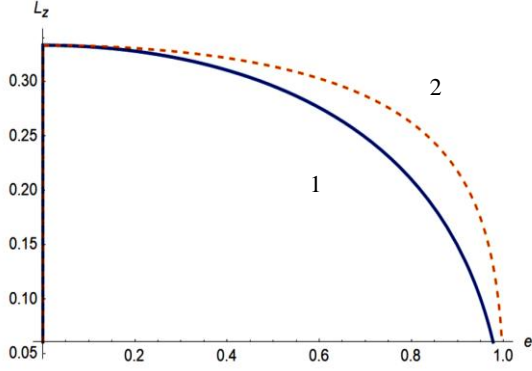
Fig. 5. Dependence of longitudinal geometric factors for elongated (*1*) and flattened (*2*) spheroids on the eccentricity [10].

(local) field generated in the nanoparticle $\vec{E}_l^j$ and the external electric field of the laser wave $\vec{E}_0^j$ is given by the following relation [11]:

$$\vec{E}_l^j = \frac{\varepsilon_m \vec{E}_0^j}{\varepsilon_m + L_j\left(\varepsilon(\omega) - \varepsilon_m\right)}.$$ (3)

If we now substitute (3) into (1), then we find the energy absorbed by the metal particle per unit time W_e for the case where the main mechanism of energy absorption is electrical absorption:

$$W_e = \frac{1}{2}V\sum_{j=1}^{3}\frac{\varepsilon_m^2\left|\vec{E}_0^j\right|^2}{\left[\varepsilon_m + L_j\left(\varepsilon' - \varepsilon_m\right)\right]^2 + \left(\frac{4\pi L_j\sigma_{jj}}{\omega}\right)^2}.$$ (4)

Here, ε' is the real part of the complex dielectric function of a metal nanoparticle.

For the frequencies of electromagnetic field ω those are large as compared to the frequency of electron collisions with scatterers γ within the Drude model, we can assume that $\varepsilon'(\omega) = 1 + \varepsilon_{\text{int}} - \left(\omega_p/\omega\right)^2$ (ε_{int} – an additive to the dielectric function of the nanoparticle that takes into account the interband transitions) [12].

Upon receipt (5), the imaginary part of the dielectric function of the metal nanoparticle material was considered to have the form $\text{Im}\,\varepsilon(\omega) = 4\pi\sigma_{jj}(\omega)/\omega$. Now, taking into account the approximations made, instead of (4) we obtain the following expression for the energy absorbed by the metal nanoparticle per unit time:

If we introduce the notation $L_{jm} = L_j/\left[\left(1 - L_j\right)\varepsilon_m + L_j\varepsilon_\infty\right]$, then from (5) for W_e we get the following expression:

$$W_e = \frac{1}{2}V\sum_{j=1}^{3}\frac{\left(\varepsilon_m\omega^2 L_{jm}/L_j\right)^2\left|\vec{E}_0^j\right|^2\sigma_{jj}}{\left[\omega^2 - \omega_{jm}^2\right]^2 + \left(4\pi L_{jm}\sigma_{jj}\right)^2\omega^2}.$$ (6)

Here, (5) and (6) introduce the notation $\varepsilon_\infty = 1 + \varepsilon_{\text{int}}$.

From (6), it follows that the SPR frequency for the spheroidal nanoparticle ω_{res}, which is in the dielectric medium with a dielectric constant ε_m, will now be given by the following expression:

$$\omega_{res} = \omega_{jm} = \sqrt{\frac{L_j}{\left(1 - L_j\right)\varepsilon_m + L_j\left(1 + \varepsilon_{\text{int}}\right)}}\,\omega_p.$$ (7)

It follows from (7) that for particles of the ellipsoidal shape there are at least two SPR frequencies – longitudinal $\omega_{res}^{\|}\left(L_j + L_\|\right)$ and transverse $\omega_{res}^{\perp}\left(L_j + L_\perp\right)$. For the spherical nanoparticle $L_j = L_\| = L_\perp = 1/3$, $\varepsilon_{\text{int}} = 0$ and for the SPR frequency, we obtain the following expression:

$$\omega_{res} = \omega_{jm} \approx \frac{\omega_p}{\sqrt{2\varepsilon_m + 1}}.$$ (8)

Excited by light plasmon vibrations of conduction electrons in metallic nanoparticles contained in a dielectric matrix, they attenuate over time due to various relaxation processes, in particular, due to interaction of the conduction electrons in the nanoparticles with the crystal lattice (electron-phonon interaction) or due to the scattering of electrons by the inner surface of the nanoparticles, when the average electron free path in the nanoparticles exceeds its size. It defines the natural width of the SPR line $\Gamma(\omega, \varepsilon_m)$ (full width at half maximum), which in general, based on (6) and (7), can be entered using the relation:

$$\Gamma(\omega, \varepsilon_m) = 4\pi L_{jm}\sigma_{jj} = \frac{4\pi L_j}{\left(1 - L_j\right)\varepsilon_m + L_j\varepsilon_\infty}\sigma_{jj}(\omega).$$ (9)

It can be seen from (9) that the width of SPR line (or as it is called the SPR attenuation rate) for a metal nanoparticle contained in a dielectric matrix depends on the corresponding (diagonal) components of the optical conductivity tensor for the nanoparticle $\sigma_{jj}(\omega)$, its geometric shape (geometric factor L_j), and dielectric constant of the dielectric matrix (environment) ε_m.

$$W_e = \frac{1}{2}V\sum_{j=1}^{3}\frac{\varepsilon_m^2\omega^4\left|\vec{E}_0^j\right|^2}{\left[\left(1 - L_j\right)\varepsilon_m + L_j\varepsilon_\infty\right]^2 \times \left\{\left(\omega^2 - \frac{L_j\omega_p^2}{\left(1 - L_j\right)\varepsilon_m + L_j\varepsilon_\infty}\right)^2 + \left(\frac{4\pi L_j\sigma_{jj}}{\left(1 - L_j\right)\varepsilon_m + L_j\varepsilon_\infty}\right)^2\omega^2\right\}}.$$ (5)

The line width (speed of extinction) $\Gamma(\omega, \varepsilon_m)$ is an important characteristic of SPR. The parameter $\Gamma(\omega, \varepsilon_m)$ is the main parameter important for evaluation of the possibility to use the SPR phenomenon in nanosensorics [13], in photovoltaics [6], and in computing [14].

Therefore, as it follows from (9), in order to find the width of SPR lines in a metal nanoparticle $\Gamma(\omega, \varepsilon_m)$, it is necessary first to ascertain the frequency dependence of the real part of the nanoparticle conductivity tensor $\sigma_{jj}(\omega)$.

There are different ways to calculate it. We turn to the method of kinetic equations proposed in [15]. Its advantages, in particular, include the ability to study nanoparticles which dimensions are so small that the scattering of conduction electrons by the inner surface of the nanoparticle begins to play a major role. We will confine ourselves to considering the nanoparticles of spheroid shape. In [15] obtained was a general view for the electric energy absorption of laser radiation (electromagnetic waves) by metal nanoparticles of the ellipsoidal shape in the form:

$$W_e = \frac{1}{2}\mathrm{Re}\int_{j=1}^{3}\left(\vec{J_e}\vec{E}_j^0\right)d\vec{r} = \frac{\pi e^2 m^2 R^3}{(2\pi\hbar)^3}\times$$
$$\times\mathrm{Re}\left[\frac{1}{\gamma-i\omega}\int\left|\vec{v}\vec{E}_j^0\right|\delta(\varepsilon-\varepsilon_F)\Psi(\vec{q})d\vec{v}\right], \quad (10)$$

where R is the radius of the sphere corresponding to the ellipsoid in the deformed coordinate system, v – velocity of conduction electron in the nanoparticle, $\varepsilon = mv^2/2$ – electron energy, ε_F – Fermi energy, γ – frequency of collisions between conduction electrons in the nanoparticle. In addition, introduced in (10) is the following notation [14]:

$$\Psi(q) = \frac{4}{3} - \frac{2}{q} + \frac{4}{q^3} - \frac{4}{q^2}\left(1+\frac{1}{q}\right)e^{-q},$$

$$q = q_1 - iq_2 = \frac{2R}{v'}(\gamma-i\omega). \quad (11)$$

Note that the formula (10) describes the electrical absorption of laser radiation by a metal nanoparticle of an ellipsoidal shape at an arbitrary ratio between bulk and surface scattering.

If $q \gg 1$, from (11) it follows that when $\Psi(q) \approx 4/3$ (bulk displacement is predominant), then from (11) we obtain:

$$W_e \approx V\frac{e^2 n\tau}{m(1+\omega^2\tau^2)}\frac{\left|\vec{E}_l^0\right|^2}{2} \equiv V\sigma(\omega)\frac{\left|\vec{E}_l^0\right|^2}{2}. \quad (12)$$

Here, $\tau = 1/\gamma$ is the time of free electron travel between collisions, $n = 8\pi(mv_F)^2/3(2\pi\hbar)^3$ – electron concentration, $v_F = \sqrt{2\varepsilon_F/m}$ – Fermi speed.

From (12), the known Drude formula for the real part of the dielectric function of the nanoparticle directly follows $\sigma(\omega) = e^2 n\tau/m(1+\omega^2\tau^2)$.

We now consider the case where nanoparticle sizes are smaller than the average electron free path (surface scattering dominates). This situation is matched by inequality $q_1 = (2\gamma/v')R \ll 1$. As for the parameter $q_2 = (2\omega/v')R$, it can be either larger or smaller than unity. Therefore, two limiting cases can be considered:

$$q_2 = \frac{2\omega}{v'}R \gg 1, \quad (13)$$

$$q_2 = \frac{2\omega}{v'}R \ll 1. \quad (14)$$

If you enter the frequency of electron oscillations between the walls of the nanoparticle $\omega_s = v_F/2R \approx v'/2R$, it can be assumed that the case (13) corresponds to high-frequency $(\omega \gg \omega_s)$ and the case (14), when $(\omega \ll \omega_s)$, to the low-frequency surface scattering.

If we neglect the bulk scattering $(q_1 \to 0)$, then for q_2 from any of (12) it follows:

$$\mathrm{Re}\left[\frac{1}{\gamma-i\omega}\Psi(\vec{q})\right] \approx \frac{2}{\omega q_2}\left[1-\frac{2}{q_2}\sin q_2 + \frac{2}{q_2^2}(1-\cos q_2)\right] \equiv$$
$$\equiv \frac{v'}{\omega^2 R}\left[1-\frac{2v'}{\omega R}\sin\frac{v'}{\omega R} + \frac{v'}{2\omega R}\left(1-\cos\frac{v'}{\omega R}\right)\right]. \quad (15)$$

Substituting (15) into (10), we obtain the general expression for the laser radiation energy (electromagnetic wave) absorbed by a metal nanoparticle of a spheroidal shape (electrical absorption) as follows:

$$W_e \approx \frac{\pi e^2 m^3 R^2}{(2\pi\hbar)^3\omega^2}\times$$
$$\times\int\left|\vec{v}\vec{E}_l^0\right|^2 v'd\vec{v}\,\delta(\varepsilon-\varepsilon_F)\left[\begin{array}{l}1-\dfrac{2v'}{\omega R}\sin\dfrac{v'}{\omega R}+\\[2mm]+\dfrac{v'}{2\omega R}\left(1-\cos\dfrac{v'}{\omega R}\right)\end{array}\right]. \quad (16)$$

To study the dependence of the influence of the shape of the nanoparticle on the absorption (to find the components of the conductivity tensor of the nanoparticle), it is sufficient to limit by the rotational ellipsoids. In this case, for the "deformed velocity" of the electron v', we can use the relation

$$v' = vR\sqrt{\left(\frac{\sin\theta}{R_\perp}\right)^2 + \left(\frac{\cos\theta}{R_\parallel}\right)^2}. \quad (17)$$

Here, θ is the angle between the axis of rotation of the spheroid and the direction of the velocity of electron, v – velocity of electron in a spherical particle of radius R.

3. Results and discussion

We apply our theory to metallic spherical nanoparticles. In this case $R_\perp = R_\parallel = R$, then v', q and $\Psi(q)$ cease to depend on the angle θ, and from (17) for the real part of the electrical conductivity of the spherical nanoparticle $\sigma_{sp}(\omega)$ we obtain the following expression (provided that $\omega_s \gg \gamma$, $v' \cong v_F$):

$$\sigma_{sp}(\omega) = \frac{3}{16\pi}\frac{\omega_p^2}{\omega^2}\frac{v_F}{R}\left[1 - \frac{2\omega_s}{\omega}\sin\frac{\omega}{\omega_s} + \frac{2\omega_s^2}{\omega^2}\left(1 - \cos\frac{\omega}{\omega_s}\right)\right].$$

(18)

For a spherical particle, the geometric factors $L_\parallel = L_\perp = 1/3$ and then from (10), taking into account (18), we obtain the following expression for the SPR attenuation rate (SPR line width) in the spherical nanoparticle $\Gamma(\omega, \varepsilon_m)$:

$$\Gamma(\omega,\varepsilon_m) = \frac{3}{2(2\varepsilon_m+1)}\left(\frac{\omega_p}{\omega}\right)^2\frac{v_F}{2R} \times$$
$$\times\left[1 - \frac{2\omega_s}{\omega}\sin\frac{\omega}{\omega_s} + \frac{2\omega_s^2}{\omega^2}\left(1 - \cos\frac{\omega}{\omega_s}\right)\right].$$

(19)

Considering only the first additive in (19), we obtain the well-known $(1/R)$ dependence for the SPR attenuation rate in a spherical particle [16]:

$$\Gamma_0 = \frac{3}{2(2\varepsilon_m+1)}\left(\frac{\omega_p}{\omega}\right)^2\frac{v_F}{2R}.$$

(20)

As it follows from (19) and (20), the lifetime of SPR (SPR line width) in a spherical metallic nanoparticle depends on both the particle radius R and the frequency of the laser-excited SPR ω and consists of two additives describing the smooth Γ_0 part and the oscillating one inherent to the SPR line width:

$$\Gamma_{osc}(\omega,\varepsilon_m) = \frac{3}{2(2\varepsilon_m+1)}\left(\frac{\omega_p}{\omega}\right)^2\frac{v_F}{2R} \times$$
$$\times\left[-\frac{2\omega_s}{\omega}\sin\frac{\omega}{\omega_s} + \frac{2\omega_s^2}{\omega^2}\left(1 - \cos\frac{\omega}{\omega_s}\right)\right].$$

(21)

For the frequency $\omega \approx \omega_{res} = \omega_p\big/\sqrt{2\varepsilon_m+1}$ corresponding to the excitation of surface plasmons in a spherical metallic nanoparticle embedded into a dielectric matrix having a dielectric constant $\varepsilon_m > 1$ from relation (21) in energy units, the following parameter can be entered:

$$\Gamma_0^{res} = \frac{3}{4}\frac{\hbar v_F}{R} \equiv \frac{3}{2}\hbar\omega_s$$

(22)

and at the SPR frequency $\omega_{res} = \omega_p\big/\sqrt{2\varepsilon_m+1}$ for the oscillating part of the line width the following expression can be obtained:

$$\Gamma_{osc}^{res}(R,\varepsilon_m) = \frac{3}{4}\frac{\hbar}{\omega_p}\left(\frac{v_F}{2R}\right)^2\sqrt{2\varepsilon_m+1}\times$$
$$\times\left[-\sin\frac{2R\omega_p}{v_F\sqrt{2\varepsilon_m+1}} + \frac{v_F\sqrt{2\varepsilon_m+1}}{2R\omega_p}\left(1-\cos\frac{2R\omega_p}{v_F\sqrt{2\varepsilon_m+1}}\right)\right]$$

(23)

provided that $\omega_s \gg \gamma$. The amplitude A_{osc}^{res} and period T of these oscillations can be estimated using the expressions:

$$A_{osc}^{res} = \frac{3}{4}\frac{\hbar}{\omega_p}\left(\frac{v_F}{2R}\right)^2\sqrt{2\varepsilon_m+1},$$

(24)

$$T = \frac{\pi}{\omega_p}\sqrt{2\varepsilon_v+1}.$$

(25)

Therefore, the total width of the full SPR line for a spherical metal nanoparticle at the plasmon resonance frequency $\omega_{res} = \omega_p\big/\sqrt{2\varepsilon_m+1}$ in energy units $\Gamma_{res}(R,\varepsilon_m)$ consists of two terms that describe the smooth Γ_0^{res} and oscillating $\Gamma_{osc}^{res}(R,\varepsilon_m)$ parts of the SPR line:

$$\Gamma_{res}(R,\varepsilon_m) = \Gamma_0^{res} + \Gamma_{osc}^{res}(R,\varepsilon_m) =$$
$$= \frac{3}{4}\frac{\hbar v_F}{R} + \frac{3}{4}\frac{\hbar}{\omega_p}\left(\frac{v_F}{2R}\right)^2\sqrt{2\varepsilon_m+1}\times$$
$$\times\left[-\sin\frac{2R\omega_p}{v_F\sqrt{2\varepsilon_m+1}} + \frac{v_F\sqrt{2\varepsilon_m+1}}{2R\omega_p}\left(1-\cos\frac{2R\omega_p}{v_F\sqrt{2\varepsilon_m+1}}\right)\right].$$

(26)

Let us consider the calculated dependences of the full and smooth width of the SPR line on the dielectric constant of the environment for K and Ag nanoparticles shown in Fig. 6. It follows, in particular, that both the amplitude and the oscillation period of the SPR line width increase in small spherical K and Ag nanoparticles placed in a dielectric matrix with a larger dielectric constant ε_m. However, the amplitude of plasmonic oscillations decreases quadratically with increasing the radius of the spherical nanoparticle.

As can be seen from Fig. 6, since the magnitude of ε_m increases, the width of the SPR line gradually increases and increases around its smooth part Γ_0^{res}. The oscillating additive to the SPR line width $\Gamma_{res}(R,\varepsilon_m)$ is an important correction to Γ_0^{res}, especially for the particles of small radius (the oscillations of the SPR line width are well expressed for K and Ag nanoparticles of small radii and practically disappear for large nanoparticles. The least admissible nanoparticle radius that can be considered in the framework of the above theory is limited by some value $R_{min} \cong 2\pi\hbar/mv_F$. For K nanoparticles, this value is $R_{min} \cong 0.855\,nm$.
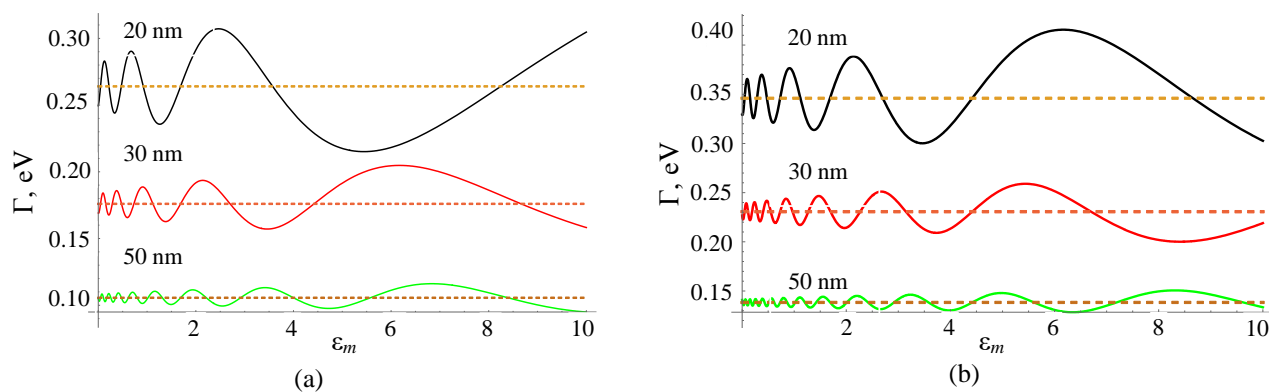
Fig. 6. The dependence of full (solid lines) and smooth (dashed lines) components of the width of the SPR line on the dielectric constant ε_m of the environment for spherical nanoparticles K (a) and Ag (b) with the radii of 20, 30 and 50 nm.

Figs 6a and 6b also show that as the radius of the spherical nanoparticle grows, the width of the SPR line decreases substantially and increases around a certain constant value in mediums of greater value ε_m. The magnitude of these oscillations is larger, the smaller the size of the nanoparticle, and the larger ε_m.

4. Conclusions

Theoretical studies have shown that in metallic nanoparticles contained in a dielectric matrix, under the conditions of surface plasmon resonance, the full width of the SPR line in a spherical metal nanoparticle depends both on the radius of particle R and laser radiation frequency ω exciting this SPR, which is described by the smooth and oscillating parts of the SPR line width. The oscillations are well expressed for nanoparticles with smaller radii and disappear for nanoparticles of larger radii. The magnitude of these oscillations increases with decreasing nanoparticle radius and increases markedly with increasing the dielectric constant of the environment.

References

1. Maier S.A. *Plasmonics: Fundamentals and Applications*. NY: Springer, New York, 2007.
2. Vinogradov S.V., Kononov M.A., Savranskii V.V., Valyanskii S.I., Urbaitis M.F. Effect of optical sensitisation on a surface plasmon resonance. *Quantum Electronics*. 2003. **33**, No 8. P. 711–713.
3. Atwater H. The Promise of Plasmonics. *Scientific American*. 2007. **17**, No 3s. P. 56–63. https://doi.org/10.1038/scientificamerican0907-56sp.
4. Noguez C. Surface plasmons on metal nanoparticles: The influence of shape and physical environment. *J. Phys. Chem. C*. 2007. **111**, No 10. P. 3806–3819. https://doi.org/10.1021/jp066539m.
5. Jeffrey N.A., Hall W.P., Lyandres O., Shah N.C., Zhao J., Van Duyne R.P. Biosensing with plasmonic nanosensors. *Nat. Mater*. 2008. **7**, No 6. P. 442–452. https://doi.org/10.1038/nmat2162.
6. Atwater H.A., Polman A. Plasmonics for improved photovoltaic devices. *Nature Materials*. 2010. **9**. P. 205–230. http://dx.doi.org/10.1038/nmat2629.
7. Jyh-Lih Wu, Fang-Chung Chen, Yu-Sheng Hsiao *et al*. Surface plasmonic effects of metallic nanoparticles on the performance of polymer bulk heterojunction solar cells. *ACS Nano*. 2011. **5**, No 2. P. 959–967. https://doi.org/ 10.1021/nn102295p.
8. Tyler Fleetham, Jea-Young Choi, Hyung Woo Choi *et al*. Photocurrent enhancements of organic solar cells by altering dewetting of plasmonic Ag nanoparticles. *Sci. Rept*. 2015. **5**. P. 1–5. https://doi.org/10.1038/srep14250.
9. Landau L.D., Lifshitz E.M. *Electrodynamics of Continuous Media*. Pergamon Press, 1984.
10. Semchuk O.Yu., Havryliuk O.O., Biliuk A.A. Energy absorption of laser radiation by metal nanoparticles in the conditions of surface plasmon resonance. *Surface*. 2019. **11**, No 26. P. 496–507. https://doi.org/10.15407/Surface.2019.11.496.
11. Petrov Yu.I. *Physics of Small Particles*. Moscow, Nauka, 1982 (in Russian).
12. Hu Min, Novo C., Funston A. *et al*. Dark-field microscopy studies of single metal nanoparticles: understanding the factors that influence the linewidth of the localized surface plasmon resonance. *J. Mater. Chem*. 2008. **18**. P. 1949–1960. https://doi.org/10.1039/b714759g.
13. Tihay F., Pourroy G., Richard-Plouet M. *et al*. Effect of Fischer-Tropsh synthesis on the microstructure of Fe-Co-based metal/spinel composite materials. *Applied Catalysis A: General*. 2001. **206**, No 1. P. 29–42. https://doi.org/10.1016/S0926-860X(00)00595-0.
14. Link S., Wang Z.L., El-Sayed M.A. Alloy formation of gold-silver nanoparticles and the dependence of the plasmon absorption on their composition. *J. Phys. Chem. B*. 1999. **103**, No 18. P. 3529–3533. https://doi.org/ 10.1021/jp990387w.
15. Tomchuk P.M., Tomchuk B.P. Optical absorption of small metal particles. *J. Exper. Theor. Phys*. 1997. **85**, No 2. P. 360–369. https://doi.org/10.1134/1.558284.
16. Kreibig U., Volmer M. *Optical Properties of Meta Clusters*. Springer-Verlag, Berlin, 1995.

Ширина лінії поверхневого плазмонного резонансу в сферичних металевих наночастинках

А.А. Білюк, О.Ю. Семчук, О.О. Гаврилюк

Анотація. В останні роки зріс інтерес до вивчення оптичних властивостей металевих наноструктур. Цей інтерес у першу чергу пов'язаний з можливістю практичного застосування таких наноструктур у квантових оптичних комп'ютерах, мікро- та наносенсорах. В основі цих застосувань лежить фундаментальний оптичний ефект збудження поверхневих плазмонів. Поверхневі плазмони – це електромагнітні збудження електронної плазми металів на границі метал-діелектрик, які супроводжуються флуктуаціями густини поверхневого заряду. Наслідком цього явища є поверхневий плазмонний резонанс (ППР) – зростання перерізу поглинання енергії металевою наночастинкою при наближенні частоти падаючого світла (лазерного випромінювання) до частоти ППР наночастинки. Знайдено частоту ППР для металевих наночастинок, що знаходяться в діелектричній матриці. Збуджені світлом плазмонні коливання електронів провідності у металевих наночастинках, що знаходяться в діелектричній матриці, з часом затухатимуть за рахунок різних релаксаційних процесів, зокрема за рахунок взаємодії електронів провідності наночастинок з кристалічною ґраткою (електрон-фононна взаємодія), або за рахунок розсіяння електронів на внутрішній поверхні наночастинки, коли середня довжина вільного пробігу електронів у наночастинці перевищує її розмір. Це зумовлює природну ширину лінії ППР. Показано, що в сферичних металевих наночастинках можуть спостерігатися осциляції ширини лінії ППР зі зміною діелектричної проникності середовища, в якому вони знаходяться. Осциляції добре виражені для наночастинок з меншими радіусами і зникають для наночастинок великих радіусів. Величина цих осциляцій збільшується зі зменшенням радіусу наночастинки і помітно зростає зі збільшенням діелектричної проникності оточуючого середовища.

Ключові слова: металеві наночастинки, електрони провідності, поверхневі плазмони, плазмонна частота, поверхневий плазмонний резонанс, ширина лінії ППР, діелектричне середовище, діелектрична проникність.