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DEPENDENCES OF DIPOLE PLASMON RESONANCE DAMPING CONSTANTS ON THE SHAPE OF METALLIC NANOPARTICLES

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A theory describing the dependence of the damping constants of dipole plasmon resonances on the shape of metallic nanoparticles has been developed. Analytical expressions for the damping constants as functions of the ratio between the curvature radii are derived in the case of spheroidal particles and provided the dominating role of electron scattering at the surface. The corresponding plots are drawn. A considerable dependence of the damping constants on the nanoparticle shape is illustrated. It is shown that the incorporation of metallic nanoparticles of a certain shape into a dielectric matrix with a high dielectric permeability can lead to a resonance caused by the coincidence of the plasmon resonance frequency with the frequency of individual electron oscillations (between the potential walls). This resonance is responsible for the appearance of a quasi-oscillating dependence of the plasmon resonance damping constants on the nanoparticle size.

K e y w o r d s: damping constants, plasmon resonances, metallic nanoparticles.

1. Introduction

The physical properties of metallic nanoparticles (MNPs) and their ensembles have been studied for rather a long time, but those researches were strongly intensified in recent years. Emission [1], optical and plasma [2, 3], and other properties [4] are researched. The interest in those objects is associated with the fact that they reveal new physical regularities that are absent in the case of massive metals. First of all, this is surface plasma resonances (collective oscillations in the electron subsystem of the cluster with respect to its frame) in MNPs and a modification of the electron–lattice energy exchange at small particle sizes, which favors the appearance of hot electrons, when the energy is introduced into MNPs.

The number of plasma resonances (PRs) and their frequency positions depend on the MNP shape. There is one dipole plasma resonance in a spherically symmetric MNP, two in a particle with the cylindrical symmetry, and three in an ellipsoidal particle. The PR frequencies belong to the visible spectral range; therefore, their presence substantially governs the optical properties of MNPs and their ensembles. In particular, the matter concerns the light absorption and scattering by MNPs and their ensembles. In addition, the PR excitation stimulates the generation of high local electric fields. This effect is widely used in biophysics [5].

If the energy is introduced into MNPs or their ensembles (island metallic films) by means of laser radiation or current transmission, the electron gas in such systems becomes "hot". The temperature of hot electrons crucially depends on the character of electron–

lattice energy exchange [1]. The intensity of the latter, as was showed in works [1, 6, 7], starts to decrease in a quasi-oscillating manner as the clusters become smaller, if the sizes of MNPs do not exceed the electron mean free path length; at certain sizes, the energy exchange in the bulk disappears altogether. In this case, only the surface energy exchange survives, the intensity of which is by orders of magnitude lower than the bulk one. Due to this feature of the electron–lattice energy exchange in island metallic films, hot electrons can be obtained not only if the power is introduced in the pulse regime, but also in the stationary one [1]. It is known that hot electrons are not obtained under stationary (quasi-stationary) conditions in massive metals and continuous metallic films, because the intensive electron–lattice exchange favors the heating of the lattice and its thermally induced destruction.

Plasma resonances in MNPs are characterized by their characteristic frequencies ω_α and damping constants γ_α. The dependences of the frequencies ω_α on the shape and the size of MNPs are well studied (see e.g., work [3]). The situation is worse for the size dependences of decrements γ_α, especially if the MNP sizes are smaller than the electron mean free path length. Even in the simplest case of a spherically symmetric MNP and when the electron scattering [8–10] both in the bulk and at the surface is taken into account, the decrement of the dipole PR damping is often written in the form

$$\gamma = \nu + A\frac{\upsilon_{\rm F}}{R},$$

where ν is the frequency of collisions in the bulk, $\upsilon_{\rm F}$ the Fermi velocity, and R the MNP radius. The constant A either is accepted to equal $3/4$ or is considered to be a fitting parameter [8–10]. Actually, the "constant" A may depend on the MNP size and shape (see below). Its explicit form can be obtained only in the framework of the kinetic approach, while describing the electron scattering in the MNP bulk and at the MNP surface [11, 12]. The necessity of using the kinetic approach becomes especially actual in the case where the MNP has an asymmetric shape, and the optical conductivity becomes a tensor quantity [11–13]. In this case, the "constant" A mentioned above will have different forms for different dipole PRs in the same metallic particle.

In this work, a theory describing the size dependence of the PR damping constants in small ellipsoidal metallic particles will be developed in the framework of the kinetic approach. It will be shown that, under certain conditions, the quasi-oscillating size dependences of PR decrements are possible. An analytical dependence of those decrements on the particle shape, provided a dominating role of the surface electron scattering in MNPs, is obtained for the first time.

2. Statement of the Problem

Let us consider an ellipsoidal metallic nanoparticle in the electromagnetic wave field

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{-i(\omega t - \mathbf{kr})}, \tag{1}$$

where $\mathbf{E}_0$ is the amplitude of the electromagnetic wave, ω its frequency, $\mathbf{k}$ its wave vector, and $\mathbf{r}$ and t are the coordinate vector and the time, respectively. The choice of the ellipsoidal shape for the particle is attractive, because the results obtained can be extended to a wide spectrum of shapes (from disk-like to rod-like ones) by changing the curvature radii of the ellipsoid [11, 13].

Let us suppose that the electromagnetic wave length is much longer than the particle size, i.e.

$$kL \ll 1, \tag{2}$$

where $L = \max R_i$, R_i is the i-th curvature radius, and $i = 1, 2, 3$. If condition (2) is satisfied, the electromagnetic wave (1) induces a spatially uniform electric field in the ellipsoidal metallic nanoparticle [14],

$$E_{in}^{\beta} e^{-i\omega t} = \frac{E_0^{\beta} e^{-i\omega t}}{1 + L_\beta[\epsilon_{\beta\beta} - 1]}, \tag{3}$$

where L_β is the depolarization factor, and $\epsilon_{\beta\beta}$ the diagonal component in the tensor of dielectric permittivity ϵ. In the case of spherical particle, ϵ becomes a scalar and looks like

$$\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega) = 1 - \frac{\omega_{pl}^2}{\omega^2 + \nu^2} + i\frac{\nu}{\omega}\frac{\omega_{pl}^2}{\omega^2 + \nu^2}. \tag{4}$$

In Eq. (4),

$$\omega_{pl} = \sqrt{\frac{4\pi n e^2}{m}} \tag{5}$$

is the bulk plasma frequency. Here, e is the elementary charge, m the electron mass, and n the electron concentration.

For an ellipsoidal metallic nanoparticle with dimensions less than the electron mean free path length (this means that the electron scattering at the cluster surface dominates), the imaginary part of the dielectric permittivity becomes a tensor [11, 13],

$$\epsilon''(\omega) \to \epsilon''_{\beta\beta}(\omega) = \frac{4\pi}{\omega}\sigma_{\beta\beta}(\omega), \tag{6}$$

where $\sigma_{\beta\beta}$ are the components of the tensor of optical conductivity.

The internal electric field (3) generates a high-frequency current in the nanocluster,

$$j_\alpha(\mathbf{r},\omega) = 2e\left(\frac{m}{2\pi\hbar}\right)^3 \int v_\alpha f_1(\mathbf{r},\mathbf{v})d^3v =$$

$$= \sum_{\beta=1}^{3} \sigma_{\alpha\beta}(\mathbf{r},\omega)E^\beta_{\text{in}}, \tag{7}$$

where $f_1(\mathbf{r},\mathbf{v})$ is the distribution function of electrons in the field $\mathbf{E}_{\text{in}}$. It can be written in the form

$$f(\mathbf{r},\mathbf{v}) = f_0(\varepsilon) + f_1(\mathbf{r},\mathbf{v}), \tag{8}$$

where $f_0(\varepsilon)$ is the Fermi distribution function of electrons over the energy ε, and $f_1(\mathbf{r},\mathbf{v})$ is a correction to $f_0(\varepsilon)$ linear in $\mathbf{E}_{\text{in}}$. In order to determine the function $f_1(\mathbf{r},\mathbf{v})$, the following kinetic equation linearized in $\mathbf{E}_{in}$ is used:

$$(\nu - i\omega)f_1(\mathbf{r},\mathbf{v}) + \mathbf{v}\frac{\partial f_1(\mathbf{r},\mathbf{v})}{\partial \mathbf{r}} + e\mathbf{E}_{\text{in}}\mathbf{v}\frac{\partial f_0}{\partial \varepsilon} = 0, \tag{9}$$

with the boundary conditions at the surface

$$f_1(\mathbf{r},\mathbf{v})|_S = 0,\ v_n < 0, \tag{10}$$

where v_n is the velocity component normal to the surface. Condition (10) corresponds to the diffusion mechanism of electron scattering by the surface of a metallic nanocluster.

The normal to ellipsoid's surface depends on all coordinates and all R_i. This circumstance makes the solution of Eq. (9) more complicated. In order to avoid those difficulties, it is expedient to change in Eq. (9) to a deformed coordinate system and velocities:

$$x'_i = \gamma_i x_i,\ v'_i = \gamma_i v_i,\ \gamma_i = \frac{R}{R_i},\ R = (R_1R_2R_3)^{1/3}. \tag{11}$$

In the deformed (primed) coordinate system, the nanoparticle takes the spherical form, with the volume equal to that of initial ellipsoidal particle. Boundary condition (10) becomes strongly simplified at that.

The solution of Eq. (9) with boundary conditions (10) in the deformed coordinate system looks like [15]

$$f_1(\mathbf{r},\mathbf{v}) = -e\mathbf{E}_{\text{in}}\mathbf{v}\frac{\partial f_0}{\partial \varepsilon}\frac{1-\exp[-(\nu-i\omega)t_0(\mathbf{r}',\mathbf{v}')]}{\nu - i\omega}, \tag{12}$$

where

$$t_0(\mathbf{r}',\mathbf{v}') = \frac{1}{v'^2}\left[\mathbf{r}'\mathbf{v}' + \sqrt{(\mathbf{R}^2 - \mathbf{r}'^2)\mathbf{v}'^2 + (\mathbf{r}'\mathbf{v}')^2}\right] \tag{13}$$

is the characteristic of Eq. (9). After determining, with the help of Eqs. (7) and (12), the high-frequency current generated in the metallic nanoparticle by the internal field $\mathbf{E}_{\text{in}}$, it is possible to obtain an expression for the energy absorbed by the particle per time unit [11]:

$$W = \frac{1}{2}\text{Re}\int d^3r\mathbf{j}(\mathbf{r})\mathbf{E}^*_{\text{in}}(\mathbf{r}) =$$

$$= \frac{V}{2}\sum_{\alpha=1}^{3}\frac{\sigma_{\alpha\alpha}\left(\epsilon_m\omega^2/g_\alpha\right)^2|E^\alpha_0|^2}{(\omega^2_\alpha - \omega^2)^2 + \left(4\pi L_\alpha\sigma_{\alpha\alpha}/g_\alpha\right)^2\omega^2}. \tag{14}$$

Expression (14) corresponds to the general case where the metallic particle is located in a dielectric matrix with the dielectric permittivity ϵ_m. In this case,

$$g_\alpha = \epsilon_m + L_\alpha(1-\epsilon_m), \tag{15}$$

and the characteristic plasma frequencies ω_α look like [11, 12]:

$$\omega_\alpha = \left(\frac{L_\alpha}{g_\alpha}\right)^{1/2}\omega_{pl}. \tag{16}$$

In vacuum, $\epsilon_m = 1$ and $g_\alpha = 1$. As is seen from Eq. (14), the decrement of dipole plasma oscillations equals

$$\gamma_\alpha = 4\pi L_\alpha\sigma_{\alpha\alpha}/g_\alpha. \tag{17}$$

Our problem consists in studying how the constant of dipole plasma oscillation damping γ_α varies when changing from the bulk electron scattering to the surface one as a result of the cluster size change.

3. Quasi-Oscillating Size Dependence of the Damping Constant for Dipole Plasma Oscillations

Expressions (14) and (17) contain the real parts of components of the tensor $\sigma_{\alpha\beta}(\mathbf{r},\omega)$ averaged over the volume. According to Eq. (12), we have

$$\sigma_{\alpha\alpha}(\mathbf{r},\omega)=\frac{2e}{V}\left(\frac{m}{2\pi\hbar}\right)^3\mathrm{Re}\int d^3r'\int d^3v\,v_\alpha\times$$
$$\times\left[-ev_\alpha\frac{\partial f_0}{\partial\varepsilon}\frac{1-e^{-(\nu-i\omega)t_0(\mathbf{r}',\mathbf{v}')}}{\nu-i\omega}\right]. \quad (18)$$

Till now, all calculations were made for an ellipsoidal nanoparticle with three different radii of curvature. In what follows, with the purpose to obtain the final results in an analytical form, the consideration will be confined to the case of spheroidal particle, i.e. we assume that $R_1=R_2=R_\perp$ and $R_3=R_\parallel$. Taking into account that the integral in Eq. (18) equals

$$\int\frac{d^3r'}{V}\left[1-e^{-(\nu-i\omega)t_0(\mathbf{r}',\mathbf{v}')}\right]=$$
$$=\frac{3}{4}\left[\frac{4}{3}-\frac{2}{q}+\frac{4}{q^3}-\frac{4}{q^2}\left(1+\frac{1}{q}\right)e^{-q}\right]=\frac{3}{4}\Psi(q), \quad (19)$$

where $q=2R(\nu-i\omega)/v'$, expression (18) for the diagonal components of the optical conductivity tensor takes the form

$$\sigma_{\alpha\beta}(\omega)=\frac{3}{2}\left(\frac{m}{2\pi\hbar}\right)^3\mathrm{Re}\frac{e^2}{\nu-i\omega}\int d^3v\,v_\alpha v_\beta\delta(\varepsilon-\varepsilon_\mathrm{F})\Psi(q). \quad (20)$$

Here, we took into consideration that $\frac{\partial f_0}{\partial\varepsilon}=-\delta(\varepsilon-\varepsilon_\mathrm{F})$, where ε_F is the Fermi energy.

Let the direction OZ be selected along the spheroid axis. Then, in accordance with Eq. (11), the "deformed" velocity v' in the expression for q has the form

$$v'=vR\left[\frac{\sin^2\theta}{R_\perp^2}+\frac{\cos^2\theta}{R_\parallel^2}\right]^{1/2}. \quad (21)$$

As a result, Eq. (20) yields

$$\sigma_\perp(\omega)=\sigma_{xx}(\omega)=\sigma_{yy}(\omega)=$$
$$=\frac{9ne^2}{8m}\mathrm{Re}\frac{1}{\nu-i\omega}\int\limits_0^{\pi/2}d\theta\sin^3\theta\Psi(q)|_{\varepsilon=\varepsilon_\mathrm{F}},$$
$$\sigma_\parallel(\omega)=\sigma_{zz}(\omega)=$$
$$=\frac{9ne^2}{4m}\mathrm{Re}\frac{1}{\nu-i\omega}\int\limits_0^{\pi/2}d\theta\sin\theta\cos^2\theta\Psi(q)|_{\varepsilon=\varepsilon_\mathrm{F}}. \quad (22)$$

3.1. Spherical metallic nanoparticle

In the case of a spherical nanoparticle, we have $R_\perp=R_\parallel=R$ and $v'=v$. From Eq. (22), we obtain

$$\sigma_\perp(\omega)=\sigma_\parallel(\omega)=\frac{3ne^2}{4m}\mathrm{Re}\frac{\Psi(q)|_{\varepsilon=\varepsilon_\mathrm{F}}}{\nu-i\omega}. \quad (23)$$

Expression (23) describes the optical conductivity of a spherical nanoparticle with an arbitrary relation between the bulk and surface scatterings. This expression remains to be rather cumbersome in view of the form of $\Psi(q)$. Much simpler expressions can be obtained from formula (23) in the limiting cases corresponding to the domination of either scattering mechanism.

Since the quantity $q_1=2R\nu/v'$ is defined as the ratio between the bulk, ν, and surface, $v'/2R$, scattering frequencies, the limiting expression for the purely bulk mechanism of scattering is obtained from Eq. (23) by putting $q_1\to\infty$, and the purely surface one by putting $q_1\to 0$. From Eq. (19), we have $\Psi(q)\approx 4/3$ for the bulk mechanism of scattering. Therefore, in accordance with Eq. (23), we obtain

$$\sigma=\frac{ne^2}{m}\frac{\nu}{\nu^2+\omega^2}=\frac{\omega_{pl}^2}{4\pi}\frac{\nu}{\nu^2+\omega^2}. \quad (24)$$

According to Eqs. (15) and (17), the damping constant for plasma dipole oscillations in the spherical metallic nanoparticle located in the vacuum looks like

$$\gamma(\omega)=\frac{4\pi}{3}\sigma(\omega)=\frac{\omega_{pl}^2}{3}\frac{\nu}{\nu^2+\omega^2}. \quad (25)$$

Since $\gamma(\omega)$ describes the damping of dipole oscillations at the frequency $\omega_S=\omega_{pl}/\sqrt{3}$, we are interested in the value of $\gamma(\omega=\omega_S)$. The frequency ω_S is located in the visible spectral range, so that $\omega_S\gg\nu$. Then Eq. (25) yields

$$\gamma(\omega_S)\approx\nu, \quad (26)$$

i.e. the relaxation time of dipole plasma oscillations in the case of bulk scattering is equal to the momentum relaxation time in the bulk metal.

More interesting is the case where the surface scattering dominates ($q_1\to 0$). From Eq. (19), we obtain

$$\Psi(q)|_{q_1\to 0}\to\Psi(-iq_2)=\frac{4}{3}+\frac{4}{q_2^2}\left(\cos q_2-\frac{1}{q_2}\sin q_2\right)+$$
$$+i\left[-\frac{2}{q_2}+\frac{4}{q_2^2}\sin q_2-\frac{4}{q_2^3}(1-\cos q_2)\right], \quad (27)$$

where $q_2 = 2R\omega/v'$. Using this formula, we find from Eq. (23) that

$$\sigma = \frac{3}{8\pi}\nu_s \left(\frac{\omega_{pl}}{\omega}\right)^2 \left[1 - 2\frac{\nu_s}{\omega}\sin\frac{\omega}{\nu_s} + \right.$$

$$\left. + 2\left(\frac{\nu_s}{\omega}\right)^2 \left(1 - \cos\frac{\omega}{\nu_s}\right)\right], \tag{28}$$

where $\nu_s = v_{\rm F}/2R$ is the frequency of electron oscillations between the potential walls, and $v_{\rm F}$ is the Fermi velocity. Hence, in the case of surface scattering, we obtain for a spherical nanoparticle in the vacuum that

$$\gamma(\omega) = \frac{3v_{\rm F}}{4R}\left[1 - 2\frac{\nu_s}{\omega}\sin\frac{\omega}{\nu_s} + 2\left(\frac{\nu_s}{\omega}\right)^2\left(1 - \cos\frac{\omega}{\nu_s}\right)\right]. \tag{29}$$

One can observe a quasi-oscillating size dependence that arises, when the frequency of individual electron oscillations between the potential walls ($\nu_s = v_{\rm F}/2R$) approaches the frequency of collective oscillations in the electron subsystem with respect to the ionic frame ($\omega_S = \omega_{pl}/\sqrt{3}$). In both limiting cases $\nu_s \gg \omega_S$ and $\nu_s \ll \omega_S$, the expression in the brackets in Eq. (29) tends to unity.

If the spherical metallic nanoparticle is located in the vacuum, it may be unrealistic to observe the quasi-oscillating dependence (29), because $\nu_s \ll \omega_S$ as a rule. However, as one can see from Eq. (16), those oscillations can be made observable by selecting a matrix with the corresponding dielectric permittivity ϵ_m and a particle with the corresponding shape (the parameter L_α).

It is worth emphasizing that, in accordance with Eq. (25), the high-frequency conductivity $\sigma(\omega)$ determines the plasma resonance width at the frequency $\omega = \omega_S$. However, at the frequencies far from the resonance, $\sigma(\omega)$ determines the Joule power losses of separate electrons, which are not associated with their collective motion. In this case, if the frequency of the external electric field ω coincides with the frequency of individual electron oscillations $\nu_s = v_{\rm F}/2R$, the absorbed energy also begins to depend on ν_s/ω in a quasi-oscillating manner if the surface scattering dominates. This fact was marked for the first time in works [11,16] dealing with the electric absorption and in works [15,17] dealing with the magnetic one.

3.2. Spheroidal metallic nanoparticle

In the case of spheroidal nanoparticle, the diagonal components of the tensor of optical conductivity are given by formulas (22). If the surface scattering dominates, $q_1 \to 0$ and $q \to -iq_2$. Then, in accordance with Eq. (21) and the definition of variable q, we have

$$q_2 = \frac{2R\omega}{v'} = \frac{2R_\perp\omega}{v}\left(1 - e_p^2\cos^2\theta\right)^{-1/2}. \tag{30}$$

where $e_p = \sqrt{\left|1 - R_\perp^2/R_\parallel^2\right|}$ is the spheroid eccentricity, and θ is the angle between $\mathbf{v}$ and the axis of spheroid symmetry. Formula (30) can be used to change in Eq. (22) from the integration over θ to the integration over $q_2 \equiv x$. In so doing, taking Eq. (27) into acount, we obtain from Eq. (22) in the limit $q_1 \to 0$ that

$$\sigma_\parallel(\omega) = \frac{9ne^2}{2m\omega}\left(\frac{\omega}{\nu_{s,\perp}}\right)^2\frac{1}{e_p^3}\int\limits_{\omega/\nu_{s,\perp}}^{\omega/\nu_{s,\parallel}}\frac{dx}{x^4}\left[1 - \left(\frac{\omega}{\nu_{s,\perp}x}\right)^2\right]^{1/2}\times$$

$$\times\left[1 - \frac{2}{x}\sin x + \frac{2}{x^2}(1 - \cos x)\right], \tag{31}$$

$$\sigma_\perp(\omega) = \frac{9ne^2}{4m\omega}\left(\frac{\omega}{\nu_{s,\perp}}\right)^2\frac{e_p^2 - 1}{e_p^3}\int\limits_{\omega/\nu_{s,\perp}}^{\omega/\nu_{s,\parallel}}\frac{dx}{x^4}\frac{1 - \left(\frac{\omega}{\nu_{s,\parallel}x}\right)^2}{\left[1 - \left(\frac{\omega}{\nu_{s,\perp}x}\right)^2\right]^{1/2}}\times$$

$$\times\left[1 - \frac{2}{x}\sin x + \frac{2}{x^2}(1 - \cos x)\right]. \tag{32}$$

Here, the following notations are introduced:

$$\nu_{s,\parallel} = \frac{v_{\rm F}}{2R_\parallel}, \quad \nu_{s,\perp} = \frac{v_{\rm F}}{2R_\perp}. \tag{33}$$

In accordance with Eq. (17), the damping constants for dipole plasma oscillations occurring along the spheroid axis and transverse to it look like

$$\gamma_\parallel = 4\pi L_\parallel\sigma_\parallel(\omega)|_{\omega=\omega_\parallel}, \tag{34}$$

$$\gamma_\perp = 4\pi L_\perp\sigma_\perp(\omega)|_{\omega=\omega_\perp}. \tag{35}$$

As one can see from Eqs. (31) and (32), at frequencies, including the characteristic ones, that satisfy the inequalities

$$\omega > \nu_{s,\parallel},\, \nu_{s,\perp}, \tag{36}$$

the oscillating terms in the brackets can be omitted, leaving only unity. In this case, integrals (31) and (32) are calculated exactly, and we obtain

$$\sigma_{\parallel}(\omega) = \frac{9ne^2\nu_{s,\parallel}}{16m\omega^2}\frac{1}{e_p^3}\Big[-e_p(1-2e_p^2)+ \\ +(1-e_p^2)^{-1/2}\arcsin e_p\Big]. \quad (37)$$

Analogously,

$$\sigma_{\perp}(\omega) = \frac{9ne^2\nu_{s,\perp}}{32m\omega^2}\frac{1}{e_p^3}\Big[e_p(1+2e_p^2)(1-e_p^2)^{1/2}- \\ -(1-4e_p^2)\arcsin e_p\Big]. \quad (38)$$

When obtaining expressions (37) and (38), we used the identity

$$\arcsin a \pm \arcsin b = \arcsin(a\sqrt{1-b^2} \pm b\sqrt{1-a^2}). \quad (39)$$

On the basis of Eqs. (34), (35), (37), and (38), we obtain the following expressions for the decrements of dipole plasma oscillations in metallic spheroidal nanoparticles:

$$\gamma_{\parallel}(\omega_{\parallel}) = \frac{3v_{\mathrm{F}}}{4R_{\parallel}}\phi_{\parallel}(e_p), \quad (40)$$

where

$$\phi_{\parallel}(e_p) = \frac{3}{8e_p^3}\Big[-e_p(1-2e_p^2)+(1-e_p^2)^{-1/2}\arcsin e_p\Big]. \quad (41)$$

and

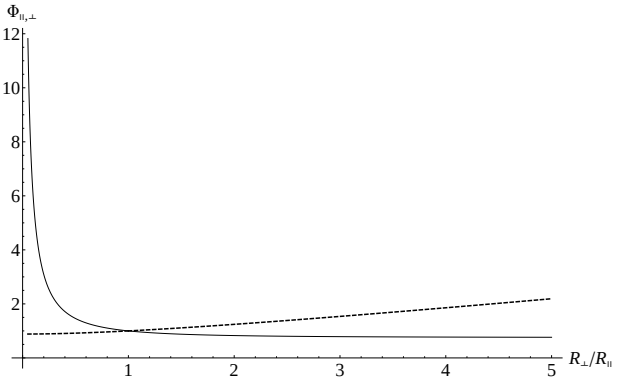
$$\gamma_{\perp}(\omega_{\perp}) = \frac{3v_{\mathrm{F}}}{4R_{\perp}}\phi_{\perp}(e_p), \quad (42)$$

where

$$\phi_{\perp}(e_p) = \frac{3}{16e_p^3}\Big[e_p(1+2e_p^2)(1-e_p^2)^{1/2}-(1-4e_p^2)\arcsin e_p\Big]. \quad (43)$$

For the spherical shape, $e_p \to 0$, and we obtain $\phi_{\parallel\parallel}(0) = \phi_{\perp}(0) = 1$. The functions $\phi_{\parallel,\perp}(e_p)$ characterize the dependence of the plasma oscillation damping on the metallic nanoparticle shape. Those dependences are plotted in Figure.

Formulas (41) and (43) are valid only for a prolate spheroid, i.e. at $0 \le e_p \le 1$. In the case of oblate spheroid, i.e. at $1 \le e_p \le \infty$, we obtain, instead of formulas (41) and (43), the following corresponding expressions:



Dependences of the plasma oscillation damping functions on the metallic nanoparticle shape: $\phi_{\parallel}(e_p)$ (solid curve) and $\phi_{\perp}(e_p)$ (dashed curve)

$$\phi_{\parallel}(e_p) = \frac{3}{8e_p^3}\Big[e_p(1+2e_p^2)- \\ -(1+e_p^2)^{-1/2}\ln(e_p+\sqrt{1+e_p^2})\Big], \quad (44)$$

$$\phi_{\perp}(e_p) = \frac{3}{16e_p^3}\Big[e_p(2e_p^2-1)(1+e_p^2)^{1/2}+ \\ +(1+4e_p^2)\ln(e_p+\sqrt{1+e_p^2})\Big]. \quad (45)$$

The spherical shape of a MNP corresponds in Figure to the value $R_{\perp}/R_{\parallel} = 1$ (or $e_p = 0$).

From Figure, one can see that the influence of the MNP shape on the PR damping constants is not reduced to small corrections to the known results obtained in the case of spherical MNP. Depending on the particle shape, the functions $\phi_{\parallel}(e_p)$ and $\phi_{\perp}(e_p)$ can change by several times. Hence, the MNP shape can substantially affect not only the PR frequency, but also the damping constants. Eventually, we note that the effect of the MNP shape on the PR damping constants has been studied in the classical case. A similar effect arises also in the quantum case due to the appearance of quantum levels determined by the boundary conditions on the surfaces of MNPs.

4. Conclusions

To summarize, a theory describing the dependence of the PR damping constants on the MNP shape is developed for the case of particle sizes where the surface electron scattering dominates. It is shown that

when MNPs are incorporated into a dielectric matrix with high dielectric permittivity, there may appear a quasi-periodic size dependence of the PR damping constant stemming from the coincidence of the dipole PR frequency with the frequency of individual electron oscillations between the potential walls. For spheroidal particles, analytical expressions are obtained, and the dependences of the PR damping constants on the ratio between the curvature radii $R_\perp/R_\parallel$ are plotted. The influence of the MNP shape on the PR decrements is shown to be substantial and is not reduced to small corrections of the known results obtained for spherical MNPs. Therefore, when interpreting the experimental results, it is necessary that the dependences of not only PR frequencies, but also PR decrements on the particle shape be taken into consideration.

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ЗАЛЕЖНІСТЬ ДЕКРЕМЕНТІВ
ЗГАСАННЯ ДИПОЛЬНИХ ПЛАЗМОВИХ РЕЗОНАНСІВ
ВІД ФОРМИ МЕТАЛЕВИХ НАНОЧАСТИНОК

Р е з ю м е

В роботі розвинута теорія залежності декрементів згасання дипольних плазмових резонансів в металевих наночастинках від їх форми. Для частинок у вигляді еліпсоїда обертання у випадку домінуючої ролі розсіяння електронів на поверхні отримані аналітичні формули (і побудовані графіки) залежності декрементів згасання як функції відношення радіусів кривизни. Проілюстрована значна залежність декрементів від форми наночастинок. Показано, що при інкорпорації металевих наночастинок певної форми у діелектричну матрицю з високою діелектричною проникністю можливий резонанс, зумовлений збіганням частоти плазмового дипольного коливання з частотою індивідуальних електронних осциляцій (від однієї потенціальної стінки до протилежної). Такий резонанс зумовлює появу квазіосциляційної розмірної залежності декремента згасання плазмових коливань.