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SURFACE PLASMON RADIATIVE DAMPING RATE IN NOBLE METAL SPHEROIDAL NANOSHELLS

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Abstract–Radiation damping rate of surface plasmon oscillations in spheroidal core-shell noble metal nanoparticles is calculated analytically. It is shown that the rate drastically decreases with decrease in the shell thickness. Calculation shows that, as in case of nanospheres, the radiation damping rate is proportional to the number of radiating electrons, i.e. to the shell volume. This result can be used in designing nanophotonic devices requiring narrow surface plasmon resonances.

Keywords: surface plasmon, radiative damping rate, spheroidal nanoshells, red shift

1. Introduction

For relatively large metallic nanoparticles (MNP) (with radii ~20 nm and more) the main limiting factor of spectral sensitivity is the radiation damping of surface plasmon (SP) oscillations. The radiation linewidth of SP spectrum in a spherical MNP is proportional to its volume [1], which makes difficult using the particles with sizes more than 20 nm in nanophotonics. This circumstance stimulates studies directed to find the ways for suppressing the SP radiation damping [2]. In this respect hollow MNPs could be good candidates if the radiation damping rate (RDR) of SP oscillations is proved to be small. It is demonstrated that SP RDR in spherical noble metal nanoshells is drastically suppressed as compared to the solid nanosphere of the same outer radius [3]. As it is shown, strong suppression of the RDR by up to two orders of magnitude takes place when shell thickness decreases only by 5–6 times. This behavior is a result of two circumstances: a) strong redshift of SP frequency ω_{sp} with decrease in the shell thickness, b) rapid raise of dielectric function of the metal with decrease in the SP frequency.

It is well known that nanoparticles of spheroidal shape often occur during the chemical synthesis [4]. For this reason it is of great interest to investigate the RDR dependence on the parameters of spheroidal nanoparticles. Note that in this case there are two degrees of freedom for tuning as compared to the spherical shape where there is only one free parameter. Indeed, for the spheroidal shape besides the shell thickness there appears the aspect ratio of nanoshell as well [5]. In this paper the RDR of longitudinal SP oscillations in noble metal prolate spheroidal nanoshells is calculated and is compared with the case of spherical nanoshells.

2. Calculation of SP RDR in Spheroidal Nanoshell

The calculation is carried out using the algorithm developed for specific systems that contain

regions with different dielectric constants [6]. We consider particles with size much smaller than the wavelength of emitted light $\lambda/2\pi \gg R$ allowing application of the quasistatic approximation. According to Eqs.1 and 2 of [3] the RDR γ in this approximation can be expressed as

$$\gamma = \left(\omega_{sp}^4 \mathbf{p}^2 / 3c^3 W\right)\sqrt{\varepsilon_3}, \tag{1}$$

where ω_{sp} is the SP frequency, $\mathbf{p}$ is the amplitude of the dipole moment of the particle, W is the electrostatic energy of the particle, ε_3 is the dielectric constant of the environment, c is the speed of light. Thus the problem of determining γ is reduced to calculating W as a function of the dipole moment **p.** This procedure in the case under consideration can be carried out by solving the electrostatic boundary problem for the two interfaces: core-shell and shell-environment. We denote the electric field potentials in the core, shell and environment regions correspondingly by φ_1, φ_2 and φ_3. Introducing the dielectric constant of the core (ε_1) and the dielectric function of the metallic shell $(\varepsilon(\omega))$ in the absence of the external field, we come to the boundary conditions for the first and second interfaces in the following form:

$$\varphi_1 = \varphi_2, \quad \left(\varepsilon_1 \mathrm{grad}\varphi_1 - \varepsilon(\omega)\mathrm{grad}\varphi_2\right)\mathbf{n}_{12} = 0, \tag{2}$$

$$\varphi_2 = \varphi_3, \quad \left(\varepsilon(\omega)\mathrm{grad}\varphi_2 - \varepsilon_3 \mathrm{grad}\varphi_3\right)\mathbf{n}_{23} = 0. \tag{3}$$

Herein, $\mathbf{n}_{12}$ and $\mathbf{n}_{23}$ are the unit vectors of normal directed from the core to the shell and from the shell into the external medium, respectively. Note that the values of $\varepsilon(\omega)$ for the noble metals are known from the experimental data of [7].

Since the solution of the boundary problem is well known [8], we present only some expressions in order to clarify our notations. Introducing spheroidal coordinates ξ and η defined according to [9], we seek the potentials in the three regions in the form of expansion in terms of Legendre functions:

$$\varphi_1 = aP_1(\xi)P_1(\eta), \ \varphi_2 = bP_1(\xi)P_1(\eta) + cQ_1(\xi)P_1(\eta), \ \varphi_3 = dP_1(\eta)Q_1(\xi), \tag{4}$$

where $P_1(\xi) = \xi$ and $Q_1(\xi) = (\xi/2)\ln\left((\xi+1)/(\xi-1)\right) - 1$. Substituting φ_1, φ_2 and φ_3 into the boundary conditions (2) and (3), we obtain homogeneous set of equations for coefficients a, b, c and d. Then the requirement of nonzero solution of the system reads

$$\begin{aligned}&\left(\varepsilon_3 - \varepsilon(\omega)\right)\left(\varepsilon_1 - \varepsilon(\omega)\right)Q_2'(\xi_2)Q_2(\xi_2)\xi_1 + \\ &\left(\varepsilon(\omega)Q_1(\xi_2) - \varepsilon_3\xi_2 Q_1'(\xi_2)\right)\left(\varepsilon_1 Q_1(\xi_1) - \varepsilon(\omega)\xi_1 Q_1'(\xi_1)\right) = 0,\end{aligned} \tag{5}$$

which determines the SP frequencies of the spheroidal shell [4].

We define the energy of the nanoparticle and its dipole moment, taking into account that the

charge arises only on the interfaces. Then the electrostatic energy equals

$$W = \frac{1}{2}\oint \sigma_{12}\varphi_1 dS_{12} + \frac{1}{2}\oint \sigma_{23}\varphi_3 dS_{23}, \tag{6}$$

where σ_{12} and σ_{23} are the surface charge densities on the core–shell and the shell–external medium boundaries, respectively. These quantities can be derived using the boundary conditions (2) and (3) on the spheroidal surfaces $\xi = \xi_1$ and $\xi = \xi_2$ with equal interfocal distances $2f$ in the form

$$\sigma_{12} = \frac{\left(\varepsilon(\omega) - \varepsilon_1\right)\eta a}{4\pi\varepsilon_2 f}\sqrt{\frac{\xi_1^2 - 1}{\xi_1^2 - \eta^2}}, \quad \sigma_{23} = \frac{\left(\varepsilon_3 - \varepsilon(\omega)\right)\eta Q_2' d}{4\pi\varepsilon(\omega) f}\sqrt{\frac{\xi_2^2 - 1}{\xi_2^2 - \eta^2}}. \tag{7}$$

Substituting the expressions for the surface charge densities into (6), we obtain the electrostatic energy in the form

$$W = \frac{\varepsilon_3 - \varepsilon(\omega)}{6\varepsilon(\omega)} f\left(\xi_2^2 - 1\right) Q_1(\xi_2) Q_1'(\xi_2)\left[1 + \frac{\xi_2^2 - 1}{\xi_1^2 - 1}\frac{\varepsilon(\omega) Q_1(\xi_2) - \varepsilon_3 \xi_2 Q_1'(\xi_2)}{\varepsilon_1 Q_1 - \varepsilon(\omega)\xi_1 Q_1'(\xi_1)}\right] d^2. \tag{8}$$

For the amplitude of the total dipole moment of the core-shell particle we come to the following expression:

$$p = 2f\oint \sigma_{12}\xi_1\eta dS_{12} + 2f\oint \sigma_{23}\xi_2\eta dS_{23} = \left(f^2/3\right)d. \tag{9}$$

Finally, the RDR is obtained in the form

$$\gamma = \frac{2\omega_{sp}^4}{9c^3}\frac{\varepsilon(\omega) f^3\sqrt{\varepsilon_3}}{\left(\varepsilon_3 - \varepsilon(\omega)\right)\left(\xi_2^2 - 1\right) Q_1(\xi_2) Q_1'(\xi_2)}\left[1 + \frac{\xi_2^2 - 1}{\xi_1^2 - 1}\frac{\varepsilon(\omega) Q_1(\xi_2) - \varepsilon_3 \xi_2 Q_1'(\xi_2)}{\varepsilon_1 Q_1(\xi_1) - \varepsilon(\omega)\xi_1 Q_1'(\xi_1)}\right]^{-1}. \tag{10}$$

As it expected expression (10) is reduced to the SP RDR of spherical nanoshell when interfocal distance $2f$ tends to zero and spheroids are transformed into spheres (see [3]). In this limit $\xi_{1,2} \to R_{1,2}/f$ where R_1 and R_2 $\left(R_2 > R_1\right)$ are the radii of the inner and outer spheres. Naturally, for a bulk spheroid the expression (10) transfers into the result of [10], e.g., γ is proportional to the particle volume. In case of bulk sphere we have from (10) the well-known result of [1]:

$$\gamma_{\text{sphere}} = (2/3)\,\omega_{sp}\left(\omega_{sp} R/c\right)^3\sqrt{\varepsilon_3} \tag{11}$$

where R is the radius of the sphere.

3. Results and Discussion

As it follows from numerical evaluation of (10) the RDR drastically decreases with decrease in the shell thickness analogously to the results for spherical nanoshell [3]. It is obvious that when the aspect ratio of the particle is kept constant the physical reason of reduction of RDR with decrease in the shell thickness is the decrease in the number of radiating electrons. Another important result is that appearance of an additional parameter in RDR as compared to sphere – aspect ratio of spheroid opens new possibility for tuning SP resonance frequency and the linewidth.

In Fig.1 we present the dependence of RDR of spheroidal shell on the shell volume, i.e. the number of radiating electrons. As seen, the decrease in the shell volume resulted in the strong decrease in RDR.

It is important to note that, as it is shown in [11], the electron-phonon interaction in thin metallic films is also suppressed due to size quantization of phonon spectra. Thus in the nanoshell the resulting linewidth of SP resonance, conditioned by the Drude relaxation and radiation damping, is drastically decreased as compared to the bulk nanoparticle of the same size. This interesting feature makes nanoshells attractive for applications in photonics and nanooptics.

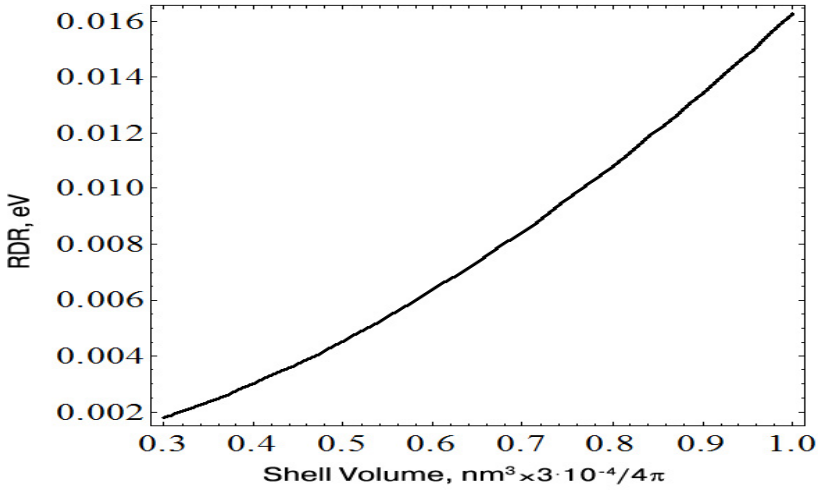

Fig.1. Dependence of RDR of a spheroidal shell on its volume.

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