Metal nanosphere at an interface: revival of degeneracy of a dipole plasmon

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Abstract. Metal nanoparticles supporting surface plasmon modes are used in many areas of science and technology. Often it is important to know the exact location of the metal nanoparticle relative to a larger dielectric object. In this paper, we demonstrate that this goal may be achieved by monitoring the localized surface plasma resonance splitting in the course of the nanoparticle movement. In particular, we simulate splitting of the plasma resonance localized in a metal nanosphere while it approaches and penetrates the interface of two dielectric media. Numerical simulations show that splitting goes through two maxima at the beginning and at the end of the penetration process while the plasmon modes become exactly degenerate at some distance near the midpoint of the nanosphere trajectory. These results may be used to real time monitoring of the exact position of the nanoparticles while they approach and penetrate different targets. Applications in the drug delivery, photodynamic therapy and other biomedicine branches are envisioned.

1. Introduction

Metal nanoparticles supporting localized surface plasma resonance (LSPR) have been applied in many areas of science and technology [1]. These particles are capable of the resonant enhancement of the density of electromagnetic radiation nearby the particle surfaces due to the collective electron oscillations in the metal and have found numerous applications [1-6]. Often it is important to know the exact location of the particle. Particles may be deposited on surface or penetrated into it, in medical applications the particles may pass through the cell membrane, wherein the frequency and properties of the resonances strongly depend on the position of the particle. Plasmon modes in particles located sufficiently far (compared with the wavelength of the exciting electromagnetic wave) from the media interface have been investigated previously in cases of different symmetries and configurations [7,8]. However, it has not been given sufficient attention to the case when the particle is located at the interface between different media, despite the fact that this case usually carried in practice. Usually in this case various approximations, which takes into account the image force, are used [9]. In [10] the perturbation theory with regard to the difference in the refractive indices of the two media was employed. Hence, the results obtained in [10] are valid only in the limit of almost equal refractive indices.

In this paper, we perform numerical simulations of the LSPR in spherical silver nanoparticles during their passage from one dielectric medium into another. The goal of our work is to establish the true LSPR frequencies and their dependence on the metal nanosphere position relative to the interface.
2. Problem statement and calculations

We consider the case of oblique incidence of light (angle of incidence is 45°) from the semi-infinite medium with a real dielectric constant $\varepsilon_1 > 0$, bordering the other semi-infinite medium with another real dielectric constant $\varepsilon_2 > 0$. Close to the surface there is a plasmonic nanosphere with the radius $r$ and the complex permittivity $\varepsilon$ (see. figure 1(a)). The right-handed Cartesian coordinate system is introduced in such a way that the plane $(x, y)$ coincide with the plane of the interface of two dielectric media. The incident wave is p-polarized, thus having non-zero components of the electric field at the axis $x$ and $z$, it excites oscillations of the electron density in the particle along the interface and perpendicular to it. Eigenfrequencies of these oscillations have different dependencies on the relative position of the particle and the surface. Resonance oscillations of the electron density correspond to the resonance absorption in the particle. So, by calculating the absorption spectrum of the energy in the particle, we can find the resonant frequency along both perpendicular directions.

![Figure 1](image1.png)

**Figure 1.** Geometry of the structure (a). Computational box parameters (b). Tetrahedral mesh view (c).

Calculations were made in the commercial software CST Microwave Studio, where in the space of a computational box Maxwell's equations are solved by the finite differences method [11]. For our calculations we used the frequency domain of the finite differences method. Dimensions of computational box (figure 1(b)) are: $a = 200$ nm, $b = 200$ nm, $c = 270$ nm. The computational grid is tetragonal, the number of cells is 52 358 (figure 1(c)). For the case when the particle is very close to the interface we introduced a finer grid in such a way that the distance between the edges of the particle and the insulator always exceeds the linear dimension of the grid. The part of the space bounded by the vertical walls with the periodic boundary conditions is also known as Floquet channel. For simulation of the excitation we use Floquet channels. In CST software Floquet ports can generate electromagnetic waves with different angle of incidence and polarization. The lattice pitch is selected such that both the near-field interaction between the particles and diffraction effects made negligible contributions to the absorption within the particle. So, despite the periodicity of the structure, the absorption in each particle is similar to the absorption in a single particle near the interface. We calculate the absorption inside the particle as a difference between the normalized energy fluxes on the surfaces labeled as $\alpha$ and $\beta$ in Figure 1(b). Since the dielectric media were chosen to be transparent, they do not contribute to the absorption. The frequency at which the absorption in the particle reaches the maximum value corresponds to the LSPR. Absorption is calculated as a function of the $z$-coordinate of the particle center $z_0$. 


3. Simulations results and discussion

Figure 2 plots the results of simulations. In the cases A and D the dielectric constants of silver were taken directly from an article by Johnson, Christy [12].

Figure 2. Splitting of the LSPR in the silver nanospheres of different radii \( r \) while they approach and penetrate an interface between two dielectric media. A: \( r = 20 \) nm, \( \varepsilon_1 = 1, \varepsilon_2 = 2.35, \varepsilon \) corresponds to silver [12]. B: \( r = 20 \) nm, \( \varepsilon_1 = 1, \varepsilon_2 = 2.35, \varepsilon \) corresponds to Drude approximation of silver with reduced damping. C: \( r = 10 \) nm, \( \varepsilon_1 = 1, \varepsilon_2 = 2.35, \varepsilon \) corresponds to Drude approximation of silver with reduced damping. D: \( r = 20 \) nm, \( \varepsilon_1 = 1.77, \varepsilon_2 = 1.96, \varepsilon \) corresponds to silver [12].

In the cases B and C the Johnson and Christy data were approximated by the Drude formula

\[
\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\gamma},
\]

where \( \omega \) is the frequency, \( \omega_p \) is the plasma frequency, \( \gamma \) is the collision frequency, \( \varepsilon_\infty \) is the ultimate high-frequency dielectric constant of silver. In the frequency range of 600-900 THz optical properties of silver are best reproduced with the following set of parameters: \( \omega_p = 2308 \) THz, \( \gamma = 70.6 \) THz, \( \varepsilon_\infty = 5.26 \). The collision frequency was halved (\( \gamma' = 35.3 \) THz) in order to obtain narrower absorption peaks, and accordingly more visible separation. For each case, a number of additional calculations has been done with the same geometry but with normal incidence of the exciting wave. It allowed us to specify the correspondence between peaks of absorption and types of electron oscillation.

It is to be noted that sometimes the widths of the LSPR do not allow for complete resolution of them. For example, there are two graphs in figure 3 In the first case (configuration A, \( z_0 = 10 \) nm) peaks are pretty clearly separated. In the second case (configuration A, \( z_0 = -22 \) nm) absorption peak is broadened, corresponding to the two resonances, but it is not possible to find the exact value of the
resonant frequencies. For a particle of radius 10 nm with silver dielectric constant from [12] we could not distinguish individual peaks, so the graph shows only the results of calculations for Drude parameters with reduced damping. In all four cases presented in figure 2 splittings of the plasmon modes behave similarly as the nanospheres approach the interface. The curves representing this splitting intersect at one point \( z = z_\omega \), and have a relatively distinct asymmetry. At \( z < z_\omega \), splitting is generally less than at \( z > z_\omega \). For a silver nanoparticle of the 20 nm radius, separation of the peaks is significant when the particle is close to the interface. If the particle is far away from the interface, the separation of the peaks is less than their widths. In this case, to visualize the positions of the resonances the imaginary part of the permittivity of silver was artificially reduced.

\[ \alpha_{1}^{(x)} = \frac{\tilde{\alpha}}{1 - \alpha\sigma_{1}^{(x)}} ; \quad \alpha_{1}^{(z)} = \frac{\tilde{\alpha}}{1 - \alpha\sigma_{1}^{(z)}} ; \quad \alpha_{2}^{(x)} = \frac{\tilde{\alpha}}{1 - \alpha\sigma_{2}^{(x)}} ; \quad \alpha_{2}^{(z)} = \frac{\tilde{\alpha}}{1 - \alpha\sigma_{2}^{(z)}} . \]  

\[ (2) \]

Here \( \tilde{\alpha} \) is the polarizability of a single particle in a vacuum [13] while \( \sigma \) accounts the image force due to the interface [14]:

**Figure 3.** Plasmon absorption in nanoparticle. 1 – configuration A, \( z_0 = 10 \) nm, 2 – configuration A, \( z_0 = -22 \) nm.

**Figure 4.** Comparison of the results of CST simulations for configuration B (magenta and cyan squares) with the results obtained in the framework of the quasistatic dipole approximation (red and blue lines).

The \( z_\omega \) values depend on the particle size and the dielectric properties of the material. So, in the cases A and B (for these cases only the absorption coefficient of the particle material is significantly different) \( z_\omega = 13 \) nm, for cases C and D \( z_\omega = -6 \) nm. In any case, the degeneracy of the plasma oscillation occurs at the point when the center of the particle resides in a medium with a lower refractive index. In the earlier work on the same subject [10] the perturbation theory was employed. Although the general trends of the mode splitting and their collapse at the interface were given correctly, the point at which the degeneracy of modes is reestablished was inevitably put \( z_\omega = 0 \). Numerical simulations performed in the present work are free from the restrictions of the perturbation theory and show the right location of the point where the plasmon modes degenerate.

The results of our calculation are in accord with the estimations that may be performed in the framework of the dipole quasi-static approximation provided the finite size of the particle is accounted for. In this approximation, the frequency of LSPR corresponds to the pole in the particle polarizability, which is given by the formulas
\[ \sigma_1^{(x)} = \frac{1}{8z_0^2} \varepsilon_2 - \varepsilon_1; \quad \sigma_1^{(z)} = \frac{1}{4z_0^2} \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 + \varepsilon_2}; \]
\[ \sigma_2^{(x)} = \frac{1}{8z_0^2} \varepsilon_1 - \varepsilon_2; \quad \sigma_2^{(z)} = \frac{1}{4z_0^2} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_2 + \varepsilon_1}. \]

The results of the quasistatic approximation are compared to the results of numerical simulations in figure 4. We see significant discrepancy between the curves when distances between particle center and dielectric surface become comparable to the radius of the particle. So, in general, if exclude the case where the particle crosses the boundary between two media, it is enough to take into account the image force in the quasi-static approximation for the correct description of the resonance. At the interface this approach, as expected, fails completely.

4. Conclusions
In this paper, we considered the passage of particles through the boundary between two dielectric media using physical modeling techniques. It was shown that when the particle edge does not intersect the media interface, the LSPR is described by the quasistatic dipole approximation quite well. On the other hand, significant difference is observed when the particle intersects the media interface. The growth of the difference between the frequencies of the modes of the collective electron oscillations along the surface and perpendicular to it stops at some point and starts to diminish. Then, the degeneracy of the modes is reestablished at the point that we designated as \( z_\ast \). This point is always located in the medium with lower refractive index. After this point, the plasmon modes split again but the sing of the splitting is reversed. Although the quasistatic approximation describes the behavior of the modes at larger distances quite satisfactory it fails to account for the mode degeneracy at \( z_\ast \).

The passage of plasmonic nanoparticles through the interface between two dielectric media is implemented in many applications [2,15]. Knowing the properties of the LSPR, we can make definite conclusions about the exact location of the particles. We expect that our results will be useful for the well-established applications, as well as for new methods of diagnosing the spread of nanoparticles in the environment. For example, using spectroscopy of particle flux in the medium with a variety of membranes (e.g., organic body) in real time and observing the kinetics of separation of resonance frequencies, it is possible to accurately determine the velocity of the particles [16].

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