Plasmonic properties of metal nanoislands: surface integral equations approach

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Abstract. The surface integral equations method is used to analyse the surface plasmon resonance position in a metal island film formed by non-interacting axisymmetrical prolate/oblate hemispheroids placed on a dielectric substrate. The approach is verified via the comparison of results obtained for a hemisphere on a substrate with the ones obtained using the multipole expansion method. The preference of the integral equations method is in obtaining a simple final analytical expression for a particle polarizability in which any dielectric function of a metal can be substituted. Such simple formulae for the hemispherical particle on the substrate and calculated dependences of the hemispheroid resonant wavelength on its aspect ratio are presented.

1. Introduction

The surface plasmon resonance (SPR) phenomenon in metal nanoparticles [1] is of a particular interest for both applied optics/plasmonics and fundamental physics. A special and interesting case of metal nanoparticles are metal island films (MIF) which can be used as polarizers and spectral filters [2] and, because of the high enhancement of the local electric field, in Raman spectroscopy [3]. The spectral position of the SPR in MIF is usually calculated for metal nanoislands of a hemispherical shape observed in experiments [4]. Using the multipole expansion method [5, 6] the dependences of the SPR wavelength on the dielectric permittivity of the substrate and on the dielectric constant and the thickness of a layer covering the nanoparticles were calculated [7]. However, not hemispherical but hemispheroidal shape of metal nanoislands has recently also been reported [8], the nanoislands being axisymmetric prolate/oblate hemispheroids (see Figure 1). This makes important the understanding of plasmonic characteristics of such nanoparticles and, respectively, of MIF formed by metal hemispheroids.

To describe plasmonic properties of a particle it is usually enough to find its polarizability dispersion. In the case of free standing spherical and spheroidal nanoparticles there are the analytical solutions allowing one to find the SPR frequency and the absorption spectrum [9, 10]. However, the majority of even relatively simple shapes of metal nanoparticles require applying numerical techniques to describe their polarizability. Diverse numerical and semi-numerical methods allow this, and below we present the application of the surface integral equations method [11, 12] to the semi-numerical
analysis of the SPR in a metal hemisphere and an axisymmetrical metal hemispheroid placed on a dielectric substrate.

2. The approach
We consider a plasmonic particle with somehow induced surface charges of a density $\sigma(r)$ and surrounded by a dielectric medium with permittivity $\varepsilon_{\text{out}}$. General relations of the Potential Theory [13] and the standard boundary conditions lead to the equation [12]:

$$
\sigma_k(r) = \frac{\lambda_k}{2\pi} \int_S \sigma_k(s) \frac{n(r)(r - s)}{|r - s|^3} dS.
$$

(1)

Here the index $k$ corresponds to a particular plasmonic mode, $\lambda_k = (\varepsilon_k - \varepsilon_{\text{out}})/(\varepsilon_k + \varepsilon_{\text{out}})$, $\varepsilon_k$ is the particle permittivity at which the $k^{th}$ plasmonic mode can be excited, $r$ and $s$ are position vectors of points on the nanoparticle surface, $n(r)$ is a unit vector normal to the surface (see Figure 2). Eq. 1 is an eigenvalue problem which determines all possible surface plasmon modes in the particle. Since the plasmonic resonant frequency is to be found, it is convenient to consider the permittivity of the surrounding dielectric, $\varepsilon_{\text{out}}$ as a parameter. Note that the particle permittivity $\varepsilon_k$ defines an eigenvalue $\lambda_k$ and corresponds to the $k^{th}$ distribution of surface charge density $\sigma_k(r)$. These values $\varepsilon_k$ are called resonant permittivities.

If an external electric field $E_0(r)$ is applied to the nanoparticle, Eq. 1 transforms to:

$$
\sigma(r) = \frac{\lambda}{2\pi} \int_S \sigma(s) \frac{n(r)(r - s)}{|r - s|^3} dS + \frac{\lambda}{2\pi} n(r)E_0(r).
$$

(2)

Note that Eq. 2, as well as Eq. 1, can be written in a more general form using the Green function $G(r,s)$:

$$
\sigma(r) = \frac{\lambda}{2\pi} \int_S \sigma(s)n(r)\nabla_s G(r,s) dS + \frac{\lambda}{2\pi} n(r)E_0(r).
$$

Here $G(r,s) = |r - s|^{-1}$ for charges distributed in a homogeneous medium. In Eq. 2, $\lambda$ is no longer an eigenvalue, and it is defined by the permittivity $\varepsilon(\omega)$ of the particle at a certain frequency $\omega$: $\lambda = (\varepsilon(\omega) - \varepsilon_{\text{out}})/(\varepsilon(\omega) + \varepsilon_{\text{out}})$. The solution of Eq. 2 can be presented through the expansion by the eigenfunctions given by Eq. 1:

Figure 1. The example of an atomic force microscope (AFM) measured profile of a particle. The nanoisland is a prolate hemispheroid with the aspect ratio $\sim 1.3$.

Figure 2. The scheme of the problem.
\[ \sigma(r) = \frac{\lambda}{2\pi \sum_k \frac{\lambda_k}{\lambda_k - \lambda} \langle n(r')E_0(r'); \tau_k(r') \rangle \sigma_k(r) }, (3) \]

where \( \tau_k \) is a corresponding eigenfunction of the equation adjoint to Eq. 1, \( \lambda_k \) is a corresponding eigenvalue, and \( \langle n(r')E_0(r'); \tau_k(r') \rangle = \int_S n(r')E_0(r')\tau_k(r')dS' \). According to Ref. 12, the solutions of Eq. 1 and the adjoint one form two biorthogonal sets: \( \int_S \tau_i(s)\sigma_j(s)dS = \delta_{ij} \), where \( \delta_{ij} \) is the Kroneckers delta. Since the eigenfunctions of Eq. (1) do not form an orthogonal set because the kernel of the equation is not symmetrical, it is convenient to use the eigenfunctions of the adjoint equation in the expansion (3). Note that the adjoint equation describes the surface dipole density which provides the same electric field as a single charged layer [12].

The particles dipole momentum, \( p \), and, respectively, the polarizability, \( \alpha \) (\( p = \alpha E_0 \)), are given by the formula:

\[ p = \int_S r\sigma(r)dS = \frac{e(\omega) - e_{\text{out}}}{4\pi e_{\text{out}}} \sum_k \frac{e_{\text{out}} - e_k}{e(\omega) - e_k} \int_S r\langle n(r')E_0(r'); \tau_k(r') \rangle \sigma_k(r)dS'. \] (4)

The values \( e_k \) are called the resonant permittivities since the polarizability increases greatly when \( e(\omega) \approx e_k \). Hereinafter, we use notification \( e_{\text{res}} \) for \( e_k \).

The substrate influence can be considered [12] using the method of mirror images. In this case the Green function transforms from \( G(r, s) = |r - s|^{-3} \) to \( G_{\text{sub}}(r, s) = |r - s|^{-3} (e_{\text{sub}} - e_{\text{out}})/(e_{\text{sub}} + e_{\text{out}}) \) [12], where \( s' \) is the mirror image of \( s \) in the substrate. This Green function should be substituted in all the equations written above instead of \( G(r, s) = |r - s|^{-3} \).

The formula (4) allows calculating the polarizability and, respectively, the SPR position. The most time-consuming routine here – eigenvalues and eigenfunctions calculation – should be run only twice (for Eq. 1 and for the adjoint one), and the calculation of the polarizability spectral dependence does not require direct numerical study that considerably simplifies the analysis. Contrary, other techniques, like the multipole expansion method [5], the discrete dipole approximation (DDA) [14] or the finite elements methods (FEM) [15], require full calculation cycle for each spectral point.

3. Polarizability of hemispherical nanoparticles

Below we present the numerical solution of Eq. 1 and the adjoint one using the surface discretization. To be more specific we consider the external electric field \( E_0 \) directed along the substrate surface; this corresponds to an incident s-polarized electromagnetic wave. We also assume that metal particles under consideration are much smaller than the light wavelength [4]. This allows neglecting retardation of the electric field phase that is to consider the problem within the frames of quasistatic (dipole) approximation [16]. In these assumptions we analyse the polarizability dispersion, \( \alpha(\omega) \), of a metal hemisphere placed on a dielectric substrate.

Keeping in (4) the resonant term only, allows obtaining a simple formula for the polarizability spectral dependence in general form:

\[ \alpha(\omega) = AR^3 \frac{e(\omega)/e_{\text{out}} - 1}{e(\omega)/e_{\text{out}} - e_{\text{res}}}, \] (5)

where scale coefficient \( A \) and resonant permittivity \( e_{\text{res}} \) depend on specific problem geometry and substrate permittivity \( e_{\text{sub}} \); \( R^3 \) is a dimensional factor.

In case of a hemispherical particle in a homogeneous medium (\( e_{\text{sub}} = e_{\text{out}} \)) and on a substrate with \( e_{\text{sub}}/e_{\text{out}} = 2.25 \) we, respectively, obtain:
\[
\alpha(\omega) = 0.63 R^3 \frac{\varepsilon(\omega)/\varepsilon_{\text{out}} - 1}{\varepsilon(\omega)/\varepsilon_{\text{out}} + 3.95}, 
\] (6)

\[
\alpha(\omega) = 0.52 R^3 \frac{\varepsilon(\omega)/\varepsilon_{\text{out}} - 1}{\varepsilon(\omega)/\varepsilon_{\text{out}} + 6.61}, 
\] (7)

where the resonant permittivities 3.95; 6.61 are the direct result of the eigenvalues calculations and the scale coefficients 0.63; 0.52 are defined by the integrals in Eq. 4. All these values depend on the substrate permittivity because it appears in the kernels of the integral equations. The results presented by formulae like (6, 7) are the indisputable advantage of the used approach: the analysis of the polarizability spectral dependence does not require direct numerical study - it is enough to substitute specific dielectric function \( \varepsilon(\omega) \) in Eqs. 6, 7. In Figure 3 we plot the dependences of the magnitude coefficient, \( A \), and the resonant permittivity, \( \varepsilon_{\text{res}} \), on the substrate dielectric constant. The plots in Figure 3 allow one to find the polarizability of a metal hemispherical particle with a dielectric function \( \varepsilon(\omega) \) for given permittivities of the substrate, \( \varepsilon_{\text{sub}} \), and the surrounding media, \( \varepsilon_{\text{out}} \).

Figure 3. The dependences of the magnitude coefficient, \( A \), and the resonant permittivity, \( \varepsilon_{\text{res}} \), on the substrate dielectric constant, \( \varepsilon_{\text{sub}} \).

Figure 4. The dispersion of the real (upper row) and the imaginary (lower row) parts of polarizability of silver and gold hemispheres on a glass substrate (\( \varepsilon_{\text{sub}} = 2.25 \)) in the air (\( \varepsilon_{\text{out}} = 1 \)). Solid lines correspond to the results of the surface integral equations method, dash lines – multipole expansion method [6, 7]. The polarizability is normalized to dimensional factor \( R^3 \).

4. Surface integral equation method vs multipole expansion method

To verify the approach under discussion, we calculate the polarizability dispersion, \( \alpha(\omega) \), of silver and gold hemispheres on a glass substrate with \( \varepsilon_{\text{sub}} = 2.25 \) in the air, \( \varepsilon_{\text{out}} = 1 \), and compare these with the results of multipole expansion method [6, 7], see Figure 4. The metals permittivities are taken from [17]. The calculated polarizability is normalized to dimensional factor \( R^3 \). Thus, the dependences in Figure 4 are dimensionless.

There is a slight discrepancy between the results given by these two approaches: 3-5 nm difference in the resonant wavelengths and about 20\% difference in magnitudes. However, inasmuch as both methods are approximate this discrepancy does not seem to be crucial.

The result for a hemisphere in a homogeneous medium also coincides well with the outcome of the multipole expansion method. According to [18], the SPR in a metal hemisphere in a homogeneous medium occurs if \( \varepsilon(\omega)/\varepsilon_{\text{out}} \approx -4 \). The surface integral equations method gives the value -3.95 (see Eq. 6).
5. Polarizability of prolate/oblate hemispheroids

We use the surface integral equations approach to find the polarizability spectra and the SPR wavelengths of axisymmetrical hemispheroids differing in aspect ratio (Figures 5, 6). Figure 5 illustrates the polarizability dispersion of silver and gold hemispheroids with aspect ratio $h/R=0.7$ and aspect ratio $h/R=1.5$.

![Figure 5](image)

**Figure 5.** The dispersion of the imaginary part of polarizability of silver (left) and gold (right) hemispheroids with different aspect ratios ($h/R$) on a glass substrate ($\varepsilon_{\text{sub}} = 2.25$). The polarizability is normalized to the dimensional factor $hR^2$.

As expected, the resonant polarizability for s-polarization grows with the redistribution of metal from height to lateral direction. SPR wavelength also grows tending to approach to the polarizability of a thin disk. One can see that the red shift of the SPR about 50 nm occurs after the decrease in the aspect ratio from 1.5 to 0.7, about two times.

In Figure 6 we present dependences of hemispheroids resonant wavelength on their aspect ratio. The curves are calculated for silver and gold particles and for different substrate dielectric constants.

![Figure 6](image)

**Figure 6.** The dependence of the resonant wavelength on the aspect ratio of silver (left) and gold (right) hemispheroids for different substrate permittivities.

Note that the higher substrate permittivity corresponds to the wider range in which the resonant wavelength varies. The behavior of the calculated dependences qualitatively corresponds to the trend well known from the analytical expressions obtained for spheroids in a homogeneous medium [9, 10].
6. Conclusion
We used the surface integral equations method to calculate the polarizability dispersion of a metal hemisphere placed on a dielectric substrate and compared the result with the one obtained using the multipole expansion method. The comparison evidenced reasonable coincidence of the results obtained with these techniques. The preference of the surface integral equations method is in the simple analytical expression for polarizability spectrum derived. The dependences of numerical parameters in the expression on a substrate dielectric constant were presented. The importance of this result is in avoiding numerical calculations for estimating a particle polarizability dispersion and the SPR wavelength. Used approach allowed us to analyze the influence of an axisymmetrical hemispheroid aspect ratio on the polarizability spectrum. Finally we presented the dependences of the SRP wavelength on silver and gold nanoislands aspect ratio. All the results presented are applicable to sparse MIF covered with dielectrics and can be used to estimate their SPR position and the polarizability.

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