

# SCATTERING OF ELECTROMAGNETIC WAVES ON METAL NANOPARTICLES

*Tomáš Váry, Juraj Chlpík, Peter Markoš*

*Institute of Nuclear and Physical Engineering, FEEIT SUT, Bratislava*

*E-mail: tomas.vary@stuba.sk*

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## 1. Introduction

Electromagnetic (EM) properties of small metallic nanoparticles, in particular the excitation of plasmon resonances, plays crucial role in various physical systems. In natural materials, plasmonic resonances are responsible for the colouring of glass. More important, plasmonic resonances are responsible for EM properties of metamaterials – artificial man-made composites with specific response to the incident EM waves [1]. In technology, metallic nanoparticles strongly influences EM properties of new composite materials used in bio-medicine, sensors and other applications. Qualitative and quantitative description of EM response of small metallic particles is therefore interesting both for the basic research and for various practical applications.

The most simple metallic nanoparticle is a small metallic sphere. The diameter of the sphere can vary from 2-3 to hundreds nanometers. Regular structures of nanoparticles: dimers, one dimensional chains, planar structures and multilayered systems are of particular interest. The aim of this paper is to describe, by means of numerical simulations, the EM response of some of these plasmonic structures. EM properties of abovementioned structures are determined by the excitation of localized plasmons excited by incident EM wave. In the static limit, when the diameter  $d$  of the particle is much smaller than the wavelength of incident radiation, it is possible to estimate the resonant frequency analytically from the equation [2]

$$2\varepsilon_m + \varepsilon_d = 0 \quad (1)$$

Here,  $\varepsilon_m$  is the (frequency dependent) permittivity of the metallic particle and  $\varepsilon_d$  is the permittivity of surrounding media.

The quantitative description of EM properties of nanoparticles requires the solution of following problems: (i) The static limit, given by Eq. (1) gives us only quantitative, not qualitative estimation of the plasmonic resonance, especially for particles with larger diameter. True resonant frequency must be estimated either experimentally, or by numerical simulations. (ii) For small particles, the permittivity of metal differs considerably from the permittivity of bulk material [3]. The main reason for this difference is that the size of the nanoparticle is smaller than the electron mean free path. This introduces new loss mechanism, not present in bulk material. (iii) Plasmonic resonance concentrates EM field in the small volume around the nanoparticle. For higher concentration of nanoparticles, the interaction of particles with the field excited by neighbouring particles strongly influences the EM response of entire systems.

Especially the third problem makes analytical solution of the problem difficult.

## 2. Method

For numerical analysis of the EM response of system of nanoparticles, we use the transfer matrix method, developed by MacKinnon and Pendry [4] (details of numerical algorithm are given in the Appendix of Ref. 5). We assume that the sample lies in the  $xy$  plane, and the EM wave with a given frequency propagates in the  $z$  direction. To simplify

numerical simulations, it is assumed that the structure of the sample is periodic in both  $x$  and  $y$  directions. Then, it is sufficient to reduce numerical analysis to the volume of one unit cell in the  $x$ - $y$  plane and use periodic boundary conditions in transversal directions. In the program, the unit cell is divided into  $N_x \times N_y \times N_z$  elementary units with a given permittivity, and Maxwell equations for EM waves are discretized according to the Yee algorithm [6]. This treatment influences the accuracy of numerical data: small values of  $N_x$  mean lower computing time cost but might not be able to sufficiently model structures containing curved surfaces and interfaces (spherical particles); on the other hand, increase of  $N_x$  increases size of transfer matrix which has effect on computation time cost by the factor  $(N_x N_z)^{5/2}$ .

Numerical simulation provides us with all three scattering parameter: transmission, reflection and absorption coefficients. The last is of particular interest for the identification of plasmonic resonances. Besides the structure of material, the program needs as an input the permittivity of each component of the structure. In our simulations, we consider the permittivity of surrounded media  $\epsilon_d = 1$  and the metallic permittivity is given by Drude formula

$$\epsilon_m = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \quad (2)$$

with parameters for plasmon bulk resonance  $\omega_p = 13.6 \times 10^3$  THz and absorption coefficient  $\gamma = 27.3$  THz [7].

### 3. Results

#### 3.1 Plasmonic resonance of isolated silver nanoparticle

To verify the validity of the approximation (Eq. 1) we consider the planar structure of silver nanoparticles, located in the centers of the rectangular lattice. In order to avoid mutual interaction between particles, the distance  $a$  between centers of neighbouring particles is much larger than the diameter  $d$  of particles. We use  $a = (29/7) d$ . The left Fig. 1 shows typical frequency dependence of the transmission, reflection and absorption coefficients for the single metallic sphere of diameter  $d = 96.6$  nm. The maximum of the absorption peak clearly identifies plasmon resonance. The wavelength  $\lambda = 570$  nm differs considerably from

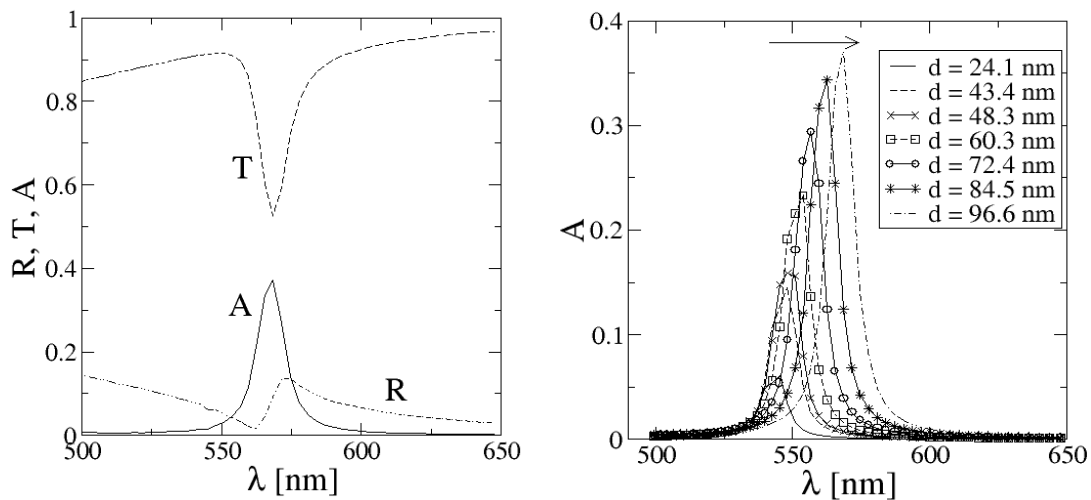


Fig. 1: Left: Transmission, reflection and absorption coefficients for single nanosphere of diameter  $d = 96.6$  nm particles. Right: Dependence of an absorption spectra of metallic particles on nanoparticle size.

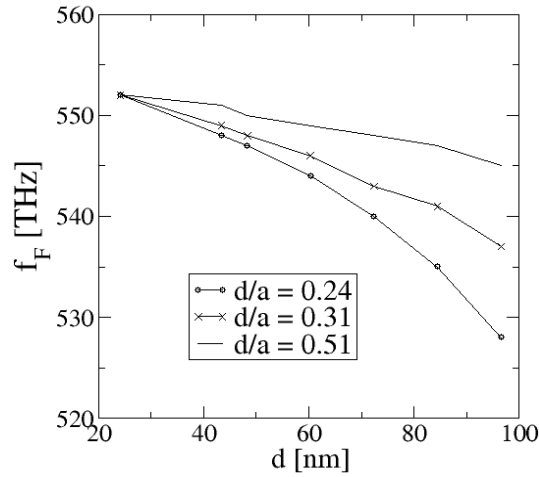


Fig. 2: Position of resonant peak as a function of particle diameter for three different distances between particles.

the static limit (Eq. 1) which is 239 nm. This indicates that the diameter of nanoparticle is too large so that the static approximation is not applicable. In the right of Fig 1. the absorption as a function of the frequency for various diameters of the nanoparticle is plotted. Small shift of the resonant frequency confirms again that the static limit is not applicable for spheres of radius  $> 20$  nm.

To estimate the shift of the plasmonic resonance quantitatively, we show in Fig. 2 the  $d$ -dependence of the resonant frequency for three different concentrations of nanoparticles. For small diameter  $d$ , the resonant frequency does not depend on the distance between neighbouring particles. When  $d$  increases the resonance frequency depends on the distance between nanoparticles. Closer the particles are to each other the lesser pronounced is the shift. This indicates that the spatial distribution of EM field around the particle is broader for larger particles and it influences oscillations of electrons in nearby particles.

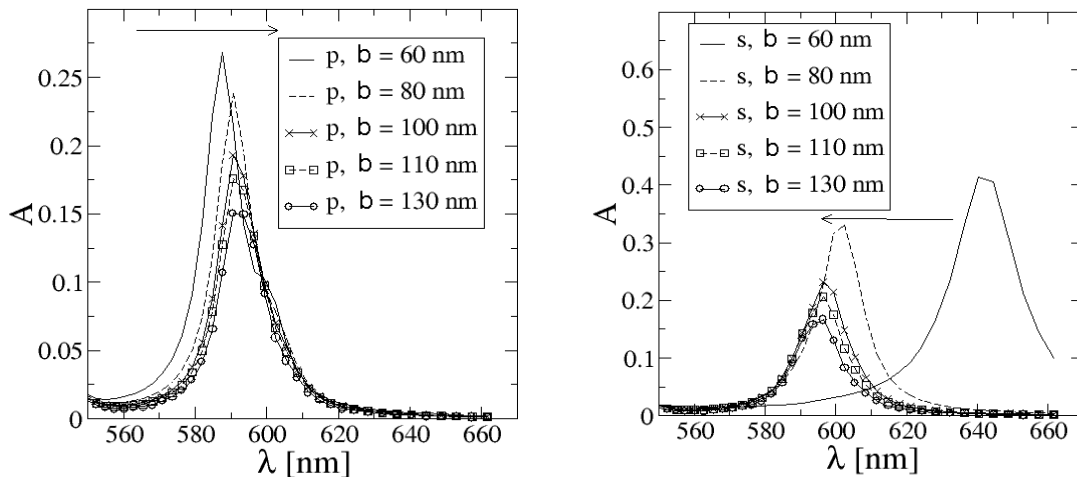


Fig. 3: Absorption spectra of linear chains of metallic nanoparticles . Left: s-polarization ( $E$  field parallel to the chain). Right: p-polarization ( $E$  perpendicular to the chain). The diameter of nanoparticles  $d = 50$  nm in rectangular cell with longer size  $a = 250$  nm and for interparticle spacing inside chain  $b = 57, 64, 78, 107, 128$ . Arrows show trend of interparticle distance increase.

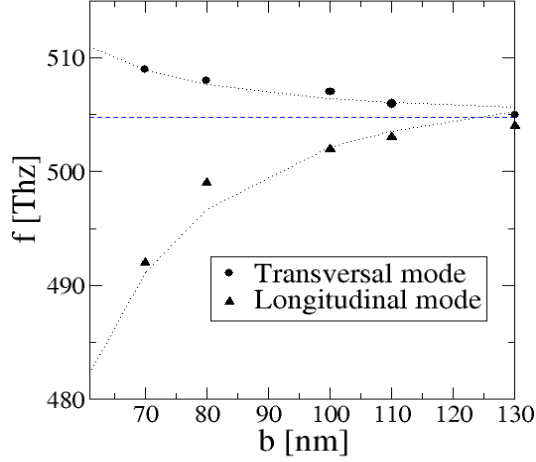


Fig. 4: Absorption maxima position dependence on interparticle distance inside nanoparticle chain. Fits show dipole character of interactions  $\sim 1/b^3$ ,  $d = 50$  nm,  $a = 300$  nm.

### 3.2. Linear chain of nanoparticles

To investigate the mutual interaction of neighbouring nanoparticles, we reduce the distance  $b$  between neighbouring particles in the  $x$  direction;  $a \gg b$  ( $b$  is the distance of particles in the  $y$  direction). Resulting structure consists of mutually non-interacting chains of nanoparticles. As expected, the EM response of resulting linear chain depends on the polarization of incident wave. Fig. 3 shows absorption for  $s$ -polarized wave (electric field parallel to the chain), and  $p$ -polarized wave (electric field perpendicular to the chain). For  $s$  polarization with particles spaced further away from each other the absorption peak is shifted towards smaller wavelengths. For  $p$  polarization we observe an opposite behaviour. This is due to dipole character of interactions between closest particles. Dipoles oscillate with higher frequency when they are directed perpendicularly to the chain axis ( $p$ -polarization). Effect is more pronounced when particles lie closer to each other. The dependence of resonant frequency on distance  $b$  is shown on Fig. 4. Calculated resonance frequency behaves as  $\sim 1/b^3$  and agree with with experiment of Maier et al. [2].

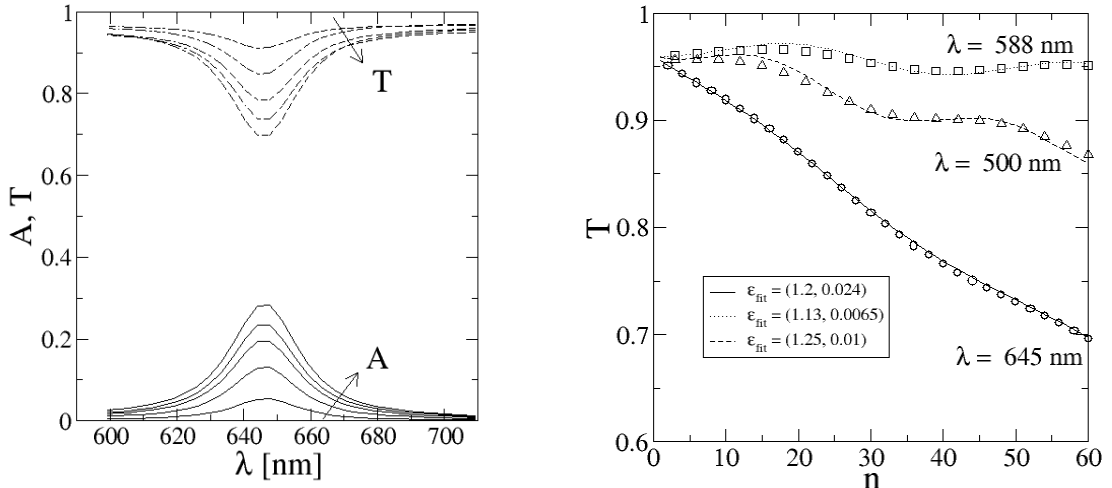


Fig 5.: Left: Transmission and absorption spectra for different lengths of nanoparticles chain. The chain is placed along  $z$  direction in which incident planewaves propagate. Right: Transmission coefficient as a function of chain length for three wavelengths of incident waves. Dashed lines represent transmission calculated from effective permittivity fit for given structure.

### 3.3 Linear chain of nanoparticles parallel to the propagation of EM wave

This structure is represented by three dimensional lattice of nanoparticles. The distance along the  $z$  direction (direction of propagation of EM wave) is much smaller (7 nm) than the lattice constant in the  $x$ - $y$  plane ( $a = 26$  nm). We considered  $d = 6$  nm silver nanoparticles. The left Fig. 5 shows that absorption increases with the length of the linear chain, but the position of the absorption peak does not depend on the length of the system. The right Fig. 5 shows how the transmission coefficient depends on the length of the chain (given in number of nanoparticles). Besides the decrease of the transmission, which is due to the absorption along the chain, the transmission coefficient exhibits Fabry-Perot oscillations, typical for the transmission of the EM wave through planar slab [8]. Therefore, we replace our structure by homogeneous slab with effective permittivity. The last can be estimated from the distance between two transmission maxima and is given in the legend of the Fig. 5. It is worth to mention, that although the structure is composed of metallic nanoparticles with negative permittivity embedded in vacuum  $\epsilon_d = 1$ , the effective relative permittivity is larger than 1.

## 4. Conclusion

We calculated numerically transmission, reflection and absorption spectra of various structures of silver nanoparticles. Our method enables us to identify the frequency of the plasmon resonance, which depends on the size of the nanoparticle as well as on mutual interaction of EM field excited in neighbouring particles. The possibility to estimate both reflection and absorption enables us to interpret numerical data and distinguish between plasmon resonance and Fabry-Perot resonances observed in multilayered structures.

The main constrain of our program is that we need to know the permittivity of the metal, which might differ considerably from the bulk permittivity. To the best of our knowledge, no data for nanoparticles permittivity are available, since the permittivity depends not only on frequency, but also on the size and shape of nanoparticles. On the other hand, numerical simulations opens the possibility to estimate the value of nanoparticle permittivity, by looking for the value for which experimental data agree with numerical ones.

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