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Plasmon resonance in ellipsoidal nanoparticles with shells

D.V. Guzatov, A.A. Oraevsky, A.N. Oraevsky

***Abstract*. The phenomenon of plasmon resonance in ellipsoidal nanoparticles with shells is considered. Based on the geometrical sizes of a nanoparticle and its components, the theory is developed which allows the calculation of absorption spectra. Using the Maxwell – Garnett theory, a collective plasmon resonance is considered, which represents a nonlinear dependence of the plasmon frequency on the concentration of nanoparticles.**

Keywords: *plasmon resonance, nanoparticles.*

1. Introduction

Continuos metal nanoparticles and dielectric nanoparticles with a metal shell (NPSs) attract attention first of all by the ability to change their absorption spectrum depending on their geometry [1, 2]. Such nanoparticles can find applications in biomedical technology as contrast agents for the optoacoustic imaging of biological tissues [3, 4] and optoacoustic tomography of tumors [5, 6].

This is explained by the fact that nanoparticles introduced to biological tissues substantially enhance the sensitivity of the methods of optical and optoacoustic tomography because absorption of light by nanoparticles in the IR spectral region at the plasmon-resonance frequency greatly exceeds absorption of light by the tissue itself. The alexandrite and yttrium – aluminium garnet lasers are used, as a rule, as radiation sources in this spectral range. The optical properties of metal nanoparticles are described, for example, in papers [7 – 10].

For practical applications in biomedical technology, nanoparticles are required that would strongly absorb light in a specified frequency range. In this respect, ellipsoidal particles are very efficient [11], which have the absorption coefficient almost an order of magnitude greater than that for spherical NPSs of the same volume.

In this paper, we study first of all ellipsoidal NPSs, whose absorption coefficient is not lower than that for continuous ellipsoidal nanoparticles, but a number of their properties are substantially different.

D.V. Guzatov, A.N. Oraevsky P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninskii prosp. 53, 119991 Moscow, Russia; e-mail: dm_guzatov@mail.ru;
A.A. Oraevsky Fairway Medical Technologies, Inc., Houston 77099, USA; e-mail: aoraevsky@fairwaymed.com

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2. Electromagnetic field of an ellipsoidal nanoparticle with a shell

An exact solution of the problem of diffraction of an electromagnetic wave from an ellipsoid is extremely cumbersome and complicated mathematically [12, 13]. The reason is that variables in the wave equation for the ellipsoid cannot be completely separated as, for example, in equations for a sphere or an infinite circular cylinder. Because of this, the diffraction problem is solved by expanding the fields of an ellipsoid in Mie spherical vectors [12, 14], which leads, however, to expressions for the field in the form of a vector series and to complicated methods for calculating the expansion coefficients [14].

The solution of the problem on the fields in a spherical shell [15] shows that, due to the presence of the second boundary surface, the number of Mie coefficients doubles and, hence, the number of required equations also doubles. Therefore, the calculation of the exact values of the fields in the ellipsoid with a shell by the method of expansion in a system of Mie vectors should involve, at the first glance, complicated equations for the Mie coefficients and complicated expressions for the fields. The solution of such a problem is substantially simplified in the case of a homogeneous external field, which is a good approximation for an ellipsoidal nanoparticle, whose size is much smaller than the wavelength of incident radiation, in the incident-wave field. In this case, the field inside the nanoparticle can be calculated without using the Mie vectors.

Consider an ellipsoidal nanoparticle made of a material with the dielectric constant ε_c, which represents an ellipsoid of revolution with the semi-axes a_1 and b_1 ($b_1 > a_1$). Let the major semi-axis of the nanoparticle be directed along the z axis, then the ellipsoid surface will be described by the equation $(x^2 + y^2)/a_1^2 + z^2/b_1^2 = 1$.

Let us cover the ellipsoidal nanoparticle with a shell made of a material with the dielectric constant ε_s. In this case, the external surface of the shell is described by the equation $(x^2 + y^2)/a_2^2 + z^2/b_2^2 = 1$ (here, $b_2 > b_1$ and $a_2 > a_1$). Then, we introduce the nanoparticle into a matrix with the dielectric constant ε_m. Hereafter, the dielectric constants of materials of the nanoparticle and matrix are assumed real, if not stated otherwise.

Because the nanoparticle under study has the rotation symmetry axis, it is convenient to study separately two types of the incident field: when the field strength vector is

directed parallel to the z axis and when it is perpendicular to the rotation axis of the particle (for example, it is directed along the x axis). A nanoellipsoid with a shell is described by the expression $(b_2 - b_1)\varepsilon_s^{1/2} + b_1\varepsilon_c^{1/2} < c/2\omega$, where ω is the incident-wave frequency and c is the speed of light in vacuum.

The problem of the field in an ellipsoidal NPS can be reduced to the solution of the Laplace equation for the field potential in spheroidal coordinates [14, 16]. The internal surface of the ellipsoid is defined by the condition $\xi_1 = 1/e_1$ and the external surface by the condition $\xi_2 = 1/e_2$ (here, ξ is one of the spheroidal coordinates of a prolate ellipsoid of revolution and $e_{1,2} = [1 - (a_{1,2}/b_{1,2})^2]^{1/2} = (1 - q_{1,2}^2)^{1/2}$ are the eccentricities of the external and internal shells of the NPS. Therefore, by solving the Laplace equation in a spheroidal coordinate system, we can find explicitly the field potentials inside the shell and expressions for the field strength.

The difficulty is, however, that the expression for the field inside the shell contains explicitly the focal distance, which is different for the internal and external shells in the non-confocal case. This focal distance is $d_1 = (b_1^2 - a_1^2)^{1/2}$ on the internal surface of the shell and $d_2 = (b_2^2 - a_2^2)^{1/2}$ on the external surface. The solution of the problem with the non-confocal shell requires the use of a special method, which is cumbersome and inconvenient [17, 18]. We will restrict our calculations to a confocal ellipsoidal shell, for which $d_1 = d_2$. In this case, most simple expressions are obtained.

We will consider the confocal shells of an ellipsoid of revolution by introducing the following convenient notation: $p_\| = b_2/b_1$, $p_\perp = a_2/a_1$, and $q = q_1$, $e = e_1$. In this case, the confocality condition has the form $p_\|^2 = e^2 + p_\perp^2 q^2$.

It is clear from physical considerations that the field amplitude excited in a nanoparticle is proportional to the incident-wave field amplitude. The field is homogeneous in the particle core and directed along the exciting field [11, 19]. The fields inside the shell and matrix are inhomogeneous.

For the incident field $\boldsymbol{E}_i^{(\|)} = E_0\boldsymbol{e}_z$, the components of the induced field in the NPS core, the shell, and in the environment, written in the spheroidal coordinate system, have the form

$$\boldsymbol{E}_c^{(\|)} = -\gamma_1^{(\|)}\left\{p_\| \frac{e^2}{q^2}\,\varepsilon_m\varepsilon_s E_0\boldsymbol{e}_z\right\},$$

$$\boldsymbol{E}_s^{(\|)} = \gamma_1^{(\|)}\left\{\frac{p_\|}{e}\,\varepsilon_m(\varepsilon_s - \varepsilon_c)E_0\left(\xi^2 - \eta^2\right)^{-1}\xi\eta\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2}\right.$$

$$\times[\boldsymbol{e}_x\cos\varphi + \boldsymbol{e}_y\sin\varphi] + \varepsilon_m E_0\boldsymbol{e}_z\left[\frac{p_\|}{e}\,(\varepsilon_s - \varepsilon_c)\left[\frac{\xi}{\xi^2-\eta^2}\right.\right.$$

$$\left.\left.-\frac{1}{2}\ln\left(\frac{\xi+1}{\xi-1}\right)\right] + p_\|\left[(\varepsilon_s - \varepsilon_c)\frac{e^2}{2q^2}\,A^{(\|)} - \varepsilon_s\frac{e^2}{q^2}\right]\right]\right\}, \quad (1)$$

$$\boldsymbol{E}_m^{(\|)} = \gamma_2^{(\|)}\left\{\frac{p_\|}{e}\left[\frac{e^2}{2q^2}\,B^{(\|)}\right]^{-1}E_0\left(\xi^2-\eta^2\right)^{-1}\xi\eta\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2}\right.$$

$$\times[\boldsymbol{e}_x\cos\varphi + \boldsymbol{e}_y\sin\varphi] + \frac{p_\|}{e}\left[\frac{e^2}{2q^2}\,B^{(\|)}\right]^{-1}E_0\boldsymbol{e}_z\times$$

$$\left.\times\left[\frac{\xi}{\xi^2-\eta^2} - \frac{1}{2}\ln\left(\frac{\xi+1}{\xi-1}\right)\right]\right\},$$

where η is the variable in the spheroidal coordinate system. In these expressions, the functions

$$A^{(\|)} = -\frac{2q^2}{e^2}\left[1 - \frac{1}{2e}\ln\left(\frac{1+e}{1-e}\right)\right],$$

$$B^{(\|)} = -\frac{2q^2}{e^2}\left[1 - \frac{p_\|}{2e}\ln\left(\frac{p_\|+e}{p_\|-e}\right)\right] \quad (2)$$

and the coefficients

$$\gamma_1^{(\|)} = \frac{e^2}{p_\perp^2 q^2}\left\{(\varepsilon_s - \varepsilon_c)\left[\varepsilon_m\frac{e^2}{p_\perp^2 q^2} + \frac{e^2}{2q^2}B^{(\|)}(\varepsilon_s - \varepsilon_m)\right]\right.$$

$$\times\frac{e^2}{2q^2}\left(p_\| A^{(\|)} - B^{(\|)}\right) - \varepsilon_s\frac{e^2}{2q^2}B^{(\|)}\left[(\varepsilon_s - \varepsilon_m)p_\|\frac{e^2}{q^2}\right.$$

$$\left.\left.-(\varepsilon_s - \varepsilon_c)\frac{e^2}{p_\perp^2 q^2}\right] - \varepsilon_m\varepsilon_s\frac{e^2}{p_\perp^2 q^2}\,p_\|\frac{e^2}{q^2}\right\}^{-1},$$

$$\gamma_2^{(\|)} = 1 - \varepsilon_m\gamma_1^{(\|)}\left[(\varepsilon_s - \varepsilon_c)\frac{e^2}{2q^2}\left(p_\| A^{(\|)} - B^{(\|)}\right) - \varepsilon_s p_\|\frac{e^2}{q^2}\right] \quad (3)$$

are used.

When the incident field has the form $\boldsymbol{E}_i^{(\perp)} = E_0\boldsymbol{e}_x$, the components of the induced field are

$$\boldsymbol{E}_c^{(\perp)} = \gamma_1^{(\perp)}\left\{p_\perp\frac{2e^2}{q}\,\varepsilon_m\varepsilon_s E_0\boldsymbol{e}_x\right\},$$

$$\boldsymbol{E}_s^{(\perp)} = \gamma_1^{(\perp)}\left\{-\frac{p_\perp q}{e}\,\varepsilon_m E_0\boldsymbol{e}_x\left[\frac{e}{q}\,(\varepsilon_s - \varepsilon_c)\frac{e^2}{q}A^{(\perp)} - \varepsilon_s\frac{2e^2}{q^2}\right]\right.$$

$$+\frac{p_\perp q}{e}\,\varepsilon_m(\varepsilon_s - \varepsilon_c)E_0 R(\xi)\,\frac{\sin\varphi}{(\xi^2-1)^{1/2}}(\boldsymbol{e}_x\sin\varphi - \boldsymbol{e}_y\cos\varphi)$$

$$+\frac{p_\perp q}{e}\,\varepsilon_m(\varepsilon_s - \varepsilon_c)E_0\,\frac{\cos\varphi}{\xi^2-\eta^2}\left\{\left[\xi\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2}\right.\right.$$

$$\left.\left.+\eta\left(\frac{\xi^2-1}{1-\eta^2}\right)^{1/2}\right]R(\xi)\left(1-\eta^2\right)^{1/2} + 2\left(\frac{1-\eta^2}{\xi^2-1}\right)\right\}$$

$$\times(\boldsymbol{e}_x\cos\varphi + \boldsymbol{e}_y\sin\varphi) + 2\,\frac{p_\perp q}{e}\,\varepsilon_m(\varepsilon_s - \varepsilon_c)E_0\boldsymbol{e}_z$$

$$\left.\times\,\frac{\cos\varphi}{\xi^2-\eta^2}\,\eta\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2}\right\}, \quad (4)$$

$$\boldsymbol{E}_m^{(\perp)} = \gamma_2^{(\perp)}\left\{-\frac{p_\perp q}{e}\left[\frac{e^2}{q}\,B^{(\perp)}\right]^{-1}E_0 R(\xi)\,\frac{\sin\varphi}{(\xi^2-1)^{1/2}}\right.$$

$$\times(\boldsymbol{e}_x\sin\varphi - \boldsymbol{e}_y\cos\varphi) - \frac{p_\perp q}{e}\left(\frac{e^2}{q}\,B^{(\perp)}\right)^{-1}E_0\,\frac{\cos\varphi}{\xi^2-\eta^2}$$

$$\times\left\{\left[\xi\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2} + \eta\left(\frac{\xi^2-1}{1-\eta^2}\right)^{1/2}\right]R(\xi)\left(1-\eta^2\right)^{1/2} +\right.$$

$$+2\left(\frac{1-\eta^2}{\xi^2-1}\right)\Big\}(\boldsymbol{e}_x\cos\varphi+\boldsymbol{e}_y\sin\varphi)-2\,\frac{p_\perp q}{e}\left(\frac{e^2}{q}B^{(\perp)}\right)^{-1}$$

$$\times E_0\boldsymbol{e}_z\,\frac{\cos\varphi}{\xi^2-\eta^2}\,\eta\left(\frac{1-\eta^2}{\xi^2-1}\right)^{1/2}\Big\}.$$

Here,

$$A^{(\perp)}=\frac{1}{e^2}\left[1-\frac{q^2}{2e}\ln\left(\frac{1+e}{1-e}\right)\right];$$

$$B^{(\perp)}=\frac{1}{e^2}\left[\frac{p_\parallel}{p_\perp}-\frac{p_\perp q^2}{2e}\ln\left(\frac{p_\parallel+e}{p_\parallel-e}\right)\right]; \tag{5}$$

$$R(\xi)=\frac{(\xi^2-1)^{1/2}}{2}\ln\left[\frac{\xi-1}{\xi+1}\right]+\frac{\xi}{(\xi^2-1)^{1/2}}; \tag{6}$$

$$\gamma_1^{(\perp)}=\frac{2e^2}{p_\perp^2p_\parallel q^2}\Big\{(\varepsilon_s-\varepsilon_c)\Big[\varepsilon_m\,\frac{2e^3}{p_\perp^2p_\parallel q^2}+\frac{e}{p_\perp q}(\varepsilon_s-\varepsilon_m)$$

$$\times\frac{e^2}{q}B^{(\perp)}\Big]\frac{e^2}{q}\left(B^{(\perp)}-p_\perp A^{(\perp)}\right)+\varepsilon_s\frac{e^2}{q}\,B^{(\perp)}$$

$$\times\left[(\varepsilon_s-\varepsilon_m)\frac{2e^3}{q^2}-(\varepsilon_s-\varepsilon_c)\,\frac{2e^3}{p_\perp^2p_\parallel q^2}\right]$$

$$+\varepsilon_m\varepsilon_s\,\frac{2e^2}{q}\,p_\perp\,\frac{2e^3}{p_\perp^2p_\parallel q^2}\Big\}^{-1}; \tag{7}$$

$$\gamma_2^{(\perp)}=1-\varepsilon_m\gamma_1^{(\perp)}\left[(\varepsilon_s-\varepsilon_c)\frac{e^2}{q}\left(B^{(\perp)}-p_\perp A^{(\perp)}\right)+\varepsilon_s p_\perp\frac{2e^2}{q}\right].$$

The indices $\parallel$ and $\perp$ denote that the rotation axis of an ellipsoidal particle is parallel or perpendicular to the incident-wave field strength vector.

Despite a relative simplicity of the problem formulated, expressions (1) and (4) are rather cumbersome. Nevertheless, they can be easily analysed. For example, assuming that $\varepsilon_s=\varepsilon_m$ or $p_\parallel=1=p_\perp$, we obtain expressions for the field induced in a matrix by a continuous ellipsoidal nanoparticle made of a material with the dielectric constant ε_c [19]. Expressions (1) or (4) can be transformed to similar formulas for a spherical shell by setting $p_\perp=p_\parallel=p$ and $q\to1$.

3. Absorption by an ellipsoidal NPS

The absorption cross section for an ellipsoidal NPS having a dielectric core with the dielectric constant ε_c and a metal shell with the complex dielectric constant ε_s has the form [20]

$$\sigma_{abs}^{(\parallel,\perp)}=\frac{3}{4\pi}\,V_{es}\,\frac{e^3}{p_\perp^2p_\parallel q^2}\,E_0^{-2}\mathrm{Im}\,\varepsilon_s\,\frac{\omega}{c}\int_{1/e}^{p_\parallel/e}\mathrm{d}\xi$$

$$\times\int_{-1}^{1}\mathrm{d}\eta\left(\xi^2-\eta^2\right)\int_0^{2\pi}\mathrm{d}\varphi\left|\boldsymbol{E}_s^{(\parallel,\perp)}\right|^2, \tag{8}$$

where V_{es} is the total volume of a nanoellipsoid with a shell. The field inside the metal shell is described by expression (1) for the parallel orientation of a nanoparticle or by expression (4) for its perpendicular orientation. Expression (8) is written for an ellipsoidal nanoparticle in a matrix with the dielectric constant ε_m. The absorption cross section (8) has the resonance shape. The approximate conditions allowing one to determine the position of the absorption peak for an ellipsoidal particle having the parallel or perpendicular orientation can be obtained by setting the real part of denominators $\gamma^{(\parallel)}$ or $\gamma^{(\perp)}$ equal to zero.

For a nanoparticle with the parallel orientation, this condition has the form

$$(\mathrm{Re}\,\varepsilon_s-\varepsilon_c)\left[2\varepsilon_m+(\mathrm{Re}\,\varepsilon_s-\varepsilon_m)p_\perp^2B^{(\parallel)}\right]\left(p_\parallel A^{(\parallel)}-B^{(\parallel)}\right)$$

$$-4\mathrm{Re}\,\varepsilon_s\varepsilon_m p_\parallel+2\mathrm{Re}\,\varepsilon_s\left[\varepsilon_m p_\parallel p_\perp^2-\varepsilon_c-\mathrm{Re}\,\varepsilon_s\left(p_\parallel p_\perp^2-1\right)\right]B^{(\parallel)}$$

$$=[\mathrm{Im}\,\varepsilon_s]^2\left[p_\perp^2\left(p_\parallel A^{(\parallel)}-B^{(\parallel)}\right)-2\left(p_\parallel p_\perp^2-1\right)\right]B^{(\parallel)}. \tag{9}$$

For a nanoparticle with the perpendicular orientation, this condition takes the form

$$(\mathrm{Re}\,\varepsilon_s-\varepsilon_c)\left[2\varepsilon_m+(\mathrm{Re}\,\varepsilon_s-\varepsilon_m)p_\perp p_\parallel B^{(\perp)}\right]\left(B^{(\perp)}-p_\perp A^{(\perp)}\right)$$

$$+4\mathrm{Re}\,\varepsilon_s\varepsilon_m p_\perp+2\mathrm{Re}\,\varepsilon_s\left[\mathrm{Re}\,\varepsilon_s\left(p_\perp^2p_\parallel-1\right)-\varepsilon_m p_\perp^2p_\parallel+\varepsilon_c\right]B^{(\perp)}$$

$$=[\mathrm{Im}\,\varepsilon_s]^2\left[p_\perp p_\parallel\left(B^{(\perp)}-p_\perp A^{(\perp)}\right)+2\left(p_\perp^2p_\parallel-1\right)\right]B^{(\perp)}. \tag{10}$$

The exact position of the resonance can be obtained by setting the derivative of (8) with respect to the wavelength equal to zero. Our calculations show that the difference between the position of the resonance determined from expressions (9) and (10) from its exact value does exceed a few percent.

Assuming in (9) that $p_\parallel=p_\perp=p$, $A^{(\parallel)}=2/3$, and $B^{(\parallel)}=2/(3p^2)$, we obtain the condition of the plasmon resonance for a spherical NPS, for which p is the ratio of the radii of the external and internal surfaces of the shell.

According to expression (8), the absorption cross section divided by the NPS volume depends only on the axial ratio q, the incident-wave frequency, and the parameter $p_\parallel$. Therefore, by specifying q, we can choose the values of $p_\parallel$ corresponding to the position of the absorption maximum at the specified frequency.

Figs 1 and 2 show the absorption cross sections for a NPS with a quartz core ($\varepsilon_c=2.347$) and a gold shell as functions of the wavelength. The particle has the specified values of q and shell thickness, which give the position of the absorption maximum at 755 nm. The absorption data for gold used in all calculations were taken from Ref. [21].

One can see from Figs 1 and 2 that, for the specified volume of the NPS, both in parallel and perpendicular orientations, the absorption cross section increases with decreasing parameter q.

A decrease in q also results in the shift of the resonance wavelength. Therefore, to maintain the resonance tuning to the specified wavelength, it is necessary to decrease $p_\parallel$ in the case of parallel orientation of the NPS or to increase $p_\perp$ in the case of its perpendicular orientation.

The presence of a metal shell around a dielectric ellipsoidal nanoparticle leads to the enhancement of absorption of light by the particle almost by an order of magnitude compared to a continuous metal nanoparticle only in the case of perpendicular orientation. A comparison of the absorption spectra of these nanoparticles in the case of parallel orientation shows that absorption of light by a

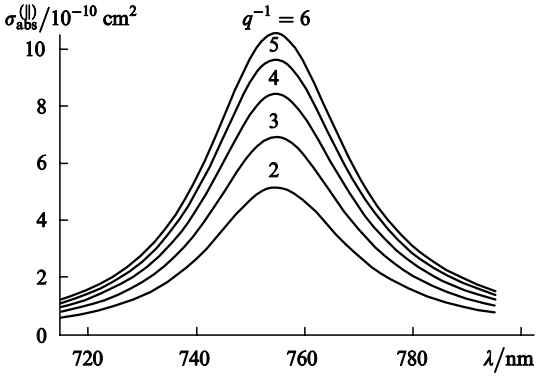

Figure 1. Dependences of $\sigma_{abs}^{(\|)}$ on λ for an ellipsoidal NPS of volume $V_{nps} = 5 \times 10^4$ nm^3 oriented parallel to the incident field for different q^{-1}. The value of $p_\|$ corresponds to the absorption maximum located at 755 nm.

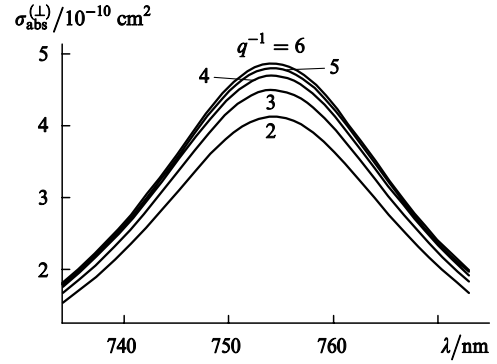

Figure 2. Dependences of $\sigma_{abs}^{(\perp)}$ on λ for an ellipsoidal NPS of volume $V_{nps} = 5 \times 10^4$ nm^3 oriented perpendicular to the incident field for different q^{-1}. The value of $p_\perp$ corresponds to the absorption maximum located at 755 nm.

continuos particle, for example, at 755 nm is greater by a factor of ~ 1.5.

Consider now absorption by a metal ellipsoid of revolution surrounded by a dielectric shell. Such a structure can be formed, for example, when a metal nanoparticle penetrates into a biological tissue of a microorganism. We will study the properties of absorption of light by such a nanoparticle by the example of a gold ellipsoid surrounded by a dielectric shell with the dielectric constant $\varepsilon_s \approx 4$ and placed in water. We assume that the nanoellipsoid has a parallel orientation because in this case the properties of a nanoparticle are manifested most distinctly [11].

We will write the absorption cross section of a nanoparticle with the parallel orientation (the complex dielectric constant of the core is ε_c and the dielectric constant of the shell is ε_s) in a matrix with the dielectric constant ε_m in the form

$$\sigma_{abs} = V_{me} p_\|^2 \frac{e^4}{q^4} \varepsilon_m^2 \varepsilon_s^2 \mathrm{Im}\, \varepsilon_c \frac{\omega}{c} \left| \gamma_1^{(\|)} \right|^2, \qquad (11)$$

where V_{me} is the volume of the metal nanoellipsoid. This formula is obtained by integrating expression (1) for the modulus of the field $\boldsymbol{E}_c^{(\|)}$ over the volume V_{me}. The expression for the absorption cross section in the case of perpendicular orientation can be obtained by integrating the modulus of $\boldsymbol{E}_c^{(\perp)}$ (4) over the volume V_{me}.

Our calculation shows that the absorption cross section (11) has a resonance shape as function of the wavelength, similarly to the shapes presented in Figs 1 and 2. The resonance wavelength corresponding to the maximum of the absorption cross section depends on the dielectric shell thickness (Fig. 3). As the shell thickness increases (for the given volume of the nanoellipsoid and the given axial ratio q), the resonance wavelength λ_{res} also increases, tending to the limiting value corresponding to the case when the ellipsoid is placed in an infinitely extended medium. Such a dependence of the resonance wavelength on the shell thickness was recently observed experimentally [22]. Note also that λ_{res} also increases with decreasing q.

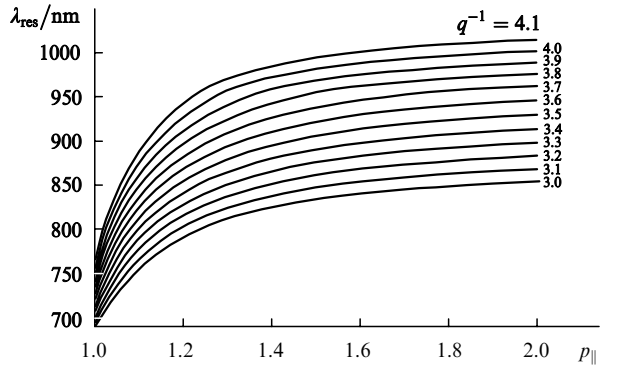

Figure 3. Dependences of λ_{res} on $p_\|$ for a gold nanoellipsoid of volume $V_{nps} = 5 \times 10^4$ nm^3 with a protein shell in water oriented parallel to the incident field for different q^{-1}.

The dependence of the resonance maximum of the absorption cross section (11) on the shell thickness is shown in Fig. 4. One can see that, for the specified axial ratio q, there exists the optimal thickness of the shell providing the maximum of the absorption cross section. However, in the region of large values of $p_\|$, a nonmonotonic variation in the absorption cross section can be expected for the given wavelength. This is explained by the appearance of resonances when the shell size becomes comparable with the wavelength in the dielectric. This effect is not reflected in our

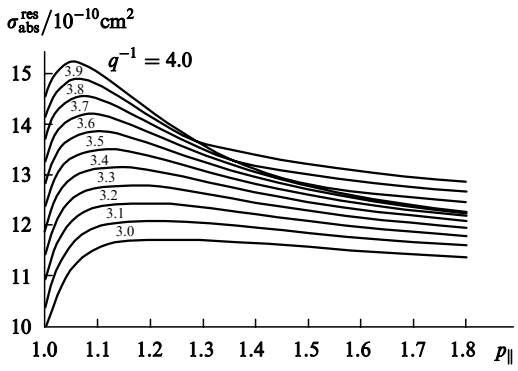

Figure 4. Dependences of σ_{abs}^{res} on $p_\|$ for a gold nanoellipsoid with a protein shell in water oriented parallel to the incident field for different q^{-1}.

calculations because it cannot be explained within the framework of the quasi-static approximation used here. To analyse this effect, it is necessary to solve exactly the problem of scattering from a metal ellipsoid with a dielectric shell.

4. Collective absorption by ellipsoidal NPSs

Consider a heterogeneous medium representing a matrix with the dielectric constant ε_m doped with ellipsoidal NPSs. We assume that all nanoparticles have cores made of the same material with the dielectric constant ε_c and shells with the dielectric constant ε_s. The values of parameters q and $p_\parallel$ (or $p_\perp$) are assumed the same for all NPSs.

The optical properties of heterogeneous media are studied using the Maxwell–Garnett formula [22, 23]. This formula gives the dependence of the dielectric constant ε_{eff} of a heterogeneous medium on the concentration of nanoparticles χ assuming that the polarisability of an individual nanoparticle is known. In the case of ellipsoidal NPSs, the dipole moments of a nanoparticle are different for different orientations of the nanoparticle with respect to the incident wave. Therefore, the dielectric constant ε_{eff} of a heterogeneous medium will be a tensor. Consider the cases of two different orientations of all the nanoparticles – parallel and perpendicular to the incident field. In these particular cases, the Maxwell–Garnett formula for diagonal elements $\varepsilon_{eff}^{(\parallel)}$ and $\varepsilon_{eff}^{(\perp)}$ has the form

$$\varepsilon_{eff}^{(\parallel,\perp)} - \varepsilon_m = \chi\gamma_{np}^{(\parallel,\perp)}\left[\varepsilon_{eff}^{(\parallel,\perp)} + 2\varepsilon_m\right]. \tag{12}$$

Here,

$$\gamma_{np}^{(\parallel)} = \frac{1}{3}\gamma_1^{(\parallel)}\left\{(\varepsilon_s - \varepsilon_c)\left[(\varepsilon_s - \varepsilon_m)\frac{e^2}{2q^2} \times\left(p_\parallel A^{(\parallel)} - B^{(\parallel)}\right) + \varepsilon_s\frac{e^2}{p_\perp^2 q^2}\right] - \varepsilon_s(\varepsilon_s - \varepsilon_m)p_\parallel\frac{e^2}{q^2}\right\} \tag{13}$$

for NPSs oriented parallel the incident field, and

$$\gamma_{np}^{(\perp)} = \frac{1}{3}\gamma_1^{(\perp)}p_\perp q\left\{(\varepsilon_s - \varepsilon_c)\left[(\varepsilon_s - \varepsilon_m)\frac{e^2}{p_\perp q^2} \times\left(B^{(\perp)} - p_\perp A^{(\perp)}\right) - \varepsilon_s\frac{2e^2}{p_\parallel p_\perp^2 q^2}\right] + \varepsilon_s(\varepsilon_s - \varepsilon_m)\frac{2e^2}{q^2}\right\} \tag{14}$$

for nanoparticles oriented perpendicular to the incident field.

Heterogeneous media consisting of metal nanoparticles suspended in an active laser medium can have the giant nonlinearity and gain when the concentration of nanoparticles is close to the critical one [24]. Such media can be also useful in studies of some exotic phenomena in electrodynamics [25]. One can hope that a heterogeneous medium containing ellipsoidal NPSs also will have similar properties, which can be obtained by selecting materials for the matrix and nanoparticles in a proper way. The search for such materials and analysis of the optical properties of prepared heterogeneous media requires a special investigation. Below, we consider absorption and reflection of light by heterogeneous media containing NPSs.

Conditions for the resonance absorption of light by a suspension of ellipsoidal NPSs, as a specific plasmon resonance of a large group of nanoparticles, can be obtained by setting the real part of the dominator in the expression for ε_{eff} equal to zero. These conditions can be written in the form

$$\begin{aligned}&(\mathrm{Re}\,\varepsilon_s - \varepsilon_c)\left\{2\varepsilon_m + (\mathrm{Re}\,\varepsilon_s - \varepsilon_m)\left[p_\perp^2 B^{(\parallel)} - \frac{2}{3}\chi\right]\right\}\\ &\times\left(p_\parallel A^{(\parallel)} - B^{(\parallel)}\right) - 4\mathrm{Re}\,\varepsilon_s\varepsilon_m p_\parallel + 2\mathrm{Re}\,\varepsilon_s\left[\varepsilon_m p_\parallel p_\perp^2 - \varepsilon_c\right.\\ &\left. - \mathrm{Re}\,\varepsilon_s\left(p_\parallel p_\perp^2 - 1\right)\right]\left(B^{(\parallel)} - \frac{2}{3p_\perp^2}\chi\right) =\\ &= [\mathrm{Im}\,\varepsilon_s]^2\left[p_\perp^2\left(p_\parallel A^{(\parallel)} - B^{(\parallel)}\right) - 2\left(p_\parallel p_\perp^2 - 1\right)\right]\\ &\times\left(B^{(\parallel)} - \frac{2}{3p_\perp^2}\chi\right)\end{aligned} \tag{15}$$

for NPSs oriented parallel to the incident field and

$$\begin{aligned}&(\mathrm{Re}\,\varepsilon_s - \varepsilon_c)\left\{2\varepsilon_m + (\mathrm{Re}\,\varepsilon_s - \varepsilon_m)\left[p_\perp p_\parallel B^{(\perp)} - \frac{2}{3}\chi\right]\right\}\\ &\times\left(B^{(\perp)} - p_\perp A^{(\perp)}\right) + 4\mathrm{Re}\,\varepsilon_s\varepsilon_m p_\perp + 2\mathrm{Re}\,\varepsilon_s\left[\mathrm{Re}\,\varepsilon_s\left(p_\perp^2 p_\parallel - 1\right)\right.\\ &\left. - \varepsilon_m p_\perp^2 p_\parallel + \varepsilon_c\right]\left(B^{(\perp)} - \frac{2}{3p_\perp p_\parallel}\chi\right) = [\mathrm{Im}\,\varepsilon_s]^2\left[p_\perp p_\parallel\right.\\ &\left.\times\left(B^{(\perp)} - p_\perp A^{(\perp)}\right) + 2\left(p_\perp^2 p_\parallel - 1\right)\right]\left(B^{(\perp)} - \frac{2}{3p_\perp p_\parallel}\chi\right)\end{aligned} \tag{16}$$

for NPSs oriented perpendicular to the incident field.

Assuming that the concentration $\chi = 0$ in (15) and (16), we obtain expressions (9) and (10) for a plasmon resonance for an individual ellipsoidal NPS. By setting $p_\parallel = p_\perp = p$, $A^{(\parallel)} = 2/3$, and $B^{(\parallel)} = 2/(3p^2)$ in (15), we obtain the condition for collective absorption of light by spherical NPSs.

Figs 5 and 6 show the dependences of the reflection coefficient of a semi-infinite heterogeneous aqueous medium containing NPSs on the wavelength of light incident from vacuum perpendicular to the interface. Nanoparticles have a quartz core and a gold shell and are oriented parallel or perpendicular to the incident field. Although the parameters of an individual NPS are selected so that the absorption maximum is located at 755 nm, the reflection and absorption maxima are shifted to the red with increasing NPS

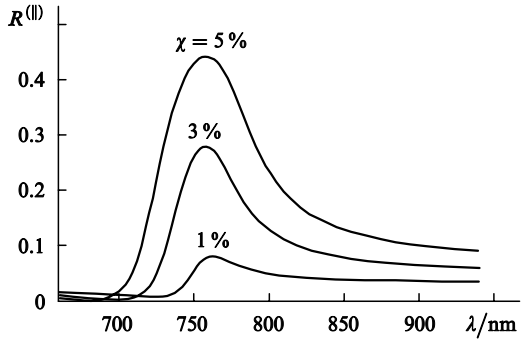

Figure 5. Dependences of the reflection coefficient $R^{(\parallel)}$ on λ for the parallel orientation, $q = 1/3$, and different χ. The value of $p_\parallel$ corresponds to the absorption maximum located at 755 nm.

Table 1.

q	$p_\parallel$				$p_\perp$			
	$\chi = 0$	$\chi = 1\,\%$	$\chi = 3\,\%$	$\chi = 5\,\%$	$\chi = 0$	$\chi = 1\,\%$	$\chi = 3\,\%$	$\chi = 5\,\%$
1/2	1.073	1.076	1.074	1.074	1.198	1.212	1.207	1.205
1/3	1.054	1.056	1.055	1.055	1.211	1.226	1.221	1.22
1/4	1.046	1.048	1.047	1.047	1.214	1.229	1.225	1.223
1/5	1.042	1.043	1.042	1.042	1.215	1.23	1.226	1.224
1/6	1.04	1.04	1.04	1.04	1.215	1.23	1.226	1.224

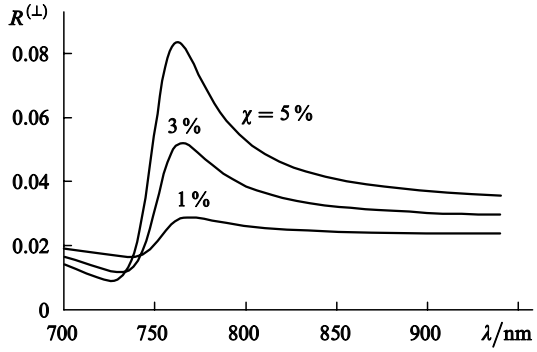

Figure 6. Dependences of the reflection coefficient $R^{(\perp)}$ on λ for the perpendicular orientation, $q = 1/3$, and different χ. The value of $p_\perp$ corresponds to the absorption maximum located at 755 nm.

concentration. This is typical for collective absorption [26]. Reflection from a heterogeneous medium, in which all ellipsoidal NPSs are oriented parallel to the incident field, is greater than in the case of perpendicular orientation of nanoparticles.

Table 1 shows the values of parameters $p_\parallel$, $p_\perp$, and q corresponding to collective absorption at a wavelength of 755 nm.

One can see from Table 1 that the value of $p_\parallel$ for NPSs oriented parallel to the incident field is almost independent of the concentration of nanoparticles in the matrix. The value of $p_\parallel$ decreases only with decreasing q. In the case of perpendicular orientation of NPSs, the value of $p_\perp$ decreases with increasing concentration, while $p_\perp$ increases with decreasing the axial ratio q.

5. Conclusions

Our study has shown that the thickness of a metal shell surrounding a dielectric ellipsoidal nanoparticle can be selected so that it will correspond to the absorption maximum of a NPS at a given wavelength for the specified axial ratio of the NPS core. In this case, absorption of light by an ellipsoidal NPS oriented parallel to the incident-radiation polarisation can be an order of magnitude greater than for the perpendicular orientation.

A dielectric shell surrounding a metal nanoellipsoid allows one to shift the absorption maximum to the red. This effect can be used in optoacoustic tomography of biological tissues.

It is important for the study of biological tissues that the spectrum of emission scattered by a nanoparticle with a metal shell coincides with in its shape with the absorption spectrum. Both these spectra have maxima at the plasmon resonance frequency. Our study has shown that the main contribution is made by NPSs oriented parallel to the incident field because in the case of perpendicular orientation, the absorption of light is almost an order of magnitude lower. In the case of parallel orientation, the reflection maximum experiences a greater shift depending on the NPS concentration.

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