Kinetic theory of absorption of ultrashort laser pulses by ensembles of metal nanoparticles under conditions of surface plasmon resonance

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Introduction. Metal nanoparticles are interesting objects both because of the review of the physics of the condensed state, and from a practical point of view. The collection of local electric fields near nanoparticles, due to surface plasma resonance, makes them useful for use, in particular, in solar energy, biology, medicine. Metal nanoparticles use a basic new development of electronics - nanoplasmonics [1]. With the beginning of the XXI century. Intensive research has begun on the creation of elements basic for integrated circuits on plasmons that use plasmons in energy and the creation of spazers (SPASER - surface amplification of plasmon due to stimulated radiation) - analogs of a laser that uses plasmons instead of photons [2].

Model and problem statement. Consider the case when an ensemble of metal nanoparticles is irradiated with a laser pulse, the electric field of which is given by the following expression:

$$\vec{E}(\vec{r},t)=\vec{E}_0\left[-\Gamma_0^2\left(t-\frac{\bar{k}_o\vec{r}}{\omega_0}\right)^2\right]\cos\left[\omega_0\left(t-\frac{\bar{k}_o\vec{r}}{\omega_0}\right)\right], \quad (1)$$

Where ω_0 - is the carrier frequency of the electromagnetic wave of the laser pulse $|\vec{k}_0|=\omega_0/c$, and Γ_0 - is the value inverse of the duration of the laser pulse, $\vec{E}_0$ is the maximum value of the electric field strength in the laser pulse.

The electric field of the laser pulse induces a potential electric field $\vec{E}_{in}(\vec{r},t)$ inside the metal nanoparticle, and the magnetic field induces a vortex electric field $\vec{E}_{vr}(\vec{r},t)$. If the characteristic size of the nanoparticle R is such that the inequality holds $k_0R<<1$, then in this case the Fourier coordinate dependence of the components of the electric and magnetic fields of the laser wave can be neglected (2).

Internal fields $\vec{E}_{in}(\vec{r},t)$ and $\vec{E}_{vr}(\vec{r},t)$ induce in the nanoparticle the corresponding currents $\vec{j}_{in}(\vec{r},t)$ and $\vec{j}_{vr}(\vec{r},t)$. Therefore, the total energy absorbed by the metal nanoparticle will be equal to [3]

$$W=\int_{-\infty}^{\infty}w(t)dt=W_e+W_m=\frac{1}{2}\mathrm{Re}\int_{-\infty}^{\infty}dt\int_V d\vec{r}\left[\vec{j}_e(\vec{r},t)\vec{E}_{in}^{*}(\vec{r},t)+\vec{j}_{vr}(\vec{r},t)\vec{E}_{vr}^{*}(\vec{r},t)\right] \quad (2)$$

Turning to the Fourier representation, relation (2) can be rewritten as follows:

$$W=\frac{1}{4\pi}\int_{-\infty}^{\infty}d\omega\,\mathrm{Re}\int_V d\vec{r}\left[\vec{j}_e(\vec{r},\omega)\vec{E}_{in}^{*}(\vec{r},\omega)+\vec{j}_{vr}(\vec{r},\omega)\vec{E}_{vr}^{*}(\vec{r},\omega)\right]. \quad (3)$$

In the general case, the current $\vec{j}(\vec{r},\omega)$ at a point $\vec{r}$ inside the nanoparticle caused by internal fields $\vec{E}_{in}(\vec{r},t)$ and $\vec{E}_{vr}(\vec{r},t)$ can be written as follows [4]:

$$\vec{j}(\vec{r},\omega)=2e\left(\frac{m}{2\pi\hbar}\right)^3\int_{-\infty}^{\infty}\vec{v}f_1(\vec{r},\vec{v},\omega)d\vec{v}, \quad (4)$$

where e - is the charge of the electron, m - is the mass of the electron, $f_1(\vec{r},\vec{v},\omega)$- is the Fourier component of the nonequilibrium electron distribution function in the nanoparticle, which serves as an additive to the equilibrium Fermi distribution function $f_0(\varepsilon)$.

An nonequilibrium $f_1(\vec{r},\vec{v},\omega)$ additive can be found as a solution of the corresponding linearized Boltzmann kinetic equation for nanoparticle electrons. Given that

$$f_1(\vec{r},\vec{v},\omega)=\int_{-\infty}^{\infty}f_1(\vec{r},\vec{v},t)\exp(i\omega t)dt, \quad (5)$$

then as a result to find $f_1(\vec{r},\vec{v},\omega)$ we get the following equation:

$$(\gamma-i\omega)\,f_1(\vec{r},\vec{v},\omega)+\vec{v}\frac{\partial f_1(\vec{r},\vec{v},\omega)}{\partial\vec{r}}+e\vec{v}\left[\vec{E}_{in}(\omega)+\vec{E}_{vr}(\vec{r},\omega)\right]\frac{\partial f_0(\varepsilon)}{\partial\varepsilon}=0. \quad (6)$$

Here, γ - the volume frequency of electron collisions with the scatterer, $f_0(\varepsilon)$ - is the equilibrium Fermi function of electron distribution in the nanoparticle.

In this paper, we consider the absorption of ultrashort laser pulses in the region of plasmon resonance. Thus, we will take into account the collective (plasmon) absorption mechanism. In this case, the solution of equation (5) can be found as follows:

$$f_1(\vec{r},v',\omega)=-e\vec{v}'\vec{E}_{in}\frac{1-\exp\left[-(v-i\omega)t'(\vec{r}',v')\right]}{\gamma-i\omega}\frac{\partial f_0}{\partial\varepsilon}. \quad (7);\quad f_1(\vec{r},v',\omega)=-e\vec{v}'\vec{E}_{in}\frac{1-\exp\left[-(v-i\omega)t'(\vec{r}',v')\right]}{\gamma-i\omega}\frac{\partial f_0}{\partial\varepsilon}. \quad (8)$$

For the total energy absorbed by the metal particle under plasmon resonance conditions, we obtained the following expression:

$$W\approx\frac{V}{64}\left(\frac{\omega_p}{\Gamma_0}\right)^2\sum_{j=1}^{3}\left|E_0^j\left(\exp\left[\frac{\left(\sqrt{L_j}\omega_p-\omega_0\right)^2}{4\Gamma_0^2}\right]+\exp\left[\frac{\left(\sqrt{L_j}\omega_p+\omega_0\right)^2}{4\Gamma_0^2}\right]\right)\right|^2, \quad (9)$$

Here $\omega_p=\sqrt{4\pi ne^2/m}$ - is the plasmon frequency.

To illustrate the effect of particle shape on the nature of the absorption of pulsed laser radiation, we limit ourselves to considering nanoparticles in the form of ellipsoids of rotation (spheroids). The geometric factors L_j included in (7) for nanoparticles having the shape of an elongated ($R_\perp<R_\parallel$) or flattened ($R_\perp>R_\parallel$) spheroid ($R_\perp$ and $R_\parallel$ - half-axis along and across the axis of rotation of the spheroid) have the form (7)

$$L_\perp=L_x=L_y=\frac{1}{2}(1-L_\parallel), \quad (10)$$

$$L_\parallel=L_z=\begin{cases}\dfrac{1-\varepsilon_p^2}{\varepsilon_p^2}\left[\dfrac{1}{2\varepsilon_p}\ln\left(\dfrac{1+\varepsilon_p}{1-\varepsilon_p}\right)-1\right], & \text{elongated spheroid, } R_\perp<R_\parallel,\\ \dfrac{1+\varepsilon_p^2}{\varepsilon_p^3}\left[\varepsilon_p-\mathrm{arctg}\,\varepsilon_p\right], & \text{flattened spheroid, } R_\perp>R_\parallel,\end{cases} \quad (11)$$

Where $\varepsilon_p^2=\left|1-R_\perp^2/R_\parallel^2\right|$.

Now from (7) we can obtain the expression for the ratio of the energy absorbed per unit volume of the metal nanoparticle to the energy of the incident laser wave

$$S_e=\frac{\pi}{8}\left(\frac{\omega_p}{2\Gamma_0}\right)^2\left|\begin{array}{l}\cos\theta\left(\exp\left[\dfrac{\left(\sqrt{L_\parallel}\omega_p-\omega_0\right)^2}{4\Gamma_0^2}\right]+\exp\left[\dfrac{\left(\sqrt{L_\parallel}\omega_p+\omega_0\right)^2}{4\Gamma_0^2}\right]\right)+\\ \sin\theta\left(\exp\left[\dfrac{\left(\sqrt{L_\perp}\omega_p-\omega_0\right)^2}{4\Gamma_0^2}\right]+\exp\left[\dfrac{\left(\sqrt{L_\perp}\omega_p+\omega_0\right)^2}{4\Gamma_0^2}\right]\right)\end{array}\right|^2. \quad (12)$$

Now evaluate the parameters included in formula (11). Let's choose $\omega_0=\Omega=\omega_p/\sqrt{3}$, $\theta=\frac{\pi}{4}$ and we will choose the frequency of plasmon resonance from the book of Kitel. Choose the plasmon frequency for the three metals Na ($\omega_p=8{,}57\cdot10^{15}$с$^{-1}$), Ka ($\omega_p=5{,}65\cdot10^{15}$с$^{-1}$) and Ag ($\omega_p=13{,}8\cdot10^{15}$с$^{-1}$).

Graphical dependences S_e from $R_\perp/R_\parallel$ for Ka nanoparticles are shown in Fig.1

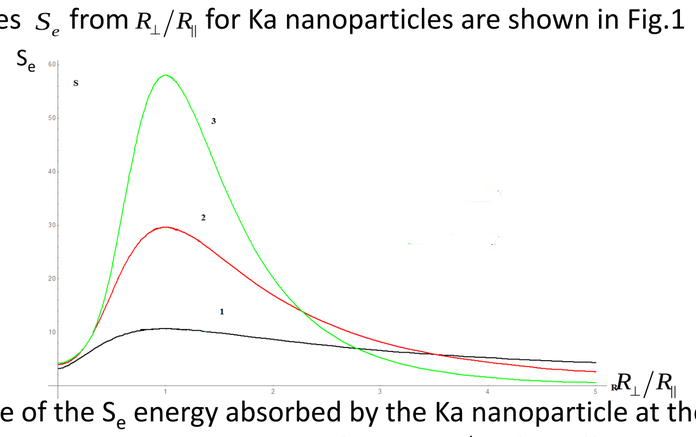

Fig.1. The dependence of the S_e energy absorbed by the Ka nanoparticle at the plasmon resonance frequency on the ratio between the spheroid half-axes $R_\perp/R_\parallel$ for different values of the laser pulse duration с$^{-1}$: 1 - $1.085\cdot10^{15}$, 2 - $0.6512\cdot10^{15}$с$^{-1}$, 3 - $0.465\cdot10^{15}$с$^{-1}$.

From Fig.1, in particular, it follows that better absorbed laser pulses with a longer duration. The maximum absorption is observed at $R_\perp/R_\parallel$ = 1, ie for spherical particles.

We now calculate the value of S_e for the case when the carrier frequency of the laser pulse differs from the plasmon resonance frequency in the spherical nanoparticle $\Omega=\omega_p/\sqrt{3}$. Choose $\omega_0=3.0\cdot10^{15}$с$^{-1}$. In fig. Figure 2 shows the results of numerical calculations of the energy absorbed by the metal nanoparticle Na at different laser pulse durations depending on the shape of the nanoparticle.

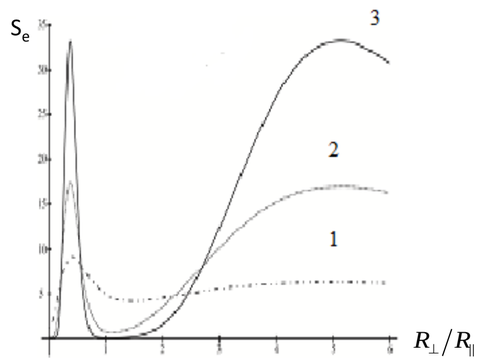

Fig.2. Dependence of S_e energy absorbed by Na nanoparticle at frequency $\omega_0=3.0\cdot10^{15}$ с$^{-1}$ on the ratio between spheroid half-axes $R_\perp/R_\parallel$ for different values of laser pulse duration

From the analysis of Fig.2 it follows that as soon as the carrier frequency deviates from the frequency of the surface plasmon in the spherical nanoparticle $\Omega=\omega_p/\sqrt{3}$, the peak of energy absorption, depending $R_\perp/R_\parallel$ on the ratio is split into two. The first maximum corresponds to the elongated($R_\perp/R_\parallel$ <1) and the second to the flattened ($R_\perp/R_\parallel$ > 1) ellipsoids.

Conclusion. We have developed the theory which describes the features of the absorption of ultrashort laser pulses by metallic nanoparticles, depending on the particle shape and the pulse duration in the area of excitation of surface plasmon resonance.. The simple analytic expressions are obtained, which make it possible to study the absorption of these pulses by surface plasmons, i.e. by the high-energy excitation of the electron gas in such nanoparticles. The analysis of the dependence of the energy absorbed by a spheroidal metal nanoparticles on the degree of its prolateness or oblateness is carried out for the different values of pulse duration and frequencies higher, lower, or identical to the plasmon resonance frequency. At the frequency of a carrier wave which coincides with that of the surface plasmon, the maximum absorption is observed for spherical metal nanoparticles. As soon as the carrier frequency deviates from that of the surface plasmon in a spherical particle, two maxima appear in the dependence of the absorbed energy on the ratio of spheroid semiaxes: one of them corresponds to the prolate particles, while the other – to the oblate particles. As the frequency deviates from the resonance one, the peak of the absorbed energy first decreases in absolute value, then splits and finally stabilizes for the more and more prolate or oblate particles. For the case of spheroidal metal nanoparticles subjected to the laser irradiation, with increase in the pulse duration, the peak in the dependence of the absorption on the frequency of a carrier wave also splits into two peaks located on the opposite sides of the value corresponding to the resonance frequency of a spherical particle. The peaks oscillations along or across the spheroid rotation axis. A distance from the minimum in a dip between the doublet peaks to the frequency of the plasmon resonance for a spherical particle provides the information about the degree of prolateness or oblateness of a nanoparticle. As the degree of prolateness or oblateness increases, the distance between the doublet components grows. At the fixed incident angle of a laser pulse, the peak height keeps constant, with its value being dependent only on the pulse duration. The features of the change of the relative absorption intensity of a pulse along and across the spheroid rotation axis with change in the angle of incidence are traced.

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