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MODELING OF THE LASER METAL NANOPARTICLES FRAGMENTATION

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Abstract. The paper considers a physical model of metal nanoparticles fragmentation in liquids under the action of femtosecond laser pulses at the example of gold particles in water. The model is based on the electrolization of metal nanoparticles heated by a laser pulse, and their division under the development of instability of a charged drop of liquid metal. The process of hot electrons emission from the surface of a nanoparticle and further solvation in liquid has been studied. The critical fragmentation parameter, namely a particle charge, has been defined.

1 INTRODUCTION

Laser nanostructuring of materials is important in many scientific, technological and medical applications [1-4]. Of special interest are the metal nanoparticles, in particular the gold ones. Their unique optical properties stimulate the research of possible applications in optics, photonics, and biomedicine [5-15]. All the methods of producing nanoparticles may be conventionally divided into two groups: *wet chemistry* i.e., the chemistry using liquid components [16,17] and *dry processes* i.e., the processes with the use of plasma discharge or those that make use of the synthesis of the needed product in flame, as well as the material evaporation under the action of a laser pulse.

Laser ablation has manifested itself as one of most effective physical methods of nanofabrication [18-25]. However, the laser methods form rather large-sized nanoparticles with a wide size spectrum. In this connection, in order to reduce the size of nanoparticles their colloids are additionally treated by ultrashort laser pulses [25-28]. The mechanism of laser nanoparticles fragmentation in liquids has not been much studied and there is no consensus on this problem. They name the following possible mechanisms: the hydrodynamic instability of the melted metal drop arising due to its interaction with the liquid vapor [25]; the evaporation of gold atoms under heating the nanoparticles by laser radiation [26]; the Coulomb explosion [27,28].

A physical model of gold nanoparticles fragmentation in water under the action of femtosecond laser pulses is presented in this paper. When the colloids of relatively large gold nanoparticles (several tens of *nm*) are irradiated by femtosecond laser pulses, one can observe their fragmentation into smaller nanoparticles (up to several nm). In the process the particle is heated up to the melting temperature and turns into a drop of liquid. The heating is accompanied by thermionic emission from the drop surface. The emitted electrons take away the negative charge, and the drop of melted metal turns to be positively charged. Thus the model of fragmentation is based on the electrolization of metal nanoparticles heated by a laser

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pulse, and their division under the development of instability of a charged drop of liquid metal. As a mechanism of electrolization we have considered the emission of hot electrons from the surface of a nanoparticle with further salvation in liquid. The problem of gold particles heating at femtosecond laser pulse absorption has been solved. Time dependence of electron thermionic emission current from the particle surface has been found. The particle fragmentation parameter has been defined. The estimates are given of nanoparticle charge gained under the action of the laser pulse in water.

2 EXPERIMENTAL RESULTS

Laser ablation is an effective method of nanofabrication. The method presents an ablation of a solid target by strong laser radiation, and this leads to the ejection of the target components, and formation of nanoclusters and nanostructures. Generally, the size and structure of nanoobjects produced with the help of laser ablation are influenced by the following factors:

- The laser radiation characteristics: intensity, pulse duration, and the wavelength.
- Target material properties: absorption at different wavelengths, the melting, vaporization and crystallization temperatures.
- The environment properties: vacuum, gas, liquid.

When laser radiation is focused onto the solid target surface there takes place the absorption of the laser energy, which results in thermal and nonthermal heating of the target material, melting and ablation of the material in the form of atoms and nanoclusters.

At the same values of laser intensity the mass of particles produced by ablation depends on the amount of energy absorbed from the laser pulse. Micro- and nanosecond pulses contain more energy as compared to pico- and femtosecond ones, and this makes the ablation with longer pulses more effective to produce a greater mass of particles. However, one should note that ultrashort pulse ablation leads to the ejection of particles of higher energy due to high intensity of the laser pulse.

Target laser ablation may be accompanied by hot plasma formation. If the plasma is produced near the target, it may decrease the efficiency of energy transfer to the target surface, as well as give rise to secondary ablation of the material due to the target heating or cavitation phenomena (in liquid media). These effects are well illustrated in [21], in which the authors studied the dependence of the size of nanoparticles produced in water on the position of the focal plane of the lens focusing the laser radiation relative to the target surface. The produced nanoparticles may be devided into two groups: narrow-dispersed (particle average size, 10-20 *nm*) nanoparticles and wide-dispersed ones (particle average size, 60-70 *nm*). The authors attribute the origin of the first group to the ablation due to the laser interaction with target material, and the second group is a result of interaction with the produced plasma. It was found that the produced plasma intensity correlates with the amount of ablated material, as well as the average size of nanoparticles related to the wide-dispersed group. The authors assume that plasma heating of the target or mechanical target destruction due to the collapse of plasma-induced cavitation bubble are possible mechanisms of secondary ablation connected with plasma.

If the target is ablated in vacuum or gas medium, the nanoclusters may be transported to a substrate located at some distance from the target and form a nanostructured film. Ablation in

liquids (e.g., water solutions) leads to the ejection of nanoparticles into the environment and to the formation of colloidal solutions.

Ablation in liquids makes it possible to obtain pure nanomaterials, which are free of surface contamination typical of chemical methods. Nanoparticles obtained in a pure well-controlled medium are especially important for the application *in vivo* biodetection and visualization. Ablation in liquids has a number of specific features, namely:

- The presence of an optical breakdown in a dense medium, which absorbs a significant part of laser energy (typical time up to 50 μm); an effective transfer of energy from the laser plasma to the ambient liquid and formation of a cavitation bubble that is growing up to 150-250 μs and then collapsing yielding a large amount of mechanical energy;
- Absorption of an incident laser radiation by produced suspended nanoparticles. May cause various effects: secondary ablation of the material [29], fragmentation of colloidal particles [30], formation of complex chemical structures [31].
- The presence of self-focusing phenomenon and generation of a continuum for ultrashort pulses. In particular, the filamentation may take place when ultrashort laser pulses pass through the optical medium, and appears as a result of a balance between the laser pulse self-focusing and de-focusing effect of the plasma produced under high laser intensity in self-focusing area [32].

Laser ablation in liquids is an effective method to produce nanoparticles in the form of colloidal solutions. One should note that at ablation in water or other solutions under the absence of chemically active components the produced nanoparticles are of rather large size. This is associated with the coagulation and aggregation of atoms subjected to ablation. Nanosecond laser pulses, for example, give the particles of 10-300 *nm* in size and 50-300 *nm* dispersion [33].

Ultrashort laser pulse ablation offers better chances to control the size and dispersion of nanoparticles. A possibility to control effectively the nanoparticle size by changing the the laser flux density (F) has been shown in [23]. The size of nanoparticles varied from 4 to 120 *nm* when F changed from 60 up to 1000 J/cm^2. Two populations of nanoparticles have been produced in the experiments. The first one was produced under low density of the laser flux and included the particles of small size and narrow dispersion. At average F values both populations were observed. At high F the particles had large average size and wide dispersion. The mentioned populations are similar to those produced in the experiments on changing the position of the focal surface of a focusing lens discussed above. So, one can conclude that different mechanisms are responsible for the occurrence of each of the populations: the ablation due to the incident radiation and ablation due the effects caused by plasma formation.

To control the size of produced nanoparticles the water solutions of surface-active agents are used frequently, for example, sodium dodecyl sulfate, which cover the nanoparticles just after the ablation and prevent further agglomeration [34]. A drawback of the method lies in the fact that the nanoparticles covered by surface-active agents have no free chemical bonds, and the area of its further application is limited.

Paper [14] presents the results from the experiments on the ablation of gold in water solutions containing neutral α-cyclodextrins, β-cyclodextrins, or γ- cyclodextrins. A Ti/sapphire laser was used in the experiments (pulse duration, 110 *fs*; wavelength, 800 *nm*;

pulse maximum energy, 1 *mJ*). A sharp decrease in the size of nanoparticles was observed in comparison with the experiments in water. The nanoparticles produced at ablation in the solution of β-cyclodextrins (10 *mMole*) had the average size 2.1-2.3 *nm*, the dispersion did not exceed 1 nm. The solution was of saturated red color. The produced colloids turned to be very stable.

To make smaller the nanoparticles produced by ablation in a liquid medium the colloids are additionally treated by ultrashort laser pulses. In [27] the 11±5 *nm* nanoparticles were produced by laser ablation of a gold plate in a sodium dodecyl sulfate solution. Then, using a sprayer, the colloid 80 μm droplets were produced and subjected to structural changes with the help of single nanosecond laser pulses (wavelength, 532 *nm*; pulse duration, 10 *ns*; pulse energy, 30 *mJ*). The experiment resulted in obtaining the nanoparticles of 3.7 *nm* average size. The authors assume that, as a result of laser energy absorption, nanoparticles are heated up to the temperature of metal melting, and then are ionized due to thermal emission. The electrons emitted from the particles' surface are temporarily solvated in water. As a result, a multiply charged gold nanoparticle becomes unstable and fragmented owing to the Coulomb explosion. A similar scenario of fragmentation is considered in [28]. At the first stage the 8±5 *nm* nanoparticles were produced by ablation of a gold plate in sodium dodecyl sulfate solution. Then, the nanoparticles were subjected to laser radiation (the wavelength, 355 *nm*; pulse duration, 10 *ns*; pulse energy, 50 *mJ*; pulse repetition rate, 10 *Hz*). The nanoparticles reduced in size to 1.5 *nm*.

In [15], as a result of gold shells ablation in pure deionized water the produced gold nanoparticles had an average size of 55 *nm* and 34 *nm* dispersion. At the second stage, the obtained colloids were subjected to laser irradiation with the following characteristics: (pulse duration, 140 *fs*; wavelength, 800 *nm*; pulse energy, 500 *mJ*; pulse repetition rate, 1 *kHz*). After 30 minutes of irradiation of the colloid, the average size of nanoparticles reduced to 11±5 *nm*. Figures 1 and 2 illustrate size distribution of nanoparticles before and after irradiation.

Under further treatment (up to two hours) the nanoparticle average size increased gradually, and finally stabilized at 20-30 *nm*. The obtained colloids demonstrated excellent stability – up to several months. The authors consider the nanoparticle fragmentation to be a consequence of Coulomb explosion. Originally the size of nanoparticles reduces sharply due to the absorption of the incident 800 *nm* laser radiation. Further decrease is caused by absorption of energy from the white continuum, which occurs due to nonlinear optical interaction between the incident radiation and medium.

An absence of nanoparticles of intermediate size even at a very short time of irradiation speaks in favor of a concept of Coulomb explosion. The presence of such particles is typical for nanoparticle size reduction due to thermal evaporation of matter.

In [26] the colloids of gold 5-50 *nm* nanoparticles were obtained by the method of chemical reduction. Later, a laser with the wavelength of 532 nm, pulse duration 7 ns and flux density 210 mJ/cm^2 was used in the experiments on nanoparticle size reduction. The time of laser irradiation was 10 minutes. As a result, the nanoparticles having the size of 20 to 50 *nm* disappeared, and the number of nanoparticles of the size up to 10 nm sharply increased. TEM pictures of nanoparticles before and after laser irradiation are shown in Fig. 3.

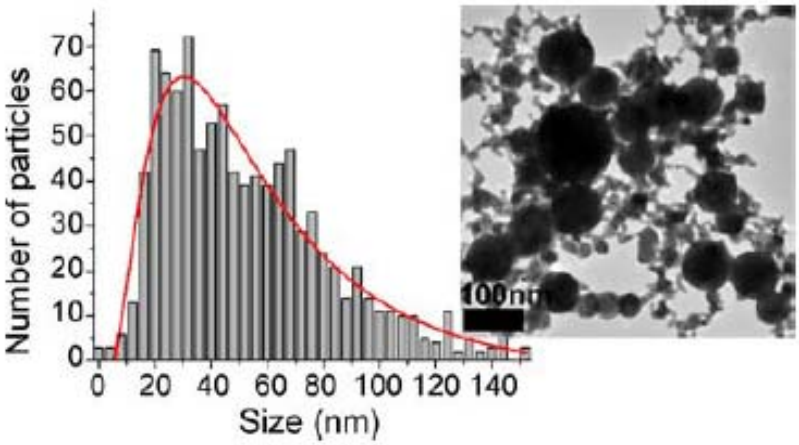

Fig. 1. TEM picture of Au nanoparticles produced by target ablation in water. Size distribution of nanoparticles.

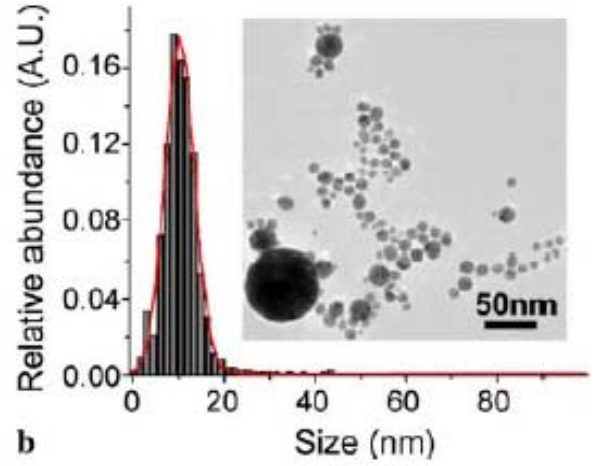

Fig. 2. TEM picture of Au nanoparticles after 30 minutes of irradiation by femtosecond laser pulses. Size distribution of nanoparticles.

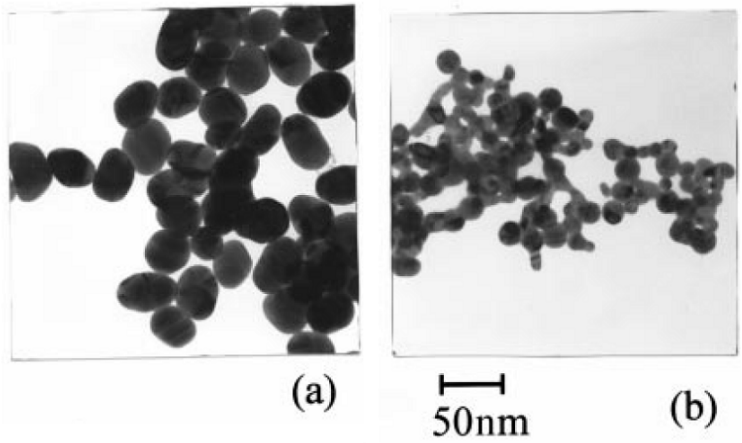

Fig. 3 TEM picture of Au nanoparticles before (a) and after (b) 10 minutes of laser irradiation; the laser flux density 210 mJ/cm^{-2}

The influence of laser irradiation time and laser flux density on nanoparticle size distribution was also studied in the paper. At a fixed laser flux density of 140 mJ/cm^2 , the maximum size of nanoparticles after 5 minutes of irradiation was 22 *nm*. Further irradiation did not change this value, and this shows that nanoparticle maximum size value may be considered as a certain threshold value. When laser flux density increased from 30 up to 500 mJ/cm^2 , there was observed a decrease in nanoparticle maximum size. The authors suggested as a mechanism of nanoparticle size reduction the evaporation of Au atoms under nanoparticle heating by laser radiation up to the temperature exceeding the gold melting temperature.

A possibility to reduce the nanoparticle size by means of laser treatment has been demonstrated for silver as well [35]. The colloids of silver 40-60 *nm* nanoparticles were obtained by the method of chemical reduction of $AgNO_3$ in water with an addition of sodium citrate at a temperature close to the boiling temperature. Then, the produced nanoparticles were subjected to laser radiation: pulse duration, 18 *ps*; wavelength, 355 and 532 *nm*; pulse energy, 2-3 *mJ*. As a result, 5-10 *nm* nanoparticles were produced. It was established that the choice of laser wavelength affects the selectivity of cluster fragmentation. For example, when the wavelength was changed for 532 *nm*, there was observed the fragmentation of large nanoparticles only, or irregular-shaped nanoparticles. The authors stated that there takes place an electron photoemission as a result of laser action on silver nanoparticles. The nanoparticles become charged and disintegrate into the smaller ones.

3 THEORETICAL MODELING

The papers are available which consider various aspects of laser interaction with metal nanoparticles. Paper [36] is devoted to numerical simulation of the interaction between short laser pulses and gold nanoparticles in water. The authors made use of a hydrodynamic model, which describes, with the help of Navier-Stokes equations, the heat and mass transfer in the system, and includes the equations of state (EOS) for water, two-temperature description of electron-phonon equilibrium in a metal nanoparticle, as well as the description of thermoelastic response of the particle matter. The modeling was made for moderate laser fluxes ($F < 100$ J/m^2), when the temperature is lower or slightly higher than the critical temperature in water; nanoparticle radius lies within the limits 25-200 *nm*; pulse duration is 0.1-1 *ps*. It was found that irradiation of nanoparticles by femtosecond laser pulses results in a propagation of a compression wave in the direction from the particle, and the width of the wave depends on the viscosity and heat conductivity of the ambient liquid. For 50 *nm* nanoparticles irradiated by 200 *fs* laser pulses and $F = 60$ J/m^2, the vapor formation on the surface of the particle starts at $t \approx 23$ ps, and the vapor layer is produced up to the time $t \approx 84$ *ps*. It was established that a total amount of evaporated matter remains relatively small, and the effect ofvapor formation on the temperature profilesis insignificant. The water temperature near the nanoparticle surface reaches the boiling temperature at flux density of 18 J/cm^2, and the critical temperature at 72 J/cm^2. At higher fluxes there is observed a continuous transition from liquid to the vapor without vapor-liquid common existence near the surface of a nanoparticle.

Paper [37] presents a kinetic theory of laser-metal nanoparticle interaction in a matrix of a wide-band dielectric (SiO_2). The formalism is based on Boltzmann equation for the electrons of an open system adapted to the description of nanoparticle electron losses owing to

thermionic emission and photoelectric effect. The simulations of energy transfer and re-distribution are presented, as well as those of electron emission within the framework of the study into the destruction processes resulting from laser-gold nanoparticle interaction in a SiO_2 matrix. The calculations were made for 1.3 *nm* and 2.6 *nm* nanoparticles in SiO_2 matrix irradiated by 351 nm laser pulses with pulse duration 0.5 ns and 50 *ps*, and flux density 0.3 *J/cm2* and 0.15 *J/cm2*, respectively. It was shown that under such regimes a considerable number of electrons can be ejected from the nanoparticles due to thermionic emission. In both cases the electron effective temperature in nanoinclusions reached saturation at > 1*eV* (5000-6000*K*), and the grating temperature was relatively low (620*K* and 390*K*, respectively) due to energy transfer to the aambient glass and the emission of high-energy electrons.

Paper [38] presents a model which allows one to determine the dynamics of electron and ion temperature in a gold nanoparticle dipped into dielectric of a finite volume under the action of subpicosecond laser pulses. The model is based on a two-temperature model destined for the calculation of nanoparticle temperature and ballistic-diffusion approximation (BDA) for the estimation of heat transfer from the particle and its propagation in a dielectric environment. The model was applied to gold 10 *nm* nanoparticles in Al_2O_3 shell, and the shell thickness varied from 0.54 to 54 *nm*. The laser pulse duration constituted 110 *fs*. Time dependences of electron and grating temperature were found with the help of Fourier law and BDA for 5.4 *nm* thick shell.

We consider such scenario of gold nanoparticles fragmentation in water under the action of femtosecond laser pulses. When the colloids of relatively large gold nanoparticles (several tens of *nm*) are irradiated by femtosecond laser pulses, one can observe their fragmentation into smaller nanoparticles (up to several *nm*). In the process the particle is heated up to the melting temperature and turns into a drop of liquid. The heating is accompanied by thermionic emission from the drop surface. The emitted electrons take away the negative charge, and the drop of melted metal turns to be positively charged. Thus the model of fragmentation is based on the electrolization of metal nanoparticles heated by a laser pulse, and their division under the development of instability of a charged drop of liquid metal. As a mechanism of electrolization we have considered the emission of hot electrons from the surface of a nanoparticle with further salvation in liquid. The problem of gold particles heating at femtosecond laser pulse absorption has been solved. Time dependence of electron thermionic emission current from the particle surface has been found. The particle fragmentation parameter has been defined. The estimates are given of nanoparticle charge gained under the action of the laser pulse in water.

To develop a physical model and optimize the regimes of laser irradiation for producing nanoparticles one needs to solve the following problems:

- The problem of nanoparticle heating under the action of laser radiation;
- Find the current of electron thermionic emission from the surface of a nanoparticle;
- Calculate the fragmentation parameter for gold nanoparticles;
- Evaluate the charge gained by the nanoparticle as a result of thermionic emission and electron salvation

4 THE PROBLEM OF NANOPARTICLE HEATING

A two-temperature model [3] has been used to solve the problem of metal nanoparticles heating by femtosecond laser pulses:

$$\begin{cases} C_e \dfrac{\partial T_e}{\partial t} - div(\lambda \cdot grad T_e) = \dfrac{P}{V} - g(T_e - T_{ph}) \\ C_{ph} \dfrac{\partial T_{ph}}{\partial t} = g(T_e - T_{ph}) \end{cases} \quad (1)$$

T_e , is the electron subsystem temperature; T_{ph} , the phonon subsystem temperature; C_e, C_{ph} , the electron and phonon heat capacity; *g*, the factor of electron-phonon coupling, which describes the rate of energy exchange between the electrons and the lattice; λ, the coefficient of heat conductivity; *P,* the laser radiation power absorbed by a nanoparticles; V , the nanoparticles volume.

Each of the equations represents the energy conservation law. The equation for the electrons illustrates the change in their temperature due to the heat transfer to the phonons, and laser radiation and laser radiation absorption. The phonons' temperature changes only due to the heat exchange with electron, since the phonons do not absorb the laser radiation.

One can use an approximation of homogeneously heated nanoparticle for the nanoparticles with the radii smaller than the distance covered by the heat from the incident radiation during the pulse action. The distance covered by the heat during the pulse is:

$$l = 2\sqrt{\chi_e \tau}\ ,\ \chi_e = \frac{\upsilon_F^2}{3\nu_e}$$

where τ is the pulse duration; χ_e the temperature conductivity of the metal electron subsyste; υ_F , the Fermi velocity; ν_e, the frequency of electron collisions. For the metals the electron collision frequency consists of the electron-phonon and electron-electron collisions. The grating temperature При температурах решетки T_{ph} being higher than Debye temperature Θ_D (for Au $\Theta_D = 170K$), the frequency of electron-phonon collisions is proportional to T_{ph} . When the electron thermal energy $k_B T_e$ is snaller than Fermi energy ε_F , the frequency of electron-electron collisions ν_{e-e} depends quadratically on the electron temperature. Bearing this in mind, let us neglect the contribution of electron-phonon collisions and consider $\nu_e \approx \nu_{e-e}$. At $\nu_{e-e} = 0.93 \cdot 10^{14}\, s^{-1}$, $\upsilon_F = 1.4 \cdot 10^8\, cm/s$, we get $\chi_e = 70\, cm/s$. At 100 *fs* pulse duration we get $l = 52$ nm. So, for the particles having the radii smaller than 52 nm, one can neglect the thermal fluxes directed from the areas with higher temperatures to the areas with lower temperatures. Finally we have the following system of equations:

$$\begin{cases} C_e \dfrac{\partial T_e}{\partial t} = -g(T_e - T_{ph}) + \dfrac{P}{V} \\ C_{ph} \dfrac{\partial T_{ph}}{\partial t} = g(T_e - T_{ph}) \end{cases} \quad (2)$$

The initial conditions:

$$\begin{cases} T_e(0) = T_{in} \\ T_{ph}(0) = T_{in} \end{cases}$$

Here T_{in} is the temperature of the environmental area considered to be equal to 300K.

If the electron subsystem temperature is much lower than Fermi temperature (for Au T_F = 63 900), only the electrons near Fermi surface are charged, and the electron heat capacityis presented in the form of linear temperature dependence:

$$C_e\left(T_e\right) = C_e^{'} \cdot T_e \tag{3}$$

where $C_e' = \pi^2 k_B^2 n_e / 2\varepsilon_F$ and n_e is the concentrationof free electrons; k_B, the Boltzman constant; ε_F, the Fermi energy.

Theoretical and experimental research shows that the Au d zone, located close to Fermi level, has a very complex structure. The electrons of U d zone introduce significant correction into the number of thermally excited electrons, and, hence, influence the electron heat conductivity [39]. The use of linear approximation for temperature dependence of electron heat conductivity may lead to an essential overestimation of electron subsystem temperature in a state of partial thermodynamic equilibrium with the phonon subsystem. Such equilibrium is usually realized under the action of femtosecond laser pulses onto the metals.

Thermally excited electrons of *d* zone also make contribution into the interaction between the electron and phonon susbsystems. That is why the temperature dependence of *g* was taken into account in the solution of the thermal problem. Figure 4 illustrates the temperature dependence of *g* factor.

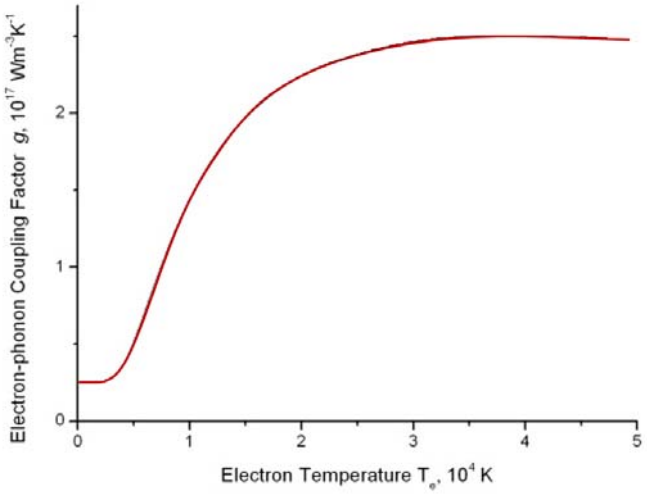

Fig.4. Dependence of electron-phonon coupling factor on the electron subsystem temperature.

Define the dependence of electron maximum temperature on the laser pulse energy density using a linear dependence between the electron heat conductivity and temperature. At the stage of heating by the laser pulse (100 *fs*) one can neglect the term responsible for the energy exchange between the electrons and phonons in the first equation of system (2). We get:

$$V \cdot C_e \cdot \frac{\partial T_e}{\partial t} = P = \sigma_{abs} \cdot q\,, \tag{4}$$

where V is the nanoparticle volume; P , the absorbed laser radiation; σ_{abs}, the absorption crosssection considered to be equal to a geometrical crosssection πa^2; and a, the nanoparticle radius; q, the laser flux. After time integration of equation (4) to the pulse duration we get the ratiobetween the electron maximum temperature $T_e^{(0)}$ on the laser pulse energy density F:

$$T_e^{(0)} = \sqrt{\frac{3}{2}\frac{F}{a \cdot C_e'}} \tag{5}$$

The obtained dependences between the maximum electron temperature $T_e^{(0)}$ and laser pulse energy density are given in Fig. 5. As seen from the figure, the maximum electron temperature calculated with the use of linear approximation for electron heat capacity is twice as much as the one obtained with account for d-electron contribution to heat conductivity.

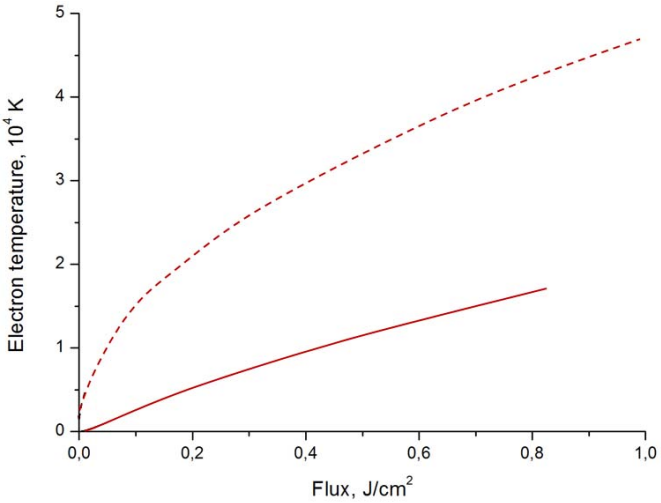

Fig. 5 Electron subsystem temperature vs flux density. Solid line: d-electron contribution taken into account; dashed line: linear approximation with no account for d-electron contribution.

At the initial stages of heating the electron subsystem temperature is much higher than the temperature of phonon subsystem ($T_e >> T_{ph}$), and, so, we may neglect the grating temperature in the system (2):

$$\begin{cases} C_e' \cdot T_e \dfrac{\partial T_e}{\partial t} = -g \cdot T_e \\ C_{ph} \dfrac{\partial T_{ph}}{\partial t} = g \cdot T_e \end{cases} \tag{6}$$

The solution of the system (6) has the following form:

$$\begin{cases} T_e(t) = T_e^{(0)}\left(1 - \dfrac{g \cdot t}{C_e' \cdot T_e^{(0)}}\right) = T_e^{(0)}\left(1 - \dfrac{t}{\tau_c}\right) \\ T_{ph}(t) = \dfrac{g \cdot T_e^{(0)}}{C_{ph}}\left(t - \dfrac{t^2}{2\tau_c}\right) \end{cases} \tag{7}$$

τ_c, the typical time of electron subsystem cooling. For Au we have $g = 2.5\times10^{10}$ W/cm^3K, $C_e'=6.27\times10^{-5}$ J/cm^3K^2. From the first equation of the system (7) we may estimate the typical time of electron subsystem cooling: if $T_e^{(0)} \approx 10^4\,K$, then $\tau_c \approx 25nc$.

Figure 6 illustrates the results from solution of systems (2) and (6) for the laser pulse energy density 100 mJ/cm^2.

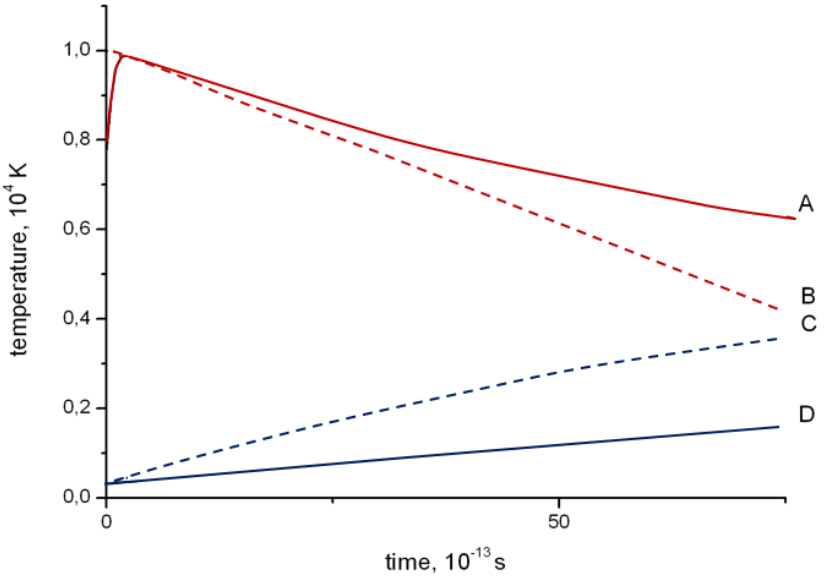

Fig.6 Time temperatures profile of the electron (A,B) and phonon (C,D) subsystems. Solid lines – numerical solution; dashed lines – analytical solution.

In the calculations the absorption cross-section was assumed to be equal to the geometrical cross-section πa^2, where a = 100 nm is the particle radius. As seen from Fig.1, after the end of the laser pulse the electron temperature reaches about ten thousands degrees, and then drops linearly during the time of tens of picoseconds. The final temperature of the nanoparticles lattice exceeds the melting temperature of gold (T=1337 K), i.e. the nanoparticles is transformed into a liquid state.

5 DEPENDENCE ON THE SIZE OF NANOPARTICLES

The absorption crosssection σ_{abs} for the nanoparticles depends on their size. The efficiency of laser radiation absorption Q_{abs} is defined as follows: $Q_{abs} = \dfrac{\sigma_{abs}}{\pi a^2}$. The

dependence of the efficiency of laser radiation (800 *nm*) absorption by gold nanoparticles in water is shown in Fig. 7.

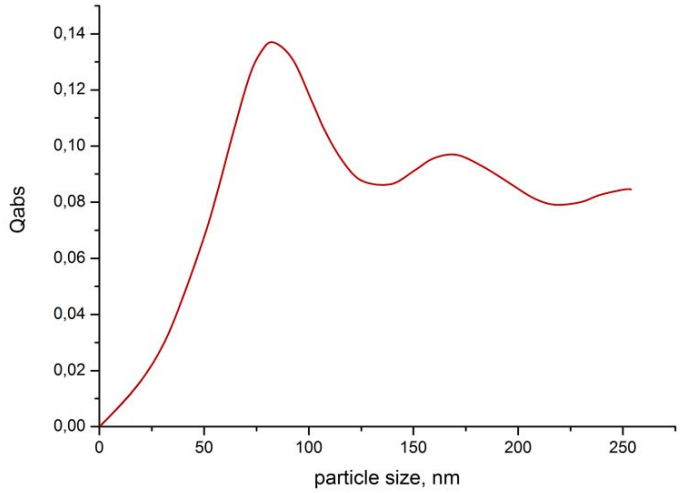

Fig.7. The dependence of absorption efficiency for for the incident laser radiation with λ=800 nm.

For the calculations we have used the program package MatLab [40], based on the Mie scattering theory of a plane electromagnetic wave on a homogeneous sphere of random size. As seen from the figure 7, the absorption crosssection increases with an increase in the nanoparticle size, and reaches its maximum for the nanoparticles with the radius of about 75 nm.

The incident laser energy is absorbed by the metal electron subsystem and leads to its heating. This means that that the change in the absorption crosssection under the change of nanoparticle size results in the change of electron temperature. Figure 8 presents the dependence of electrom maximum temperarture on the size of nanoparticles for different densities of the the incident laser flux obtained by equation (4). Maximum temperature of the heated electron subsystem corresponds to the absorption maximum efficiency, and falls at 75 nm nanoparticles.

The electron subsystem transfers the energy to the grating, and this leads to the temperature growth. Let us estimate estimate the amount of heat *H*, which is necessary for the gold nanoparticle to be melted under the action of a laser pulse. $H = C_{Au} \cdot (T_{пл} - T_0) + \Delta H_{пл}$, here $C_{Au} = 25.4\ J/mole \cdot K$ is the gold heat capacity; $T_{пл}$, the melting temperature of Au; $T_0 = 300K$, the initial temperature; $\Delta H_{пл} = 12.6 \cdot 10^3\ J/mole$, the melting molar heat. Then $H = 3.8kJ/mole \cdot K = 3{,}7kJ/cm^3$.

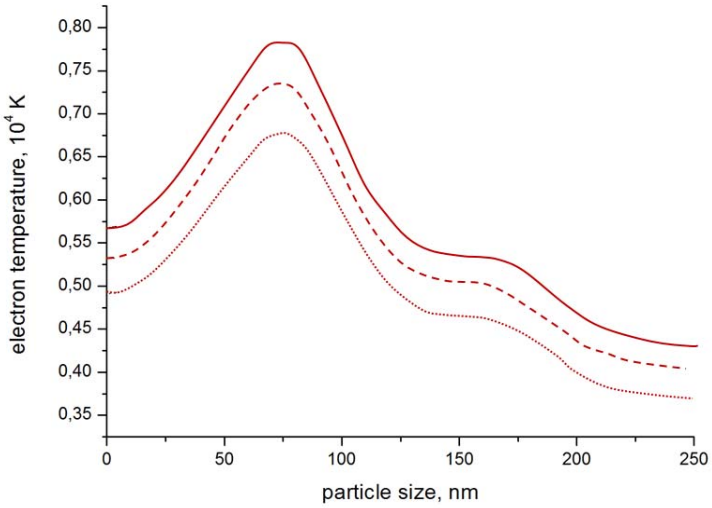

Fig. 8. Maximum electron temperature vs nanoparticle size for the laser flux density of 200 mJ/cm^2 (dotted line), 250 mJ/cm^2 (dashed line), 300 mJ/cm^2 (solid line).

If one knows the H value, the, by using formula (4) it is possible to find the dependence between the threshold flux density of the laser flux F_{th} and the nanoparticle size. Under the threshold density of the laser flux we mean here its minimal value needed to transfer to the particle the amount of heat sufficient to melt it.

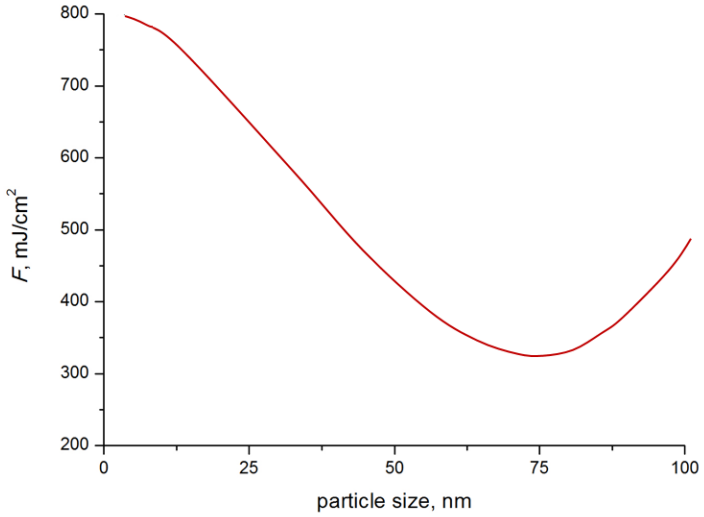

Fig. 9. Laser flux threshold density vs nanoparticle size.

One can see from Fig. 9 that the F_{th} value lies within the limits of 300 to 800 mJ/cm^2 for 100 *nm* nanoparticles. The smaller is the absorption efficiency the more energy should be given to the nanoparticle in order to reach the metal melting temperature. This is well seen from a comparison of Fig.8 and Fig. 9: the growth of absorption efficiency corresponds to the decrease in laser flux density.

6 THERMIONIC EMISSION

A thermionic emission from the surface of heated gold nanoparticles is observed. The value of electron thermionic emission current is defined by the temperature of the metal electron subsystem:

$$j = A \cdot T_e^2 \cdot \exp(-\frac{W}{kT_e}) \tag{8}$$

Here A, is the Richardson constant; $A \approx 120 \ \frac{A}{cm^2 \cdot K^2}$, W=5,1 eV, the work of the gold yield; T_e, the electron temperature.

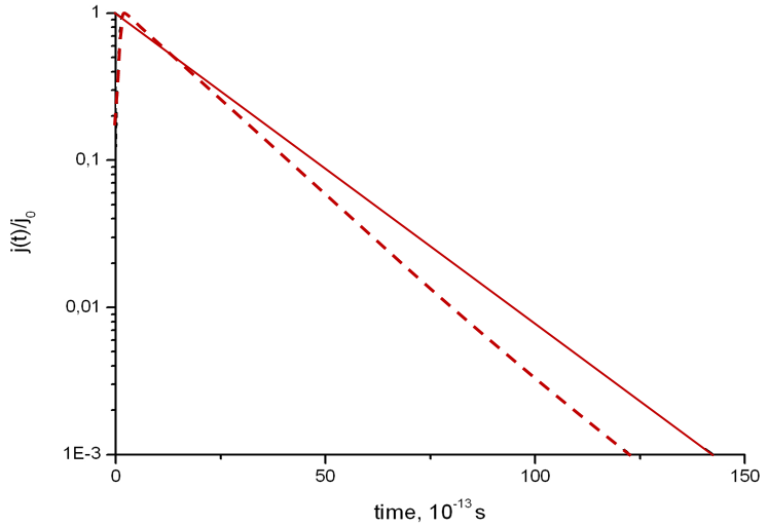

Fig. 10. Time profile of thermionic emission current. Solid line –analytical solution, dashed line – numerical solution.

Fig. 10 illustrates time dependence of thermionic emission current for laser fluence $F = 100\ mJ/cm^2$. Maximal density of thermionic current is ~ $10^6\ A/cm^2$. One can see from the Fig. 10 that, in accordance with the numerical and analytical solutions, the current drops exponentially after the end of the laser pulse during a typical time of several picoseconds.

7 SALVATION OF ELECTRONS IN WATER

The electrons emitted from the surface of a nanoparticle are rapidly thermolized.

The interaction electrostatic forces occurr berween the water dipoles and electrons emitted from the nanoparticle surface due to thermionic emission. Water molecules are polarized by electron and captured, i.e. the electrons are solvated in water.

Typical time of salvation is about 250 fs [3]. The mobility of electrons sharply drops here. As a result, an electric double layer of a space charge is formed near the nanoparticle surface.

Pure deionized water presents an amorphous dielectric with the forbidden zone E_g=6.5±0.5 eV [3]. Hence, the motion of emitted electrons in water can be considered as electron motion in a semiconductor in the space charge self-field.

This field grows with the growth of the number of emitted electrons, and it becomes more and more difficult for the new electrons to leave the nanoparticle surface. As a result, the emission current decreases, and, hence, the field becomed weaker. When the field decreases, it is easier for the electrons to leave the nanoparticle surface, and the emission current grows. Such electric field is called a self-consistent field.

Water molecules are heavier than electrons, and, so, the capture of electrons by water molecules in salvation prevents the electron motion by the electric field. Consequently, the molility and the depending (by Einstein relation) diffusion coefficient of slvated electrons sharply drop down to ~ 10^{-4} cm^2/s [3].

In this case salvation is similar to electron capture on a capture center. The above considerations allow one to use the elements of the solid body theory to describe the electron motion in water. Namely, the equations of electron motion in a dielectric medium with account for the space self-charge have the form [41]:

$$\begin{cases} \dfrac{\partial n_e}{\partial t} = D_e \Delta n_e - \mu_e \cdot div\left(n_e \cdot \vec{E}\right) - \dfrac{n_e}{\tau_s} \\ \dfrac{\partial n_s}{\partial t} = D_s \Delta n_s - \mu_s \cdot div\left(n_s \cdot \vec{E}\right) + \dfrac{n_e}{\tau_s} \\ -\varepsilon_0 \Delta\varphi = 4\pi e\left(n_e + n_s\right) \\ \vec{E} = -grad\varphi \end{cases} \tag{9}$$

e is the electron charge; n, the concentration of electrons; D, the electron diffusion coefficient in water; μ, the electron mobility in water; E, the electron spatial self-consistent field; ε_0, the dielectric constant of water; φ, the electric potential of the self-field of electrons, the indices e and s refer to the emitted and solvated electrons, respectively.

The first two equations in (9) describe the motion of the emitted and solvated electrons due to the diffusion and drift in a self-consistent electric field and the solvation in water, respectively. The third equation of the system is derived from the Maxwell equation for the rotor of the magnetic field vector provided that our problem is a spherically symmetric one (assume the nanoparticle to be sphere-shaped).

The boundary conditions are as follows:

$$\begin{cases} n_e\big|_{r=a} = \dfrac{j_T}{\langle \upsilon_T \rangle \cdot e} \\ \left(D_s \dfrac{\partial n_s}{\partial r} - \mu_s n_s \vec{E} \right)\Bigg|_{r=a} = 0 \end{cases} \tag{10}$$

Here j_T is the emission current and $\langle \upsilon_T \rangle$, the average velocity of the emitted electrons.

The first equation of system (10) shows that the concentration of electrons emitted at nanoparticle boundary is defined by the emission current only; the second one shows that the current at the boundary of a nanoparticle equals zero.

Since the mobility and diffusion coefficient of solvated electrons are small, we neglect the terms corresponding to the diffusion and drift of solvated electrons. Finally, instead of system (9) we get the following system of equations:

$$\begin{cases} \dfrac{\partial n_e}{\partial t} = D_e \Delta n_e - \mu_e \cdot div\left(n_e \cdot \vec{E}\right) - \dfrac{n_e}{\tau_s} \\ \dfrac{\partial n_s}{\partial t} = \dfrac{n_e}{\tau_s} \\ -\varepsilon_0 \Delta\varphi = 4\pi e\left(n_e + n_s\right) \end{cases} \tag{11}$$

Systems (10) and (11) determine the electric field *E(r,t)* and *n(r,t)*, at the given parameters j_T and $\langle \upsilon_T \rangle$, and the parameters ε_0, μ and *T*. For further solution of the system it is convenient to introduce dimensionless functions and variables. In a dimensionless form in a spherical system of coordinates we have the system of equations where all the values are dimensionless:

$$\begin{cases} \dfrac{\partial n_e}{\partial t} = \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2 \dfrac{\partial n_e}{\partial r}\right) - \dfrac{1}{r^2}\dfrac{\partial}{\partial r} r^2\left(n_e E_r\right) - \dfrac{n_e}{\tau_s} \\ \dfrac{\partial n_s}{\partial t} = \dfrac{n_e}{\tau_s} \\ \dfrac{1}{r^2}\dfrac{\partial}{\partial r}\left(r^2 E_r\right) = n_e + n_s \end{cases} \tag{12}$$

Numerical solution of (12) resulted in obtaining time dependence of a space charge self-consistent field value. It is well known that the field value and the value of the generating charge are related as follows: $E = \dfrac{Ze}{a^2}$, *E* is the electric field; *Ze* , the charge, *a* , the size of a nanoparticle.

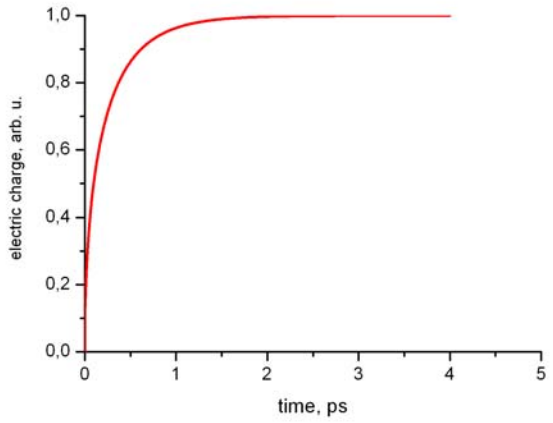

Fig.10. Electric charge (in relative units) vs time.

Figure 10 illustrates the time of a space charge. The obtained time dependence of the space charge indicates that a sharp growth of the electric field is observed for the times of ~1 *ps*, i.e., the times corresponding to a sharp growth of the thermionic emission current (see Fig. 10).

After this one can observe an exponential drop of the thermionic emission current, and the electric charge reaches the saturation. The estimated electric charge gained by a nanoparticles as a result of electron emission from its surface $Z_0 \approx 10^6$.

8 FRAGMENTATION PARAMETER

It has been shown that under irradiation of colloids of relatively large gold nanoparticles (several tens of ns) by femtosecond laser pulses one observes the fragmentation of these nanoparticles into smaller nanoparticles (up to several ns). The nanoparticle is heated to up to the metal boiling temperature and turns into a drop of liquid. The heating is accompanied by electron thermionic emission from the surface of a drop. The emitted electrons take away the negative charge, and the drop of melted metal becomes positively charged.

The problem of charged spherical drop stability depending on the ratio between the surface and Coulomb energy was solved by Rayleigh in 1882 [42]. The fission parameter X is defined as follows:

$$X = \frac{E_c}{2E_s}$$

where E_c, is the Coulomb repulsion force, E_s, the surface tension force.

It's well known that the fragmentation is observed at $X \geq 1$; at $0.3 < X < 1$ one can observe both the fragmentation and evaporation of single atoms from the the nanoparticle surface; at $X < 0.3$ only the evaporation of single atoms is observed [43].

The fission parameter for the metal (gold) nanoparticles is defined as $X = A\frac{q^2}{n}$, q, the particle charge; n, the number of atoms in the nanoparticle; $A = \frac{e^2\rho}{6 \cdot \sigma \cdot M_a} \approx 2$; e, the electron charge; $\rho = 19.3 g/cm^3$, the gold density; $\sigma = 1.125 \cdot 10^3 erg/cm^2$, the surface tension coefficient of melted gold; $M_a = 196.97 g/mole$, the gold molar mass.

The drop is stable in the face of extreme deformations – splitting into two identical parts at $Q_{cr}^2 = 0{,}36 \times 16\pi a^3 \sigma$, where a - particle size, $Q=Ze$, σ, surface tension coefficient of the liquid.

One can estimate the minimal number of electrons, q_{min}, which should leave the drop surface to make it unstable and fragmented.

Figure 12 presents the dependence of q_{min} on the size of nanoparticle. Mimimum number of electrons needed for fragmentation grows as function $a^{2/3}$, where a is the nanoparticle radius.

The typical values of q_{min} for the nanoparticles at a diameter $a=100nm$ should be an order $Z_{cr}=10^4$. Comparing the typical values with the charge estimates obtained from numerical solution of (9), one can obtain that

$$Z_0 / Z_{cr} >> 1$$

The charge gained by the nanoparticle from the electron thermionic emission is sufficient to make the particle unstable and fragmented.

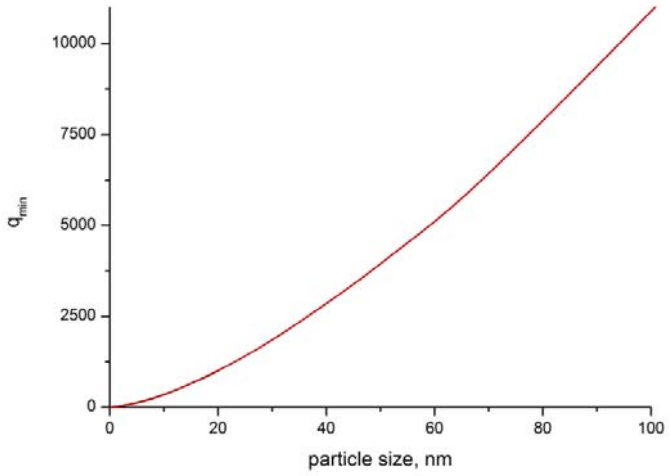

Fig. 12. Minimum number of electrons needed for fragmentation vs nanoparticle size. .

9 CONCLUSION

Theoretical modeling of metal nanoparticles fragmentation in water under the action of femtosecond laser pulses is discussed. The problem of heating a gold nanoparticle by laser pulses of femtosecond duration has been solved. The value and typical time of the drop of thermionic emission current from the nanoparticle surface due to the heating of the particle by the laser radiation field has been found. On the basis of the Rayleigh drop model the criterion of nanoparticle fragmentation has been found. The estimates of the charge gained by the nanoparticle due to the electron thermionic emission and their further solvation have been obtained. It was shown that the charge exceeds the threshold value given by the Rayleigh criterion. It is possible to conclude that as a result of the influence of laser radiation the particle becomes unstable and the nanoparticles fragmentation takes place.

The results of theoretical modeling may be used to optimize the laser operation regime destined to produce the nanoparticles of the given size.

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