On one mechanism of light ablation of nanostructures

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ABSTRACT

The mechanism of mechanical ablation of nanoparticles during the interaction with a high-power laser radiation pulse is proposed. A particle is polarized under a laser electric field, and electric forces acting on field-induced opposite-sign charges cause rupture stresses. Upon reaching the stresses exceeding the maximum allowable values for a given material, a nanoparticle decays into two ones. This effect can be used for narrowing the size distribution of nanoparticles produced by the laser ablation method.

Ablation of nanoparticles, field-induced charges, rupture stresses.

1. INTRODUCTION

Metal ablation by laser radiation is widely used to fabricate thin films, nanoparticles, and other nanoobjects[1]. Thermal and nonthermal ablation mechanisms are distinguished. During thermal ablation upon exposure to LPs, the target surface is locally heated above a certain critical temperature, which results in target material vaporization with the solid-gas or solid-plasma transition followed by NP condensation. During nonthermal ablation, target material is detached by electric forces. The determining factor in nonthermal ablation is the Coulomb explosion effect[2] at which electrons gain the LP energy and are vaporized from the target surface, having no time to transfer the energy to the lattice. The appearing positive space charge causes ion ejection. The characteristic time of this process is ~100 fs.

2. OBJECTIVE OF THE STUDY

In this paper, we consider the mechanism of mechanical grinding of metal NPs under an electric field of LP. The electric field polarizes NPs with the result of the formation of opposite-sign surface charges to which electric forces are applied, which cause mechanical stresses in the particle volume.

3. THEORETICAL TREATMENT OF THE INTERACTION OF HIGH-POWER LASER RADIATION WITH NANOSTRUCTURES

3.1. Interaction of the high-power laser pulse (LP) with a nanoparticle

Let us consider the interaction of the high-power laser pulse (LP) with a nanoparticle (NP). What time scales will be considered? First, we note that the time of field propagation over the nanoparticle volume is small, $\tau = 2a/c \leq 10^{-17}$ s, for particles with diameters smaller than 10 nm. This time is smaller than the oscillation period in the incident optical-range wave, $\tau_v = 1.6\cdot 10^{-15}$ s, and is much smaller than the particle thermalization time, i.e., the characteristic time of the energy transfer from the electron gas to the lattice, $\tau_i \sim 10^{-12}$ s.

Let us consider two models describing the interaction of the NP and radiation, relevant to various LP durations. The first model deals with femtosecond pulses, when the LP duration $\tau_p << \tau_i$; the second model concerns pico- and nanosecond pulses, when $\tau_p >> \tau_i$. Let us begin with the first one.

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The optical frequency field for NPs can be considered to be quasi-static, $\tau_c << \tau_\nu$; $\tau_c << \tau_\nu$; the electron gas can be considered to be an ideal conductor. The field induced when a metal sphere is polarized in a uniform electric field can be described by the potential

$$\Phi = -\left(\vec{E}_0, \vec{r}\right) \cdot \left(1 - \frac{a^3}{r^3}\right) \tag{1}$$

where $\vec{E}_0$ is the external electrostatic field strength, a is the sphere radius, and $\vec{r}$ is the vector from the sphere center to the observation point. The electric field strength on the sphere surface is written as

$$\vec{E} = -\nabla\Phi\Big|_{r=a} = 3 \cdot \left(\vec{E}_0, \vec{n}\right) \cdot \vec{n}\,, \tag{2}$$

where $\vec{n} = \dfrac{\vec{r}}{r}$ is the outward normal vector to the sphere surface. The surface electric charge density corresponding to (2) is $\sigma = \dfrac{3}{4\pi} \cdot \left(\vec{E}_0, \vec{n}\right)$. The force acting on the surface element dS is given by

$$d\vec{f} = \frac{1}{2} \cdot \sigma \vec{E} \cdot dS = \frac{9}{8\pi} \cdot \left(\vec{E}_0, \vec{n}\right)^2 \cdot \vec{n} \cdot dS\,, \tag{3}$$

Let us calculate the force acting on the sphere surface element cut by a cone with an axis coinciding with the direction $\vec{E}_0$ and the opening angle ϑ,

$$f = \frac{9}{16} \cdot E_0^2 \cdot a^2 \cdot \left(1 - \cos^4 \vartheta\right), \tag{4}$$

The stress arising at the base of the corresponding spherical segment is obtained by dividing Eq. (4) by the segment area $\pi a^2 \sin^2 \vartheta$, where $I = \dfrac{c}{4\pi} \cdot \sqrt{\varepsilon_o} \cdot E_0^2$ is the LP intensity and c is the speed of light. Thus, we have

$$T = 75MPa \cdot \left(\frac{I}{10^{12}\, W/cm^2}\right) \cdot \left(1 + \cos^2 \vartheta\right), \tag{5}$$

As can that during the interaction of the gold NP with LPs, even at an intensity of 10^{12} W/cm^2, stresses comparable with ultimate rupture stresses for macroscopic gold arise in the NP, $T_{Au} \sim 100MPa$. We can see from Eq. (5) that the maximum stress appears near sphere poles at small angles ϑ; in the equatorial plane ($\vartheta = \pi/2$), the stress is minimum. The effect of electron loss upon exposure to LPs, causing a positive NP charge, increases mechanical stresses in the NP volume; however, a moderate NP charge is insufficient to detach ions from the NP surface and to develop the Coulomb explosion.

Let us pay attention to the possible effect of laser cleaning or nanopolishing. If an NP contains any defect leading to an NP shape deviation from spherical, a larger higher charge will concentrate on a corresponding bump during NP polarization, which will result in detachment of exactly this bump in the first place. The energy transferred to the electron gas can be estimated having calculated the potential energy of charges on the polarized sphere surface, $W = \dfrac{1}{2} \oiint \Phi \sigma dS$, where the potential Φ contains two terms (see (1)): the potential induced by external charges, $\Phi_1 = -\left(\vec{E}_0, \vec{r}\right)$, and the potential of charges on the polarized sphere $\Phi_2 = \left(\vec{E}_0, \vec{r}\right) \cdot \dfrac{a^3}{r^3}$. In calculating the energy of separated charges, we should take into account only Φ_2,

$$W = \frac{1}{2}\oiint \Phi_2 \sigma dS = \frac{E_0^2 \cdot a^3}{2}, \tag{6}$$

Considering that this energy after pulse passing transforms to heat, we estimate the particle temperature change, taking the macroscopic value of the gold specific heat,

$$\Delta T = \frac{W}{C_{Au} \cdot m} = \frac{3I}{2c} \cdot \frac{1}{C_{Au} \cdot \rho} = 20K \cdot \left(\frac{I}{10^{12}\, W/sm^2} \right), \tag{7}$$

where m is the particle mass, $C_{Au} = 130 \frac{J}{kg \cdot K}$ is the gold specific heat, and $\rho = 19.3 \frac{g}{cm^3}$ is the gold density.

3.2 Case of long laser pulses

Let us now consider the sufficiently long-term NP--NP interaction, i.e., $\tau_p >> \tau_i$. For the time τ_p, collective processes have time to be included, and we can describe NP electromagnetic properties in terms of the permittivity, expecting that the values of ε will appear close to those measured for macroscopic samples.

Let us calculate the fields induced during scattering of a monochromatic plane wave of frequency ω by a metal sphere. As is known, the field components $\vec{E}, \vec{H}$ can be expressed in spherical coordinates in terms of the potentials denote here by R_p, Q_p,

$$\begin{aligned}
E_r &= k^2 \cdot rR_p + \partial_r^2 \left(rR_p\right) & H_r &= k^2 Q_p r + \partial_r^2 \left(rQ_p\right) \\
E_\vartheta &= \frac{1}{r} \cdot \partial_\vartheta \partial_r \left(rR_p\right) + \frac{i\omega}{\sin\vartheta} \cdot \partial_\varphi Q_p & H_\vartheta &= \frac{1}{r} \cdot \partial_\vartheta \partial_r \left(rQ_p\right) - \frac{i\varepsilon\omega}{\sin\vartheta} \cdot \partial_\varphi R_p \\
E_\varphi &= \frac{1}{r \cdot \sin\vartheta} \cdot \partial_\varphi \partial_r \left(rR_p\right) - i\omega \cdot \partial_\vartheta Q_p & H_\varphi &= \frac{1}{r \cdot \sin\vartheta} \cdot \partial_\varphi \partial_r \left(rQ_p\right) + i\varepsilon\omega \cdot \partial_\vartheta R_p
\end{aligned} \tag{8}$$

Here ϑ, φ are the polar and azimuthal angles of the spherical coordinate system. Let (r, ϑ, φ) be the spherical coordinates in the system with the polar axis directed along the wave vector $\vec{k}$, $|k| = \sqrt{\varepsilon\omega^2}$, where ε is the permittivity of the corresponding medium at the wave frequency. The subscript p indicate the values related to the incident wave; the subscript i,o relate to the transmitted and reflected waves, respectively. The continuity conditions on the surface of the sphere of tangential E_t and H_t strength components and normal εE_r and H_r induction components lead to the conditions

$$\begin{aligned}
\varepsilon_i R_i &= \varepsilon_o R_o + \varepsilon_o R_p & \partial_r \left(rR_i\right) &= \partial_r \left(rR_o\right) + \partial_r \left(rR_p\right) \\
Q_i &= Q_o + Q_p & \partial_r \left(rQ_i\right) &= \partial_r \left(rQ_o\right) + \partial_r \left(rQ_p\right)
\end{aligned} \tag{9}$$

Let us consider a linearly polarized wave. The nonzero components are given by

$$E_x = E_p \cdot \exp\left(ikr\cos\vartheta\right) \quad H_y = -H_p \cdot \exp\left(ikr\cos\vartheta\right), \tag{10}$$

where $kE_p = \omega H_p$. Since the potentials R_p and Q_p satisfy the wave equation, they can be presented as expansions in spherical functions,

$$R_p = \sum_{lm} \left(a_{p,lm} \Psi^J_{p,lm} + b_{p,lm} \Theta^J_{p,lm} \right) \quad Q_p = \sum_{lm} \left(c_{p,lm} \Psi^J_{p,lm} + d_{p,lm} \Theta^J_{p,lm} \right), \tag{11}$$

where eigenfunctions are chosen in the form

$$\Psi^J_{p,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{kr}}\cdot\frac{2l+1}{2}\cdot J_{l+1/2}(kr)\cdot P_l^m(\cos\vartheta)\cdot\cos(m\varphi)$$
$$\Theta^J_{p,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{kr}}\cdot\frac{2l+1}{2}\cdot J_{l+1/2}(kr)\cdot P_l^m(\cos\vartheta)\cdot\sin(m\varphi), \quad (12)$$

For the expansion coefficients, we can obtain the expressions

$$a_{p,l1}=\frac{i\cdot E_p}{k\cdot l(l+1)} \quad d_{p,l1}=\frac{i\cdot H_p}{k\cdot l(l+1)}, \quad (13)$$

Other coefficients disappear.

We present the potentials of scattered and transmitted waves also in the form of expansions,

$$R_o=\sum_{lm}\left(a_{o,lm}\Psi^H_{o,lm}+b_{o,lm}\Theta^H_{o,lm}\right) \quad Q_o=\sum_{lm}\left(c_{o,lm}\Psi^H_{o,lm}+d_{o,lm}\Theta^H_{o,lm}\right), \quad (14)$$

$$R_i=\sum_{lm}\left(a_{i,lm}\Psi^I_{i,lm}+b_{i,lm}\Theta^I_{i,lm}\right) \quad Q_i=\sum_{lm}\left(c_{i,lm}\Psi^I_{i,lm}+d_{i,lm}\Theta^I_{i,lm}\right) \quad (15)$$

where eigenfunctions have the form

$$\Psi^H_{o,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{kr}}\cdot\frac{2l+1}{2}\cdot H_{l+1/2}(kr)\cdot P_l^m(\cos\vartheta)\cdot\cos(m\varphi)$$
$$\Theta^H_{o,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{kr}}\cdot\frac{2l+1}{2}\cdot H_{l+1/2}(kr)\cdot P_l^m(\cos\vartheta)\cdot\sin(m\varphi) \quad (16)$$

$$\Psi^I_{i,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{pr}}\cdot\frac{2l+1}{2}\cdot I_{l+1/2}(pr)\cdot P_l^m(\cos\vartheta)\cdot\cos(m\varphi)$$
$$\Theta^I_{i,lm}(r,\vartheta,\varphi)=(i)^l\cdot\sqrt{\frac{2\pi}{pr}}\cdot\frac{2l+1}{2}\cdot I_{l+1/2}(pr)\cdot P_l^m(\cos\vartheta)\cdot\sin(m\varphi) \quad (17)$$

The scattered wave (-length) is described by the Hankel function $H_\nu(z)=J_\nu(z)+i\cdot Y_\nu(z)$; the field within the particle is described by the modified Bessel function $I_\nu(pr)$, where $p=\omega\cdot\sqrt{-\varepsilon_i}$.

From boundary conditions (9), we can obtain equations for the coefficients $a_{o,lm}, a_{i,lm}, b_{o,lm}\ldots$ which include the values of the radial functions $J_{l+1/2}(kr), H_{l+1/2}(kr), I_{l+1/2}(pr)$ on the sphere surface. Taking into account that we assume the NP size to be much smaller than the incident radiation wavelengths, $ka \ll 1; pa \ll 1$, we use the Bessel function expansions at small argument values,

$$J_\nu(z)\cong\frac{1}{\Gamma(\nu+1)}\cdot\left(\frac{z}{2}\right)^\nu \quad H_\nu(z)\cong-\frac{i\cdot\Gamma(\nu)}{\pi}\cdot\left(\frac{2}{z}\right)^\nu \quad I_\nu(z)\cong\frac{1}{\Gamma(\nu+1)}\cdot\left(\frac{z}{2}\right)^\nu, \quad (18)$$

Solving the system of linear equations obtained taking into account (18), we find

$$a_{i,lm}=\frac{\varepsilon_o\cdot(2l+1)}{\varepsilon_i\cdot l+\varepsilon_o\cdot(l+1)}\cdot\left(\frac{k}{p}\right)^l\cdot a_{p,lm} \quad d_{i,lm}=d_{p,lm}\cdot\left(\frac{k}{p}\right)^l, \quad (19)$$

$$a_{o,lm}=-i\cdot\frac{\pi}{\Gamma\left(l+\frac{1}{2}\right)\cdot\Gamma\left(l+\frac{3}{2}\right)}\cdot\left(\frac{ka}{2}\right)^{2l+1}\cdot\frac{(\varepsilon_o-\varepsilon_i)\cdot(l+1)}{\varepsilon_i\cdot l+\varepsilon_o\cdot(l+1)}a_{p,lm}, \quad (20)$$

Other coefficients are zero.

Now, from Eq. (8), we can calculate radial components of the electric field strength on the sphere surface,

$$E_{r,ol} = -(i)^l \cdot \frac{l\cdot(l+1)}{a}\cdot\frac{2l+1}{2}\cdot\frac{\sqrt{\pi}}{\Gamma\left(l+\frac{3}{2}\right)}\cdot\frac{(\varepsilon_o-\varepsilon_i)\cdot(l+1)}{\varepsilon_i\cdot l+\varepsilon_o\cdot(l+1)}\cdot\left(\frac{ka}{2}\right)^l\cdot a_{p,l1}\cdot P_l^1(\cos\vartheta)\cdot\cos\varphi$$

$$E_{r,pl} = (i)^l \cdot \frac{l\cdot(l+1)}{a}\cdot\frac{2l+1}{2}\cdot\frac{\sqrt{\pi}}{\Gamma\left(l+\frac{3}{2}\right)}\cdot\left(\frac{ka}{2}\right)^l\cdot a_{p,l1}\cdot P_l^1(\cos\vartheta)\cdot\cos\varphi \quad , \tag{21}$$

$$E_{r,il} = (i)^l \cdot \frac{l\cdot(l+1)}{a}\cdot\frac{2l+1}{2}\cdot\frac{\sqrt{\pi}}{\Gamma\left(l+\frac{3}{2}\right)}\cdot\frac{\varepsilon_o\cdot(2l+1)}{\varepsilon_i\cdot l+\varepsilon_o\cdot(l+1)}\cdot\left(\frac{ka}{2}\right)^l\cdot a_{p,l1}\cdot P_l^1(\cos\vartheta)\cdot\cos\varphi$$

The jump of the radial field component on the sphere surface is related to the polarization sphere phenomenon and the surface charge formation,

$$\sigma_l = \frac{1}{4\pi}\cdot\left(E_{r,ol}+E_{r,pl}-E_{r,il}\right), \tag{22}$$

We can see from Eq. (21) that the effect decreases with increasing harmonic number l due to the multiplier $(ka)^l$. Let us consider the harmonic with $l = 1$. From Eq. (21), we find

$$\sigma_1 = -\frac{3}{4\pi}\cdot\left(\frac{\varepsilon_o-\varepsilon_i}{\varepsilon_i+2\cdot\varepsilon_o}\right)E_p\cdot\sin\vartheta\cdot\cos\varphi, \tag{23}$$

Let us calculate the tangential components of the electric field on the sphere surface. Due to the continuity of the tangential components, it is sufficient to calculate $E_{\vartheta i,11}, E_{\varphi i,11}$. Near the sphere surface, the potentials have the form

$$R_i = \frac{3\cdot\varepsilon_o}{\varepsilon_i+2\cdot\varepsilon_o}\cdot\frac{E_p}{2}\cdot r\cdot\sin\vartheta\cdot\cos\varphi \quad Q_i = \frac{H_p}{2}\cdot r\cdot\sin\vartheta\cdot\sin\varphi, \tag{24}$$

From Eqs. (1-7), we find

$$E_{i\vartheta} = \frac{3\cdot\varepsilon_o}{\varepsilon_i+2\cdot\varepsilon_o}\cdot E_p\cos\vartheta\cdot\cos\varphi \quad E_{i\varphi} = -\frac{3\cdot\varepsilon_o}{\varepsilon_i+2\cdot\varepsilon_o}\cdot E_p\cdot\sin\varphi \ , \tag{25}$$

The calculation of the normal force component acting on the surface charge is nontrivial, since the normal component exhibits a surface discontinuity. Solving this problem, we come to the result

$$E_{r,ef} = \frac{1}{2}\left(E_{r,p}+E_{r,o}+E_{r,i}\right) = \frac{3}{2}\cdot\frac{(\varepsilon_o+\varepsilon_i)}{\varepsilon_i+2\cdot\varepsilon_o}\cdot E_p\cdot\sin\vartheta\cdot\cos\varphi, \tag{26}$$

where $\vec{E}_{ef}$ is the effective field acting by force on the surface element dS. From Eqs. (25) and (26), we can see that the effective field can be presented by the sum $\vec{E}_{eff} = \vec{E}_a + \vec{E}_b$. Introducing the Cartesian unit vector $\vec{i}$ and the normal vector to the sphere surface $\vec{n}$, we find

$$\vec{E}_a = \vec{i}\cdot\frac{3\cdot\varepsilon_o}{\varepsilon_i+2\cdot\varepsilon_o}\cdot E_p \quad \vec{E}_b = \vec{n}\cdot\left(\vec{n},\vec{i}\right)\cdot\frac{3}{2}\cdot\frac{(\varepsilon_i-\varepsilon_o)}{\varepsilon_i+2\cdot\varepsilon_o}\cdot E_p, \tag{27}$$

The charge density is also expressed in terms of the vectors $\vec{i}$ and $\vec{n}$,

$$\sigma_1 = -\frac{3}{4\pi}\cdot\left(\frac{\varepsilon_o-\varepsilon_i}{\varepsilon_i+2\cdot\varepsilon_o}\right)E_p\cdot\left(\vec{n},\vec{i}\right), \tag{28}$$

Let us calculate the force averaged over the period, acting on a three-dimensional sector cut on a sphere by a cone with an axis coinciding with the vector $\vec{i}$ and the opening angle γ. We introduce an alternate spherical coordinate system $(r,\tilde{\vartheta},\tilde{\varphi})$ with a polar axis directed along the incident wave polarization vector $\vec{E}_p$ collinear to $\vec{i}$. Then the sought force can be expressed through the integrals

$$f_\gamma = \frac{\langle E_b \cdot Q\rangle}{4\pi} \cdot \int_0^\gamma \cos^3\tilde{\vartheta} \cdot a^2 \cdot \sin\tilde{\vartheta} \cdot d\tilde{\vartheta} \int_0^{2\pi} d\tilde{\varphi} + \frac{\langle E_a \cdot Q\rangle}{4\pi} \cdot \int_0^\gamma \cos\tilde{\vartheta} \cdot a^2 \cdot \sin\tilde{\vartheta} \cdot d\tilde{\vartheta} \int_0^{2\pi} d\tilde{\varphi}, \tag{29}$$

Here

$$E_a = 3E_p \cdot \frac{\varepsilon_o}{\varepsilon_i + 2\cdot\varepsilon_o}; \quad E_b = \frac{3}{2}E_p \cdot \frac{\varepsilon_i - \varepsilon_o}{\varepsilon_i + 2\cdot\varepsilon_o}; \quad Q = -3\cdot E_p \cdot \frac{\varepsilon_o - \varepsilon_i}{\varepsilon_i + 2\cdot\varepsilon_o}\cdot, \tag{30}$$

Angle brackets mean averaging over the oscillation period.

We calculate the stress as the ratio of the force to the sector base area $\pi\rho^2 \sin^2\gamma$.

$$T_\gamma = \xi(\gamma,\lambda) \cdot 1MPa \cdot \left(\frac{I}{10^{12}\,\frac{W}{cm^2}} \right), \tag{31}$$

Let us estimate the NP temperature change for the LP passage time. The energy released per unit volume per unit time is given by the relationship

$$Q = \frac{\omega}{8\pi} \cdot \varepsilon'' \cdot |E_i|^2, \tag{32}$$

Substituting the gold specific heat and density, we find

$$\Delta T = \frac{Q\cdot\tau_p}{C_{Au}\cdot\rho} = 2.4\cdot 10^3 K \cdot \beta(\lambda) \cdot \left(\frac{I}{10^{12}\,W/cm^2}\right) \cdot \left(\frac{\tau}{10^{-12}\,s}\right), \tag{33}$$

4. CONCLUSIONS

It was shown that NP heating by fs pulses plays an important role at LP radiation densities above 10^{14} W/cm^2. At the same time, we can see that, at the chosen LP intensities and durations when operating, the temperature reaches values exceeding the gold boiling point $T_{ev} = 3129K$. However, when using the laser in the near infrared region, the effect of NP heating is no longer determining. From this, we can conclude that such LP intensity and duration in the near IR region can be selected for gold NPs that the ablation effect can be observed without NP vaporization.

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