Equation of state for computer simulation of metal ablation by femtosecond laser pulses

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Abstract. In this paper a wide-range equation of state for computer simulation of metal ablation by femtosecond laser pulses is proposed. The simulation results are compared with experimental data for several metals (Al, Au, Cu, Ni). A good agreement for numerical results with experimental data shows that this equation of state together with two-temperature hydrodynamic model can be employed for choosing laser parameters to receive better accuracy in simulation of metal ablation.

1. Introduction
The rapid development of ultra-short lasers over the past decades make them very useful tool for laser materials processing. A great deal of progress in nanofabrication of materials has relied on the use of them. Production of nanoparticles can be done in several ways, one of them is laser ablation [1].

Despite extensive research work, accurate prediction of the ablation process is still lacking, because it significantly depending on laser parameters, surrounding medium and target material characteristics. Furthermore, to analyze the physical processes at high energy densities, when laser is used, an adequate description of the thermodynamic properties of matter over a broad region of states including the normal conditions and plasma at high pressures and temperatures is required.

Nowadays a two-temperature model has been widely employed for solving ultra-short laser processing of metals [2-5]. This continuous model describes the energy transfer inside a metal with two coupled generalized heat conduction equations for the temperatures of the electrons and the lattice. To describe the material removal processes two-temperature model is often inserted into a hydrodynamic code. But the choice of equations of state for materials, required for solving hydrodynamic equations, can significantly affect the results.

2. Equation of state
To solve the system of hydrodynamic equations in the two-temperature model we construct wide-range semi-empirical two-temperature equation of state. In this equation a metal is expected to consist of the same electrically neutral atomic cells with atomic weight \( A \) and charge \( Z \). To describe thermodynamic properties (such as pressure, temperature and internal energy) we use the Helmholtz free energy. For the single atomic cell it is proposed as the sum of three terms, describing the electronic and ionic components, and the interaction between them:

\[ F = F_e + F_i + F_{ei} \] (1)
As the main thermodynamic parameters we use atomic cell volume \( V \) and two temperatures: \( T_e, T_i \). The number of free electrons in one atomic cell we call the degree of ionization and denote by the letter \( y \). The pressure of the electrons is assumed to be the pressure of an ideal Fermi gas of electrons with density \( y/V \) and temperature \( T_e \), where \( y \) is the solution of the modified equation of ionization:

\[
\mu_F (\frac{y}{V}, T_e) + I(y) - B(V, T_e) = 0 \tag{2}
\]

Here \( \mu_F \) - the chemical potential of an ideal Fermi gas, \( I(y) \) - ionization potential, which is a smooth function of \( y \) and is constructed as a smoothing spline on the known experimental values of the successive stages of ionization \( I(1), I(2) \) etc. \( B(V, T_e) \) - negative correction, which purpose is the description of cold ionization of highly compressed matter:

\[
B(V, T_e) = b \left( \frac{y}{V} \right)^\delta (1 + \mu T_e V^\sigma)^{-1} \tag{3}
\]

where \( b, \beta, \sigma, \mu \) - parameters, determined from shock compression data of metals.

For the free energy of an ideal Fermi gas we use approximation:

\[
F_e = y T_e \left( \frac{3}{2} \phi - \frac{3}{2} \ln \left( 1 + \frac{5}{2\phi} \right) \right) \tag{4}
\]

where

\[
\phi = \frac{1}{2} \left( \frac{3\pi^2}{\sqrt[3]{y}} \right)^\frac{2}{3} / T_e \tag{5}
\]

From (4) we get formulas for the chemical potential, pressure and internal energy of the free electrons:

\[
\mu_F = \frac{1}{2} \left( \frac{3\pi^2}{\sqrt[3]{y}} \right)^\frac{2}{3} + T_e \left[ \left( 1 + \frac{2}{3} \phi \right)^{-1} - \frac{3}{2} \ln \left( 1 + \frac{5}{2\phi} \right) \right] \tag{6}
\]

\[
P_e = \frac{1}{5} \left( \frac{3\pi^2}{\sqrt[3]{y}} \right)^\frac{5}{3} + T_e \left( \frac{y}{V} \right)^\frac{2}{3} \left( 1 + \frac{2}{3} \phi \right)^{-1} \tag{7}
\]

\[
\varepsilon_e = \frac{3}{2} V P \tag{8}
\]

\( F_i \) is describing the transition from the crystal state at low temperatures to the state of an ideal ion gas at high temperatures:

\[
F_i = \frac{3}{2} T_i \ln \frac{1 + \lambda G}{\sqrt[3]{V}} \tag{9}
\]

where

\[
G = \left( \frac{4\pi}{3} \right) \frac{1}{\sqrt[3]{V}} \frac{y^2 (V)}{V^{3T_i}} \tag{10}
\]

and \( y_c (V) \) assumed to be a known function of the atomic volume \( V \), defined by the equation of ionization, \( \lambda \) - parameter of interpolation.

From (9) we get:

\[
P_i = T_i \frac{1 + 3\lambda G}{\sqrt[3]{V}} \frac{d \ln y_c (V)}{d \ln V} \frac{1 + \lambda G}{1 + \lambda G} \tag{11}
\]

\[
\varepsilon_i = \frac{3}{2} T_i \frac{1 + 2\lambda G}{1 + \lambda G} \tag{12}
\]

And finally, for \( P_{ei} \) we take into account that it should not affect the equation of ionization, full pressure should be equal zero at normal density and zero temperature, component of the internal energy must take into account the Coulomb attraction between the free electrons, at low densities \( P_{ei} \) must decrease rapidly, electron-ion interaction at a fixed density should decrease as the temperature increases:

\[
P_{ei} = - \frac{1}{5} \left( \frac{3\pi^2}{\sqrt[3]{V}} \right)^\frac{2}{3} \frac{y^2}{y_0^3} \frac{V^2}{1 + \delta + (1 + \delta) T_e / T^* (\sqrt[3]{V})^\rho} \tag{13}
\]
Here $V_0$, $\gamma$, $\delta$, $T^*$ are the parameters, determined from the known values of density, sublimation energy, isothermal compressibility and thermal expansion coefficient.

3. Two-temperature model

In this work we describe the evolution of material parameters using the conservation of mass, momentum and energy of electron and ion subsystems in a two-temperature single-fluid 1D Lagrangian form:

$$\frac{\partial}{\partial t} \left( \frac{1}{\rho} \right) + \frac{\partial v}{\partial m} = 0$$

(14)

$$\frac{\partial v}{\partial t} + \frac{\partial P_i}{\partial m} = 0, \quad v = \frac{\partial x}{\partial t}$$

(15)

$$\frac{\partial \varepsilon_i}{\partial t} + P_i \frac{\partial v}{\partial m} = \frac{\alpha_{ei}}{\rho} (T_e - T_i)$$

(16)

$$\frac{\partial \varepsilon_e}{\partial t} + P_e \frac{\partial v}{\partial m} = \frac{\partial}{\partial m} \left( k \frac{\partial T_e}{\partial m} \right) - \frac{\alpha_{ei}}{\rho} (T_e - T_i) + J_L$$

(17)

where $m$ is the mass coordinate, $dm = p dx, m = \int_0^x p dx$, direction of $x$-axis is chosen perpendicular to the irradiated surface of the metal, $v$ is the velocity, $t$ is the time, $\rho$ is the density, $\rho_0$ is the initial density, $P_e$ and $P_i$ are the pressures of electrons and ions, $T_e$ and $T_i$ are the temperatures of electrons and ions, $\varepsilon_e$ and $\varepsilon_i$ are the internal energies of electrons and ions, $\varepsilon = \varepsilon_e + \varepsilon_i$ are the full pressure and the internal energy.

For the coefficient of electron-ion relaxation $\alpha_{ei}$ we use formula from work [6] and energy of the absorbed laser radiation $J_L$, described by:

$$J_L = \frac{F_{abs}}{\tau_L \delta \sqrt{\pi \rho}} \exp \left( -\frac{t^2}{\tau_L^2} \right) \exp \left( -\frac{x(m,t)-x(m_0,t)}{\delta} \right)$$

(18)

where $\tau_L$ is the laser pulse duration, $\delta$ is the skin depth of metal, $F_{abs}$ is the laser radiation energy.

The electron wide-range thermal conductivity coefficient $k$ is constructed as an interpolation between limiting metal and hot plasma cases [7]. The viscosity and thermal conductivity of the ions are neglected in this model. To calculate the ablation depth, we perform an integration of the mass flux through the surface using the expression:

$$d = \frac{1}{\rho_0} \int_0^{\tau_L} J_L \rho v \big|_{x=x_0} dt'$$

(19)

4. Results

We compare simulation results (ablation depth) after a single laser shot with experimental data for aluminium, gold, copper and nickel. Ultrashort laser pulses are generated by an amplified all-solid-state Ti:Saphire laser chain [8]. Low energy pulses are extracted from a mode-locked oscillator. The pulses are then injected into an amplifying chain including: an optical pulse stretcher, a regenerative amplifier associated with a two-pass amplifier using a 20 W Nd:YLF laser as pumping source, and a pulse compressor. Linearly polarized pulses with wavelength centered on 800 nm, an energy of 1.5 mJ at 1 kHz repetition rate and typical duration of 100 fs were delivered.

The samples are mounted on a three-motorized-axes system with 0.5 $\mu$m accuracy. Experiments are performed in the image plane of an aperture placed before the objective. Focusing objectives of 25 mm or 10 mm focal lengths to obtain fluences in a range of 0.1 to 10 J/cm$^2$ with the same beam size, 16 $\mu$m in diameter, in the image plane.

For ablation depth measurements, grooves are machined by moving the sample, which is adapted such that each point on the groove axis undergoes 8 consecutive irradiations at each target pass. The number of times the sample passes in front of the fixed beam can be adjusted. Figure 1 shows a scanning electron microscopy (SEM) picture of the machined grooves on copper for 2, 4, 6, 8 and 10 passes.
The groove depth is measured by an optical profilometer with a 10 nm depth resolution. The ablation rates for each groove are deduced taking into account the sample speed, the repetition rate of the laser, the beam size and the number of passes. For each energy density an ablation depth averaged over a few tens of laser shots.

Figure 1. SEM picture of machined-groove profiles, from 2 to 10 passes, on a copper sample.

As we can see in figure 2 results of the simulation are close to experimental data for all metals in the range of 0.1 to 10 J/cm².

Figure 2. Experimental and numerical ablation depth on a target of different metals as a function of the laser fluence obtained with a 100 fs laser pulse.
Some disagreement is observed for gold and further investigation is required. The possible explanation of this problem is ignoring thermal excitation of d band electrons in Au [9]. These electrons can significantly contribute into heat capacity and electron-ion interaction and provide some underestimation of ablated depth.

5. Conclusion

A wide-range equation of state for computer simulation of metal ablation by femtosecond laser pulses is constructed. The simulation results for ablation depth using this equation together with two-temperature hydrodynamic model are in good agreement with experimental data for aluminum, gold, copper and nickel. It shows that this equation of state together with two-temperature hydrodynamic model can be employed for choosing laser parameters to receive better accuracy in simulation of metal ablation.

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