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Phase transitions in femtosecond laser ablation

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ABSTRACT

In this study we simulate an interaction of femtosecond laser pulses (100 fs, 800 nm, 0.1–10 J/cm²) with metal targets of Al, Au, Cu, and Ni. For analysis of laser-induced phase transitions, melting and shock waves propagation as well as material decomposition we use an Eulerian hydrocode in conjunction with a thermodynamically complete two-temperature equation of state with stable and metastable phases. Isochoric heating, material evaporation from the free surface of the target and fast propagation of the melting and shock waves are observed. On rarefaction the liquid phase becomes metastable and its lifetime is estimated using the theory of homogeneous nucleation. Mechanical spallation of the target material at high strain rates is also possible as a result of void growth and confluence. In our simulation several ablation mechanisms are taken into account but the main issue of the material is found to originate from the metastable liquid state. It can be decomposed either into a liquid–gas mixture in the vicinity of the critical point, or into droplets at high strain rates and negative pressure. The simulation results are in agreement with available experimental findings.

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1. Introduction

Ultrashort laser–matter interaction has become the subject of thorough investigations over the past years. Subpicosecond lasers have proved their efficiency in machining, microstructuring, synthesis of nanoparticles, and many other applications. To gain a better understanding of ultrashort nonlinear processes in targets after the laser irradiation a numerical modeling is used. Simulation is based mainly on continual models [1–5] or molecular dynamics [6,7]. The first approach can deal with the real-scale problems. To achieve good agreement with experiment semiempirical models with adjustable coefficients are also used [8]. Nevertheless, continual models have a difficulty of taking into account the micro-level effects such as evaporation, void growths and confluence. On the contrary, molecular dynamics operates with individual atoms and thus reproduces the micro-level mechanisms naturally. The basic problem of molecular dynamics is a choice and adjustment of an interatomic potential that must be in agreement with experimental data for a substance under consideration.

In this work we extend our hydrodynamic approach with kinetic models of evaporation, nucleation, pressure and temperature relaxations to describe the main processes of laser ablation of metals.

2. Computational model

In metals the conduction band electrons absorb laser energy in a skin layer and then transmit it into the bulk of the target. At the same time the temperature of the lattice rises due to electron–ion collisions. In this initial stage the temperature of electrons and ions can be essentially different [9].

Our present model is based on the multi-material Eulerian hydrodynamics with separate description of energy for electrons and ions [3,4]. Initially, the target occupies a half-space $x \geq 0$ and the laser pulse has a Gaussian profile in time. The parameters of the laser pulse are $\tau_L = 100$ fs, $\lambda_L = 800$ nm and $F_L = 0.1$ –10 J/cm², where τ_L , λ_L and F_L are the full width at half maximum of the pulse, wavelength and fluence, respectively. For relatively weak intensities the power density of the laser pulse, absorbed in a skin layer can be approximated by the Beer's law:

$$Q(x, t) = \frac{F_L(1-R)}{\sqrt{\pi/\ln(16)}\tau_L\lambda_{\text{opt}}} \exp\left[-\ln(16)\frac{(t-t_0)^2}{\tau_L^2}\right] \exp\left[\frac{-x}{\lambda_{\text{opt}}}\right].$$

Here R is the reflectivity, known at particular intensity from the pump-probe experiments [8], t is the time ($t \geq 0$) and $t_0 = 5\tau_L$. Optical penetration depth λ_{opt} is taken from the experiment [10].

The laser spot size is typically much bigger than the characteristic depth of the heat affected zone (micrometers versus nanometers) and for this reason we can consider the problem in one-dimensional geometry, at least for subnanosecond time

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delays. For longer time delays one needs to consider the problem setting in multi-dimensional case.

3. Equation of state

To complete the hydrodynamic equations we use a semiempirical multi-phase equation of state (EOS) with the separate expressions for the subsystems of heavy particles and electrons. The specific Helmholtz free energy has a form $F(\rho, T_i, T_e) = F_i(\rho, T_i) + F_e(\rho, T_e)$. Here ρ is the material density, while T_i and T_e are the temperatures of heavy particles (atoms, ions, nuclei) and electrons, respectively. The first term describes the contribution of heavy particles and the second one gives that of electrons. The ionic term F_i in turn consists of two parts: the electron–ion interaction part F_c (calculated at $T_i = T_e = 0$ K) and the contribution of thermal motion of heavy particles F_a . The analytical form of F_i has different expressions for the solid, liquid, and gas phases. Our EOS contains information about phase boundaries which are determined from the equality conditions for the temperatures T_i , pressures $P_i = \rho^2(\partial F_i / \partial \rho)_T$, and Gibbs potentials $G_i = F_i + P_i / \rho$ for each pair of phases. Tables of thermodynamic parameters are calculated taking into consideration the information about the phase transitions and metastable regions [11,12]. The free energy of electrons in metal F_e has a finite-temperature ideal Fermi-gas form [13].

4. Treatment of metastable states

In our model a special treatment of metastable states has been realized. It is known that a subpicosecond laser pulse can result in high-rate isochoric heating (see dashed thermodynamic paths AB1 and AB2 in Fig. 1) followed by the rarefaction of a substance (paths B1C1 and B2C2 in Fig. 1). On the rarefaction the thermodynamic pathway can cross the liquid branch of the binodal and enter into the metastable region (C1D1 and C2D2 in Fig. 1). The lifetime of the metastable state decreases exponentially in the vicinity of the spinodal because of the avalanche-like growth of bubble population. The typical space and time scales of nucleation are nanometers and picoseconds, and this process can be far from thermodynamic equilibrium. To remedy this problem additional kinetic models should be applied.

We consider the homogeneous nucleation as the basic mechanism of metastable liquid separation. It is assumed, that the nucleation process has three basic stages: (i) spontaneous appearance of critical size gas bubbles in liquid, (ii) growth of these

bubbles, and (iii) confluence of bubbles and final relaxation of pressure and temperature.

The first stage can be described by the critical bubble waiting time $\tau = (J_1 \nu)^{-1}$ [14], where J_1 is the nucleation rate and ν is the volume under consideration. The stability and growth of a new bubble is governed by the condition:

$$p^g > p^l + \frac{2\sigma}{r},$$

where p^g and p^l are the pressures in the gas bubble and liquid, respectively, r is the radius of the bubble and σ is the surface tension. The nucleation rate has a general form [14]:

$$J_1 = Cn \exp\left(\frac{W_c}{k_B T}\right),$$

where $C \approx 10^{10} \text{ s}^{-1}$ is the kinetic coefficient [15], n is the concentration, W_c is the work to create a bubble of critical radius and k_B is the Boltzmann constant. The work of the critical bubble formation can be derived as [14]:

$$W_c = \frac{16\pi\sigma^3}{3(p^g - p^l)^2}.$$

For bubbles of a nanometric radius the surface curvature contributes a lot into the mechanical balance and thus an appropriate wide-range expression for the surface tension is needed. Dependencies known from literature describe the surface tension mainly in the vicinity of the critical or triple points, ignoring the large area in the metastable liquid state where pressure is negative, see region below isobar 1 in Fig. 1. Keeping in mind the fact that the surface tension must tend to zero on the spinodal and knowing the experimental value at the melting temperature we can extend the Eötvös's law for liquid metals into the metastable liquid state:

$$\sigma(T, \rho) = \sigma_0 \left(\frac{T_c - T}{T_c - T_0} \right) \left(\frac{\rho_{bn}^l(T) - \rho_{bn}^g(T)}{\rho_{bn}^l(T_0) - \rho_{bn}^g(T_0)} \right)^{2/3} \left(\frac{\rho - \rho_{sp}^l(T)}{\rho_{bn}^l(T) - \rho_{sp}^l(T)} \right)^{1/2}.$$

Here T_c is the temperature in the critical point, σ_0 is the surface tension in the triple point at temperature T_0 , $\rho_{bn}^l(T)$ and $\rho_{bn}^g(T)$ are the densities on the liquid and gas branches of the binodal, respectively, and $\rho_{sp}^l(T)$ is the density on the liquid branch of the spinodal. The growth of bubbles on the second stage is governed by the pressure gradient. On the third stage the confluence of bubbles results in the final lost of uniformity by the liquid and formation of a stable two-phase liquid–gas mixture.

5. Model of evaporation

We use the model of Hertz–Knudsen [16] to calculate the mass flow of atoms leaving the unit surface during the unit time, $J_{\text{evap}} = p_{bn}^g \sqrt{m/2\pi k_B T}$.

Here p_{bn}^g is the pressure of the saturated gas (pressure at the binodal) at temperature T of the condensed phase. Taking into account the back flux in the form $J_{\text{cond}} = p^g \sqrt{m/2\pi k_B T^g}$ we can estimate the total volume fraction of evaporated or condensed substance on the surface S in any volume of interest ν during the time Δt as follows:

$$f_{\text{evap}} = (J_{\text{evap}} - J_{\text{cond}}) \frac{S \Delta t}{(\rho^l \nu)}.$$

The negative value of f_{evap} indicates that the condensation process predominates.

We adopt the procedures of pressure and temperature relaxation in any multi-phase cell of the size Δx using the relaxation law $dP/dt = -(P - P_{\text{eq}})/\tau_{\text{mech}}$, $dT/dt = -(T - T_{\text{eq}})/\tau_{\text{therm}}$. Here $\tau_{\text{mech}} \approx \Delta x / c_s$ and $\tau_{\text{therm}} \approx \Delta x^2 / \chi$ are the mechanical and

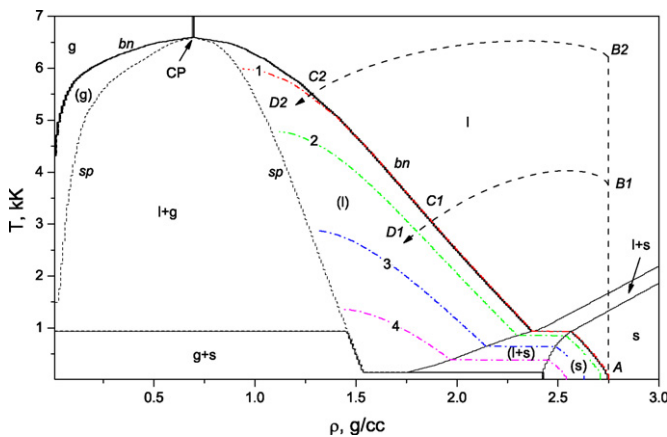


Fig. 1. Phase diagram of aluminum. Here sp: spinodal; bn: binodal; g: stable gas; l: stable liquid; s: stable solid; l + s: stable melting; l + g: liquid–gas mixture; g + s: sublimation zone; (g): metastable gas; (l): metastable liquid; (l + s): metastable melting; (s): metastable solid; CP: critical point. Dash-dot lines: isobars; 1: 0 GPa; 2: –1 GPa; 3: –3 GPa; 4: –5 GPa.

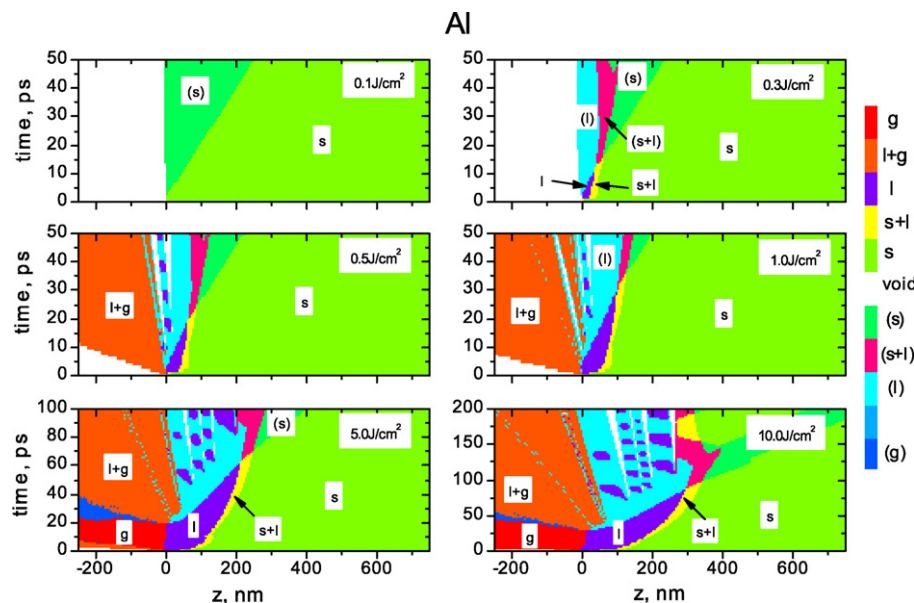


Fig. 2. Time-space diagram of distribution of phase states for Al. Here g: stable gas; l: stable liquid; s: stable solid; l + s: stable melting; l + g: liquid–gas mixture; g + s: sublimation zone; (g): metastable gas; (l): metastable liquid; (l + s): metastable melting; (s): metastable solid.

thermal relaxation time, respectively. Sound speed c_s and thermal diffusivity χ as well as equilibrium pressure P_{eq} and temperature T_{eq} are calculated on each time step [4]. This gives us the opportunity to describe the mechanical, thermal, and chemical relaxation in the system. Similar to the earlier work [5], we observe that this effect gives a small contribution into the entire amount of ablated material (the typical rate of ablation is about 1 nm per 100 ps).

6. Results and discussion

We perform the simulation of laser–matter interaction for Al, Au, Cu, and Ni and study the dependence of the results on the laser fluence. In Figs. 2–5 we present x – t diagrams of the phase states for these metals after irradiation. At fluences close enough to the

ablation threshold (~ 0.1 J/cm²) only the mechanical response is observed (the formation of a weak shock wave).

For fluence $F_L = 0.3$ J/cm², it is seen that the melted zone in Al is about 100 nm, whereas for other metals it varies from 20 to 40 nm. The process of melting is reversible as soon as the heat wave moves into the bulk and the temperature on the surface of the target drops. The melted layer becomes thinner at 20 ps for Au, at 10 ps for Cu and Ni, and almost disappears by the moments 50, 30, and 20 ps, respectively. For Al the melted layer is thick enough and stops to grow only at about 50 ps.

For higher fluence $F_L = 0.5$ J/cm², the picture of the target response differs a lot. Firstly, an intensive evaporation from the free surface takes place for all metals under consideration and the vapor moves away from the target at high speed (~ 10 km/s). Then, one can see that the nature of the melted front propagation into the

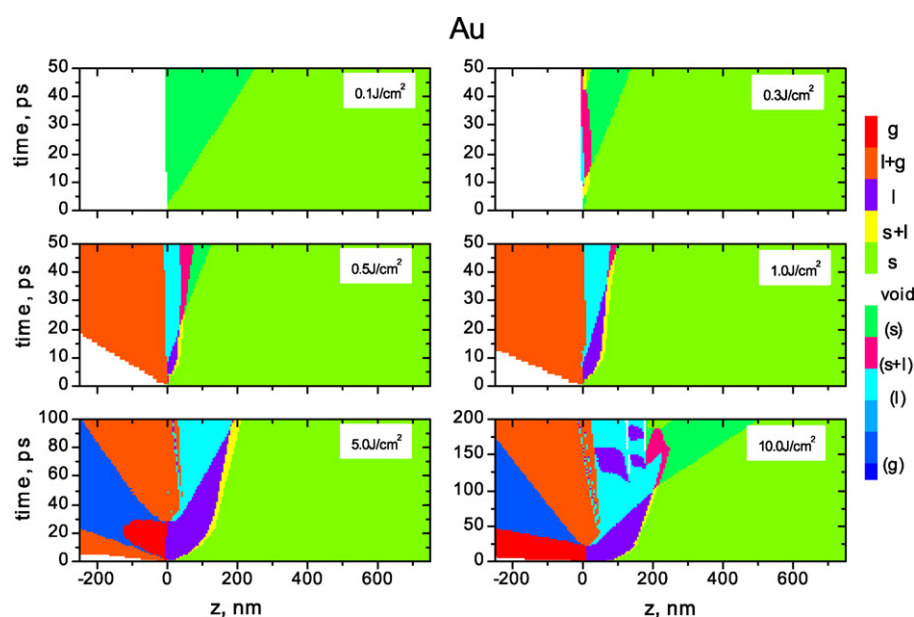


Fig. 3. The same as in Fig. 2, but for Au.

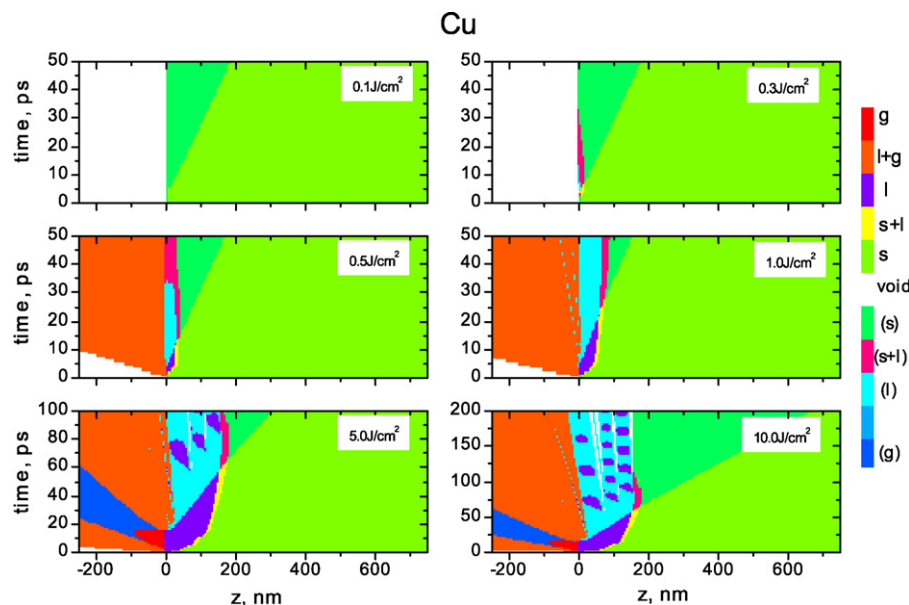


Fig. 4. The same as in Fig. 2, but for Cu.

bulk is essentially nonlinear. During several picoseconds the front goes deep into the bulk overtaking the shock wave. Finally, owing to the intensive tension of the melted layer on rarefaction the fragmentation (cavitation) starts and results in droplet formation (plates in 1D case). Drops have a typical size of tens of nanometers and are ejected at about 1 km/s.

Further increase of the fluence results in new physical effects. At 5 J/cm^2 an intensive evaporation takes place in a super-critical regime (the thermodynamic path goes above the critical point on rarefaction) when the transition from the liquid state to the gas one occurs without nucleation. The highest fluence in our simulation is 10 J/cm^2 because at bigger laser fluxes ionization effects cannot be neglected.

The simulation shows that the ablated material may consist of a gas fraction, liquid–gas mixture and liquid droplets. The mass balance between these fractions depends on the laser fluence at a

fixed wavelength and the pulse duration. Equilibrium melting and evaporation processes are taken into account based on the enthalpy of melting and evaporation, which are determined by the EOS.

We suppose here that the crater formation is governed by the evacuation of evaporated and melted fractions. Under this assumption we can estimate the depth of the crater explicitly considering the position of a new interface between the condensed phase and either void or gas, see Figs. 2–5. The results of simulation are in a reasonable agreement with the experiment [10,17]. The ablation depth per pulse is presented in Fig. 6. Some disagreement is observed for Au and further investigation is required. The possible explanation of underestimation of the ablated depth in our simulation is ignoring the fact that for Au the so-called d-electrons can be excited in this regime [18]. These electrons can contribute significantly into the heat capacity and

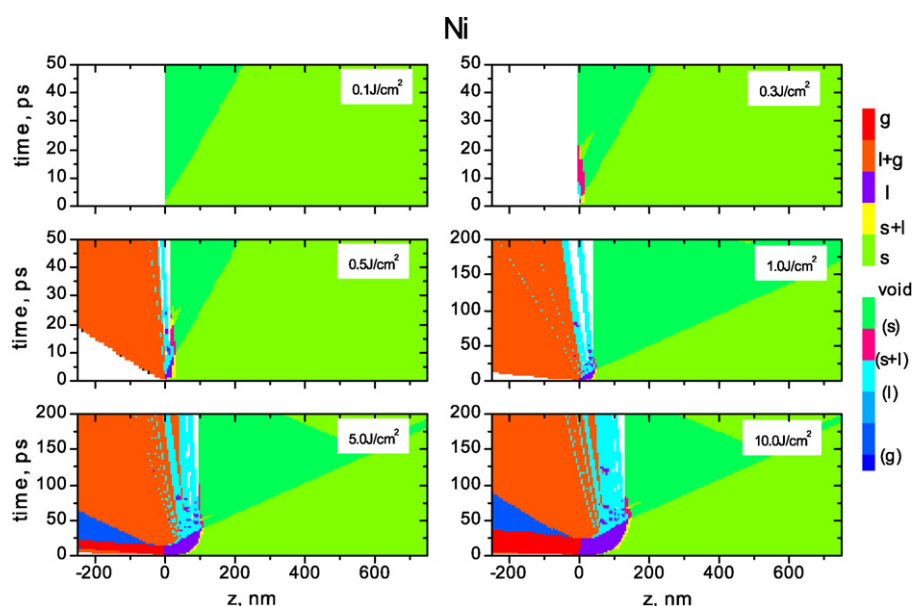


Fig. 5. The same as in Fig. 2, but for Ni.

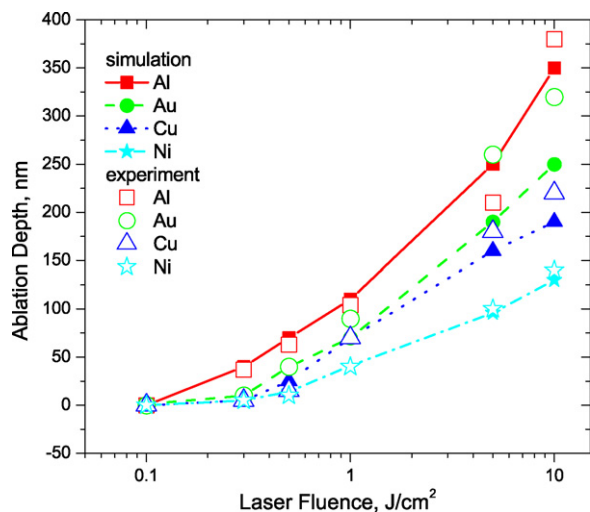


Fig. 6. Dependence of ablation depth on laser fluence for Al, Au, Cu, and Ni. Comparison with experiment is made for Al, Cu, and Ni [5] and for Au [17].

give rise to a faster electron–ion exchange and less energy dissipation into the bulk of the target.

7. Summary

The self-consistent model is developed for the description of femtosecond laser–metal interaction. Phase transitions are taken into account using a multi-phase EOS with separate electron and ion subsystems. Transport properties are modeled using a wide-range model of electron–ion collisions. We observe three mechanisms of laser ablation: (i) direct evaporation from the free surface, (ii) homogeneous nucleation in the neighborhood of the critical point, and (iii) mechanical cavitation in a liquid phase. The

mass fraction of the ablated material is mainly due to the mechanism (iii) (~80%), while the effect (ii) produces ~10–15% of the ablated material. Consideration of mechanical effects gives better description of the experiment.

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