

Equation of state for simulation of nanosecond laser ablation aluminium in water and air.

R. Davydov, V. Antonov, N. Kalinin

Peter the Great St.Petersburg Polytechnic University, Saint Petersburg, Russia

E-mail: davydovroman@outlook.com

Abstract. To analyze the physical processes at high energy densities, when laser is used, an adequate description the thermodynamic property of matter over a broad region of states including the normal conditions and plasma at high pressures and temperatures is required. For describing the thermodynamic properties of metals in nanoparticles production using laser ablation a semi-empirical equation of state model is proposed. To verify this model, an equation of state of aluminum was constructed. Using this equation was calculated ablation depths and crater profile for aluminum and compared with experimental data. Received results are in a good match with experiment.

1. Introduction

There is a growing interest in the nanofabrication of materials and their applications in various fields of life and technology, such as electronics, energy generation, health care and storage. A great deal of progress in this field has relied on the use of lasers. Production of nanoparticles can be done in several ways; one of them is laser ablation [1]. Evidence shows that this method is superior to other methods. Indeed, laser ablation in liquids, which consists of the pulverization of a solid target in liquid environment, gives a unique opportunity to solve the toxicity problems. In contrast to chemical nanofabrication methods, laser ablation can be performed in a clean, well-controlled environment, such as deionized water, giving rise to the production of ultrapure nanomaterial. The use of these particles decreases toxicity risks, which is especially important in vivo bio sensing and imaging applications [2].

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. For that a semi-empirical equation of state model is proposed, based on Thomas–Fermi model with quantum, exchange and oscillation corrections.

2. Equation of state for metal

The thermodynamic properties of metal are described by the Helmholtz free energy, which is considered as a sum of three components, describing the thermal contributions of electrons (F_e) and atoms (F_a) and the elastic part of the interaction at $T = 0$ K (F_c):

$$F = F_e + F_a + F_c$$

The first component is calculated within the framework of the Thomas–Fermi model with quantum, exchange and oscillation corrections [3]. The advantage of this model is easy expansion on mixtures and materials in the liquid medium, but it needed some corrections at normal conditions and



very high pressures. For that, two other components of the equation of state are calculated by empirical way.

The second component is given by formula:

$$F_a = 3RT \ln \left(\frac{\alpha(V_0/V)^{2/3} \exp \left(\left(\gamma_0 - \frac{2}{3} \right) \frac{B^2 + D^2}{B} \arctg \frac{B \ln(V_0/V)}{B^2 + D(\ln(V_0/V) + D)} \right)}{T^2} + \frac{\beta(V_0/V)^{2/3}}{T} \right)$$

Here γ_0 is the value of Gruneisen coefficient under normal conditions and coefficients A, B, C and D are determined comparing with available thermodynamic data for metals on high pressures.

The third component is given by interpolation formula [4]:

$$F_c = a_0 V_{0c} \ln(V_{0c}/V) - 3V_{0c} \sum_{i=1}^3 \frac{a_i}{i} \left((V_{0c}/V)^{-\frac{i}{3}} - 1 \right) + 3V_{0c} \sum_{i=1}^2 \frac{b_i}{i} \left((V_{0c}/V)^{\frac{i}{3}} - 1 \right)$$

The value of coefficient b_1 and b_2 are determined by expressions:

$$b_1 = - \left[Z^2 \frac{3}{10} \left(\frac{4\pi}{3} \right)^{\frac{1}{3}} + Z^{\frac{4}{3}} \frac{11}{36} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \right] a_B E_H (A m_u V_{0c})^{-\frac{4}{3}}$$

$$b_2 = Z^{\frac{5}{3}} \frac{1}{5} (3\pi^2)^{\frac{2}{3}} a_B^2 E_H (A m_u V_{0c})^{-\frac{5}{3}}$$

Here V_{0c} is the specific volume at $P = 0$ and $T = 0$ K, E_H is the Hartree energy, a_B is the Bohr atomic radius, m_u is the atomic mass unit (amu), A is the atomic mass (in amu), Z is the atomic number of an element.

To determine the coefficients a_i we must solve the problem of minimization of the root-mean-square deviation of pressure at points $V_n = \frac{V_{0c}}{10n}$, $n = 1, \dots, 100$ from the results of calculation by the Thomas–Fermi model with corrections subject to the conditions for the pressure, bulk modulus and its first and second derivative with respect to pressure at $V = V_{0c}$:

$$P(V_{0c}) = 0$$

$$B_c(V_{0c}) = - \frac{V dP_c}{dV} = B_0$$

$$\dot{B}_c(V_{0c}) = - \frac{dB_c}{dP_c} = \dot{B}_0$$

$$\ddot{B}_c(V_{0c}) = - \frac{d^2 B_y}{dP_y} = \ddot{B}_0$$

The problem of conditional minimization is solved with the introduction of Lagrange factors [5]. The values of the parameters V_{0c} , B_0 , \dot{B}_0 , \ddot{B}_0 are fitted by iterations so as to satisfy under normal conditions the tabular value of specific volume V_0 and the values of isentropic compression modulus and its pressure derivative determined by the data of dynamic measurements.

The received coefficients for aluminium:

$$V_{0c} = 0.36, a_0 = 6940.1, a_1 = -4772.4, a_2 = 1265.4, a_3 = 50.1, b_1 = -5061.1, b_2 = 1597.1, \beta = 0.001, D = 0.4, B = 0.4, \gamma_0 = 1.95, \alpha = 0.2, V_0 = 0.3687$$

3. Mathematical model of laser ablation

In this work, the nanosecond laser ablation rate of aluminum is investigated from low fluence to high fluence in air and water. For nanosecond pulses the plasma induced by laser ablation of metal targets can be described by the hydrodynamic equations [6]:

$$\begin{aligned} & \frac{\partial}{\partial t} \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho u \\ \rho v \\ E + 0.5\rho(u^2 + v^2) \end{pmatrix} + \frac{\partial}{\partial r} \begin{pmatrix} \rho_1 u \\ \rho_2 u \\ \rho u^2 + P \\ \rho uv \\ u(E + 0.5\rho(u^2 + v^2) + P) + q_r + Q_r \end{pmatrix} \\ & + \frac{\partial}{\partial z} \begin{pmatrix} \rho_1 v \\ \rho_2 v \\ \rho uv \\ \rho v^2 + P \\ v(E + 0.5\rho(u^2 + v^2) + P) + q_z + Q_z - I \end{pmatrix} \\ & + \frac{1}{r} \begin{pmatrix} \rho_{env} u \\ \mu_i \rho_i u \\ \rho u^2 \\ \rho uv \\ u(E + 0.5\rho(u^2 + v^2) + P) + q_r + Q_r \end{pmatrix} = 0 \end{aligned}$$

where ρ_1 and ρ_2 are the densities of the metal and air (or water), ρ is the total density defined as $\rho = \rho_1 + \rho_2$, u and v are the velocities in r and z direction, P the pressure, E the volumetric internal energy, I the net flux in laser radiation in the z direction, q_r and q_z the heat flux of thermal conduction in r and z direction, and Q_r and Q_z the radiative heat flux in r and z direction.

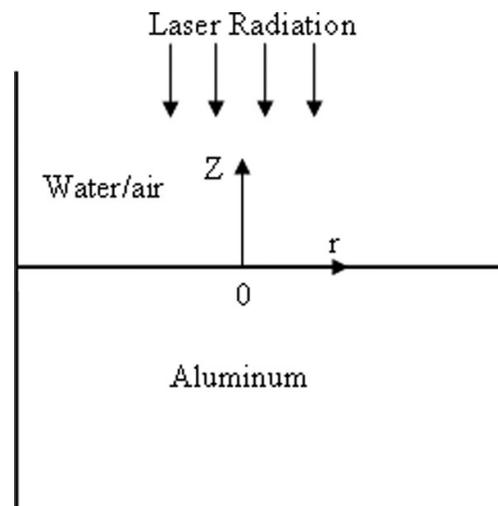


Figure 1. Schematic diagram of the model.

To solve the hydrodynamic equations, appropriate equations of state must be employed. For the aluminum targets we use equation of state constructed in previous chapter, for air and water we use equations described in articles [7, 8].

4. Results

Using the model were received the dependence of ablation depth on the laser pulse duration and also the profile of crater after a single laser shot:

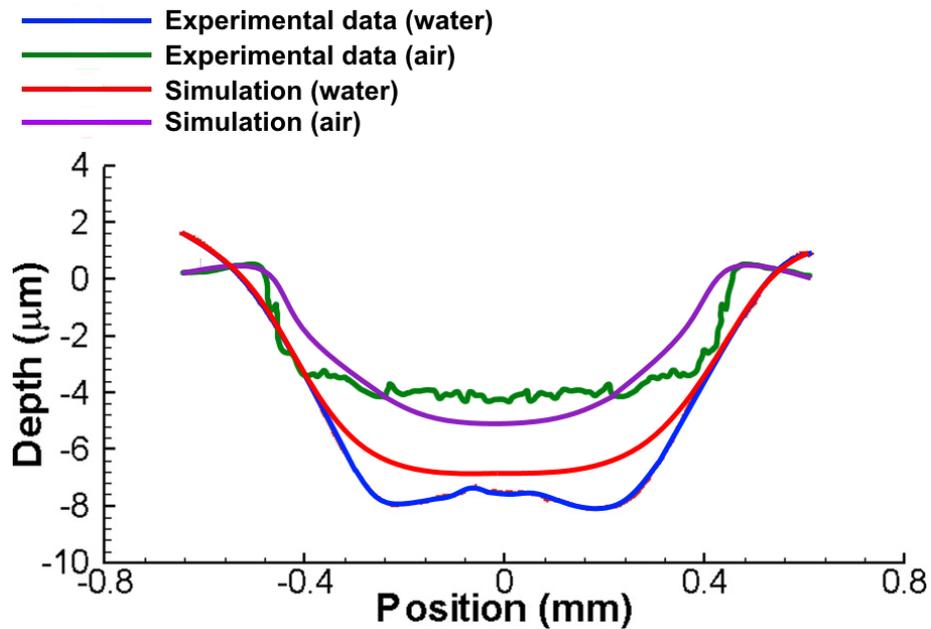


Figure 2. Crater profile after a single shot laser ablation (laser pulse duration 6 ns, wavelength 1064 nm, beam diameter 1 mm, laser fluence 24 J/cm², single shot laser ablation).

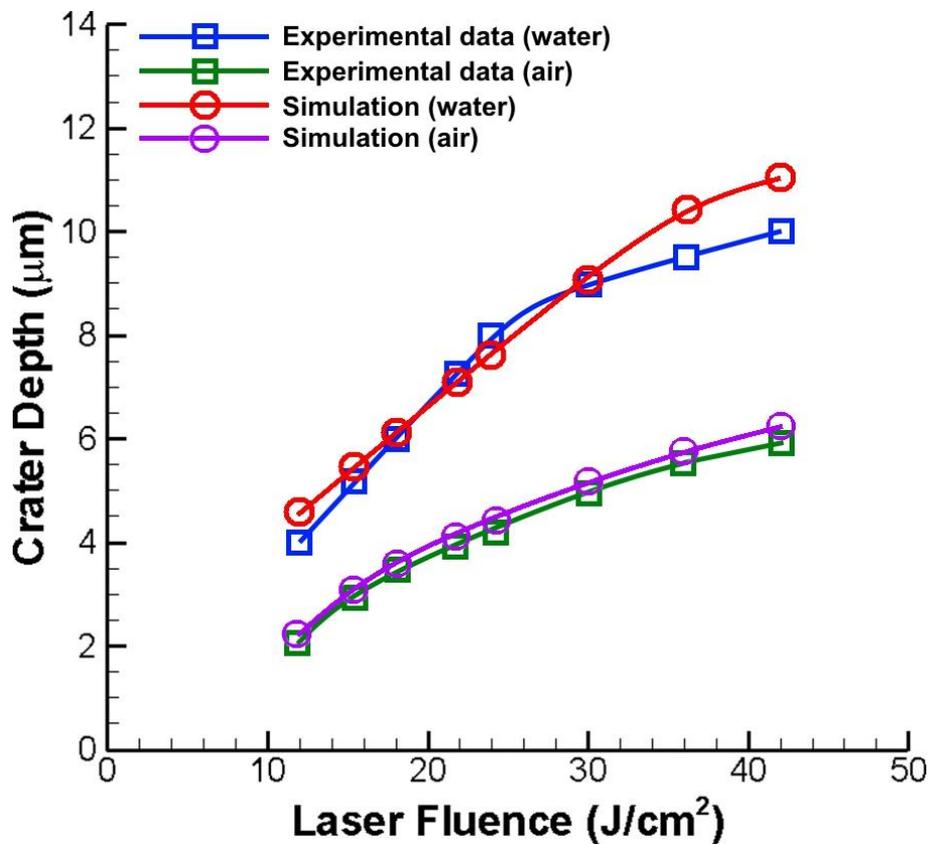


Figure 3. Crater depth under different laser fluences (laser pulse duration 6 ns, wavelength 1064 nm, beam diameter 1 mm, single shot laser ablation).

The ablation depths predicted agreed well with the experiments both in air and water. Also the simulated crater profile is relatively close to the experimentally (on the bottom and on the edges too). The described equation of state can be modified for other metals and used for improving accuracy simulation laser ablation.

References

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