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Dynamics of liquid nanodroplet formation in nanosecond laser ablation of metals

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ABSTRACT

The laser ablation mechanisms of metallic targets leading to liquid nanodroplet ejection are of wide interest both from a fundamental point of view and for applications in various fields, especially when nanoparticle synthesis is required. The phase explosion process was recognized as the driving mechanism of the expulsion of a mixture of vapor and liquid nanodroplets in the short pulse laser ablation of metals. A model based on thermodynamics that links the theory of homogeneous vapor bubble nucleation to the size distribution of the generated liquid nanoclusters has been recently proposed. The present work aims to take a step ahead to remove some assumptions made in previous work. Here an improved computational approach allows us to describe time-dependent nucleation in a homogeneous system with no temperature spatial gradients under nanosecond laser irradiation. Numerical results regarding the size distribution of formed liquid clusters and the time evolution of the process are shown for aluminum, iron, cobalt, nickel, copper, silver and gold. Connections with experimental data and molecular dynamics simulations, when available from literature, are reported and discussed.

1. Introduction

The synthesis of metallic and metal-based nanoparticles (NPs) by pulsed laser ablation has recently met new promising applications in materials science. In this field, the development of physically grounded theoretical models of the NPs formation mechanisms in the laser irradiation of metal targets is clearly important from both a basic point of view as well as to engineer the nanostructures. In a recent work [1] we directly connected the theory of homogeneous nucleation to the size distribution of the liquid nanodroplets that are formed in the phase explosion of metals.

Here we present the results of computational simulations that describe time-dependent nucleation in 3D systems of 100 nm side with several heating rate values used as input parameters. Moreover, we numerically solved the hydrodynamic–thermodynamic problem of spherical vapor bubble growth as function of time in a uniform superheated metal by implementing the method proposed by Lee and Merte [2]. The process of vapor bubble growth was parametrized for the different metals, temperatures and heating rates and was then included in the phase explosion simulation. The expansion of the whole system due to the increasing temperature and to the liquid-vapor phase transition is computed as a function of time.

In particular we studied the size distribution of the liquid nanodroplets generated in the phase explosion process and the characteristic time scales of the phenomena involved (the time lag of homogeneous nucleation, the characteristic time of the bubble growth process and the typical time duration of phase explosion). The numerical results of our modeling are here reported for aluminum, iron, cobalt, nickel, copper, silver and gold.

2. Theory and calculation

2.1. Thermodynamics of metastable liquid metals

In order to study the thermodynamics of liquid metals in the vicinity of the thermodynamic critical temperature T_c, we considered some semi-empirical scaling laws consistent with the theory of critical exponents [3]. In this context, the thermodynamic quantities can be expressed as functions of the expansion parameter $\Delta T = (T_c - T)/T_c$. The analytical approximated expressions describing the critical behavior of the thermodynamic quantities are obtained by fitting the experimental data available in literature for liquid metals with the theoretical scaling laws.

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As regards the temperature dependence of the enthalpy of vaporization Δh_v, we applied the Watson model [4]:

$$\Delta h_v(T) = \Delta h_v(T_b)\left(\frac{\Delta T}{\Delta T_b}\right)^{0.38}, \quad (1)$$

where ΔT_b is referred to the normal boiling point T_b. The surface tension σ was expressed as a function of the temperature through the Guggenheim formula [5]:

$$\sigma(T) = \sigma_m\left(\frac{\Delta T}{\Delta T_m}\right)^{11/9}, \quad (2)$$

where σ_m and ΔT_m are the surface tension and the expansion parameter at the melting point, respectively. The liquid-vapor coexistence curve was modeled as in our previous work [1].

To find a reliable temperature-dependent expression for the thermal conductivity of metastable liquid metals, we first considered the Wiedemann–Franz law, that establishes the relation between the thermal conductivity and the electrical conductivity and which was proven to be valid for Fermi liquids up to the metal-insulator transition [6]:

$$\frac{K_e}{\sigma_{el}T} = \frac{\pi^2 k_B^2}{3e^2} = L, \quad (3)$$

where K_e is the electron contribution to the thermal conductivity, σ_{el} is the electrical conductivity, and $L = 2.44 \times 10^{-8}\,\mathrm{W\,\Omega\,K^{-2}}$ is known as the Lorentz number. Then we adopted the model proposed by Korobenko et al. [7] for the electrical conductivity of liquid metals at high temperatures, based on the Drude–Sommerfeld free electron model. Finally we assumed the thermal conductivity of liquid metals to be entirely due to the electron contribution, so that $K \approx LT\sigma_{el}$. The effective valence z_{ion} used in this model was taken as reported in Table 1.

Provided that the critical behavior of the specific heat capacity at constant volume c_v is described by the universal law with the critical exponent $\alpha \approx 0.1$, the temperature dependence of the isobaric specific heat capacity of the liquid phase $c_{p,l}$ was approximated by a semi-empirical rule [8]:

$$c_{p,l}(T) = c_{p,l}(T_m)\left(\frac{\Delta T}{\Delta T_m}\right)^{-0.24}. \quad (4)$$

The binodal line in the phase diagram is established by the Clausius–Clapeyron equation,

$$\frac{dp_s}{dT} = \frac{\Delta h_v(T)}{T[v_v(T) - v_l(T)]}, \quad (5)$$

where v_v and v_l are the vapor and liquid molar volumes, respectively. The vapor pressure inside the nucleated vapor bubbles p_v and the liquid pressure p_l due to the recoil effect in the fast vaporization from the free surface, as well as the thermodynamic critical parameters, were calculated as in our previous study [1]. The main parameters used for the estimation of the thermophysical quantities are summarized in Table 1.

2.2. Homogeneous vapor bubble nucleation

If we assume that the vapor bubbles nucleated in the metastable liquid are spherical, the classical expression for the critical radius of the vapor bubbles r_c (i.e. the vapor bubbles which are in labile equilibrium with the liquid phase) is:

$$r_c = \frac{2\sigma}{p_v - p_l}, \quad (6)$$

with σ being the surface tension. Within the framework of the classical theory of homogeneous nucleation, as discussed by Skripov [18], the nucleation frequency of near-critical vapor nuclei per unit volume can be expressed as:

$$J_s = \frac{\rho_l}{m}\sqrt{\frac{6\sigma}{(3-b)\pi m}}\, e^{-\frac{\Delta h_v}{RT}} e^{-\frac{W_c}{k_B T}}, \quad (7)$$

where m is the atomic mass, $b = 1 - (p_l/p_v)$ and W_c is the free energy of critical vapor bubble formation. Eq. (7) holds in case of a steady nucleation process, but in real systems (in particular in the fast thermal processes that occur in the pulsed laser heating of metals) the steady conditions can only be attained asymptotically with a characteristic time lag expressed as [18]:

$$\tau_{lag} = \sqrt{\frac{2\pi m}{k_B T}}\frac{4\pi\sigma p_v}{(p_v - p_l)^2}. \quad (8)$$

The effective nucleation frequency, J^*, can be found by solving the following differential equation [19] for a given time evolution of the liquid temperature:

$$\frac{dJ*}{dt} + \tau_{lag}^{-1} J* = \tau_{lag}^{-1} J_s. \quad (9)$$

If we assume as a simplifying hypothesis that the liquid temperature is constantly increasing, with an arbitrary time derivative dT/dt, we can solve numerically Eq. (9) as shown in Fig. 1.

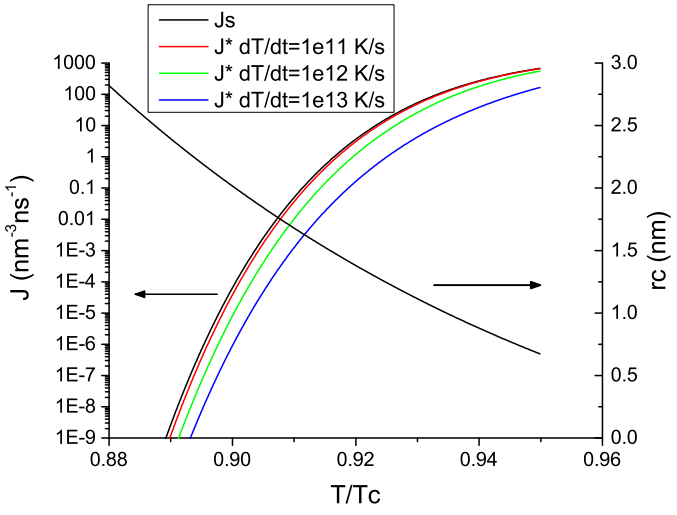

Fig. 1. Vapor bubble nucleation frequency in both steady and unsteady cases for aluminum. Three different constant heating rates were considered. On the right axis the critical radius is reported in the same temperature range.

2.3. Single bubble expansion in superheated liquid metal

The dynamics of a single vapor bubble in a homogeneous liquid metal was studied by adopting the model developed by Lee and Merte [2] for water, sodium and other low T_b substances. This approach includes the influences of surface tension, liquid inertia and heat diffusion and consists of the following coupled equations:

$$\begin{cases} R\dfrac{d^2R}{dt^2} + \dfrac{3}{2}\left(\dfrac{dR}{dt}\right)^2 = \dfrac{P_v(T) - P_\infty}{\epsilon\rho_l} - \dfrac{2\sigma(T)}{\epsilon\rho_l R} - 4\dfrac{\mu}{\epsilon\rho_l R}\dfrac{dR}{dt} & (10a) \\ \dfrac{\partial T}{\partial t} + \epsilon\dfrac{R^2}{r^2}\dfrac{dR}{dt}\dfrac{\partial T}{\partial r} = \dfrac{K}{\rho_l c_{p,l}}\left(\dfrac{\partial^2 T}{\partial r^2} + \dfrac{2}{r}\dfrac{\partial T}{\partial r}\right). & (10b) \end{cases}$$

Eq. (10a) is the equation of expansion, where R is the bubble radius, $\epsilon = 1 - \rho_v/\rho_l$ and μ is the dynamic viscosity defined as:

$$\mu = \frac{1}{3}\left(\frac{2\sigma K}{\pi\rho_l c_{p,l}}\right)^{1/2}\rho_v\frac{\Delta h_v}{K}(T_\infty - T_{sat})^{-1} \times\left\{\rho_v[p_v(T_\infty) - p_\infty]\right\}^{-1/4}. \quad (11)$$