The Direct Simulation Monte Carlo Of Cluster Formation Processes In Laser Plume

N.Y. Bykov, G.A. Lukyanov

Saint-Petersburg State Polytechnical University, Polytechnicheskaya 29, 195251 St.-Petersburg, Russia
nbykov@nm.ru, nbykov2006@yandex.ru

Abstract. A model of neutral cluster formation for the direct simulation Monte Carlo (DSMC) method has been elaborated. This model was united with the hybrid model of pulsed laser ablation process which based on joint solution of the thermal problem of laser-induced material vaporization and the gasdynamic problem of ablated products vapor expansion. The general model was applied for simulation of cluster growth processes in laser plume. The ablation of niobium target by laser pulse of moderate intensity and nanosecond scale was considered as an example. The analysis of cluster growth process and time evolution of particles size distributions revealed two characteristic stages: the stage of clusterization and stage of flow with frozen composition of vapor. For considering parameters clusterization degree for the second stage was approximately 0.007 and largest clusters consisted of 7 atoms. It was not observed the strong influence of cluster formation processes on flow parameters. The dynamics of clusters motion was analyzed in details. It was revealed that velocity of clusters is practically the same as monomers velocity.

Keywords: Cluster formation, pulsed laser ablation, laser plume, the direct simulation Monte Carlo (DSMC).
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INTRODUCTION

Pulsed laser ablation (PLA) of solids is a powerful technique in a variety of scientific and technological applications such as thin film deposition, micromachining and nanostructures synthesis [1]. The PLA is very complex phenomenon that includes a variety of interrelated processes such as laser radiation absorption, heating, melting, and vaporization of the material and expansion of the ablation products into surroundings.

Usually the PLA is accompanied by clusters formation process. Depending on initial parameters clusters may be ejected from the target with following growth in flowfield or formed directly in expanding vapor. Presence of clusters in laser plumes under PLA has crucial significance for the efficiency of different technologies. Understanding of such complicated phenomenon as PLA and estimation of technology convenience require development of mathematical models and approaches which describe in details all processes including clusters formation.

The development of cluster formation model for PLA in vacuum or rarefied ambient gas is rather difficult problem because of the intricate flow dynamics with very high rate of vapor expansion, cooling and existence of flow thermal non-equilibrium. It seems that the direct simulation Monte Carlo (DSMC) method is more adequate technique for process modeling in this situation.

Some attempts to formulate model of neutral cluster formation were made recently [2-5]. The first paper devoted to DSMC of cluster growth processes was [2]. The modeling was fulfilled for null dimension case without taking into account internal degrees of freedom and some classes of reactions as three body collisions. In paper [3] processes of three-body recombination and particles dissociation were considered under DSMC modeling of laser ablation of germanium target. Some future steps were made by employment of classical RRK theory results for description of atom evaporation in work [4] devoted to modeling of the agglomeration and fragmentation processes of Cu atoms and clusters in an Ar buffer gas. A two-stage computational model based on both the molecular dynamics (MD) method and the DSMC technique was developed in [5] for the case of picoseconds laser ablation of an organic solid with consideration of cluster ejection and growth processes.

This paper is devoted to the elaboration of neutral clusters formation model in terms of DSMC, unification this model with hybrid model of target vaporization and ablated products expansion [6,7] and investigation by the general approach of cluster growth and decay processes in laser plume. The important features of our cluster formation model for DSMC method are in accurate consideration of all possible reactions including three body collisions for dimers formation and accurate treatment with energy exchange processes that involve translation, rotation and vibration degrees of freedom with taking into account energy release or absorption under reactions of association or destruction.

Finally we present general model of PLA and results of laser plume simulation including clusterization process for the case of metal target vaporization by nanoseconds laser pulse of moderate intensity.

MODEL AND NUMERICAL METHOD

The scheme of considering PLA process is shown in Fig.1 and includes interrelated processes in target volume and surface (heating and evaporation by laser radiation) and into surrounding above the surface (flow of ablated products with physic-chemical processes in a volume). The presented general model is an extension of PLA model without processes of condensation [6,7]. The model may be divided into three parts: the model which describes absorption of laser radiation by target volume, heating and evaporation of a target (the heat model), the model for description of evaporated vapor dynamics (the model of expansion) and related to the last one the model of cluster formation and growth processes (the cluster formation model).

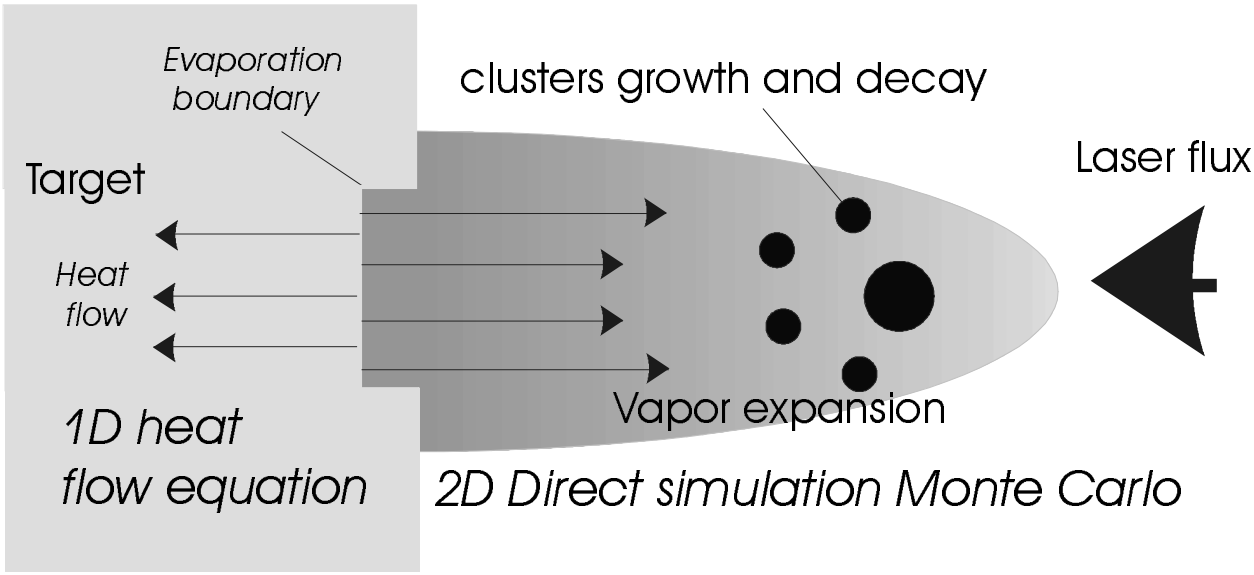

FIGURE 1. The general scheme of the PLA process modeling.

The Heat Model

To describe the thermal state of the laser-irradiated material, the heat flow equation is used in a one-dimensional form, as appropriate to many experimental situations:

$$c\rho\left(\frac{\partial T}{\partial t}-\omega(t)\frac{\partial T}{\partial x}\right)=\frac{\partial}{\partial x}\lambda\frac{\partial T}{\partial x}+\alpha I(x,t). \quad (1)$$

Here x-coordinate, t – time, T – temperature; c, λ, and ρ are the thermal capacity, thermal conductivity, and target material density, respectively, and $\omega(t)$ is the velocity of surface recession. Laser radiation is distributed in the irradiated target as a volume source related to incident laser power $I_0(t)$ of Gaussian temporal shape as

$$I(x,t)=I_0(t)(1-R)\exp(-\alpha_r x) \quad (2)$$

with R and α_r to be the coefficients of reflection and absorption.

The velocity of surface recession is determined as $\omega(t) = mF/\rho$ where F is the total particle flux through a surface which is conterminous with the vaporization front and m is the mass of an atom. We supposed that only atoms are evaporated from the surface. The rate of evaporation follows the Hertz-Knudsen equation and the vapor pressure above the vaporized surface is estimated with the Clausius-Clapeyron equation [8,9]. The boundary conditions and peculiarities of numerical method are discussed in [6].

The Model Of Vapor Expansion

For the description of vapor motion we employ the DSMC method in cylindrical symmetry. The numerical scheme with no time counter (NTC) is realized with the hard-sphere (HS) collision dynamics [10]. The cross-section for particles collisions for HS-model is defined as

$$\sigma = \pi(r_i + r_j), \tag{3}$$

where r_i, r_j – the radii of particles i and j correspondingly.

The calculated region in the simulation represents a cylinder with sizes of 3r in radius and 5r in length (r is the irradiation spot radius). For re-indexing the particles and choosing the macroparameters, a rectangular zone grids are used whose parameters were varying during calculations.

The boundary conditions at the surface are defined by the solution of the equation (1) with the temperature-dependent parameters c and λ according to methodology suggested by [7].

The Clusters Formation Model

We suppose that all particles are neutrals, only atoms are evaporated from the surface and cluster formation in laser plume is the result of particles collisions. We consider elastic collision of atoms

$$A + A \longrightarrow A' + A', \tag{4}$$

atomic recombination by three body collision

$$A + A + A \xrightarrow{p1} A_2' + A', \tag{5}$$

association of atoms and clusters

$$A_i + A \xrightarrow{p2} A_k'(k = i + 1), \tag{6}$$

association of clusters

$$A_i + A_j \xrightarrow{p3} A_k'(k = i + j), \tag{7}$$

atom evaporation from a cluster

$$A_k \longrightarrow A_{k-1}' + A'. \tag{8}$$

Index $'$ relates to the particles after collision (reaction).

In case of three body collision (5) or pair collisions (6), (7) association takes place with probabilities p_1, p_2, p_3 correspondingly. These probabilities in general case are functions of energy of relative motion, values of internal energy of colliding particles, configurations of clusters and geometry of collision.

A cluster is described by number of atoms k, mass m_k, radius r_k, velocity $\vec{v}_k$, internal energy $E_{int,k}$, and binding energy $E_b(k)$. Cluster radius is defined by spherical drop liquid model [11]

$$r_k = r_w k^{1/3}, r_w = \left(\frac{3m_k}{4\pi\rho}\right)^{1/3}. \tag{9}$$

In considering model clusters have fully excited rotation and vibration degrees of freedom. The internal energy of a cluster is presented as

$$E_{\text{int},k} = E_{r,k} + E_{v,k}, \tag{10}$$

$$E_{r,k} = \frac{\zeta_r}{2} k_b T_{r,k}, E_{v,k} = \frac{\zeta_v}{2} k_b T_{v,k}, \tag{11}$$

where $E_{r,k}$ and $E_{v,k}$ – energies of rotation and vibration degrees of freedom, ζ_r and ζ_v – number of rotation and vibration degrees of freedom, $T_{r,k}$ and $T_{v,k}$ – rotation and vibration temperature of a cluster, k_b – Boltzmann's

constant. It is regarded $\zeta_r=2$, $\zeta_v=2$ for dimers, $\zeta_r=3$, $\zeta_v=6k-12$ for other clusters. It is supposed that $T_{r,k} = T_{v,k} = T_{int,k}$, $T_{int,k}$ – internal temperature of a cluster.

The binding energy of a cluster may be presented as [11,12]

$$E_b(k) = a_v k - a_s k^{2/3}, \tag{12}$$

where a_v and a_s – constants depending on target material.

We employ Larsen-Borgnakke (LB) model [10] for description of energy exchange between reacting particles and theirs vibration-rotation-translation (VRT) degrees of freedom. In case where all reaction probabilities are unities this model is used only for description of processes (5) and (8).

For determination of atom evaporation frequency according to process (8) we use next equation:

$$\nu = \nu_0 k_s \exp[-\frac{\zeta_v \Delta E_b}{2E_{v,k}}], \tag{13}$$

$$\Delta E_b = E_b(k) - E_b(k-1). \tag{14}$$

Here k_s – number of surface atoms ($k_s=k$ for small clusters), $\nu_0 = 10^{13}$ c^{-1} – characteristic frequency of vibration. The equation (13) is the variant of approximate equation of RRK theory [13].

RESULTS AND DISCUSSION

We employ the general model for description of PLA processes including cluster formation and growth in a vapor for the simulation of laser plume from niobium target. The surrounding was vacuum. The energy of laser radiation was 5 J/cm^2. The pulse had gaussian temporal profile with full width half maximum (FWHM) time τ_L=13ns. The radius of irradiated spot r was 0.3mm. Thermophysical parameters of a target were borrowed from [8]. All probabilities of association processes were unities. The constant in equation (12) for the case of small niobium clusters were a_v = 9.5eV and a_s =8.3eV [12].

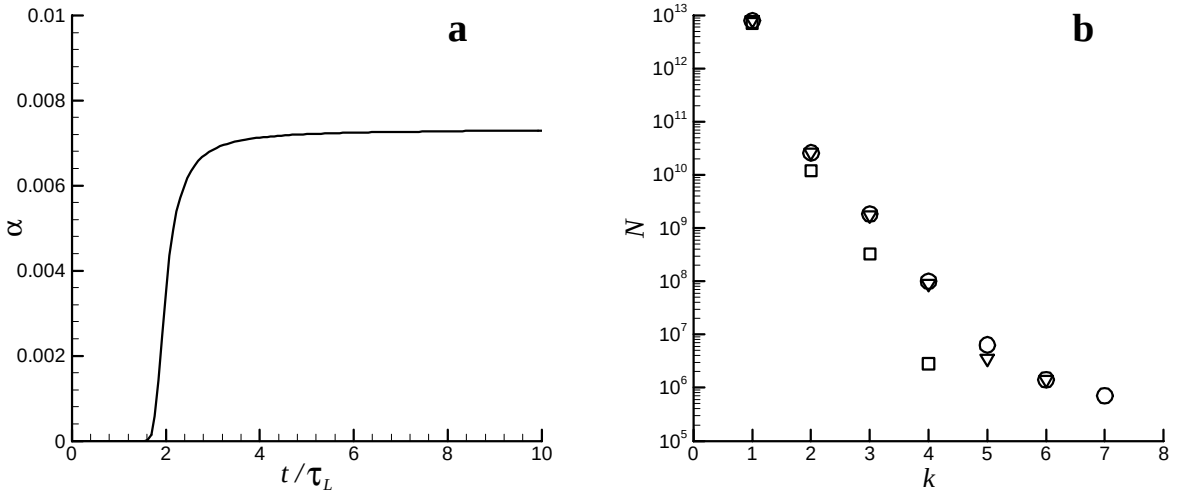

FIGURE 2. The time dependence of clusterization degree (a) and size distributions of clusters for time moments t/τ_L = 2 (□), 4 (▽) and 6 (○).

For characterization of the vaporization process, it is convenient to use some average parameters. An average surface temperature may be determined, according to [9], as $T_{AV} = \sum T_i N_i / \sum N_i$ (T_i is the mean temperature corresponding to a time step i and N_i is the number of the molecules vaporized at this time step). An average density may be presented as $n_{AV} = 4N/(v_T \tau_L \pi r^2)$, where N is the total number of vaporized atoms, v_T is the average thermal velocity of the particles determined by T_{AV}. Using these average parameters, we can determine two characteristic Knudsen numbers for nonstationary axisymmetrical flow: $Kn_1 = \lambda / r$ and $Kn_2 = \lambda/(v_T \tau_L)$ (λ is the

mean free path determined by n_{AV}). The Knudsen numbers and the average parameters are given in Table 1. The calculated ablation rate is 2 monolayers.

TABLE 1. Average parameters of the ablation process.

E_0, J/cm^2	T_{AV},K	n_{AV},m^{-3}	Kn_1	Kn_2
5	5871	$9.26*10^{24}$	$0.97*10^{-3}$	0.019

The time evolution of a degree of vapor clusterization $\alpha = \sum_{k=2} kc_k / c_1$ (c_k – is the volume fraction of A_k clusters in a vapor) is presented in Fig.2a. The results demonstrate the presence of two stages of clusterization process: (i) the stage of clusters formation; (ii) the stage of expansion with frozen vapor composition. The duration of clusters formation stage is approximately 1-1.2 τ_L. For this stage the degree of vapor clusterization reaches value 0.007 and remains constant for the next stage.

The clusters size distributions (for whole modeling field) for time moments t/τ_L = 2, 4 and 6 are shown in Fig.2b. There are only small clusters (up to 7 atoms) in laser plume for considering case. The main part of clusters is dimers. Theirs volume fraction in the mixture for $t/\tau_L > 4$ is of the order 0.006. The size distribution after $t/\tau_L > 2$ varies slightly and stabilizes after $t/\tau_L > 4$.

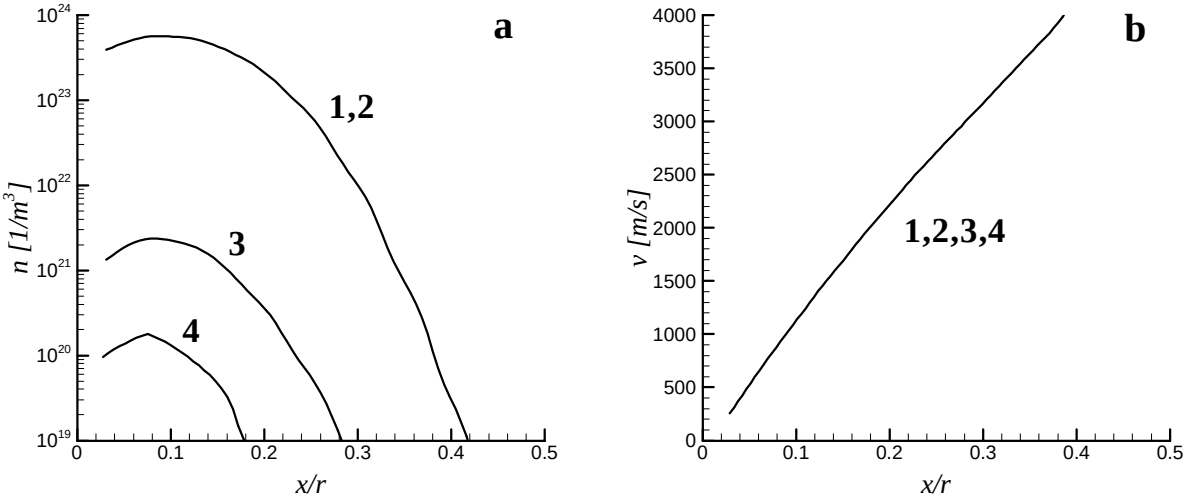

FIGURE 3. Axial distributions of density n (a) and velocity v (b) for atoms (1 – simulation without processes (5)-(8); 2 – simulation with processes (5)-(8)), dimers (3) and trimers (4) for the time t/τ_L = 4.

Weak influence of condensation process on gasdynamic parameters may be predicted for such low clusterization degree. We fulfilled the same simulation without taking into account cluster formation and decay processes (5)-(8) with the purpose of comparison. Fig.3 demonstrates axial distributions of density and velocity of monomers, dimers and trimers for the time moment t/τ_L = 4. The flow has one-dimension structure in the considering case [14] so these distributions characterize main part of real vapor. Practically there is not influence of cluster growth process on expansion gasdynamics. The density and velocity of atoms for both calculation variants coincides with each other. It is very interesting fact that velocities of atoms and clusters are approximately the same in depended of mass. The coordinates of density maximums are also very close to each other. There is a little difference in axial distributions of temperature (Fig.4a). The temperature of atoms for simulation with taking into account cluster formation process is slightly more in comparison with non-reactive flow. Shapes of temperature curves are typical for expansion in vacuum [14].

Results presented in Fig.4b demonstrate the time evolution of average per simulation volume internal energy distribution functions for trimers. The data correspond the time moments t/τ_L =2, 2 – 4, 3 – 6. For the cluster formation stage internal energy of clusters is in range 6-7eV. For the stage of vapor expansion with frozen composition internal energy has values from 0 to 2-3eV. Internal energy equilibrium functions are also shown in Fig.4b. These functions correspond to equation [10]

$$f(E_{\text{int},k}) \propto E_{\text{int},k}^{\zeta/2-1} \exp[-\frac{E_{\text{int},k}}{k_B T_{\text{int},k}}], \tag{15}$$

where $\zeta = \zeta_v + \zeta_r$ is the total number of internal degrees of freedom. The simulated distribution functions have approximately the same shape as equilibrium ones. The nature of cluster cooling (decreasing of internal energy in time) is explained by the presence of considering processes with main role of clusters decay by atom evaporation (8).

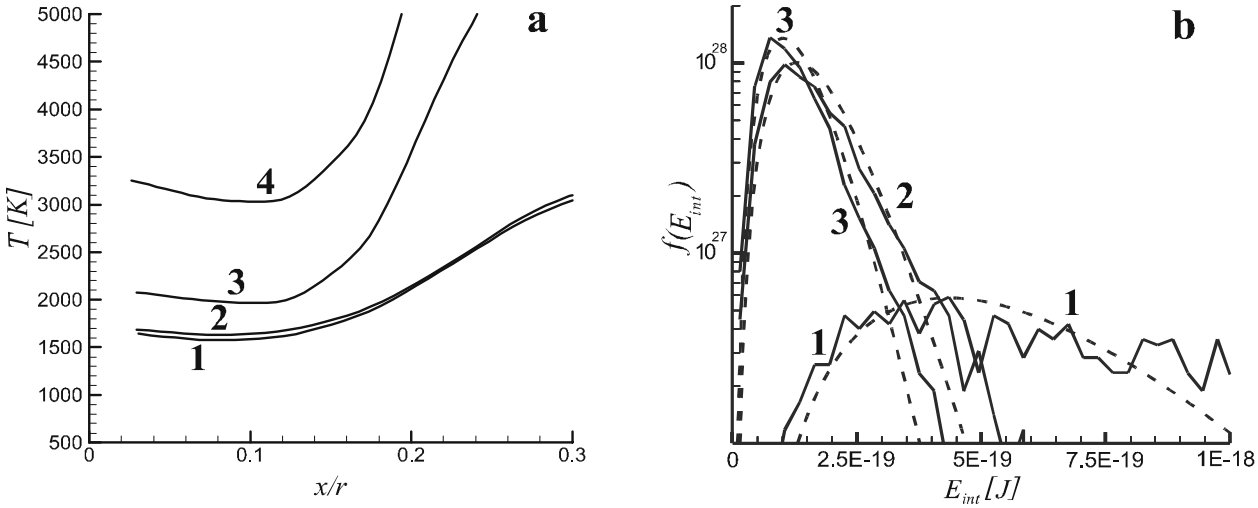

FIGURE 4. Axial distributions of translation temperature for the time $t/\tau_L = 4$ (a) and distribution function (average per volume) of internal energy of trimers (b): 1 - t/τ_L =2, 2 – 4, 3 – 6 (solid line – simulation results, dashed line – calculation by (15)).

CONCLUSIONS

We have developed the general model of PLA including cluster formation process in laser plume. The ablation in vacuum of niobium target by laser pulse of moderate intensity and nanoseconds time scale was considered as an object for simulation. Low values of clusterization degree with maximum clusters consisted of 7 atoms and weak influence of condensation process on plume gasdynamics were observed. The efficiency of the model for clusters parameters prediction was demonstrated.

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