Formation of nanoparticles by short and ultra-short laser pulses

K. Gouriet*[a], T. E. Itina[a], S. Noël[a], J. Hermann[a], M. Sentis[a], and L. Zhigilei[b]
[a]Laboratory of Lasers, Plasmas and Photonics Processing, CNRS, 128 av. de Luminy, Case 917, 13288 Marseille Cedex 9, France;
[b]Dep. of Materials Science & Engineering, University of Virginia, 395 McCormick Road, P.O. Box 400745 Charlottesville, VA USA 22904-4745

ABSTRACT

The main objective of this study is to explain the experimental observations. To simulate material ablation, plume formation and its evolution, we developed a combined molecular dynamics (MD) and direct simulation Monte Carlo (DSMC) computational study of laser ablation plume evolution. The first process of the material ablation is described by the MD method. The expansion of the ejected plume is modelled by the DSMC method. To better understand the formation and the evolution of nanoparticles present in the plume, we first used separate MD simulations to analyse the evolution of a cluster in the presence of background gas with different properties (density, temperature). In particular, we examine evaporation and growth reactions of a cluster with different size and initial temperature. As a result of MD calculations, we determinate the influence of the background gas parameters on the nanoparticles. The reactions rates such as evaporation/condensation, which are obtained by MD simulations, are directly transferred to the DSMC part of our combined model. Finally, several calculations performed by using MD-DSMC model demonstrate both plume dynamics and longer-time cluster evolution. Calculations results are compared with experimental findings.

Keywords: Laser Ablation, Molecular Dynamics, Direct simulation Monte Carlo, Evaporation, Condensation

1. INTRODUCTION

In recent years, pulsed laser ablation (PLA) has become a promising nanoclusters synthesis technique for photonics, electronics and medicine [1]-[12]. One of the several advantages of this method is the chemically clean synthesis and the control of the cluster size distribution by carefully choosing the laser irradiation parameters and properties of the background gas. The understanding of the physical and chemical processes that affect the time-evolution of the nanoclusters in the presence of a gas is extremely important for further development of this technique. The mechanisms of clusters formation are still not enough understood.

Previously, only several theoretical models have been proposed to explain the evaporation-condensation process, such as the statistical model of Rice, Ramsperger and Kassel (RRK) [13], [14] and the Classical Nucleation theory [15]-[17]. Molecular dynamics (MD) method [15]-[20] directly simulates molecular movement and interactions and can be used to investigate the evaporation process or to study the formation and evolution processes of clusters of many materials [13], [16], [21]-[23]. Several MD simulations [24], [25] and experiments [26]-[28] of laser ablation solids shown, that clusters are observed in the expanding plume of ablation. To describe clusters formation in the laser ablation process, a combination of the MD technique and the direct simulation Monte Carlo (DSMC) method [29] is developed [14], [28], [30]-[33]. The MD method described the initial stage of laser ablation (laser coupling to the target, ejection of molecules and clusters). Then, the DSMC method was used to model the long-term expansion of the ejected plume. Furthermore, the dynamics of the expanding plume [22] revealed that a different distribution of the clusters in the plume following their size.

The cluster parameters, such as cluster temperature and size, are changed following the position of the cluster in the expanding plume. In the same way, the corresponding characteristics surrounding the cluster, such as the density and temperature of monomers, are varied. In the present paper, we investigate the evolution of clusters of a molecular material in presence of the same background gas with different properties by using the molecular dynamics method and breathing sphere [19], [20] model. The main objective is to study the influence of background gas and cluster parameters on the evolution of molecular nanoclusters, to investigate the longer-time evolution of the cluster with DSMC.

*gouriet@lp3.univ-mrs.fr; phone 0033 491 829 286; fax 0033 491 829 289; www.lp3.univ-mrs.fr

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2. MOLECULAR DYNAMICS SIMULATION

2.1 Computational model

In this section, we review the features of breathing sphere model developed for MD simulation of organic solids ablation. This model is described in detail in [19], [20]. Briefly, the model assumes that each molecules (or group) can be represented by a single spherical particle. The parameters of interparticle interaction are chosen to reproduce the properties of a molecular solid. In order to simulate molecular excitation by photon absorption and vibrational relaxation of the excited molecules, on additional internal degree of freedom is attributed to each molecule. This internal degree of freedom, or breathing mode, is realized by allowing the particles to change their size. The parameters of a potential function ascribed to the internal motion can be used to change the characteristic frequency of the breathing sphere. The rate of vibrational transfer is determined by the size of the anharmonic of potential function and frequency mismatch between the internal motion and phonon modes in a molecular solid.

Thus the parameters of internal potential can be used to control the coupling between internal and translational molecular motions [19].

The system used in simulations is a molecular cluster in the presence of the same background gas. The parameters of intermolecular potential (Morse potential) are chosen to represent the van der Waals interaction in a molecular solid with the cohesive energy of 0.6 eV, elastic bulk modulus of ~5 GPa, and density of 1.2 g/cm^3. A mass of 100 Dalton is attributed to each molecule [19], [20]. For the simulation performed in this study a computational cell of dimensions 100×100×100 nm^3 is used. Periodic boundary conditions in all directions are imposed. These conditions simulate a cluster in a little volume of the expanding ablation plume represented by the background gas. A neighbour definition is used to distinguish clusters from gas.

The clusters used in this study were prepared as follows: starting with a sphere of N particles, the sphere is quenched to obtain a molecular solid sphere with constant potential energy and constant total energy. After quenching, the cluster is slowly heated in order to obtain a liquid sphere. This sphere is quenched again. We then obtain an amorphous cluster with N particles at 0 K. This cluster is then heated to melt and obtain a cluster with a temperature T_0. The heating is slow, so as the total and potential energies are constant at the end of simulation. This kind of heating allows us to obtain a stable cluster. To verify the stability of the cluster, we control over the evaporation of the cluster without background gas during 3 ns. No evaporation process is observed after 3 ns whatever the initial temperature of the cluster used.

Next, the background gas is generated based on the gas density and temperature. The volume of the computational cell and the gas density determine the number of gas particle in our simulation. The volume of the cell is constant and equal to 100×100×100 nm^3. Then, for the gas with the number density of 2.0 10^{19} part/cm^3, we use 20 000 particles of gas. To heat the gas, each particle of gas is given a velocity (Maxwell-Boltzmann distribution) according to the initial temperature.

In NVT simulations, we put a cluster in the center of our computational cell, in the gas with given temperature and density. Therefore, we can modify 4 parameters: 2 for the cluster (initial temperature, size), 2 for the gas (temperature, density).

2.2 Cluster evolution

MD simulations are performed until a time delay of 3 ns for a molecular cluster made up with different initial size and internal temperature, in the presence of a molecular background gas. Simulations results show that the cluster grows with time [Figure 1] and the cluster size converges to a constant value dependent on both cluster and gas parameters. In the presence of a gas with a high density (2.0 10^{19} part./cm^3), the size of clusters rapidly increases. The lower is the gas density, the more the size of clusters slowly increases. During the simulation, monomers collide with the cluster. Evidently, the number of collision between the gas particles and the cluster increase with the gas density.

To simplicity, we consider only these kinds of reactions:

(1) simple collision with the rate of collisions ν_{coll};

$$A_i + A \xleftrightarrow{\nu_{coll}} A_i + A \qquad (1)$$

(2) evaporation and condensation reactions,

$$A_i + A \xleftrightarrow{\nu_e,\nu_c} A_{i+1} \qquad (2)$$

where ν_e and ν_c are respectively the evaporation and condensation rates.

The simple collision does not affect the growth of the cluster. This kind of collision (1) allows a rearrangement of the cluster configuration and the change of cluster internal energy. So only the second reaction (2) is analyzed in this study. The evolution of a cluster depends on its evaporation and condensation processes. These processes change the size and the internal energy of the cluster. Following the gas properties, the collisions with the cluster play more or less role in the evolution of the cluster.

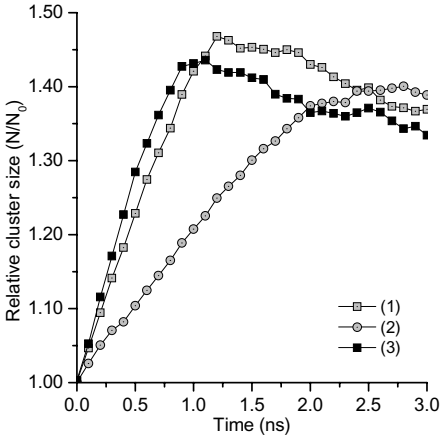

Fig. 1: Time-evolution of the cluster's size for (1) a cluster composed of 1500 particles and initially heated to 800 K in a background gas with the density of 2.0 10^{19} part/cm^3 and at 827 K; (2) a cluster composed of 1500 particles initially at 800 K in a background gas with the density of 1.0 10^{19} part/cm^3 and at 735 K and (3) a cluster of 1250 particles initially at 800 K in a background gas with the density of 2.0 10^{19} part/cm^3 and at 827 K.

To study the evolution of the cluster, we follow the size of the cluster every 100 ps and the number of cluster particles which evaporate (low potential energy) and the number of gas monomers which condensate on the cluster (high potential energy), as shown in Figure 2. When cluster grows, the number of particles on its surface with a high potential energy increases. In addition, large clusters have lower potential energy (high negative value) than medium clusters and they grow more rapidly due to sticking collisions (or, condensation).

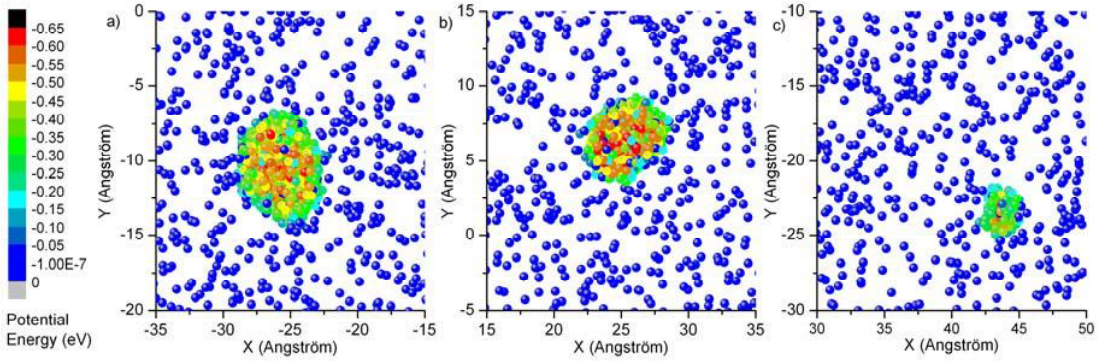

Fig. 2: Snapshots from the simulation showing clusters in the presence of a background gas (1.0 10^{19} part/cm^3 and at 800 K). The cluster contains (a) 750 particles, (b) 500 particles and (c) 100 particles at the end of simulation (3 ns). The colors correspond to the potential energy. The blue and gray colors represent gas particles (higher potential energy) and black and red colors are for particles inter the cluster (lower potential energy).

The calculation results show that the number of particles that belong to the cluster (or, with low potential energy per particle) increases in the presence of gas [Figure 3], and reaches a constant value at the end of the simulations. When the number of particles in cluster becomes constant, this result indicates that the condensation and evaporation processes compensate each other. The formation of clusters and the condensation of the gas are higher in a dense gas. We can predict a high rate of formation of small clusters and the growth of clusters in the center of the plume, which is the denser region, if the temperature is not too large (at low laser fluence).

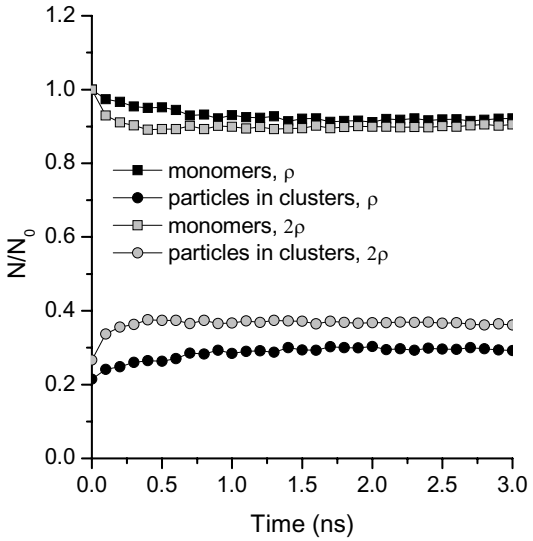

Fig. 3: Number of particles in the gas (squares) and in the cluster (circles) obtained in the MD study of cluster evolution composed of 1000 particles at initially 800 K in presence of a background gas with the density (black symbols) $\rho = 1.0\ 10^{19}$ part/cm^3 or (dot symbols) $\rho'=2\rho$ at 550 K.

The calculated evaporation rate for molecular clusters surrounded by a monomer gas can be used to predict the evaporation rates of molecular cluster in expanding plume of laser ablation. The large-scale three-dimensional plume evolution is simulated by using the DSMC part of our combined model.

3. LONG-TIME SIMULATION OF LASER ABLATION

3.1 Combined MD-DSMC computational Model

A combined MD-DSMC model is developed for the investigation of the laser plume formation and long-term evolution. In the model, two different numerical methods are used (i) molecular dynamics for target material disintegration and ejection of mixture monomers and clusters [24], [30] and (ii) direct simulation Monte Carlo for calculation of large scale three-dimensional plume evolution. Here, the breathing sphere model is adopted to model laser pulse absorption and relaxation processes in the MD part, for a molecular solid target. The pulse duration was set to be 15 ps. The transition between the DSMC and MD calculations is performed by using the MD results obtained at 1 ns after the laser pulse. These MD results defined the initial conditions for the DSMC simulations in the hybrid model. The collision probabilities in DSMC calculations are parameterized to describe the material properties in a gas phase [34].

In the present study, we assume that the spatial laser beam profile is top hat and the radial expansion of ablation plume is small during the first MD stage. Therefore, the radial distributions parameters of the simulation are assumed to be uniform with the laser spot. The axial density distributions of the initial DSMC parameters are fitted by using a normal distribution functions:

$$f_i(z) = \frac{d_i}{\sigma_i \sqrt{2\pi}} \exp\left[-\frac{(z-\mu_i)}{2\sigma_i^2} \right], \tag{3}$$

where z is the distance from initial target surface. The parameters d_i, μ_i and σ_i are calculated from numerical fits to MD results performed for each species group, and i is the number of group. The species groups are chosen as follow: 1- monomers, 2- dimmers to 15-mers species, 3- clusters of 16-100 molecules, 4- clusters of 101-1000 molecules and 5- clusters of more than 1000 molecules. The linear dependencies:

$$g_i(z) = A_i z - B_i, \tag{4}$$

are used to fit axial velocity distributions, where A_i and B_i are fitting parameters for each component [24] The distributions of the axial and radial temperatures and internal temperatures of clusters are fitted by six-order polynomial dependencies.

In the DSMC simulation, the laser plume is modeled by a representative ensemble of particles (here, about 8 10^6). The simulated particles are introduced based on the gas-dynamic parameters obtained from MD simulations of the initial stage of the plume formation. The physical space is divided into a network of cells with dimensions smaller than the local mean free path and a small time step Δt incremented the time. The calculations are performed with the three following main steps:

(1) Indexing of the simulated particles;

(2) Calculation of a representative set of collisions and chemical reactions in each cell;

(3) Movement of the simulated particles and calculation of the interactions with the boundaries [29].

In the present study of cluster formation, all simulated particles are divided into several simulation groups according to their size, although collisions are calculated for all particles together based on their probabilities by using a no-time-counter technique [29].

At the beginning, simulated particles are introduced according to the distributions calculated by previous MD calculations [24], [30]. The axis r=0 is set to be the axis of radial symmetry. At the target surface (Z=0), a partial diffuse reflection and redeposition of particles is sampled by using an accommodation coefficient. The accommodation coefficient of the target surface is set to be 0.5 in this work. The simulated volume is increased several times during the calculation to cover the plume expansion region. The calculation of collisions and reactions in the present DSMC includes the treatment of the following processes:

(i) Elastic collisions;

(ii) Inelastic non-reactive collisions;

(iii) Sticking reactions in cluster-molecule collisions;

(iv) Clusters evaporation reactions.

For simplicity, the cluster-cluster collisions were not considered in this first study. The non-reactive collisions are calculated based on the conservation laws of energy and momentum. For clusters, the reference cross-sections are computed based on their effective radii [34]. A soft-spheres collision model is used in the present modelling calculation. Sticking process is included for collisions in which the relative translational energy before the collision is smaller than the binding energy of the final cluster [35]. For the evaporation reaction, we used the results of separated MD simulations. The pulse duration was set to be 15 ps and the absorbed fluence of laser is 61.38 J/m^2.

3.2 Evolution of clusters in long-time simulation of ablation laser

Experimental study performed by Noel et al [28] has demonstrated that clusters are efficiently generated by short laser ablation. In addition, the fast CCD images have revealed two different components: one that moves rapidly and is composed of monomers (atoms), and the second one, which stays at the back part of the plume and contains clusters.

To bring more light on these observations, a series of long-scale calculations are performed with the combined MD-DSMC model. The separate MD simulation results are integrated into the DSMC simulations. To verify the validity of

our DSMC part, we compared first the modified DSMC simulation results with the long-time MD simulation result. The cluster size distribution was reproduced with reliable accuracy.

Then, we consider the laser plume dynamics. The distributions of the small clusters with a size range from dimmers to 100-mers, large clusters (size greater than 100 particles) and monomer densities [Figure 4] illustrate the laser expansion away from the irradiated target. Monomers and small clusters constitute the main components and the large clusters are present in lower fraction near the center and the rear area of the plume.

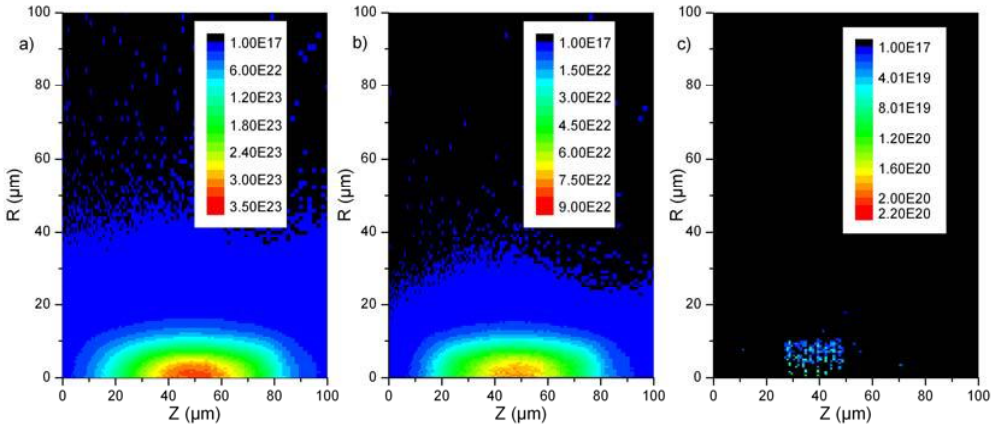

Fig. 4: Two-dimensional distributions of (a) monomers, (b) small clusters (2-100 particles) and (c) clusters (100-1000 particles) number density at time delay of 50 ns. The results are obtained with the DSMC simulation performed for pulse duration of 15 ps, laser fluence of 61 J/cm^2 and a laser spot radius of 10 μm.

The abundance of clusters in the plume with a size smaller than 500 particles in the MD-DSMC simulation of the plume expansion is shown in Figure 5. The abundance varies with time, and the number of small cluster decreases, while the bigger clusters become more abundant. During the following plume expansion, collisions take place in the plume and affect the distribution.

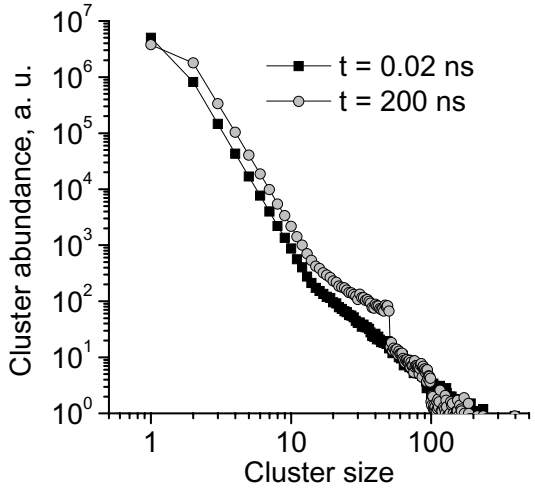

Fig. 5: Cluster abundance distribution. The results are obtained with the DSMC simulation performed for pulse duration of 15 ps, laser fluence of 61 J/cm^2 and a laser spot radius of 10 μm.

4. SUMMARY

To summarize, we presented the results of an atomistic-level modeling of nanocluster evolution in a laser ablated flow represented by a background gas with different properties of density and temperature. The calculations performed with molecular dynamics technique demonstrate the role of the presence of monomers around the cluster on the cluster evolution. The main gas parameter is the density. The results show that the high density, due to high collision rate, affected the condensation and the evaporation of clusters and the formation of clusters. The MD calculations demonstrate that evolution of large clusters in the plume is affected by collisions and located in the part of the plume which is the colder and the less dense (closer to the target).

As a result, during the expansion of the plume, modeled by the MD-DSMC simulations, the dynamics of different cluster groups is visualized. Further development of the modeling of the evaporation and condensation processes will be including for the optimization of calculation procedure and more precise treatment of clusters collisions in the ablation plume.

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