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Generation of nanoparticles by laser ablation: Combined MD-DSMC computational study

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Abstract. The early stage of the ablation plume formation and the following dynamics of the plume expansion are studied numerically using a combination of molecular dynamics and the direct simulation Monte Carlo methods. The direct cluster ejection from the target and the following cluster-monomer and cluster-cluster collisions are considered. The presence of the ablated clusters is shown to strongly affect the dynamics of the plume expansion, leading to considerable modifications of the plume structure. Plume segregation into two components observed in the simulations is in a good qualitative agreement with the results of recent plume emission measurements.

1. Introduction

Pulsed laser ablation (PLA) is one of the promising methods of the synthesis of nanoparticles for applications in optics, photonics, electronics and medicine, e.g. [1,2,3]. During the last decade, it has been demonstrated that PLA provides a possibility of chemically clean synthesis, which is difficult to achieve with conventional nanoparticle production methods. Moreover, recent experimental studies indicate that size distributions of clusters produced by PLA can be controlled by a careful choice of laser irradiation parameters and deposition conditions.

While the ability of PLA to generate nanoparticles has been demonstrated in many experimental studies and a number of mechanisms of nanoparticle formation have been discussed, a clear picture of the interplay of different physical and chemical processes during the ablation plume evolution and their relation to the parameters of the observed nanoparticles is still lacking. Both the initial material ejection and the following plume expansion occur so rapidly in PLA that the equilibrium conditions are not attained. As a result, the continuum hydrodynamics and the classical nucleation theory have limited applicability under the typical PLA conditions. Moreover, there have been experimental [4,5] and computational [6,7] reports suggesting that the direct ejection of nanoparticles from the target as a result of laser-induced explosive disintegration of the target material can play an important role in defining the final size distribution of the produced nanoparticles. In this case, the common thermal desorption and

condensation models are insufficient and only a detailed molecular-level simulation can provide the complete description of the nanoparticle formation process. A possible approach for such simulations is to combine the molecular dynamics technique (MD) with the direct simulation Monte Carlo method (DSMC) [8,9]. The combined MD-DSMC model is, up to now, the only numerical method that properly accounts for both the processes of the direct cluster ejection from the target and their following evolution in the expanding ablation plume.

In this paper, we investigate the effect of the direct cluster ejection from the target on the long-term evolution of the ablation plume. The results of two MD-DSMC simulations of PLA performed with and without the initial clusters are presented and related to recent experimental observations of plume splitting.

2. Combined MD-DSMC numerical model

A combined MD-DSMC model is developed for the calculation of the laser plume formation and its following evolution. In the model, MD is used to simulate the disintegration of the target material and the ejection of a plume consisting of clusters and monomers [6], whereas DSMC is used to study the following large-scale three-dimensional plume evolution [10]. The MD simulations are performed for laser fluence of 6.1 mJ/cm^2 and pulse durations of 15 ps and 150 ps. The target material is a molecular solid represented by the breathing sphere model [6]. The parameters of the ablation plume obtained by the end of the MD simulation, 1 ns after the laser pulse, are used as initial conditions for the following DSMC calculation. To make the connection between the MD and DSMC simulations, we describe the parameters of the ablation plume in terms of spatial distributions of different plume components, their velocities, radial and translational temperatures, and internal temperatures of the ejected clusters.

In the DSMC simulation, the laser plume is modeled by an ensemble of simulated particles (here, about $8 \cdot 10^6$). The physical space is divided into a network of cells with dimensions smaller than the local mean free path. The calculations consist in the repetition of three main steps: (i) indexing of the simulated particles (ii) calculation of a representative set of collisions and chemical reactions in each cell; (ii) movement of the simulated particles and calculation of the interactions with the boundaries. In the present work, all plume species are divided into five groups depending on their size, although collisions are calculated for all particles together based on their probabilities by using the no-time-counter method of Bird [11]. The five groups are chosen as follows: monomers, clusters of 2 to 15 molecules, clusters of 16 to 100 molecules, clusters of 101 to 1000 molecules, and clusters of more than 1000 molecules. Cluster size is sampled in each group according to the size distributions obtained in the MD calculations. The accommodation coefficient of the target surface was set to be 0.5.

The following processes are included in DSMC part of the model: (i) non-reactive collisions, (ii) sticking reaction in cluster-molecule and cluster-cluster collisions, (iii) cluster evaporation reaction, and (iv) thermal radiation emission from clusters. The non-reactive collisions are calculated based on the conservation laws of energy and momentum by using a soft-spheres model. For clusters, the reference cross-sections are computed based on their effective radius $r_n = an^{1/3} + b$, where a=3.97 Å, b=1.59 Å [12]. In cluster-molecule and cluster-cluster collisions, the choice between a simple elastic collision and a sticking process is done based on the internal energies of the clusters. To ensure the energy conservation in the sticking reaction, the relative translational energy of the monomer and cluster was transferred into the internal energy of the resulting cluster, whereas the center-of-mass velocity was conserved. The rate of evaporation from a cluster of n atoms with internal energy E_n is calculated according to the classical RRK theory [13]. After the evaporation, the remaining energy is distributed between the relative translational energies of the evaporated monomer and the remaining cluster. Thermal radiation emission from clusters is calculated with the classical Stephan-Boltzmann-Rayleigh equation for small particles. To

gain enough statistics, the DSMC calculations are repeated at least 15 times. For simplicity, cluster-cluster reactions of rearrangement and fragmentation are not considered in this study. This simplification is justified by small probabilities of such processes as compared to those of non-reactive and sticking collisions. More details of the calculation procedure will be presented in forthcoming papers.

3. Results and discussion

In this section we present the results of two MD-DSMC simulations of laser ablation plume expansion, one performed under an assumption of complete vaporisation of the ablated material and another performed for a multi-component plume containing cluster generated in an explosive material ejection from the irradiated target.

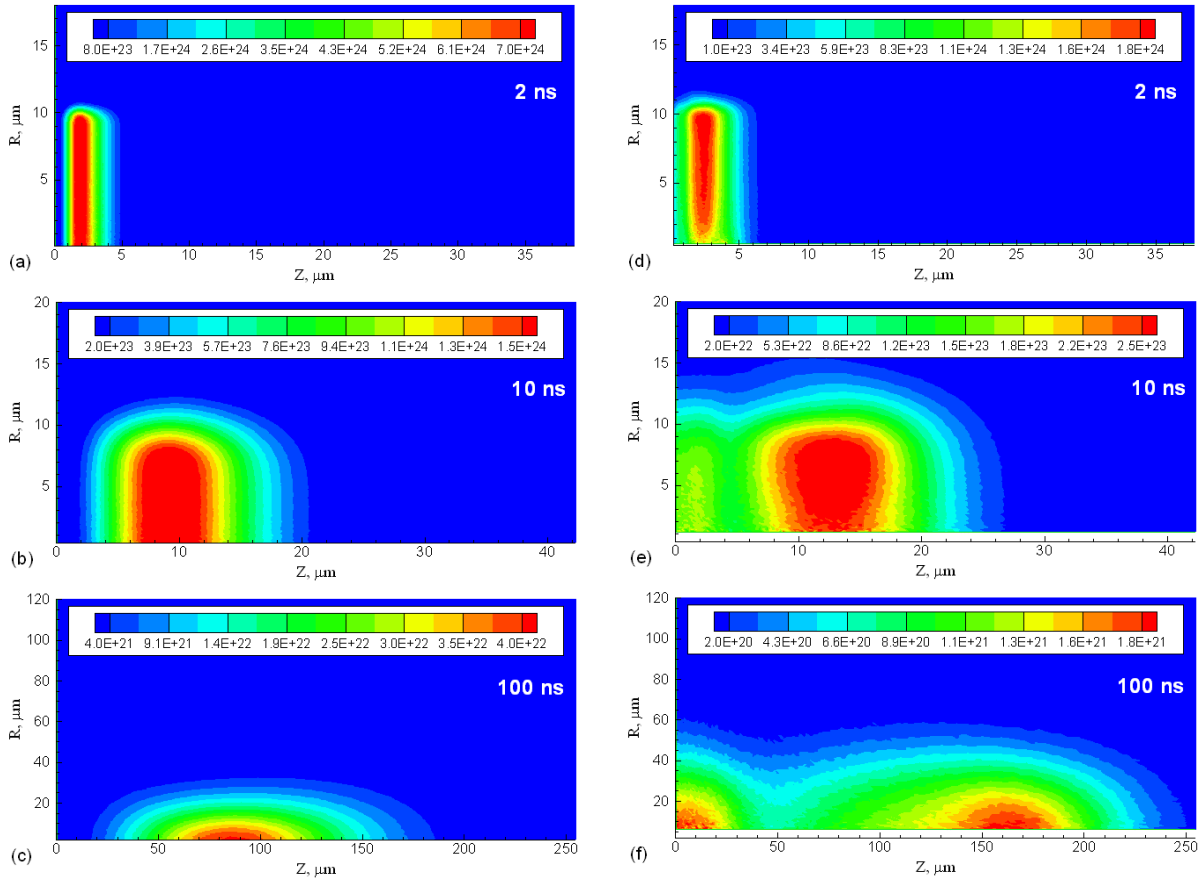

Figure 1. Number density distributions of molecules obtained for different times during the ablation plume expansion in DSMC simulations of laser ablation of a molecular target. The simulations are performed for a flat-top laser beam directed in *Z* direction and irradiating the target surface located at *Z*=0. Only monomer component of the plume is considered in the simulation illustrated by the left frames (a-c), whereas a multi-component plume consisting of a mixture of individual molecules and clusters of different sizes, as predicted in MD simulation, is used as the initial condition in DSMC calculation illustrated by the right frames (d-f). Laser pulse duration of 15 ps, laser fluence of 6.1 mJ/cm^2, and aser beam radius of 10 μm are used in both simulations. Simulation results are shown for different delay times after the beginning of the DSMC simulation: (a,d) 2 ns, (b,e) 10 ns, and (c,f) 100 ns. The scales show the number density in units of molecules/m^3.

The effect of the presence of clusters on the following plume dynamics is apparent from Figure 1, where a flat-top laser beam with a laser spot radius of 10 μm is assumed. The absorbed laser fluence and the initial density distributions are, therefore, uniformly distributed in the radial direction within the laser spot. In the absence of clusters in the initial plume (Figures 1a-c), the shape of the plume evolves from a pancake-type during the first ~10 ns, to a spherical at ~20 ns, and to an oval elongated in the direction normal to the target surface, as observed at 100 ns in Figure 1c. The density maximum is located on the plume axis and the plume moves from the laser-irradiated target with a center-of-mass velocity of ~850 m/s.

In the presence of different cluster components, the plume dynamics looks similar to that described above during the first nanoseconds, Figure 1d. At a delay of about 10 ns, however, the monomer density distribution exhibits splitting, with a second gas cloud appearing close to the target surface, Figure 1e. The following plume evolution shows that the density distribution stays segregated into two clouds. The first cloud is of an oval shape, and it moves away from the target with a velocity of 1600 m/s, about twice as high as that in the absence of clusters. The second cloud has zero center-of-mass velocity and stays in the vicinity of the target. The splitting is observed only for monomers, whereas each cluster group forms only one cloud that moves behind the fast monomer component with about twice as small velocity, Figure 2.

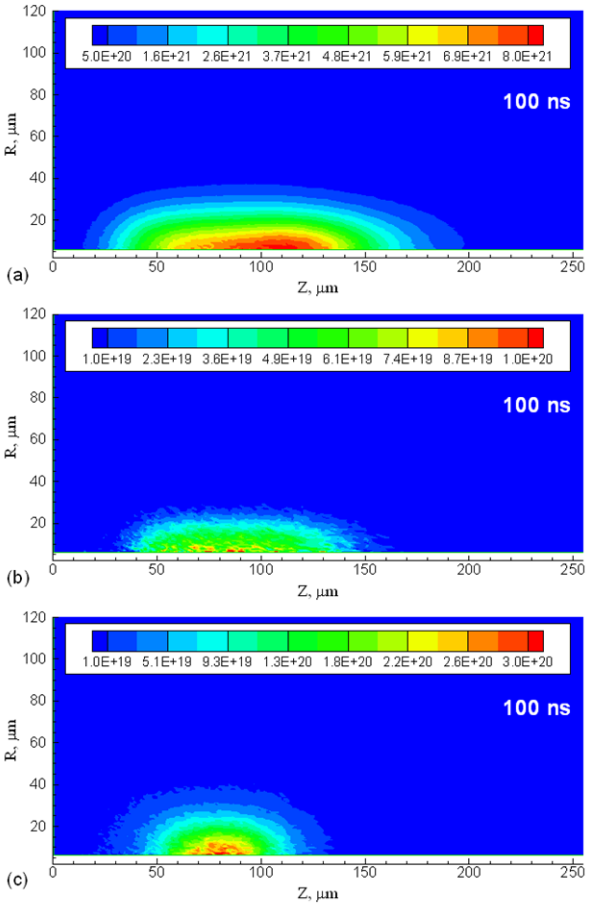

Figure 2. Number density distributions obtained in a simulation illustrated in Figure 1(d-f) at a delay time of 100 ns for different groups of clusters: (a) clusters of 2 to 15 molecules, (b) clusters of 16 to 100 molecules, (c) clusters of 101 to 1000 molecules. The scales show the number density in units of number of clusters per m^3.

To elucidate the effect of the pulse duration on the calculation results, we compared the results shown in Figures 1 and 2 for 15 ps laser pulse with those obtained for 150 ps pulse at the same laser fluence (not shown). A short laser penetration depth of 50 nm is used in the MD simulations and the change of the laser pulse duration results in the transition of the physical regime of laser ablation from the stress confinement with 15 ps pulse to the thermal confinement with 150 ps pulse [7,14]. For both pulse durations, however, similar formation of a two-cloud structure in monomer distributions is observed in the presence of clusters directly ejected from the target. For 150 ps pulse, the MD-DSMC simulation with clusters yields the first cloud velocity of about 1300 m/s.

The two-cloud structure observed in the multi-component flow expanding in the vicinity of the laser-irradiated target can be attributed to the initial plume composition with larger clusters ejected at the back of the plume and to the sticking and evaporation reactions involving clusters. In particular, the monomers evaporating from clusters attain velocities in all directions with equal probability and, therefore, enhance the back-scattered flow. The boundary-conditions effect was excluded by varying the accommodation

coefficient of the surface from 0.5 (half of the backscattered molecules are diffusively reflected and other half is re-deposited) to 0 (complete re-deposition). It should be noted, furthermore, that similar two-cloud plume structures were recently observed in a number of experimental studies of short pulse laser ablation, e.g. Figure 3 [15,16]. These observations were explained by the presence of clusters in the expanding ablation plume.

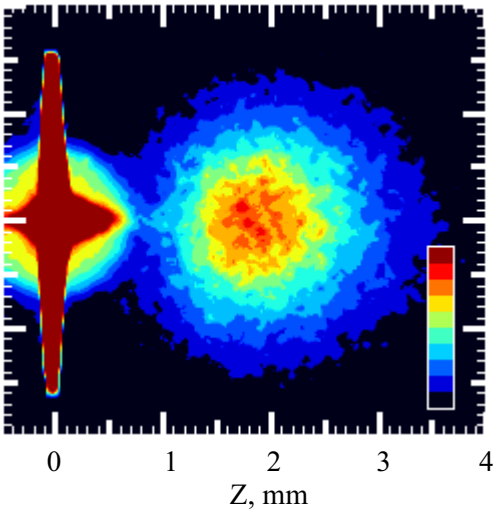

Figure 3. Laser plume emission recorded at t=540 ns in the femtosecond laser ablation of a gold target. Laser beam comes from the right, laser fluence is 0.8 J/cm^2, laser energy distribution is uniform within the spot of about 35×35 μm^2. Courtesy of Hermann et al. [16].

4. Summary

The ablation plume generation and the following long-term expansion are investigated with a recently developed two-stage computational model that combines two particle-based numerical methods, MD and DSMC. MD simulations are used at the initial stage of laser ablation, when an explosive decomposition of the irradiated target leads to the ejection of a plume of vapour and clusters of different sizes. The parameters of the ablation plume predicted in MD simulations are used as initial conditions for DSMC simulations of the long-term evolution of the multi-component ablation plume. The combined model provides a unique tool for investigation of the evolution of a laser-generated plume containing nanoparticles.

The results of the simulations performed for a flat-top laser pulse indicate that the presence of the ablated clusters strongly affects the dynamics of the plume expansion and leads to the development of a two-component plume structure, where the first component stays near the target and the second component moves outward with a considerable center-of-mass velocity. The observation of the plume segregation into two components is in a good qualitative agreement with the results of recent plume emission measurements.

Acknowledgments

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