A Hybrid MD-DSMC Model of Picosecond Laser Ablation and Desorption

Michael I. Zeifman[*], Barbara J. Garrison[*] and Leonid V. Zhigilei[¶]

[*]*Department of Chemistry, 152 Davey Laboratory, The Pennsylvania State University, University Park, PA 16802, USA*

[¶]*Department of Material Science and Engineering, 116 Engineer's Way, University of Virginia, Charlottesville, Virginia 22904, USA*

Abstract. A two-stage computational model of the evolution of a plume generated by laser ablation of an organic solid is presented and discussed. The first stage of the laser ablation involves laser coupling to the target and ejection of the plume and is described by molecular dynamics (MD) simulations. The following stage of a long-term expansion of the ejected plume is modeled by the direct simulation Monte Carlo (DSMC) method. The results of the MD simulations demonstrate that the physical mechanism of material ejection at sufficiently high laser fluences is a phase explosion of the overheated material followed by a homogeneous decomposition of the expanding plume into a mixture of liquid droplets (molecular clusters) and gas phase molecules. The extremely low proportion of large-size clusters hinders both statistical description of their parameters from the results of MD simulations and the following representation of each cluster size as a separate species, as required in the conventional DSMC. Therefore, a new computational scheme, which treats the size of large clusters as a random variable, is developed. The results of the hybrid model demonstrate that even for low laser fluences and short pulse duration, the evolution of the plume differs considerably from that predicted by pure thermal desorption models. For high fluences, the phase explosion of the target material and intensive processes of particle interactions within the plume are responsible for dramatic changes in the plume evolution as compared to that at low fluences.

INTRODUCTION

Several applications of pulsed laser ablation, such as thin film deposition [1,2], micromachining [3] and mass spectrometry [4,5] require detailed modeling of the ablated vapor cloud (plume). Very often, the time of the energy deposition on the target surface is shorter than the time of dissipation of the absorbed laser energy by the thermal conduction, turning a normal surface evaporation at low laser fluences into an explosive vaporization, or phase explosion, at higher fluences [6]. In this situation, existing theoretical models of plume formation and evolution, which are suitable for the thermal evaporation process [7,8,9,10], may fail. Indeed, such experimental facts as the presence of submicro- and micron-size particles in the plume [11,12] and the very high actual speed of the expansion front [9] cannot be explained in the framework of the thermal desorption model.

Phase explosion is just one of a wide range of diverse processes, from molecular excitation to generation of pressure wave in the target to a collective expulsion of part of the target material into an ambient background to interactions among particles forming the plume and/or the background gas, which are triggered by a pulse laser beam. These processes occur at different time- and length scales and may require different models for adequate description. Recently, the molecular dynamics (MD) and the direct simulation Monte Carlo (DSMC) methods have been coupled to study the evolution of a plume in laser ablation of organic solids [13,14]. The first stage of the laser ablation resulting in the formation of the initial plume is described by the MD model, while the following stage of a long-term expansion of the ejected plume is inaccessible by MD and is described by the DSMC simulation. In this hybrid model, the coupling between the MD and DSMC parts is through the initial conditions and via interaction cross sections.

The MD breathing sphere model [15], used for simulation of the initial stage of the laser ablation process, provides coordinates, velocities, sizes and internal energies of the ejected particles. This information in statistical

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form is then transformed into the initial conditions of the DSMC model, used for simulation of a long-term expansion of the ejected plume. Separate MD calculations provide the essential cross sections of interparticle interactions for the DSMC calculations.

The composition of the ejected plume strongly depends on the laser fluence [6]. For low fluence (desorption regime), the main ejected species is molecules, and only molecular coordinates and velocities should be statistically characterized based on the results of the MD model. For high fluences (ablation regime), clusters of sizes up to tens of thousands of molecules constitute major part of the plume mass, therefore, particle coordinates, velocities, internal energies and sizes must be characterized. The available number of clusters in the output of a typical MD simulation, however, is too small to permit straightforward statistical characterization of the MD results [13]. Moreover, direct representation of each cluster size as a separate species, as required in the conventional DSMC, is computationally prohibitive. Therefore, a new computational scheme, which treats the size of large clusters as a random variable, has been developed.

In the present work we focus on the differences between the plume evolutions in the regimes of laser desorption and ablation. We perform two series of large-scale simulations for two different sets of the irradiation parameters which are chosen in order to make sure that the desorption regime is realized in one set of the simulations and the ablation regime is achieved in another. The computational setup and the irradiation parameters are given in the next section. The analysis of the plume evolution in the desorption regime and ablation regime is given and related to experimental data and existing theoretical models in the subsequent section.

THE HYBRID MODEL

In this section we briefly review the basic features of the breathing sphere model developed for MD simulation of laser ablation of organic solids, describe the proposed DSMC model as well as the coupling between the MD and DSMC parts of the hybrid model.

The MD Model

Complete details of the breathing sphere model are given in reference [15]. The model assumes that each molecule (or appropriate group of atoms) can be represented by a single particle. The parameters of interparticle interaction are chosen to reproduce the properties of an organic material, in this case a molecular solid. In order to simulate molecular excitation by photon absorption and vibrational relaxation of the excited molecules, an 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 sizes. The parameters of a potential function ascribed to the internal motion can be used to change the characteristic frequency of the breathing mode and to affect the coupling between internal and translational molecular motions. In effect one can control the rate of the conversion of internal energy of the molecules excited by the laser to the translational and internal motion of the other molecules. The laser irradiation is simulated by vibrational excitation of molecules that are randomly chosen during the laser pulse duration within the penetration depth appropriate for a given wavelength. Vibrational excitation is modeled by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal motion of a given molecule. Since in this model each molecule is represented by a single particle and explicit atomic vibrations are not followed, the system size and the time-step in the numerical integration of the equations of motion can be large enough to reproduce the collective dynamics leading to laser ablation and damage on the time length of up to few nanoseconds. The parameters of the intermolecular 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 ~5GPa, and density of 1.2 g/cm3. A mass of 100 Dalton is attributed to each molecule. For the simulation performed in this work a computational cell of dimensions 40x10x90 nm (253,808 molecules) is used. Periodic boundary conditions in the directions parallel to the surface are imposed. These conditions simulate the situation in which the laser spot diameter is large compared to the penetration depth so that the effects of the edges of the laser beam are neglected or the situation of a flat laser profile.

The MD breathing sphere model is computationally limited in both time (few nanoseconds) and length (a few tens of nanometers). At about one nanosecond after the laser irradiation, the local Knudsen number in the ablated plume becomes high enough to provide the rarified conditions; therefore, the following long-term plume evolution can be modeled using the DSMC method. Some of the findings of the MD model pertinent to the following DSMC modeling are listed below.

- When the laser fluence is low (desorption regime), the only ejected species is molecules. A one-dimensional self-similar flow in the direction normal to the ablated surface (axial direction) is developed within the entire plume. The dependence of the plume flow velocity and temperature on height above the surface, however, deviates from that predicted by models based on pure thermal desorption mechanism. Moreover, there is no thermal equilibrium within the plume so that the corresponding velocity distributions of molecules must be characterized, at least, by local flow velocity and local axial and radial temperatures.
- When the laser fluence exceeds a threshold value (ablation regime), clusters in a very broad size range from dimers to clusters composed of tens of thousands of molecules constitute a major part of the plume mass. The available number of large clusters in a typical MD model output, however, can be as small as several dozens. A one-dimensional self-similar flow in the axial direction is also formed within the entire plume.

The following subsection describes the proposed DSMC model and the means of statistical characterization of the MD results in order to establish information transfer between the MD and DSMC parts of the hybrid model.

The DSMC Model and the MD-DSMC Coupling

As it was mentioned earlier, the presence of severely underpopulated large clusters in the MD output poses the main challenge for both statistical description of the cluster parameters from the results of MD simulations and the following representation of each cluster size as a separate species as required in the conventional DSMC. The proposed remedy is to represent a statistical sample of large clusters in a DSMC cell rather than clusters of each possible size. This simplification implies that the cluster size is treated as a random variable, which makes it possible to estimate otherwise indeterminable distributions of cluster parameters such as internal energy, velocity and location in the plume from the available sample of large clusters in the MD output.

The additional computational restrictions to the proposed DSMC procedure are at least eight large clusters in an initial cell and at least 50 runs of the code for the ensemble averaging [14]. Complete details of the DSMC model and the estimation procedure are given in references [14,16]. Here we only briefly outline the main points. In the case of a flat-profile laser, the laser fluence is uniform throughout the spot, and the results of a single run of the MD model can be used as the initial conditions for the DSMC calculations.

The characterization of the results of MD simulations obtained in the desorption regime includes the estimation of the velocity and density distributions for molecules located at a given height above the surface. Since these estimations are only needed for the subsequent initialization of the DSMC calculations, a non-parametric statistical scheme can be used. In the employed Bootstrap scheme [16] the variables are resampled directly from the MD data. The obvious advantage of this procedure is that no assumptions about specific analytical forms of the distribution functions need to be made.

The same non-parametric scheme could be applied for monomers in the ablation regime. As for the clusters, there are more variables to be statistically characterized (internal energy and size in addition to velocity) while the data pool is too small to permit a non-parametric scheme. As it was mentioned earlier, the periodic boundary conditions implemented in the breathing sphere model reduce the spatial dependence of cluster properties to the dependence on height above the surface (coordinate z). Physical reasoning and an initial statistical analysis of the data [14,16,17] allows us to design analytical distribution models so that only several parameters of the distributions need to be estimated. For a given height above the surface, the cluster size distribution is lognormal, the velocity components are normally distributed about the axial flow velocity, and the internal energy has a Gamma distribution.

Besides the initial conditions, a variety of possible particle interactions should be addressed in the DSMC procedure. The initial MD study has shown that the main reactions are elastic collisions, sticking collisions and evaporation of monomers from clusters. The hard-sphere cross-sections are evaluated numerically for monomers and approximated for clusters. A collision is classified either as a sticking or elastic one with the aid of sticking probability, which ranges from zero for monomer-monomer collisions to unity for collisions involving a large cluster. Evaporation of a monomer from a cluster has been found to comply with the classic RRK model [18].

In our no-time-counter [19] DSMC simulation, the cylindrical volume surrounding the axial-symmetric plume above the laser-irradiated surface is divided into cells and filled with simulation particles, representing the real molecules or molecular clusters as shown in Fig. 1. The characteristics of the simulation particles in a given DSMC cell at the beginning of the DSMC simulation are defined by the parameters of molecules and clusters located in the corresponding region of the plume obtained by the end of the MD simulation, as schematically shown in Fig. 1.

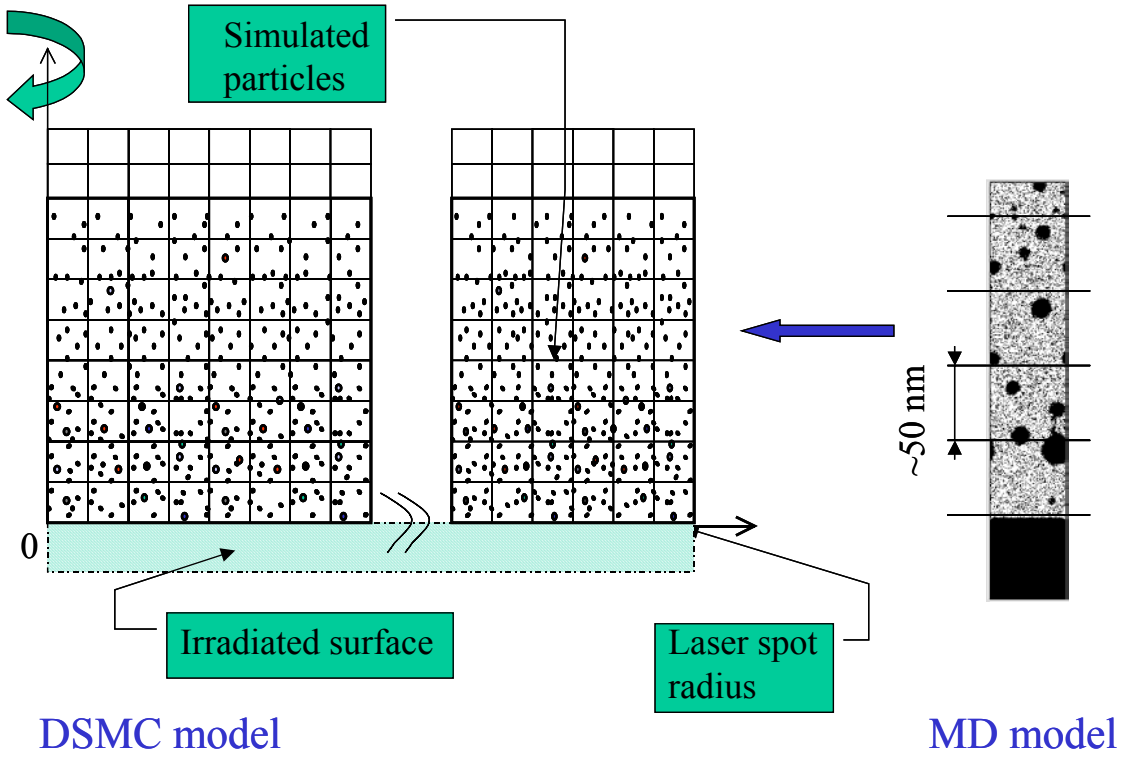

FIGURE 1. The interconnection between the MD model and the DSMC model. The MD model is represented by a snapshot, the horizontal lines correspond to the cells in the DSMC model, the black spots are clusters and the dots are molecules.

In this study, a laser penetration depth of 50 nm, a pulse duration of 15 ps, and fluences of 28 and 61 J/m^2 are used as the irradiation conditions in the MD calculations to simulate the desorption and the ablation regimes, respectively. The radius of the laser spot simulated in the DSMC calculations is 10 μm. The results of the hybrid model are discussed in the next section.

RESULTS

In this section, results of the simulations performed with the hybrid model for the desorption and ablation irradiation regimes are presented and discussed.

Desorption Regime

The results of the MD model calculations in terms of density, velocity variances and flow velocity profiles are shown in Figure 2. It is observed that the monomer density monotonically decreases with height, the flow velocity almost linearly increase with height and the variances of axial and radial velocity components are statistically different within the initial plume. The formation of an initial plume in laser desorption was studied earlier both theoretically and by Monte-Carlo simulations. Kelly, who studied 1D thermal desorption of molecules [7], has claimed that if the desorption yield exceeds about 0.5 monolayers in 10 ns, a Knudsen layer, characterized by thermal equilibrium, is formed near the surface. He also provided analytical results for the density and temperature profiles based on a self-similar solution of ideal gas equations. For the chosen simulation setup of the MD model, about one monolayer in 0.1 ns has been desorbed. While the density profile agrees with the analytical power-law prediction of Kelly as shown in Fig. 2a and the axial flow velocity depends linearly on the height above the surface as seen in Fig. 2b, which is characteristic of self-similar flows, the inequality of radial and axial velocity variances indicates the lack of thermal equilibration within the initial plume as seen in Fig. 2c.

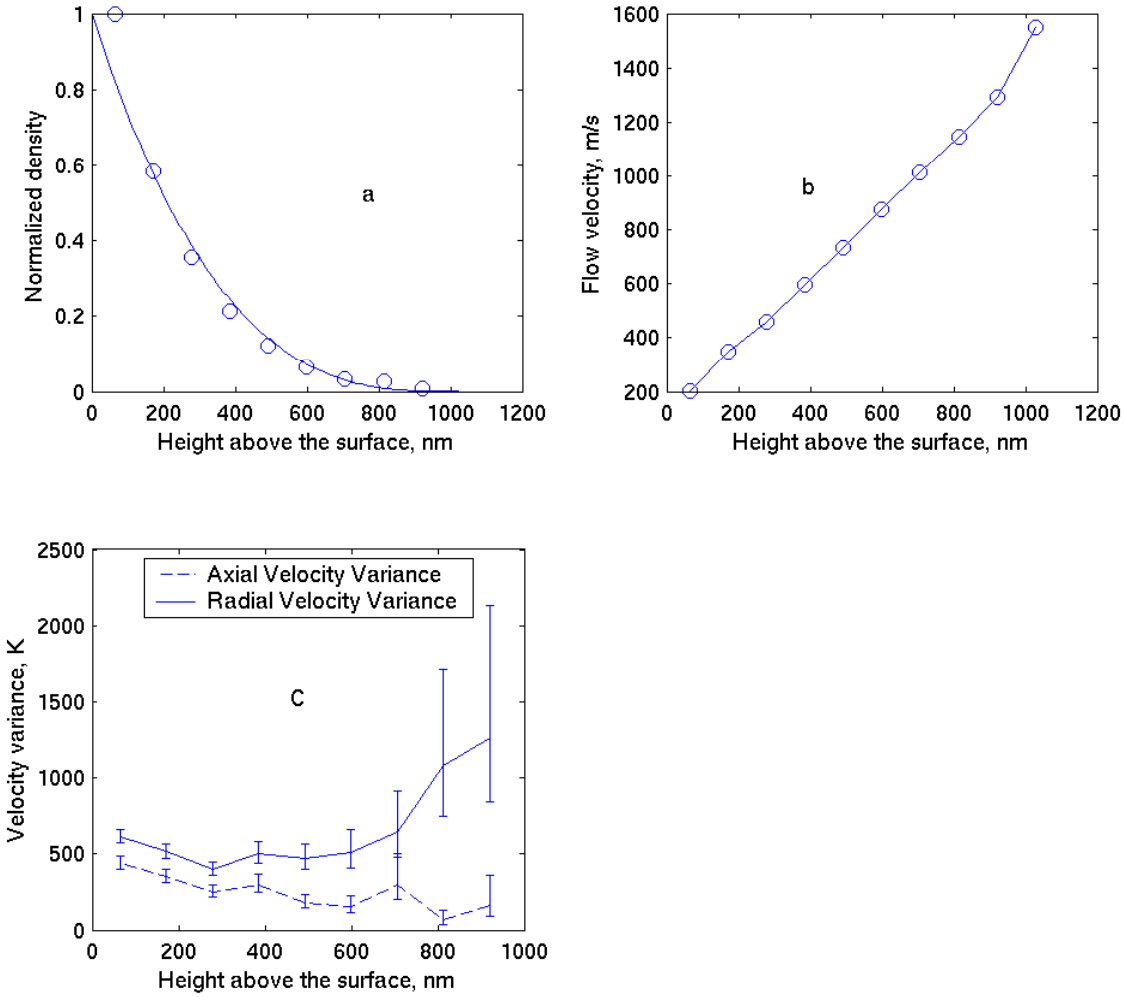

FIGURE 2. The results of MD simulations used as initial conditions for the DSMC calculations. (a) Density profile (circles) and the predicted power-law [7] curve. (b) Flow velocity profile. (c) Velocity variance (axial and radial temperature) profiles. Error bars correspond to 90% confidence interval.

Sibold and Urbassek studied a thermal desorption flow both analytically and with the aid of DSMC calculations [20]. They identified three distinctive desorption regimes with respect to the number of desorbed monolayers θ. While the two extremes, collisionless flow ($\theta<<1$) and very intensive flow ($\theta>>1$) allowed for analytical description, in the transitional regime, when few monolayers were desorbed, the ideal gas equations were not applicable and the flow could not be characterized analytically. The translational temperature profiles, given in reference [20] for the transitional regime are very close to the results of our MD model, Fig. 2c.

One essential characteristic of the flow, the expansion front speed, however, differs from the one predicted by Kelly [7] and Sibold and Urbassek [20]. For the actual irradiated surface temperature of 700 K, Kelly's prediction of the expansion front speed is 980 m/s, which is about 1.5 times lower than the front speed observed in the simulation as seen in Fig. 2b. Sibold and Urbassek [20] did not provide an analytical expression for the expansion front speed in the transitional regime, but their simulation values are very close to the Kelly one. The high speed of the front can be attributed to the high velocities of the molecules directly ejected in the course of the relaxation of the molecules excited by laser irradiation. This ejection mechanism is beyond the capabilities of the conventional models of thermal desorption, which reduce the laser-surface interaction to the uniform heating of the irradiated surface.

The results of the DSMC model calculations performed with the initial conditions described above are shown in Fig. 3. It is observed that the initially oblate cloud changes its shape and becomes prolate, which is consistent with

the results of Sibold and Urbassek for the thermal desorption in the transitional regime [10]. The long-term interactions among molecule result in the forward peaking of the angular distribution of the molecular cloud, Fig. 3c. The higher flow velocities in the upper part of the plume result in the higher degree of the plume forward peaking as compared to the pure thermal desorption. More precisely, the terminal angular distribution of the ejected molecules in our hybrid model (circles on Fig. 3c) is much narrower as compared to the angular distribution given in Ref. [10] (squares in Fig. 3c). The collisions cease at about 60 ns and the plume expansion becomes fully self-similar thereafter.

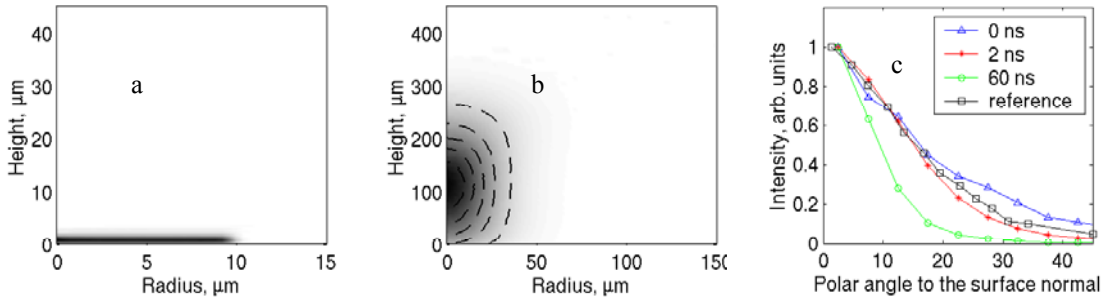

FIGURE 3. Density of the plume at 2 ns (a) and 300 ns (b) after the switching from the MD model to the DSMC model. The aspect ratio is the same in both contour plots. (c) Evolution of the angular distribution of molecules in the plume, the data of reference [10] are designated by squares.

Ablation Regime

The results of our MD modeling of the ablation regime have been published elsewhere [6,14,17] and here we only briefly review the main points pertinent to the chosen computational setup.

- A self-similar axial flow is formed for all the particles within the plume.
- The lower part of the plume, where all the clusters and most of monomers are located, is characterized by translational temperature equilibrium, while monomers located at the upper part of the plume are characterized by different axial and radial temperatures.
- The internal energies of clusters are characterized by Gamma distributions. The corresponding mean internal temperatures are not correlated with the translational ones.
- For large clusters, the dependence between logarithm of cluster size and height is close to a linear regression model with a negative slope, i.e., the lighter the cluster, the higher it is located. The unconditional cluster size distribution is close to a power-law distribution; the maximum observed cluster consists of about 13,000 molecules.

The results of the DSMC model calculations subject to the initial conditions provided by the MD model are represented in Fig. 4. As compared to the desorption regime profile shown in Fig. 3b, changes in both the shape and dimensions are noticeable for the monomer density profile in the ablation regime at 300 ns, as shown in Fig. 4a. Although the monomer density pattern remains prolate, it is not elliptical. Rather, a characteristic two-fold shape of the monomer density profile is formed, which consists of a slow, less forward-peaked fraction and a fast fraction, which is directed more towards the plume axis. Sticking reactions between large clusters and monomers are found to be the main reason of the monomer bifurcation [13]. The region of low intermediate density of monomers corresponds to the region of high population of clusters in the size range of 50 to 1000 molecules as shown in Fig. 4b. Evaporation of monomers, modeled in this study by RRK theory, can partially cancel the effect of the sticking collisions between clusters and monomers. The lifetime of a cluster or the sticking collision complex, i.e., time to the evaporation of a monomer, however, depends on the cluster size and internal temperature. For the clusters in the mentioned size range, the mean lifetime for a typical internal temperature of 300 K is greater than 1 μs [14], whereas at heights less than 200 μm at 300 ns the cluster size is larger than 1000 and the estimated lifetime is less than 10 ns. Therefore, in the lower part of the plume the sticking collisions are almost instantly followed by evaporation, while at the middle of the plume there is no monomer evaporation on the considered time scale. The intensive evaporation of monomers from very large clusters located at the lower part of the plume as shown in Fig. 4b leads also to a significantly larger radial extension of the monomer profile at 300 ns as compared to that in the desorption regime, Fig. 3b. The higher axial extension of the monomer density in the ablation regime, about 600 μm as compared to 300 μm in the desorption regime, can be attributed to the collective phenomena initiated by a pulse laser beam at a

fluence above the ablation threshold. Phase explosion of the overheated surface material, which is the main mechanism of material expulsion at high laser fluences, imparts much higher kinetic energies to the ejected particles.

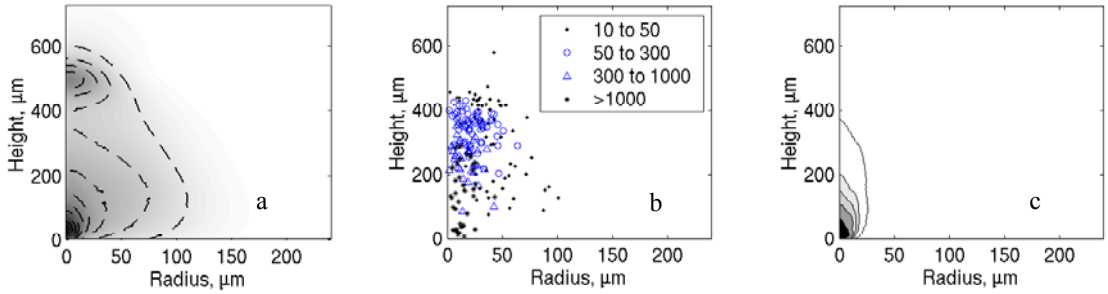

FIGURE 4. (a) Density of monomers at 300 ns when the interaction processes cease. (b) Location of clusters of different sizes at 300 ns, the legend designates cluster sizes. (c) Overall plume density at 300 ns.

Interactions between clusters and monomers in the plume also cause the appearance of the radial flow of clusters [14]. Obviously, the lighter the cluster, the larger the radial velocity it has acquired, which is seen in Fig. 4b. The axial distribution of large clusters remains practically unaltered in the course of the plume expansion, the lighter the clusters, the higher they are located in the plume.

Since large clusters constitute a major part of the plume mass, the plume density profile, Fig. 4c, has little relation with the monomer density profile, Fig. 4a. Because of the rapid plume expansion in the axial direction, very large clusters located at the lower part of the plume do not succeed in acquiring significant radial velocity in the collisions with monomers and light clusters. As a result, the aspect ratio of the overall mass density profile is about three times higher as compared to the one of the monomer density profile, and no bifurcation is seen on the plume density pattern.

Although numerous experimental studies confirmed the presence of large clusters in the plume [11,12] as well as non-thermally high speed of the expansion front [9], direct experimental verification of the presented theoretical results is still lacking. The spatial distribution of clusters in the plume can be visualized by laser-induced fluorescence (LIF) and Rayleigh scattering imaging techniques [21]. The effect of bifurcation of monomers, however, may not be seen by the standard methods, since when the plume expands to the size accessible for image processing, the monomer density in the upper part of the plume may be too low. We believe that sophisticated experimental setup may facilitate verification of the predicted results.

SUMMARY

We have presented a hybrid MD-DSMC model for the evolution of a desorption/ablation plume for short laser pulses, when the common thermal desorption scenario may be inapplicable. Even for relatively low laser fluences, when the desorption of single molecules is the main ejection mechanism, our model yields a higher speed of the expansion front and narrower angular distribution of the ejected molecules than those predicted by the thermal desorption models. For high fluences (ablation regime), the phase explosion of the target material and intensive processes of particle interactions within the plume are responsible for dramatic changes in the plume evolution as compared to that at low fluences. Relatively high axial and radial expansion, a bifurcation of a density profile of monomers, presence of large strongly forward peaked clusters, absence of the correlation between the monomer density profile and the plume density profile are the characteristics of the plume evolution in the ablation regime.

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