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Multiscale simulation of laser ablation of organic solids: evolution of the plume

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Abstract

A computational approach that combines the molecular dynamics (MD) breathing sphere model for simulation of the initial stage of laser ablation and the direct simulation Monte Carlo (DSMC) method for simulation of the multi-component ablation plume development on the time- and length-scales of real experimental configurations is presented. The combined multiscale model addresses different processes involved in the laser ablation phenomenon with appropriate resolutions and, at the same time, accounts for the interrelations among the processes. Preliminary results demonstrate the capabilities of the model and provide new insights into complex processes occurring during the ablation plume expansion. The spatial distribution of monomers in the plume is found to be strongly affected by the presence of large clusters. Interaction between the clusters and monomers can result in splitting of the monomer distribution into faster and slower components. The overall spatial mass distribution is found to have little relation with the monomer distribution.

Keywords: Molecular dynamics; Monte Carlo; Clusters; Spatial distribution

1. Introduction

The need to understand the mechanisms of plume expansion in laser ablation is defined by a rapid growth in the practical applications of this phenomenon, particularly for desorption–ionization of biomolecules in mass-spectrometric investigations [1–3] for surface microfabrication of polymer films [4–6] and in laser surgery [7]. The main obstacle for further progress in the modeling of laser ablation is the lack of connections between the different levels of description of this complex multiscale phenomenon. Different models address specific processes with specific resolutions, whereas the real processes occurring at different time- and length-scales are strongly coupled and interrelated.

On the microscale, the processes involved in plume formation include laser excitation of molecules, energy transfer from the excited molecules into the internal and translational modes of the surrounding molecules, formation of a highly energized high-temperature and high-pressure region, explosive disintegration and prompt ejection of a volume of material, and initial energy and composition redistribution within the plume. This stage is characterized by relatively high material density and molecular dynamics (MD) technique combined with the breathing sphere model [8] which has been demonstrated to be adequate for simulation of the

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initial stage of laser ablation [9,10]. Some of the findings of this model with regard to the ablated plume features are listed below.

- Clusters in a very broad size range from dimers to clusters composed of tens of thousands of molecules constitute a significant part of the plume in the ablation regime.
- A nearly identical linear increase of the flow velocity in the axial direction (i.e., normal to the surface) as a function of the distance from the initial surface is established for all components of the plume. The clusters of different sizes are entrained in the expanding plume and are moving along with the individual molecules with nearly the same flow velocity.

In the following stage of plume evolution, elastic and inelastic collisions among particles forming the plume and/or the background gas are dominant processes. The rarefied conditions make it possible to use either continuum analytical models [11–13] or Monte Carlo simulations [14–17]. In Monte Carlo simulations, it is typically assumed for initial conditions that the plume consists of monomers with thermal velocities. The results of the MD simulations, however, suggest that the ablation plume can have a complex composition, with clusters of different sizes comprising a major fraction of the ejected material [9,10]. It is therefore of scientific and practical interest to study how the nano-scale plume characteristics will affect the plume behavior on the larger time- and length-scale.

In this paper, a two-stage computational model of laser ablation of organic solids is discussed. One of the most appropriate MC methods for the rarefied flow description, direct simulation Monte Carlo (DSMC) [18], is chosen for extending the MD breathing sphere model into the larger scale. In order to adopt the results of MD simulation as input for the DSMC calculation, we have to characterize both the statistical distribution of the MD output (e.g., spatial monomer and cluster distributions, translational and internal energy distributions) and possible reactions between monomers, clusters and/or the background gas. In the MC description, clusters of each size constitute a separate species. The maximum number of species considered to date in DSMC calculations have been about 25 [19]. In ablation, the number of molecules in the ejected clusters can be as high as tens or even hundreds of thousands [20]. It is computationally impossible to include thousands of species into a simulation [21]. This computational challenge and the non-trivial issue of statistical characterization of limited data from the breathing sphere model are addressed in the following section.

The initial results of the combined two-stage model are discussed in this paper. The spatial density of monomers is strongly affected by large clusters in the plume. At the same time, collisions between monomers and clusters cause redistribution of large clusters within the plume. Finally, the overall spatial mass distribution is predicted to have little relation with the monomer distribution.

2. Computational setup

The chosen form of the Monte Carlo procedure dictates what kind of statistical information we need to retrieve from the MD model. Briefly, in the DSMC method the entire flow volume is divided into cells with dimensions of about one mean free path. Each cell is filled with simulated particles that are characterized by spatial coordinates, velocities, internal energy, mass, cross-sections and weight factor. The weight factor is the number of real particles that are represented by each simulated particle. The basic principle of DSMC is that the continuous process of particle movement and interaction is uncoupled. First, at each time step every particle is moved according to its velocity. Next, the interaction between the particles is modeled by collisions. Collision pairs are selected at random within each cell and the probability of collision acceptance is calculated with regard to the relative velocity and the reaction cross-section. Once accepted, the collision alters the particle velocities in elastic collisions and the internal energies in inelastic collisions. Reactions other than two-particle interactions (e.g., three-body collisions and evaporation from clusters [19]) can be incorporated in the interaction stage.

Therefore, we need to provide the following information for each cell.

- Number density for monomers and clusters of each size.
- Velocity distribution for monomers and clusters of each size.
- Internal energy distribution for cluster of each size.

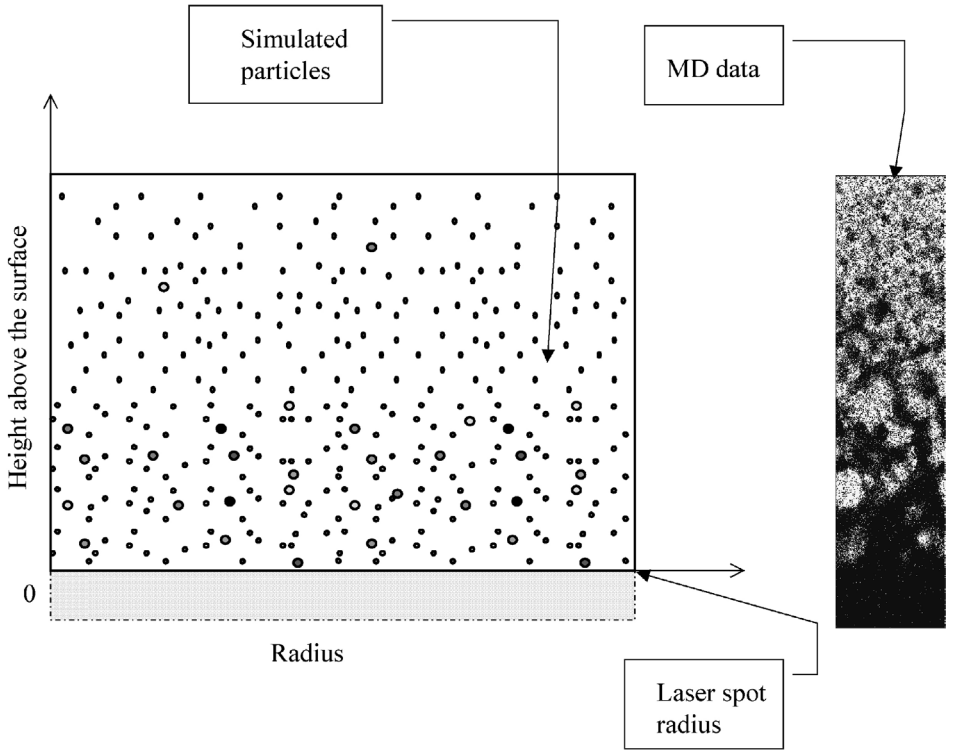

Fig. 1. The initial cylindrical volume of a plume above the ablated surface is filled with simulated particles in accordance with the results of the MD simulation. The flat-profile laser pulse simulated here imposes the same initial and boundary conditions for the MD simulations throughout the laser spot. Thus, it is possible to use the results of a single run of the MD calculations within a thin bar as the input for the entire plume.

We also have to characterize reactions between clusters, including monomers.

For this study, we chose a simple case of a laser pulse with a flat spatial profile, a fluence of 61 J/m^2, a penetration depth of 50 nm and a pulse duration of 15 ps, which makes it possible [22] to use the results of a single MD simulation as a uniform input for the region of the laser spot with radius of 10 μm (see Fig. 1).

The results of the cluster distribution from the MD simulation are given in Table 1. The size of the clusters ranges from dimers to clusters of about 14,000 molecules. If we wanted to represent directly all the clusters in the DSMC calculation, then we would need 14,000 species. For each of the 14,000 species, we would need to estimate the spatial and velocity distribution functions. As can be seen from Table 1, there are relatively few large clusters. In particular, the available information of clusters larger than pentamers is insufficient for a proper estimation of the needed distributions [21].

Table 1
MD data of the initial plume composition

Cluster size range, number of molecules	1	2	3–8	9–14000
Number of clusters in MD output	18999	2105	672	56
Contribution to the total yield (%)	24.9	5.5	3.1	66.5

The two computational challenges for using the MD output in the DSMC calculation are thus the vast number of cluster sizes and the low frequency of occurrence of large clusters. The maximum number of different species which have been used in DSMC simulations is about 25 [19]. It is computationally impossible to use 14,000 species in a simulation [21]. The suggested remedy for these computational challenges is the introduction of cluster groups, which combine clusters with similar physical features. In this study we have grouped the clusters by the main type of

collision reaction, although other features such as size and spatial density could also be used [22]. The main reactions are identified as elastic collisions (e.g., monomer–monomer, monomer–small cluster), sticking collisions (e.g., cluster–cluster, monomer–large cluster) and evaporation of monomers from clusters. The hard-sphere cross-sections are evaluated numerically for monomers and approximated for clusters [21]. Evaporation is modeled by the classic RRK model [23].

More details of the estimation procedure are given elsewhere [21] and here we briefly outline the main points:

- The underrepresented clusters are divided into the following two groups—"small" clusters in the size range 6–9 and "large" clusters comprising 10 molecules or greater.
- The spatial number density is estimated for monomers, dimers, trimers, tetramers, pentamers and for each cluster group separately.
- The velocity distributions are assessed based on the effect of entrainment of clusters into the plume and the estimated axial and radial temperatures of the monomers and clusters [22].
- The internal energy distribution was confirmed to be of a known analytical type [18] and its parameters were estimated.

In our DSMC simulation the cylindrical volume surrounding the plume above the laser-ablated surface is divided into cells and filled with the particles, representing one of the above-mentioned seven species. The number of the particles of each species in a cell is proportional to their estimated number density. Then if the species belongs to one of the two cluster groups, the particle mass is assigned in accordance with the cluster size distribution within the group. The velocity and internal energy for each particle are sampled from the corresponding estimated distribution, and the particle position is chosen at random within the cell. For monomers and well-represented clusters (dimers through pentamers), the procedure is the same except for the random mass. The use of only seven species allows us to represent each species with at least two particles in an initial cell, thus assuring that possible cluster reactions are represented in full.

Our simulations stopped at a time of 800 ns when the collision frequency approaches zero. The results obtained are discussed in the next section.

3. Results and discussion

The spatial density of plume components is discussed below. Figs. 2 and 3 show the spatial density of monomers and large clusters (>10 molecules in size) at time 20 ns after switching from MD to DSMC. The radius of the simulated laser spot is 10 μm. The density distributions at this early time of the plume

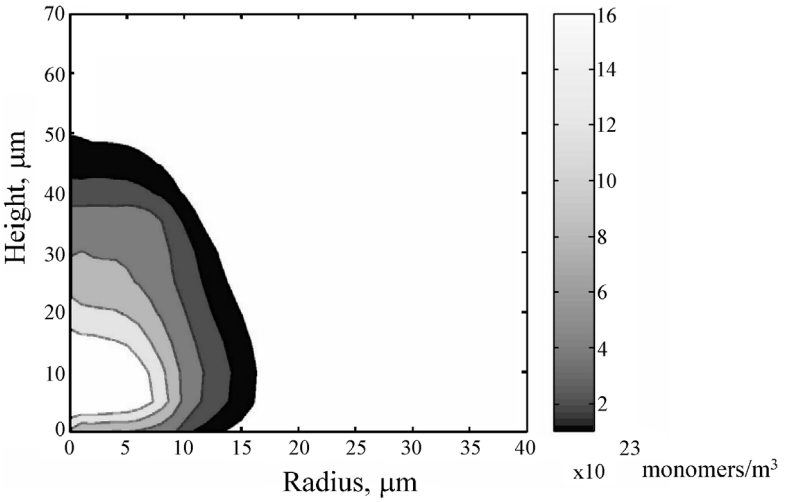

Fig. 2. Monomer density at time 20 ns after switching from MD to DSMC.

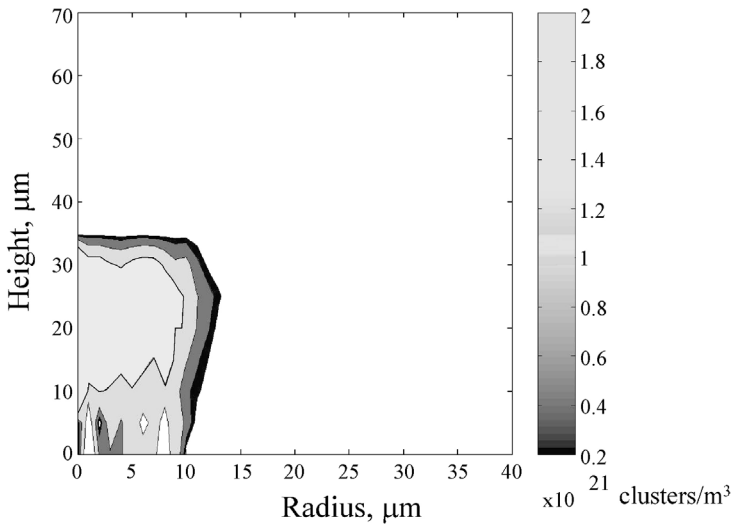

Fig. 3. Density of large clusters containing more than 10 molecules at time 20 ns after switching from MD to DSMC.

expansion are strongly affected by the initial parameters obtained from the MD simulation. The MD simulation shows that the particles near the top of the plume have a much larger axial flow velocity than the particles near the bottom [22]. Therefore, the plume expands mainly in the axial direction. The height above the surface of large clusters is bounded by 35 μm, whereas the maximum height reached by monomers is about 50 μm. The region of maximum density of large clusters is located between 10 and 32 μm. The region of maximum density of monomers is located closer to the surface between 3 and 17 μm. These characteristics are similar to the results of the MD simulation [22].

Figs. 4 and 5 show the spatial density of monomers and large clusters at time 500 ns after switching from MD to DSMC. Dramatic changes are noticeable for this time for both monomers and large clusters. For monomers, two separate regions of enhanced density are clearly seen on the plot with the second region

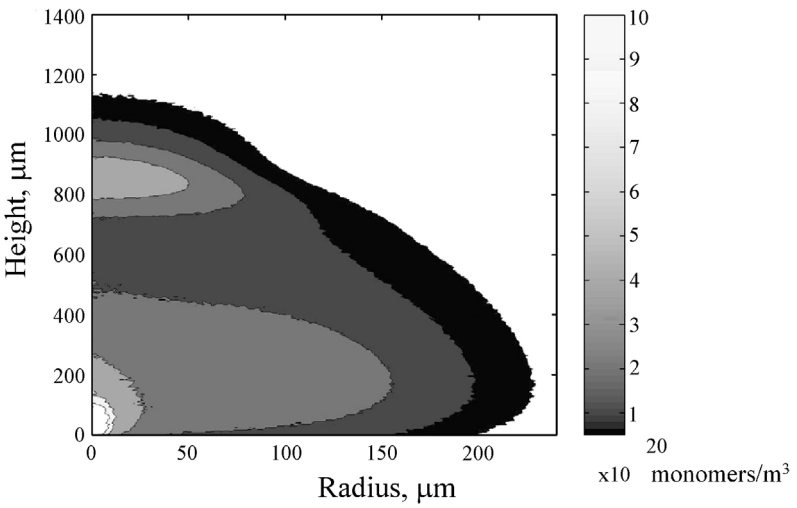

Fig. 4. Monomer density at time 500 ns after switching from MD to DSMC.

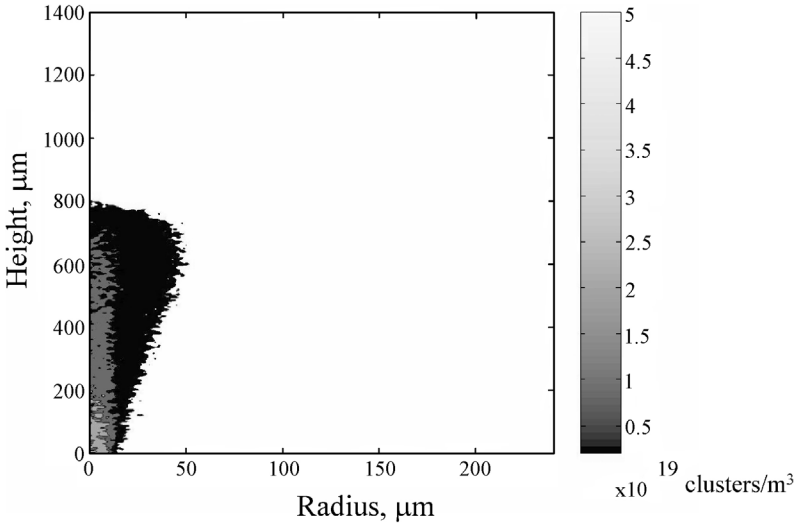

Fig. 5. Density of large clusters containing more than 10 molecules at time 500 ns after switching from MD to DSMC.

located near the height of 850 μm. Sticking reactions between large clusters and monomers are found to be the main reason for the monomer bifurcation. Indeed, the region of high density of large clusters at time 20 ns (Fig. 3) corresponds to the region of 20–64% of the maximum height of the monomers at time 20 ns. Because of the self-similarity of the plume expansion in the axial direction and due to the effect of the entrainment of clusters in the plume [20], the majority of large clusters remain at the same region of 20–64% of the maximum height of the monomers, i.e. between 230 and 740 μm at time 500 ns. Evaporation of monomers, modeled in this study by RRK theory, can balance sticking collisions between large clusters and monomers. The lifetime of a cluster or the sticking collision complex, i.e. time for the evaporation of a monomer, depends on the cluster size and internal temperature. The strong correlation between cluster size and its height above the surface (the smaller the cluster size, the higher it is located—see Fig. 6) and

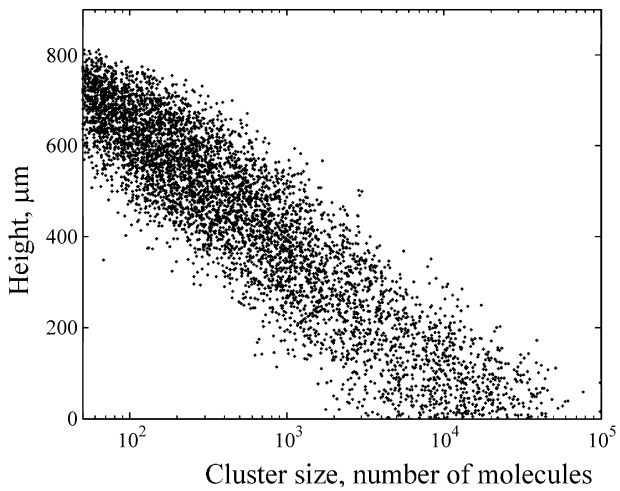

Fig. 6. Cluster size–height above the surface dependence for large clusters at time 500 ns after switching from MD to DSMC. Each point corresponds to a cluster.

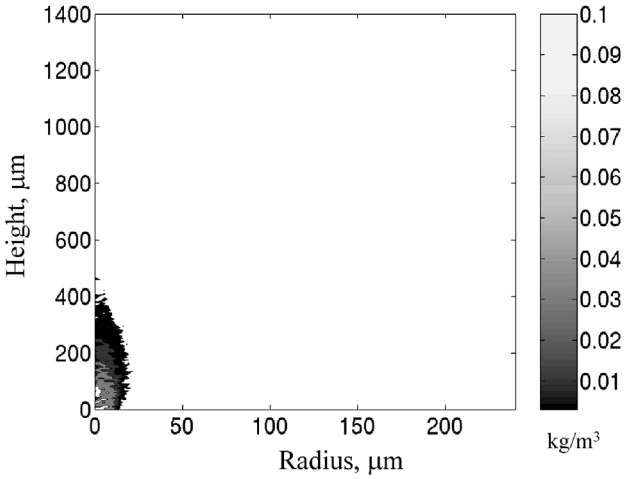

Fig. 7. Total mass density in the plume at time 500 ns after switching from MD to DSMC.

similar correlation between cluster size and its internal temperature [21] leads to the dramatic difference in lifetimes. At the upper part of the large clusters (at height 500–800 μm in Fig. 5), where the cluster size is in the range 10–200, the mean lifetime for a typical internal temperature of 300 K is greater than 1 μs [21], whereas at the bottom part (height less than 200 μm), the cluster size is larger than 1000 and the estimated lifetime is less than 10 ns. Therefore at the bottom of the plume, the sticking collisions are almost instantly followed by evaporation, while at heights above 500 μm there is no monomer evaporation on the considered time-scale.

Another interesting feature of the evolution of the plume composition is an unusual expansion of large clusters (Figs. 3 and 5). The higher the clusters are, the more they expand in the lateral direction. This expansion can be explained by the dependence of initial thermal radial velocity of large clusters on their sizes. As the estimated initial translational temperatures of clusters are nearly independent of the cluster size [22], the dependence of cluster size on the height above the surface (Fig. 6) results in the unusual shape of large cluster density.

Finally, the distribution of the plume mass at time 500 ns is shown in Fig. 7. As large clusters constitute the major part of the plume mass, there is no relation between monomer density (Fig. 3) and the actual overall mass density.

4. Conclusion

This paper describes a two-stage computational model, in which the results of the nano-level breathing sphere model of laser ablation of organic solids are adopted as the initial conditions for a Monte Carlo simulation of the following plume expansion. New insights into the evolution of the spatial plume composition were gained by the combined model.

- The monomer density distribution in the ablation plume is strongly affected by the presence of clusters and bifurcate at time above 500 ns for the chosen laser fluence (about twice the ablation threshold) and duration (15 ps).
- The overall mass density is characterized by much stronger forward peaking than the density of monomers.

These findings are of relevance to both mass spectrometry applications and pulsed laser deposition (PLD) of thin organic films.

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