

# Molecular Dynamics Study of Laser Ablation Plume Formation and Cluster Ejection: Implications for Laser-Driven Mass Spectrometry Techniques

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**Introduction.** Computational modeling has a potential of making an important contribution to the advancement of laser-driven methods in mass spectrometry. In particular, recent molecular dynamics (MD) simulations have provided insights into various aspects of matrix assisted laser desorption/ionization (MALDI).<sup>1,2,3,4</sup> The microscopic mechanisms of laser ablation/desorption, parameters of the ejected molecules and their dependence on the irradiation conditions has been analyzed with both atomistic<sup>1,2</sup> and mesoscopic resolutions.<sup>3,4,5</sup> In the present study we perform a computational analysis of the initial stage of the ablation plume formation and analyte ejection in MALDI. Active processes occurring during the first hundreds of picoseconds of the plume development play an important part in defining the survivability and desolvation of large analyte molecules. A better understanding of the dynamics of the plume formation can also provide necessary input for ionization models being developed for MALDI.<sup>6,7</sup>

**Computational Method.** In simulations of MALDI we use the breathing sphere model,<sup>5</sup> which provides an adequate description of a molecular system, allows us to expand the length- and time- scales of the simulations up to the ones comparable to the experimental conditions, and provides an effective means for incorporation of the description of the primary laser excitations and the vibrational relaxation of excited molecules into the model. Analyte molecules in the model are represented by a bead-and-spring model. A new computational setup aimed at investigation of surface-assisted laser desorption is also presented and preliminary results are discussed. In this case the two-temperature model is coupled to the atomistic MD model to account for the laser energy absorption into the electronic system and fast electron heat conduction through the film.

## Results and Discussion

*The dynamics of the early stages of the ablation plume formation* and the mechanisms of cluster ejection are investigated in large-scale MD simulations. The cluster composition of the ablation plume has a strong dependence on the irradiation conditions and is defined by the interplay of a number of processes during the ablation plume evolution. At sufficiently high laser fluences, the phase explosion of the overheated material leads to the formation of a foamy transient structure of interconnected liquid regions, Figure 1, that subsequently decomposes into a mixture of liquid droplets, gas-phase molecules, and small clusters. The ejection of the largest droplets has been attributed to the hydrodynamic motion in the vicinity of the melted surface, especially active in the regime of stress confinement. Spatially-resolved analysis of the dynamics of the plume formation reveals the effect of segregation of the clusters of different sizes in the expanding plume. The largest clusters are formed in the region closest to the surface, medium-size clusters are formed in the middle of the plume, and small clusters are formed in the top part of the plume, with almost no regions of coexistence of clusters of different sizes. Despite being ejected from deeper under the surface, the larger clusters in the plume have substantially higher internal temperatures as compared to the smaller clusters. The cluster size distributions can be relatively well described by a power law  $Y(N) \sim N^{-\tau}$  with exponents different for small, up to  $\sim 15$  molecules, and large clusters, Figure 2. The decay is much slower in the high mass region of the distribution. The revealed characteristics of cluster ejection provide a basis for discussion of the ionization mechanisms in MALDI,<sup>6,7</sup> the efficiency of postionization, and desolvation of the analyte molecules.

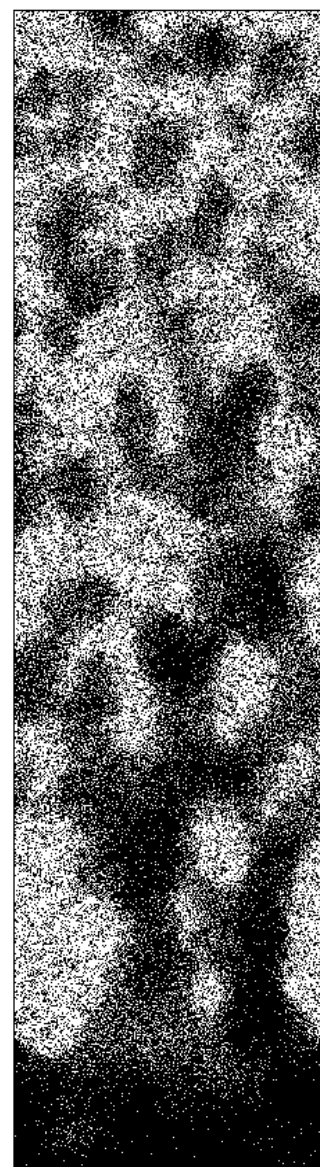
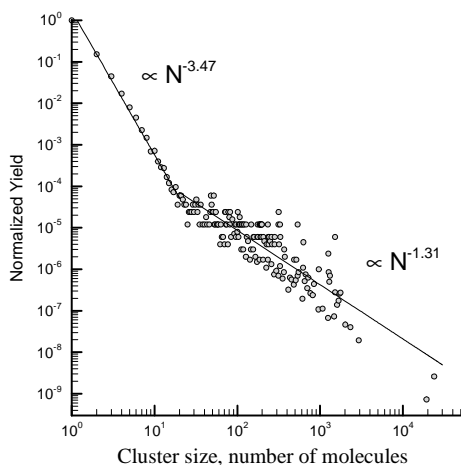
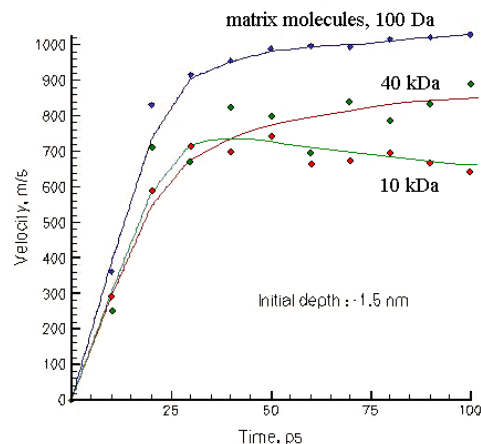


Figure 1. Formation of a foamy transient structure of interconnected liquid clusters and gas-phase molecules in MD simulation of laser ablation of a molecular system.



**Figure 2.** Cluster abundance distribution in the ablation plume observed at 1 ns after irradiation of a molecular solid with 150 ps laser pulses at laser fluence of 61 J/m<sup>2</sup>.



**Figure 3.** Velocities of matrix and analyte molecules as function of time in simulation of laser irradiation of a molecular solid with 15 ps laser pulses at laser fluence of 55 J/m<sup>2</sup>. The data is shown for molecules initially located at 1.5 nm below the surface.

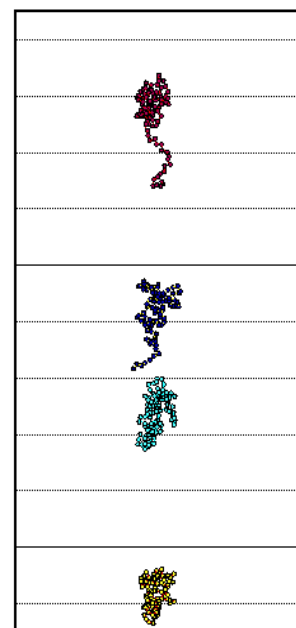
We continue<sup>4</sup> computational investigation of the ejection of analyte molecules in MALDI. The ejection velocities of analytes of different masses are investigated for different initial location of the analytes in the sample. We find that the analyte molecules are entrained into expanding plume of matrix molecules and, for the same depth of origin, their velocities exhibit only a weak dependence on molecular mass, Figure 3. The observed values of the ejection velocities, hundreds of m/s, and the weak dependence of the velocities on molecular mass are in agreement with experimental measurements. At the same time, we find that irradiation conditions (laser fluence and pulse duration) and the degree of incorporation of analyte molecule into matrix have strong effect on the ejection velocities. In agreement with earlier atomic-level simulations,<sup>2</sup> we find that the entrainment of the analyte molecule into expanding plume of matrix leads to conformational changes of the analyte molecules, Figure 4. The extension of the analyte molecule along the plume flow direction can reduce the efficiency of entrainment and the final velocities of the analyte molecules.

**Summary and Future Work.** A detailed microscopic picture of matrix disintegration and ablation plume formation is revealed in MD simulations. Future directions include a more systematic analysis of the effect of mass and geometrical parameters (e.g. globular vs. linear) of analyte molecules on their ejection velocities. Events leading to the fragmentation of analyte molecules during the matrix disintegration the initial stage of the plume expansion will be studied for analytes with different degree of incorporation into matrix crystal.

A computational model for atomic-level simulation of laser interaction with metals has been designed and tested. The model can be applied for simulations of surface-assisted laser desorption, when molecular ejection is due to the fast energy transfer from the metal film to an organic overlayer.

## References

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**Figure 4.** Ejection of a globular polymer chain in MALDI. Matrix molecules are not shown in the figure.