

Ejection of matrix-polymer clusters in matrix-assisted laser evaporation: Coarse-grained molecular dynamics simulations

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Abstract. Molecular-level dynamic simulations are performed to investigate the mechanisms of molecular ejection and transport in laser ablation of frozen polymer solutions, as related to the matrix-assisted laser evaporation (MAPLE) technique for polymer film deposition. Coarse-grained description of molecular matrix and polymer molecules is used in the model, allowing for large-scale simulations of the ejection of multiple polymer molecules from MAPLE targets with different polymer concentrations, from 1 to 6 wt.%. The ejection of polymer molecules is observed only above the threshold for the collective material ejection (ablation). Ablation is driven by the phase explosion of the overheated matrix material, which proceeds through the formation of a foamy transient structure of interconnected liquid regions that subsequently decomposes into a mixture of liquid droplets and gas-phase matrix molecules. The polymer molecules resist the decomposition of the transient foamy liquid structure and stabilize the matrix droplets. In all simulations the polymer molecules are ejected as parts of large matrix-polymer droplets/clusters that are likely to retain a large fraction of matrix material at the time of the deposition on a substrate. The ejection and transport of large matrix-polymer droplets is related to high-resolution scanning electron microscopy (SEM) images of polymer films deposited in MAPLE, where morphologies of the films are found to be indicative of active processes of matrix vaporization and escape from the deposited matrix-polymer droplets.

1. Introduction

The Matrix Assisted Pulsed Laser Evaporation (MAPLE) technique is a process of molecular entrainment for deposition of thin polymer films, developed with the goal to minimize chemical modification of the target material [1,2]. In MAPLE, the target is prepared by dissolving the material to be deposited in a volatile solvent, freezing the homogeneous dilute solution (0.1-5 wt.%) and placing it into a vacuum chamber for deposition. Short pulse laser irradiation of the target results in a collective ejection or ablation of the matrix which entrains the polymer molecules along into the plume. The ejected polymer molecules are deposited on a substrate, whereas the volatile solvent molecules are pumped away from the deposition chamber.

First investigations have demonstrated that, with an appropriate choice of experimental parameters, MAPLE is capable of providing conditions for “soft” ejection and deposition of polymer and biological molecules. Recent developments include deposition of very thin (10-50 nm) and highly uniform films for biosensor fabrication [3] and exploration of the potential of water ice as a matrix [4,5]. Further optimization of experimental parameters in current applications of MAPLE and the emergence of new methods and areas of application can be facilitated by a better understanding of the

relation between the basic mechanisms of laser interaction with the target material, non-equilibrium processes caused by the fast deposition of laser energy, parameters of the ejected ablation plume, and the resulting morphological characteristics of the growing film. Molecular-level computer modeling, in particular, has a potential of revealing the mechanisms of molecular ejection and transport in MAPLE. Molecular dynamics (MD) simulations reported to date have been limited to the analysis of matrix-assisted ejection of individual macromolecules [6,7,8,9] and the effects of the polymer concentration on the ablation process has not been addressed.

In this paper we present first results of coarse-grained molecular dynamics simulations of the early stages of laser ablation of MAPLE targets. The characteristics of molecular ejection and the composition of the ejected plume are studied for a range of laser fluences and different polymer concentrations in the target. Polymer molecules are found to be ejected within extended matrix droplets/clusters which undergo significant changes in shape, size, and composition during the first nanosecond of the plume expansion. The ejection and transport of large matrix-polymer droplets observed in the simulations is related, at a qualitative level, to the morphologies of polymer films deposited in MAPLE.

2. Computational model

The laser-driven material ejection from the target is described in this work by a coarse-grained molecular dynamics model built around the “breathing sphere” model [10]. The model has been actively used for investigation of laser interaction with molecular targets [9,10]. It adapts a coarse-grained representation of the molecules by particles with real translational degrees of freedom, but approximate representation of the internal degrees of freedom. The model is capable of describing molecular excitation by laser irradiation, intermolecular energy transfer, as well as the collective molecular dynamics induced by laser irradiation. The polymer molecules are represented by the bead-and-spring model, commonly used in polymer modeling [11]. The “beads” representing functional groups of a polymer molecule (monomers) are connected by anharmonic springs with strengths appropriate for chemical bonding. The chains can dissociate if the local forces applied to the chemical bonds are sufficiently large.

The discussion of laser ablation of polymer-matrix targets reported in this paper is based on nine simulations performed at three laser fluences of 4, 6, and 8 mJ/cm² and three concentrations of polymer molecules in the MAPLE target, 1, 3 and 6 wt.%. The laser pulse duration of 50 ps and optical penetration depth in pure matrix of 50 nm are chosen to reproduce the conditions of thermal confinement characteristic of the parallel experimental study performed for toluene/PMMA system. In this irradiation regime, the heat conduction does not contribute to the energy redistribution during the laser pulse and the thermal energy is largely confined within the absorbing region. The absorption by polymer molecules is neglected in this study and the effective penetration depth is increased with increasing concentration of polymer molecular in the MAPLE target. Computational cell with dimensions of 40×40×60 nm (~650,000 molecules) is used in the simulations with the polymer chains randomly and uniformly distributed in the sample. Each chain contains 100 monomer units with each unit being of the same molecular weight as a single matrix molecule, 100 Da. This weight corresponds to the weight of a PMMA monomer and is close to the weight of a toluene molecule, 92 Da.

3. Results and discussion

In this section we briefly discuss the results of MD simulations of laser ablation of the matrix-polymer target. The mechanisms of explosive matrix disintegration are discussed first, followed by the analysis of the evolution of the ejected matrix-polymer clusters during the first nanosecond of the plume expansion and comparison between the computational results and experimental observations.

3.1. The effect of polymer molecules on the mechanisms of laser ablation

Figure 1 shows snapshots from two simulations performed for the same polymer concentration in the target and different laser fluences. In both simulations the ablation mechanism can be described as an

explosive decomposition of the target material overheated above the limit of its thermodynamic stability. The phase explosion of the overheated material leads to the formation of a foamy transient structure of interconnected liquid regions that subsequently decomposes into a mixture of liquid droplets, gas-phase molecules, and small clusters. In the simulation performed at 4 mJ/cm^2 , close to the ablation threshold, the characteristic size of the liquid regions is large and the ejection process is relatively slow, Fig. 1a. Most of the material ejected in this simulation is contained in a few large droplets. As the fluence increases, the fraction of the matrix turning into vapor and driving the ejection of the liquid droplets is increasing and a more violent “phase explosion” takes place, Fig. 1b. The overall picture of laser ablation is similar to the one observed in earlier simulations performed for pure matrix [12]. The presence of polymer chains adds stability to the transient liquid structures generated in the ablation process and facilitates the formation of larger matrix droplets. While the initial orientation of the polymer chains in the target is random, they have a clear tendency to extend along the flow of the ablation plume and to thread through the liquid regions. The decomposition of the transient liquid structure is hampered by the necessity to pull out and, at higher polymer concentrations, disentangle the polymer chains.

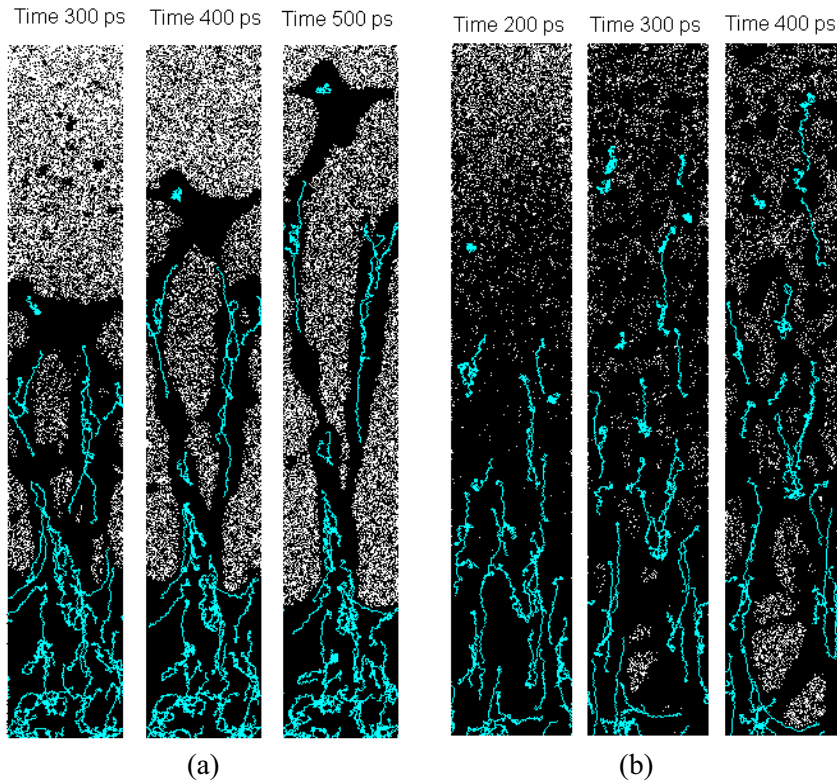


Figure 1. Snapshots from simulations of laser ablation of a MAPLE target with 1 wt. % polymer concentration irradiated at two laser fluences: a) 4 mJ/cm^2 and b) 6 mJ/cm^2 .

Polymer chains are shown in blue colour and are superimposed on the matrix shown in the background.

3.2. Ejection of matrix-polymer clusters

In all simulations performed so far we find that the polymer molecules are ejected only as parts of matrix-polymer droplets/clusters. For the same polymer concentration, a higher fluence yields more clusters with a broader range of sizes. Smaller clusters are typically generated in the upper part of the expanding plume, whereas large clusters are formed in the deeper regions, e.g. Fig. 1b. The dynamics of cluster formation is reflected in Fig. 2, where spatial distributions of clusters in the plume are shown for two simulations performed at the same laser fluence but different polymer concentrations. In both cases, clusters that are generated in the top parts of the expanding plume are smaller and typically contain one or two polymer chains. The clusters that are formed in the deeper parts of the plume are larger and contain more polymer chains.

For the same laser fluence we observe that an increase in the polymer concentration tends to break a continuous distribution of cluster sizes into a distinct bi-modal distribution with a few very large droplets on one side of the distribution and numerous small clusters on the other side. An example of the bi-modal cluster size distribution is shown in Fig. 2b, where a large fraction of the ejected polymer molecules is contained in the two largest clusters.

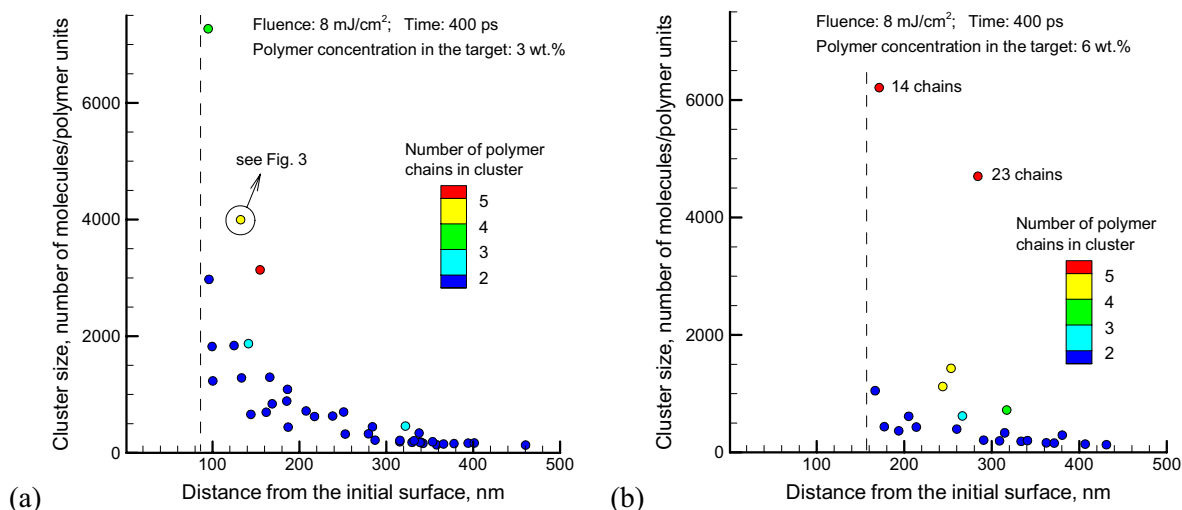


Figure 2: Distribution of matrix-polymer clusters in the ejected plume at 400 ps after the beginning of the laser pulse. Polymer concentration in the target is a) 3 wt.% and b) 6 wt.% and a laser fluence of 8 mJ/cm² is used in both simulations. Colour coding corresponds to the number of polymer chains in each cluster. Dashed lines separate the ejected plume from the regions where the process of decomposition of the foamy liquid structure is not complete at 400 ps and individual clusters cannot be identified. Additional detachment of large liquid droplets from these regions takes place at later times.

3.3. Evolution of matrix-polymer clusters in the plume

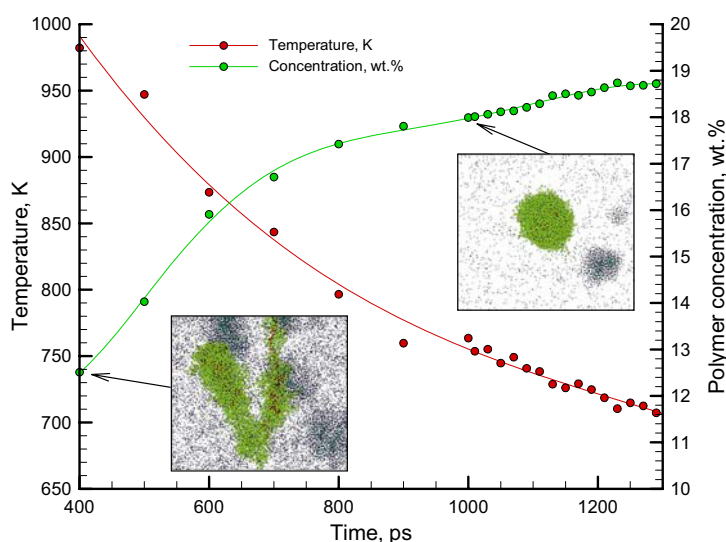


Figure 3. Internal temperature and composition (polymer concentration) of a cluster ejected in the simulation illustrated in Fig. 2a. The cluster contains 5 polymer chains. Snapshots of the cluster taken at 400 and 1000 ps are shown in the insets.

Figure 3 provides information on the evolution of a single matrix-polymer cluster containing five polymer chains. Within 600 ps following the detachment of the cluster, its internal temperature decreases by about 300 K and the polymer concentration in the cluster increases by about 6%. The increase in the polymer concentration and the fast cooling are related to the evaporation of matrix molecules from the surface of the cluster. The snapshots taken at 400 and 1000 ps also reveal significant changes in the shape of

the cluster which attains an equilibrium spherical shape over time. The dramatic change of the shape converts the potential energy

of the surface to the internal kinetic energy of the cluster and additionally contributes to the matrix evaporation. Importantly, the saturation in the composition and temperature suggests that the composition observed at 1.3 ns is close to the one to be expected at the time it would reach a substrate in MAPLE polymer film deposition.

3.4. Connection to the experimental results

The ejection of large matrix-polymer droplets observed in simulations can be related to SEM images of polymer films deposited with MAPLE technique. The images show the morphology of films deposited from a target containing 5% PMMA in a toluene matrix. A deposition of several large droplets is observed at a laser fluence of 50 mJ/cm^2 , Fig. 4a. This fluence is close to the threshold below which no deposition is observed. As laser fluence is increased we see an increase in the number of deposited clusters, with both small and large clusters present on the substrate, Fig. 4b. Qualitatively, the observation of large droplets just above the ablation threshold can be related to the computational results, suggesting that only large matrix-polymer clusters are ejected at the ablation threshold (e.g. Fig. 1a) and the ejection of clusters with a broad size distribution takes place at higher fluences (e.g. Fig. 1b and Fig. 2). Large quantitative differences in the ablation threshold fluences and the droplet sizes observed in the simulations and experiments are related to the smaller length and time-scales of the simulated MAPLE process as compared to the experiment (e.g. laser pulse duration and penetration depth are 50 ps and 50 nm in simulations and 25 ns and $\sim 4.0 \mu\text{m}$ in experiments). Nevertheless, both the simulations and experiments are performed in the same physical regime of thermal confinement and the same physical processes are expected to be responsible for the molecular ejection in both cases.

The results of the simulations can also provide a clue for explaining the interesting shapes of the deposited polymer droplets that contain distinct features of collapsed pipes and shells/popped balloons. In simulations we observe that polymer molecules are always ejected as parts of matrix droplets/clusters. Thermal evaporation of matrix molecules leads to the fast cooling of the droplets but cannot completely desolve the polymer molecules (remove all the matrix from the droplets), e.g. Fig. 3. As a result, the droplets reaching the surface can still retain a significant amount of volatile matrix material. Therefore, we can propose the following scenario for the formation of the observed droplet morphologies. Active evaporation of matrix molecules from the surface of a large droplet could result in the formation of a polymer-rich surface layer, hampering the escape of the remaining matrix molecules. The droplets are deposited on a substrate that is maintained at a room temperature. The internal pressure from the volatile matrix molecules trapped inside the droplet could lead to the formation of the escape passes through the viscous polymer material. The escape of the matrix vapor

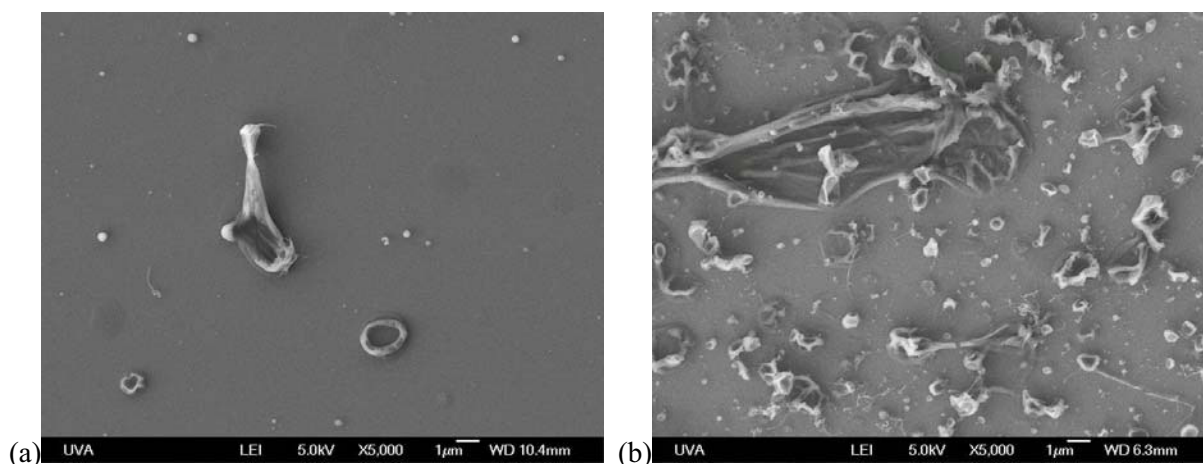


Figure 4. SEM images of MAPLE deposited PMMA films. Toluene matrix with 5% PMMA is used as a target. Laser fluence is 50 mJ/cm^2 in (a) and 130 mJ/cm^2 in (b).

could result in the collapse of the polymer surface layer into the wrinkled patterns, such as the ones observed in Fig. 4. We are currently verifying this speculative scenario in a series of specially designed simulations and experiments.

4. Summary

Molecular dynamic simulations of the initial stage of molecular ejection in MAPLE reveal the microscopic picture of laser ablation of matrix-polymer composite targets. The polymer molecules are found to stabilize the matrix droplets generated as a result of the explosive decomposition of matrix material overheated by short pulse laser irradiation. In all simulations the polymer molecules are ejected within matrix-polymer droplets/clusters that are likely to retain a large fraction of matrix material at the time of deposition on a substrate. Under no conditions we observe the ejection that would be limited to single polymer molecules. This observation suggests that deposition of uniform thin films may be difficult to achieve due to the unavoidable contribution of droplets and clusters to the film morphology. Indeed, experimental results presented in this paper for the toluene/PMMA system and recent results reported for water ice/PEG MAPLE targets [5] confirm the prominent presence of polymer droplets in the deposited films. The morphologies of experimentally observed polymer droplets, with distinct features of collapsed pipes and popped balloons, are interpreted in terms of the active processes of matrix vaporization and escape from the deposited matrix-polymer droplets.

Acknowledgments

Financial support of this work is provided by the National Science Foundation through grant DMII-0422632.

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