# Molecular dynamics simulation study of the ejection of polymer molecules and generation of molecular balloons in matrix-assisted pulsed laser evaporation

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## ABSTRACT

Coarse-grained molecular dynamics simulations are performed to investigate the origins of the surface features observed in films deposited by the Matrix-Assisted Pulsed Laser Evaporation (MAPLE) technique. The simulations of MAPLE are performed for polymer concentrations up to 6 wt.% and a broad range of laser fluences. The polymer molecules are found to be ejected only in the ablation regime and are always incorporated into polymer-matrix clusters/droplets generated in the process of the explosive disintegration of the overheated matrix. The entanglement of the polymer molecules facilitates the formation of intricate elongated viscous droplets that can be related to the complex morphologies observed in polymer films deposited by MAPLE. The effect of dynamic molecular redistribution in the ejected matrix-polymer droplets, leading to the generation of transient "molecular balloons" in which polymer-rich surface layers enclose the volatile matrix material, has been identified as the mechanism responsible for the formation of characteristic wrinkled polymer structures observed experimentally in films deposited by MAPLE.

**Keywords:** Matrix-assisted pulsed laser evaporation, MAPLE, film deposition, laser ablation, molecular dynamics

## 1. INTRODUCTION

Matrix-assisted pulsed laser evaporation (MAPLE) is a technique developed for deposition of high-quality ultra-thin organic, bioorganic, and composite films with minimum chemical modification of the target material [1-5]. In this technique, the target is prepared by dissolving the material to be deposited in a volatile solvent, freezing the homogeneous dilute solution (typically 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. Since most of the laser energy is absorbed by the volatile matrix rather than polymer molecules, the photochemical decomposition of polymers can be minimized or even completely eliminated. Moreover, since the ablation onset in MAPLE is defined by the thermodynamic parameters of the volatile solvent rather than the polymeric material, deposition can proceed at a significantly lower, as compared to the conventional PLD technique, energy densities, minimizing thermal decomposition of the polymer molecules.

No cluster formation is expected in MAPLE as the polymer concentration is low, the polymer molecules are dissolved down to the molecular level in the target, and the entrainment of the polymer molecules in the expanding plume of the volatile matrix does not provide an environment suitable for condensation of polymer clusters. It comes as a surprise, therefore, when high-resolution scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging of MAPLE deposited films reveal significant surface roughness, with well-defined aggregates or clusters with characteristic sizes ranging from tens of nanometers to tens of microns [6-15]. For example, SEM images of PMMA (polymethyl-methacrylate) films deposited in MAPLE with toluene used as a matrix reveal complex morphologies with distinct features of "collapsed pipes," "deflated balloons," and elongated nanofibers [12,13,16]. In order to explain the experimental observations and to reveal the processes responsible for the formation of the large polymer aggregates with complex morphology, a series of large-scale MD simulations of the early stages of laser ablation of frozen polymer

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solutions have been recently performed for a wide range of laser fluences and for targets with different polymer concentrations, from 1 to 6 wt.% [17]. In this paper, we review the results of the simulations and relate them to several distinct types of surface features observed in MAPLE deposited films.

## 2. COMPUTATIONAL MODEL

A coarse-grained MD model, combining the breathing sphere model [18,19] for simulation of the molecular matrix and the bead-and-spring model [17,20] for representation of polymer molecules, is used in the simulations. The model is schematically illustrated in Figure 1. The breathing sphere model assumes that each molecule can be represented by a single particle, Figure 1a. The parameters of interparticle interaction are chosen to reproduce the properties of the material, in this case, a molecular solid. In particular, the cohesive energy, vibrational/elastic properties, as well as speed of sound, thermal conduction, melting and boiling temperatures, strength and plasticity of the material are defined by the interparticle interaction potential. The equilibrium distance in the interparticle potential is defined as the distance between the edges of the spherical particles rather than their centers.

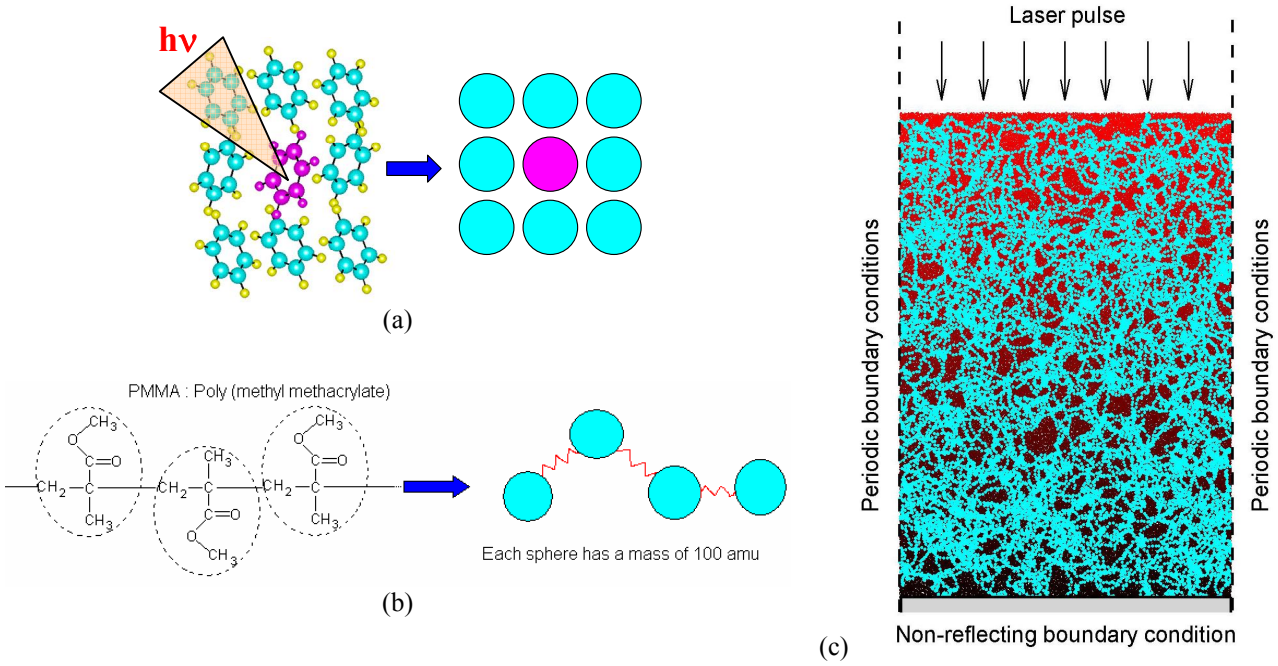


**Figure 1.** Schematic representation of the approximations used in the design of coarse grained breathing sphere (a) and bead-and-spring (b) MD models. A simulation setup used in modeling of molecular ejection in MAPLE is illustrated in (c), where the polymer chains are shown in blue color and are superimposed on top of the image of matrix molecules shown in the background.

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. The internal degree of freedom, or breathing mode, is implemented by allowing the particles to change their sizes and is used for simulation of molecular excitation by photon absorption and vibrational relaxation of the excited molecules. In the case of UV laser irradiation, the breathing mode can be considered as the recipient of the energy released by internal conversion from electronically excited states. The parameters of a potential function attributed to the internal motion 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 [18,19]. 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. The total number of photons entering the model during the laser pulse is determined by the laser fluence, incident laser energy per unit surface area. The absorption probability is modulated by Lambert-Beer's law to reproduce the exponential attenuation of the laser

light with depth or can be restricted to a certain component within a complex material. The laser properties are thus explicitly included in the model.

In order to enable simulations of laser interaction with polymer solutions, the breathing sphere model has been recently combined with the bead-and-spring model, commonly used in polymer modelling [17,20]. In the bead-and-spring model, schematically illustrated in Figure 1b, the "beads" representing functional groups of a polymer molecule (monomers) are connected by anharmonic springs with strengths appropriate for chemical bonding. The depth of the potential well is chosen to reproduce the value of the dissociation energy of a particular polymer molecule [17] and the chains can dissociate if the local forces applied to the chemical bonds are sufficiently large. While the radii of the breathing spheres are dynamic variables for which equations of motion are solved during the simulation, the radii of "beads" in the polymer bead-and-spring model are kept fixed during the simulation.

Since both the breathing sphere model and the bead-and-spring model adopt a coarse grained representation of molecules, in which each molecule or monomer unit are represented by a single particle, the system size can be sufficiently large to reproduce the collective dynamics in a molecular system leading to laser ablation and damage. Moreover, since explicit atomic vibrations are not followed, the time-step in the numerical integration of the equations of motion can be much longer and the dynamics in the irradiated sample can be followed for as long as nanoseconds. The limitations of the breathing sphere model are related to the approximation of all the internal degrees of freedom of a molecule by one internal mode. The rates of intermolecular energy transfer cannot be studied within the model, but have to be specified through the input parameters, as discussed above. The accuracy in quantitative description of the thermodynamic and transport properties of the materials represented at the coarse-grained level is limited and the models are appropriate for investigation of general, rather than material-specific, characteristics of the ablation process. A smaller number of degrees of freedom in the model system should also be taken into account when performing a quantitative comparison with experimental data, e.g. of the threshold fluence for the ablation onset [21].

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, Figure 1c. Each monomer unit in a polymer molecule has the same molecular weight as a single matrix molecule, 100 amu. This weight corresponds to the weight of a PMMA monomer and is close to the weight of molecules typically used as MAPLE matrices, e.g. toluene (92 Da), chloroform (118 Da), glycerol (92 Da). Each polymer chain contains 100 monomer units and has a total molecular weight of 10 kDa. A pressure-transmitting boundary condition [22,23] is applied at the bottom of the computational cell in order to avoid reflection of the laser-induced pressure wave from the boundary.

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 [19] characteristic of the experiments performed for toluene/PMMA system [12-16,24]. Although the length and time-scales of the simulated MAPLE process are very different from the experimental ones (laser pulse duration of 25 ns, penetration depth of ~4.0 μm), the fact that in the simulations and experiments the MAPLE process takes place under similar physical conditions (the same physical regime of thermal confinement) suggests that the ejection mechanisms revealed in the simulations are also at work in experiments, albeit at much larger time and length scales.

## 3. SIMULATIONS OF LASER ABLATION OF POLYMER SOLUTIONS

In the simulations of laser irradiation of MAPLE targets, the ejection of polymer molecules is observed only above the threshold for the collective material ejection (ablation). A typical dynamics of the ablation process is illustrated in Figure 2, where snapshots from two simulations performed for a target containing 1 and 6 wt.% of polymer molecules are shown. Similarly to the ablation of one-component molecular systems [19,25], the ablation of MAPLE targets starts from a homogeneous expansion of a significant part of the surface region overheated above the limit of its thermodynamic stability and 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 (shown in blue in the snapshots) extend along the flow of the ablation plume, thread through the liquid regions and resist the decomposition of the transient foamy liquid structure generated in the ablation process.

At low polymer concentration, Figure 2a, the chains are not heavily entangled and the presence of individual polymer chains in the expanding overheated matrix has a relatively weak effect on the overall dynamics of the ablation plume formation. As the polymer concentration increases, the chains become more entangled, leading to the formation

of intricate elongated structures that extend far above the ablating surface, e.g. Figure 2b. While the expanding liquid structures eventually disintegrate into individual liquid regions, the elongated shapes characteristic for these regions (e.g. a droplet in the top part of a snapshot taken at 800 ps in Figure 2b) are very different from the spherical droplets observed in simulations of laser ablation of pure matrix targets [25].

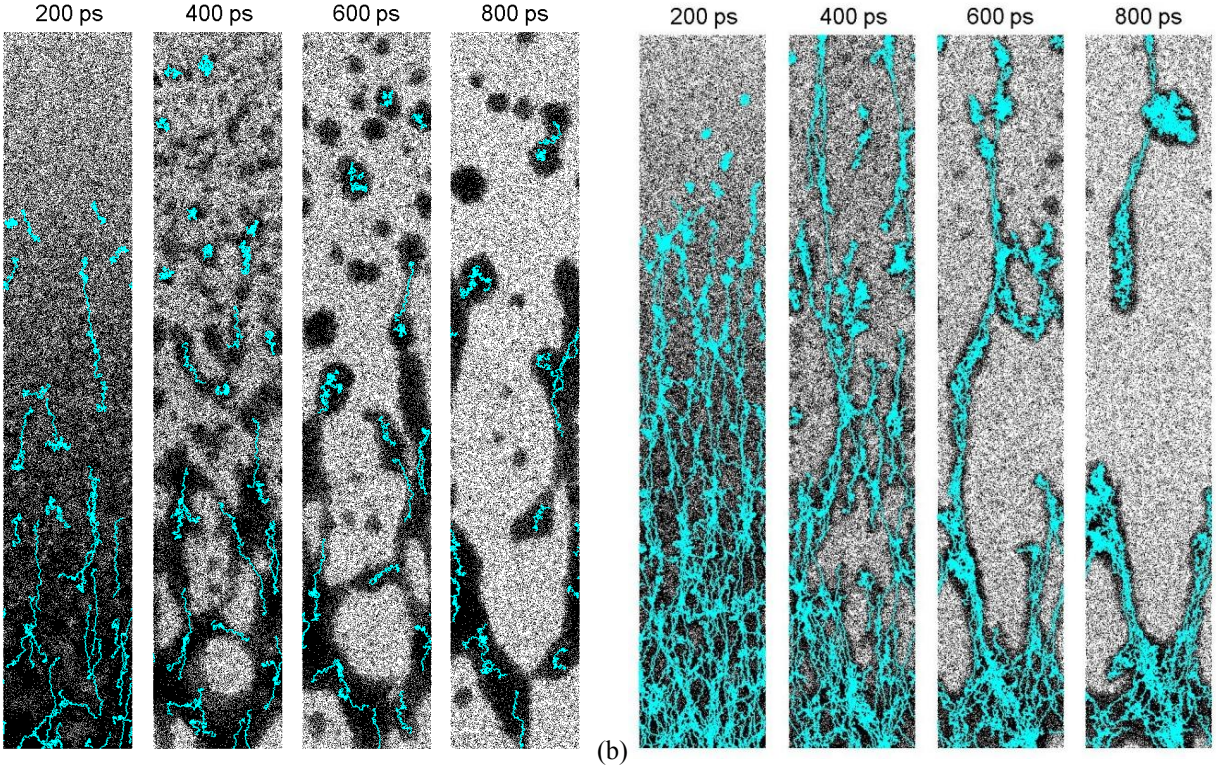


**Figure 2.** Snapshots from simulations of laser ablation performed for MAPLE targets with polymer concentrations of 1 wt.% (a) and 6 wt.% (b). The same fluence of 8 mJ/cm$^2$ is used in both simulations. Matrix molecules and units of polymer chains are shown by black and blue dots, respectively. In order to provide a clear picture of the distribution of the polymer molecules within the matrix, the polymer chains are superimposed on top of the image of matrix molecules shown in the background.

The elongated liquid structures can be stabilised by evaporative cooling in the expanding plume and can reach the substrate in MAPLE film deposition, contributing to the film roughness. The effect of the evaporation process on parameters of liquid matrix-polymer droplets is illustrated in Figure 3, where the size evolution is shown for two of the large clusters ejected in a simulation for which snapshots are shown in Figure 2b. The clusters emerge from the phase explosion at 500 ps with temperatures as high as 92 and 93% of the threshold temperature for the phase explosion T* [17,26], but cool down to temperatures of 0.70T* and 0.72T* by the time of 2.5 ns. The rate of the evaporative cooling has strong temperature dependence, with the most active cooling occurring within the first nanosecond after the laser pulse. Importantly, the quickly decreasing rates of evaporation of the ejected clusters suggest that the sizes and compositions of the clusters observed at 2.5 nm are close to the ones to be expected at the time when they reach the substrate in MAPLE deposition of polymer films.

Since in all simulations the polymer molecules are ejected only as parts of large matrix-polymer droplets/clusters that do not have enough thermal energy to evaporate during the flight to the substrate, one can expect that the growth of polymer films in MAPLE proceeds mainly through the deposition of matrix-polymer clusters. This observation goes against the notion of the ejection and transport of individual polymer molecules in MAPLE [1-3] but is consistent with observations of surface roughness in the experimental AFM and SEM images [6-16]. Indeed, the ejection of the extended liquid structures observed in the simulations, e.g. Figure 2b, can be related to "nanofiber" or "necklace" polymer surface features observed in SEM images of PMMA films deposited in MAPLE [12-15,24], as well

as in films fabricated by IR laser ablation of poly(vinil chloride) involving a partial thermal decomposition of the target material [27]. Some of the transient liquid structures do not separate from the target or can be redeposited within or outside the laser spot, resulting in the formation of complex surface morphology at the target. Experimentally, the generation of extended nanofibers [28,29] and surface swelling and foaming [30-33] have been reported for polymer and biopolymer targets subjected to short pulse laser irradiation.

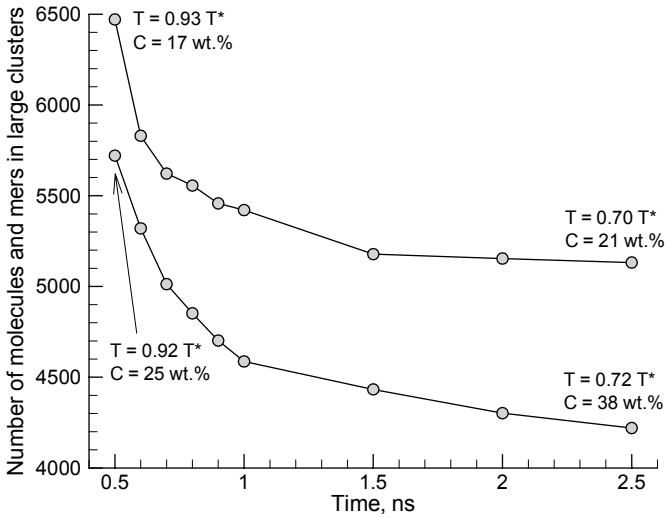


**Figure 3.** Evolution of the sizes of two clusters ejected in a simulation performed at a fluence of 8 mJ/cm$^2$ and polymer concentration of 6 wt.%. Internal temperatures and polymer concentrations in the clusters at 500 ps after the laser pulse, as well as at the end of the simulation, 2.5 ns, are shown in the figure. The temperature values are expressed through the threshold temperature for the phase explosion, T*. This temperature is determined in a constant pressure MD simulation of a very slow heating of a metastable liquid [17]. The threshold temperature T* manifests itself by the onset of the phase separation and a sharp increase of the volume of the system.

The prediction of the simulations that the matrix-polymer clusters/droplets ejected in MAPLE are likely to retain a significant amount of volatile matrix at the time of the deposition, Figure 3, can be related to the formation of wrinkled surface features observed in recent MAPLE experiments [12,13,16]. Such features, sometimes resembling "collapsed pipes" or "deflated balloons," may form as a result of the vaporisation and escape of the deposited matrix trapped within the polymer material. Large quantitative differences in length and time-scales of the simulated and experimental MAPLE process (laser pulse duration and penetration depth are 50 ps and 50 nm in simulations and 25 ns and ~4.0 μm in experiments), however, do not allow us to directly relate the ejection of relatively small matrix-polymer clusters observed in the simulations to the formation of complex micron-size surface morphologies observed in the experiments.

## 4. MOLECULAR REDISTRIBUTION IN OVERHEATED MATRIX-POLYMER DROPLETS

To investigate the collective molecular rearrangements responsible for the formation of the "deflated balloon" type of surface features observed in experiments, a series of targeted MD simulations focused on the evolution of individual large matrix-polymer droplets experiencing the heating conditions similar to the ones realised in the simulations of the MAPLE process have been performed [16,24]. In these simulations, the evolution of droplets with the initial diameter of 60 nm, initial polymer concentration of 16 wt.%, and the amount of thermal energy ranging between 60 and 80% of the cohesive energy of the matrix material, $E_c$, is studied. Both the initial polymer concentration and the amounts of the deposited energy are typical for droplets generated in different parts of the ablation plume in the MAPLE simulations. The time-scale of the energy deposition at the beginning of the simulations reported in Ref. [16] is chosen to ensure that the droplets have time to expand during the heating process and, similarly to the MAPLE simulations and experiments discussed above, the conditions of the inertial stress confinement are not realized in the simulations of droplets. The effect of the heating rate on the behavior of the matrix-polymer droplets is further investigated in additional simulations performed with a faster heating rate, resulting in the condition of partial inertial stress confinement [24].

Snapshots from a simulation performed at the deposited thermal energy density of $0.7E_c$ are shown in Figure 4. The temperature that corresponds to this level of thermal energy exceeds the threshold temperature T* for phase explosion, Figure 5. Above this temperature a fast homogeneous nucleation of vapor takes place inside the droplet,

leading to the appearance of multiple vapor regions inside the superheated liquid. Fast evaporation of the volatile matrix molecules from the surface of the droplet takes place simultaneously with the expansion of the droplet driven by the pressure generated by the internal release of the matrix vapor. The size of the droplet increases during the first 150 ps of the simulation, stays at approximately the same level up to 500 ps, and then decreases and stabilizes by ~1.5 ns. As the droplet expands, the entangled chains form a continuous network arranged in a spherical shell partially encasing the volatile matrix vapor and forming a balloon-like transient structure. Although the size of the droplet decreases below the original size by 900 ps and the vapor region collapses by 1.5 ns, the new distribution of the polymer molecules within the droplet is very different from the original one. The polymer molecules are clearly segregated to the outskirts of the droplet, forming a polymer-rich shell around the volatile matrix trapped in the central part of the droplet. The average polymer concentration in the droplet increases up to 25 wt.% by 1 ns, whereas the maximum polymer concentration in the polymer shell is reaching 42 wt.% by this time, more than twice the concentration in the initial droplet. Note that the fast collapse of the transient balloon-like structure into a compact droplet is driven by the surface tension that is particularly large in small 60 nm droplets used in the simulations. The transient hollow structures are likely to be more stable in the case of much larger μm-size droplets ejected under experimental conditions [16].

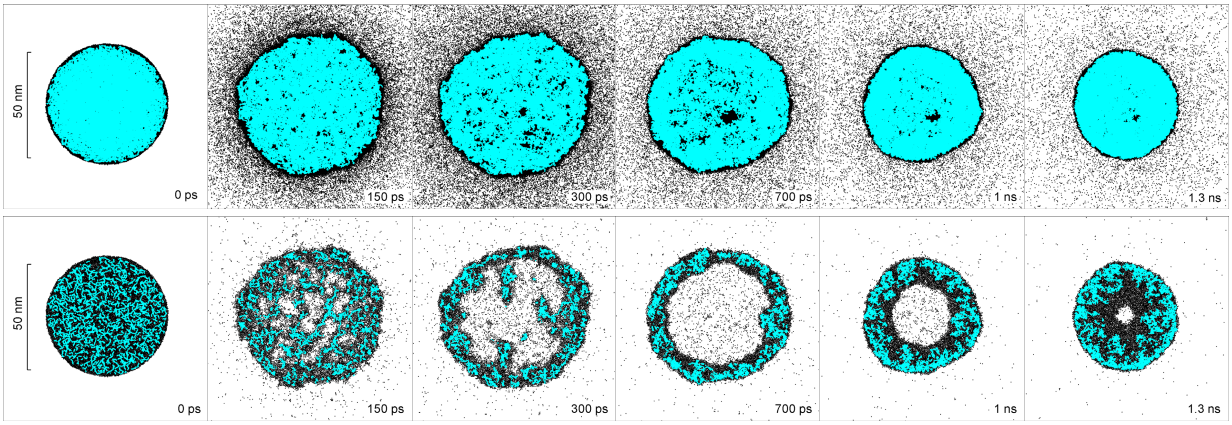


**Figure 4.** Snapshots from MD simulations of a 60 nm droplets with the initial polymer concentration of 16 wt.% and the initial amount of thermal energy equal to 70 % of the cohesive energy of the matrix material, $E_c$. Matrix molecules and units of polymer chains are shown by black and blue dots, respectively. In order to provide a clear picture of the distribution of the polymer molecules within the matrix, polymer molecules are superimposed on top of the matrix molecules. All molecule representation is shown in the top row of images and 2 nm slices cut through the centre of the droplet are shown in the bottom row.

The condition for the internal boiling and generation of "molecular balloons" identified in the simulations of matrix-polymer droplets is the same as the condition for the onset of laser ablation, discussed in Section 3. As soon as the material is overheated above a well-defined threshold temperature T*, a fast homogeneous nucleation of the vapor takes place, driving the expansion of the droplet in Figure 4 or material ejection in Figure 2. The explosive decomposition into liquid regions and vapor results in the fast temperature drop below T*, Figure 5. The second, slower stage of the temperature decrease in Figure 5 is mainly defined by the continued evaporation of matrix molecules from the surface of the droplet. The evaporation is also reflected by the increase of the polymer concentration in the droplet, Figure 5. The evaporation slows down as the temperature of the droplet continues to decrease and time dependence of the polymer concentration shows signs of saturation by the end of the simulation, 1.5 ns.

Thus, the results of the MD simulations of MAPLE and large matrix-polymer droplets, briefly discussed above, suggest the following scenario of the formation of the experimentally observed "deflated balloon" surface features. Short pulse laser irradiation produces an explosive decomposition of the overheated surface region of a MAPLE target into a mixture of liquid polymer-matrix droplets and vapor-phase matrix molecules. Although the exact heating regime experienced by droplets ejected in nanosecond pulse MAPLE experiments is not clearly established yet, one can expect that the droplets emerge in the overheated state from the explosive boiling of the irradiated target and, at laser fluences significantly exceeding the ablation threshold, can be further heated by the tail of the laser pulse. An internal release of the vapor of matrix molecules in a sufficiently large droplet is capable of pushing the polymer

molecules to the outskirts of the droplet, forming a transient "molecular balloon" expanding under the action of the internal vapor pressure. Active evaporation of matrix molecules from the surface of the droplet contributes to the formation of a polymer-rich surface layer, hampering the escape of the remaining matrix molecules. Following the deposition of the droplet to a room-temperature substrate, the volatile matrix material enclosed by a polymer-rich layer expands and makes escape passes through the polymer layer, leaving behind a characteristic wrinkled "deflated balloon" and "collapsed pipes" polymer structures [12,13,16].

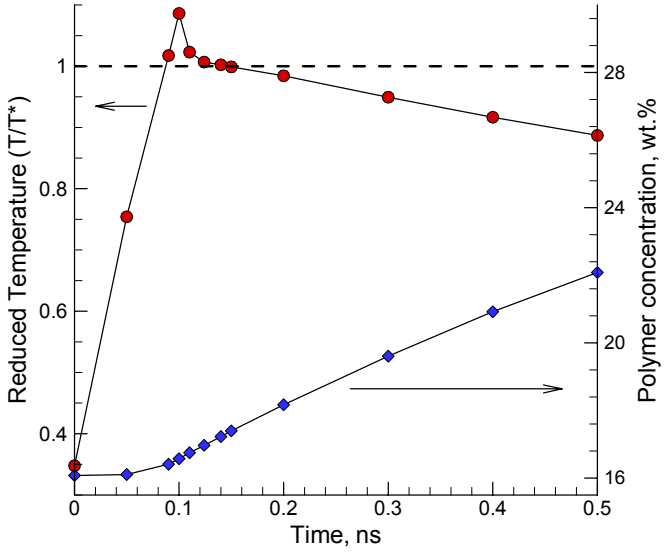


**Figure 5.** Evolution of temperature and polymer concentration during the first 500 ps of the simulation of an overheated matrix-polymer droplet illustrated in Figure 4. Only molecules that belong to the continuous droplet are included in the evaluation of the average temperature and concentration. The temperature values are normalised to the threshold temperature for phase explosion, T*.

## 5. SUMMARY

Molecular dynamic simulation technique has been playing an increasingly important role in the advancement of theoretical understanding of laser ablation. The results of large-scale MD simulations of laser ablation have provided insights into complex processes occurring at the early stages of the ablation plume development and their relation to the parameters of the ejected particles. One of the conclusions from MD simulations performed for different target materials is that particles and small atomic/molecular clusters are unavoidable products of the processes responsible for the material ejection in the ablation regime. Phase explosion of the overheated material, identified as the main mechanism of laser ablation in the regime of thermal confinement, is found to proceed through 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.

MD simulations performed for molecular systems consisting of polymer molecules dissolved in a volatile molecular matrix have revealed a significant influence the polymer molecules have on the ablation process even at relatively low concentrations of several weight percent. The polymer molecules are found to be ejected only in the ablation regime and are always incorporated into polymer-matrix clusters/droplets generated in the process of the explosive disintegration of the overheated matrix. The entanglement of the polymer molecules facilitates the formation of intricate elongated viscous droplets that can be related to the complex morphologies of polymer films deposited by MAPLE. Moreover, the effect of dynamic molecular redistribution in the ejected matrix-polymer droplets, leading to the generation of transient "molecular balloons" in which polymer-rich surface layers enclose the volatile matrix material, has been identified as the mechanism responsible for the formation of characteristic wrinkled polymer structures observed in MAPLE experiments.

## ACKNOWLEDGEMENTS

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