

## Making Molecular Balloons in Laser-Induced Explosive Boiling of Polymer Solutions

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The effect of the dynamic molecular rearrangements leading to compositional segregation is revealed in coarse-grained molecular dynamics simulations of short pulse laser interaction with a polymer solution in a volatile matrix. An internal release of matrix vapor at the onset of the explosive boiling of the overheated liquid is capable of pushing polymer molecules to the outskirts of a transient bubble, forming a polymer-rich surface layer enclosing the volatile matrix material. The results explain unexpected “deflated balloon” structures observed in films deposited by the matrix-assisted pulsed laser evaporation technique.

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Irradiation of a solid target with a laser pulse of a sufficiently high energy can result in material removal from the target. One of the characteristic features of this phenomenon, called laser ablation, is the generation of particles (small polyatomic clusters, droplets, or solid fragments). The applications based on particle generation in laser ablation include fabrication of ultrafine powders and nanostructured materials, as well as deposition of metal particles for catalysis or medical applications. At the same time, the presence of clusters or particulates in the ablation plume can have an adverse effect on the quality of thin films grown in pulsed laser deposition [1].

In the area of fabrication of high-quality ultrathin organic films with stringent requirements for uniformity and maintaining the native molecular structure, a technique dubbed matrix-assisted pulsed laser evaporation (MAPLE) [2] has been developed with the intention of avoiding the particle formation and achieving a soft molecule-by-molecule deposition of uniform films [3]. In MAPLE, the target is prepared by dissolving the material to be deposited in a volatile solvent (matrix) and freezing the homogeneous dilute solution (0.1–5 wt. %). Short pulse laser irradiation of the target results in a collective ejection (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. 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) images of PMMA (polymethyl-methacrylate) films deposited by toluene-matrix MAPLE [4] reveal complex morphologies with distinct features of “collapsed pipes,” “deflated balloons,” and elongated nanofibers, e.g., Fig. 1.

In order to explain the experimental observations and to reveal the processes responsible for the formation of the large polymer aggregates with complex morphologies, we undertake molecular-level computer modeling of the early stages of laser ablation of frozen polymer solutions. The laser-driven material ejection from a MAPLE target is simulated with a coarse-grained molecular dynamics (MD) model based on the “breathing sphere” model developed and actively used for investigation of laser interaction with molecular targets [5]. The polymer molecules are represented by the bead-and-spring model, commonly used in polymer modeling [6]. Each monomer unit in a polymer molecule has the same molecular weight as a single matrix molecule, 100 amu. This weight corresponds to the actual weight of a PMMA monomer and is close to the weight of a toluene molecule, 92 amu.

Large-scale MD simulations of MAPLE have been performed for a wide range of laser fluences and for targets with polymer chains randomly and uniformly distributed in the sample at different polymer concentrations, from 1 to 6 wt. %. The laser pulse duration of 50 ps and optical penetration depth in pure matrix of 50 nm are chosen to

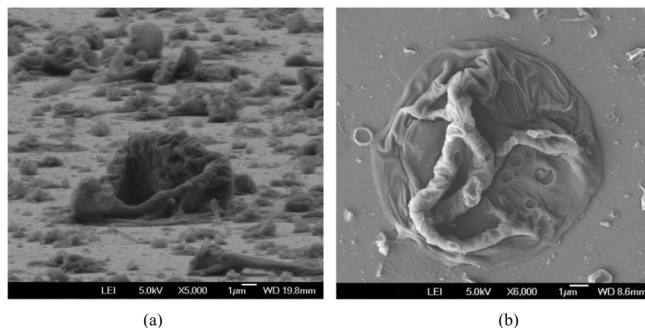


FIG. 1. SEM images of a typical thin film morphology produced by MAPLE deposition from a target containing 5 wt. % of PMMA in a toluene matrix (a), and a top view of a characteristic deflated balloon surface feature (b).

reproduce the conditions of thermal confinement [5] characteristic of the experimental study performed for the toluene/PMMA system; Fig. 1. At the same time, the rate of the laser energy deposition is sufficiently low to allow for the mechanical relaxation (expansion) of the absorption region of the target during the laser pulse (the conditions of inertial stress confinement [5,7] are not achieved). 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  $\sim 4.0 \mu\text{m}$ ), 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.

In the simulations of MAPLE, the ejection of polymer molecules is observed only above the threshold for collective material ejection (ablation). The ablation starts from an expansion of a 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. In all MAPLE simulations, the polymer molecules are ejected only as parts of large matrix-polymer droplets or clusters that are likely to retain a large fraction of matrix material at the time of the deposition on a substrate. This observation goes against the notion of the ejection and transport of individual polymer molecules in MAPLE [2,3] and provides a hint for explaining the observed surface roughness in the experimental SEM images, e.g., Fig. 1. Large quantitative differences in length and time scales of the simulated and experimental MAPLE process, 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 shown in Fig. 1. The evolution of much larger droplets, expected to be ejected under experimental conditions, has to be studied in order to understand the collective molecular rearrangements responsible for the formation of the deflated balloon type of features observed in experiments.

Based on the results of the MAPLE simulations, we perform a series of targeted MD simulations focused on the evolution of individual large matrix-polymer droplets experiencing the heating conditions similar to the ones realized in the simulations of MAPLE. Droplets with the initial diameter of 60 nm and 16 wt. % of randomly oriented and distributed polymer chains (50 mers and 5000 amu each) are used in the simulations. The droplets are heated during the first 100 ps of the simulation, with the total amount of the deposited thermal energy ranging between 60% and 80% of the cohesive energy of the matrix material  $E_c$ . The time scale of the energy deposition 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 the droplets.

Snapshots from a simulation performed at the highest energy density,  $0.8E_c$ , are shown in Fig. 2(a) [8]. During the first hundreds of picoseconds, 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 formation of a hollow structure of the expanding polymer-matrix shell filled with matrix vapor is evident in the snapshot taken at 300 ps. By the time of 700 ps the expansion of the polymer shell results in disintegration into several elongated clusters with an average polymer concentration of 32 wt. %. The conditions leading to the explosive decomposition of the droplet into vapor and liquid clusters are apparent from Fig. 3(a), where the evolution of the internal temperature of the droplets is shown. By the end of the heating process, the temperature of the cluster significantly exceeds the threshold temperature  $T^*$  for “phase explosion” [9,10]. The threshold temperature  $T^*$  is determined in a series of constant temperature and pressure MD simulations performed for a matrix-polymer system consisting of 134 000 matrix molecules and having the same 16 wt. % of polymer chains as in the simulations of droplets. This temperature  $T^*$  corresponds to the onset of the phase separation and sharp increase of the volume of the system. A sharp transition from a metastable superheated liquid to a two-phase mixture of liquid and vapor at a temperature of approximately 90% of the critical temperature has been predicted in the classical nucleation theory [9] and confirmed in simulations [10]. As soon as temperature exceeds  $T^*$ , a fast homogeneous nucleation of matrix vapor takes place inside the droplet, driving the expansion and eventual disintegration of the droplet. The explosive decomposition into liquid regions and vapor results in the temperature drop that is particularly sharp during the initial stage of the phase explosion; Fig. 3(a).

In the simulation performed at a lower energy density of  $0.7E_c$ , the temperature reached by the end of the heating process also exceeds  $T^*$ , Fig. 3(a), leading to the appearance of multiple vapor regions inside the superheated liquid. 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  $\sim 1.5$  ns. As the droplet expands, the entangled chains form a continuous network arranged in a spherical shell partially encasing the volatile matrix vapor. Minor ruptures or holes, which appear in the transient shell structure at the time of the maximum expansion, gradually close during the contraction stage. The formation of the polymer-rich layer at the surface of the droplet is apparent in Fig. 2(b),

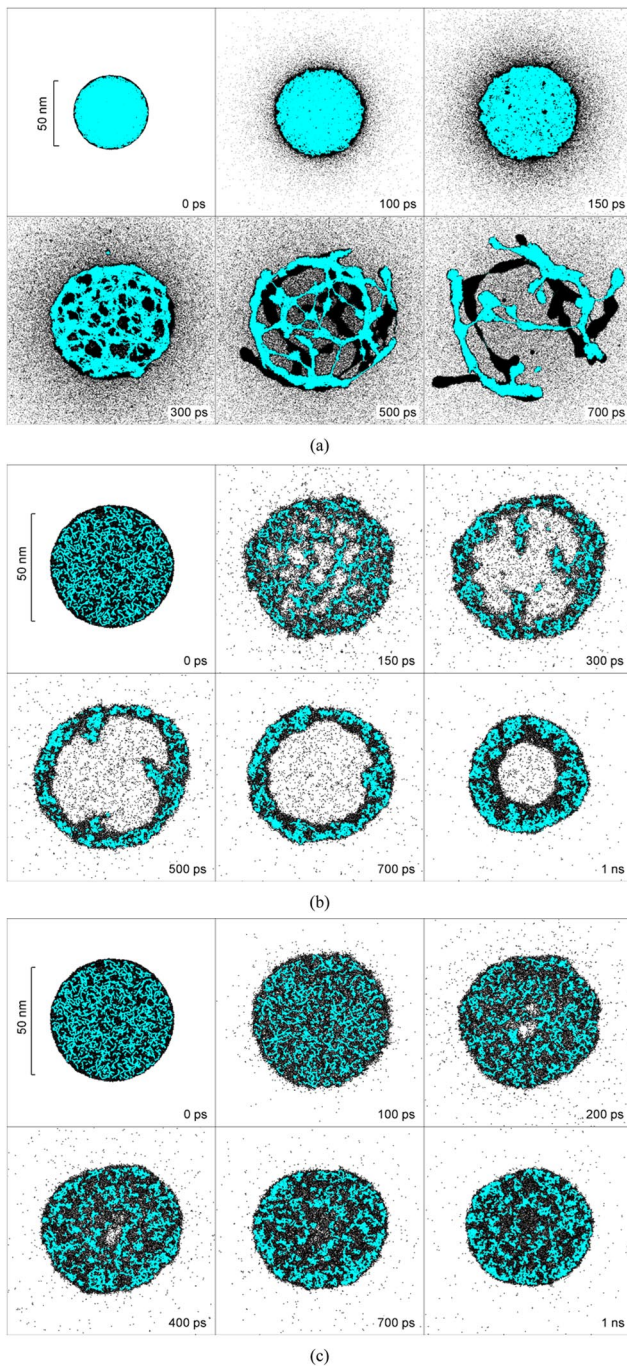


FIG. 2 (color online). Snapshots from MD simulations of the response of 60 nm droplets containing 16 wt.% of polymer molecules to a constant rate energy deposition. Droplets are heated during the first 100 ps of the simulation, with the total amounts of the deposited thermal energy equal to (a)  $0.8E_c$ , (b)  $0.7E_c$ , and (c)  $0.6E_c$ . Matrix molecules and units of polymer chains are shown by black and gray (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. Only 2 nm slices cut through the center of the droplet are shown in (b) and (c). Animated sequences of snapshots from the simulations illustrated in (a) and (b) can be found at [8].

where 2 nm slices cut through the center of the droplet are shown. Fast internal release of the matrix vapor (homogeneous boiling) starts at the end of the heating process, pushes the polymer molecules toward the surface of the droplet, and leads to the formation of a well-defined balloonlike structure by  $\sim 500$  ps. Although the size of the droplet decreases below the original size by 900 ps and the vapor region collapses by 1350 ps, 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 reaches 42 wt.% by this time, more than twice the concentration in the initial droplet. Two-stage temperature decrease, similar to the one at  $0.8E_c$ , is also observed at  $0.7E_c$ ; Fig. 3(a). The second stage, however, is significantly slower at  $0.7E_c$  and the temperature of the droplet exceeds the one calculated for  $0.8E_c$  after 220 ps. More violent phase decomposition and rapid expansion of the vapor and small liquid fragments at  $0.8E_c$  [Fig. 2(a)] provide conditions for faster cooling as compared to the evaporation of matrix from the polymer-rich shell enclosing the hot vapor at  $0.7E_c$  [Fig. 2(b)].

At the lowest energy density used in the simulations,  $0.6E_c$ , the temperature barely reaches  $T^*$  by the end of the heating process; Fig. 3(a). In this case, the phase separation occurs only in a small central region of the droplet and does not lead to the formation of a balloonlike structure with a well-defined polymer-rich surface layer; Fig. 2(c). As the droplet retains, to a large extent, its mechanical integrity, the initial expansion of the droplet is followed by an elastic contraction that takes place between 120 and 140 ps, on the time scale that corresponds to half the period of an elastic oscillation of the droplet. The relaxation of the potential (bonding) energy in the droplet during the contraction results in a slight increase of the kinetic (thermal) energy that can be observed in Fig. 3(a).

The changes in the polymer concentration in the droplets, Fig. 3(b), reflect the explosive vaporization of the matrix described above. By the time of 500 ps, the average polymer concentration in the droplets increases up to 19.1, 22.1, and 30.1 wt.%, in simulations performed at  $0.6E_c$ ,  $0.7E_c$ , and  $0.8E_c$ , respectively. Notably, the matrix content in the polymer-matrix droplets emerging from the phase explosion remains high even at the highest energy density used in the simulations. Further long-term evaporative cooling would slow down the evaporation and the droplets reaching the surface of the substrate in MAPLE film growth experiments can be expected to retain a significant amount of volatile matrix material [11].

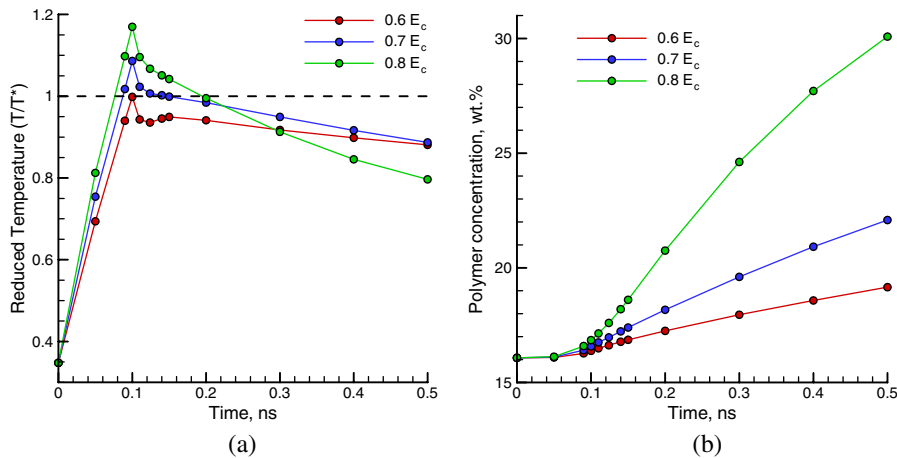


FIG. 3 (color online). Evolution of temperature and polymer concentration during the first 500 ps of the simulations of the three droplets illustrated in Fig. 2. Only the molecules that belong to the continuous droplets are included in the evaluation of the average temperatures and concentrations. The temperature values are normalized to the threshold temperature for the phase explosion  $T^*$ .

Thus, the following scenario of the formation of the experimentally observed surface features emerges from the simulations. In contrast to the generally accepted picture of the desorption and transfer of individual polymer molecules in MAPLE [2,3], simulation results suggest that polymer molecules are ejected as parts of matrix droplets or clusters generated in the process of explosive decomposition of the overheated surface region of a MAPLE target into a mixture of liquid polymer-matrix droplets and vapor-phase matrix molecules. An internal release of the vapor of matrix molecules in a sufficiently large droplet is capable of pushing 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 the polymer-rich layer expands and makes escape passes through the polymer layer, leaving behind a characteristic wrinkled, deflated balloonlike polymer structure, such as the one shown in Fig. 1(b) [12].

The effect of the dynamic spatial segregation of polymer and matrix molecules, discussed here for molecular droplets, may also occur in the bulk of the overheated solution, where the transient appearance and collapse of vapor bubbles at the onset of the explosive boiling can result in a similar molecular redistribution leading to the formation of polymer-rich spherical layers enclosing the volatile matrix material. Beyond MAPLE, the generation of molecular balloons demonstrated in the simulations may have implications for a broad range of practically important processes, from production of micro- or nanocapsules for medical applications to interpretation of mass spectrometry data in analysis of organic aerosol particles.

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- [12] Experiments performed by drying a droplet of polymer-matrix solution on a substrate do not produce the wrinkled patterns observed in MAPLE experiments, supporting the role of the molecular segregation in the initial phase explosion and in-flight processes, revealed in the simulations, in the formation of the observed surface morphologies.