Ablation of molecular solids under nanosecond laser pulses: The role of inertial confinement

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The thermal routes to ablation in molecular solids having a long (micron scale) optical penetration depth are investigated under nanosecond laser pulses using a two-dimensional molecular-dynamics model. The authors demonstrate that the mechanisms of matter removal are mainly determined by the local degree of inertial confinement; by increasing level of confinement, these are (trivial) fragmentation, phase explosion, and heterogeneous nucleation of vapor bubbles at solid-liquid boundaries. The thermodynamic pathways to ablation are shown to be different from those predicted by the model of Miotello and Kelly [Appl. Phys. Lett. **67**, 3535 (1995); Appl. Phys. A: Mater. Sci. Process. **69**, S67 (1999)]. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358941]

The ejection of macroscopic amounts of material from solids following irradiation with a short, intense laser pulse above a well-defined threshold fluence (energy per unit area) is a process known as *laser ablation*.[1] It is routinely used in a number of technological applications ranging from nanoparticle synthesis[2] and surface micromachining[3] of metals and semiconductors to mass spectrometry and analytical chemistry[4] of molecular solids.

From a fundamental standpoint, opposing views regarding the *thermal* (i.e., occurring under local electron-ion equilibrium) mechanisms behind laser-induced matter removal can be found in the literature.[5–9] In a scenario proposed by Miotello and Kelly (MK), it is suggested that ablation under long (nanosecond) pulses results from homogeneous nucleation of vapor bubbles upon rapid *heating* of a metastable, superheated liquid.[5,6] Commonly termed "phase explosion" or "explosive boiling," this scenario has been invoked by numerous authors to describe ablation of various materials under femtosecond,[10] picosecond,[11,12] and nanosecond[4,13,14] pulses.

However, the MK picture has been challenged by several experimental,[15] analytical,[16] and numerical[7–9,17] studies of short-pulse laser ablation of metals and semiconductors characterized by a metallic liquid phase with a small ($\sim 10^{-8}$ m) optical penetration depth. For ultrashort pulses ($\lesssim 10^{-12}$ s), on the one hand, heating is isochoric and the material is initially pulled *away* from the region of superheated liquid states; depending on the locally deposited energy, the irradiated matter may then undergo a phase explosion or a "nontrivial" fragmentation process as it rapidly *cools* within the metastable or supercritical region of the phase diagram, respectively.[7,9] For longer pulses ($\gtrsim 10^{-11}$ s), on the other hand, heating is nonisochoric and access to the subcritical, superheated states is hampered by a combination of slower expansion and efficient thermal conduction; as a result, explosive boiling is suppressed and ablation involves the near-equilibrium dissociation of a homogeneous, supercritical fluid, a process called "trivial" fragmentation.[8,9]

Nevertheless, in materials having a relatively long optical penetration depth ($\sim 10^{-7}$–10^{-6} m), which is the case of a large number of molecular solids, the MK model is often called on to explain, e.g., the appearance of large cavities and the subsequent ejection of liquid droplets upon nanosecond irradiation (see, for example, Ref. 4 and references therein). In this case, however, the increased confinement of the irradiated matter is expected, instead, to pull the heated system away from the region of metastable liquid states.

Clearly, a definite assessment of the mechanisms of laser-induced matter removal—and of the validity of the MK model—in molecular solids has yet to come. This is the object of this letter. Using a two-dimensional molecular-dynamics model, we demonstrate that matter removal under nanosecond pulses in solids characterized by a large optical penetration depth is determined by the local level of inertial confinement. By following the thermodynamic evolution of the laser-heated material, as in previous work,[7,8] we find that three mechanisms are responsible for ablation as a function of increasing inertial confinement (or depth): fragmentation, explosive boiling, and heterogeneous nucleation of vapor embryos at solid-liquid boundaries; in particular, the large, micron-scale absorption length of the laser energy is found to provide a natural pathway—but *not* that proposed by MK—to phase explosion in molecular solids under nanosecond pulses.

In our molecular-dynamics model, the atoms interact via the classical Lennard-Jones (LJ) potential. The incoming photons are absorbed by "carriers" whose role is to redistribute the energy to the surrounding atoms, which is done by adding an appropriate component to their velocity (see Refs. 7 and 8 for details). The model is thus "generic" and has previously been used to study short-pulse laser ablation in materials where the energy is deposited over a relatively short distance beneath the surface.[7,8] It is not meant to reproduce laser-matter interactions (such as, e.g., electronic excitations in molecular solids) in a rigorous manner. However, as previous studies have shown,[7,8,17] it captures the essential

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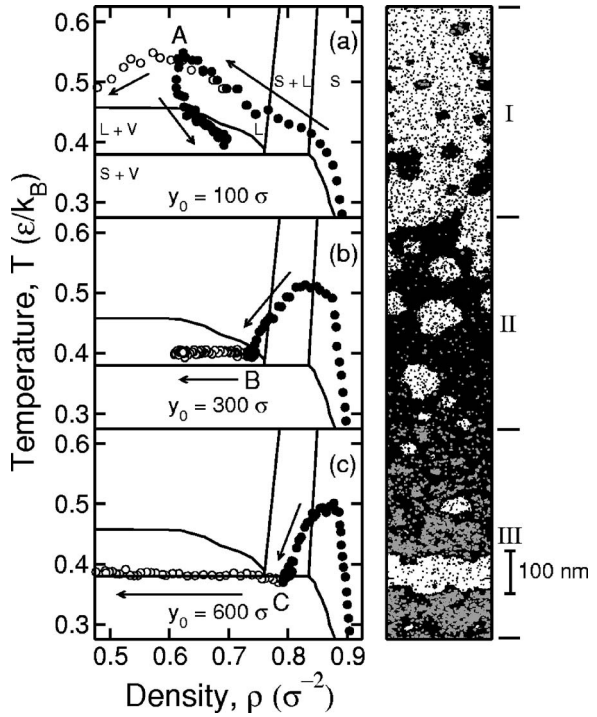

FIG. 1. Left: time evolution of the irradiated system in the ρ-T plane for different depths y_0 below the original surface (as indicated). White circles: macroscopic branch; black circles: dense branch; the gas branch is out of range. Arrows indicate the flow of time. *S*: solid; *L*: liquid; *V*: vapor. Other capital letters refer to locations in the phase diagram of which a detailed description is given in Ref. 7. Right: snapshot of the corresponding simulation at a fluence $F=1.25F_{th}=2000\epsilon/\sigma$ and time $t=2500\tau$. Gray: locally crystalline structure; black: locally disordered structure; a common-neighbor-analysis procedure has been used to infer the local structure (see Ref. 19). Note that only the near-surface, ablating region is shown.

physics of the problem, thus offering a simple, yet powerful approach to describe the *thermal* excitation of absorbing solids.[15]

The results below are quoted in reduced LJ units, i.e., σ^{-2} for density, ϵ/k_B for temperature, ϵ/σ^2 for pressure, and $\tau=(m\sigma^2/\epsilon)^{1/2}$ for time; ϵ and σ are the usual energy and length scales; m is the atomic mass. For a typical molecular solid (see, e.g., Ref. 12), $\epsilon\simeq 0.2$ eV, $\sigma\simeq 2$ nm, and $m\simeq 100$ amu; hence, $\tau\simeq 5$ ps. Simulations have been carried out for a pulse duration (full width at half maximum) $\tau_p=500\tau$ (≈ 2.5 ns) and an optical penetration depth $\delta=2000\sigma$ (≈ 4 μm); the initial width and height of the target were set to 180σ and 1800σ, respectively, for a total of about 300 000 particles. Note that the above values of τ_p and δ are at least an order of magnitude larger than those used in previous simulations involving short-pulse laser ablation of molecular solids.[12,18]

Figure 1, which summarizes our simulations, illustrates the thermodynamic pathways (left) and related structural modifications (right) at a fluence slightly above the ablation threshold $F_{th}=1600\epsilon/\sigma$. Three regions, associated with different removal mechanisms, can be identified in the ablating material:[20] (i) In the topmost region (marked I), the system is composed of a rapidly expanding mixture of liquid droplets and gas. (ii) Further down into the plume (II), *homogeneously* nucleating gas bubbles in a slowly expanding melt are observed. (iii) Finally, cavities are found to grow *heterogeneously* in the underlying solid-liquid region (III). Note that regions III ($F\gtrsim 0.95F_{th}$), II ($F\gtrsim 1.05F_{th}$), and I ($F\gtrsim 1.1F_{th}$) appear sequentially as a function of increasing fluence. The nucleation of gas bubbles at fluences starting slightly below F_{th} and the ejection of liquid droplets together with the nonselective nature of the ablation process above F_{th} are features in qualitative agreement with experiments on molecular solids using nanosecond pulses.[4]

As discussed in Ref. 7, the mechanisms responsible for ablation can be unambiguously identified by following the thermodynamic trajectories of the irradiated material in ρ-T-P space. Briefly, the density ρ, temperature T, and pressure P of various sections of the target are computed at regular intervals in time and the results assigned to either dense (solid and/or liquid), gas, or macroscopic (average) "branches." The nature of the process by which matter removal (locally) takes place is then determined by locating the point where void nucleation causes the dense and macroscopic branches to split in the ρ-T (or ρ-P) plane of the material's equilibrium phase diagram.

A typical trajectory for region I is displayed in Fig. 1(a). As a consequence of the relatively weak inertial confinement near the surface, the irradiated solid expands almost freely into vacuum; the solid-liquid coexistence region is eventually reached and melting takes place. The resulting melt is then further heated to a supercritical state where—as indicated by the separation of the dense and macroscopic branches (marked *A*)—void nucleation gives rise to the breakup of the initially homogeneous fluid into clusters. Clearly, matter removal cannot be attributed to the phase explosion (or spinodal decomposition) of a subcritical, metastable (or unstable) liquid; instead it results from a "trivial" fragmentation process, as is observed upon nonisochoric heating of metals and semiconductors under picosecond pulses.[8,9]

The thermodynamic evolution of the system is fundamentally different further down into the expanding plume where the neighboring material locally gives rise to significant inertial confinement [region II, Fig. 1(b)]. Consequently, heating is nearly isochoric and expansion occurs upon cooling rather than heating. In the process, the system melts and ultimately enters the liquid-vapor coexistence region where homogeneous nucleation of gas bubbles takes place (*B*). Such a scenario, which provides unambiguous evidence for the occurrence of phase explosion, is analogous to that observed upon isochoric heating of metals and semiconductors under near-threshold femtosecond pulses;[7,9,15] it is, however, fundamentally different from the predictions of the MK model.

Finally, in regions located even further down into the ablating plume, a third mechanism operates [region III, Fig. 1(c)]. As in region II, the system is first heated at nearly constant volume. However, owing to the increased confinement, mechanical expansion is now slow enough that thermal diffusion becomes an additional, effective cooling process. As a result, the material expands almost entirely within the solid-liquid region where it only partially melts—visual inspection of the target confirms that liquid droplets develop within the cooling solid (see Fig. 1)—before reaching the metastable, solid-vapor region. Shortly after, *heterogeneous* nucleation of gas bubbles takes place at the solid-liquid boundaries (*C*); the cavities eventually coalesce, causing the ejection of a relatively large (few hundred nanometer thick) piece of material. This ejection mechanism is observed at all fluences above F_{th}.

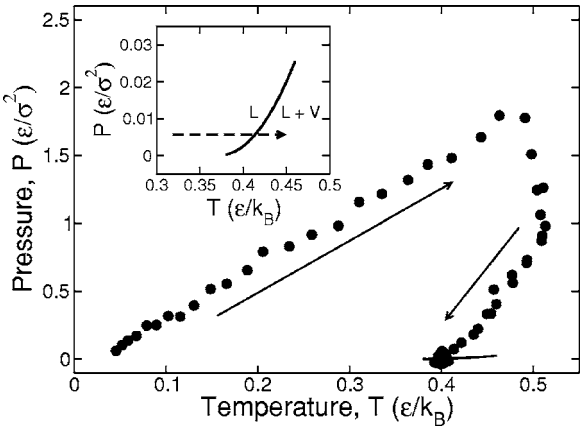

FIG. 2. Time evolution of the irradiated system in the T-P plane for a depth $y_0=300\sigma$ below the original surface (region II). Solid line: binodal (liquid-vapor coexistence); the spinodal (limit of mechanical stability) is not shown. Inset: thermodynamic trajectory (dashed arrow) of the heated system under nanosecond irradiation, as predicted by the MK model.

Under long, nanosecond pulses, the MK model predicts a superheated liquid material which undergoes a phase-explosion process as it is rapidly *heated* into the liquid-vapor region at nearly constant pressure (see inset to Fig. 2).[5,6] This scenario is not supported by the thermodynamic trajectories in region II, of which a typical illustration in the T-P plane is displayed in Fig. 2. Here and contrary to the MK picture, the irradiated matter under inertial confinement is heated *away* from the region of metastable, superheated states (located below the binodal); the latter is accessed, instead, as the pressure buildup is gradually released upon subsequent expansion and cooling.

The magnitude of the pressure buildup is (locally) related to the amount of absorbed energy and level of inertial confinement. The latter can be quantified by comparing the pulse duration $\tau_p=500\tau$ with the characteristic time scale for mechanical equilibration of the irradiated material. More specifically the mechanical relaxation of a region originally located at depth y_0 is commonly argued to take place in a time $\tau_s(y_0)=y_0/c_s$,[4] where the sound velocity c_s in a LJ system is typically on the order of $10\sigma/\tau$. Hence, for the present optical penetration depth ($\delta=2000\sigma$), $\tau_s(\delta)\simeq 200\tau < \tau_p$ and the entire system (or at least its topmost region) would be expected to evolve near mechanical equilibrium during laser irradiation. However, in conditions where ablation is thermal, expansion velocities are usually much smaller than the sound velocity;[21] here, these are approximately equal to $0.01c_s$. Therefore, the typical time for mechanical relaxation is, rather, $\tau_s(y_0)=100y_0/c_s$. In regions I–III this corresponds to $\tau_s^{\mathrm{I}}\simeq 1000\tau$, $\tau_s^{\mathrm{II}}\simeq 3000\tau$, and $\tau_s^{\mathrm{III}}\simeq 6000\tau$, respectively; regions II and III are thus expected to be significantly more confined than region I, in agreement with the results presented in Fig. 1.

We have shown that thermal ablation in molecular solids under nanosecond pulses is governed by local inertial confinement effects. As can be seen in Fig. 1, the long, micron-scale penetration of the laser energy results in a maximum temperature ($\approx 0.5\epsilon/k_B$) that is nearly *independent* of the distance from the original surface. In this context, the routes to matter removal are (locally) determined by the level of inertial confinement, in increasing degree of which these are (trivial) fragmentation, phase explosion, and heterogeneous nucleation of vapor embryos at solid-liquid interfaces. This picture is expected to remain valid as the pulse duration is decreased, except in region I where the increased confinement will eventually cause the breakup of the expanding supercritical matter through, rather, a "nontrivial" fragmentation process.[7] This is different from the case of metals and semiconductors where ablation is essentially determined by the local amount of deposited energy.[7,9]

The strong inertial confinement of the irradiated matter provides a natural pathway to phase explosion upon *cooling* of the laser-heated material. Taken together with our previous studies,[7–9] the present simulations further demonstrate that the model of Miotello and Kelly is not adequate to describe ablation of absorbing solids under femtosecond to nanosecond laser pulses.

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