

Insight from molecular dynamics simulation into ultrashort-pulse laser ablation

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ABSTRACT

Ultrashort-pulse laser irradiation may melt the target and, at higher intensities, lead to ablation. The state of the material shortly after irradiation is characterized by high temperatures and pressures (both tensile and compressive). In addition, the material may not yet be in thermal equilibrium. Molecular dynamics simulation is well suited to model the state of matter under these conditions. We give several examples of how molecular dynamics simulations have contributed to understanding the ablation phenomena after ultrashort-pulse laser irradiation.

Keywords: Laser ablation, molecular-dynamics simulation

1. INTRODUCTION

The interaction of intense ultrafast (fs- or ps-) laser pulses with metal surfaces heats the crystal, melts it, and may – at even higher intensities – lead to ablation.^{1–11} A modeling of these processes is best based on atomistic simulation by molecular dynamics (MD), since it allows to treat the extreme states satisfactorily, to which matter is excited under the irradiation – such as high tensile and compressive pressures and high temperatures – and the nonequilibrium states through which the material evolves after irradiation. Hence, in the past ten years, the technique of molecular dynamics simulation has been applied successfully to model laser ablation, and a number of interesting insights have been obtained. In this paper we shall outline by way of example several of the features investigated in this area.

To set the scene, and to outline the relevant time and length scales involved in laser irradiation, we shall focus on the irradiation of a metallic target, with numbers corresponding to gold.^{12,13} In a metal, the laser irradiation is absorbed very close to the surface, in the skin layer, with a depth of the order of 10 nm. However, due to the high diffusivity of electrons, these diffuse quickly into the target inner. Simultaneously electrons impart their energy to atoms. The electron-atom coupling time τ characterizes the time after which the electron and atom system have reached thermal equilibrium. For gold, $\tau \cong 20$ ps. At this time, the electrons have diffused to a heated depth of $d_T = 250$ nm. In this region a zone of hot, thermally equilibrated material has been created.

Concomitant with heating, due to the thermoelastic effect the material is under high compressive pressure. For ultrashort pulses, during the time mentioned above, the material has no time to relax the pressure. For a velocity of sound of $v_{\text{sound}} = 3$ km/s, pressure needs for relaxation a time equivalent to the acoustic response time, $d_T/v_{\text{sound}} = 80$ ps. This feature that high pressures are generated after irradiation with no time for relaxation is called *stress confinement*. It is characteristic of ultrashort pulses; processes occurring after nanosecond laser irradiation do not exhibit stress confinement, but are purely thermal in nature.

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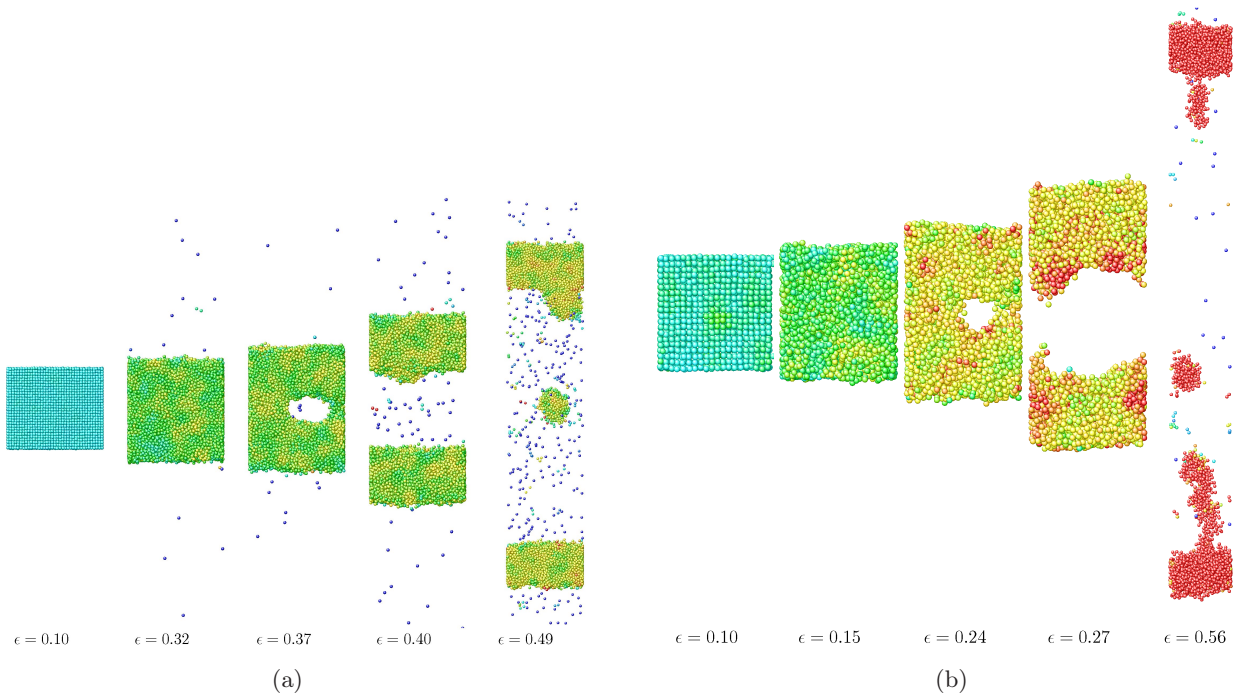


Figure 1. Series of snapshots of an energized Lennard-Jones film (a) and an Al film (b) featuring the materials processes occurring after laser irradiation. The energization ϵ , Eq. (1), is indicated in the figures. Data have been taken at a time $t \gg d/v_{\text{sound}}$, typically between 5 and 20 ps after energization. Colour denotes the local temperature and increases from blue to red; green characterizes the melting point. The subplots visualize from left to right the effect of increasing energization: crystalline solid; molten; temporary void formation; spallation, cluster formation. From Refs. 9,22.

2. MODEL

The method of molecular dynamics simulation is well established and has been described in a number of textbooks and reviews.^{14–19} An important aspect of the problem addressed here is the coupling of molecular dynamics to the electronic system, and the modeling of the dynamics within the electronic system. For metals, the method of the two temperature model (TTM) has been developed to describe these processes in a continuum model.²⁰

When a continuum description of the electronic system is coupled to an atomistic simulation of the atoms, a hybrid simulation scheme is generated which has been called TTM-MD.⁴ In molecular dynamics, the coupling can be effected by introducing additional forces acting on the atoms. One ansatz uses velocity-proportional forces, which assure that the power imparted to an atom by the electrons equals the power lost by the electronic system in this space region.^{3,4} An alternative procedure uses velocity scaling on the atoms with a scaling factor proportional to the power input by the electronic system.²¹

This scheme assumes the electron system to be thermalized. Shortly after irradiation this will not be the case. When it seems important to model processes in the nonthermal electron regime – e.g., for an insulator or a semiconductor –, a Monte Carlo description of the electron system may be appropriate. This has been done in the context of laser irradiation by Lorazo et al. for silicon.⁷

3. THIN FILMS

In view of the length scales described in Sect. 1, thin films are those whose thickness $d \leq \tau v_{\text{sound}}$.¹³ In this case, due to the fast homogenization of the electrons in the film, a homogeneous pressure and temperature distribution will be set up in the film. This gives rise to a quite universal sequence of events occurring.

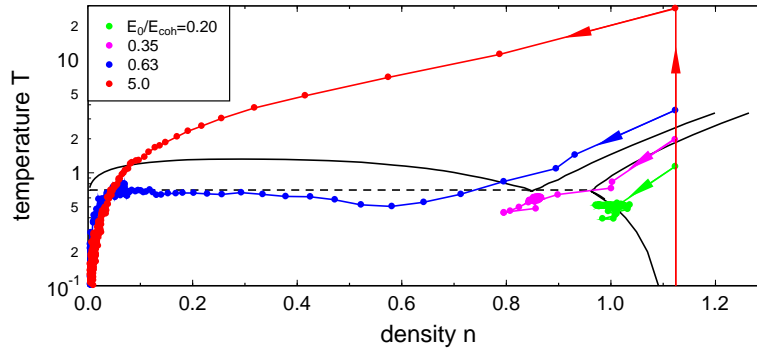


Figure 2. Phase-space (T - n) trajectories of the path of the simulation volume in a laser-irradiated Lennard-Jones film. Data are given in normalized Lennard-Jones units. Four different energizations $\epsilon = E_0/E_{\text{coh}}$ have been studied. The phase boundaries of the Lennard-Jones system have been included (full lines). The horizontal dashed line indicates the triple point temperature. From Refs. 9, 23.

Fig. 1 shows the processes occurring in laser irradiated materials as a function of excitation energy. It is convenient to normalize the energy given by the laser to an atom, E_0 , to the cohesive energy of the material, E_{coh} , and to introduce the *energization*

$$\epsilon = E_0/E_{\text{coh}}. \quad (1)$$

For the two materials simulated for Fig. 1 – a Lennard-Jones material and aluminum – with increasing energization, the crystal is heated, then melts, then temporary voids (or gas-filled bubbles) form. Eventually the material fractures: This indicates the energy needed for ablation, and thus the ablation threshold. For even higher energization, multifragmentation occurs.

The ablation mechanism is as follows. After the high compressive pressure has been set up by the laser pulse, the pressure relaxes, leading to a series of acoustic oscillations of the entire film, cf. also Fig. 7 below. In these oscillations, when the thickness reaches largest values, the film is under tensile pressure. If this pressure exceeds the yield strength of the material it will break. Due to the symmetry of the system (homogeneous excitation) the largest pressure is reached in the center of the film and hence ablation results in two symmetric fragments. A closer inspection reveals that a Lennard-Jones material fractures in the solid phase; this process can be called spallation. Metals, however, break in the liquid phase. The fracture process can be characterized as the nucleation of voids, their growth, and coalescence.

Fig. 2 shows the processes occurring in Fig. 1(a) as phase space trajectories in a thermodynamic temperature-density diagram. It allows to view the high temperatures reached after irradiation and the different paths that the system takes to release the pressure and thereby to cool. Note that the points where the trajectories are in the (metastable or instable parts of the) coexistence region are an artifact of the evaluation: Here averages over all atoms in the systems have been plotted.

4. THICK FILMS AND BULK SOLIDS

A film may be called thick if its thickness d is larger than a few times the heated depth d_T ; Demaske et al. propose $d > 3d_T$.¹³ In this case the film is no longer heated homogeneously but strong temperature and pressure gradients have built up after the electron-atom coupling time τ . These gradients start waves in the material, which contribute additional physics on top of the oscillations observed for thin films. In particular, the region of high compressive stress close to the surface will start a compressive wave running into the film; it is followed by an unloading tensile wave. In this unloading wave, ablation may occur for the same reason as in the thin film, viz. by mechanical fracture. Fig. 3 shows a close-up view of the ablation process in the unloading wave for the case of a thick (semi-infinite) Cu target. It is seen how the tensile pressure in the region of the void is relaxed after spallation occurred in the molten phase.

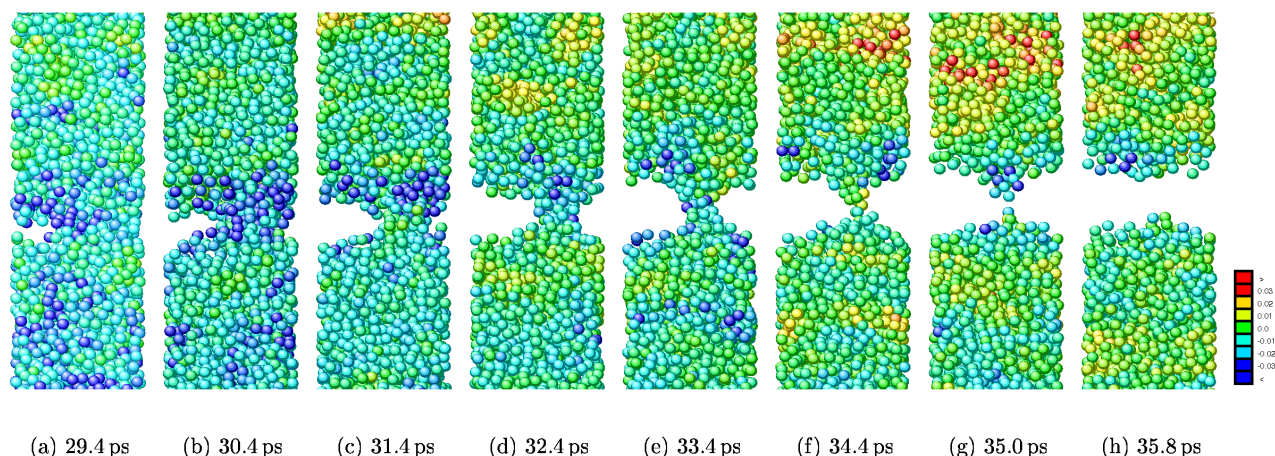


Figure 3. Atomistic view of part of the laser-irradiated Cu solid during ablation. Cross sections (height 60 \AA , width 21 \AA , thickness 10 \AA) through the simulation volume are shown at various times after laser irradiation. Atoms are coloured according to their local pressures, in units of the bulk modulus, $B = 137 \text{ GPa}$. The local pressure of an atom is defined as the average virial within a sphere of radius of 6.2 \AA (cutoff of the interaction potential). From Ref. 3.

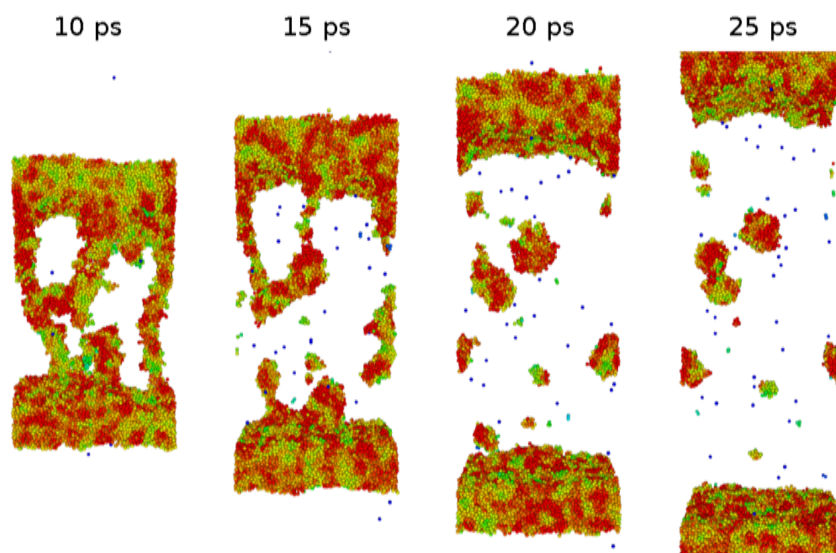


Figure 4. Ablating Al film of 12.8 nm thickness, and 12.8 nm lateral width, energized with 1.2 eV/atom laser irradiation.

These processes occur both for thick films and for bulk solids. For a thick film, however, also spallation may occur at the rear side, after the compressive pulse generated at the front side has been reflected at the back and changed its phase to a tensile pulse.¹³

5. MECHANISMS: SPALLATION VS PHASE EXPLOSION

Above we described how ablation under ultrafast (femtosecond or few-picosecond pulses) occurs. It is a mechanistic process mediated by the tensile pressure in the material, cf. Fig. 4. When the condition of stress confinement (cf. Sect. 1) is no longer fulfilled, no huge pressures will build up, and this mechanism does no longer work. Then ablation occurs by thermal processes; this is the usual scenario for nanosecond pulses. In a

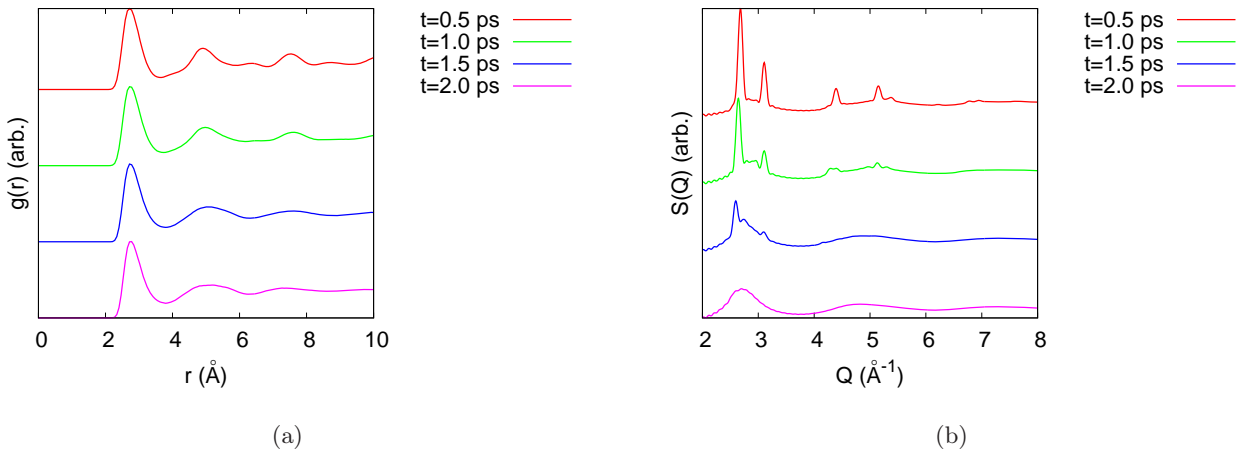


Figure 5. Time evolution of the pair distribution function $g(r)$ (a) and of the structure factor $S(Q)$ (b) in an Al film after laser irradiation. Film thickness 12.8 nm, number of atoms 1.21×10^5 , laser excitation 0.31 eV/atom.

recent paper, Zhigilei et al. compared ablation of a Ni target induced by 1 ps and 50 ps pulses.¹¹ In the latter case the condition of stress confinement is no longer fulfilled. Then ablation occurs by a mechanism which has traditionally been termed *phase explosion* or explosive boiling. This term describes the situation where the system enters the spinodal region, which is thermodynamically unstable; hence instantaneous decomposition of the system into two phases, here liquid and gas, results. In a molecular dynamics simulation, this happens on the time scale of picoseconds. In our scenario, it means that the energized liquid expands until it fragments upon reaching the spinodal. Garrison et al. found with the help of molecular dynamics simulations that at temperatures $T > 0.90T_c$, where T_c is the critical temperature of the liquid-gas phase transition, the rate of homogeneous nucleation increases so strongly that phase explosion occurs within picoseconds.²⁴

Zhigilei et al. found that outside the regime of stress confinement, spallation cannot occur,¹¹ and the mechanism of ablation is phase explosion. In the particular case investigated, phase explosion was characterized by a rather high percentage of atoms in the ablation plume. They also demonstrate that in the regime of stress confinement, i.e., for ultrashort pulses, a regime of phase explosion exists for energizations above the spallation regime; its signature is the high percentage of atoms in the ablated flux, besides liquid droplets or clusters, which dominate the pure spallation regime.

6. MELTING

For laser intensities below the ablation threshold, materials will be heated and may melt. It is of interest to investigate the laser-induced melting process also for higher intensities, since – as we saw above – metals will usually melt before ablation.

For a number of years it has been known that the melting process can be studied experimentally with picosecond time resolution using a pump-probe technique based on electron or X-ray diffraction. Thus it was shown experimentally that a 20 nm aluminum film irradiated by 120 fs laser pulse at 84 J/m^2 intensity melts within less than 6 ps.²⁵

Lin and Zhigilei could corroborate these results using molecular dynamics simulation and showed that melting of an aluminum film can occur within 3 ps.²⁶ We show in Fig. 5 the time evolution of the pair distribution function and its Fourier transform, the structure factor, in an aluminum film after irradiation with an ultrashort laser pulse. Here the destruction of the crystalline order within approximately 2 ps can be seen.

Since the structure factor $S(Q)$ is experimentally observable, and a time resolution of 0.1 ps appears feasible, such measurements can give valuable insight both into the melting mechanism, and into the reliability of the TTM-MD model.

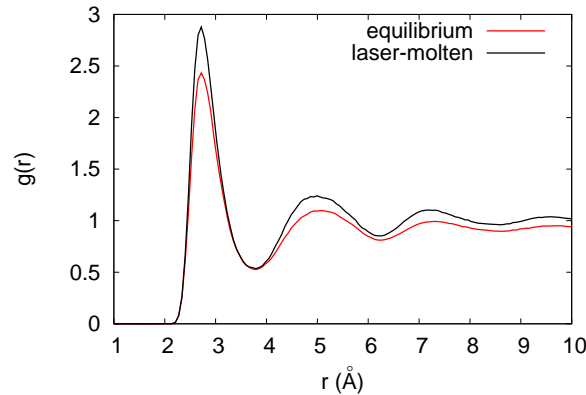


Figure 6. Pair distribution function $g(r)$ for a laser molten liquid 6 ps after irradiation compared to an equilibrium liquid at the same temperature, 1400 K. To prepare the laser-molten liquid, we employed the same system as in Fig. 5, but energized to 0.47 eV/atom.

Fig. 6 demonstrates that the pair distribution function of a laser-melted aluminum film – at 6 ps after irradiation where it is entirely molten – does not coincide with that of an equilibrium liquid at the same temperature. The reason hereto are the acoustic oscillations in the film, which are strong shortly after the laser pulse (here at 6 ps, in the expanded tensile-stress phase of the oscillation, cf. Fig. 7). The nonequilibrium liquid shows density maxima at slightly larger distances and of reduced height, compatible with its reduced density, than the equilibrium liquid.

Lin and Zhigilei found in their study²⁶ that for metals which melt more slowly – due to an increased electron-atom coupling time τ , such as for gold – the structure factor shows an additional feature, besides the typical results of peak broadening due to the temperature increase in the crystalline phase and the destruction of the crystalline order: When the crystal expands uniaxially due to the acoustic oscillation, a characteristic splitting of the diffraction peaks is observed. They also note that melting usually starts from the surface, i.e., as homogeneous melting, for not too strong laser intensities. Otherwise homogeneous melting will occur, where liquid regions nucleate throughout the thin film.^{4,26}

7. TIME STRUCTURE OF LASER PULSE: DOUBLE PULSES

In recent experiments the time structure of the laser pulse was changed from its usual Gaussian shape in order to inquire into its effects on materials processes in general, and ablation in particular. The simplest change is if instead of one Gaussian pulse, two Gaussian pulses with a time delay δ are employed. In a specific experiment the irradiation of Cu with two pulses, each with a width of 0.1 ps and a fluence of 2 J/cm², showed a strong effect on the ablation depth.²⁷ For time delays $\delta \lesssim 1$ ps, the ablation depth of two pulses is smaller than two times the ablation depth of a single pulse; even more surprisingly, for pulse delay times between around 20 and 200 ps, the ablation depth for two pulses is even smaller than that of one pulse.

In their analysis,²⁷ these authors show that in the latter regime of delays the second laser pulse is absorbed in the ablation plume generated by the first pulse rather than in the target. As a consequence part of the ablation plume of the first pulse is re-deposited on the surface, reducing the ablation depth to values below that of a single pulse. These authors point out that also the interference of pressure waves by the two pulses may lead to effects on the ablation behavior. This issue was investigated in detail in a recent publication, in which the acoustic oscillations induced by the two pulses and the melting of the film were investigated.²¹ Fig. 7 shows the acoustic oscillations in an aluminum film of 30 nm thickness after absorption of a single pulse (absorption 0.5 eV/atom), and with two such identical pulses with a time delay of $\delta = 4$ ps and 10 ps. Note that the acoustic oscillation period in this film amounts to $2d/v_{\text{sound}} = 8$ ps. When the two pulses are roughly in phase ($\delta = 10$ ps) the pressure oscillations may be increased, while they are decreased for a time delay of $\delta = 4$ ps, where destructive interference occurs.

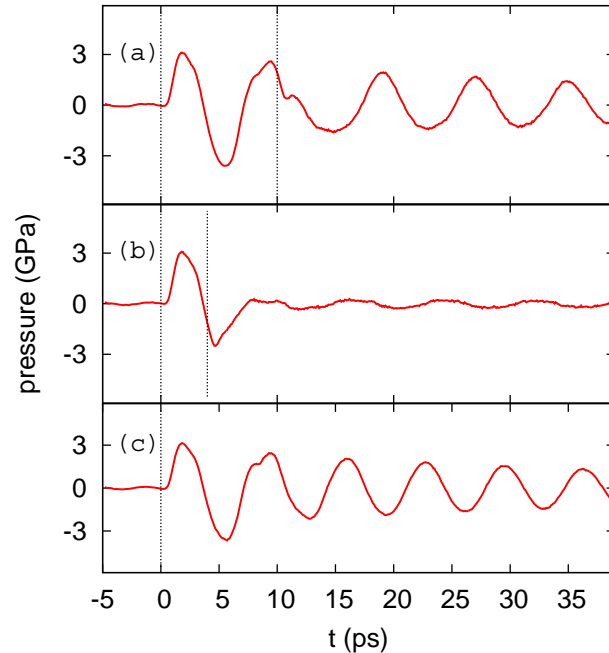


Figure 7. Time evolution of pressure in a thin Al film irradiated by a double pulse with time delay $\delta = 10$ ps (a) and 4 ps (b). (c) shows the pressure after a single pulse (time delay $\delta = \infty$). Vertical dotted lines mark the start of the second (delayed) laser pulse. Compressive (tensile) pressure has positive (negative) values. Data partially taken from Ref. 21.

8. CONCLUSIONS

In this paper we showed by way of example how molecular dynamics simulation may lead to insight into the mechanisms and processes occurring during ablation induced by short-pulse laser irradiation. Apart from the electron dynamics, which needs to be modeled separately, molecular dynamics allows to model the processes without any physical input – besides the interatomic interaction potential. As long as this potential is reliably known, this simulation procedure is able to describe strongly nonequilibrium processes, such as the superheating of the melt, nucleation processes, such as void formation in the liquid, the physics occurring in the metastable gas-liquid coexistence region, etc. Since matter is subject to high heating (and cooling) rates, strong tensile and compressive stresses and high strain rates, it is important that the interatomic potential is able to describe all these processes satisfactorily.

This potential may change after high excitation rates, leading for example to the well known phenomenon of nonthermal melting observed in silicon and other semiconductors.²⁸ The treatment of such phenomena is outside the method of classical molecular dynamics and requires quantum techniques.

The simulation of laser ablation phenomena poses particular problems, since the dynamics of the electronic system must also be modeled, simultaneously with the molecular dynamics simulation of the atom evolution. A number of schemes have been set up in the past to describe quantitatively the electron dynamics, and to couple it to the molecular dynamics simulation. We mention the well established two temperature model,^{3,4} the application of continuum (plasma) equations to describe ionization and recombination processes in the conduction band,¹² particularly in insulators, and Monte Carlo schemes for the early electron dynamics.⁷

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