Mesoscopic Breathing Sphere Model for Computer Simulation of Laser Ablation and Damage

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ABSTRACT

A breathing sphere model has been developed for molecular dynamics simulations of laser ablation of organic solids. The novel feature of this model is an approximate representation of the internal molecular motion, which permits a significant expansion of the time and length scales of the model, and yet still allows one to reproduce a realistic rate of the vibrational relaxation of excited molecules. A dynamic boundary condition that accounts for the laser induced pressure wave as well as the direct laser energy deposition in the boundary region allows one to focus the computational effort to the region where active processes of laser ablation and damage occur. The model has been applied to study the mechanisms of laser ablation of molecular solids, velocity distributions of ejected molecules, and laser damage in the case of spatially localized absorbers. The results for different laser fluences and pulse durations have been analyzed and related to available experimental data.

Keywords: molecular dynamics simulation, laser ablation, mesoscopic model, pressure waves, non-reflecting boundary condition.

INTRODUCTION

The interaction of laser pulses with organic matter leading to massive material removal (ablation) from a target is a subject of scientific as well as applied interest [1,2]. Important practical applications include laser surgery [3], matrix-assisted laser desorption/ionization (MALDI) of biomolecules for mass - spectrometric investigations [1,2,4] and surface microfabrication of polymer thin films [1,2].

Laser ablation of organic solids is a complex collective phenomenon that includes processes occurring at different length and time scales. The processes involved in laser ablation include laser excitation of absorbing molecules, energy transfer from the excited molecules into the internal and translational modes of other molecules in the solid, formation of a highly energetic high-temperature and high-pressure region, explosive disintegration and prompt forward ejection of a volume of material, intensive processes in the ejected plume, and propagation of the pressure wave away from the ablation region. The complex character of the involved intertwined processes hinders an adequate analytical formulation for a continuum description of the phenomenon whereas a collective character of the laser ablation occurring at the mesoscopic rather than molecular scale does not permit a direct application of the atomistic simulation approach.

An alternative mesoscopic model has been developed recently for molecular dynamics (MD) simulation of laser ablation and damage of organic solids [5,6]. The model has advantage of both addressing the effects of laser irradiation at a submicron resolution and yet incorporating a realistic description of energy relaxation of individual molecules internally excited by photon absorption.

The laser induced buildup of a high pressure within the absorbing volume and generation of the pressure waves propagating from the absorption region poses an additional challenge for molecular-level simulation. A new dynamic boundary condition is developed to account for the laser induced pressure wave propagation through the boundary of the computational cell as well as for the direct laser energy deposition in the boundary region [7].

In this paper we give a brief description of the breathing sphere model and the dynamic boundary conditions. This is followed by a discussion of application of the model to the analysis of the basic physical mechanisms of laser ablation of molecular solids. The existence of two distinct regimes of molecular ejection and the fluence dependence of the monomer yield measured in mass specrtometry experiments are addressed.

THE BREATHING SPHERE MODEL

The model assumes that each molecule (or appropriate group of atoms) can be represented by a single particle that has the true translational degrees of freedom but an approximate internal degree of freedom [5,6]. The internal degree of freedom is attributed to each molecule by allowing the particles to change their sizes. The characteristic frequency of the internal motion is controlled by the parameters of an anharmonic potential. The rate of the intermode energy transfer is determined by the size of the anharmonicity and frequency mismatch between vibrational modes. Thus, the parameters of the internal potential can be used to affect the coupling between internal and translational molecular motions and to achieve a desired rate of the conversion of internal energy of the molecules excited by the laser to the translational and internal motion of the other molecules. The rate of the vibrational relaxation of excited molecules is an input parameter in the model and can be either estimated from experimental data or modeled with atomistic or *ab initio* molecular dynamics simulations [8,9].

Because the molecules and not the atoms are the particles of interest, the system size can be significantly larger. Moreover, since explicit atomic vibrations are not followed, the timestep in the numerical integration is longer. One more advantage of the breathing sphere model is the ability to simulate complex multicomponent organic materials [10]. One can easily include bonding interactions, different strengths and absorptions of different components. The rate of energy transfer within an individual component as well as between components can be precisely controlled.

The effect of laser irradiation is simulated by vibrational excitation of random molecules during the time of the laser pulse within the penetration depth appropriate for a given wavelength. Vibrational excitation is modeled by depositing a quantum of energy equal to the photon energy into the kinetic energy of internal vibration of a given molecule. The absorption probability can be modulated by 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.

Owing to the approximations adopted in the breathing sphere model, computational cells can be large enough to reproduce the collective dynamics leading to laser ablation and damage. One effect, however, that can not be directly simulated within the MD model is propagation of the laser induced elastic wave. The method used to minimize the effects of the reflection of the wave from the boundary of the computational cell are discussed in the next section.

DYNAMIC BOUNDARY CONDITION

The generation of stress waves is a natural result of the fast energy deposition in the case of short pulse laser irradiation and inhomogeneous absorption [7,9,11]. This is illustrated in Figure 1 where the energy contour plots reflect the formation and propagation of a plane pressure wave within the MD computational cell. In this case the high pressure builds up during the 15 ps laser pulse within the penetration depth, 32 nm, of the irradiated sample. The high pressure contributes to the ablation of a part of the irradiated volume and drives a strong compression wave into the bulk of the sample. Simulation of the propagation of the pressure wave requires the size of the MD computational cell to be increased linearly with the time of the simulation. For times longer than ~100 ps the size of the model required to follow the wave propagation becomes computationally prohibitive and artificial border effects can interfere with the simulation results. Both rigid and free boundary conditions lead to the complete reflection of the pressure wave, as shown in Figure 1a. This reflection of the pressure wave can cause the effect known as back spallation [7,11], when the tensile strength of the material is exceeded and fracturing occurs at a certain depth near the back surface of the sample. The reflected wave can also reach the front surface of the irradiated sample and contribute to the material ejection.

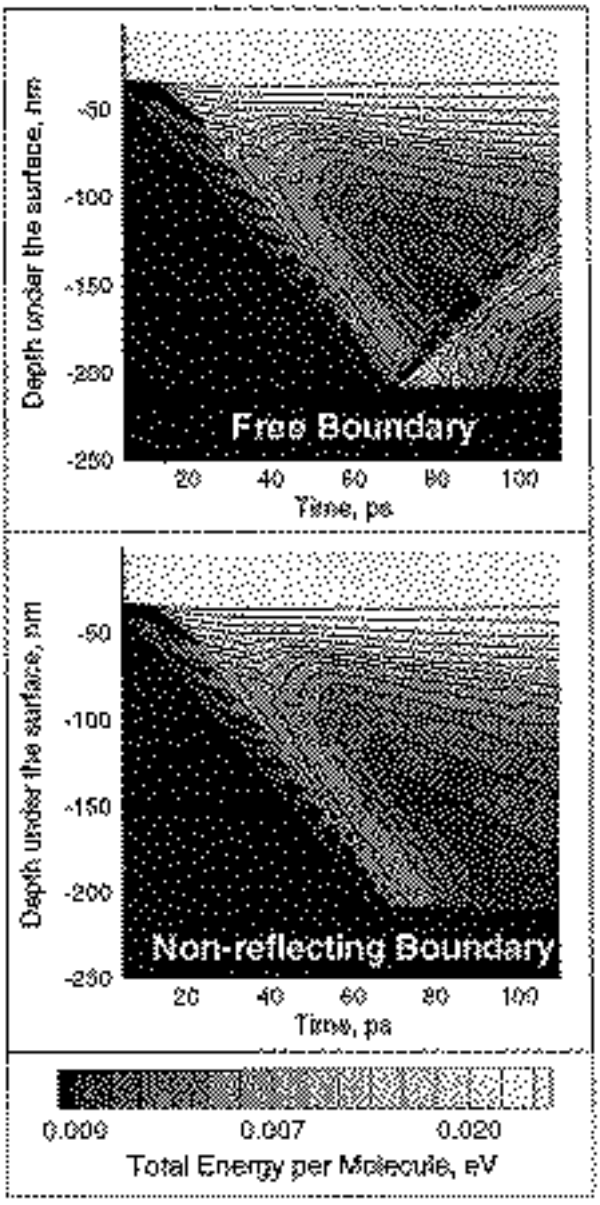


Figure 1: Energy contour plots for free and non-reflecting boundary condition applied at the bottom of the computational cell.

In order to avoid artifacts due to the pressure wave reflection, we have developed a simple and computationally efficient non-reflecting boundary condition based on analytical evaluation of the forces acting at the molecules in the boundary region from the outer "infinite medium" [7]. In this approach the boundary condition is a set of terminating forces that are applied to the molecules in the boundary region. In the calculation of the terminating forces, that are updated at each integration step, we take into account three effects, namely, the static forces that mimic interaction with molecules beyond the computational cell, the forces due to the pressure wave propagation

through the boundary region, and the forces due to the direct laser energy absorption in and around the boundary region during the laser pulse.

As shown in Figure 2b, the dynamic boundary condition allows us to completely eliminate simulation artifacts associated with the reflection of the pressure wave from the boundary of the MD computational cell and to restrict area of the MD simulation to the region where active processes of laser induced melting, ablation and damage occur. In effect, this significantly expands the scope of phenomena that can be addressed and allows to use irradiation parameters comparable to the experimental values [12].

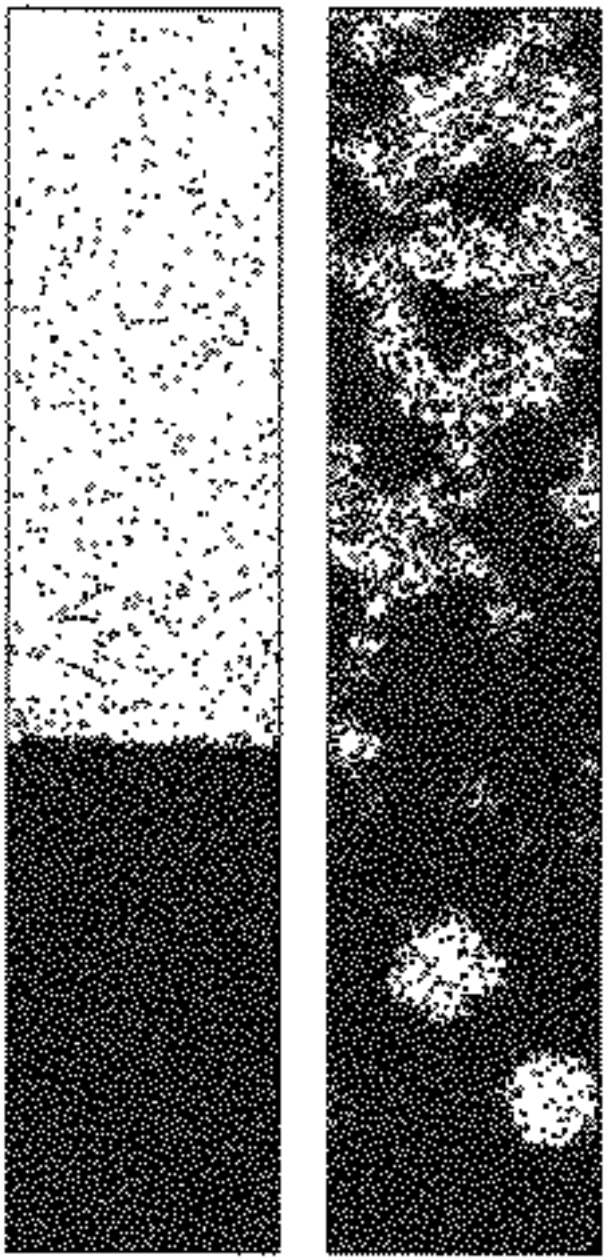
SIMULATION RESULTS

The mechanisms of laser ablation

In order to understand the basic processes leading to the material ejection, we performed a series of simulations of short pulse laser irradiation of a model molecular solid with a range of laser fluences. We found that there are two distinct regimes of molecular ejection separated by a well-defined threshold fluence. At fluences below threshold thermal desorption from the surface is observed, the desorption yield consists primarily of monomers, Figure 2a, and the desorption yield has an Arrhenius-type dependence on the laser fluence. At the threshold fluence the ejection mechanism changes from desorption to ablation, in which a collective ejection of a volume of irradiated material occurs. The change in the ejection mechanism manifests itself in more than an order of magnitude stepwise increase in the amount of ejected material, Figure 3, and in a drastic change in the plume composition. Large clusters become a major constituent of the plume above threshold, Figure 2b, and the total amount of ejected material follows the critical volume energy density deposited by the laser pulse[12]. The laser induced pressure buildup and the phase explosion due to overheating of the irradiated material are identified as the key processes responsible for material ejection in the ablation regime [5,6,12,13].

Total yield vs. yield of monomers

One important result from the simulations is an indication on a drastic difference in the fluence dependence of the total ablation yield and a yield of individual molecules, measured as a count rate in mass spectrometry experiments [12]. This difference is obvious from Figure 3 where both total yield and monomer yield are plotted. There is no step increase in the number of ejected monomers at the ablation threshold and one can hardly identify the threshold fluence from this dependence. An Arrhenius-type dependence of the monomer yield on fluence, albeit appropriate for the regime of thermal desorption only, appears to work over a larger fluence region, Figure 3. This observation provide an explanation for recent experimental results in MALDI [4]. Simulation



(a) (b)

Figure 2: Snapshots from the simulation of irradiation of molecular solid with 150 ps laser pulse at laser fluences of (a) 34 J/m^2 and 55 J/m^2.

results clearly demonstrate that the yield of individual molecules does not reflect in any quantitative extent the total amount of material ejected in the ablation regime. The difference in the physical mechanisms of molecular ejection below and above the ablation threshold leads to a drastically different plume composition and should be taken into account in order to provide an adequate analytical description of the yield vs fluence dependence in mass spectrometry experiments.

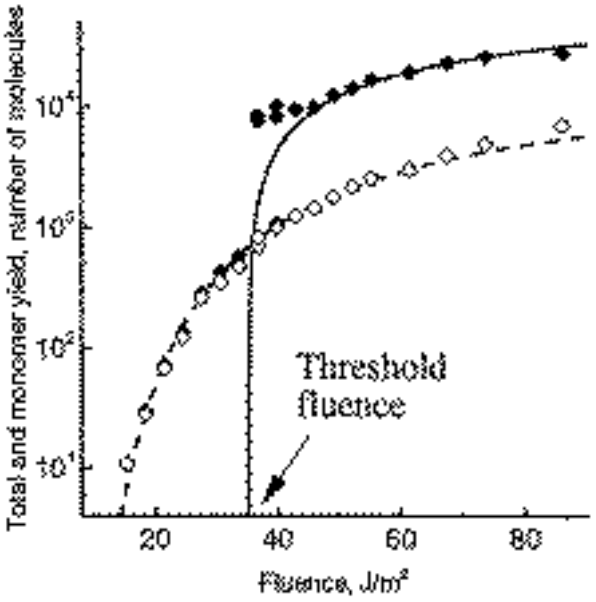


Figure 3: Total and monomer yield, vs. laser fluence. The solid line represent predictions of the ablation model (volume energy density criteria), the dashed line represents prediction of the thermal desorption model [12]. The closed and open symbols show the data points for total yield and monomer yield, respectively.

Other recent applications of the model include development of a consistent analytic description of the velocity distributions of matrix and analyte molecules in MALDI [14,15], analysis of the mechanisms of laser damage to spatially localized absorbers [10,16], and development of a combined molecular dynamics – finite element method for multiscale simulations [17].

SUMMARY

First results of the microscopic simulations of laser ablation and damage of organic solids demonstrate that with growing computer power and certain reasonable approximations it is now possible to apply the MD simulation technique for analysis of complex collective phenomena of laser ablation. Molecular-level simulations provide a comprehensive picture of the processes leading to ablation and damage both at mesoscopic level, in terms of energy, temperature and pressure development in the irradiated material, and at microscopic level, in terms of laser induced molecular motions. In effect, one has a unique opportunity to relate detailed information on the physical processes to experimentally observed results of laser irradiation.

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