1 Introduction

Laser ablation with the use of ultrashort pulsed laser has been widely used in material processing in recent years. It involves the removal of material from a solid (or occasionally liquid) surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically converted to plasma. Usually, laser ablation refers to removing material with a pulsed laser, but it is possible to ablate a material with a continuous wave laser beam if the laser intensity is high enough. The depth over which the laser energy is absorbed, and thus the amount of material removed by a single laser pulse, depends on the material’s optical properties and the laser wavelength. Laser pulses can vary over a wide range of duration (milliseconds to femtoseconds) and fluxes and can be precisely controlled. This makes laser ablation very valuable for both research and industrial applications.

The phenomena of Coulomb explosion require the consideration of special relativity due to the involvement of high energy electrons or ions. It is known that laser ablation processes at high laser intensities may lead to the Coulomb explosion, and their released energy is in the regime of keV to MeV. In contrast to conventional molecular dynamics (MD) simulations, we adopt the three-dimensional relativistic molecular dynamics (RMD) method to consider the effects of special relativity in the conventional MD simulation for charged particles in strong electromagnetic fields. Furthermore, we develop a Coulomb force scheme, combined with the Lennard-Jones potential, to calculate interactions between charged particles, and adopt a Verlet list scheme to compute the interactions between each particle. The energy transfer from the laser pulses to the solid surface is not directly simulated. Instead, we directly assign ion charges to the surface atoms that are illuminated by the laser. By introducing the Coulomb potential into the Lennard-Jones potential, we are able to mimic the laser energy being dumped into the xenon (Xe) solid, and track the motion of each Xe atom. In other words, the laser intensity is simulated by using the repulsive forces from the Coulomb potential. Both nonrelativistic and relativistic simulations are performed, and the RMD method provides more realistic results, in particular, when high-intensity laser is used. In addition, it is found that the damage depth does not increase with repeated laser ablation when the pulse frequency is comparable to the duration of the pulse. Furthermore, we report the time evolution of energy propagation in space in the laser ablation process. The temporal-spatial distribution of energy indirectly indicates the temperature evolution on the surface of the Xe solid under intense laser illumination. [DOI: 10.1115/1.3056607]

Keywords: relativistic molecular dynamics, Coulomb explosion, laser ablation, xenon solid
by electron gas by the finite difference method based on the thermal conductivity of metal [13]. Furthermore, it is known that the atomic absorption of energy increase in its atomic lattice position and vibration and the range increases with increasing temperature, and makes the energy of mutual impact of atomic energy transfer increase [14–17]. Hence, it can be observed that the amplitude of stress wave will increase with the positive charges. In order to identify the Coulomb explosion experimentally, the ions will have to be detected time-resolved in situ, which is difficult. On the other hand, simulations provide a convenient means of probing the phenomenon. In the case of the Coulomb explosion, the smallest distance between 2 atoms is 4.3 Å, and the average distance between atoms at maximum compression is 4.56 Å and reached 250 fs after the onset of the laser. As for cluster problems, simulation results have been shown to be in agreement with the experimental findings obtained from field ionization of the atoms and the solid by the strong electric field of the infrared laser [18,19].

In the present work, we carried out MD simulations, both non-relativistic and relativistic ones, with the combination of the Lennard-Jones and Coulomb potentials to simulate the laser ablation process. Focus is placed on the effects of relativistic effects. As for the energy transfer from the laser to the material surface, we adopt the method of direct assignment of charges to the atoms in the hemispherical region of the laser spot. The radius of the laser spot is 8 Å. The rationale is that ionization occurs under ultrashort laser illumination, and hence the atoms are assumed to be fully ionized. In this paper, we compare three cases, different in their charge levels. Atoms in the hemispherical region under the surface laser spot are also assumed to be ionized. For the three charge states, the laser fluences are 0.13 J/m², 0.2 J/m², and 0.4 J/m². The ionization for the singly, doubly, and triply charged states is 1170.4 kJ/mol, 2046.4 kJ/mol, and 3099.4 kJ/mol [20].

2 Relativistic Molecular Dynamics Modeling

In the present study, the xenon solid is chosen due to the simplicity of its atomic interactions. The Xe potential used in the MD code is of the Lennard-Jones type [21]. Hence, the total potential was modified by the electrostatic Coulomb potential and the Lennard-Jones potential. Figure 1 shows the schematic of the physical problem of laser ablation. In this paper, the energy transfer process from the laser to the Xe solid is simulated by directly assigning ionization charges to the atoms being irradiated by the laser. Emphasis is placed on the difference between conventional and relativistic MD simulations. The plume of sputtered particles are depicted.

For the charge particle interactions, we describe the repulsion between such ionized atoms using a Coulomb potential in addition to the Lennard-Jones potential. The interactions are modeled using the Coulomb potential smoothly splined to the electrostatic term. Although it can be argued that more highly charged ions would experience even greater core-core repulsion than singly charged Coulomb repulsion, for simplicity, this is not considered here. Our focus is to study relativistic effects in the molecular dynamics simulation. The Coulomb force is specially developed in the present work to simulate the phenomena of the Coulomb explosion. It is noted that the Coulomb force is the most computationally intensive part of the MD model [22–25]. Hence, we adopt a Verlet list scheme to compute the interactions among particles.

The Xe+ – Xe+n interactions were assumed to be purely electrostatic and repulsive. The total potential for the Xe+n – Xe interactions can be calculated with Eqs. (1)–(3) as follows:

\[
V_{\text{LJ}}(r_{ij}) = 4\varepsilon \left( \frac{\sigma}{r_{ij}} \right)^{12} - 2\varepsilon \left( \frac{\sigma}{r_{ij}} \right)^{6}
\]  

(1)

\[
V_{\text{C}}(r_{ij}) = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}
\]  

(2)

\[
V_{\text{total}}(r) = V_{\text{LJ}}(r_{ij}) + V_{\text{C}}(r_{ij}) = \sum_{i<j} \left[ (\frac{\sigma}{r_{ij}})^{12} - 2(\frac{\sigma}{r_{ij}})^{6} \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}
\]  

(3)

The constants in the Lennard-Jones potential are given as \(\sigma = 4.3\) Å and \(\varepsilon = 0.0197\) eV. In Fig. 2, the interatomic force and distance relationships for the combination of the Lennard-Jones and Coulomb potentials are shown. The inset shows the Lennard-Jones potential for neutral xenon atoms with \(\sigma = 4.3\) Å and \(\varepsilon = 0.0197\) eV.
With the force acting on ion \( i \) being known, the equations of motion for this particle can be solved according to

\[
F = \frac{ma}{\left(1 - \frac{v^2}{c^2}\right)^{3/2}}, \quad P = \gamma mV = \frac{mV}{\sqrt{1 - \frac{v^2}{c^2}}}
\]

where \( V \) is the velocity of the particle and \( t \) is the duration of a time step in the simulation.

In our simulations, the \( Xe \) solid lattice (fcc) is used as target and \( Xe^{+1} \), \( Xe^{+2} \), and \( Xe^{+3} \) are considered as being ionized by the femtosecond laser in the laser spot. All the particles in the system were evaluated using both the relativistic and nonrelativistic methods. The \( y \) direction is perpendicular to the surface, and fixed boundaries were taken along the \( x \) and \( z \) directions. The system size is on the order of \( 140,000 \) atoms, and from the total energy calculation of the \( Xe \) system, the laser flux transmitted to the solid is about a few tenths of \( J/\text{m}^2 \). The simulations are run for times not exceeding about 10 ps. The velocity Verlet algorithm was used to integrate the equations of motion with a time step of \( 10^{-3} \) fs. Three sets of simulations are carried out: Charge +1, Charge +2, and Charge +3 are assigned to the ionized \( Xe \) atoms in the laser spot, assumed to be 8 Å in diameter.

The system size representing all particles (atom, ion) in our RMD code was chosen to be of the order of \( 120 \times 60 \times 60 \) Å\(^3\). In this limit, the microscopic interactions of all charged particles are taken care of by the relativistic molecular dynamics formalism. The RMD code contains no free parameters and presents a virtual experiment.

We remark that ionization [26–30] in a cluster of bombarded particles is a combined process of optical field and collisional ionization. The newly created electrons from these are generally placed inside the solid, treated as inner electrons. Accordingly, the ion charge of all ions is increased. For solids, electrons can be removed from or recaptured by the solids. Outer ionization is the process in which an inner electron leaves the parent solid and becomes an outer electron. The reverse process of electron recapture is also possible. It can occur when an outer electron is attracted to the positively charged particles through Coulomb forces or due to Coulomb explosion. In the present work, these phenomena are not included in our models.

3 Results and Discussion

Results and discussion are presented in this section. First, damages on the surface of the xenon solid are discussed, and then the propagation of laser energy inside the solid is presented.

3.1 Damages on the Surface of the \( Xe \) Solid Due to Laser Ablation. In our simulation from the energy due to Coulomb repulsion, the three cases studied here, Charges +1, +2, and +3, are equivalent to laser fluences \( 0.13 \) J/cm\(^2\), \( 0.2 \) J/cm\(^2\), and \( 0.4 \) J/cm\(^2\), respectively. Considering the time step (\( 10^{-3} \) fs), these fluences are equivalent to the laser intensities 3 \( \times \) \( 10^{18} \) W/cm\(^2\), 1.2 \( \times \) \( 10^{19} \) W/cm\(^2\), and 2.56 \( \times \) \( 10^{19} \) W/cm\(^2\).

The total energy of the \( Xe \) system under laser ablation with Charge +1, Charge +2, and Charge +3 is shown in Fig. 3. The short dashed-line (black) labeled with “no laser” indicates the baseline case that no laser energy is applied to the \( Xe \) system. The laser energy is applied by assigning charges to the atoms in the laser spot, assumed to be 8 Å in diameter. The system size representing all particles (atom, ion) in our RMD code was chosen to be of the order of \( 120 \times 60 \times 60 \) Å\(^3\). The system size representing all particles (atom, ion) in our RMD code was chosen to be of the order of \( 120 \times 60 \times 60 \) Å\(^3\). From the total energy calculation of the \( Xe \) system, the laser flux transmitted to the solid is about a few tenths of \( J/\text{m}^2 \). The simulations are run for times not exceeding about 10 ps. The velocity Verlet algorithm was used to integrate the equations of motion with a time step of \( 10^{-3} \) fs. Three sets of simulations are carried out: Charge +1, Charge +2, and Charge +3 are assigned to the ionized \( Xe \) atoms in the laser spot, assumed to be 8 Å in diameter.

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ablation. For low energy laser, repeated bombardments can lead to similar transmissivity with the high energy one. The plateau region of the Charge 1 case indicates that low energy laser processing can make the dimple deeper by repeating bombardments. However, the Charge 2 and 3 cases show that repeated processing does not increase the aspect ratios of the dimples.

As shown in Fig. 9, mean speeds of the particles in the nonrelativistic and relativistic models are significantly different. The speeds are in units of multiples of light speed, and the particles move away from the top surface. To calculate the mean speed of the atoms moving away from the surface, we fix the observation time equal to 10^{-2} fs, and average the speeds of atoms layer by layer away from the top surface. In the calculation, each layer is assumed to be about 1 Å. The results in Fig. 9 are from the case Charge +3. From the distribution of the mean speed, it can be seen that the particles with the highest speed are located at about 2–3 Å away from the top surface. This finding shows that nonrelativistic models cannot reflect reality.

3.2 Spatiotemporal Energy Propagation of Laser Ablation.

The surface morphologies of the laser-processed Xe solid are shown in Figs. 10–12 for the three cases, Charges +1, +2, and +3, respectively. In all of the cases, the initial laser spot size is 8 Å. In Figs. 10(a) and 10(b), it can be seen that the initial periods of the ablation processes create local melting and transient to equilibrium. The local melting can be identified by observing the atomic arrangements on the figures as they lose their crystallinity. To be able to quantitatively distinguish crystalline and amorphous regions requires further analysis of their structural factors. Figures 10(c)–10(f) delineate the energy propagation away from the ablation center. When equilibrium is reached, Fig. 10(f) shows a triangular finish (40 Å), indicating that low energy ablation cannot form a circular hole even though the laser spot has a circular shape. Again, in this case, the penetration depth is 20 Å. For the Charge +2 case, Fig. 11 shows a similar feature to Fig. 10 in terms of the time evolution of energy distribution in space. When equilibrium is reached, Fig. 11(f) shows a most circular finish (90 Å in diameter). It is noted that the penetration depth in this case is 25 Å. We remark that the circularity of the damage depends on the interaction between the material and the laser intensity. When the laser energy increases to Charge +3, Fig. 12 shows large local melting. A high energy wave front is formed around the ablation hole (Fig. 12(c)). Figures 12(c)–12(f) delineate the energy propagation away from the ablation center. When equilibrium is reached, Figure 12(f) shows a rough circular finish (110 Å in
diameter), indicating that high energy ablation cannot form a circular hole even though the laser spot has a circular shape (8 Å in diameter). The less noncircular shape may be due to the defect formation. The penetration depth is 50 Å. Remark that in Figs. 10–12 the simulation time runs from 1 ps to 25 ps, less than 100 ps (stabilized, as shown in Fig. 7), and hence the surface features continuously change, as well as the depth of the laser ablation.

Snapshots of the spatiotemporal distribution of energy wave are shown in Fig. 13 at time equal to 1 fs, 5 fs, and 10 fs after laser irradiation for the case of Charge +3. The inset shows the schematic of the direction of energy propagation away from the dimple. Remark that the atoms moving away from the surface more than 100 Å are not included in the energy calculation. Energy peaks are at \( D = 10 \text{ Å}, 15 \text{ Å}, \) and 25 Å away from the center of ablation for \( t = 1 \text{ fs}, 5 \text{ fs}, \) and 10 fs, respectively. It is noted that the energy wave is circularly symmetric when observed on the surface of xenon. The speed of wave is not constant. From 1 fs to 5 fs, the wave speed is about 1 Å/fs (or 100 m/s), and from 5 fs to 10 fs, it reduces to about 0.5 Å/fs (or 50 m/s). The reduction in the wave speed indicates that wave propagation is not reversible. Energy loss occurs in the process of propagation. Furthermore, the
energy peaks 0.055, 0.041, and 0.031 at $D = 10$, 15, and 25 Å, respectively, for the three cases show that the energy wave is of the dispersive type. The decay rate of the energy peaks is 0.71. The tail behavior of the energy wave for the case of $t = 5$ and 10 fs shows no exponential decay. Remark that periodic boundary conditions are adopted. The mechanisms for the wave propagation are related to diffusional processes and a high thermal gradient due to laser ablation. The connection between classical continuum modeling and RMD simulation in this respect needs to be further explored in a later paper.

Fig. 10  Time evolution of energy distribution for the Charge 1 case. (a) $t = 1$ ps, (b) $t = 5$ ps, (c) $t = 10$ ps, (d) $t = 15$ ps, (e) $t = 20$ ps, and (f) $t = 25$ ps.
Figure 14 below shows the temperature versus time right of center, 50 Å on the top surface. During laser ablation at the center point at time of 40 fs, the temperature wave propagates to view points first at 59 fs with a temperature of 157 K. As shown in Fig. 15, the initial energy is about 52 MeV during the first 40 fs in the simulation. This energy is the equilibrium energy before the laser is illuminated on the xenon surface. At 40 fs, the system receives energy from assigning charges to the atoms in the laser spot;
maximum energy is about 83 MeV. From 40 fs to 60 fs, the drop of total energy is associated with (1) the numerical error induced from the prechosen cutoff radius in our molecular dynamics simulation, (2) the existence of temperature control layers above the fixed substrate, and (3) atoms moving away from the top surface by more than 100 Å. The temperature control layers behave as an

Fig. 12 Time evolution of energy distribution for the Charge 3 case. (a) t=1 ps, (b) t=5 ps, (c) t=10 ps, (d) t=15 ps, (e) t=20 ps, and (f) t=25 ps.
energy source or sink to maintain the temperature of the model. Therefore, our system is not a conserved system. Between 60 fs and 80 fs, the system energy reaches about 30 MeV, different from the initial 52 MeV due to the removal of atoms.

4 Conclusions

With the consideration of relativistic effects, our particle-dynamics simulations of the interaction of intense (being inferred from ionized charges) femtosecond (being considered as the atoms in the laser spot being ionized in the single time step of our molecular dynamics simulation) laser pulses have shown that the damage shape depends on the fluence of the laser and the number of laser pulses being received by the surface atoms. The novel combination of the Coulomb and Lennard-Jones potential, as well as the consideration of special relativity in the conventional molecular dynamics simulation, enables realistic predictions of the ablation process. The results of our simulations show that using the Coulomb potential is suitable to simulate the Coulomb explosion phenomenon of the laser ablation process. Furthermore, we show that to reach the same damage depth, one can use low laser ablation fluence with several repeated laser pulse bombardments, or a high fluence laser. From the present simulations, it is found that low energy laser pulses may induce certain thermal expansion and vibration with no removal of surface atoms. However, for high energy pulses, surface atoms may be removed and the shapes of final finishing can be controlled by the level of energy, as well as the illumination time for moderate laser power. Longer illumination time ensures that several pulses will be received by the surface atoms. When the energy of laser pulses is too high, damage in terms of the activation of slip systems may occur.

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