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Molecular dynamics study of solid melting and vaporization by laser irradiation

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Abstract—The molecular processes of the phase change of melting and vaporization of solid materials by laser beam irradiation were studied numerically by using the molecular dynamics method. By absorbing the laser light energy, the solid atoms or molecules are excited in the interatomic or intermolecular potential energy to change their interacting forces. The resulting Hamiltonian equations of atomic or molecular motions are solved with the molecular dynamics method to understand the molecular behavior of the phase changing process. The excitation strength, that is, the laser energy of irradiation, has the most predominant effect on the phase change of vaporization and melting. The laser energy absorbed is converted to the kinetic energy of the evaporating particles and that of the lattice particles. This process of energy transfer is controlled by the irradiation period as well as the excitation life.

1. INTRODUCTION

MATERIAL processing and manufacturing by using laser irradiation have been of interest in various fields of engineering. The laser light can transfer high energy of a specified level to a small confined area within a time such that the atoms or molecules outside the area are hardly disturbed in their kinetic states. The phase change of vaporization and melting of solid material by laser irradiation is the fundamental of such material processing. Heating the material to evaporate and melt is a macroscopic process of heat and mass transfer, whereas absorbing light energy is of atomic or molecular matters. Between these macroscopic and molecular processes, there is a large gap of physical understanding. In order to predict the phase change of solid material by laser irradiation, the process should be understood from the standpoint of atomic or molecular motions. The reaction process of a laser beam with solid materials is the interaction between the electromagnetic field of light and the electric field of atoms or molecules of the solid material. For a complicated system of many electric charges, it is too difficult to predict quantitatively such an electric interaction between light and matter. Due to this difficulty, little work has been reported of the phase change of melting and vaporization of solid materials by laser irradiation [1, 2].

The light absorbed by matter can be considered in three categories depending on the strength of light energy; (1) the excitation of electronic state of atoms and molecules of the lattice particle, (2) the excitation of intramolecular vibrational state of the lattice molecules, and (3) the excitation of intermolecular (or interatomic) vibrational or rotational state of the lattice molecules. In order to result in the phase change of melting and vaporization, the atoms or molecules of the particle lattice should obtain enough energy for their translational motion to overcome the potential barrier which confines them in the vibrational motion of lattice structure. Depending on the light energy and the electric field of the lattice particle, there is some possibility that the lattice atoms or molecules get such energy directly through the light absorbing process of category (3). For this process of light absorption, it is necessary that the lattice particles have changes in the electric dipole moment with respect to the intermolecular vibrational motion and those in the intermolecular vibrational state corresponding to the incident light energy. The first or second process of light absorption makes the lattice particle change in the potential which leads to the translational motion through interacting with each other.

Fundamentally, it can be considered that the interaction between light and matter is the change of atomic or molecular potential which is the energy of electric Coulomb work. In the present study, the light absorption is assumed to excite the potential energy of the lattice particle in such a way. By solving the resulting Hamiltonian equations of particle motion with the molecular dynamics method, the phase change processes of melting and vaporization of solid materials by laser irradiation are studied to understand their molecular features and dynamic structures.

2. LIGHT ABSORPTION AND LATTICE-PARTICLE MOTIONS

Lattice particles of a solid material consist of atoms or molecules depending on the solid structure. Light irradiation makes these atoms or molecules change in the dynamic structure of their electric field to result in relative motions of the particles such as intramolecular vibration, intermolecular vibration and intermolecular rotation. For the phase changing process, the relative motion of the lattice particles is the most controlling factor so that only its translational

NOMENCLATURE

E	electric field of light	μ	dipole moment
H	Hamiltonian	τ_{ex}	time duration of excitation
M	mass of lattice particle	τ_{rd}	time duration of light irradiation
R	coordinates of lattice particle	τ_{sp}	pause time of irradiation
R_{ij}	distance between i-th and j-th particles, $R_i - R_j$	Φ	potential energy.
t	time		
V	velocity		
x, y, z	coordinates.	Superscripts	
		0	ground state
Greek symbols		*	excited state
ε	energy of potential depth	~	change due to excitation.

motion can be taken into account by considering the potential between the lattice particles.

The lattice particles of a solid material, in which the coordinates of the i-th particle are denoted by R_i, are irradiated by a laser light of electric field E. The potential energy of the lattice particle can then be expressed as

$$\Phi^*(R_i) = \Phi^0(\{R_i\}) + \tilde{\Phi}(\{R_i\}; E) + [\mu^0(\{R_i\}) + \tilde{\mu}(\{R_i\}; E)] \cdot E \quad (1)$$

where Φ^0 and μ^0 are the electronic energy and the electric dipole moment of the particle without the light irradiation or at the ground state, and $\tilde{\Phi}$ and $\tilde{\mu}$ are changes in the electronic energy and the electric dipole moment with the light irradiation or at the excited state, respectively. $\{R_i\}$ denotes the relative distances between the i-th particle and others;

$$\{R_i\} = (R_{i1}, R_{i2}, R_{i3}, \ldots), \quad R_{ij} \equiv R_i - R_j. \quad (2)$$

Although the ensemble of particles is not always considered as the total of pair-wise particles concerning the potential energy, the assumption of pair-wise potential may provide sufficiently qualitative features of the particle motions. The expression of pair-wise potential leads to

$$\Phi^*(R_i) = \sum_j \Phi^0(R_{ij}) + \sum_j \tilde{\Phi}(R_{ij}; E) + \sum_j \{\mu^0(R_{ij}) + \tilde{\mu}(R_{ij}; E)\} \cdot E \quad (3)$$

which can be expressed as the sum of the potential at the ground state and the change due to the excitation by light irradiation as shown in Fig. 1;

$$\Phi^*(R_i) = \Phi^0(R_i) + \tilde{\Phi}(R_i) \quad (4)$$

where

$$\Phi^0(R_i) = \sum_j \Phi^0(R_{ij}),$$

$$\tilde{\Phi}(R_i) = \sum_j \tilde{\Phi}(R_{ij}; E) + \sum_j \{\mu^0(R_{ij}) + \tilde{\mu}(R_{ij}; E)\} \cdot E.$$

It is not easy to obtain an appropriate potential for the lattice particles of a solid material, especially at the excited state with the light interaction. From the standpoint of understanding the physical features qualitatively, the 12–6 Lennard–Jones potential may be assumed. At the ground state, the potential can be then given by

$$\Phi^0(R_{ij}) = 4\varepsilon^0 \left\{ \left(\frac{\sigma^0}{R_{ij}}\right)^{12} - \left(\frac{\sigma^0}{R_{ij}}\right)^{6} \right\} \quad (5)$$

and at the excited state

$$\Phi^*(R_{ij}) \equiv \Phi^0(R_{ij}) + \tilde{\Phi}(R_{ij}) = 4\varepsilon^* \left\{ \left(\frac{\sigma^*}{R_{ij}}\right)^{12} - \left(\frac{\sigma^*}{R_{ij}}\right)^{6} \right\} \quad (6)$$

where

$$\varepsilon^* = \varepsilon^0 + \tilde{\varepsilon}, \quad \sigma^* = \sigma^0 + \tilde{\sigma}.$$

Between excited and unexcited particles, the potential

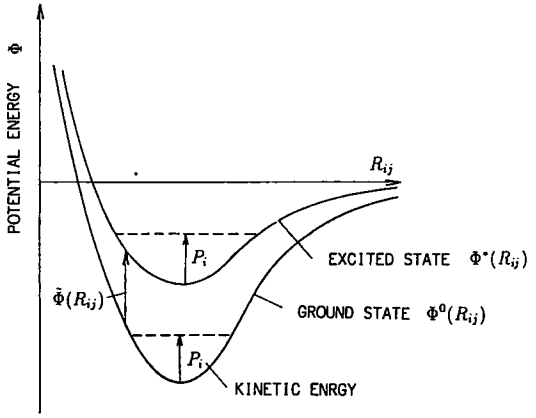

FIG. 1. Excitation of potential energy of lattice particles by light irradiation.

can be assumed with the assumption

$$\varepsilon = (\varepsilon^* \varepsilon^0)^{1/2}, \quad \sigma = (\sigma^* + \sigma^0)/2.$$

The classical Hamiltonian of the particle motion can be given by

$$H_i = \frac{1}{2M_i} P_i^2 + \Phi^*(R_i) \tag{7}$$

where M_i and P_i are the mass and the momentum of the i-th particle. The Hamiltonian describes the particle motions within the range of neglecting the quantum behavior. The equations of particle motion are then

$$M_i \dot{V}_i = -\nabla \Phi^*(R_i), \quad \dot{R}_i = V_i \tag{8}$$

where V_i is the velocity of the i-th particle and the dot denotes the time derivative.

3. NUMERICAL MODEL OF SOLID MELTING AND VAPORIZATION BY LASER IRRADIATION

The atomic or molecular particles of a solid material are considered to have a lattice configuration and are irradiated by a laser light partially in the z-direction as shown in Fig. 2. In order to consider the material of infinite length and to avoid width limit in the computational domain, the periodic boundaries are employed in the x- and y-directions. The upper surface on which the light is irradiated is free for the motion of particles vaporized, and the lower surface of the solid material is kept thermally adiabatic.

The time and space lengths are non-dimensionalized with the characteristic values of the potential at the ground state, ε^0 and σ^0 as

$$\sqrt{\left(\frac{24\varepsilon^0}{M\sigma^0}\right)} t \to t, \quad \frac{R}{\sigma^0} \to R, \quad \sqrt{\left(\frac{M}{24\varepsilon^0}\right)} V \to V,$$

$$\frac{\Phi}{24\varepsilon^0} \to \Phi, \quad \frac{\varepsilon^*}{\varepsilon^0} \to \varepsilon, \quad \frac{\sigma^*}{\sigma^0} \to \sigma. \tag{9}$$

These reference values depend on how to approximate the potential in the form of the Lennard–Jones type.

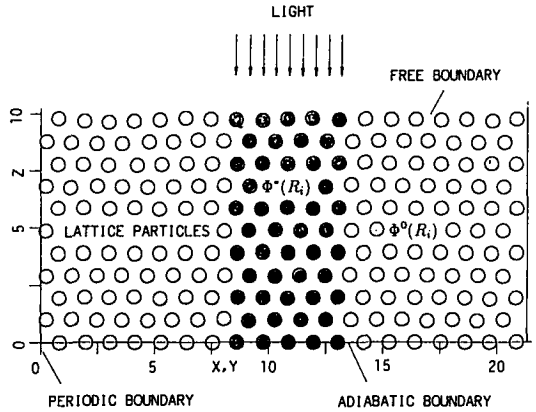

FIG. 2. Configuration of lattice particles under laser-light irradiation.

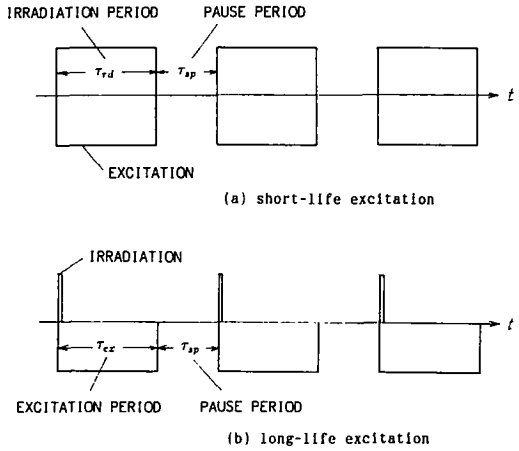

FIG. 3. Laser-light irradiation and excitation of lattice particle.

Approximately, ε^0/k and σ^0 (k: Boltzmann constant) correspond to the melting temperature and the molecular or atomic size of the lattice particle, respectively. Equations of the particle motion are then given by

$$\dot{V}_i = -\sum \varepsilon \sigma^6 \frac{R_i - R_j}{R_{ij}^8} \left\{ 2\left(\frac{\sigma}{R_{ij}}\right)^6 - 1 \right\}$$

$$\dot{R}_i = V_i. \tag{10}$$

These equations are solved numerically with the finite

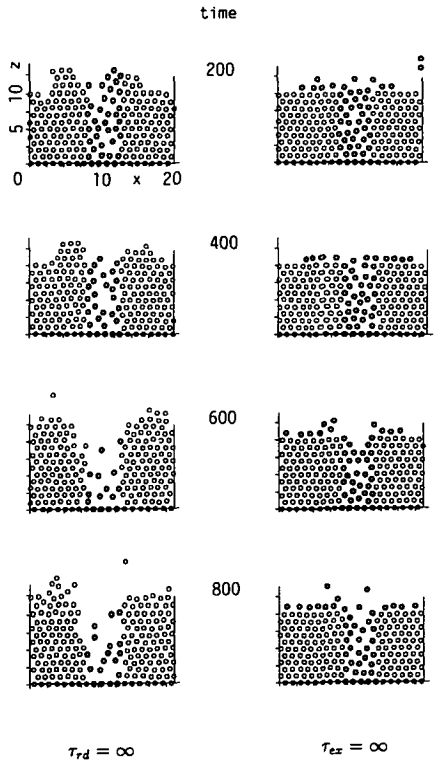

FIG. 4. Time-history of phase change of lattice particle by laser irradiation: $\varepsilon = 0.5$. (a) Short-life excitation: $\tau_{rd} = \infty$, (b) Long-life excitation: $\tau_{ex} = \infty$.

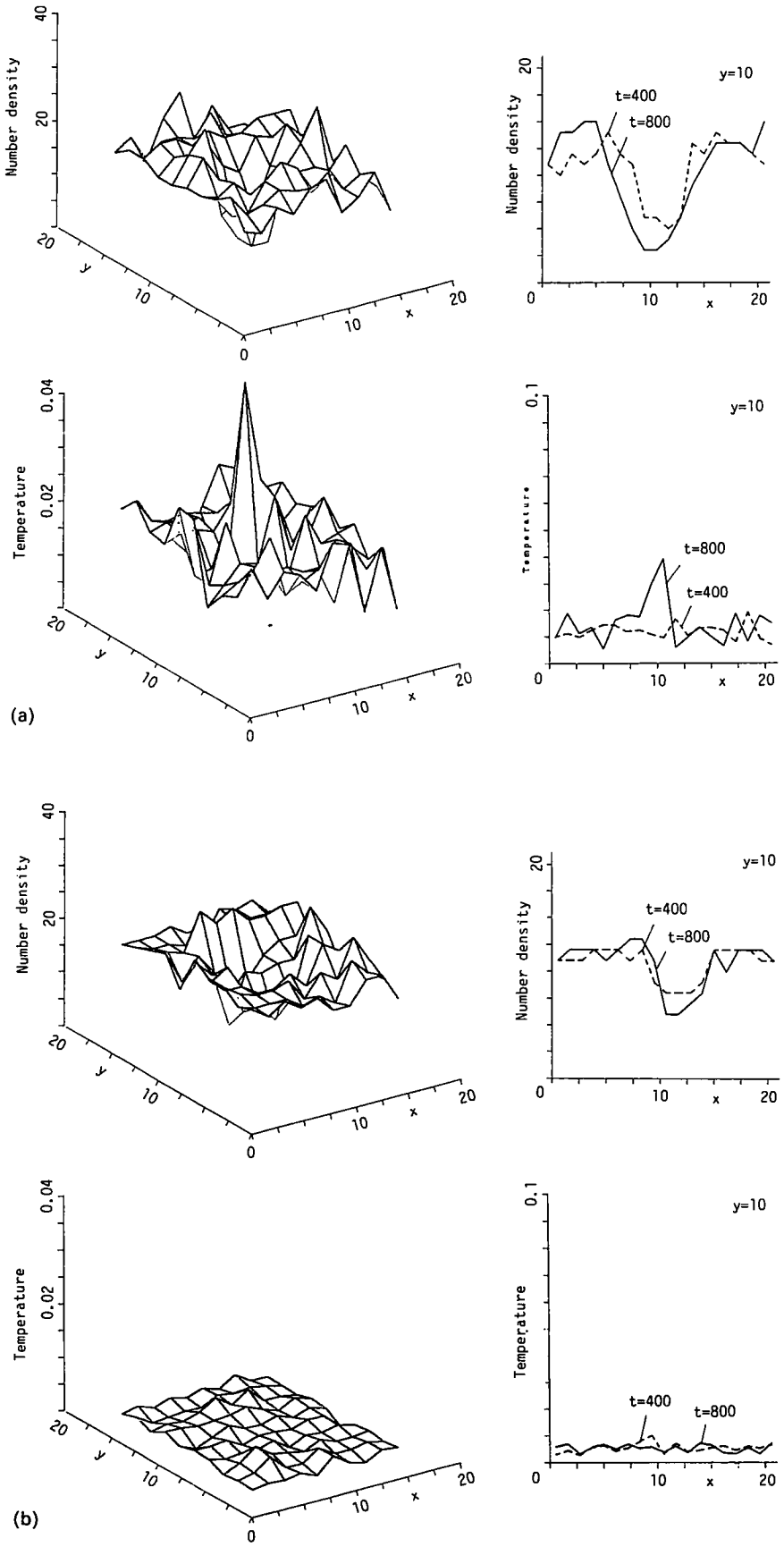

FIG. 5. Distributions of number density and temperature: $\varepsilon = 0.5$. (a) Short-life excitation: $\tau_{rd} = \infty$, (b) Long-life excitation: $\tau_{ex} = \infty$.

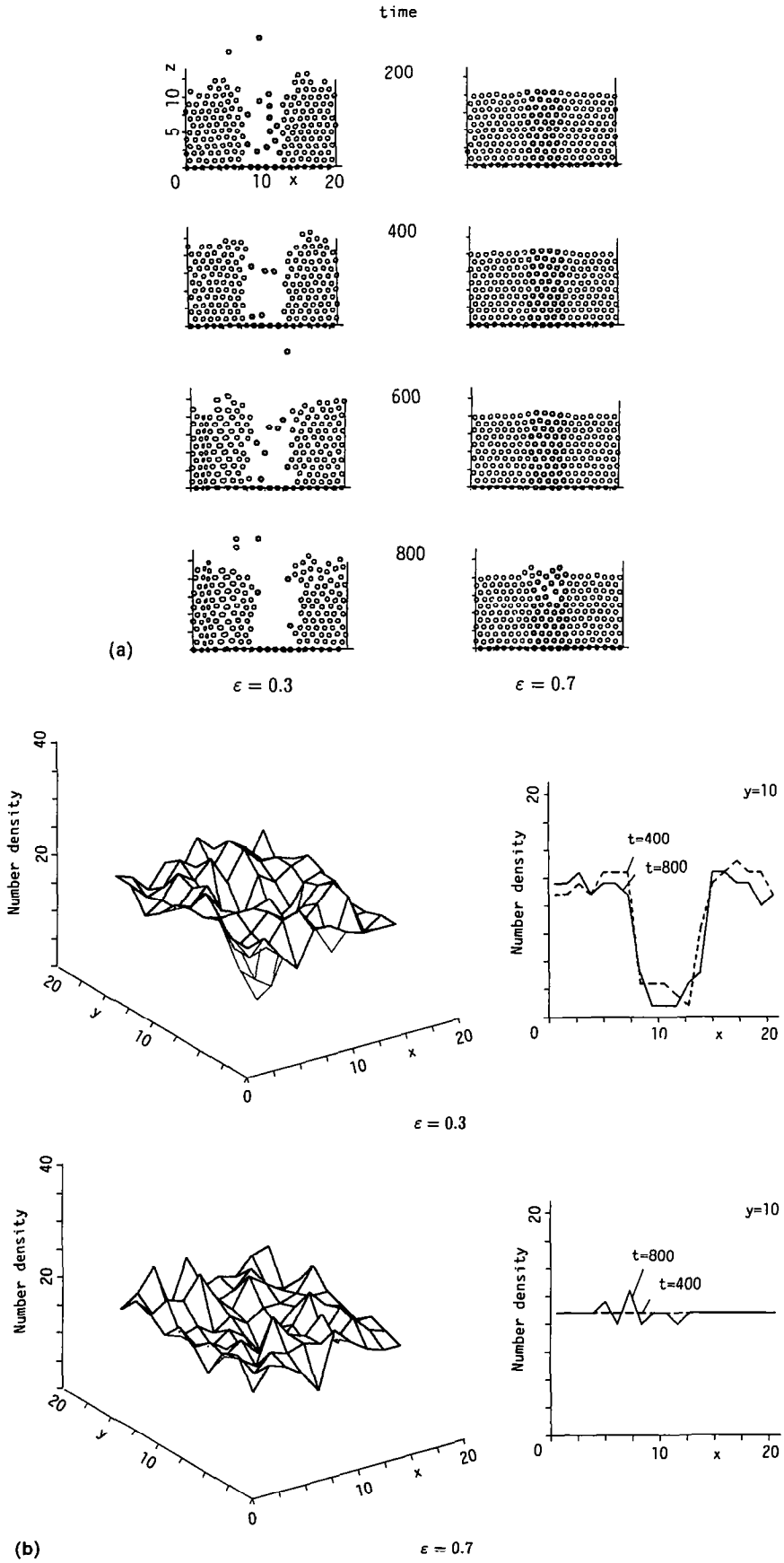

FIG. 6. Effects of excitation strength: $\tau_{rd} = \infty$. (a) Time-history of phase change, (b) density and temperature distributions.

difference method with respect to the time in the following way:

$$V_i(t+\Delta t/2) = V_i(t-\Delta t/2) + \sum_j \varepsilon\sigma^6 \frac{R_i(t)-R_j(t)}{R_{ij}(t)^8}\left\{2\left(\frac{\sigma}{R_{ij}(t)}\right)^6 - 1\right\}\Delta t$$

$$R_i(t+\Delta t) = R_i(t) + V_i(t+\Delta t/2)\Delta t \quad (11)$$

where Δt is the time step.

With the initial conditions chosen appropriately, the calculation can start to attain a thermal equilibrium state without light irradiation. After obtaining the equilibrium state, the laser is irradiated onto the lattice particles. The wave length of the light is assumed sufficiently long that the light can penetrate uniformly into the whole depth of the solid material.

The number of particles considered is $21 \times 21 \times 11$ and the time step is 0.01–0.005 with $\sigma = 1$ used for most cases of calculation.

4. RESULTS AND DISCUSSIONS

Two patterns of the potential excitation by light irradiation are considered;

(1) the potential energy is excited during only the period of the irradiation (short-life excitation), and

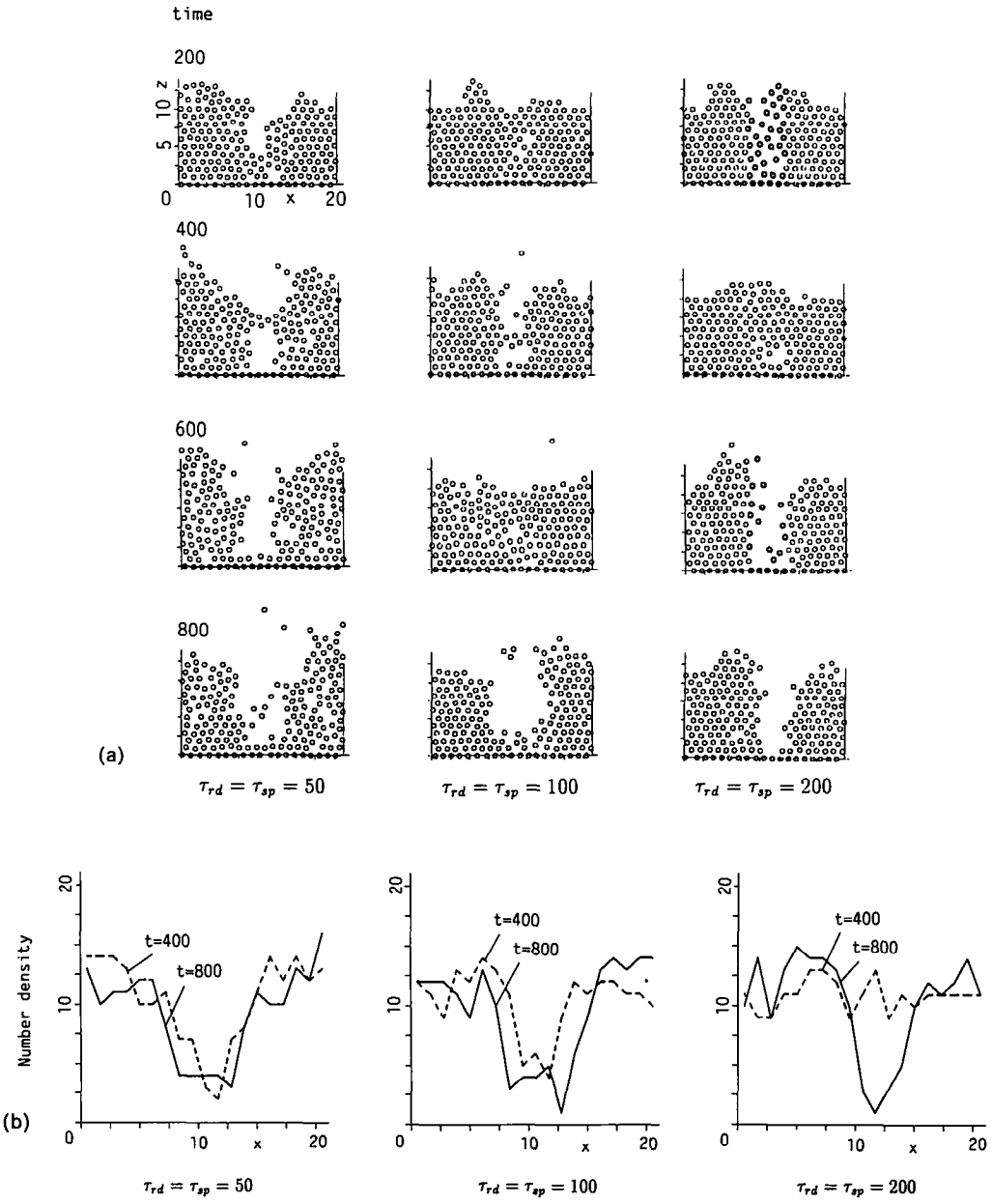

FIG. 7. Phase change with cyclic excitation: $\varepsilon = 0.5$. (a) Time-history of phase change, (b) number density distribution.

(2) the potential energy is excited for some duration after the irradiation (long-life excitation).

Figure 3 shows these patterns of excitation and irradiation. In the first case, the excitation is kept within the time of irradiation, τ_{rd}, and in the second case, it is limited within the excitation duration, τ_{ex}. For cyclic irradiation, an unexcited period τ_{sp} is followed as a pause of excitation.

Figure 4 is a typical time-history of the melting and vaporization process by laser irradiation. The laser beam is irradiated onto particles denoted by a solid circle. It is seen from the figure that the lattice particles irradiated relax and move upward, and finally depart from the irradiation space to make a hole behind. The hole made by the irradiation is not shaped sharply because of the translational motion induced on particles close to the hole wall.

In Figs. 4 and 5, two patterns of excitation are compared; (a) short-life excitation and (b) long-life excitation. Figure 5 shows the distribution of the number density and temperature in the xy plane. The number density and temperature are averaged in the z-direction, that is, in the depth of light irradiation. On the right side, the number density and temperature distribution at the center of the y-length are shown at two different times, $t = 400$ and 800. In the case of short-life excitation, the lattice particles are melted and evaporated more quickly than those which are excited for an infinite time. The difference between both excitations is whether the particle irradiated is de-excited outside of the laser-beam space or kept in the excited state. The particles of short-life excitation are de-excited outside of the laser spot. Since the de-excitation makes the potential decrease, the kinetic energy of the particle will be increased, and the increased kinetic energy is transferred to enhance the motion of surrounding particles. This leads to faster evaporation and results in a larger hole.

The strength of excitation has a considerable effect on the phase change process. In Fig. 6, the excitation level is changed from $\varepsilon = 0.3$ to $\varepsilon = 0.7$. In the case of Figs. 4 and 5, $\varepsilon = 0.5$ is used. Clearly, higher excitation makes faster melting and vaporization, producing a larger hole. In the case of $\varepsilon = 0.7$, only melting process can be observed to start partially inside the irradiation area.

In Fig. 7, the effects of periodic irradiation are studied. The excitation state is kept for the period τ_{rd} by light irradiation in the case of short-life excitation or for the time τ_{ex} in the case of long-life excitation, and then the pause state is followed for the time τ_{sp}. In the pause period of excitation, the de-excited particles can stick to the solid particles and to transfer their high kinetic energy to the condensate particles. The energy transfer increases the temperature of the particles in the solid state and induces their disordering motion of melting. This causes a large hole of vague shape. Thus, the more frequent the pauses in the irradiation, the more the kinetic energy is transferred to the solid-phase particles to enhance the melting and vaporization process. As the irradiation has more chances of de-excitation, the lattice particles tend to have motions that are more favorable for the phase change of melting and vaporization.

5. CONCLUSION

The molecular processes of the phase change of melting and vaporization of solid materials by laser beam irradiation were studied numerically by using the molecular dynamics method. By absorbing the laser light energy, the solid atoms or molecules are excited in the interatomic or intermolecular potential between them to change their interacting forces. The resulting Hamiltonian equations of atomic or molecular motions are solved with the molecular dynamics method to understand the molecular behavior of the phase changing process.

The excitation strength, that is, the laser energy, has the most predominant effect on the phase change of vaporization and melting. The laser energy absorbed is converted to the kinetic energy of the evaporating particles and that of the lattice particles. This process of energy transfer is controlled by the irradiation period and the excitation life. As the irradiation has more chances of de-excitation, the lattice particles tend to have motions that are more favorable for the phase change of melting and vaporization.

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