Limit of overheating and the threshold behavior in laser ablation

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Constant temperature and pressure molecular-dynamics simulations in conjunction with constant pressure and enthalpy simulations, designed to examine the threshold behavior in laser ablation, demonstrate that the rate of homogeneous nucleation (explosive boiling) increases sharply in a very narrow temperature range at approximately 90% of the critical temperature. Moreover, the homogeneous nucleation is sufficiently rapid to prevent the superheated liquid from entering the spinodal region at densities greater than the critical density.

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Numerous experiments [1,2] have demonstrated and analytic theories [3] have predicted that there is a threshold for pulsed laser ablation of a wide range of materials. Recent computer simulations of laser interactions with organic materials make obvious that an onset of massive material removal or ablation occurs at a well-defined threshold fluence [4]. The amount of ejected material increases sharply at the threshold and the composition of the ejected plume changes from mostly individual molecules below the threshold fluence to a mixture of molecules and liquid droplets above the threshold. The initial plume development visually shows a homogeneous decomposition of the material leading to a foamy transient structure of interconnected liquid clusters and individual molecules [5,6]. The phase transition has been ascribed to explosive boiling, i.e., homogeneous nucleation, as originally conceptualized by Martynyuk for discharging a condenser into a wire [7] and advocated by Miotello and Kelly [8] as being the prime phase transition in laser ablation in the thermal confinement regime. Homogeneous nucleation occurs when a system (liquid) is superheated to a temperature of approximately 90% of the critical temperature, T_c [9–11]. Both experiments and classical nucleation theory propose that there is a sharp transition with temperature from a metastable superheated liquid to a gas for homogeneous nucleation.

The relationship between the sharp transition region in homogeneous nucleation theory and the ablation threshold is implied by the interpretations of Miotello and Kelly [8] as well as Martynyuk [7]. The conditions for laser ablation include the presence of a free surface, confinement in the lateral directions, a Beer's law energy deposition profile, and temporal variations of temperature and pressure. These nonuniform and nonequilibrium conditions of laser ablation make the interpretation of the connection of the sharp ablation threshold and the temperature dependence of homogeneous nucleation a challenging problem. Since laser ablation of a vast array of materials has similar general characteristics [12], we would expect that, in the thermal ablation regime, the essence of the phenomenon is similar for different materials and is reproducible in a model system. Thus, in order to obtain a relatively simple scenario that is applicable to the onset of a phase transition in laser ablation, we probe the dynamics of a superheated liquid in a series of constant pressure and temperature (NPT) as well as constant pressure and enthalpy (NPH) molecular-dynamics computer simulations [13,14] performed for a well-characterized Lennard-Jones (LJ) argon system [15,16]. The liquid-gas phase diagram of a LJ argon system is given in Fig. 1. The binodal coexistence curve [15] and the spinodal curve from an empirical equation of state [16] are shown. The NPT simulations allow us to model a superheated liquid at a series of temperatures for a constant pressure as shown by the solid line in Fig. 1. The NPH simulations allow us to add in a controlled manner small amounts of energy (enthalpy) to a superheated liquid near the region of instability. We find that homogeneous boil-

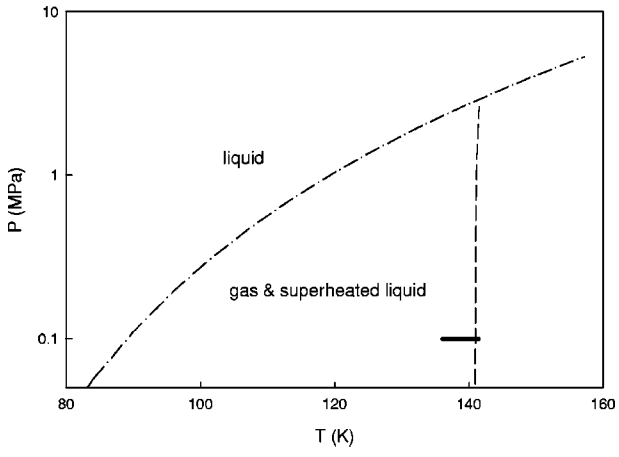

FIG. 1. Pressure vs temperature phase diagram for Lennard-Jones Ar. The binodal line (dot-dashed) is taken from Ref. [15] and the spinodal line (dashed) from the equation of state in Ref. [16]. The region of these simulations is shown by the short solid line segment.

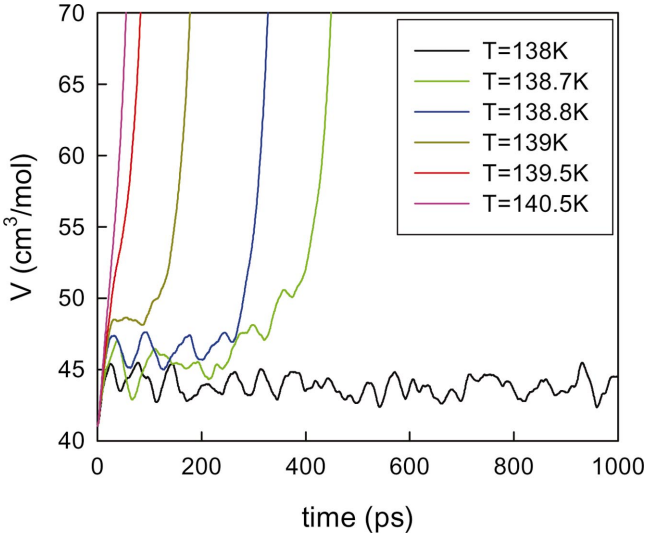

FIG. 2. (Color) Volume vs time at different temperatures in the NPT simulations. The system size is 6912 atoms.

ing of the overheated liquid occurs in a very narrow temperature interval at around $0.9T_c$, and the incubation period for the onset of the homogeneous boiling drops from more than a nanosecond to picoseconds as the temperature increases by $\sim 1\%$. This observation is consistent with the threshold behavior in laser ablation [4] and suggests that homogeneous nucleation is connected to the ablation threshold. Moreover, these simulations demonstrate that the narrow temperature range of the explosive boiling regime can be modeled with molecular-dynamics simulations.

The argon LJ system has values for the LJ well depth ε of 0.0103 eV and σ of 3.405 Å. In all simulations, the pressure is 0.1 MPa (~ 1 atm). Empirically we determined that stable gas-phase regions are formed in the overheated liquid within less than one ns slightly above a temperature of 138 K. By equilibrating a system of 6912 argon atoms in small temperature increments, we obtained a metastable liquid at 136 K. This base sample is used as a starting point for the simulations [17]. In addition to this system size, a number of NPT simulations were performed for systems sizes of 1372, 2048, and 32 000 atoms. The value of the piston mass used to maintain constant pressure [13] is 2×10^9 kg/m^4 for 6912 atoms and the value of the friction parameter used to maintain constant temperature [14] is 64 kJ ps^2. The cutoff distance for the interaction potential is $6\sigma = 20.43$ Å, as was used by Lotfi [15].

The volume versus time dependences are shown for the NPT simulations in Fig. 2 for several temperatures at and above 138 K. There is an incubation time in which the vol-

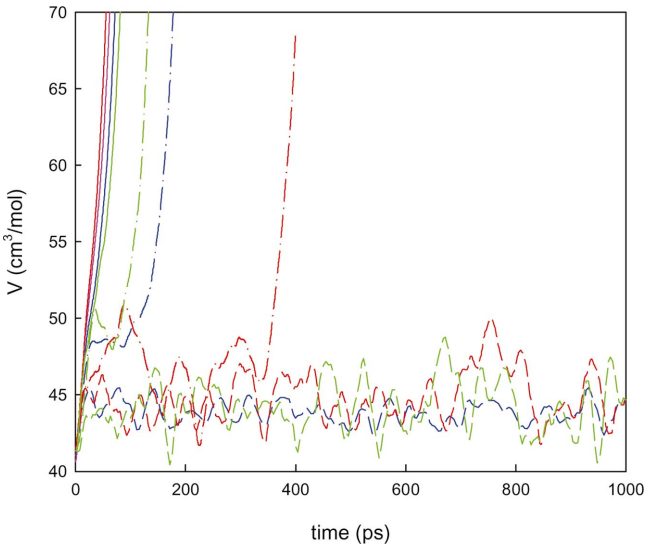

FIG. 3. (Color) Volume vs time at different temperatures in the NPT simulations for different system sizes. Green, red, and blue lines are for simulations performed for systems of 1372, 2048, and 6912 atoms, respectively. The solid lines are for 140 K, the dot-dash lines are for 139 K, and the dashed lines are for 138 K, except for the 2048-atom system, for which the temperature is 138.5 K. The pink line is for a simulation performed for a system of 32 000 atoms at 140 K. The piston mass in the constant pressure algorithm is 9×10^9, 6×10^9, and 4×10^8 kg/m^4 for the 1372-, 2048-, and 32 000-atom systems, respectively.

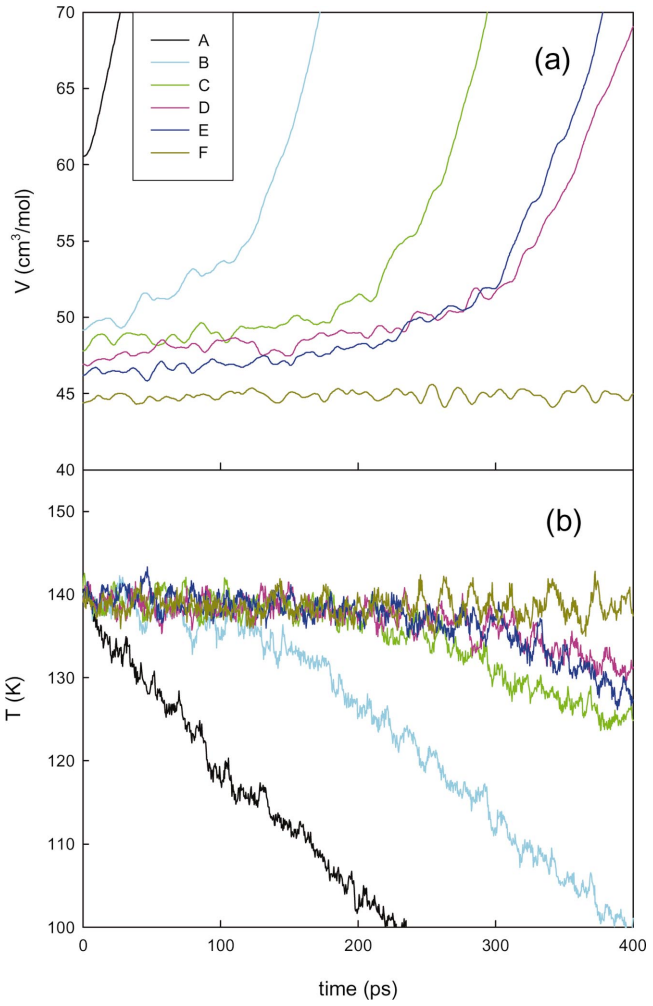

FIG. 4. (Color) Volume and temperature vs time at different enthalpies in the NPH simulations. The relative values of the enthalpy in kJ/mol for the runs *A*, *B*, *C*, *D*, *E*, and *F* are 0, -0.28, -0.35, -0.43, -0.46, and -0.59 kJ/mol, respectively. The system size is 6912 atoms.

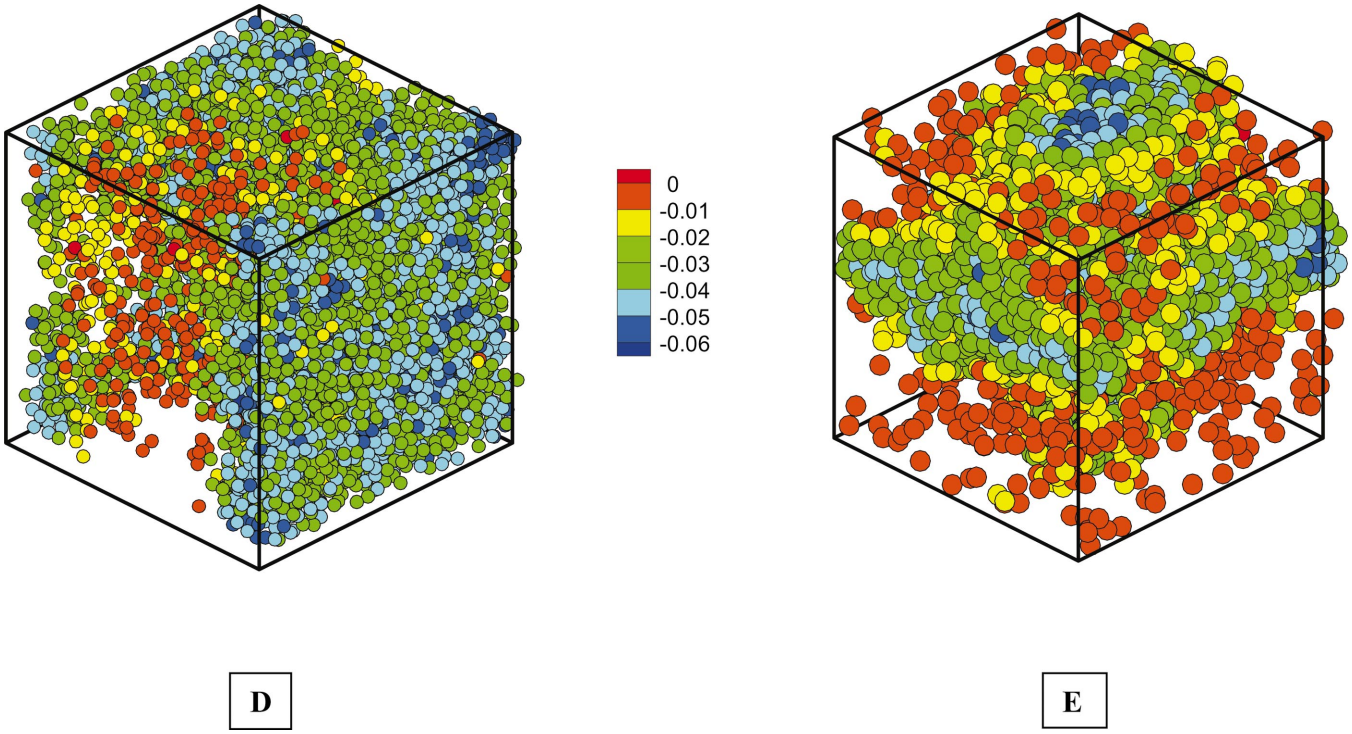

FIG. 5. (Color) Final configurations of atoms for simulations marked *D* and *E* of Fig. 4. The atoms are colored by potential energy in eV as shown in the legend. The diameter of the spheres is 3.82 Å, the distance of the minimum in the LJ pair potential. The box size is 95 Å on a side, which corresponds to a volume of 76 cm^3/mol.

ume is approximately constant before a sharp volume increase indicating the phase transition. The curves in Fig. 2 show clearly that the length of the incubation period has a very strong temperature dependence. The volume at 138 K fluctuates but no nucleation of a stable gas-phase region is observed in the 1 ns simulation time. For temperatures between 138 K and 139 K, the volume fluctuates for a short time and then starts to monotonically increase. For temperatures above ~139.5 K or ~90% of T_c, the volume increases immediately. Simulations at intermediate temperatures between 138 K and 139 K show similar behavior but have different incubation times. At 138 K, we performed several simulations for the various system sizes for a total run time of almost 20 ns and observed no phase transition, that is, the system remained a metastable liquid. Volume versus time dependences for different system sizes are shown in Fig. 3. The general characteristics of the incubation times do not depend on the system size. Comparable volume versus time trends are observed in NPH simulations as shown in Fig. 4(a) for different values of deposited enthalpy or, in the language of laser ablation, for different absorbed fluences and/or different depths under the surface of the irradiated target. Simultaneously with the large volume expansion, the temperature of the system declines as shown in Fig. 4(b). The temperature decrease associated with the phase transformation can be related to the fast cooling of the ablation plume observed in simulations of laser ablation [4]. The crossing of the curves for runs *D* and *E* at about 300 ps reflects a statistical fluctuation. Although fluctuations are not negligible, the qualitative features are verified to be consistent in different runs at the same temperature. To obtain reliable incubation times as a function of enthalpy, many initial configurations would have to be sampled.

From a microscopic picture, the phase transition initiates when atoms with negligible potential energies start to localize and grow into gaslike regions with a concomitant localization and growth of liquidlike regions with large negative potential energies. In agreement with recent Monte Carlo simulations of homogeneous nucleation in an overheated LJ liquid [18], the regions of low and high density at the onset of the phase separation are relatively small and irregular in shape and are not spherical bubbles as assumed in analytic theories. The final configurations from simulations marked as *D* and *E* in Fig. 4 are shown in Fig. 5. The atoms are colored by potential energy and the radius of spheres representing atoms is 3.82 Å. Low-density regions are shown by orange/red spheres and high density regions are blue. Some periodic boundary condition effects are present but the separation of the high- and low-density regions is obvious. Run *E* is characterized by a liquid drop surrounded by gas whereas a columnlike low-density region surrounded by liquid is formed in run *D*.

The temperature region of the explosive boiling can be compared to the Johnson *et al.* [16] empirical equation of state. The predicted spinodal temperature at 0.1 MPa is 141 K, a value slightly above the temperature range in which we observe the fast phase transition of the superheated liquid. We thus conclude that the phase transition proceeds through homogeneous nucleation and growth of gas-phase regions, albeit at a temperature very near the spinodal region. The simulations presented in this paper do not support the possibility of the system crossing deep into the spinodal region by

laser-initiated fast overheating of a metastable liquid at these densities, which are well above the critical density. We find that the incubation time for the homogeneous nucleation vanishes as the system approaches the spinode. In the NPH simulations, the onset of the homogeneous nucleation is manifested by a sharp volume increase with a concomitant temperature decrease.

The conditions under which laser ablation occurs are more complex than the controlled conditions in the simulations performed here. The initial temperature, pressure, and density in the system are functions of the depth in the sample due to the Beer's law penetration depth, any inhomogeneities in the material, the lateral position due to the Gaussian beam profile, the temporal profile of the beam, the laser fluence, and the pulse width. The relaxation of the deposited laser energy can lead to the material disintegration and associated fast cooling [4,19]. As a result, the material achieves a range of temperature and pressure conditions, leading to different phase-separation scenarios in different parts of the ablation plume. In particular, recently it has been suggested [20] that an adiabatic cooling of a part of an irradiated target, initially heated well above the vapor-liquid critical temperature, results in the phase separation via spinodal decomposition of the material that reaches the spinodal region in a close vicinity of the critical point, without ever entering the region of superheated liquid where the nucleation and growth of the gas phase is possible. While this possibility may be realized for a small fraction of the ejected plume, an adiabatic cooling of the largest fraction of the ablation plume is likely to proceed through the path that misses the critical point. At very high energy densities that can be realized in the top layer of the irradiated target, the material will go directly into the vapor phase and will not enter the liquid-vapor coexistence region. At lower energy densities, material will enter the superheated liquid region and the phase separation will proceed via homogeneous nucleation before the spinodal region is reached, as is demonstrated in the present paper.

The very strong temperature dependence of the incubation time for the homogeneous nucleation in the overheated liquid implies that as the laser fluence increases in ablation experiments, there will be a well-defined fluence at which the proper conditions are attained for the phase transition. Consequently, there will be a well-defined threshold fluence for ablation as observed in experiment [1,2] and MD simulations [4]. In addition to providing insight into the threshold behavior in laser ablation, these simulations suggest a computational pathway for exploring the microscopic nature of homogeneous nucleation near the spinodal region, a process that does not fit analytic theories [9,11].

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