Multi-Vapor Embryos Nucleation Process and Spinodal Analyses of Expandable Superheated Water System

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MULTI-VAPOR EMBRYOS NUCLEATION PROCESS AND SPINODAL ANALYSES OF EXPANDABLE SUPERHEATED WATER SYSTEM

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A homogeneous nucleation process in superheated water is studied with molecular dynamics simulation. System temperature and pressure are controlled with Langevin dynamics and the volume is variable. During the simulation, there can be seen many regions with no molecules, which are termed vapor embryos here. *The vapor embryo nucleation and phase transition process of the system is studied phenomenologically. Vapor embryos violate some predictions of classical bubble dynamics theory, which indicate that it is different from bubble. Systems under different temperature are simulated to investigate the effects of superheated rate. The spinodal limit of superheated water at atmospheric pressure is determined at about 535 K.*

KEY WORDS: molecular dynamics, phase transition, vapor embryos, spinodal analysis

INTRODUCTION

According to classical boiling nucleation theory, a superheated liquid system can stay in the metastable state instead of nucleating and boiling instantly when the boiling point is reached. The superheated rate of the system cannot increase unrestricted. There is a spinodal limit after which when exceeded the liquid system becomes unstable and will skip to a vapor state instantly. Boiling-related regions on a pressure–volume diagram can be found in Figure 1. In the metastable state, the system is under fluctuation microscopically. The energy of molecules in some regions can deviate from the system-averaged value and bubbles may form there first [1]. The size of these bubbles is on the order of 10^{-9} m, and their formation duration is in order of 10^{-12} s. Experimental studies of boiling phase transition at such short time and length scales are currenlty limited.

Molecular dynamics (MD) simulation starts from a simplified model of molecule interactions. By solving an equation of motion for every molecule in the system numerically, detailed information of the entire system can be attained. It is applicable for examination of various fundamental mechanisms of thermal phenomena from the microscopic point of view [2–4]. A number of studies have been conducted on both heterogeneous and homogeneous boiling processes with MD simulation.

NOMENCLATURE

F_i	resultant force acts on molecular i	ε_{00}	energy scale of the potential function
k_b	Boltzmann constant	σ_{00}	length scale of the potential function
m_i	mass of molecular i		
$P_{sat}(T_l)$	saturation pressure at the temperature of T_l	σ	surface tension
		σ_f	standard deviation of the random force in Langevin function
R_{fi}	random force in Langevin equation		
R_i	position coordinate of water molecular	φ	total potential energy of the system
R_{ij}	distance between two oxygen atoms	φ_{ij}	potential energy of two molecules i and j
r	distance between molecules		
r_e	critical radius for bubble in equilibrium	**Subscripts**	
		l	liquid
r_{ij}	distance between oxygen and hydrogen atom	ve	vapor
		sat	saturation
T	temperature		
t	simulation time		

Greek Symbols

γ	damping coefficient
ε_0	dielectric constant
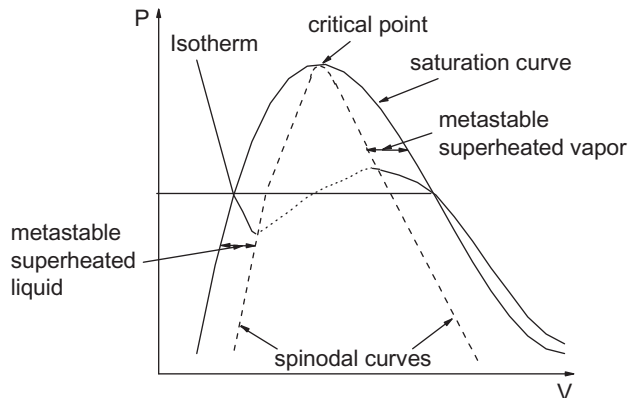
Figure 1. Isothermal curves and boiling-related regions on pressure–volume diagram of pure substance.

Bubble nucleation on a solid wall was studied with a system composed of 5,488 argon molecules [5]. MD simulation of the bubble nucleation process inside a nanoscale channel was carried out and comparison with classical nucleation theory was studied [6]. Novak used MD simulation to investigate the bubble nucleation mechanism, especially the effect of surface properties and topology [7]. Carey and Wemhoff compared thermodynamics analysis with MD simulation results to study the near-wall effects on phase stability and homogeneous nucleation during rapid surface heating [8]. A study by Dirk Zahn, which made use of a transition phase-sampling method and a system of 256 water molecules, stated that the boiling process starts from unstable

vacuum cavities in the length scale of 10^{-10} m [9]. Okumura and Ito heated up local molecules artificially and captured the phenomenon that heated molecules scatter the neighboring nonheated molecules and form a bubble [10]. Li et al. studied bubble growth phenomenologically and divided it into four processes: a clustering period, a nucleation period, an isothermal growth period, and a constant pressure growth period [11]. Yasuoka and Matsumoto investigated the dynamics of vapor phase nucleation at 350 K with a specific supersaturation ratio [12].

Nevertheless, application of MD simulation in the study of a boiling nucleation process is still inadequate. Classical MD simulations use a microcanonical ensemble and control the volume and energy of the system [13]. However, the boiling phase transition is in nonequilibrium and is a nonlinear expanding process, so a classical MD simulation method is insufficient to deal with the entire phase transition process. Most of the studies still use the classical Lennard-Jones 12-6 potential for the simulation of inert molecules. The interaction between water molecules is much more complicated than that of inert molecules, so the boiling phase transition of a water system needs further exploration.

The present study makes use of NAMD [14] molecular dynamics simulation codes to study a water system made up of 11,273 molecules. The temperature and pressure of the system are controlled with Langevin dynamics and the system volume is variable. Nucleation and phase transition processes from the liquid state to the vapor state were studied. Energy fluctuation and the effect of superheated rate were analyzed.

SIMULATION MODEL

For an intensive study of the boiling process, MD simulation of an isothermal isobaric ensemble instead of the classical microcanonical ensemble was carried out. In the present study, Langevin dynamics [15–17] instead of Newton's second law of motion is used to describe the interaction between molecules. The Langevin equation of a particle is

$$m_i \frac{d^2 \overrightarrow{r_i}}{dt^2} = \overrightarrow{F_i} - \gamma_i m_i \frac{d\overrightarrow{r_i}}{dt} + R_{fi} \tag{1}$$

where $\overrightarrow{F}_i$ is the resultant force acts on particle i, and m_i is the mass of particle i. Compared with the classical equation of Newton's second law, two additional terms, on the right side of the above equation, accompany the ordinary force that particle i experiences. The second term represents a frictional damping with the frictional coefficient $\gamma_i m_i = 5[\text{kg}/(\text{ps})]$. The third term stands for the random force according to a Gauss distribution with the mean value of 0 and the standard deviation $\sigma_f = \sqrt{2\gamma_i k_b T m_i}$, k_b is the Boltzmann constant, and T is the temperature of the system. These additional terms complicate the calculation process, but the application of Langevin dynamics can maintain particle kinetic energy to control temperature and pressure.

TIP3P potential for water was chosen to describe the interaction between two molecules:

$$\phi_{ij}(\mathrm{R}_i, \mathrm{R}_j) = 4\varepsilon_{\mathrm{OO}} \left[\left(\frac{\sigma_{\mathrm{OO}}}{\mathrm{R}_{ij}} \right)^{12} - \left(\frac{\sigma_{\mathrm{OO}}}{\mathrm{R}_{ij}} \right)^6 \right] + \sum_i \sum_j \frac{\mathrm{q}_i \mathrm{q}_j}{4\pi\varepsilon_0 \mathrm{r}_{ij}} \tag{2}$$

Table 1 Parameters for TIP3P potential of water

Items	r_{OH}	$<HOH$	σ_{00}	ε_{00}	q_H	Qo
Dimension	[nm]	[°]	[nm]	[kJ/mol]	[C]	[C]
Value	0.9572	104.52	0.3151	0.6363	+0.417e	−0.834e

$e = 1.60219 \times 10^{-19}$ C.

R_i, R_j stand for the positions of the two molecules, R_{ij} is the distance between two oxygen atoms, and r_{ij} is the distance between oxygen and hydrogen atoms. The first term on the right side of Eq. (2) stands for the Lennard-Jones potential between oxygen atoms, and the second term is the electrical force between hydrogen and oxygen atoms. Properties of the potential function are listed in Table 1.

The potential energy of the entire system is the summation of the potential between molecules:

$$\phi = \sum_i \sum_{j>i} \phi_{ij}(R_i, R_j) \tag{3}$$

Then, the resultant force exerted on a particle is

$$F_i = -\frac{d\phi}{dr_i} \tag{4}$$

A Nose-Hoover Langevin piston [18] is used to control the pressure of the simulation system. The Langevin piston period of 0.1 ps and the Langevin piston decay of 0.05 ps were used, and the target pressure was held at 0.1 MPa. The time step was 0.5 fs and 100,000 more steps were calculated after the system reached equilibrium.

RESULTS AND DISCUSSION

Phenomenological Study of the Nucleation Process

The phase transition and the expanding process of the system was simulated, and representative snapshots of the process under temperature control of 525 K are shown in Figure 2, which display the central slab of the cubic simulation system. During the expansion process, great numbers of nanoscale regions, with no or few molecules inside, occur and in the present study these regions are referred to as *vapor embryos*. These vapor embryos are unstable in nature and are deforming with time. With the evolution of the vapor embryos, the liquid system disaggregates gradually, the distance between molecules increases, and finally the system stays in the vapor state. The distance between molecules in the vapor state is about 10 times that of the liquid state and the concentration of molecules is about one thousandth that of liquid state. As can be seen in the subgraph (h) of Figure 2, in the vapor state, the space that used to be full of molecules was taken up by only several molecules.

In the simulation region there are many vapor embryos, which are evolving spontaneously. Because the interactions between water molecules are more complicated, the vapor embryos of the water system are much less stable than those of an inert
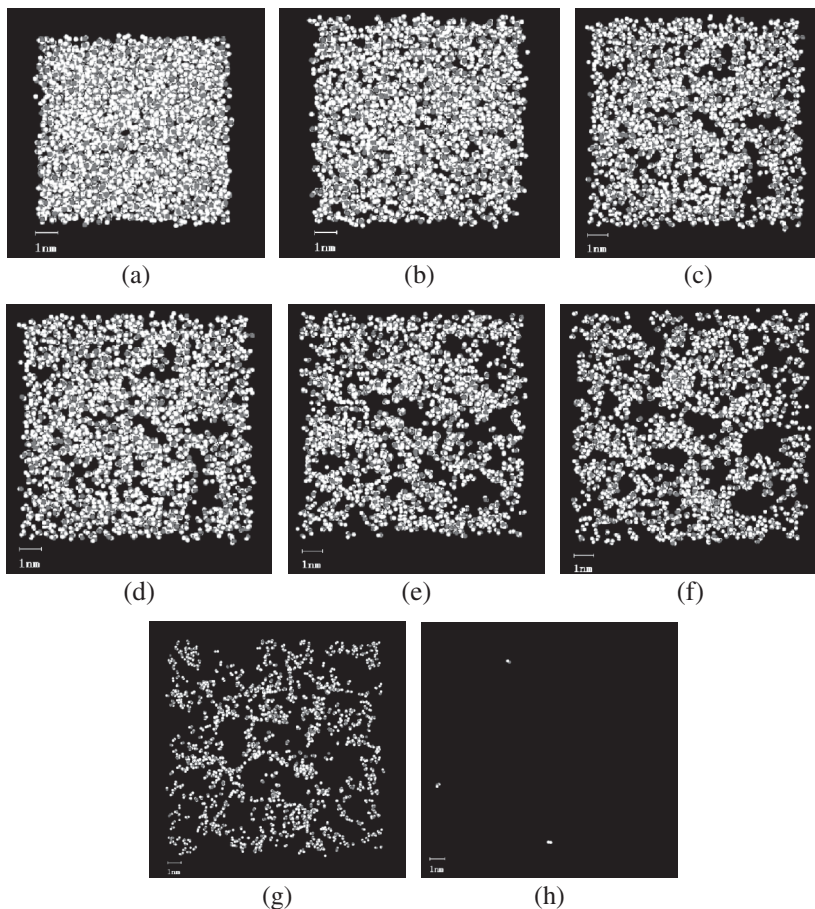
Figure 2. Snapshots of water systems under temperature control of 525 K. (a) $t = 0$ fs; (b) $t = 2,500$ fs; (c) $t = 5,000$ fs; (d) $t = 7,500$ fs; (e) $t = 12,500$ fs; (f) $t = 15,000$ fs; (g) $t = 17,500$ fs; (h) $t = 20,000$ fs.

molecule system [11]. As can be seen in the snapshots, only a few vapor embryos are approximately spherical, and others are in the process of deforming and assume anomalous shapes. The number density of molecules in the vapor embryos is much lower than in the surrounding areas. In the MD simulation of a classical microcanonical ensemble, the formation of the regions with lower number density will definitely lead to an increase in density of other areas, because the total volume remains constant. An isothermal isobaric ensemble with changeable system volume can simulate the boiling process in a better way.

According to the potential equation of water, when the distance between two molecules $r \leq \sigma_{00}$, the repulsion force between them increases dramatically; when $r \geq \sigma_{00}$ the attraction changes gradually. The water system is under the resulting effect of these two kinds of forces continuously. When a vapor embryo forms, the distances between molecules increase and result in a sharp drop of repulsions as well as a slight change of the attractions. At that time, the molecules in the low-density region will move toward the high-density region due to the attraction of the molecules in the high-density region, as shown in Figure 3. When the distance between some molecules reduces
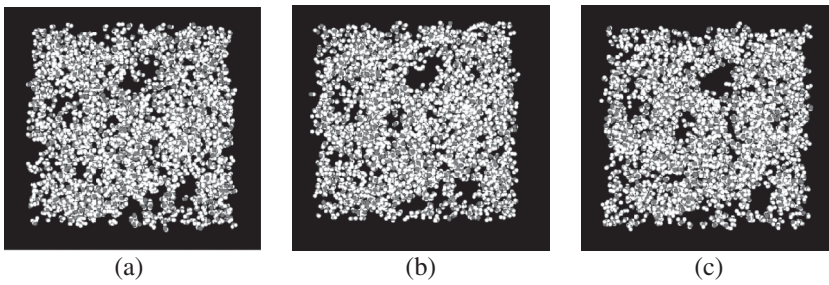
Figure 3. Formation process of a vapor embryo.

to less than σ_{00}, the molecules will be pushed away and the vapor embryo annihilates. As can be seen in Figure 4, this process will lead to a disturbance in the high-density region and a decrease in density. Under the collective effect of the attractions and the repulsions, vapor embryos form, deform, and annihilate, and the liquid system expands gradually toward the vapor state as shown in Figure 2. Molecules moving from the low-density region toward the high-density region form vapor embryos and cause the system to expand, whereas molecules moving from the high-density region toward the low-density region increase the distance between molecules, which enhances the possibility of the formation of larger vapor embryos.

The influence of the nearby vapor embryos on each other is critical for the boiling nucleation process. If several vapor embryos occur at a close distance, they tend to merge into larger vapor embryos, as can be seen in Figure 5.
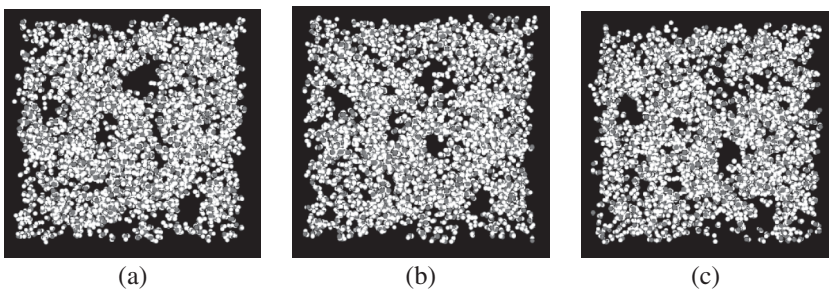
Figure 4. Annihilation process of a vapor embryo.
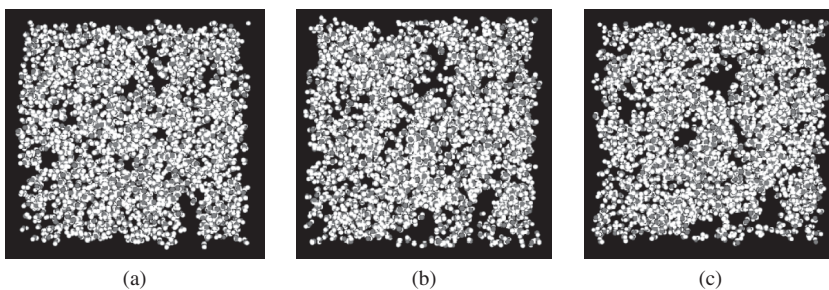
Figure 5. Merging process of vapor embryos into a larger one.

Comparison with Classical Theory

According to classical nucleation theory, a bubble in equilibrium obeys the Young-Laplace equation:

$$P_{ve} = P_l + \frac{2\sigma}{r_e} \tag{5}$$

where P_l is the pressure of the liquid phase, P_{ve} is the pressure of the vapor phase inside the bubble, σ represents surface tension, and r_e is the bubble radius. However, as shown in the snapshot of the simulation, there are few molecules inside the spherical vapor embryos and the pressure of that region is much lower than that required by the Young-Laplace equation. Nagayama et al. noticed this phenomenon in their study [6]. The size of the vapor embryos in the present study and the size of bubbles mentioned in MD simulation literature are much smaller than those of theoretical analysis. According to the classical bubble dynamics theory [1], the critical radius of the bubble in equilibrium is

$$r_e = \frac{2\sigma}{P_{sat}(T_l) \exp\{v_l[P_l - P_{sat}(T_l)]/RT_l\} - P_l} \tag{6}$$

According to the above equation, the critical radius of a bubble at atmospheric pressure and 523 K is 13.8 nm; the critical radius increases to 1130 nm at atmospheric pressure and 393 K. Currently, it is impractical to simulate the nucleation process of such a large bubble. Until now, to the authors' knowledge, there are no three-dimensional MD simulations that present a bubble system chime in with Young-Laplace equation, and is composed of a liquid phase, liquid–vapor interface, and vapor phase inside the bubble. Therefore, in the present study, in order to distinguish it from a bubble, the low-density region is referred to as a vapor embryo. There is a great possibility that the vapor embryo formation process is more fundamental and microcosmic than bubble formation, and the formation of vapor embryos engenders the formation of the vapor phase inside a bubble.

The Effect of Superheated Rate

Cases under different temperature controls were studied, as can be seen in Table 2.

For case A, the system stays in the liquid state, although a few small vapor embryos may occur inside it. When the set temperature increases to 515 and 525 K, the simulation system can stay in a metastable liquid state for a while. When the fluctuation of energy surpasses the spinodal limit, the system will start to nucleate dramatically and change from the metastable liquid state to the stable vapor state. For cases F and G, the system cannot reach the set temperature under the liquid state and will expand directly in an explosive way. This is because 550 K is past the spinodal temperature of water under 0.1 MPa and the liquid system becomes unstable in nature. The temperature evolution of representative cases can be seen in Figure 6.

Table 2 Simulation cases with corresponding temperatures

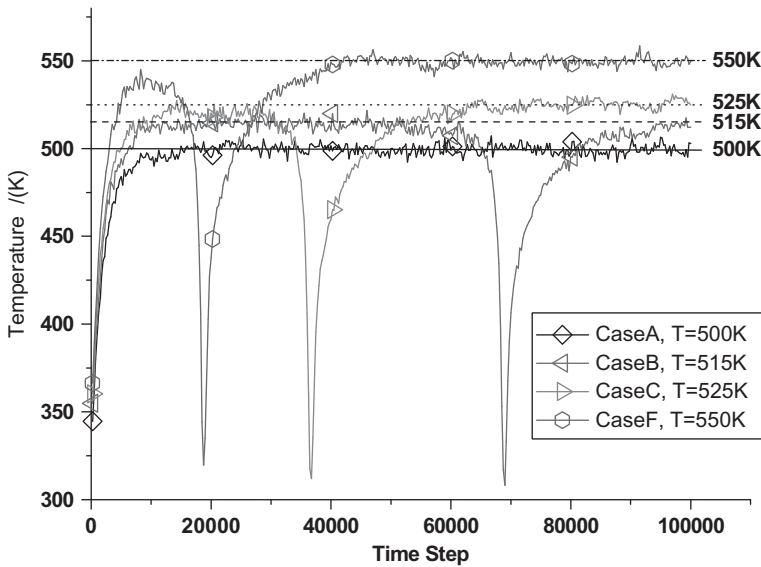| Cases	A	B	C	D	E	F	G
Temperature (K)	500	515	525	533	537	550	573

Figure 6. Temperature against time step of different simulation cases.

During the dramatic nucleation and phase transition process, the system changes from a metastable liquid state to a vapor state in a short time. During this process, the energy of the system changes dramatically. The system temperature will fall bellow the set temperature so that the system can absorb energy from the thermostat. After the dramatic phase transition the system temperature will return to the set value. So, an undershoot of temperature can be observed in every case, which indicates the dramatic phase transition process. With the increase of the set temperature, phase transition is more likely to occur and an undershoot of temperature will come into being earlier, as indicated in Figure 6.

At temperature control of 525 K, as can be seen in Figure 6, the temperature undershoot comes into being at the time step of approximately 35,000 ($t = 17,500$ fs). At the time step of about 40,000 ($t = 20,000$ fs), the system temperature has already returned to the set value. Compared with snapshot of the system in Figure 2, in the subgraph (g), $t = 17,500$ fs, the molecular number density starts to drop sharply; in the subgraph (h), $t = 20,000$ fs, the system is already in the vapor state and only several molecules can be seen in the snapshot. Generally, the temperature diagram is in chime with the snapshot and can also indicate the phase transition process.

The exact value of the spinodal temperature for homogeneous nucleation in liquid water is still controversial. According to theoretical analysis, the spinodal temperature for water at atmospheric pressure is as high as 573 K [1]. Experimental study has shown that the value is within the range of 523 and 556 K [19, 20]. As the system surpasses the spinodal curve, it will enter the unstable region where small perturbations will grow spontaneously. Thus, a liquid system under a temperature higher than the spinodal temperature is unstable in nature, and phase transition will take place before the system can reach the set temperature. From the temperature curve of case F in Figure 6, it is clear that the phase transition will occur before the liquid system can obtain the temperature of 550 K. At the temperature control of 525 K, the liquid system temperature can fluctuate around 525 K before phase transition occurs. So, under our simulation conditions, the spinodal
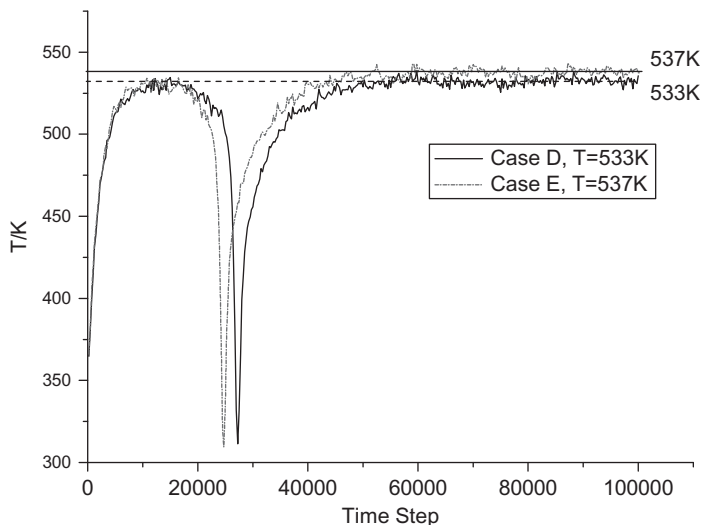
Figure 7. Temperature evolution of systems under 533 and 537 K.

temperature of water at atmospheric pressure is between 525 and 550 K. Similarly, cases under temperature control between 525 and 550 K were studied to determine the spinodal temperature more precisely. The temperature evolution of systems under temperature control of 533 and 537 K can be seen in Figure 7, which indicates that the system can reach the set temperature of 533 K in a liquid state but not below 537 K. This leads to the conclusion that the spinodal temperature of liquid water under our simulation conditions is between 533 and 537 K, or about 535 K.

Energy Evolution of the System

Evolution of the total energy against time step can be seen in Figure 8. The total energy is the sum of the various potential energies and the kinetic energy. The total energy is negative because the potential energies are negative. During the boiling process, the liquid system absorbs energy from the thermostat and the total energy increases to the vapor state level. During the dramatic phase transition process, there is energy fluctuation, which is in chime with the temperature undershoot.

Figure 9 shows the energy evolution of case C under the temperature control of 515 K. When the liquid–vapor phase transition takes place, the temperature and kinetic energy of the system fall and then resume quickly. The temperature difference between the system and the thermostat acts as the driving force for energy absorbance. The energy absorbed during this process is mainly used to increase the potential energies of the system and increase the distance between molecules.

CONCLUSION

In the present work, a homogeneous nucleation process in the superheated water system has been studied with molecular dynamics simulation of an isothermal isobaric ensemble. Temperature and pressure of the system are controlled with Langevin
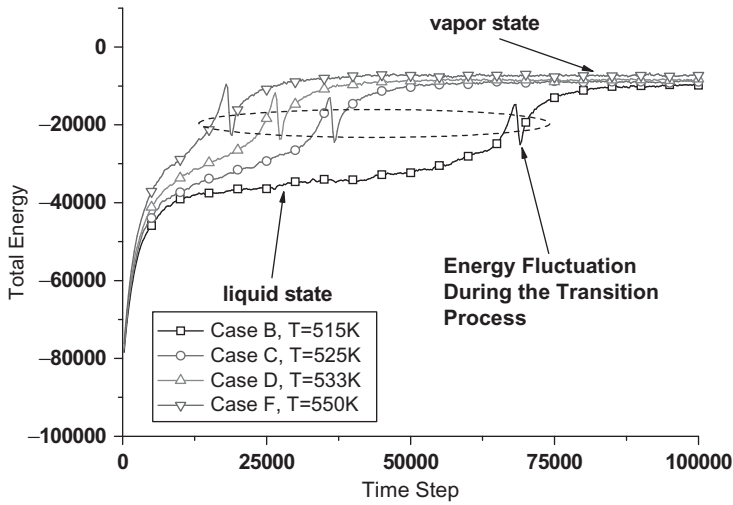
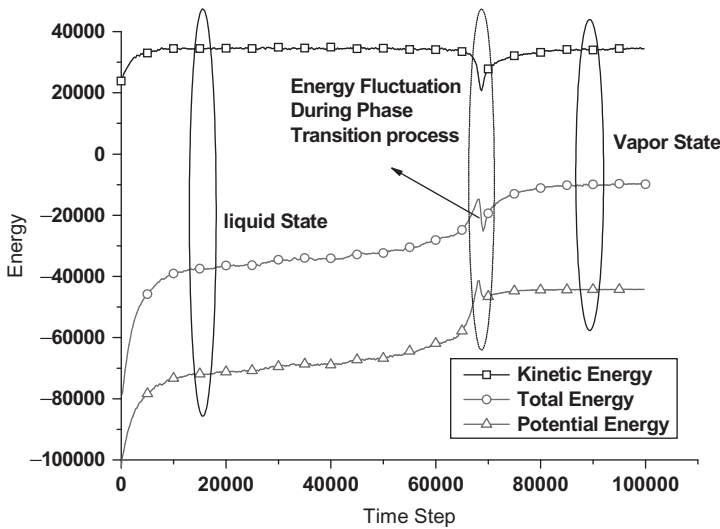**Figure 8.** Evolution of total energy against time step.

Figure 9. Evolution of energy at temperature control of 515 K.

dynamics and the volume is expandable. According to the simulation results, great numbers of nearly spherical low-density regions can be seen, which are referred to as vapor embryos in this article. The size of these vapor embryos is much smaller than the size of equilibrium bubbles predicted by classical nucleation theory. Vapor embryos also violate the Young-Laplace equation. These points indicate the differences between vapor embryos and bubbles.

Under the combined effect of the repulsion and the attraction forces between molecules, the vapor embryos form, evolve, and annihilate continuously. Formation and evolvement of vapor embryos causes an increase in both system volume and distance between molecules. Finally, the system no longer remains in the metastable liquid state and stays in the stable vapor state.

Systems under different temperature control have been studied in this work. With the increase of temperature, local fluctuation will be more likely to surpass the spinodal limit and phase transition will take place instantly. During the phase transition process, the liquid system absorbs energy dramatically, which is mainly used to increase the potential energy of the system.

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