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Continuous liquid–vapor phase transition in microspace[1]

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Abstract — Molecular dynamics and Monte Carlo methods are adopted to predict thermodynamic parameters of small argon systems. Simulation results of isotherms are similar to the van der Waals loop in the P–V diagram, which implies the continuity between the liquid and gas states. Both simulation and experiment of argon system indicate that the density variation inside the liquid–vapor interface is gradual and the interface may become considerably thick as the saturation temperature is close to the critical point. The temperature in the interface region is not uniform and higher than the saturation temperature, which is another example of the continuous phase transition between liquid and vapor. © 2000 Éditions scientifiques et médicales Elsevier SAS

phase transition / microspace / molecular simulation

1. INTRODUCTION

The liquid–vapor phase change has been an active area of current research because it is of both fundamental interest in thermal science and practical significance in various heat transfer related engineering. Boiling or condensation is a very efficient mode of heat transfer and as such is employed in component cooling and in energy conversion systems. In view of the fact that phase change heat transfer is an extremely complex process, a number of problems remain unsolved. For instance, various models [1–4] of microlayer under a vapor bubble have been developed to describe the dramatic rise of heat flux with the formation and growth of vapor bubble. However, their results about the thickness of microlayer may be quite different (10–1000 μm). With the rapid development of microelectronics and microelectromechanical systems (MEMS) the phase change heat transfer is adopted not only for the purpose of cooling electronic and mechanical components [5], but also for pumping fluid in microactuators [6, 7]. It is worth noting that the phase change in the microscale space exhibits some unusual features. For example, the critical temperature and critical pressure of fluids in microtubes became much lower than the ones in normal-scale space [8], and boiling-like high heat flux was obtained, while no bubbles were observed, in preliminary experiment of water flow in microchannels [9].

There are some phase transition phenomena in microscale cases as mentioned above, including various interphase properties, which are not, or hardly available from experiment. On the contrary, computer simulations based on molecular dynamics or/and Monte Carlo method can be used to predict such properties and to improve our understanding of phase transition in extreme cases. This paper is to investigate the characteristics of liquid–vapor phase transition in microspace based on MC/MD simulation of argon fluid with some experiment of freon fluid (R13).

2. LIQUID–VAPOR TRANSITION AND PHASE DIAGRAM

2.1. Basic concepts

2.1.1. Saturation line and critical point

A P–V diagram is schematically given in *figure 1*. Below a certain pressure, the liquid phase may exist in equilibrium with the vapor phase in the liquid–vapor

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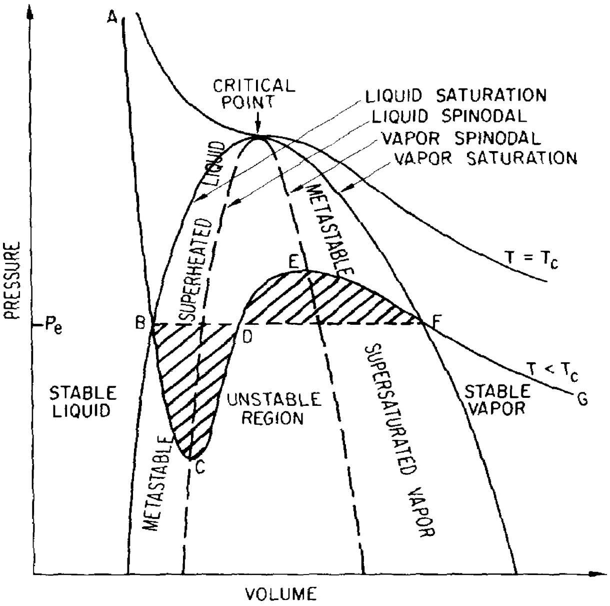


Figure 1. Schematic of a thermodynamic pressure–volume diagram.

coexisting region, which is confined by vapor saturation and liquid saturation lines. The junction of these two saturation lines is the critical point beyond which there is no latent heat of vaporization (condensation) and no other characteristic changes, such as phase separation, distinct phase interface and so on.

2.1.2. Van der Waals loop

Van der Waals developed his famous equation of state in 1873 in an attempt to show the intrinsic continuity between the liquid and gas states. It is utterly simple and plausible. A line of constant temperature ($T < T_c$) on the van der Waals surface is also illustrated in *figure 1*, where the specific volume becomes triple-valued in pressure but the conventional liquid–vapor transition is not in evidence. The two regions of negative slope, B to C (superheated liquid) and E to F (supersaturated vapor), are regions of metastable equilibrium. The region of positive slope, C to E, has been proved to be unstable—no states can persist in it.

2.1.3. First- and second-order phase transition

The phase transition is referred to as the first-order phase transition at which the thermodynamic potentials (free energy or internal energy) are continuous and their first-order derivatives are discontinuous (volume or entropy). The liquid–vapor phase transition under subcritical conditions belongs to the first-order phase transition, which is characterized by the distinct interface between liquid and vapor phases in space and the liquid–vapor coexisting region in the P–V diagram. The phase transition at the critical point is referred to as the second-order phase transition at which both thermodynamic potentials and their first-order derivatives are continuous but their second-order derivatives are discontinuous. It is characterized by the sharp changes in specific heat.

2.2. Computer simulation methods

In the molecular dynamics simulations one solves directly the equation of motion of particles in the system:

$$m\frac{\mathrm{d}^2 r_i}{\mathrm{d}t^2} = -\nabla_i U \tag{1}$$

Positions and momenta are then recorded at successive instances of time, and thermodynamic and transport properties could be obtained. In Monte Carlo simulations one performs a biased random walk which generates configurations of the molecules with probability proportional to $\exp(-U/kT)$. The thermodynamic properties are then obtained as configurational averages. Hundreds to thousands of argon molecules in a cubic box with periodic boundary conditions are calculated in present simulations. Intermolecular potential is given by the Lennard-Jones (12–6) potential

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2}$$

where $\sigma = 3.405$ Å and $\varepsilon = 119.8$ K. The potentials are truncated at a distance $r_c = 2.5\sigma$.

The pressure is calculated based on the virial theorem:

$$\frac{p}{\rho kT} = 1 - \frac{1}{6NkT}\left\langle \sum_i \sum_{j>i} r_{ij}\frac{\partial v_{ij}}{\partial r_{ij}} \right\rangle \tag{3}$$

where the second term on the right-hand side of this equation is the time average of the virial.

In the molecular dynamics simulations, it is very important to choose a highly effective algorithm to calculate intermolecular forces because of the large computation demands. For reducing the calculation amount and storage on the computer, a cell-table method is used to describe the molecule positions and their interactions, and a fourth-order difference method is used to solve the Newton's motion equations in present work. The chosen time

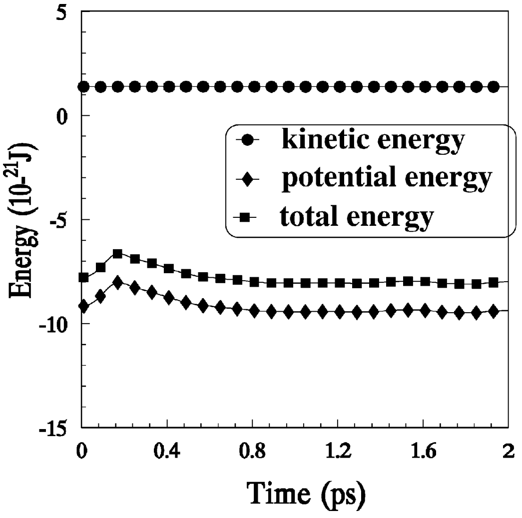


Figure 2. Process from the initial to equilibrium state.

step is 10^{-14} s, and the thermodynamic properties are obtained as time averages over 2 000 time steps. An example of the equilibrium process is given in *figure 2*. In the Monte Carlo simulations, all thermodynamic properties are obtained as configurational averages of 10^5 steps after more than 10^5 equilibration steps.

2.3. MD/MC simulational results on the saturation line

The simulational results on saturation lines for 3D argon system of 1 000 particles by MD and MC methods, together with the corresponding experimental data for comparison, are given in *figure 3*, where the periodic boundary condition is adopted in computations. A good agreement can be seen except for the area near the critical point in *figure 3*.

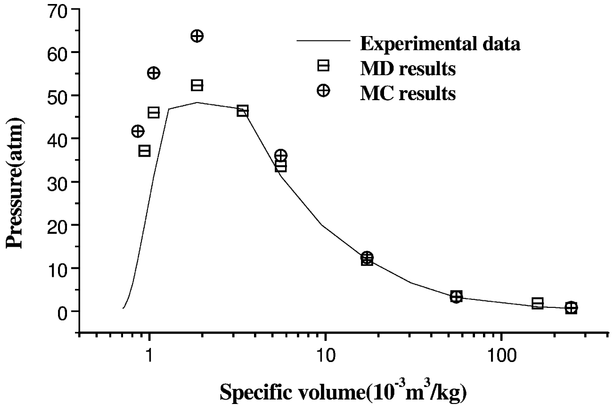
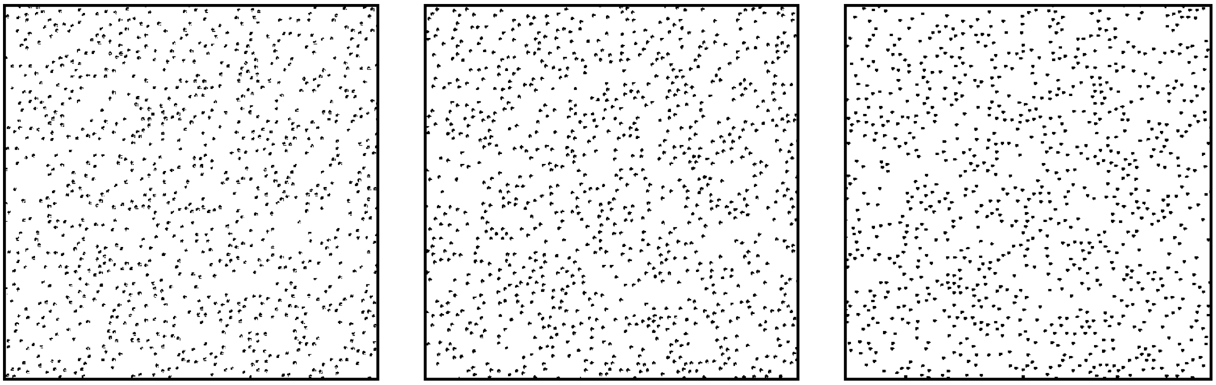


Figure 3. Saturation line of argon.

2.4. MD/MC simulational results on liquid–vapor coexisting region

MD simulation of small argon system indicates that no phase change evidence have been observed for thermodynamic parameters in the liquid–vapor coexisting region (not only in the metastable regions, but also in the unstable region). That is, no stable/growing bubbles or droplets can be seen during computations. *Figure 4* illustrates the distribution of molecules in the cell at different



$\tau = \tau_1$ $\tau = \tau_1 + \Delta\tau$ $\tau = \tau_1 + 2\Delta\tau$

Figure 4. Snapshots of the MD simulation ($\Delta\tau = 10$ ps).

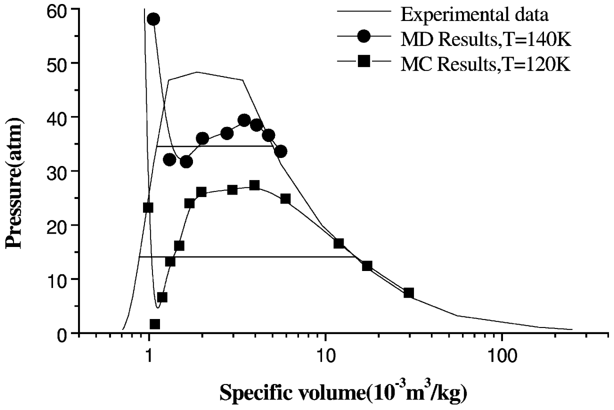


Figure 5. Van der Waals loop of argon at 140 K and 120 K.

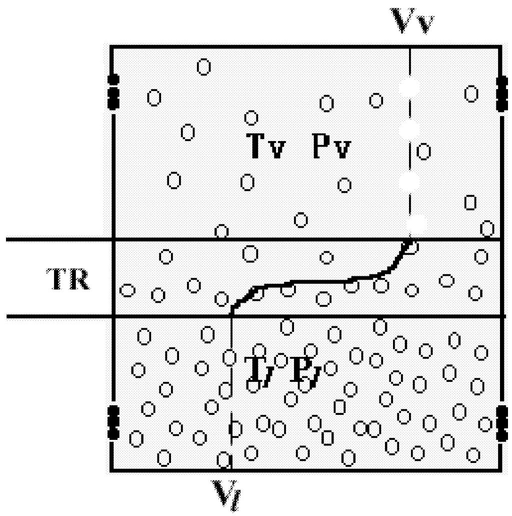


Figure 6. Schematic of transition region.

times, where a lot of clusters of various sizes can be seen. They are not stable or growable, but go rupture or coagulation with time.

The constant temperature MD/MC simulations give isotherms in the *P–V* diagram, which are similar to the van der Waals loop resulting from the van der Waals equation, as plotted in *figure 5*. In order to examine the effect of boundary conditions, the rigid wall boundary conditions are used to predict the isotherms, which are still like van der Waals loop except for that the location of the loop is lower than that for the periodic boundary conditions.

It has been suggested by Kido et al. [10] that the apparent "loop" is due to the finite-size effect in the simulation, which can be removed when a large-size system is employed in the computation simulation. They also demonstrated that the "loop" phenomena can be largely suppressed by reducing the attractive part of intermolecular potential, while retaining the repulsive part of the potential at the same system temperature [11]. On the contrary, our point of view is that such "loop" behavior from MD/MC simulation may exist in the reality if the system scale is down to the same order of the critical (equilibrium) radius of nucleus (bubble or droplet). This is because the system size reduction prevents the nucleus from kinetic stability and growing, and from the consequent phase separation. It turns out that the phase transition between liquid and vapor becomes gradual. This means, the continuous phase transition may appear too in the subcritical cases under the microspace condition. In other words, the second-order phase change may occur in the subcritical cases, where the second-order derivatives are discontinuous. For example, the specific heat passes through infinity at point C and E in *figure 1* and is negative in between. If it were possible to add heat in this range, the result would actually be to lower the fluid temperature, because the resulting expansion returns more potential energy of interaction than it would absorb kinetic energy.

3. LIQUID–VAPOR INTERFACE UNDER EQUILIBRIUM CONDITIONS

The liquid–vapor interface is usually regarded as a mathematical surface in the macroscopic analyses as it is very thin. As a matter of fact, the interface is of finite thickness, which should be a transition region between liquid and vapor phases. Study on the characteristics of interface is important for understanding the phase change process and surface tension behavior.

3.1. Planar interface

An argon liquid–vapor two-phase system in the cell is shown in *figure 6*, where the density variation in the interface region is assumed to be gradual from liquid to vapor. This has been verified by MD simulation in the following.

3.1.1. Density profile and interface thickness

Figure 7 gives MDS results on the density profile, which confirm the gradual variation of density in the interface. Computational results on the thickness of interface at different saturation temperatures for 2D system of

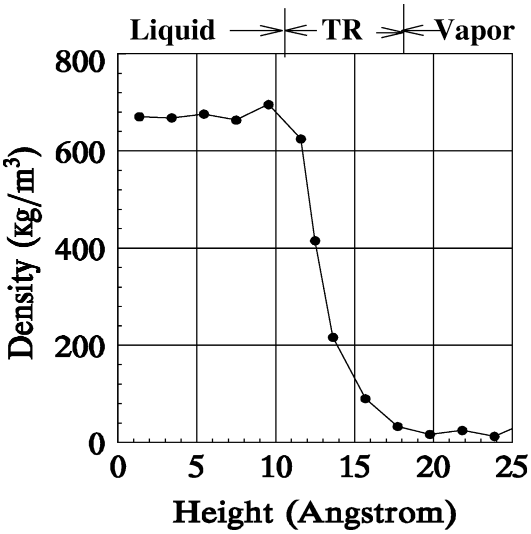


Figure 7. Density variation in transition region at 55 K.

5 000 argon particles are listed in *table I*. It can be found that the interface is very thin and its thickness is weakly temperature dependent as the saturation temperature is far below the critical temperature. However, the interface thickness increases remarkably with the temperature rise, as it is close to the critical temperature. *Figure 8* shows the distribution of molecules at different temperatures. It can be seen in *figure 8* that the planar surface is not a real flat plane from the viewpoint of molecular scale, rather, it behaves as a wave-like surface.

TABLE I
Interface thickness.

Temperature, K	40	45	50	55	60
Interface thickness, nm	4.1	4.4	5.5	8.5	11.9

3.1.2. Temperature profile

The temperature in the interface between saturated vapor and liquid phases was conventionally assumed to be constant and equal to the saturation temperature in the existing literature. Now let us view this problem at different angle. In the case of planar interface there is no effect of the surface tension on the fluid pressure, and consequently, the pressure in the interface region should be the same as the saturation pressure because of no fluid motion. In this connection, the temperature in the transition region is impossible to be constant and equal to the saturation temperature when the fluid in the interface is uniform in pressure but non-uniform in density. MD simulation indicates that the temperature profile inside the interface region exhibits a nonmonotonical variation, as shown in *figure 9*. Interesting is that this temperature profile in the interface region is similar to the van der Waals loop (T–V plane) at constant pressure (see *figure 10*). This implies that liquid–vapor phase transition

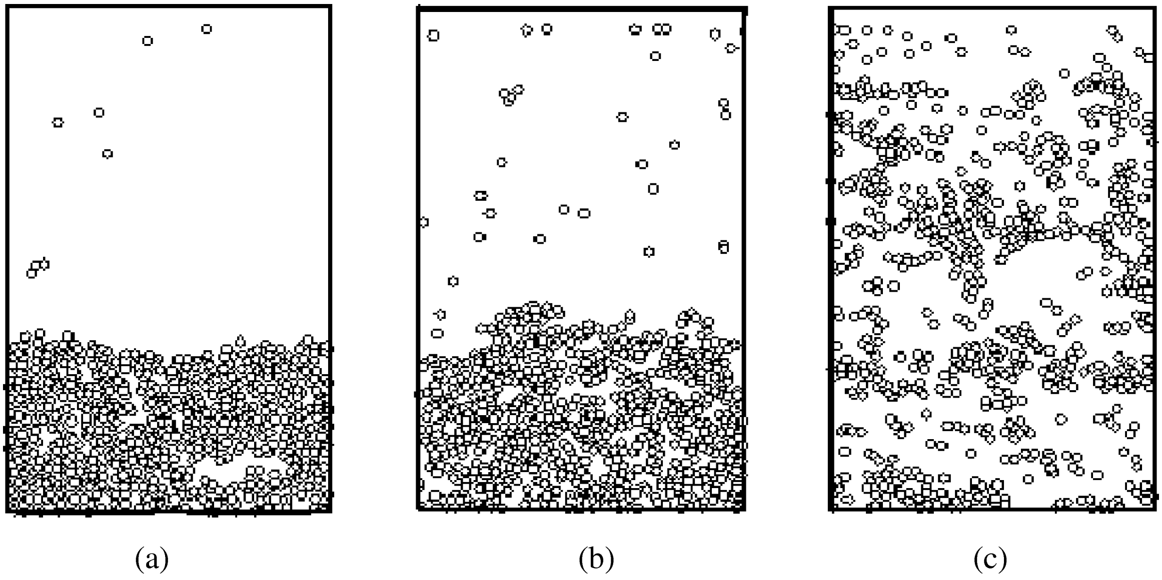

(a) (b) (c)

Figure 8. Diagram of molecule distribution. (a) $T = 45$ K, (b) $T = 55$ K, (c) $T = 65$ K.

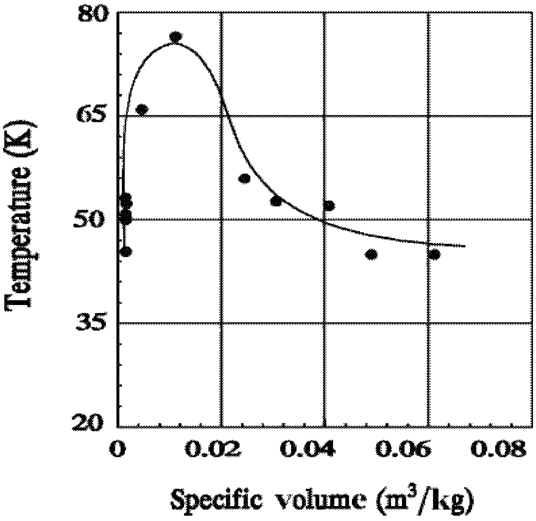


Figure 9. T–V line in transition region.

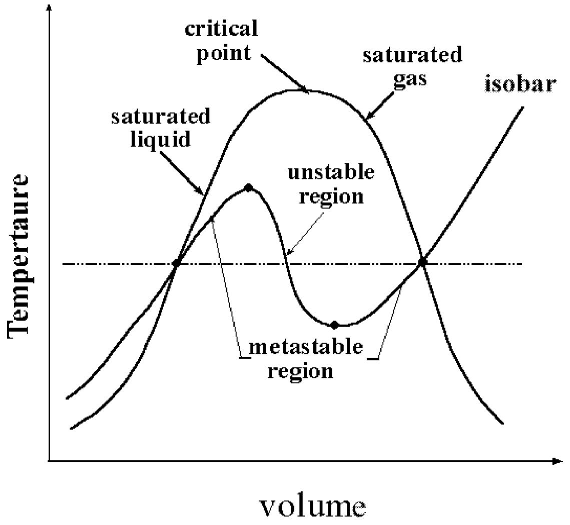


Figure 10. Schematic of a T–V diagram.

proceeds continuously across the interface region without boiling or condensation. The explanation for that is that the length scale of interface thickness is too small for the stability or/and growth of nucleus.

3.2. Curved interface

Maruyama [12] simulated liquid droplets of water and argon surrounded by their vapor by the molecular dynamics method to explore the surface phenomena of clusters. He assumed the temperature in the interface region to be constant and equal to the saturation temperature in his computations of pressure profiles. In present MD simulation of argon droplet surrounded by argon vapor shown in *figure 11*, the assumption of the constant saturation temperature in the interface region has been abandoned. The results on the density, pressure and temperature profiles in the interface are given in *figures 12–14*, respectively. It can be found once again in *figure 14* that the temperature profile inside the interface is nonmonotonical, and

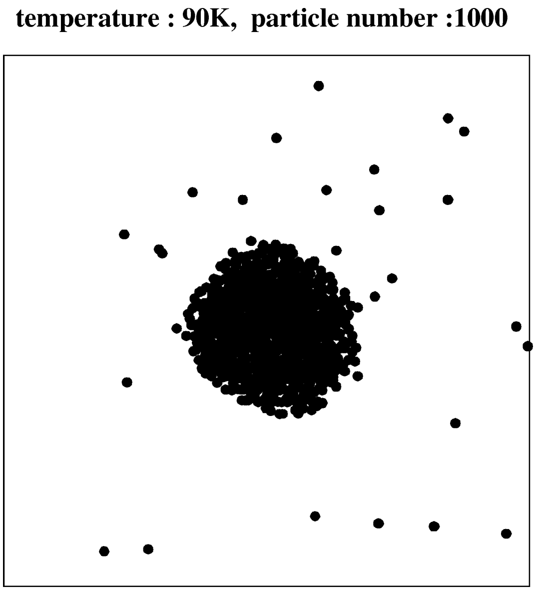


Figure 11. A snapshot of argon droplet.

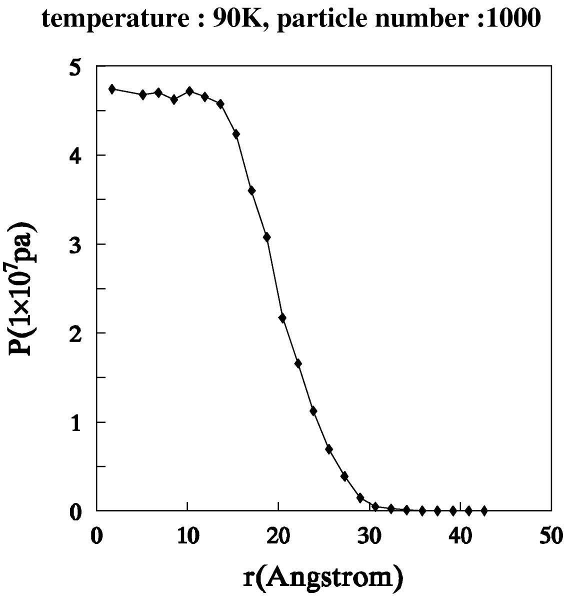


Figure 12. Pressure distribution of argon droplet.

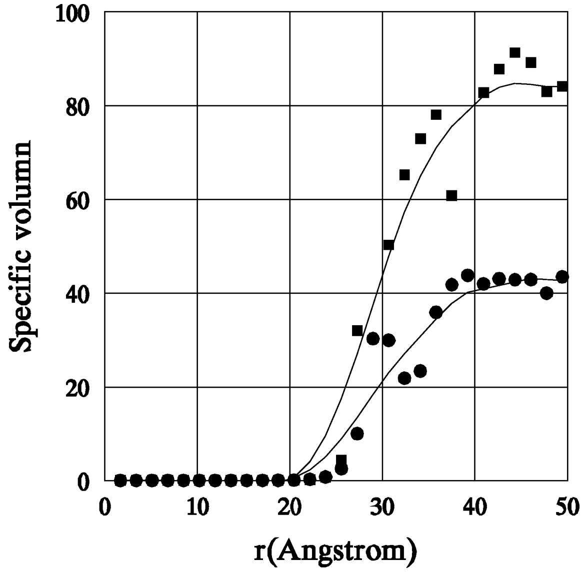


Figure 13. Density distribution of argon droplet.

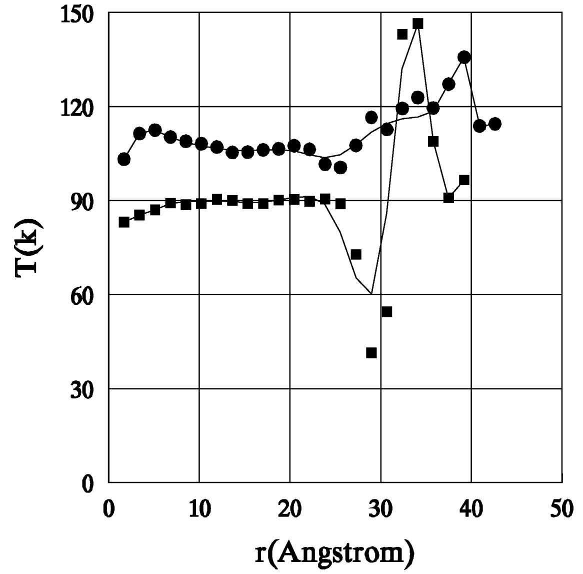


Figure 14. Temperature distribution of argon droplet. ■: $T =$ 90 K, ●: $T = 110$ K.

some part of that falls into the unstable region of the van der Waals loop at constant pressure. These results may further confirm the phenomena of continuous phase transition in the microspace.

3.3. Experiment

Experiment was carried out about the density variation and interface thickness in a stainless vessel (made in Technical University of Munich, Germany). The stainless vessel with two glass windows is tightly fitted in a copper block. The two-phase freon system in the vessel was heated by the warm air through the copper block, which guarantees the peripherally uniform heating of freon (R13). The heating rate was maintained very slow in order to make the temperature field of freon approximately homogeneous. Laser Speckle technique was used to measure the density variation in freon fluid. The experimental rig is schematically given in *figure 15*. The liquid and vapor are approximately of the same volume in the vessel at room temperature, as shown in *figure 16(a)*. The liquid–vapor interface is very thin, so that the measurement of the density variation in the interface region is not available by laser Speckle technique. No bubble could be observed during the heating process due to very small superheat. The height of liquid surface did not change (*figure 16(b)*) as the temperature rose to 26.5 °C. This is because the volume increase of liquid due to expansion is compensated by the volume reduction of liquid due to evaporation at interface.

In *figure 16(c)*, three fringes can be seen between the liquid and vapor phases. The region being of fringes represents the region of density variation, namely, the phase transition region. As the temperature was further close to the critical temperature, the vapor phase disappeared and the transition region became large up to 7.8 mm, as illustrated in *figure 16(d)*. *Figure 16(e)* shows the argon fluid at critical point, where no difference exists between the liquid and vapor phases. When the argon fluid was cooled from the supercritical state down to the temperature a little below the critical point, the condensation suddenly occurred and numerous tiny droplets appeared. As a result, the image becomes very dark due to strong scattering by droplets, as shown in *figure 16(f)*.

4. CONCLUDING REMARKS

- MD/MC simulation results show that isotherms in the P–V diagram are similar to the van der Waals loop, that is, the continuous phase transition between liquid and vapor appears as the space scale is down to the order of the critical radius of nucleus (bubble or droplet). This is because the reduction of length scale prevents the nucleus from kinetic stability and growth.

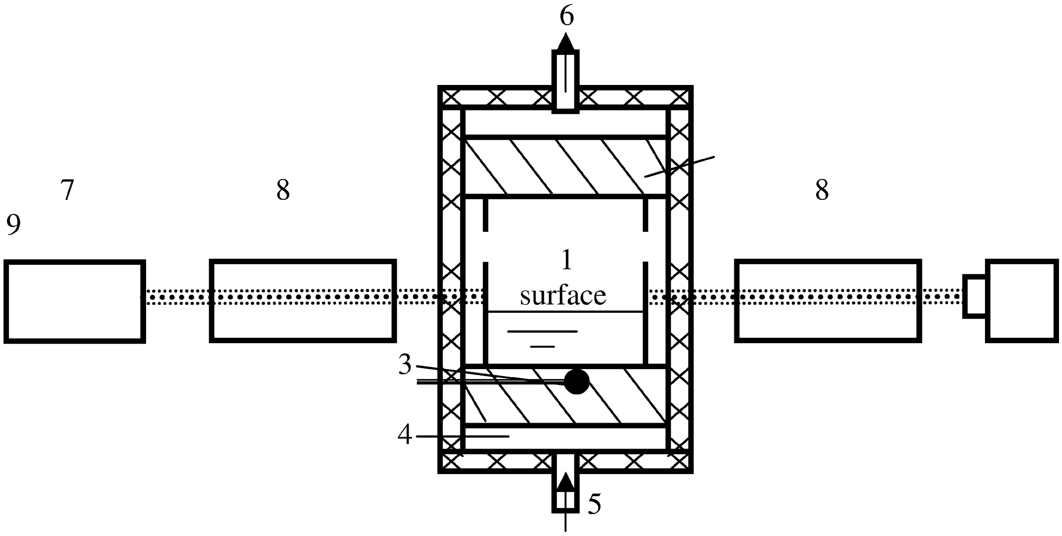
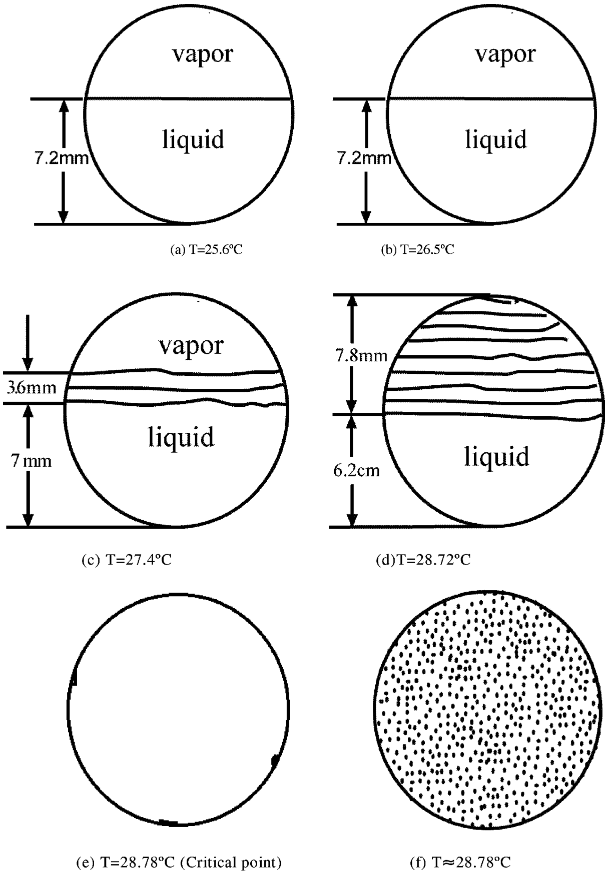


Figure 15. Experimental rig. 1: two-phase freon test section; 2: copper block; 3: thermocouple; 4: air chamber; 5: warm air inlet; 6: warm air outlet; 7: laser; 8: optical component; 9: CCD.



(a) T=25.6°C (b) T=26.5°C

(c) T=27.4°C (d)T=28.72°C

(e) T=28.78°C (Critical point) (f) T≈28.78°C

Figure 16. Schematic of interface characteristics of freon system.

- MD simulation of argon and experiment of freon (R13) indicate that the density variation in the liquid–vapor interface is gradual and the interface thickness increases remarkably as the saturation temperature is close to the critical point.
- Analyses and MD calculation demonstrate that the temperature inside the interface region is higher than the saturation temperature. It is similar to the van der Waals loop in the $T-V$ diagram. This implies that the liquid–vapor phase transition proceeds continuously across the interface region without boiling or condensation.
- The characteristics of interface, including the continuous phase transition and the temperature distribution, may be used to clarify the mechanism of heat transport in the microlayer in nucleate boiling and some unusual phenomena of phase change heat transfer in microchannels.

Acknowledgement

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