MOLECULAR DYNAMICS SIMULATION OF LIQUID-VAPOR BINARY MIXTURE OF LENNARD-JONES FLUIDS

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Summary Molecular dynamics simulation is used to investigate the property of liquid-vapor system of Ar-Kr binary mixture. The local profiles of density, normal & tangential pressure, and surface tension are analyzed. The variations of saturation pressures with temperature and the equilibrant concentrations of mixture are discussed.

INTRODUCTION

Due to the fundamental importance for many technological processes, such as coating, adsorption, industrial separation, or tertiary oil recovery, liquid-vapor systems and liquid-vapor interface have been a matter of great interest in many experimental and theoretical investigations. A detailed understanding of interfacial structure and mixture behavior is crucial to many technological processes. In the last decade, computer simulations became more and more an important tool to obtain information on the properties of pure homogeneous fluids and mixtures as well as on their interfacial behavior.

Among these simulation methods, the molecular dynamics simulation is considered to be one of the best methods to study the detailed property of liquid-vapor systems. Mecke *et al.* performed molecular dynamics simulations to investigate the liquid–vapor interfacial properties of the Lennard-Jones fluid[1]. Trokhymchuk investigated the orthobaric densities, normal and tangential pressure profiles, and surface tension of liquid-vapor systems[2]. While most researchers focused on liquid-vapor system of pure material, few researchers studied the liquid-vapor property of mixture. Olivier *et al.* studied the rates of evaporation and condensation in a mixture of Lennard-Jones particles using equilibrium and non-equilibrium molecular dynamics simulations[3]. Recently, Inzoli *et al.* investigated the thermodynamic properties and transfer coefficients of a liquid-vapor interface in a two-component system[4].

SETUP OF MOLECULAR DYNAMICS SIMULATION

We performed molecular dynamics simulation of a three-dimensional liquid mixture in equilibrium with its own vapor. The particles interact via a Lennard-Jones 12-6 potential. For argon, σ=0.3405nm and ε/K_B=119.8K. While for krypton, σ=0.3633nm and ε/K_B=167.0K. The Lorentz-Berthelot mixture rule was used to calculate the interaction between argon and krypton molecules. 8000 molecules were initially placed at the center region of simulation box using body-centered cubic lattice method. The cut-off radius was 4.5σ. Our simulations were performed in a NVT ensemble. The temperature was kept constant by the velocity scaling method and the equations of motion were solved using leap-frog algorithm. The reduced time step Δt^* was 0.005. During the computation, the first 200,000 time steps was used to lead the system to equilibrium. Another 800,000 time steps were carried out to sample macro properties, such as density, temperature, pressure and surface tension. The simulation box was cut into 300 slices in z direction to get local quantities.

The local density profiles under three temperatures (T=95.8K, 119.8K and 143.8K) are shown in Fig. 1. Liquid and vapor coexist in the system. The density at center region (liquid region) is large, while at both sides, the density is much smaller. The liquid density decreases with the increase of temperature, while the gas density increases. Molecular velocity increases with the increase of temperature, so the molecule is easy to escape from the surface and enter into vapor. The interface thickness increases with the increase of temperature.

Saturation pressure at certain temperature can also be achieved when the system is in equilibrium. The variation of saturation pressure at different temperatures is shown in Fig. 2, with experimental data of Chen *et al.* also provided[5]. As can be found from the figure, the present calculated saturation pressures agree very well with experimental data, less than 1%. In some situations, experimental data is hard to achieve. For example, the pressure is too large near critical point for some materials. While in molecular dynamics simulation, it is easy to handle in these situations. So, the molecular dynamics simulation can be a good supplement to experiment. And this method can be used to forecast the property of new materials.

RESULTS AND DISCUSSIONS

Apart from the determination of phase equilibrium and coexisting densities, the surface tension has been of great interest in these studies. The surface tension is calculated from the profiles of the components of pressure tensor by using the mechanical definition. The normal and tangential pressure components are the same in pure vapor and liquid region. So the surface tension is zero in these two regions, as can be seen in Fig. 3. But in interfacial region, the normal and tangential pressure components are different and the local surface tension is not zero. This value decreases with the

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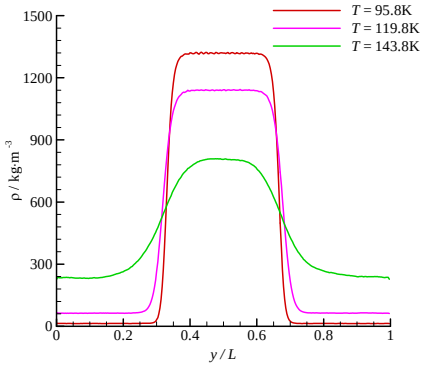

Fig. 1 Local density distributions at different temperatures

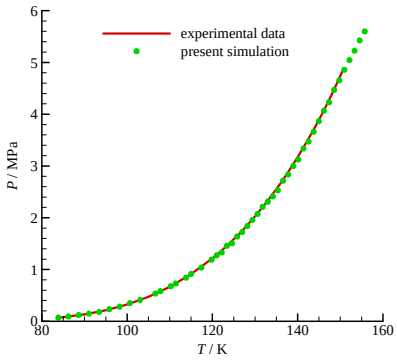

Fig. 2 Saturation pressures at different temperatures

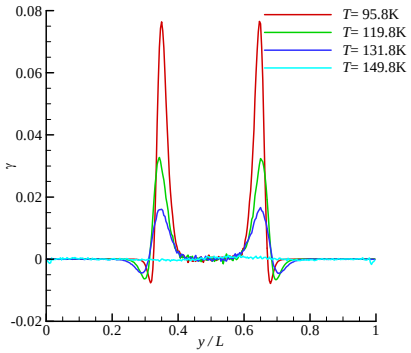

Fig. 3 Local surface tension profiles at different temperatures

increase of temperature. When the temperature is high enough, no different exist between vapor and liquid and the surface tension is zero, such as T=149.8K in the figure.

The property of liquid-vapor binary mixture of argon and krypton is then studied. The mole percentage of Ar and Kr in vapor region at different temperatures are first analyzed. The initial percentages of Ar and Kr are both 50%. The boiling point of Ar is lower than that of Kr, so Ar is easier to evaporate. The mole percentage of Ar is larger than that of Kr, as can be found in Fig. 4. The influence of initial percentage on equilibrium Kr percentage in vapor region is shown in Fig. 5. The temperature is kept at 95.8K. The equilibrium Kr percentage depends greatly on initial Kr concentration. This feature can be utilized in rectification process to increase the rectifying efficiency by choosing appropriate initial concentration.

The saturation pressures of mixture at different temperatures are also analyzed. Because of space limit, only the result of 50-50% Ar-Kr mixture is shown in Fig. 6. The saturation pressures at different temperatures are hard to measure in experiment or hard to estimate through state equation, especially for multi-component mixtures. While molecular dynamics simulation can easily estimate the properties of multi-component mixtures.

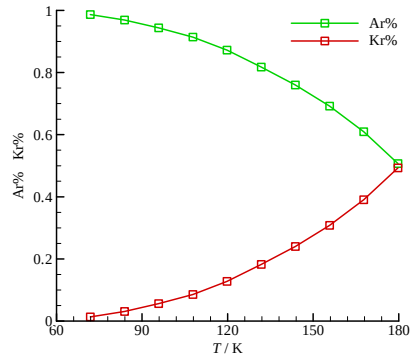

Fig. 4 Percentage of Ar and Kr in vapor at different temperatures

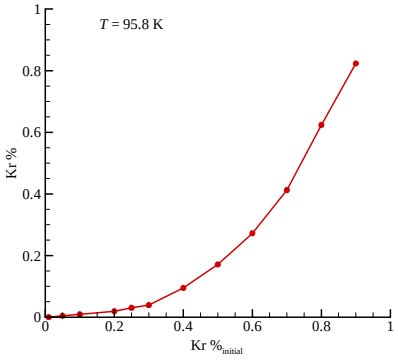

Fig. 5 Percentage of Kr in vapor at different initial concentrations

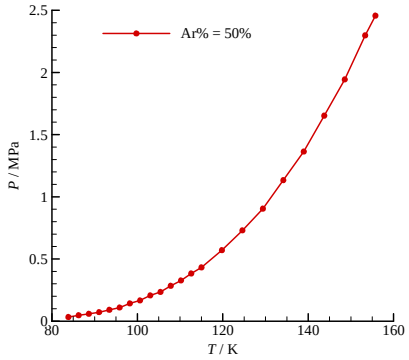

Fig. 6 Saturation pressures of mixture at different temperatures

CONCLUSIONS

Molecular dynamics simulation was adopted to investigate the property of liquid-vapor system of Ar-Kr binary mixture. The saturation pressures of argon at different temperatures were first compared with experimental data, and excellent agreement was achieved. The local profiles of density, normal and tangential pressures, and surface tension are then analyzed. At last, the characteristics of Ar-Kr mixture at different initial concentrations and different temperatures are discussed.

Acknowledgement

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