Nonequilibrium Molecular Dynamics Simulation of Evaporation and Condensation

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Evaporation and condensation at the liquid-vapor interface have draw considerable attention from the physical and chemical community for many years. However, due to its complexity of the physical mechanism, there are still many questions remained unsolved. It is much difficult to accurately predict the phase change flux.

Assuming an ideal gas and neglecting interactions between individual molecules, the net mass flux of the evaporation and condensation can be estimated as

$$\dot{m}_{net} = \sqrt{\frac{M}{2\pi R}} \cdot \left(\frac{p_v}{\sqrt{T_v}} - \frac{p_;}{\sqrt{T_l}} \right) \tag{1}$$

from the kinetic theory [1]. Considering the real gas effects, the classical theories of evaporation and condensation introduce the evaporation/condensation coefficients, which are defined as the ratio of the evaporated/condensed molecules to the incident ones into the interface, into Eq. (1) to adapt the experimental data to the simplified theoretical predictions:

$$\dot{m}_{net} = \sqrt{\frac{M}{2\pi R}} \cdot \left(\alpha_c \frac{p_v}{\sqrt{T_v}} - \alpha_e \frac{p_;}{\sqrt{T_l}} \right). \tag{2}$$

Eq.(2) is the so-called Hertz-Knudsen-Langmuir equation [1]. Schrage and Labuntsov [2] respectively modified the Eq.(2) for near-equilibrium and non-equilibrium conditions as following:

$$\dot{m}_{net} = \frac{2}{2-\alpha_c} \cdot \sqrt{\frac{M}{2\pi R}} \cdot \left(\alpha_c \frac{p_v}{\sqrt{T_v}} - \alpha_e \frac{p_;}{\sqrt{T_l}} \right) \quad , \tag{3}$$

$$\dot{m}_{net} = \frac{2}{2-0.798\alpha_c} \cdot \sqrt{\frac{M}{2\pi R}} \cdot \left(\alpha_c \frac{p_v}{\sqrt{T_v}} - \alpha_e \frac{p_;}{\sqrt{T_l}} \right) \quad . \tag{4}$$

Eq.(3) is known as Hertz-Knudsen-Schrage Equation and Eq.(4) is called as Hertz-Knudsen- Labuntsov Equation. Furthermore, a more complex kinetic evaporation and condensation equation taking into account the velocity distribution of the reflected molecules is given by Ytrehus, and Rose gave an overview on the liquid-vapor interphase mass transfer.

For the evaporation/condensation coefficients, a lot of experimental investigations have been carried out, but there are often discrepancies among the measured evaporation/condensation coefficients from the different experiments [1], e.g., for the evaporation/condensation coefficients of water, at the same temperature, the measured data vary over more than three orders [1]. In recent years, with molecular dynamics (MD) simulations, the evaporation/condensation coefficients under equilibrium were statistically computed by Tsuruta et al. [3], Mosumoto et al. [4] and us [5] respectively with the different statistical method and physical model, and the different values were obtained. In addition, the condensation coefficients can be theoretically predicted. The evaporation/condensation coefficients from the modified transition state theory by us [6] agree well with the data from the molecular dynamics calculations by both Tsuruta and us. However, It is difficult to give merit for these simulated and theoretical results since these currently available data are under equilibrium conditions, while in practice the evaporation and condensation are carried out under quasi-equilibrium or nonequilibrium conditions.

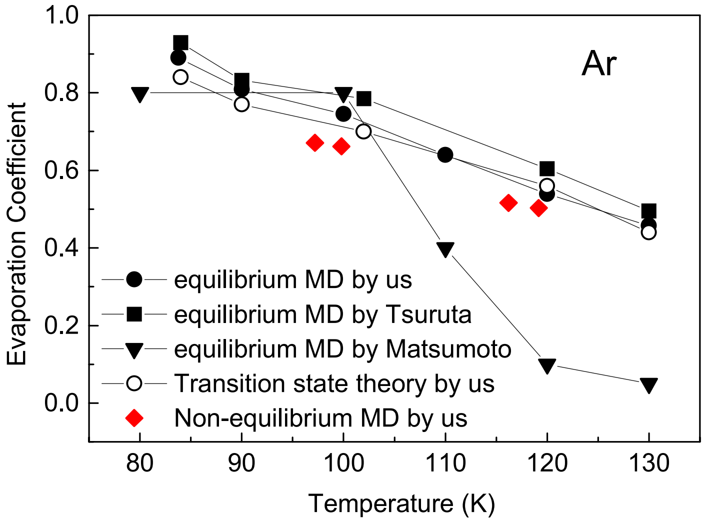
In this contribution, nonequilibrium molecular dynamics simulations (NEMD) are performed to study the evaporation and condensation processes. Evaporation coefficients are obtained under nonequilibrium and compared with the data from the equilibrium molecular dynamics simulations.

12,000 molecules with the nonpolar interacting force expressed by the 12-6 Lennard-Jones potential [7] are used to simulate the evaporations of the liquid argon. Time step is 1.19fs, and the cut-off is 4.0σ. Periodic boundary conditions are used in all three directions. Firstly, the molecules are enclosed in an empty cubic box, and canonical ensemble (*NVT*) MD simulations are carried out to model the saturated liquid system at 100K and 120K respectively. The initial distance between molecules is the average distance of the saturated liquid molecules. The constant bulk temperature is performed with the constraint method [7]. The static parameters, the pressure P and the density ρ, of the simulated liquid at the saturated temperature T are compared with the reported data [8] to judge whether the simulated liquid is the saturated liquid under equilibrium. Secondly, by elongating the simulated system in z direction, expand the saturated liquid system under equilibrium from the volume $V=SL$ to the volume $S(L+\Delta L)$, in which S is the area of the surface perpendicular to z direction, L is the length in z direction of the original system, and $L+\Delta L$ is the length in z direction of the expanded system. The saturated liquid film is settled in the middle of the expanded system. Then in the simulated system, the evaporation begins at the two surfaces of the saturated liquid film. During the simulation of the evaporation, the number of molecules N and the volume of the system V are settled constant. In order to prevent the wandering of the liquid film, adjusting the mass center of the system to be in the middle of the system is performed at every MD step. The intial 10,000 MD steps (11.9ps) are used to produce the liquid-vapor interface. Then After expanding the system for 10000 MD steps (11.9ps), we begin to record the number of the vapor molecules N to obtain the evaporation flux $\dot{m}_{net}$ from the molecular level. By calculate the change of number of the vapor molecules every 50,000 MD steps (dt =55.9ps), the net evaporated fluxes every 50,000 MD steps (55.9ps) are obtained as following

$$\dot{m}_{net} = \frac{m \cdot \left(N(t+dt) - N(t)\right)}{2 \cdot S \cdot dt} , \qquad (5)$$

Moreover, the pressure profile $P(z)$, the temperature profile $T(z)$ and the density profile $\rho(z)$ are statistically calculated every 50,000 MD steps (55.9ps), and the liquid and vapor average thermodynamic parameters P_l, T_l, and P_v, T_v, every 50,000 MD steps (55.9ps) are obtained. The local pressure is computed with the method presented by Hoover et al [9]. Assuming $\alpha_c=\alpha_e$, with Eq.(4) the evaporation coefficient can be calculated.

The evaporation coefficients obtained from the NEMD simulations are compared with the data from the MD simulations under equilibrium and the transition state theory as shown in the following figure. Good agreements are reached among the evaporation coefficients from our NEMD simulations and those from the modified transition state theory and the MD simulations under equilibrium by Tsuruta et al. and by us. Between the NEMD simulations and the modified transition state theory or the equilibrium MD (EMD) calculations by us, the difference of evaporation coefficients is within 10%, and between the NEMD simulations and the EMD calculations by Tsuruta et al. it is about 15%. However, between the NEMD calculations and the EMD simulations by Matsumoto et al. et al., there exist large differences of the evaporation coefficients at the higher temperatures. If using Hertz-Knudsen-Labuntsov equation to predict the net evaporation/condensation mass flux, the statistical model presented by Masumoto et al is not appropriate for the calculation of the evaporation/condensation coefficient in the high temperature region.



Comparison of the evaporation coefficients

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