A nonequilibrium molecular dynamics simulation of evaporation

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ABSTRACT

The net evaporation process is investigated by performing non-equilibrium molecular dynamics simulations. The transient density, temperature and pressure profiles are statistical calculated, and the net evaporation flux is obtained from molecular level. With Hertz-Knudsen- Labuntsov equation, the evaporation coefficients based on nonequilibrium molecular dynamics simulations are computed and compared with the data calculated by the equilibrium molecular dynamics simulations and the transition state theory. The evaporation coefficients of the nonequilibrium molecular dynamics agree with those from the transition state theory and some data of equilibrium molecular dynamics calculations in literature within 15%. However, if using Hertz-Knudsen-Labuntsov equation to predict the net evaporation/condensation mass flux, the statistical model presented by Matsumoto et al., (1995) does not show reasonable agreement with present simulation and some other data in literature, especially in the high temperature region.

1. INTRODUCTION

Evaporation and condensation at the liquid-vapor interface have drawn considerable attention from the physical and chemical community for many years. Extensive researches have been carried out, which involve the liquid-vapor interface, the interphase transport dynamics, evaporation/condensation coefficient, etc. However, due to the complexity of its physical mechanism, there are still many challenges remained unsolved. For instance, it is still difficult to accurately predict the phase change flux in many situations.

From the kinetic theory view (Collier and Thome, 1994; Cammenga, 1980), assuming an ideal gas and neglecting interactions between individual molecules, the net mass flux of the evaporation and condensation can be estimated as:

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

where $\dot{m}_{net}$ is the net mass flux of phase change, M is the molar mass, R is the gas constant, p_v and p_l are the vapor and the liquid pressures separately, T_v and T_l are the vapor and the liquid phases temperatures separately. Considering the real gas effects, the classical theories of evaporation and condensation has to introduce the evaporation/condensation coefficients, which are defined as the ratio of the evaporated/condensed molecules to the incident ones into the interface. Generally, the evaporation/condensation coefficients are put into Equation (1) to adapt the experimental data to the simplified theoretical prediction, in the form of:

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

Equation (2) is the so-called Hertz-Knudsen-Langmuir equation (Cammenga, 1980), where α_c is the condensation coefficient and α_e is the evaporation coefficient. Schrage (Schrage,

1953) and Labuntsov (Labuntsov, 1967) respectively modified Equation (2) for near-equilibrium and non-equilibrium conditions as following,

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

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

Equation (3) is known as Hertz-Knudsen-Schrage Equation and Equation (4) is so 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 (Ytrehus, 1997), and Rose gave an overview on the liquid-vapor interphase mass transfer (Rose, 1998).

For the evaporation/condensation coefficients, a number of experimental investigations have been carried out, but there are often discrepancies among the measured evaporation/condensation coefficients from the different experiments (Cammenga, 1980; Eames et al., 1997; Bedeaux and Kjelstrup, 1999; Marek and Straub, 2001). As an example, checking the evaporation/condensation coefficients of water, at the same temperature, the measured data vary over more than three orders (Eames et al., 1997; Bedeaux and Kjelstrup, 1999; Marek and Straub, 2001). In recent years, by using molecular dynamics (MD) simulations, the evaporation/condensation coefficients under equilibrium were statistically computed by Matsumoto et al. (1995), Tsuruta and Nagayama (2000), and us (Wang et al., 2003) respectively, with different statistical methods and physical models, and different values were obtained. Meanwhile, the condensation coefficients can be theoretically predicted. The evaporation/condensation coefficients calculated by a modified transition state theory by us (Wang et al., 2002) agree well with the simulated data in the molecular dynamics calculations by both Tsuruta and Nagayama, (2000) 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 processes take place mostly 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 equilibrium molecular dynamics simulations.

2. SIMULATION DETAILS

12,000 molecules with the non-polar interacting force expressed by the 12-6 Lennard-Jones potential are employed to simulate the evaporations of the liquid argon. The Lennard-Jones potential has the form (Allen and Tildesley, 1987),

$$U(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5)$$

where r is the molecular pair separation, and parameters of the potential are $\sigma = 3.405 \times 10^{-10} m$, ε/k_B=119.8K, in which k_B is Botlzman's constant. The time step is 1.19fs, and the cut-off radius is 4.0σ. Periodic boundary conditions are applied to all three directions. Firstly, the molecules are enclosed in an empty cubic box, and canonical ensemble (the number of the molecules N, the volume of the system V and the temperature T are fixed) 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 (Allen and Tildesley, 1987). The static parameters, the pressure P and the density ρ, of the simulated liquid at saturated temperature T are compared with other reported data (Dunikov et al., 2001) 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 vol-

Table 1: The size parameters of the simulated system.

T (K)	S (10^{-20}m^2)	L (10^{-10}m)	ΔL (10^{-10}m)
100	74.2^2	111.4	334.1
120	77.2^2	115.7	347.2

ume $V=SL$ 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. S, L, ΔL at two different simulation temperatures are given in Table 1.

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. 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. 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, are obtained every 50,000 MD steps (55.9ps). The local pressure is computed with the method presented by Hoover et al. (Hoover et al., 1991). Assuming $\alpha_c=\alpha_e$, with Equation (4) the evaporation coefficient can be calculated.

3. RESULTS AND DISCUSSIONS

The density profile, temperature profile and the pressure profile in the direction normal to the interface are statistically calculated every 59.5ps from 11.9ps. For an initial temperature of 100K, the change of the density, the temperature, and the pressure profiles with respect to time are shown in Figures 1, 2 and 3.
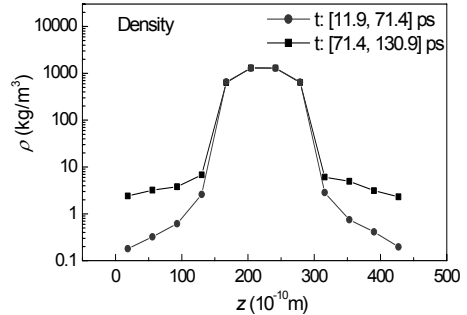
The density of vapor increases with time as

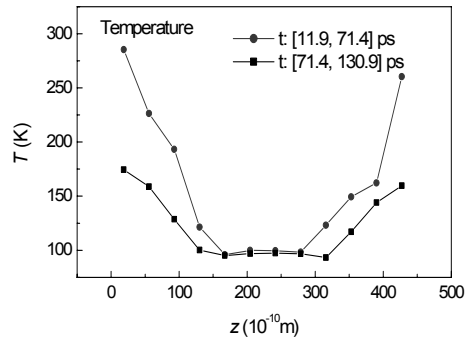Figure 1: Change of the density profile with respect to time.

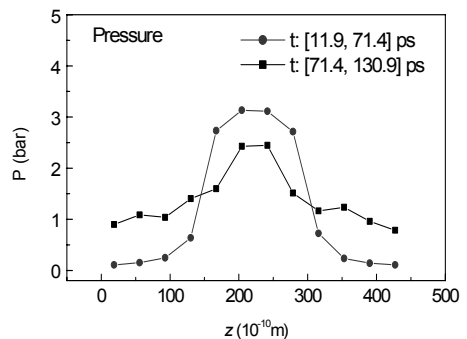Figure 2: Change of the temperature profile with respect to time.

Figure 3: Change of the presure profile with respect to time.

expected. The temperature gradually decreases with time because of the latent heat absorption, and because of the rapid heat conduction of liquid argon, no clear temperature gradient was seen in the temperature profile of the liquid

film. The pressure of the liquid decreases with time, while the pressure of the vapor increases with time, i.e. the driving pressure of the evaporation decreases.

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 (dt=55.9ps) are obtained as following,

$$\dot{m}_{net} = \frac{m \cdot (N(t+dt) - N(t))}{2 \cdot S \cdot dt} \qquad (6)$$

where, m is the molecular mass, $N(t+dt)$ and $N(t)$ are respectively the number of the vapor molecules at time t and $t+dt$, S is the area of the interface. Assuming $\alpha_c = \alpha_e$, the evaporation coefficients are predicted with Equation (4) as shown in Table 2.

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 Figure 4.

Reasonable 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 and Nagayama, (2000) 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 and Nagayama it is about 15%. However, between current NEMD calculations and the EMD simulations by Matsumoto et al., there exist large differences of the evaporation coefficients at higher temperatures. If using Hertz-Knudsen-Labuntsov equation to predict the net evaporation/condensation mass flux, the statistical model presented by Matsumoto et al. (Matsumoto et al., 1995) does not show reasonable agreement with present simulation and some other data in literature, especially in the high temperature region.

Table 2: Net evaporation flux and evaporation coefficient.

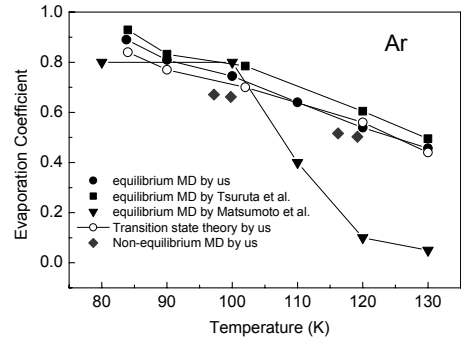| T (K)	Time (ps)	Evaporation flux (kg/m^{2}s)	Evaporation coefficient
100	11.9-71.4	716.98	0.662
100	71.4-130.9	383.19	0.671
120	11.9-71.4	1814.91	0.503
120	71.4-130.9	1209.74	0.516

Figure 4: Comparison of the evaporation coefficients.

4. CONCLUSIONS

Molecular dynamics simulations are carried out to study the evaporation and condensation under non-equilibrium conditions. By using the Hertz-Knudsen-Labuntsov equation for the non-equilibrium conditions, we calculate the evaporation coefficients of argon at four average liquid temperatures and compare them with other data available in literature. The comparisons show that:

1. The evaporation coefficients from the non-equilibrium molecular dynamics can agree with the data from our modified transition state theory, the data from equilibrium molecular dynamics simulations by Tsuruta and Nagayama and by us. The differences are within 15%.

2. For evaporation coefficients at higher temperatures, there is a large discrepancy between current non-equilibrium molecular dynamics and the equilibrium molecular dynamics calculation by Matsumoto et al. If using Hertz-Knudsen-Labuntsov equation to calculate the net evaporation/condensation

mass flux, the statistical method proposed by Masumoto et al. does not show reasonable agreement with present simulation and some other data in literature, especially in the high temperature region.

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REFERENCES

Allen, M.P. and D.J. Tildesley, 1987. Computer Simulation of Liquids, Arrowmith, Bristol, 1987.

Bedeaux, D. and S. Kjelstrup, 1999. Transfer coefficient for evaporation, Phys. A 270: 413-426.

Cammenga, H.K., 1980. Evaporation mechanisms of liquids, in Current Topics in Materials Science 5, Kaldis ed., Amsterdam, North-Holland.

Collier, J.G. and J.R. Thome, 1994. Convective Boiling and Condensation, Oxford: Clarendon, 3rd ed..

Dunikov, D.O., S.P. Malyshenko and V.V. Zhakhovskii, 2001. Corresponding states law and molecular dynamics simulations of the Lennard-Jones fluid, J. Chem. Phys. 115: 6623-6631.

Eames, I.W., N.J. Marr and H. Sabir, 1997. The evaporation coefficient of water: a review, Int. J. Heat Transfer, 4(12): 2963-2973.

Hoover, W.G., 1991. Computational Statistical Mechanics, Elsevier, Amsterdam.

Labuntsov, D.A., 1967. An analysis of intensive evaporation and condensation, High Temperature (Engl. Transl.), 5: 579-647.

Marek, R. and J. Straub, 2001. Analysis of the evaporation coefficient and the condensatio coefficient of water, Int. J. Heat Transfer, 44: 39-53.

Matsumoto, M., K. Yasuoka and Y. Kataoka, 1995. Molecular mechanism of evaporation and condensation, Thermal Science & Engineering, 3(3): 27-31.

Rose, J.W., 1998. Interphase matter transfer, the condensation coefficient and dropwise condensation, Proceedings of the 11th International Heat Transfer Conference, Kyongiu, Korea, vol.1: 89-104.

Schrage, R.W., 1953. A Theoretical Study of Interphase Mass Transfer, Columbia University Press, New York.

Tsuruta, T. and G. Nagayama, 2000. A molecular dynammics approach to interphase mass transfer between liquid and vapor, Proceedings of the international conference on heat transfer and transport phenomena in microscale, Banff, Canada, 432-439.

Wang, Z.J., M. Chen and Z.Y. Guo, 2002. Modified Transition State Theory for Evaporation and Condensation. Chinese Phys. Lett. 19(4): 537-539.

Wang, Z.J., M. Chen and Z.Y. Guo, 2003. A molecular study on the Liquid-vapor interphase transport, Microscale Thermophysical Eng., 7(4): 275-289.

Ytrehus, T., 1997. Molecular-flow effects in evaporation and condensation at interfaces, Multiphase Science and Technology 9(3): 205-325.