Molecular dynamics study of kinetic boundary condition at an interface between argon vapor and its condensed phase

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(Received 6 November 2003; accepted 29 April 2004; published online 25 June 2004)

The evaporation and condensation at an interface of vapor and its condensed phase is considered. The validity of kinetic boundary condition for the Boltzmann equation, which prescribes the velocity distribution function of molecules outgoing from the interface, is investigated by the numerical method of molecular dynamics for argon. From the simulations of evaporation into vacuum, the spontaneous-evaporation flux determined by the temperature of condensed phase is discovered. Condensation coefficient in equilibrium states can then be determined without any ambiguity. It is found that the condensation coefficient is close to unity below the triple-point temperature and decreases gradually as the temperature rises. The velocity distribution of spontaneously evaporating molecules is found to be nearly a half-Maxwellian at a low temperature. This fact supports the kinetic boundary condition widely used so far. At high temperatures, on the other hand, the velocity distribution deviates from the half-Maxwellian.

I. INTRODUCTION

The evaporation from and condensation on a liquid or solid surface have long been an important subject of fundamental researches in physics of fluids. Molecular gas dynamics (rarefied gas dynamics) can give an accurate description of the behavior of vapor adjacent to its condensed (liquid or solid) phase. This has actually been accomplished by solving the Boltzmann equation with a kinetic boundary condition at an interface between vapor and its condensed phase. The boundary condition widely used can be written as:1,2

\[ f^\text{out} = \alpha f^e + (1 - \alpha) f^r \quad (\xi_z > 0), \tag{1} \]

where \( f^\text{out} \) denotes the velocity distribution function of outgoing molecules from the interface and \( \xi_z \) is the velocity component normal to the interface. The parameter \( \alpha \) (0 \(<\alpha\leq1) \) has been called the condensation coefficient\(^3\) (the definition of condensation coefficient will be given in Sec. II). \( f^e \) is a Maxwellian with saturated vapor density \( \rho_v \) at the temperature of the condensed phase \( T_c \):

\[ f^e = \rho_v \hat{f}^e, \quad \hat{f}^e = \frac{1}{(2\pi RT_c)^{3/2}} \exp \left( -\frac{\xi_x^2 + \xi_y^2 + \xi_z^2}{2RT_c} \right), \tag{2} \]

where \( R \) is the gas constant and \( \xi_x \) and \( \xi_y \) are the velocity components tangential to the interface. The symbol \( \wedge \) signifies the distribution function normalized by the gas density and the superscript \( * \) represents a Maxwellian. For \( f^r \) in the second term, the diffuse reflection is usually used:

\[ f^r = \sigma_w \hat{f}^r, \quad \sigma_w = -\frac{2\sqrt{\pi}}{RT_c} \int_{\xi_z < 0} \xi_z f^\text{coll} d\xi_z, \tag{3} \]

where \( f^\text{coll} \) is the distribution function of molecules incident on the interface.

A number of problems have been solved on the basis of Eq. (1) (especially in the case of \( \alpha=1 \), the complete condensation), and thereby various phenomena have been found (see Refs. 1 and 2 and references therein). However, the physical appropriateness of Eq. (1) has never been verified, and the parameter \( \alpha \) in Eq. (1) cannot be determined in the framework of the molecular gas dynamics. In the present paper, we shall shed light on the first term \( \alpha f^e \) in Eq. (1), and examine its validity by the numerical method of molecular dynamics (MD) for argon.

In the following section, we shall clearly state the problem and provide the outline of the analysis. In Sec. III, we describe the method for MD simulations. The numerical results are presented and discussed in Sec. IV. Section V is devoted to conclusions.

II. PROBLEM STATEMENT

Let us consider an interface between a vapor and its condensed phase. The temperature in the bulk condensed phase \( T_c \) is assumed to be constant. In order to study the physically appropriate boundary condition, we start from not Eq. (1) but a general expression for \( f^\text{out} \),

\[ f^\text{out} = f^\text{evap} + f^\text{ref} \quad (\xi_z > 0), \tag{4} \]

where \( f^\text{evap} \) is a distribution function of molecules spontaneously evaporating from the interface and \( f^\text{ref} \) is defined as \( f^\text{ref} = f^\text{out} - f^\text{evap} \). We define the spontaneous evaporation as an evaporation that occurs independently of incident vapor

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intrinsically difficult because molecules experience compli-
cations. Application of the mass conservation law at the inter-
facial plane leads to the definition of the condensed mass flux
\begin{equation}
\langle J_{\text{cnds}} \rangle.
\end{equation}

In the equilibrium state, since \( \langle J_{\text{out}} \rangle = \langle J_{\text{coll}} \rangle \), we have
\( \langle J_{\text{cnds}} \rangle = \langle J_{\text{evap}} \rangle \) from Eqs. (6) and (7), and hence \( \alpha_c = \alpha_e \). In this paper, we define \( \alpha \) as
\begin{equation}
\alpha = \frac{\langle J_{\text{evap}} \rangle}{\langle J_{\text{out}} \rangle},
\end{equation}
which is equal to \( \alpha_c \) and \( \alpha_e \) in the equilibrium state. We shall evaluate \( \alpha \) for a wide temperature range including the triple point.

**III. COMPUTATIONAL METHOD**

We consider the dynamics of molecules at an interface between vapor and condensed phases of argon. The phenomenon concerned is assumed as one dimensional in a macroscopic sense, i.e., the interface is assumed as planar in a macroscopic sense and normal to the z axis (see Fig. 2).

**A. Equilibrium simulation**

To begin with, we describe the method for equilibrium MD simulations for argon. The computational method is almost the same as those developed in Refs. 4, 11, 12, where a system of \( N \) molecules is considered in a simulation cell with dimensions \( L_x \times L_y \times L_z \) for a specified average temperature \( T_\epsilon \). The simulations are executed for \( T_\epsilon = 70, 75, 80, 85, 90, 100, 110, 120, \) and 130 K. A vapor-liquid equilibrium is obtained between the triple-point temperature (83.8 K) and the critical-point temperature (150.7 K), and a vapor-solid equilibrium is obtained below the triple-point temperature, where the sublimation occurs.

As an intermolecular potential of argon molecules for \( 85 \, \text{K} \leq T_\epsilon \leq 130 \, \text{K} \), we use a 12-6 type Lennard-Jones potential
\begin{equation}
\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right],
\end{equation}
where the particle diameter \( \sigma \) is 3.405 Å and the potential depth \( \epsilon/k \) is 119.8 K (\( k \) is the Boltzmann constant). The Lennard-Jones potential however gives poor saturated vapor density below the triple point. To obtain reliable results for \( T_\epsilon = 70, 75, \) and 80 K, we use the Dymond–Alder potential, which is a numerically tabulated one.

![Molecular fluxes at the interface](https://example.com/image.png)
number of molecules $N = 2000$, while in higher temperature cases of $110 \, \text{K} \leq T_e \leq 130 \, \text{K}$, we increase $L_z$ to 300 Å and $N$ to 4000. The surface area $L_x \times L_y$ is fixed to 50×50 Å$^2$ in all cases.

Newton’s equations of motion for $N$ molecules in the cell are solved by the leap-frog method with the time step 1 fs. For the both potentials, the cutoff radius is set to 15 Å. The periodic boundary conditions are imposed for all three directions of the simulation cell.

When a steady state is attained, a thick condensed phase is formed at about the center of the cell as shown in Fig. 2. The thickness of the bulk condensed phase is at least 30 Å in low temperature cases and 60 Å or more in high temperature cases. After that, the simulation is continued until 10 ns and the configuration of molecules is sampled every 400 fs. This yields 25,000 samples. Since there are two interfaces in the cell, we have 50,000 samples in one simulation. The ensemble averages are evaluated from $N_e = 50,000$ sampled configurations.

In MD simulations, an averaged density can be calculated as

$$\rho = \frac{1}{N_s} \sum_p \sum_{i \in p} m^i,$$

where $\Xi_p$ is a volume element in the physical space, $m^i$ is the mass of the $i$th molecule ($m^i = m$, $m$ is the mass of a molecule). The summation $\sum_{i \in \Xi_p} m^i$ means the mass of the molecules inside $\Xi_p$. One can also calculate a flux $J$ by counting the number of molecules passing through a unit area per unit time, and then the ensemble-averaged flux is calculated as $\langle J \rangle = (1/N_s)\sum_{N_s}^\Xi J$. The averaged bulk vapor density (saturated vapor density) $\rho_v$, bulk liquid (or solid) density $\rho_e$, and $\langle J_{\text{coll}} \rangle_e$ and $\langle J_{\text{out}} \rangle_e$ obtained from the equilibrium simulations are shown in Table I, where $\langle J_{\text{coll}} \rangle_e$ is the mass flux of molecules incident on the interface in the equilibrium state. The numerical results show good agreement with corresponding experimental ones. Clearly, an equilibrium condition $\langle J_{\text{out}} \rangle_e = \langle J_{\text{coll}} \rangle_e$ is satisfied.

The averaged density profiles are shown in Fig. 4. Note that, here and hereafter, one of the two interfaces in a cell, facing in the positive $z$ direction, is presented and discussed. The density in the transition layer can be well fitted with a function,

$$\rho(z) = \frac{\rho_v + \rho_e}{2} + \frac{\rho_v - \rho_e}{2} \tanh\left(\frac{z - Z_m}{0.455\delta}\right),$$

where $Z_m$ denotes the center of the transition layer and $\delta$ the 10–90 thickness (see Table I). $Z_m$ and $\delta$ are obtained by a nonlinear least-squares method (Levenberg–Marquardt method$^{15}$). These values are affected by the simulation cell size and temperature. We introduce the following coordinate:

$$z^* = \frac{z - Z_m}{\delta},$$

and thus we can compare various physical quantities of different temperatures in the $z^*$ coordinate. As shown in Fig. 4, the bulk vapor phase is well developed in $z^* \approx 2$ for all cases of $T_e$.
B. Vacuum simulation

We now turn to the simulation method for evaporation into vacuum. As an initial condition for the vacuum simulation, a configuration at an arbitrary time in the vapor–liquid or vapor–solid equilibrium state of $T_e$ is used, for which $Z_m$ and $d$ are known. The periodic boundary conditions are applied in the $x$ and $y$ directions alone. The top and bottom of the cell are assumed to be open to the vacuum. Molecules can evaporate into vacuum but cannot come from vacuum. The number of molecules in the cell are therefore gradually reduced as time goes on. As a result, the thickness of the condensed phase decreases with time, and the transition layer moves in the negative $z$ direction, accordingly. Then, another coordinate transformation may be useful,

$$z^* = \frac{z - (Z_m - \nu_s t)}{\delta}, \quad \nu_s = \frac{J_s}{\rho_\ell},$$

(14)

where $t$ is the time from the beginning of the vacuum simulation, $J_s$ is a nonaveraged molecular flux evaporating into vacuum, and $\nu_s$ is the speed of the moving coordinate. Here, we use the same symbol $z^*$ as in Eq. (13), but this would not lead to confusion. At each time step, we estimate the evaporation flux $J_s$ at $z^* = L^*_g$, and eliminate the molecules in a region $z^* < L^*_g$, a virtual vacuum (see Fig. 5).

Using the velocity scaling method, we control the temperature of the condensed phase in the region $z^* < -L^*_g$ as shown schematically in Fig. 5. The size of $L^*_g$ is chosen so that the averaged temperature in the bulk condensed phase can be fixed to a specified $T_e$; we found that $L^*_g = 0, 0.5,$ and 1 give good results. Since $z^*$ is the moving coordinate, the molecules to which the velocity scaling is applied change with time. The temperature control technique is essential to realize a steady state. If an inadequate temperature control is applied, a steady state may not be realized or the reference temperature may not be determined uniquely. Our temperature control works well. In fact, the averaged temperature and density in the bulk condensed phase are almost uniform and equal to $T_e$ and $\rho_\ell$, respectively.

![FIG. 4. Density profiles around the interface in equilibrium simulations and vacuum simulations. The solid line represents Eq. (12) ($\Xi_e = L_x, \Sigma \Delta z^*, \Delta z^* = 0.1$). (a) $T_e = 85$ K. (b) $T_e = 130$ K.](image)

![FIG. 5. Schematic of simulation of evaporation into the virtual vacuum on the moving coordinate $z^*$ defined by Eq. (14).](image)
At the time when the number of molecules in a region $z^*<L_g$ decreases to 1000 due to the evaporation into vacuum, we stop the simulation in order to avoid sampling erroneous configurations. This sometimes leads to the shortage of the number of samples for ensemble averages. To compensate this, we execute seven more simulations starting from different initial conditions.

IV. RESULTS AND DISCUSSION

A. Spontaneous-evaporation flux and condensation coefficient in equilibrium state

The temporal evolution of molecular flux $\langle J_+ \rangle$ in the vacuum simulation is plotted for $T_e=85$ and $130$ K in Fig. 6. For the both temperatures, one can see that after an initial transient state, an almost steady state is realized and $\langle J_+ \rangle$ can be regarded as constant except for small fluctuation. In this figure, $\langle J_- \rangle$ is zero ($L_g^*=4.0$, $L_g^*=1.0$). Note that $\langle J_+ \rangle$ is defined at $z^*=L_g^*$.

In the steady evaporation state, the averaged fluxes are determined only by $L_g^*$ in the equilibrium state at low temperature. That is, the spontaneous-evaporation flux $\langle J_{\text{sp}}^{\text{evap}} \rangle$ certainly exists and can be defined by the net flux in the vacuum simulation:

$$\langle J_{\text{sp}}^{\text{evap}} \rangle = \langle J_+ \rangle - \langle J_- \rangle = \langle J_+ \rangle |_{z^*=L_g^*}.$$  \hfill (15)

The spontaneous-evaporation fluxes $\langle J_{\text{sp}}^{\text{evap}} \rangle$ obtained in the vacuum simulation are presented in Table II.

As shown in Fig. 6(a), the difference between $\langle J_{\text{out}} \rangle$ (broken line) and $\langle J_+ \rangle |_{z^*=L_g^*}$ (dash-dotted line) is small for $T_e=85$ K. This implies that $\langle J_{\text{out}} \rangle$ determined from Eq. (6) is small in the equilibrium state at low temperature. In the case of $T_e=130$ K shown in Fig. 6(b), $\langle J_{\text{out}} \rangle$ in the equilibrium state is considerably large compared with $\langle J_+ \rangle |_{z^*=L_g^*} = \langle J_{\text{sp}}^{\text{evap}} \rangle$. That is, $\langle J_{\text{out}} \rangle$ amounts to half or more of $\langle J_{\text{evap}} \rangle$ in the equilibrium state at $T_e=130$ K.

Once the flux $\langle J_{\text{sp}}^{\text{evap}} \rangle$ is obtained, the condensation coefficient in the equilibrium state $\alpha$ can be easily evaluated from its definition, Eq. (9). In Fig. 8 (see also Table II), we plot $\alpha$ for argon as a function of $T_e$. The results of previous MD simulations are also shown for comparison. As men-

<table>
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<th>$T_e$ (K)</th>
<th>$\langle J_{\text{sp}}^{\text{evap}} \rangle$ (g/cm$^2$s)</th>
<th>$\alpha$ (10$^{-3}$ g/cm$^3$ s$^{-1}$)</th>
<th>$\alpha p_e/2$ (10$^{-3}$ g/cm$^3$)</th>
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FIG. 6. $\langle J_\circ \rangle$ in vacuum simulations. (a) $T_e=85$ K, (b) $T_e=130$ K. In this figure, $\langle J_- \rangle$ is zero ($L_g^*=4.0$, $L_g^*=1.0$). Note that $\langle J_+ \rangle$ is defined at $z^*=L_g^*$.

FIG. 7. The spatial distribution of fluxes in the steady evaporation state in vacuum simulations ($T_e=85$ and $130$ K, $L_g^*=4.0$, $L_g^*=1.0$).

FIG. 8. Condensation coefficient $\alpha$ for argon at equilibrium conditions.
tioned in Sec. II, the previous authors counted reflected molecules in equilibrium states and evaluated \( \langle J_{\text{cond}} \rangle \) by using Eq. (7). Although some ambiguity is inevitably involved in such a treatment,\(^{10} \) the discrepancy of their results from ours is small except for the result in Ref. 21. It can be seen that \( \alpha \) approaches unity below the triple point and monotonically decreases as the temperature rises.

The temperature dependence of \( \alpha \) is qualitatively similar to those reported in several experimental studies for various materials other than argon (Thran et al.,\(^{22} \) Kossacki et al.\(^{23} \)). For example, Fujikawa et al.\(^{24} \) have conducted experimental studies on the condensation coefficient of methanol by combining a shock-tube experiment with an asymptotic analysis based on the kinetic theory. They have shown that \( \alpha \) is strongly affected by temperature and density conditions. The long history on the determination of the condensation coefficient can be found in Cammenga’s monograph.\(^{25} \)

**B. Velocity distribution of spontaneous evaporation**

We shall evaluate the velocity distribution of molecules evaporating into vacuum \( f_{\text{evap}} \). In MD simulations, a velocity distribution function \( f \) can be calculated as

\[
\hat{f} = \frac{1}{\rho N_s} \sum_{\Xi} \sum_{i=1}^{N_s} m^i, 
\]

where \( \hat{f} \) is the marginal distribution of the \( j \) component of molecular velocity \( (j=x,y,z) \), \( \Xi \) a one-dimensional volume element in the \( j \) direction in the molecular velocity space, and \( \Xi_p \cap \Xi_j \) four-dimensional one in the six-dimensional phase space.\(^{26} \) Note that \( \xi_j, \xi_y, \) and \( \xi_z \) are assumed to be independent random variables.\(^{27} \) In all cases, \( \hat{f}_x \) and \( \hat{f}_z \) are equal due to the isotropy in the \( (x,y) \) plane. The distributions of molecules evaporating into the vacuum at \( z^*=0, 2, \) and 4 are plotted for \( T_e = 85 \) K and 130 K in Fig. 9. The abscissa \( \xi_j = \xi_j/\sqrt{2RT_e} \) is the \( j \) component of normalized molecular velocity.

As shown in Figs. 9(a) and 9(d), at \( z^*=0 \) (center of the transition layer), all of \( \hat{f}_j \)'s agree with a solid curve, a one-dimensional normalized Maxwellian \( (1/\sqrt{\pi})\exp(-\xi_j^2) \).\(^{28} \) This means that molecules are in a local equilibrium state around \( z^*=0 \). When \( T_e = 85 \) K, at \( z^*=2, \hat{f}_z \) is distorted from Maxwellian [see Fig. 9(b)] and it develops into a one-dimensional normalized half-Maxwellian \( (2/\sqrt{\pi})\exp(-\xi_j^2/2) \exp(-\xi_z^2) \) at \( z^*=4 \) [Fig. 9(c)]. That is, in the three-dimensional form,

\[
\hat{f}_{\text{evap}} = 2\hat{f}^* (\xi_j > 0),
\]

where \( \hat{f}^* \) is the normalized Maxwellian defined in Eq. (2), \( \hat{f}_{\text{evap}} = \hat{f}^* \rho_v \), and \( \rho_v \) is the vapor density evaporating into vacuum. On the other hand, when \( T_e = 130 \) K, both \( \hat{f}_x \) and \( \hat{f}_z \)

**FIG. 9. Velocity distribution of molecules evaporating into vacuum in the case of \( L_s = 4 \). (a) \( T_e = 85 \) K and \( z^*=0 \), (b) \( T_e = 85 \) K and \( z^*=2 \), (c) \( T_e = 85 \) K and \( z^*=4 \), (d) \( T_e = 130 \) K and \( z^*=0 \), (e) \( T_e = 130 \) K and \( z^*=2 \), (f) \( T_e = 130 \) K and \( z^*=4 \). The solid curve indicates a one-dimensional normalized Maxwellian \( (1/\sqrt{\pi})\exp(-\xi_j^2) \) and the dashed curve a one-dimensional half-Maxwellian \( (2/\sqrt{\pi})\exp(-\xi_j^2/2) \exp(-\xi_z^2) \). The dotted curves are a Maxwellian with temperatures evaluated by MD simulations, \( \sqrt{T_e/(T_2-\pi)} \exp(-\xi_j^2/2) \exp(-\xi_z^2) \) with \( T_2 = 92.5 \) K at \( z^*=2 \) and \( T_2 = 84.1 \) K at \( z^*=4 \) \( (\Xi_x = L_x, \Delta z^*, \Delta z = 0.2, \Xi_x = \Delta z, \Delta \xi = 0.375) \).
become Maxwellian with lower temperatures [see Figs. 9(e) and 9(f)], and \( \hat{f} \) deviates from the half-Maxwellian at \( z^* = 4 \) [see Fig. 9(f)]. Zhakhovskii and Anisimov\(^{29} \) also examined the distribution function \( \hat{f} \) for evaporation into vacuum, and obtained the results similar to those in the present paper. Our results make \( f^p_{\text{evap}} \) more clear than their ones.

The vapor density evaporating into vacuum \( \rho_v \) can be evaluated from Eq. (11). The result is shown in Table II.

### C. Kinetic theory analysis for half-Maxwellian

In the preceding section, by using MD simulations, we have shown that \( f^p_{\text{evap}} \) is the half-Maxwellian in a low temperature case [Eq. (17)]. In this section, we shall analyze the behavior of the vapor evaporating into vacuum by using the kinetic theory of gases.

First, we shall analytically prove that \( f^p_{\text{evap}} = \alpha f^e (\xi_z > 0) \) if \( f^p_{\text{evap}} (= f^p_{\text{evap}} / \rho_s) \) is the half-Maxwellian with \( T_\ell \). Suppose that \( f^p_{\text{evap}} \) is the half-Maxwellian (17). Then,

\[
\langle J^p_{\text{evap}} \rangle = \int \xi f^p_{\text{evap}} d\xi = \rho_s \sqrt{\frac{2RT_\ell}{\pi}}.
\]

(18)

On the other hand, from the definition of \( \alpha \), Eq. (9),

\[
\langle J^p_{\text{evap}} \rangle = \alpha \langle J_{\text{out}}^e \rangle = \alpha \rho_v \sqrt{\frac{RT_\ell}{2\pi}}.
\]

(19)

Elimination of \( \langle J^p_{\text{evap}} \rangle \) from Eqs. (18) and (19) immediately gives

\[
\rho_c = \alpha \rho_v \frac{2}{\pi}.
\]

(20)

We therefore obtain

\[
f^p_{\text{evap}} = \alpha \rho_s f^* = \alpha f^e (\xi_z > 0)
\]

[see Eq. (2)]. Thus, the first term in Eq. (1) is validated physically.

In the above proof, Eq. (20) is a consequence deduced from the assumption that \( f^p_{\text{evap}} \) is the half-Maxwellian. However, the numerical result shows that Eq. (20) holds even in high temperature cases, where \( f^p_{\text{evap}} \) is not the half-Maxwellian [see Table II and Fig. 9(f)]. This may be explained as follows: although \( f^p_{\text{evap}} \) in the case of \( T_\ell = 130 \) K is distorted from the half-Maxwellian, the difference is limited for small \( |\xi| \), and therefore the difference in the mass fluxes is small [see Eq. (18)]. As a result, Eq. (20) holds approximately.

Second, we shall discuss the deviation from the half-Maxwellian in high temperature cases. To do so, we compare the velocity and temperature obtained from MD simulation and those evaluated using the kinetic theory on the assumption of the half-Maxwellian. In the kinetic theory, the velocity and temperature are given by

\[
v_j = \frac{1}{\rho} \int \xi_j f d\xi, \quad T_j = \frac{1}{\rho R} \int (\xi_j - v_j)^2 f d\xi.
\]

(22)

The temperature is retrieved by \( T = (T_x + T_y + T_z)/3 \). Substituting the half-Maxwellian \( f = 2\rho \alpha f^e (\xi_z > 0) \) into Eq. (22) gives

\[
v_x = v_y = 0, \quad v_z = \sqrt{\frac{2RT_\ell}{\pi}}.
\]

(23)

\[
T_x = T_y = T_\ell, \quad T_z = \left( 1 - \frac{2}{\pi} \right) T_\ell.
\]

(24)

Note that \( v_z \) and \( T_z \)'s are independent of \( \alpha \). On the other hand, in MD simulations, the velocity and temperature can be calculated as

\[
v_j = \frac{1}{\rho \sum_{i,j} N_i \sum_{ \sum_{\xi_j} } m^i \xi_j},
\]

(25)

\[
T_j = \frac{1}{\rho R \sum_{i,j} N_i \sum_{ \sum_{\xi_j} } m^i (\xi_j - v_j)^2},
\]

(26)

where \( \xi_j \) is the \( j \) component of molecular velocity of the \( i \)th molecule. From Fig. 10(a), we can confirm that, at \( z^* = 4 \) when \( T_\ell = 85 \) K, the results from MD simulation agree with those by the kinetic theory on the assumption of the half-Maxwellian. In the case of \( T_\ell = 130 \) K, however, the results from MD do not agree with those by the kinetic theory. In particular, the temperatures of tangential components to the interface \( T_x \) and \( T_y \) become definitely small compared with \( T_\ell \) [see also Figs. 9(e) and 9(f)].
The most important factor that leads to the deviation form the half-Maxwellian in high temperature cases may be the molecular interaction in the transition layer. The useful measure for the molecular interaction is the Knudsen number for the transition layer Kn. A very rough estimation of Kn is \(1/(\sqrt{2} \pi \sigma^3 (p_e/m) \delta)\), where \(\sigma = 3.405 \text{Å}\) [see Eq. (10)] and \(\delta\) is the 10–90 thickness of the transition layer in the equilibrium state [see Eq. (12)]. Since \(Kn = 43.1\) for \(T_e = 130\text{K}\), molecular collisions rarely happen in the transition layer in the low temperature case. Accordingly, the distribution function in the bulk condensed phase propagates toward the outside of the transition layer without deformation except for loosing the negative \(v^e\) component of molecular velocity. As a result, the vapor evaporates into the vacuum with the half-Maxwellian distribution. On the other hand, in the case of \(T_e = 130\text{K}, Kn = 0.8\) and therefore molecular collisions occur around \(v^e = 0\) [see Fig. 4(b)]. Since the intermolecular interaction promotes the local equilibration, \(f_x\) and \(f_z\) approach each other [see Figs. 9(e) and 9(e)].

V. CONCLUSIONS

Using the MD simulation of evaporation into vacuum, we have studied the physical appropriateness of the first term in the right-hand side of Eq. (1). First, we have demonstrated the existence of the spontaneous-evaporation flux \(\langle J^\text{evap}\rangle\) determined only by the temperature in the bulk condensed phase. The existence of \(\langle J^\text{evap}\rangle\) enables us to define \(\langle J^\text{red}\rangle\) and \(\langle J^\text{cond}\rangle\) by Eqs. (6) and (7), and hence the condensation coefficient \(\alpha\) in equilibrium state is determined without any ambiguity. We have found that \(\alpha\) is close to unity below the triple-point temperature and decreases as the temperature rises. Second, we have found that the distribution function of spontaneous evaporation \(f^\text{w}_{\text{evap}}\) is equal to the half-Maxwellian \(\alpha^e\chi^e\) for high temperature cases.

A number of analytical and numerical studies have so far been carried out in the area of molecular gas dynamics, where in addition to boundary condition, Eq. (1), the assumption of ideal gas also is important. By introducing \(1 - p_e/(p_e RT_e)\) as a measure of the deviation from the ideal gas, we have 0.03 for argon at 85 K and 0.28 at 130 K. The assumption of ideal gas may therefore be a good approximation for argon in low temperature cases treated here.

2. Y. Sone, Kinetic Theory and Fluid Dynamics (Birkhäuser, Boston, 2002).
3. The parameter \(\alpha\) in the first term in Eq. (1) is sometimes called the evaporation coefficient and distinguished from the condensation coefficient. See Eq. (8), and also, R. Meland and T. Ytrehus, “Evaporation and condensation Knudsen layers for nonunity condensation coefficient,” Phys. Fluids 15, 1348 (2003).

25. The volume element in the vacuum simulation is fixed on the moving coordinate defined by Eq. (14).
26. As a check of a necessary condition for statistical independence, we have confirmed that the correlation coefficients are small compared with unity.
27. Exactly speaking, the condensed phase has a velocity \(\approx (J^\text{evap})/p_e\) in the moving coordinate. However, it is too small to be seen in Figs. 9(a) and 9(d).