Comparison study on the calculation formula of evaporation mass flux through the plane vapour-liquid interface

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Abstract. In order to understand the influence of various factors on the evaporation rate on the vapor-liquid interface, the evaporation process of water in pure steam environment was calculated based on the statistical rate theory (SRT), and the results were compared with those from the traditional Hertz-Knudsen equation. It is found that the evaporation rate on the vapor-liquid interface increases with the increase of evaporation temperature and evaporation temperature difference and the decrease of vapor pressure. When the steam is in a superheated state, even if the temperature of the liquid phase is lower than that of the vapor phase, the evaporation may also occur on the vapor-liquid interface; at this time, the absolute value of the critical temperature difference for occurring evaporation decreases with the increase of vapor pressure. When the evaporation temperature difference is smaller, the theoretical calculation results based on the SRT are basically the same as the predicted results from the Hertz-Knudsen equation; but the deviation between them increases with the increase of temperature difference.

1. Introduction

The evaporation phenomenon exists widely in daily life and industrial production process, such as, spray drying, electronic cooling, spray printing, DNA detection and protein chip technology and so on, in which the calculation and control of evaporation rate has a very important influence on many industrial production process, and has already attracted the attention of many scholars [1-3].

Many factors will affect the interfacial evaporation rate, including gas composition, temperature, pressure and flow velocity and so on. When the evaporation of liquid is in the static pure steam environment, the evaporation mass flux $j_m$ can be calculated according to the theory of Classical Kinetic Theory (CKT) [4-7], in which Hertz-Knudsen-Schrage equation or Hertz-Knudsen equation is used commonly

$$j_m = \alpha \sqrt{\frac{M}{2\pi R}} \left[ \frac{P(T_l)}{\sqrt{T_l}} - \frac{P_v}{\sqrt{T_v}} \right] \quad (1)$$

In the formula, $M$ is the medium molar mass, $R$ the universal gas constant, $R=8.314 \text{ J/(mol·K)}$, $P_v$ the saturation pressure corresponding to interfacial liquid-phase temperature $T_l$, $P_v$ and $T_v$ as the vapor pressure and the vapor temperature respectively, and $\alpha$ the evaporation adaptation coefficient determined by the experiment.
The equation (1) shows that the relationship of the evaporation flux and the temperature difference between two sides of vapor-liquid interface is nonlinear. If the vapor and the liquid are in equilibrium state, $T_l = T_v$, then the evaporation flux $j_m = 0$, and no evaporation occurs. The Hertz-Knudsen equation (1) is linearized around equilibrium, and becomes the following form [8-9]

$$ j_m = \alpha \rho_v h_{fg} \sqrt{\frac{M}{2\pi R T_v}} (T_I - T_v) = \alpha \rho_v h_{fg} \sqrt{\frac{M}{2\pi R T_v}} \Delta T $$

in which, $\rho_v$ is the vapor density, $h_{fg}$ the latent heat of vaporization, $\Delta T$ the temperature difference between the liquid and vapor phases, namely, $\Delta T = T_l - T_v$.

It should be noted that both the equations (1) and (2) are the calculation formulas of vapor-liquid interfacial evaporation flux on basis of the experiment, in which the evaporation coefficient $\alpha$ is constant and is determined by the experiment. Therefore, Ward and Fang [10] derived the evaporation mass flux formula according to the Statistical Rate Theory (SRT) in 1999, which was certified by a series of experimental results [11-14]. Compared with the classical Hertz-Knudsen equation, there is no empirical constant in this expression, which not only can calculate the interfacial evaporation rate more accurately, but also can make up for the deficiencies of the classical kinetic theory that cannot reflect the interfacial non-equilibrium effect.

Based on the interfacial evaporating statistical rate theory and taking water as the working medium, this paper analyzes the effects of various non-equilibrium thermodynamic factors on the interfacial evaporation mass flux at the vapor-liquid interface. The results are compared with those of the classical Hertz-Knudsen equation.

2. Evaporation statistical rate theory

Take the single component steady evaporation system with the liquid phase, the vapor phase and the interface, as shown in figure 1. The temperatures of vapor phase and liquid phase in the vapor-liquid interface were $T_I^V$ and $T_I^L$, the vapor pressure $P_v^*$, the saturation pressure $P_s(T_I^L)$ corresponding to the liquid phase temperature. To maintain steady state evaporation, the liquid is continually supplied from the bottom part, and the steam from evaporating is continuously removed from the upper part. The liquid supplement rate should be equal to the evaporation rate to maintain the vapor-liquid interfacial position. Simultaneously, the liquid phase is touched with the constant temperature heat source $T_I^L$, and all the heat for vaporization comes from the heat source.

![Figure 1. Schematic diagram of a single component steady state evaporation system.](image)

For simplicity, assume that the interfacial thickness is zero, so there is no adsorption process at the interface. Namely, a liquid-phase molecule enters the vapor phase through the interface and does not stay at the interface, and vice versa. Meanwhile, each phase of vapor and liquid is homogeneous and all the intensive parameters are constant. According to the statistical rate theory, the evaporation mass rate at the vapor-liquid interface can be deduced [10-14]:

\[ j_m = \alpha \rho_v h_{fg} \sqrt{\frac{M}{2\pi R T_v}} \Delta T \]
pressure and the vapor pressure increase, so the interfacial evaporation rate increased rapidly with the increase of temperature, which makes the difference between the saturation vapor pressure and the liquid phase pressure constant, so the interfacial evaporation flux increases linearly with the increase of temperature difference, as shown in figure 2 (b). Special attention should be paid to that the evaporation interface is flat, the curvature radius of the interface is \( r_i = 0 \), and the equation (7) becomes \( \rho = \rho_i^{LV} \).

3. Results and discussion

The working medium is water, the atomic number is \( n = 3 \), and the molar mass is \( M = 0.018015 \text{ kg/mol} \). For the sake of simplicity, assume that the evaporating vapor-liquid interface is flat and the thermodynamic properties of water and steam are calculated according to the method in the literature [15]. Vibrational frequency of covalent bond of water molecules includes symmetric stretching vibration frequency, anti-symmetric stretching vibration frequency and flexural vibration frequency. Stretching vibration frequency is usually about 2 times of flexural vibration frequency. The values for the vibrational frequencies of water molecules include symmetric stretching \( \omega_s \) as the surface tension of vapor-liquid interface, \( \theta \) as the characteristic temperature, \( \omega_i \) as the phonon frequency, and \( q_{iv} \) as the vibrational partition function. If the evaporation interface is flat, the curvature radius of the interface is \( r_i = 0 \), and the equation (7) becomes \( \rho = \rho_i^{LV} \).

\[
\begin{align*}
\Delta s_{LV} &= 4 \left( 1 - \frac{T_i^L}{T_i^V} \right) + \ln \left[ \frac{T_i^V}{T_i^L} \right] + \ln \left[ \frac{p_i}{p_i^{LV}} \right] \left[ \frac{q_{iv} (T_i^L)}{q_{iv} (T_i^L)} \right] \\
&\quad + \left( \frac{1}{T_i^V} - \frac{1}{T_i^L} \right) \sum_{i=1}^{n} \left[ \frac{\theta_i}{2} + \frac{\theta_i}{e^{\theta_i/T_i^V} - 1} \right] + \frac{\omega_i (T_i^L)}{k_b T_i^L} \left[ p_i^{LV} - p_i (T_i^L) \right] \\
q_{iv} (T) &= \sum_{i=1}^{n} e^{\omega_i/T_i} \frac{\theta_i}{\theta_i - e^{\omega_i/T_i} - 1} \quad \theta_i = \frac{\hbar \omega_i}{2 \pi k_b}
\end{align*}
\]
when the steam is saturated, if the liquid-phase temperature is lower than the steam temperature $\Delta T<0$, the liquid phase must be in a supercooled state, and not the evaporation process but the condensation process occurs at the vapor-liquid interface, so the interfacial evaporation flux is negative value.

Figure 2. Variation of evaporation mass flux with the liquid-phase temperature (a) and evaporation temperature difference (b) in saturated steam environment.

In the experimental studies on vapor-liquid interfacial evaporation phenomenon [11-14], the continuous pumping on the steam chamber is to maintain a constant pressure. At this time, the steam is usually in a superheat state. When the steam is superheated, a new parameter $\eta$ is introduced to describe the superheat degree and is defined as the ratio of steam pressure and saturation pressure corresponding to steam temperature, i.e.

$$\eta = \frac{P_v}{P^*_v} \left( T^*_v \right)$$

(9)

Obviously, $\eta$ is smaller, the superheat is higher; $\eta=1$ means the saturated steam.

Figure 3. Variation of evaporation mass flux with the liquid-phase temperature (a) and temperature difference (b) in superheated steam environment at $\eta=0.5$.

Figure 3 gives the variation of evaporation mass flux with the liquid-phase temperature and the evaporation temperature difference in superheated steam environment at $\eta=0.5$. Overall, the variation of mass flux in the superheated steam is similar to that in the saturated vapor. However, there are three differences. (1) Because the steam is superheated, the pressure dropped, the vapor-phase chemical potential decreased, the chemical potential difference between liquid phase and vapor phase as the vaporizing driving force increased, so the interfacial evaporation mass flux increased. (2) The chemical potential of the pure substance is not only related to the pressure, but also depends on the temperature. The lower the pressure is and the higher the temperature is, the lower the chemical potential is. Therefore, when the steam is in the superheated state, even if its temperature is higher than the liquid-
phase temperature $\Delta T = T_l - T_v < 0$, it also ensures that the chemical potential of the vapor phase is lower than that of the liquid phase. Therefore, the evaporation process can still be carried out and evaporation mass flux is still positive value, which has been confirmed by a large number of experimental results [11-14]. (3) Due to the superheated steam, the Clausius-Clapeyron equation is no longer applicable, and the evaporation mass flux no longer increases linearly with the increase of evaporation temperature difference, as shown in figure 3 (b).

From figure 2, when the steam is saturated, if the liquid-phase temperature is lower than the steam temperature, $\Delta T < 0$, not the evaporation but the condensation occurs on the interface. When the steam is superheating, whether the evaporation process occurs or not depends on the two phase temperature difference and the vapor-phase pressure. Obviously, when the liquid-phase temperature is low enough, the condensation process will occur. Figure 4 shows the critical conditions whether the evaporation process can occur on the interface under two typical liquid-phase temperatures. The left-upper part is the evaporation region, and the right-lower part is the condensation region. The absolute value of the critical temperature difference in the evaporation process decreases with the increase of the vapor-phase pressure. At $\eta = 1$, the steam is saturated and the vapor and the liquid are in equilibrium state, therefore, $\Delta T_{cr} = 0$.

Compared with the traditional Hertz-Knudsen equation, the greatest merit of the SRT theory for calculating the evaporation rate on the vapor-liquid interface is that it does not require any empirical constant or coefficient, and is a pure theoretical calculation formula. The comparison between the two calculation results of evaporation mass flux for water is shown in figure 5. Here, the evaporation adaptation coefficient $\alpha$ in equation (1) is fittingly determined according to the calculation results of
the SRT. From the figure, when the steam is saturated and the evaporation temperature difference is small, the calculated results of SRT theory are very close to those of the Hertz-Knudsen equation, which is in the vicinity of the equilibrium state. As long as the suitable evaporation coefficient is selected, both calculation results are basically the same. However, when the temperature difference is larger, such as, $\Delta T=8K$, the difference between the calculated results increases, and the increasing speed of the evaporation rate predicted by SRT theory with the liquid-phase temperature is slower than that of the Hertz-Knudsen equation. On the other hand, when the vapor is in a superheat state, the difference of the evaporation rate between the two indicating results increases, as shown in figure 5 (b).

4. Results and discussion

The evaporation process of water in pure steam environment was calculated by adopting the statistical rate theory (SRT), and the main factors that affect the interfacial evaporation rate were analyzed. The calculation results were compared with those of the traditional Hertz-Knudsen equation, and the main conclusions were as follows: (1) the evaporation rate of vapor-liquid interface increases with the increase of evaporation temperature difference and evaporation temperature and the decrease of vapor pressure; (2) when the steam is in a superheated state, even if the liquid-phase temperature is lower than the vapor-phase temperature, the evaporation may also occur. At this point, the absolute value of the critical temperature difference decreases with the increase of vapor pressure; (3) when the evaporation temperature difference is smaller, the calculation results for the SRT theory and the Hertz-Knudsen equation are basically the same, but the deviation increases with the increase of temperature difference.

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