PERGAMON

International Journal of Heat and Mass Transfer 44 (2001) 1681–1686

International Journal of
HEAT and MASS
TRANSFER

www.elsevier.com/locate/ijhmt

Thermodynamic aspect of the shift of concave liquid–vapor interfacial phase equilibrium temperature and its effect on bubble formation

J.T. Zhang, B.X. Wang *, X.F. Peng

Department of Thermal Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 14 April 2000; received in revised form 27 June 2000

Abstract

The thermodynamic analysis conducted here demonstrates that the capillary pressure discontinuity at the concave liquid–vapor interface could promote interfacial evaporation. The phase equilibrium temperature of the concave liquid interface decreases with increasing surface tension and/or decreasing radius of curvature of the concave liquid–vapor interface. The shift of phase equilibrium temperature and, hence, of latent heat implies that interfacial evaporation may even occur at a temperature lower than the nominated saturation temperature. According to these analytical results, bubbles can initiate from active cavities as long as the temperature of the liquid microlayer under the bubbles is higher than the phase equilibrium temperature, which may even be lower than the nominated saturation temperature. The conclusion is consistent with experimental observations about bubble formation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial evaporation; Surface tension; Bubble formation

1. Introduction

The phase change at the liquid–vapor interface is of great importance in many heat transfer phenomena, such as bubble formation, evaporation at the liquid–vapor interface, mass transport phenomena in porous materials, etc. A good understanding of evaporation or phase change phenomena at the liquid–vapor interface is crucial to the realization of the corresponding mechanisms of the abovementioned processes. Many efforts [1–15] have been made to investigate the liquid–vapor interfacial phase-change phenomena. An interfacial evaporation model has been proposed from molecular kinetic analysis [1,2] such that

$$J = \left(\frac{\alpha}{2-\alpha}\right)\left(\frac{M}{2\pi R}\right)^{1/2}\left[\frac{P_{\mathrm{iv}}}{T_{\mathrm{iv}}^{1/2}} - \frac{P_{\mathrm{v}}}{T_{\mathrm{v}}^{1/2}}\right], \tag{1}$$

where J is the interfacial evaporation mass flux per unit interface area, α the accommodation coefficient, M the molar weight of the vapor, P_{iv} the interfacial vapor pressure, T_{iv} the saturation temperature with respect to interfacial pressure, P_{v} the bulk vapor pressure away from the interface, T_{v} the bulk vapor temperature with respect to the pressure P_{v} and R is the universal gas constant. From Eq. (1), the driving force for evaporation is the pressure difference between the interfacial and bulk vapor pressures. If the interfacial temperature T_{iv} is taken as approximately equal to the bulk vapor temperature T_{v}, i.e., $T_{\mathrm{iv}} = T_{\mathrm{v}}$, the interfacial evaporation will be driven by the interfacial and the bulk vapor pressure difference from the viewpoint of molecular kinetics. This driving pressure difference can be effectively changed so as to produce supersaturated bulk vapor for condensation or to superheat bulk vapor for evaporation.

The difference between interfacial and bulk vapor can also result from the effect of surface tension. This is the basis for many interfacial phenomena and applications, such as bubble formation, processes in heat pipes, etc. As a result, studies of interfacial evaporation by the

---

* Corresponding author. Tel.: +86-10-6278-4530; fax: +86-10-6277-0209.

E-mail address: bxwang@mail.tsinghua.edu.cn (B.X. Wang).

PII: S0017-9310(00)00224-6

Nomenclature

f	fugacity
ΔH^{i}	ideal molar heat of vaporization
h_{fg}	latent heat of liquid
J	interfacial evaporation mass flux
K	curvature of the liquid–vapor interface
M	molar weight of vapor
P	pressure
R	universal gas constant
r_e	effective radius of interface curvature
T	temperature
w	molecular interaction potential
U	molar cohesive energy
V	specific volume
v	molar volume
X	concentration
Greek symbols	
Π	dispersion force
α	accommodation coefficient
κ	Boltzman constant
μ	chemical potential
μ^{i}	cohesive energy
ρ	density
σ	surface tension
Subscript	
iv	liquid–vapor interface
l	liquid
v	vapor

effect of surface tension have attracted much attention in the last two decades, among which the viewpoint of Wayner and his co-workers [4–11] prevails. They have proposed an expression for the description of interfacial evaporation on the liquid–vapor interface, as:

$$J = C\left(\frac{M}{2\pi R T_l}\right)^{1/2}\left[\frac{P_v M h_{fg}}{R T_v T_{iv}}(T_{iv} - T_v) - \frac{v_l P_v}{R T_{iv}}(\Pi + \sigma K)\right], \tag{2}$$

where v_l is the molar volume of vapor, Π connects with the dispersion force of extremely thin films, σ is the surface tension and K is the curvature of the interface. The first term on the right-hand side of Eq. (2) reflects the effect of superheat, which demonstrates the role of wall heating and drives interfacial evaporation. The second term on the right-hand side of Eq. (2) is treated as the interfacial resistance resulting from the surface tension and the dispersion force. Here, the dispersion force is neglected and the curvature, K, is a positive value for the concave liquid–vapor interface. However, the conclusion to consider the resistance of surface tension to interfacial evaporation is questionable.

Consideration of interfacial evaporation is generally based on the Kelvin equation [1,16], and interfacial interaction analysis [17] gives

$$P_v = P_{iv}\exp\left(-\frac{2\sigma}{r_e \rho_l R T_l}\right), \tag{3}$$

where r_e is the effective capillarity radius of liquid–vapor interface curvature, σ the surface tension and ρ_l is the liquid density. Assuming the term in the bracket to be small, Eq. (3) can be approximately expressed by the following polynomial as

$$P_v = P_{iv}\left\{1 - \frac{2\sigma}{r_e \rho_l R T_l} + O\left[\left(\frac{2\sigma}{r_e \rho_l R T_l}\right)^2\right]\right\} \tag{4}$$

and, hence,

$$P_{iv} - P_v \cong \frac{2 P_{iv}\sigma}{r_e \rho_l R T_l}. \tag{5}$$

This shows that the pressure difference ($P_{iv} - P_v$) would be positive if interfacial tension existed.

For a saturated, flat liquid–vapor interface, as shown by the dashed line in Fig. 1, there is no pressure difference between the vapor and the liquid neighboring the interface because the liquid and vapor are in thermodynamic equilibrium. However, if the interface is concave, as shown by the solid line in Fig. 1, by the use of Fig. 2, (μ being the chemical potential), it can be seen [17] that, as the liquid pressure goes down due to capillarity according to the Young–Laplace equation, the saturated liquid state B gets into the metastable superheated state a. In this case, outside disturbance easily makes this metastable superheated liquid evaporate to the saturated vapor state b, with $\mu_b = \mu_a$ for thermal equilibrium and $\mu_b < \mu_a$ for non-equilibrium. The saturated vapor evaporates from the liquid–vapor interface and move into the bulk vapor with the reduction of vapor pressure due to kinetics. This saturated vapor

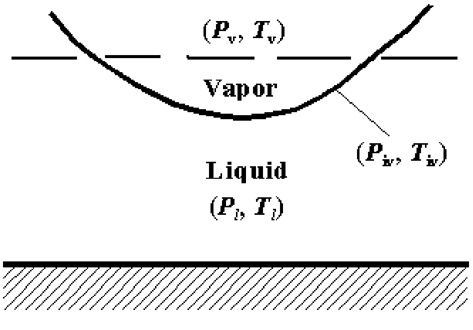


Fig. 1. The diagram of the physical model.

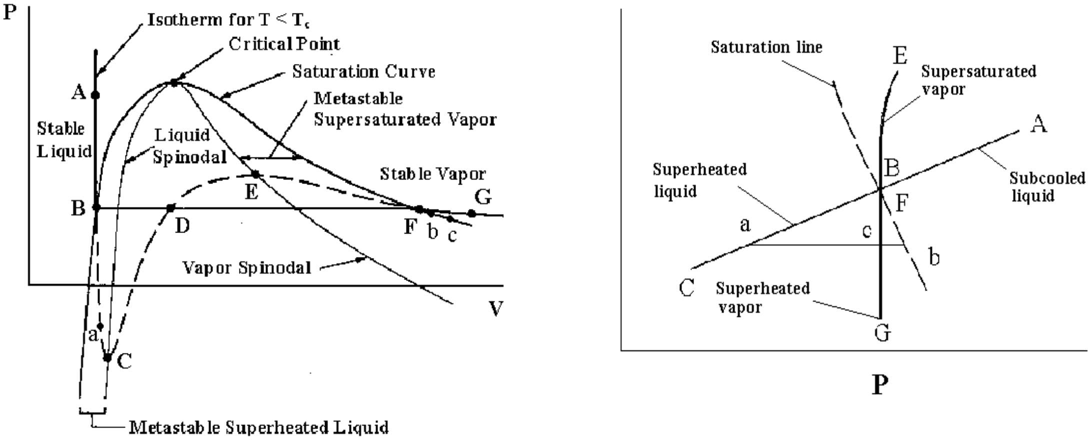


Fig. 2. *P–V* diagram and *μ–P* diagram [16].

state b is further transformed into superheated vapor state c under the given vapor pressure. Thus, a positive pressure difference between the interfacial and bulk vapors promotes interfacial evaporation. Referring to the thermodynamic analysis of Udell [16], we have [18]

$$RT_{\mathrm{iv}} \ln \frac{P_{\mathrm{iv}}}{P_{\mathrm{v}}} = (P_{\mathrm{iv}} - P_{\mathrm{l}})V_{\mathrm{l}} \tag{6}$$

and

$$\frac{P_{\mathrm{iv}} - P_{\mathrm{v}}}{P_{\mathrm{iv}} - P_{\mathrm{l}}} \cong \frac{V_{\mathrm{l}}}{V_{\mathrm{v}}}, \tag{7}$$

where V_{l} and V_{v} are the specific volumes of the liquid and vapor, respectively.

The present paper will focus on the thermodynamic aspect for detecting the effect of shifting phase equilibrium temperature and latent heat on interfacial evaporation and bubble formation.

2. The shift of phase equilibrium temperature of interfacial capillary evaporation

Suppose the interfacial evaporation process is to be in asymptotic equilibrium, the Clausius–Clapeyron equation is applied as

$$\frac{1}{P}\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{Mh_{\mathrm{fg}}}{RT^2}. \tag{8}$$

This indicates that increase in pressure would bring about a rise in temperature.

Integrating Eq. (8) through the path from (P_{l}, T_{l}) to (P_{iv}, T_{iv}) yields

$$\ln \frac{P_{\mathrm{iv}}}{P_{\mathrm{l}}} = \frac{(T_{\mathrm{iv}} - T_{\mathrm{l}})Mh_{\mathrm{fg}}}{RT_{\mathrm{iv}}T_{\mathrm{l}}}. \tag{9}$$

For a small pressure change, Eq. (9) can be approximated by the Taylor expansion to yield

$$P_{\mathrm{iv}} - P_{\mathrm{l}} = \frac{P_{\mathrm{l}}(T_{\mathrm{iv}} - T_{\mathrm{l}})Mh_{\mathrm{fg}}}{RT_{\mathrm{iv}}T_{\mathrm{l}}}, \tag{10}$$

where T_{l} is the phase equilibrium temperature with respect to liquid pressure P_{l}.

As indicated by the approximated Kelvin equation and Eq. (7), the pressure difference ($P_{\mathrm{iv}} - P_{\mathrm{l}}$) is positive for the concave interface and related to the interfacial capillary pressure discontinuity. An increase in surface tension or decrease in radius of the interface curvature increases the pressure difference. So, the phase equilibrium temperature of liquid declines according to Eq. (10), implying that the liquid microlayer beneath the nucleated vapor gets into its superheated state at a lower temperature compared to the general saturation temperature with respect to interfacial or bulk vapor pressure. As a result, interfacial capillary evaporation from the metastable liquid microlayer occurs if its temperature is higher than the phase equilibrium temperature determined by Eq. (10); this indicates that interfacial phase change can occur at a temperature lower than the nominated phase-change temperature when the interface is concave, i.e., the concave liquid–vapor interface could promote interfacial evaporation.

As indicated by the Young–Laplace equation, the bulk liquid pressure of the concave interface decreases due to the action of surface tension. Based on the well-known fundamental thermodynamic relation,

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{1}{\rho}, \tag{11}$$

a fall in liquid pressure results in a decrease in chemical potential, μ, of the liquid adjacent to the interface.

Referring to molecular interaction, the chemical potential μ comprises the cohesive energy of molecules, μ^{i}, and the thermal energy associated with entropy, $\kappa T \ln X$, such that [19]

$$\mu = \mu^{\mathrm{i}} + \kappa T \ln X, \tag{12}$$

where X is the concentration and κ is the Boltzmann constant. As indicated by Eq. (12), since X is invariant, the decrease of chemical potential leads to a decrease in the cohesive energy μ_1^{i}.

As demonstrated by Israelachvili [19] the liquid cohesive energy, μ_{l}, is related to the molecular interaction potential, w, by

$$\mu_1^{\mathrm{i}} \approx nw, \tag{13}$$

where n ranges from 4 to 6 depending on the molecule. Since the molecular interaction potential, w, is always negative, a decrease in μ_1^{i} results in the increase of the absolute value of w as well as μ_1^{i}. The molar cohesive energy U is related to the molecular interaction potential by [19]

$$U = -N_0 nw \tag{14}$$

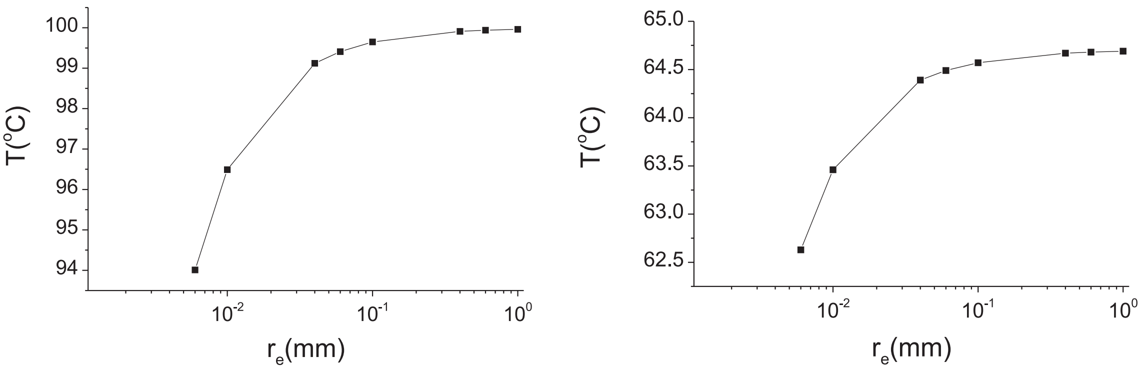
and the latent heat of vaporization, h_{fg}, is related to U as [19]

$$h_{\mathrm{fg}} = U + RT_{\mathrm{iv}}, \tag{15}$$

where T_{iv} is the liquid–vapor phase change interfacial temperature. Eqs. (14) and (15) show that the increase in the absolute value of the molecular interaction potential, w, leads to an increase in the latent heat of vaporization and decrease in the relevant saturation temperature. This conclusion indicates that interfacial capillary evaporation occurs at a lower temperature with a higher latent heat for the concave liquid–vapor interface.

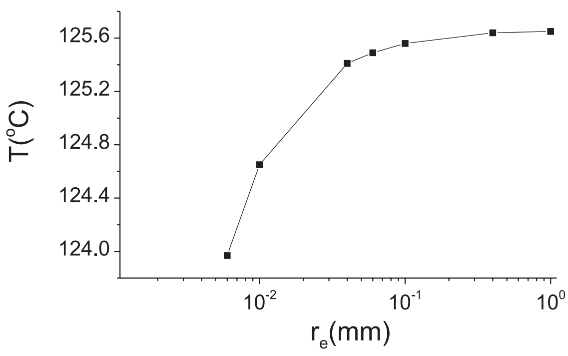
3. On bubble formation

Bubbles are considered generally as being formed from active gas cavities of the heated wall [1,20,21]. Gas can be entrapped in some cavities if the cavity side angle and the contact angle of the filling liquid meet some



(a) water

(b) methanol



(c) octane

Fig. 3. Variation of phase equilibrium temperature with the effective radius of the interface curvature: (a) water; (b) methanol; (c) octane.

criteria. From this viewpoint, bubble formation is based on the interfacial evaporation mechanism. The liquid microlayer exists between the bubble and the heated wall in the active cavity. It is assumed primarily that vapor evaporates from the interface if the temperature within the microlayer is slightly higher than the saturation value with respect to the pressure of the liquid, and the bubble forms and grows as long as the wall heat flux or the superheating is sufficient. Accordingly, interfacial evaporation plays a role in the process of bubble formation. The required superheat for the bubble formation is [1]

$$[T_\mathrm{l} - T_\mathrm{sat}(P_\mathrm{l})] > \frac{2\sigma T_\mathrm{sat} v_\mathrm{v}}{h_\mathrm{fg} r}, \tag{16}$$

where $T_\mathrm{sat}(P_\mathrm{l})$ is the saturation temperature with respect to the liquid pressure P_l and r is the required radius of the liquid microlayer curvature of the active cavity. Eq. (16) indicates that, if the cavity is active, the bubble can form in the case of the liquid temperature being higher than the saturation temperature of the liquid with respect to local pressure and the wall being heated to reach or exceed the required superheated temperature.

However, experimental observations have been reported in open literature to show that bubble formation may occur even though the temperature of the heated wall is lower than the liquid saturation temperature at the local pressure. We suppose that this disagreement comes from the fact that Eq. (16) does not involve the effects of interfacial evaporation of the liquid microlayer. As is being analyzed, the pressure discontinuity caused by the capillarity of the concave interface of an active cavity can increase the latent heat and decrease the interfacial phase-change temperature of its liquid microlayer. Accordingly, the bubble may form and grow though the liquid temperature is lower than the saturation value with respect to the vapor pressure, as long as interfacial evaporation is sufficient to sustain this bubble formation. Based on Eq. (15), variations of the phase equilibrium temperature of the liquid microlayer with the radius of liquid interface curvature have been predicted as shown in Fig. 3, where water, methanol and octane were chosen as the working substances. For water, the phase equilibrium temperature of an assumed active cavity with a radius of 10 μm can be 3°C lower than the saturation temperature with respect to the pressure of the cavity vapor, which implies that the bubble can form and grow at a temperature lower than the nominated saturation temperature. As a result, this bubble formation temperature is a little lower than the superheat predicted by Eq. (16).

As there exist suitable limits for the cavities to be active, it should be noted that the radii of active cavities cannot be arbitrarily small. However, Fig. 3 illustrates that the higher the surface tension, the stronger its influence on the phase equilibrium temperature. The surface tension of saturated water at standard atmospheric pressure is much higher than that of octane, and, hence, the shift of phase equilibrium temperature is obvious for water but much less so for octane.

4. Conclusions

The thermodynamic analysis conducted in this paper demonstrates that the pressure discontinuity due to the capillarity of the concave liquid–vapor interface shifts the phase equilibrium temperature and corresponding latent heat and therefore promotes interfacial evaporation. The application of these results in the microlayer evaporation model for bubble formation indicates that bubbles can be formed from active cavities at a temperature lower than the nominated saturation temperature. The prediction for water, methanol and octane demonstrate that the shift effect is more obvious for substances with high surface tension, such as water. These conclusions are consistent with the experimental observations that bubbles can be formed before the normal superheat, or even the nominated saturation temperature, is reached.

Acknowledgements

The project is financially supported by the National Natural Science Foundation of China, Grant No. 59995550-3. The discussion on bubble formation with Professor G.P. Peterson of Texas A&M University (USA) is also acknowledged.

References

[1] V.P. Carey, Liquid–Vapor Phase-Change Phenomena: An Introduction to The Thermophysics of Vaporization and Condensation Process In Heat Transfer Equipment, Hemisphere, Washington, DC, 1992, pp. 112–120.

[2] I.W. Eames, N.J. Marr, H. Sabir, The evaporation coefficient of water: a review, Int. J. Heat Mass Transfer 40 (12) (1997) 2963–2973.

[3] B.V. Deryagin, S.V. Nerpin, N.V. Churayev, Effect of film transfer upon evaporation of liquids from capillaries, Bull. RILEM 29 (1965) 93–98.

[4] M. Potash, P.C. Wayner, Evaporation from a two-dimensional extended meniscus, Int. J. Heat Mass Transfer 15 (1972) 1851–1863.

[5] P.C. Wayner, Y.K. Kao, L.V. Lacroix, The interline heat-transfer coefficient of an evaporating wetting film, Int. J. Heat Mass Transfer 19 (1976) 487–492.

[6] C. Peter, P.C. Wayner, The effect of interfacial mass transport on flow in thin liquid films, Colloids and Surfaces 52 (1991) 71–84.

[7] S. DasGupta, J.A. Schonberg, P.C. Wayner, Investigation of an evaporating extended meniscus based on the augmented Young–Laplace equation, J. Heat Transfer 115 (1993) 201–208.

[8] S. DasGupta, I.Y. Kim, P.C. Wayner, Use of the Kelvin–Clapeyron equation to model an evaporating curve microfilm, J. Heat Transfer 116 (1994) 1007–1015.

[9] P.C. Wayner, Thermal and mechanical effects in the spreading of a liquid-film due to a change in the apparent finite contact-angle, J. Heat Transfer 116 (1994) 938–945.

[10] P.C. Wayner, Interfacial forces and phase change in thin liquid films, in: C.L. Tien, A. Majumdar, F.M. Gerner (Eds.), Microscale Energy Transport, Taylor & Francis, Washington, 1997.

[11] I.Y. Kim, P.C. Wayner, Shape of an evaporating completely wetting extended meniscus, J. Thermophys. Heat Transfer 10 (2) (1996) 320–325.

[12] Y. Kobayashi, S. Ikeda, M. Iwasa, Evaporative heat transfer at the evaporative section of a grooved heat pipe, J. Thermophys. Heat Transfer 10 (1) (1996) 83–89.

[13] D. Khrustalev, A. Faghri, Thermal analysis of a micro heat pipe, J. Heat Transfer 116 (1994) 189–198.

[14] D. Khrustalev, A. Faghri, Heat transfer during evaporation on capillary-grooved structures of heat pipes, J. Heat Transfer 117 (1995) 740–747.

[15] D. Khrustalev, A. Faghri, Thick-film phenomenon in high-heat-flux evaporation from cylindrical pores, J. Heat Transfer 119 (1997) 272–278.

[16] K.S. Udell, Heat transfer in porous media heated from above with evaporation, condensation, and capillary effects, J. Heat Transfer 105 (1983) 485–492.

[17] B.X. Wang, J.T. Zhang, X.F. Peng, The effect of interfacial evaporation on heat and mass transfer of falling liquid film, Science in China Series E 30 (3) (2000) 216–221.

[18] J.T. Zhang, B.X. Wang, X.F. Peng, The capillary pressure for concave liquid–vapor interface and its effect on interfacial evaporation (paper submitted to Science in China, Series E, May 2000).

[19] J.N. Israelachvili, Intermolecular and Surface Forces, second ed., Academic Press, San Diego, 1991, pp. 176–212.

[20] C.H. Wang, V.K. Dhir, On the gas entrapment and nucleation site density during pool boiling of saturated water, J. Heat Transfer 115 (1993) 670–679.

[21] V.K. Dhir, Boiling heat transfer, Annu. Rev. Fluid Mech. 30 (1998) 365–401.