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# Interfacial behaviour of growing bubbles in concentration boundary layer

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**Abstract**

The vapor bubble interface for nucleate pool boiling of a binary mixture subjects to both concentration gradient and temperature gradient, which give rise to interfacial shear, and may create Marangoni flow. A proposed microwedge model is adopted to demonstrate that, variation of surface tension along microwedge interface would be beneficial for liquid layer merging each other, and consequently, detaching fully grown bubbles from the heated surface even under microgravity. This is in quite good agreement with the experimental observations in the literature. The model can be further extended to explain pool boiling phenomena of binary mixtures at high heat fluxes or even CHF under microgravity. © 1998 Elsevier Science Ltd. All rights reserved.

**Nomenclature**

| | |
|---|---|
| $a$ | constant |
| $b$ | constant |
| $A$ | constant, surface area [m$^2$] |
| $B$ | surface area [m$^2$] |
| $Bo$ | Bond number |
| $h_{fg}$ | latent heat [W kg$^{-1}$ K] |
| $k$ | curvature [m$^{-1}$] |
| $\dot{m}(x)$ | mass flow rate [kg s$^{-1}$] |
| $p, P$ | pressure [N m$^2$] |
| $\dot{q}, q''$ | heat flux [W m$^{-2}$] |
| $r$ | bubble radius [cm] |
| $R$ | dimensionless variable |
| $s$ | interface tangential direction [m] |
| $T$ | temperature [°C] |
| $u$ | velocity [m s$^{-1}$] |
| $x$ | component concentration, mass percentage, $x$ direction coordination |
| $y, z$ | coordinations. |

*Greek symbols*

| | |
|---|---|
| $\theta$ | liquid superheat [°C] |
| $\sigma$ | surface tension [N m$^{-1}$] |
| $\xi, \lambda$ | dimensionless variables, constant |
| $\gamma$ | activity coefficient [N s m$^{-2}$] |
| $\mu$ | viscosity [N s m$^{-2}$] |
| $\delta$ | concentration boundary thickness, liquid layer thickness [m]. |

*Subscripts*

| | |
|---|---|
| l | liquid |
| lg | liquid–gas interface |
| w | wall surface |
| $\infty$ | bulk liquid |
| s | saturated liquid |
| 1 | component 1 |
| 2 | component 2. |

## 1. Introduction

There is much published information regarding experiments on pool boiling of mixtures, and considerable effort has been made to develop physical models describing the phenomena. The pool boiling heat transfer rate of binary mixtures is generally lower than that of an equivalent ideal pure component. Most of the investigators attribute the lower heat transfer coefficients in the mixtures to the additional mass diffusion resistance of the volatile component to the vapor bubble. Several

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semi-empirical correlations for the prediction of the boiling heat transfer coefficient are available in the literature [1–3]. It can be seen that most of these correlations were derived assuming that vapor bubbles grew in a uniformly superheated infinite liquid. However, it is not true for vapor bubbles growing on a heated surface. Thus, despite decades of efforts, there is still a lack of techniques and methods for the prediction of nucleate pool boiling heat transfer of binary mixtures.

It is well known that surface tension is a strong function of component concentration. In the so-called positive binary systems, the volatile component has a lower surface tension. Hovestreijdt [4] demonstrated that surface tension gradients along the vapor-liquid interfaces between neighboring bubbles may build up due to concentration gradients caused by preferential evaporation. This is probably the earliest study on the effect of concentration gradients on boiling of mixtures. More recently, Abe et al. [5] have conducted pool boiling experiments with non-azeotropic water-ethanol mixtures under 10 s microgravity conditions available from a drop shaft facility with a 490 m free fall, from which they concluded that boiling heat transfer is enhanced under microgravity compared with terrestrial conditions due to the Marangoni effect in positive binary mixtures caused by concentration gradient. This phenomena will be focused in the present study. Examining the role of Marangoni effect on boiling will not only be beneficial for proposing more satisfactory heat transfer correlations, but will also provide some new insight into our fundamental understanding of the heat transfer mechanism of binary mixtures both under microgravity and under terrestrial conditions. The study of Marangoni effect caused by concentration gradient would be an area that merits further study.

Another portion of the current investigation presents a renewed effort in the study of the bubble detachment mechanism, especially under microgravity. Boiling heat transfer will play an important role in future thermal engineering in space. Siegel [6] did several early studies on microgravity pool boiling up to the mid 1960s. Lately, Merte [7], Abe et al. [5], Christopher et al. [8] and Straub et al. [9] carried out microgravity pool boiling experiments or/and theoretical research. Boiling experiments in microgravity exhibit the high heat transfer coefficients as under terrestrial conditions, where the bubble also departs from the heater surface and thus contributes to the agitation of the liquid.

In search of an explanation of the high heat transfer rate associated with nucleate boiling, a liquid layer evaporation model was first developed by Snyder et al. [10]. The model attributes a significant portion of the total heat transfer rate in boiling to the rapid evaporation of the microlayer which forms underneath a growing bubble on a heater surface. Many investigators have conducted indirect experimental or direct measurements of the microlayer thickness to predict indicate microlayer formation in nucleate boiling. Their experimental results showed that the liquid microlayer was almost wedge shaped and as the bubble grew in size, the microlayer thickness decreased and the radius of the dry spot forming underneath the bubble increased. They attribute the reduction in the microlayer thickness with time solely to liquid evaporation and concluded that radial flow of liquid into the microlayer was negligible.

Recently, Straub et al. [9] propose a microwedge model to describe the primary mechanism of boiling heat transfer under microgravity. The model considers the evaporation at the interface of the bubble base and mass flow in the wedge between the interface and the heater surface due to capillary forces. This microwedge effect is regarded as the primary mechanism of boiling. It is caused by surface tension and is therefore independent of gravity.

For nucleate pool boiling of binary mixtures under microgravity conditions, surface tension is typically a strong function of concentration. Depending on the binary mixtures, the surface tension gradient caused by the concentration gradient can be quite large. Therefore, some special effects may result at the interface of the microwedge layer.

We propose a method for calculating surface tension of binary mixtures with a bubble growing in the concentration boundary layer. A microwedge model for nucleate pool boiling of binary mixtures under microgravity is suggested. The characteristics of the microwedge layer change is demonstrated by solving the phase interface, momentum, and energy equations, and the bubble detachment mechanism is shown accordingly.

## 2. Physical considerations

### 2.1. General concept

As shown in Fig. 1, in the so-called positive non-azeotropic binary mixtures system, such as water-ethanol and water-methanol mixtures, the preferential evaporation of

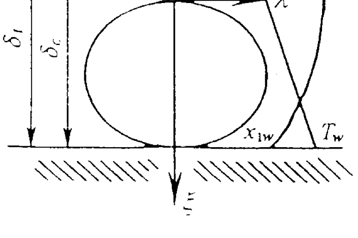

Fig. 1. Physical model.

the more volatile component into the bubble from its surface is more intensive in the zone closer to the heater. The liquid, adjacent to the heater surface where bubbles are generated at the specific nucleation sites, would be depleted of the higher volatile component. This forms a concentration gradient from the bulk fluid to the wall with the high volatile component diffusing from the bulk fluid to the liquid layer adjacent to the heater surface. Therefore, the growing bubble in the thermal boundary layer, is also existing in a concentration boundary layer. As shown in Fig. 1, $\delta_t$ is the thermal boundary layer thickness in which liquid temperature varies from wall temperature $T_w$ to the bulk liquid temperature $T_\infty$ (or $T_s$ for saturated boiling). The steady-state temperature profile will ultimately establish a linear profile between the wall surface ($y = 0$) and $y = \delta_t$,

$$\frac{\theta}{\theta_w} = \frac{\delta_t - y}{\delta_t} \tag{1}$$

where $\theta = (T - T_s)$ or $(T - T_\infty)$.

In the concentration boundary layer $\delta_c$, the volatile component concentration varies from wall concentration $x_{1,w}$ to bulk liquid concentration $x_{1,0}$ as shown in Fig. 1.

### 2.2. Surface tension model for growing bubble on a heating wall surface

For a binary mixture such as water–ethanol or water–methanol, the surface tension can be adequately expressed as

$$\sigma = x_1\sigma_1(T_i) + (1 - x_1)\sigma_2(T_i) \tag{2}$$

$x_1$ is the interfacial concentration of one component 1. This is different from those based on bulk liquid composition and are unfit for our analysis of a growing bubble in the concentration boundary layer.

As is the case for most pure liquids, the surface tension decreases almost linearly with temperature. Consequently, curve-fit equations for surface tension data are almost linear in nature and the surface tension of each component are assumed to be linear relation of the form

$$\sigma(T) = C_0 - C_1 T \tag{2a}$$

The constants $c_0$ and $c_1$ are given by Jaspar [11].

The growth of a bubble controlled by heat transfer would stand for the case that the bubble grew large enough, so as the vapor bubble pressure is nearly equal to liquid saturated pressure which may be assumed to be constant. In addition, tangential vapor flow along the bubble interface often occurs rapidly. In terms of this opinion, the vapor pressure of a binary mixture can be expressed as

$$P_v = x_1\gamma_1 P_1 + (1 - x_1)\gamma_2 P_2 \tag{3}$$

Here the activity coefficient $\gamma_i$ is not unity for most liquid mixtures with strong molecular interactions, which can be usually determined from the two-parameters Wilson equations [12],

$$\ln\gamma_i = -\ln(x_i + x_j\lambda_{ij}) + \left[\frac{\lambda_{ij}}{x_i + x_j\lambda_{ij}} - \frac{\lambda_{ji}}{x_i + x_j\lambda_{ji}}\right] \tag{4}$$

The constants $\lambda_{ij}$ and $\lambda_{ji}$ can be determined from experimental data for mixtures and are independent of temperature over the range of interest.

The vapor pressures of pure components $P_i$, are calculated from the Antoine equation, i.e.

$$\ln P_i = A_i - \frac{B_i}{T + C_i} \tag{5}$$

where the constants $A_i$, $B_i$, and $C_i$ can be found in the literature.

Using the chain rule, the following equation is obtained from equation (2)

$$\frac{d\sigma}{dT} = [\sigma_1(T_i) - \sigma_2(T_i)]\frac{dx_1}{dT} + \left[x_1\frac{dx_1}{dT} + (1 - x_1)\frac{d\sigma_2}{dT}\right] \tag{6}$$

Differentiating equation (3) with respect $T_i$ and setting the result equal to zero, we have

$$\frac{dx_1}{dT} = \frac{\left[x_1\dfrac{d\ln P_1}{dT} + (1 - x_1)\dfrac{\gamma_2}{\gamma_1}\dfrac{P_2}{P_1}\right]}{\dfrac{\gamma_2}{\gamma_1}\dfrac{P_2}{P_1} - 1 - x_1\dfrac{d\ln\gamma_1}{dx_1} - (1 - x_1)\dfrac{\gamma_2}{\gamma_1}\dfrac{d\ln\gamma_2}{dx_1}\dfrac{P_2}{P_1}} \tag{7}$$

The variation of surface tension with respect to volatile component concentration is given as

$$\frac{\partial\sigma}{\partial x_1} = \frac{\partial\sigma}{\partial T}\frac{\partial T}{\partial x_1} \tag{8}$$

The surface tension gradient in tangential directions can be obtained as

$$\frac{d\sigma}{ds} = \frac{d\sigma}{dT}\frac{dT}{ds} \tag{9}$$

From equations (6) and (7), then,

$$\frac{d\sigma}{dx_1} \quad \text{and} \quad \frac{d\sigma}{ds}$$

can be calculated for a given temperature distribution.

### 2.3. Discussion

As a typical illustrating example, if the temperature gradient along bubble interface is assumed to be $-2.67 \times 10^{3}$°C m$^{-1}$, for ethanol–water and methanol–water mixtures, the results are shown in Figs 2–5.

The surface tension of the more volatile component may be smaller than that of the less volatile component. Hence, the concentration gradient along the bubble interface will generate a force which drags the liquid adjacent to interface toward the bubble bottom on the heating wall. Though surface tension gradients caused by tem-

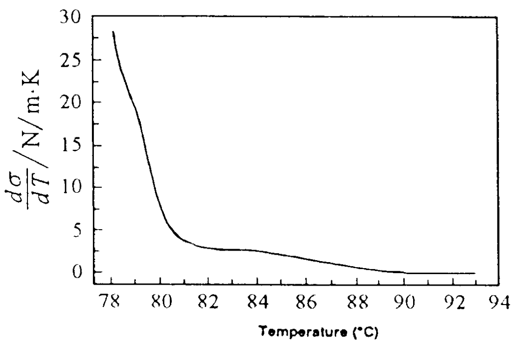

Fig. 2. Surface tension derivative vs temperature as a function of temperature for ethanol–water.

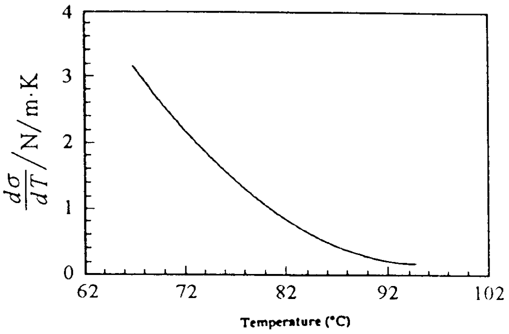

Fig. 3. Surface tension derivative vs temperature as a function of temperature for methanol–water.

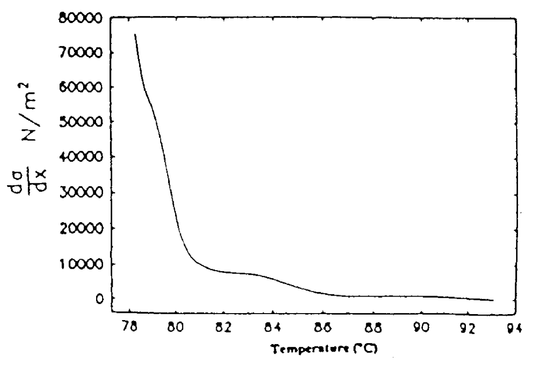

Fig. 4. Surface tension gradient as a function of temperature for ethanol–water.

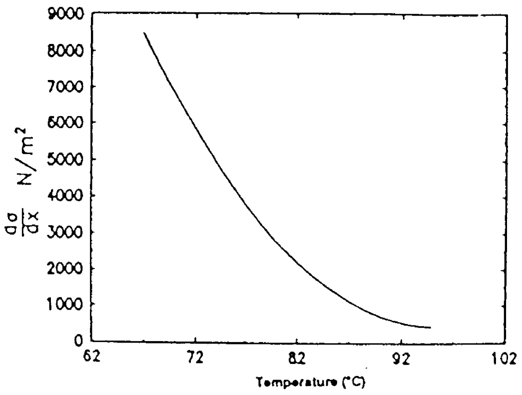

Fig. 5. Surface tension gradient as a function of temperature for methanol–water.

perature gradients have the opposite effect, the above mentioned predicted results show that the concentration effect is larger than the temperature effect on surface tension for growing bubbles in a thermal boundary layer. Therefore, compared with pure liquid boiling where the bubble surface tension is only subjected to the temperature gradient, the vapor bubble of binary mixtures under microgravity could experience a Marangoni force directed from the top to the bottom of the bubble. This kind of Marangoni flow may be very intensive.

Depending on the mixture component, the liquid flow induced by the Marangoni force can prompt bubble detachment and enhance convective heat transfer along the surface.

## 3. Microwedge model

### 3.1. Proposed analytical model

The physical model shown in Fig. 1, with the consideration of surface tension as discussed above, could hold true also for nucleate pool boiling of binary mixtures under microgravity. Under the action of surface tension gradient and pressure gradient caused by the interface curvature, the liquid will flow toward the heating surface with a microwedge interface. Besides it may exist a very thin liquid layer adhered on the surface beneath the growing bubble. Analysis of the flow in microwedge liquid layer will not only play an important role in explaining heat transfer mechanism, but also be beneficial for the analyzing bubble detachment mechanism.

Referred to Fig. 1, defining dimensionless variables $\xi$ and $\lambda$ as

$$\xi = \frac{z}{r_0} \quad \text{and} \quad \lambda = \frac{r}{r_0},$$

$r_0$ is the radius of curvature at point 0 in Fig. 1. The bubble interface equation considering surface tension varies with temperature and composition can be written [13] as

$$\frac{\xi''}{[1+(\xi')^2]^{3/2}}+\frac{\xi'}{\lambda[1+(\xi')^2]^{1/2}}=\frac{2\sigma_0}{\sigma(T,x_1)}+\frac{(\rho_v-\rho_l)gr_0^2}{\sigma(T,x_1)}\xi \tag{10}$$

where the $'$ and $''$ denote 1st and 2nd derivatives with respect to $\lambda$, respectively. For such a second-order ordinary differential equation, two boundary conditions are required. As a consequence of the choices of coordinate systems and the symmetry of the bubble, it is required that

$$\lambda = 0, \quad \xi = 2R, \quad \xi' = 0 \tag{11}$$

where $2R$ is dimensionless bubble height in Fig. 1.

Supposed that the bubble surface tension of binary mixtures varied with temperature, $\sigma = a+bT$. However, whether the condition is true or not, it does not affect the essence of our analysis. Solving equation (10) analytically is virtually impossible, but for the microwedge liquid layer, $(\xi')^2 \ll 1$, equation (10) can be simplified as

$$\xi''+\frac{\xi'}{\lambda}=\frac{2-Bo\xi}{1+A\xi} \tag{12}$$

Two solutions exist for equation (12) depending upon the gravitational environment:

(1) when $Bo \approx 0$, combining equation (11) and equation (12) yields the solution

$$\xi+\frac{A\xi^2}{2}=-\frac{1}{2}\lambda^2+2R+2AR^2 \tag{13}$$

(2) when $Bo \neq 0$, combining equation (11) and equation (12) yields the solution

$$\frac{A}{Bo}\xi^2-\frac{4(2A+Bo)}{Bo^3}\left[\left(1-\frac{Bo}{2}\xi\right)\right]\left[\left(1-\frac{Bo}{2}\xi\right)\times\ln\left(1-\frac{Bo}{2}\xi\right)-\left(1-\frac{Bo}{2}\xi\right)\right]\Bigg]=-\frac{1}{2}\lambda^2+\frac{A}{Bo}4R^2$$
$$-\frac{4(2A-Bo)}{Bo^3}[(1-BoR)[(1-BoR)\times\ln(1-BoR)-(1-BoR)] \tag{14}$$

It is shown from the results plotted in Fig. 6 that, under terrestrial conditions, buoyancy plays a dominant role and the microwedge interface deflects above for both binary mixture and single components. While under microgravity, $A < 0$ for single components, the microwedge interface still deflects upward, which means the surface tension gradient plays a similar role as buoyancy in bubble detachment. For binary mixtures, $A > 0$, the microwedge interface flattens thereby. The change of the microwedge interface has a direct relationship with changing of contact line in a macroscopic sense. For single components, microwedge interface deflects above, just the same as being analyzed in Ref. [13]. The mechanism of bubble detachment for binary mixtures differs from single components under microgravity which has been reported in previous experimental observation [5].

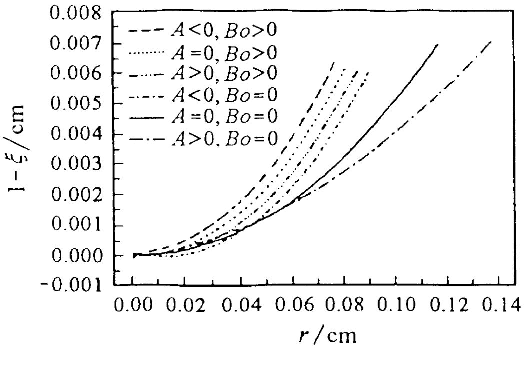

Fig. 6. Change of microwedge interface.

The liquid is driven mainly by the surface tension gradient and the curvature gradient, the simplified Navier–Stokes equation can be written for the velocity in the microwedge layer as

$$\frac{d^2u}{dy^2}=\frac{1}{\mu}\frac{dp_1}{dx} \tag{15}$$

with the boundary conditions

$$y = 0, \quad u = 0 \tag{16}$$

$$y = \delta, \quad \mu\frac{\partial u}{\partial n}=\frac{\partial \sigma}{\partial s} \tag{17}$$

For binary mixtures, the second boundary condition significantly affects the velocity distribution because of large gradients in concentration and temperature, and consequently the surface tension gradient.

Solving equations (15)–(17), we obtain

$$u=\frac{1}{\mu}\frac{dp_1}{dx}\left(\frac{y^2}{2}-\delta y\right)+\frac{y}{\mu}\frac{d\sigma}{dx} \tag{18}$$

Integrating equation (18) across the liquid film, yields the mass flow rate in the liquid film, $\dot{m}(x)$, as

$$\dot{m}(x)=\left(\frac{\delta^3\sigma}{3\nu}\frac{dk}{dx}+\frac{\delta^2}{2\nu}\frac{d\sigma}{dx}\right)2\pi x \tag{19}$$

Therefore, the mass flow rate is related to the heat flux by the following equation

$$\dot{q}(x) = +\dot{m}(x)h_{fg}/\pi x^2 \tag{20}$$

That is, low heat flux means low mass flow rate. With the data presented for ethanol–water and methanol–water mixtures in Fig. 4 and Fig. 5, the lower surface superheat, the larger the surface tension gradients, and hence, the more important role the second term in equation (19) will play. Figures 7 and 8 show the mass flow rate as a function of $x$. The surface tension gradient strongly affects the change of interface curvature and prompts liquid layers to be connected to each other. For illustration, considering two liquid layers formed by a liquid phase (1), surrounded by a gas phase (g), as shown in Fig.

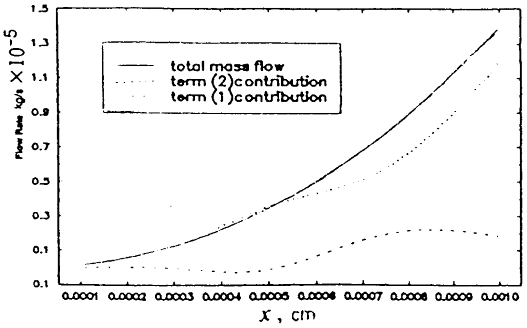

Fig. 7. Mass flow rate and individual contributions to mass flow rate vs position for ethanol–water.

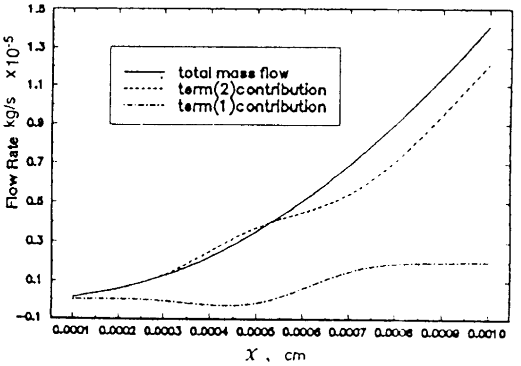

Fig. 8. Mass flow rate and individual contributions to mass flow rate vs position for methanol–water.

9 once merging takes place, the total work interaction for the processes is given by

$$w_{sp} = \sigma_{lg}(2A - B) \tag{21}$$

for $2A > B$, $w_{sp}$ is also greater than zero, which implies that work can be extracted and change to kinetic energy of liquid layer, thus enhance the merging process.

Higher heat fluxes mean higher evaporation mass rates which results in much larger radial mass flow rate. However, as shown in Fig. 4 and Fig. 5, the higher superheat means a smaller surface tension gradient. Therefore, for a given large evaporation mass rate, the interface curvature must change greatly to enhance the radial mass flow rate. This kind of interface change results in formation of dry spots, which will increase the local temperature and enhance evaporation. Consequently, the interface will change continuously and move backward. If the contact angle is approximately 90°, a local instability follows and a critical heat flux may result. In other words, the model proposed here can be extended to describe the critical heat flux.

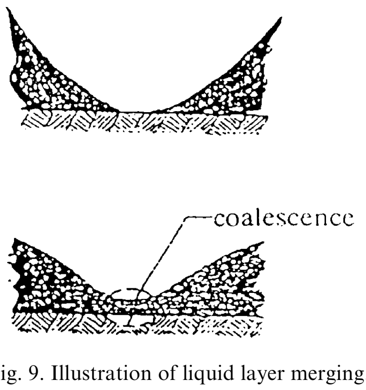

Fig. 9. Illustration of liquid layer merging.

### 3.2. An alternate analysis

In order to emphasize the role of $d\sigma/dx$, we consider the role of the curvature gradient term being unchangeable. Then for steady flow, the combined mass and energy balances will be

$$q''2\pi x\,dx = -h_{fg}\,d\dot{m}(x) \tag{22}$$

Equation (19) can be accordingly simplified as

$$\dot{m}(x) = \frac{\delta^2}{2\nu}\left(c + \frac{d\sigma}{dx}\right)2\pi x \tag{23}$$

Combining equations (22) and (23), we have

$$q''2\pi x = -h_{fg}\frac{\delta^2}{2\nu}\left(\frac{d\sigma}{dx}+c\right)2\pi x - 2\pi x\left(\frac{d\sigma}{dx}+c\right)\frac{\delta}{\nu}h_{fg}\frac{d\delta}{dx} \tag{24}$$

Solving equation (24) gives

$$\delta = \left[\frac{2\nu q''}{-3\left(\frac{d\sigma}{dx}+c\right)h_{fg}}\right]^{1/2} x^{1/2} \tag{25}$$

From equation (25), for binary mixtures, $d\sigma/dx$ would be a negative value, and hence reduces the liquid layer thickness, i.e. the liquid layer will become flatter when considering the effect of the surface tension gradient. This conclusion is consistent with above analysis. In addition, the effect of heat flux is more obvious from equation (25). The larger the heat flux, the larger the liquid layer thickness will be. This means that microwedge layer interface will move outward at a higher heat flux, which is also consistent with the above analysis.

## 4. Conclusions

Interfacial behavior of vapor bubbles growth in binary mixtures (ethanol–water, methanol–water) is studied. For nucleate pool boiling of binary mixtures, the bubble growing in a thermal boundary layer is also existing in a concentration boundary layer. The nonuniform mixture concentration has a great effect on bubble interface behavior. A model for surface tension at the interface is developed. Differing from pure liquid component vapor bubbles, Marangoni flow around binary mixture bubbles are directed from the top to the bottom of the bubbles.

A reasonable microwedge model for nucleate pool boiling of binary mixtures under microgravity is proposed. The surface shear due to composition gradients and temperature is an important factor which affects the behavior of the microwedge interface and thus bubble detachment. At different levels of heat flux, the interfacial curvature of the microwedge is subjected to different modes of change. The theory proposed here verifies the phenomena reported previously and even can be extended to explain the CHF phenomena of pool boiling of binary mixtures under microgravity conditions.

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