ADSORPTION AND CAPILLARY CONDENSATION AT THE CONTACT LINE IN CHANGE OF PHASE HEAT TRANSFER

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Abstract—A model based on adsorption and capillary condensation which describes the wetting characteristics of the contact line in change of phase heat transfer is proposed. A relationship between the equilibrium shape of a thin film at the contact line, superheat, and interfacial forces is derived for both zero and finite contact angle systems on "smooth" surfaces. Contact line boundary conditions which are a function of temperature, superheat and interfacial forces are presented. Homogeneous and heterogeneous nucleation at the minimum film boiling temperature is discussed.

NOMENCLATURE

a, see equation (9) $[m^{-2}]$;
$\bar{A}$, dispersion constant $[J]$;
A, Hamaker constant $[J]$;
b, see equation (10), $[T^{-1}]$;
f, fugacity $[N \cdot m^{-2}]$;
H, molar heat of vaporization $[J \, mol^{-1}]$;
$h2\pi$, Planck's constant $[J \cdot s]$;
K, curvature $[m^{-1}]$;
P, pressure $[N \cdot m^{-2}]$;
q, heat flux $[W \cdot m^{-2}]$;
R, universal gas constant $[J \cdot mol^{-1} \cdot K^{-1}]$;
T, temperature $[K]$;
V, molar volume $[m^3 \cdot mol^{-1}]$;
x, x coordinate distance $[m]$.

Greek symbols

γ, surface tension $[N \cdot m^{-1}]$;
Δ difference;
δ, film thickness $[m]$;
η, dimensionless film thickness;
θ, contact angle;
μ, chemical potential $[N \cdot m^{-2}]$;
ξ, dimensionless distance;
τ, dimensionless temperature;
ψ, see equation (8);
$\bar{\omega}$, characteristic frequency for van der Waals interaction.

Subscripts

a, apparent;
ai, apparent for isothermal condition;
c, critical;
ca, atmospheric critical;
cal, atmospheric critical, limiting value;
e, evaporative;
k, evaluated with $\gamma(\delta) = \gamma_{lv}$
l, liquid;
llv, liquid side of liquid–vapor interface;

ll, liquid–liquid interaction;
ls, liquid–solid;
lv, liquid–vapor;
o, contact line, interline;
oi, contact line for isothermal condition;
s, solid;
v, vapor.

Superscripts

d, dispersion;
*, differentation with respect to ξ;
', differentation with respect to x.

INTRODUCTION

THE MECHANISM whereby the stationary leading edge of a steady state thin evaporating film can stay in contact with a superheated surface is discussed herein. It is of interest to many heat transfer processes such as steady state evaporation from stationary thin films, evaporation from the leading edge of a rewetting film and evaporation at the Leidenfrost point. Due to interfacial forces, the liquid–solid system can either be spreading (zero apparent isothermal contact angle) or non-spreading (finite apparent isothermal contact angle). The modifier apparent is used to emphasize the fact that we cannot see the real contact angle which is at the molecular level. The zero apparent contact angle case has been extensively discussed using the disjoining pressure concept which is based on the London–van der Waals dispersion force [1–5]. Segev and Bankoff used a model based on the Langmuir adsorption isotherm to discuss the minimum film boiling temperature [6]. Rewetting finite contact angle systems have been discussed using simple macroscopic models based on the contact angle, e.g. [7–12]. Herein we make use of recent insights concerning isothermal finite contact angle systems to generalize and extend previous microscopic results [1–5] to include systems which have apparent isothermal contact angles in the

range $0 \leq \theta_{ai} < 90^\circ$. Since we are primarily concerned with presenting a simple conceptual view of the contact line, we restrict our analysis to simple systems that interact primarily by the London–van der Waals dispersion force. On the other hand, it should be possible to extend this approach to include other phenomena. We emphasize that we are primarily concerned herein with the leading edge at equilibrium which might be viewed as having negligible extent. However, we note that this edge is critical because it represents the boundary condition for flow in the adjacent film where evaporation occurs.

For a zero apparent contact angle system, it has been proposed that the leading edge is kept from evaporating by multilayer adsorption [1–6]. A reasonable assumption is that the principal interaction is due to the London–van der Waals dispersion force. This leads to a chemical potential which decreases with thickness and an equilibrium film thickness at the leading edge which decreases with an increase in superheat. For a non-isothermal system, fluid flow and evaporation in the adjacent film results from an increase in the film thickness relative to its equilibrium value. The curvature at the contact line is taken to be equal to zero. As the thickness in the adjacent evaporating film increases the curvature also increases until a maximum value is reached. From this region on, fluid flow is due to a curvature gradient.

For a non-spreading system, this simple model does not describe a stable system because the chemical potential of a flat ultra-thin film based on a London–van der Waals model increases with a decrease in film thickness and an additional physicochemical effect is needed at the contact line for stability. We propose that this additional effect can be conceptualized as simply a curvature effect which has been extensively used in adsorption in porous media and which is known as capillary condensation. Although its application to a very rough surface is more obvious, we apply it herein to "smooth" surfaces. However, we note that all surfaces are non-uniform at sufficient magnification. A physicochemical model for the superheat dependent curvature at the contact line which leads to a stable nonisothermal finite contact angle system is presented. This gives a clearer conceptual view of the contact line of an evaporating film and leads to a consistent model for systems with apparent isothermal contact angles in the range $0 \leq \theta_{ai} < 90^\circ$. For $\theta_{ai} > 0$, the maximum curvature is located at the contact line. For the non-isothermal case, fluid flow towards the contact line is due to a curvature gradient in the adjacent liquid film.

The use of a curvature effect is partially supported by two recent publications. Adamson and his colleagues have been optically measuring the adsorption isotherms for vapors near their saturation pressure on "smooth" surfaces [13–15]. They have also measured the contact angles for the corresponding liquids on the same surfaces. In one of their latest publications, [15], they suggest the possibility that the adsorption they

measure is mainly due to capillary condensation in surface "dimples." In this vein, we note that all surfaces have some type of non-uniformity on the microscopic level where condensation can occur. In another recent publication, the Young–Laplace equation of capillarity augmented by disjoining pressure concept of Deryagin was used to obtain the interfacial profile in the contact line region of a finite contact angle system on a "smooth" surface [16]. An initial liquid–vapor interfacial slope identical to zero and an initial effective film thickness of the order of interatomic spacing led to substantial initial curvature and a finite apparent contact angle. The theoretical results based on this model agreed with published data on the measured apparent contact angles for the alkane–PTFE system. We note that these results were based on a continuum model and applied in a regime with some dimensions of the order of a molecular diameter. This has been accomplished in closely related analyses by the inclusion of a critical cut-off parameter which is closely related to the molecular diameter. Considerable physical insight and (at least) apparent experimental verification has been attained by this approach in [16] and in the past, e.g. [17–19]. In addition, this approach allows us to use the wealth of previous results which are given in terms of macroscopic measurements and models like the apparent contact angle.

CONTACT LINE MODEL

A conceptional drawing of the contact line region of a thin film of liquid in contact with a solid substrate is shown in Fig. 1. Spreading ($\theta_{ai} = 0$) and non-spreading ($0 < \theta_{ai} < 90^\circ$) contact line regions are presented for both equilibrium ($q_c = 0$) and evaporating conditions. In the non-spreading model there is a non-spreading contact "line" of small but finite extent (molecular size) with a thickness of δ_o. In the spreading case, the concept of an interline thickness, δ_o, which is the thickness at the junction of the evaporating and non-evaporating segments of a thin film has been used in [1–5]. Herein, this is also called the contact line. The contact line is at equilibrium in all cases. The substrate is non-uniform on at least the molecular level. However, the exact nature of these surface non-uniformities is unimportant at the present time. For the $\theta_{ai} > 0$ system, net evaporation or condensation does not occur at the contact line becuse of the interfacial forces associated with both surface curvature and film thickness. For the spreading system, interfacial forces associated with film thickness are sufficient to reduce the vapor pressure so that evaporation does not occur. Outside this contact line region of interest, evaporation or condensation can occur when $T_l > T_v$ because of a change in curvature, thickness and/or temperature. Herein, we are not particularly concerned with this outer region and focus on the characteristics of the contact line. The analysis is
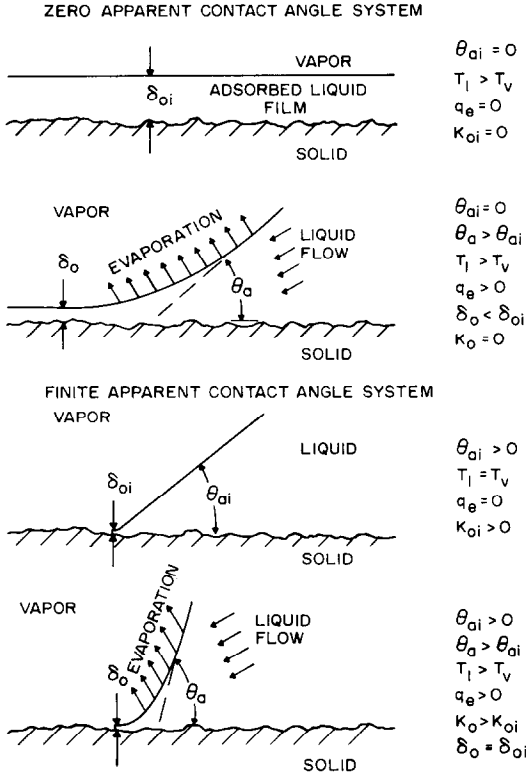
ZERO APPARENT CONTACT ANGLE SYSTEM

$\theta_{ai} = 0$
$T_l > T_v$
$q_e = 0$
$K_{oi} = 0$

$\theta_{ai} = 0$
$\theta_a > \theta_{ai}$
$T_l > T_v$
$q_e > 0$
$\delta_o < \delta_{oi}$
$K_o = 0$

FINITE APPARENT CONTACT ANGLE SYSTEM

$\theta_{ai} > 0$
$T_l = T_v$
$q_e = 0$
$K_{oi} > 0$

$\theta_{ai} > 0$
$\theta_a > \theta_{ai}$
$T_l > T_v$
$q_e > 0$
$K_o > K_{oi}$
$\delta_o = \delta_{oi}$

FIG. 1. Conceptual view of contact line represented by thickness δ_o. Since the surface inhomogeneities are extremely small, the substrate appears "smooth" to the unaided eye.

restricted to simple non-polar, liquid–solid systems which have an isothermal apparent contact angle (as given by the Young–Dupre equation) in the range $0 \leq \theta_{ai} < 90°$.

The thermodynamic equation for the change in liquid fugacity with liquid pressure and temperature is

$$d \ln f_l = \frac{V_l}{RT_l} dP_l + \frac{H}{RT_l^2} dT_l \qquad (1)$$

where H is the molar heat of vaporization for an adsorbed liquid expanding into a vacuum. Integrating equation (1) first along an isobaric path between the vapor phase temperature, $T_l = T_v$, and a new liquid–vapor interfacial temperature in the liquid, $T_l = T_{llv}$, and then along an isothermal path between the vapor phase pressure, $P_l = P_v$, and the effective liquid phase pressure $P_l = P_{llv}$ gives

$$\ln \frac{f_{llv}}{f_v} = \frac{V_l(P_{llv} - P_v)}{RT_{llv}} + \frac{H(T_{llv} - T_v)}{RT_v T_{llv}}. \qquad (2)$$

Equilibrium at the contact line requires that $f_{llv} = f_v$. Therefore,

$$V_l \Delta P + \frac{H \Delta T}{T_v} = 0 \qquad (3)$$

where $\Delta P = P_{llv} - P_v$ and $\Delta T = T_{llv} - T_v$.

The effective pressure change across a liquid-vapor interface due to interfacial forces for a thin curved film adsorbed on a solid substrate is a function of both the curvature of the liquid–vapor interface, $K(x)$, and the thickness of the adsorbed film, $\delta(x)$, e.g. [16]:

$$\Delta P = -\gamma_{lv} K + \frac{\hbar \omega}{8\pi^2 \delta^3}. \qquad (4)$$

Equation (4) is the Young–Laplace equation of capillarity modified to include the effect of film thickness on the effective pressure. This equation states that for a non-spreading system at isothermal equilibrium, the vapor pressure increase due to interfacial forces has to be offset by an equal vapor pressure change of opposite sign due to capillarity. For a non-spreading system, $\bar{\omega} > 0$ is a "characteristic frequency" for this interaction. For the non-isothermal spreading case, $\bar{\omega} < 0$, the second effect in equation (4) is sufficient for stability until a critical superheat is reached. Various forms of equation (4) have been used in the literature on isothermal films, e.g. [16, 20–23]. Herein, we take γ_{lv} to be a constant.

Using equations (4)–(6), equation (3) is expanded and made dimensionless to obtain equations (7)–(10)

$$K = \delta'' [1 + (\delta')^2]^{-1.5} \qquad (5)$$

in which $\delta' = d\delta/dx$ and $\delta'' = d^2\delta/dx^2$. Taking

$$x = (1.5)^{0.5} \delta_o \xi; \; \delta(x) = \delta_o \eta(\xi); \; \Delta \tau = \frac{\Delta T}{T_v} \qquad (6)$$

in which δ_o represents the thickness at the contact line,

$$a_k \delta_o^2 \psi - \eta^{-3} - b\Delta\tau = 0. \qquad (7)$$

The non-dimensional curvature is given by

$$\Psi = \eta^{**} [1 + \tfrac{2}{3}(\eta^*)^2]^{-1.5} \qquad (8)$$

in which $\eta^* = d\eta/d\xi$, $\eta^{**} = d^2\eta/d\xi^2$ and

$$a_k = \frac{16\pi^2 \gamma_{lv}}{3\hbar\omega}, \qquad (9)$$

$$b = \frac{8\pi^2 H \delta_o^3}{\hbar\omega V_l}. \qquad (10)$$

At the contact line, $\eta = 1$ and equation (7) leads to equation (11) for the non-dimensional curvature at the contact line, $\Psi(0)$:

$$\Psi(0) = \frac{1 + b\Delta\tau}{a_k \delta_o^2}. \qquad (11)$$

Equation (11) relates the equilibrium shape of a thin film at the contact line to the superheat and interfacial forces.
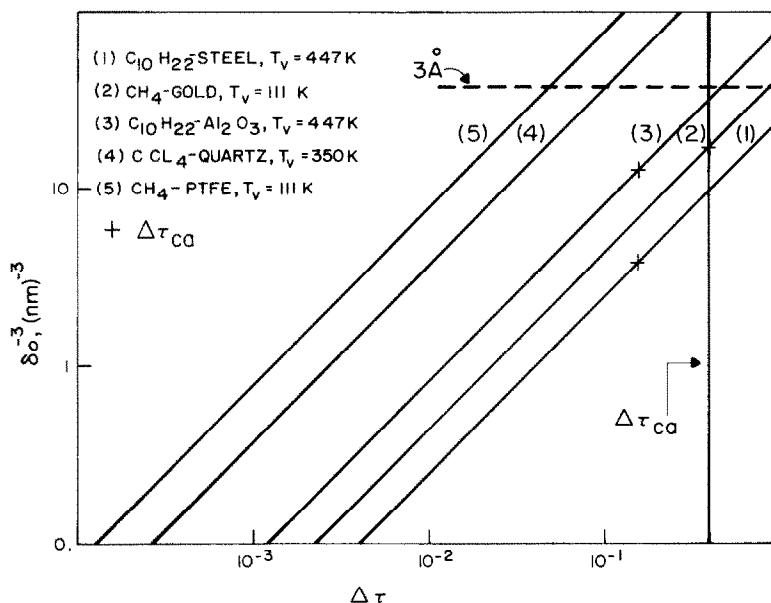
FIG. 2. Reciprocal of adsorbed liquid film thickness cubed vs substrate reduce superheat for a zero apparent isothermal contact angle. Numerical values were obtained from the reviews in [3,4]. However, the values for CH_4-PTFE were adjusted to be consistent with results presented in [17].

For a superheated contact line, $\Delta\tau > 0$, equation (11) describes the following two physical systems. Non-spreading systems: $90° > \theta_{ai} > 0$, $\bar{\omega} > 0$, $a_k \delta_o^2 > 0$ and $\Psi(0) > 0$. In this case, the vapor pressure decrease due to curvature offsets the vapor pressure increase due to superheat and interfacial forces, thereby giving stable contact between the liquid and solid at the contact line. Spreading systems: $\theta_{ai} = 0$, $\bar{\omega} < 0$, $a_k < 0$ and $\Psi(0)$. In this case, curvature is not needed at the contact line since the vapor pressure increase due to superheat is offset by the vapor pressure decrease due to the London–van der Waals dispersion force. However, curvature could be present in some systems as an additional effect. These results are discussed below and given in graphical form in Figs. 2 and 3.
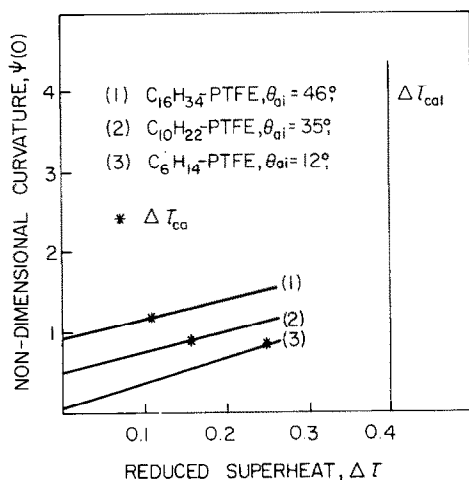
Based on the London–van der Waals equation of state, the reduced limit for superheating a homogeneous liquid at pressures well below the critical pressure is $T_l/T_c = 0.84$, e.g. [24]. Spiegler et al. [25] suggested that this is the minimum film boiling temperature for a liquid. The Berthelot equation of state leads to $T_l/T_c = 0.92$ [24]. For the purpose of a reference point it is desirable to relate the results in Figs. 2 and 3 to the reduced limit for superheating a liquid. For our model, the vapor is at the saturation temperature. Therefore we use the approximation $T_v \approx 0.6\ T_c$, which applies to lower molecular weight liquids at atmospheric pressure along with $T_l/T_c \approx 0.84$ to obtain a limiting value of the atmospheric critical reduced superheat, $\Delta\tau_{cal} \approx 0.4$. This reference line is given in Figs. 2 and 3. Values of $\Delta\tau_{ca}$ are also given in which T_v is equal to the atmospheric boiling point and $T_l \approx 0.84\ T_c$. As indicated below, we note that some of the values of a_k and b were calculated at temperatures below the atmospheric boiling temperature.

THEORETICAL ESTIMATION OF PHYSICAL PROPERTIES

Spreading systems

$\theta_{ai} = 0$, $\bar{\omega} < 0$, $a_k < 0$ and $\Psi(0) = 0$. Using equation (11)

$$\Delta\tau = b^{-1} = -\frac{h\bar{\omega}V_l}{8\pi^2 H \delta_o^3}.$$ (12)

Equation (12) can also be written in the following form [3, 4]:

$$\delta_o^3 = \frac{V_l \bar{A}}{H\Delta\tau}.$$ (13)

FIG. 3. Non-dimensional contact line curvature vs reduced substrate superheat for a finite contact angle system.

Table 1. Numerical values for Fig. 3

	From [17]				
	δ_o $m \times 10^{10}$	γ_{lv} $Jm^{-2} \times 10^2$	A_{sl} $J \times 10^{20}$	$a_k\delta_o^2$	b
C_6H_{14}	1.67	1.84	3.83	15.0	47.0
$C_{10}H_{22}$	1.59	2.38	4.14	1.88	4.9
$C_{16}H_{34}$	1.57	2.75	4.33	1.09	2.6

The theoretical estimation of the value of the equilibrium film thickness, δ_o, using equation (13) has been discussed in [2–4]. Results based on these methods are given in Fig. 2.

Nonspreading systems

$90° > \theta_{ai} > 0$, $\bar{\omega} > 0$, $a_k\delta_o^2 > 0$ and $\Psi'(0) > 0$. The variation of the non-dimensional contact line curvature with superheat is obtained using equation (11). Substituting equation (14) from [3] and $A_{ll} = 24\pi r^2\gamma_{lv}$ from [26] with $r = \delta_o$ into equation (9) gives equation (15):

$$\frac{3\hbar\bar{\omega}}{4\pi} = A_{ll} - A_{sl}, \qquad (14)$$

$$a_k\delta_o^2 = \frac{4\pi\gamma_{lv}\delta_o^2}{24\pi\gamma_{lv}\delta_o^2 - A_{sl}}. \qquad (15)$$

Results based on these equations are given in Table 1 and Fig. 3 for a series of alkanes on PTFE. To calculate b, bulk values for V_1 and H at a consistent temperature, $T_v = 293$ K, were used.

Although the availability of complete sets of data is limited, the above procedures demonstrate the use of the model and the need for additional data at higher temperatures.

HOMOGENEOUS VS HETEROGENEOUS NUCLEATION

In the above model the contact line occupies a particularly stable reference position on the surface because the interfacial forces are sufficiently flexible along this line to maintain equilibrium. The local thickness and/or curvature can vary to offset the local superheat. For the spreading case as the superheat increases the contact line thickness as represented by the thin film thickness in Fig. 2 decreases. For the non-spreading case as the superheat increases the effective curvature at the contact line as represented by the curvature of a film in Fig. 3 increases. In an adjacent region where the interfacial effects are less because of either the basic heterogenity of all solid surfaces or the longer distance to an interface, instability in the form of nucleation can occur with superheating before it occurs along the contact line. If the increase in free energy associated with the formation of a bubble

attached to the solid is greater than that associated with a detached bubble, homogeneous nucleation occurs. If the reverse is true, heterogeneous nucleation occurs. A review of the past research on nucleation is given in [27].

For the spreading case, the results presented in Fig. 2 demonstrate that for those systems with films present above $\Delta\tau_{ca}$ nucleation should occur first in the thin film if the effect of non-condensibles in surface cavities is relatively small. In this case, the bond of adhesion is significantly stronger than the bond of cohesion. As a result past researchers have been able to correlate the Leidenfrost temperature and the minimum film boiling temperature for the spreading case with either the thermodynamic limit of superheat or values close to it [6, 25, 28, 29]. The results presented in Fig. 2 numerically emphasizes the point that superheats greater than this value are needed to prevent the first few monolayers of an adsorbed film from forming on the solid substrate because the solid–liquid intermolecular bond is significantly stronger than the liquid–liquid bond. The thermodynamic limit of superheat is an upper limit for rewetting with a liquid film in these systems. Those systems in which the thickness at the contact line decreases to the monolayer level before the homogeneous nucleation temperature is reached are controlled by both a change in thickness and curvature.

The non-spreading case is more involved because the interfacial force of adhesion is less than that of cohesion and heterogeneous nucleation can occur at a lower superheat as a result of surface roughness and/or variations in the interfacial forces along the solid–liquid interface. In addition, due to the shape of the resulting bubble and its effect on the relative size of the liquid–vapor and liquid–solid areas formed, past theoretical research has suggested the possibility that homogeneous nucleation can also occur in systems with moderate contact angles [27]. Further, the effect of solid surface contamination on the surface free energy varies with temperature. At this point, we neglect the effect of non-condensibles on nucleation. Again, the contact line can be viewed as a stable reference line for discussion using equation (11). In this case, the effective curvature at the contact line as given in Fig. 3 can vary with superheat to give added stability to the adhesion of a thin film. In the adjacent region, the physical situation at the liquid–solid interface can be sufficiently different so that heterogeneous nuc-

leation occurs at a lower superheat. A detailed surface description would be needed for a quantitative prediction. However, qualitatively we would expect that for a series of liquids with finite contact angles, as the difference between the energy of cohesion and the energy of adhesion increases (increase in $\bar{\omega}$) heterogeneous nucleation should occur at superheats further below the thermodynamic homogeneous limit. This point is emphasized by the decrease in the value of b in Table 1 and Fig. 3 with an increase in contact angle. Therefore, past researchers have demonstrated that the Leidenfrost point and the minimum film boiling temperature are less than the homogeneous nucleation temperature for these systems and are a function of the liquid–solid interfacial free energy [28–30].

BOUNDARY CONDITIONS FOR FLOW WITH EVAPORATION IN THE CONTACT LINE REGION OF AN ADSORBED FILM

Using the above model of the contact line, it is now possible to develop a unified view of the zero and finite contact angle systems. Previous theoretical work on the zero apparent contact angle system demonstrated that liquid flow with evaporation in the contact line region was primarily due to the local liquid–vapor interfacial slope and the extreme thinness of the film [1–5]. The minimum thickness occurred at the contact line and was found to be a function of temperature. This thickness and a small interfacial slope are the boundary conditions for the zero contact angle case. On the other hand, analyses of experimental results on the zero apparent contact angle system indicated that the curvature increased as the contact line was approached [31]. However, thickness below 10^{-7} m were not analyzed in [31] and a model which includes the concepts associated with equation (7) leads to the conclusion that the curvature reaches a maximum in the region around $\delta = 10^{-7}$ m and decreases from that point to the contact line [31].

Analyses of past experimental results on the finite apparent contact angle system indicated that the fluid flow with evaporation in the contact line region was primarily due to the gradient of the interfacial curvature [32]. For the non-spreading case, the maximum curvature occurred at the contact line and was found to increase with overall evaporation rate and temperature. This curvature along with the contact line thickness are the boundary conditions for the finite apparent isothermal contact angle case. The above model describes the physical phenomena, adsorption and capillarity, that lead to contact line stability and boundary conditions which vary with superheat. In addition, this model gives consistent contact line boundary conditions for both the $\theta_{ai} = 0$ and $0 < \theta_{ai} < 90°$ cases. The relative effect of the various forces and superheat can now be calculated using equation (11). However, the relative stability of the adjacent field depends in a complex way upon surface heterogeneity and local nucleation sites. A complete integration of

these effects into the model is outside the scope of this paper.

REFERENCES

1. M. Potash, Jr. and P. C. Wayner, Jr., Evaporation from a two-dimensional extended meniscus, *Int. J. Heat Mass Transfer* **15**, 1851–1863 (1972).
2. P. C. Wayner, Jr., Y. K. Kao and L. V. LaCroix, The Interline Heat Transfer coefficient of an evaporating wetting film, *Int. J. Heat Mass Transfer* **19**, 487–492 (1976).
3. P. C. Wayner, Jr., The effect of the London–van der Waals disperion force on interline heat transfer, *Trans. ASME, J. Heat Transfer* **100**, 155–159 (1978).
4. P. C. Wayner, Jr., Effect of interfacial phenomena in the interline region on the rewetting of a hot spot, *Int. J. Heat Mass Transfer* **22**, 1033–1040 (1979).
5. S. Moosman and G. M. Homsy, Evaporating menisci of wetting fluids, *J. Colloid Interface Sci.* **73**, 212–223 (1980).
6. A. Segev and S. G. Bankoff, The role of adsorption in determining the minimum film boiling temperature, *Int. J. Heat Mass Transfer* **23**, 637–642 (1980).
7a. W. S. Norman and V. McIntyre, Heat transfer to a liquid film on a vertical surface, *Trans. Inst. chem. Engrs* **38**, 301–307 (1960).
7b. W. S. Norman and D. T. Binns, The effect of surface tension changes on the minimum wetting rates in a wetted-rod distillation column, *Trans. Inst. Chem. Engrs* **38**, 294–300 (1960).
8. D. E. Hartley and W. Murgatroyd, Criteria for the break-up of thin liquid layers flowing isothermally over solid surfaces, *Int. J. Heat Mass Transfer* **7**, 1003–1015 (1964).
9. N. Zuber and F. W. Staub, Stability of dry patches forming in liquid films flowing over heated surfaces, *Int. J. Heat Mass Transfer* **9**, 897–905 (1966).
10. A. Orell and S. G. Bankoff, Formation of a dry spot in a horizontal liquid film heated from below, *Int. J. Heat Mass Transfer* **14**, 1835–1842 (1971).
11. F. F. Simon and Y. Y. Hsu, Effect of contact angle hysteresis on moving liquid film integrity, NASA TM X-68071 (1972).
12. P. C. Wayner, Jr., Fluid flow in the interline region of an evaporating non-zero contact angle meniscus, *Int. J. Heat Mass Transfer* **16**, 1777–1783 (1973).
13. A. W. Adamson, An adsorption model for contact angle and spreading, *J. Colloid Interface Sci.* **27**, 180–187 (1968).
14. P. Hu and A. W. Adamson, Adsorption and contact angle studies II **59**, 605–614 (1977).
15. J. Tse and A. W. Adamson, Adsorption and contact angle studies III **72**, 515–523 (1979).
16. P. C. Wayner, Jr., Interfacial profile in the contact line region of a finite contact angle system, *J. Colloid Interface Sci.* **77**, 495–500 (1980).
17. N. F. Owens, P. Richmond, D. Gregory, J. Mingins and D. Chan, Contact angles of pure liquids and surfactants on low-energy surfaces. In *Wetting Spreading and Adhesion*, (Edited by J. Padday), Paper No. 5. Academic Press, N.Y. (1978).
18. D. J. Mitchell and P. Richmond, A general formula for the calculation of free energies of inhomogeneous dielectric and electrolytic systems, *J. Colloid Interface Sci.* **46**, 118–127 (1974).
19. V. A. Parsegian, G. H. Weiss and M. E. Schraeder, Macroscopic continuum model of influence of hydrocarbon contaminate on forces causing wetting of gold by water, *J. Colloid Interface Sci.* **61**, 356–360 (1977).

20. B. V. Deryagin, Definition of the concept of, and magnitude of the disjoining pressure and its role in the statics and kinetics of thin layers of liquids, *Colloid J. (USSR)* **17**, 191–197 (1955).

21. F. Renk, P. C. Wayner, Jr. and G. M. Homsy, On the transition between a wetting film and a capillary meniscus, *J. Colloid Interface Sci.* **67**, 408–414 (1978).

22. B. V. Zheleznyi, Form of the equilibrium contact angle, *Dokl. Akad. Nauk. SSSR* **206**, 377–380 (1972).

23. K. K. Mohanty, H. T. Davis and L. E. Scriven, Thin fluid films at rest on simply shaped solids, *Bull. Am. Phys. Soc.* **23**, 996 (1978).

24. J. G. Eberhart and H. C. Schnyders, Application of the mechanical stability to the predictions of the limit of superheat for normal alkanes, ether, and water, *J. Phys. Chem.* **77**, 2730–2736 (1973).

25. P. Spiegler, J. Hopenfeld, M. Silberberg, C. F. Bumpus, Jr. and A. Norman, Onset of stable film boiling and the foam limit, *Int. J. Heat Mass Transfer* **6**, 987–994 (1963).

26. J. F. Padday and N. D. Uffindell, The calculation of cohesive and adhesive energies from intermolecular forces at a surface, *J. Phys. Chem.* **72**, 1407–1414 (1968).

27. R. Cole, Boiling nucleation. In *Advances in Heat Transfer*, Vol. 10, pp. 85–166. Academic Press, N.Y. (1974).

28. K. J. Baumeister and F. F. Simon, Leidenfrost temperature—its correlation for liquid metals, cryogens hydrogens and water, *J. Heat Transfer* **95C**, 166–173 (1973).

29. K. L. Waldram, H. K. Fauske and S. G. Bankoff, Impaction of volatile liquid droplets onto a hot liquid surface, *Can. J. Chem. Engng* **54**, 456–458 (1976).

30. R. E. Henry, D. J. Quinn and E. A. Spleha, An experimental study of the minimum film boiling point for liquid–liquid systems, *5th Int. Heat Transfer Conf.* Tokyo, Japan (1974).

31. R. Cook, C. Y. Tung and P. C. Wayner, Jr., Use of scanning of microphotometer to measure *in situ* the evaporating meniscus profile. Manuscript No. 4491, presented at 73rd Annual Meeting AIChE, Chicago, IU, (Nov. 1980); *ASME J. Heat Transfer* **103**, 325–330 (1981).

32. F. J. Renk and P. C. Wayner, Jr., An evaporating ethanol meniscus: Part II, theoretical studies, *J. Heat Transfer* **101C**, 59–62 (1979).

ADSORPTION ET CONDENSATION CAPILLAIRE A LA LIGNE DE CONTACT DANS LE TRANSFERT THERMIQUE AVEC CHANGEMENT DE PHASE

Résumé—On propose un modèle basé sur l'adsorption et la condensation capillaire qui décrit les caractéristiques de mouillage de la ligne de contact dans le transfert thermique avec changement de phase. Une relation entre la forme d'équilibre d'un film mince à la ligne de contact, la surchauffe et les forces interfaciales est établie à la fois pour les systèmes à angle de contact nul ou fini sur des surfaces "lisses". On présente des conditions aux limites de ligne de contact qui sont fonctions de la température, de la surchauffe et des forces interfaciales. La nucléation homogène et hétérogène à la température d'ébullition en film minimale est discutée.

ADSORPTION UND KAPILLAR-KONDENSATION AN DER KONTAKTLINIE BEIM WÄRMEÜBERGANG MIT PHASENWECHSEL

Zusammenfassung—Es wird ein Modell mit Adsorption und Kapillar-Kondensation vorgelegt, welches die Benetzungseigenschaften der Kontaktlinie beim Wärmeübergang mit Phasenwechsel beschreibt. Es wird eine Beziehung zwischen der Gleichgewichtsform eines dünnen Films an der Kontaktlinie, der Überhitzung und der Grenzflächenkräfte für Systeme mit endlichem Kontaktwinkel und dem Kontaktwinkel null an glatten Oberflächen abgeleitet. Die Randbedingungen an der Kontaktgrenzlinie, welche eine Funktion der Temperatur, der Überhitzung und der Grenzflächenkräfte sind, werden vorgestellt. Die homogene und heterogene Keimbildung bei der kleinsten Filmverdampfungstemperatur wird diskutiert.

АДСОРБЦИЯ И КАПИЛЛЯРНАЯ КОНДЕНСАЦИЯ НА ЛИНИИ КОНТАКТА ПРИ ТЕПЛООБМЕНЕ С ИЗМЕНЕНИЕМ АГРЕГАТНОГО СОСТОЯНИЯ

Аннотация — Предложена модель для исследования адсорбции и капиллярной конденсации, которая учитывает характеристики смачиваемости на линии контакта при теплообмене с изменением фаз. Выведено соотношение между равновесной формой тонкой пленки на линии контакта, перегревом и межфазными силами как для систем с нулевым, так и с конечным значением угла смачиваемости на «гладких» поверхностях. Представлены граничные условия на линии контакта, которые зависят от температуры, перегрева и межфазных сил. Обсуждается гомогенное и гетерогенное зарождение пузырьков.