Int. J. Heat Mass Transfer. Vol. 16, pp. 1777–1783. Pergamon Press 1973. Printed in Great Britain

FLUID FLOW IN THE INTERLINE REGION OF AN EVAPORATING NON-ZERO CONTACT ANGLE MENISCUS

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(*Received* 13 *October* 1972 *and in revised form* 29 *January* 1973)

Abstract—The transport processes in the interline region of a stationary evaporating meniscus with a non-zero contact angle are qualitatively described. Previously published data on evaporating drops are then discussed. A change in the thickness of the adsorbed thin film in the interline region resulting from evaporation can cause both contact angle hysteresis and fluid flow.

NOMENCLATURE

f,	fugacity [N/m^2];
H,	latent heat of evaporation [J/mole];
$\mathscr{R}$,	gas constant [J/Kmole];
S,	spreading coefficient [N/m];
t,	film thickness [m];
T,	temperature [K];
v,	specific volume [m^3/kg];
V,	molar volume [m^3/kg];
Γ,	amount adsorbed per unit area [mole/m^2];
γ,	interfacial free energy [N/m];
π,	film pressure [N/m].

Subscripts

d,	disjoining pressure dynamic;
e,	equilibrium;
l,	liquid;
ls,	liquid–solid interface;
lsv,	liquid–(solid–vapor) interface;
lv,	liquid–vapor interface;
r,	reference pressure;
s,	solid surface;
v,	vapor;
vlv,	vapor pressure at liquid–vapor interface;
$vlvt$,	saturation vapor pressure at liquid–vapor interface at surface temperature.

Superscripts

d,	due to dispersion forces;
id,	ideal;
0,	adsorbed at saturation.

HEAT and mass transfer in the vicinity of the triple interline is of major importance in change-of-phase heat transfer. For the purpose of this study, the triple interline is viewed as the junction on a solid substrate of a thin film in which the pressure is a function of the film thickness and a meniscus in which the pressure drop across the liquid–vapor interface is described by Laplace's equation of capillarity. The importance of this region is exemplified by recent work on the formation of dry spots [1, 2], the stability of dry spots [3, 4], heat transfer at the base of bubbles in boiling [5–7] and evaporation from an extended meniscus-thin film [8, 9]. The references in these papers are a good guide to the extensive literature in these areas. In [8, 9] a procedure to analyze the effects of disjoining pressure, capillarity, thermocapillarity, substrate thermal conductivity and superheat on the transport processes in a meniscus with a zero contact angle was presented. The objective of the present study is to relate the analysis of transport processes in the triple interline region of a wetting meniscus (zero contact angle) with that for a nonwetting meniscus (non-zero contact angle). The results are then used to qualitatively analyze experimental results concerning evaporating drops of liquid. Although the analysis primarily concerns systems in which interfacial effects predominate, the development enhances our understanding of the evaporating interline in general. The results will be useful in the design of future experiments and equipment in this area.

ISOTHERMAL SYSTEM

The following concepts for a single component, liquid–vapor isothermal system in contact with a solid substrate are useful to the understanding of the evaporating system. In Fig. 1, this system is presented for the interline region of a meniscus in contact with a horizontal solid surface covered with an adsorbed film. The meniscus curvature is not apparent over the short distance presented. The spreading coefficient, S_{ls}, is defined as the change in free energy per unit area for a liquid spreading over a bare solid [10]

$$S_{ls} \equiv \gamma_s - \gamma_{ls} - \gamma_{lv}. \qquad (1)$$

The coefficient is positive for spontaneous spreading. Its relation to the contact angle is obtained by using the definition of the film pressure [11],

$$\pi_e \equiv \gamma_s - \gamma_{sv} \qquad (2)$$

and the Young–Dupré equation,

$$\gamma_{lv} \cos \theta_e = \gamma_{sv} - \gamma_{ls} \qquad (3)$$

to obtain equation (4)

$$S_{ls} = \pi_e + \gamma_{lv}(\cos \theta_e - 1). \qquad (4)$$

The use of both the surface free energy for the base solid, γ_s and the surface free energy for the solid covered by an equilibrium adsorbed film, γ_{sv}, enhances the description and shows that the spreading coefficient is related to the film pressure. The decrease in the surface free energy of the solid surface (π_e) resulting from adsorption can be obtained by an integration of the Gibbs adsorption equation [12]:

$$\pi_e = \mathcal{R}T \int_0^{p_v} \Gamma \, \mathrm{d} \ln p_v. \qquad (5)$$

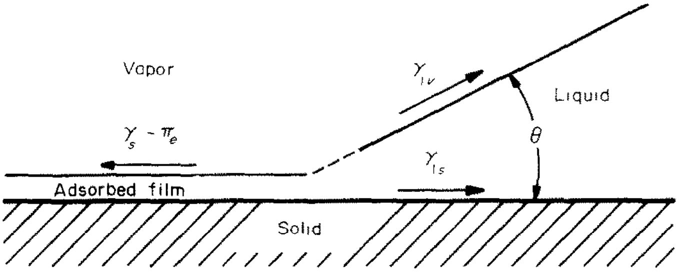

FIG. 1. Interline region for a non-zero contact angle meniscus on a solid surface covered by an adsorbed film.

There are various techniques to relate the contact angle on a smooth surface with the chemical nature of the surface. Using a geometric mean technique based on London dispersion forces, Fowkes [13] has suggested that, for a liquid–solid system that interact by dispersion forces only,

$$\cos \theta_e = \frac{2\sqrt{(\gamma_s^d \gamma_{lv}^d)}}{\gamma_{lv}} - \frac{\pi_e}{\gamma_{lv}} - 1. \qquad (6)$$

Deryagin and Zorin [14] measured the thickness of an adsorbed film as a function of the superheat of the solid substrate. Their results were presented so as to correlate the film thickness with the reduced vapor pressure of the adsorbed film, and are reproduced in Fig. 2. The vapor pressure of the adsorbed film, p_{vlv}, is reduced from its thermodynamic saturation value, p_{vlvt}, at the substrate temperature, T_s, by dispersion forces. The experiments were designed to study the disjoining pressure which is defined as [15]

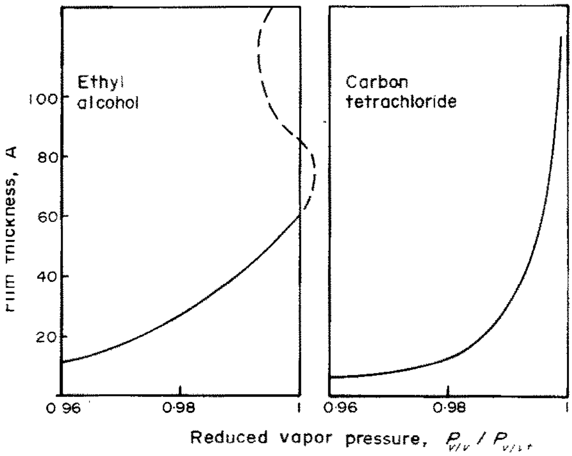

FIG. 2. Reduced vapor pressure of adsorbed film vs film thickness [14].

$$p_d \equiv -\frac{\mathscr{R}T_s}{V_l}\ln\frac{p_{vlv}}{p_{vlvt}} \tag{7}$$

and is related to the pressure in the liquid film, p_l, by

$$p_d = p_r - p_l. \tag{8}$$

Sheludko [16] presents the following connection between the film pressure and the disjointing pressure:

$$d\pi = -t\,dp_d. \tag{9}$$

These results demonstrate that for polar substances the adsorption isotherm intersects the saturation ordinate, whereas, the isotherm asymptotically approaches the saturation ordinate for non-polar liquids. Following Frumkin [17], Deryagin and Zorin [14] pointed out that "the contact angle can differ from zero only if no continuous transition from the adsorption layer to the bulk phase through a series of increasing thickness corresponding to thermodynamically stable states is possible." Based on this hypothesis, there should be a step-change or series of step-changes in thickness at the interline leading to a macroscopic contact angle greater than zero in Fig. 1. The extension of the adsorption isotherm could have the general shape depicted by the dashed line in Fig. 2. As outlined in Adamson [18] an integration of the Gibbs adsorption equation to the first crossing of the adsorption isotherm presented in Fig. 3 gives

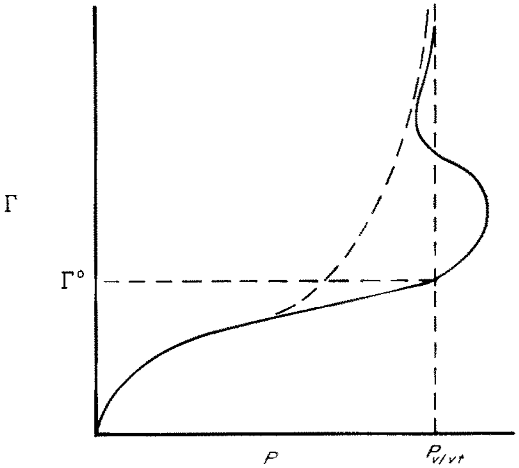

FIG. 3. Amount adsorbed vs pressure [18].

$$\gamma_s - \gamma_{sv} = \pi_e = \mathscr{R}T\int_{\Gamma=0}^{\Gamma=\Gamma 0}\Gamma\,d\ln p_v \tag{10}$$

while an integration to an infinitely thick film gives

$$\gamma_s - \gamma_{ls} - \gamma_{lv} = S_{ls} = \mathscr{R}T\int_{\Gamma=0}^{\Gamma=\infty}\Gamma\,d\ln p. \tag{11}$$

The difference between the two is just the spreading coefficient for the liquid on an adsorbed film:

$$S_{lsv} = S_{ls} - \pi_e = \gamma_{lv}(\cos\theta_e - 1). \tag{12}$$

Therefore, the adsorbed equilibrium thin film can decrease the observed spreading coefficient. As an example of this, Hare and Zisman [19] have presented data for many fluids that cannot spread on their own adsorbed films.

The thermodynamic equation for the change in the fugacity (escaping tendency) with pressure and temperature of a three dimensional single component liquid phase is [20]

$$\mathrm{d}\ln f = \frac{V_l}{\mathscr{R}T}\,\mathrm{d}p + \frac{H^{id}}{\mathscr{R}T^2}\,\mathrm{d}T. \qquad (13)$$

This equation shows how a decrease in the fugacity of a liquid resulting from a decrease in the pressure on a liquid can be offset by an increase in the temperature. Integrating equation (13) at constant temperature over a fugacity range where the fugacity is approximately equal to the vapor pressure gives

$$\Delta p = \frac{\mathscr{R}T_s}{V_l}\ln\frac{p_{vlv}}{p_{vlvt}} \qquad (14)$$

which is Deryagin's equation for the disjointing pressure.

EVAPORATING EXTENDED MENISCUS WITH A CONTACT ANGLE EQUAL TO ZERO

In [8], the transport processes in an evaporating extended meniscus formed on a superheated vertical flat plate which was immersed in a pool of saturated carbon tetrachloride, were modeled and analyzed. The process operates as follows. The pressure in the thin film portion of the extended meniscus is a function of only the thickness, whereas, the pressure in the intrinsic portion of the meniscus is a function of only the curvature. In an isothermal system, the pressure drop in the vertical extended meniscus is equal to the hydrostatic pressure drop. With a superheated plate, evaporation causes a decrease in the thin film thickness and a decrease in the intrinsic meniscus height. Both of these changes give the increased pressure gradient which is necessary to balance the viscous shear stresses in the liquid flowing up the meniscus. It has been shown that the disjointing pressure is primarily a function of the film thickness [21], therefore, it is possible to offset the effect on the vapor pressure of the tension in the liquid by an increase in the temperature (see equation 13). Phenomenologically, the same result would be obtained by maintaining the temperature of the extended meniscus using a suitable supply of energy while decreasing the temperature and pressure in the surrounding vapor using a suitable heat sink. The results of the analysis demonstrate that the most significant characteristic of the evaporating extended meniscus is that its profile can adjust to fit a given heat flux. The results also demonstrate how it is possible for the heat flux and velocity to have a zero value where the thickness is fixed by adsorption, go through a maximum value, and then decrease to a negligible value where the meniscus becomes relatively thick.

EVAPORATING EXTENDED MENISCUS WITH A FINITE CONTACT ANGLE

Equations (10)–(12) outline why the meniscus with a contact angle may be viewed as the result of the coexistence of an intrinsic meniscus and an adsorbed thin film. Since π_e can be greater than S_{ls} it is possible to have both a non-zero contact angle and an adsorbed film when $S_{ls} > 0$. Considerable data that confirm this concept for high energy surfaces are available (e.g. [19]). In this vein, Deryagin and Zorin [14] discuss adsorbed layers with an oriented structure and discontinuous liquid profiles. These concepts suggest that the analysis presented in [8] for a wetting meniscus is applicable to the nonwetting case with a few modifications. First, at the junction of the intrinsic meniscus and the thin film, there would be a discontinuous change in the angle that an extension of the liquid–vapor interface makes with the solid substrate. For the non-zero contact angle case, the discussion presented below suggests that a dynamic contact angle should be used regardless of the angle in the adjacent film. Second, Deryagin and Zorin [14] suggest that the thickness of the liquid at the junction is not continuous. Third, if there are structural changes in the liquid film, the bulk properties of the liquid are not applicable in the thin film. Unfortunately, sufficient data to make these changes are presently unavailable. However, the use of the analysis presented in [8] should give the same qualitative results. Therefore, a qualitative description of the non-zero contact angle system is available.

The thin film has a significant effect on both spreading and heat transfer. For the spreading process, it is the "surface" in contact with the meniscus and it is a path of non-zero thickness for fluid flow at the interline. For the heat transfer process, it is an extended "surface" for evaporation and fluid flow. Using the result of [8, 9], it is possible to approximate the size of the heat sink in that portion of an evaporating thin film with a thickness less than 10^{-8} m. This thickness represents an upper limit on that anticipated for a simple fluid with a non-zero contact angle meniscus but not for a zero contact angle meniscus. For carbon tetrachloride evaporating from a smooth surface with a constant superheat of 0·82 K, the length of this portion of the thin film was 2×10^{-7} m and had a heat flux of $4{\cdot}23 \times 10^5$ W/m^2. For a superheat of 2·82 K, the corresponding numbers are 10^{-7} m and $1{\cdot}56 \times 10^6$ W/m^2. Therefore, the total heat flow from this region is not large when the interline length is short. However, the effect on the spreading process is critical in this region and for evaporation from small pores, the interline length is relatively large.

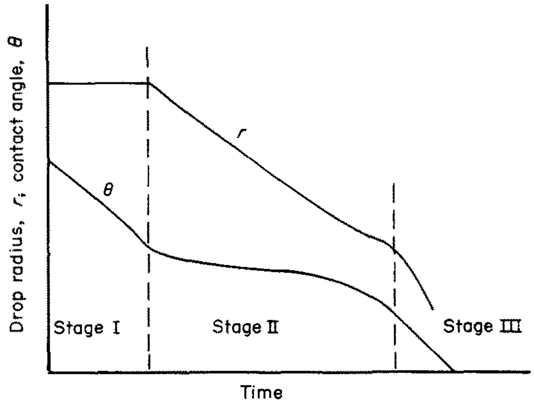

FIG. 4. Idealized history of an evaporating drop [2].

EVAPORATING DROP OF CONSTANT RADIUS

Simon and Hsu [2] experimentally measured the wetting dynamics of evaporating drops of water on various surfaces and reported the idealized history of drop radius and contact angle presented in Fig. 4. Of particular importance herein is the fact that the contact angle decreased while the radius of the drop remained constant during stage (I) of the evaporative cycle. In their study of the copper–water system, stage (I) predominated. Equation (6) relates the equilibrium contact angle to the various surface free energies and film pressure. Assuming that the surface free energies remain constant during that portion of the slow evaporation process which occurs at constant drop radius, equation (6) can be rewritten for stage (I) as

$$\cos\theta_d = \frac{2\sqrt{(\gamma_s^d \gamma_{lv}^d)}}{\gamma_{lv}} - \frac{\pi_d}{\gamma_{lv}} - 1. \qquad (15)$$

Essentially, this is a dynamic Young–Dupré equation, which has been previously used in interline motion.

Subtracting equation (6) from equation (15) gives

$$\gamma_{lv}(\cos\theta_d - \cos\theta_e) = \pi_e - \pi_d. \qquad (16)$$

This suggests that the change in contact angle during stage (I) reported in [2] is just a measure of the change in film pressure (adsorption in the thin film). During evaporation the thin film thickness decreases and the liquid drop is in contact with a thinner adsorbed film. Since the film pressure is a measure of the decrease in the free energy of the base solid resulting from adsorption of the vapor, the free surface energy of the evaporating adsorbed layer is larger than the nonevaporating film. Therefore, the balance of forces at the interline requires a smaller contact angle. Since the thin film thickness is less than 10^{-8} m and would follow the contour of the surface, the surface roughness effect on the contact angle would be in addition to the film pressure effect.

Numerous articles have been written concerning contact angle hysteresis. Indeed it is difficult to ascertain whether the hysteresis is due to any one of the various possible mechanisms suggested (e.g. surface roughness, surface heterogeneities, surface penetration, and friction). However, it is interesting to extend the use of the "simple friction of the liquid on the surface" concept presented by Adam and Jessop [22] to the evaporating interline system. Phenomenologically, this extension suggests that fluid flows across the junction of the drop and the thin adsorbed film as a result of a pressure gradient. This pressure gradient results from a change in the fluid profile in the interline region during evaporation. The pressure in the adsorbed thin film and its reduced vapor pressure are functions of the film thickness. The pressure in the drop is a function of the curvature of the liquid–vapor interface. Therefore, the direction of flow depends on the detailed description of the heat flux distribution and the resulting pressure distribution. If sufficient information were available, the transport processes could be quantitatively described using the procedures outlined above. Although this task is formidable, improved heat transfer equipment would surely result from the complete solution of this problem.

CONCLUSIONS

Sufficient information is available to qualitatively describe the transport processes in the interline region of a stationary evaporating meniscus which has a non-zero contact angle. Additional data concerning such concepts as anomalous fluid properties and discontinuous film thicknesses are needed for the quantitative description of the evaporative process. A decrease in the thickness of the adsorbed thin film in the interline region resulting from evaporation can cause both fluid flow and contact angle hysteresis.

ACKNOWLEDGEMENT

The support of N.S.F. Grant #GK-24223 entitled "Heat and Mass Transfer in Evaporating Menisci" is gratefully acknowledged.

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ECOULEMENT FLUIDE AU VOISINAGE D'UN MENISQUE EN EVAPORATION ET A ANGLE DE CONTACT NON NUL

Résumé—On décrit les mécanismes de transport dans la région d'un ménisque immobile en évaporation et à angle de contact non nul. Sont ensuite discutés des résultats déjà publiés sur des gouttes en évaporation. Un changement dans l'épaisseur du film mince adsorbé dans la région interfaciale résultant de l'évaporation peut provoquer à la fois une hystérésis de l'angle de contact et un écoulement fluide.

FLÜSSIGKEITSSTRÖMUNG IM RANDBEREICH EINES VERDAMPFENDEN MENISKUS MIT RANDWINKEL

Zusammenfassung—Die Tranportvorgänge im Randbereich eines stationären, verdampfenden Meniskus mit einem vorhandenen Randwinkel werden qualitativ dargestellt. Weiter werden früher veröffentlichte Daten für verdampfende Tropfen diskutiert. Eine Dickenänderung des adsorbierten dünnen Filmes im Randbereich, die von der Verdampfung herrührt, kann sowohl eine Hysterese im Benetzungswinkel wie auch eine Flüssigkeitsströmung hervorrufen.

ТЕЧЕНИЕ ЖИДКОСТИ НА ГРАНИЦЕ ИСПАРЯЮЩЕГОСЯ МЕНИСКА С НУЛЕВЫМ УГЛОМ СМАЧИВАНИЯ

Аннотация—Дается качественное описание процессов переноса при стационарном испарении на границе мениска при нулевом угле смачивания. Проводится анализ ранее опубликованных данных по испарению капель. Изменение толщины адсорбированной тонкой пленки на границе мениска в результате испарения может вызвать как гистерезис угла смачивания, так и течение жидкости.