Experimental investigation of contact angle, curvature, and contact line motion in dropwise condensation and evaporation

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Received 21 June 2002; accepted 17 December 2002

Abstract

Image-analyzing interferometry is used to measure the apparent contact angle and the curvature of a drop and a meniscus during condensation and evaporation processes in a constrained vapor bubble (CVB) cell. The apparent contact angle is found to be a function of the interfacial mass flux. The interfacial velocity for the drop during condensation and evaporation is a function of the apparent contact angle and the rate of change of radius of curvature. The results support the hypothesis that evaporation/condensation is an important factor in contact line motion. The main purpose of this article is to present the experimental technique and the data. The equilibrium contact angle for the drop is found experimentally to be higher than that for the corner meniscus. The contact angle is a function of the stress field in the fluid. The equilibrium contact angle is related to the thickness of the thin adsorbed film in the microscopic region and depends on the characteristics of the microscopic region. The excess interfacial free energy and temperature jump were used to calculate the equilibrium thickness of the thin adsorbed film in the microscopic region.

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Keywords: Contact angle; Condensation; Evaporation; Interfacial forces and fields; Wetting; Capillarity; Interfacial excess free energy; Spreading; Contact line motion

1. Introduction

Interfacial phenomena in the three-phase contact line region, where a liquid–vapor interface intersects a solid surface, are of importance to many equilibrium and nonequilibrium phenomena such as contact angle, adsorption, surface patterning, spreading, evaporation, condensation, boiling, wetting, and stability. Herein, we address small liquid regions formed within a quartz cuvette partially filled with n-butanol during condensation and evaporation of a sessile droplet. Generically, the versatile but simple experimental system employed is called a constrained vapor bubble (CVB). A cross-sectional view of the experimental CVB system partially filled with a partially wetting fluid, n-butanol, is presented in Fig. 1a. Depending on the imposed temperature field, menisci can form in the sharp corners and sessile drops can form on the flat walls. The shapes of the regions are easily viewed through a microscope because of the presence of naturally occurring interference fringes. These regions are connected by ultrathin liquid films and through the vapor. The liquid in the top corners is also connected to the bottom corners by the meniscus in the vertical corners. Since the chemical potential is a function of both pressure and temperature, a Kelvin–Clapeyron (K–C) continuum model for small regions, which includes these effects on the local vapor pressure, gives an enhanced understanding of both equilibrium and nonequilibrium processes.

The chemical potential and the change in the chemical potential energy per unit volume of a single component liquid in a gravitational field [1–7] are given by

\[ \mu_{ig} = \mu_i(T_i, P_i) + \rho_l g x, \]  
\[ \Delta \mu_g = -(K \gamma + \Pi - \rho_l g x) + \frac{\rho_l D_h m}{T} (T_{lv} - T_v), \]  
\[ \Delta \mu_g = \rho_l m R_g T_{lv} \ln \frac{P_{vlv}}{P_v}. \]  

The pressure in the bulk vapor at \( x \) is \( P_v \), whereas \( P_{vlv} \) is the vapor pressure at the liquid–vapor interface at \( x \). The difference between these two vapor pressures is used to obtain the interfacial mass flux. At equilibrium these two vapor pressures are equal. The interfacial vapor pressure is affected

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by capillarity ($K\gamma$), disjoining pressure ($\Pi$), the hydrostatic head ($\rho g x$), and temperature, $\rho_{lm}$ is the liquid molar density (mol/m$^3$), while $\rho_l$ is the liquid density (kg/m$^3$). The interfacial temperature jump is $\Delta T = T_{lv} - T_v$. The product of the density, $\rho$, and the latent heat of vaporization, $\Delta h_m$, in the volumetric heat of vaporization at the average phase change temperature, $T$. Various forms of these equations have been used to study the phase change phenomenon in small dimensions (e.g., [1–16]). Using Eq. (2) for both completely wetting and partially wetting and nonisothermal and isothermal cases, equilibrium results can be obtained and verified, experimentally. For example, for isothermal equilibrium, the extended Young–Laplace equation is obtained, which includes the definition of the disjoining pressure, $\Pi > 0$ for complete wetting:

$$K\gamma + \Pi = \rho_l g x = P_v - P_t.$$  \hspace{1cm} (4)

In Fig. 1a, $K\gamma > 0$ for the corner meniscus and the pressure in the liquid $P_l < P_v$. Experimentally, the measured shape of the liquid regions gives the isothermal interfacial free energy per unit volume or the pressure jump at the interface [17].

Since our particular interest is in nonisothermal systems, the effects of both temperature and pressure changes are important. The nonisothermal equilibrium use of Eq. (2) leads to the equation for the effect of the excess interfacial temperature on the shape of small liquid regions (e.g., [1,3,6]):

$$K\gamma + \Pi - \rho_l g x = \frac{\rho_l \Delta h_m}{T}(T_{lv} - T_v).$$ \hspace{1cm} (5)

This versatile equation demonstrates that the thickness and thickness profile are strongly coupled with the temperature and the excess temperature fields. For the experimental conditions employed in the present study, $\rho_l$ is 810 kg/m$^3$, $\Delta h_m$ is 591.3 kJ/kg.

For $\Delta \mu \neq 0$, Eqs. (2) and (3) can be used with interfacial kinetic theory to obtain an equation that gives a Kelvin–Clapeyron model for interfacial mass flux written as a net heat flux associated with interfacial condensation or evaporation (e.g., [3–5,8,10,16,18]):

$$q'' = h_{lv}(T_{lv} - T_v)$$

$$= h_{lv}(T_{lv} - T_v) - h_{lv}(\Pi + K\gamma - \rho_l g x).$$ \hspace{1cm} (6)

$$h_{lv}^{kl} = \left(\frac{C^2 M}{2\pi R_g T_{lv}}\right)^{(1/2)} \frac{V_{lm} P_v \Delta h_m}{R_g T_{lv}}.$$ \hspace{1cm} (7)

The net mass flux is a function of the interfacial temperature jump and the interfacial pressure jump due to the shape. The classic heat transfer coefficient, $h_{lv}$, which is viewed as a function of only the temperature jump, is replaced in Eq. (6) by coefficients for the temperature and pressure jumps. Due to the effect of temperature on the vapor pressure, the coefficients are strong functions of the temperature level and increase rapidly with temperature. The values of the coefficients demonstrate that it is much easier to measure (or, simply, observe) the interfacial pressure jump via the profile than the interfacial temperature jump. For example, the following equation is obtained for n-butanol at $T = 45^\circ$C, $P_{lv} = 3.42 \times 10^3$ Pa:

$$q'' = 5.02268 \times 10^5(T_{lv} - T_v) + 0.31792(P_l - P_v).$$ \hspace{1cm} (7)

For a partially wetting n-butanol sessile drop with a radius of curvature of 140 µm, $\Delta P = 363$ N/m$^2$. For an equivalent temperature jump effect in Eq. (7), $\Delta T = 2.3 \times 10^{-4}$ K. Therefore the effects of extremely small interfacial temperature gradients are significant in many nonisothermal and apparently "isothermal" systems.

Herein we describe the use of a very simple experimental setup to study the dynamics of the dropwise condensation and evaporation process. We use image-analyzing interferometry to calculate the curvature and the apparent contact angle of the liquid drop and the meniscus in the corner. Combining with the microscopic region analysis, we use our experimental data to obtain useful information about the equilibrium behavior for a partially wetting fluid on a solid surface. The main purpose of this article is to present the experimental technique and the data. There is an extensive literature on dropwise condensation and evaporation. For example, Bourgès-Monnier and Shanahan studied the influence of evaporation on the contact angle using a projection method [19]. Birdi et al. [20] found that the evaporation rates of water droplets on a solid surface are determined by the
rate of vapor diffusion in the medium. They developed a correlation between the rate of vapor diffusion and the radius of curvature of the drop and concluded that the evaporation rate of a spherical drop depends on the radius of a solid–liquid interface. De Ruiter et al. [21] found that the driving force for the droplet spreading is the loss of the droplet’s free energy due to increase in its base radius, while dissipation occurs because of viscous flows in the droplet core. Our technique is useful particularly for fluids with small contact angles.

2. Materials and experimental setup methods

A simple experimental setup based on the CVB concept is used to study the contact angle and curvature during the condensation and evaporation of an n-butanol drop. The experimental setup consists of a quartz cell of square cross section with inside dimensions of 3 × 3 mm, outside dimensions 5.5 × 5.5 mm, and length 40 mm. The quartz cell is partially filled with n-butanol (from Sigma–Aldrich Inc., purity 99.8%). The liquid forms a meniscus in the corners of the cell, as shown in Fig. 1a. A schematic diagram of the experimental setup is shown in Fig. 1b. The cell is mounted axially on a grooved copper plate of rectangular cross section (60 × 35 × 6 mm). A patch heater is attached to the bottom of the copper plate using high-temperature epoxy to reduce the contact resistance. The copper plate, because of its high conductivity, ensures approximately uniform temperature along its surface. For studying the condensation of n-butanol, a very small amount of power is applied to this heater. Vapors of n-butanol formed inside the quartz cell condense on the upper surface inside the cell, as it is at a slightly lower temperature compared with the saturation temperature corresponding to the vapor. n-Butanol partially wets the quartz surface. Hence we can observe dropwise condensation of n-butanol. By changing the power applied to the bottom heater, we can change the rate of condensation. The same setup can be used to study the evaporation of n-butanol. To facilitate this, a thermoelectric heater is attached to the upper surface of the cell. When the drops are formed on the upper surface inside the quartz cell, power is applied to the thermoelectric heater attached to the upper surface, while the patch heater at the bottom of the copper plate is turned off. So the drops evaporate inside the cell. The rate of evaporation is changed by changing the power applied to the upper thermoelectric heater. This entire setup is mounted on the microscope table as shown in Fig. 1b.

Optical interferometry has been used previously to observe interfacial phenomena. Jawurek [22] studied bubble dynamics and microlayer geometry in nucleate boiling using interferometry. Voutsinos and Judd [23] employed laser interferometry to investigate microlayer evaporation phenomena. Chen and Wada [24] used laser light interference microscopy to study the dynamics of liquid drop spreading. Ludviksson and Lightfoot [25] and Bascom et al. [26] analyzed the effect of surface shear in a climbing liquid using optical technique. Recently Zheng et al. [27] described an expression for film thickness as a function of order of interference for a sessile drop on a quartz surface.

In our experimental setup monochromatic light (λ = 543.5 nm) from a Hg arc is used to illuminate the cell through the objective of the microscope. Naturally occurring interference fringes result due to reflection of monochromatic light at the liquid–vapor and liquid–solid interfaces. A CCD camera is used to record the images. Based on the images, the drop is assumed to be a spherical cap. There is a small region near the apparent contact line where this does not apply. The corner meniscus is considered to be a part of a circle in the region δ > 0.097 µm. Recorded images of the interference fringes for the meniscus and the drop are analyzed using Image-Pro Plus software to extract gray value plots. Using the gray value plots and the geometry of the cell, the film thickness profiles for the meniscus and the drop are obtained [27,28]. The curvature and the apparent contact angle are then calculated simultaneously by best fitting the experimental film thickness profile [28]. Even though the previous studies of the CVB heat pipe concept used an evacuated cell [18,27,28], simplicity dictated the current use of a vapor–air bubble.

3. Observations and results

The region of dropwise condensation and evaporation is viewed through a microscope with a 50× objective using monochromatic light (λ = 543.5 nm) from a Hg arc. Naturally occurring interference fringes appear due to the reflection of light at the liquid–vapor and liquid–solid (quartz surface) interfaces. The images are captured using a CCD camera. With this setting, each of 640 × 480 pixels measures average reflectivity of a region with a 0.177-µm diameter. The recorded images are analyzed using an image processing technique based on interferometry to get the curvature and the apparent contact angle. In all the experiments for condensation and evaporation, we used the same location in the cell to observe the drop.

3.1. Condensation

During the condensation of n-butanol, we monitor the growth of a single drop as a function of time until that drop merges with another drop. The image analysis shows that the radius of curvature of the drop increases linearly as a function of time as the drop grows, while the apparent contact angle remains constant for a given rate of condensation. The same experiment is repeated for different rates of condensation (by changing the power applied to the bottom heater). The experimental data of radius of curvature as a function of time for each run during condensation are shown in Figs. 2a–2e. As the rate of condensation increases, the contact angle increases. In Figs. 3a–3e, the images of the drop growth during condensation corresponding to Fig. 2c
are shown. Thus the rate of condensation increases from Figs. 2a–2e. For all the data points in Fig. 2a, the rate of condensation and hence the contact angle are constant. Similarly, for all the data points in Fig. 2b, the rate of condensation and hence the contact angle are constant but higher than those corresponding to Fig. 2a and so on. Thus Figs. 2a–2e represent increasing rate of condensation and hence increasing contact angle; while Figs. 3a–3e, which correspond to different data points of Fig. 2c, represent a constant rate of condensation and, hence, a constant contact angle and increasing radius of curvature.

The thickness profile for the drop shown in Fig. 3c, is illustrated in Fig. 3f. With the interferometry technique, the minimum film thickness we can measure is 0.097 µm for n-butanol on a quartz surface using green light (λ = 543.5 nm). The points show the experimental profile obtained from analysis of the interference fringes, while the solid line represents the best-fit profile. The best-fit line is obtained using the experimental data and the geometry of the cell [27,28]. The least-squares method in MATLAB is used to perform the calculations for best fitting. A detailed description of how the profile is obtained is given elsewhere [27] and is beyond the scope of this article.

3.2. Evaporation

Also during the evaporation, we monitored a single drop as a function of time. We observed that the radius of curvature of the drop decreases linearly with time, while the apparent contact angle remains constant for a given rate of
evaporation. The same experiment is repeated for different rates of evaporation (by changing the power applied to the top thermoelectric heater). The experimental data of radius of curvature as a function of time for each run during evaporation are shown in Figs. 4a–4d. As the rate of evaporation increases, the contact angle decreases. In Figs. 5a–5e, the images of the drop during evaporation corresponding to Fig. 4c are shown. Thus, the rate of evaporation increases from Figs. 4a–4d. For all the data points in Fig. 4a, the rate of evaporation and hence the contact angle are constant. Similarly, for all the data points in Fig. 4b, the rate of evaporation and hence the contact angle are constant, but the contact angle is lower than that corresponding to Fig. 4a and so on. Thus, Figs. 4a–4d represent increasing rate of evaporation and hence decreasing contact angle, while Figs. 5a–5e, which correspond to different data points of Fig. 4c, represent a constant rate of evaporation and hence a constant contact angle and decreasing radius of curvature.

The apparent contact angle during condensation was always higher than that during evaporation for all the experiments. This is in agreement with the principle that the advancing contact angle is always higher than the receding contact angle.

3.3. Corner meniscus

The contact angle and the curvature for the corner meniscus, at the same axial location as the drop, remains constant in all the above experiments when a drop is not merging with the corner film. Also the contact angle for
Fig. 4. Radius of curvature versus time for n-butanol evaporation: (a) contact angle = 4.6°, (b) contact angle = 4.4°, (c) contact angle = 4.2°, (d) contact angle = 3.9°.

The drop merges into the corner meniscus only when it contacts the corner meniscus. Snapshots of the drop merger process in the corner meniscus during condensation at the interfacial mass flux of 20.9 mg/m² s (corresponding to the corner meniscus is always lower than that for the drop. The drop merges into the corner meniscus only when it contacts the corner meniscus. Snapshots of the drop merger process in the corner meniscus during condensation at the interfacial mass flux of 20.9 mg/m² s (corresponding to
Fig. 6. Drop merging into the corner meniscus during condensation at the same interfacial mass flux as in Fig. 2e. Relative time: (a) $t = 0\, \text{s}$, (b) $t = 0.33\, \text{s}$, (c) $t = 0.66\, \text{s}$, (d) $t = 0.99\, \text{s}$, (e) $t = 2.64\, \text{s}$.

Fig. 2e) are shown in Figs. 6a–6e. The front of the corner meniscus during the merger of the drop is unstable. Hence a disturbance develops that causes the front to shed mass as shown in Fig. 6e. The meniscus then recedes back into the corner. We monitored the motion of this retracting corner meniscus and calculated its contact angle and curvature as a function of time. The curvature and contact angle data of this corner film are shown in Figs. 7 and 8, respectively. As the corner film retracts toward the corner, its contact angle and curvature approach the steady-state contact angle and curvature values of the corner meniscus present, when the drop is not merging with the corner meniscus. The observed steady-state and equilibrium contact angles for the corner film were both $2.2^\circ$. In the experiments, the condensate could flow from the horizontal corners to the bottom of the cell via the vertical corners.

Fig. 7. Curvature versus time for the meniscus retracting toward the corner during $n$-butanol condensation.
4. Discussion

4.1. Relation between contact angle and interfacial mass flux during phase change

Based on the observed images, we assume that the drop of n-butanol forms a spherical cap on the quartz surface. The volume of this spherical cap and the area of the liquid–vapor interface are given by the relations [29]

\[
V_l = \left(\frac{\pi R^3}{3}\right) \left(2 - 3 \cos(\theta_d) + \cos^3(\theta_d)\right)
\]
or

\[
V_l = \left(\frac{\pi R^3}{3}\right) (1 - \cos \theta_d)^2 (2 + \cos \theta_d)
\]

and

\[
A_{lv} = 2\pi R^2 (1 - \cos \theta_d).
\]

Hence, the mass flux of condensation (or evaporation) based on unit area of the liquid–vapor interface is

\[
\dot{m} = \frac{d}{dt} \left\{ \rho_l V_l A_{lv} \right\}.
\]

During condensation (or evaporation) at constant rate, the observed contact angle does not change with time. Therefore,

\[
\dot{m} = \frac{\rho_l}{6} (1 - \cos(\theta_d))(2 + \cos(\theta_d)) \frac{dR}{dt}.
\]

Let \( f(\theta_d) = (1 - \cos(\theta_d))(2 + \cos(\theta_d)) \). Therefore,

\[
\dot{m} = \frac{\rho_l}{6} f(\theta_d) \frac{dR}{dt}.
\]

For complete wetting, \( \theta_d = 0^\circ \), \( f(\theta_d) = 0 \). For \( \theta_d = 90^\circ \) and \( \theta_d = 180^\circ \), \( f(\theta_d) = 2 \). Since, from the data, we know \( \theta_d \) at each constant value of \( dR/dt \), we get \( f(\theta_d) \) as a function of mass flux of condensation (or evaporation). The results are plotted in Fig. 9 for both the condensation process and the evaporation process. The interfacial heat flux calculated from Eq. (6) gives the local mass flux, while the mass flux calculated from Eq. (11) using the experimental data gives the total mass flux through the interface. Also, the local flux changes rapidly near the contact line region [11]. Hence integration has to be performed to get the total interfacial mass flux from Eq. (6). Since the experimental technique used in this study gives an average value of the total interfacial mass flux based on Eq. (11), the need for an integration to get the total interfacial mass flux is avoided.

Extrapolating the results gives \( f(\theta_d) \approx 0.012 \) at \( \dot{m} = 0 \). Solving the nonlinear equation \( f(\theta_d) = 0.012 \) in MATLAB gives the equilibrium contact angle for the drop, \( \theta_d \approx 5.1^\circ \) at \( \dot{m} = 0 \). Independently, \( \theta_d = 5.2^\circ \) at \( \dot{m} = 0 \) for the condensation data and \( \theta_d = 5^\circ \) at \( \dot{m} = 0 \) for the evaporation data. The value at \( \dot{m} = 0 \) for each process demonstrates the correct type of hysteresis for each contact line movement.

We define the characteristic length of the drop based on the liquid–vapor interfacial area and drop volume as

\[
L_d = \frac{V_l}{A_{lv}}.
\]

Thus, the characteristic interfacial velocity for the drop is given by

\[
U_d = \frac{d}{dt} \left( \frac{V_l}{A_{lv}} \right),
\]

\[
U_d = \frac{1}{6} f(\theta_d) \frac{dR}{dt}.
\]

Hence, the characteristic interfacial velocity of the drop during the condensation and evaporation processes is a function of the contact angle and the rate of change of curvature. The characteristic drop velocity for both evaporation and condensation as a function of contact angle is plotted in Fig. 10. The data fit the scaling law \( U_d \propto \theta_d^3 \). The equation
of the polynomial fit is
\[ U_d = 0.0002 \theta^3 - 0.0029 \theta^2 + 0.0197 \theta - 0.0463. \] (15)

This dependence of interfacial velocity on the apparent contact angle is consistent with Tanner’s scaling equation [30] for the spreading of a drop. It also provides another way of getting the equilibrium contact angle. From Fig. 10, we get an equilibrium contact angle for the drop as 5.3°, which agrees with the value we get from the interfacial mass flux calculations. Depending on the spreading regime, there are various forms of Tanner’s scaling equation in the literature [31]. We observed only a single scaling law for our data on contact angle and interfacial velocity. We do not have enough data to support all the different scaling models reported in [30,31]. Anderson and Davis [11] used a linear combination of Tanner’s law and a term signifying the contribution due to evaporation flux to relate the contact line velocity to the contact angle. But in our analysis, the spreading is due to the interfacial phase change (condensation or evaporation). So we used a characteristic interfacial velocity based on the interfacial area. According to Ref. [11], the fluid velocity is equal to the spreading velocity at zero interfacial evaporation flux. In our case, at equilibrium, the interfacial velocity is zero. Thus, the interfacial velocity used here is the velocity of spreading due to phase change. Even though Tanner’s law is for the contact line without phase change, we can use a form of Tanner’s scaling equation (cubic dependence) to relate the apparent contact angle to the velocity of spreading [30]. Thus, we can use Tanner’s scaling equation for the phase change. In doing so, we have to use a characteristic interfacial velocity for phase change, which is different from the contact line velocity in the horizontal direction used by Anderson and Davis [11]. Thus, \( U_d \) signifies a combined effect of the contact line velocity and the fluid velocity defined in [11]. We feel that our experimental results add support to Wayner’s model [8,13] for the presence of phase change in forced spreading.

4.2. Relation between contact angle and interfacial force field

The shape of the drop and the meniscus is characterized by their curvature and contact angle. These parameters decide the interfacial free energy and hence the force field in the fluid [32]. Because of the differences in the shape-dependent intermolecular force field, there is a pressure difference between the liquid drop (\( K_d < 0 \)) and the meniscus in the corner (\( K_c > 0 \)) of the cell. The dimensionless free energy difference for the flow of condensate from the drop to the corner during condensation was obtained as [18]

\[
\frac{F}{d\gamma} = (\cos \theta_c - \cos \theta_d) + \delta(K_c - K_d). \] (16)

Thus, the dimensionless difference in free energy represents the relative magnitude of the resistance force due to shear as compared with the free energy of the surface of a flat liquid film.

From the condensation data shown in Fig. 9, as the interfacial mass flux for condensation increases, the apparent contact angle of the drop increases. The contact angle and the curvature of the corner meniscus remain constant when the drop is not merging into the corner meniscus. Therefore, increasing the interfacial mass flux of condensation causes an increase in the dimensionless free energy difference for flow associated with the condensing drop. Thus the contact angle is a function of the stress field in the fluid. A theoretical discussion of this phenomenon awaits additional data.

The effect of the liquid–vapor interfacial pressure jump and the temperature jump on the interfacial mass flux can be analyzed in view of the Kelvin–Clapeyron model [3,6] of the interface. DasGupta et al. [16] used this model to study the evaporation process of a curved completely wetting microfilm near the contact line region. The model equation includes an isothermal change in the interfacial pressure jump (Kelvin effect) and an isobaric change in the interfacial temperature (Clapeyron effect) as given by Eq. (6). The interfacial pressure jump can be obtained from Eq. (4), which is the augmented Young–Laplace equation.

To calculate the interfacial temperature jump, first we calculate the value of interfacial heat flux [27] as

\[ q'' A_N = -\frac{d(\Delta h_m \rho l V_l)}{dt}, \] (17)
\[ q'' = -\frac{\Delta h_m \rho l (1 - \cos \theta_d)(2 + \cos \theta_d) \frac{dR}{dt}}{2}. \] (18)

The nonequilibrium interfacial pressure jump is calculated from Eq. (4) using the experimental data of the curvature and the apparent contact angle. Since for the macroscopic profile the film thickness is large, the disjoining pressure is very small. Still it was taken into account to calculate the pressure jump from Eq. (4). Thus in Eq. (6), we know the values of \( P_l - P_v \) and \( q'' \). The interfacial temperature jump \( T_N - T_c \) for a drop during condensation and evaporation is then calculated using the Kelvin–Clapeyron model.
given by Eq. (6). The calculated values of interfacial temperature jump for the condensation data corresponding to Fig. 2c are reported in Fig. 11. This interfacial temperature jump for the condensation data corresponding to given by Eq. (6). The calculated values of interfacial temperature jump at equilibrium as a special case of Eq. (5):

\[ \Pi = \frac{\Delta h_{lv}}{T_i} (T_{lv} - T_v), \]

where

\[ T_i = \frac{T_{lv} + T_v}{2}. \]

Based on the definition of excess free energy of adhesion, Sharma [12,33] calculated the spreading coefficient with only apolar interaction and \( A > 0 \) (partially wetting) as

\[ \Delta \Pi_{LW} = \Delta \Pi_{vdW} = \frac{-A}{12\pi d_0^2}, \]

where \( A \) is the Hamaker constant, which is related to the disjoining pressure, \( \Pi \), by

\[ \Pi = \frac{A}{6\pi \delta_e^3}. \]

Therefore, from Eqs. (19) and (21),

\[ \delta_e = \left(\frac{-A T_v}{6\pi (T_{lv} - T_v) \Delta h_{lv}}\right)^{1/3}. \]

The spreading coefficient is related to the macroscopic contact angle based on Young’s equation,

\[ \delta_{LW} = \gamma (\cos \theta_e - 1). \]

We note here that \( n \)-butanol is apolar while the quartz surface is polar. So the polar interaction does not play any role in determining the interfacial behavior of this system.

We calculate the spreading coefficient using Young’s equation at \( \dot{m} = 0 \) and from that the Hamaker constant using Eq. (20) with \( d_0 = 0.158 \text{ nm} \). Then using the calculated value of the interfacial temperature jump \( (T_{lv} - T_v) = -10^{-4} \) \text{ K} \) we solve Eq. (22) to get the equilibrium thickness of the thin adsorbed film in the microscopic region. Because the interfacial temperature jump is small and almost constant, we use the average value of \( -10^{-4} \) \text{ K} \) for the interfacial temperature jump. Assuming the interfacial temperature difference \( (T_{lv} - T_v) \) is the same for the drop and the corner meniscus, we get the results

\[ \delta_{LW} = -1.89 \times 10^{-5} \text{ J/m}^2, \]

\[ \delta_{vdW} = -1.01 \times 10^{-5} \text{ J/m}^2, \]

\[ \delta_{efc} = 1.8 \times 10^{-9} \text{ m}, \]

\[ \delta_{efd} = 3.2 \times 10^{-9} \text{ m}, \]

where \( \delta_{efd} \) and \( \delta_{efc} \) represent the equilibrium thickness of the thin film adjacent to the drop and the corner meniscus, respectively;

\[ d_0 = 0.158 \text{ nm} [34], \]

\[ \gamma = 25.4 \times 10^{-3} \text{ J/m}^2 [35], \]

\[ \theta_{ed} = 5.1^\circ, \]

\[ \theta_{ec} = 2.2^\circ. \]

Here the subscripts \( ed \) and \( ec \) represent the equilibrium drop and the equilibrium corner meniscus, respectively. Thus, the spreading coefficient of the drop is more negative than that of the corner meniscus. Therefore, the drop wants to spread out and there is a driving energy to merge the drop with the meniscus. Also, the equilibrium film thickness of the adsorbed film in the microscopic region adjacent to the drop \( (\delta_{efd}) \) is higher than that of the equilibrium adsorbed film in the microscopic region adjacent to the corner meniscus \( (\delta_{efc}) \). So, the magnitude of the film pressure (which is of the order of \( \Pi \delta_e \)) is higher for the thin film adjacent to the drop than for the thin film adjacent to the corner meniscus.

The spreading coefficient signifies the excess free energy due to van der Waals forces. This can be related to the excess free energy due to adhesion. The resulting equation, which relates the microscopic and the macroscopic parameters of
wetting [33], is written as

$$\Delta G^{\text{LW}} = S^{\text{LW}} \left( \frac{d^2}{\delta^2} \right). \quad (24)$$

The resulting values for the thin film adjacent to the drop and the corner meniscus at equilibrium ($\dot{m} \to 0$) are

$$\Delta G_{\text{fc}}^{\text{LW}} = -1.39 \times 10^{-7} \text{ J/m}^2,$$

$$\Delta G_{\text{fd}}^{\text{LW}} = -2.43 \times 10^{-7} \text{ J/m}^2.$$

Here the subscripts fc and fd represent the thin film adjacent to the corner meniscus and to the drop, respectively. The difference in the thickness of the thin adsorbed film in the microscopic region results in the difference in the excess free energy of the microscopic regions of the drop and the meniscus. Because of the difference in the characteristics of microscopic regions of the drop and the corner film, there is a difference in the equilibrium characteristics of the drop and the corner film. The difference between the experimental values of the equilibrium contact angles of the drop and the corner meniscus thus signifies an effective difference in the excess free energy contribution from the thin adsorbed film in the microscopic region. Using the concept of spreading coefficient, from Eq. (23), the difference in the excess free energy per unit area of the drop and the corner meniscus can be expressed as

$$\gamma (\cos \theta_{\text{ec}} - \cos \theta_{\text{ed}}) = 8.25 \times 10^{-5} \text{ J/m}^2. \quad (25)$$

We can invoke the concept of line tension to explain this excess free energy difference between the drop and the corner meniscus. Line tension is the reversible work done to expand a unit length of the three-phase contact line [36]. Thus it is the excess energy contribution by the three-phase contact line region. Including the effect of line tension, the modified Young equation can be written as [37]

$$\gamma_{\text{lv}} = \gamma_{\text{lv}} + \gamma_{\text{lv}} \cos \theta_e + \frac{\omega}{I}. \quad (26)$$

Here, $\omega$ is the line tension (J/m) and $l$ is the characteristic length for the contact line in the lateral direction. Writing this equation for the drop and the meniscus, we get

$$\gamma (\cos \theta_{\text{ec}} - \cos \theta_{\text{ed}}) = \frac{\alpha_d}{I_d} - \frac{\alpha_c}{I_c}. \quad (27)$$

Thus the difference in the equilibrium contact angles of the drop and the meniscus can be expressed in terms of the difference in the line tensions of the microscopic regions of the two.

The equilibrium contact angle can be analyzed using two approaches, macroscopic and microscopic, as discussed by Sharma and co-workers [12,33,38–40]. There can be an associated thin uniform film adsorbed on the solid surface in the microscopic region. For a drop of nonvolatile fluid sitting on a solid surface Sharma and co-workers obtained the modified equation of capillarity as

$$\delta_{\text{ls}} \left( 1 + \frac{\delta_{\text{ls}}^2}{\delta_{\text{ls}}^2} \right)^{-3/2} - \phi(\delta)/\gamma + K = 0. \quad (28)$$

Here, $K$ is the curvature of the drop at the center ($x = 0$). Integrating the above equation,

$$(1 + \delta_{\text{ls}}^2)^{-1/2} + \frac{1}{\gamma} \int \phi(\delta) d\delta - K\delta + C' = 0, \quad (29)$$

where $C'$ is an integration constant. This analysis does not consider the effect of interfacial temperature jump. In his analysis as $x \to \infty$, Sharma neglects the term $K\gamma$. Instead, we include this term. At large distance ($x \to \infty$), the microscopic analysis simplifies to a uniform film of equilibrium thickness $\delta_e$. The condition for this from Eq. (29) becomes

$$\phi(\delta_e) = K\gamma. \quad (30)$$

For the case of a partially wetting fluid with phase change, Sharma [12] studied the effect of adsorption on nucleation and film stability and analyzed the equilibrium vapor pressure of a curved liquid surface in view of the macroscopic wetting parameters. For the case of isothermal equilibrium the modified Young–Laplace equation was obtained [12] as

$$\gamma (1 + \delta_{\text{ls}}^2)^{-3/2} + \Pi = C_0. \quad (31)$$

where $C_0$ is a constant and is related to the curvature and disjoining pressure of the macroscopic interfacial profile. However, this analysis considered the isothermal equilibrium. The thin film region was studied in [12] using an equilibrium thickness obtained from the adsorption isotherm.

Total excess free energy in the microscopic region is a combination of the effect of the curvature, excess free energy due to adhesion, and the interfacial temperature difference. A detailed theoretical analysis of the relationship between the equilibrium contact angles (of the drop and the meniscus) and the excess free energy contribution from the thin adsorbed film on the surface based on a comprehensive model described by Eqs. (5), (28), and (31) awaits additional data and is beyond the scope of this article. The additional data needed are the equilibrium values of the wetting parameters for drops and the meniscus as a function of fluid wettability and thickness of the thin film adjacent to the drop and the meniscus. Also numerical data of the profiles of film thickness, curvature, contact angle, interfacial potential, etc. in the microscopic region are required. We have to use the concept of nonisothermal equilibrium based on Eq. (5) to model the microscopic (thin film) region. Then these results can be studied using the concepts of interfacial excess free energy in the microscopic region and Kelvin–Clapeyron model of phase change. This work is currently in progress. The main purpose of this article is to present the experimental technique and the data.

5. Conclusions

Dropwise condensation and evaporation of n-butanol on a quartz surface was studied in a constant contact angle mode. The experimental results showed that as the rate of condensation increased, the contact angle increased, while at the
same location, as the rate of evaporation increased, the contact angle decreased. The contact angle during condensation was found to be higher than that during evaporation. The interfacial mass flux and the characteristic interfacial velocity during condensation and evaporation are a function of the contact angle and the rate of change of radius of curvature. The interfacial temperature jump is of the order of $10^{-4}$ K and is too small to measure experimentally for the observed contact line velocity. The value can be calculated using the Kelvin–Clapeyron model.

The contact angle for the drop was always higher than that for the corner meniscus. The contact angle is thus a function of the stress field in the fluid. The equilibrium thickness of the adsorbed thin film in the microscopic region was different for the drop and the meniscus. The difference in the equilibrium contact angles of the drop and the meniscus in the macroscopic region is a result of the difference in the excess free energy contribution of the thin adsorbed film in the microscopic region. Thus the adsorbed thin film in the microscopic region plays an important role in determining the equilibrium behavior of the drop and the corner meniscus. The results support the hypothesis that evaporation/condensation is an important factor in contact line motion.

Acknowledgments

This material is based on the work supported by the National Aeronautics and Space Administration under Grant NAG3-2383. Any opinions, findings, and conclusions expressed in the article are those of the authors and do not necessarily reflect the view of NASA.

Appendix A. Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$DG$</td>
<td>free energy (J/m$^2$)</td>
</tr>
<tr>
<td>$\Delta h_m$</td>
<td>heat of vaporization (kJ/kg)</td>
</tr>
<tr>
<td>$\Delta h_{lv}$</td>
<td>heat of vaporization per unit volume (kJ/m$^3$)</td>
</tr>
<tr>
<td>$q''$</td>
<td>interfacial heat flux (W/m$^2$)</td>
</tr>
<tr>
<td>$m$</td>
<td>mass flux (kg/m$^2$s)</td>
</tr>
<tr>
<td>$A$</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>$A_{lv}$</td>
<td>liquid–vapor interfacial area (m$^2$)</td>
</tr>
<tr>
<td>$C$</td>
<td>accommodation coefficient = 2</td>
</tr>
<tr>
<td>$d_0$</td>
<td>equilibrium cutoff distance decided by short-range Born repulsion (0.158 nm)</td>
</tr>
<tr>
<td>$d_s$</td>
<td>width (m)</td>
</tr>
<tr>
<td>$F$</td>
<td>driving force for liquid flow per unit width (J/m)</td>
</tr>
<tr>
<td>$g$</td>
<td>acceleration due to gravity (m/s$^2$)</td>
</tr>
<tr>
<td>$h$</td>
<td>heat transfer coefficient (J/m$^2$K)</td>
</tr>
<tr>
<td>$K$</td>
<td>curvature (m$^{-1}$)</td>
</tr>
<tr>
<td>$l$</td>
<td>length (m)</td>
</tr>
<tr>
<td>$P$</td>
<td>pressure (N/m$^2$)</td>
</tr>
<tr>
<td>$R$</td>
<td>radius of curvature (m)</td>
</tr>
<tr>
<td>$R_g$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$S$</td>
<td>spreading coefficient (J/m$^2$)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>$\bar{T}$</td>
<td>average phase change temperature (K)</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s)</td>
</tr>
<tr>
<td>$U$</td>
<td>interfacial velocity (m/s)</td>
</tr>
<tr>
<td>$V$</td>
<td>volume (m$^3$)</td>
</tr>
<tr>
<td>$x$</td>
<td>distance (m)</td>
</tr>
</tbody>
</table>

Subscripts

- $0$ flat liquid film on the solid surface
- $c$ corner film
- $d$ drop
- $e$ equilibrium
- $fc$ thin film adjacent to the corner meniscus
- $fd$ thin film adjacent to the drop
- $l$ liquid
- $lm$ liquid molar amount
- $ls$ liquid–solid interface
- $lv$ liquid–vapor interface
- $sl$ solid–liquid interface
- $sv$ solid–vapor interface
- $v$ vapor

$\delta$ film thickness (m)
$\lambda$ wavelength (nm)
$\gamma$ surface tension (J/m$^2$)
$\phi$ excess energy per unit volume (J/m$^3$)
$\Pi$ disjoining pressure (J/m$^3$)
$\rho$ density (kg/m$^3$)
$\theta$ contact angle (degrees)
$\mu$ chemical potential (J/m$^3$)
$\tau$ average shear stress (J/m$^3$)
$\omega$ line tension (J/m)

Superscripts

- $cl$ Clapeyron
- $kl$ Kelvin
- $LW$ apolar component

Greek symbols

- $\delta$ film thickness (m)
- $\lambda$ wavelength (nm)
- $\gamma$ surface tension (J/m$^2$)
- $\phi$ excess energy per unit volume (J/m$^3$)
- $\Pi$ disjoining pressure (J/m$^3$)
- $\rho$ density (kg/m$^3$)
- $\theta$ contact angle (degrees)
- $\mu$ chemical potential (J/m$^3$)
- $\tau$ average shear stress (J/m$^3$)
- $\omega$ line tension (J/m)

References