Proceedings of the ASME 2010 3rd Joint US-European Fluids Engineering Summer Meeting and
8th International Conference on Nanochannels, Microchannels, and Minichannels
FEDSM-ICNMM2010
August 1-5, 2010, Montreal, Canada

FEDSM-ICNMM2010-31201

SESSILE-WATER-DROPLET CONTACT ANGLE: THE EFFECT OF ADSORPTION

H. Ghasemi[*]
Thermodynamics and Kinetics Laboratory
Department of Mechanical and Industrial Engineering
University of Toronto
Toronto, Ontario M5S 3G8
CANADA
Email: hadi.ghasemi@utoronto.ca

C. A. Ward
Thermodynamics and Kinetics Laboratory
Department of Mechanical and Industrial Engineering
University of Toronto
Toronto, Ontario, M5S 3G8
CANADA
Email: charles.ward@utoronto.ca

ABSTRACT

A method has been recently proposed for determining the surface tension of solid-vapor interfaces. The proposed method was used in conjunction with Gibbsian thermodynamics to investigate both analytically and experimentally the possible role of line tension in determining the contact angle of sessile-water-droplets. After forming a sessile-water-droplet in a closed system, its contact angle was determined by measuring the curvature of three-phase contact line and the height of the axisymmetric droplet on its centerline. The total number of the moles in the closed system was determined from the minimum in the Helmholtz function. The total number of moles in the system was then changed to a new value and the system allowed to come to equilibrium again. The contact angle in the new equilibrium condition could be measured and predicted by taking the adsorption at the solid-liquid and solid-vapor interfaces into account but with line tension completely neglected. The predicted values of contact angle are in closed agreement with those measured indicating line tension plays no role in determining the contact angle of mm-sized water droplets on a polished Cu surface. The surface tension of the solid-vapor interface was approximately constant and equal to the surface tension of adsorbing fluid; that is, the Young equation could be simplified.

INTRODUCTION

In a closed system when a sessile droplet contacts an ideal solid surface (smooth, homogeneous, nondissolving), the thermodynamics postulates leads to a coupled system of equations as the necessary conditions for equilibrium [1–3]. However, the equations do not form a closed set of equations for determining the surface tension of solid-liquid and solid-vapor interfaces, γ^{SL} or γ^{SV}. Equations of state must be added to close system of equations. Those for the bulk phases may be added with no controversy (liquid phase approximated as incompressible fluid and vapor phase as an ideal gas). However, the existing equation of states for the surface phases have not been supported by the experimental data. A common assumption is that adsorption, especially at the solid-liquid interface, may be neglected. This assumption have been shown to be a poor approximation for many systems [4–9]. We show that the contact angle is sensitive to the liquid phase pressure at the three-phase contact line [10,11]. The observations indicate that the contact angle should be viewed as a thermodynamic property of the system and not as a material property which is fixed for a combination of a solid-liquid system.

Although several solid-vapor adsorption isotherms such as BET [12], FHH [13–15] are suggested, none of them have been proved by the experimental data for pressure near the saturation-vapor pressure. A solid-vapor adsorption isotherm called $\zeta-$isotherm [16] was recently proposed. It has been examined for

---

[*] Address all correspondence to this author.

the several systems. When the measurement of adsorbed vapor on a solid-vapor interface is available, one may find the ζ-isotherm parameters by fitting the isotherm relation to the measurements. The ζ- isotherm expression may be tested by comparing the calculated amount with that measured. When the ζ-isotherm parameters are known, one may use the isotherm in conjunction with the Gibbsian thermodynamics to obtain the expression for the surface tension of solid-vapor interface in terms of isotherm parameters and the surface tension of the adsorbing fluid. As will be seen, including the adsorption at the solid-vapor and solid-liquid interface actually simplifies the wetting problem, as compared with the approaches that neglect adsorption.

In this study, the method for determining γ^{SV} has been examined in the low pressure limit by using it to predict γ^{S0}, the surface tension of the solid in the absence of adsorption. This approach has been applied to four solid surfaces to examine the ζ-isotherm expression. After, the expression is examined at pressures close to the saturation pressure. In this range, the pressure is such that the contact angle can exist. In each experiment, an equilibrium sessile water droplet is formed in a closed system. The state of the system is changed by decreasing the total number of moles present in the system. The contact angle of the droplet in the new state is predicted by the minimum in the Helmholtz function of the system and compared with the measured one. The predicted and measured values of θ differ little. Since no line tension effects are included in the analysis, the agreement suggests that line tension plays no role in determining θ for the system considered.

ADSORPTION AT SOLID-VAPOR INTERFACES

The ζ-isotherm approximates the adsorbed phase as a collection of molecular clusters [16]. Each adsorbed cluster was assumed to be a quantum-mechanical-harmonic oscillator with a binding energy depended on the number of molecules in the cluster. The maximum number of molecules in a cluster was denoted as ζ. If the number of adsorption sites per unit area of a solid surface is denoted M, according to the ζ-isotherm the amount adsorbed, n^{SV}, as a function of $x^V (\equiv P^V/P_s)$, the ratio of the vapor phase pressure to the saturation pressure, is:

$$n^{SV} = \frac{Mc\alpha x^V[1-(1+\zeta)(\alpha x^V)^{\zeta}+\zeta(\alpha x^V)^{1+\zeta}]}{(1-\alpha x^V)[1+(c-1)\alpha x^V - c(\alpha x^V)^{1+\zeta}]}, \qquad (1)$$

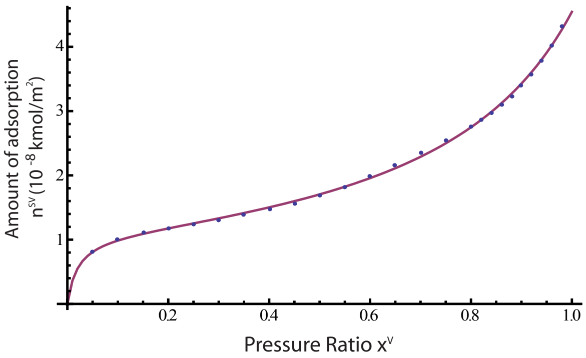

FIGURE 1. THE MEASURED AMOUNT OF ARGON ADSORBED ON TITANIA AT 77 K IS SHOWN AS SOLID DOTS [17]. THE SOLID LINE WAS CALCULATED USING EQN. 1 AND THE VALUES OF THE ADSORPTION PARAMETERS LISTED IN TAB. 1.

where c and α are temperature dependent parameters that are to be determined along with M and ζ from measurements of the amount adsorbed as a function of x^V. The accuracy of the ζ-isotherm description of a given set of isothermal adsorption measurements may be assessed by calculating the mean-square difference between the measured amount adsorbed and that calculated to be adsorbed, $\Delta(\zeta)$:

$$\Delta(\zeta) \equiv \frac{\sqrt{\sum_{j=1}^{N_m}[n^{SV}_{mes}(x^V_j) - n^{SV}_{cal}(\zeta, x^V_j)]^2}}{\sum_{j=1}^{N_m} n^{SV}_{mes}(x^V_j)}, \qquad (2)$$

where $n^{SV}_{mes}(x^V_j)$ is the amount measured at x^V_j, and $n^{SV}_{cal}(\zeta, x^V_j)$ is the amount calculated to be adsorbed at this condition. The number of measurements is denoted N_m. For a given set of adsorption measurements, the parameter ζ is treated as a threshold parameter. If it is taken to be smaller than the threshold value, and the isotherm parameters determined from the nonlinear regression package available in Mathematica, the value of the error, $\Delta(\zeta)$, is larger than when ζ is the threshold value. If ζ is taken to be larger than the threshold value, the error in calculations does not decrease further [16].

The ζ-isotherm expression was examined for four solid-vapor systems. The measured amount of Ar adsorbing at 77 K on titania that was reported by Matejova et al [17] is shown as solid dots in Fig. 1. The amount of N_2 adsorbing on titania at 77 K has been reported by [17]. These measurements are shown in Fig. 2. The solid lines in these two figures were calculated using Eqn. 1, the value of ζ, and the mean values of the isotherm parameters that are listed in Tab. 1. The mean-square difference between the calculations and the measurements, $\Delta(\zeta)$, for Ar and N_2 adsorbing on titania was 0.2% and 1.1%, respectively. We treat these parameters and ζ listed in Tab. 1 as material properties.

From the ζ-isotherm, one then finds an expression for the surface tension of the solid-vapor interface, $\gamma^{SV}_{[1]}$ in terms of the

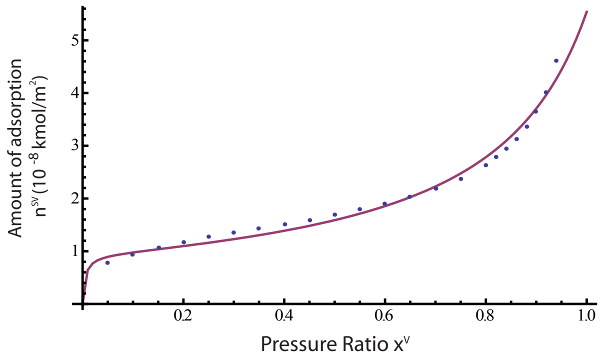

FIGURE 2. THE MEASURED AMOUNT OF NITROGEN ADSORBED ON TITANIA AT 77 K IS SHOWN AS SOLID DOTS [17]. THE SOLID LINE WAS CALCULATED USING EQN. 1 AND THE VALUES OF THE ADSORPTION PARAMETERS LISTED IN TAB. 1.

isotherm parameters and x^V

$$\gamma^{SV}_{[1]}(x^V) = \gamma^{LV} - Mk_bT\ln\left(\frac{(\alpha-1)[1+(c-1)\alpha x^V]}{(\alpha x^V-1)[1+(c-1)\alpha]}\right), \qquad (3)$$

where the subscript indicates the Gibbs dividing surface has been chosen to be at a position where the excess of the solid component vanishes. We will suppress this notation in subsequent equations [11]. One may take the limit of the expression for the surface tension of a solid-vapor interface as x^V goes to zero. Explicitly, the expression obtained for γ^{S0} is

$$\gamma^{S0} = \gamma^{LV} + Mk_bT\ln(1+\frac{c\alpha}{1-\alpha}). \qquad (4)$$

This equation could be interpreted as indicating that γ^{S0} depends on the values of the adsorption parameters and γ^{LV}. However, γ^{S0} is a material property of a solid, and its value cannot depend on the the vapor used to determine its value. Therefore, two possibilities arise. If the value of γ^{S0} determined for a solid surface depends on the vapor used, it would means the proposed method for determining γ^{SV} is incorrect in some fundamental sense. The other possibility is that the value of γ^{S0} is found to be same using different vapors, supporting the proposed approach and indicating that for a particular solid surface at a given temperature, a relation exists between γ^{LV} and the adsorption-isotherm parameters. For Ar and N_2 adsorbing on titania, the results are shown in Fig. 3. Different vapors are seen to indicate the same value of γ^{S0}.

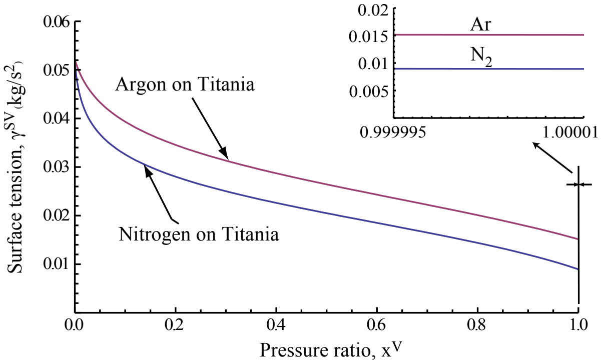

FIGURE 3. THE CALCULATED VALUES OF γ^{S0} ARE SHOWN FOR TITANIA EXPOSED TO Ar AND N_2 AT 77 K. NOTE THAT TWO STUDIES INDICATE THE SAME VALUE OF γ^{S0} FOR TITANIA AT 77 K.

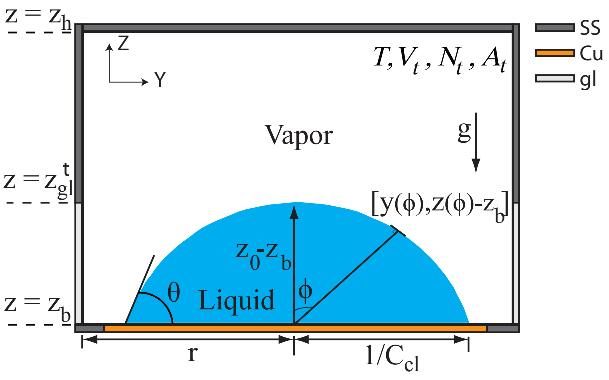

FIGURE 4. THE ISOTHERMAL SYSTEM HAS A FIXED TOTAL VOLUME, NUMBER OF MOLES, SURFACE AREA AND CONTAINS AN AXISYMMETRIC SESSILE WATER DROPLET THAT CONTACTS A POLISHED COPPER SURFACE. THE WALLS OF THE COMPOSITE SYSTEM CONSIST OF STAINLESS STEEL, COPPER, AND BOROSILICATE GLASS.

SYSTEM DEFINITION

The composite system considered is shown schematically in Fig. 4. The constraints of the isothermal system are a total volume V_t, a total surface area A_t, and a total of N_t water molecules. The molecules can be either in bulk or adsorbed on surface phases. There are three substrates: stainless steel, copper, and borosilicate glass denoted by subscripts ss, Cu, and gl, respectively. Each type of phase, liquid, vapor, liquid-vapor, solid-vapor or solid-liquid is denoted by a superscript L, V, LV, SV and SL respectively.

TABLE 1. ζ-ISOTHERM PARAMETERS AND SURFACE TENSIONS OF SEVERAL OXIDES AT 77K

Material	Vapor	γ^{LV} (kg/s^2)	M(10^{-9} kmol/m^2)	c	α	ζ	$\Delta(\zeta)$, %	γ^{S0} (kg/s^2)
$\alpha-$Alumina [17]	Ar	0.01514	10.769 ±0.1572	37.60 ±5.41	0.7726 ±0.0045	100	0.2	0.0486 ±0.0017
$\alpha-$Alumina [17]	N_2	0.00895	10.4974 ±0.1205	102.33 ±52.07	0.7727 ±0.0041	140	0.8	0.0483 ±0.0032
$\alpha-$Alumina [18]	N_2	0.00895	10.9844 ±0.3776	80.48 ±22.74	0.7643 ±0.0156	100	0.8	0.0481 ±0.0042
Titania [17]	Ar	0.01514	10.8066 ±0.1734	64.51 ±14.03	0.7632 ±0.0052	130	0.2	0.0521 ±0.0025
Titania [17]	N_2	0.00895	9.3383 ±0.6851	253.90 ±201.45	0.8315 ±0.0215	120	1.1	0.0516 ±0.0031
Magnesia [17]	Ar	0.01514	13.2577 ±0.1200	59.23 ±4.68	0.6622 ±0.0063	140	0.1	0.0556 ±0.0012
Magnesia [17]	N_2	0.00895	9.5109 ±0.2406	270.00 ±202.45	0.8808 ±0.0271	100	1.2	0.0552 ±0.0041
Borosilicate Glass [17]	Ar	0.01514	11.4864 ±0.1564	52.10 ±4.90	0.6476 ±0.0085	80	0.1	0.0475 ±0.0014
Borosilicate Glass [17]	N_2	0.00895	9.9651 ±0.4056	32.06 ±20.08	0.9163 ±0.0211	130	1.6	0.0463 ±0.0041

The total surface area may be expressed

$$A_t = A_{ss}^{SV} + A_{Cu}^{SV} + A_{Cu}^{SL} + A_{gl}^{SV}. \tag{5}$$

The conservation of moles gives

$$N_t = N^L + N_{Cu}^{SL} + N^{LV} + N^V + N_{Cu}^{SV} + N_{ss}^{SV} + N_{gl}^{SV}. \tag{6}$$

The total system volume is the sum of the liquid and vapor volumes:

$$V_t = V^L + V^V. \tag{7}$$

Based on the system constraints, the Helmholtz function acts as the thermodynamic potential for the composite system with T, V_t, A_t, and N_t as the independent variables. The conditions that the intensive properties must satisfy in order for equilibrium to exist in the composite system may be obtained by determining the conditions that the thermodynamic potential is an extremum [1, 3]. One then finds the chemical potential in phase j must satisfy

$$\mu^j + Wgz = \lambda \qquad j = L, V, SL, SV; \tag{8}$$

where W denotes the molecular weight, g the acceleration of gravity, and z the height above z_b, the base of the system. If the vapor phase is approximated as an ideal gas, then

$$\mu^V[T, P^V(z)] = \mu^V[T, P_s] + k_b T \ln[\frac{P^V(z)}{P_s(T)}], \tag{9}$$

and if the liquid phase as incompressible, then

$$\mu^L[T, P^L(z)] = \mu^V[T, P_s] + v_f[P^L(z) - P_s(T)], \tag{10}$$

where the saturation-vapor pressure is denoted $P_s(T)$, the vapor-phase pressure as P^V, the liquid-phase pressure as P^L, and the specific molar volume of the liquid at saturation as v_f. If the pressures in the liquid and vapor phases at height z divided by $P_s(T)$, are denoted $x^L(z)$ and $x^V(z)$ respectively, then at the liquid-vapor interface where $z = z_I$, the Laplace equation gives

$$x^L(z_I) - x^V(z_I) = \frac{\gamma^{LV}}{P_s}(C_1^{LV} + C_2^{LV}), \tag{11}$$

where the curvatures at a point on the liquid-vapor interface are denoted C_1^{LV} and C_2^{LV}. If the molar specific volume of the vapor at saturation is denoted $v_g(\equiv \bar{R}T/P_s(T))$, application of Eqn. 8, at the liquid-vapor interface of the droplet where $z = z_I$ requires the chemical potentials of each phase to be equal or

$$x^V(z_I) = \exp\left[\frac{v_f}{v_g}(x^L(z_I) - 1)\right]. \tag{12}$$

Note then that $x^L(z_I)$ and $x^V(z_I)$ are not independent. If one is known the other may be calculated.

DETERMINATION OF CONTACT ANGLE

The Bashforth and Adams [19] procedure is modified to impose the necessary conditions for thermodynamic equilibrium at the droplet apex [19–22]. The sessile droplet is assumed axisymmetric; at the apex ϕ vanishes and we denote properties evaluated there with the subscript zero. Since the curvatures of liquid-vapor interface at the droplet apex are equal, one may apply Eqns. 11 and 12 at the sessile droplet apex and find

$$C_0^{LV} = \frac{P_s}{2\gamma^{LV}}\left(x_0^L - \exp\left[\frac{v_f}{v_g}(x_0^L - 1)\right]\right). \tag{13}$$

When Eqn. 8 is applied at the droplet apex and at an arbitrary position on the liquid–vapor interface, λ may be eliminated. By making use of Eqn. 10 between these two points, one then finds

$$x^L(\phi) = x_0^L + \frac{Wg}{v_f P_s}[z_0 - z(\phi)]. \tag{14}$$

The curvature C_2^{LV} may be expressed

$$C_2^{LV} = \frac{\sin\phi}{y(\phi)}. \tag{15}$$

At an arbitrary position on the liquid-vapor interface, the Laplace equation, Eqn. 11, combined with Eqns. 12, 13, 14 and 15 gives

$$C_1^{LV}(\phi) = \frac{P_s x_0^V}{\gamma^{LV}}\left(1 - \exp\left[\frac{Wg[z_0 - z(\phi)]}{v_g P_s}\right]\right) + \frac{Wg[z_0 - z(\phi)]}{\gamma^{LV} v_f} + 2C_0^{LV} - \frac{\sin\phi}{y(\phi)}, \tag{16}$$

and from differential geometry

$$\frac{dy(\phi)}{d\phi} = \frac{\cos\phi}{C_1^{LV}}; \tag{17}$$

$$\frac{dz(\phi)}{d\phi} = -\frac{\sin\phi}{C_1^{LV}}. \qquad (18)$$

The boundary conditions at the droplet apex are

$$\begin{aligned} y(0) &= 0; \\ z(0) &= z_0 - z_b. \end{aligned} \qquad (19)$$

The maximum value of the turning angle, ϕ_m, is determined from:

$$\begin{aligned} y(\phi_m)C_{cl} &= 1; \\ z(\phi_m) &= z_b. \end{aligned} \qquad (20)$$

The value of θ is given by

$$\theta = \phi_m. \qquad (21)$$

In order to close the system of equations, C_0^{LV} must be determined.

MEASUREMENTS: THE CONTACT ANGLE FROM C_{cl} AND x_3^L

To close the system of equations, one method is to measure both C_{cl} and the droplet height $z_0 - z_b$. When Eqn. 12 is applied at the apex

$$x_0^V = \exp[\frac{v_f}{v_g}(x_0^L - 1)]. \qquad (22)$$

If the value of C_0^{LV} is assumed, the value of x_0^L may be calculated from Eqn. 13, and the value of x_0^V from Eqn. 22. Then the expression for $C_1^{LV}(\phi)$ may be obtained from Eqn. 16 and used in Eqs. 17 and 18 to close the system of equations. The system of equations may then be numerically integrated, and the boundary conditions given in Eqs. 19 imposed. At the three-phase line, the solution obtained from the assumed value of C_0^{LV} must satisfy Eqn. 20. If it does not, another value of C_0^{LV} is assumed and the process repeated. Once Eqn. 20 is satisfied the value of θ may be determined from Eqn. 21. Thus, θ may be viewed:

$$\theta = \phi_m(C_{cl}, z_0 - z_b). \qquad (23)$$

From Eqn. 14, the height of the droplet may be expressed in terms of the liquid-phase pressure at the three-phase line, x_3^L

$$z_0 - z_b = \frac{v_f P_s[x_3^L - x_0^L(C_{cl})]}{Wg}, \qquad (24)$$

where the value of $x_0^L(C_{cl})$ is determined from the assumed value of C_0^{LV}, see Eqn. 13. Thus the contact angle may viewed as a function of C_{cl} and x_3^L

$$\theta = \phi_m(C_{cl}, x_3^L). \qquad (25)$$

The procedure described in this section uses numerical methods to determine θ as a function of C_{cl} and x_3^L, but we note that for sessile droplets with spherical liquid-vapor interfaces, it may be shown analytically that θ is a function of C_{cl} and x_3^L [22].

PREDICTION: THE CONTACT ANGLE FROM N_t AND C_{cl}

One may form the Helmholtz function of the system by adding the Helmholtz potential of each existing phase including bulk and surface phases. The total Helmholtz function of the system shown schematically in Fig. 4 may be written [23]

$$\begin{aligned} F = &\int_{z_b}^{z_0} \pi y^2 f^L(z)dz + \int_{z_b}^{z_h} \pi r^2 f^V(z)dz - \int_{z_b}^{z_0} \pi y^2 f^V(z)dz + \\ &\int_{z_b}^{z_0} 2\pi y f^{LV} dz + \pi C_{cl}^{-2} f_{Cu}^{SL}(z_b) + f_{ss}^{SV}(z_b)(\pi r^2 - A_{Cu}) + \\ &\int_{z_{gl}^t}^{z_h} 2\pi r f_{ss}^{SV}(z)dz + \pi r^2 f_{ss}^{SV}(z_h) + (A_{Cu} - \pi C_{cl}^{-2}) f_{Cu}^{SV}(z_b) + \\ &\int_{z_b}^{z_{gl}^t} 2\pi r f_{gl}^{SV}(z)dz \end{aligned} \qquad (26)$$

A reference state is defined such that no droplet exists in the system and the vapor phase is in equilibrium with the adsorbed phases. Properties of the phases in the reference state are denoted with subscript I.The total Helmholtz function of the system in the reference state may be written as

$$\begin{aligned} F_I = &\int_{z_0}^{z_h} \pi r^2 f_I^V(z)dz + f_{I-ss}^{SV}(z_b)(\pi r^2 - A_{Cu}) + \\ &\int_{z_{gl}^t}^{z_h} 2\pi r f_{I-ss}^{SV}(z)dz + \pi r^2 f_{I-ss}^{SV}(z_h) + \\ &A_{Cu} f_{I-Cu}^{SV}(z_b) + \int_{z_b}^{z_{gl}^t} 2\pi r f_{I-gl}^{SV}(z)dz. \end{aligned} \qquad (27)$$

Therefore, the difference in the total Helmholtz potentials may be expressed as a function of $T, V_t, N_t, C_{cl}, \theta$:

$$F - F_I = F[T, V_t, N_t, C_{cl}, \theta] - F_I[T, V_t, N_t]. \qquad (28)$$

When a sessile droplet exists in the system, an iteration procedure may be used to plot $(F - F_I)$ as a function of θ. For instance, the Helmholtz potential of the system shown schematically in Fig. 4 for a known values of the T, V_t, N_t and C_{cl} is shown in Fig. 5.

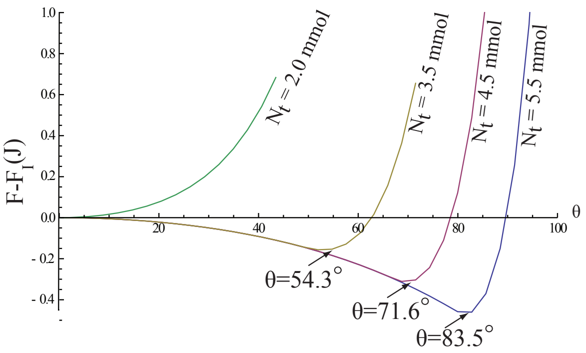

FIGURE 5. THE HELMHOLTZ FUNCTION RELATIVE TO THE REFERENCE STATE FOR A CLOSED SYSTEM INCLUDING A SESSILE DROPLET IN CONTACT WITH ITS OWN VAPOR WITH C_{cl} OF 0.2222 mm^{-1} IS SHOWN. THE THERMAL RESERVOIR HAD A TEMPERATURE OF 30 °C, $z_{gl}^{t} - z_b$ HAD A VALUE OF 0.068 m, THE SURFACE AREA OF THE STAINLESS STEEL HAD A VALUE OF 0.145 m^2, THE BOROSILICATE GLASS SURFACE AREA HAD A VALUE OF 0.0105 m^2, AND THE POLISHED COPPER SURFACE HAD AN AREA OF 0.0015 m^2. THE SYSTEM WAS APPROXIMATED AS A CYLINDER WITH A RADIUS OF 0.029 m AND A TOTAL VOLUME OF 0.001416 m^3. THE VALUES OF N_t CONSIDERED ARE INDICATED, AND THE DEPENDENCE OF θ TO N_t IS ILLUSTRATED [23].

EXPERIMENTAL INVESTIGATION

The prediction of the equilibrium contact angles in the previous section was experimentally investigated. The objective of the experiments was to examine the prediction of change in contact angle due to change in the total number of moles in the system shown schematically in Fig. 4. A sessile-water droplet was formed on the polished Cu surface by injecting water. After it reached to equilibrium condition, the total number of moles in the system was determined. Then the total number of moles in the system was changed by a known amount. In the new state, the contact angle was predicted and compared with the measured one.

EXPERIMENTAL PROCEDURE AND APPARATUES

For the experiments, water was deionized, distilled, and nano filtered until it had a resistivity of 18.2 MΩ. cm. Experimental procedure is described in detail in [23]. A sessile droplet was formed on the polished Cu surface. After the droplet had reached the equilibrium state, the droplet height, $z_0 - z_b$, was measured with an accuracy of ± 10 μm. A camera was placed in front of one of the glass viewports. The curvature of three-phase contact line was measured by image taken by camera using public domain software Imagej. The symmetry of the droplet was examined by measuring the droplet diameter at different positions on the perimeter of the droplet base. In each experiment, two sets of measurements were made. The first set was used to determine N_t^a from the measurement of C_{cl} and $z_0 - z_b$. The value for each experiment is listed in Tab. 2. Each portion of an experiment was labeled Enj where $1 \leq n \leq 5$, and j is either a or b. The value of θ observed in state-a of each experiment is also listed in Tab. 2. The second portion of each experiment was begun by purging some vapor from the system by a mechanical pump in a short period of time, ≈ 3 s. The vapor phase pressure decreased rapidly as the total number of moles in the system was reduced to N_t^b. We neglect any evaporation or desorption that occurred when the valve to mechanical pump was open. The value of N_t^b is then given by

$$N_t^b = N_t^a - \frac{\Delta P^V (V_t - V^L)}{\bar{R}T}, \tag{29}$$

where the ΔP^V is measured pressure drop due to valve opening and $\bar{R}$ is the gas constant. Once the value of N_t^b is known, the equilibrium contact angle in the new state, θ^b may be *predicted* using Helmholtz potential of the system. The value of θ^b may also be *measured* from direct measurement of $z_0 - z_b$ and C_{cl}. The measured and predicted values of θ^b are listed in Tab. 2.

1 Discussion

In an isothermal closed system, when the total volume, total surface area of the materials used to construct the chamber along with the ζ-isotherm parameters are known, provided that the total moles of the fluid is more than a limiting value, the contact angles of the stable equilibrium-sized droplet can be predicted as a function of N_t and C_{cl}. These prediction are examined for a series of sessile water droplets on a polished Cu surface. When a water sessile droplet in contact with a solid surface is in a equilibrium condition, the contact angle may be determined by measuring the values of $z_0 - z_b$ and C_{cl}. We refer this contact angle as the measured one. The predicted contact angle can be determined as the one corresponding to a minimum in the Helmholtz function. We emphasize that the Young equation used in the calculations, does not include any line tension effects; thus, line tension play no role in determining the contact angle of millimeter-sized water droplets on a Cu substrate. Thus, the contact angle cannot be viewed as a material property of a fluid-solid combination, but must be viewed as a thermodynamic property of a material-fluid combination that depends on the thermodynamic state of the system [10, 11, 16]. The effect on γ^{SV} of these changes in the thermodynamic state may also be determined.

TABLE 2. SUMMARY OF EXPERIMENTAL INVESTIGATION

Experiment	E1a	E1b	E2a	E2b	E3a	E3b	E4a	E4b	E5a	E5b
T^V(°C)	29.98 ±0.04		30.04 ±0.04		29.92 ±0.02		30.04 ±0.02		30.00 ±0.02	
T^L_{th}(°C)	29.95 ±0.04		29.94 ±0.02		29.88 ±0.02		30.01 ±0.02		30.01 ±0.02	
$V_t(10^{-3}\text{m}^3)$	2.103*		1.416		1.416		1.416		1.416	
N_t(mmol)	3.81 $\pm 10^{-6}$	3.74 $\pm 10^{-6}$	2.59 $\pm 10^{-6}$	2.57 $\pm 10^{-6}$	2.82 $\pm 10^{-6}$	2.77 $\pm 10^{-6}$	2.73 $\pm 10^{-6}$	2.70 $\pm 10^{-6}$	2.96 $\pm 10^{-6}$	2.87 $\pm 10^{-6}$
C_{cl} (mm^{-1})	0.333 ±0.006		0.501 ±0.004		0.435 ±0.005		0.402 ±0.008		0.357 ±0.005	
Measured θ (°)	45.0 ±0.4	37.4 ±0.4	63.4 ±0.4	61.1 ±0.4	76.5 ±0.4	71.9 ±0.4	63.1 ±0.4	60.4 ±0.4	69.2 ±0.4	65.0 ±0.4
Predicted θ (°)	–	38.3 ±0.3	–	61.6 ±0.3	–	72.7 ±0.3	–	60.8 ±0.3	–	64.6 ±0.3

* Note that the total volume of experiment E1 was larger than that of the other experiments.

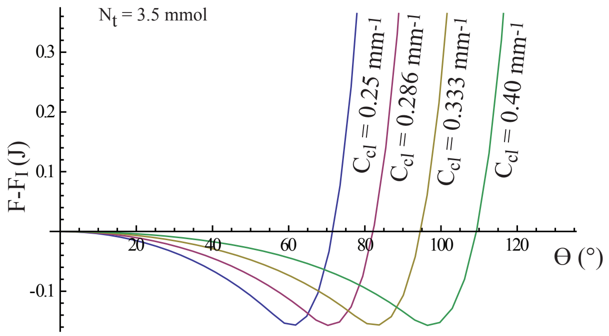

FIGURE 6. FOR THE CLOSED ISOTHERMAL SYSTEM CONSIDERED IN FIG. 4, THE HELMHOLTZ FUNCTION IS SHOWN AS A FUNCTION OF θ WITH N_t=3.5 mmol AND FOUR VALUES OF C_{cl}. A STABLE EQUILIBRIUM STATE IS PREDICTED IN EACH CASE [23].

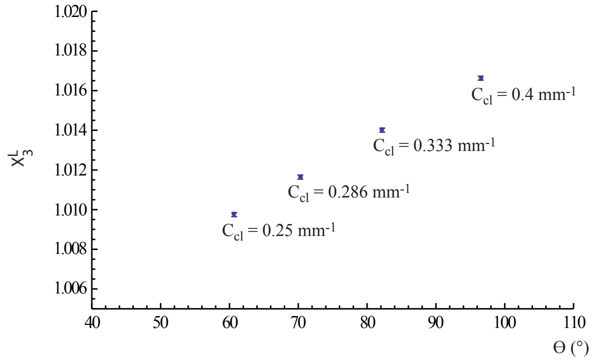

FIGURE 7. THE DEPENDENCE OF θ ON C_{cl} AND x_3^L FOR THE ILLUSTRATED EQUILIBRIUM STATES IN FIGURE 6 IS SHOWN.

The calculated values of γ^{SV} for Cu is very near the values of γ^{LV} of the adsorbing fluid; thus, the Young equation reduces to:

$$\gamma^{SL} = \gamma^{LV}(1-\cos\theta). \tag{30}$$

The dependence of θ on C_{cl}, x_3^L may be illustrated by calculating the Helmholtz function of an isothermal system containing a sessile droplet with a fixed value of N_t and different values of C_{cl}, see Fig. 6. In each case there is a stable equilibrium state for one value of θ, and as indicated in Fig. 7, the value of θ is predicted to be sensitive to both x_3^L and C_{cl}.

It is reported by Sefiane [24] and Chan and Pierce [25] that as a sessile droplet evaporates, it depins before it evaporates completely. Sefiane considered sessile water droplets on an Al substrate, and found that as the droplet evaporated, the contact angle decreased with the contact line pinned until the contact angle had reached $\sim 50°$. Then it depinned. The results shown in Fig. 5 provide a possible explanation for their observations. For the system that we consider, if the pressure were reduced and held at the reduced value so the droplet on the Cu substrate would evaporate slowly, then N_t would be progressively reduced, and the system would be expected to go through the sequence of states illustrated in Fig. 5. Note that when N_t is reduced from 5.5 to 3.5 mmol, the contact angle is reduced from 83.5 to 54.3°, and that in each of these stable states C_{cl} had the same value, i.e., the contact line was pinned. However, when the N_t was reduced further, it was no longer possible to find a stable equilibrium state corresponding to this value of C_{cl}. This suggests that complete depining is a non-equilibrium phenomena that occurs when N_t is reduced below a limiting value.

2 Conclusion

When the ζ-isotherm [16] is used in conjunction to Gibbsian thermodynamics, the value of θ for an axisymmetric, sessile droplet held in a closed isothermal container can be both measured and predicted. The measurement is obtained by measuring the droplet height on the center line, the value of C_{cl} and iteratively integrating the Laplace equation to obtain a droplet shape that satisfies these two conditions. The value of θ can also be predicted by measuring the Helmholtz variables: T, V_t, N_t and C_{cl}, calculating the Helmholtz potential as a function of θ and identifying the predicted contact angle as the one corresponding to the minimum value of the Helmholtz potential. For a range of N_t and C_{cl}, the results indicate a sessile droplet can be in a stable equilibrium state. A comparison of the predicted and measured values of θ are shown in Tab. 2. In the prediction of θ, no line tension effects were included. The agreement seen in Tab. 2 indicates that line tension does not play any role in determining the contact angle of the droplets investigated in this study, but indicates that the dependence of θ on C_{cl} can be predicted by including adsorption.

With the temperature maintained at 30 °C, N_t and C_{cl} were changed as indicated in Tab. 2. The observed contact angles were in the range from $37.4 \pm 0.4 \leq \theta \leq 71.9 \pm 0.4$. The effect of changing N_t and C_{cl} was to change the pressure in the liquid phase. As a result, the value of γ^{SL} was changed by a factor of more than 3.3 in these experiments, while γ^{SV} was approximately constant and equal to the surface tension of the adsorbing fluid. Thus, the Young equation reduces to Eqn. 30. As shown in this analytical and experimental investigation, the contact angle must be viewed as a thermodynamic property; not as a material property of a fluid-solid combination. Its value depends on the thermodynamic state of the system.

The Helmholtz function of the considered system in Fig. 4

indicates that the stability of a sessile droplet depends on both values of N_t and C_{cl}. For a given value of C_{cl}, N_t may be reduced to a limiting value, while the contact line remains pinned, and the contact angle is reduced (see Fig. 5). But if N_t is reduced further, there is no longer a stable equilibrium state for the droplet with that value of C_{cl}, and the droplet depins. Depending on the value of N_t, the droplet may come to a new equilibrium state or may evaporates completely.

ACKNOWLEDGMENT

We gratefully acknowledge the support of the Canadian Natural Sciences and Engineering Research Council, the Canadian Space Agency and the European Space Agency.

REFERENCES

[1] Ward, C. A., and Sasges, M. R., 1998. "Effect of gravity on contact angle: A theoretical investigation". *J. Chem. Phys.,* ***109***, pp. 3651–3660.

[2] Liu, Z., Muldrew, K., Wan, R. G., and Elliott, J. A. W., 2003. "Measurement of freezing point depression of water in glass capillaries and the associated ice front shape". *Phys. Rev. E,* ***67***, p. 061602.

[3] Gibbs, J. W., 1961. "On the equilibrium of heterogeneous substances". In *The Scientific Papers of J. Willard Gibbs*, H. A. Bumstead and R. G. V. Name, eds., Vol. 1. Dover, New York, pp. 55–349.

[4] Ghasemi, H., and Ward, C. A., 2009. "Surface tension of solids in the absence of adsorption". *J. Phys. Chem. B,* ***113***, pp. 12632–12634.

[5] Schneider, R., Chadwick, B., Jankowski, J., and Acworth, I., 1997. "Determination of physicochemical parameters of solids covered with conditioning films from groundwaters using contact angles. comparative analysis of different thermodynamic approaches utilizing a range of diagnostic liquids". *Colloids Surf. A: Physicochem. Eng. Asp.,* ***126***, pp. 1–23.

[6] Vogler, E. A., 1998. "Structure and reactivity of water at biomaterial surfaces". *Advances in Colloid and Interface Science,* ***74***, pp. 69–117.

[7] Schrader, M. E., 1996. "Contact angle and vapor adsorption". *Langmuir,* ***12***, pp. 3728–3732.

[8] Douillard, J. M., 1997. "Concerning the thermodynamic consistency of the "surface tension components" equations". *J. Colloid Interface Sci.,* ***188***, pp. 511–515.

[9] Chibowski, E., and Perea-Carpio, R., 2002. "Problems of contact angle and solid surface free energy determination". *Adv. Colloid Interface Sci.,* ***98***, p. 245.

[10] Wu, J., Farouk, T., and Ward, C. A., 2007. "Pressure dependence of the contact angle". *J. Phys. Chem. B,* ***111***, pp. 6189–6197.

[11] Ward, C. A., Wu, J., and Keshavarz, A., 2008. "Measurement of the adsorption at solid-liquid interfaces from the pressure dependence of contact angles". *J. Phys. Chem. B,* ***112***, pp. 71–80.

[12] Brunauer, S., Emmett, P. H., and Teller, E., 1938. "Adsorption of gases in multimolecular layers". *J. Am. Chem. Soc.,* ***60***, pp. 309–319.

[13] Frenkel, Y. I., 1946. *Kinetic Theory of Liquids*. Clarendon Press: Oxford, U.K.

[14] Halsey, G., 1948. "Physical adsorption on non-uniform surfaces". *J. Chem. Phys.,* ***16***, p. 931.

[15] Hill, T. L., 1986. *An Introduction to Statistical Thermodynamics*. Dover, Mineola, NY.

[16] Ward, C. A., and Wu, J., 2007. "Effect of adsorption on the surface tensions of solid-fluid interfaces". *J. Phys. Chem. B,* ***111***, pp. 3685–3694.

[17] Matejova, L., Solcova, O., and Schneider, P., 2008. "Standard (master) isotherms of alumina, magnesia, titania and controlled-pore glass". *Microporous and Mesoporous Materials,* ***107***, pp. 227–232.

[18] Cejka, J., Zilkova, N., Rathousky, J., and Zukal, A., 2001. "Nitrogen adsorption study of organised mesoporous alumina". *Phys. Chem. Chem. Phys.,* ***3***, pp. 5076–5081.

[19] Bashforth, F., and Adams, J. C., 1883. *An attempt to test the theories of capillary action by comparing the theoretical and measured forms of drops*. Cambridge University Press: Cambridge.

[20] Sasges, M. R., Ward, C. A., Azuma, H., and Yoshihara, S., 1996. "Equilibrium fluid configurations in low gravity". *J. Appl. Phys.,* ***79***, pp. 8770–8782.

[21] Elliott, J. A. W., Ward, C. A., and Yee, D. J., 1996. "Bubble shapes in rotating two-phase fluid systems: a thermodynamic approach". *J. Fluid Mech.,* ***319***, pp. 1–23.

[22] Ward, C. A., and Wu, J., 2008. "Effect of contact line curvature on solid-fluid surface tensions without line tension". *Phys. Rev. Lett.,* ***100***, p. 256103.

[23] Ghasemi, H., and Ward, C. A., 2010. "Sessile-water-droplet contact angle dependence on adsorption at the solid-liquid interface". *J. Phys. Chem. C,* ***114***, pp. 5088–5100.

[24] Sefiane, K., 2004. "Effect of nonionic surfactant on wetting behavior of an evaporating drop under a reduced pressure environment". *J. Colloid Interface Sci.,* ***272***, pp. 411–419.

[25] Chan, K. B., and Pierce, S. C., 2007. "Sessile droplet depinning: New life for gravimetric data". *J. Colloid Interface Sci.,* ***306***, pp. 187–191.