

## Effect of Contact Line Curvature on Solid-Fluid Surface Tensions Without Line Tension

C. A. Ward\* and Jiyu Wu

*Department of Mechanical and Industrial Engineering, Thermodynamics and Kinetics Laboratory, University of Toronto,  
5 King's College Road, Toronto, Ontario Canada, M5S 3G8*

(Received 10 January 2008; published 25 June 2008)

For sessile droplets partially wetting a solid surface, it has been observed experimentally that the value of the contact angle depends on the contact line curvature and this dependence has been attributed to tension in the contact line. But previous analyses of these observations have neglected adsorption at the solid-liquid interface and its effect on the surface tension of this interface. We show that if this adsorption is taken into account the relation between the contact angle and contact line curvature is completely accounted for without introducing line tension. Further, from the observed relation between the contact angle and contact line curvature, the adsorption at the solid-liquid interface can be determined, as can the surface tensions of the solid-liquid and solid-vapor interfaces.

DOI: [10.1103/PhysRevLett.100.256103](https://doi.org/10.1103/PhysRevLett.100.256103)

PACS numbers: 68.35.Md

In sessile droplet experiments, a number of investigators have observed that the contact angle  $\theta$  changes as the curvature of the three-phase line  $C_{cl}$  is changed. This relation has been suggested to result from line tension, but line tension has not provided a consistent explanation. Both positive [1–3] and negative values [4,5] have been reported, and the reported values differ in magnitude by several orders. An oft used method for determining the line tension is to plot measurements of  $\cos\theta$  versus  $C_{cl}$ , neglect any effects on the surface tension of the solid-liquid interface resulting from changes in  $\cos\theta$  and  $C_{cl}$ , and determine the line tension from the slope of the  $\cos\theta$ - $C_{cl}$  relation [1–7]. We show that when  $\theta$  and  $C_{cl}$  are changed, the pressure in the liquid phase at the three-phase line  $P_3^L$  is necessarily changed. This changes the adsorption at the solid-liquid interface,  $n^{SL}$ , and therefore the surface tension of this interface,  $\gamma^{SL}$ .

For water held in borosilicate glass cylinders, the sensitivity of  $\theta$  to changes in  $P_3^L$  has been shown to be surprisingly large [8,9]: when  $C_{cl}$  had a value of  $0.9 \text{ mm}^{-1}$ , the contact angle was observed to change by as much as  $79^\circ$  when  $P_3^L$  was changed by 235 Pa [8]. This pressure change is small compared to some that have resulted from changing  $C_{cl}$  and  $\theta$  in the process of measuring line tension [4]. The source of the sensitivity of  $\theta$  to  $P_3^L$  for water-borosilicate glass cylinders cannot be line tension, since  $C_{cl}$  was constant in each of these experiments [8,9]. This sensitivity has been suggested to result from  $n^{SL}$ , and its effect on  $\gamma^{SL}$  [8,9]. The dependence of  $\theta$  on  $P_3^L$  had been observed in earlier studies [10–13], but it could not be related to  $n^{SL}$  until an adsorption isotherm had been established for the *solid-vapor* interface that was valid when the vapor-phase pressure was near the saturation-vapor pressure [10,14].

Since the effect of  $n^{SL}$  on the  $\theta$  can now be taken into account, we examine its effect on sessile droplets of dodecane partially wetting very carefully prepared silanized silicon wafers [4]. The values of  $C_{cl}$  for the sessile droplets

in the study reported in [4] ranged up to  $6.7 \mu\text{m}^{-1}$  (or down to a radius of 75 nm). This is the  $C_{cl}$  range where line tension is suggested to be most important [7], but in the pressure range where line tension can exist (i.e., where a  $\theta$  can exist), we show that  $n^{SL}$  completely accounts for the observed  $\theta$ - $C_{cl}$  relation, and that there is no need to introduce line tension for this purpose. Further, a measured  $\theta$ - $C_{cl}$  relation can be used to determine the values of  $n^{SL}$ , of  $\gamma^{SL}$ , and of  $\gamma^{SV}$ , the surface tensions of the solid-vapor interface.

Consider a sessile droplet in a closed container maintained isothermal at a temperature  $T$ , exposed to a gravitational field that has an acceleration of  $g$ , and suppose the droplet is in contact with a smooth, homogeneous and rigid surface. If the chemical potential of the molecules in phase  $j$  is denoted  $\mu^j$ , the molecular weight as  $W$ , and the height in the field as  $z^j$ , then one of the conditions for equilibrium may be written [10,15] as

$$\mu^j[T, P^j(z^j)] + Wgz^j = \lambda, \quad (1)$$

where  $\lambda$  is a constant for the system and  $P^j(z^j)$  is the pressure in phase  $j$  at  $z^j$ . In [10], this is seen to result from allowing the molecules to be in any bulk or surface phase, but in total to be conserved. Physically, it ensures the potential for molecular transport is the same in all phases [10].

We approximate the liquid as incompressible. Then  $\mu^L[T, P^L(z)]$  may be expanded in a Taylor series at constant temperature about  $P_s(T)$  and only the first term of the expansion retained. Each of the other terms in the expansion vanishes, since the liquid-specific volume is constant for all values of  $P^L$ . Equation (1) for the liquid phase becomes

$$\mu^L(T, P_s) + v_f[P^L(z^L) - P_s(T)] + Wgz^L = \lambda, \quad (2)$$

where  $v_f$  is the specific volume of the saturated liquid.

TABLE I. Calculated values of  $x_3^L$ ,  $n_{[1]}^{SL}$ ,  $\gamma_{[1]}^{SL}$ , and  $\gamma_{[1]}^{SV}$  for dodecane adsorbing on silanized silicon at 22 °C.

$\cos\theta$	$C_{cl} \mu\text{m}^{-1}$	$x_3^L$	$n_{[1]}^{SL} \text{mmol/m}^2$	$\gamma_{[1]}^{SL} \text{mJ/m}^2$	$\gamma_{[1]}^{SV} \text{mJ/m}^2$
0.916	1.01	1518.21	-0.954	2.13	25.4
0.935	2.01	2662.67	-0.414	1.64	25.4
0.951	3.01	3490.00	-0.238	1.25	25.4
0.963	4.01	4039.59	-0.153	0.936	25.4
0.973	5.01	4350.43	-0.105	0.692	25.4

If the vapor is approximated as an ideal gas, one finds from the Gibbs-Duhem equation that Eq. (1), for the vapor phase, may be written

$$\mu^V(T, P_s) + \bar{R}T \ln\left[\frac{P^V(z^V)}{P_s}\right] + Wgz^V = \lambda, \quad (3)$$

where  $\bar{R}$  denotes the gas constant.

Another condition for equilibrium is the Laplace equation. If  $x_I^V$  denotes the pressure in the vapor at the liquid-vapor interface divided by  $P_s(T)$ , and directly across the interface in the liquid phase, this pressure ratio is denoted  $x_I^L$ , then the Laplace equation may be written

$$x_I^L - x_I^V = \frac{\gamma^{LV}}{P_s}(C_1^{LV} + C_2^{LV}), \quad (4)$$

where the surface tension of the liquid-vapor interface is denoted  $\gamma^{LV}$ , and  $C_i^{LV}$  is one of its curvatures. When Eq. (1) is applied in the liquid and vapor phases at the liquid-vapor interface where  $z_I^L = z_I^V$ , one finds

$$\mu^L(T, P_I^L) = \mu^V(T, P_I^V). \quad (5)$$

Since the vapor phase has been approximated as an ideal gas, its specific volume at saturation  $v_g$  is given by  $\bar{R}T/P_s(T)$ , and when Eqs. (2) and (3) are combined with Eq. (5), one finds

$$x_I^V = \exp\left[\frac{v_f}{v_g}(x_I^L - 1)\right]. \quad (6)$$

We limit our attention to the range of conditions where the contact angle can exist and use the measured  $C_{cl}$ - $\theta$  relation reported in [4] for spherical, sessile dodecane droplets to determine  $n^{SL}$ ,  $\gamma^{SV}$ , and  $\gamma^{SL}$ .

Suppose the uniform curvature of the liquid-vapor interface is denoted  $C_0^{LV}$  (i.e.,  $C_1^{LV} = C_2^{LV} \equiv C_0^{LV}$ ), then from geometry

$$\sin\theta = \frac{C_0^{LV}}{C_{cl}}, \quad (7)$$

and when Eq. (4) is simplified and combined with Eqs. (6) and (7), one finds at the three-phase line

$$\sin\theta = \frac{P_s}{2\gamma^{LV}C_{cl}} \left\{ x_3^L - \exp\left[\frac{v_f}{v_g}(x_3^L - 1)\right] \right\}, \quad (8)$$

where the subscript 3 on a quantity indicates it is to be evaluated at the intersection of the liquid-vapor, the solid-liquid, and the solid-vapor interfaces, i.e., at the three-phase line. Note then for a sessile, spherical droplet, at wetting ( $\theta \equiv 0$ ,  $x_3^L = x_w^L$ ,  $x_w^L = 1$ ).

We simplify the relations further by taking advantage of the nonvolatility of dodecane: the ratio  $v_f/v_g$  for dodecane at the temperature considered (22 °C) is  $\sim 10^{-6}$ , and in the experiments of [4],  $x_I^L$  had a maximum value of 4350. Thus,  $x_I^V$  deviated from unity by a maximum of  $\sim 0.5\%$ , and this deviation may be neglected. Equation (8) then becomes

$$\sin\theta = \frac{P_s}{2C_{cl}\gamma^{LV}}(x_3^L - 1). \quad (9)$$

From Eq. (9), the expression for  $\cos\theta$  may be obtained:

$$\cos\theta = \left[ 1 - \frac{P_s^2(x_3^L - 1)^2}{4C_{cl}^2(\gamma^{LV})^2} \right]^{1/2}. \quad (10)$$

The results obtained from Eq. (10) for the range of  $C_{cl}$  and  $\cos\theta$  values considered by [4] are shown as solid lines in Fig. 1. These curves are independent of the solid surface.

In order for them to be specific to a particular solid surface, measurements must be made of two of the three variables:  $\theta$ ,  $x_3^L$ ,  $C_{cl}$ . To illustrate, the measurements of [4] were given in the form of a fitting relation for  $\cos\theta$  as a

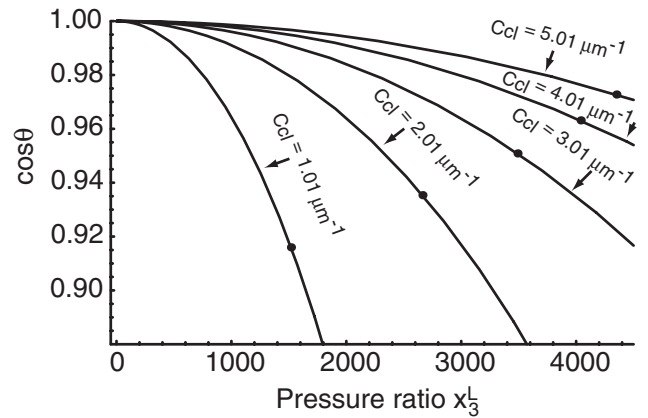


FIG. 1. The solid lines were calculated for the range of  $C_{cl}$  values given in [4]. The data points shown were obtained from their measurements of  $\cos\theta$  and  $C_{cl}$ .

function of  $C_{cl}$ . For a given value of  $C_{cl}$ , a value of  $\cos\theta$  is first calculated from their fitting relation, then Eq. (10) is used to determine the corresponding value of  $x_3^L$ . In Table I, the five data points obtained from this procedure are listed. These points are specific to the dodecane-silanized silicon surface. They give the values of  $x_3^L$  that would have existed at the three-phase line when these values of  $C_{cl}$  and  $\cos\theta$  were observed. These data points are also shown in Fig. 1.

We use the Gibbs model of the interphase and take the position of the dividing surface at the solid-liquid and solid-vapor interfaces to be such that there is no adsorption of the solid component. If a subscript [1] indicates this position of the interface has been chosen, the Gibbs adsorption equations may be written [15]:

$$d\gamma_{[1]}^{SV} = -n_{[1]}^{SV}v_fP_s dx_3^L, \quad (11)$$

and

$$d\gamma_{[1]}^{SL} = -n_{[1]}^{SL}v_fP_s dx_3^L, \quad (12)$$

where  $n_{[1]}^{SL}$  and  $n_{[1]}^{SV}$  are the adsorptions at the solid-liquid and solid-vapor interfaces, respectively.

The Young equation is also a condition for equilibrium:

$$\gamma_{[1]}^{SV} - \gamma_{[1]}^{SL} = \gamma^{LV} \cos\theta. \quad (13)$$

If a partial differential is taken of Eq. (13) with respect to  $x_3^L$ , the result combined with Eqs. (11) and (12), one finds

$$n_{[1]}^{SL} - n_{[1]}^{SV} = \frac{\gamma^{LV}}{v_f P_s} \left( \frac{\partial \cos\theta}{\partial x_3^L} \right)_{C_{cl}}. \quad (14)$$

Since dodecane is such a nonvolatile substance, we neglect the adsorption at the solid-vapor interface compared to that at the solid-liquid interface. Such an approximation has been shown to be valid for water adsorbing on borosilicate glass [8,9], and the approximation would be expected to be even better for the dodecane-silanized silicon system.

Equation (10) may be used in Eq. (14) to express  $n_{[1]}^{SL}$  in terms of  $x_3^L$  and  $C_{cl}$ :

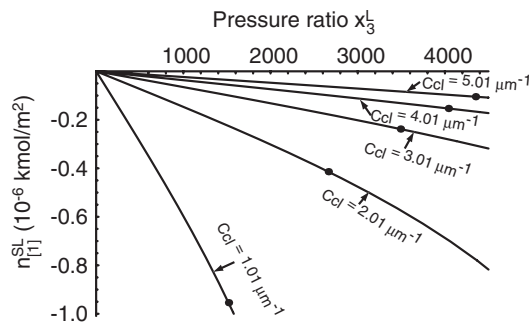


FIG. 2. The solid lines were obtained from Eq. (15). The data points were calculated from a fitting relation given in [4].

$$n_{[1]}^{SL} = \frac{P_s(1 - x_3^L)}{4v_f C_{cl}^2 \gamma^{LV} \left(1 - \frac{P_s^2(1 - x_3^L)^2}{4C_{cl}^2(\gamma^{LV})^2}\right)^{1/2}}. \quad (15)$$

The functional relation between  $n_{[1]}^{SL}$ ,  $x_3^L$ , and  $C_{cl}$  is illustrated in Fig. 2 by the solid curves. Like the curves shown in Fig. 1, these curves would be true for a sessile dodecane droplet on any solid surface, but when measurements are made of  $\theta$  and  $C_{cl}$ , the adsorption at the solid-liquid interface required to produce that value of  $\theta$  can be determined. The measured  $\theta$ - $C_{cl}$  relation, reported by [4], has been used to determine the five data points shown in Fig. 1. The corresponding adsorptions at the solid-liquid interface, calculated from Eq. (15), are listed in Table I and shown in Fig. 2. Thus, a measurement of any two of the three variables,  $C_{cl}$ ,  $\theta$ ,  $x_3^L$ , can be used to determine the adsorption at the solid-liquid interface.

Note the adsorption  $n_{[1]}^{SL}$  is negative. Negative adsorption at the solid-liquid interface means physically that the concentration of the fluid component is smaller in the interphase than in the bulk liquid [9]. For a given value of  $C_{cl}$ , the adsorption of dodecane on silanized silicon becomes more negative as  $x_3^L$  is increased (see Fig. 2). The same data trend has been found for water adsorbing on borosilicate glass. This conclusion is supported by independent studies of water density in small pores where the interphase fills a significant portion of the volume. Water concentration in such pores was found to be smaller than that of bulk water [16–18].

For a given  $C_{cl}$ , as seen from a comparison of Figs. 1 and 2, for dodecane adsorbing on silanized silicon,  $\theta$  is predicted to decrease as the  $n_{[1]}^{SL}$  becomes less negative. This prediction was also examined for water in borosilicate glass cylinders by rotating each cylinder about its longitudinal axis. Progressively increasing the rotation rate had the effect of lowering  $x_3^L$ . That made  $n_{[1]}^{SL}$  become less negative, and in each cylinder,  $\theta$  was observed to decrease [9].

The expression for the surface tensions or surface energies,  $\gamma_{[1]}^{SL}$  and  $\gamma_{[1]}^{SV}$ , may now be determined. We use the

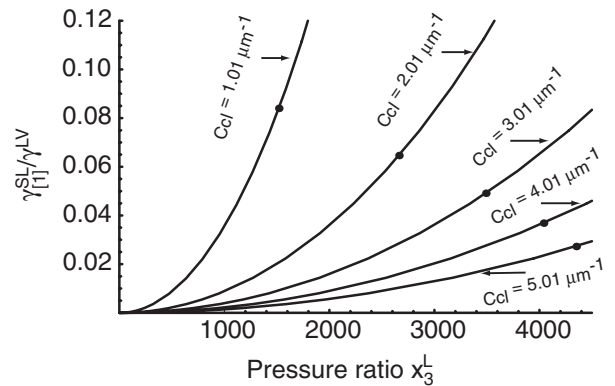


FIG. 3. Value of  $\gamma_{[1]}^{SL}$  as a function of  $x_3^L$  and  $C_{cl}$ .

wetting hypothesis [14] to assign a reference condition where the surface energy  $\gamma_{[1]}^{SL}$  vanishes. For any value of  $C_{cl}$ , the wetting condition is reached when  $\theta$  is  $0^\circ$  or  $x_3^L = 1$  [see Eq. (9)]. Integrating Eq. (12) across the phase transition from no liquid to some liquid phase being present gives

$$\gamma_{[1]}^{SL}(1^+, C_{cl}) - \gamma_{[1]}^{SL}(1^-, C_{cl}) = -v_f P_s \int_{1^-}^{1^+} n_{[1]}^{SL} dx_3^L. \quad (16)$$

The wetting hypothesis assumes  $n_{[1]}^{SL}$  is continuous, and takes  $\gamma_{[1]}^{SL}(1^-, C_{cl})$  as zero. Both the integral and  $\gamma_{[1]}^{SL}(1^+, C_{cl})$  then vanish. Using this hypothesis, substituting Eq. (14) into Eq. (12), neglecting  $n_{[1]}^{SV}$ , and integrating the result from unity to  $x_3^L$  gives

$$\gamma_{[1]}^{SL}(x_3^L, C_{cl}) = \gamma^{LV}[1 - \cos\theta(x_3^L, C_{cl})]. \quad (17)$$

When Eq. (17) is inserted in Eq. (13), one finds

$$\gamma_{[1]}^{SV}(x_{[1]}^{SV}, C_{cl}) = \gamma^{LV}. \quad (18)$$

The calculated values of  $\gamma_{[1]}^{SL}$  and  $\gamma_{[1]}^{SV}$  obtained from the data of [4] are listed in Table I. We emphasize that Eqs. (17) and (18) are valid only when the pressure is such that  $\theta$  can exist.

When Eqs. (10) and (17) are combined, one obtains an expression for  $\gamma_{[1]}^{SL}$  in terms of  $C_{cl}$  and  $x_3^L$ . This relation is illustrated in Fig. 3. By comparing Figs. 2 and 3, the effect of adsorption on  $\gamma_{[1]}^{SL}$  may be determined. For a given  $C_{cl}$ , an increase in  $x_3^L$  is seen in Fig. 2 to cause  $n_{[1]}^{SL}$  to become more negative, meaning the concentration of dodecane in the interphase is decreased relative to that in the bulk liquid [9]. This is seen in Fig. 3 to increase the value of  $\gamma_{[1]}^{SL}$ . By contrast, for a given value of  $x_3^L$ , increasing  $C_{cl}$  is seen in Fig. 2 to make  $n_{[1]}^{SL}$  less negative, indicating that the concentration in the interphase is increased, and as seen in Fig. 3,  $\gamma_{[1]}^{SL}$  is decreased. Hence, the value of  $\gamma_{[1]}^{SL}$  depends on the fluid concentration in the solid-liquid interphase relative to that in the bulk: when the concentration in the interphase is increased, the value of  $\gamma_{[1]}^{SL}$  is decreased, and when this concentration is decreased,  $\gamma_{[1]}^{SL}$  increases. The variables that control this concentration are seen to be any two of the three:  $\theta$ ,  $x_3^L$ ,  $C_{cl}$ . Note that the predicted effect of liquid concentration in the solid-liquid interphase is analogous to the effect of adsorption at the solid-vapor interface with interphase concentration replacing surface concentration.

The adsorption at the solid-liquid interface fully accounts for the measured dependence of  $\theta$  on  $C_{cl}$ . A measurement of  $\theta$  and  $C_{cl}$  determines the value of  $x_3^L$  (see Fig. 1). The values of  $C_{cl}$  and  $x_3^L$  determine the adsorption  $n_{[1]}^{SL}$  (see Fig. 2). They also determine the surface tension  $\gamma_{[1]}^{SL}$  (see Fig. 3) that gives the observed value of  $\theta$ . Thus,  $C_{cl}$  does affect  $\theta$ , but through its effect on  $n_{[1]}^{SL}$ . There is no basis for introducing line tension to explain the dependence of  $\theta$  on  $C_{cl}$  while neglecting adsorption at the solid-liquid interface.

We wish to acknowledge the support of the Canadian Space Agency and the Natural Sciences and Engineering Research Council of Canada.

\*ward@mie.utoronto.ca

- [1] J. Gaydos and A. W. Neumann, *J. Colloid Interface Sci.* **120**, 76 (1987).
- [2] D. Li, *Colloids Surf. A* **116**, 1 (1996).
- [3] W. C. Jensen and D. Li, *Colloids Surf. A* **156**, 519 (1999).
- [4] A. Checco, P. Guenoun, and J. Daillant, *Phys. Rev. Lett.* **91**, 186101 (2003).
- [5] R. J. Good and M. N. Koo, *J. Colloid Interface Sci.* **71**, 283 (1979).
- [6] T. Getta and S. Dietrich, *Phys. Rev. E* **57**, 655 (1998).
- [7] T. Pompe and S. Herminghaus, *Phys. Rev. Lett.* **85**, 1930 (2000).
- [8] J. Wu, T. Farouk, and C. A. Ward, *J. Phys. Chem. B* **111**, 6189 (2007).
- [9] C. A. Ward, J. Wu, and A. Keshavarz, *J. Phys. Chem. B* **112**, 71 (2008).
- [10] C. A. Ward and M. R. Sasges, *J. Chem. Phys.* **109**, 3651 (1998).
- [11] M. R. Sasges and C. A. Ward, *J. Chem. Phys.* **109**, 3661 (1998).
- [12] C. A. Ward, P. Rahimi, M. R. Sasges, and D. Stanga, *J. Chem. Phys.* **112**, 7195 (2000).
- [13] P. Rahimi and C. A. Ward, *Microgravity Sci. Technol.* **16**, 231 (2005).
- [14] C. A. Ward and J. Wu, *J. Phys. Chem. B* **111**, 3685 (2007).
- [15] *The Scientific Papers of J. Willard Gibbs*, edited by H. A. Bumstead and R. G. Van Name (Dover, New York, 1961), Vol. 1, p. 55.
- [16] F. M. Etzler and D. M. Fagundus, *J. Colloid Interface Sci.* **93**, 585 (1983).
- [17] F. M. Etzler and D. M. Fagundus, *J. Colloid Interface Sci.* **115**, 513 (1987).
- [18] T. Takei, K. Mukasa, M. Kofuji, M. Fuji, T. Watanabe, M. Chikazawa, and T. Kanazawa, *Colloid Polym. Sci.* **278**, 475 (2000).