Surface Tension of Solids in the Absence of Adsorption

H. Ghasemi and C. A. Ward*

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

Received: July 20, 2009; Revised Manuscript Received: August 13, 2009

A method has been recently proposed for determining the value of the surface tension of a solid in the absence of adsorption, $\gamma^{S0}$, using material properties determined from vapor adsorption experiments. If valid, the value obtained for $\gamma^{S0}$ must be independent of the vapor used. We apply the proposed method to determine the value of $\gamma^{S0}$ for four solids using at least two vapors for each solid and find results that support the proposed method for determining $\gamma^{S0}$.

The surface tension of a solid in the absence of adsorption, $\gamma^{S0}$, is of central importance in characterizing a solid; however, previously proposed methods for determining its value have led to controversy and a lack of experimental support.1–4 Recently, a new method was proposed5 that only requires a suitable amount is adsorbed in this limit. The in the proposed method since both indicate that an infinite phase pressure, $\gamma$S0, is of central importance in characterizing a solid; however, Wu5 is incorrect in some fundamental sense. The other possibility is that $\gamma^{S0}$ is found to be the same for all vapors, supporting the proposed approach and indicating that for a particular solid surface at a given temperature, a relation exists between $\gamma^{LV}$ and the adsorption-isotherm parameters. Using adsorption data from the literature, we examine these possibilities for four solids using at least two vapors in each case to determine the value of $\gamma^{S0}$. The value of $\gamma^{S0}$ for each solid is found to be independent of the vapor used. Thus, we find results that support the second possibility.

The $\zeta$ isotherm was obtained by approximating the adsorbed vapor as a collection of molecular clusters with at most one cluster adsorbed at one of the M adsorption sites. Each adsorbed cluster was approximated as a quantum-mechanical-harmonic oscillator with a binding energy that depended on the number of molecules in the cluster. The maximum number of molecules that could be in a cluster was denoted as $\zeta$. Using a canonical ensemble, the amount adsorbed at a solid–vapor interface, $n^{SV}$, was expressed as

$$n^{SV} = \frac{M c \alpha \sqrt{[1 - (1 + \zeta)(\alpha \gamma_{V})^\zeta + \zeta(\alpha \gamma_{V})^{1+\zeta}]} \right)}{(1 - \alpha \gamma_{V})[1 + (c - 1) \alpha \gamma_{V} - c(\alpha \gamma_{V})^{1+\zeta]}}$$

A comparison between the measured amount adsorbed and that calculated is assessed using the parameter $\Delta(\zeta)$ which, for a given value of $\zeta$, is a measure of the mean-square difference between the measured amount adsorbed and that calculated

$$\Delta(\zeta) = \frac{\sqrt{\sum_{j=1}^{N_{m}}(n^{SV}_{\text{mes}}(x_{j}) - n^{SV}_{\text{cal}}(\zeta, x_{j}))^{2}}}{\sum_{j=1}^{N_{m}}n^{SV}_{\text{mes}}(x_{j})}$$

where $n^{SV}_{\text{mes}}(x_{j})$ is the amount measured at $x_{j}$ and $n^{SV}_{\text{cal}}(\zeta, x_{j})$ is the amount calculated. The number of measurements is denoted as $N_{m}$. For a given set of adsorption measurements, the

*To whom correspondence should be addressed. E-mail: charles.ward@utoronto.ca.
The measured amount of argon adsorbed at 77 K is shown as solid dots. The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

Figure 1.

The measured amount of nitrogen adsorbed at 77 K is shown as solid dots. The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

Figure 2.

The measured amount of nitrogen adsorbed at 77 K is shown as solid dots. The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

Figure 3.

The measured amount of argon adsorbed at 77 K is shown as solid dots. The solid line was calculated using eq 2 and the values of the adsorption parameters listed in Table 1.

The mean-square difference between the calculations and the values of the adsorption parameters are shown in Figures 2 and 3. The solid lines in these three figures were calculated using eq 2, the value of \( \gamma \) is taken to be larger than the threshold value, the error in the calculations does not decrease further.

The measured amount of Ar adsorbing at 77 K on \( \alpha \)-alumina that was reported by Matejova et al.\(^\text{11} \) is shown as solid dots in Figure 1. The amount of N\(_2\) adsorbing on \( \alpha \)-alumina at 77 K has been reported by two laboratories.\(^\text{11,12} \) These measurements are shown in Figures 2 and 3. The solid lines in these three figures were calculated using eq 2, the value of \( \gamma \) and the mean values of the isotherm parameters that are listed in Table 1. The mean-square difference between the calculations and the measurements, \( \Delta(\gamma) \), for Ar and N\(_2\) adsorbing on \( \alpha \)-alumina was 0.2 and 0.8\%, respectively. Note that for the measurements from two independent laboratories, there is no measurable difference between the inferred values of the isotherm parameters. We treat these parameters and \( \gamma \) listed in Table 1 as material properties.

When the solid surface is exposed to a vapor phase, the expression for \( \gamma^\text{SV}(x^v) \) obtained by Ward and Wu\(^\text{1} \) is

\[
\gamma^\text{SV}(x^v) = \gamma^\text{LV} + Mk_b T \ln \left( \frac{1 - \alpha x^v}{1 - \alpha x^v_w} \frac{[1 + (c - 1)\alpha x^v]}{[1 + (c - 1)\alpha x^v_w]} \right)
\]

(4)

Note that the value of \( \gamma^\text{SV}(x^v) \) depends on the value of \( x^v_w \), the relative vapor-phase pressure at wetting. The contact angle formed when a liquid and its vapor are held in a cylinder has been shown to depend on the pressure at the three-phase line.\(^\text{5,14,15} \) To estimate the value of \( x^v_w \), we consider liquid N\(_2\) or liquid Ar at 77 K held in a cylinder that has a radius of 0.3 mm, which is exposed to normal gravity, \( g \), and forms a contact angle of zero. If the molecular weight of the fluid is denoted \( W \) and the specific volume of the liquid at saturation as \( LV \), then the Bond number \( (\equiv Wg r^2_v/(\rho V^3)) \) is 0.085 or less. Thus, the liquid—vapor interface may be approximated as spherical.\(^\text{16} \) The conditions for equilibrium at the liquid—vapor interface in the cylinder require the equality of the chemical potentials in the liquid and vapor phases and the validity of the Laplace equation.\(^\text{5} \) If the liquid is approximated as incompressible and the vapor as an ideal gas, then\(^\text{15} \)

\[
x^v_w = \exp \left[ \frac{LV}{Wg} \left( x^v - \frac{2\gamma^\text{LV}}{P^c_{cy}} - 1 \right) \right]
\]

(5)

This equation may be solved iteratively to determine \( x^v_w \). For Ar and N\(_2\), one finds that \( x^v_w \) deviates from unity by less than 10\(^{-5} \). If cylinders larger that 0.3 mm were considered, the deviation from unity would be even smaller.\(^\text{5} \) Thus, we approximate \( x^v_w \) as unity. Then, eq 4 simplifies to

\[
\gamma^\text{SV}(x^v) = \gamma^\text{LV} - Mk_b T \ln \left( \frac{(\alpha - 1)[1 + (c - 1)\alpha x^v]}{(\alpha x^v_w - 1)[1 + (c - 1)\alpha]} \right)
\]

(6)

The value of \( \gamma^\text{SV} \) may now be calculated as a function of \( x^v \) using eq 6 and the values of the isotherm parameters listed in Table 1. If the limit is taken of eq 6 as \( x^v \) goes to zero, one obtains eq 1. We emphasize that the values of the adsorption parameters were determined strictly from the adsorption measurements. Thus, the calculated value of \( \gamma^\text{SV} \) for each vapor may be viewed as a prediction. For Ar and N\(_2\) adsorbing on \( \alpha \)-alumina, the results are shown in Figure 4. This figure includes results obtained from two independent studies of N\(_2\) adsorption on \( \alpha \)-alumina. In each case, the different vapors indicate the same value of \( \gamma^\text{SO} \). In Table 1, note that the adsorption of Ar and N\(_2\) on titania, magnesia, and borosilicate glass indicate the same value of \( \gamma^\text{SO} \).
pressures are indicated to be essentially constant; thus, the contact angle for this range of pressures is predicted to depend only on the value of $\gamma_{SL}$, and this surface tension is controlled by the adsorption at the solid–liquid interface.5,15,17

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

References and Notes

(1) Vogler, E. A. Adv. Colloid Interface Sci. 1998, 74, 69–117.
(2) Schrader, M. E. Langmuir 1996, 12, 3728–3732.
(3) Douillard, J. M. J. Colloid Interface Sci. 1997, 188, 511–515.
(4) Chibowski, E.; Perea-Carpio, R. Adv. Colloid Interface Sci. 2002, 98, 245.
(5) Ward, C. A.; Wu, J. J. Phys. Chem. B 2007, 111, 3685–3694.
(6) Ward, C. A.; Sasges, M. R. J. Chem. Phys. 1998, 109, 3651–3660.
(7) Brunauer, S.; Emmett, P. H.; Teller, E. J. Am. Chem. Soc. 1938, 60, 309–319.
(8) Frenkel, Y. I. Kinetic Theory of Liquids; Clarendon Press: Oxford, U.K., 1946.
(9) Halsey, G. J. Chem. Phys. 1948, 16, 931.
(10) Hill, T. L. An Introduction to Statistical Thermodynamics; Dover: Mineola, NY, 1986; p 161.
(11) Matejova, L.; Solcova, O.; Schneider, P. Microporous Mesoporous Mater. 2008, 107, 227–232.
(12) Cejka, J.; Zilkova, N.; Rathousky, J.; Zakal, A. Phys. Chem. Chem. Phys. 2001, 3, 5076–5081.
(13) Jasper, J. J. J. Phys. Chem. 1972, Ref. Data 1, 841.
(14) Wu, J.; Farouk, T.; Ward, C. A. J. Phys. Chem. B 2007, 111, 6189–6197.
(15) Ward, C. A.; Wu, J.; Keshavarz, A. J. Phys. Chem. B 2008, 112, 71–80.
(16) Sasges, M. R.; Ward, C. A.; Azuma, H.; Yoshiihara, S. J. Appl. Phys. 1996, 79, 8770–8782.
(17) Ward, C. A.; Wu, J. Phys. Rev. Lett. 2008, 100, 256103.

Table 1: $\zeta$-Isotherm Parameters and Solid Surface Tension

| Material     | Vapor | T (K) | $\gamma_{LV}$ (kg/s²) | $M$ (10⁻⁹ kmol/m²) | $c$ | $\alpha$ | $\zeta$ | $\Delta(\zeta)$, % | $\gamma$ (kg/s²) |
|--------------|-------|-------|------------------------|---------------------|-----|----------|---------|---------------------|-----------------|
| α-alumina¹¹  | Ar    | 77    | 0.01514                | 10.769 ± 0.1572     |     | 37.60 ± 5.41 | 0.7726 ± 0.0045 | 100     | 0.2       | 0.0486 ± 0.0017    |
| α-alumina¹¹  | N₂    | 77    | 0.00895                | 10.4974 ± 0.1205    |     | 102.53 ± 52.07 | 0.7727 ± 0.0041 | 140     | 0.8       | 0.0483 ± 0.0032    |
| TiO₂¹¹       | N₂    | 77    | 0.00895                | 10.9844 ± 0.3776    |     | 80.48 ± 22.74 | 0.7643 ± 0.0156 | 100     | 0.8       | 0.0481 ± 0.0042    |
| TiO₂¹¹       | Ar    | 77    | 0.01514                | 10.8066 ± 0.1734    |     | 64.51 ± 14.03 | 0.7632 ± 0.0052 | 130     | 0.2       | 0.0521 ± 0.0025    |
| magnesia¹¹   | N₂    | 77    | 0.00895                | 9.3383 ± 0.6851     |     | 253.90 ± 201.45 | 0.8315 ± 0.0215 | 120     | 1.1       | 0.0516 ± 0.0031    |
| borosilicate glass¹¹ | N₂ | 77 | 0.00895 | 9.5109 ± 0.2406 | 270.00 ± 202.45 | 0.8808 ± 0.0271 | 100  | 1.2       | 0.0552 ± 0.0041    |
| magnesia¹¹   | Ar    | 77    | 0.01514                | 13.2577 ± 0.1200    |     | 59.23 ± 4.68  | 0.6622 ± 0.0063 | 140     | 0.1       | 0.0556 ± 0.0012    |
| borosilicate glass¹¹ | N₂ | 77 | 0.00895 | 9.9651 ± 0.4056 | 32.06 ± 20.08  | 0.9163 ± 0.0211 | 130  | 1.6       | 0.0463 ± 0.0041    |

Figure 4. The calculated values of $\gamma_{SV}$ are shown for α-alumina exposed to Ar and to N₂ at 77 K. The results shown for N₂ are based on adsorption measurements made in two independent laboratories.¹¹,¹² Note that all three studies indicate the same value of $\gamma_{SV}$ for α-alumina at 77 K.

JP9068653