

DETERMINATION OF THE CAPILLARY PRESSURE IN MENISCI OF MOLECULAR DIMENSIONS

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The measured adhesion force arising from the Laplace pressure in capillary condensed liquid between two curved molecularly smooth surfaces is well described by the Gibbs–Kelvin equation of classical thermodynamics for liquid hydrocarbons with meniscus radii down to 0.5–1.0 nm. The corresponding limit for liquid water is much higher, about 5 nm.

1. Introduction

The difference ΔP in hydrostatic pressure between a pure liquid and its vapour depends on the mean radius of curvature r_m of the liquid/vapour interface. The Gibbs–Kelvin equation [1,2] of classical thermodynamics gives, for a liquid of surface tension γ ,

$$\Delta P = \gamma/r_m, \quad (1)$$

an equation which can also be derived from hydrostatic principles, when it is known as the Young–Laplace equation [3]. We define r_m here by $1/r_m = 1/r_1 + 1/r_2$, where r_1 and r_2 are the principal radii of curvature of the surface. r_m is positive for droplets, negative for concave menisci.

For highly curved menisci the surface tension γ may be a function of r_m [4]. However, this and other theoretical corrections so far proposed (e.g. refs. [4–6]) become significant only when r_m approaches molecular dimensions, when the meaning of r_m also becomes problematic.

The question arises: below what absolute value of r_m does bulk thermodynamics break down, and the Gibbs–Kelvin equation consequently fail? The ques-

tion is fundamentally significant and also of practical importance, particularly for capillary-condensed liquids (r_m negative), where meniscus forces often make the major contribution to the adhesion between solid surfaces in a vapour atmosphere [7]. So far the question has not admitted of an answer. In an attempt to provide an experimental answer, we have measured the force of adhesion between crossed cylinders of molecularly smooth mica with capillary-condensed liquid in the contact zone. Comparison of measured and theoretical adhesion forces at various meniscus radii allows us to draw conclusions about the lower limit of meniscus radius to which the equations of macroscopic thermodynamics may be applied.

2. Experimental technique and results

The apparatus is an adaptation of that previously used [8] to study the short-range forces between two cylindrical mica surfaces immersed in a liquid. In the present experiments the crossed mica cylinders are first brought into contact in a vapour atmosphere, when multiple beam interferometry [9,10] allows us to observe the formation of an annulus of capillary-condensed liquid and to measure the mean radius of

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curvature r_m of the liquid/vapour interface. With one surface held rigidly, a gradually increasing tensile force is then applied to the other surface via a cantilever spring. When the force reaches a critical "pull-off" value F the mica surfaces jump apart, and the value of F is then readily obtained from the measured jump distance and the known spring constant. Accurate adhesion measurements between solid surfaces in a dry nitrogen atmosphere have been reported [11], and a more detailed description of this method of measuring adhesion forces is given elsewhere [8].

The equilibrium mean radius of curvature of the meniscus depends on the relative vapour pressure p/p_s [12]. By varying p/p_s as described in ref. [10] we could thus monitor how the adhesion force varies with p/p_s and hence with the meniscus radius r_m .

The theoretical attractive force due to the Laplace pressure in a bridging meniscus between two contacting crossed cylinders is

$$F = 4\pi R \gamma \cos \theta \quad (2)$$

where R ($\gg |r_m|$) is the (measured) local radius of curvature of the mica surfaces, γ the surface tension of the liquid, and θ the contact angle. Note that eq. (2) is independent of r_m ! Eq. (2) also holds even when pull-off occurs while the contact region between the curved surfaces is still flattened [11]. Thus deviations from bulk or macroscopic thermodynamics should be reflected as deviations in the measured adhesion force from that predicted by eq. (2).

We first studied adhesion in cyclohexane vapour ($\cos \theta$ is in the range 0.98–1.00 for this [13] and all other liquids used in this study), having previously verified [10] that r_m is well described by the Kelvin equation [12] for this liquid for $|r_m|$ down to at least 4 nm. Fig. 1 shows results for the adhesion force, plotted as $F/4\pi R \cos \theta$, as a function of relative vapour pressure p/p_s and r_m . We note that the adhesion force remains within $\approx 10\%$ of that expected theoretically with γ independent of r_m down to $p/p_s \approx 0.1$. The Kelvin equation [12], derived from the Gibbs–Kelvin equation, predicts that the meniscus

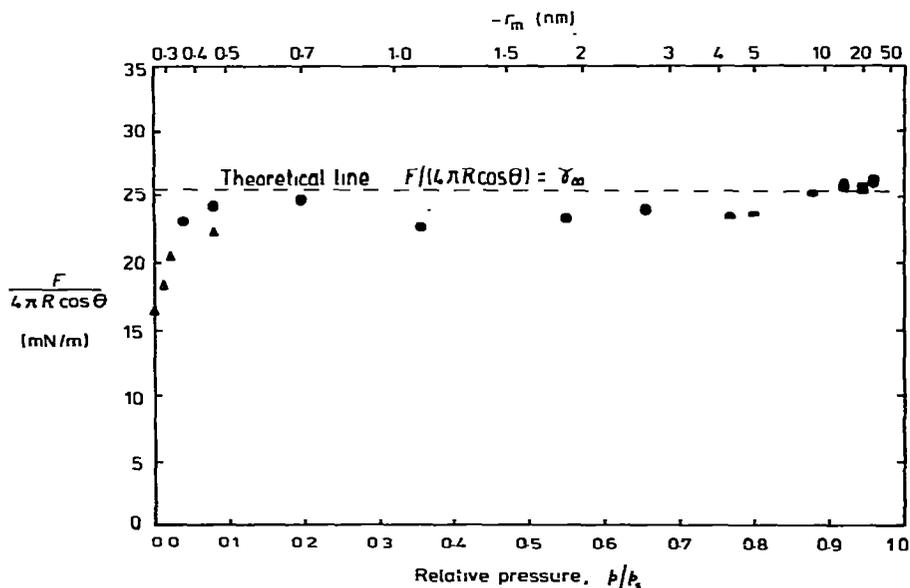


Fig. 1. Measured force of adhesion F , scaled by $4\pi R \cos \theta$, between cylindrical mica surfaces of radius $R \approx 2$ cm as a function of relative vapour pressure p/p_s of cyclohexane ($\gamma = 25.5$ mN/m at 22°C). Results of three separate experiments with curved surfaces of different radii R . The relative vapour pressure was controlled either by admission of a measured volume of liquid cyclohexane into the constant volume chamber ($p/p_s < 0.9$) or by temperature control (for $p/p_s \geq 0.9$) [10]. Standard error in values of F was better than $\pm 0.2\%$; random errors in R are about $\pm 1\%$; errors in p/p_s are negligible. The values of r_m are calculated from the Kelvin equation, which we have now found to be valid for cyclohexane for $|r_m| > 2.5$ nm (ref. [10] and unpublished results). — — — Predicted values of $F/4\pi R \cos \theta$ from the uncorrected Gibbs–Kelvin equation (2).

radius is 0.5 nm, i.e. about a molecular diameter, at this relative vapour pressure. Very similar results were obtained with benzene and *n*-hexane. These measurements therefore show that the Gibbs–Kelvin equation, with the assumption that γ is independent of r_m , is applicable to menisci with radii as low as a molecular diameter.

These results appear to be contrary to the predictions of the Gibbs–Tolman–Koenig equation [4] where the surface tension is given by, to a first approximation:

$$\gamma = \gamma_\infty(1 - \Delta\lambda/r_m), \quad (3)$$

where γ_∞ is the macroscopic surface tension and $\Delta\lambda$ is the “thickness” of the interfacial region, estimated by Choi et al. [14] to be 0.49 nm for cyclohexane. Since r_m is negative for concave menisci, eq. (3) predicts that γ will increase with decreasing meniscus radius. One possible reason for the lack of such an effect is that the Gibbs–Tolman–Koenig equation takes no account of density variation with r_m . Dilation must occur under the very large negative pressure, up to about 10^8 N/m², existing in the capillary condensed cyclohexane, and the decrease in density will produce a decrease in the surface tension γ . This effect could well offset the increase in γ predicted by eq. (3). Data are not available to calculate the magnitude of this effect.

We performed a similar set of experiments with capillary condensed water. The results (not shown) were quite different from those for cyclohexane, and showed a *monotonic* decrease in the adhesion force with decreasing relative vapour pressure. The adhesion force was within 10% of that expected from macroscopic thermodynamics only for relative vapour pressures above 0.9, corresponding to meniscus radii $\gtrsim 5$ nm. This result may reflect the long-range cooperative nature of the hydrogen-bonding interaction in water, although the equally long-range effects of double-layer forces may also play a part by reducing the effective surface tension of water.

In all of the above experiments, meniscus forces dominate the adhesion. It is of interest to know whether this is always the case, so we extended our measurements to include 2-methylbutane, whose surface tension (13.72 mN m⁻¹ [15]) is sufficiently low that the meniscus force is expected to be less than the measured force of adhesion between dry mica surfaces. If

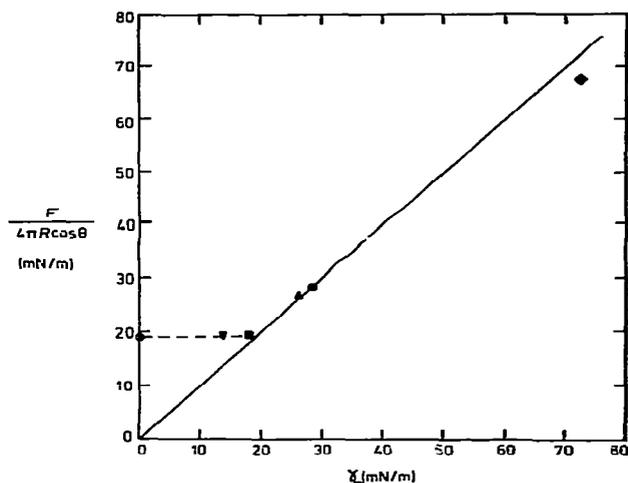


Fig. 2. Force of adhesive F , scaled by $4\pi R \cos \theta$, between mica surfaces of radius R , as a function of macroscopic surface tension γ_∞ of meniscus liquid in equilibrium with vapour, all at $p/p_S \approx 0.95$ and $T = 22 \pm 1^\circ\text{C}$. \blacklozenge : water ($\gamma_\infty = 72.5$ mN/m); \bullet : benzene ($\gamma_\infty = 28.9$ mN/m); \blacktriangle : cyclohexane ($\gamma_\infty = 25.5$ mN/m); \blacksquare : *n*-hexane ($\gamma_\infty = 18.4$ mN/m); \blacktriangledown : 2-methylbutane ($\gamma_\infty = 13.7$ mN/m); \circ : nitrogen at atmospheric pressure; —: $F/4\pi R \cos \theta = \gamma_\infty$. Standard error in values of $F/4\pi R \cos \theta$ was generally better than $\pm 3\%$, i.e. about the size of the plotted points, except in dry nitrogen where the scatter was larger.

the adhesive force F at high values of r_m is always determined by meniscus forces alone, then F (scaled by $R \cos \theta$) should be proportional to the macroscopic surface tension γ_∞ of the particular liquid. Fig. 2 shows that this is true for all the liquids studied except 2-methylbutane, where the adhesive force is just that between the dry mica surfaces. It appears from this result that for liquids with low surface tensions, such that $4\pi R \gamma \cos \theta$ is below the adhesive force between dry surfaces, the presence of a liquid meniscus does not affect the adhesion.

3. Conclusions

The adhesive forces due to the Laplace pressure in simple hydrocarbon liquids are adequately described by the macroscopic laws of classical thermodynamics for meniscus radii down to one or two molecular diameters, i.e. the Gibbs–Kelvin equation of classical thermodynamics is applicable to such small menisci

on the assumption that the surface tension is curvature independent. We further find that meniscus forces in capillary-condensed liquid completely dominate the adhesion between molecularly smooth mica surfaces unless the meniscus force is such that $4\pi R\gamma \cos \theta$ is below the adhesive force between the dry surfaces, in which case the presence of the meniscus does not affect the adhesion.

Water menisci do not follow the simple behaviour of hydrocarbon liquids, and much larger meniscus radii are needed before the Gibbs–Kelvin equation is applicable. A full account of these and related studies is in preparation.

References

- [1] J.W. Gibbs, *Trans. Conn. Acad. Arts Sci.* III (1874–1878) 108, 343.
- [2] W. Thomson, *Proc. Roy. Inst.* 11 (1886) 483.
- [3] P.R. Pujado, C. Huh and L.E. Scriven, *J. Colloid Interface Sci.* 38 (1972) 662.
- [4] J.C. Melrose, *Ind. Eng. Chem.* 60 (1968) 53.
- [5] F.P. Buff, in: *Handbuch der Physik*, Vol. 10, ed. S. Flügge (Springer, Berlin, 1960) p. 281.
- [6] L. Boruvka and A.W. Neumann, *J. Chem. Phys.* 66 (1977) 5464.
- [7] J. Visser, *Surface Colloid Sci.* 8 (1976) 3.
- [8] J.N. Israelachvili and G.E. Adams, *J. Chem. Soc. Faraday Trans. I* 74 (1978) 975.
- [9] J.N. Israelachvili, *Nature* 229 (1971) 85; *J. Colloid Interface Sci.* 44 (1973) 259.
- [10] L.R. Fischer and J.N. Israelachvili, *Nature* 277 (1979) 548.
- [11] J.N. Israelachvili, E. Perez and R.K. Tandon, *J. Colloid Interface Sci.*, to be published.
- [12] W. Thomson, *Phil. Mag.* 42 (1871) 448.
- [13] L.R. Fisher, *J. Colloid Interface Sci.* 72 (1979) 200.
- [14] D.S. Choi, M.J. Jhon and H. Eyring, *J. Chem. Phys.* 53 (1970) 2608.
- [15] *Handbook of Chemistry and Physics*, 53rd Ed. (Chemical Rubber Company, Cleveland, 1970).