can become positive. For a sinusoidal variation of the temperature between $T_{max} = 500$ K at the subsolar point and $T_{min} = 200$ K at the opposite point, and a uniform density distribution $n_c = 1.5 \times 10^4$, we computed this net upward ballistic flux to be 5×10^7 atom cm^{-2} s^{-1} for the subsolar point. This upwards flux could very well play the role of the nonthermal escape flux ϕ_{nt} introduced by Liu and Donahue[10] and Sze and McElroy[11]. When reported on their Figs 2, 3, 4, $\phi_{nt} = 5 \times 10^7$ cm^{-2} s^{-1} implies low values of K of the order of 10^6 cm^2 s^{-1}. This value could, therefore, allow the atomic oxygen to build up and the 1,304 Å emission would be explained by resonance scattering.

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1. Chamberlain, J. W. *Planet. Space Sci.* **11**, 901 (1963).
2. Liu, S. C. & Donahue, T. M. *J. atmos. Sci.* **31**, 1118 (1974).
3. Hunten, D. M. & Strobell, D. *J. atmos. Sci.* **31**, 305–17 (1974).
4. Bertaux, J. L. *et al. Planet. Space Sci.* **26**, 817 (1978).
5. Bertaux, J. L. *et al. Astr. Astrophys.* **46**, 19 (1976).
6. Thomas, G. E. *J. geophys. Res.* **80**, 2247 (1975).
7. Blamont, J. E., Cazes, S. & Emerich, C. *J. geophys. Res.* **80**, 2247 (1975).
8. Marcelin, M. thesis Univ. Paris VII (1978).
9. Broadfoot, A. L., Kumar, S., Belton, M. J. S. & McElroy, M. B. *Science* **183**, 1315 (1974
10. Liu, S. C. & Donahue, T. M. *Icarus* **24**, 148 (1975).
11. Sze, N. D. & McElroy, M. B. *Planet. Space Sci.* **23**, 763 (1975).
12. Anderson, D. E. *J. geophys. Res.* **81**, 1213 (1976).
13. Dickinson, R. E. & Ridley, E. C. *Icarus* **30**, 163 (1977).

Direct experimental verification of the Kelvin equation for capillary condensation

THE thermodynamic properties of liquids trapped in microscopic pores or existing as very small, highly curved droplets are described by the Kelvin equation[1]. This equation forms the basis of critical nucleation theory[2] and has been used in interpreting such diverse phenomena as adhesion[3], the enhanced solubility of small particles[2] and the retention and flow of liquids in porous materials[4–6]. The validity of the application of the Kelvin equation to such highly curved interfaces (where the mean radius of curvature can be in the range 1–100 nm) has been questioned[1,4], but has never been tested by direct experiment. We have used multiple beam interferometry to observe the formation of capillary condensed liquid between crossed cylinders of molecularly smooth mica. We report here that the Kelvin equation is obeyed by cyclohexane menisci with mean radius of curvature as low as 4 nm. We further conclude that the application of the laws of thermodynamics, and the concept of a bulk surface tension, are valid in principle for such highly curved interfaces.

The Kelvin equation[1] (equation (1)) gives the equilibrium mean radius of curvature r_m of a liquid–vapour interface in terms of the actual vapour pressure p and the saturated vapour pressure p_s. The equation can be applied to both liquid drops (r_m positive) and to bubbles and capillary-held wetting liquids (r_m negative)[2]. We have measured the mean radius of curvature of cyclohexane menisci at the periphery of liquid bridges trapped between two crossed cylindrical mica surfaces (Fig. 1) at equilibrium with relative vapour pressures in the range $0.71 < (p/p_s) < 0.94$, giving mean radii of curvature in the range $4 \text{ nm} < -r_m < 19$ nm. The experiments were carried out using an apparatus[7] in which the distance D between the molecularly smooth surfaces of a pair of rigidly mounted crossed cylindrical mica sheets was controlled and measured to ±0.1 nm. Distances were measured by multiple beam interferometry, which also

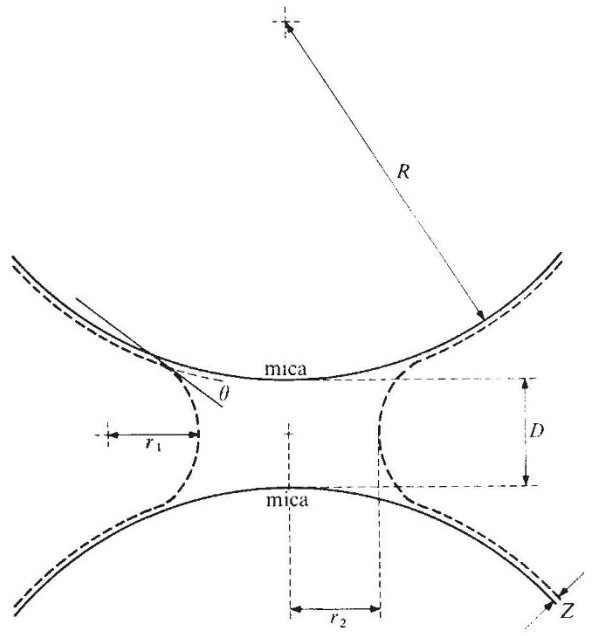

Fig. 1 Space between crossed mica cylinders with bridging meniscus (section through 45° plane of symmetry). Not drawn to scale: $R \approx 10^7$ nm, $r_2 \approx 10^4$ nm, $r_1 \approx -10$ nm. The mean radius of curvature r_m is defined as $1/r_m = 1/r_1 + 1/r_2$. By convention, r_1 is negative and r_2 positive in the configuration shown here. The equation used to calculate values of r_m from experimental values of the critical distance $D = D_c$ (see text) was $r_m \simeq r_1 = -(D_c - 2Z)/2 \cos\theta$. This equation is accurate to within 0.5% for the range of values of r_m examined. The measured value of the contact angle θ was $\theta = (6 \pm 1)°$ (L.R. F., to be published).

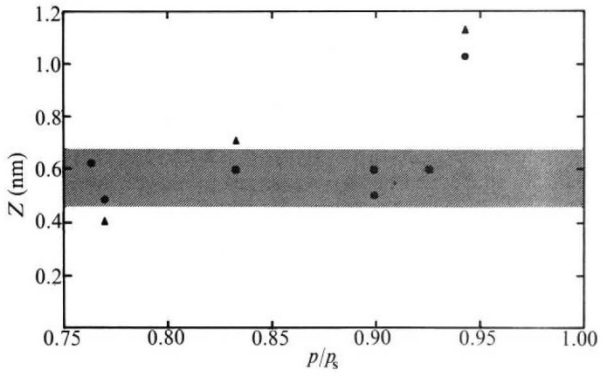

Fig. 2 Adsorption isotherm of cyclohexane on cleaved mica. Values of the adsorbed film thickness Z were determined (1) by measuring the distance ($D_{contact}$) between the mica surfaces at the moment of first contact, and assuming that $Z = D_{contact}/2$; or (2) by calculation from the measured root mean square refractive index (μ_{rms}) of the medium between the surfaces when the surfaces were held at a constant small distance (D) apart[8]. △, Points calculated from spacing at contact; ○, points calculated from r.m.s. refractive index. Shaded band: range of possible values of the thickness of a cyclohexane monolayer, calculated from measurements on a Courtauld spacefilling molecular model. We have taken $Z = (0.6 \pm 0.1)$nm for relative pressures below 0.93 and $Z = (1.05 \pm 0.1)$nm for $p/p_s = 0.943$.

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permitted observation of the presence of a bridging meniscus and measurement of the refractive index of the material between the surfaces[8]. For distances D greater than a critical distance D_c, the liquid bridge evaporated irreversibly. Values of r_m were calculated from the experimental values of D_c, with allowance by simple subtraction for the thickness Z of the adsorbed film. Values of Z were determined from the adsorption isotherm at 293 K (Fig. 2).

The Kelvin relation between r_m and (p/p_s) is[9]:

$$\ln(p/p_s) = \{M/\rho_l RT\}\{(\gamma/r_m) - (p - p_s)\} \quad (1)$$

where M is the molecular weight, ρ_l is the liquid density, p/p_s is the relative vapour pressure, γ is the liquid–vapour interfacial tension at the absolute temperature T, and R is the gas constant. As $|\gamma/r_m| \gg |(p - p_s)|$ for the range of values of r_m measured, this equation gives an almost linear plot of $\ln(p/p_s)$ versus $1/r_m$, with a slope of $[\gamma M/\rho_l RT]$. Two theoretical plots of $\ln(p/p_s)$ versus

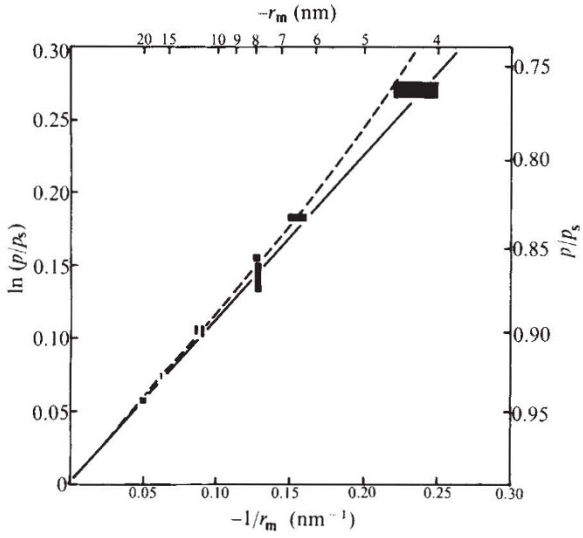

Fig. 3 Comparison of theoretical (Kelvin equation) plot of $-\ln(p/p_s)$ versus $-1/r_m$ with experimental results. The solid line corresponds to the assumption that γ ($=25.5$ mN m^{-1}) is independent of r_m. The dashed line is calculated assuming the approximate relation[10] $\gamma = \gamma_\infty(1 + \Delta\lambda/r_m)$, where γ_∞ is the surface tension of a planar cyclohexane liquid–vapour interface and $\Delta\lambda$ is the 'thickness' of the interfacial region. We have taken $\Delta\lambda = 0.49$ nm (ref. 12). The relative pressure p/p_s was controlled by maintaining a constant temperature difference between the mica surfaces and a pool of liquid cyclohexane in the chamber of the apparatus. Errors in (p/p_s) are due to temperature drifts during an experiment. The principal errors in r_m arise from uncertainty in the thickness of the adsorbed film (about ±0.1 nm) and from errors in establishing the limits at which menisci were clearly observed to evaporate irreversibly (upper limit for D_c) or to grow (lower limit for D_c).

$1/r_m$ are shown in Fig. 3, together with the values of $1/r_m$ calculated from the experimental values of Z, D_c and θ at various experimental values of $\ln(p/p_s)$. The experimental points agree closely with those predicted by the Kelvin equation, assuming γ = constant, down to the smallest mean radius of curvature examined ($r_m = -4.2$ nm). If allowance is made for the effect of curvature on surface tension[10], a theoretical line is obtained with a slightly better fit to the experimental points. The assumption that an equilibrium adsorbed monolayer affects only the geometry of the system and not the meniscus curvature seems to be justified, although this assumption may need modification for thicker adsorbed layers[11].

In conclusion, we have verified that the Kelvin equation for cyclohexane condensed on to mica surfaces is satisfied to within ±6% of r_m down to meniscus radii of 4 nm. A more detailed account of this work will be published elsewhere.

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1. Thomson, W. *Phil. Mag.* **42,** 448–452 (1871).
2. Defay, R., Prigogine, I., Bellemans, A. & Everett, D. H. *Surface Tension and Adsorption,* 310–348 (Longman and Green, London, 1966).
3. Visser, J. *Surface Colloid Sci.* **8,** 3–83 (1976).
4. Everett, D. H. & Haynes, J. M. *Colloid Sci.* **1,** 123–172 (1973).
5. Dullien, F. A. L. & Batra, V. K. *Ind. Eng. Chem.* **62,** 25–51 (1970).
6. Boucher, E. A. *J. Mater. Sci.* **11,** 1734–1750 (1976).
7. Israelachvili, J. N. & Adams, G. E. *Nature* **262,** 774–776 (1976); *JCS Faraday Trans I* **74,** 975–101 (1978).
8. Israelachvili, J. N. *Nature* **229,** 85–86 (1971); *J. Colloid Interface Sci.* **44,** 259–272 (1973).
9. Melrose, J. C. *Am. Inst. Chem. Engng. J.* **12,** 986–994 (1966).
10. Melrose, J. C. *Ind. Eng. Chem.* **60,** 53–70 (1968).
11. Philip, J. R. *J. chem. Phys.* **66,** 5069–5075 (1977); **67,** 1732–1741 (1977).
12. Choi, D. S., Jhon, M. S. & Eyring, H. *J. chem. Phys.* **53,** 2608–2614 (1970).

Measurement of carbon tetrafluoride in the atmosphere

ATMOSPHERIC trace concentrations of carbon tetrafluoride (CF_4) in a variety of ambient air samples have been measured. The air samples were concentrated by a cryogenic trapping technique and the CF_4 species identified by combined gas chromatography–mass spectrometry (GC–MS) with single ion monitoring. The contribution of natural and/or anthropogenic sources to the global burden of CF_4 is unknown. CF_4 may be one of the atmosphere's rare gases.

CF_4 is a very stable compound that behaves like an inert gas up to a temperature of about 2,000 °C. The presence of CF_4 in the atmosphere at a concentration of approximately 0.1 to parts per 10^9 (p.p.b.) was deduced by Gassman[1] from MS analyses of contaminant levels of CF_4 in high-purity krypton samples. Gassman suggested[1] that CF_4 was enriched from the atmosphere during the cryogenic preparation of high-purity krypton. The GC–MS analyses made at Harwell were conducted to determine whether CF_4 is indeed a common constituent of the ambient atmosphere, and if so at what concentration.

A pre-concentration technique was used to provide samples for GC–MS analysis. A glass U-tube equipped with Teflon stopcocks was immersed in liquid nitrogen and air was allowed to liquify until the tube was approximately two-thirds full. Clean helium was then bubbled slowly through the trap until the liquid air had evaporated. The trap was then removed from the liquid nitrogen and thermally equilibrated at room temperature. This created a positive pressure of helium in the trap containing enriched concentrations of the trace species present in the air at the time of trapping. Samples of the mixture were then simply taken off the side arms of the trap with a syringe and injected directly into the chromatographic column. The helium gas used in the enrichment process was cleaned before passage into liquid air by passing through 40 ft of stainless steel tube ($\frac{1}{8}$ inch outer diameter), immersed in liquid nitrogen. This effectively removed all CF_4 and Xe that may have collected in the liquid air trap in the evaporation process. Analysis of blanks made by passing helium through the cold empty trap for 30 min showed no signs of either CF_4 or Xe.

For quantification both ^{84}Kr (boiling point −158 °C) and ^{132}Xe (boiling point −107 °C) were measured directly in 5 ml air samples and in the cryogenic preparations. Essentially 100%

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