FURTHER COMMENT ON THE VERTICAL-PLATE BALANCE

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Several years ago,[1] we analysed the measurement of surface tension using the Wilhelmy[2] vertical plate balance with either smooth or roughened plates. Our analysis for smooth plates appears to be correct, but the treatment of roughened plates was criticized by Kawanishi *et al.*[3] More recently[4] we attempted to correct the analysis for roughened plates, simulating the roughness by regular grooves of arbitrary shape running in either the horizontal or the vertical direction. The theoretical results were checked with data obtained experimentally, and the agreement for horizontal grooves was excellent, but only moderate for plates having vertical grooves. Princen[5] has independently examined theoretically the expected behaviour of plates having vertical grooves and obtained a similar expression to our own. In both analyses[4,5] the most useful method of obtaining the surface tension involves the weighing of the grooved plate plus adhering liquid after immersion and complete withdrawal from the liquid phase. We were concerned only with the liquid trapped in the grooves but Princen[5] attempted to correct for the pendent liquid which hangs from the base of the plate following complete withdrawal from the liquid. We omitted this correction, and if Princen's result is applied directly to our experimental results, it improves considerably the agreement between theory and experiment for vertical grooves, with some decrease in agreement for horizontal grooves. This result would be gratifying, but closer examination of the correction term indicates that it is not directly applicable to our experiments.

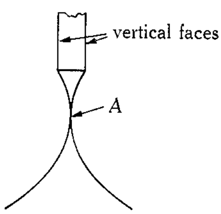

Fig. 1.—Position of plate of infinite width when it is about to separate from the liquid phase.

Princen[5] considered a plate of infinite width but finite thickness and height. Because the vertical faces have infinite width, any line of triple contact between plate, liquid, and fluid must be horizontal. Figure 1 shows a vertical section through the

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[2] Wilhelmy, L., *Ann. Phys.*, 1863, **199**, 177.

[3] Kawanishi, T., Seimiya, T., and Sasaki, T., *Aust. J. Chem.*, 1969, **22**, 2247.

[4] Lane, J. E., and Jordan, D. O., *Aust. J. Chem.*, 1970, **23**, 2153.

[5] Princen, H. M., *Aust. J. Chem.*, 1970, **23**, 1789.

system, normal to the vertical faces, the plate extending an infinite distance in the direction normal to the paper. The plate is at a level such that the line of triple contact lies in the two parallel edges formed by the intersection of the horizontal base with the vertical faces, and simultaneously the two curved liquid–fluid interfaces on opposite sides of the plate meet in a horizontal line A of infinite length. In this position, the whole of the horizontal base is in contact with the liquid. If the plate is raised further, the liquid ruptures at the line A, and the liquid above this line will remain attached to the plate. The contribution to the mass of attached liquid is the same for any unit subdivision of the infinite width of plate. We consider Princen's result to be correct for a plate with infinite width.

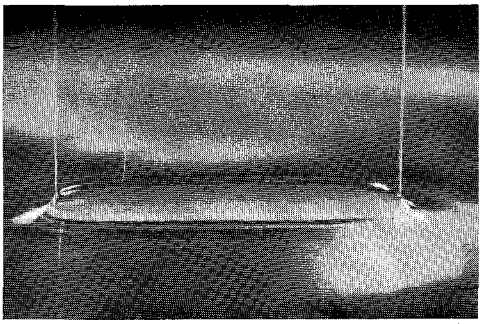

Fig. 2

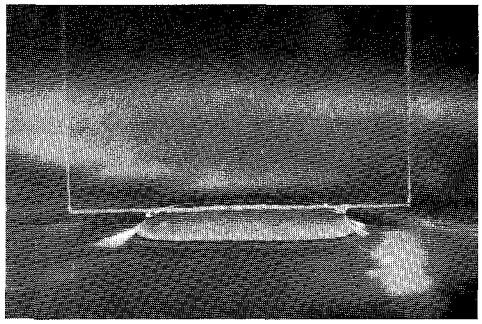

Fig. 3

Fig. 2.—Curved line of triple contact on the vertical face of a plate of finite width.
Fig. 3.—Draining of liquid from below the base of a plate of finite width before the plate is separated from the liquid phase.

No real flat plate can have infinite width, so that a smooth flat plate with *finite width*, if partly submerged in a liquid, has a line of triple contact that is not horizontal (Fig. 2). If the plate is raised, the shape of the liquid–fluid interface is not changed until the line of triple contact first meets the intersection of the base and vertical edge of each face. If the plate is raised further, the shape of the liquid–fluid interface is altered, and the line of triple contact retracts from the edges of the plate (Fig. 3). In addition, much of the liquid below the base of the plate has been drained away. As the plate is raised further, the centre section of the plate, which contains a line of triple contact, becomes narrower and eventually reaches a critical width when rupture of the liquid occurs. We have been unable to estimate theoretically the critical distance, but for plates of equal thickness it is expected to be not very dependent upon the width. Most importantly, a large proportion of the base has been drained of pendent liquid before the plate separates from the bulk of the liquid, and hence the value will be less than for a section of the infinite plate having the same width as the finite plate.

We have checked the base correction for a smooth glass microscope slide $0 \cdot 096$ cm thick, $2 \cdot 49$ cm wide, and $7 \cdot 58$ cm long, using de-ionized water with a surface tension of $71 \cdot 0 \pm 0 \cdot 2$ mN m^{-1} at 20°C. According to equations (35) and (36) of ref.[5], the mass of water attached to the plate should be approximately 9 mg for

$2 \cdot 49$ cm of a plate of infinite width and thickness $0 \cdot 096$ cm. We measured the actual increase in mass and found it to be $1 \cdot 3 \pm 0 \cdot 3$ mg. However, if the plate is withdrawn rapidly, so that equilibrium is not maintained, we found it possible to withdraw 6 ± 1 mg. We also tilted the plate on its side to obtain a width of $7 \cdot 58$ cm. The mass of water attached after withdrawal was 3 ± 1 mg.

If we now consider our results for grooved plates,[4] the correction to our force term $F_{\sigma,c}$ (defined in equations (26) and (46) of ref.[4]) based on an infinite plate is approximately $-1 \cdot 2$ mN. However, the actual correction is likely to be between $-0 \cdot 1$ and $-0 \cdot 3$ mN, which is of the order of the experimental error, and does not affect any of the conclusions we reached.

The uncertainty of the magnitude of this particular correction provides an additional argument in support of our claim[4] that roughened plates are only useful for those systems in which a zero contact angle between plate and liquid cannot be achieved and where accuracy is not required. This correction is unnecessary for a smooth plate as the surface tension of the liquid–fluid interface is obtained without the need to withdraw the plate completely from the liquid.[1] This provides a further reason for using smooth plates for surface tension measurements when accuracy is desired.