The role height plays in the spreading of liquid droplets over sharp edges

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Summary A study has been conducted to investigate how the volume which can be held on the top of a pillar is dependant on the pillar's height. When a fluid which is spreading across a surface encounters an edge between two surfaces of equal contact angle, then the subsequent behaviour will depend on the inclination angle between the surfaces, in the case of a downward step effectively the inclination acts to increase the hysteresis. Such increased hysteresis at the rim of a circular pillar is well known, in this work this hysteresis will be examined as a function of pillar height. Circular pillars of various heights down to 0.2µm we fabricated in silicon, it was found that as the height went below 7µm there was a marked and almost linear decline in the additional hysteresis offered by the step.

INTRODUCTION

The spreading behaviour as a droplet placed on a solid surface reaches an equilibrium contact angle or a metastable state has been studied extensively both experimentally [1, 2] and theoretically [3 - 5]. The wetting properties which dictate such behaviour can be altered by surface structures. When the surface structure is large enough (> 100nm), laws applying to macroscopic scale can still be applied locally. However, when structures are on the nanoscale, the fine details of the three-dimensional variation of intermolecular forces and the thermal fluctuating effects such as interfacial capillary waves become important [6]. Three-phase contact lines can, for example, cross boundaries of microchannels but for nanochannels or nanostrips such events lose sharpness and therefore meaning.

The equilibrium at a contact angle, θ_0, that is formed by a liquid droplet / fluid interface on an isotropic, smooth and rigid solid is given by the Young-Dupre equation:

$$\gamma_{lv}\cos(\theta_0) = \gamma_{vs} - \gamma_{ls} \tag{1}$$

the surface tensions being defined by subscripts abbreviating solid, vapour and liquid. When the three-phase contact line comes in contact with a mathematically sharp solid edge, then a condition of equilibrium exists over a range of angles (θ) defined by [7]:

$$\theta_0 \le \theta \le (180 - \phi) + \theta_0 \tag{2}$$

where ϕ is the angle between the surfaces forming the edge. On a real surface this range of possible angles is in addition to the contact angle hysteresis related to energies required to move the contact line.

In this work droplets are deposited on the horizontal top of a pillar, the sharp edge being formed the vertical walls of the pillar. The validity of the angle range given above will be examined as the height of the pillar is reduced into the nanometer scale. The pillars used are circular, as other shapes can contain fluid in manners in which the contact line passes onto the walls of the pillar in a stable manner [8].

METHODS

Circular pillars of varying heights were fabricated from (100)-oriented Si wafers through deep reactive ion etching. The pillars were of 2, 3 or 4 mm diameter and had heights of 0.2, 0.63, 1.17, 3.5, 7.2, 8.7 and 31.8 µm (as measured by a stylus profiler). Fluid was deposited onto the raised platforms using a fine needle positioned close to the centre of the raised circles, the flow rate being governed by a syringe pump, the flow rates used being 4, 32 and 96 µL/min (no flow rate dependency was observable over this range). Images of the growing fluid volume were captured in the vertical or horizontal planes using CCD cameras fitted with microscopic lens. For the critical measurement of the contact angle, images of the drops were taken in the vertical plane under diffuse back lighting. The video images were analysed to give data on the change of contact angle over time. Deionised water was used. Prior to each experiment compressed air was used to ensure the surfaces were dry, furthermore data was checked carefully for any trends which would indicate a deteriorating surface quality, none were found.

RESULTS

Figure 1 shows the profile of the contact angle for two pillars. For the 32 µm pillar it can be seen from the inset images, that initially the drop grows at 100^o, once the edge of the pillar is reached this grows until a maximum value is obtained, prior to rapid reduction at spillage, this is as would be expected for a large height pillar and allows the various contact angles to be determined. There are three contact angles of interest, that on the upper surface, the side wall and lower surface. On the upper surface a range of contact angles (for the example given is 100^o) were produced by cleaning the photoresist off to varying degrees, however for a given height value, this had no influence on the maximum contact angle prior to spillage. This confirms that the critical relationship is with the wall, we have no direct way of measuring this contact angle due to the small heights involved, even with a high speed camera spillage was too fast to observe a transition state, however from Gibbs it is clear that the angle is in the order of 70^o as the maximum angle prior to

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spillage is approximately 160°, this conclusion is supported by the fact that no increase is observed in this value between the 8.7 µm and 32 µm pillars (i.e. a large enough height has been achieved above which further addition of height plays no further role). The contact angle on the lower surface is 60° but this only plays a role once spillage has occurred, so beyond the realm of interest for these experiments. For the 0.2 µm pillar the sequence is very different, the droplet progresses at the angle of the upper surface (again 100°), when the edge is reached no growth is seen, rather spillage is immediate and the angle of the etched lower surface is obtained. As no rise in the angle is seen prior to spillage, the presence of the edge plays no role.

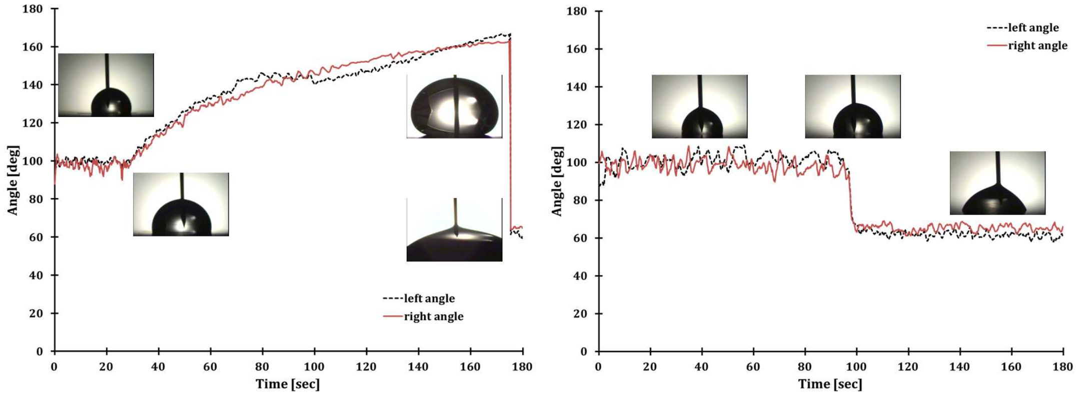

Figure 1: The contact angle over time for the growing droplet, left for a 32 µm pillar and right for a 0.2 µm pillar, inserts are included of the side view of the droplet.

Figure 2 shows the value of the maximum contact angle prior to spillage for each pillar height, it can be seen that as the height is reduced from 7.2 µm to 0.2 µm there is a transition between the pillar acting as Gibbs predicts to not being "noticed" by the droplet. The data takes average values over numerous (over 200) tests once spread of data was minimised through careful experimental setup and image analysis. The diameter plays no significant role over the range tested.

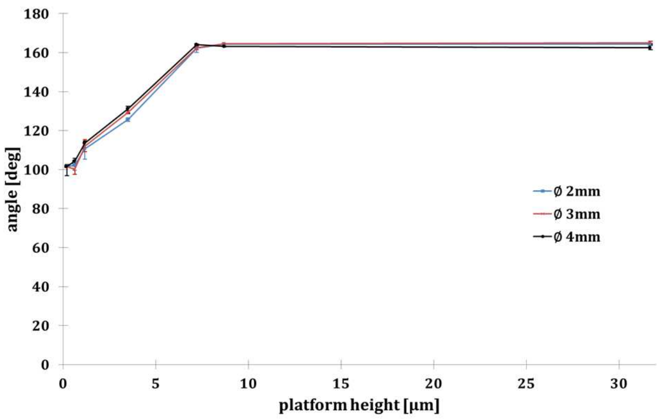

Figure 2: A plot of the angle at which spilling occurred, i.e. when the contact line moves beyond the edge of the pillar as a function of height, plotted for three pillar diameters.

CONCLUSIONS

A height based relationship for the spillage angle has been demonstrated for a circular pillar. It has been shown that for pillars etched into silicon, that above a height of 7.2 µm the behaviour is accurately predicted by Gibbs, whilst below that value there is a steady drop off in spillage angle until, at 0.2 µm the presence of the step in at the edge of the pillar has no influence on the wetting behaviour.

References

[1] Tanner, L. H.: The spreading of silicone oil drops on horizontal surfaces. *J.Phys*. **12**: 1473, 1979.
[2] McHale, M. I.; Newton S. M.; Rowan M. B. G.: The spreading of small viscous stripes of oil. *J. Phys*. **28**: 1925, 1995.
[3] Voinov, O. V.: Hydrodynamics of wetting. *Fluid Dyn*. **11**: 714, 1976.
[4] Hocking, L. M.: The spreading of a thin drop by gravity and capillarity. *Q. J. Mech. Appl. Math*. **36**: 55, 1983.
[5] Bonn, D.; Eggers, J.; Indekeu, J.; Meunier, J.; Rolley, E.: Wetting and spreading, *Rev. Mod. Phys*. **81**: 739, 2009.
[6] Dietrich, M. N. P. S.; Rauscher, M.: Wetting on structured substrates. *J. Phys.: Condens. Matter* **17**: 577, 2005.
[7] Gibbs, J. W.: Scientific Papers. Dover, New York 1961
[8] Tóth, T.; Ferraro, D.; Chiarello, E.; Pierno, M.; Mistura, G.; Bissacco, G.; Semprebon C.: Suspension of Water Droplets on Individual Pillars, *Langmuir*, **27**: 4742–4748, 2011.