Movement of drops on a solid surface due to a contact angle gradient

Experimental results on the motion of liquid drops on horizontal surfaces resulting from a contact angle gradient are presented. Silicon surfaces were modified using dodecyltrichlorosilane to generate the gradient. Water drops with initial diameters of 0.31 - 0.5 mm (15 - 65 nl) were placed on the surface, their movement videotaped, and subsequently analyzed. To characterize the gradient surface the static contact angle was measured along the surface.

1. Introduction

The possibility of drop movement resulting from a contact angle gradient was noted by Greenspan[1] in 1978 and experimentally demonstrated by Chaudhry and Whitesides[2] in 1992. The applications for this phenomenon are numerous as it represents a new way to transport fluids. The development of complex silicon microfabricated systems that would make procedures such as blood chemistry analysis, DNA screening, or pollution analysis both rapid and inexpensive has been hindered in part by the lack of a simple and general method for the pumping and positioning of liquids on submillimeter scales. Mechanical systems cannot conveniently be used for this purpose. Nonmechanical positioning and pumping can be achieved by several means, including thermal[3-6], chemical[2,3,7,8] and electrochemical[9,10] methods. More applications arise from using such a gradient surface to remove fluids on it automatically. Daniel et al. [11] have shown that the efficiency of heat exchangers can be dramatically improved by using gradient surfaces that continuously remove condensing water drops. This can be useful especially under a \( \mu \)g-environment. Another practical example is the removal of liquid debris that collects around the nozzles of ink jet devices.

2. Experiments

The experiments were carried out on strips (15x30 mm\(^2\)) that were cut out of polished silicon wafers. Each strip was first rinsed with deionized water, then cleansed using acetone and again thoroughly rinsed with DI water. After each rinsing, the water was blown off the surface using a nitrogen jet. Subsequently the surface was treated with a propane flame to remove any remaining organic material. The process of generating the gradient was carried out in a desiccator to provide a dry environment. The main idea is to allow the vapour of dodecyltrichlorosilane to diffuse over the surface and to react with it. The method employed here is based on the procedure used by Daniel et al. [11]. A cotton thread uniformly soaked with dodecyltrichlorosilane was placed over one end of the silicon surface. The treatment time was about 1 - 2 min. The gradients were not reproducible from one day to the next, likely because of variations in the humidity. After the treatment the end of the strip closest to the string was strongly hydrophilic with a contact angle of 100\(^\circ\) - 110\(^\circ\). The contact angle progressively decreased farther away from the hydrophobic end. The experiments were carried out in a plexiglas box providing a water ring around the pedestal on which the silicon strip was placed. The purpose of the water ring was to maintain a saturated atmosphere to minimize evaporation of the small drops. A nanoliter pump pushing water through a small capillary with a tip diameter of \( \sim 75 \) \( \mu \)m was used to generate the drops. The drops were placed on the hydrophobic end of the surface and their movement videotaped. The video was subsequently digitized and analyzed. To measure the contact angle gradient, small drops (small enough not to move) were placed along the surface and videotaped. The static shape was then analyzed and the contact angle determined.

3. Theory

The change of the static contact angle \( \theta \) along the surface is due to the change of the surface free energies of the solid-liquid (\( \gamma_{SL} \)) and the solid-gas (\( \gamma_{SG} \)) interfaces. A drop placed on the hydrophobic end of the gradient surface will move in the direction of lower surface energies, that is, towards the hydrophilic end. Brochard [3] has provided an approximate analysis of the motion of the drop using lubrication theory.

4. Results

Figure 1 shows the results of the static contact angle measurement along a silicon surface. The plot of \( d\cos(\theta)/dx \) vs \( x \) shows a distinct maximum near the hydrophobic end. In the experiments, the motion of the drop
occurred in two or three stages, depending on the position where the drop was placed on the surface. When placed at a location to the left of the maximum in $d\cos(\theta)/dx$, the drop first crept slowly before it rapidly accelerated to a peak velocity and then decelerated to creep slowly until it stopped. When placed at the location of this maximum or to the right of it the initial slow creeping behavior was not observed.

![Image of a graph showing $\theta$, $\cos(\theta)$ and $d\cos(\theta)/dx$ along the surface](image1)

**Fig. 1:** $\theta$, $\cos(\theta)$ and $d\cos(\theta)/dx$ along the surface

Figure 2 shows an example of a velocity plot of three drops of nearly the same size. The last part of the rapid deceleration phase and the final creeping stage are depicted. During the final creeping, the drops move with an average speed of 0.02 mm per second. Other drops of the same size reached much higher speeds on different surfaces. This is an example that illustrates problems with reproducibility of the generation of the gradient surfaces. The kink at $x \sim 1.9$ mm is probably due to a surface defect; it occurs also in other velocity plots (same surface). The experiments showed a clear increase in the velocity with increasing drop size (not shown here). The fastest drops ($d = 0.5$ mm) reached peak velocities of up to 50 mm/s. It is not possible to compare the results with the predictions made by Brochard [3] because the theoretical model assumes a constant driving force and a steady velocity. Neither assumption is satisfied in the present experiments.

5. Summary

Experimental results on the movement of drops on a surface with a contact angle gradient are presented. Water drops moving on chemically modified silicon surfaces were videotaped and their movement analyzed. The velocity increased with increasing drop size with an observed maximum velocity of 50 mm/s. Preparing well-defined and reproducible gradient surfaces was found to be a major obstacle that needs to be resolved in future work.

Acknowledgements

The first author gratefully acknowledges the helpful scholarship by the German Academic Exchange Service DAAD. This work was supported in part by NASA Grant NAG3-2703. The authors gratefully acknowledge helpful discussions with Ms. Susan Daniel and Professor Manoj K. Chaudhury of Lehigh University.

6. References


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