Experimental investigations of the behaviour of droplets on surfaces that exhibit a gradient in wettability

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Summary: The paper presents our activities on the field of moving droplets on solid surfaces due to a wettability gradient. The main focus lies on the theoretical basics and the experimental set up. Droplets are known to move along horizontal solid surfaces that exhibit a gradient in wettability. The driving force in the direction of increasing wettability arises from an imbalance of forces acting on the contact line around the droplet periphery. Contact angle measurements are used to characterize the wettability of the surfaces, force measurements will be applied to determine the driving force.

1. INTRODUCTION

The possibility of drop movement due to a contact angle gradient was noted first by Greenspan [1] in 1978 and experimentally demonstrated by Chaudhury and Whitesides [2] in 1992. The main applications for this phenomenon are the directed and the undirected transport of fluids. The development of complex silicon micro fabricated systems such as MEMS (MicroElectroMechanicalSystems) is in need of a simple method for the pumping and positioning of liquids on sub millimetre scales (directed transport). Mechanical systems cannot conveniently be used for this purpose because of the dominance of capillary forces on those scales. More applications arise from using such a gradient surface to remove fluids on it automatically (undirected transport). As Daniel et al. [11] could show, the efficiency of heat exchangers can be improved by using gradient surfaces that continuously remove condensing water drops. This can be useful especially under a µg environment.

The objective of this work is to provide an overview over the project and a basic understanding of the underlying mechanism of the phenomenon.

2. THEORETICAL BASICS

2.1 YOUNG’S EQUATION

Usually a liquid that is placed on a solid surface, as shown in Fig. 1, will form a drop having a definite angle of contact between the liquid and the solid. This angle which is a measure of wettability is called (equilibrium) contact angle $θ$. $γ_{SG}$, $γ_{SL}$ and $γ_{LG}$ are the surface tensions of the three interfaces solid-gas, solid-liquid and liquid-gas, respectively.

Figure 1: Drop on a homogeneous solid surface
Young’s equation, one of the governing equations of wettability, describes the mechanical equilibrium of forces acting on the contact line, the forces being represented by the surface tensions:

\[ \gamma_{LG} \cdot \cos(\theta) = \gamma_{SG} - \gamma_{SL} \]  

(1)

2.2 GRADIENT SURFACES

Common surfaces exhibit everywhere the same wettability represented by identical contact angles (within experimental error) measured from drops placed on the surfaces (see Fig 2a). A surface with a gradient of wettability in one direction, say along the x-axis as shown in Fig. 2b, shows a distinct change of wettability in this direction.

When a droplet is placed on such a gradient surface it may begin to move in the direction of increasing wettability (decreasing contact angle), depending on its size. Drops smaller than a critical size do not move and thus can be used to measure the static contact angle along the surface.

2.3 DRIVING FORCE

A simplified physical explanation for the driving force is as follows. The 2D case is considered, the drop is assumed being a strip of liquid (in y-direction). The wettability of the surface on the left side of the drop is lower (higher equilibrium contact angle \( \theta_A \)) than on the right side. The drop is small and the influence of gravity negligible. Due to an uniform pressure in the droplet its shape is a circular section (constant radius of curvature) with equal contact angles \( \theta_0 \) at both ends [3, 4] (Fig. 3).

However, the equilibrium contact angles \( \theta_A \) and \( \theta_B \) which represent balance of forces at the contact line differ from \( \theta_0 \). This leads to resulting forces at both ends of the drop as shown in detail in Fig. 4:

Let us consider the left side of the drop, referred to as point A. The horizontal component of \( \gamma_{LG} - \cos(\theta_A) \cdot \gamma_{LG} \) — together with \( \gamma_{SG} \) and \( \gamma_{SL} \) must be present at the contact line for the balance of forces according to Young’s equation (1). Instead, \( \cos(\theta_0) \cdot \gamma_{LG} \) is present at the contact line. The result is a force \( dF_A = \gamma_{LG} \cdot [\cos(\theta_0) - \cos(\theta_A)] \cdot dy \) in direction of higher wettability (right side). The analogue treatment of point B yields \( dF_B = \gamma_{LG} \cdot [\cos(\theta_B) - \cos(\theta_0)] \cdot dy \) which leads to the driving force:

\[ dF = \gamma_{LG} \cdot [\cos(\theta_B) - \cos(\theta_A)] \cdot dy \]  

(2)

It must be emphasized here that this model does not account for the effect of contact angle hysteresis. The speed of movement is assumed small and dynamic effects are neglected.
2.4 CONTACT ANGLE HYSTERESIS

It is a general observation that the contact angle of a liquid advancing across a surface exceeds that of one receding from the surface. It is possible to change the volume of a drop resting on a surface by adding or withdrawing liquid without the contact line moving (Fig. 5). When adding liquid the contact angle increases to a maximum – the advancing contact angle $\theta_a$. If still more liquid is added the contact line advances, retaining $\theta_a$. In the case of withdrawing liquid a minimum value is achieved – the receding contact angle $\theta_r$. The difference between the advancing and receding contact angle is known as contact angle hysteresis. The equilibrium contact angle $\theta$ lies somewhere between these two limits. Contact angle hysteresis is generally attributed to surface roughness, heterogeneity and contamination or swelling, rearrangement or alteration of the surface by the liquid [5].

![Figure 5: Demonstration of contact angle hysteresis by adding and withdrawing liquid](image)

3. SURFACE PREPARATION

3.1 BASIC COATING

Strips of 30 mm x 6 mm are cut from a silicon wafer (p-type, 525 ± 15 µm thick, <1-0-0>). The surface is cleaned in a first step using a CO2-snow jet to remove micron and sub micron particles from cutting the wafers. The samples are then degreased with ethanol in a heated ultrasonic bath and further cleaned by dipping in freshly prepared “piranha solution” for 15 min at 150 °C. This is a strong acid (70% H2SO4 + 30% H2O2) that removes residual contamination (caution: this mixture reacts violently with organic materials and must be handled with extreme care). After excessive rinsing with deionised water and drying with a nitrogen jet the samples are coated with an octadecyltrichlorosilane self assembled monolayer (OTS-SAM). The cleaned samples are allowed to react for 1h in a reaction solution composed of 70 mL hexadecane, 30 mL CCL₄ and 5·10⁻³ M of OTS. After a final cleaning with CCL₄ the samples show strong hydrophobicity, represented by a contact angle of 113°.

3.2. GRADIENT PREPARATION

The samples undergo a final treatment based on UV-exposure to form the wettability gradient. The new method developed at our laboratory makes it possible to form defined gradient surfaces. Length scale and steepness of the wettability gradient (as well as the shape to some extent) can be controlled. Surfaces with a linear gradient of \( \cos(\theta) \) are of special interest (Fig. 6).

![Figure 6: Example of a gradient surface on a length scale of 15 mm; water drops placed at an interval of 2mm](image)

4 EXPERIMENTAL MEASUREMENTS

4.1 STATIC CONTACT ANGLE

Contact angles are measured on sessile drops as they are at hand as object of interest. Backlight illumination is used, digital images are taken using a CCD-camera coupled with a telecentric objective.
Contact angles are determined from the images by fitting the Laplacian curve of capillarity to the shape of the drops [6]. The measured contact angles are considered as advancing contact angles due to the nature of spreading of drops where the contact line advances. Accuracy of measurements is on the order of ± 1°.

4.2 DYNAMIC CONTACT ANGLE AND DROP VELOCITY

Dynamic contact angles are measured on moving droplets with the image acquisition unit tracking the moving drop using the same procedure as for static angles. The velocity of the drop is derived from the position of the drop versus time [7].

4.3 FORCE MEASUREMENTS

The first attempt to measure the force acting on a drop on a gradient surface was made by Suda and Yamada [8] using a flexible glass micro needle. The drop on the gradient surface adhered to the needle and deformed it from which the force could be determined. We have developed a new non invasive method based on the centrifugal force imposed on the drop by rotation.

5. PRELIMINARY RESULTS AND OUTLOOK

To perform and evaluate experiments in the right way it is necessary to provide reproducible initial conditions. In this project it is the gradient surfaces that have to be produced reproducibly. At this time this is our main focus. A first result is shown in Fig. 6. However, we still lack satisfactory reproducibility in fabricating the gradient surfaces. The apparatus for the force measurements will be put into operation soon.

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REFERENCES


