Towards Smart Substrates for Controlling Micrometric Droplet Motion

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Abstract. In this contribution, we describe a novel approach to the problem of setting micrometric droplets in motion. First, this paper reviews the state-of-the-art methods to enable millimetric droplet motion, and investigates the scalability of the most promising techniques on the basis of preliminary experiments. Then, we propose a novel approach based on substrates with radial 3D pattern. In the poster, we will investigate this approach in further details using numerical models and systematic experiments.

1 Introduction and Background

Droplets capture both hydrophilic and hydrophobic components, owing to capillarity if no stronger force such as gravity is acting against it. Therefore, moving droplets are an efficient way of transporting and/or collecting sensitive and fragile material such as cells, nanotubes, and different micro/nano-objects.

For a liquid droplet, two possible motions may occur: (1) if the droplet partially wets the surface, it slides along it; (2) if the droplet is in a superhydrophobic state, it can roll on the surface [1], much like a marble on a rough inclined plane. In both cases, an external driving force such as gravity is needed.

Unfortunately, setting a partially wetting droplet in motion requires non-negligible forces because the contact angle hysteresis generates a force opposing the motion [2] (Figure 1). Contact angle hysteresis is due to non-idealities of the substrate such as small heterogeneities, wetting/non-wetting contrast, and roughness [3].

Several authors have proposed different approaches to this problem based on electro-wetting [4], electric fields [5], and chemical reactions [6]. Chaudhury et al. [7] have successfully fabricated a surface having a spatial gradient in its surface free energy that is capable of causing drops of water placed on it to move uphill. However, the fabrication process is not straightforward and the surface needs to remain perfectly clean so that the hysteresis is small. Khoo et al. have demonstrated self-propelled millimetric droplets on radially, chemically patterned surfaces [8].

In the second type of motion, the design of a super-hydrophobic surface is required. Chemically treated smooth surfaces do not allow contact angles higher
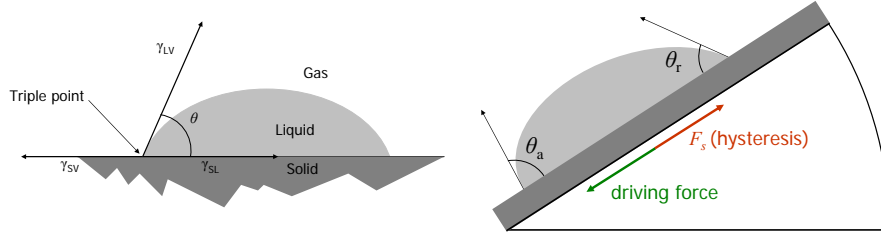
Fig. 1. *Left:* The contact angle θ of a liquid droplet on a solid surface is given by the Young's equation: $\gamma_{LV} \cdot \cos \theta_e = \gamma_{SV} - \gamma_{SL}$ where γ_{LV}, γ_{SV} and γ_{SL} are the liquid-vapor, solid-vapor and solid-liquid surface tensions, respectively. One can distinguish complete wetting ($\theta \to 0°$), partial wetting ($0° < \theta < 180°$) and no wetting ($\theta \to 180°$). *Right:* Under real conditions, the equilibrium contact angle θ is not exactly that provided by the Young's equation, but it can oscillate between two values $\theta_r < \theta < \theta_a$ without making the contact line move. We call θ_a and θ_r respectively the advancing and the receding contact angles. Contact angle hysteresis involves a constant sliding force F_s acting against the movement.

than 120°. Several authors have reported that hydrophobic rough surfaces can enable contact angles very close to 180° [9,10]. It is known that there are typically two states in which a droplet can reside on a given rough surface [11]: (1) the droplet may sit on air pockets which remain trapped in the roughness asperities underneath the droplet (Figure 2) or (2) the droplet may wet the grooves and thus increase its contact area with the substrates, which geometrically enhances hydrophobicity. The apparent contact angle of a droplet is given by Cassie's formula [12] in the former state and by Wenzel's formula [13] in the latter. Generally speaking, a droplet tends to reside in the lowest-energy state, i.e. the state in which the apparent contact angle is minimal. However, an energy barrier separates the two states so that a droplet may reside in Cassie state even though Wenzel state has a lower energy, and inversely [14]. He et al. [15] have demonstrated that the Cassie state shows much less hysteresis compared to the Wenzel state and is therefore preferred in applications involving moving droplets.

An interesting alternative to these approaches consists of encapsulating a liquid droplet with a hydrophobic powder. The resulting liquid marbles are found to behave like a soft solid showing dramatically reduced adhesion to a solid surface [16].

Such extreme contact angles dramatically reduce both hysteresis and viscous friction. Therefore, very high speeds of motion are theoretically possible. However, the solid-liquid area of pearl drops tends towards zero so that one cannot exploit the surface-energy gradient as a driving force.

Several authors have proposed an intermediate approach which consists of exploiting a partial super-hydrophobicity in order to reduce hysteresis and viscous friction while keeping the solid-liquid surface of the droplet large enough to exploit surface-energy gradient as a driving force. Shastry et al. [17] describe surface-energy gradients created by varying the dimension d and spacing s of mi-
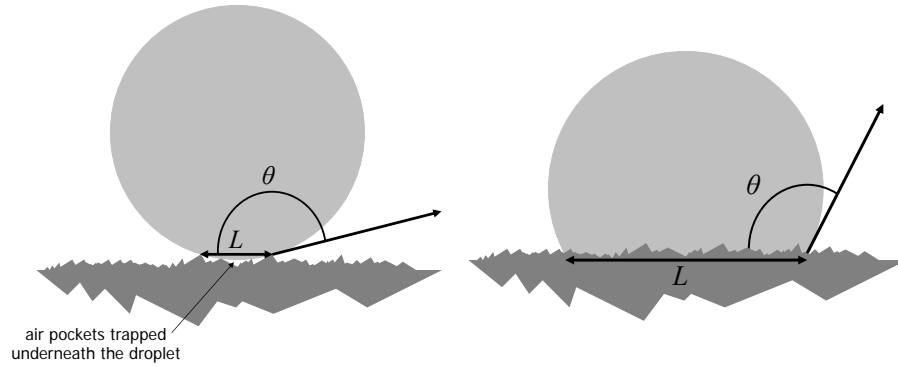
Fig. 2. *Left:* This droplet sits on air pockets which remain trapped in the roughness asperities underneath the droplet, leading to a composite contact with air and solid substrate. The apparent contact angle θ is given by Cassie's formula. *Right:* This droplet wets the asperities. The apparent contact angle is given by Wenzel's formula. In both cases, the contact length L is proportional to the initial droplet radius and inversely proportional to the apparent contact angle.

crofabricated pillars[1]. They demonstrate that millimetric Cassie droplets move down such gradients if and only if vibration of the substrate provides the force required to overcome pinning.
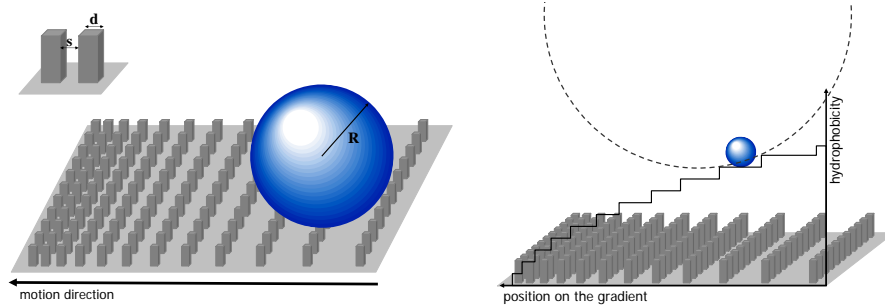

Fig. 3. *Left:* This droplet in a super-hydrophobic state may move towards the region of higher hydrophilicity, i.e. towards the pillars that are closer to each other. *Right:* Pillar-based gradients have an inherent discreteness which may prevent small droplets from moving. In this figure, the radius of the large droplet (depicted by a dashed circle) is only ten times larger than the radius of the blue droplet which does not sense the gradient at all, thus experiencing a zero driving force.

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[1] On one hand, the height of the pillars does not play a role for Cassie droplets themselves. On the other hand, the higher the pillars, the higher the energy barrier between Cassie and Wenzel states and subsequently the larger the stability of Cassie droplets.

2 Preliminary Results

Our contribution investigates the pillar-based approach at the micrometer scale. We are currently collecting data from systematic experiments with Gamma-Butyrolactone (GBL) droplets of radius $R = 75\,\mu m$ (on flight or at generation) and pillars of dimension d and spacing s ranging from $2\,\mu m$ to $20\,\mu m$. We introduce a very simple metric, $\xi = \frac{L}{d+s}$, that is basically the number of pillars sensed by the droplet at a given position on the gradient. We demonstrate that the factor ξ is proportional to the driving force. The average value of ξ in our case is much smaller than reported in the work of Shastry et al..

Furthermore, a small ξ might render droplets very sensitive to the discreteness of the gradient (Figure 3). Depending on the initial conditions and their historical motion, droplets remain stuck in local minima because they are sensing only a very small section of the gradient. Furthermore, very recent work has impressively demonstrated that Wenzel's and Cassie's equations are valid only to the extent that the structure of the contact area reflects the ground-state energies of contact lines, and the transition states between them [18]. Therefore, one cannot rely on these equations to model the behavior of droplets in the case of small ξ, owing to the predominance of the deformations of the contact line (which scales linearly with the radius) with respect to those of the contact area (which scales with the second power of the radius).
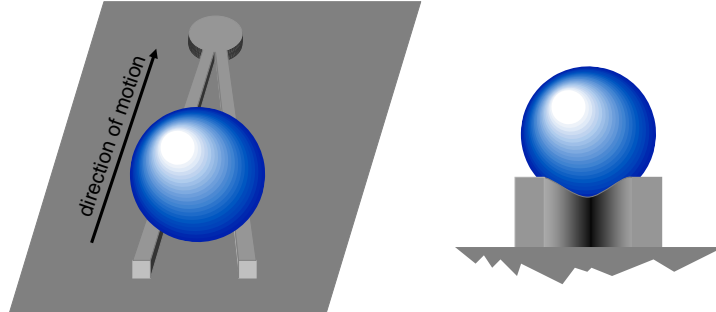

Fig. 4. *Left:* Two branches of a radial pattern guide a Cassie droplet towards the center of the pattern. Indeed, they form an increasing wettability gradient because the liquid-solid contact area is increasing as the branches are getting closer. *Right:* this side view illustrates that the radial topology is not so different from the pillar-based topology from a local point of view.

Given the above remarks, we investigate a novel type of surface energy gradients based on radial patterns. Our approach differs from that of Khoo et al. [8] in at least one fundamental aspect—our patterns are 3-dimensional and they may enable super-hydrophobicity. Radial gradients are interesting because they are continuous even at very small length-scales. Furthermore, their geometry naturally enables the alignment of moving droplets with their center (Figure 4).

Current experimental results demonstrate that micrometric droplets deposited on pillar-based substrates using an Inkjet printer do not reside in Cassie state, most likely because of their considerable velocity at the moment of the impact. Those results are confirmed by Lattice Boltzmann simulations. We are currently investigating whether the radial patterns suffer from similar problems. The poster will provide detailed numerical models validated by systematic experimental results regarding this novel approach to micrometric droplet motion.

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