BOUNDS ON CONTACT ANGLE HYSTERESIS OF TEXTURED SUPER-HYDROPHOBIC SURFACES

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Abstract

This paper presents the fabrication of rough super-hydrophobic surfaces, dynamic measurements of sliding angles of water droplets, and a modeling approach to estimate bounds on contact angle hysteresis—the major dissipative mechanism in droplet based microfluidic systems. We investigate the dependence of hysteresis on texture parameters, evaluate the current model, propose a modification, and show that the two models—current and proposed—are useful bounds on the hysteresis of the surface.

Keywords: droplet microfluidics, contact angle hysteresis, surface characterization

1. Introduction

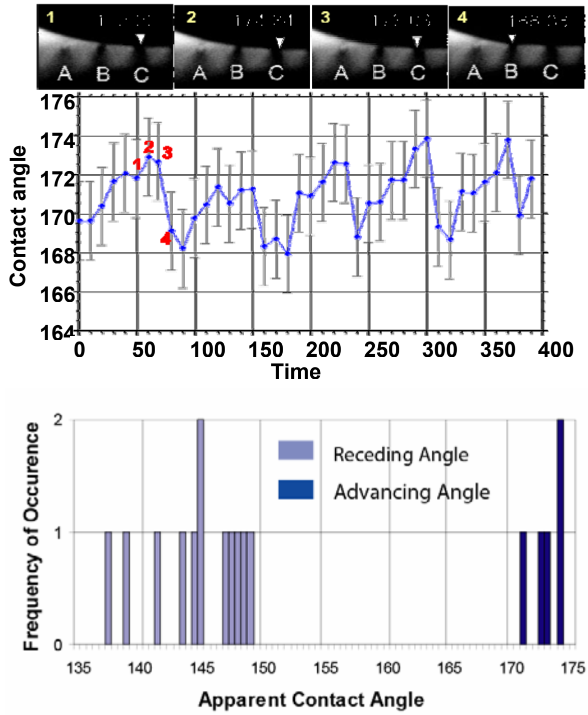
Droplet based systems make temporally and spatially resolved chemistries possible—creating exciting possibilities for lab-on-chip assay. A low hysteresis surface translates to low energy requirements for droplet actuation. For electrowetting based devices [1], low-hysteresis and low-drag surfaces [2, 3] could make sub-CMOS actuation voltages possible—enabling totally integrated microfluidic platforms. Understanding the quantitative relationship between the impeding force of contact angle hysteresis and surface parameters is therefore an important milestone in this pursuit.

2. Experimental

We built rough surfaces realized by pillars of controlled geometry in silicon. The texture is characterized by ϕ, the solid-liquid contact area fraction. The two states in which a sessile droplet can rest on a rough hydrophobic surface are explained in Fig. 1.

Pillars are fabricated in silicon using standard Bosch process for DRIE and Teflon AF 1600 is spin coated on them to create the test surfaces. We mounted the test surfaces on the goniometer stage and deposited measured droplets, ensuring Fakir state [4]. These droplets were expanded and contracted using a syringe pump. A video was recorded and contact angles measured in each frame.

Figure 1: Droplets of volume 5 μl, on a Teflon-coated silicon surface with ϕ = 0.05 and r = 1.4 in a) Fakir state with a footprint diameter of 1 mm, θ_F = 156.6^o (expected: 164.5^o) and b) Wenzel state with a footprint diameter of 1.96 mm, θ_W = 118^o (expected: 112.8^o). Air pockets are visible between pillars under the Fakir state droplet. Pinning of the droplet edge causes significant deviations from the predicted equilibrium value.



2a)

2b)

Figure 2: a) The advancing contact angle is plotted as a function of time for a sessile droplet (on a surface with $\phi = 0.04$). b) Contact angle values in the entire video for the advancing angle measurements were used to create the histogram shown.

In Fig. 2a, the contact angle of the expanding droplet increases till the advancing edge lands on the next pillar, at which point it drops. For the contracting droplet, the receding angle decreases till the edge snaps off a pillar. The mode value of contact angle is reported (Fig. 2b) for each case. Movies were made for surfaces of varying texture ϕ ranging from 0.025 to 1, data plotted, and trends analyzed.

3. Results and Discussion

The cosines of advancing and receding angles were observed to decrease linearly with ϕ (Fig. 3). The advancing angle model is $\cos\theta_A = -1+\phi\,(1+\cos\theta_{i,A})$, a heuristic relation proposed by He et al. [5] —obtained by replacing the intrinsic equilibrium contact angle θ_i with the intrinsic advancing angle $\theta_{i,A}$. These results provide the first experimental validation of this relation. The current model for receding angle in the Fakir state, $\cos\theta_{R,} = 2\phi-1$, is obtained assuming a trailing film remains on the pillar tops [5]. As seen in Fig. 4a, this assumption, originally proposed for hydrophilic surfaces [6], expectedly overestimates hysteresis—providing an upper bound (for $\phi>0.1$).

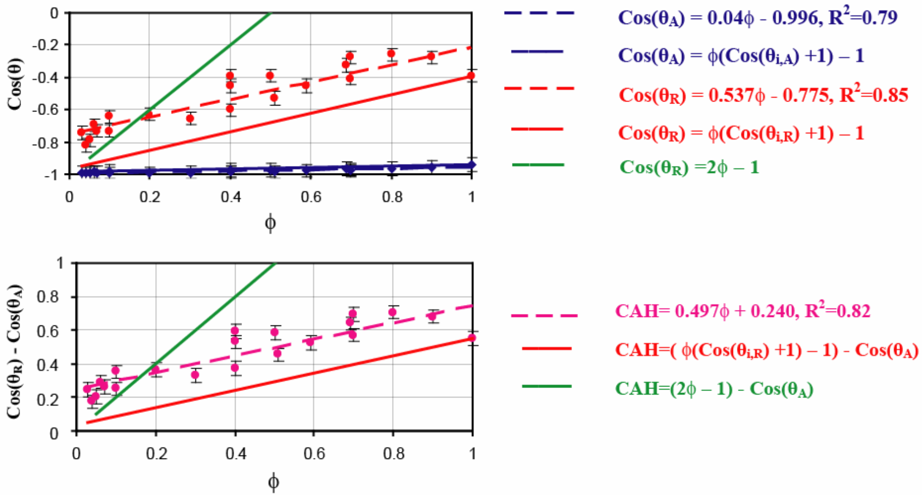


Figure 3: a) Mode values of advancing and receding contact angles obtained on Teflon coated surfaces are plotted as a function of ϕ along with the linear fit lines and model predictions. b) The contact angle hysteresis (CAH) is plotted as a function of ϕ for Teflon, as well as model lines and a fit line.

We re-derived the relation from first principles, heuristically replacing "1" (=cos0) by $\cos\theta_i$ in the coefficient of ϕ to obtain $\cos\theta_R = (1+\cos\theta_{i,A})\phi - 1$. The model accounts for partial coverage of pillars by the trailing film—which is expected for a hydrophobic coating. Our model provides the lower bound to hysteresis (Fig. 3b). For very low ϕ (ϕ<0.1), experiments are underway to validate our hypothesis that the perimeter per unit area and not ϕ controls the behavior.

This work marks an important step towards engineering droplet behavior on textured super-hydrophobic surfaces.

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