Contact Angle Hysteresis on Superhydrophobic Stripes

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We study experimentally and discuss quantitatively the contact angle hysteresis on striped superhydrophobic surfaces as a function of a solid fraction, \(\phi_s\). It is shown that the receding regime is determined by a longitudinal sliding motion the deformed contact line. Despite an anisotropy of the texture the receding contact angle remains isotropic, i.e. is practically the same in the longitudinal and transverse directions. The cosine of the receding angle grows nonlinearly with \(\phi_s\), in contrast to predictions of the Cassie equation. To interpret this we develop a simple theoretical model, which shows that the value of the receding angle depends both on weak defects at smooth solid areas and on the elastic energy of strong defects at the borders of stripes, which scales as \(\phi_s \ln \phi_s\). The advancing contact angle was found to be anisotropic, except as in a dilute regime, and its value is determined by the rolling motion of the drop. The cosine of the longitudinal advancing angle depends linearly on \(\phi_s\), but a satisfactory fit to the data can only be provided if we generalize the Cassie equation to account for weak defects. The cosine of the transverse advancing angle is much smaller and is maximized at \(\phi_s \simeq 0.5\). An explanation of its value can be obtained if we invoke an additional energy due to strong defects in this direction, which is shown to be proportional to \(\phi_s^2\). Finally, the contact angle hysteresis is found to be quite large and generally anisotropic, but it becomes isotropic when \(\phi_s \leq 0.2\).

1 Introduction

Surface texture can change wetting properties in a very important way. On a surface, which is both rough and hydrophobic, the contact angle of water is often observed to be very large. This situation is referred to as superhydrophobic (SH). Two states are possible for a drop on such SH solid. The first, so-called impaled state, where liquid penetrates the texture completely, is known since Wenzel.\textsuperscript{2,3} The second idea, first expressed by Cassie and Baxter,\textsuperscript{4} assumes air is trapped by texture, so that liquid sits on the top of the asperities, being in the so-called fakir state. In such a situation the effective (Cassie) contact angle is expressed as

\[
\cos \theta^* = \phi_s \cos \theta - 1 + \phi_s,
\]

with \(\theta\) the contact angle on the bare, smooth surface with the same chemical characteristics, and \(\phi_s\) the solid fraction.

Attempts to understand SH surfaces were mostly focussed on wetting of a low density array of pillars. In this situation the Wenzel contact angle is close to Young’s angle, but the hysteresis, which is usually defined as a difference between the advancing and receding contact angles, maybe very large, owing to the strong pinning of the contact line in the texture. In the Cassie state, the advancing and even receding water contact angles are outstandingly large,\textsuperscript{4} and hysteresis is often very low.\textsuperscript{10,11} These remarkable (‘super’) properties of the SH Cassie materials have macroscopic implications in the context of self-cleaning\textsuperscript{2} and impact processes.\textsuperscript{4} However, in some recent studies of dense SH Cassie textures a contact angle hysteresis has been observed and analyzed theoretically,\textsuperscript{5–13} similarly to reported earlier for the Wenzel state.\textsuperscript{14,15} These investigations again have been mostly focussed on the isotropic arrays of pillars\textsuperscript{16,17} and natural SH surfaces.\textsuperscript{18}

SH surfaces could also revolutionize microfluidic lab-on-a-chip systems\textsuperscript{19} since the large effective slip of SH surfaces\textsuperscript{20,21} can greatly lower the viscous drag and amplify electrokinetic pumping\textsuperscript{22,23} in microfluidic devices. A physical parameter that quantifies flows is an effective slip length\textsuperscript{24} which is not directly related to a contact angle.\textsuperscript{25} Moreover, optimization of robust transverse flows in SH devices, which is important for flow detection, droplet or particle sorting, or passive mixing, requires highly anisotropic textures which significantly differ from those optimizing effective slip.\textsuperscript{25} In particular, it has been shown that transverse flow in thin channels is maximized by stripes with a rather large solid fraction, where the contact angle and the effective slip are relatively small, but the Cassie state is generally stable.

These directional textures exhibit anisotropic wetting behavior.\textsuperscript{26,27} It is natural to suggest that on materials with a high density of anisotropic patterns, the contact angle hysteresis can be relatively large owing to an enhanced solid/liquid contact (compared to dilute micropillars). Here we discuss this quantity for striped superhydrophobic Cassie surfaces.

Our paper is organized as follows. Sec.2 contains a description of our surfaces and experimental methods. Results are discussed in Sec.3 and we conclude in Sec.4.

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2 Experimental

Fluorinated superhydrophobic rectangular grooves (see Fig. 1) of width \( w \) separated by distance \( d \) (both varied from 3 to 100 \( \mu m \)) and depth \( h \) (5 \( \mu m \)) have been prepared to provide \( \phi_S \) from 0.12 to 0.88 in the Cassie state. To manufacture the surfaces we used two methods. First, we employed the projection photolithography on silicon wafers. Silicon surfaces have been oxidized by plasma treatment, and coated with a chlorotrifluorosilane. Second, we used similarly hydrophobized PDMS replicas fabricated from silicon patterns by a common soft lithography (cross-linking at 60\(^{\circ}\)C). Note that flat silicon surfaces have been also hydrophobized similarly.

The geometry of the patterns after hydrophobisation has been validated by using the interference profilometry (WYKO NT2000, Veeco, USA) and optical microscopy (Axioplan 2 Imaging System, Zeiss, Germany), which also allowed obtaining exact values of \( w, d, h \) and \( \phi_S \) for each sample.

![Fig. 1 A droplet on a striped surface: a) transverse side view; b) longitudinal side view.](image)

To measure the receding and advancing contact angles we use the Drop Shape Analysis System (DSA100, Krüss, Germany) by employing two independent methods. In the first method\(^{30} \) the volume of the sessile drop on the pattern oscillated in the range 7\( \pm \)5 \( \mu L \) being fed with a syringe. The advancing angle is then measured by introducing purified milli-Q water and is the largest before the drop advances. Similarly, as water is drawn out of the drop, the smallest angle possible before the drop retracts is the receding contact angle. In the second method we investigated the directed motion of the droplet of a volume ca. 4 \( \mu L \) driven by the syringe needle placed inside the droplet with constant (low) velocity.\(^{31, 32} \) The angle at the front edge is the advancing, and that at the rear, the receding contact angle. Note that first method gives the maximal values of advancing contact angles, while the second method gives lowest values of receding angles. Values of contact angles were obtained by averaging over 5 – 10 measurements. In case of striped surfaces all contact angles were measured in two, longitudinal and transverse, eigendirections of the surface pattern. The notations we use below are summarized in Table 1. We monitor the local shape of triple contact line by using optical microscopy (Axioplan 2 Imaging System, Zeiss, Germany) and confocal microscopy (Leica TCS SP8, Germany).

### Table 1: Notations of different contact angles on flat and patterned surfaces

| Type of surfaces | receding | advancing |
|------------------|----------|-----------|
| Flat             | \( \theta_r \) | \( \theta_a \) |
| Patterned        | \( \theta^*_r \) | \( \theta^*_a \) |

3 Results and discussion

3.1 Contact angles on the flat hydrophobic surface

We begin by studying contact angles on the flat hydrophobized silicon surface. The cosines of measured contact angles are presented in Table 2 and clearly show that there is some contact angle hysteresis. Our data are in good agreement with prior work\(^{32} \) which has been interpreted by the static friction for the contact line displacement.\(^{33} \)

### Table 2: Contact angles of water on the flat hydrophobized surface used in the study. For all the measurements errors did not exceed instrumental error of 1\(^{\circ}\)

| \( \theta, \circ \) | receding | static | advancing |
|-------------------|----------|--------|-----------|
| \( \cos \theta \) | 84       | 109    | 115       |

Measured hysteresis indicates that flat hydrophobic surface contains weak defects, likely small scale chemical heterogeneities or some roughness elements.\(^{14} \)

3.2 Contact angle hysteresis on the patterned surface

Now, we measure contact angles on the striped superhydrophobic surface with different \( \phi_S \). Fig. 1 shows the typical sessile drop on a grooved Cassie surface. We see that the contact angle is different in transverse and longitudinal directions. A typical (bottom) view of the droplet baseline is shown in Fig. 2. It can be seen that the shape of the contact line base slightly deviates from circular. Thus, unlike the homogeneous flat surface, hydrophobic striped surface demonstrates anisotropic wetting properties, which depend on \( \phi_S \).

Below we summarize our data for receding and advancing contact angles. Taking into account the anisotropy of wetting we measure contact angles in two eigendirections.
3.2.1 Receding Contact Angles. Let us first consider the receding contact angle. Note that it was measured only for patterns with $\phi_S < 0.7$ since experiment in a high $\phi_S$ regime was affected by the Cassie-to-Wenzel transition. In Fig. 3, we have plotted the experimental results for the longitudinal and transverse receding contact angle as a function of $\phi_S$. A first striking and a counterintuitive result is that it is the same in the longitudinal and transverse direction, i.e., practically isotropic. Note, however, that observations of an isotropic receding angle for a drop on striped surfaces have been reported before. There have been also similar observations made for anisotropic arrays of pillars. As expected, the cosine of the receding contact angle is close to that for a smooth surface in the dilute regime and increases for denser patterns. However, an this is the most important result emerging from this plot, the increase is nonlinear in contrast to predictions of classical Eq. (1).

To understand this isotropic behavior we explored the local motion of the contact line, and found it to be irregular. In other words, the contact line does not move smoothly, it sticks and slips. This is illustrated in Fig. 4 which shows a sequence of snapshots of the contact line near the edge of the drop. In the transverse direction, $x$, the line recedes in abrupt steps of the size $w + d$ and remains pinned for a period before next step. The pinned state of the contact line in transverse direction indicates, that in this situation the contact line slides in the longitudinal direction $y$. These features are qualitatively similar to described before for stripes in the Wenzel state, and is likely responsible for an observed isotropy of the receding angle. Fig. 5(a) and (b) show the shape of the contact line during receding in smaller scale. It is well seen that at gas areas the contact line is bent in the direction of motion (or of a force), and is always ahead the contact line at solid areas, being pinned by edges.

Now we propose a simple description to explain the non-linearity of the receding angle. The observations of the motion and shape of the receding contact line suggest arguments, based on the earlier model of hysteresis on a flat surface, which has been recently adapted for isotropic superhydrophobic textures. We first modify the Cassie equation, by substituting $\theta$ by $\theta_r$.

$$
\cos \theta_r = \phi_S \cos \theta - 1 + \phi_S,
$$

(2)

The physical idea underlying this relationship is to account for weak defects that lead to a hysteresis on a flat solid areas.

To take into account the strong defects at the borders of stripes we evaluate the elastic energy per unit length of contact line, $E$, similarly to suggested in prior work for an isotropic array of pillars.
\[ E = \frac{a}{\gamma} \frac{d}{2 w + d} \ln \left( \frac{w + d}{w} \right) = -\frac{a}{2} S \ln S. \]  

Here \( a \) is a parameter, which reflects the geometry of pinning centers and indicates how strongly the contact line is deformed. By adding this expression to Eq. (2) we finally get

\[ \cos \theta^* = \phi_S \cos \theta_0 - 1 + \phi_5 = -\frac{a}{2} S \ln S. \]  

We fitted the experimental data to Eq. (4) taking \( a \) as a fitting parameter, and the value of \( a = 2.2 \) was obtained from fitting. The theoretical curves are included in Fig. 3. A general conclusion from this plot is that the theoretical predictions are in good agreement with experimental results, confirming the validity of the approach, based on elastic distortion of the contact line, for an anisotropic striped surface. Note that the larger value of \( a = 3.8 \) has been obtained for pillars, which obviously reflects that in case of pillars the contact line is less deformed. We finally remark that previous work reported the low \( \phi_5 \) regime and ignored the presence of weak defects at the solid area, i.e. used \( \theta \) instead of \( \theta_0 \) in Eq. (4). We have therefore tried to make a similar analysis, but were unable to provide a reasonable fit to the data for the whole range of \( \phi_5 \). This clearly shows the importance of weak defects on smooth solid sectors in determining the behavior of receding contact angles on patterned surfaces.

Let us now turn to the advancing contact angle.

### 3.2.2 Advancing contact angles

The experimental results for two eigendirections are shown in Fig. 5. The main conclusion from this plot is that the advancing angle is strongly anisotropic, except as in a very dilute regime. For the longitudinal direction the cosine of the advancing angle depends linearly on \( \phi_5 \). The data obtained for a transverse direction generally show smaller \( \cos \theta^*_a \), which is maximized by stripes with \( \phi \simeq 0.5 \).

The data for a longitudinal angle are well fitted by straight line, but deviate from the Cassie predictions, Eq. (1). Therefore, we try to generalize the above ideas that led to Eq. (4) to predict

\[ \cos \theta^*_a = \phi_S \cos \theta_0 - 1 + \phi_5 \]  

Theoretical curves are included in Fig. 6 and we conclude that they are in good agreement with experimental results. This suggests that the advancing longitudinal angle is hindered or restricted by weak defects, and that the contact line is not pinned at the edges of stripes.

Monitoring of the shape of the contact line during the longitudinal advancing shows (see Fig. 5(c) and (d)) that the solid part of the contact line moves ahead its gas sector, which is indeed not pinned. A conclusion emerging from this observation is that in contrast to receding (sliding) regime, the advancing of the drop represents rather its smooth rolling motion, which immediately explains Eq. (5). Indeed, by assuming the rolling of the drop, one can speculate that a precursor contact line on solid areas, which is likely formed since their wetting by a liquid is more preferable than that of the gas parts, determines the longitudinal advancing angle.

The transverse advancing of the contact line represents a stick-slip motion due to presence of strong defects (borders of gas/solid areas) in this direction. An explanation for smaller transverse angle can be obtained if we invoke additional energy due to these defects. The contact line of length \( dy \) pins as we move the liquid, by applying a force. The line meets \( \phi_5 \) defects for a displacement \( dx \), or \( \phi_5 dx \) defects per unit length. Passing each of them, an energy \( dE \) is stored and then released in the liquid as the line depins. We now make a simple suggestion that depinning happens when adhesion on the solid area \( \phi_S \gamma (1 + \cos \theta_0) dy \) is equal to applied force, which immediately leads to
Contact angle hysteresis $\Delta \cos \theta^*$ for different solid liquid fractions. Squares are experimental data for transverse direction, circles — for longitudinal direction. Solid and dashed curves show theoretical predictions.

Inclusion of this term to Eq. (5) gives

$$ \frac{E}{\gamma} = \phi_S^2 (1 + \cos \theta_a) $$

(6)

We emphasize that this is merely a simple-minded approach which we will use in an attempt to fit experimental data. In particular, we should like to note that it does not provide a correct asymptotics at $\phi_S \simeq 1$. However, the predictions of Eq. (7) included in Fig. 6 are in quantitative agreement with experiment, proving that our tentative model is physically correct in a very large range of $\phi_S$.

3.2.3 Contact angle hysteresis. Finally, we consider in this paragraph the contact angle hysteresis, $\Delta \cos \theta^* = \cos \theta^* - \cos \theta^*_a$. We have plotted in Fig. 7 experimental and theoretical $\Delta \cos \theta^*$ as a function of $\phi_S$. This plot illustrates immediately that hysteresis is quite large and generally strongly anisotropic, but it becomes isotropic for $\phi_S \leq 0.2$. We emphasize that altogether the experimental results are in surprisingly good quantitative agreement the predictions of our simple models.

4 Conclusions

We have measured receding and advancing contact angles of a droplet on the striped Cassie surfaces with a different fraction of solid areas. Our experiment demonstrated that the receding angle is isotropic, and increases nonlinearly with $\phi_S$. The receding contact line shows irregular sliding motion. Results were found to be in excellent agreement with predictions of a simple theoretical model, which takes into account the role of both weak defects at smooth solid areas and of strong defects at the borders of stripes. The later contribution scales as $\phi_S \ln \phi_S$. The advancing of the drop represents a rolling motion, and the advancing contact angle was found to be generally anisotropic. The cosine of the longitudinal advancing angle increases linearly on $\phi_S$. The data are well fitted by our simple model, which reflects that the the motion of the contact line at the smooth solid areas is hindered by weak defects. The cosine of the transverse advancing angle is much smaller and has a maximum at $\phi_S \simeq 0.5$. An explanation of this different from the longitudinal angle can be obtained if we invoke an additional energy due to strong defects in this direction which is shown to be proportional to $\phi_S^2$. This was explained by invoking an additional energy due to strong defects, which scales as $\phi_S^2$. Finally, we evaluated the contact angle hysteresis, which was found to be quite large and generally anisotropic. However it becomes practically isotropic in the dilute regime, $\phi_S \leq 0.2$.

Altogether, our study shows that both weak defects at the solid areas and strong defects at the borders of stripes are crucial in determining the contact angle hysteresis. Globally the experimental results are in agreement with the theoretical estimates, confirming that the our simple approach captures the physical mechanisms at play; although our models may be seen as oversimplified, theoretical results were shown to be predictive over a broad range of solid surface fraction.

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