Ratchet-Like Anisotropic Slip Angle Behavior on Printed Superhydrophobic Surfaces

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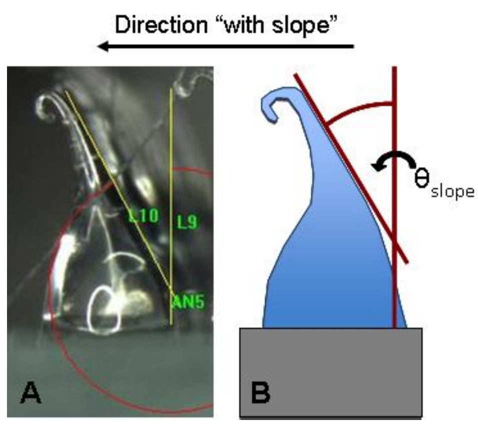
Supplementary Materials

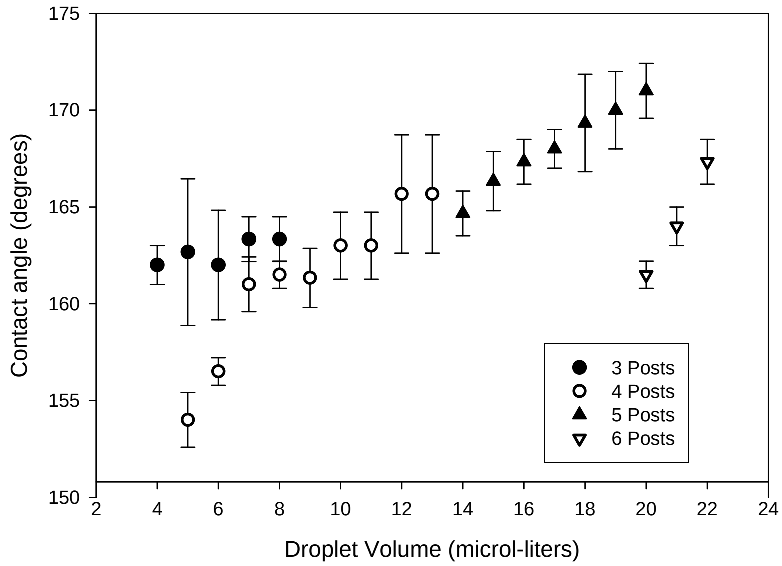
I. Slope and length measurements:

Images of the superhydrophobic surfaces were captured digitally using a microscope (Nikon SMZ1500) and Image-Pro software. The slopes of the posts and dimensions such as the width of the droplet or the height of the posts were measured manually using Image-Pro software. Slope values were measured as shown in **SF1**.; the average of 10 or more randomly selected posts is reported.



Supp. Figure 1: A: Post slope determination from stereomicroscope image; B: cartoon illustrating post slope measurement. Note slip direction labeled "with slope".

II. Static contact angles on superhydrophobic surfaces with straight posts: Effect of droplet

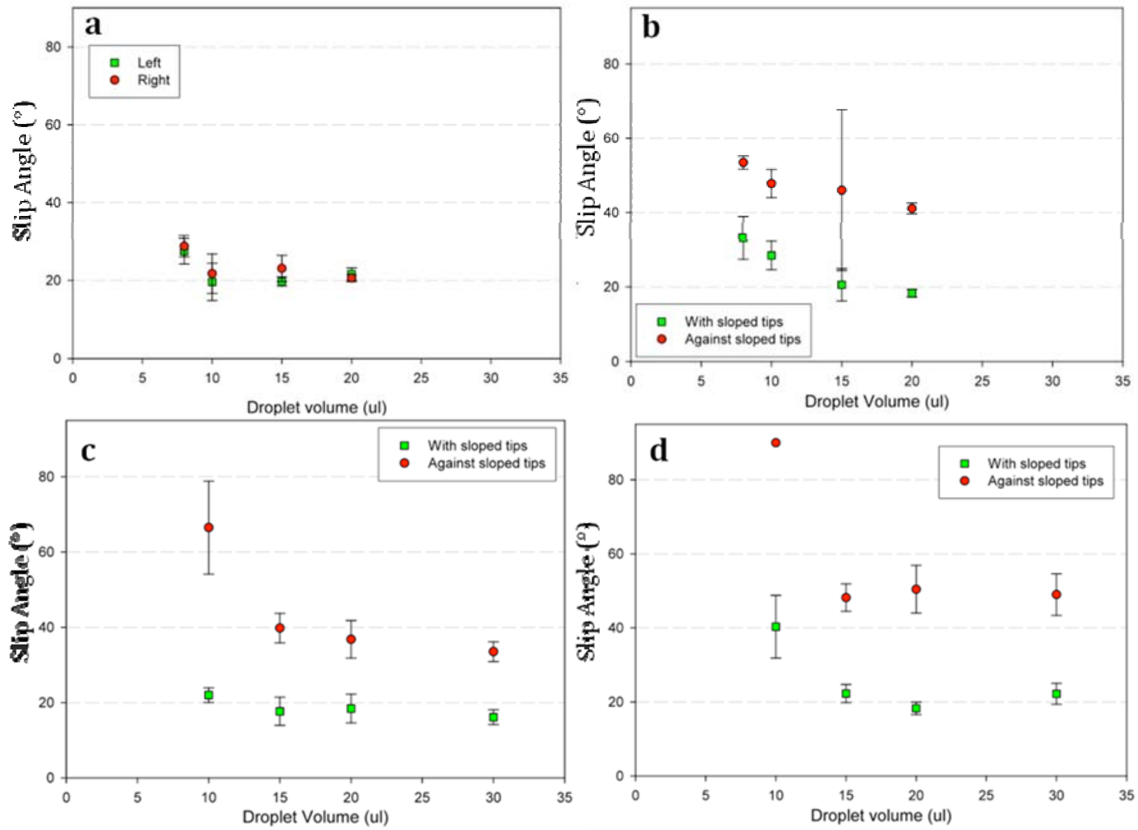


Supp. Figure 2. Effect of droplet volume on the apparent static contact angle on DAP-00-8 (straight posts). Graph showing dependence of contact angle on post coverage.

The effect of droplet volume on the apparent static CA observed on a PDMS surface with straight posts is shown in **Figure SF2**. As droplet volume increases from 3 to 22 μl, the apparent static CA also shows an overall increase from 154 to 170^{o}. The dependence of the contact angle on the droplet volume can be understood in terms of the number of posts which support the droplet. Compared to most studies of superhydrophobic surfaces, the post pitch of these surfaces is comparable in scale to the diameter of the droplets. This is especially true for small, < 10 μl droplets; for example a 5 μl spherical water droplet would have a diameter of 2.1mm which is approximately 4 times the post pitch. For the smallest volume of water tested, the drop is supported by a span of 3 posts in the lateral direction. As the volume increases, the drop can be supported by either a span of 3 or 4 posts depending upon how the drop is placed on the surface and how deeply into the surface the droplet penetrates. When a 5μl droplet spans 4 posts, its apparent contact angle (154°) is significantly lower than when the same volume drop spans 3 posts (163°). By contacting fewer posts, the droplet perimeter extends beyond the post edge thus exhibiting a higher apparent CA. When the drop contacts more posts, the drop perimeter is pinned by the outermost posts and exhibits a lower apparent CA. As the drop volume increases to 8 μl the difference in contact angle between the two positions decreases, mainly because the CA of the drop which spans 4 posts continues to increase. Between 8 and 14 μl, the droplet is only stable when spanning 4 posts. Another bi-stable state was observed for 20 μl volumes where the drop could be supported by spans of either 5 or 6 posts. Again, by spanning a larger number of posts, a reduction in apparent CA is observed for droplets of the same volume. These observations indicate that interactions between the droplet and surface features can have a significant effect on the behavior of droplets on superhydrophobic surfaces. This is especially true when the liquid-solid contact line is closely aligned to the droplet surface (i.e. 20 μl drop spanning 6 posts) as opposed to when the contact line is separated from the droplet surface (i.e. 20 μl drop spanning 5 posts).

III. <u>Effect of Droplet Volume on Slip Angle.</u>

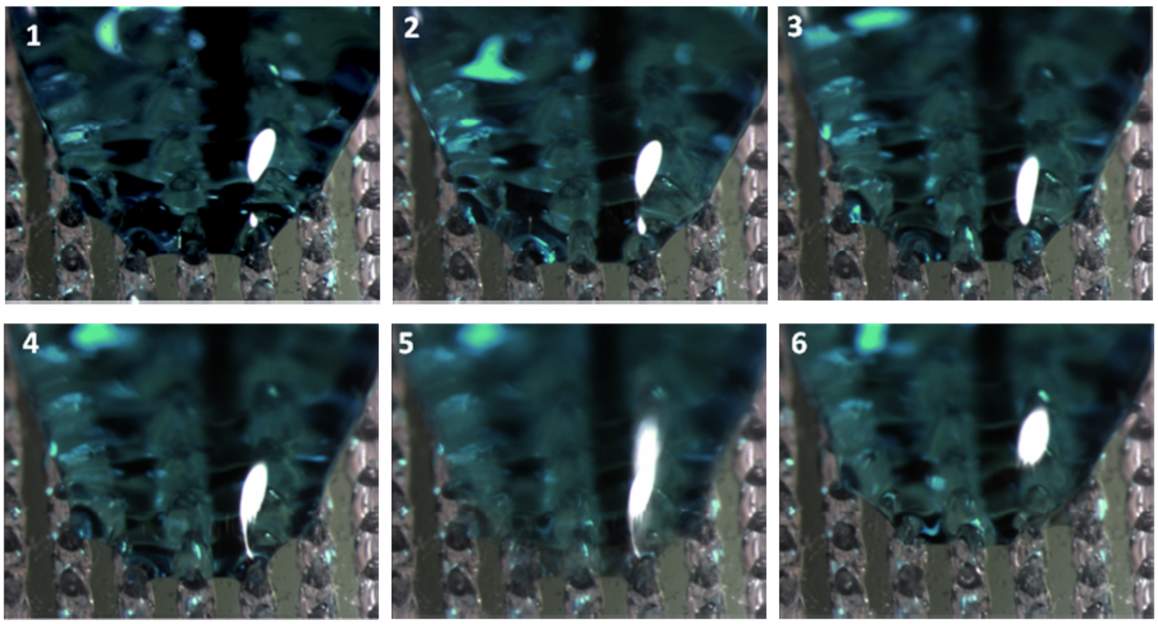
Supp. Figure 3. Slip angle dependence direction of inclination and droplet volume for (a) DAP 00-9; (b)



DAP 35-20; (c) DAP 44-20; and (d) DAP 50-20.

Plots of slip angle vs droplet volume are shown in SF3 for samples prepared from straight posts as well as posts with slopes of 35, 44 and 50 degrees. Data from these plots, along with those shown in Figure 3 in the text were used to construct Figure 5 in the main text. We observe two general trends: the mean slip angle decreases with larger droplets and the variance with respect to slip angle measurements decreases as larger droplets are used. Slip angle and slip angle variance both increase with decreasing droplet volume because the droplet diameter begins to approach the post pitch. As a result, droplet behavior can be more strongly influenced by the particular geometry of an individual post. In addition, the effect of liquid-surface interactions are relatively more important than gravitational forces. Indeed, the largest slip angles are observed for 10μl drops on the surfaces with the most highly sloped posts (SF 3d).

IV. Images of droplets moving against the post slope direction.

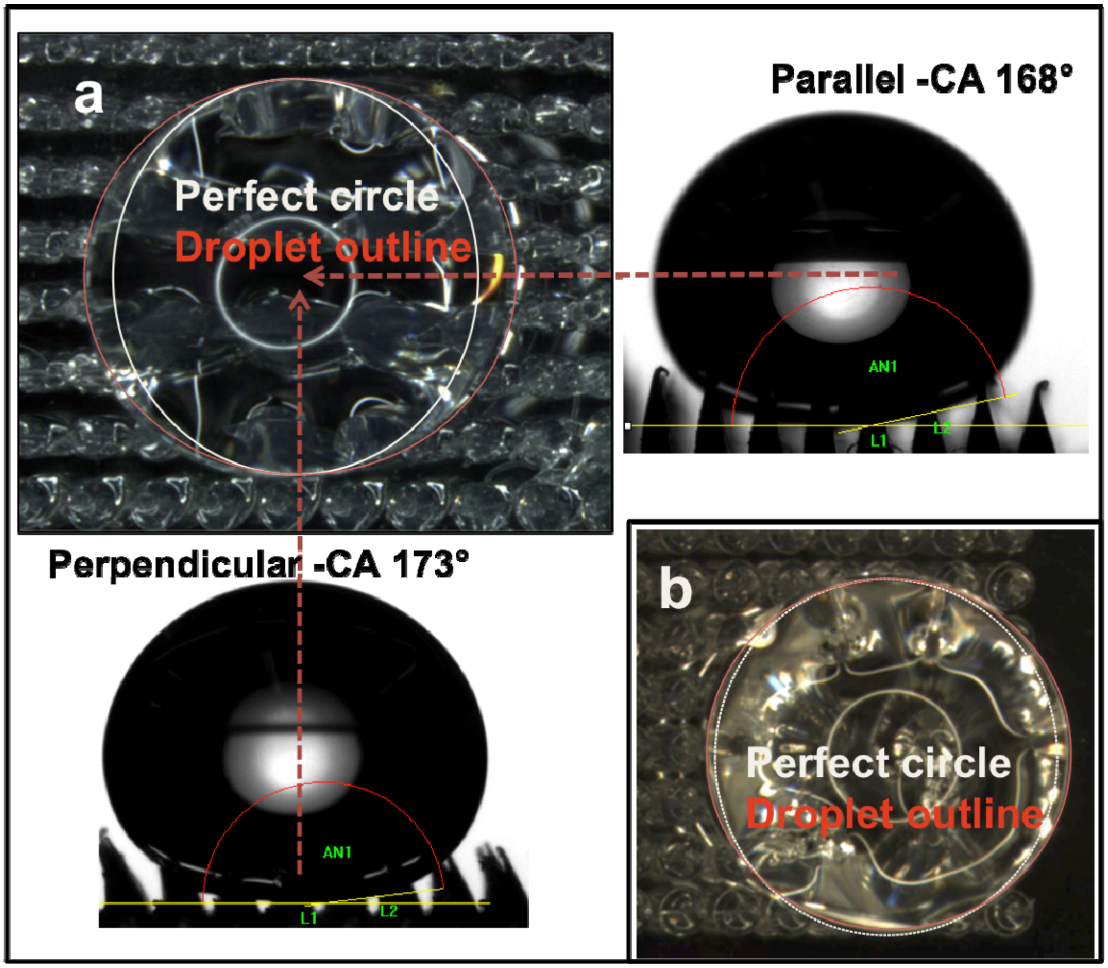


Supp. Figure 4. A 20ul droplet moving away from the camera (images SF4.1-6) traversing against the direction of the posts' slope.

The trailing end of a water droplet (containing blue dye to enhance contrast) is shown in Fig SF4 as it disengages from the posts during a tilting stage experiment. During the early stage of the experiment (SF4.1), the trailing edge of the drop penetrates into the trailing line of 3 posts. Each post is surrounded by fluid and the TCL is composed of a circle on each post. As the stage is tilted the leading edge of the droplet moves away from camera, but the trailing edge remains pinned. The TCL continues to increase in length in images SF4.2 – SF4.5 changing shape from a circle (approximately parallel to the surface) to an ellipse (approximately parallel to the post slope). When the trailing posts penetrate into the droplet, the reflection in the droplet is dark (SF4.1), but when the droplet is only contacting the back of the post, the reflection is more transparent (SF4.2-3). At a sufficiently high angle, the droplet disengages completely from this row of posts and becomes pinned along the next row as shown in figure SF4.6. Only a small incremental increase in tilt angle is required for the droplet to move completely off the surface.

V. Effect of post slope orientation on static contact angle and droplet shape

We observed the behavior of a 20ul droplet on a 'ratchet-like' surface (DAP 21-20) and an isotropic surface (DAP-00) using bright field microscopy. We recorded images of the droplet when viewed from the side, either parallel or perpendicular to the sloped posts (**SF 5a**). These images were analyzed to measure contact angle. A small degree of contact angle anisotropy was observed as a function of the direction of observation only for the sample with sloped posts. Contact angle when viewed perpendicular to the post slope was 173°, vs. 168° when viewed parallel. In addition, an aerial image was taken to observe droplet shape as a function of post slope (**SF5 a & b**). We observed some droplet elongation in the aerial image for a droplet on a surface with 21^{o} post slope, but no droplet anisotropy on the sample with straight posts.



Supp. Figure 5. Droplet elongation on (a) DAP-21-20, depicting slight droplet elongation with contact angle measurements measured perpendicular and parallel to the sloped posts and; (b) on DAP-00, depicting good agreement with perfectly circular prediction. For clarity, pink lines outline the droplet perimeter whereas white lines illustrate perfect circles.

VI. Video #1- 20µl droplet moving in the easy direction on DAP 21-20

VII. Video #2 - 20µl droplet moving in the hard direction on DAP 21-20

VIII. Video #3 -20µl droplet moving to the left on DAP 00

IX. Video #4 -20µl droplet moving to the right on DAP 00