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Mapping microscale wetting variations on biological and synthetic water-repellent surfaces

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Droplets slip and bounce on superhydrophobic surfaces, enabling remarkable functions in biology and technology. These surfaces often contain microscopic irregularities in surface texture and chemical composition, which may affect or even govern macroscopic wetting phenomena. However, effective ways to quantify and map microscopic variations of wettability are still missing, because existing contact angle and force-based methods lack sensitivity and spatial resolution. Here, we introduce wetting maps that visualize local variations in wetting through droplet adhesion forces, which correlate with wettability. We develop scanning droplet adhesion microscopy, a technique to obtain wetting maps with spatial resolution down to 10 µm and three orders of magnitude better force sensitivity than current tensiometers. The microscope allows characterization of challenging non-flat surfaces, like the butterfly wing, previously difficult to characterize by contact angle method due to obscured view. Furthermore, the technique reveals wetting heterogeneity of micropillared model surfaces previously assumed to be uniform.
Superhydrophobic surfaces enable exceptional functions in biology and technology\textsuperscript{1–5}. Understanding how water repellency emerges from the microscale and nanoscale features\textsuperscript{6–8} is critical to advance the development of these surfaces\textsuperscript{9–12}. Biological superhydrophobic surfaces often contain irregular surface texture and details\textsuperscript{9, 10}, such as creases or veins, and synthetic surfaces are prone to fabrication defects. Such irregularities in surface texture and chemical composition lead to spot-to-spot variation of wetting properties\textsuperscript{9, 12}, which may affect or even govern droplet mobility\textsuperscript{13, 14}, icing\textsuperscript{15}, and condensation\textsuperscript{16}. Even though these variations have been considered in theory\textsuperscript{1}, so far they have not been probed experimentally, partly because existing contact angle and force-based methods lack sensitivity and spatial resolution\textsuperscript{17–19}. The contact angle method, describing a surface by a single pair of apparent advancing and receding contact angle values, is still viewed as the gold standard in hydrophobic surface characterization. As the measurement is based on observing a moving contact line, it is inherently unsuitable for precise spatial mapping. Moreover, as an optical method, contact angle measurements become increasingly inaccurate for contact angles beyond 150°\textsuperscript{17, 18} due to resolution limit of the optical system, and often suffer from obscured view of the contact line on curvy surfaces\textsuperscript{9}. Wetting properties have also been characterized by droplet friction forces, i.e., resistance to lateral motion\textsuperscript{20–22} and by droplet adhesion forces, i.e., resistance to detaching a droplet in the normal direction\textsuperscript{8, 19, 23, 24}. It has been experimentally verified that snap-in (first droplet contact) and pull-off (droplet separation) adhesion forces on hydrophobic surfaces are related to, respectively, the advancing contact angle (θ\textsubscript{adv}) and the receding contact angle (θ\textsubscript{rec})\textsuperscript{19}. Smaller forces correspond to larger contact angles. However, current tensiometers are not sensitive enough to detect droplet adhesion forces below 1 µN. On the other hand, scanning probe microscopy techniques, e.g., atomic force microscopy (AFM), can have nN or even better force resolution, though so far have not been used to map spatial wetting variations. To study wetting in ambient air, the water droplet must be large enough so that evaporation during a single measurement becomes insignificant, and nN sensitive AFM cantilevers cannot support such large droplets in air. Droplet–surface interactions have therefore previously been measured by AFM not in ambient air but instead in liquid–liquid and bubble–liquid systems\textsuperscript{25}, or by using the AFM tip itself as the surface under study\textsuperscript{26–28}, hence greatly limiting the scope of AFM to study wetting of surfaces.

Here, we introduce scanning droplet adhesion microscopy, a technique for obtaining wetting maps of surfaces based on high-precision force measurements. The technique enables us to map in extraordinary detail the wetting forces, even on challenging, non-flat, biological surfaces. Since butterfly wings and their eyespots have sparked tremendous scientific interest\textsuperscript{26, 27}, we select...
the wing of the striped blue crow butterfly (Euploea mulciber) as a model surface. Wetting maps obtained on an eyespot of the wing show correlation between wetting and visual appearance. We also show that on micropillared model surfaces, the wetting forces can vary pillar-to-pillar.

Results

Measurement concept. The apparatus we built comprises a vertically mounted force sensor with a liquid droplet probe (e.g., water) and a multi-axis sample stage (Fig. 1a and Supplementary Fig. 1) for measuring normal forces point-by-point in a fully automated manner (Supplementary Movie 1). By scanning an eyespot area (Fig. 1b) on the striped blue crow butterfly wing (Fig. 1c), we obtain snap-in (Fig. 1d) and pull-off (Fig. 1e) force maps. Force measurement on a single point starts with moving up the sample surface to approach the droplet, followed by first contact (snap-in) with the droplet, then the sample surface moves down until it separates from the droplet (pull-off) (Fig. 1f). A typical force curve with nanonewton resolution, recorded at 100 Hz sampling rate, is shown in Fig. 1g. The droplet volume is filled to 1.5 µl before every measurement; the effect of evaporation is not significant as only ~1% of the volume evaporates during a typical single measurement lasting around 20 s.

Accuracy and repeatability. To verify accuracy and repeatability of the microscope, we measured snap-in and pull-off forces on single silicon pillars (Fig. 2a–c and Supplementary Fig. 2) of varying radius, one pillar at a time. For each radius, the measurement is carried out on ten different pillars, with ten repetitions on each pillar. The mean snap-in force for ten 10 µm radius pillars is 125.9 nN with pooled standard deviation of 6.6 nN (Fig. 2b), and the mean pull-off force is 4606.4 nN with pooled standard deviation of 5.3 nN (Fig. 2c). Analysis of variance indicates that pillar-to-pillar variation of snap-in force is six times larger than within-pillar variation and nine times larger in case of pull-off force. For the larger pillars, this difference is even clearer (Supplementary Table 1). We are thus capable of measuring tiny but significant differences in adhesion force from one pillar to another, likely caused by tiny structural variations on the pillar tops (see Fig. 2a). The 6.6 nN standard deviation in within-pillar measurements is predominantly attributed to sensor noise of the microscope (measured as 5 nN), verifying excellent repeatability of the method. We measured snap-in and pull-off forces for pillar radii between 10 and 400 µm. The results (Fig. 2d, e) show high consistency for each radius and agree well with numerical simulation. The simulation uses Young–Laplace equation and boundary conditions to solve the shape of the droplet, which can be used to compute the forces18. A detailed discussion on modelling and simulation can be found in Supplementary Note 1.

Wetting forces on superhydrophobic surfaces. We also compared snap-in and pull-off forces to optically measured contact angles for various hydrophobic and superhydrophobic surfaces. The results are shown in Supplementary Table 2 and Supplementary Figs. 3 and 4. The smallest measured snap-in force, 7.8 ± 1.9 nN, was obtained on Hydrobead-coated silicon wafer with optically measured contact angles $\theta_{adv}/\theta_{rec} = 169°/168°$. The smallest pull-off force, 218.5 ± 9.7 nN, was measured on a silicon
nanograin surface coated with fluoropolymer, where the optically measured contact angles were \( \theta_{adv}/\theta_{rec} = 175°/169° \). In contrast to a recent study, there seems to be no contact angle limit beyond which the snap-in or pull-off force becomes zero. Therefore, using force sensors with enhanced sensitivity should allow characterization of even higher contact angle superhydrophobic surfaces.

Micropillar arrays are common model superhydrophobic substrates\(^1\)-\(^3\), \(^28\), \(^29\), and water droplets have been imaged to advance and recede step-wise, respectively, by pinning and depinning from pillar to pillar\(^29\), \(^30\). Droplets rolling off such micropillar surfaces may oscillate due to the pinning and depinning steps\(^31\), \(^32\). Here we quantify, for the first time, the tiny forces during pinning and depinning in great detail (Fig. 3). While a water droplet advances, in total 16 pinning steps were detected with forces ranging from 20 to 60 nN. Eight depinning steps were detected during droplet receding, with forces ranging from hundreds of nN to more than 10 \( \mu \)N. The butterfly wing exhibits similar pinning/depinning steps (Supplementary Fig. 6). The number of pinning steps in Fig. 3 is much higher than the number of depinning steps, because depinning from multiple pillars are combined into larger steps. It should be noted that the number of depinning steps, because depinning from multiple pillars (Fig. 1g), except for the final depinning step. It should also be noted that during a long measurement such as the one presented in Fig. 3, the volume loss due to evaporation of the droplet may affect the magnitude of the pinning and depinning steps (see Supplementary Note 1 for further theoretical discussion on the volume dependency).

**Wetting force mapping.** To challenge the sensitivity of the scanning droplet adhesion microscope, we measured snap-in and pull-off forces on a superhydrophobic-superhydrophobic patterned surface consisting of parallel stripes (\( \theta_{adv}/\theta_{rec} = 175°/174° \)) on background (\( \theta_{adv}/\theta_{rec} = 173°/170° \)) (Fig. 4a, b). \( \theta_{adv} \) and \( \theta_{rec} \) are all beyond 170°, and thus difficult to determine accurately with contact angle measurement\(^18\). We performed a line scan across the stripes, recording snap-in and pull-off forces every 75 \( \mu \)m. Whereas the snap-in force is too small to be detected for this surface, the pull-off force shows a clear difference between the stripes and the background (Fig. 4c).

While contact angle measurements of biological surfaces are often impossible due to an obscured baseline (Supplementary Fig. 7), we constructed detailed wetting force maps of striped blue crow butterfly wing. We probed an area of 2.2 \( \times \) 3.2 mm covering one of the eyespots on the wing, with 200 \( \mu \)m spacing between measurement points, resulting in snap-in and pull-off force maps (Fig. 1b, d, e). We probed furthermore a smaller area (400 \( \times \) 50 \( \mu \)m) of the eyespot in greater detail, with 10 \( \mu \)m spacing between measurement points (Fig. 4d, e). The corresponding snap-in and pull-off force maps are shown in Fig. 4f, together with an optical micrograph of the area. The wetting force maps reveal variations...
in snap-in and pull-off force when moving across the edge of the eyespot. The wetting variations correspond to variations in structural colour, and are thus due to subtle structural differences of the wing surface (scanning electron microscopy (SEM) micrographs of the probed area in Fig. 4e).

Discussion

Microscale spatial heterogeneity is generally acknowledged as a major source of contact angle hysteresis and droplet friction, though how wetting on model surfaces and especially on irregular surfaces is related to the microscopic surface features is still not completely understood. Scanning droplet adhesion microscopy provides the sensitivity and the resolution that is critical to create wetting maps, a concept for hydrophobic surface characterization to study this relation in both biology and materials science. Using a sensor probe with increased sensitivity in pN range, measurement could become possible of superhydrophobic surfaces exhibiting even lower adhesion forces. Combination of scanning droplet adhesion microscopy with optical microscopy techniques would open the way to multimodal characterization of pinning and depinning events towards comprehensive understanding of wetting. Whereas this study focused on water, arguably the most understood how wetting on model surfaces and especially on irregular surfaces is related to the microscopic surface features is still not completely understood. Scanning droplet adhesion microscopy provides the sensitivity and the resolution that is critical to create wetting maps, a concept for hydrophobic surface characterization to study this relation in both biology and materials science. Using a sensor probe with increased sensitivity in pN range, measurement could become possible of superhydrophobic surfaces exhibiting even lower adhesion forces. Combination of scanning droplet adhesion microscopy with optical microscopy techniques would open the way to multimodal characterization of pinning and depinning events towards comprehensive understanding of wetting. Whereas this study focused on water, arguably the most well-studied wetting liquid, the scanning droplet adhesion microscopy could in principle be extended to study wetting of other liquids, including organic liquids on oleophobic surfaces.

Methods

Silicon micropillars. Silicon micropillars were fabricated by deep reactive ion etching. First, a plasma-enhanced chemical vapour deposited (PECVD) oxide (Oxford PlasmaLab 80+, 300 °C, 8.5 sccm SiH4, 1000 mTorr, 20 W) was deposited on a 4-inch silicon wafer (<100>, p-type doping 1–20 ohm-cm). The thickness of the oxide was 750 nm (12 min deposition time). The oxide was patterned by UV lithography and reactive ion etching (Oxford PlasmaLab 80+, 25 sccm Ar, 25 sccm CHF3, 200 W, 30 mTorr, 21 min etching time). The pillar radius was 5 μm. The silicon pillars were then etched by cryogenic deep reactive ion etching (Oxford PlasmaLab System 100, –110 °C, 40 sccm SF6, 6 sccm O2, 1050 W ICP power, 3 W platen power, 8 mTorr). The etch depth was 20 μm. The oxide mask was then removed by hydrofluoric acid. Finally, a thin hydrophobic fluoropolymer coating was deposited on top of the pillars by PECVD (Oxford PlasmaLab 80+, 100 sccm CHF3, 50 W, 30 mTorr, 5 min).

Silicon undercut micropillars. Silicon undercut micropillars with a silicon dioxide top were fabricated for the accuracy and repeatability experiments. Undercut pillars with radius 10 μm - 50 μm were fabricated with the following process: a thermally oxidized (oxide thickness 1.2 μm) silicon wafer was used as a substrate. The oxide was patterned by UV lithography and reactive ion etching (Oxford PlasmaLab 80+, 25 sccm Ar, 25 sccm CHF3, 200 W, 30 mTorr, 38 min). The samples were then etched anisotropically by cryogenic deep reactive ion etching (Oxford PlasmaLab System 100, –110 °C, 40 sccm SF6, 6 sccm O2, 1050 W ICP power, 3 W platen power, 8 mTorr, 10 min) to the depth of 22 μm. Finally, an isotropic silicon etching step was performed to create the undercut (Oxford PlasmaLab 80+, 100 sccm SF6, 100 W, 100 mTorr, 18 min). Undercut pillars with radius 75 μm - 200 μm were fabricated by a process reported before.

Silicon nangrass coated with fluoropolymer. The substrate was a 4-inch silicon wafer (<100>, p-type doping 1–20 ohm-cm). Silicon nangrass was created by maskless cryogenic deep reactive ion etching (the so-called black silicon process) (Oxford PlasmaLab System 100, –110 °C, 40 sccm SF6, 18 sccm O2, 1000 W ICP power, 6 W platen power, 10 mTorr, 7 min etching time). The nangrass was made superhydrophobic by a PECVD deposition of a fluoropolymer thin film (Oxford PlasmaLab 80+, 100 sccm CHF3, 50 W, 30 mTorr, 5 min deposition time).

Fluoropolymer on Si wafer. Fluoropolymer coated silicon surface was fabricated by the same PECVD process as with the fluoropolymer coated silicon nangrass. The substrate was an unprocessed 4 inch silicon wafer (<100>, p-type doping 1–20 ohm-cm).

Silicon nangrass patterned surface for line scan. To pattern the nangrass, a 500 nm thick silicon dioxide film was deposited (Oxford PlasmaLab 80+, 300 °C,
Copper (II) hydroxide nanowires were prepared by injecting methyltrichlorosilane (99%, Aldrich) through a silicone septum until the relative humidity reached ca. 30% followed by sealing the reactor and flushing with nitrogen. Glucose on Si wafer. Test-grade silicon (100) wafers were cleaned with an alkaline solution (Deconex 11 Universal, VWR), rinsed thoroughly with Milli-Q water, and dried under nitrogen flow. Afterwards, commercial Glucose Standard was applied on Si wafer and dried for 10 min.

Silicone nanofilaments on Si wafer. Surface was prepared as described in the literature. Similarly, silicon (100) wafer was cleaned by ultrasonication in alkaline solution (Deconex 11 Universal, VWR), rinsed thoroughly with Milli-Q water, and dried under nitrogen flow. Silicon nanofilaments were grown onto the surface using a parylene deposition system (SCS Labcoter 2 PDS M-122.2DD, 0.15 µm thick layer of parylene-C thickness.

Copper (II) hydroxide nanowires. Copper (II) hydroxide nanowires were prepared as described in literature. Similarly, (NH₄)₂S₂O₈ for 20 min at room temperature and washed afterwards with Milli-Q water and dried under nitrogen flow. Chemical modification was performed by immersing substrate into 5 mM lauric acid (ethanol solution) for 20 min, followed by washing with Milli-Q water and drying under nitrogen flow. Subsequently, the substrate was immersed into a mixed solution of 2.5 M NaOH and 0.13 M (NH₄)₂S₂O₈ for 20 min at room temperature and washed afterwards with Milli-Q water and dried under nitrogen flow. Chemical modification was performed by immersing substrate into 5 mM lauric acid (ethanol solution) for 20 min, followed by rinsing with Milli-Q water and drying under ambient conditions for a few minutes.

Silicon nanoglass coated with parylene-C. Parylene-C coated silicon nanoglass was fabricated as described in literature. Similarly, cryogenic deep reactive ion etching (Oxford Plasmalab System 100, −110 °C, 40 sccm SF₆, 18 sccm O₂, 100 W ICP power, 6 W platen power, 10 mTorr, 7 min etching time). The stage keeps moving up either for a fixed time delay or the fixed force limit was used to minimize variation between measurements. The maximum force depends on the distance moved up during the time delay, or is directly the preset force limit. The stage is then retracted down to 10 µm s⁻¹ until the droplet separates from the surface (pull-off), i.e., a step up is detected in the force. The volume of water droplet used in the measurements is 1.5 µl. After each measurement, the droplet is refilled up to 1.5 µl using the microdispenser. The above-mentioned low approach speeds (2 µm s⁻¹ or 5 µm s⁻¹), and moderate retraction speed (10 µm s⁻¹) were chosen to avoid dynamic effects while keeping the measurement duration reasonable.

Approach/retraction speed characterization. The effect of approach speed on snap-in force, and the effect of retraction speed on pull-off force, was characterized for five different speeds. Measurements were carried out on a fluoropolymer-coated silicon nanoglass surface (slightly less superhydrophobic than the one listed in Supplementary Table 2). A force vs. speed comparison is shown in Supplementary Fig. 8.

Automated scanning. The measurements were fully automated for accuracy and repeatability testing on micropillars, line scanning, and area scanning of wetting maps. The force readout of the probe is used as feedback to detect contact when probing a surface, and to monitor the droplet volume when refilling the droplet after every measurement. Measurement locations are generated beforehand, but after that hundreds of measurements can be carried out automatically without human intervention.

Data analysis. Snap-in and pull-off events are extracted from individual force recordings using a step detection algorithm based on Student’s t-test metric:

\[ t = \frac{\mu_1 - \mu_2}{\sqrt{\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}}} \] (1)

where, for each force value in the signal, \( \mu \) is the mean of the \( N \) previous values, \( \sigma \) is the mean of the \( N \) subsequent values, \( \sigma' \) is the variance of the \( N \) previous values, and \( \sigma'' \) is the variance of the \( N \) subsequent values. The threshold \( t \) is adjusted based on the magnitude of measured forces and the sensor noise. In practice, \( t \) varied from 20 to 80. The value of \( N \) depends on the force data sampling rate and was set to 8 for the 100 Hz used in the measurements. After detection of snap-in event in the force recording (time of snap-in, polynomial curves are fitted to the preceding and succeeding values, so that magnitude of the step (snap-in force) can be extracted from the difference between the fitted curves at the time of the event. Pull-off force is determined by the difference in the force after the detected pull-off event (time of pull-off) and the minimum force in the recording.

Numerical simulation. For detailed discussion on modelling and simulation, see Supplementary Note 1.
Contact angle measurements. Contact angles were measured using sessile drop method by Attension Theta optical tensiometer with automated liquid pumping system. Advancing contact angles were measured by placing a 0.2 µl droplet on the surface and increasing its volume to 40 µl, at a rate of 0.10 µl s⁻¹. Receding contact angles were measured by decreasing droplet volume at a rate of 0.10 µl s⁻¹, starting with a drop volume of 40 µl.

Data availability. The data that support the findings of this study are available from the corresponding author on reasonable request.

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Author contributions
R.H.A. conceived the research. Q.Z. designed the apparatus. Q.Z., R.H.A.R., V.L. and M.V. designed the sensor probe. V.L. and M.V. constructed the apparatus. V.L. and Q.Z. designed the measurement algorithms. R.H.A.R., Q.Z., M.V., V.L. and V.J. designed the experiments and analysed the results. M.V., V.L. and M.J.H. performed experiments. V.J. fabricated the sensor probe disc and microstructured Si samples. V.S. carried out modelling and numerical simulations. All authors discussed and co-wrote the paper.

Additional information
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Competing interests: The authors have filed a patent application based on the content of the manuscript.

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