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Toward vanishing droplet friction on repellent surfaces

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Superhydrophobic surfaces are often seen as frictionless materials, on which water is highly mobile. Understanding the nature of friction for such water-repellent systems is central to further minimize resistance to motion and energy loss in applications. For slowly moving drops, contact-line friction has been generally considered dominant on slippery superhydrophobic surfaces. Here, we show that this general rule applies only at very low speed. Using a micropipette force sensor in an oscillating mode, we measure the friction of water drops approaching or even equaling zero contact-line friction. We evidence that dissipation then mainly stems from the viscous shearing of the air film (plasmen) trapped under the liquid. Because this force is velocity dependent, it can become a serious drag on surfaces that look highly slippery from quasi-static tests. The plasmen thickness is found to be the key parameter that enables the control of this special friction, which is useful information for designing the next generation of ultraslippery water-repellent coatings.

Significance
A small raindrop will easily slide off the surface of a lotus leaf or the feathers of a bird. These natural systems are beautiful examples of superhydrophobic surfaces. Today, there is a strong focus on mimicking this natural surface design to manufacture artificial liquid-repellent substrates for a wide range of applications, such as self-cleaning and nonwetting materials. The physics describing how water drops move on these surfaces has been studied extensively to find even better surface designs. Here, we developed a technique to measure the tiny friction of drops moving on extremely slippery superhydrophobic surfaces. We found an important plasmen friction force that needs to be considered when designing the next generation of ultraslippery water-repellent coatings.
important step to understand the high mobility of drops on repellent materials (1, 8, 11, 22, 23).

In this paper, we probe this system in depth, which we achieve by developing an oscillating MFS technique. This provides a direct measurement of the friction force and damping coefficient of drops on repellent surfaces in two complementary cases, either with a strictly zero contact-line friction or on slippery black silicon. In the first case, we consider a carbonated water drop levitating \( (F_\mu = 0) \) on a transparent superhydrophobic material. In the second case, we study water drops moving on black silicon with various texture heights, yet with constant contact angles and hysteresis, which eventually confirms the existence of a previously disregarded friction for water drops moving on repellent materials. We finally introduce a sample design usable in the future to minimize this source of resistance.

**Results**

**Friction Forces.** In addition to contact-line friction, drop motion can be influenced by electrostatic forces \((11)\), aerodynamic resistance \((8)\), and viscous resistance inside the drop \((3, 4, 8)\). The two first effects should be negligible in our case. First, we did not detect any sign of electrostatic forces in our MFS measurements, with no difference in the forces as a function of scanning distance or after changing the drop for a new one. Second, it is known that aerodynamic friction is only relevant when the drop speed is a few tens of cm/s, far above the range explored in this study \((8)\). Denoting \( \eta_\text{a} \) and \( \rho_\text{a} \) as the air viscosity and density, viscous and inertial frictions in air respectively scale as \( \eta_\text{a} V R^2 \) and \( \rho_\text{a} V^2 R^2 \), both on the order of 0.1 nN for \( V = 1 \) cm/s, far below the frictions reported in Fig. 1C. A more subtle air friction takes place in the wedge of air present around the drop. Following Scriven's analysis \((24, 25)\) and denoting \( \varepsilon = \pi - \theta \) as the wedge angle (Fig. 1A), we expect this friction to scale as

\[
\eta_\text{a} V / \varepsilon \ln(R/H)
\]

where the logarithmic factor accounts for the singular character of the friction in the wedge, but also from the fact that air can slip on the air trapped in the texture with height \( H \). This force is typically around 1 nN, ten times larger than the viscous friction in air, but small compared to our data. In addition, it can be tested in our experiment, in particular as a function of the contact area radius \( l \), to which it is expected to be proportional. As emphasized by Mahadevan and Pomeau \((8)\), a nonwetting contact results from a balance between weight and surface tension, which yields \( l \sim R^2/l_c \), where \( l_c = (\gamma/\rho p)^{1/2} \) is the capillary length \((2.7 \text{ mm for water})\). All drops in this study will be smaller than the capillary length, that is, rounded by surface tension rather than flattened by gravity—but they will keep a gravity-induced contact \( l < R \), a crucial point for understanding their friction.

The viscous friction in the drop is also natural to consider \((3, 4, 8)\). At high liquid viscosity \( \eta_\text{l} \), we expect the viscous friction to scale at most as \( (\eta_\text{l} V / \rho V^2 R^2) \), that is, \( \eta_\text{l} V^2 R^2 / \rho V^2 R^2 \), after using the Mahadevan–Pomeau law of contact \((3, 4, 8)\). For water \((\rho = 1 \text{ mPa.s})\), this force is expected to be on the order of 1 nN, again significantly smaller than the force of about 10 nN measured in the velocity-dependent regime in Fig. 1C. This law, however, can be questioned for a liquid with low viscosity such as water. Then, dissipation might rather occur in the viscous boundary layer localized in the contact zone. With a thickness \( \delta \) scaling as \( (\eta_\text{l} V / \rho)^{1/2} \), we find a force \( \eta_\text{l} V^2 R^2 / \rho V^2 R^2 \), whose dependency remains in \( V^2 \) and magnitude of order 1 nN. Hence, we conclude that the viscous friction in the drop is negligible compared to the observed one.

After eliminating these canonical sources of dynamic friction, we finally consider a force specific to repellent materials, arising from the viscous dissipation in the plastron of air trapped within the microtexture or present below drops when they levitate above their substrate. Here, the term ’plastron’ specifically refers to the air layer trapped within the microstructure of a superhydrophobic coating. In contrast to other air or gas films present in the levitation \((2, 26–30)\) or bouncing \((31)\) dynamics of drops, the plastron of superhydrophobic substrates remains stable for a long time also for stationary drops or submerged surfaces \((32)\). The plastron is thus highly important to a broad range of wetting phenomena on superhydrophobic materials, including drop bouncing and splashing, but also steady drop sliding and rolling motion. Slippery surfaces have a minimized contact with drops, and they provide an ultralow contact angle hysteresis so that we consider that water can slip on the plastron. This generates velocity gradients on the order of \( V/H \) inside the plastron, assuming that the viscous boundary layer in air has invaded the whole texture, which it does at micrometric scales. The corresponding plastron friction thus scales as \( (\eta_\text{l} V / H)^{1/2} \), a quantity expected to be on the order of 10 nN for micrometric texture, consistent with our observations. This force exceeds line friction for \( V > \gamma \Delta \cos \theta \eta_\text{l} l_c / \rho \), that is, around 1 m/s for \( \Delta \cos \theta = 10^{-3} \) and 1 cm/s for \( \Delta \cos \theta = 10^{-2} \), again in accordance with data in Fig. 1C where we only see a plateau for micropillars with high hysteresis (black data), contrasting with the

![Fig. 1. Friction mechanisms.](https://doi.org/10.1073/pnas.2315214121)
deviations linear in velocity around 1 cm/s on black silicon of ultralow hysteresis (red data).

In the following sections, we present an experimental technique developed to directly probe the friction on such low-friction surfaces. This allows us to test the model by playing separately with the parameters $k$, $V$, and $H$. In addition, we can test the case of levitating drops for which we have an air cushion yet no contact line ($F_B = 0$), a situation where the cushion friction can be tested independently of the presence of a line friction.

**Oscillating MFS Measurements.** In the oscillating MFS technique (Fig. 2A), a substrate-supported drop is attached through capillary forces at the end of a glass fiber (spring constant $k_p$, see Materials and Methods for experimental details). The drop-fiber device is deflected from the equilibrium position $x = 0$ and the subsequent oscillations are followed with a side-view camera, that gives the position $x$ of the drop center of mass as a function of time $t$ (Fig. 2B). The motion is opposed by an elastic force $kx$ caused by the MFS cantilever, the line friction $F_p$ and a dissipative force we assume to be proportional to the velocity $\dot{x}$, as suggested by our first experiments. Denoting the drop mass as $m$, the solution of the equation of motion $m(d^2x/dt^2) = -kx - F_p - F_m$ (33–36) is a damped harmonic oscillator function that successfully fits the data in Fig. 2B.

This oscillating droplet tribology approach has been robustly used for magnetic drops (33–35) and lubricated sliders (37) to probe wetting properties of superhydrophobic surfaces. Here we use the oscillating droplet tribometry (ODT) analysis methodology in the context of oscillating micropipettes. The ODT fit is performed for data with oscillation amplitudes that are small enough to be in the harmonic regime, but large enough to correspond to actual center-of-mass motion of the drop and not to the final "wiggle" motion of the drop interface. The output of the fit are $k$, $F_p$, and $\beta$. Since the contact-line friction force $F_p$ has been studied in detail in previous work (9), the damping coefficient $\beta$ is the main focus of this study. As described in detail below, great care has been taken in experimentally and theoretically verifying the physical meaning of each of the three fitting parameters used by the ODT model. In addition, the ODT model was validated by measuring simulated data (see SI Appendix, Supplementary Text for more details).

The spring constant $k$ of the drop-micropipette system can be described as a series of the spring-like micropipette, with known stiffness $k_p$, and the spring-like deformation of the drop interface at the micropipette-drop contact line (Inset in Fig. 2C). The spring constant $k_p$ in the $x$-direction of the latter can be calculated by considering the left and right-hand contact angles $\theta_L$ and $\theta_R$ made by the drop with the micropipette (Fig. 2A): $k_p = γ(\sin\theta_L - \sin\theta_R)$. This gives a total (theoretical) spring constant of

$$k_t = \frac{1}{1/k_p + 1/k_m(\sin\theta_L - \sin\theta_R)}.$$  \[1\]

By analyzing the contact angles at the largest deflections of the drop-pipette system, at the beginning and end of the region used for the ODT fit, an average value of the surface tension–related spring constant was calculated and included in Eq. 1. In Fig. 2C, the spring constant $k$ from the ODT fits for all oscillating MFS data on Glaco and black silicon is plotted for three different micropipettes as a function of the spring constant $k_p$ given by Eq. 1. These two are in excellent agreement, as shown by the collapse of the data on a line with a slope one. This implies that neither $k_t$ (described by Eq. 1) nor $F_p$ (confirmed at low speed with independent scanning MFS experiments or made null as described in the following section) are fitting parameters in our study, which aims at extracting and understanding the sole friction coefficient $\beta$.

**Drops with Zero Contact-Line Friction.** We first discuss the friction of a drop slightly levitating above a flat solid. Here, we were inspired by recent work reporting a reduced adhesion of carbonated water on hydrophobic and superhydrophobic surfaces (26, 27, 38), where it was proposed that the main resistance to motion arises in the thin CO$_2$ gas film supporting the drops (26), whose viscosity $\eta_g$ is 15 μPa·s (39). In our work, MilliQ water was carbonated using a commercial SodaStream system, and a drop of sparkling water was placed onto the micropipette just above a transparent superhydrophobic Glaco-treated substrate (see Materials and Methods for all experimental details). After gently pushing on the micropipette to the side, the drop-micropipette started to oscillate (Fig. 2A and B and Movie S1). Experiments were performed with drops from 1 to 10 μL and slightly different...
CO₂ concentrations (rendering different levitation times, see Materials and Methods), and the center-of-mass drop oscillations were fit with the ODT model. In all experiments, the fit gave values on the order of \( F_\mu \approx 10^{-20} \text{ N} \) with errors on the order of \( \Delta F_\mu \approx 10^{-21} \text{ N} \). However, this value reflects more the properties of the ODT method rather than the friction force for the levitating carbondated drops with zero friction force. Based on the validation data of ODT, such extremely low values reflect real values of \( F_\mu < 1 \text{ nN} \) (see SI Appendix, Supplementary Text for more details). We estimate the contact-line friction force to be zero in this case.

To understand the damping in this system, the oscillating MFS experiments were performed together with reflection interference contrast microscopy (RICM) (28–30, 40) from below (see Materials and Methods for details). The RICM gave time-resolved images of the contact region between water and its substrate with interference fringes indicating the shape and thickness of the gas film (Fig. 3A and Movie S2). By analyzing the position of these Newton rings (crosses in Fig. 3A, see Materials and Methods), the CO₂ film profile can be plotted as a function of radial distance \( r \) (Fig. 3B). The Newton rings are symmetrically centered around the contact region center (Movie S2), and the data are well described by a spherical cap on top of a very thin film. Hence, the thickness of this gas “blister” can be written \( h = H_b - r^2/2R_b + h_0 \) where \( H_b \) is the height of the blister, \( h_0 \) the thickness of the gas film at the perimeter of the contact region, and \( R_b = (l^2 + H_b^2)/2H_b \) is the radius of curvature of the spherical cap. We deduce the viscous damping coefficient of this cap-shaped film:

\[
\beta_{\text{cushion}} \approx \eta_g \int \frac{dA}{b(r)} \approx -2\pi \eta_g R_b \ln \left( \frac{l^2}{2(h_0 + H_b)H_b} - 1 \right) \approx 2\pi \eta_g \frac{l^2}{H_b} \ln \frac{l}{H_b},
\]

where we take advantage of the hierarchy in the distances \( (h_0 \approx H_b \ll l \ll R_b) \). The damping coefficients of the carbonated water drops (measured with MFS combined with ODT) from all experiments are plotted in Fig. 3C as a function of the value expected from Eq. 2 and deduced from RICM. Data collapse onto a line with a slope of one. The micropipette stiffness and LED wavelength do not affect the scaling (SI Appendix, Fig. S4). This experiment thus confirms that the friction of these levitating drops is dominated by the viscous friction in the gas that supports them.

**Drops with Vanishing Contact-Line Friction.** We now discuss whether these results can be generalized to the case of repellent slippery surfaces such as black silicon, where a velocity-dependent force was found to add to and even dominate the line friction (Fig. 1C). We used oscillating MFS to measure the damping coefficient on four different black silicon samples (Fig. 4 A–D), the same surfaces as studied with scanning MFS in ref. 9, see Materials and Methods. All samples exhibit conical microstructures, with heights \( H \) varying from 1 to 4 μm. Looking at the damped oscillations of water drops with \( R \approx 0.8 \text{ mm} \) on samples bSi A and D shows that friction markedly depends on the sample: Oscillations are damped in ~0.25 s on bSi D instead of ~1 s on bSi A (Fig. 4E). After using ODT to successfully fit the data, we extract the damping coefficients for differently sized drops (volumes between 1 and 9 μL, allowing us to vary the contact area radius \( l \)) on the four samples. As seen in Fig. 4F, the coefficient \( \beta \) strongly varies with both the black silicon sample and the contact area radius \( l \), by a factor 30 between the smallest \( l \) on sample bSi B to the largest \( l \) on sample bSi D. Furthermore, this logarithmic representation suggests that data can be described by a quadratic law \( (\beta \sim l^2) \) for all samples, which implies proportionality between friction and contact surface area.

We can compare these observations with the behaviors expected from the various sources of friction discussed earlier. On the one hand, the contact-line friction \( F_c \) is sensitive to the perimeter of the contact and thus scales as \( l^2 \) (SI Appendix, Fig. S5), with no dependency on velocity at low speed, which makes it essential when drops are moving slowly (Fig. 1C). In contrast, the Scriven force in the wedge of air bounding the drop is velocity dependent, but it also scales as the contact perimeter, unlike data in Fig. 4F. On the other hand (in the liquid), the viscous friction in the drop is velocity dependent, but it scales as \( l^{1/2} \), that is, with an exponent smaller than observed in Fig. 4F. The picture is very different at large viscosities \( \eta_g \), as confirmed in SI Appendix, Fig. S6 for glycerol on bSi A. Then, the viscous friction \( F_\mu \sim \eta_g V^3 l^{1/2} \eta_g \) is found to become dominant at speeds larger than 0.2 mm/s. Other mechanisms (aerodynamic resistance, viscous friction in air) are global, at the scale of the drop, and thus not sensitive to the contact area radius \( l \). Hence, none of these forces agree with a friction scaling

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**Fig. 3.** Friction of levitating carbondated water drops on a transparent repellent substrate. (A) The contact region between the drop and the substrate as imaged from below with RICM. Each subsequent bright Newton ring (marked with red crosses) shows a change of \( \lambda/2 \) in the thickness of the CO₂ film, where \( \lambda \) is the wavelength of the LED. (B) The gas film height \( h \) as a function of radial distance \( r \) from the center of the contact region in (A). The CO₂ blister is a spherical cap (red solid line) with a maximum height \( H_b \approx 3.5 \mu \text{ m} \) placed on a film with a height \( h_0 \approx 0.2 \mu \text{ m} \). (C) Damping coefficient \( \beta \) of the moving drop obtained from oscillating MFS combined with ODT and plotted as a function of the theoretical damping coefficient \( \beta_{\text{cushion}} \) given by Eq. 2. The data collapse onto a solid line of \( \beta = 2\beta_{\text{cushion}} \) (slope of 1 in graph due to log-log axes). The error bars are the 95% CI of the ODT fit for \( \beta \) and the error propagation for the components (and their SD) of Eq. 2 for \( \beta_{\text{cushion}} \).
as $\bar{l}$; in addition, and consistently, the expected magnitudes of these forces are at least ten times smaller than measured.

Hence, we are left with the plastron friction. It scales as $(\eta_a V/H) \pi \bar{l}$, that is, as $V$ and $\bar{l}$, as respectively observed in Figs. 1C and 4F and its magnitude is around 10 nN, agreeing again with the data. Furthermore, the phenomenon is general: First, the same $\beta$ ~ $\bar{l}$ scaling has been reported for magnetic water drops oscillating on a very slippery superhydrophobic copper surface (33); second, the inverse of the damping time $(1/\tau \sim \bar{l})$ was also shown to scale linearly with the contact area $\bar{l}$ of oscillating magnetic drops on four different commercial superhydrophobic coatings (Neverwet, WX2100, Ultra-Ever Dry, and Hydrobead) (41).

The damping coefficient $\beta_{\text{plastron}} \sim \eta_a \bar{l}/H$ is expected to be sensitive to the texture design, through its height $H$. This prediction qualitatively agrees with Fig. 4F where $\beta$, at fixed $\bar{l}$, decreases when increasing $H$, that is, when going from sample bSi D to sample bSi A. We can further examine this dependency, after evaluating the average thickness $H$ of the black silicon microstructure (SI Appendix; Table S1) from side-view scanning electron microscopy (SEM) imaging (Fig. 4A–D, see Materials and Methods). This allows us to calculate the expected damping coefficient $\beta_{\text{plastron}}$ with the air viscosity $\eta_a = 18 \mu\text{Pa}\cdot\text{s}$ (38). When plotting the results of Fig. 4F as a function of $\beta_{\text{plastron}}$ (Fig. 4G), all data collapse onto a line with a slope of 1. Hence, we could separately verify the scaling in $\bar{l}^2$ (Fig. 4F), $H^{-1}$ (Fig. 4G), and $V$ (Fig. 1C) expected from the model, which confirms that the resistance opposing the motion of drops on black silicon at intermediate velocity mainly arises from the shearing of the plastron that cannot be considered a purely passive support (42). This scenario is verified for both levitating drops and deposited ones, with differences in the geometry: levitating droplets have a cap-shaped cushion, while droplets on black silicon have a “flat” plastron trapped within the microstructured coating. Other than this, the damping mechanism is the same.

As a final demonstration, we compare the scanning MFS experiments at different drop speeds on the most slippery bSi A sample (Fig. 1C) with the results from the oscillating MFS experiments (Fig. 5A). The averaged quantitative results $F_{\mu}/2\bar{l}$ and $\beta V/2\bar{l}$ from the oscillating MFS are plotted as lines in the graph—these lines are not fits to the scanning MFS data. The dimensionless contact-line friction force measured with scanning MFS in the low drop speed regime is thus in excellent agreement with $F_{\mu}/2\bar{l}$ measured with oscillating MFS on the same sample. Furthermore, the two techniques indicate the same onset and scaling of the viscous friction in the plastron. Finally, the total dissipative force $F_{\text{tot}} = F_{\mu} + F_{\text{cushion}}$ is plotted in Fig. 5A as a solid black line where it fits convincingly the data. Hence, our two experimental techniques clearly evidence a previously disregarded friction mechanism on highly slippery materials, that occurring in the plastron.

The Plastron Thickness as a Design Parameter for Minimizing Drop Friction Forces. In order to minimize plastron friction on ultraslippery repellent surfaces, we introduce here a criterion for their design: The plastron must both be thick and maintain a low contact angle hysteresis. One option for such a design is a dual-scale roughness, for example by etching the slippery black silicon bSi A onto micropillars with height $H_p \approx 44 \mu\text{m} \gg H$ (Fig. 5B and C). The samples “$\mu_b + \text{bSi}$” and “$\mu_b + \text{bSi}$” have micropillars (samples $\mu_b$ and $\mu_b$) with different densities (or Cassie fraction) $\phi^\alpha = 0.04 \pm 0.02$ and $\phi^B = 0.13 \pm 0.06$, as measured from top-view SEM images (SI Appendix; Fig. S3 and Materials and Methods). Similar samples have been made before (43), but the design process here is unique: Our aim is not to reduce the Cassie fraction but to keep it low while increasing the plastron depth. The dimensionless total friction was measured with scanning MFS on these samples (Fig. 5D) and the contact-line friction remains comparable to that on bSi A at low $V$. However, the plastron friction on these samples occurs both in the air between the micropillars and between the bSi cones (with height $H$ measured with side-view SEM, see SI Appendix, Fig. S7 and Table S1). This provides $\beta_{\text{plastron}} \sim \eta_a \pi^2 [\phi_b / H + (1 - \phi_b) / H_p] \sim \eta_a \pi^2 \phi_b / H$ (Fig. 5E), i.e., reduced by a factor $\phi_b$ compared to bSi samples in Fig. 4. The damping coefficients on these samples were measured.

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Fig. 5. Friction of water drops on the most slippery samples. (A) The dimensionless total friction $F_{\text{tot}}/2\gamma$ as a function of the drop speed, as measured by scanning MFS on bSi A (red markers, $H = 0.92 \pm 0.05$ mm and $l = 270 \pm 30$ $\mu$m). Red lines show the average $\beta \gamma/2\gamma$ and $F_{\text{tot}}/2\gamma$ from the oscillating MFS experiments (Fig. 4) on the same sample, and the black line shows $(F_{\mu} + \beta\gamma)/2\gamma$. (B and C) SEM image at 45° tilt of the $\mu_b + \text{bSi}$ and $\mu_c + \text{bSi}$ samples. Pillars are less dense on the $\mu_c$ sample and microtexture on both micropillared samples is bSi A (Fig. 4A). The bar shows 10 $\mu$m. (D) Scanning MFS measured $F_{\text{tot}}/2\gamma$ vs. $V$ on $\mu_b + \text{bSi}$ ($l = 280 \pm 30$ $\mu$m) and $\mu_c + \text{bSi}$ ($l = 290 \pm 30$ $\mu$m). Solid lines are the results from oscillating MFS, and dashed lines are averages from low-speed scanning MFS. (E) The damping coefficient $\beta$ from oscillating MFS experiments as a function of the theoretical plastron damping coefficient $\beta_{\text{plastron}} = \eta \pi l^2 / H$, on bSi and $\mu_b + \text{bSi}$ samples. All data collapse onto a line of slope 1. The error bars are the 95% CI of the ODT fit for $\beta$ and the error propagation for the components (and their SD) of $\beta_{\text{plastron}}$. (F) The dominating friction as a function of plastron thickness and drop speed for a water drop with $R = 1$ mm and $l = 0.2$ mm on a surface with $F_{\mu} = 10$ nN. The $\eta$ denotes the region where viscosity in the drop dominates. Error bars in A, D, and F are error propagations of the SD.

Discussion

There is a strong focus on developing extremely slippery repellent surfaces for applications in drag reduction, antifogging, and antiwetting, to name a few. Low friction is attained on superhydrophobic surfaces by reducing the contact made by the drop with the inherently hydrophobic surface. This is achieved through the trapping of an air film (plastron) between the microstructures of the surface, allowing the drop to glide on a cushion of air. Here, we report a plastron friction force on such a slippery repellent surface, as revealed by a MFS in conventional scanning mode as well as in an oscillating mode. We measure the contact-line friction and damping of water drops moving in regimes of vanishing and even zero contact-line friction. We show the importance of the viscous resistance in the seemingly passive air plastron. This force can become dominant for drops with low viscosity ($\eta \ll 100$ mPa.s) moving at 1 to 10 mm/s (a range that depends on the drop size and plastron thickness) on “ultraslippery” materials where line friction $F_{\mu}$ is on the order of 10 nN. The plastron friction increases linearly with the drop speed so that it can become at higher velocity (10 cm/s to 1 m/s) comparable to the line friction of a not-so-slippery repellent sample made of micropillars. This effect thus cannot be neglected in the design of future ultraslippery surfaces. For slightly less slippery samples ($F_{\mu}$ around 300 nN), such as bSi C, superhydrophobic copper surfaces (33), and commercial Glaco and Ultra-Ever Dry samples (18), the transition to the plastron dissipative force-dominated regime occurs at drop speeds in the range of 10 to 100 mm/s, still well below the typical terminal velocity on superhydrophobic surfaces (~m/s).

The current understanding of superhydrophobic sample design has been that reducing the length scale of microstructure (nano- or microcones) and diluting it strongly reduces friction. Our work shows that this rule breaks down when plasitrons are too thin (see critical plastron thickness values illustrated in Fig. 5F and SI Appendix, Figs. S9 and S10). Then, friction can drastically
increase despite the slippery character of the material. We carefully considered and excluded other velocity-dependent dissipation mechanisms and evidenced the situations where friction mainly originates from the plastron. For a millimeter water drop moving on samples with microscopic structures \((H \approx 1 \text{ \mu m})\) and a vanishing contact-line friction force \((F_c < 100 \text{ nN})\), the plastron dissipative force becomes key at drop speeds \(V < 10 \text{ mm/s}\). For the special case of a zero contact-line friction, as demonstrated here with levitating carbonated water drops, plastron friction is dominant at most drop speeds. We have found a total of six different highly slippery materials, including well-known commercially available coatings, that all show indications of leading plastron friction. The phenomenon is general, and it needs to be considered in future research and applications. We use our findings to introduce an additional design principle that minimizes contact-line friction and simultaneously reduces the plastron friction, which achieves highly slippery samples at all drop speeds. Our work thus provides the means to design more formative ultraslippy samples in the future.

**Materials and Methods**

**Scanning MFS Measurements.** Scanning MFS experiments were performed according to a previously developed protocol (9). Micropipettes were pulled from thick glass capillaries (i.d./o.d. = 0.75 mm/1 mm, World Precision Instruments, model no. TW100-6) using a micropipette puller (Narishige, model no. PN-31). The straight cantilever was cut to a desired length using a microforge (Narishige, model no. MF-900) and calibrated (spring constant \(k_p\)) with a small water droplet as control weight (19). The force-calibrated micropipette was then mounted vertically above the substrate, which rested on a motorized xyz-stage. The entire setup was mounted on an active antivibration table (Halcyonics_i4large, Accurion) and shielded by a cardboard box to damp out noise. For the experiments in this study, the micropipette in the equilibrium position of the pipette (Canon 90D capturing at 60 to 120 fps using a Canon MP, 800 ISO) was started to capture the equilibrium position of the pipette (Fig. S2). The friction force was finally measured in the regime of uniform sliding.

**RICM Image Analysis.** Using a home-written MATLAB code, the Newton rings from the RICM experiments were counted as a function of radial distance from the contact region center. Knowing that each subsequent ring corresponds to a change in \(\Delta z\) thickness of \(\Delta z/2\), where \(\Delta z\) is the wavelength of the LED (26), the change in film height could be determined. To quantify the absolute thickness of the gas film, we followed the procedure by Panchanathan et al. (26), where the first frame showing the collapse of the gas film was used as a reference for \(h_0 = 0\). By playing the video backward and counting the appearance/disappearance of fringes, the levitation height \(h_0\) could be determined. The resulting height profile of the gas film (see example in Fig. 3b) was plotted as a function of time during the same time range as analyzed with ODT in the side-view MFS experiments. A spherical cap function was fit to the data, and the time-averaged \(h_0, h_p, \text{ and } l\) were used to calculate the damping coefficient online in the side-view oscillating MFS experiments (see above).

**ODT analysis and simulations.** ODT was done based on the model of oscillating droplet tribometer (33–35, 37). The same model can be used since the forces in our system are similar. The solution of the general harmonic oscillator with viscous and contact-line friction is a piecewise solution for each half-oscillation as

\[
x(t) = x \left(\frac{nT}{2} + \tau\right) = x_{n+1}(\tau),
\]

where we have:

\[
x_{n+1} = (-1)^n A_0 \sqrt{1 + \beta} \left(1 + \frac{F_p}{k_p} \right) e^{-\frac{1}{2} \sum_{j=0}^{n} e^{-\frac{2}{k_p} x_j^2}} e^{-\frac{\omega^2 x^2}{2 \beta}} \cos \left(\omega \tau - \cos^{-1} \left(\frac{1}{\sqrt{1 + \beta}}\right)\right) + \tilde{F}.
\]

A_0 is the starting amplitude, \(\omega\) the angular frequency of the oscillation, \(\tilde{F} = F_p / k_p A_0\) the normalized sliding friction, and \(\beta = \beta / \omega m\) the normalized viscous friction coefficient (33, 36). The drop location data were fit to the model based on nonlinear least squares method and interpolating the data to time steps of 1 ms based on smoothing spline using MATLAB. The ODT model was validated for these parameter values by fitting the ODT model to simulated data with similar parameters as the experimental data (SI Appendix, Supplementary Text). The simulations were done by solving the drop’s equation of motion forward in time using Runge-Kutta of 4(5) order algorithm using Python package SciPy 1.0 (34, 44, 45). There was good agreement between the used simulation parameters and the parameters obtained from the ODT model, which shows the viability of using the ODT model for oscillating MFS measurements.

**Carbonated Water.** MilliQ water was carbonated using a commercial SodaStream system. A range of different CO2 concentrations was used, rendering different levitation times (a few to tens of seconds) of the drop. By measuring the pH of the sparkling water using a micro-pH meter (Mettler Toledo SevenExcellence), the
concentrations could be calculated as $C_0 = 10^{-2 \cdot \text{pH}}/K_a$, where $K_a = 4.33 \cdot 10^{-7}$ is the first dissociation constant of $\text{H}_2\text{CO}_3$ (46). Our concentrations ranged between $C_0 = 14 \pm 0.6 \text{mM (pH = 4.1)}$ and $C_0 = 44 \pm 0.2 \text{mM (pH = 3.86)}$, assuming an error of $\Delta \text{pH} = \pm 0.01$ for the pH meter. According to the work of Panchanathan et al. (26), these concentrations should yield levitation times of 3 to 12 s, which corresponds to what we observed.

Preparation of the Glaco Sample. Microscope glass slides were thoroughly cleaned by rinsing and scrubbing with cotton sticks in acetone ($\geq 99.5 \%$, Sigma-Aldrich). Then, they were ultrasonicated for 10 min in acetone ($\geq 99.5 \%$), followed by rinsing with isopropyl alcohol ($\geq 99.7 \%$, Sigma-Aldrich). After drying under nitrogen flow, the slides were treated for 5 min with oxygen plasma for homogenization of surface chemistry. Finally, the samples were sprayed with Glaco, following the instructions from the supplier. Both spraying and drying were done on vertically mounted slides. The drying time was 24 h. The advancing and receding contact angles of water on these Glaco samples were $\theta_{\text{adv}} = (168 \pm 4)°$ and $\theta_{\text{rec}} = (166 \pm 5)°$, confirming that these samples are superhydrophobic. These contact angle measurements were done using conventional contact angle goniometry (Biolin Attention Theta) by growing a 1 µL droplet, bringing it in contact with the surface, growing the drop 1 µL more, and then centering the needle in the backside of the droplet. The growth speed for this process was 0.05 µL/s. Then, the droplet volume was grown for 15 µL more at the rate of 0.05 µL/s while it was recorded, giving the advancing contact angle. For the receding angle, the droplet was grown for 10 µL more with a rate of 0.05 µL/s, and then, it was sucked in for 25 µL. After each receding angle experiment, a volume of 50 µL was dispensed aside to prevent contamination of water, and then, the next advancing angle was measured. The measurement was repeated 10 times giving an average advancing and receding contact angle with their SD.

Fabrication of Black Silicon Samples. Black silicon nanopillars were fabricated with a maskless anisotropic deep reactive etching process (47). The plasma etcher used was Oxford Plasmalab System 100, Oxford Instruments. For all types of black silicon, the etching temperature $-110 \, ^\circ\text{C}$, the pressure $10 \, \text{mTorr}$, and the etching time 7 min were kept constant. To obtain the different black silicon topographies A, B, C, and D, the SF$_6$ gas flows (in sccm) were 40, 37.6, 35.3, and 32.9, the O$_2$ gas flows (in sccm) were 18, 20.4, 22.8, and 25.1, and the forward powers (in W) were 6, 6.5, 4, and 4, respectively. The samples were then made superhydrophobic by applying a plasma-enhanced chemical vapor deposited (PECVD) fluoropolymer coating (Oxford Plasmalab 80+, Oxford Instruments). The parameters for this coating were 50 W power, 250 mTorr pressure, 100 sccm Ar flow, and 40 sccm SF$_6$ flow. The etching time was 18 min. Afterward, the oxide mask was removed with buffered HF. The depth of the micropillars was measured by a profilometer (Bruker Dektak XT) to be 44 ± 0.6 µm. Finally, the same PECVD fluoropolymer coating as for the black silicon samples was deposited on top of the micropillars. SEM images of the final samples are shown in SI Appendix, Fig. S3.

Fabrication of Etched Micropillared Samples. The samples with black silicon on top of micropillars were fabricated by a combination of the two processes. First, the micropillars were fabricated as described above and coated with PECVD fluoropolymer. These conventional superhydrophobic samples were probed with MF5 (black data in Fig. 1C). Then, the fluoropolymer coating was removed with oxygen plasma, and the black silicon A process (described above) was applied. As a last step, the same PECVD fluoropolymer coating that was used for both the black silicon and the micropillars was deposited on the combined micropillars + bSi samples.

SEM Measurements. The SEM imaging was done using Zeiss Sigma VP SEM at a low acceleration voltage (1.0 kV) with an in-lens detector. Before imaging, the samples were coated with gold--palladium (Au/Pd) coating with Leica EM ACE600 high-vacuum sputter coater in the following manner. The bSi A (Fig. 4A) and bSi + bSi A sample (Fig. 5B) was coated with 5 nm Au/Pd from the top and 5 nm Au/Pd from the side, while samples bSi-B were coated with 8 nm Au/Pd from the side. No conductive coating was applied on the samples bSi + bSi and bSi shown in SI Appendix, Fig. S7. The SEM imaging of micropillared samples µbSi and µbSi A before the black silicon etching was done with 4.0 kV acceleration voltage with an SE2 detector, and no conductive coating was applied on these samples.

Data, Materials, and Software Availability. All data needed to evaluate the conclusions in the paper are present in the paper and SI Appendix, Tables S2-S16. The raw data files and MATLAB codes are shared on Zenodo (48).

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