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Quantifying microdroplet contact-line friction using atomic force microscope

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Controlling the wetting and spreading of microdroplets is key to technologies such as microfluidics, ink-jet printing, and surface coating. Contact angle goniometry is commonly used to characterize surface wetting by droplets, but the technique is ill-suited for sub-millimetric droplets. Here, we attach a micrometric-sized droplet to an Atomic Force Microscope (AFM) cantilever to directly quantify contact-line friction on different surfaces (superhydrophobic and underwater superoleophobic) with sub-nanonewton force resolutions. We demonstrate the versatility of our approach by performing friction measurements using different liquids (water and oil droplets) and under different ambient environments (in air and under water). Finally, we show that underwater superoleophobic surfaces can be qualitatively different from superhydrophobic surfaces: contact-line friction is highly sensitive to contact-line speeds for the former but not for the latter surface.

INTRODUCTION

Sub-millimetric or microdroplets are formed during various processes such as condensation and human respiratory activities, with implications for heat transfer [1, 2] and disease spread [3, 4]. At the same time, the ability to control surface wetting by microdroplets is key to optimizing the performance of various technologies, such as ink-jet printing [5, 6] and enhanced oil-recovery techniques [7, 8]. Contact angle goniometry is the most common approach to quantify the wetting properties of surfaces especially by a millimetric-sized liquid droplet [9, 10]. The adhesion and friction forces required to remove the droplet can also be deduced, albeit indirectly, from the advancing and receding contact angles [11, 12]. However, contact angle goniometry does not work well for microdroplets. Moreover, contact angle measurements are inaccurate for large values close to 180° and for rough surfaces [9, 13].

Recently, we introduced a modified Atomic Force Microscopy (AFM) method to precisely measure adhesion forces of small droplets (tens of micron in size) with nN force resolutions [14–16]. The microdroplet is attached to and spatially manipulated by a tipless AFM cantilever, and the forces acting on the droplet can be deduced from the cantilever deflection. This technique is sometimes known as droplet probe AFM and has been used to study various interfacial problems [17–22], but its potential as a surface wetting characterization tool—especially to measure contact-line friction—remains untapped.

Here, we used droplet probe AFM to directly quantify the contact-line friction (with sub-nN force resolutions) for a sub-millimetric water or oil droplet moving laterally (with controlled speeds $U = 2$–$600$ $\mu$m s$^{-1}$) on superhydrophobic and underwater superoleophobic surfaces (Fig. 1). We explain how to convert the raw voltage signal from the four-quadrant sensor first to the moment $M$ and ultimately the friction force $F_{\text{fric}}$ acting on the droplet. Measuring droplet-solid friction using AFM presents unique challenges as compared to traditional solid-solid friction measurements [23–25]. For example, the droplet probe is much more easily deformed compared to a solid tip, and special care has to be taken to disentangle contact-line friction from other effects, e.g.,

Figure 1. (a) Measuring friction force $F_{\text{fric}}$ for a water droplet moving on black silicon superhydrophobic surface. Inset shows the scanning electron micrograph of the surface. (b) Measuring $F_{\text{fric}}$ for an oil droplet on hydrated polyzwitterionic brush surface (underwater superoleophobic). Inset shows AFM topography of the brush layer with thickness $h$. 

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viscous drag acting on the droplet [21].

In this paper, we chose a black silicon surface [26] and a zwitterionic poly(sulfobetaine methacrylate) (pSBMA) brushes [27, 28] as the archetypal superhydrophobic and underwater superoleophobic surfaces, respectively. Black silicon consists of micron-sized cones with hierarchical nanotextures to trap an air layer beneath the water droplet (Fig. 1a), while the polymer brushes in pSBMA play a similar role by trapping a stable water film under the oil droplet (Fig. 1b). Previously, it was thought that zwitterionic polymer brushes (and other underwater superoleophobic surfaces) are simply oil-repellent analogues of superhydrophobic surfaces [29]. This view is partly based on the experimental observations that droplets on both surfaces exhibit high contact angles close to 180°.

Here, we show how this view is inaccurate and that contact-line friction is not just quantitatively but qualitatively different for the two surfaces. Firstly, we found that $F_{\text{tric}}$ is one to two orders of magnitude lower for underwater superoleophobic surface compared to superhydrophobic surface for similarly sized droplets. More interestingly, $F_{\text{tric}}$ increases with contact-line speed $U$ for underwater superoleophobic surface but is independent of $U$ for superhydrophobic surface, reminiscent of the distinction between lubricated and dry frictions in tribology [30].

**RESULTS AND DISCUSSIONS**

We start by addressing the deformability of the droplet probe. We can control the contact radius $r$ by varying the normal force $F_N$ acting on the droplet. For example increasing $F_N$ from 8 to 350 nN results in an increase of $r$ from 10 to 18 μm for an underwater oil droplet (radius $R = 50$ μm) sitting on the pSBMA surface (Fig. 2a); a similar increase in $F_N$ results in an increase of $r$ from 4 to 10 μm for a water droplet ($R = 20$ μm) on a superhydrophobic surface (Fig. 2b). For a droplet of radius $R$ and surface tension $\gamma$ making a contact angle $\theta$, $r$ results from a balance between the Laplace pressure $(2\gamma/R)\pi r^2$, the capillary adhesion force $2\pi r\gamma \sin \theta$, and the applied $F_N$, i.e.,

$$ (2\gamma/R)\pi r^2 - 2\pi r\gamma \sin \theta = F_N $$

$$ (r/R)^2 - (r/R) \sin \theta = F_N/(2\pi R\gamma) $$

(1)

, where $\tilde{r} = r/R$ and $\tilde{F}_N = F_N/(2\pi R\gamma)$ are non-dimensional, normalized contact radius and normal force. Experimentally, we observed that $r$ increases with increasing $F_N = 5$–400 nN for droplets of different sizes $R = 11$–70 μm for both surfaces (Fig. 2c). More importantly, the data for superhydrophobic and underwater superoleophobic surfaces collapse into their respective master curves when $r$ and $F_N$ are normalized by $R$ and $2\pi R\gamma$, as predicted by Equation 1 (Fig. 2d).

We can obtain the contact angles $\theta$ from the plot of $\tilde{r}$ vs. $\tilde{F}_N$ since $\sin \theta = \tilde{r} - \tilde{F}_N/\tilde{r}$. In the limit of small $\tilde{F}_N \approx 0$, both surfaces have similar $\theta \approx 170°$ (Fig. 2e). As we increase $\tilde{F}_N$ from 0 to 0.08, $\theta$ for the superhydrophobic surface falls from 170° to 155°. This is likely because the water droplet penetrates deeper into the cones at higher $F_N$, resulting in increasing solid contact fraction and decreasing $\theta$ consistent with predictions by Cassie-Baxter [31]. In contrast, $\theta$ for the underwater superoleophobic surface remains relatively constant between 165° and 170° for the same increase in $F_N$. As explained in our previous paper, the polymer brushes become charged when submerged under water, resulting in repulsive electric double-layer forces that can sustain strong hydration layers [28], i.e., the oil droplet cannot penetrate into the polymer brush layer even with increasing $F_N$. The difference between the two surface classes will become even more apparent from the contact-line friction measurements presented later.

Before we can quantify the friction force $F_{\text{tric}}$ accurately, we need to perform several calibration steps to convert the raw voltage signal $V_{\text{lat}}$ (due to torsional deflection of the cantilever) from the four-quadrant sensor.
Figure 3. To obtain $k_\phi$ and $S_\phi$ for the two cantilevers TL-Cont and Arrow-TL we fitted the power spectral density (PSD) in (a, b) air and (c, d) under water with Equation (3), using Sader’s method. Experimental points are in gray, while blue lines show the best-fit curves. (e, f) Contact method: alternatively, we can obtain the lateral sensitivity $LS$ by applying a known moment $M = F \omega^2/2$ (where $w$ is the cantilever width) and recording the signal response $V_{\text{lat}}$. The slope of $|V_{\text{lat}}|$ against $M$ corresponds to $1/LS$.

(volts) into forces (newtons) [25]. To do this, we need to know (1) the sensitivity $S_\phi$ [V$^{-1}$] which relate the voltage signals to the torsional deflections $\Delta \phi$ [rad], (2) the spring constant $k_\phi$ [N m] which convert the deflections into moment $M$, and (3) the droplet height $H$ since $M = F \omega^2 H$, i.e.,

$$V_{\text{lat}} \xrightarrow{S_\phi} \Delta \phi \xrightarrow{k_\phi} M \xrightarrow{1/H} F_{\text{tric}}$$

$$V_{\text{lat}} \xrightarrow{LS} M \xrightarrow{1/H} F_{\text{tric}}$$

(See schematic in Fig. 1). We can also define a lateral sensitivity $LS = k_\phi S_\phi$ to convert $V_{\text{lat}}$ directly to $M$, i.e., $M = LS V_{\text{lat}}$.

The droplet height $H$ can be obtained from sideview images such as in Figs. 2a, b. To determine $k_\phi$ and $S_\phi$, we follow the approach first proposed by Sader [32, 33], who realized that the thermal response of the cantilever beam (its resonant frequency and the quality factor) is determined by the equipartition theorem and damping due to the surrounding fluid, which in our case is either air or water. Hence, by looking at fluctuations of $V_{\text{lat}}$ of an unloaded cantilever with time, it is possible to deduce $k_\phi$ and $S_\phi$ with about 10–20 % accuracy.

In many commercial AFM systems, there is no automatic option to implement Sader’s method for torsional deflection. Here, we describe a practical implementation of Sader’s method for two different cantilevers: TL-Cont and Arrow-TL used to measure friction for the superhydrophobic and underwater superoleophobic surfaces, respectively. We first measured the thermal fluctuations of $V_{\text{lat}}$ in air and under water as a function of time (at a rate of 600 kHz) and performed a fast fourier transform to obtain the power spectral density (PSD), which is then fitted with a simple harmonic oscillator model

$$\text{PSD}(f)^2 = A_{\text{DC}}^2 \left( \frac{f_0^2}{f_0^2 - f^2} \right)^2 + \left( \frac{f_0}{Q} \right)^2 + A_{\text{fric}}^2,$$  \tag{3}$$

where $f_0$ is the resonant frequency, $Q$ is the quality factor, and $A_{\text{DC}}$ and $A_{\text{fric}}$ are fitting parameters [34]. $k_\phi$ and $S_\phi$ can then be determined using the following equations:

$$k_\phi = 6.285 \rho \omega^4 LQ f_0^2 \Gamma_i / f_0 k_\phi,$$

$$S_\phi = \sqrt{ \frac{2 K_B T}{\pi A_{\text{DC}}^2 Q f_0 k_\phi} }.$$  \tag{4}$$

where $\Gamma_i$ is the hydrodynamic function described in Green et al. (2002) [33] and $\rho = 1.205 \text{ kg m}^{-3}$ or 998 kg m$^{-3}$ is the air or water density depending on the ambient environment. $w$ and $L$ are the width and length of the cantilevers, while $K_B$ is the Boltzmann constant and $T$ is the absolute temperature.

Depending on the choice of cantilever and the ambient environment (air vs. water), we obtained different $f_0$ and $Q$ values when fitting the experimental PSD data with Equation 3 as shown in Figures 3a–d (See [35] for our Python programming code). We can then obtain $k_\phi$ and $S_\phi$ (and hence $LS$) by applying Equation 4, which we summarize in Table I. Note that while $S_\phi$ and $LS$ values in air and water can differ, the spring constant $k_\phi$ cannot. Experimentally, we found that the fitted values of $k_\phi$ in air and water do not vary by more than 33%; 2.9×10$^{-8}$ vs. 2.1×10$^{-8}$ N m for TL-Cont; 4.3×10$^{-9}$ vs. 5.0×10$^{-9}$ N m for Arrow-TL.

To confirm the accuracy of the Sader’s method, we used a direct contact method to obtain $LS$ in air [36, 37]. We pushed the cantilever edge against a hard solid tip (i.e., at $w/2$ away from the cantilever central axis) to apply a known force $F$ and hence a resultant moment $M = F w/2$, while recording the signal response $V_{\text{lat}}$ (Fig. 3e, f). Depending on the cantilever side, we can apply either a clockwise or anti-clockwise rotation/moment. The slopes of $|V_{\text{lat}}|$ against $M$ correspond to $1/LS$. Experimentally, we found that the two methods, Sader and contact, give similar $LS$ values: 1.2×10$^{-11}$ vs. 0.9×10$^{-11}$ N m/V for TL-Cont; 7.6×10$^{-13}$ vs. 8.7×10$^{-13}$ N m/V for Arrow-TL (See Table I). Once the calibration has been performed, the raw signal $V_{\text{lat}}$ can be converted into $F_{\text{tric}}$ using the relation $F_{\text{tric}} = (k_\phi S_\phi / H) V_{\text{lat}} = (LS / H) V_{\text{lat}}$.

We first performed friction measurements for a water droplet ($F_N = 5 \text{ nN}$, $R = 30 \mu \text{m}$, and $r = 6 \mu \text{m}$) moving on the superhydrophobic surface. Figure 4a shows the...
Table I. Calibration results from Figure 3

<table>
<thead>
<tr>
<th>Cantilever</th>
<th>( S_\theta ) (V(^{-1}))</th>
<th>( k_\phi ) (N m)</th>
<th>( LS ) (N m/V)</th>
<th>( S_\theta ) (V(^{-1}))</th>
<th>( k_\phi ) (N m)</th>
<th>( LS ) (N m/V)</th>
<th>Contact (air) LS (N m/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL-Cont</td>
<td>4.1(\times)10(^{-4})</td>
<td>2.9(\times)10(^{-8})</td>
<td>1.2(\times)10(^{-11})</td>
<td>1.1(\times)10(^{-4})</td>
<td>2.1(\times)10(^{-8})</td>
<td>0.6(\times)10(^{-11})</td>
<td>0.9(\times)10(^{-11})</td>
</tr>
<tr>
<td>Arrow-TL</td>
<td>1.8(\times)10(^{-4})</td>
<td>4.3(\times)10(^{-9})</td>
<td>7.6(\times)10(^{-13})</td>
<td>1.7(\times)10(^{-4})</td>
<td>5.0(\times)10(^{-9})</td>
<td>8.7(\times)10(^{-13})</td>
<td>6.5(\times)10(^{-13})</td>
</tr>
</tbody>
</table>

Figure 4. (a) Contact-line friction for a water droplet \( (F_N = 5 \text{ nN}, R = 30 \text{ \(\mu\)m}) \) moving at a speed \( U = 30 \text{ \(\mu\)m s}^{-1} \) on the superhydrophobic surface. (b) Raw force data for an oil droplet \( (F_N = 30 \text{ nN}, R = 55 \text{ \(\mu\)m}) \) moving at a speed \( U = 40 \text{ \(\mu\)m s}^{-1} \) on the superoleophobic surface. (c) Reference data for an oil droplet not touching the surface. (d) Friction data after subtracting c from b.

Correctly measure contact-line friction for the oil droplet, it is important to disentangle \( F_{\text{fric}} \) from other effects. To do this, we repeated the same force measurements as in Figure 4b except with the oil droplet lifted up from the surface (by about 100 \(\mu\)m). We observed a clear signal despite there being no contact-line friction. The observed force is partly due to viscous drag (i.e., Stokes’s law) \( F_{\text{drag}} \approx 6\pi r \eta U \approx 40 \text{ pN} \) where \( \eta \) is water’s viscosity. A more significant effect is likely due to the misalignment of the optical lever which causes a signal that varies with cantilever position as clearly seen in Figure 4c. In any case, we can obtain \( F_{\text{fric}} = 120 \pm 20 \text{ pN} \) (much smaller than \( F_{\text{fric}} \) in superhydrophobic surface) correctly by subtracting the reference data in Figure 4c from the raw data in Figure 4b (Fig. 4d).

The difference between the two surfaces goes beyond the magnitude of \( F_{\text{fric}} \) and is evident in the force fluctuations \( \Delta F_{\text{fric}} \). Previously, we and others showed that electric double layer forces in pSBMA can sustain nanometric water film beneath the oil droplet preventing contact with the polymer brushes [18, 28, 38]. This explains why the force curve are smooth for the underwater superoleophobic surface (Fig. 4d), and the observed \( \Delta F_{\text{fric}} = 80 \text{ pN} \) is mostly due to thermal fluctuations (We measured similar magnitude of signal fluctuations for a stationary cantilever when performing calibration using Sader’s method). In contrast, the force curve is more jagged with larger \( \Delta F_{\text{fric}} = 0.7 \text{ nN} \) for the superhydrophobic surface, which we attribute to pinning-depinning events as the moving droplet detaches from individual cones (Fig. 4a and later schematic in Fig. 5b).

To better illustrate the difference in contact-line behaviours, we repeated the friction measurements over a wide range of \( U = 2–600 \text{ \(\mu\)m s}^{-1} \) and applied \( F_N = 5–580 \text{ nN} \) (which translates to different contact radii \( r \)). Firstly, we observed that \( F_{\text{fric}} \) for underwater superoleophobic surface is one to two orders of magnitude lower as compared to superhydrophobic surface (Fig. 5a). We have chosen to present the friction force in its non-dimensional form \( F_{\text{fric}}/2r\gamma \) to allow us to compare results between different surfaces, droplet sizes, and applied \( F_N; F_{\text{fric}}/2r\gamma \) is also equivalent to the contact angle hysteresis \( \Delta \cos \theta \approx \Delta \theta^2/2 \) [28, 39, 40]. For underwater superoleophobic surface, we measured \( F_{\text{fric}}/2r\gamma \) as low as \( 3\times10^{-5} \) which is equivalent to \( \Delta \theta \approx 8\times10^{-3} \text{ rad} \) or 0.4\(^\circ\), a value that would be too low to measure accurately using conventional contact angle goniometry.

More interestingly, we found that \( F_{\text{fric}} \propto U \) for underwater superoleophobic surface (Inset, Fig. 5a), but is independent of \( U \) for superhydrophobic surface. This dis-
crepancy points to different dissipation processes for the two surfaces (Fig. 5b, c). For superhydrophobic surface, \( F_{\text{fric}} \) is dominated by contact-line pinning, while for underwater superoleophobic surface, \( F_{\text{fric}} \) is dominated by viscous flow in the nanometric water film beneath the droplet. This is reminiscent of the distinction between dry and lubricated frictions in tribology [30].

Previously, we experimentally verified the presence of water film thickness \( h_{\text{water}} \approx 100 \) nm that is stabilized by electric double layer forces for polyzwitterionic brushes [28]. Most of the viscous dissipation occurs in the advancing and receding front of size \( \lambda \approx \sqrt{R h_{\text{water}}} \). Hence, we expect

\[
F_{\text{fric}} \approx 2\pi r \lambda \left( \frac{\eta U}{h_{\text{water}}} \right) = 2\pi r \eta U \sqrt{R h_{\text{water}}}
\]

which is consistent with the experimental observation that \( F_{\text{fric}} \propto U \). Equation 5 can be rearranged to its non-dimensionalized form

\[
F_{\text{fric}}/2r\gamma \approx \pi \text{Ca} \sqrt{R h_{\text{water}}}
\]

where \( \text{Ca} = \eta U/\gamma \) is the capillary number. Both equations are consistent with our experimental results. For example, Equation 5 predicts \( F_{\text{fric}} \approx 100 \) pN for the oil droplet in Figure 4d consistent with the experimentally measured value.

Note that here we assume that the water inside the brush layer is bound and does not contribute to viscous dissipation. We also could not rule out the presence of non-viscous component to \( F_{\text{fric}} \) in underwater superoleophobic surface which can be important at lower contact line speed \( U \ll 1 \) \( \mu \) m s\(^{-1}\).

Finally, we would like to point out that the AFM technique described here measures surface wetting under dynamic conditions (i.e., with controlled contact-line speeds), which is different from conventional contact angle measurements which is primarily a static/quasi-static measurement with poorly controlled contact-line speeds. This is a point often ignored in the literature, which we discussed at lengths in a recent review paper [40].

**CONCLUSIONS**

In this paper, we demonstrated the versatility of droplet probe AFM as a surface wetting characterization tool by measuring contact-line frictions (with sub-nN resolutions) for different liquids (water and oil droplets) and under different ambient environments (in air and under water). Our approach can quantify surface wetting properties with controlled contact-line speeds, and when combined with the sensitivity of the technique allows us to probe the physical origins of the observed liquid-repellency for superhydrophobic and underwater superoleophobic surfaces.

**MATERIALS AND METHODS**

**Superhydrophobic Surfaces.** Black silicon surface was fabricated as described previously in the literature [26, 39]. Briefly, a maskless deep reactive ion etching (Oxford Plasmalab System 100, Oxford instruments UK) process was used to create the cone-shaped topography (7 min etch time, +110 degree celsius temperature, forward power 6 W, ICP power 1000W, 18 sccm of O\(_2\), and 40 sccm of SF\(_6\)). The surface was made superhydrophobic by depositing a nominally 40 nm thick fluoropolymer coating using a plasma-enhanced chemical vapour deposition process (Oxford Plasmalab 80+, 50 W power, 5 min deposition time, 100 sccm of CHF\(_3\)).

**Zwitterionic PSBMA surface preparation.** The polymer brush surfaces are prepared using surface initiated Atom Transfer Radical Polymerization (ATRP) using a protocol adapted from Azzaroni et al. (2006) [27] and described in details in our previous papers [16, 28].

**Probe liquid droplets:** Silicone oil (polyphenylmethyliolsiloxane, viscosity \( \sim 100 \) mPa.s, density 1.06g/ml) was purchased from Sigma-Aldrich. The water-oil interfacial tension is 40 mN/m for silicone oil as measured using the pendant drop method. Deionized water with a resistivity of 18.2 M\(\Omega\).cm was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).
We dissolved a small amount of salt (3 wt% CaCl$_2$) to water to prevent the microdroplets from drying out.

**Droplet probe AFM.** In our experiment, we used two different tipless cantilevers purchased from NanoSensors: TL-Cont (width $w = 40 \mu m$, length $L = 450 \mu m$, and thickness $t = 2 \mu m$) and Arrow-TL (width $w = 100 \mu m$, length $L = 500 \mu m$, and thickness $t = 1 \mu m$).

To create water microdroplets, we forced aqueous 3 wt% CaCl$_2$ solution through the nozzle of a conventional spray bottle onto the superhydrophobic surface. To create small oil droplets, we force 50 $\mu l$ of oil through a small capillary tube with inner and outer diameters of 360 $\mu m$ and 290 $\mu m$ into a petri-dish of water. The two methods generate multiple droplets with a broad range of sizes $2R = 20–200 \mu m$. We can then pick up a droplet of the desired size to perform contact-line friction measurements.

Sideview images in Figure 2 is taken using a special sideview cantilever holder provided by Bruker which incorporates a 45° mirror.

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**AUTHORS’ CONTRIBUTIONS**

D.D. conceived and planned the experiments. X.Q.K and C.T. executed the experimental work. V.J. fabricated the black silicon sample and provided helpful suggestions. D.D. analysed the experimental results and wrote the manuscript. All authors reviewed the manuscript.

**CONFLICTS OF INTEREST**

The authors declare no competing interests.

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