Quantifying contact line friction via oscillating droplet dynamics

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NEWS

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Quantifying contact line friction via oscillating droplet dynamics

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It was Wolfgang Pauli who famously said that "*God made the bulk, but the surface was invented by the devil*". The intermediate case of a liquid droplet sitting on a hydrophobic textured surface thus represents a very special kind of Purgatory—as anyone who has tried to measure the apparent contact angle in such a three-phase equilibrium configuration can attest. As Robin Ras and his coworkers note[1] the inherent hysteresis associated with contact line pinning events, the vanishing size of the contact area patch and the difficulty of resolving and imaging the exact location of the interface all conspire to dramatically increase the experimental uncertainty of the reported values of the contact angle. In this first issue of the new journal *Droplet* the authors report on a novel approach to making quantitative measurements of such situations using an Oscillating Droplet Tribometer (ODT). Using this technique, they show greatly improved resolution of the contact angle hysteresis that exists on a range of superhydrophobic surfaces, as well as the ability to resolve small systematic trends in the change of surface wettability associated with thermal treatments or fouling by other environmental factors.

To understand the devilish difficulty in making goniometric measurements on a superhydrophobic surface it is first important to recognize that the shape and mobility of a nonwetting liquid droplet placed on such a solid substrate is governed by not one, but *two*, contact angles; the advancing angle (as the liquid droplet advances over a dry clean surface) and a receding angle (as the liquid drop recedes from a bulk material that is now in thermodynamic equilibrium with an overlying liquid). The situation is further complicated by the presence of molecular scale wetting films with their own dynamics that are controlled by parameters such as the Hamaker constant and the topography of the surface (for more details of this microstructural viewpoint see the seminal review by De Gennes[2]). A range of different physicochemical phenomena associated with wetting, adhesion, and droplet dynamics are governed by these different measures of the three-phase contact line. I find a particularly useful way of representing this is in the form of the triangular diagram sketched in Figure 1. On the abscissa, the relative stickiness of a surface is quantified by a dimensionless thermodynamic work of adhesion $W_{adh}/\gamma_{lv} = 1 + \cos\theta_{rec}$ (where γ_{lv} is the interfacial tension of the liquid/vapor interface), which provides one measure of the work required to remove a liquid droplet from a wetted solid. On the vertical axis the contact angle hysteresis—as measured by the difference in cosines ($\cos\theta_{rec} - \cos\theta_{adv}$) provides a dimensionless measure of the pinning and frictional dynamics associated with moving a sessile droplet across a surface—and is sometimes reported alternatively in terms of a *roll-off angle* for droplet shedding.

Unfortunately, in many older publications often only one of these two contact angles is reported, and it is thus impossible to identify the precise locus of a droplet/surface pair on such a nomogram. This is critical because the surface mobility and dynamics of drops on surfaces vary dramatically with the values of these two coordinates. Superhydrophilic surfaces, and droplets sitting on liquid-infused surfaces or "LIS" (with very low resistance to droplet mobility) are located near the lower right corner of such a diagram.[3] The diagonal lines on this state diagram each correspond to a constant value of the advancing contact angle, θ_{adv}, but the specific locus on the line changes with varying levels of chemical and/or topological surface pinning. Flat and dry perfluorinated surfaces can achieve a maximum advancing contact angle of around 120–130°; to generate higher advancing angles

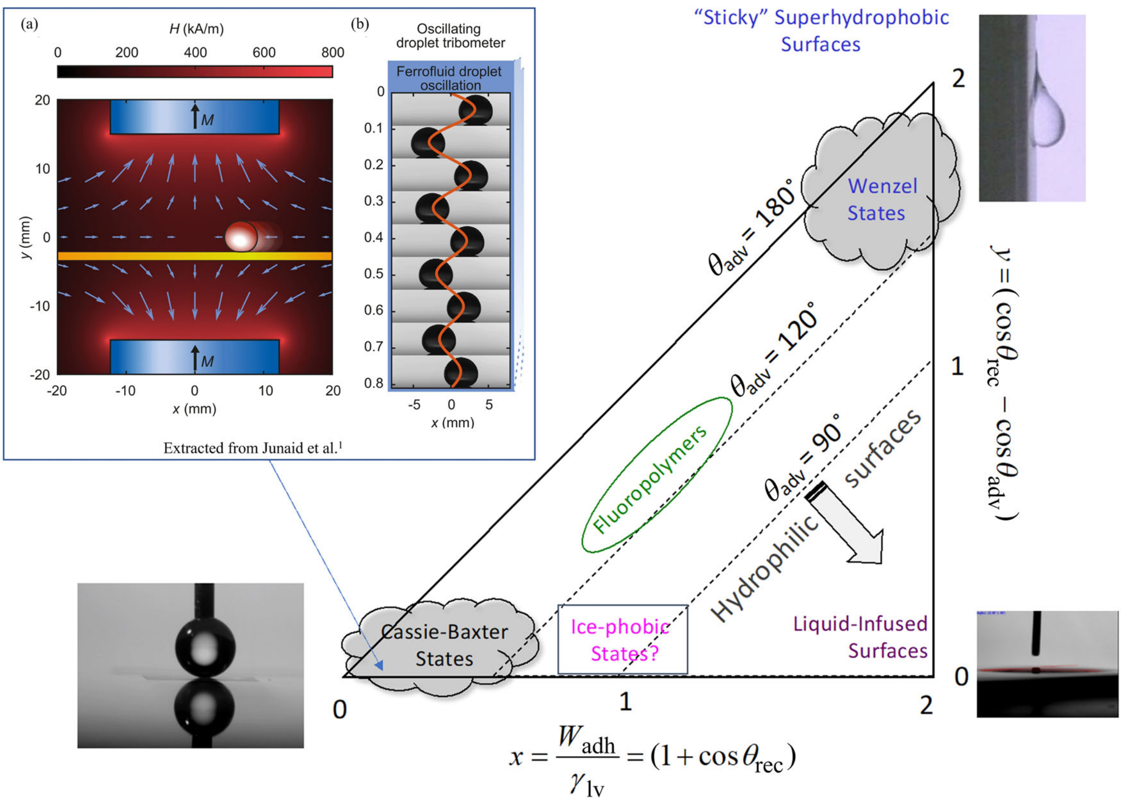

FIGURE 1 A triangular state diagram for conveniently locating and identifying the locus of different wetting states achievable with textured surfaces. The inset image shows the configuration of the oscillating droplet tribometer[1] that can be used to accurately measure the contact angle hysteresis and dynamic contact line friction of Cassie–Baxter droplets resting on textured superhydrophobic surfaces.

than represented by this contour line requires progressively greater levels of surface texturing. Strongly nonwetting surfaces are commonly identified by verbal statements such as "a contact angle of greater than 150°", but on hearing such statements one should ask *which contact angle is this referring to*? This is where the second measure comes in. Sticky superhydrophobic textured surfaces (or *Wenzel states*) with very high hysteresis and high levels of contact line pinning sit near the upper rightmost apex. Truly superhydrophobic surfaces typically correspond to a contact angle of more than 150° *and also* a contact angle hysteresis of less than 5° or 10°. Such surfaces are located near the lower left apex of this triangular state diagram, and it is this region that the work of Junaid et al.,[1] focuses on. Making accurate experimental measurements in this region is especially difficult because both the work of adhesion and the contact angle hysteresis approach zero. The shape of a sufficiently small droplet (so that gravity plays no role) approaches a perfect sphere that is singularly perturbed by a small-flattened region near its south pole. This small deformed region can dominate the dynamical mobility of a nonwetting droplet,[4] and special techniques are required to make reliable contact angle measurements in this region.[5,6] It is here that the ODT mapping technique, first described by Liimatainen et al.,[7] comes into its own. In the improved version of the instrument, described in this inaugural issue of *Droplet*, a small aqueous droplet of ferrofluid is carefully placed onto a surface between the poles of two rare earth permanent magnets as indicated in the upper left sketch. At equilibrium the droplet sits on the superhydrophobic surface at the focus of the magnetic trap (as indicated by the blue arrows). A small and rapid lateral perturbation of the droplet (or the trap) results in a series of damped oscillations as the system returns to equilibrium; the magnetic field imposes a lateral restoring force on the magnetically susceptible aqueous droplet, and the viscous dissipation associated with the local advancing and receding of the viscous drop's contact region across the textured surface dampens each successive oscillation. Similar under-damped oscillations can be observed in the motion of room-temperature Leidenfrost droplets as they skitter across a curved surface,[8] where in this case the restoring force is provided by gravity instead.

Measuring the droplet dynamics with a high-speed camera, and fitting the resulting motion to the second order equation for a damped oscillator, leads to exquisite sensibility in measuring the contact angle hysteresis. The authors report that with droplet volumes on the order of 10 µL their two-magnet ODT technique can resolve lateral forces as small as 0.5 µN and values of the contact angle hysteresis as small as $\Delta \cos\theta = \cos\theta_{rec} - \cos\theta_{adv} \approx 0.02$. As the authors explain, a unique benefit of this technique is that the sensitivity of their instrument actually *increases* as the hysteresis reduces (and the locus of the droplet on the triangular state diagram in Figure 1 approaches the apex). This is because the degree of damping progressively reduces and so the data series used for fitting and extracting $\Delta\cos\theta$ has more and more points to fit! Furthermore, by adjusting the vertical position of the substrate in the magnetic trap the vertical body force partially impaling the droplet on the textured surface can be systematically varied. In such a configuration the complex local hydrodynamic flow near the distorted liquid–vapor interface can be investigated. This may help guide selection of superhydrophobic topographies for advanced applications such as frictional drag reduction, where experiments show that the attainable level of friction reduction best correlates with contact angle measurements at elevated droplet pressures.[9]

Combining novel techniques such as this two magnet ODT (2mODT) to probe $\Delta\cos\theta = \cos\theta_{rec} - \cos\theta_{adv}$, together with conventional instrumentation such as dynamic surface tensiometry (which can directly probe the dynamics of θ_{adv} and θ_{rec} individually as a function of velocity) should provide unprecedented resolution of the dynamics of wetting on microstructured and textured substrates and provide data to help validate emergent molecular kinetic models of contact line friction.[10] We hope that *Droplet* will publish a range of experimental, computational, and theoretical contributions from the scientific community in this broad area in our future issues.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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REFERENCES

1. Junaid M, Nurmi HA, Latikka M, Vuckovac M, Ras RHA. Oscillating droplet tribometer for sensitive and reliable wetting characterization of superhydrophobic surfaces. *Droplet*. 2022. https://doi.org/10.1002/dro2.9
2. de Gennes PG. Wetting: Statics and dynamics. *Rev Mod Phys*. 1985;57:827-863.
3. Smith JD, Dhiman R, Anand S, et al. Droplet mobility on lubricant-impregnated surfaces. *Soft Matter*. 2013;9(6):1772-1780.
4. Mahadevan L, Pomeau Y. Rolling droplets. *Phys Fluids*. 1999;11(9):2449-2453.
5. Srinivasan S, McKinley GH, Cohen RE. Assessing the accuracy of contact angle measurements using sessile drops on liquid-repellent surfaces. *Langmuir*. 2011;27(22):13582-13589.
6. Vuckovac M, Latikka M, Liu K, Huhtamäki T, Ras RHA. Uncertainties in contact angle goniometry. *Soft Matter*. 2019;15(35):7089-7096.
7. Liimatainen V, Vuckovac M, Jokinen V, et al. Mapping microscale wetting variations on biological and synthetic water-repellent surfaces. *Nat Commun*. 2017;8:1798.
8. Panchanathan D, Bourrianne P, Nicollier P, Chottratanapituk A, Varanasi KK, McKinley GH. Levitation of fizzy drops. *Sci Adv*. 2021;7(28):eabf0888.
9. Golovin KB, Gose JW, Perlin M, Ceccio SL, Tuteja A. Bioinspired surfaces for turbulent drag reduction. *Philos Trans A Math Phys Eng Sci*. 2016;374(2073):20160189.
10. Lee E, Müller-Plathe F. Contact line friction and dynamic contact angles of a capillary bridge between superhydrophobic nanostructured surfaces. *J Chem Phys*. 2022;157(2):024701.

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