MATERIALS SCIENCE

Improving surface-wetting characterization

Awareness of instrument inaccuracies will boost the development of liquid-repellent coatings

By **Kai Liu,[1] Maja Vuckovac,[1] Mika Latikka,[1] Tommi Huhtamäki,[1] Robin H. A. Ras[1,2]**

Highly hydrophobic surfaces have numerous useful properties; for example, they can shed water, be self-cleaning, and prevent fogging (*1*, *2*). Surface hydrophobicity is generally characterized with contact angle (CA) goniometry. With a history of more than 200 years (*3*), the measurement of CAs was and still is considered the gold standard in wettability characterization, serving to benchmark surfaces across the entire wettability spectrum from superhydrophilic (CA of 0°) to superhydrophobic (CA of 150° to 180°). However, apart from a few reports [e.g., (*4*–*8*)], the inherent measurement inaccuracy of the CA goniometer has been largely overlooked by its users. The development of next-generation liquid-repellent coatings depends on raising awareness of the limitations of CA measurements and adopting more sensitive methods that measure forces.

CAs reveal the equilibrium states of droplets deposited on surfaces. However, each surface has a range of metastable CAs, and a static CA has a random value in this range. Thus, measuring the minimum and maximum values of the range, termed the receding and advancing contact angles (RCA and ACA), is recommended. This is done by decreasing (RCA) or increasing (ACA) the droplet volume with a needle until the contact line starts to recede or advance on the surface (*9*). RCA and ACA are often confusingly called "dynamic CAs," although this terminology should be avoided because the measurements are performed slowly and quasi-statically. Droplet mobility is related to the difference between ACA and RCA, called contact angle hysteresis (CAH). In addition to CAH, mobility is often quantified by tilting the surface below the test droplet until the sliding angle is reached and the droplet begins to move. However, sliding-angle measurements are sensitive to details of the experiment, such as droplet volume and how the droplet was placed on the surface, which can make comparison of results challenging (*10*).

Despite being useful quantities in wetting characterization, CAs suffer from practical limitations. The results obtained by independent scientists can vary by up to 10° even with the same setup, especially for CAs exceeding 150° (*4*, *5*), which makes meaningful comparisons almost impossible.

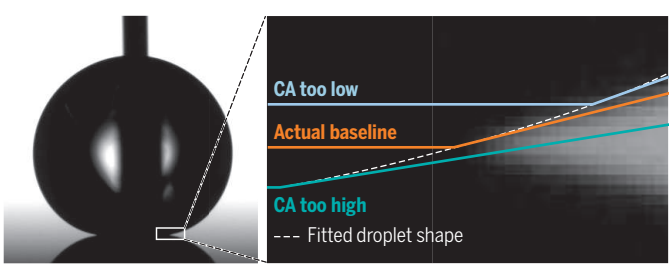
All measurements of CA involve taking a profile image of the droplet followed by image analysis (*4*–*9*). The inaccuracies mainly originate from optical distortions and are affected by experimental parameters such as magnification, lighting, contrast, and camera resolution. The optical distortions are large near the baseline (i.e., the boundary between the solid surface and the liquid droplet in the two-dimensional image; see the figure, top). Not only is the droplet edge diffuse, but it also becomes heavily pixelated, even when a goniometer with a high-resolution camera is used. The diffuse edge and pixelation necessarily introduce a substantial systematic error in CA from about 1° to beyond 10° because of the uncertainty in baseline placement, which becomes subjective. Even the automatic baseline detection feature in goniometer software often fails, likely because of the short baseline length on highly hydrophobic surfaces. Despite the continuous improvement of experimental procedures (*9*, *11*) and analysis methods (*6*–*8*) of CA goniometry, these problems still persist.

The errors in CA resulting from one-pixel displacement of the baseline are shown in the bottom panel of the figure. Simulations (*5*) and experiments match and demonstrate how the error increases substantially for increasing CA, especially upon reaching the superhydrophobic regime. The uncertainty range in CA corresponds to ~1° for CAs less than 120°, ~2° for CAs of ~150°, and ~5° for CAs of ~162°. Propagation of errors in subtraction make the uncertainty of CAH even worse, up to $\sqrt{2}$ times greater than for single CA values. Droplet reflection (as depicted in the figure, top) can somewhat facilitate the baseline determination, but only for reflective surfaces. Moreover, macroscopically rough surfaces, such as woven textiles, have an irregular baseline and the contact angle is ill-defined.

Droplet shedding and sliding on repellent surfaces are governed by adhesion and friction forces, which are related to con-

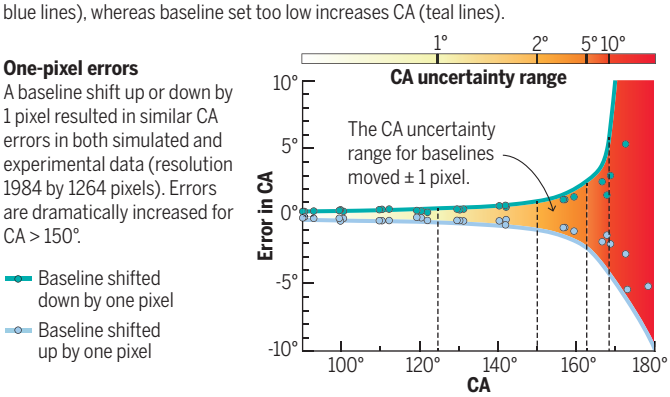
Tricky contact angle imaging

A simple method for determining surface wetting, measuring contact angles (CAs) of water droplets, can be misleading for superhydrophobic surfaces because of difficulties in positioning the baseline (for more details, see supplementary materials).



(Mis)placing baselines
A droplet image (camera resolution 1984 by 1264 pixels) during CA measurement on a superhydrophobic surface and high-magnification zoom image. Inaccurate baseline position causes errors in CA measurement; baseline set too high decreases CA (light-blue lines), whereas baseline set too low increases CA (teal lines).

One-pixel errors
A baseline shift up or down by 1 pixel resulted in similar CA errors in both simulated and experimental data (resolution 1984 by 1264 pixels). Errors are dramatically increased for CA > 150°.



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tact angles: $F \sim \cos RCA - \cos ACA$. When CAH is low, even a small error in baseline placement causes huge relative errors in CAH and in the calculated adhesion force. For example, for a superhydrophobic surface with RCA of 170°, an error of just one pixel in the baseline height can result in at least 300% error in CAH and adhesion force. Thus, CAH is in practice poorly suited for characterization of highly repellent surfaces. Even with improved optics, such as enhanced camera resolution, the error near the upper CA limit will remain high.

We propose the use of force measurements to characterize hydrophobic surfaces. The classic Wilhelmy plate technique is limited by strict constraints on sample geometry and gives no information about local wetting properties (*12*). However, it is now possible to detect tiny forces between droplets and surfaces. Measuring the deflection of a thin capillary inserted in a droplet (*13*) can determine droplet friction. The oscillating droplet tribometer uses back-and-forth motion of a magnetic water droplet to measure droplet friction forces down to 10 nN (*14*). Scanning droplet adhesion microscopy can measure adhesion forces as small as 5 nN and map wetting properties at microscale spatial resolution (*15*). These newer methods offer more accurate wetting measurements, especially on highly hydrophobic surfaces. ■

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SUPPLEMENTARY MATERIALS

www.sciencemag.org/content/363/6432/1147/suppl/DC1
Supplementary Text
Table S1
Fig. S1
Numerical Modeling (Simulations)

10.1126/science.aav5388

SIGNALING

Histone modifiers are oxygen sensors

Hypoxia signals directly to chromatin via histone demethylases to alter gene expression

By **Paolo Gallipoli** *and* **Brian J. P. Huntly**

Approximately 2.6 billion years ago, during the Proterozoic period, the evolution of photosynthesis in cyanobacteria led to the introduction of the by-product of this reaction, oxygen, into Earth's atmosphere (*1*). This great oxidative event heralded the rise of multicellular organisms, which are almost totally dependent on oxygen as an efficient fuel for metabolism and as a cofactor in many critical physiological enzymatic reactions. Central to this adaptation, and to allow cellular physiology across a wide range of oxygen concentrations (tensions), metazoans have evolved the highly conserved hypoxia-inducible factor (HIF) pathway (*2*). This is important for both physiological and pathological processes that occur in a hypoxic microenvironment, including embryogenesis, stem cell homeostasis, cancer, and cardiovascular disease. It has long been observed that hypoxia induces histone lysine hypermethylation, a form of epigenetic chromatin modification. However, whether this represents a direct sensing of oxygen tension or an indirect effect, perhaps through the HIF pathway, has not been established (*3*). On pages 1222 and 1217 of this issue, Batie *et al.* (*4*) and Chakraborty *et al.* (*5*), respectively, resolve this question, demonstrating in different cellular systems that the activity of the lysine-specific demethylases (KDMs) KDM5A and KDM6A is oxygen sensitive, and thereby identifying them as oxygen sensors.

> ***"...oxygen sensing by [lysine-specific demethylases] might also be therapeutically targeted..."***

In ambient normoxic conditions, HIF-1α, the DNA-binding component of the HIF heterodimeric transcription factor complex, is targeted for ubiquitylation and destruction. This occurs through hydroxylation on proline residues in HIF-1α by the EglN family of prolyl hydroxylases (PHDs), which are 2-oxoglutarate– and oxygen-dependent dioxygenase enzymes that sense physiological changes in oxygen tension and are activated in normoxia. However, in hypoxic conditions, PHD activity is lost and HIF-1α is stabilized so that it can bind to its partner ARNT (aryl hydrocarbon nuclear translocator; also called HIF-1β). The HIF complex translocates to the nucleus and induces hypoxia-specific gene expression programs that mediate altered cellular metabolism and survival through binding to specialized hypoxia response elements (HREs) in target gene promoters. The family of 2-oxoglutarate– and oxygen-dependent dioxygenases is large, with more than 60 members (*6*), and also includes the TET and JmjC (Jumonji-C) KDM families of epigenetic regulators.

Using biochemical analysis of recombinant proteins, Batie *et al.* and Chakraborty *et al.* have added KDM5A and KDM6A to the list of dioxygenases that have low oxygen affinities (K_M values) comparable to those of the EglN PHD family. Batie *et al.* also used time course experiments to show that histone methylation changes after the induction of hypoxia were rapid and preceded subsequent transcriptional events. Using cellular systems expressing loss-of-function and gain-of-function mutant proteins in the HIF pathway and through documenting the speed of HIF-1α stabilization following induction of hypoxia, histone methylation changes were found to be independent of HIF as well as independent of other known hypoxia-inducible inhibitors of KDM activity, such as reactive oxygen species and 2-hydroxyglutarate.

Linking direct histone hypermethylation to cellular function, Chakraborty *et al.* demonstrated that hypermethylation of lysine 27 of histone H3 (H3K27), a histone change that is associated with gene repression, prevented differentiation in different cell line model systems. Conversely, these effects could be antagonized by inhibition of the reciprocal histone methyltransferase EZH2 (enhancer of zeste homolog 2).

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