Liu, Kai; Vuckovac, Maja; Latikka, Mika; Huhtamäki, Tommi; Ras, Robin H.A.

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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. Ras1,2*

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°–180°). However, apart from a few reports, including (4–8), the measurement inaccuracy has been largely overlooked by users of the CA goniometer. Raising awareness of the limitations of CA measurements and the development of alternative, more sensitive methods is essential for the development of next-generation liquid-repellent coatings for advanced applications.

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, giving only limited information about surface wettability. Therefore, measuring the minimum and maximum values of the range, termed 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,” though we discourage that terminology 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 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 using the same setup, especially for CAs > 150° (4, 5). Such huge inaccuracy entails that it becomes difficult if not impossible to meaningfully compare CA values for superhydrophobic surfaces toward the upper CA limit. 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 significant near the baseline, i.e., the boundary between the solid surface and the liquid droplet in the two-dimensional image (Figure 1a). 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 (Figure 1b). Even 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 contact angle goniometry, these problems still persist.

The errors in CA resulting from one-pixel displacement of the baseline are shown in Figure 1c. Simulations (S) and experiments match well and demonstrate how the error increases substantially for increasing CA, especially upon reaching the superhydrophobic regime. The uncertainty range in CA corresponds to approximately 1° for CAs below 120°, 2° for CA around 150° and 5° for CA around 162°. Note that errors will be more significant for goniometers with poorer camera resolution. Due to the propagation of error in subtraction, the uncertainty of CAH is even worse, up to v = 1.4 times greater than for single CA values. Droplet reflection (as in Figure 1a) 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 contact angles: $F \propto \cos \text{RCA} - \cos \text{ACA}$. 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 will result in at least 300% error in CAH and adhesion force. As a result, CAH is in practice poorly suited for characterization of highly repellent surfaces. Even if future CA goniometers were to feature improved optics, such as enhanced camera resolution, the error near the upper CA limit will remain high.

We encourage researchers to rethink the relevance of contact angles in hydrophobic surface characterization and propose force as the next-generation benchmark quantity. In classic Wilhelmy plate technique, the whole sample is dipped in water while measuring the force acting on it. However, this method sets strict constraints on sample geometry and gives no information about local wetting properties (12). Recent progress has enabled the detection of the (previously undetectable) tiny forces between droplet and surfaces, making local measurements possible. Droplet friction force can be determined by measuring the deflection of a thin capillary inserted in a droplet (13). The oscillating droplet tribometer uses back-and-forth motion of a magnetic water droplet to measure droplet friction forces down to 10 nN (14). Droplet adhesion forces as small as nN can be measured by scanning droplet adhesion microscopy, allowing mapping of wetting properties at nanoscale spatial resolution (15). These novel methods avoid the optical limitations present in goniometry and offer more accurate wetting measurements especially on highly hydrophobic surfaces.

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