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Surface-wetting characterization using contact-angle measurements

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Wetting, the process of water interacting with a surface, is critical in our everyday lives and in many biological and technological systems. The contact angle is the angle at the interface where water, air and solid meet, and its value is a measure of how likely the surface is to be wetted by the water. Low contact-angle values demonstrate a tendency of the water to spread and adhere to the surface, whereas high contact-angle values show the surface's tendency to repel water. The most common method for surface-wetting characterization is sessile-drop goniometry, due to its simplicity. The method determines the contact angle from the shape of the droplet and can be applied to a wide variety of materials, from biological surfaces to polymers, metals, ceramics, minerals and so on. The apparent simplicity of the method is misleading, however, and obtaining meaningful results requires minimization of random and systematic errors. This article provides a protocol for performing reliable and reproducible measurements of the advancing contact angle (ACA) and the receding contact angle (RCA) by slowly increasing and reducing the volume of a probe drop, respectively. One pair of ACA and RCA measurements takes ~15–20 min to complete, whereas the whole protocol with repeat measurements may take ~1–2 h. This protocol focuses on using water as a probe liquid, and advice is given on how it can be modified for the use of other probe liquids.

Introduction

Surface wettability has an important role in many biological, chemical and physical processes. Development of a water-repellent cuticle, which covers and protects the aboveground organs of flowers, leaves and fruits, was one of the key evolutionary developments that allowed plants to spread from their primarily aquatic environment to land[1]. Some plants and animals have developed unique wetting properties to facilitate life in extreme circumstances: water-striders have legs that facilitate floatation to allow walking on water[2], lotus leaves have self-cleaning properties to keep themselves clean in marshy environments[3] and the Namib desert beetle harvests water vapor to survive in an arid desert environment[4], to name a few. In agriculture, the efficiency of pesticides is strongly affected by the wettability of the plants, as well as the surface tension and viscosity of the liquid pesticide formulations. In medicine, decreasing the contact angle of titanium implants allows for better bone-cell attachment, enabling better integration of the implant with the bone[5]. Antimicrobial properties of food packaging can be optimized by increasing the contact angle of the package materials, which allows for prolonged release of antimicrobial agents and leads to increased shelf life of, for example, meat products and poultry[6].

Wetting also has an important role in many industrial processes: for painting and printing, both the liquid surface tension and the properties of the solid must be optimized to ensure suitable adhesion of the liquid to the solid[7]. Solid surface energy must be considered in many processes requiring, for example, heat transfer or lubrication. In oil recovery, the solid material must be designed to selectively absorb oil but not water, a quality also determined by its wetting properties[8].

Wetting is commonly characterized by the contact angle, which is defined as the angle between the tangent to the liquid–vapor interface and the solid surface at the three-phase contact line (Fig. 1). By convention, the contact angle is measured from the liquid side. The contact angle between liquid and

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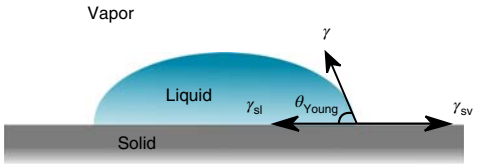

Fig. 1 | A drop of water on an ideal solid substrate. Young contact angle (θ_{Young}) is determined by a balance of the horizontal projection of the surface tension of the water along the solid surface ($\gamma \cos\theta_{Young}$) and interfacial tensions γ_{sv} and γ_{sl}.

an ideal solid surface (i.e., one that is atomically smooth, chemically homogeneous, nonreactive and nondeformable by the liquid) has traditionally been defined using the Young equation:[9]

$$\cos\theta_{Young} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma},$$

where θ_{Young} is the Young contact angle, γ_{sv} and γ_{sl} the solid–vapor and solid–liquid interfacial tensions, respectively, and γ the surface tension of the liquid. From the Young equation, it is known that a solid surface with high surface energy (i.e., high solid–vapor interfacial tension γ_{sv}) tends to show a low contact angle, whereas a low-energy surface would exhibit a high contact angle.

A real surface that is considered to be close to ideal is a high-quality silicon wafer: it is smooth at the atomic level and can be chemically homogeneous when handled in clean-room environment. Yet, even silicon wafers, chemically unmodified ones as well as those coated with high-quality smooth films with various surface energies, have a range of stable static contact angles[10]. The phenomenon is evident from our everyday experiences: if solid surfaces were to have only a single stable contact angle, the slightest tilt of a solid would lead to movement of a drop. This is because tilting the solid surface would lead the contact angles to deviate from the Young contact angle, and a drop at an unstable contact angle would not be able to resist the force of gravity and would therefore move. Yet we see stable water drops on inclined surfaces all the time, for example, on a windshield of a car and on various parts of plants (Fig. 2).

Sessile-drop goniometry

The method of measuring contact angles in the protocol is called sessile-drop goniometry. It is performed by recording a video of a water drop on a solid surface and determining the contact angle from the images of the video by a fitting procedure. The apparent simplicity of the method is misleading: when contact-angle measurements are published in the literature, often a 'static' or 'as-placed' contact angle is reported, as measured by depositing a drop on the surface. This approach presumes that the deposited drop would be in a global energy minimum and therefore in a stable state that corresponds to the Young contact angle (Fig. 3a). However, the drop can be in any local energy minimum within the hysteresis range and would in other words be metastable (Fig. 3b). The measurements of a static contact angle are therefore not necessarily reproducible, and a single contact-angle value fails to provide important information about solid–water interactions determined by contact-angle hysteresis[11]. A method enabling the drop to reach the most stable contact angle, by overcoming the energy barriers separating the local energy minima using mechanical vibrations of the sample surface, has been demonstrated in the literature[12]. However, this technique is currently not found in commercially available goniometers.

The two reproducibly measurable contact angles are the ACA and the RCA, the highest and the lowest angle in the hysteresis range, as measured by increasing and decreasing, respectively, the droplet volume (Fig. 4). When the drop volume increases, the contact angle of the drop will increase, and the contact line will remain pinned until the ACA is reached (Fig. 4a–c). Further increase of drop volume will lead to movement of the contact line, whereas the contact angle remains constant.

Conversely, when drop volume decreases, the contact line of the drop will remain static and only the shape of the drop changes until the RCA is reached (Fig. 4d,e). Further decrease of drop volume will lead to movement of the contact line, whereas the contact angle remains ideally constant but can vary in measurements because of nonuniformity of the sample. Contact-angle hysteresis, which is critical for evaluating the mobility of a drop on a surface, can be defined as the difference between the ACA and the RCA ($\theta_a - \theta_r$)[13], or alternatively as the difference between their cosines ($\cos\theta_r - \cos\theta_a$)[14].

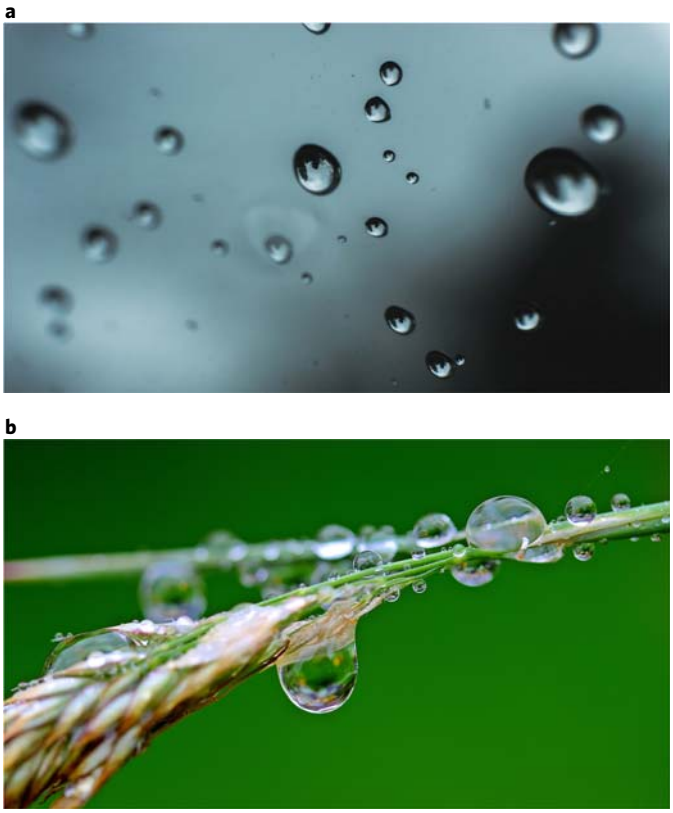

Fig. 2 | Static water drops. a,**b**, Static water drops on a glass window (**a**) and on a plant surface (**b**). Images were taken from https://www.pexels.com/photo/clear-close-up-dew-drop-of-water-371075/ and https://www.pexels.com/photo/macro-photography-of-morning-dew-drop-on-the-plants-stem-144241/.

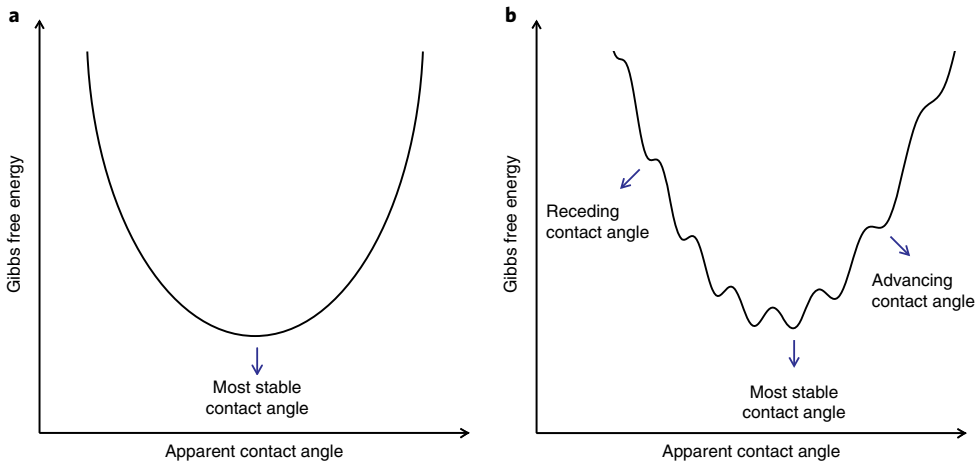

Fig. 3 | Sketch of the Gibbs free energies of ideal and real wetting systems as a function of the apparent contact angle. a, Free energy of a wetting system between an ideal solid surface, water and gas. The wetting system has only a single free-energy minimum, corresponding to the most stable contact angle, which is also the Young contact angle. **b**, The wetting system of a real solid surface has the most stable contact angle at the global minimum free energy but also has several metastable static contact angles, corresponding to the local free-energy minima. Owing to the energy barrier between the local free-energy minima of a real solid surface, a deposited 'static' drop can be in any of the free-energy minima within the hysteresis range. As it is not possible to know in which free-energy minima a static drop is by current contact-angle characterization methods, the advancing and the receding contact angles are the only reproducibly measurable contact angles.

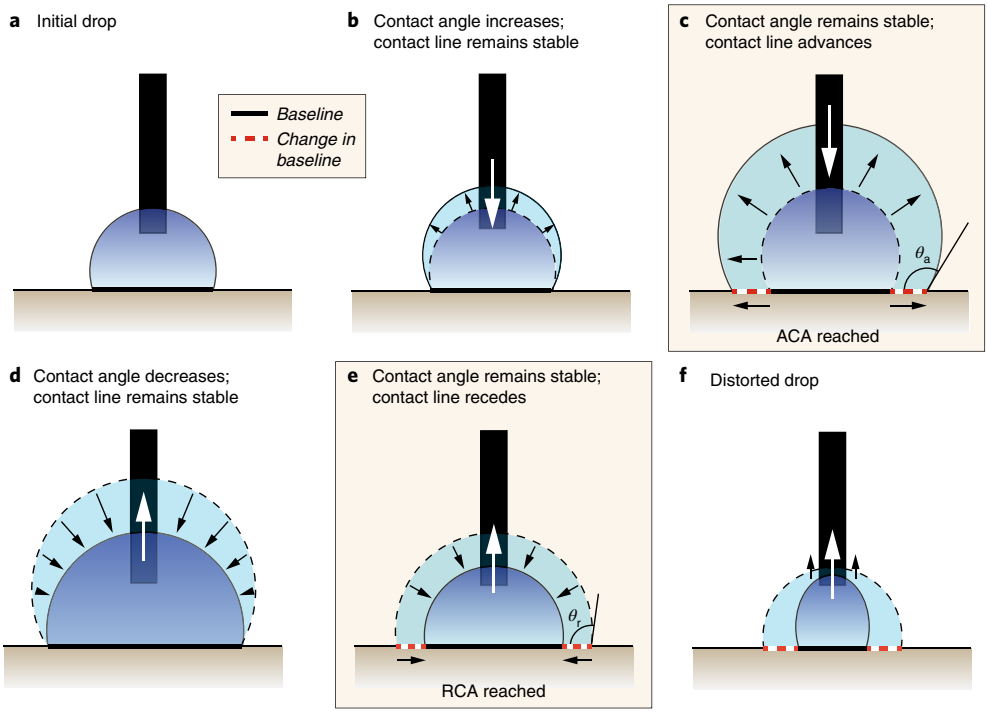

Fig. 4 | Different stages of ACA and RCA measurement. The white arrows point to water pumped in during the ACA measurement, and pumped out of the droplet during the RCA measurement. The ACA and RCA are reached in stages **c** and **e**, respectively, and are highlighted with boxes. **a**, An initial 2-μL droplet is deposited. **b**, Water is added to the drop before the measurement is started. At this stage, the ACA is not necessarily reached: the shape of the droplet changes, but the baseline (highlighted with a black line) remains stable. **c**, The ACA is reached, the baseline advances steadily as water is added, and the droplet volume increases from 3 to 10 μL while a video is recorded. **d**, In RCA measurements, water is first removed from an initial drop before recording of the video is started. At this stage, the RCA is not yet necessarily reached; the shape of the drop changes, and the baseline remains stable. **e**, RCA is reached, and the baseline recedes steadily as droplet volume is decreased from 10 to 3 μL while a video is recorded. **f**, A droplet smaller than 3 μL becomes distorted by the needle and the data are not reliable.

The larger the difference between the ACA and the RCA, the less mobile the drop is. Although the difference in cosines is more closely based on the physics underlying the measurement, it is often simpler to just report the difference between the angles.

The ACA and the RCA are often misleadingly called dynamic contact angles. They are not dynamic, however, but (quasi-)static instead. Care should therefore be taken in the measurements to avoid dynamic effects. We encourage the restriction of the term dynamic contact angle to dynamic events in which the contact angle changes rapidly and the value of the contact angle depends on the speed of the moving contact line, such as in the cases of forced flow, and spontaneous spreading and penetration[15,16]. In this protocol, we provide instructions on how to generate reproducible and meaningful contact-angle data. The protocol is based on our own experience of contact-angle measurement and on the measurement guides previously published in the literature[11,17–20].

Comparison of different methods for surface-wetting characterization

Most methods for wetting characterization can be classified into two main groups. In optical methods, the shape of a droplet is measured, whereas most other methods assess the force exerted by water on the solid. Owing to its versatility and ease of use, the optical method called sessile-drop goniometry is probably the most widely used. Other optical methods include, for example, the tilting-plate method, in which the tilt angle of a sample surface with a drop is gradually increased until the drop starts moving, and this so-called sliding angle is recorded. The Wilhelmy plate technique is an example of a force-based method: the sample is dipped in water and the force acting on the sample is measured, from which the contact angle can be calculated[21]. Recently, we introduced scanning droplet adhesion microscopy, which allows measurement of droplet adhesion forces as small as a nanonewton and construction of wetting maps that depict microscale spatial variation in wettability[22].

Table 1 | Different wetting characterization methods

Method	Description	Advantages	Disadvantages
Direct methods			
Sessile-drop goniometry	The volume of a drop deposited on the measured surface is increased, and the value of the ACA is obtained from the advancing contact line. For the RCA, the volume of the drop is reduced, and the value of the RCA is obtained from the receding contact line	Simple	Susceptible to operator error if a strict protocol is not used
		Small amounts of water are required	Collecting information from a large area requires measurements at multiple locations, and is thus time consuming
		It is possible to measure samples with small surface areas	Small amounts of impurities in the water may cause experimental error
		Provides information about the uniformity of the sample	
Tilting plate	Contact angles are measured from the leading edge and the trailing edge of a distorted drop on an inclined plane when the drop starts sliding. The tilt angle at which the drop starts sliding is called 'sliding angle', and is a measure of droplet mobility.	Simple	The measured contact angles do not necessarily correspond to the ACA and the RCA. The sliding angle does not necessarily correspond to the contact angle hysteresis.
		It is quick to perform	The recorded values also depend on the size of the drop used in the measurements—the obtained values are not necessarily a property of the measured surface alone
Indirect methods			
Wilhelmy plate	The sample surface in the form of a thin plate is dipped vertically into water, and the contact angle is determined from the measured force. The change in the force is a combination of buoyancy and the force of wetting	No operator error	Does not provide information about the uniformity of the surface
	The ACA and the RCA can be measured by dipping the sample into the water or withdrawing the sample from the water	Ease of automation	There is no visual feedback to help detect how wetting occurs
		Information from large areas of the sample is gathered quickly	The sample should have the same composition and morphology on all surfaces: front, back and sides
			The relationship between the measured force and the obtained contact angle depends on the length of the contact line, which may be hard to determine for rough surfaces

The tilting-plate method is sometimes used to measure ACAs and RCAs, although that method is not recommended, for the reasons explained below. In this approach, the tilt angle of the plate is increased, and the contact angles on the upper and the lower side of the drop are measured just before the drop starts moving. The lower angle of the drop is taken to represent the ACA, and the upper angle is taken to represent the RCA. The contact angles on opposite sides of a drop on a tilted plate are not independent of each other, however, and the lower angle does not in general reach the ACA simultaneously with the upper angle reaching the RCA. In addition, for the reason stated above, the

sliding angle as measured by the tilting-plate method does not necessarily represent the contact-angle hysteresis. The sliding angle has been shown to depend on the size of the drop, whereas the contact-angle hysteresis is a surface property and does not depend on drop size[23,24].

Each measurement technique has its own strengths and shortcomings, and the most suitable technique depends on the application. An overview of some of the techniques available for contact-angle measurement is provided in Table 1. Details of the various methods are out of the scope of this article and can be found elsewhere in the literature[11,12,17,18,20].

Experimental design

The measurements in this protocol are performed using the so-called needle-in-drop sessile drop. The ACAs and the RCAs are measured by slowly pumping water in and out of a needle using a motorized syringe. The needle is located in close proximity to the sample, so that the tip of the needle is embedded in the water drop.

Video is recorded when water is being pumped to the drop slowly from the syringe via the needle, and the water front advances on the sample. Each image of this video is later analyzed to determine the contact angle at the moment the image was captured, and the contact-angle values from all the images are averaged to gain the ACA of the measurement. Video for the RCA is recorded when water is being removed from the surface, and the results are analyzed in the same way as for the ACA.

The analysis is performed by a software-based fitting procedure that finds the edge between the water drop and the surrounding gas. The analysis is done after the measurement and the recording of the video have been stopped, not during the measurement itself. The baseline, which is the line between the solid surface and the water in the two-dimensional images, can be determined automatically by the software or placed manually by the operator. We recommend placing it manually to avoid errors from the automatic procedure, as differences in contrast between water and the solid are often low, and automatic determination can be problematic.

The value of the contact angle in a single measurement is determined by performing a software-based fitting procedure on each of the recorded images and calculating the average of the obtained values (see Box 1 for details about different fitting methods). The relatively large volume range of a single measurement ensures that there is statistical averaging of several dozens of data points in the result obtained (see Box 2 for details on the effects of drop size on the results of the measurements).

Calculate the ACA and the RCA values of a sample as an average of five or more measurements. Vary the position of the measurement on the sample each time to gain information about the homogeneity of the wetting properties. Report both the ACA and the RCA averages, as well as the standard deviation of the measurements.

Materials

Reagents

- Sample
- Milli-Q water (Millipore, water purification system model Direct-Q 3 UV)

Equipment

- Goniometer (Biolin Scientific, model Attension Theta)

Equipment setup

Goniometer setup

Commercial goniometers typically include a motorized syringe for precisely controlling the volume of the deposited drop and a software-operated camera for capturing images of the drop. The contact angle is determined for each image by a software-operated fitting procedure, but it requires operator input.

The current generation of goniometers usually have modular design, enabling the accommodation of additional capabilities, for example, a high-temperature environmental chamber, pressure chamber, tilting base and automated droplet dispensing. If a high-speed camera system is installed, the dynamics of the wetting process can also be studied. The goniometer should be set on a sturdy table to prevent the disturbance of external vibrations, as vibrations can cause error in the measurement. Airflow from room ventilation may also cause droplet vibrations and, if needed, can be avoided by placing the goniometer in a cabinet. The measurements are best carried out in air sufficiently clean of

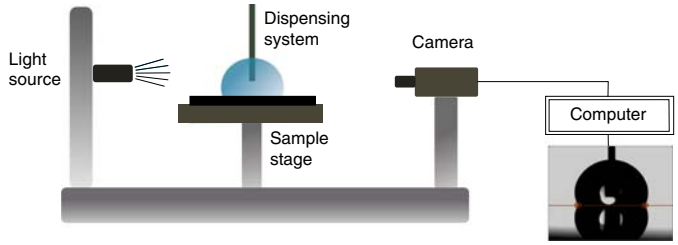

Fig. 5 | Sketch of a goniometer setup. A basic goniometer consists of a light source, an adjustable sample stage, a dispensing system (motorized syringe connected to a needle by tubing), a camera to record video and a computer for data analysis.

Box 1 | Considerations about curve fitting

Curve fitting is performed to determine the profile of the droplet using the contrast gradient between the liquid and the gas phases in the recorded images. Automatic fitting is a feature in the manufacturer-provided software, and usually several possible fitting methods are provided. The 'baseline'—the line of contact between the solid, liquid and gas in the two-dimensional image—must be determined before the curve fitting can be performed. The baseline can be placed either automatically (using the manufacturer-provided software), or manually (by the operator). We recommend doing it manually, as the automatic determination often fails. The contact angle is then measured by the manufacturer-provided software from the contact point of the baseline and the fitted curve.

The accuracy of the fitting procedure will eventually determine the quality of the data, and considerable errors may result from incorrect procedures. Several mathematical methods can be used for curve fitting, including but not limited to the following: Young–Laplace, circle, elliptical, polynomial and B-spline snakes. Their suitability varies depending on the type of the sample and the size of the drop.

- The Young–Laplace method (also called axisymmetric drop-shape analysis (ADSA)[27]) is the only curve-fitting method with a physical basis, as it analyzes the drop shape based on the Young–Laplace equation. Axisymmetry means rotational symmetry around an axis—in this instance, the rotational axis is normal to the solid surface, and as a result, the solid–liquid–gas contact line is circular. The method uses a strategy to fit the shape of the drop in the recorded image to a theoretical drop profile according to the Young–Laplace equation of capillarity, which describes the pressure inside a drop based on the curvature and the surface tension: $\Delta p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$.

  In the fitting procedure, the surface tension is used as an adjustable parameter. The best fit identifies the correct surface tension from which the contact angle can be determined by a numerical integration of the Laplace equation. We recommend using the Young–Laplace method in most circumstances, not only because it has a physical basis, but because it also provides excellent reproducibility and precision. Because it assumes an axisymmetric drop, it will give large errors in the case of nonaxisymmetric drops (e.g., when measuring very hydrophilic or macroscopically rough surfaces). However, the contact angle is ill-defined in the absence of axisymmetry anyway.
- The circle method assumes a circular shape for the drop in the two-dimensional images recorded by the camera and therefore works best for drops with diameters much smaller than the capillary length on hydrophobic surfaces. Capillary length (λ_c) is the characteristic length scale for the interface between a liquid and a gas, and is defined as $\lambda_c = \sqrt{\frac{\gamma}{\rho g}}$, where γ is the liquid surface tension, ρ the density of the liquid and g the gravitational acceleration. For water and air, the capillary length is ~2.7 mm.
- Polynomial and B-spline snakes make no assumption of the drop shape but fit a polynomial equation locally at the contact point.
- The fitting error should be checked after the fitting procedure by comparing the fitted curve and the actual profile of the drop in the recorded image. If the fitted line does not follow the edge of the drop, the data should be discarded and the video should be reanalyzed. Potential causes that can be adjusted for reanalysis are the fitting method and the location of the baseline. If reanalysis does not lead to improvement, a new measurement must be performed.
- In general, different fitting methods give different sizes of errors depending on the size of the drop and the type of surface characterized.

organic vapors and dust. Organic vapors may adsorb on the sample surface or on the probe droplet and modify their surface properties. Airborne dust adsorbing on the sample or the water can also have adverse effects on the measurements.

Room conditions

The humidity and temperature of the room are preferred to be kept steady. For water, for example, temperatures between 20 and 40 °C have been shown to have little effect on the surface tension[25,26], therefore, small changes in temperature are not expected to affect contact-angle measurements

Box 2 | What drop size to use?

Despite the size of the drop being absent from the Young equation, the results of contact-angle measurements are sensitive to the size of the drop used to measure them. The appropriate size of the drop is a balance between the deviations from the theoretical contact angles caused by small drops and those caused by big drops. In our protocol, the drop sizes used to measure ACAs and RCAs, respectively, increase and decrease between 3 and 10 μL to balance the errors for small and large drops. Drops smaller than 3 μL should not be used when executing the protocol, as several factors, such as disturbance by the needle, cause large errors for them. The upper limit of 10 μL is not as strict and can be varied if needed. It is important that the range of drop sizes is large enough to ensure statistical validity and to enable detection of possible invalid data due to random errors, as many of the errors do not remain constant over a large range. The selected size range is determined based on the factors listed below:

- The size ratio between the needle tip and the drop affects how much the needle distorts the drop shape, which can cause fitting errors. It is recommended that the diameter of the drop be at least five times the diameter of the needle tip.
- The drop base area should be much larger than the chemical or topographical heterogeneity of the surface. Marmur[11] recommends that the drop base be preferably 100–1,000× larger than the typical heterogeneity length scale to avoid substantial distortion of the contact line. The actual roughness length scale is not always known, however, and relatively large drops are used to ensure that this condition is fulfilled.
- The drop also must be axisymmetric in order for the measurement and interpretation to be meaningful. The larger the drop, the more it tends toward axisymmetry.
- Smaller drops are more sensitive to evaporation and optical errors associated with light scattering and diffraction. In addition, the difficulty of precisely locating the baseline for small drops causes larger uncertainty, as does the drop profile discretization, as each pixel of the image is either on the liquid or the gas side of the interface.
- The larger the drop is, the more gravity distorts its shape, leading to larger fitting errors.
- The drop must be large at first and then reduced to 10 μL before RCA measurement due to contact-angle hysteresis. Otherwise, the RCA is not reached at the beginning of the measurement, and the value of the contact angle will reduce during the recording of data. This will cause error in the measured contact-angle values.

The recommended starting volume (V_a) for RCA measurement (Step 10 in the protocol) depends on the ACA and RCA (Fig. 6)[29]. In Fig. 9b, typical behavior of the data is shown for using an advancing drop volume equal or larger than V_a, whereas Fig. 9a shows data for an experiment in which the initial drop volume was smaller than V_a and thus too small for a reliable measurement.

greatly. However, we recommend measuring and reporting room temperature and humidity together with the contact-angle data. If needed, an environmental chamber can be used to ensure a constant atmosphere during the measurement.

Camera setup

Vendors may have a selection of different camera options. The resolution of the camera may influence the error in the contact-angle measurement, as the fitting procedure is more precise with higher-quality images and accuracy of the placement of the baseline increases with resolution. Everyone should choose the camera according to the precision needed in their application. Although it is not possible for us to present quantified information about the size of the error, we assume that other uncertainties in the measurements are more substantial. A high-speed camera is not needed for the measurements performed in this protocol.

The sample should be placed horizontally, and the camera view should be on the same plane as the sample (Fig. 5). If the contact line between water and the sample is not visible due to roughness or shape of the sample, the camera view can be tilted downward by 1–3°. Substantial tilt in the camera view, however, can be a source of error. If tilt is needed to ensure visibility of the contact line, one must take into account the fact that the results may differ from the value of the contact angle in the horizontal plane. If the results are published, the tilt angle of the camera should be reported. Camera settings can influence the results of contact-angle measurements. Used parameters are bound to vary from lab to lab, making comparison of results potentially difficult, so it is most important to use the same parameters for every measurement when comparing surface properties of different samples in a given lab. The exact details of how the settings affect the results are beyond this protocol, but a few general guidelines are listed in Box 3.

Water dispensing system

The water dispensing system consists of a motorized syringe dispenser, tubing and a needle. The dispenser uses a step motor to dispense and draw liquid from the syringe into the needle via the tubing. The dispensing system is operated by using the software of the goniometer. It is recommended to use a different set of syringe, needle and tubing for each probe liquid to prevent

Box 3 | Guidelines on camera settings

Exposure
Increase exposure until the histogram optimum is reached (255), but no more. Too brief an exposure will cause reduced contrast, which may lead to failure to fit the curve. Exposure for too long may cause the fitted curve to be located 'inside' the droplet, instead of at the real water–gas interface, reducing the accuracy of the measurement.
Gain
If the histogram optimum can be reached without gain, the gain should be set to zero. After all, if gain is increased when the histogram is already at an optimum, it will only increase noise. If the histogram optimum cannot be reached even at full exposure, the gain can be increased until the optimum is reached, but no more.
Frame rate
Increasing the number of frames per second taken by the camera will decrease the resolution of the images, which will reduce the accuracy of the measurement. Therefore, the frame rate should be kept as low as possible.
Magnification
In general, higher magnification of the camera leads to more accurate data. In the case of ACA measurement, it must be taken into account that the drop should fit into the images even as it grows. Otherwise, as high a magnification as the size of the drop allows is recommended.
Focus
Lack of focus will affect the fitting procedure, reducing the accuracy of the measurements. The focus should be adjusted so that the contact points on both sides of the drop are optimal. Optimally, the needle should be in the middle of the probe liquid drop from every perspective, as the contact points on the sides of the drop will stay in focus when the volume of the probe liquid drop is varied (Fig. 6). For superhydrophobic samples, the needle must be at the back of the drop as seen from the camera perspective (see Step 6 in the Procedure).
Calibration
Calibration is performed to facilitate calculation of the volume of the drop from the fitted curve on the images. It is usually done by using either a metal sphere of specific size or using the width of the needle. Calibration should be done each time the distance between the measured drop and the camera changes, or when magnification is adjusted.

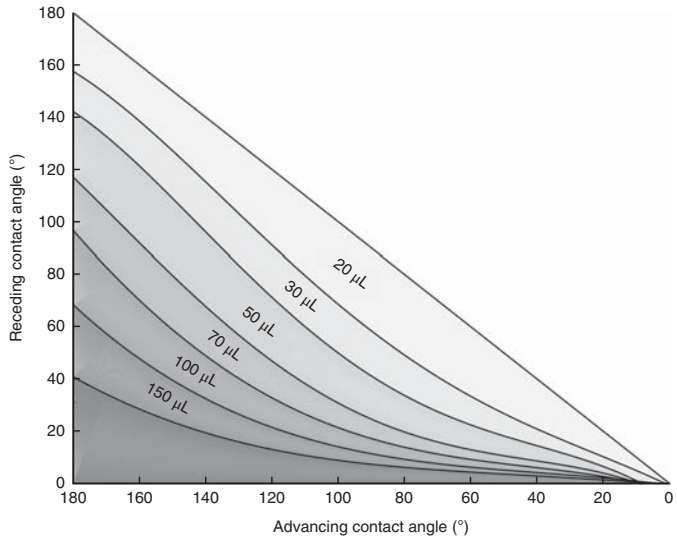

Fig. 6 | Recommended starting volume for RCA measurement, i.e., minimum advancing drop volume (V_a) needed to reach RCA at 10 µL. By estimating the ACA and the RCA of the sample to be measured, a recommended starting volume can be determined from the plot. The plot was obtained by numerical integration of the Young–Laplace equation. The code for calculating contour lines is provided in the Supplementary Methods.

cross-contamination and thereby ensure the purity of the liquid. Spare kits can usually be obtained from the manufacturer of the goniometer. The width of the needle should be as small as possible, as the needle distorts the shape of the drop and may affect the fitting procedure. The syringe and tubing should be cleaned regularly, as impurities in water can alter the surface tension and therefore affect the measured contact angles.

The connections in the syringe–tube–needle set must be tight, as even a small leak will cause a loss of control in the dispensing mechanism. This will make it hard to control the exact volume of the drop, as the flow of water does not stop at the same instant the dispensing is stopped, nor will withdrawal of water start at the instant suction is started.

Material surface preparation

The sample should be clean, macroscopically flat and rigid whenever possible. Samples can be cleaned using a suitable solvent that does not damage or contaminate the surface or using pressurized gas (e.g., N_2). Care should be taken with compressed air, as it may contain small oil droplets originating from the compressor. For sample preparation, it is not recommended to use water from plastic bottles as it may contain dissolved plasticizer compounds that can affect wetting.

The sample should be chemically inert to water, as dissolving of the sample may affect the properties of the surface as well as the surface tension of the water. The sample should also be nondeformable, as changes to the topography of the sample caused by water can affect the acquired data. Lightweight samples can be picked up by capillary action of the probe droplet. This can be avoided by attaching the sample by two-sided tape to either the sample stage or, alternatively, a microscopy slide. Sometimes it is necessary to tolerate imperfect or contaminated samples and measure them as provided. This must be taken into account in the way the results are understood and reported. Although it is not possible to give instructions for how to prepare each individual sample, some typical categories of samples and how samples in these categories are typically prepared are listed in Table 2.

Liquid preparation

Water is usually the preferred probe liquid because of the importance of aqueous systems in science and technology. It also has the highest surface tension of commonly available liquids[27]. If possible, use freshly purified water in the measurements to avoid organic contamination, which will affect its surface tension. In addition, deionized water is preferred. Probe liquids should be stored in closed containers, preventing organic vapors and particles present in air from contaminating the liquid. It is critical to ensure that the containers are made out of material that does not dissolve in the liquid—do not use plastic bottles, as plasticizers may leach into the water.

Dynamic effects can affect the results for probe liquids of high viscosity if the flow rates and equilibration times of this protocol are used. The presence of dynamic effects can be checked by lowering the flow rate in a stepwise manner and checking whether the results vary from those published by Tavana and Neumann[28]. When lowering the rate does not affect the measured contact angles anymore, the flow rate is low enough to avoid dynamic effects.

Dispense deionized water from the purifier into a clean beaker, and then fill the syringe from the beaker through the needle and tubing, using the manufacturer-provided software. The purity of the water is measured by its resistance. The needed level of purity depends on individual application of the measurements. Filling the syringe before a set of measurements will ensure that one does not run out of liquid during the measurements. A 1-mL syringe is sufficient for this protocol. After the syringe is full, dispensing ~20 μL of liquid will usually reveal any possible leaks in the liquid dispensing system.

Procedure

Advancing-contact-angle measurement ● Timing 5 min

1 Prepare and clean the sample.

2 Prepare the goniometer syringe and tubing. Fill the syringe with more water, if necessary, and check the tightness of the water tubing. If you use other probe liquids with the same goniometer, use different tubing and needle for each probe liquid.

3 Dispense ~20–100 μl of water into a spare cup or a piece of paper to remove possible air bubbles or impurities in the needle tip.

4 Place the sample on the sample stage. Check that the stage is horizontal (no tilt in any direction).
? TROUBLESHOOTING

5 Dispense a 2-μL drop of water so that it freely hangs on the tip of the needle. Lower the needle so that the drop is on the lower part of the computer screen. Position the needle so that it is in the middle of the screen, pointing directly downward.

6 Raise the sample stage so that the drop comes into contact with the sample, until the tip of the needle is about halfway inside the drop and is in the middle of the drop from the perspective of the camera (see Fig. 4 for the needle position from the camera perspective).
? TROUBLESHOOTING
Dispense 1 μL of water at a flow rate of 0.05 μL/s, so that the overall size of the drop is 3 μL. The low flow rate is necessary to avoid dynamic effects. Wait for 30 s to make sure that the system is in equilibrium.

Table 2 | Sample preparation: examples of how some sample types are prepared for contact angle measurement, with anticipated results.

Sample type	Surface preparation	Possible cleaning procedure when needed	Issues	Solutions	Anticipated results
Lightweight, e.g., paper, plant leaves, films and foils	Cut, shape and attach to a pad	Blow dust off with pressurized nitrogen/ compressed dry air	Capillary forces lift the sample or deform it	Attach the sample to a pad before the measurement	Reproducible
		Gently wash with water or another suitable solvent if possible	Solid surface is not macroscopically flat	Stretch the sample carefully when attaching it to a pad. Touch only areas of the sample where no measurements will take place	
Absorbing, e.g., paper, certain films and textiles	Cut, shape and attach to a pad	Blow dust off with pressurized nitrogen/ compressed dry air	Drop slowly absorbs into the sample, leading to lack of reproducibility	Use a smaller range of drop volume in the measurements to reduce measurement time	Not always reproducible
		Gently wash with water or another suitable solvent, if possible	Solid surface properties change as a function of time	Check whether the pumping speed of the water can be increased without creating dynamic contact-angle effects	
Reflective, e.g., silicon wafers and metals	Use as is	Wash with a solvent + water; dry with pressurized nitrogen/ compressed dry air	Difficult to place baseline when the RCA is ~90°	Locate the baseline position from a drop that has not reached the receding angle (by reducing the starting drop size). Repeat the measurement according to the protocol, and use the same location for the baseline	Reproducible
		Ultrasonicate in a detergent/solvent			
Very hydrophilic, e.g., glass, silicon and activated surfaces	Use as is	Wash with a solvent + water; dry with pressurized nitrogen/ compressed dry air	Drops tend toward nonaxisymmetric shapes	Do not report exact contact-angle values if the contact angle varies based on the direction of observation	Not always reproducible
	Cut and shape		In the RCA measurement, the needle detaches from the drop	Place the tip of the needle very close to the sample. Use the data until the moment of detachment to calculate the RCA	
Hydrophobic, high-hysteresis surfaces, e.g., biological and biomimetic materials	Use as is	Blow dust off with pressurized nitrogen/ compressed dry air	The needle detaches from the drop when the drop size is reduced before the receding angle measurement	When you reach the advancing drop volume (Step 9): (i) lower the stage, so that the needle is at the top part of the drop meniscus. (ii) Move the stage toward the light source, so that the needle is in the middle of the drop when looking from a birds-eye perspective. (iii) Raise the stage back to its original position and perform Step 11 of protocol. (iv) Move the stage toward the camera so that the needle is at the back of the drop from the camera perspective (Step 10)	Reproducible

Table continued

Table 2 (continued)

Sample type	Surface preparation	Possible cleaning procedure when needed	Issues	Solutions	Anticipated results
	Cut, shape and attach to a pad	Gently drop a couple of drops of water onto the surface and let them roll off			
Macroscopically rough, soft materials, e.g., papers, textiles, plant leaves and insect wings	Use as is	Blow dust off with pressurized nitrogen/ compressed dry air	Drops are not axisymmetric; the contact angle depends on the direction of observation	Tilt the camera so that it looks down	Not always reproducible, and results depend on the direction of observation. Report camera tilt angle along with the results
	Cut, shape and attach to a pad		Time-dependent behavior due to interactions between the probe liquid and the sample	Use a higher flow rate, if allowed, without dynamic effects. Use a smaller drop size range when measuring, ACAs and RCAs	
Macroscopically rough, hard materials, e.g., ceramics and minerals	Use as is	Wash with solvent + water; dry with pressurized nitrogen/ compressed dry air			Not always reproducible; water may cause permanent changes in the solid material properties
	Polish				

7 Start recording the video. Continue quickly to the next step (Step 8).

8 Dispense 8 μL of water at a flow rate of 0.05 μL/s.

▲ **CRITICAL STEP** Avoid any disturbances to the drop during this phase. The flow rate must be low enough to avoid dynamic effects.

? TROUBLESHOOTING

9 Stop the video. The recorded images are used for analyzing the ACA (see the Analysis section).

Receding-contact-angle measurement ● Timing 5 min

10 Estimate the recommended starting droplet volume for RCA measurement (V_a) (see Fig. 6 for instructions on how to determine V_a and the Supplementary Methods for the computer code used to produce the figure). If you have no approximation of the receding angle of the sample, perform a measurement to find out the contact angle at which the baseline starts to move.

? TROUBLESHOOTING

11 Deposit a drop with a volume larger than V_a onto the sample. The flow rate can be high at this stage, for example, 2 μL/s.

12 Adjust the height of the stage so that the needle is close to the sample surface without touching it.

13 Remove water from the drop at a flow rate of 2 μL/s until it is ~13 μL in size. Adjust the position of the needle again, if needed.

14 Remove 2 μL at 0.05 μL/s. The low flow rate is used to avoid dynamic effects.

15 Wait for 30 s to make sure that the system is in equilibrium.

16 Start recording the video. Continue quickly to the next step (Step 17).

17 Withdraw water at a flow rate of 0.05 μL/s until the droplet is completely removed.

? TROUBLESHOOTING

18 Stop recording the video after removal of water. The recorded images are used for analyzing the RCAs (see the Analysis section).

19 Lower the sample stage to avoid contact between the needle and the sample. Clear any possibly remaining water off the sample with a stream of pressurized gas or a lint-free paper tissue.

Move either the stage or the sample so that the next measurements of ACA and RCA will be on a different location, raise the stage back into close proximity with the needle and start again from Step 5. If the size of the sample does not allow measurements on different locations, repeat the measurement on the same location.

Analysis ● Timing 10 min

20 Expand the window showing the first recorded image of the droplet to ensure that you can distinguish the interface between the droplet and the sample surface as well as possible.

21 Use the manual baseline option and place the baseline on this interface. If there is any tilt on the surface, tilt the baseline so that it is in the correct position on both sides of the drop.

22 Analyze all the recorded images.

? TROUBLESHOOTING

23 After the analysis is complete, check from images of a different-sized drop that the baseline was placed in the correct position.

▲ **CRITICAL STEP** If there is a need to adjust it, check carefully in which direction and how far it needs to be shifted, and return to Step 20. Start again, making the appropriate corrections. If there is no need to adjust the baseline position, continue to Step 24.

24 Check the fitting error of the analyzed images by comparing the fitted curves to the actual drop profile. Remove the data points with clearly visible fitting errors (Figs. 7 and 8).

25 Plot the average of the contact angle on the left- and right-hand sides of the drop as a function of the drop volume (Figs. 7 and 8).

26 Plot the baseline length as a function of the drop volume.

▲ **CRITICAL STEP** Check that the three-phase contact line is moving (i.e., that the length of the baseline increases steadily during the ACA measurements, and that it reduces steadily during the RCA measurements) (Fig. 9).

27 If all the above tests were passed, calculate an average of the contact-angle value obtained from each image in a measurement.

? TROUBLESHOOTING

28 Calculate the ACA and the RCA values of a sample as an average of five or more measurements each. Report both the advancing- and the receding-angle averages, and the standard deviations of the measurements.

Troubleshooting

Troubleshooting advice can be found in Table 3 and Fig. 10.

Table 3 | Troubleshooting table

Step	Problem	Possible reason	Solution
4	Sample is not horizontal	Sample stage is tilted	Move the needle a couple of millimeters above the sample stage. Move the sample stage from left to right, and check from the magnified image on the computer screen whether the distance between the needle and the stage remains constant. If not, adjust and repeat until it does. Turn the sample stage 90° and repeat the procedure
	Baseline is not visible	Roughness of the sample	Reliable ACA and RCA measurements are not possible for macroscopically rough samples
		Camera tilted upward	Tilt the camera down a couple of degrees. If the camera is tilted downward during the measurements, report the tilt angle with the results. Do not use tilt angles >3°
6	Not able to get the needle into the correct position relative to the drop	The sample is highly hydrophobic and has low contact-angle hysteresis	Place the needle toward the back side of the drop, as seen from the camera perspective (Fig. 10). If this is difficult to do, use the following procedure: test on which side of the needle a free-hanging drop prefers to go by lifting a hydrophobic sample from below into contact with the drop. After finding this out, lower the sample and turn the needle to make the hydrophilic side face toward the camera. Lift the sample back up, and if the drop is not closer to the camera than the needle, move the sample

Table continued

Table 3 (continued)

Step	Problem	Possible reason	Solution
			stage carefully in the direction away from the camera until the drop is in the desired position
8	Dynamic effects on viscous liquids	Flow rate is too high	Start with a measurement with an extremely low flow rate. Repeat the measurements by increasing the flow rate stepwise between measurements. When the results of a measurement with a higher flow rate start deviating from the ones with a lower flow rate, the limit for dynamic effects has been surpassed. Repeat the original measurements with a flow rate below this limit[30]
10	RCA approximation is not known	No operator experience with similar samples/no previous literature for similar samples	Conduct one RCA measurement with a very large drop, for example, 100 μL. Plot the data with the contact angle as a function of the drop volume, and check the volume at which the contact angle starts decreasing. This is the advancing droplet volume (V_a). Perform the rest of the RCA measurements according to the protocol
	Not able to use a large enough advancing drop volume for the RCA measurement	Either the overall size of the sample is too small, or the sample does not have a large enough homogeneous area	If possible, use a larger sample. If this is not possible, use only the plateau of the data where the contact angle is constant (Fig. 9a). If a plateau cannot be reached, no reliable RCA data can be gathered
17	Not all water can be removed	Hydrophilic sample, water sticks to the solid surface	Remove water until the needle detaches from it. Check the video to see when the detachment happens, and analyze the results only to this point. For the next measurement, the air drawn into the syringe will be removed in Step 3
22	Fitting fails	Improper needle position	Make sure the needle is vertically positioned and in the center of the camera view
		Location of the sample in the recorded image is incorrect	Adjust the height of the sample stage so that the sample is in the middle of the recorded image
		Lack of contrast between the phases in the recorded image	Try (i) increasing the exposure of the camera, (ii) adding gain on the camera settings and (iii) removing disturbing external light, using only the light source of the goniometer during the measurement
		Wrong curve-fitting method was used	Test whether other fitting methods work better. Methods that do not make assumptions about the shape of the drop, such as polynomial fitting, are less prone to failure of fitting
27	Measured contact angle values are not constant for parts of the data	Sample is nonuniform	Try repeating the measurement on a different part of the sample. If there is no improvement, report the nonuniformity with the data
		Drop is vibrating during parts of the measurement	Repeat the measurement. Take extra care to remove all possible external vibrations and air flow

Timing

- Steps 1–9, advancing contact angle measurement: 5 min
- Steps 10–19, receding contact angle measurement: 5 min
- Steps 20–28, analysis: 10 min

Anticipated results

Using this protocol, one should be able to measure the ACA and the RCA on a wide variety of surfaces in a reproducible manner. The results give information on the solid surface properties and give insights into solid–water interactions.

The measured ACA is expected to correlate well with the tendency of the surface to either attract or repel the probing water. The measured RCA, on the other hand, is expected to correlate well with the adhesion force between the surface and water.

Because a droplet moving horizontally on a surface has both an advancing contact line in the front and a receding contact line at the back, the measured hysteresis is expected to correlate well with horizontal mobility of water on the surface. It must be stressed, however, that the contact angles at the

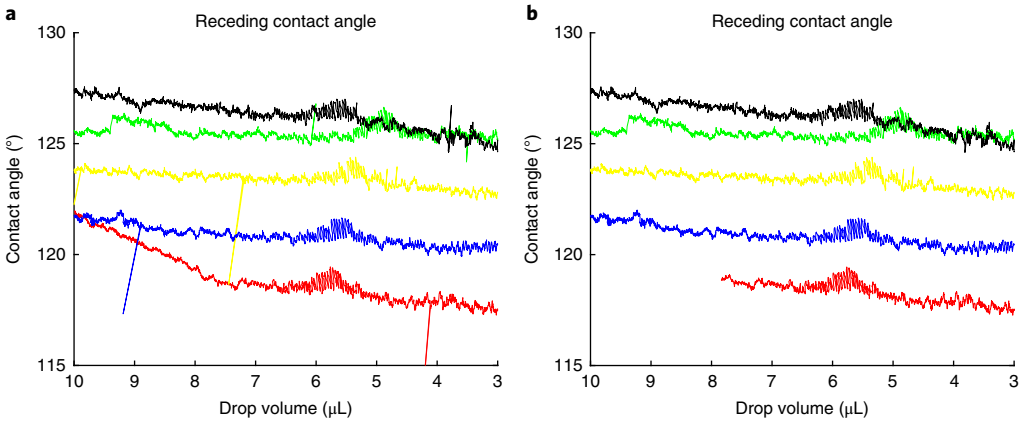

Fig. 7 | Receding-contact-angle data of a nanostructured polysiloxane film on silicon substrate. Five different measurements were performed on different locations of the sample. **a**, Raw data that include some outlier data points in which the automatic fitting procedure has failed. **b**, The same data with the measured value of the contact angle at the outlier points removed. The average receding contact angle (122.7 ± 3.3°) of the sample is calculated as an average of the data points of the five curves shown here. For the measurement with the data shown by the red curve, the contact angle had not achieved the RCA phase, even though an identical advancing drop volume was used in all the measurements. In such a case, the optimal procedure would be to repeat the measurement with a larger advancing drop volume for this measurement. If this is not allowed by the sample size, one should remove the data for which the receding contact angle has not been reached, as shown here.

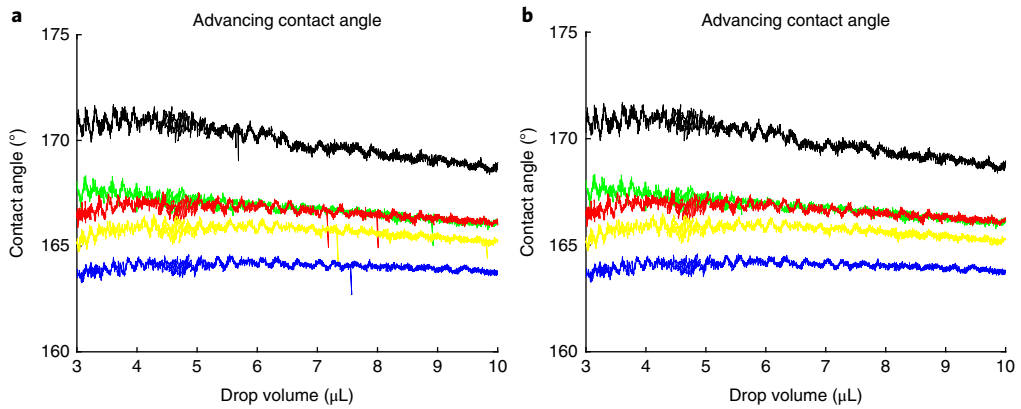

Fig. 8 | Advancing contact-angle data of a nanostructured polysiloxane film on silicon substrate. Five different measurements were performed on different locations of the sample. **a**, Raw data that include some outlier data points in which the automatic fitting procedure has failed. **b**, The same data with the measured value of the contact angle at the outlier points removed. The average contact angle of the sample (166.6 ± 1.8°) is calculated as an average of the data points of the five curves shown in **b**.

opposing fronts of the droplet do not necessarily correspond to the ACA and the RCA simultaneously.

When a contact line is made to either advance or recede, it moves over macroscopic areas of the surface. Therefore, the results obtained from the measurements in this protocol give an indication of the homogeneity of the surface. Repeated measurements on several different locations of the surface increase the areal coverage of this information. Repeated measurements also give an indication of the reliability of the data and allow one to recognize possible random errors in a given measurement.

An example of data collected from contact-angle measurements performed on one sample is shown for the ACA in Fig. 8 and the RCA in Fig 7. Five individual measurements are performed on separate locations of the sample, and as the wetting properties of the sample are not perfectly homogeneous, the results deviate slightly from one measurement to another. In Fig. 8a, all the obtained data points between a 3- and a 10-μL drop size are shown, and in Fig. 8b, only the data points used to calculate the average ACA of the sample are shown; the data points removed at this step are outliers in which the automatic fitting procedure has failed. The oscillations seen on each of

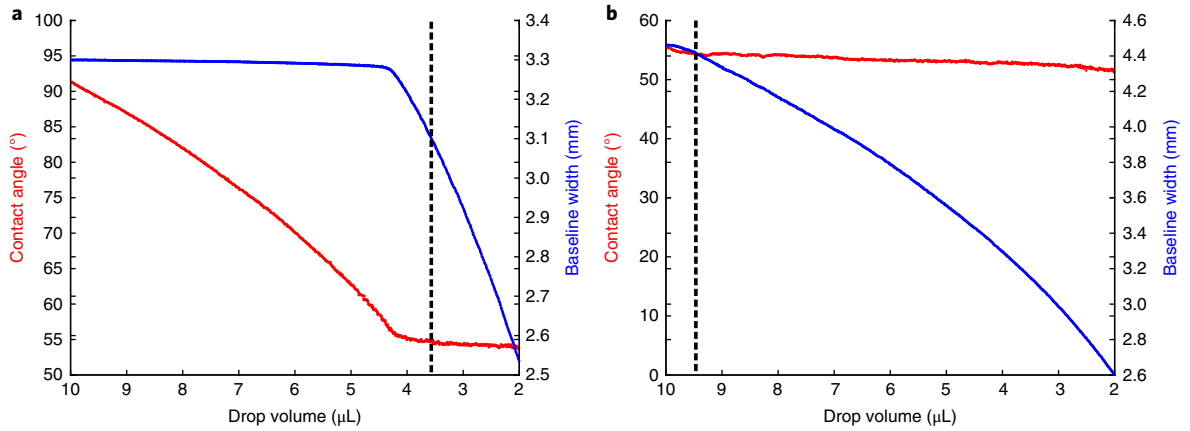

Fig. 9 | Effect of advancing drop volume (V_a) on the receding contact-angle measurement. Both measurements are performed on the same sample, a polysiloxane film deposited on a silicon wafer. The red line corresponds to the value of the measured contact angle as a function of drop volume, and the blue line corresponds to the width of the baseline as a function of drop volume. **a**, The advancing drop volume is smaller than V_a, and the receding contact angle is reached only near the end of the measurement, as marked by the dashed line. **b**, When an advancing drop volume of at least V_a is used, the receding contact angle is reached before the start of measurement, and useful data are gathered over the entire measured range. Data collected before the dashed line are not directly useful in wetting characterization, and useful data are obtained from only a very limited region of the sample. Even after the receding contact angle is reached, the measured value of the contact angle may decrease slightly as the volume of the drop decreases. This can be due to the location of the baseline varying slightly during the measurement and the needle affecting smaller drops more strongly.

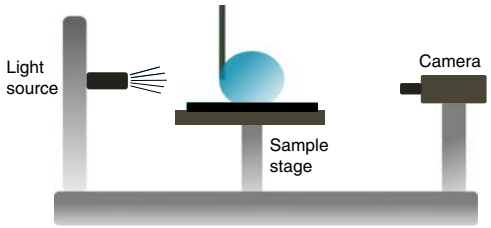

Fig. 10 | Needle position for a very hydrophobic surface with low contact-angle hysteresis. The needle will not remain in the middle of the drop (from this side perspective) on highly hydrophobic surfaces, as the friction is too low. If the needle is not in the middle of the drop (as seen from the camera perspective), it may lead to failure in the automatic fitting procedure, as the software sometimes assumes the position of the needle to be in the middle. The pictured location for the needle will cause the least inaccuracy in the results obtained.

the curves up to a volume of ~6 μL are not an error of measurement but are caused by stick-and-slip behavior of the moving contact line.

In one of the RCA measurements (Fig. 7; red curve), the advancing drop volume was not large enough to reach the RCA, because of differences in the wetting properties between different areas of the sample. An optimal procedure would be to repeat this one measurement with a larger advancing drop volume. If this cannot be done, due to, for example, restricted size of the sample, only the 'plateau' in the data should be used. In Fig. 8a, all the measured data points are shown, and in Fig. 8b, only the data points used for calculation of the average contact angle of the sample are shown.

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Author contributions

R.H.A.R. coordinated the project. T.H., X.T. and J.T.K. performed the experiments. All authors participated in designing the protocol. T.H. and R.H.A.R. wrote the manuscript with contributions from all authors. J.T.K. wrote the Python code.

Competing interests

The authors declare no competing interests.

Additional information

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