Huhtamäki, Tommi; Tian, Xuelin; Korhonen, Juuso T.; Ras, Robin H.A.

Surface-wetting characterization using contact-angle measurements

Published in:
Nature Protocols

DOI:
10.1038/s41596-018-0003-z

Published: 09/07/2018

Document Version
Peer reviewed version

Please cite the original version:
Huhtamäki, T., Tian, X., Korhonen, J. T., & Ras, R. H. A. (2018). Surface-wetting characterization using contact-angle measurements. *Nature Protocols*, *13*(7), 1521-1538. https://doi.org/10.1038/s41596-018-0003-z

PROTOCOL METADATA

Manuscript number: NP-P160155B

DOI: 10.1038/nprot.2018.032

Number of:

Figs: 10

Tables: 3

Boxes: 3

List of SI:

CFIs: (y/n)

Surface Wetting Characterization using Contact Angle Measurements

Tommi Huhtamäki[1], Xuelin Tian[1,2], Juuso T. Korhonen[1,a] and Robin H. A. Ras[1,3]*

[1]Department of Applied Physics, School of Science, Aalto University, Puumiehenkuja 2, 02150 Espoo, Finland

[2] School of Materials Science and Engineering, Sun Yat-sen University, 510275 Guangzhou, China

[3] Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, Kemistintie 1, 02150 Espoo, Finland

[a]Current address: Department of Neuroscience and Biomedical Engineering, School of Science,

Aalto University, Rakentajanaukio 2 C, 02150 Espoo, Finland

*e-mail: robin.ras@aalto.fi

Abstract

Wetting, the process of water interacting with a surface, is crucial in our everyday life 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, while 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 wide variety of materials, from biological surfaces to polymers, metals, ceramics, minerals, etc. The apparent simplicity of the method is misleading, however, and obtaining meaningful results requires minimizing random and systematic errors. This article provides a protocol for performing reliable and reproducible measurements of the advancing contact angle and the receding contact angle by slowly increasing and reducing the volume of a probe drop, respectively. One pair of advancing and receding contact angle measurement takes approximately 15-20 minutes to complete, while the whole protocol with repeat measurements may take about 1-2 h. This protocol focuses on using water as a probe liquid, but advice is given how it can be modified for the use of other probe liquids.

Introduction

Surface wettability plays an important role in many biological, chemical and physical processes. Development of a water-repellent cuticle, which covers and protects the above-ground organs of flowers, leaves and fruits, was one of the key evolutionary developments allowing 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-strider legs that facilitate floatation to allow walking on water,[2] Lotus leafs have self-cleaning properties to keep them clean in marshy environments,[3] 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 to 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 plays an important role in many industrial processes: For painting and printing, both the liquid surface tension and the properties of the solid need to be optimized to ensure suitable adhesion of the liquid to the solid. [7] Solid surface energy needs to be considered in many processes requiring for example heat transfer or lubrication. In oil recovery, the solid material needs to be designed to selectively absorb oil but not water, a quality also defined by its wetting properties.[8]

Wetting is commonly characterized by the *contact angle*, which is defined as the angle between the tangent to the water-gas interface and the tangent to 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 water and an ideal solid surface (i.e. atomically smooth, chemically homogeneous, non-reactive and non-deformable by water) has traditionally been defined using the Young equation:[9]

$$\cos\theta_{\mathrm{YOUNG}} = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma}$$

where θ_{YOUNG} is the Young contact angle, γ_{sv} and γ_{sl} solid-gas and solid-water interfacial tension respectively, and γ surface tension of water. 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 on the atomic level, and can be chemically homogeneous when handled in cleanroom environment. Yet, even silicon wafers, chemically unmodified as well as 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 would only have a single stable contact angle, a slightest tilt of the solid would lead to movement of the drop. This is due to the fact that tilting the solid surface will lead the contact angles to deviate from the Young angle, and unstable contact angles will not be able to resist the force of

gravity from moving the drop. 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 to measure contact angles in the protocol is called *sessile drop goniometry.* It is performed by recording 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 vibrations, has been demonstrated in the literature.[12] However, this technique is not currently available in the commercially available goniometers.

The two reproducibly measurable contact angles are the *advancing contact angle* and the *receding contact angle*, the highest and the lowest angle in the hysteresis range. When the drop volume increases, the contact angle of the drop will increase and the contact line will remain pinned until the advancing contact angle is reached (Fig. 4a-c). Further increase of drop volume will lead to movement of the contact line, while 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 receding contact angle is reached (Fig. 4d-e). Further decrease of drop volume will lead to movement of the contact line, while the contact angle remains ideally constant, but can vary in measurements due to non-uniformities of the sample. Contact angle hysteresis, which is crucial for evaluating mobility of a drop on a surface, can be defined as the difference between the advancing and the receding contact angle ($\theta_a - \theta_r$),[13] or alternatively as the difference between their cosines ($\cos\theta_r - \cos\theta_a$).[14] The larger the difference between the advancing and the receding contact angle, the less mobile the drop is. While 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 advancing and the receding contact angle 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 to restrict the term *dynamic contact angle* for dynamic events where 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 in two main groups. In optical methods, the shape of a droplet is measured, whereas most other methods assess the force exerted by a water on the solid. Due to its versatility and ease of use, the optical method called *sessile drop goniometry* is probably 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 contact angle can be calculated.[21] Recently, we introduced *scanning droplet adhesion microscopy*, allowing to measure droplet adhesion forces and construct wetting maps that depict microscale spatial variation in wettability.[22]

The tilting plate method is sometimes used to measure the advancing and the receding contact angles, although that method is not recommended due to 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 advancing contact angle, and the upper angle the receding contact angle. 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 advancing contact angle simultaneously with the upper angle reaching receding contact angle. For the reason stated above, also 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, while the contact angle hysteresis is a surface property, and does not depend on the 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 measurements is given in the **Table 1** below. Details of the various methods are out of the scope of this article, and can be found elsewhere in the literature.[11,17,18,25,26]

Method	Description	Advantages	Disadvantages
Direct Methods			
Sessile drop goniometry	The volume of a drop deposited on the measured surfaced is increased, and the value of the advancing contact angle is obtained from the advancing contact line. For the receding contact angle, the volume of the drop is reduced, and the value of the receding contact angle is obtained from the receding contact line.	Simple	Susceptible to operator error if a strict protocol is not used
		Small amounts of water required	Collecting information from large area requires time
		Possible to measure samples with small surface areas	Small amounts of impurity in the water may cause experimental error
		Gives information about the uniformity of the sample	

			Tedious to measure large areas of the surface
Tilting plate	Contact angles are measured from the lead edge and the trail edge of a distorted drop on an inclined plane when the drop starts sliding	Simple	The measured angles do not necessarily correspond to the advancing and the receding contact angle
		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 a 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 give information about the uniformity of the surface

	The advancing and the receding contact angles can be measured by dipping the sample into the water, or withdrawing the sample from the water.	Ease of automation	No visual feedback to detect how wetting occurs
		Information from large areas of the sample is gathered quickly	Sample should have same composition and morphology on all surfaces: front, back and sides
			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

Table 1: *Different wetting characterization methods.*

Experimental Design

The measurements in this protocol are performed using the so-called needle-in-drop sessile drop. The advancing and the receding contact angles are measured by slowly pumping water in and out of a needle using a motorized syringe. The needle is located in close proximity of 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 advancing contact angle of the measurement. Video for receding contact angle is recorded when water is being removed from the surface, and the results analyzed in the same way as for advancing contact angle.

The analysis is performed by software-based fitting procedure, which finds the edge between the water drop and the surrounding gas. The analysis is done after the measurement and the recording of the video is 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, since difference in contrast between water and the solid is 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 2 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 3 for details on the effects of drop size on the results of the measurements).

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

MATERIALS

Equipment setup

Goniometer setup

Commercial goniometers typically include a motorized syringe for precisely controlling the volume of the deposited drop, and 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 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 disturbance of external vibrations, as vibrations can cause error in the measurement. Air flow 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 from 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.

The humidity and temperature of the room are preferred to be kept steady. For water, for example, temperature between 20 and 40°C has been shown to have little effect on the surface tension,[27,28] therefore small changes in temperature are not expected to affect contact angle measurements 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 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, since the fitting procedure is more precise with higher quality images, and also 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 significant. 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. 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 to 3 degree. Significant tilt in the camera view, however, can be a source of error. If tilt is needed to ensure visibility of the

contact line, one needs to take into account 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 is beyond this protocol, but a few general guidelines are listed in Box 1.

Box 1: Guidelines on camera settings.

Exposure. Increase exposure until the histogram optimum is reached (255), but no more. Too small exposure will cause reduced contrast, which may lead to failure to fit the curve. Too large exposure 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, gain should be set to zero. After all, in case gain is increased when histogram is already in an optimum, it will only increase noise. If the histogram optimum cannot be reached even at full exposure, 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, frame rate should be kept as low as possible.

Magnification. In general, higher magnification of the camera leads to more accurate data. In case of advancing contact angle measurement, it needs to be taken into account that the drop should fit into the images even as it grows. Otherwise, as high 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. 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 side of the drop will stay in focus when volume of the probe liquid drop is varied (Fig. 5). For superhydrophobic samples, the needle needs to 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 calculating 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 every time the distance between the measured drop and the camera changes, or when magnification is adjusted.

End of Box

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 to the needle via the tubing. The dispensing system is operated using the software of the goniometer.

It is recommended to use a different set of syringe, needle and tubing for each probe water to prevent cross-contamination, and thereby ensure purity of the water. Spare kits can usually be obtained from the manufacturer of the goniometer.

The width of the needle should be as small as possible, since 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 dispense 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 on 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. It is not recommended to use water from plastic bottles in sample preparation, 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 surface tension of water. The sample should also be non-deformable, 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 either to the sample stage, or alternatively to a microscopy slide.

Sometimes it is necessary to tolerate imperfect or contaminated samples and measure them as provided. This needs to 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, in Table 2 are listed some typical categories of samples, and how samples in these categories are typically prepared.

Sample type	**Surface preparation**	**Possible cleaning procedure when needed**	**Issues**	**Solutions**	**Anticipated results**
Lightweight *e.g. Paper, plant leaves, films, foils*	Cut, shape, 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 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, textiles*	Cut, shape, 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 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 if pumping speed of water can be increased without creating dynamic contact angle effects	
Reflective *e.g. Silicon wafers, metals*	Use as is	Wash with a solvent+water, dry with pressurized nitrogen / compressed dry air	Difficult to place baseline when receding contact angle is ~90 degrees	Locate the baseline position from a drop that has not reached the receding angle (by reducing the starting drop size).	Reproducible

				Repeat the measurement according to the protocol, and use the same location for the baseline.	
		Ultrasonicate in a detergent / solvent			
Very hydrophilic *e.g. Glass, silicon, activated surfaces*	Use as is	Wash with a solvent+water, dry with pressurized nitrogen / compressed dry air	Drop tends toward non-axisymmetric 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 receding contact angle measurement 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 receding contact angle.	
Hydrophobic, high hysteresis surfaces *e.g. Biological, biomimetic*	Use as is	Blow dust off with pressurized nitrogen / compressed dry air	Needle detaches from the drop when the drop size is reduced before receding angle measurement	When you reach advancing drop volume (Step 9 in protocol): 1. Lower the stage, so that the needle is at the top part of the drop meniscus 2. Move the stage towards the light source, so that the needle is	Reproducible

				in the middle the drop when looking from a birds-eye perspective 3. Raise the stage back to its original position and perform Step 11 of the protocol 4. Move the stage towards the camera so that the needle is at the back of the drop from camera perspective (Step 10)	
	Cut, shape and attach to a pad	Gently drop and let roll off a couple of drops of water			
Macroscopically rough, soft materials *e.g. Papers, textiles, plant leaves, insect wings*	Use as is	Blow dust off with pressurized nitrogen / compressed dry air	Drop not axisymmetric, contact angle depends on the direction of observation	Tilt the camera so that it looks down	Not always reproducible, 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 water and the sample	Use higher flow rate if allowed without dynamic effects. Use smaller drop size range when measuring	

				advancing and receding contact angles.	
Macroscopically rough, hard materials *e.g. Ceramics, 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				

Table 2: *Sample preparation. Examples on how some sample types are prepared for contact angle measurement, and what kind of results are anticipated.*

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.[29] If possible, use purified water in the measurements to avoid organic contamination affecting its surface tension. Also, de-ionized 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 crucial to ensure that the containers are made out of material that does not dissolve to 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 step-wise manner, and checking if the results vary, as published by Tavana and Neumann.[30] When lowering the rate does not affect the measured contact angles anymore, the flow rate is low enough to avoid dynamic effects.

Dispense de-ionized water from the purifier to a clean beaker, 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 a couple of tens of microliters of liquid will usually reveal any possible leaks in the liquid dispensing system.

Procedure

Advancing contact angle (ACA) <5 minutes>

1. Prepare and clean the sample.
2. Prepare the goniometer syringe and tubing. Fill the syringe with more water if necessary, check the tightness of the water tubing. If you also use other probe liquids with the same goniometer, use different tubing and needle for each probe liquid.
3. Dispense some tens of µL of water to 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 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 downwards.
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 in the middle the drop from the perspective of the camera (see Fig. 4 for the needle position from the camera perspective). **[Troubleshooting]** Dispense 1 µL 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.
7. Start recording the video. Continue quickly to the next step (8).
8. Dispense 8 µL at a flow rate of 0.05 µL/s. **[Troubleshooting]**
   <CRITICAL STEP> Avoid any disturbances to the drop during this phase. The flow rate needs to be low enough to avoid dynamic effects.
9. Stop the video after the 8 µL has been dispensed. The recorded images are used for analyzing the advancing contact angle (see **Analysis** –section).

Receding contact angle (RCA) <5 minutes>

10. Estimate the minimum advancing droplet volume (V_a) (see Fig. 6 for instructions how to determine V_a and Supplementary Method 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 the base line starts moving on. **[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 about 1/4 of the drop height as measured from the sample stage.
13. Remove water from the drop at a flow rate of 2 µL/s until it is approximately 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 (17).
17. Remove 11 µL at a flow rate of 0.05 µL/s. **[Troubleshooting]**
18. Stop recording the video after removal of water. The recorded images are used for analyzing the receding contact angles (see **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 towel. 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 to a 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 <10 minutes>

20. Expand the window showing the first recorded image of drop in a measurement to ensure that you can distinguish the interface between the drop and the sample surface as good 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 on 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 way and how much 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 (see Figure 7).
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
26. Plot the baseline length as a function of the drop volume.
    <CRITICAL STEP> Check that the baseline is moving (i.e. that the length of the baseline increases steadily during the advancing contact angle measurements, and that it reduces steadily during the receding contact angle measurements (Figure 8).
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 advancing and the receding contact angle value of a sample as an average of five or more measurements each. Report both the advancing and the receding angle averages, and the standard deviation of the measurements.

BOX 2: 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 2-dimensional image - needs to 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, since 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[29]) 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: $\Delta p = \gamma(\frac{1}{R_1} + \frac{1}{R_2})$. 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. As it assumes an axisymmetric drop, it will give large errors in the case of non-axisymmetric 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 interface between liquid and 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.
- 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 re-analyzed. Potential causes that can be adjusted for re-analyzing are the fitting method, and the location of the baseline. If re-analysis does not lead to improvement, a new measurement needs to be performed.
- In general, different fitting methods give different size of errors depending on the size of the drop, and the type of surface characterized.
  END OF BOX 2

BOX 3: What drop size to use?

Despite the size of the drop being absent from 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 advancing and receding contact angles respectively increase and decrease between 3-10 µL to balance the errors for small drops 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 should be at least 5 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 should be preferably 100-1000 larger than the typical heterogeneity length scale to avoid significant distortion of the contact line. The actual roughness length scale is not always known, however, and relatively large drops are used to ensure this condition is fulfilled.
- The drop also needs to be axisymmetric in order for the measurement and interpretation to be meaningful. The larger the drop, the more it tends towards axisymmetry.
- Smaller drops are more sensitive to evaporation and optical errors associated with light scattering and diffraction. Also, 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 has to be large at first, and then reduced to 10 µL before receding contact angle measurement due to contact angle hysteresis. Otherwise, the receding contact angle is not reached at the beginning of the measurement, and the value of contact angle will reduce during the recording of data. This will cause error in the measured contact angle values.

The required advancing drop volume (V_a) from which step (9) in the protocol starts depends on the advancing and receding contact angles (see Fig. 6).[31] In Figure 9a typical behavior of the data is shown for using an advancing drop volume equal or larger than V_a, while Figure 9b shows data for an experiment where the initial drop volume was smaller than V_a, thus too small for a reliable measurement.

End of Box 3

Troubleshooting

Troubleshooting advice can be found in Table 3.

Step	Problem	Possible reason	Solution
4	Sample not horizontal	Sample stage is tilted	Move the needle a couple of mm 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 stays constant. If not, adjust and repeat until it does. Turn the sample stage 90 degrees, and repeat the procedure.
4	Baseline not visible	(a) Roughness of sample b) Camera tilted upwards	Tilt camera down a couple of degrees. If camera is tilted downwards during the measurements, report the tilt angle with the results. Do not use tilt angles greater than 3 degrees.
6	Not able to get the needle in the correct position in relation to the drop	Sample is highly hydrophobic and has low contact angle hysteresis	Place the needle to the back 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 down, and turn the needle to make the hydrophilic side face towards the camera. Lift the sample back up, and if the drop is not closer to the camera than the needle, move the sample stage carefully to the direction away from the camera until the drop is in the desired position.
8	Dynamic effects on viscous liquids	Too high flow rate	Start with a measurement with extremely low flow rate. Repeat 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 lower flow rate, the limit for dynamic effects has been surpassed. Repeat the original measurements with a flow rate under this limit.[32]
10	Receding contact angle approximation not known	No operator experience with similar samples / no previous literature of similar samples	Conduct one receding contact angle measurement with a very large drop, for example 100 µL. Plot the data with 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 receding contact angle measurements according to the protocol.
10	Not able to use big enough advancing drop volume for receding contact angle measurement	Either the overall size of the sample is too small, or 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 CA is constant (see Fig. 9). If the plateau cannot be reached, no reliable contact angle data can be gathered.
17	Not all water can be removed	Hydrophilic sample, water sticks to the solid surface	Remove water until needle detaches from it. Check from the video to see when the detachment happens, and analyze results only to this point. For the next measurement, the air drawn to the syringe will be removed in Step 3.
22	Fitting fails	(a) Needle position (b) Location of the sample in the recorded image (c) Lack of contrast between the phases in the recorded image (d) Wrong curve fitting method	(a) Needle not being in the middle of the recorded image, pointing straight down may distort the drop and cause lack of axisymmetry (b) Adjust the height of the sample stage so that the sample is in the middle of the recorded image (c) Try (1) increasing the exposure of the camera, (2) adding gain on the camera settings, (3) removing disturbing external light, using only the light source of the goniometer during the measurement. (d) Test if other fitting methods work better. Methods that don't make assumptions about the shape of the drop, like polynomial fitting, are less prone to failure of fitting.
27	Measured CA values not constant on parts of the data	(a) Sample is non-uniform (b) Drop is vibrating during parts of the measurement	(a) Try repeating the measurement on a different part of the sample. If there is no improvement, report the non-uniformity with the data. (b) Repeat the measurement. Take extra care of removing all possible vibrations and air flow.

Table 3: Troubleshooting

Anticipated Results

With this protocol, one should be able to measure the advancing contact angle and the receding contact angle on a wide variety of surfaces in a reproducible manner. The results give information on the solid surface properties and give insights to solid-water interactions.

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

As a droplet moving horizontally on a surface has both an advancing contact line in the front and a receding contact line in 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 opposing fronts of the droplet do not necessarily correspond to the advancing contact angle and the receding contact angle 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 to recognize possible random errors in a given measurement.

An example of data collected from contact angle measurements performed on one sample are shown below, the advancing contact angle in Figure 8 and the receding contact angle in Figure 7. Five individual measurements are performed on separate locations of the sample, and since the wetting properties of sample are not perfectly homogeneous, the results deviate slightly from one measurement to another. In Figure 8 a) are shown all the obtained data points between 3 and 10 µL drop size, in 8 b) only the data points used to calculate the average advancing contact angle of the sample are shown: the data points removed before this step are outliers in which the automatic fitting procedure has failed. The oscillations seen on each of the curves up to the volume of some 6 µL is not an error of measurement, but is caused by stick-and-slip behaviour of the moving contact line.

In one of the receding contact angle measurements (Figure 7; red curve), the advancing drop volume has not been large enough to reach the receding contact angle, due 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 can't be done, due to for example restricted size of the sample, only the 'plateau' in the data should be used. In Figure 7 a) are shown all the

measured data points, in Figure 7 b) are shown only the data points used for calculation of the average contact angle of the sample.

Competing financial interests

The authors declare no competing financial interests.

Acknowledgements

The protocol is the result of a procedure gradually developed since wetting research was started in the group of R.H.A.R., and we acknowledge the contributions from Henrikki Mertaniemi, Tuukka Verho and Mika Latikka This work was supported by the European Research Council ERC-2016-CoG (725513- SuperRepel) and Academy of Finland (Centres of Excellence Programme 2014-2019). X.T. thanks the support of One Hundred Talents Program of SYSU and One Thousand Youth Talents Program of China.

Author contributions statement

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

Supplementary Information

Supplementary Method: Python code for solving the Young-Laplace equation

The minimum advancing drop volumes (= the recommended starting volume for receding contact angle measurement) needed to reach RCA at 10 µL (Fig. 6), were obtained by solving the Young-Laplace equation by numerical integration, using Python programming language with Scipy library. The shape and size of the drop for different pairs of contact angle and drop volume were solved using a code that is provided in this supplementary file.

FIGURE LEGENDS

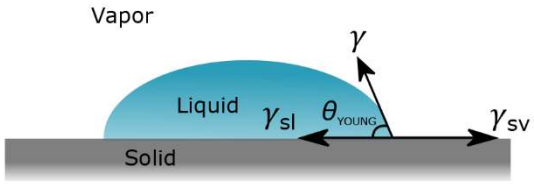

Figure 1: *A drop of water on an ideal solid substrate. Young contact angle* $(\theta_{\mathrm{YOUNG}})$ *is determined by a balance of the horizontal projection of the surface tension of water along the solid surface (*γ**cos(*θ_{YOUNG}*)) and interfacial tensions* γ_{sv} and γ_{sl}.

Figure 2: Static water drops on a window, and on a plant stem. 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/

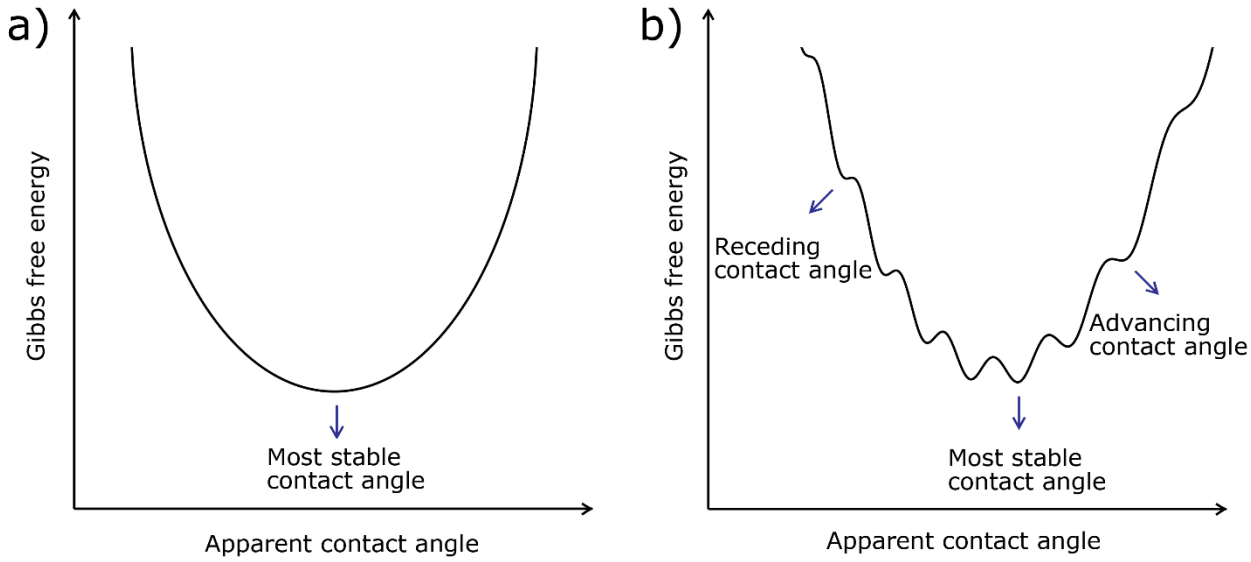

***Figure 3**: Sketch of the Gibbs free energies of ideal and real wetting system as a function of the apparent contact angle. a) Free energy of a wetting system between an ideal solid surface, water and gas. The wetting system only has a single energy minimum, corresponding to the most stable contact 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 several metastable static contact angles, corresponding to the local energy minima.*
Due to the energy barrier between the local energy minima of a real solid surface, a deposited "static" drop can be in any of the energy minima within the hysteresis range. Since it is not possible to know in which 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.

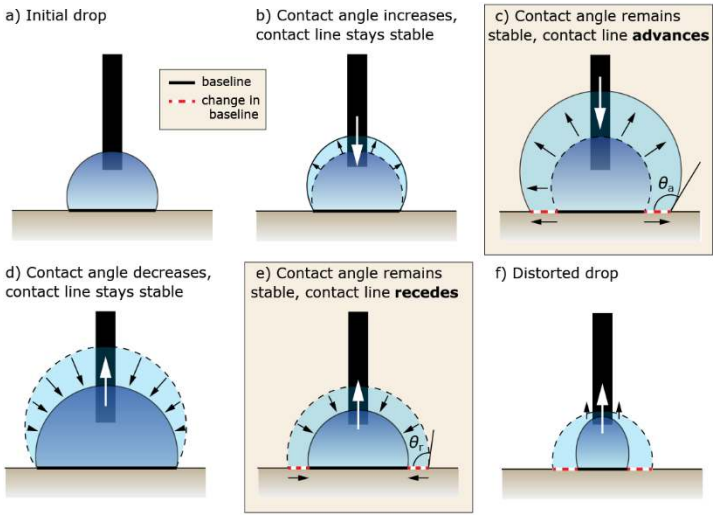

***Figure 4**: Different stages of the advancing and the receding contact angle measurement. The white arrows point to water pumped in during the advancing contact angle measurement, and pumped out of the droplet during the receding contact angle measurement. The advancing*

contact angle and receding contact angle are reached respectively in stage (c) and (e) as highlighted with a box.
(a) An initial 2 µL droplet is deposited. b) Water is added to the drop before the measurement is started. At this stage, the advancing contact angle is not necessarily reached: The shape of the droplet changes, but the baseline (highlighted with a black line) remains stable. c) The advancing contact angle is reached, and baseline advances steadily as water is added and the droplet volume increases from 3 to 10 µL while video is recorded. In receding contact angle measurements, (d) water is first removed from an initial drop before recording of the video is started. At this stage, the receding contact angle is not yet necessarily reached; the shape of the drop changes, and the baseline remains stable. (e) Receding contact angle is reached, and baseline recedes steadily as droplet volume is decreased from 10 to 3 µL while video is recorded.

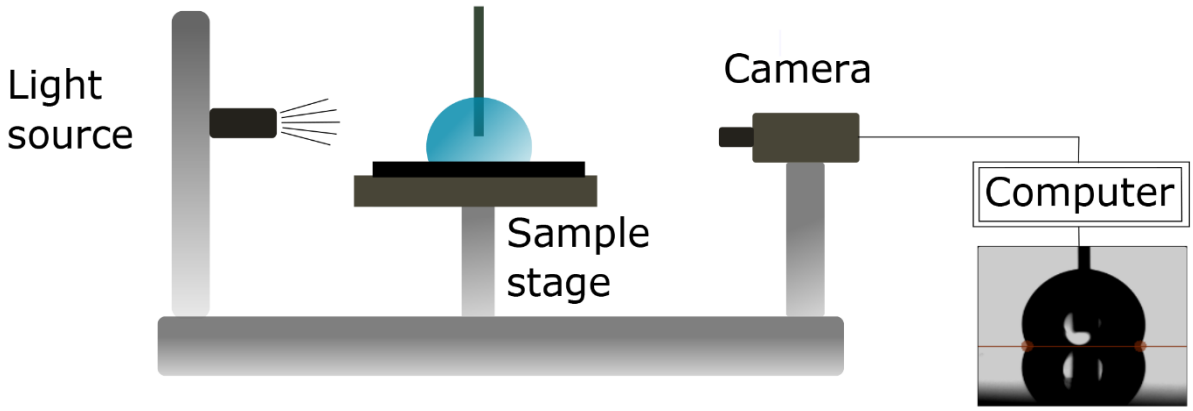

Figure 5: *Sketch of a goniometer set-up. Basic goniometer consists of a light source, an adjustable sample stage, a dispensing system (motorized syringe connected to a needle by tubing), and a CCD camera to record video and a computer for data analysis.*

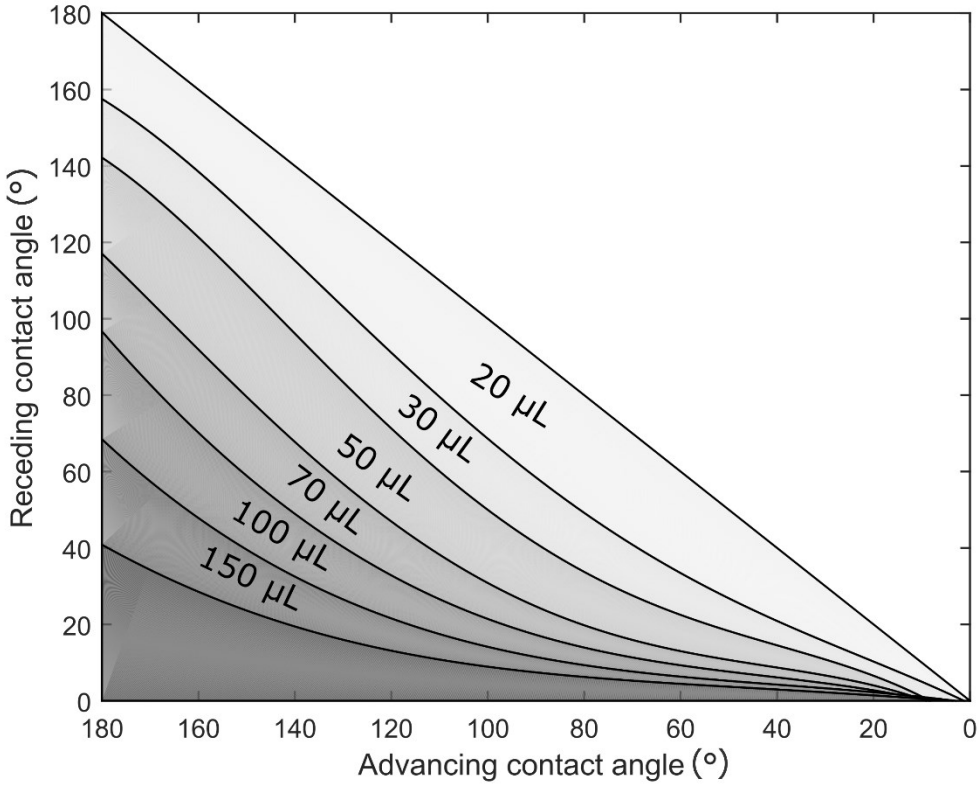

Figure 6: *Recommended starting volume for RCA measurement, i.e. minimum advancing drop volume (V_a) needed to reach RCA at 10 µL. By estimating the advancing and the receding contact angle of the sample to be measured, a recommended starting volume can be found from the plot. The plot was obtained by numerical integration of the Young-Laplace equation. The code for calculating contour lines is provided in Supplementary Method 1.*

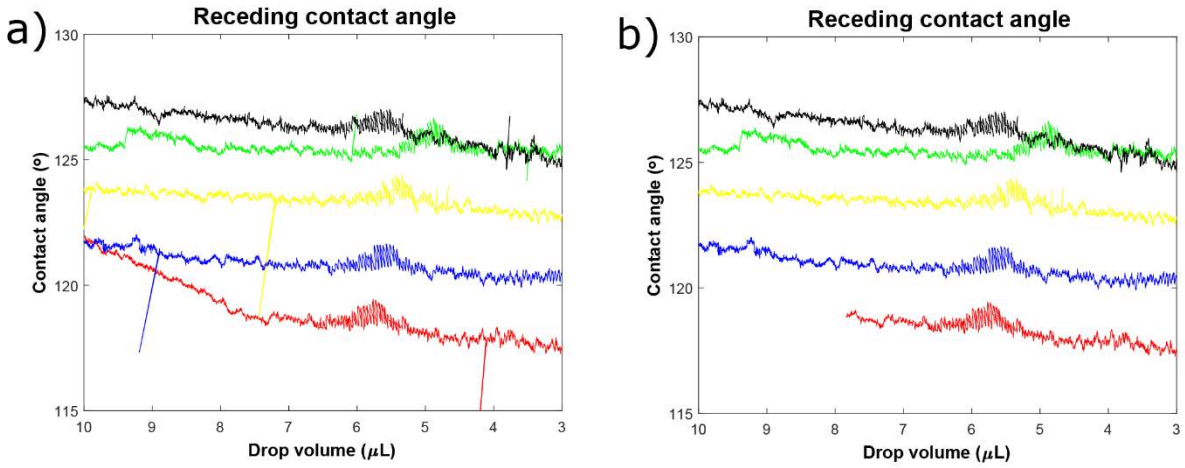

Figure 7: *Receding contact angle data of a nanostructured polysiloxane film on silicon substrate. Five different measurements performed on different locations of the sample. In a) is shown the raw data,*

which includes some outlier data points in which the automatic fitting procedure has failed, and the measured value of contact angle in these points has been removed from the data shown in b). The average receding contact angle (122.7 ± 3.3°) of the sample is calculated as an average of the data points of the 5 curves shown in b). For the measurement with the data shown by the red curve, the contact angle had not achieved the receding contact angle 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.

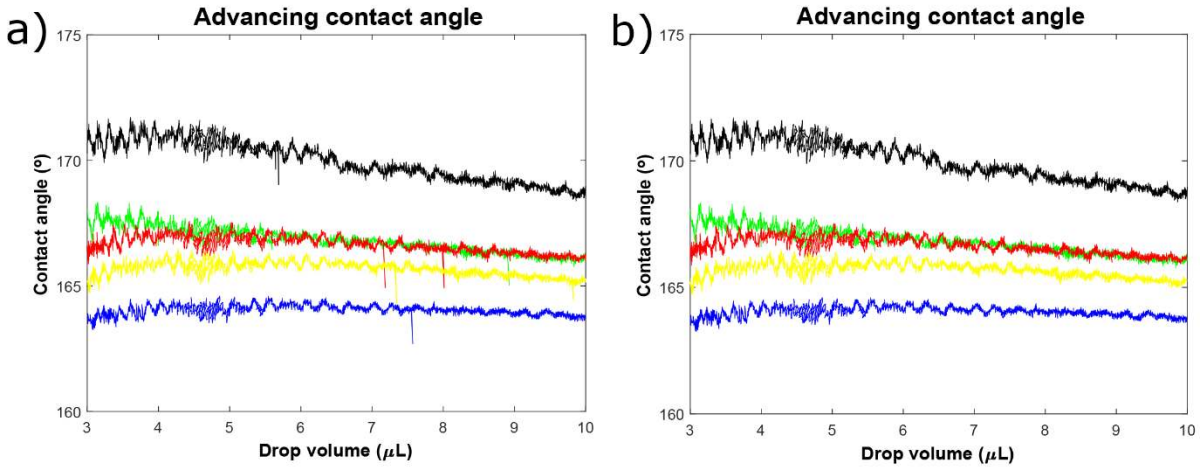

***Figure 8**: Advancing contact angle data of a nanostructured polysiloxane film on silicon substrate. Five different measurements performed on different locations of the sample. In a) is shown the raw data, which includes some outlier data points in which the automatic fitting procedure has failed. The measured value of contact angle in these points has been removed from the data shown in b). The average contact angle of the sample (166.6 ± 1.8°) is calculated as an average of the data points of the 5 curves shown in b).*

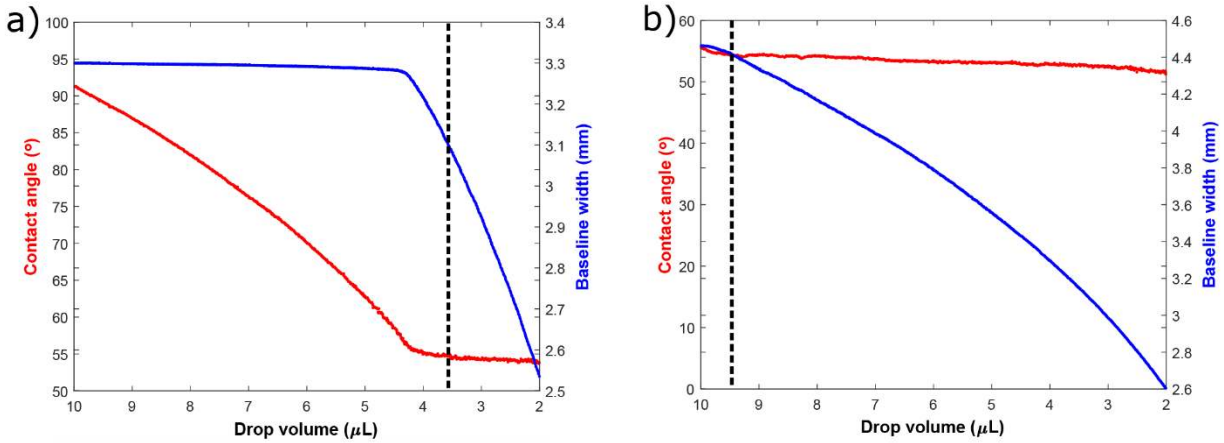

***Figure* 9:** *Effect of advancing drop volume (V_a) on the receding contact angle measurement. Both measurements are performed on the same sample, a polysiloxane film deposited on a silicon wafer. The green line corresponds to the value of the measured contact angle as a function of drop volume, blue line to the width of the baseline as a function of drop volume. a) The advancing drop volume is smaller than V_a, and receding contact angle is only reached near the end of the measurement, as marked by the dashed line. b) When advancing volume of at least V_a is used, RCA is reached before the start of measurement, and useful data is gathered over the entire measured range. Data collected before the dashed line is not directly useful in wetting characterization, and useful data is obtained only from a very limited region of the sample. Even after the receding contact angle is reached, 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.*

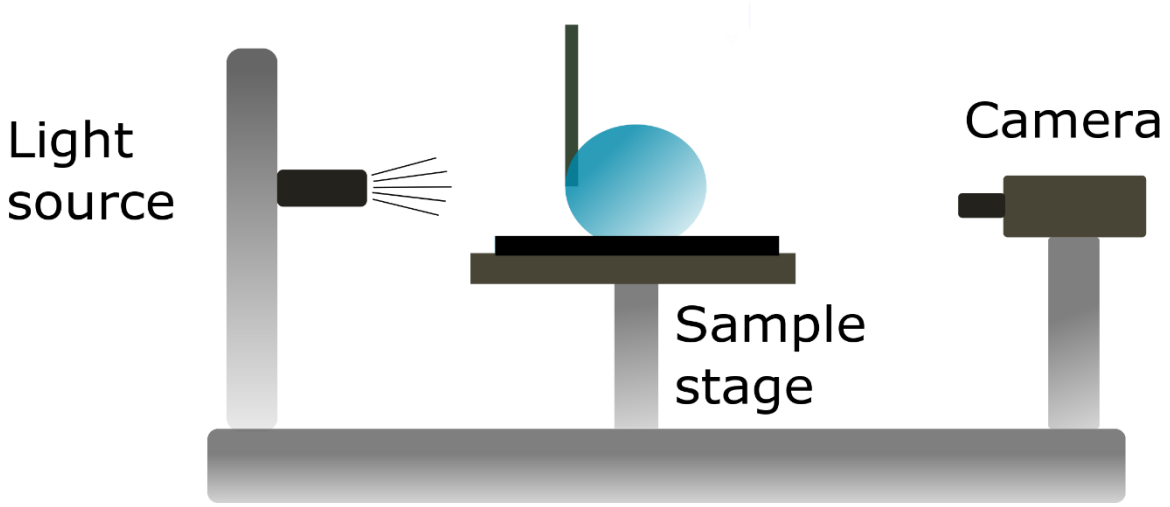

Figure 10*: Needle position for a very hydrophobic surface with low contact angle hysteresis. The needle will not stay in the middle of the drop from this side perspective on highly hydrophobic surfaces, since the friction is so low for it. If the needle is not in the middle of the drop as seen from 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 above location for the needle will cause the least inaccuracy in the results obtained.*

References

1. Riederer, M. & Schreiber, L. Protecting against water loss: analysis of the barrier properties of plant cuticles. *J. Exp. Bot.* **52,** 2023–2032 (2001).

2. Gao, X. & Jiang, L. Water-repellent legs of water striders. *Nature* **432,** 36 (2004).

3. Barthlott, W. & Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **202,** 1–8 (1997).

4. Parker, A. R. & Lawrence, C. R. Water capture by a desert beetle. *Nature* **414,** 33–34 (2001).

5. Zhao, G. *et al.* High surface energy enhances cell response to titanium substrate microstructure. *J. Biomed. Mater. Res. - Part A* **74,** 49–58 (2005).

6. Pankaj, S. K. *et al.* Applications of cold plasma technology in food packaging. *Trends in Food Science and Technology* **35,** 5–17 (2014).

7. Tian, D., Song, Y. & Jiang, L. Patterning of controllable surface wettability for printing techniques. *Chem. Soc. Rev. Chem. Soc. Rev* **42,** 5184–5209 (2013).

8. Korhonen, J. T., Kettunen, M., Ras, R. H. A. & Ikkala, O. Hydrophobic nanocellulose aerogels as floating, sustainable, reusable, and recyclable oil absorbents. *ACS Appl. Mater. Interfaces* **3,** 1813–1816 (2011).

9. Young, T. An Essay on the Cohesion of Fluids. *Philos. Trans. R. Soc. London* **95,** 65–87 (1805).

10. Extrand, C. W. & Kumagai, Y. An Experimental Study of Contact Angle Hysteresis. *J. Colloid Interface Sci.* **191,** 378–383 (1997).

11. Marmur, A. Solid Surface Characterization by Wetting. *Annu. Rev. Mater. Res.* **39,** 473–489 (2009).

12. Marmur, A. Guide to the Equilibrium Contact Angles Maze. in *Contact Angle, Wettability and Adhesion* (ed. Mittal, K. L.) 3–18 (2006).

13. Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **38,** 71–99 (2008).

14. Andrieu, C., Sykes, C. & Brochard, F. Average Spreading Parameter on Heterogeneous Surfaces. *Lan* **104,** 2077–2080 (1994).

15. de Gennes, P. G. Wetting: statics and dynamics. *Rev. Mod. Phys.* **57,** 827–863 (1985).

16. Blake, T. D. The physics of moving wetting lines. *J. Colloid Interface Sci.* **299,** 1–13 (2006).

17. Drelich, J. Guidelines to measurements of reproducible contact angles using a sessile-drop technique. *Surf. Innov.* **1,** 248–254 (2013).

18. Good, R. J. Contact angle, wetting, and adhesion: a critical review. *J. Adhes. Sci. Technol.* **6**, 1269–1302 (1992).

19. Kwok, D. Y. & Neumann, A. W. *Contact angle measurement and contact angle interpretation*. *Advances in Colloid and Interface Science* **81,** 167– 249 (1999).

20. Lam, A. N. C., Lu, J. J. & Neumann, A. W. Measuring Contact Angle. *Appl. Surf. Colloid Chem.* **2,** 251–277 (2002).

21. Della Volpe, C. & Siboni, S. The Wilhelmy method : a critical and practical review. *Surf. Innov.* (2018). doi:https://doi.org/10.1680/jsuin.17.00059

22. Liimatainen, V. *et al.* Mapping microscale wetting variations on biological and synthetic water-repellent surfaces. *Nat. Commun.* **8,** 1798 (2017).

23. Pierce, E., Carmona, F. J. & Amirfazli, A. Understanding of sliding and contact angle results in tilted plate experiments. *Colloids Surfaces A Physicochem. Eng. Asp.* **323,** 73–82 (2008).

24. Krasovitski, B. & Marmur, A. Drops down the hill: Theoretical study of limiting contact angles and the hysteresis range on a tilted plate. *Langmuir* **21,** 3881–3885 (2005).

25. Lam, C. N. C., Lu, J. J. & Neumann, a. W. Measuring Contact Angle. *Handb. Appl. Surf. Colloid Chem.* **1,** 251–280 (2002).

26. Marmur, A. in Contact Angle, Wettability and Adhesion, Volume 6, Ed. Mittal K. L. A Guide to the Equilibrium Contact Angles Maze. 3–18 (2009).

27. Rudawska, A. & Jacniacka, E. Analysis for determining surface free energy uncertainty by the Owen-Wendt method. *Inernational J. Adhes. Adhes.* **24,** 451–457 (2009).

28. Zhao, Q., Liu, Y. & Abel, E. W. Effect of temperature on the surface free energy of amorphous carbon films. *J. Colloid Interface Sci.* **280,** 174–183 (2004).

29. Hoorfar, M. & Neumann, A. W. Recent progress in Axisymmetric Drop Shape Analysis (ADSA). *Adv. Colloid Interface Sci.* **121,** 25–49 (2006).

30. Tavana, H. & Neumann, A. W. On the question of rate-dependence of contact angles. *Colloids Surfaces A Physicochem. Eng. Asp.* **282–283,** 256–262 (2006).

31. Korhonen, J. T., Huhtamäki, T., Ikkala, O. & Ras, R. H. A. Reliable Measurement of the Receding

Contact Angle. *Langmuir* **29,** 3858–3863 (2013).

32. Grundke, K. *et al.* Experimental studies of contact angle hysteresis phenomena on polymer surfaces - Toward the understanding and control of wettability for different applications. *Adv. Colloid Interface Sci.* **222,** 350–376 (2015).