

Contact Angle Measurements Using a Simplified Experimental Setup

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Contact angle measurements are often used to evaluate surface and liquid cleanliness and the effects of surface treatments developed as a part of fundamental research in surface science, as well as for industrial applications. An accurate characterization of surfaces is required in a wide range of research fields, such as surface chemistry and biomaterials (1). In addition to techniques such as Fourier-transform infrared spectroscopy (2), second-harmonic generation or sum-frequency generation (3), atomic force microscopy (4), X-ray photoelectron microscopy (5), and ellipsometry (6), contact angle measurement is useful in the evaluation of surface macroscopic properties, such as surface energy (7) and wettability (8).

A drop of pure liquid on a plane solid surface experiences adhesive forces acting between the liquid and the solid surface that favor spreading, whereas the cohesive forces within the liquid counteract the spreading. The balance between these forces determines the contact angle, θ (Figure 1). This balance is described by Young's equation (9) that relates the contact angle to the surface free energies of a system containing solid (S), liquid (L), and vapor (V) phases

$$\gamma^{SV} - \gamma^{SL} = \gamma^{LV} \cos \theta \quad (1)$$

where γ^{SV} is the solid surface free energy, γ^{LV} is the liquid surface free energy (also called surface tension), and γ^{SL} is the solid–liquid interfacial free energy. A solid surface with a surface energy that is higher than the surface tension of a liquid drop will undergo complete wetting so that adhesiveness dominates, and the drop spreads such that the contact angle is 0° . This can be illustrated by the complete spreading of water on any substrate that has a higher surface energy than that of water itself (i.e., $> 72.8 \text{ mN m}^{-1}$, water surface tension). If the substrate has a relatively high surface energy, yet lower than the liquid's surface tension, the liquid will wet the solid surface and the resulting contact angle is $0^\circ < \theta < 90^\circ$ (Figure 1C). Conversely, if the surface energy of the solid surface is low, it will undergo poor wetting and poor adhesiveness of the drop, resulting in a larger contact angle. For example, a water drop that has a contact angle $> 90^\circ$ (Figures 1A and 2B) is characterized as nonwetting, and the solid surface is said to be hydrophobic.

Measuring contact angles with a high level of precision usually requires high-tech contact angle goniometers that can perform a great number of automated measurements ($N = 50\text{--}100$) per drop, thus, reducing the error on each returned average value (10). Such goniometers may not be needed, especially for researchers that are

mainly concerned with performing routine controls on the quality of their sample surfaces, rather than making wetting studies that require the best equipment available. For instance, when making self-assembled monolayer (SAM) covered substrates for cell culture (1), a precision of $\pm 1\text{--}2^\circ$ in one single measurement is sufficient, as biological response, by nature, will not be critically sensitive to small variations in substrate wettability. Therefore, the simple experimental apparatus described here provides a convenient alternative to commercial goniometers because the method allows measurements with sufficient precision to be obtained while being accessible in terms of cost and ease of construction.

Practical experience in determining contact angle and surface energies would be advantageous to students in a course such as physical chemistry. In addition to learning how to optimize the configuration of the apparatus, the students would be acquainted with the sensitivity of contact angle measurements, which highly depend on the quality of the solid surface and on the cleanliness of the test liquid(s). Therefore, the students would learn the importance of cleaning and drying the sample surface, that is, performing experiments carefully and with attention to detail. More generally, and beyond experimental considerations, it should be emphasized that the contact angle measurement is a reliable technique to characterize solid–liquid interfaces, and the most simple and accessible technique available to measure the surface tension of solid surfaces. Step-by-step instructions on how to make a contact angle measurement are provided in the supporting information.

Hardware Assembly

A schematic view of the setup is shown in Figure 2C. All parts, except the lighting system, are mounted on an aluminum breadboard. Thus, the optical components are kept stable and fixed, while the sample support is mounted on a translation system, allowing for subtle focus adjustments. Details of all the parts used to assemble the system are listed in Table 1.

The optical parts include a basic digital camera (Sony, Cyber-shot, 5.1 megapixels) and an optical lens with a focal distance of 50.0 mm (Thorlabs, BK7 A-coated plano-convex lens, 25.4 mm diameter) that is situated between the camera and the sample (Figure 2A). A lamp is positioned behind the sample to make the liquid drop to appear black, which is necessary for measurement precision as well as for image processing. A box (Figure 2B), covered with sheets of aluminum foil, is positioned over the lens and the sample, thus, rejecting stray light. The box

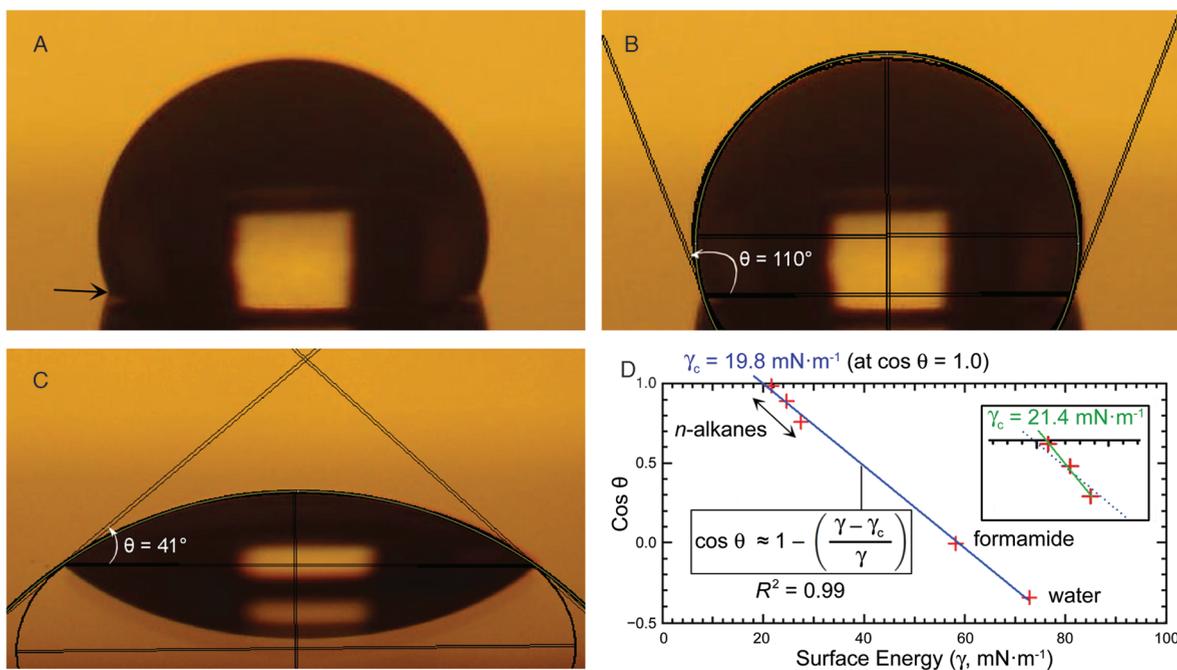


Figure 1. Liquid drops in contact with a solid surface (ODS SAM on glass slide). (A) A drop of deionized water ($5 \mu\text{L}$) on ODS surface. The arrow points the solid–liquid–air point, where the contact angle is measured. (B) Same drop as in (A) processed with the ImageJ software using the contact angle plugin. (C) A drop of *n*-Hexadecane ($5 \mu\text{L}$) on ODS SAM, processed with ImageJ. The profiles of the drops in (B) and (C) are automatically fitted using the ellipse approximation. A possible application of contact angle measurements is to determine critical surface energy (γ_c) of the solid surface using a Zisman plot (D). Inset box at top right represents the line fit for data for *n*-alkanes liquids only that supposedly returns a more accurate value for the critical surface tension of an ODS SAM. The dashed line in the inset box is equivalent to the line fit for all liquids.

dimensions are not critical, providing that the box covers the sample and lens assembly. The liquid drop should not reflect any stray light that could spoil the measurement. The use of the box can be avoided, providing the experiments are conducted in a room where light intensity is lower than the light intensity produced by the lamp. Nevertheless, the box is also useful to prevent drops being polluted by air contaminants such as dust.

The most critical element relating to the precision of measurements is the lighting system. Careful attention should be given to generate a background behind the drop that is homogeneous (Figure 1A). Good results in homogenizing the background are obtained through positioning a diffuser such as tracing paper between the drop and the lamp as (Figure 2C). A commercial lamp with power between 50 and 200 W can be used to provide the light source.

In addition, the height of the camera should be adjusted so that the actual drop and its reflection on the glass substrate can be observed. Thus, one can precisely determine position of the triple line (at intersection of solid–liquid–air interfaces) between the two, marked by an arrow in Figure 1A.

Hazards

The organic reagents may cause irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled. They are also flammable.

Measuring Contact Angles

The contact angle measurement is illustrated in the case of drops ($5 \mu\text{L}$) of deionized water (Figure 1A,B) and of *n*-hexadecane

(Figure 1C) (Sigma, >99%) on a glass slide (VWR microslides, $25 \text{ mm} \times 75 \text{ mm} \times 1 \text{ mm}$, cut with a diamond tip) modified with octadecyltrichlorosilane (OTS, Gelest, Inc.), so as to obtain a surface evenly coated with monolayer of octadecylsilane (ODS) groups: an ODS SAM. The procedure to make this substrate can be found elsewhere (11). The ODS SAM has hydrophobic terminal methyl groups, and thus, the contact angle for water is $>90^\circ$ (Figure 1A,B). The images in Figure 1 are taken directly with the camera. No image treatment, such as contrast enhancing, has been done to further process images to determine contact angles.

The same drop of deionized H_2O on an ODS SAM (as in Figure 1A) is shown in Figure 1B after processing by ImageJ free software (12) using the contact angle plugin (13). For each measurement, the user must choose two points to manually define the baseline and three points along the drop profile (see the supporting information that features a set of instructions supplying all the details on the procedure used to make the measurement). The program then fits the profile of the drop and calculates the contact angle using the sphere approximation or the ellipse approximation. In our study, the ellipse approximation gave consistent results for contact angles $>40^\circ$. For drops with contact angles $<40^\circ$, the sphere approximation was used.

To evaluate the level of precision on the analysis of a single drop obtained using this method, the image of the drop shown in Figure 1A was processed 50 times by the ImageJ contact angle plugin (as in Figure 1B). The returned value of contact angle was $110.2 \pm 0.4^\circ$. The difference between the maximum and minimum measured values was 1.7° . For an *n*-hexadecane drop, which has a lower contact angle on the same surface (Figure 1C), the contact angle was $40.7 \pm 0.6^\circ$, with a difference between

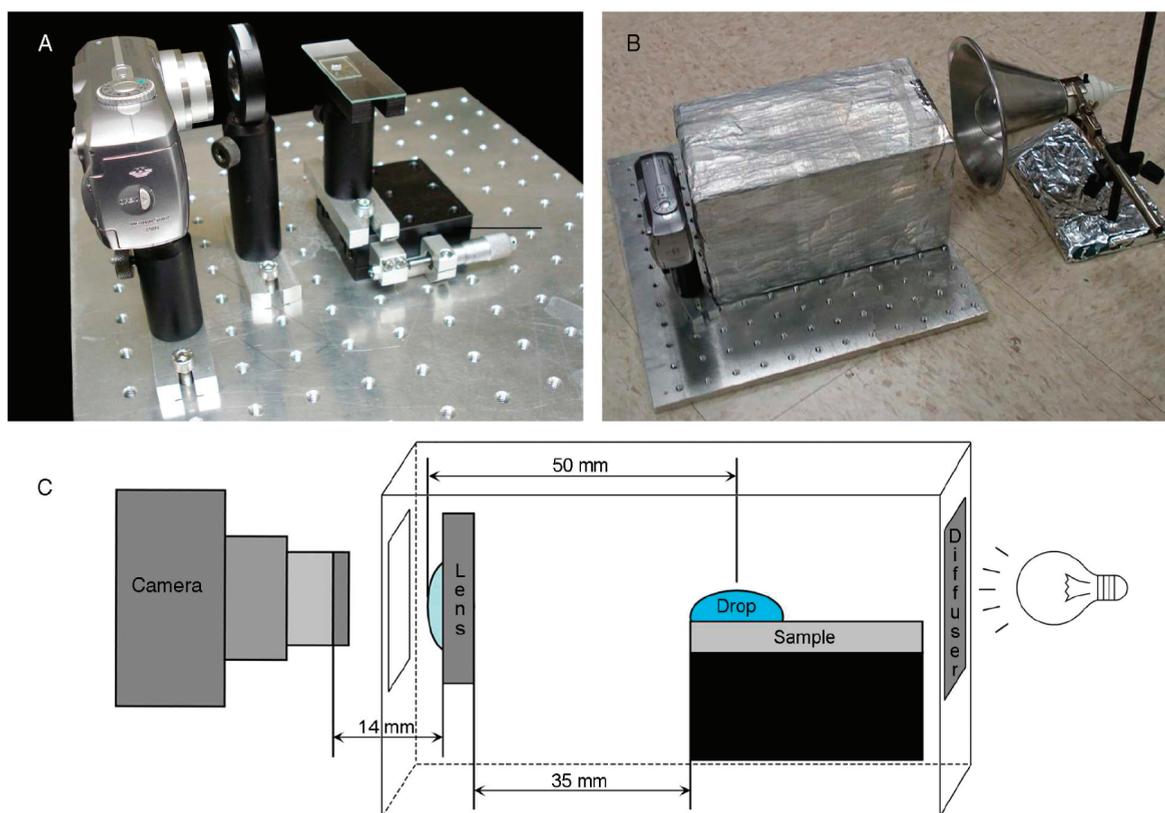


Figure 2. Setup used to measure contact angles. All the “internal” elements of the experimental apparatus are shown in picture (A), whereas picture (B) depicts elements external to the box, such as lighting system. The sketch in (C) precisely describes the configuration, along with the critical distances between some essential parts, such as camera, lens, and sample area.

Table 1. List of All Components Used To Make the Contact Angle Measurement Experimental Apparatus, as Presented in Figure 2A

Brand	Specification	Part number	Quantity
Sony	Cyber-Shot Digital Camera, 5.1 Mpxl	DSC-P93	1
OptoSigma	Aluminum Linear Ball Bearing Stage	123-0710/0715	1
Thorlabs	Aluminum Breadboard, 8" x 8" x 1/2", 1/4-20 Threaded	MB8	1
Thorlabs	Mounting Base, 1" x 3" x 3/8" (25 x 75 x 10 mm)	BA1	4
Thorlabs	Post Holder with Spring-Loaded Thumbscrew, L = 3"	PH3-ST	1
Thorlabs	Post Holder with Spring-Loaded Thumbscrew, L = 2"	PH2-ST	2
Thorlabs	Adapts $d = 1''$ – Optic to $d = 2''$ – Mount	AD2	1
Thorlabs	SM1 Retaining Ring for $d = 1''$ Lens Tubes and Mounts	SM1RR	1
Thorlabs	1/4"-20 Locking Thumbscrew for Post Holders, Brass, 10 Per Box	TS25B031	1
Thorlabs	($d 1/2'' \times 1.5''$)-Post	TR1.5	3
Thorlabs	Cap Screw Kit	HW-KIT2/M M6-1.0 Screws	1
Thorlabs	BK7 A-Coated Plano-Convex Lens, $d = 25.4$ mm, $f = 50.0$ mm	LA1131-A	1

maximum and minimum measured values equal to 2.4° . These values obtained for water and *n*-hexadecane drops are in good agreement with those reported in the literature for the same substrate (14–16). Moreover, the level of precision obtained for the analysis of one single drop appears to be comparable to those obtained with commercial contact angle goniometers (10). The same type of measurements was done with drops of formamide, *n*-undecane, and *n*-octane on the same surface, displaying similar results in terms of precision. The results of all measurements made are summarized in Table 2. To obtain reasonable precision

on one single measurement of a specific liquid on a specific substrate, the user should perform the analysis of multiple drops (at least 3). The mean value of the analysis of these drops is the contact angle value for the liquid and surface under consideration. It is noted that according to experimental conditions, the standard deviation of the mean contact angle value may be higher than the uncertainty on the analysis of one single drop, reported in Table 2. Thus, the user is not requested to perform more than one single analysis per image, providing the line fit of the drop profile looks accurate.

Table 2. Static Contact Angles Measured for Several Test Liquids

	Water ^a	Formamide ^a	<i>n</i> -Hexadecane ^a	<i>n</i> -Undecane ^a	<i>n</i> -Octane ^a
Surface tension, γ /(mN m ⁻¹)	72.80	58.20	27.47	24.66	21.62
θ /deg, min value	109.6	88.6	39.4	26.5	9.4
θ /deg, mean \pm std dev (no. of times the contact angle was evaluated for a single image)	110.2 \pm 0.4 (50)	90.3 \pm 0.8 (50)	40.7 \pm 0.6 (50)	27.3 \pm 0.4 (20)	9.8 \pm 0.4 (20)
θ /deg, max value	111.3	92.2	41.8	27.9	10.8

^aUsing one drop per liquid on octadecylsilane self-assembled monolayer (ODS SAM) on glass. All values were obtained by fitting the images of the drops with the ImageJ contact angle plugin. Drops of water, formamide, and *n*-hexadecane were fitted using the ellipse approximation, whereas drops of *n*-undecane and *n*-octane were fitted using the sphere approximation.

Determination of the Critical Surface Tension of the Solid Substrate

Determining contact angles using several liquids that display different surface tensions can help in establishing the critical surface tension, γ_c , of the organic monolayer when surfaces are modified. As an example, the critical surface tension γ_c of the ODS substrate has been determined by measuring the static contact angle of liquid droplets (see Table 2). The values of γ_c are calculated using the Fox–Zisman approximation (17). In this article, it can be understood as a first-order approximation of the Good–Girifalco equation (18) for a surface tension of the liquid γ ($\gamma \geq \gamma_c$) close to the critical surface tension γ_c of the solid. Thus, a better plot of the contact angle is $\cos \theta$ versus $\gamma^{1/2}$, that is,

$$\cos \theta = -1 + 2 \left(\frac{\gamma_c}{\gamma} \right)^{1/2} \quad (2)$$

A linear approximation of eq 2 in the vicinity of γ_c (Fox–Zisman) gives

$$\cos \theta \approx 1 - \left(\frac{\gamma - \gamma_c}{\gamma} \right) \quad (3)$$

implying that when $\cos \theta = 1$, then $\gamma = \gamma_c$. This relationship is presented graphically in Figure 1D. It is made by fitting the data for the test liquids, using a linear regression analysis, to $\cos \theta = 1$, as described by Zisman (17). As a result, the critical surface energy determined for the ODS SAM is $\gamma_c = 19.8 \pm 1.5$ mN m⁻¹. In considering surface tensions, the “more energetic” component is wetted by the “less energetic”. Because γ_c is assimilated to the surface tension (i.e., surface energy) of the solid, all liquids that have a surface tension $\gamma > \gamma_c$ will not wet this solid (i.e., $\theta > 0$), and conversely, all liquids with $\gamma < \gamma_c$ will wet the solid surface (i.e., $\theta = 0$). Thus, the ODS SAM will undergo complete wetting of any liquid that has a surface tension below $\gamma_c = 19.8$ mN m⁻¹. This value compares favorably with literature values determined by Tillman et al. ($\gamma_c = 20.2$ mN m⁻¹) (14) and Kulkarni et al. ($\gamma_c = 20.7$ mN m⁻¹) (19) using the same method.

Here, the line fit of data obtained for H₂O, formamide, and *n*-alkanes was made considering that the ODS SAM is homogeneous and does not exhibit large roughness and polar contributions, known to be able to critically influence contact angles (20, 21). Starting from this postulate, we can also consider that, because *n*-alkane liquids have no polar contribution in their surface tensions (contrary to water and formamide), a more accurate line fit is obtained when fitting the data using only *n*-alkane liquids (inset box in Figure 1D). The result is

$\gamma_c = 21.4 \pm 0.5$ mN m⁻¹, which is probably an estimation closer to the “real” surface tension of the ODS substrate.

Conclusion

We considered a simple, efficient, and inexpensive apparatus for equilibrium contact angle measurements that proved to be adequate for measuring contact angles and thus to correctly estimate the critical surface tension, using the model derived from the theory of Good and Girifalco. The experimental results, summarized in Table 2, were obtained with ImageJ. This free and easily accessible image analysis software (with macros), returned precise and stable values of the contact angles in both relatively high ($\theta \geq 90^\circ$) and rather low ($\theta \leq 40^\circ$) degree regions. The setup described in this work can be a valuable instrument when a low-cost routine characterization of the surface is needed. It can be used for student laboratory instruction in educational institutions as well as for performing surface studies for actual research applications, for instance in biomedical fields.

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Supporting Information Available

Step-by-step instructions on how to make a contact angle measurement. This material is available via the Internet at <http://pubs.acs.org>.