Contact Angle Measurements with Sessile Drops and Bubbles

In this note a simple and precise method for measurement of contact angles in the range 0°–180° on solid surfaces is proposed. In the case when the three-phase contact line is irregular due to surface roughness and inhomogeneity, the method provides an effective averaged value of the contact angle. The method is based on a numerical solution of the Laplace equation for the interfacial profile. The input parameters used are the liquid–gas surface tension and a pair of the following parameters of the drop (bubble) shape: volume, height, contact radius, and equatorial radius. Depending on the magnitude of the contact angle different pairs of parameters are to be measured for the purpose of best accuracy.

1. INTRODUCTION

The contact angle is an important macroscopic characteristic of the surface wettability and of the interfacial free energy (1). The contact angle also characterizes the biological compatibility of different surfaces (2, 3).

The most popular way of determining contact angles with sessile drops is the goniometric technique. A tangent to the drop surface is placed at the point of contact and direct measurement is conducted. This method has a relatively large error of ±2° and is not suitable for small angles and irregular contact lines.

Different interferometric techniques (4, 5) can be used for measuring the contact angle, even for irregular contact lines. These methods are based on restoring the liquid meniscus profile in close vicinity of the contact line by processing the data for the interference fringes. In some cases the interference pattern can be time consuming.

An alternative possibility for contact angle measurements is provided by a method called axisymmetric drop shape analysis (ADSA). The version ADSA-P of this technique (6, 7) is based on computer processing of many experimental points for the drop profile in accordance with the Laplace equation. In particular, the measured drop height is also used for contact angle calculation. Cheng *et al.* (8) improved ADSA-P by using an automatic digitization technique utilizing recent developments in digital image acquisition and analysis. This technique was applied (9) for line tension measurements.

When the contact angle is small and the drop profile is flat ADSA-P is difficult to apply. To avoid this difficulty Skinner *et al.* (10) developed another technique, called ADSA-CD, based on measurements of only two geometrical parameters. These are the contact diameter and the drop volume. This method is conceptually simpler and does not require a special digital image analyzer. ADSA-CD can also be applied for contact angle measurements on imperfect solids (11).

The experimental techniques presented below in this note are closely related to ADSA-CD. The contact angle is determined from different pairs of measurable geometrical parameters. The numerical data processing is simple and fast. The different versions of the method are compared and discussed with respect to their accuracy and applicability.

2. METHOD DESCRIPTION AND ERROR ANALYSIS

Let us consider a liquid drop on a flat solid surface. Depending of the solid–liquid interactions two different configurations of the drop can be observed—see Figs. 1a, b.

In the case depicted in Fig. 1a (contact angle $\theta_c < 90°$) one can measure the volume, V, the contact radius, r_c, and the height of the drop, h. For the configuration shown in Fig. 1b one can measure in addition the equatorial radius of the drop, R. The generatrix of the upper drop surface satisfies the known Laplace equation. For axisymmetric liquid surfaces this equation reads (12, 13)

$$\sigma \frac{d(x \sin \theta)}{x(dx)} = P_c + \Delta\rho g z. \qquad [1]$$

Here σ is the liquid/gas surface tension, $\Delta\rho$ is the density difference between the two fluid phases, g is the gravity acceleration, P_c is the capillary pressure at the level $z = 0$, and θ is the running slope angle:

$$\frac{dz}{dx} = \tan \theta. \qquad [2]$$

If the drop profile $x = x(z)$ is known one can calculate the drop volume V by integrating the equation:

$$\frac{dv}{dz} = \pi x^2. \qquad [3]$$

Hartland and Hartley (13) demonstrated that for computational purposes it is convenient to use the length s of the generatrix as a parameter. One has

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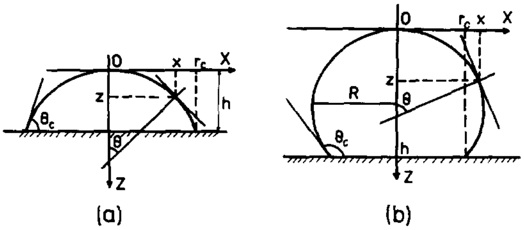

FIG. 1. Profile and geometrical parameters of a sessile drop on a solid surface with contact angle $\theta_c < 90°$ (a) and $\theta_c > 90°$ (b). R and r_c are the equatorial and the contact radii of the drop, respectively, h is the height, and θ is the running slope angle.

$$\frac{dx}{ds} = \cos\theta, \quad \frac{dz}{ds} = \sin\theta, \qquad [4]$$

and hence Eqs. [1] and [3] can be transformed to read

$$\frac{d\theta}{ds} = \frac{P_c + \rho g z}{\sigma} - \frac{\sin\theta}{x} \qquad [5a]$$

$$\frac{dv}{ds} = \pi x^2 \sin\theta. \qquad [5b]$$

We will use the above equations to calculate the contact angle θ_c by numerical integration (for details, see below). The boundary conditions at the drop (bubble) apex are

$$z = 0, \quad \theta = 0, \quad v = 0 \text{ at } x = 0. \qquad [6]$$

The parameter P_c on the right-hand side of Eq. [5a] is not directly measurable. To determine P_c and θ_c from the above set of equations one needs the values of two other parameters. For $\theta_c < 90°$ (Fig. 1a) these parameters can be

(1) volume (V) and height (h);
(2) volume (V) and contact radius (r_c)—see Ref. (10);
(3) height (h) and contact radius (r_c).

For $\theta_c > 90°$ (Fig. 1b) there are three additional possibilities:

(4) contact radius (r_c) and equatorial radius (R);
(5) height (h) and equatorial radius (R);
(6) volume (V) and equatorial radius (R).

It should be noted that the pair (V, r_c), case B, was used by Skinner *et al.* (10) in their method called ADSA-CD.

To integrate Eqs. [4] and [5] we used the standard method of Runge–Kutta–Felberg (RKF45)—see, e.g., Ref. (14). $\Delta\rho$ and σ are input parameters, which are supposed to be known from the experiment. The computer program is designed to account for the following two experimental situations:

(i) Let (u, w) be one of the pairs of measured geometrical parameters A, B, or C (see above). At a given (trial) value of the capillary pressure, P_c, the integration starts from the drop (bubble) apex with Eq. [6] as a boundary condition. The integration proceeds with appropriate increments in s up to the point where parameter u acquires its experimental value. At this point one also calculates some value of w which depends on u and P_c:

$$w = \zeta(u, P_c).$$

At given experimental values of u and w the later equation allows determining of P_c. Thus P_c is calculated by using trials and errors. Simultaneously the contact angle θ_c is calculated as the value of θ at the contact line.

(ii) Let (u, R) be one of the pairs of measured geometrical parameters D, E, or F (see above). At a given (trial) value of P_c Eqs. [4] and [5] are integrated numerically from the drop (bubble) apex (Eq. [6]) with appropriate increments in θ up to the point $\theta = 90°$, i.e., up to the drop (bubble) equator. Thus some value $R = R(P_c)$ of the equatorial radius is calculated. The real value of P_c is the one yielding the experimental value of R. Once P_c has been determined, the integration proceeds from the drop equator up to the contact line, i.e., up to the point where parameter u acquires its experimental value. The value of θ at this point is the sought for contact angle θ_c.

The accuracy of the calculated value of the contact angle depends on the experimental errors of the two measured parameters. The standard deviation $\Delta\theta_c$ can be calculated from the equation

$$\Delta\theta_c = \left\{\left[\left(\frac{\partial\theta_c}{\partial u}\right)_w \Delta u\right]^2 + \left[\left(\frac{\partial\theta_c}{\partial w}\right)_u \Delta w\right]^2\right\}, \qquad [7]$$

where the pair of variables (u, w) is to be replaced by (V, h) in case A, by (V, r_c) in case B, etc. The derivatives in Eq. [7] have been calculated numerically by using small increments in u at fixed w or vice versa.

It is expedient for one to measure this pair of parameters, which provides the best accuracy (least value of $\Delta\theta_c$). We tested the errors in all the cases, A, B, C, D, E, and F, at different experimental conditions and our suggestions are given at the end of this paper.

It should also be mentioned that the method based on numerical integration of Eqs. [4] and [5] is not accurate for angles very close to 180°, because the error of θ_c is relatively large (from 1 to 3 degrees in our experiments). In this case interferometric determinations of θ_c are advisable (5).

The method based on Eqs. [4] and [5] can be used not only with drops, but also with bubbles attached to a solid surface. For example, the variants D, E, and F of the method (see above) cannot be realized with sessile drops for $\theta_c < 90°$, but they can be realized with bubbles situated under the solid surface. Comparison between the contact angles measured with drops and those measured with bubbles is presented in the next section.

3. EXPERIMENTAL RESULTS

In our experiments we observed the drop (bubble) by using a horizontal and a vertical microscope. The horizontal microscope allows measurements of h and R, whereas the vertical microscope can be used for measurements of r_c if the contact line is a regular circumference. In addition, the vertical microscope allows independent interferometric measurement of the contact angle as described in Ref. (5). Some illustrative experimental data are presented in Tables I–III, θ_c in the tables is determined from the measured values of a pair of parameters (one of the sets A–F above) and θ_c^g is determined by using the goniometric method.

Table I contains experimental data for the height h and the volume V (set A) of sessile drops on a horizontal glass surface. The drop was formed from a 0.001 mol/liter aqueous solution of sodium dodecyl sulfate by using a syringe. The contact line was not a regular circumference and the interferometric measurements (common interference in reflected light—see Ref. (5)) showed that because of the hysteresis the contact angle varied between 3.7° and 4.5°. Supposing that the drop is axisymmetric, from the values of h and V we calculated an effective averaged value of the contact angle, θ_c, by means of the procedure based on Eqs. [1-6]. In Table I this value is compared with θ_c^g, measured by means of the goniometric method. One sees that the values of θ_c agree well with the interferometric measurements, whereas the values of θ_c^g are systematically higher.

In the same surfactant solution we formed air bubbles under a horizontal glass plate and measured the contact and equatorial radii, r_c and R (set D), by means of the vertical microscope. The results are presented in Table II. In this case the contact line turned out to be a perfect circumference and the interferometrically measured contact angle was $\theta_c = 0.85°$. These results imply that a thin foam film intervenes between the glass plate and the air bubble. The value of θ_c, determined by means of our method, and the goniometrically determined contact angle θ_c^g are also shown in Table II. One sees that the accuracy of our method in this case is not satisfactory, whereas the goniometric method provides strongly exaggerated values of θ_c.

Table III contains data for the height, h, and the equatorial radius, R (set E), of sessile pure aqueous drops on a homogeneous horizontal teflon surface. The contact angle, θ_c, calculated from the values of h and R by means of our method turns out to be well reproducible—see Table III. The goniometrically determined angle, θ_c^g, is again systematically higher. In this case the contact angle is too large and measurements of θ_c by means of the common interference are not possible.

Finally, we measured $V = 3.0 \pm 0.2$ μl and $r_c = 3.3 \pm 0.02$ (mm) (set B) for a pure aqueous drop on glass and then we calculated $\theta_c = 6.4° \pm 0.3°$. This value is to be compared with $\theta_c = 5.5° \pm 1.9°$, calculated by us from the shape of an air bubble in pure water with equatorial radius $R = 1.25 \pm 0.02$ (mm) and contact radius $r_c = 0.475 \pm 0.02$ (mm)—set D. The results demonstrate that for small contact angles set B (with sessile drops) yields the contact angle with considerably better accuracy than set D (with bubbles).

Similar experiments led us to the following conclusions:

(1) V and h are appropriate for use when the contact line is irregular (the surface is not perfectly smooth) or with large contact angles less than 90°;

(2) V and r_c are appropriate parameters for small contact angles, when the contact line is a regular circumference:

(3) h and r_c are suitable in all cases when the contact line is regular and h is not too small to be accurately measured;

(4) r_c and R are appropriate parameters for contact angles close to 180°;

TABLE I

Contact Angles of Sessile Drops from Surfactant Solution on a Glass Plate

h (μm)	v (μl)	θ_c (degree)	θ_c^g (degree)
56	0.2	4.4 ± 0.6	5.5 ± 1.0
60	0.3	4.0 ± 0.6	6.0 ± 1.0
73	0.5	4.2 ± 0.6	5.0 ± 1.0
100	1.5	4.1 ± 0.6	3.5 ± 1.0

TABLE II

Contact Angles of Bubbles in Surfactant Solution under a Glass Plate

R (μm)	r_c (μm)	θ_c (degree)	θ_c^g (degree)
919 ± 20	240 ± 20	0.0 ± 2.7	4.0 ± 1.0
927 ± 20	260 ± 20	0.3 ± 2.7	3.5 ± 1.0

Note. Interferometric measurement of θ_c is 0.85°.

TABLE III

Contact Angles of Sessile Drops from Distilled Water on a Horizontal Teflon Surface

h (μm)	R (μm)	θ_c (degree)	θ_c^g (degree)
945 ± 20	638 ± 20	121.4 ± 3.1	129 ± 6.5
1613 ± 20	1140 ± 20	121.7 ± 1.7	125 ± 3.0
1925 ± 20	1412 ± 20	121.2 ± 1.4	130 ± 5.0

(5) h and R can be used for angles between 90° and 180° but preferably for those close to 90°;

(6) R and V provide relatively large experimental error in the calculated contact angle and this pair of parameters is useful only for drops on not perfectly smooth surfaces at large ($\theta_c > 90°$) contact angles.

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