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# Contact angle calculations from the contact/maximum diameter of sessile drops

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## SUMMARY

This paper presents two algorithms for computing the contact angle of sessile liquid drops given data about the drops. The first yields the contact angle given the volume, surface tension and maximum diameter (or contact diameter) of a single drop. This algorithm is an extension of existing algorithms based on knowledge of the maximum diameter or of the contact diameter of a drop. A sensitivity analysis is included for this algorithm, allowing estimates to be made of the error in computed contact angle caused by errors in the measurement of the volume and/or diameter. The second algorithm requires only the volume and maximum or contact diameter of two different drops as input, and it produces both the contact angle and surface tension as output. Both algorithms are based on Newton's method applied to a function whose value is computed by solving a system of ordinary differential equations obtained from the Laplace equation of capillarity. The techniques are applicable to both hydrophobic and hydrophilic surfaces. Copyright © 2000 John Wiley & Sons, Ltd.

KEY WORDS: contact angle; contact diameter; sessile drops

## 1. INTRODUCTION

Finding the contact angle between a liquid and solid substrate by using small axisymmetric sessile drops has been the subject of several papers [1–3]. Experimentally, the method requires only small amounts of liquid and only a few square millimeters of substrate. There are several different techniques for calculating the contact angle formed. Probably the simplest consists of taking a photograph of the drop from the side and using a protractor to measure the contact angle. More sophisticated methods involve approximating the drop shape with ellipses [4,5] or fitting prescribed curves to specific data points on the drop profile. The axisymmetric drop shape analysis-profile (ADSA-P) [6] improves the method by fitting an arbitrary set of profile co-ordinate points to the Laplace equation of capillarity. In addition, this method can be used, at the expense of more points and computational effort, to estimate other drop parameters, such as the interfacial tension, volume and surface area.

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However, these methods have serious shortcomings. They are inaccurate for biological and other hydrophilic surfaces because the extremely flat profiles of the drop make it difficult to acquire accurate co-ordinates along the drop surface. Moreover, they are inapplicable to situations in which a side view of the drop cannot be obtained. To address the first problem, Reference [7] introduced the ADSA-CD (contact diameter) method in which the contact angle is calculated, again by integrating the Laplace equation of capillarity, from knowledge of the drop surface tension, volume and contact diameter. This method was subsequently modified in Reference [8] as the ADSA-MD (maximum diameter) method to use not the contact diameter but the maximum diameter. Thus, drops for which the contact angle exceeds 90° can be analyzed with only an overhead view and the advantages of the ADSA-CD method are retained. A generalized algorithm that includes both References [7,8] as special cases is given in Reference [9].

In the present paper, a modification and extension of the ADSA-CD/MD methods are proposed. The volume and drop diameter (either contact or maximum) of two different sized drops are used, but the liquid/air surface tension as input is no longer required—instead this parameter is calculated as part of the algorithm. Because the single drop theory of References [7,8] is required in the two-drop problem, a unified and slightly enhanced treatment of these methods, including an analysis of the sensitivity of the procedure to input errors, is presented first. The analysis applies specifically to the maximum diameter problem—the small changes required for the contact diameter set-up are indicated where appropriate. The results are then extended to include the two-drop experiment.

## 2. SINGLE DROP—THEORY

The Laplace equation of capillarity arises from the balance of pressure and tension forces in the drop surface

$$\gamma(\kappa_1 + \kappa_2) = \Delta P \tag{1}$$

where $\kappa_1$ and $\kappa_2$ are the principal curvatures and $\Delta P$ is the pressure difference across the interface. With gravity as the only external force, this pressure difference is a linear function of height

$$\Delta P = \Delta P_0 + g(\Delta\rho)z \tag{2}$$

where $\Delta P_0$ is the difference across the droplet interface at the top of the drop, $\Delta\rho$ is the density difference between the drop and the surrounding medium, and $z$ is the distance below the top of the drop (Figure 1). Equations (1) and (2) then reduce to

$$\kappa_1 + \kappa_2 = 2\kappa + \alpha z \tag{3}$$

where $\kappa$ is the mean curvature at the origin and $\alpha = g(\Delta\rho)/\gamma$.

 

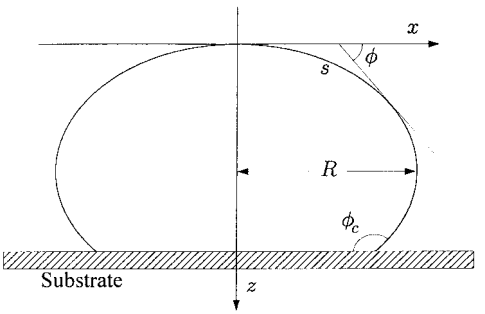


Figure 1. Co-ordinate system for the sessile drop. $s$ is arc length along the drop measured from the origin and $\phi$ is the angle of the tangent below the $x$-axis. The radius of the drop is $R$ and $\phi = \phi_c$ at the point of contact with the substrate. For the CD experiment, $R$ is the radius of the drop at the substrate level.

For an axisymmetric drop, the shape is completely determined by a single meridian, which it is convenient to parametrize in terms of arc length $s$ measured from the origin. The two principal curvatures are given [10, p. 3] by the formulae

$$\kappa_1 = \frac{\mathrm{d}\phi}{\mathrm{d}s} \quad \text{and} \quad \kappa_2 = \frac{\sin\phi}{x}$$

and so Equation (3) can be written as the system of ordinary differential equations (ODE)

$$\left.\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}s} &= \cos\phi, & x(0) &= 0 \\ \frac{\mathrm{d}z}{\mathrm{d}s} &= \sin\phi, & z(0) &= 0 \\ \frac{\mathrm{d}\phi}{\mathrm{d}s} &= 2\kappa + \alpha z - \frac{\sin\phi}{x}, & \phi(0) &= 0 \end{aligned}\right\} \tag{4}$$

Since the solution of these equations depends on $\kappa$ as well as $s$, we write $x(s, \kappa)$, $z(s, \kappa)$ and $\phi(s, \kappa)$. In order to compute the volume $V$ of the drop, we augment this system with the additional equation

$$\frac{\mathrm{d}v}{\mathrm{d}s} = \pi x^2 \sin\phi, \quad v(0) = 0 \tag{5}$$

whose integral gives the volume $v(s, \kappa)$ of liquid above the point with parameter $s$.

In Equation (4) for this single drop case, the parameter $\alpha$ is assumed known. The drop volume $V$ and outer radius $R$ (as viewed from above) are measured and therefore also known.

 

Once the value of $\kappa$ has been determined, the desired contact angle $\phi_c$ is found by solving Equations (4) and (5) until $v = V$ and then $\phi = \phi_c$ (or if $\phi = \pi$ before $v = V$, then the volume of the drop is too large for the given radius and the drop is unrealistic). To compute the value of $\kappa$, the shooting method is employed as follows. For a given $\kappa$, let $S(\kappa)$ be the value of $s$ at which the solution of Equations (4) and (5) satisfies either $\phi = \pi/2$ or $v = V$, whichever occurs first. To find $\kappa$ we need to solve the equation $X(\kappa) \equiv x(S(\kappa), \kappa) = R$. This is accomplished by iterating the Newton algorithm

$$\kappa \leftarrow \kappa - \frac{X(\kappa) - R}{X'(\kappa)}$$

until the desired accuracy is obtained. The derivative $X'(\kappa)$ is found from

$$X'(\kappa) = x_\kappa + (\cos\phi)S'(\kappa)\big|_{s = S(\kappa)}$$

where the subscript $\kappa$ denotes differentiation with respect to $\kappa$. The last term disappears in the case $\phi = \pi/2$. In the other case, $v(S(\kappa), \kappa) \equiv V$ with derivative $v_\kappa + (\pi x^2 \sin\phi)S'(\kappa) = 0$. Substituting for $S'(\kappa)$ above yields

$$X'(\kappa) = x_\kappa - \frac{v_\kappa}{\pi x^2}\cot\phi\Big|_{s = S(\kappa)}$$

and since $\cot\phi = 0$ when $\phi = \pi/2$ this equation holds in all cases. Finally, $x_\kappa$ and $v_\kappa$ are computed by numerically solving Equations (4) and (5) together with the following system, obtained by differentiating (4) and (5) with respect to $\kappa$

$$\left.\begin{aligned}
\frac{dx_\kappa}{ds} &= -(\sin\phi)\phi_\kappa, & x_\kappa(0) &= 0\\
\frac{dz_\kappa}{ds} &= (\cos\phi)\phi_\kappa, & z_\kappa(0) &= 0\\
\frac{d\phi_\kappa}{ds} &= 2 + \alpha z_\kappa - \frac{\cos\phi}{x}\phi_\kappa + \frac{\sin\phi}{x^2}x_\kappa, & \phi_\kappa(0) &= 0\\
\frac{dv_\kappa}{ds} &= 2\pi x(\sin\phi)x_\kappa + \pi x^2(\cos\phi)\phi_\kappa, & v_\kappa(0) &= 0
\end{aligned}\right\} \tag{6}$$

Precise details on the numerical methods used to implement the described scheme are given in Section 4.

Note that the previous analysis recovers the ADSA-CD method by letting $S(\kappa)$ be the value of $s$ when $v = V$.

 

## 3. SINGLE DROP—SENSITIVITY ANALYSIS

The computed value of the contact angle $\phi_c$ is a function of the data $R$ and $V$. The following analysis shows how errors in the data, $\Delta R$ and $\Delta V$ respectively, are reflected in the calculated value of $\phi_c$. Writing $\phi_c = \Phi(R, V)$ and using matrix notation, the error $\Delta\phi_c$ in the computed value of $\phi_c$ is approximated by

$$\Delta\phi_c \simeq \Phi_R \Delta R + \Phi_V \Delta V = (\Delta R, \Delta V)\Delta\Phi, \quad \text{where } \nabla\Phi = (\Phi_R, \Phi_V)^T \tag{7}$$

in which the $R$ and $V$ subscripts denote partial derivatives. The gradient $\nabla\Phi$ is calculated as follows. Write $K(R, V)$ for the computed value of the curvature $\kappa$, $S_1(R, V)$ for the value of $s$ at which $x$ attains the maximum and $S_2(R, V)$ for the value of $s$ at which the drop contacts the substrate (so $S_1 = S_2$ in the hydrophilic case $\phi_c < \pi/2$). Then, $\Phi(R, V) = \phi(S_2(R, V), K(R, V))$, so by the chain rule

$$\nabla\Phi = \begin{pmatrix} S_{2R} & K_R \\ S_{2V} & K_V \end{pmatrix} \begin{pmatrix} (2\kappa + \alpha z - (\sin\phi)/x)_2 \\ (\phi_\kappa)_2 \end{pmatrix} \tag{8}$$

where $(\cdot)_j$ indicates evaluation at $s = S_j$. On the other hand, differentiating the identities

$$x(S_1(R, V),\ K(R, V)) \equiv R \quad \text{and} \quad v(S_2(R, V),\ K(R, V)) \equiv V$$

with respect to $R$ and $V$ yields the four equations

$$(\cos\phi)_1 S_1 R + (x_\kappa)_1 K_R = 1$$

$$(\cos\phi)_1 S_{1V} + (x_\kappa)_1 K_V = 0$$

$$(\pi x^2 \sin\phi)_2 S_{2R} + (v_\kappa)_2 K_R = 0$$

$$(\pi x^2 \sin\phi)_2 S_{2V} + (v_\kappa)_2 K_V = 1$$

Now $S_1 \equiv S_2$ or $(\cos\phi)_1 \equiv 0$. In either case we can replace $S_1$ by $S_2$ in these equations, which leads to

$$\begin{pmatrix} S_{2R} & K_R \\ S_{2V} & K_V \end{pmatrix} \begin{pmatrix} (\cos\phi)_1 & (\pi x^2 \sin\phi)_2 \\ (x_\kappa)_1 & (v_\kappa)_2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and substituting into Equation (8) shows finally

 

$$\nabla\Phi = \begin{pmatrix} (\cos\phi)_1 & (\pi x^2 \sin\phi)_2 \\ (x_\kappa)_1 & (v_\kappa)_2 \end{pmatrix}^{-1} \begin{pmatrix} (2\kappa + \alpha z - (\sin\phi)/x)_2 \\ (\phi_\kappa)_2 \end{pmatrix}$$

In terms of relative errors, Equation (7) can be written in the form

$$\frac{\Delta\phi_c}{\phi_c} \simeq F_R \frac{\Delta R}{R} + F_V \frac{\Delta V}{V}, \quad \text{where } F_R = \frac{R}{\phi_c}\Phi_R \quad \text{and} \quad F_V = \frac{V}{\phi_c}\Phi_V$$

For extremely hydrophobic substrates $(\phi)_1 = \pi/2$ and $\phi_c = (\phi)_2 \to \pi$ so the coefficient matrix in $\nabla\Phi$ becomes singular. This suggests (and Table II confirms) that both $F_R$ and $F_V$ become infinite, rendering this method of calculating contact angles unsuable. At the other extreme for small $s$ is it easy to see that, to leading order as $s \to 0$,

$$x \sim s, \qquad z \sim \frac{1}{2}\kappa s^2, \qquad \phi \sim \kappa s, \qquad v \sim \frac{\pi}{4}\kappa s^4$$

$$x_\kappa \sim -\frac{1}{3}\kappa s^3, \qquad z_\kappa \sim \frac{1}{2}s^2, \qquad \phi_\kappa \sim s, \qquad v_\kappa \sim \frac{\pi}{4}s^4$$

Now at the point of contract, $x(s) = R$ and $v(s) = V$ so $s \sim R$ and $(\pi/4)\kappa s^4 \sim V$, which yields

$$F_R \to -3 \quad \text{and} \quad F_V \to 1 \quad \text{as } \phi_c \to 0$$

Thus, the method is viable for extremely hydrophilic surfaces, although $R$ must be determined accurately. These results are borne out in Table I in Section 4.

Note that the ADSA-CD method is again recovered by replacing all occurrences of $(\cdot)_1$ with $(\cdot)_2$. In particular, the coefficient matrix in $\nabla\Phi$ no longer becomes singular in the limit $\phi_c \to \pi$ since the $(\cos\phi)_1$ entry now approaches $-1$ instead of 0. Thus, ADSA-CD remains a viable method even for extremely hydrophobic surfaces, although measuring the contact diameter accurately becomes difficult since the actual point of contact is hard to determine with certainty. Again these results are evident in Table III.

## 4. SINGLE DROP—NUMERICAL EXPERIMENTS

Tables I, II and III show the results of implementing the algorithm discussed in the previous sections for various values of $V$ and $\alpha$ on both hydrophilic (in which case the CD and MD methods coincide) and hydrophobic surfaces. In each case, the sensitivity factors are also computed and displayed.

The solution of Equations (4)–(6) was computed using the standard fourth-order Runge–Kutta algorithm with an initial step length of $R/10$. (Reducing the initial step length to $R/100$ had no effect on the calculated values to the precision shown.) Precise values for $S$, $S_1$ and $S_2$ were determined by stepping forward until the required criterion was exceeded, taking one step back, decreasing the step length by a factor of 10 and repeating the process until the desired accuracy was attained. See Sections 2 and 3 for the definitions of $S$, $S_1$ and $S_2$.

 

Table I. Computed contact angles (°) and sensitivity factors for various drop volumes and surface tension on hydrophilic surfaces[a].

| $\alpha$ | $V$ | $\kappa$ | $\phi_c$ | $F_R$ | $F_V$ |
|---|---|---|---|---|---|
| 0.0 | 0.5 | 0.563 | 34.3 | −2.7 | 0.9 |
| | 1.0 | 0.863 | 59.7 | −2.1 | 0.7 |
| | 1.5 | 0.973 | 76.6 | −1.6 | 0.5 |
| | 2.0 | 1.000 | 88.2 | −1.3 | 0.4 |
| 1.0 | 0.5 | 0.515 | 35.9 | −2.6 | 0.9 |
| | 1.0 | 0.774 | 63.2 | −2.1 | 0.7 |
| | 1.5 | 0.852 | 82.5 | −1.6 | 0.6 |
| 5.0 | 0.5 | 0.365 | 41.6 | −2.4 | 0.9 |
| | 1.0 | 0.512 | 75.7 | −2.0 | 0.8 |

[a] The maximum/contact radius of the drop $R = 1$.

The Newton algorithm to determine $\kappa$ was started with the initial estimate $\kappa = 1/R$ or, if the drop parameters were close to those of the previous run, the previous value of $\kappa$ was used. Since Equations (4)–(6) are invariant under the (non-dimensionalizing) transformation

$$s \to \frac{s}{R}, \quad x \to \frac{x}{R}, \quad z \to \frac{z}{R}, \quad \phi \to \phi, \quad v \to \frac{v}{R^3}, \quad \kappa \to \kappa R, \quad \alpha \to \alpha R^2$$

we lose no generality in considering only $R = 1$ in the computed results.

Table II. Computed contact angles (°) and sensitivity factors for various drop volumes and surface tension on hydrophilic surfaces using the MD method[a].

| $\alpha$ | $V$ | $\kappa$ | $\phi_c$ | $F_R$ | $F_V$ |
|---|---|---|---|---|---|
| 0.0 | 2.5 | 1.000 | 97.5 | −1.4 | 0.5 |
| | 3.0 | 1.000 | 107.3 | −1.8 | 0.6 |
| | 3.5 | 1.000 | 119.1 | −2.4 | 0.8 |
| | 4.0 | 1.000 | 138.0 | −5.3 | 1.8 |
| 1.0 | 2.0 | 0.858 | 97.5 | −1.7 | 0.6 |
| | 2.5 | 0.858 | 114.9 | −2.4 | 0.9 |
| | 3.0 | 0.858 | 147.4 | −7.0 | 2.7 |
| 5.0 | 1.5 | 0.525 | 104.9 | −2.2 | 0.9 |
| | 2.0 | 0.525 | 177.1 | −81.5 | 35.0 |

[a] The maximum/contact radius of the drop $R = 1$.

 

Table III. Computed contact angles (°) and sensitivity factors for various drop volumes and surface tension on hydrophilic surfaces using the CD method[a].

| $\alpha$ | $V$ | $\kappa$ | $\phi_c$ | $F_R$ | $F_V$ |
|---|---|---|---|---|---|
| 0.0 | 2.5 | 0.993 | 96.6 | −1.1 | 0.4 |
| | 3.0 | 0.975 | 102.8 | −1.0 | 0.3 |
| | 3.5 | 0.952 | 107.8 | −0.9 | 0.3 |
| | 4.0 | 0.929 | 111.7 | −0.8 | 0.3 |
| 1.0 | 2.0 | 0.853 | 96.8 | −1.4 | 0.5 |
| | 2.5 | 0.827 | 107.9 | −1.2 | 0.5 |
| | 3.0 | 0.792 | 117.2 | −1.1 | 0.4 |
| 5.0 | 1.5 | 0.516 | 103.1 | −1.7 | 0.7 |
| | 2.0 | 0.469 | 126.5 | −1.5 | 0.7 |

[a] The contact radius of the drop $R = 1$.

## 5. TWO DROPS

Given the radius $R$ and volume $V$ of the sessile drop, the single drop analysis calculates the contact angle. The angle thus determined depends on $\alpha$; denote it by $\Phi_{R,V}(\alpha)$. Figure 2 shows the graph of $\Phi_{R,V}$ versus $\alpha$ for two different sized drops $(R_1, V_1)$ and $(R_2, V_2)$. The surface tension parameter $\alpha$ can be found by solving the single equation

$$\Phi_{R_1,V_1}(\alpha) = \Phi_{R_2,V_2}(\alpha) \tag{9}$$

and then the contact angle is simply the common $\Phi$ value.

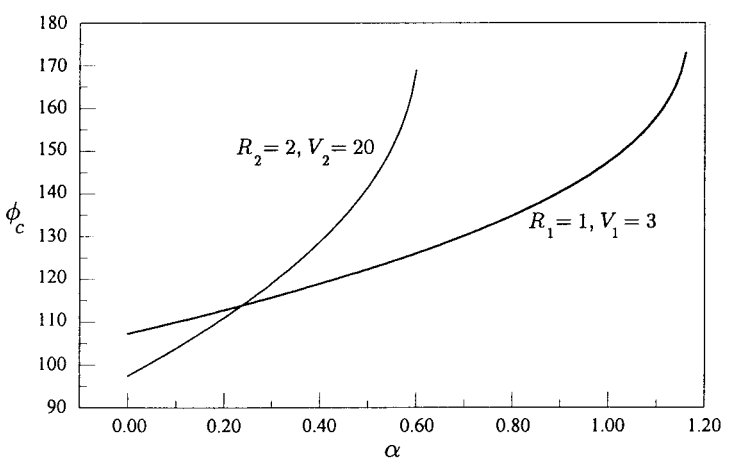


Figure 2. Graphs showing the contast angle $\phi_c$ versus $\alpha$ for two drops of given volume and radius. The intersection of the graphs gives the contact angle and surface tension $\gamma = g(\Delta\rho)/\alpha$. Here $R_1$ and $R_2$ are the maximum drop diameters.

 

To solve Equation (9) we again use Newton's algorithm

$$\alpha \leftarrow \alpha - \frac{\Phi_{R_1,V_1}(\alpha) - \Phi_{R_2,V_2}(\alpha)}{\Phi'_{R_1,V_1}(\alpha) - \Phi'_{R_2,V_2}(\alpha)}$$

To calculate the derivate $\Phi'_{R,V}(\alpha)$ we proceed as follows. Begin by augmenting the system (4)–(6) to include $\alpha$ derivatives

$$\frac{\mathrm{d}x_\alpha}{\mathrm{d}s} = -(\sin\phi)\phi_\alpha, \quad x_\alpha(0) = 0$$

$$\frac{\mathrm{d}z_\alpha}{\mathrm{d}s} = (\cos\phi)\phi_\alpha, \quad z_\alpha(0) = 0$$

$$\frac{\mathrm{d}\phi_\alpha}{\mathrm{d}s} = z + \alpha z_\alpha - \frac{\cos\phi}{x}\phi_\alpha + \frac{\sin\phi}{x^2}x_\alpha, \quad \phi_\alpha(0) = 0$$

$$\frac{\mathrm{d}v_\alpha}{\mathrm{d}s} = 2\pi x(\sin\phi)x_\alpha + \pi x^2(\cos\phi)\phi_\alpha, \quad v_\alpha(0) = 0$$

and write $x(s, \kappa, \alpha)\ldots$ for all the dependent variables to show their dependence on $s$, $\kappa$ and $\alpha$. Let $K(\alpha)$ be the computed value of the curvature $\kappa$, $S_1(\alpha)$ be the value of $s$ at which $x$ attains its maximum and $S_2(\alpha)$ be the value of $s$ at which the drop contacts the substrate. Then, $\Phi_{R,V}(\alpha) = \phi(S_2(\alpha), K(\alpha), \alpha)$ and so

$$\begin{aligned}\Phi'_{R,V}(\alpha) &= \left(2\kappa + \alpha z - \frac{\sin\phi}{x}\right)_2 S'_2 + (\phi_\kappa)_2 K' + (\phi_\alpha)_2 \\ &= (S'_2, K')\begin{pmatrix}(2\kappa + \alpha z - (\sin\phi)/x)_2 \\ (\phi_\kappa)_2\end{pmatrix} + (\phi_\alpha)_2 \end{aligned} \tag{10}$$

To find $S'_2$ and $K'$, we differentiate the identities

$$x(S_1(\alpha), K(\alpha), \alpha) \equiv R \quad \text{and} \quad v(S_2(\alpha), K(\alpha), \alpha) \equiv V$$

with respect to $\alpha$ to obtain the equations

$$(\cos\phi)_1 S'_1 + (x_\kappa)_1 K' + (x_\alpha)_1 = 0, \qquad (\pi x^2 \sin\phi)_2 S'_2 + (v_\kappa)_2 K' + (v_\alpha)_2 = 0$$

As in Section 3, we can replace $S_1$ by $S_2$, so

$$(S'_2, K')\begin{pmatrix}(\cos\phi)_1 & (\pi x^2 \sin\phi)_2 \\ (x_\kappa)_1 & (v_\kappa)_2\end{pmatrix} = -((x_\alpha)_1, (v_\alpha)_2)$$

 

Table IV. Newton iterations for drops $R_1 = 1$, $V_1 = 3$ and $R_2 = 2$, $V_2 = 20$[a].

| $\alpha$ | $\Phi_{R_1,V_1}(\alpha)$ | $\Phi_{R_2,V_2}(\alpha)$ |
|---|---|---|
| 1.000 | 147.4 | Undefined |
| 0.500 | 122.3 | 141.5 |
| 0.342 | 117.1 | 122.9 |
| 0.249 | 114.2 | 114.8 |
| 0.237 | 113.9 | 113.9 |
| 0.237 | 113.9 | 113.9 |

[a] Here $R_1$ and $R_2$ are the maximum drop diameters.

Inverting the matrix and substituting into Equation (10) yields

$$\Phi'_{R,V}(\alpha) = -((x_\alpha)_1, (v_\alpha)_2)\nabla\Phi + (\phi_\alpha)_2$$

where $\nabla\Phi$ is the vector defined in Section 3. Again, evaluating all expressions at $s = S_2$ generalizes the ADSA-CD method to the two-drop experiment.

A little care is required in the Newton iteration because $\Phi_{R,V}(\alpha)$ is defined only for values of $\alpha$ within some interval (assuming the given radius and volume are physically realizable). For too large a value of $\alpha$, the drop becomes flat and the required volume cannot be attained. Moreover, Equation (9) may have no solution if the drops have grossly disparate shapes. In light of these remarks, we implemented the algorithm as follows, starting with the value $\alpha = 1$. If for a given $\alpha$ either $\Phi_{R_1,V_1}(\alpha)$ or $\Phi_{R_2,V_2}(\alpha)$ is undefined, simply divide $\alpha$ by 2. Otherwise, perform a Newton step. If convergence is not attained after 20 Newton iterations, it is assumed the drops are incompatible. (In all our numerical simulations convergence, when it occurred, took no more than six iterations.) Table IV shows the iterations for the drops described in Figure 2. From the sensitivity analysis of Section 3 it is clear that this method is inapplicable to systems for which the contact angle is very large.

Application of this method to actual experiments performed at the University of Toronto using a variety of liquids is reported in Reference [11]. There it was found that the algorithm performed flawlessly with idealized data. In real applications the estimation of the surface tension was very sensitive to input errors, particularly the radius of the drops when the drops were small, and it was concluded that the method in its present form is viable for measuring contact angle but not surface tension.

**Remark**

The dependence of contact angle on drop size is a matter of debate—some experiments in the literature report an increase in contact angle with drop size and some a decrease. Gaydos and Neumann [12] give experimental results of contact angle versus maximum drop radius for *n*-alkane (do- through to hexa-) drops on carefully prepared Teflon (FEP) surfaces. They show that the dependence of contact angle on drop radius is marked for small drops but less so for large drops—contact angles varied by only 1° and 2° for radii larger than 3 mm or so. This is consistent with the modified Young equation (14) of Reference [12]

 

$$\cos \phi_c \propto C - \frac{1}{x_c}$$

where $C$ (related to the substrate surface tension) is a constant and $x_c$ is the contact radius of the drop.

## 6. CONCLUSIONS

This paper describes two numerical schemes for estimating the contact angle of sessile drops. The first yields the contact angle given the volume, interfacial tension and maximum diameter (or contact diameter) of a single drop, while the second yields estimates of both the contact angle and surface tension of a liquid from the volume and outer radius measurements of two different sized sessile drops. Sensitivity analysis indicates that the results are accurate for drops on all but highly hydrophobic surfaces. Experiments performed at the University of Toronto show that the second method works well for estimating the contact angle but fails to determine the interfacial tension reliably. It should, therefore, be used to determine the contact angle when the interfacial tension is not known and is not required.

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