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Uncertainty in contact angle measurements from the tangent method

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ABSTRACT

The uncertainty in contact angles from sessile drops measured by the tangent method was estimated using a standard error propagation technique involving partial derivatives. If contact angles are <60°, then uncertainty of the tangent method appears to be quite small, ≤ ± 2°. However, as θ values approach 90°, uncertainty increases asymptotically and can exceed ±5°.

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Introduction

Contact angle measurements are frequently used to assess cleanliness of surfaces and the potential for creating a high-quality adhesive bond.[1–3] The most common technique employs a sessile drop, where a small volume of liquid is deposited onto a horizontal solid surface and allowed to spread. Liquid may be added to or withdrawn from the drop to advance or retract its contact line, then an image of the drop is captured, as depicted in Figure 1. A base line (b) with a slope of $m_b \approx 0$ is drawn that passes through the triple point on each side of the drop where the liquid, solid and the surrounding fluid meet. Another line (t) is drawn tangent to the side of the drop with a slope of m_t, which also originates from the triple point. Finally, the so-called contact angle (θ) between these two lines is measured.

The uncertainty in contact angle measurements is generally reported to be ±1–2°.[4] However, depending on the measurement method and the wettability of the solid, these values can vary significantly. A number of investigators have examined the Wilhelmy tensiometry method and have shown that uncertainty in contact angles grows asymptotically as $\theta \to 0°$ or 180°.[5–8] Uncertainty in indirect estimates from the dimensions and/or volumes of sessile drops also is higher at the limits of wettability.[9] Relative uncertainty of the height–diameter[10–12] and the volume–diameter methods[13] increases as θ approaches 0°; whereas uncertainty in the height–diameter method grows as θ tends towards 180°.[9]

Even though the uncertainties of many techniques for measuring wettability have been well documented, surprisingly, error propagation of the tangent method has received little

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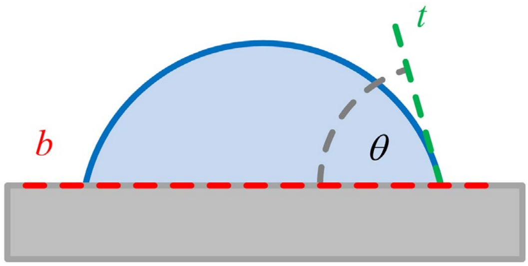

Figure 1. A depiction of a sessile liquid drop and its contact angle (θ).

attention. Therefore, in this work, the uncertainty in direct measurement of contact angles by the tangent method was analyzed for $0° < \theta < 180°$.

Analysis

We begin the analysis by defining several parameters. The absolute uncertainties in the measurement of the tangent and base line slopes (m_t and m_b) are δm_t and δm_b. Their corresponding relative uncertainties are defined as

$$\Delta_t = \frac{\delta m_t}{m_t} \tag{1}$$

and

$$\Delta_b = \frac{\delta m_b}{m_t}. \tag{2}$$

If it is supposed that the uncertainties of m_t and m_b are independent of each other and random, then uncertainty in contact angle ($\delta\theta$) can be estimated using standard error propagation techniques,[14]

$$\delta\theta = \left[\left(\frac{\partial\theta}{\partial m_t}\right)^2 (\delta m_t)^2 + \left(\frac{\partial\theta}{\partial m_b}\right)^2 (\delta m_b)^2\right]^{1/2}, \tag{3}$$

where $\partial\theta/\partial m_t$ and $\partial\theta/\partial m_b$ are partial derivatives. Values of θ from the tangent method can be determined from the slopes of tangent line (m_t) and base line (m_b) using the following expression,[15]

$$\theta = \mathrm{ArcTan}\left|\frac{m_t - m_b}{1 + m_t \cdot m_b}\right|, \tag{4}$$

Differentiating Equation (4) with respect to m_t and m_b, inserting those partial derivatives into Equation (3) and assuming that the solid surface is indeed horizontal ($m_b = 0$) produces the following expression for $\delta\theta$,

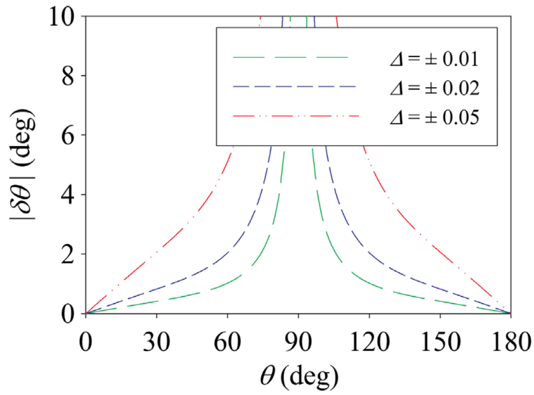

Figure 2. Absolute uncertainty of the contact angle ($|\delta\theta|$) estimated from Equation (11) as a function of the contact angle (θ) and the relative uncertainties in the slopes of the tangent line (Δ_t) and base line (Δ_b), where $\Delta = \Delta_t = \Delta_b$.

$$\delta\theta = \frac{1}{1+m_t^2}\left[\left(\delta m_t\right)^2 + \left(\delta m_b\right)^2\left(1+m_t^2\right)^2\right]^{1/2}, \tag{5}$$

Because the contact angle (θ) is related directly to the slope of the tangent line (m_t) through the tangent function,

$$\left|m_t\right| = \mathrm{Tan}\theta, \tag{6}$$

Equation (5) can be recast as,

$$\delta\theta = \mathrm{Cos}^2\theta\left[\left(\delta m_t\right)^2 + \left(\delta m_b\right)^2\mathrm{Sec}^4\theta\right]^{1/2}, \tag{7}$$

To reduce the complexity of the analysis, it is assumed that the absolute uncertainties in the slopes of the base and tangent lines are equal,

$$\delta m = \delta m_t = \delta m_b \tag{8}$$

and Equation (7) simplifies to an expression that allows for the estimation of the absolute uncertainty in contact angles from the tangent method in terms of absolute uncertainty in tangent and baseline slopes,

$$\delta\theta = \left[1 + \mathrm{Cos}^4\theta\right]^{1/2}\delta m. \tag{9}$$

Often, it is easier to think in terms of relative uncertainty. Therefore, to further simplify, it is assumed that relative uncertainties of the slopes are also equal,

$$\Delta = \Delta_t = \Delta_b = \frac{\delta m}{m_t}. \tag{10}$$

Substituting Equations (6) and (10) into Equation (9) yields the absolute uncertainty in contact angles in terms of relative uncertainty in the tangent and baseline slopes,

$$\delta\theta = \mathrm{Tan}\theta\left(1 + \mathrm{Cos}^4\theta\right)^{1/2}\Delta. \tag{11}$$

Results and discussion

Figure 2 shows the absolute uncertainty of the contact angle ($|\delta\theta|$) estimated from Equation (11) as a function of the contact angle (θ), where the relative uncertainties in the slopes of the tangent line (Δ_t) and base line (Δ_b) are equal, $\Delta = \Delta_t = \Delta_b$. Over most of the range of wettability, the uncertainty of the tangent method appears to be quite small. For $\theta < 60°$ or $> 120°$, $|\delta\theta| \leq \pm 2°$, where $\Delta \leq \pm 0.02$. However, as θ approaches 90°, from either $\theta < 90°$ or $> 90°$, $|\delta\theta|$ increases asymptotically. For contact angles in the vicinity of 90°, $|\delta\theta|$ can exceed ±5°. Why? The slope of the tangent line (m_t) and its absolute uncertainty (δm_t) grow as $\theta \rightarrow 90°$, causing a steep rise in $|\delta\theta|$. These findings will likely resonate with anyone who has used the tangent method to manually measure contact angles – confidence in precise placement of the tangent line is generally greater for sessile drops that exhibit $\theta < 60°$ than drops where $\theta \sim 90°$. Consequently, for surfaces with $\theta \sim 90°$, measurement of contact angles by other methods, such as the height–width method with small sessile drops, may be more precise than by the tangent method.[9]

When considering uncertainty in contact angle measurements by the tangent method, error in the tangent and base line slope is only part of the story. Other experimental factors also may play a role and could further contribute to uncertainty. For example, precise measurements on super hydrophobic surfaces generally are more difficult than surfaces with moderate to low contact angles due to difficulties in locating the point of contact, positioning of the baseline, gravitational distortion of the drop and erroneous assumptions regarding the extent of spreading.[4,9,16–22]

The analysis done here focuses on an axisymmetric drop sitting on a horizontal surface. The tangent method is also used to assess contact angles of drops that are distorted by body forces, such as those that arise from gravitational (e.g. an inclined plane) or centrifugal (e.g. a rotating disk) acceleration.[23–26] This analysis also should be generally applicable to distorted drops.

Conclusions

Uncertainty in contact angles measured by the tangent method appears to be quite small over most of the range of wettability, but increases asymptotically near 90°.

Disclosure Statement

No financial interest or benefit has arisen from the direct application of this research.

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