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The Cassie equation: How it is meant to be used

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ABSTRACT

A review of literature shows that the majority of papers cite a potentially incorrect form of the Cassie and Cassie–Baxter equations to interpret or predict contact angle data. We show that for surfaces wet with a composite interface, the commonly used form of the Cassie–Baxter equation, $\cos\theta_c = f_1 \cos\theta - (1-f)$, is only correct for the case of flat topped pillar geometry without any penetration of the liquid. In general, the original form of the Cassie–Baxter equation, $\cos\theta_c = f_1 \cos\theta_1 - f_2$, with $f_1 + f_2 \geq 1$, should be used. The differences between the two equations are discussed and the errors involved in using the incorrect equation are estimated to be between ~3° and 13° for superhydrophobic surfaces. The discrepancies between the two equations are also discussed for the case of a liquid undergoing partial, but increasing, levels of penetration. Finally, a general equation is presented for the transition/stability criterion between the Cassie–Baxter and Wenzel modes of wetting.

Contents

1. Introduction

A rough surface can be wet in one of two modes, the Cassie–Baxter mode [1–4] (for which parts of the interface under the drop is liquid–vapor due to vapor remaining beneath the drop in the troughs of the rough surface), or the Wenzel mode [5] (for which the entire solid area under the drop is wetted). The works of Cassie and Cassie/Baxter [1–4] have been greatly referenced in recent years, since their equation can be used to help describe the phenomenon of superhydrophobicity (extreme water repellency) displayed both by natural surfaces (e.g. such as lotus leaves and ducks feathers) and by surfaces manufactured using lithography, micromachining, etching, or similar techniques. Superhydrophobic surfaces are surfaces with extremely high contact angles and low contact angle hysteresis, commonly understood to be due to the low adhesion properties of the air remaining below the drop in the Cassie–Baxter wetting mode.

A combined Web of Science and Google Scholar search[1] returns 2686 papers referencing the works of Cassie and Cassie/Baxter

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[1] Baxter, S.; Cassie, A. B. D. *Journal of the Textile Institute Transactions* **1945**, *36*, 67–90 was not indexed in Web of Science, and so could not be searched there. A Google Scholar search found only 35 references to this work, which were included. In general, Web of Science returned more results than Google Scholar, and so its results were used for the other three works of Cassie and Baxter [2–4]. Further, Cassie, A. B. D. *Discussions of the Faraday Society* **1948**, *3*, 11 is sometimes incorrectly cited as Cassie, A. B. D. *Transactions of the Faraday Society*. **1948**, *3*, 11. Thirty-six references to the later were found with a Web of Science search, even though no such volume or issue were published in *Transactions* in that year. The thirty-six references were included in the total count of references to Cassie and Baxter's works. Finally, of the original 100 references randomly selected, 7 could not be retrieved/were in a foreign language. Seven additional references were chosen at random and used in the sample.

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[1–4]. A *random* sample of 100 of these papers [6–105] gives 53 that present some form of the Cassie/Cassie–Baxter equations [53–105], of which 40 use a form of the equation to interpret contact angle data on rough surface [66–105] (instead of e.g. heterogeneous smooth surfaces). Of these 40 references, the majority (~65%) use Eq. (1) to interpret or explain their data [80–105]; this can be a cause for alarm on three different fronts as explained below. Consider Eq. (1):

$$\cos\theta_c = f\cos\theta - (1-f) \tag{1}$$

where θ_c is the predicted Cassie–Baxter contact angle, and f is thought to be the fractional projected area of a material with smooth surface contact angle, θ, and the $(1-f)$ term is thought to reflect the contribution of air remaining under the drop. The use of Eq. (1) potentially introduces errors in (at least) three aspects of wetting: 1) the prediction and/or interpretation of contact angle data on surfaces, 2) the effect on contact angle predictions as liquids penetrate into rough surfaces, and 3) the stability or transition criterion of the Cassie–Baxter and Wenzel wetting modes on rough surfaces.

The concerns with Eq. (1) stem from the definition of f. Eq. (1) defines f as the *projected* area of the solid–liquid interface per unit projected area under the drop. This means that Eq. (1) is *not, in general*, the Cassie–Baxter equation. The original *proper* Cassie–Baxter equation, as formulated by Cassie and Baxter [1–4], is Eq. (2):

$$\cos\theta_c = f_1\cos\theta_1 - f_2 \tag{2}$$

Cassie and Baxter defined f_1 as the *total* area of solid under the drop per unit projected area under the drop, with θ_1 as the contact angle on a smooth surface of material 1. Likewise, f_2 is defined in an analogous way, with material 2 as air ($\theta_2 = 180°$). Cassie and Baxter thought that θ_1 could be either of the advancing or receding smooth surface contact angles, giving advancing and receding predictions of the Cassie–Baxter contact angle, respectively. Johnson and Dettre [106] later rederived Cassie and Baxter's equation using thermodynamic principles, showing that θ_c and θ_1 must each be equilibrium contact angles. However, the form of the equation derived [106] remained the same as Eq. (2), with the same definitions for f_1 and f_2. Marmur and Bittoun have more recently shown that the Cassie–Baxter, (and Cassie, and Wenzel) equations are approximations which become valid as the drop size becomes sufficiently large compared to the wavelength of the roughness/heterogeneity of the surface [107]. However, when this requirement is satisfied, they find the same form for the equations. In this review we also focus on cases where drop size is much larger than the wavelength of the roughness/heterogeneity of the surface.

Fig. 1(i) shows how the values of f_1 and f (and by extension, Eqs. 1 and 2) can be identical in the limiting case of coplanar interfaces. Fig. 1(ii) and (iii) shows how f_1 and f_2 are different from the values of f and 1-f in the general case. As the first problem then, Eq. (1) will not generally return correct predictions of contact angles on rough surfaces, while Eq. (2) will. To put the difference between Eqs. (1) and (2) in another way, using Eq. (1) effectively ignores any roughness at the solid–liquid and liquid–vapor interface, and is thus only valid for surfaces such as those in Fig. 1(i). Fig. 1(i) is obviously not a general rough surface, and thus Eq. (1) is not a general correct form of the Cassie–Baxter equation. However, many studies [83–105] (~58% of the *randomly* selected references which study rough surfaces), and four works by the present authors [108–111] examine general rough surfaces such as those in Fig. 1(ii) and (iii), and use Eq. (1) nevertheless.

The second problem with the use of Eq. (1) stems from its mathematical inconsistency as liquid penetrates the troughs of a rough surface (i.e. as $f \rightarrow 1$). As $f \rightarrow 1$, Eq. (1) returns the behavior of the Young equation. In their largely forgotten passage, however, Cassie and Baxter noted, “When [f_2 is zero equation [2]] reduces to Wenzel's equation for the apparent contact angle of a rough surface with the roughness factor f_1.”. The Wenzel roughness factor, identical to f_1 in Cassie and Baxter's work if the surface is fully penetrated, is commonly given the symbol, r. The correct form of the Cassie–Baxter equation (Eq. 2) therefore must, and does, capture both the Wenzel equation:

$$\cos\theta_c(f_1 \rightarrow r, f_2 \rightarrow 0) = \cos\theta_w = r\cos\theta_1 \tag{3}$$

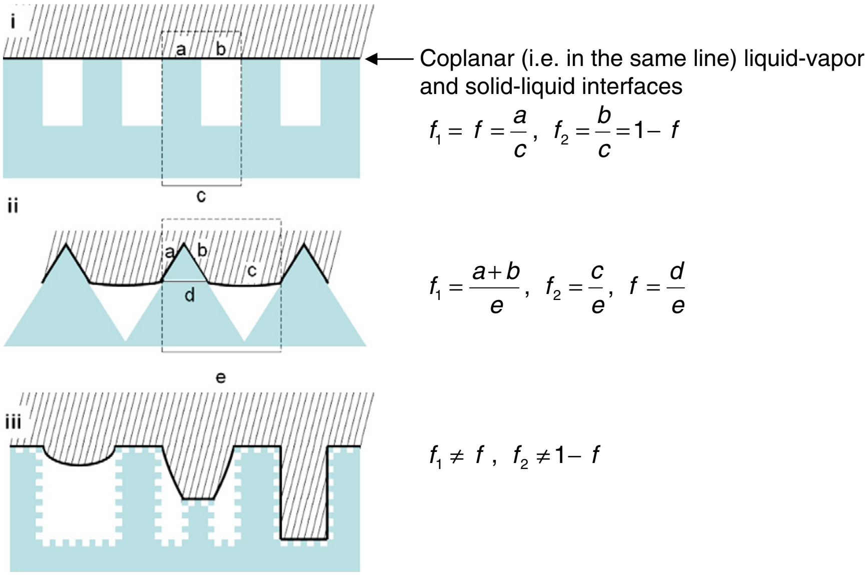

Fig. 1. Schematic close up of three rough 2-D surfaces. Solid is blue/gray, air is white, liquid is the cross-hatched area above the surface. Liquid–vapor and solid–liquid interfaces of drop are denoted by the black line. (i) A smooth-topped rough surface, which (for zero penetration of liquid) has coplanar solid–liquid and liquid–vapor interface (i.e. interfaces are in line with each other). This yields $f_1 = f$ and $f_2 = (1\text{-}f)$ for (i). (ii) An arbitrary rough surface showing the values of f_1, f_2 and f, with $f_1 \neq f$ and $f_2 \neq (1\text{-}f)$ in general. (iii) A dual-scale rough surface showing (left) a curved liquid–vapor interface, (middle) contact of the drop with pillars of different heights, and (right) partial penetration into a dual scale structure, all of which increase the effective area of the liquid–vapor interface under the drop. Neither f_1 nor f_2 are functions of f in all three case of (iii). Further, f_1 and f_2 can *both* be greater than unity (depending on spacing, etc.).