Wetting on Hydrophobic Rough Surfaces: To Be Heterogeneous or Not To Be?

Abraham Marmur*

Department of Chemical Engineering, Technion – Israel Institute of Technology, 32000 Haifa, Israel

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Equilibrium wetting on rough surfaces is discussed in terms of the "competition" between complete liquid penetration into the roughness grooves and entrapment of air bubbles inside the grooves underneath the liquid. The former is the homogeneous wetting regime, usually described by the Wenzel equation. The latter is the heterogeneous wetting regime that is described by the Cassie–Baxter equation. Understanding this "competition" is essential for the design of ultrahydrophobic surfaces. The present discussion puts the Wenzel and Cassie–Baxter equations into proper mathematical–thermodynamic perspective and defines the conditions for determining the transition between the homogeneous and heterogeneous wetting regimes. In particular, a new condition that is necessary for the existence of the heterogeneous wetting regime is added. It is demonstrated that when this condition is violated, the homogeneous wetting regime is in effect, even though the Cassie–Baxter equation may be satisfied.

Introduction

Understanding wetting on rough surfaces[1–29] is essential for designing and controlling wetting processes in general. Of special interest is the extreme case of ultrahydrophobic surfaces, for which roughness results in very high water contact angles and very low water roll-off angles.[1–8,11–13,17–19] Leaves of some plants, notably the Lotus flower leaves, have this property as an essential part of a self-cleaning mechanism.[18] The application of this mechanism is desirable also for nonbiological systems, such as windows, painted exterior surfaces, and so forth.[7,8] In addition, ultrahydrophobic surfaces may have many other applications, such as in microfluidics.

The above two requirements of ultrahydrophobic surfaces, namely, very high water contact angles and very low water roll-off angles, are closely related but not necessarily equivalent. In particular, the mechanism of roll-off is not yet fully understood. However, complete understanding of this dynamic process can be achieved only if its starting point, namely, the equilibrium state of a drop on a hydrophobic surface, is well understood. One of the most important underlying questions is: does the liquid fill up the roughness grooves (Figure 1a) or are air bubbles entrapped inside the grooves, underneath the liquid (Figure 1b)? The former situation is the "homogeneous wetting regime", while the latter is the "heterogeneous wetting regime". The relationship between roll-off and the wetting regime is not yet clear and will be discussed elsewhere. The present discussion focuses on the conditions for existence of either wetting regime, in terms of the topography characteristics of the solid surface.

The basis for studying equilibrium wetting on rough hydrophobic surfaces was established many years ago by Wenzel[23] and Cassie and Baxter[24] (CB). The Wenzel equation relates to the homogeneous wetting regime and yields the Wenzel apparent contact angle, θ_W, in terms of the Young contact angle, θ_Y, and the roughness ratio, r:

$$\cos \theta_W = r \cos \theta_Y \qquad (1)$$

The roughness ratio is defined as the ratio of the true area of the solid surface to its nominal area. This equation shows, as is well-known, that when the surface is hydrophobic ($\theta_Y > \pi/2$), roughness increases the contact angle.

The CB equation describes the heterogeneous wetting regime and gives θ_{CB}, the CB apparent contact angle, as

$$\cos \theta_{CB} = r_f f \cos \theta_Y + f - 1 \qquad (2)$$

* Fax: 972-4-829-3088. E-mail: marmur@tx.technion.ac.il.

(1) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377.
(2) Patankar, N. A. *Langmuir* **2003**, *19*, 1249.
(3) Yoshimitsu, Z.; Nakajima, A.; Watanabe, T.; Hashimoto, K. *Langmuir* **2002**, *18*, 5818.
(4) Quere, D. *Physica A* **2002**, *313*, 32.
(5) Extrand, C. W. *Langmuir* **2002**, *18*, 7991.
(6) Li, S.; Li, H.; Wang, X.; Song, Y.; Liu, Y.; Jiang, L.; Zhu, D. *J. Phys. Chem. B* **2002**, *106*, 9274.
(7) Kijlstra, J.; Reihs, K.; Klamt, A. *Colloids Surf., A* **2002**, *206*, 521.
(8) Duparre, A.; Flemming, M.; Steinert, J.; Reihs, K. *Appl. Opt.* **2002**, *41*, 3294.
(9) Della Volpe, C.; Maniglio, D.; Morra, M.; Siboni, S. *Colloids Surf., A* **2002**, *206*, 47.
(10) Palasantzas, G.; de Hosson, J. T. M. *Acta Mater.* **2001**, *49*, 3533.
(11) Thieme, M.; Frenzel, R.; Schmidt, S.; Simon, F.; Hennig, A.; Worch, H.; Lunkwitz, K.; Scharnweber, D. *Adv. Eng. Mater.* **2001**, *3*, 691.
(12) Herminghaus, S. *Europhys. Lett.* **2000**, *52*, 165.
(13) Oner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777.
(14) Chow, T. S. *J. Phys.: Condens. Matter* **1998**, *10*, L445.
(15) Nakae, H.; Inui, R.; Hirata, Y.; Saito, H. *Acta Mater.* **1998**, *46*, 2313.
(16) Topolski, K.; Urban, D.; Brandon, S.; DeConinck, J. *Phys. Rev. E* **1997**, *56*, 3353.
(17) Tadanaga, K.; Katata, N.; Minami, T. *J. Am. Ceram. Soc.* **1997**, *80*, 3213.
(18) Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1.
(19) Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. *Langmuir* **1996**, *12*, 2125.
(20) Li, H.; Kardar, M. *Phys. Rev. B* **1990**, *42*, 6546.
(21) Huh, C.; Mason, S. G. *J. Colloid Interface Sci.* **1977**, *60*, 11.
(22) Eick, J. D.; Good, R. J.; Neumann, A. W. *J. Colloid Interface Sci.* **1975**, *53*, 235.
(23) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988.
(24) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
(25) Wolansky, G.; Marmur, A. *Colloids Surf., A* **1999**, *156*, 381.
(26) Brandon, S.; Haimovich, N.; Yeger, E.; Marmur, A. *J. Colloid Interface Sci.* **2003**, *263*, 237.
(27) Johnson, R. E.; Dettre, R. H. In *Contact Angle, Wettability, and Adhesion*; Advances in Chemistry Series 43; American Chemical Society: Washington, DC, 1964.
(28) Wolansky, G.; Marmur, A. *Langmuir* **1998**, *14*, 5292.
(29) Marmur, A.; Krasovitsi, B. *Langmuir* **2002**, *18*, 8919.

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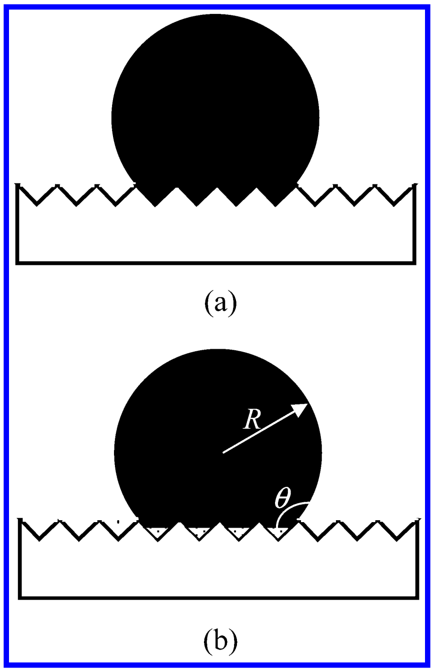

Figure 1. (a) Homogeneous wetting on a hydrophobic, rough surface. (b) Heterogeneous wetting on a hydrophobic, rough surface.

In this equation, f is the fraction of the projected area of the solid surface that is wet by the liquid, and r_f is the roughness ratio of the wet area. When $f = 1$, $r_f = r$, and the CB equation turns into the Wenzel equation. As recently realized,[25,26] both equations are correct only if the drop is sufficiently large compared with the typical roughness scale. As will be shown below, these equations are necessary but not sufficient conditions for describing wetting equilibrium on rough surfaces.

Johnson and Dettre[27] demonstrated for a sinusoidal surface that, above a certain value of r, the CB contact angle is the preferred equilibrium state (i.e. the Gibbs energy is lower in the CB case). Above this r, a further increase in the roughness ratio seems inefficient, since the slope of the increase in θ_{CB} with r is much lower than that of θ_W. As mentioned above, the role of this transition between wetting regimes in ultrahydrophobicity is not yet clear. However, it certainly is essential to understand the conditions for this transition. Therefore, the goal of this paper is to formulate the complete set of equilibrium conditions of a drop on a hydrophobic rough surface, emphasizing the relationship between the solid surface topography and the transition between the homogeneous and heterogeneous wetting regimes.

Theory

The problem of determining the equilibrium conditions of a drop on a rough surface is, as is well-known, a problem of minimization of the Gibbs energy of the system. It is convenient (though not necessary[28]) to perform the minimization under the constraint of a constant volume of the liquid drop. In the minimization of the Gibbs energy of a drop on an *ideal* (i.e. flat, rigid, homogeneous, nonreactive, and insoluble) solid surface, the only independent variable is the contact angle. In contrast, the case of rough surfaces needs to be described by two independent variables: the apparent contact angle, θ, and f. The addition of f as a variable is necessary, since the extent of penetration into the roughness grooves is initially unknown. The extremum conditions of functions of two independent variables are somewhat more intricate than those for a function of one independent variable, and the implications of the additional conditions are essential, as will be shown below.

In general, the Gibbs energy of the system is given by

$$G = \sigma_{lf} A_{lf} + \sigma_{sl} A_{sl} + \sigma_{sf} A_{sf} \qquad (3)$$

where σ is the interfacial tension, A is the interfacial area, and the subscripts s, l, and f stand for the solid, liquid, and fluid, respectively. For generality, the term fluid is kept in the following, although in many cases of practical interest the fluid is a vapor. In formulating the detailed expression for the Gibbs energy of the system, it will be assumed that the drop is sufficiently large compared with the typical scale of roughness. This assumption has important implications: (a) The equilibrium shape of the drop, in the absence of gravity (as is assumed for simplicity), is spherical, and all distortions due to the roughness are limited to the contact line region.[25,26] (b) The radius of curvature of the liquid−fluid interface inside the grooves must equal the radius of the drop itself (that is, very large); therefore, it is assumed that this interface is approximately planar. (c) The volume of liquid inside the roughness grooves is negligible compared with the drop volume. (d) The projected solid−liquid area is approximately equal to the base area of the spherical drop; that is, the area of the protrusions in the contact line is negligible compared with the base area of the drop. In addition, line tension effects are assumed to be negligible.[29]

On the basis of these assumptions, the interfacial areas and drop radius are calculated as follows. The liquid−fluid interfacial area consists of two parts, the outside interface of the spherical cap and the liquid−fluid interface within the grooves:

$$A_{lf} = 2\pi R^2(1 - \cos\theta) + (1 - f)\pi R^2 \sin^2\theta \qquad (4)$$

Here, R is the radius of the sphere, and θ is the apparent contact angle at a given state of the drop (see Figure 1b), not necessarily at equilibrium. The solid−liquid interfacial area is given by

$$A_{sl} = \pi R^2 r_f f \sin^2\theta \qquad (5)$$

The solid−fluid interfacial area also consists of two parts, the interface outside the drop and the solid−fluid interface within the grooves:

$$A_{sf} = [A_{tot} - \pi R^2 r \sin^2\theta] + \pi R^2 r_{1-f}(1 - f)\sin^2\theta \qquad (6)$$

Here, A_{tot} is the total area of the solid surface, and r_{1-f} is the roughness ratio of the dry part. The roughness ratios of the wet and dry areas are related by

$$r_f f + r_{1-f}(1 - f) = r \qquad (7)$$

and the drop radius is related to its volume by

$$R^2 = \left(\frac{3V}{\pi}\right)^{2/3}(2 - 3\cos\theta + \cos^3\theta)^{-2/3} \qquad (8)$$

Introducing eqs 4−8 into eq 3, one gets the expression for the Gibbs energy, which can be written in the following dimensionless form

$$G^* \equiv \frac{G}{\sigma_{lf}\pi^{1/3}(3V)^{2/3}} = F^{-2/3}(\theta)[2 - 2\cos\theta - \Phi(f)\sin^2\theta] \qquad (9)$$

where

$$F(\theta) \equiv (2-3\cos\theta + \cos^3\theta) \tag{10}$$

and

$$\Phi(f) = r_f f \cos\theta_Y + f - 1 \tag{11}$$

It should be noted that A_{tot} is a constant that does not affect the minimization; therefore, it is taken as zero, for convenience. It is also important to note that the roughness ratio of the wet area depends on f, $r_f = r_f(f)$, and that the overall roughness ratio, r, does not explicitly appear in eq 9 (except for being the limiting value of r_f). The complete analysis of the extrema of a function needs to include local as well as border extrema. It will be shown below that the distinction between local and border minima plays a very important part in wetting of rough hydrophobic surfaces.

Local Extrema

Necessary conditions for local extrema consist of vanishing of the first partial derivatives[30] (assuming the function is differentiable). Applying these conditions to G^*, one gets

$$\frac{\partial G^*}{\partial f} = -F^{-2/3}(\theta)\sin^2\theta\left[\cos\theta_Y\frac{d(r_f f)}{df} + 1\right] = 0 \tag{12}$$

$$\frac{\partial G^*}{\partial \theta} = 2F^{-5/3}\sin\theta(\Phi - \cos\theta)(1-\cos\theta)^2 = 0 \tag{13}$$

The latter condition is fulfilled when

$$\cos\theta = \Phi \tag{14a}$$

or when

$$\theta = \pi \tag{14b}$$

Equation 12 is fulfilled when

$$\frac{d(r_f f)}{df} = -(\cos\theta_Y)^{-1} \tag{15a}$$

or when

$$\theta = \pi \tag{15b}$$

Equations 12 and 13 need to be simultaneously fulfilled; therefore, in principle, there exist four combinations of eqs 14 and 15 that need to be considered. Equation 14a is the CB equation. When combined with eq 15a, the value of f at equilibrium is determined by this equation, which is equivalent to the statement[28] that the actual contact angle that the liquid makes with the solid inside the groove must be the Young contact angle. Thus, eqs 14a and 15a are consistent with previous knowledge. The combination of eq 14a with eq 15b is valid only when $\theta_{CB} = \pi$, implying that $f = 0$, as concluded from eq 2. The combination of eq 14b with eq 15a is valid only if the latter is fulfilled by $f = 0$. The combination of eq 14b with eq 15b simply implies $\theta = \pi$ and $f = 0$. So, in fact, the four combinations are reduced to two possibilities: (a) the CB equation with f being determined by eq 15a, and (b) $\theta = \pi$ and $f = 0$.

(30) Rektorys, K. *Survey of Applicable Mathematics*, 2nd ed.; Kluwer Academic Publishers: Dordrecht/Boston/London, 1994.

However, in addition to eqs 12 and 13, the following condition must be met[30] for a local extremum to exist:

$$AC - B^2 > 0 \tag{16}$$

where (assuming that the first derivatives are differentiable)

$$A \equiv \frac{\partial^2 G^*}{\partial f^2} = -F^{-2/3}\sin^2\theta\cos\theta_Y\frac{d^2(r_f f)}{df^2} \tag{17}$$

$$B \equiv \frac{\partial^2 G^*}{\partial\theta\,\partial f} = 2F^{-5/3}\sin\theta(1 - 2\cos\theta + 2\cos^2\theta - \cos^4\theta)\left[1 + \cos\theta_Y\frac{d(r_f f)}{df}\right] \tag{18}$$

and

$$C \equiv \frac{\partial^2 G^*}{\partial\theta^2} = 2F^{-5/3}\{\sin^2\theta[2(\Phi - \cos\theta)(1-\cos\theta) + (1-\cos\theta)^2] + (\Phi-\cos\theta)\cos\theta(1-\cos\theta)^2\} - 10F^{-8/3}\sin^4\theta(\Phi-\cos\theta)(1-\cos\theta)^2 \tag{19}$$

When $AC - B^2 = 0$, there may be but does not need to be a local extremum, and the function needs to be further checked in order to verify it.

At the f value that is necessary for the local minimum, $B = 0$, by eqs 15 and 18. Therefore, the existence of local extrema is determined only by the value of AC. For θ given by the CB equation, eq 14a

$$AC = -2F^{-7/3}\sin^4\theta(1-\cos\theta)^2\cos\theta_Y\frac{d^2(r_f f)}{df^2} \tag{20}$$

Since F is always positive and $\cos\theta_Y$ of interest is negative (hydrophobic surfaces), the sign of AC is the same as the sign of $d^2(r_f f)/df^2$. Thus, as long as $\pi/2 < \theta < \pi$, only if

$$d^2(r_f f)/df^2 > 0 \tag{21}$$

there exists a local extremum in G^* for θ given by the CB equation. The nature of this extremum is determined by the sign of A:[30] it is a minimum when $A > 0$. According to eq 17, the sign of A is the same as the sign of $d^2(r_f f)/df^2$. Thus, if this second derivative is positive, it is a minimum. Since a local extremum may exist only when this sign is positive (eq 21), it turns out this local extremum must be a minimum. The value of this energy minimum explicitly depends on θ_{CB}:

$$G^*_{minCB} = F^{-2/3}(\theta_{CB})[2 - 2\cos\theta_{CB} - \cos\theta_{CB}\sin^2\theta_{CB}] = F^{1/3}(\theta_{CB}) \tag{22}$$

It should be noted that, mathematically, the Wenzel equation can be derived as a specific case of the CB equation, when $f = 1$. However, when $f = 1$, eq 15a cannot be fulfilled for $\theta_Y < \pi$. This is so, since at the bottom of a roughness valley the local actual contact angle should be π, and this value does not match the Young contact angle value. Thus, although, in principle, the Wenzel equation could be a limiting case of a local minimum, in practice, it is impossible, since Young contact angles that are close to π do not exist in nature.

By eq 14b or 15b, a local extremum may possibly exist also for $\theta = \pi$. In this case

$$A \equiv \frac{\partial^2 G^*}{\partial f^2} = 0 \tag{23}$$

$$C \equiv \frac{\partial^2 G^*}{\partial \theta^2} = 2^{-1/3}(\Phi + 1) \tag{24}$$

Therefore, $AC = 0$, a local extremum is, in principle, possible, and the situation has to be checked independently for each specific case. The dimensionless Gibbs energy for $\theta = \pi$ is given, independently of the value of f, by

$$G^*|_{\theta=\pi} = 4^{1/3} \geq F^{1/3}(\theta_{CB}) \tag{25}$$

Thus, the local minimum given by the CB equation when $\theta_{CB} < \pi$ is lower in energy than the one given by $\theta = \pi$, when the latter exists.

The above analysis leads to the conclusion that the mainly relevant local minimum that the dimensionless Gibbs energy may have is given by the CB equation. However, there may be situations for which the conditions for a local minimum cannot be fulfilled. This may be the case when $\Phi < -1$ (eq 14a becomes meaningless for hydrophobic surfaces, $\theta_Y > \pi/2$) or when no value of $d(r_f f)/df$ equals $(-\cos^{-1}\theta_Y)$ (eq 15a cannot be fulfilled) or when $d^2(r_f f)/df^2 < 0$ (eq 21 is not fulfilled). In these cases one needs to seek the minimum of the function at the borders. It should be emphasized though that the border minimum needs to be checked in all cases and compared with the local minimum if it exists.

The Border Minimum

The borders of the range of independent variables are $\theta = 0$, $\theta = \pi$ and $f = 0$, $f = 1$. For $\theta = 0$, it can be shown that, independently of f, $G^* \rightarrow \infty$; so, obviously this is not a minimum. For $\theta = \pi$, independently of f, $G^* = 4^{1/3}$, as shown above.

When the borders in f are considered, the problem turns into a minimization in θ only, since the value of f is fixed. The extremum in G^* is then given by eq 14a, since this condition was derived from the partial derivative with respect to θ. If eq 14a can be fulfilled for hydrophobic surfaces, $\theta_Y > \pi/2$ (namely, if $\Phi \geq -1$), then from eq 19 it can be concluded that the second derivative at the extremum point is always positive, so the extremum is a minimum. For $f = 0$, $\Phi = -1$, so the minimum is at $\theta = \pi$, and $G^* = 4^{1/3}$. For $f = 1$, $\Phi = r\cos\theta_Y$, and the minimum is at $\cos\theta = r\cos\theta_Y$ if $\Phi \geq -1$ (for hydrophobic surfaces, $\theta_Y > \pi/2$) or at $\theta = \pi$ if $\Phi < -1$. The former is, of course, the Wenzel equation, and then $\theta = \theta_W$. The value of the dimensionless Gibbs energy at the minimum given by the Wenzel equation is

$$G^* = (2 - 3\cos\theta_W + \cos^3\theta_W)^{1/3} < 4^{1/3} \tag{26}$$

This is an important result, since it shows that whenever there is no local minimum in the Gibbs energy, the homogeneous wetting regime is lower in energy than the case of $\theta = \pi$. Of course, θ_W could equal π, or θ could equal π when $\Phi < -1$; in these cases, there is no practical distinction between the homogeneous and heterogeneous wetting regimes.

Results and Discussion

The above analysis answers the question posed in the Introduction regarding the transition between the homogeneous and the heterogeneous regimes of wetting on hydrophobic, rough surfaces. This is done in terms of criteria based on the detailed solid surface topography, which are completely general. These criteria apply to all cases and, therefore, are both more fundamental and more useful than empirical criteria that are sometimes used, such as the aspect ratio of the asperities. It turns out that the CB equation applies when a local minimum exists, and the Wenzel equation or $\theta = \pi$ applies when it does not. Comparing eqs 22, 25, and 26, it turns out that (a) the case of $\theta = \pi$ always has the highest energy and (b) the lower contact angle, θ_W or θ_{CB}, is associated with the lower energy, since $F(\theta)$ is a monotonic function in θ.

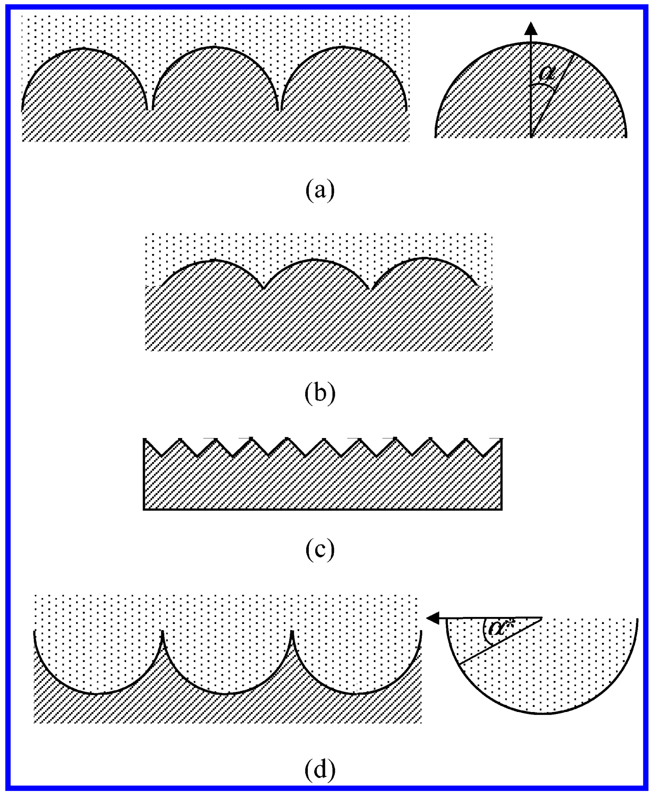

Figure 2. Examples of simple rough surfaces: (a) semicircular protrusions; (b) circular protrusions, the cross section of which is smaller than a semicircle; (c) saw-toothed surface; (d) semicircular grooves.

To demonstrate the application of the criteria presented in the Theory section, the following discussion is divided according to the type of the solid surface topography, in terms of $d^2(r_f f)/df^2$. In real surfaces, the sign of $d^2(r_f f)/df^2$ may vary along the surface. To emphasize the important points in the present analysis, the following discussion focuses on simple examples for which the sign of $d^2(r_f f)/df^2$ is the same for the whole surface. For simplicity, the examples below are of surfaces with two-dimensional profiles; however, the drops on them are three-dimensional. When the drops are sufficiently large, they should be axisymmetric (based on numerical simulations with two-dimensional patterns on heterogeneous, smooth surfaces, a ratio greater than 10 of the typical drop size to the typical heterogeneity scale may be sufficient to render axisymmetry).[25,26]

The Case of $d^2(r_f f)/df^2 > 0$. A simple example for this case is the two-dimensional surface profile shown in Figure 2a, which consists of semicircular protrusions. For this case

$$f = \sin\alpha \tag{27}$$

and

$$r_f = \frac{\alpha}{\sin \alpha} \quad (28)$$

where α is the angle shown in Figure 2a. Equation 15a turns into

$$\frac{d(r_f f)}{df} = \frac{d\alpha}{d \sin \alpha} = (\cos \alpha)^{-1} = -(\cos \theta_Y)^{-1} \quad (29)$$

The solution of this equation is $\alpha = \pi - \theta_Y$, which is feasible for $\pi/2 \le \theta_Y \le \pi$, since $\alpha \le \pi/2$. The next stage is to check the sign of $d^2(r_f f)/df^2$, which is given by (noting that $\alpha \le \pi/2$)

$$\frac{d^2(r_f f)}{df^2} = \frac{d \cos^{-1} \alpha}{d \sin \alpha} = \frac{\sin \alpha}{\cos^3 \alpha} > 0 \quad (30)$$

Thus, a local minimum in G^* may exist at $\alpha = \pi - \theta_Y$, if eq 14a is fulfilled. The CB equation, eq 14a, in this case is

$$\cos \theta_{CB} = (\pi - \theta_Y) \cos \theta_Y + \sin \theta_Y - 1 \quad (31)$$

This equation has a solution for the whole range of relevant Young contact angles, so indeed a local minimum in G^* exists.

A variation on this case is the subcase, where the protrusion vertical cross section is smaller than a semicircle (see Figure 2b) in such a way that eq 15a cannot be fulfilled. In other words, $\alpha_{max} < \pi - \theta_Y$, where α_{max} is the maximum value of α. This situation calls for a border minimum, which, as explained above, leads to the homogeneous wetting regime. The apparent contact angle in this case is

$$\cos \theta = \begin{cases} \cos \theta_W = r \cos \theta_Y = \dfrac{\alpha_{max}}{\sin \alpha_{max}} \cos \theta_Y & \text{if } r \cos \theta_Y \ge -1 \\ -1 & \text{otherwise} \end{cases} \quad (32)$$

The Case of $d^2(r_f f)/df^2 = 0$. A simple example for this case is the saw-toothed profile. This profile is characterized by $r_f = r = \cos^{-1} \beta$, where β is the inclination angle (see Figure 2c). Equation 15a for this case,

$$\frac{d(r_f f)}{df} = r = (\cos \beta)^{-1} = -(\cos \theta_Y)^{-1} \quad (33)$$

may be fulfilled only for a single value $\theta_Y = \pi - \beta$ within the range $\pi \ge \theta_Y \ge \pi/2$.

Next,

$$\frac{d^2(r_f f)}{df^2} = 0 \quad (34)$$

On the basis of eqs 34 and 20, a local minimum in G^* may be possible, but the details need to be checked. The value of Φ (eq 11) for θ_Y and β related by eq 33 is −1, independently of *f*. Therefore, a local minimum is possible, according to eq 14a, at $\theta = \pi$.

If the inclination angle is different than $\pi - \theta_Y$, no local equilibrium is possible. Then, the border minimum leads to

$$\cos \theta = \begin{cases} r \cos \theta_Y = \dfrac{\cos \theta_Y}{\cos \beta} & \text{if } \beta < \pi - \theta_Y \\ -1 & \text{otherwise} \end{cases} \quad (35)$$

Thus, if $\beta < \pi - \theta_Y$, the drop is in the homogeneous wetting regime based on a border minimum. If $\beta = \pi - \theta_Y$, the drop is floating on the surface ($\theta = \pi$) as a consequence of a local minimum. If $\beta \ge \pi - \theta_Y$, the drop is floating on the surface ($\theta = \pi$) as a consequence of a border minimum.

The Case of $d^2(r_f f)/df^2 < 0$. A simple example for this case is the two-dimensional surface profile shown in Figure 2d, which consists of semicircular grooves. It is of special interest to compare this case with that of the semicircular protrusions, since both have the same roughness ratio, $r = \pi/2$. However, the difference in the details of their topography makes wetting on them extremely different. For this case

$$f = 1 - \cos \alpha^* \quad (36)$$

and

$$r_f = \frac{\alpha^*}{1 - \cos \alpha^*} \quad (37)$$

where α* is the angle shown in Figure 2d. Equation 15a turns into

$$\frac{d(r_f f)}{df} = \frac{d\alpha^*}{d(1 - \cos \alpha^*)} = \sin^{-1} \alpha^* = -\cos^{-1} \theta_Y \quad (38)$$

This equation has a solution at $\alpha^* = \theta_Y - \pi/2$. However, the sign of $d^2(r_f f)/df^2$ is given by (noting that $\alpha^* \le \pi/2$)

$$\frac{d^2(r_f f)}{df^2} = \frac{d \sin^{-1} \alpha^*}{d(1 - \cos \alpha^*)} = -\frac{\cos \alpha}{\sin^3 \alpha} < 0 \quad (39)$$

Thus, a local minimum in G^* may not exist, although eq 15a may be fulfilled. This situation indicates a border minimum, which, as explained above, leads to the homogeneous wetting regime. No heterogeneous solution is possible for this type of surface. The apparent contact angle in this case is

$$\cos \theta = \begin{cases} \cos \theta_W = r \cos \theta_Y = \dfrac{\pi}{2} \cos \theta_Y & \text{if } \theta_Y \le \arccos\left(\dfrac{2}{\pi}\right) \\ -1 & \text{otherwise} \end{cases} \quad (40)$$

Summary and Conclusions

The question of complete liquid penetration into roughness grooves (homogeneous wetting regime) versus entrapment of air bubbles inside the grooves underneath the liquid (heterogeneous wetting regime) is of utmost importance for understanding wetting on hydrophobic, rough surfaces. Specifically, the design of ultrahydrophobic surfaces critically depends on understanding this "competition." The present discussion puts the Wenzel and Cassie−Baxter equations into proper mathematical−thermodynamic perspective and defines the conditions for determining the transition between the homogeneous and heterogeneous wetting regimes. The detailed results of the present analysis are summarized in Figure 3, in the form of a flow chart. The main results are summarized by the following conclusions:

1. In addition to the previously known equilibrium conditions, the sign of $d^2(r_f f)/df^2$ determines whether a

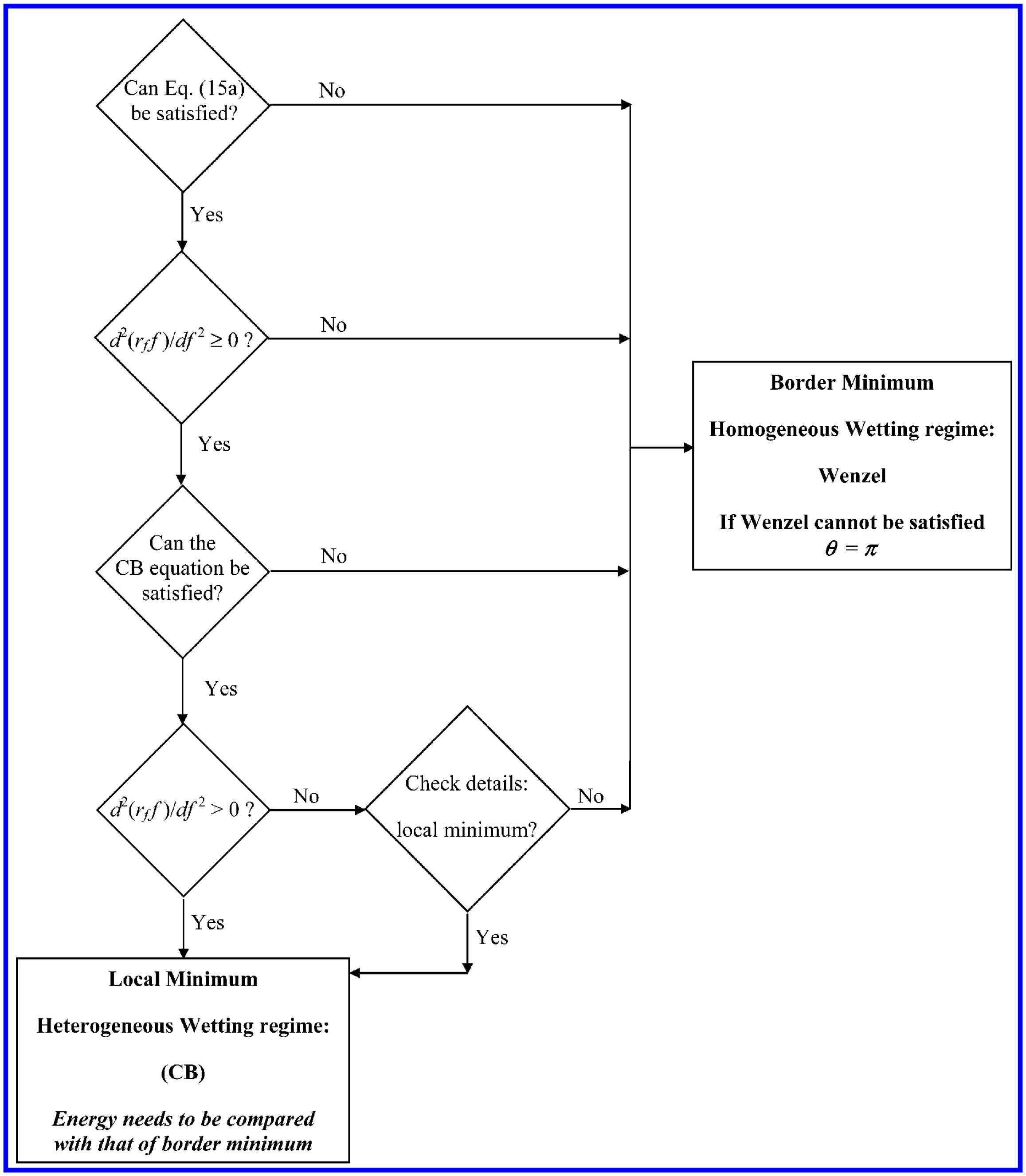

Figure 3. Flow chart for determining the equilibrium state of a drop on a hydrophobic, rough surface.

local minimum in G^* may exist. If $d^2(r_f f)/df^2 < 0$, a local minimum does not exist even if the CB equation may be satisfied.

2. The heterogeneous wetting regime exists when a local minimum in G^* is possible. It is expressed by the CB equation.

3. The homogeneous wetting regime exists as a border minimum in G^* and is expressed by the Wenzel equation. If the latter cannot be satisfied, the border minimum occurs at $\theta = \pi$ (in this case there is no distinction between the homogeneous and heterogeneous wetting regimes).

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