

# A new model for the formation of contact angle and contact angle hysteresis\*

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The formation mechanism of the contact angle and the sliding angle for a liquid drop on a solid surface plays an important role in producing hydrophobic surfaces. A new half soakage model is established in this paper as a substitute for Wenzel (complete soakage) and Cassie (no soakage) models. The model is suited to many solid surfaces, whether they are hydrophilic or hydrophobic, or even superhydrophobic. Based on the half soakage model, we analyse two surfaces resembling lotus, i.e. taper-like surface and corona-like surface. Furthermore, this new model is used to establish a quantitative relationship between the sliding angle and the parameters of surface morphology.

**Keywords:** contact angle, half soakage model, contact angle hysteresis

**PACC:** 6810C, 6810, 6770

## 1. Introduction

Due to the growing importance of hydrophobic or oleophobic surface in industry and daily life, research on the three-phase contact line on solid surface has become more and more important.<sup>[1]</sup> The relationship between contact angle and surface tension was first investigated by Young,<sup>[2]</sup> Wenzel<sup>[3]</sup> and Cassie *et al.*,<sup>[4]</sup> who established their own models. In the Wenzel's model it was assumed that liquid wetted the whole rough surface (i.e. completely soaks into the surface), while in the Cassie *et al.*'s model it was assumed that the droplet just floated on the rough surface due to the support of the trapped air inside it. The Wenzel's model is often used to describe the contact angle on solid surfaces which are hydrophilic or less hydrophobic, while the Cassie *et al.*'s model is often used to describe the contact angle on the solid surfaces which are more hydrophobic or super-hydrophobic.<sup>[5–10]</sup> Much research has focused on distinguishing the two models given a certain condition.<sup>[11–20]</sup> However, the practical case does not suit either model.<sup>[21,22]</sup> In the present paper, we establish a new half soakage model to substitute both the Wenzel's model and the Cassie *et al.*'s model. Since this new model suits nearly every kind of surface whether they are hydrophilic, hydrophobic or even superhydrophobic, the distinction between the Cassie *et al.*'s model and the Wenzel's model seems unnecessary.

Sliding angle and contact angle hysteresis are important indicators in hydrophobicity studies. Surfaces with a sufficiently large contact angle and sufficiently small sliding angle (or contact angle hysteresis small enough) also have a better self-cleaning effect.<sup>[23–25]</sup> Furmidge<sup>[26]</sup> pointed out that the smaller contact angle hysteresis results in a smaller sliding angle. Many different views exist on the formation mechanism of contact angle hysteresis: Adam and Jessop<sup>[27]</sup> pointed out that the friction at the three-phase interface contributes to the contact angle hysteresis. Kamusewitz *et al.* adopted Mises condition to calculate the contact angle hysteresis but found that contact angle did not increase with the increase of surface roughness, which was in disagreement with the experimental results.<sup>[28]</sup> Cao and Jiang<sup>[29]</sup> tried to adopt the Amonton condition to explain the formation of the contact angle hysteresis. However, they did not give an analytic relationship between contact angle hysteresis and parameters of surface morphology. Using the half soakage model, we analyse two lotus-like surfaces in this paper, and obtain an analytic expression.

## 2. Half soakage model

Young's equation describes the relation between contact angle and surface tension for a liquid droplet on a smooth and uniform solid surface, and it is ex-

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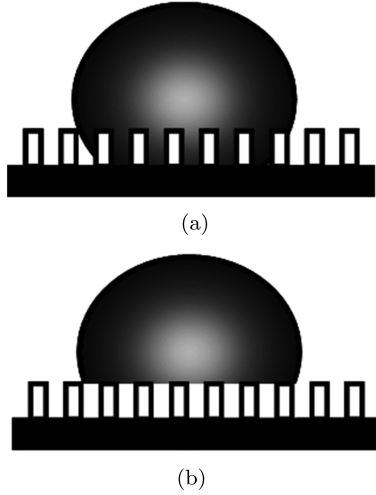
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pressed as

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta^*, \quad (1)$$

where  $\gamma_{sv}$ ,  $\gamma_{sl}$  and  $\gamma_{lv}$  denote the surface tensions of solid/air, solid/liquid, and liquid/air interfaces, respectively;  $\theta^*$  is the Young's contact angle. However, on the rough surface or composite surface, the contact angle is much larger and cannot be explained by the change of chemical components.<sup>[1]</sup> In order to explain this phenomenon, Wenzel and Cassie *et al.* established their own models. The former believed that the increasing contact angle should be attributed to the increase of contact area, caused by the complete soaking on the rough solid surface (see Fig. 1(a)), while the latter argued that the formation of composite surface (air–solid) would result in a larger contact angle (see Fig. 1(b)). Both Cassie *et al.* and Wenzel considered only an extreme condition in their models. More commonly, the liquid usually partially soaks into the surface as shown in Fig. 2(a).



**Fig. 1.** (a) Wenzel's model showing that the liquid drop completely soaks into the solid surface; (b) Cassie *et al.*'s model indicating that liquid floats on the microstructure, and only liquid/solid contact and liquid/air contact are considered, while the air/solid contact is neglected.

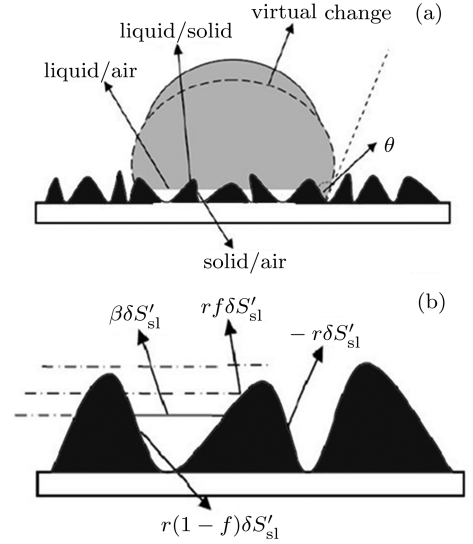
Consider a virtual change shown in Fig. 2. Assume that  $r$  is the ratio of the actual surface area to ideal area (the area of the smooth and uniform surface),  $f$  is the ratio of the area of the liquid/solid interface to the whole solid surface area,  $\delta S'_{sl}$  is the change of the area of the apparent solid/liquid interface, and  $\delta S_{lv}$  is the change of the area of the upper liquid/air interface. Then the geometrical relationship between  $\delta S'_{sl}$  and  $\delta S_{lv}$  is

$$\delta S'_{sl} \cdot \cos \theta = \delta S_{lv}. \quad (2)$$

The change of the area of real solid/liquid interface is denoted with  $rf\delta S'_{sl}$ ,  $r(1-f)\delta S'_{sl}$  is the change of the area of solid/air interface in the groove. If  $\beta$  denotes the ratio of the area of the liquid/air interface in the groove to the apparent area of a smooth and uniform surface, the change of the area of the liquid/air interface in the groove should be expressed as  $\beta\delta S'_{sl}$ . In the right zone, the change of the area of the solid/air interface is  $-r\delta S'_{sl}$ . Thermodynamic equilibrium requires the variation of Helmholtz free energy to equal zero, i.e.,

$$\begin{aligned} \delta F &= \gamma_{sl}rf\delta S'_{sl} + \gamma_{sv}r(1-f)\delta S'_{sl} + \gamma_{lv}\beta\delta S'_{sl} \\ &\quad + \gamma_{lv}\delta S_{lv} - \gamma_{sv}r\delta S'_{sl} \\ &= 0. \end{aligned} \quad (3)$$

Helmholtz free energy is more important than Gibbs energy because the temperature and the volume of this system, rather than pressure, are constant.



**Fig. 2.** Half soakage model. Panel (a) is for a composite solid–liquid–air interface, showing that this model considers not only the liquid/solid and liquid/air contacts, but also the solid/air contact, and panel (b) shows the area change caused by the virtual motion of the three-phase contact line.

Substituting Eq. (2) into Eq. (3) leads to

$$\cos \theta = rf \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} - \beta. \quad (4)$$

Substituting Eq. (1) into Eq. (4) yields

$$\cos \theta = rf \cos \theta^* - \beta. \quad (5)$$

If  $\delta S_{sl}$  denotes the change of the actual area of the solid/liquid interface, and  $\delta S$  refers to the total change of the solid area, then  $f = \delta S_{sl}/\delta S$  and  $r = \delta S/\delta S'_{sl}$ , thus  $rf = \delta S_{sl}/\delta S'_{sl}$ . So  $\varepsilon = rf = \delta S_{sl}/\delta S'_{sl}$ , which

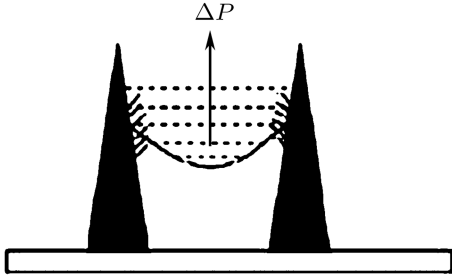
expresses the ratio of the actual area of solid/liquid interface to the apparent area of a smooth and uniform surface. Then, we obtain

$$\cos \theta = \varepsilon \cos \theta^* - \beta. \quad (6)$$

This equation uses  $\varepsilon$  and  $\beta$  to take the place of  $r$  and  $f$ , which are used in the Wenzel's and the Cassie *et al.*'s models to demonstrate the effect of surface structure on contact angle, and is closer to the experimental results. When  $\varepsilon = r$  and  $\beta = 0$ , equation (6) returns to Wenzel's equation, i.e.  $\cos \theta = r \cos \theta^*$ . When  $\varepsilon = f$  and  $\beta = 1 - f$ , equation (6) returns to Cassie *et al.*'s equation, i.e.  $\cos \theta = f \cos \theta^* + f - 1$ .

Equation (6) allows us to quantitatively calculate the contact angle on the solid surface with a certain structure. Its accuracy could be proved by the method of photoetching.<sup>[30]</sup>

Take the lotus-like surface for example. It is generally deemed that the lotus surface is comprised of micropapillas (5~9  $\mu\text{m}$ ) and nanoneedles (120 nm).<sup>[31]</sup> Nanoneedles have two main effects: bending the droplet under surface tension in order to create the Laplace pressure difference so as to hold the droplet<sup>[32]</sup> (shown in Fig. 3), and increasing the area of the solid/liquid interface, i.e.  $\varepsilon$  (while  $\beta$  remains the same).



**Fig. 3.** Nanoneedles that can hold the droplet, where the curvature of the droplet has been magnified in order to express that the nanostructure can hold the droplet.

Although the Laplace pressure difference which contributes mainly to holding the droplet is caused by the surface curvature, the following analysis will show that the undersurface can still be regarded as flat in contact angle calculation.

The volume of the droplet is

$$V = \pi a^3 (1 - \cos \theta)^2 (2 + \cos \theta) / 3, \quad (7)$$

where  $a$  is the radius of the droplet. The apparent area of the solid/liquid interface is

$$S = \pi a^2 \sin^2 \theta. \quad (8)$$

So the pressure caused by the gravitation is

$$P = V \rho g / S = \frac{a}{3} (1 - \cos \theta) (2 + \cos \theta) \rho g / (1 + \cos \theta). \quad (9)$$

If this pressure is totally offset by the Laplace pressure difference, then we have

$$P = \Delta P = 2\gamma / R, \quad (10)$$

where  $R$  is the radius of the liquid/air interface (see Fig. 3) and  $\gamma$  is the tension of the interface. Under the experimental condition, the size of the droplet is about several micrometers, and the surface tension of water at room temperature is about 20 mN/m. For  $\theta = 120^\circ$ ,  $R = 2.67$  m, which is much larger than the distance between papillae. Thus, the interface can still be treated as a flat surface.

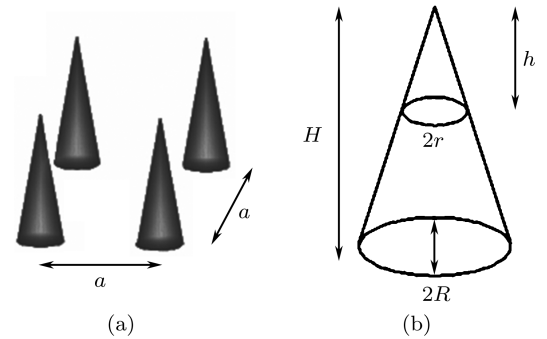
First, we analyse the surface with taper structure. As is illustrated in Fig. 4,  $R$  and  $H$  denote the radius and the height of the taper. The tapers are equally spaced with a distance  $a$ . Letter  $r$  is the radius of the circle which contacts three-phase contact line and its distance to the top of the taper is  $h$ . From geometry, we obtain  $h = rH/R$ . If the effect of nanostructure on  $\varepsilon$  is not taken into account, we can easily obtain the following equations:

$$\varepsilon = \pi r \sqrt{r^2 + h^2} / a^2 = \pi r^2 \sqrt{1 + \frac{H^2}{R^2}} / a^2, \quad (11)$$

$$\beta = (a^2 - \pi r^2) / a^2. \quad (12)$$

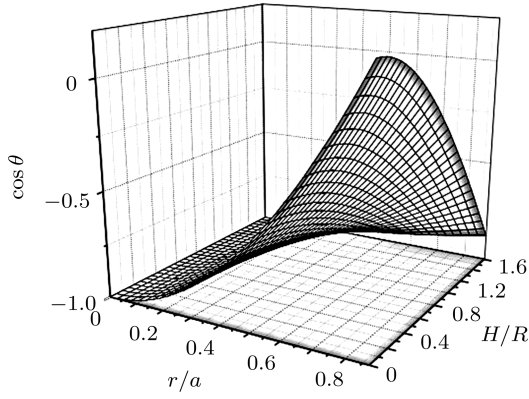
Substituting Eqs. (11) and (12) into Eq. (6) leads to

$$\cos \theta = \pi r^2 \sqrt{1 + \frac{H^2}{R^2}} / a^2 \cos \theta^* + \pi r^2 / a^2 - 1. \quad (13)$$



**Fig. 4.** Sketches of the lotus-like surface with taper structure (only microstructure is shown). In panel (a) the tapers are assumed to be equally separated with a distance  $a$ , and in panel (b) shown is the detailed geometry structure of a single taper, where  $h$  is the soakage length.

As shown in Fig. 5,  $\cos \theta$  decreases with  $r/a$  decreasing and  $H/R$  increasing. Thus, we should appropriately reduce  $r/a$  and increase  $H/R$  in order to create high hydrophobic surfaces.



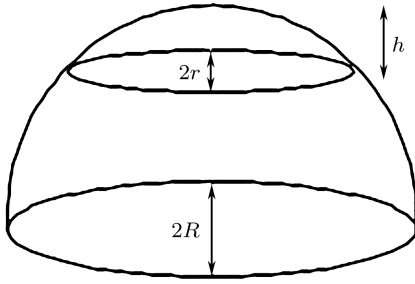
**Fig. 5.** Effect of geometrical parameters on contact angle, with assuming  $\theta^* = 120^\circ$ , considering only hydrophobic area, i.e.  $-1 \leq \cos \theta \leq 1$ , and  $\cos \theta$  decreasing with the reduction of  $r/a$  and the increase of  $H/R$ .

Considering the effect of nanoneedles on  $\varepsilon$ ,  $\tau$  can be introduced to characterize the increase

$$\cos \theta = \tau \pi r^2 \sqrt{1 + \frac{H^2}{R^2}} / a^2 \cos \theta^* + \pi r^2 / a^2 - 1. \quad (14)$$

When  $\cos \theta^* < 0$ ,  $\cos \theta$  decreases significantly because  $\tau > 1$ .

Another lotus-like surface is analysed in Fig. 6, where  $R$  denotes the radius of the corona,  $r$  is the radius of the circle which contacts the three-phase contact line,  $h$  represents the depth of soakage.



**Fig. 6.** Geometric structure of corona.

Similarly, we obtain

$$\varepsilon = 2\pi Rh/a^2, \quad (15)$$

$$\beta = (a^2 - \pi r^2)/a^2. \quad (16)$$

The relationship among  $r$ ,  $h$ , and  $R$  can be geometrically expressed as  $r^2 + (R - h)^2 = R^2$ , so

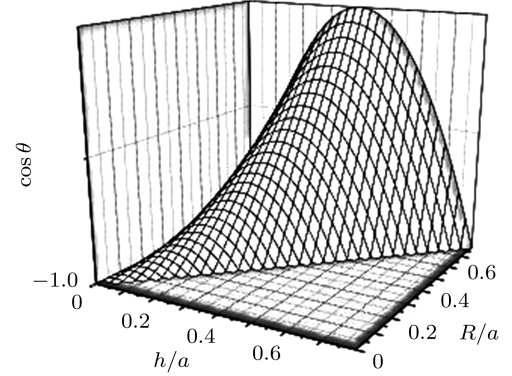
$$\beta = \{a^2 - \pi [R^2 - (R - h)^2]\} / a^2. \quad (17)$$

Substituting Eqs. (15) and (17) into Eq. (6), we can obtain

$$\cos \theta = 2\pi Rh/a^2 \cos \theta^* + \frac{\pi [R^2 - (R - h)^2]}{a^2} - 1$$

$$= -\pi h^2/a^2 + 2\pi Rh/a^2 (\cos \theta^* + 1) - 1. \quad (18)$$

As shown in Fig. 7, when  $h = R(\cos \theta^* + 1)$ ,  $\cos \theta$  has a maximum function  $\pi R^2(\cos \theta^* + 1)/a^2 - 1$ . In order to obtain high hydrophobicity,  $R$  should decrease and  $a$  should increase to reduce  $\pi R^2(\cos \theta^* + 1)/a^2 - 1$ . However, too small  $R$  and too large distance  $a$  would result in large curvature of the liquid/air interface.



**Fig. 7.** Effect of geometrical parameters on contact angle with assuming  $\theta^* = 120^\circ$ , considering only hydrophobic area, i.e.  $-1 \leq \cos \theta \leq 1$ , and the curve of  $\cos \theta - h/a$  being parabolic for a given value of  $R/a$ .

Similarly, the nanostructure would increase  $\varepsilon$  so as to reduce  $\cos \theta$ .

### 3. Sliding angle and contact angle hysteresis

In fact, the contact angle is not a constant but varying in a continuous range. The maximum value of contact angle is referred to as advancing angle  $\theta_A$  and the minimum value is named receding angle  $\theta_B$ , and  $\Delta \cos \theta = \cos \theta_B - \cos \theta_A$  is called the contact angle hysteresis.

The existence of the contact angle hysteresis can be explained in the following.<sup>[33]</sup> When liquid is added into a drop on a horizontal surface, the three-phase contact line is pinned by the coherent force and the contact angle increases until it reaches  $\theta_A$ . Further addition of liquid leads to the motion of the contact line. When liquid is vapourized or absorbed from a droplet, the contact line is again pinned and the contact angle decreases down to  $\theta_B$ . Further vapourization or absorption leads to the motion of the contact line. If this reasoning is applied to a droplet on the inclined surface, it can be concluded that the droplets can stand in equilibrium as long as the contact angles with respect to the front line and the rear line

do not become greater than  $\theta_A$  and smaller than  $\theta_B$ , respectively.

Furmidge<sup>[26]</sup> pointed out the relationship between the sliding angle and the contact angle hysteresis, expressed as

$$mg \sin \alpha / \omega = \gamma_{lv} \Delta \cos \theta, \quad (19)$$

where  $m$  is the mass of the droplet,  $\alpha$  is the sliding angle,  $\omega$  is the perimeter of three-phase contact line, and  $\gamma_{lv}$  is the tension of liquid/air interface. Thus the effective way to reduce the sliding angle is to reduce the contact angle hysteresis.

In order to gain its quantitative expression to calculate the contact angle hysteresis, the parameter ' $\mu$ ' is introduced to describe the coherent force between the solid/air interfaces per unit area, where the contact line must overcome its movement. So equation (3) will change into

$$\begin{aligned} \delta F &= \gamma_{sl} \varepsilon \delta S'_{sl} + \gamma_{sv} r (1 - f) \delta S'_{sl} + \gamma_{lv} \beta \delta S'_{sl} \\ &\quad + \gamma_{lv} \delta S'_{sl} \cdot \cos \theta_A + \mu \varepsilon \delta S'_{sl} - \gamma_{sv} r \delta S'_{sl} \\ &= 0, \end{aligned} \quad (20)$$

$$\begin{aligned} \delta F &= -\gamma_{sl} \varepsilon \delta S'_{sl} - \gamma_{sv} r (1 - f) \delta S'_{sl} - \gamma_{lv} \beta \delta S'_{sl} \\ &\quad - \gamma_{lv} \delta S'_{sl} \cdot \cos \theta_B + \mu \varepsilon \delta S'_{sl} + \gamma_{sv} r \delta S'_{sl} \\ &= 0. \end{aligned} \quad (21)$$

From Eq. (20) the advancing angle is obtained as

$$\cos \theta_A = \varepsilon \cos \theta^* - \beta - \mu \varepsilon / \gamma_{lv}. \quad (22)$$

From Eq. (21) the receding angle is obtained as

$$\cos \theta_B = \varepsilon \cos \theta^* - \beta + \mu \varepsilon / \gamma_{lv}. \quad (23)$$

Thus the angle hysteresis is given as

$$\Delta \cos \theta = \cos \theta_B - \cos \theta_A = 2\mu \varepsilon / \gamma_{lv}. \quad (24)$$

From Eq. (24) it can be observed that lower  $\varepsilon$  and larger  $\gamma_{lv}$  would result in lower contact angle hysteresis. This may explain why the sliding angle of oil

on an inclined solid surface is larger than that of water. In addition, when the solid surface is hydrophilic or less hydrophobic, the liquid completely soaks into the solid surface, thus  $\varepsilon = r$ , meeting the requirement of the Wenzel's model; with the increase of  $r$ , the contact angle  $\theta$  and the contact angle hysteresis  $\Delta \cos \theta$  both increase. However, when the solid surface is more hydrophobic or superhydrophobic, the droplet almost floats on the solid surface, thus  $\varepsilon = f$ , satisfying the requirement of the Cassie *et al.*'s model. With a decrease of  $f$ , the contact angle increases while the contact hysteresis decreases. Therefore, the surface satisfying the requirement of Cassie *et al.*'s model is more advantageous to achieve better self-cleaning effect, because of the contrary orientation of the contact angle to that of the sliding angle.

Now, we consider the contact angle hysteresis of the surface with taper structure as shown in Fig. 4. Substituting Eq. (11) into Eq. (24) yields

$$\Delta \cos \theta = 2\mu \varepsilon / \gamma_{lv} = 2\mu \pi r^2 \sqrt{1 + \frac{H^2}{R^2}} / (a^2 \gamma_{lv}). \quad (25)$$

Smaller values of  $r/a$  and  $H/R$  result in smaller  $\Delta \cos \theta$ . However, smaller  $H/R$  would result in smaller  $\theta$ . Thus appropriate values of  $H$ ,  $R$ ,  $r$ , and  $a$  should be chosen so as to satisfy different needs for hydrophobicity.

## 4. Conclusion

In the present paper, we established a half soakage model which is advantageous compared with the Wenzel's model and the Cassie *et al.*'s model, then we quantitatively analysed two lotus-like surfaces and determined the relationship between contact angle and parameters of surface morphology. Furthermore, we made use of this new model to calculate the contact angle hysteresis and gave a reasonable explanation to the formation of the contact angle hysteresis.

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