Microstructure Design for Artificial Superhydrophobic Surfaces

Shailendra Deva, Anil Kumar, Ravindra Kumar

Abstract: Superhydrophobic surfaces are the surfaces that do not allow the droplets of liquid to spread and wet it. Ideally, the droplets remain almost spherical in shape and with a very small angle of tilt, slide away from the surface. This occurs due to very high contact angle. A perfectly spherical droplet would make 180^0 angle of contact, but practically this high contact angle is never possible for a stable droplet. The surfaces that make contact angle (CA)>90^o are said to be hydrophobic surfaces. If CA is greater than 150^o, the surface is known as superhydrphobic surface. This property of the surface is termed as superhydrophobicity.

In this paper, the surface morphology to be engineered is studied, which is governed by certain principles. Theories of Thomas Young [1], Wenzel [2] and Cassie-Baxter [3] are reviewed and effect of micro and nano level of roughness, producing hierarchical structures is analyzed. Subsequently, the designing of such super hydrophobic surfaces is attempted.

Keywords: Hierarchical, Lotus, Roughness Superhydrophobic

I. INTRODUCTION

Wetting of surfaces by certain liquid is dependent on the property of hydrophobicity of the surface in respect of that fluid. In fact, hydrophobic surfaces do not allow retaining the liquid droplets on them; rather, those surfaces tend to repel the liquid from their surfaces. This property was first observed on lotus leaves, on which droplets of water slide away without making it wet. Therefore, this phenomenon is known as 'Lotus Effect'. Contact angle, the drop makes with the surface is the factor responsible for the degree of hydrophobicity. For hydrophobic surfaces, the contact angle is greater than 90^o. The surfaces are known as superhydrophobic surfaces, if this contact angle is greater than 150^O. Conversely, the surfaces that do not repel the liquid from the surface are known as hydrophilic surfaces.

Roughness profile of the surface decides the contact angle on which superhydrophobicity is dependent. In order to engineer a surface that is superhydrophobic, and at the same time having control on desired degree of its superhydrophobicity, it is significant to study the texture of the surface. It is the combination of micro roughness and superimposed upon it the nano scale roughness that affects the contact angle and subsequently the superhydrphobicity. Such combination of micro and nano scale roughness is termed as hierarchical structure of the surface roughness.

In this paper, attempt is made to review and understand first the various wetting theories, as given by Thomas Young [1] for smooth surfaces and by Wenzel [2] and by Cassie-Baxter [3] for rough surfaces. Thereafter, attempt is made to design the microstructure of the surface to mimic the lotus leaf. Micro and nano scale roughness of the surface is controlled and measured, along with the measurement of contact angle. Clearly, it can be stated that the attempt is to design the hierarchical structure of the surface to obtain the desired level of superhydrphobicity on the surface.

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II. THEORIES OF WETTING ON ROUGH SURFACES: SUPERHYDROPHOBICITY

When a small droplet of liquid is deposited on solid surface, it may spread to form a film or may form a spherical cap shape. This spreading behavior in general is said as the *wetting* property of a solid surface. Thomas Young [1] first described in 1805 that surface energy is the interaction between the forces of cohesion and adhesion which determines whether or not the wetting i.e. the spreading of a liquid over a surface occurs. If complete wetting does not occur, then a bead of liquid while in contact will form an angle with the solid surface which is a function of the surface energies of the system. The wetting property of the solid surface is specified by the contact angle that a drop of fluid makes at the solid surface.

According to Thomas Young's [1] theory, the incremental change in surface free energy, ΔG, accompanying a small displacement of the liquid with an incremental change in area of solid covered by the liquid can be given as

$$\Delta G = \Delta A_{sl}(\gamma_{sl} - \gamma_{sv}) + \Delta A_{lv}\gamma_{lv} \qquad \text{(Ia)}$$

where, γ_{lv}, γ_{sv} and γ_{sl} are the surface free energy at the interface of the liquid- vapour, solid-vapour and solid-liquid, respectively; A_{sl} and A_{lv} are contact areas of the liquid with solid and vapour respectively.

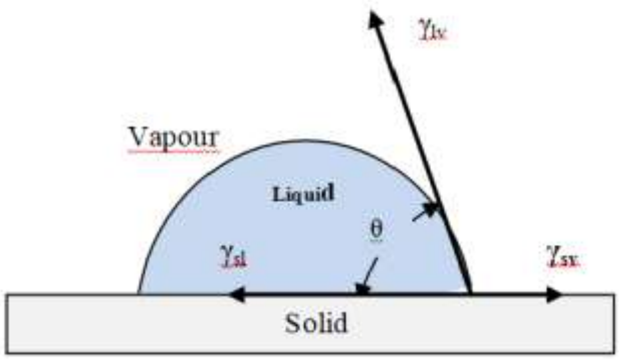

Fig.1: The wetting behavior, expressed by the contact angle (θ) of a liquid drop on a smooth solid substrate with a vapor phase, surrounding the solid and liquid.

Considering that $\Delta\theta$ is a corresponding incremental change in contact angle due to ΔG, it can be shown that

$$\Delta\, Alv \;=\; \Delta\, Asl\,\cos(\,\theta - \Delta\theta)$$

Therefore,

$$\Delta G \;=\; \Delta Asl\,(\gamma s - \gamma sv) + \Delta Asl\,cos(\theta - \Delta\theta)\,\gamma_{lv} \qquad \text{(Ib)}$$

at equilibrium, $\Delta G=0$, when $\Delta\theta$ goes to zero, the equation (I b) is reduced to-

$$\gamma_{sl} - \gamma_{sv} + \gamma_{lv}\; cos\theta = 0 \qquad \text{(Ic)}$$

Above equation is the Young's equation [1].

The Young's static (at equilibrium) contact angle, θ_y in the notation $\theta=\theta_y$, such as in Fig1, for an ideal solid surface that is a flat, rigid, homogeneous, and insoluble and also the three media, solid liquid and vapour do not chemically react. From equation (Ic), we get,

$$cos\;\theta y = \frac{(\gamma sv - \gamma sl)}{\gamma lv} \qquad \text{(I d)}$$

Surfaces for which θ_y *is* smaller than 90° are considered intrinsically hydrophilic, whereas, those having θ_y greater than 90° are considered intrinsically hydrophobic.

The hypothesis of Young [1] assumed an idealized smooth and inert surface that also did not interact with fluid coming in contact with it. The significant phenomenon of contact angle has been widely studied later, on non-ideal rough surfaces from both academic and practical perspectives. The theories Wenzel [2] and Cassie-Baxter [3] have been mostly applied to explain and understand the wetting behavior of rough solid surfaces.

Wenzel Model

The wetting behavior for a rough surface, according to Wenzel [2] model is illustrated in Figure 2a. According to Wenzel [2], the contact angle or strictly speaking an 'apparent' contact angle θ_a for the rough surface such as modeled in Figure 2a is governed by a roughness coefficient *r*

$$\text{Roughness factor}, r = \frac{\text{actual surface area}(A_{\text{actual}})}{\text{projected surface area}(A_{\text{projected}})} \qquad \text{(II a)}$$

The coefficient *r* is the ratio of actual area of the rough surface to its projected area. Clearly, for a rough surface, *r>1*, since $A_{actual} > A_{projected}$

For water droplets on rough surfaces, according to equation (Ia) and (IIa),

$$\Delta G = \Delta A_{actual}\,(\gamma_{sl} - \gamma_{sv}) + \Delta A_{projected}\,\cos(\theta_\alpha - \Delta\theta_\alpha)\,\gamma_{lv} \qquad \text{(II b)}$$

For the condition $\Delta G=0$, when $\Delta\theta_a$ goes to zero, above equation (IIb) is reduced to:

$$r\,(\gamma sl \;-\; \gamma sv\,) + \cos(\theta\alpha)\gamma lv \;=\; 0 \qquad \text{(II c)}$$

Here, denoting the apparent contact angle for the case of Wenzel wetting as, $\theta_a = \theta_f^w$, from above,

$$\cos\theta_f^w = r\,\frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}} \qquad \text{(II d)}$$

The equation (IId) is modified Young's equation (Id). This can be written involving Young's angle θ_y, as

$$\cos\theta_f^w = r cos\theta y \qquad \text{(II e)}$$

Equation [II c to II e] is Wenzel's equation for wetting on a rough surface of roughness factor '*r'*.

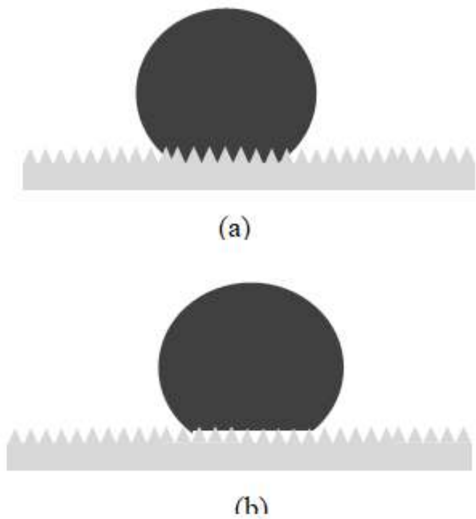

Fig2 (a) Homogeneous wetting on hydrophobic (θ_y>90^0) surface; Wenzel model[2] (b) Inhomogeneous wetting on hydrophobic (θ_y>90^0) surface) Inhomogeneous wetting on hydrophobic (θ_y>90^0) surface; Cassie-Baxter model[3]

Referring to Fig2a, the fluid penetrates fully in the recess or grooves and thus the surface in contact with fluid drop is enhanced. It is obvious that the coefficient r is >1.0. It may be seen that Wenzel equations [IIc, d, e] predict that wetting is enhanced by roughness i.e. $\theta_f^w < \theta y$ when, θ_y is < 90°; and the wetting is lessened by roughness, i.e. $\theta_f^w > \theta y$ when θy is > 90°. This implies that a hydrophobic surface (θ_y > 90^0) will become more hydrophobic with increasing degree of roughness while a hydrophilic surface (θ_y<90^0) will become more hydrophilic, if the same type of roughness is introduced. That is, the surface roughness leads to an amplification of the wetting properties of the smooth material.

It may be noted that the Wenzel equation, being a development over the Young's model, yet assumes that wetting surface under discussion is homogeneous and of a single chemical composition. Water is in complete contact with the solid rough surface in Wenzel state of wetting.

Cassie-Baxter Model

Cassie and Baxter [3] explained the wetting on a rough surface particularly of very high roughness by modeling the rough surface/fluid drop system as in Fig 2b. According to them a rough surface comprises of air as a second phase besides its own composition and thus is a composite surface on which the fluid drop is situated. Below the drop, the air is trapped in grooves of the rough surface. It is observed in Fig 2b that the fluid at the rough surface encounters two interfaces, a fluid-solid interface and a fluid-vapour interface. This implies that rough surface is chemically inhomogeneous or heterogeneous or a composite surface comprised of a solid (phase1) and a vapour phase (phase2); this is a key assumption in Cassie- Baxter [3] model of rough solid surface wetting (rather non-wetting or hydrophobicity).

Accordingly, from Cassie-Baxter[3] model, the overall wettability is the consequence of composite wetting and now the apparent contact angle, θ_a (here denoted, $\theta_a = \theta_f^c$) has contributions from phase1 and 2, as following-

$$cos\theta_f^c = f_1 cos\theta_1 + f_2 cos\theta_2 \qquad \text{(III a)}$$

$$with, \quad f_1 + f_2 = 1$$

Where, f_1 and f_2 are the surface fractions of phase 1 and phase 2, respectively; θ_1 and θ_2 are the contact angles on phase 1 and phase 2, respectively, as if the surfaces of these phases are smooth.

For a two phase system as in equation(IIIa), a solid phase with f_s as the solid fraction, (defined as the fraction of the solid surface that is wetted by the fluid) and the air as the other remaining phase with air fraction $(1 - f_s)$, the equation(IIIa) is reduced to as following-

$$\cos\theta_f^c = f_s cos\theta_y + (1 - f_s) cos180^o$$

$$\text{Or,} \quad \cos\theta_f^c = f_s cos\theta_y + f_s - 1 \qquad \text{(III b)}$$

If we consider the ratio of the actual wetted area to the projected area, r_f which is also referred to as the roughness ratio of the solid fraction, it will give rise to the modified form of the CB equation [14]-

$$\cos\theta_f^c = r_f f_s \cos\theta_y + (1 - f_s) cos180^{\,0}$$

$$\text{or,} \quad \cos\theta_f^c = r_f . f_s \cos\theta_y + f_s - 1 \qquad \text{(IIIc)}$$

when, $r_f = r$ and f_s=1, the above CB equation turns into the Wenzel equation.

The surface roughness is sometimes invoked for explaining the extreme hydrophobicity of very rough surfaces [13], but the main parameter behind the contact angle of a drop on a hydrophobic rough surface is the fraction of solid f_s that is actually in contact with the liquid.

Equation (III c) interprets the multilayered roughness and is more suitable for the hierarchical surface structure, which has been found much morphologically closer to the natural model of superhydrophobic surfaces.

In the natural models, the water droplet sits (or rolls when surface is tilted) on nano structures with air entrapments under the drop; the interface is inhomogeneous comprised of a solid part (the nano/micro structure) and the air.

The Cassie-Baxter model with an air entrainment appears to account well for the observations of near spherical shape water droplets both in nature and on artificial superhydrophobic surfaces and predictions of contact angle or the hydrophobicity/superhydrophobicity have been made commonly by Cassie-Baxter (CB) model.

III. INADEQUACY AND LIMITATIONS OF WENZEL AND CASSIE-BAXTER THEORIES FOR SUPERHYDROPHOBICITY

The conventional theories, to begin with, provided essential academic knowledge and were used to explain, particularly the Cassie-Baxter stipulation of composite liquid-solid interface to explain the superhydrophobicity. It may be recalled that 'lotus effect' discovered in 1997 in fact stimulated an extensive artificial superhydrophobic research, focused on multi-valued roughness and a low surface energy top structure. The later research however, questioned and debated [4]-[8] the applicability of classical theories to explain the superhydrophobicity, primarily for a large CA hysteresis not explainable by these theories. Later research also did show that there were significant differences in the observed contact angles and to those predictable by the classical theories. This discrepancy was highlighted by Erbil [11] who compared the theoretical CA of several systematically prepared surfaces reported in literature of no ambiguity of structure geometry with the experimental results obtained in these studies. It was found that Wenzel equation could not predict the superhydrophobicity in most of the cases; the reason was due to full penetration of water in the microstructure grooves, as shown in Fig. 3(a). Whereas, for the Cassie-Baxter case, there were two possibilities; in the first case, the water did penetrate but limited to certain small depth contacting the microstructure lateral side walls as shown in Fig 3(b).

In this case, the Cassie Baxter equation was applicable though the values of the experimental and the theoretical solid fraction f_s were found at variance such that f_s (experimental)> f_s (theoretical). This meant that experimental CA values were smaller than those of the predictable by the CB equation.

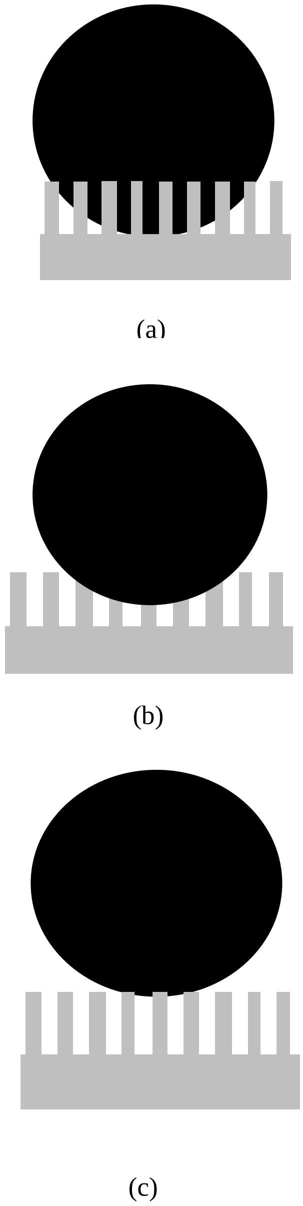

Fig.3: Three situations for water drops on microstructures; (a) Wenzel state- water fully penetrates (b) Cassie-Baxter state -water penetrates partially (c) CB- state water contacts with solid top surface

In the second case, the water drop was in partial contact to solid surface as in Fig. 3(c), and this state was closer to theoretical composite interface though for this case the values of f_s now are f_s (theoretical)> f_s (experimental), in contrast to the small penetration case said above.

In both cases, the large deviations were found in CA of theoretically predictable compared to experimentally observed. This discrepancy showed inadequacy and limitations of Cassie-Baxter theory also while Wenzel was already not being considered suitable to explain and help design the artificial superhydrophobic surfaces. The cause of creating or preparing artificial superhydrophobic surface however could advance by setting certain design rules, derived from the Lotus leaf hierarchical structure as described in the section to follow.

IV. STRUCTURAL DESIGN OF HIERARCHICAL SUPERHYDROPHOBIC SURFACES

Patankar [12] has suggested design guide lines to mimic the Lotus effect to meet the following design goals:

1. A composite drop to be formed on the coarse scale roughness to ensure that the drop has minimum hysteresis and may roll-off easily. A wetted drop (Fig.3a) exhibits much more hysteresis (about 10 times) as compared to a composite drop (Fig.3b, 3c) even if the apparent contact angles are same. However, no conditions are imposed whether water wets the fine scale grooves or not.
2. To ensure low hysteresis of superhydrophobic surface, for a composite drop the apparent contact angle as high as possible is to be obtained. It is assumed that the composite state should represent the global minimum in energy for surfaces. Hence, it becomes mandatory to ensure that the rough surface possesses geometric parameters such that the energy for composite drop is lower than that of wetted drop. This implies that the apparent contact angle of the composite drop should be less than the apparent contact angle of the wetted drop. In such a case, even though the wetted drop has a larger apparent contact angle, it should be avoided because it leads to more hysteresis.

In summary, above goals are to be met with the help of Cassie-Baxter[3] assumption of a composite interface for the water drop and rough microstructure with the minimization of energy concepts discussed in earlier section.

V. DESIGN OF SURFACE STRUCTURE:

Figure 4(a)-(c) depicts a model fine scale roughness structure. This structure is made up of square pillars arranged in a regular array, anticipated to bio-mimic the lotus leaf structure (Fig 4d). Fine scale roughness structure lies on the surface of the coarse scale roughness. Both the structures are modeled to have the same geometry as the fine scale structure, i.e., a regular array of square pillars. Finer scale structure are named the first generation scale that are on the top of a coarser square pillars –named the second generation structure.

At the first generation, the square pillars be of size a_1 x a_1 and height H_1 with the periodic spacing of the regular array as b_1 (Figure 4.a). Placing a drop on this surface (without the coarse scale roughness features), would mean in general, two drop shapes corresponding to the wetted and composite cases are possible (see Fig.4a and 4 b-c).

The apparent contact angles are given by Wenzel[2] and Cassie-Baxter[3] state wetting, respectively, by equations (IIe) and (IIIb). Taking in account the geometry of the considered pillar structure, these equations particularized here are-

Wenzel wetting,

$$\cos\theta_f^w = \left(1 + \frac{4A_1}{a_1/H_1}\cos\theta_y\right) \qquad \text{(IVa)}$$

$$\cos\theta_f^c = A_1(1 + \cos\theta y) - 1 \qquad \text{(IVb)}$$

Where, $A_1 = \dfrac{1}{\left(\left({b_1}/{a_1}\right)+1\right)^2}$

In the above equations (IVa) and (IVb) , it is easily seen that CA for the composite case depends only on ratio (b_1/a_1), whereas for the wetted case, it depends on both (b_1/a_1) and (H_1/a_1). The Figure 5 shows the plots of CA versus these geometrical ratios for both the cases of wetting regime. For the wetted case, three widely differing ratio values (H_1/a_1) =5, 37 and 100 are chosen in presently referred literature study [12]

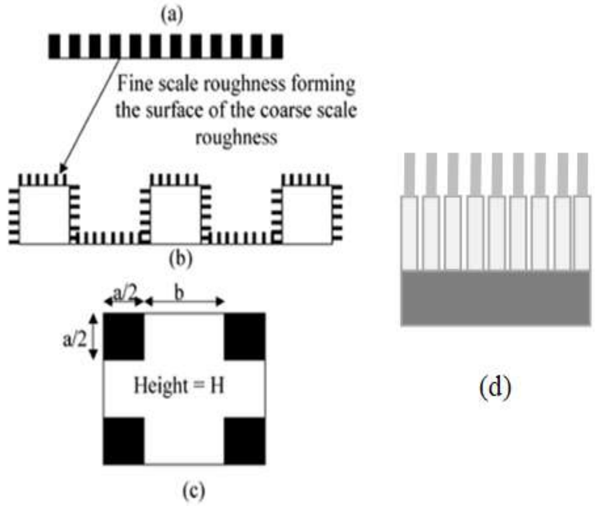

Fig.4: Roughness geometry model for theoretical analysis. (a)The first generation fine scale roughness. (b)The second generation of fine scale roughness forms on the surface of the coarse scale pillars. (c)The pillar geometry at both scales is assumed periodic. The top view of one period is shown. The pillar cross-sectional size is a_1x a_1. Subscripts "1" and "2" denote the geometric parameters for the first and second generation, structures respectively. (Acknowledgement. Patankar[12])

(d) **For a comparison, model schematic of a hierarchical structure based on lotus leaf**

Now an appropriate choice of the geometrical parameters has to be made such that not only the apparent CA is high, the hysteresis also is minimized. The design approach does not directly consider the advancing and receding CA, the characteristics of hysteresis, but first it relies on the past experimental results that high CA (say >150^0) lead to low hysteresis adequate for the roll-off desired for a superhydrophobic surface. For ensuring low CA hysteresis, the minimization of energy concept is used.

The energy change G from the initial state to the final state, for a given apparent contact angle and given volume V of the water drop, is given to be [9], [10]

$$G = (9\pi)^{1/3} V^{2/3} \gamma_{lv} (1 - \cos\theta_a)^{2/3} (2 + \cos\theta_a)^{1/3}$$

The energy of drop is dependent on apparent CA, θ_α.

Since, cosine of an angle can never exceed a value of -1, whereas from the

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Wenzel equation such values may as well be possible for very high roughness r>>1, this anomaly viewed in respect to above equation means that a fully wetted state (as shown earlier in Fig.2a) is ruled out for superhydrophobicity. Hence, only Cassie –Baxter composite wetting need be considered for the present context. Also, the plots (Fig.5a) for wetted drop are physically unrealizable whenever $\cos\theta_f^w$ < -1.

The design approach now can be explained through an example:

Finer First Generation Structure

Following two design assumptions for the structure in Fig.3 are made:

1. The equilibrium angle of smooth substrate θ_y>90^0 (~95^0 in the present context)
2. The aspect ratio (height /pillar cross section) of pillars (H_1/a_1) =5; since it is generally not easy to fabricate slender micro-pillars, this value appears appropriate choice.

The objective is to amplify the apparent contact angle as high as possible. The best way to ensure that is to pick the value of b_1/a_1 such that the apparent contact angle is maximized along the lower energy segments. This point corresponds to the intersection of the composite and wetted curves. For the chosen parameters one obtains designed value for ($b1/a1$) = 0.7 and the corresponding apparent contact angle denoted as θ_{int} =133.3° in Fig.5. Thus, the smooth θ_y =95° in the present example is amplified to 133.3°.

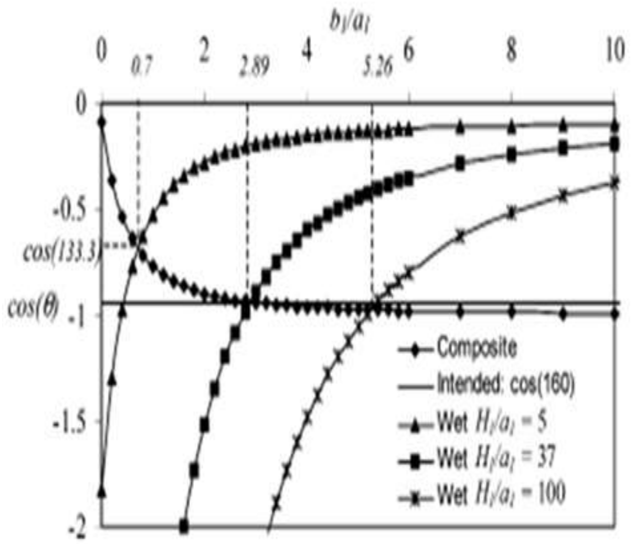

Figure 5(a). Plot of the apparent contact angles for wetted and composite drops as a function of roughness geometry of the first generation. All states for which $\cos\theta_f^w$ is less than -1 are physically unrealizable (see text) (Ack. Patankar[12])

Coarser Second Generation Structure

The coarse structure of pillars (dimensions $a_2xb_2xH_2$) has been assumed earlier to possess periodicity similar to the fine structure. (Subscript 2 denotes the second generation structure) The steps are similar to above, but now the value of equilibrium CA for the present consideration is taken as $\theta_y = \theta_{int}$ = 133.3°.

The plots of ratio (b_2 /a_2) and apparent contact angle are obtained as usual using the Wenzel and Cassie-Baxter equations (IVa) and (IVb), as shown in Fig. 5b.

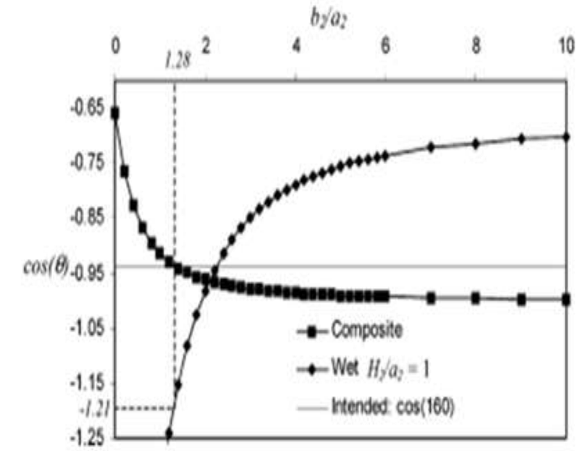

Figure 5(b). Plot of the apparent contact angles for wetted and composite drops as a function of roughness geometry of the second generation. All states for which $\cos\theta_f^w$ is less than -1 are physically unrealizable (see text) (Ack. Patankar[12])

Now, one can choose any value for the ratio (b_2 /a_2), where the energy for the Cassie-Baxter plot is lower than the Wenzel plot. Alternatively, one set design goal for apparent value, say θ=160^0 and the intersection of this straight line with the Cassie plot provides the required value for (b_2 /a_2)=1.28, ensuring however that energy of this Cassie plot point is lower than the corresponding Wenzel plot point, as may be seen in the figure. However, for obtaining Wenzel plot, it is important to choose the ratio (H_2/a_2) of similar order as of lotus leaf structure that is chosen here as the model structure. For the lotus leaf, this has been found as (H_2/a_2) ~1.0.

The above example illustrates as to how a hierarchal structure (Fig.2d) bio mimicking the lotus leaf structure as a design goal can be achieved.

VI. RESULT AND DISCUSSION

In order to make a surface possess superhydrophobicity, the surface must be engineered such that the contact angle with droplet of water is above 150^O. The hydrophilic or hydrophobic nature of surfaces is fully understood by the theories given by Thomas Young, Wenzel and Cassie & Baxter.

For understanding and explaining the phenomena of ultrahydrophobicity or superhydrophobicity, initially the classical theory for wetting on rough surfaces by Cassie-Baxter [3] had been found to be generally adequate. Experimental evidence showed that though the WCA were sufficiently high, the drop has tendency to pin-down to the rough surface and there is a phenomenon of hysteresis, requiring other considerations beyond the classical theories. According to some other theories coexistence and transition between the Wenzel and Cassie-Baxter states occur. A Cassie-Baxter metastable state of non-wetting seems to explain extreme non-wetting on rough surfaces with certain special micro /nano scale structures. There have been significant developments that put forward the explanation for the superhydrophobicity by

laying down the criteria for such surfaces.
A schematic of a bio-inspired model including the lotus leaf is shown in Figure 6.

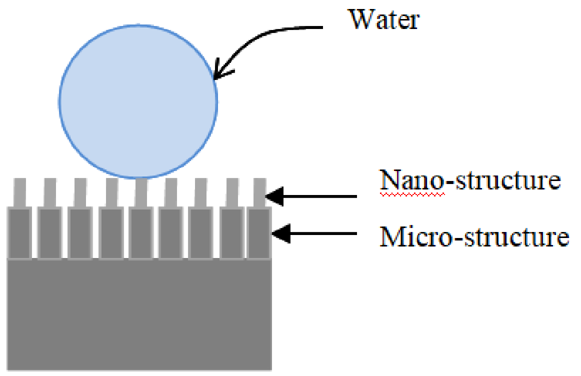

Figure 6: Bio inspired model of a superhydrophobic surface showing hierarchical roughness in two scales – micro and nano dimensions

There have been many methods to create this model lotus surface structure. A composite solid–air–liquid surface is critical to superhydrophobicity. Surface roughness on a hydrophilic or hydrophobic surface decreases or increases the contact angle, respectively, based on the so-called Wenzel effect. Air pocket formation in the valleys can increase the contact angle for both hydrophilic and hydrophobic surfaces based on the so-called Cassie–Baxter effect. Formation of air pockets, leading to a composite interface, is the key to very high contact angle and small slide angle (tilt).
A rough surface comprises of air as a second phase besides its own composition and thus, is a composite surface on which the fluid drop is situated. Below the drop, the air is trapped in grooves of the rough surface. It is observed in Fig.2 that the fluid at the rough surface encounters two interfaces, a fluid-solid interface and a fluid-vapour interface. This implies that rough surface is chemically inhomogeneous or heterogeneous or a composite surface comprised of a solid (phase1) and a vapour phase (phase 2). Nature of roughness has a great influence on hysteresis. The experimental microstructures of typical rough surfaces such as periodic array of pillars or posts, holes or stripes differentiate the hysteresis of such structures in respect to solid fraction roughness [13]. The structures are of microscale dimensions. The hysteresis is also found to depend on the direction of wetting.
Now an appropriate choice of the geometrical parameters of the surface morphology has to be made, in which the apparent contact angle becomes high and at the same time, the hysteresis also is minimized. The design approach besides advancing the Contact Angle is more based on low CA hysteresis. For ensuring low CA hysteresis, the minimization of energy concept is used.

VII. CONCLUSION

Designing the microstructure for a surface to be superhydrophobic, involves developing the hierarchy of nano scale and micro scale pattern of roughness on the surface. The primary roughness of micro scale behaves like a structure for the overriding nano scale roughness. The apparent contact angle is a function of roughness geometry of second generation. This second generation roughness alongwith the dimensions of micro-pillar of primary structure give magnified apparent contact angle. The slenderness ratio of these micopillars and their dimensions for minimum energy can be the parameters to achieve desired level of superhydrophobicity, as this affects the apparent contact angle. In turn, the surface roughness can be manipulated and surface can be engineered.

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