The rose petal effect and the modes of superhydrophobicity

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The wetting of rough surfaces remains a subject of active investigation by scientists. The contact angle (CA) is a traditional parameter used to characterize the hydrophobicity/philicity of a solid surface. However, it was found recently that high CAs can coexist with strong adhesion between water and a solid surface in the case of the so-called ‘rose petal effect’. Several additional parameters have been proposed to characterize the interaction of water with a rough solid surface, including the CA hysteresis, the ability of water droplets to bounce off a solid surface, the tilt angle needed to initiate the flow of a droplet, and the normal and shear adhesion. It is clear now that wetting is not characterized by a single parameter, since several modes or regimes of wetting of a rough surface can exist, including the Wenzel, Cassie, lotus and petal. Understanding the wetting of rough surfaces is important in order to design non-adhesive surfaces for various applications.

Keywords: rose petal; superhydrophobicity; wetting regimes; adhesion; self-cleaning

1. Introduction

The wetting of rough surfaces is a complex problem that continues to attract scientists, in particular due to the emergence of new materials with controlled surface micro-, nano- and hierarchical structures. During the past decade, the so-called ‘lotus effect’, or surface roughness-induced superhydrophobicity and self-cleaning, has become a subject of active investigation. According to the early models of Wenzel (1936) and Cassie & Baxter (1944), there are two regimes of wetting of a rough surface: a homogeneous regime with a two-phase solid–water interface, and a non-homogeneous or composite regime with a three-phase solid–water–air interface (air pockets are trapped between the solid surface and water). Both models predict that surface roughness affects the water contact angle (CA) and can easily bring it to extreme values close to 180° (superhydrophobicity) or close to 0° (superhydrophilicity). Studies of the wetting of microstructured surfaces have concentrated on the investigation of the two regimes and the factors

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that affect the transition between them (Jung & Bhushan 2006; Bormashenko et al. 2007; Nosonovsky & Bhushan 2007a,b,c,d, 2008a,b,c; Bhushan & Jung 2008; Bhushan et al. 2009; Bhushan 2010). Recent experimental findings and theoretical analyses have made it clear that the early Wenzel (1936) and Cassie & Baxter (1944) models do not explain the complexity of interactions during wetting of a rough surface, which can follow several different scenarios (Jin et al. 2005; Wang & Jiang 2007; Feng et al. 2008; Gao & McCarthy 2008; Xia & Jiang 2008; McHale 2009; Bhushan & Her 2010; Nosonovsky & Bhushan 2010). As a result, there are several modes of wetting of a rough surface, and therefore wetting cannot be characterized by a single number such as the CA.

The concept of surface (or interface) energy is central to the analysis of wetting phenomena. Atoms or molecules at the surface of a solid or liquid have fewer bonds with neighbouring atoms than those in the bulk. Energy is spent on breaking the bonds when a surface is created. As a result, the atoms at the surface have higher energy. This excess surface energy or surface tension, $\gamma$, is measured in newtons per metre, and it is equal to the energy needed to create a surface with unit area. If a liquid droplet is placed on a solid surface, the liquid and solid surfaces come together under equilibrium at a characteristic angle called the static CA, $\theta_0$, given by the Young equation (Bhushan 2002),

$$\cos \theta_0 = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \quad (1.1)$$

where $\gamma_{SL}$, $\gamma_{SA}$ and $\gamma_{LA}$ are the surface energies of the solid–liquid, solid–air and liquid–air interfaces, respectively. For a large number of combinations of materials and liquids, $\gamma_{SA} + \gamma_{LA} > \gamma_{SL}$, which means that it is energetically profitable for a liquid to wet the solid surface rather than to have an air film separating the solid and liquid. On the other hand, for many material combinations, $\gamma_{SL} + \gamma_{LA} > \gamma_{SA}$, which means that it is energetically profitable for a solid to be in contact with air rather than to be covered by a thin liquid film. As a result, in most situations $-1 < (\gamma_{SA} - \gamma_{SL})/\gamma_{LA} < 1$, and there exists a value of the CA given by equation (1.1). The CA is the angle at which the liquid–air interface comes into contact with the solid surface locally, and it does not depend on the shape of the body of water. If the water CA is $0^\circ < \theta_0 < 90^\circ$, then the surface is usually called ‘hydrophilic’, whereas a surface with water CA of $90^\circ < \theta_0 < 180^\circ$ is usually called ‘hydrophobic’.

Consider now a rough solid surface with roughness factor $R_f > 1$, equal to the ratio of the solid surface area to its flat projected area. When water comes into contact with such a surface, the effective values of the solid–liquid and solid–air surface energies become $R_f \gamma_{SL}$ and $R_f \gamma_{SA}$. This leads to the Wenzel equation for the CA with a rough surface (Wenzel 1936),

$$\cos \theta = R_f \cos \theta_0. \quad (1.2)$$

If some air is trapped between the rough solid surface and the liquid, then only the fraction $0 < f_{SL} < 1$ constitutes the solid–liquid contact interface. The area of the solid–liquid interface is now $R_f f_{SL}$ per unit area, and, in addition, there is $(1 - f_{SL})$ of the liquid–air interface under the droplet. The effective
values of the solid–liquid and solid–air surface energies become $R_f f_{SL} \gamma_{SL}$ and $R_f f_{SL} \gamma_{SA} + (1 - f_{SL}) \gamma_{LA}$. The CA is then given by the Cassie and Baxter equation (Cassie & Baxter 1944),

$$\cos \theta = R_f f_{SL} \cos \theta_0 - 1 + f_{SL}. \quad (1.3)$$

If a surface is covered by holes filled (or impregnated) by water, the CA is given by

$$\cos \theta = 1 + f_{SL}(\cos \theta_0 - 1). \quad (1.4)$$

This is the so-called ‘impregnating’ Cassie wetting regime (Nosonovsky & Bhushan 2008c).

In the ideal situation of a perfectly smooth and homogeneous surface, the static CA is a single number that corresponds to the unique equilibrium position of the solid–liquid–air contact line (the triple line). However, when the contact takes place with a rough surface, there may be multiple equilibrium positions, which results in an entire spectrum of possible values of the CA. In addition, the value of the surface energy itself exhibits so-called ‘adhesion hysteresis’ and can depend on whether it is measured during the approach of the two bodies or when they are taken apart. As a result, there is always a minimum value of the CA, called the receding CA, $\theta_{\text{rec}}$, and a maximum value of the CA, called the advancing CA, $\theta_{\text{adv}}$. The difference between the advancing and receding CAs is called CA hysteresis (figure 1).

The CA is a macroscale parameter characterizing wetting. However, hydrophobicity/philicity is dependent upon the adhesion of water molecules to the solid. On the one hand, a high CA is a sign of low liquid–solid adhesion. On the other hand, low CA hysteresis is a sign of low liquid–solid adhesion as well. There is an argument in the literature as to whether superhydrophobicity is adequately characterized only by a high CA, and whether a surface can have a high CA but at the same time strong adhesion. It is now widely believed that a surface can be superhydrophobic and at the same time strongly adhesive to water (e.g. Jin et al. 2005). The so-called ‘petal effect’ is exhibited by a surface that has a high CA, but also a large CA hysteresis and strong adhesion to water. The phenomenon of large CA hysteresis and high water adhesion to rose petals (and similar surfaces), as opposed to small CA hysteresis and low adhesion to lotus leaf, has been observed by several research groups (Bormashenko et al. 2009; Chang et al. 2009; Bhushan & Her 2010). Bormashenko et al. (2009) reported a transition between wetting regimes, e.g. the penetration of liquid into the micro/nanostructures.

Li & Amirfazli (2007) argued that, since ‘superhydrophobicity’ means a strong fear of water or lacking affinity to water, ‘the claim that a superhydrophobic surface also has a high adhesive force to water is contradictory’. Gao & McCarthy (2008) pointed out that the terms ‘hydrophobic/philic’ should be defined in a more accurate way. They suggested several experiments showing that even Teflon, which is usually considered very hydrophobic, can be, under certain conditions, considered hydrophilic, i.e. having affinity to water. They argued that the concepts of ‘shear and tensile hydrophobicity’ should be used, so that the wettability of a surface is characterized by two numbers, advancing and receding CAs, and ‘the words hydrophobic, hydrophilic and their derivatives can and should only be considered qualitative or relative terms’. Instead, shear and...
tensile hydrophobicity should be investigated, which makes wetting (‘solid–liquid friction’) similar to the friction force, as pointed out in the literature earlier (Nosonovsky 2007a). McHale (2009) noted that all solid materials, including Teflon, are hydrophobic to some extent, if they have a Young CA less than 180°. Therefore, it is energetically profitable for them to have contact with the solid, at least to some extent. Wang & Jiang (2007) suggested five superhydrophobic states (Wenzel’s state, Cassie’s state, so-called ‘lotus’ and ‘gecko’ states and a
transitional state between Wenzel’s and Cassie’s states). It may be useful also to see the transition between the Wenzel, Cassie and dry states as a phase transition, and to add the ability of a surface to bounce off water droplets to the definition of superhydrophobicity (Nosonovsky & Bhushan 2008b). In addition, there is an argument on how the various definitions of CA hysteresis are related to each other (Krasovitski & Marmur 2004; Bormashenko et al. 2007, 2009; Xia & Jiang 2008; Chang et al. 2009).

The lotus effect has been comprehensively discussed in earlier publications. The objective of this paper is to discuss various wetting modes of rough surfaces beyond the classical Wenzel (1936) and Cassie & Baxter (1944) regimes in light of recent experimental data on the petal effect and strong adhesion with superhydrophobic surfaces referred to as the rose petal effect.

2. Modelling CA hysteresis

Predicting CA hysteresis for a rough surface with a given topography is a difficult task. One approach is a numerical simulation. However, in most cases the simulations are limited to two-dimensional topography. Kusumaatmaja & Yeomans (2007) showed that CA hysteresis is sensitive to the details of the surface patterning. Despite that, certain conclusions about the relation of CA hysteresis to roughness can be made. It is known that the energy gained by surfaces during contact is greater than the work of adhesion on separating the surfaces, owing to so-called adhesion hysteresis. Factors that affect CA hysteresis include adhesion hysteresis, surface roughness and inhomogeneity. Nosonovsky & Bhushan (2007a,b,c,d) assumed that CA hysteresis is equal to the adhesion hysteresis term and the term corresponding to the pinning effect of roughness, $H_r$. They further noted that adhesion hysteresis can be assumed to be proportional to the fractional solid–liquid area $(1 - f_{LA})$. Using equation (1.3), the difference between the cosines of the advancing and receding angles is related to the difference between those angles for a nominally smooth surface, $\theta_{adv0}$ and $\theta_{rec0}$, as

$$\cos \theta_{adv} - \cos \theta_{rec} = R_f (1 - f_{LA}) (\cos \theta_{adv0} - \cos \theta_{rec0}) + H_r.$$ (2.1)

The first term on the right-hand side of the equation, which corresponds to the inherent CA hysteresis of a smooth surface, is proportional to the fraction of the solid–liquid contact area, $1 - f_{LA}$. The second term $H_r$ is the effect of surface roughness, which is proportional to the length of the triple line. Thus equation (2.1) involves a term proportional both to the solid–liquid interface area and to the triple line length. It is observed from equations (1.4) and (2.1) that increasing $f_{LA} \rightarrow 1$ results in increasing the CA $(\cos \theta \to -1, \theta \to \pi)$ and decreasing the CA hysteresis $(\cos \theta_{adv} - \cos \theta_{rec} \to 0)$. In the limiting case of a very small solid–liquid fractional contact area under the droplet, where the CA is large $(\cos \theta \approx -1 + (\pi - \theta)^2/2, \sin \theta \approx \theta - \pi)$ and the CA hysteresis is small $(\theta_{adv} \approx \theta \approx \theta_{rec})$, based on equation (2.1) one has (Nosonovsky & Bhushan 2007c)

$$\pi - \theta = \sqrt{2(1 - f_{LA})(R_f \cos \theta_0 + 1)}$$ (2.2)
and

\[ \theta_{\text{adv}} - \theta_{\text{rec}} = (1 - f_{LA}) R f \frac{\cos \theta_{\text{adv}0} - \cos \theta_{\text{rec}0}}{-\sin \theta} \]

\[ = (\sqrt{1 - f_{LA}}) R f \frac{\cos \theta_{\text{rec}0} - \cos \theta_{\text{adv}0}}{\sqrt{2(R f \cos \theta_{0} + 1)}}. \]  (2.3)

For a homogeneous interface, \( f_{LA} = 0 \), whereas for a composite interface, \( f_{LA} \) is a non-zero number. It is observed from equations (2.2) and (2.3) that, for a homogeneous interface, increasing roughness (high \( R f \)) leads to increasing CA hysteresis (high values of \( \theta_{\text{adv}} - \theta_{\text{rec}} \)), while for a composite interface, an approach to unity of \( f_{LA} \) provides both high CA and small CA hysteresis (Jung & Bhushan 2006; Nosonovsky & Bhushan 2007a,b,c; Bhushan & Jung 2008; Bhushan et al. 2009). Therefore, a composite interface is desirable for self-cleaning.

A different semi-phenomenological model of CA hysteresis was proposed recently by Whyman et al. (2008). According to their model, the CA hysteresis is given by the equation \( \theta_{\text{adv}} - \theta_{\text{rec}} = (8 U / \gamma R_0)^{1/2} h(\theta^*) \), where \( U \) is the height of the potential barrier connected with the motion of the triple line along the substrate, \( R_0 \) is the initial radius of the spherical drop before deposition on the substrate, and \( h(\theta^*) \) is a dimensionless function of the apparent CA \( \theta^* \).

Vedantam & Panchagnula (2007) suggested a semi-empirical phase field method to calculate the CA hysteresis. In this method, the order parameter \( \eta(x, y) \) is selected in such a manner that \( \eta = 0 \) for non-wetted regions of the surface and \( \eta = 1 \) for wetted regions, whereas \( 0 < \eta < 1 \) for partially wetted regions. After that, the energy function \( f(\eta) \) is constructed, and its minima correspond to the equilibrium states of the system (e.g. the Wenzel and Cassie states). The energy functional is written as

\[ L = \int_{A} \left\{ f(\eta) + \frac{\lambda}{2} |\nabla f(\eta)|^2 \right\} \, dA, \]  (2.4)

where \( \lambda \) is the gradient coefficient. The functional that should be minimized involves the free energy and the gradient of the free energy. The latter term is needed to account for the fact that creating an interface between two phases is energetically unprofitable. The kinetic equation is given in the form

\[ \beta \dot{\eta} = -\frac{dL}{d\eta} = \lambda \nabla^2 \eta - \frac{\partial f}{\partial \eta}, \]  (2.5)

where \( \beta > 0 \) is the kinetic coefficient. Vedantam & Panchagnula (2007) showed that, in the case of \( \beta = \text{const.} \) for an axisymmetric drop flowing with velocity \( V \), equation (2.5) leads to

\[ \cos \theta_{\text{adv}} - \cos \theta_{\text{rec}} = 2\alpha \beta V. \]  (2.6)

In other words, assuming that the kinetic coefficient is constant, the CA hysteresis is expected to be proportional to the flow velocity. A more complicated form of the kinetic coefficient may lead to a more realistic dependence of the CA hysteresis on the velocity.

There is an asymmetry between the wetting and dewetting processes, since less energy is released during wetting than the amount required for dewetting, due to adhesion hysteresis. Adhesion hysteresis is one of the reasons that lead to CA
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hysteresis, and it also results in hysteresis of the Wenzel–Cassie state transition. The Cassie–Wenzel transition and CA hysteresis may both be considered as different manifestations of the same wetting–dewetting cycle behaviour. Both the CA hysteresis and Cassie–Wenzel transition cannot be determined from the macroscale equations and are governed by micro- and nanoscale phenomena.

Note that the size of the surface roughness details is an important factor. It is generally assumed that the roughness factor $R_f$ as well as the fractional area of contact $f_{SL}$ can be determined by averaging the surface roughness over some area that is itself small relative to the size of the liquid droplet. For $R_f$ and $f_{SL}$ fractional areas that change with a spatial coordinate, special generalized Wenzel and Cassie equations, proposed by Nosonovsky (2007b), should be used. The size of the surface roughness also affects the ability of the interface to pin the triple line and thus affects the CA hysteresis. It could be claimed that CA hysteresis is a ‘second-order’ effect that is expected to vanish with decreasing ratio of the size of the surface roughness and heterogeneity details to the droplet radius. This, however, does not happen, since surface roughness and heterogeneity is an inherent property of any surface. There is a deep similarity between dry friction and the wetting of a solid surface (Nosonovsky 2007a). In the ideal situation of absolutely homogeneous and smooth surfaces, there would be no friction and no CA hysteresis owing to the absence of energy dissipation. However, in real situations, surfaces are not ideal, and this leads to both dry friction and CA hysteresis. The development of quantitative relationships between the degrees of surface non-ideality (e.g. the Shannon entropy of a rough surface) and CA hysteresis remains an interesting task similar to the same task for friction (Nosonovsky 2010).

3. Investigation of the petal effect

Plant leaves and petals provide an example of surfaces with high CA and high and low CA hysteresis. Bhushan & Her (2010) studied two kinds of superhydrophobic rose petals: (i) Rosa Hybrid Tea cv. Bairage and (ii) Rosa Hybrid Tea cv. Showtime, referred to as Rosa cv. Bairage and Rosa cv. Showtime, respectively. Figure 2 shows optical micrographs, scanning electron microscopy (SEM) images and atomic force microscope (AFM) surface height maps of two rose petals. Figure 3 shows a sessile and a suspending water droplet on Rosa cv. Bairage, demonstrating that it can simultaneously have high CA, high adhesion and high CA hysteresis.

The surface roughness of the two rose petals was measured with the AFM, and the results for the peak-to-base height of bumps, midwidth, peak radius and bump density are summarized in table 1. The data indicate that the low-adhesion specimen (Rosa cv. Showtime) has higher density and height of the bumps, indicating that the penetration of water between the micro-bumps is less likely. Wetting of a rough surface with a single level of hierarchy of roughness details can follow several scenarios (table 2).

For a hierarchical structure with small bumps on top of larger bumps, a larger number of scenarios is available, and they are summarized in table 3 and figure 4. Water can penetrate either into the micro- or nanostructure, or into both.

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Figure 2. Two roses with superhydrophobic petals: (a) Rosa cv. Bairage, with high adhesion; and (b) Rosa cv. Showtime, with low adhesion. (i) Optical images, fresh (scale bar, 10 mm); (ii) scanning electron micrographs of the petals, dried (scale bar, 20 µm); and (iii) atomic force microscope roughness maps of the petals, dried. Adapted from Bhushan & Her (2010).

Figure 3. Optical micrographs of a water droplet on Rosa cv. Bairage at (a) 0° and (b) 180° tilt angles. The droplet is still suspended when the petal is turned upside down (Bhushan & Her 2010). Scale bars, (a,b) 500 µm.
Table 1. Surface roughness statistics for the two rose petals (Bhushan & Her 2010).

<table>
<thead>
<tr>
<th></th>
<th>peak-to-base height (μm)</th>
<th>midwidth (μm)</th>
<th>peak radius (μm)</th>
<th>bump density (1/10⁴ μm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rosa cv. Bairage (high adhesion)</td>
<td>6.8</td>
<td>16.7</td>
<td>5.8</td>
<td>23</td>
</tr>
<tr>
<td>Rosa cv. Showtime (low adhesion)</td>
<td>8.4</td>
<td>15.3</td>
<td>4.8</td>
<td>34</td>
</tr>
</tbody>
</table>

Table 2. Wetting regimes of a surface with a single level of hierarchy of roughness.

<table>
<thead>
<tr>
<th>state</th>
<th>Cassie–Baxter</th>
<th>Wenzel</th>
<th>impregnating Cassie</th>
</tr>
</thead>
<tbody>
<tr>
<td>cavities</td>
<td>air</td>
<td>water under droplet</td>
<td>water everywhere</td>
</tr>
<tr>
<td>CA</td>
<td>high</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>CA hysteresis</td>
<td>low</td>
<td>can be high</td>
<td>low</td>
</tr>
</tbody>
</table>

Table 3. Different regimes of wetting of a surface with dual roughness.

<table>
<thead>
<tr>
<th>air in nanostructure</th>
<th>water under droplet in nanostructure</th>
<th>water impregnating nanostructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>lotus, high CA, low CA hysteresis</td>
<td>rose, high CA, high CA hysteresis</td>
<td>rose filled microstructure</td>
</tr>
<tr>
<td>Cassie (air-filled microstructure, water in nanostructure), high CA, low CA hysteresis</td>
<td>Wenzel (water in micro- and nanostructure), high CA, high or low CA hysteresis</td>
<td>Wenzel filled microstructure</td>
</tr>
<tr>
<td>water impregnating nanostructure</td>
<td>Cassie filled nanostructure</td>
<td>Wenzel filled nanostructure</td>
</tr>
</tbody>
</table>

In addition, the micro- or nanostructure can be impregnated by water or air. The regimes with water penetrating into the microstructure can have high solid–water adhesion and therefore high CA hysteresis.

Bhushan & Her (2010) conducted a series of carefully designed experiments to decouple the effects of the micro- and nanostructures. They synthesized microstructured surfaces with pillars out of epoxy resin. The epoxy surfaces were reproduced from model Si templates and were created by a two-step moulding process producing a dual replica—first a negative replica and then a positive replica of the original Si template (Bhushan et al. 2009). Surfaces with a pitch (the periodicity of the structure of the pillars) of 23, 105 and 210 μm and with the same diameter (14 μm) and height (30 μm) of the pillars were produced. After that, nanostructures were created on the microstructured sample by self-assembly of the alkane n-hexatriacontane (CH₃(CH₂)₃₄CH₃) deposited by a thermal
Figure 4. Schematic of nine wetting scenarios for a surface with hierarchical roughness.

Figure 5. SEM micrographs of the micro- and nanostructures fabricated with two different masses of \(n\)-hexatriacontane for hierarchical structure. All images were taken at 45° tilt angle. All samples are positive replicas, obtained from the negative replica with dental wax and Si micropatterned master template (14 µm diameter and 30 µm height) fabricated with epoxy resin coated with \(n\)-hexatriacontane. Adapted from Bhushan & Her (2010). (a) Low-magnification images: (i) 23 µm pitch, (ii) 105 µm pitch and (iii) 210 µm pitch. (b) High-magnification images: (i) 0.1 µg mm\(^{-2}\) and (ii) 0.2 µg mm\(^{-2}\) \(n\)-hexatriacontane. Scale bars, (a) 100 µm and (b) 2 µm.
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Figure 6. Schematic of a wetting regime map as a function of microstructure pitch and the mass of nanostructure material. A mass of nanostructure material equal to zero corresponds to microstructure only (with the Wenzel and Cassie regimes). A higher mass of nanostructure material corresponds to higher values of pitch, at which transition occurs.

Table 4. CA and CA hysteresis (degrees) for surfaces with various micro- and nano-roughness (adapted from Bhushan & Her 2010).

<table>
<thead>
<tr>
<th>mass of n-hexatriacontane (µg mm(^{-2}))</th>
<th>23 µm pitch</th>
<th>105 µm pitch</th>
<th>210 µm pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CA</td>
<td>CA hysteresis</td>
<td>CA</td>
</tr>
<tr>
<td>0.10</td>
<td>164</td>
<td>3</td>
<td>152</td>
</tr>
<tr>
<td>0.12</td>
<td>165</td>
<td>3</td>
<td>153</td>
</tr>
<tr>
<td>0.16</td>
<td>166</td>
<td>3</td>
<td>160</td>
</tr>
<tr>
<td>0.20</td>
<td>167</td>
<td>3</td>
<td>168</td>
</tr>
</tbody>
</table>

Evaporation method. Alkanes of varying chain lengths are common hydrophobic compounds of plant waxes. On smooth surfaces, alkanes can cause a large CA and a small CA hysteresis for water droplets. To fabricate the nanostructure, various masses of n-hexatriacontane were coated on a microstructure. The nanostructure is formed by three-dimensional platelets of n-hexatriacontane. Platelets are flat crystals, grown perpendicular to the surface. They are randomly distributed on the surface, and their shapes and sizes show some variation. Figure 5 shows selected images. When different masses of wax are applied, the density of the nanostructure is changed.

For surfaces with a small pitch of 23 µm, as the mass of n-hexatriacontane is changed, there are only small changes in the static CA and CA hysteresis values, which means that they are always in the lotus wetting regime. On the surface with a 210 µm pitch value, as the mass of n-hexatriacontane is increased, the static CA is increased, and the reverse trend was found for the CA hysteresis. This was interpreted as evidence that the nanostructure is responsible for the CA hysteresis and low adhesion between water and the solid surface. The results are summarized in table 4. The wetting regimes are shown schematically...
Figure 7. Shapes of droplets on various hierarchical structures. (a) Droplet on a horizontal surface of hierarchical structure with 23 μm pitch and 0.1 μg mm$^{-2}$ n-hexatriacontane, showing air pocket formation. (b) Droplet on a horizontal surface of hierarchical structure with 105 μm pitch and (i) 0.1 μg mm$^{-2}$ and (ii) 0.2 μg mm$^{-2}$ n-hexatriacontane, showing (i) no air pocket and (ii) air pocket formation, respectively. (c) Droplet on inclined surfaces of hierarchical structure with 105 μm pitch and 0.1 μg mm$^{-2}$ n-hexatriacontane, showing that droplet is still suspended when (i) vertical and (ii) upside down. Adapted from Bhushan & Her (2010). Scale bars, all 500 μm.

in figure 6 as a function of the pitch of the microstructure and the mass of n-hexatriacontane. A small mass of the nanostructure material corresponds to the Cassie and Wenzel regimes, whereas a high mass of nanostructure corresponds to the lotus and rose regimes. The lotus regime is more likely for larger masses of the nanostructure material. Figure 7 shows a droplet on a horizontal surface of hierarchical structure with 23 and 105 μm pitch and
Figure 8. Optical micrographs of droplet evaporation on hierarchical structured surfaces with 105 μm pitch value and (a) 0.1 μg mm$^{-2}$ or (b) 0.2 μg mm$^{-2}$ n-hexatriacontane. (a) The 0.1 μg mm$^{-2}$ n-hexatriacontane coated sample has no air pocket formed between the pillars in the entire contact area until evaporation was complete. (b) The 0.2 μg mm$^{-2}$ n-hexatriacontane coated sample has an air pocket, and then transition from the lotus regime to the ‘rose petal’ regime occurs. Adapted from Bhushan & Her (2010). Scale bars, both 500 μm.
$n$-hexatriacontane ($0.1 \text{gmm}^{-2}$). Air pockets are observed in the first case and not observed in the second case, indicating the difference between the two regimes (Bhushan & Her 2010).

To further verify the effect of wetting states on the surfaces, evaporation experiments with a droplet on a hierarchical structure coated with two different amounts of $n$-hexatriacontane were performed. Figure 8 shows the optical micrographs of a droplet evaporating on two different hierarchical structured surfaces. On the $0.1 \text{gmm}^{-2}$ $n$-hexatriacontane coated surface, no air pocket is visible at the bottom area of the droplet. However, the droplet on the surface has a high static CA ($152^\circ$) since the droplet still cannot completely impregnate the nanostructure. The footprint size of the droplet on the surface has only small changes from 1820 to 1791 $\mu$m. During evaporation, the initial contact area between the droplet and the hierarchical structured surface does not decrease until the droplet evaporates completely, which means complete wetting between droplet and microstructures. For the $0.2 \text{gmm}^{-2}$ $n$-hexatriacontane coated surface, the light passes below the droplet, and air pockets can be seen, so to start with the droplet is in the Cassie–Baxter regime. When the radius of the droplet decreased to 381 $\mu$m, air pockets are no longer visible. The footprint size of the droplet on the surface is changed from 1177 to 641 $\mu$m, since the droplet remained on only a few pillars until the end of the evaporation process.

The experimental observations of the two types of rose petals show that hierarchically structured plant surfaces can have both adhesive and non-adhesive properties at the same time with high CA. This is due to the existence of various modes of wetting of a hierarchical surface, so that water can penetrate either into macro- or nano-roughness, or into both. Water penetration into the micro-roughness tends to result in high adhesion with the solid surface, whereas the presence of nano-roughness still provides high CA. As a result, two distinct modes of wetting are observed. One can be called the ‘lotus’ mode (with low adhesion) and the other is the ‘rose’ mode (with high adhesion).

4. Conclusions

In this work, several modes of wetting of rough surfaces were investigated. Rose petals have different hierarchically organized surface micro- and nanostructures, and can exhibit high and low adhesion to water. The pitch spacing and height of the microstructures controls the wetting regime, since it controls the penetration of water into the microstructure. The microstructure controls the CA hysteresis, whereas the nanostructure provides high CA. As a result, a rose petal can exhibit typical lotus effect properties (high CA and low CA hysteresis) or petal effect properties (high CA and high CA hysteresis). Artificial surfaces that mimic rose petals were investigated and similar behaviour was found. Various wetting regimes are possible, depending on air and water penetration into the micro- and nanostructures. Understanding the wetting of rough surfaces is important in order to design non-adhesive surfaces for various applications, including green tribology.

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