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1 Mimicking lotus leaves for designing super-hydrophobic/hydrophilic and super-attractive/repulsive nanostructured hierarchical surfaces

Nicola M. Pugno
Department of Structural Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

Abstract

In this Chapter we demonstrate the feasibility of super-hydrophobic/hydrophilic and simultaneously super-attractive/repulsive surfaces, mimicking Nature thanks to hierarchical architectures. Super-hydrophobia is found to take place for a number of ~2 hierarchical

Correspondence/Reprint request: Dr. Nicola M. Pugno, Department of Structural Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy. E-mail: nicola.pugno@polito.it

levels, as observed in several plants, e.g. lotus. Moreover, the strength of the capillary attractive or repulsive interaction is found to be enormously enhanced by the hierarchical architecture. Thus, the analysis suggests the feasibility of innovative self-cleaning and simultaneously super-adhesive hierarchical materials, as observed in geckos.

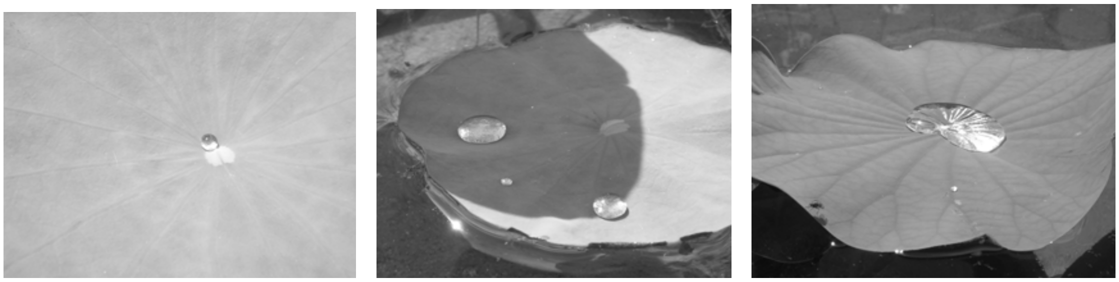
1. Introduction

Several natural materials exhibit super-hydrophobia, with contact angles between 150° and 165°, often a strategy for allowing a safe interaction with water, see the review on non-sticking drops by Quéré [1]. This is the case for the leaves of about 200 plants, including asphodelus, drosera, eucalyptus, euphorbia, gingko biloba, iris, tulipa and, perhaps the most famous, lotus [2, 3], Figure 1. Similarly, animals can be super-hydrophobic, as for the case of water strider legs, butterfly wings, duck feathers and bugs [4-6]. These surfaces are generally composed of intrinsic hydrophobic material (contact angle larger than 90°, often around 120°) with a two-level hierarchical micro-sized architecture. Super-hydrophobia (contact angle larger than ~150°, see [1]) is extremely important, e.g., in micro/nano-fluidic devices for reducing the friction associated with the fluid flow, but also for self-cleaning: super-hydrophobic materials are often called self-cleaning materials since drops are efficiently removed taking with them the dirty particles which were deposited on them [3, 7]. This effect is extremely important, (e.g., for producing self-cleaning skyscraper glass). Researchers [8] have proved that the adhesive setae of geckos become cleaner with repeated use; super-adhesion and self-cleaning are both probably a consequence of the hierarchical nature of the gecko foot. On the other hand, hydrophily (contact angle smaller than 90°) is needed to achieve high wettability, (e.g. for surfaces to be painted).

In this letter we demonstrate the feasibility of super-hydrophobic/hydrophilic and simultaneously super-attractive/repulsive surfaces, mimicking Nature thanks to hierarchical architectures.

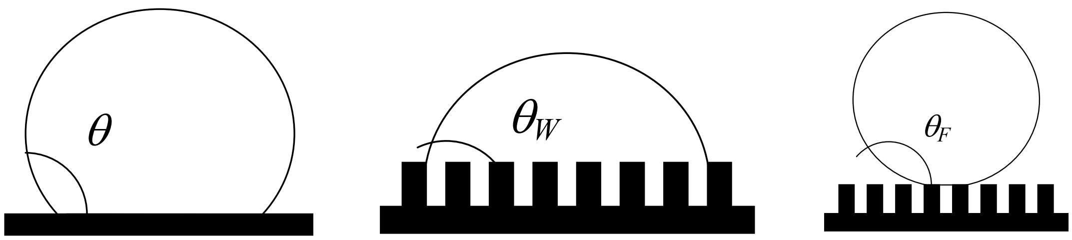
2. Super-hydrophobic/hydrophilic and super-attractive/repulsive surfaces

The contact angle (Figure 2a) between a liquid drop and a solid surface was found by Young [9] according to $\cos\theta = (\gamma_{SV} - \gamma_{SL})/\gamma_C$, where $\gamma_C \equiv \gamma_{LV}$ and the subscripts of the surface tensions describe the solid (*S*), liquid (*L*) and vapour (*V*) phases. Note that for $(\gamma_{SV} - \gamma_{SL})/\gamma_C > 1$ the drop tends to spread completely on the surface and $\theta = 0^\circ$, whereas for $(\gamma_{SL} - \gamma_{SV})/\gamma_C > 1$ the drop is in a pure non-wetting state and $\theta = 180^\circ$. According to the well-known



(a) (b) (c)

Figure 1. Super-hydrophobic behaviour in lotus leaves. Liquid drops of small (a), medium (b) or large size (c). Photos taken by the Author.



(a) (b) (c)

Figure 2. Contact angles for a drop on a flat surface (a) or on a rough surface in the Wenzel (b) or in the Fakir (c) state.

Wenzel's model [10, 11] the apparent contact angle θ_W is a function of the surface roughness w, defined as the ratio of rough to planar surface areas, namely, $\cos\theta_W = w\cos\theta$ (Figure 2b). The apparent contact angle varies also with the heterogeneous composition of the solid surface, as shown by Cassie and Baxter [12]. Consider a heterogeneous surface made up of different materials characterized by their intrinsic contact angles θ_i and let φ_i be the area fraction of each of the species; the individual areas are assumed to be much smaller than the drop size. Accordingly, the apparent contact angle θ_{CB} can be derived as $\cos\theta_{CB} = \sum_i \varphi_i \cos\theta_i$ [12].

A droplet can sit on a solid surface in two distinct configurations or states (Figure 2b,c). It is said to be in Wenzel state (Figure 2b) when it is conformal with the topography. The other state in which a droplet can rest on the surface is called the Fakir state, after Quéré [13], where it is not conformal with the topography and only touches the tops of the protrusions on the surface (Figure 2c). The observed state should be the one of smaller contact angle, as can be evinced by energy minimization [14].

Let us consider a hierarchical surface (Figure 3). The first level is composed by pillars in fraction φ (as in Figure 2b,c). Each pillar is itself structured in n sub-pillars in a self-similar (fractal) manner, and so on. Thus, the pillar fraction at the hierarchical level N is φ^N, whereas the related number of pillars at the level N is n^N. Applying the Cassie and Baxter law [12] for the described composite (solid/air) hierarchical surface (the contact angle in air is by definition equal to 180°) we find for the hierarchical fakir state:

$$\cos\theta_F^{(N)} = \varphi^N\left(\cos\theta + 1\right) - 1 \tag{1}$$

Note that for $N = 0$ $\cos\theta_F^{(0)} = \cos\theta$ as it must be, whereas for N=1 $\cos\theta_F^{(1)} = \varphi(\cos\theta + 1) - 1$, as already deduced for the case described in Figure 2c [15]. Eq. (1) quantifies the crucial role of hierarchy and suggests that hierarchical surfaces are fundamental to realize super-hydrophobic materials (effective contact angle larger than $\theta_{SHpho} \approx 150^\circ$), since we predict $\theta_F^{(\infty)} = 180^\circ$. The minimum number of hierarchical levels necessary to achieve super-hydrophobia is thus:

$$N_{SHpho}^{(F)} = \frac{\log\left(\dfrac{1+\cos\theta_{SHpho}}{1+\cos\theta}\right)}{\log\varphi} \tag{2}$$

and the logarithmic dependence suggests that just a few hierarchical levels are practically required.

By geometrical argument the roughness w of the introduced hierarchical surface (Figure 3) can be calculated in closed form. The roughness at the hierarchical level k is given by $w^{(k)} = 1 + S_L^{(k)}/A$ in which A is the nominal contact area and $S_L^{(k)}$ is the total lateral surface area of the pillars. The pillar at the level k has an equivalent radius r_k and a length l_k and the pillar slenderness s, defined as the ratio between its lateral and base areas, is

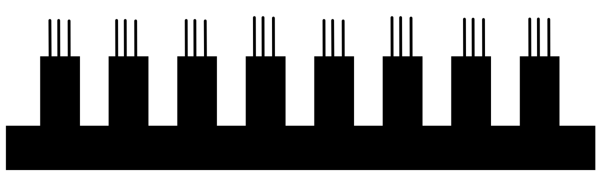


Figure 3. A hierarchical surface (with N=2 levels).

$s = 2l_k / r_k$. The air surface area at the level k can be computed as $A\left(1-\varphi^k\right)$ or equivalently as $A - n^k \pi r_k^2$, thus we deduce $r_k = r_0 (\varphi/n)^{k/2}$, with $A \equiv A_0 \equiv \pi r_0^2$. Consequently:

$$w^{(N)} = 1 + \frac{1}{\pi r_0^2} \sum_{k=1}^{N} 2\pi r_k l_k n^k = 1 + s \sum_{k=1}^{N} \varphi^k = 1 + s \frac{\varphi - \varphi^{N+1}}{1-\varphi} \quad \forall n \tag{3}$$

Note that the result becomes independent from n (and that $w^{(0)}(\varphi) = 1 = w^{(N)}(\varphi = 0)$, $w^{(1)} = 1 + s\varphi$, whereas $w^{(N \neq 1)}(\varphi = 1) = \infty$). Thus we find for the hierarchical Wenzel state:

$$\cos\theta_W^{(N)} = w^{(N)} \cos\theta = \left(1 + s\frac{\varphi - \varphi^{N+1}}{1-\varphi}\right)\cos\theta \tag{4}$$

Eq. (4) suggests that hierarchical surfaces can be interesting also to realize super-hydrophilic materials, since we predict $\cos\theta_W^{(\infty)} = w^{(\infty)} \cos\theta$ with $w^{(\infty)} = 1 + s\varphi/(1-\varphi)$; thus if $\cos\theta > 0$ $\theta_W^{(\infty)} \to 0$, for $s \to \infty$ or $\varphi \to 1$. However note that for $\cos\theta < 0$, $\theta_W^{(\infty)} \to 180^\circ$ ($s \to \infty$ or $\varphi \to 1$), and thus super-hydrophobia can take place also in the Wenzel state, without invoking fakir drops. The minimum number of hierarchical levels necessary to render the surface super-hydrophobic/hydrophilic is thus:

$$N_{SHpho,phi}^{(W)} = \frac{\log\left(1 + \frac{(1-\varphi)}{s\varphi}\left(1 - \frac{\cos\theta_{SHpho,phi}}{\cos\theta}\right)\right)}{\log\varphi} \tag{5}$$

where effective contact angles smaller than θ_{SHphi} define super-hydrophily.

Comparing $\theta_W^{(N)}$ and $\theta_F^{(N)}$, we find that the Fakir state is activated at each hierarchical level for (we omit here second order problems, related to metastability, contact angle hystheresis and limit of the Wenzel's approach, for which the reader should refer to the review by Quèrè [1]):

$$\theta > \theta_{WF}, \ \cos\theta_{WF} = -\frac{1-\varphi^N}{w^{(N)} - \varphi^N} = -\frac{1}{w^{(\infty)}} = -\frac{1-\varphi}{1+\varphi(s-1)} \quad \forall N \tag{6}$$

Note that the result is independent from N and $\theta_{WF} \to 90^\circ$ for $s \to \infty$ or $\varphi \to 1$, and thus a hydrophobic\hydrophilic material composed by sufficiently slender or spaced pillars surely will/will not activate fakir drops and will become super-hydrophobic\hydrophilic for a large enough number of hierarchical levels. Thus hierarchy can enhance the intrinsic property of a material. The role of hierarchy is summarized in Figure 4.

For example, for plausibly values of $\varphi = 0.5$ and s=10 we find from eq. (6) $\theta_{WF} = 95.2^{o}$; thus assuming $\theta = 95^{o}$ the Fakir state is not activated and the Wenzel state prevails (if the Fakir state still prevails it is metastable, see [1]). From eq. (3) $w^{(1)} = 6$, $w^{(2)} = 8.5$, $w^{(3)} = 9.75$ and $w^{(4)} = 10.375$; accordingly from eq. (4) $\theta_W^{(1)} \approx 122^{\circ}$, $\theta_W^{(2)} \approx 138^{\circ}$, $\theta_W^{(3)} \approx 148^{\circ}$ and $\theta_W^{(4)} \approx 155^{\circ}$, thus N=4 hierarchical levels are required for activating super-hydrophobia (from eq. (5) $N_{SHpho}^{(W)} = 3.2$). On the other hand, assuming $\theta = 100^{\circ}$ fakir drops are activated and from eq. (1) $\theta_F^{(1)} \approx 126^{\circ}$, $\theta_F^{(2)} \approx 143^{\circ}$ and $\theta_F^{(3)} \approx 154^{\circ}$, thus N=3 hierarchical levels are sufficient to achieve super-hydrophobia (from eq. (2) $N_{SHpho}^{(F)} = 2.6$).

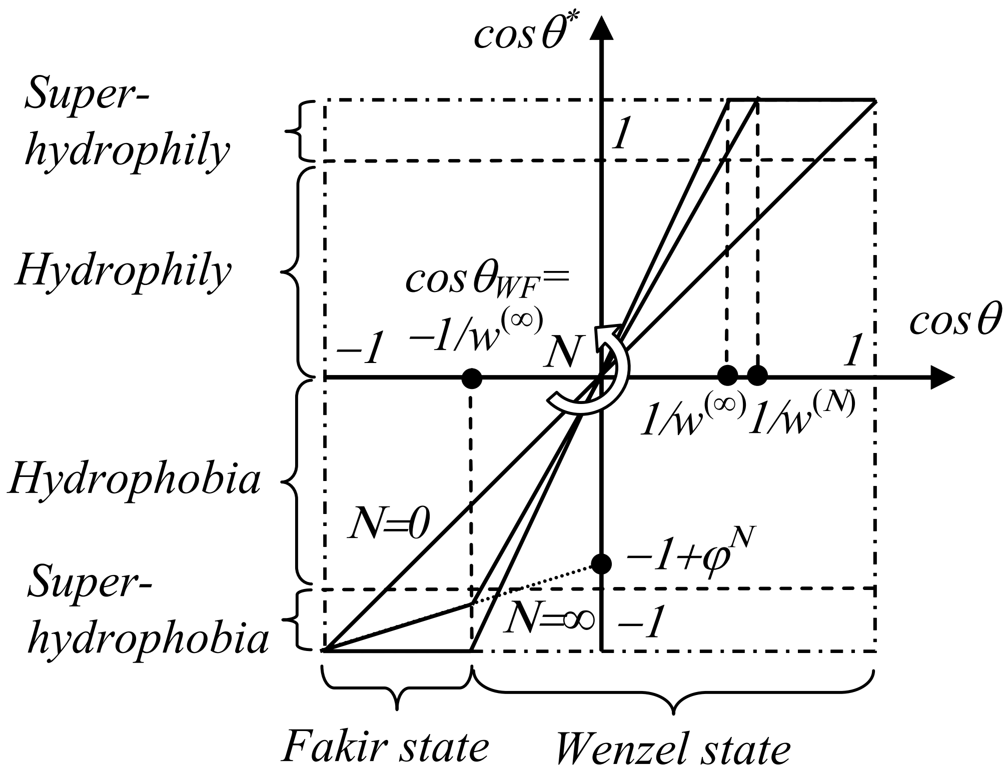


Figure 4. Effective contact angle $\theta^{*} = \theta_{F,W}^{(N)}$ as a function of the intrinsic one θ by varying the number N of hierarchical levels. Thus, super-hydrophobic/hydrophilic surfaces can be obtained by an opportune design of the hierarchical architecture, according to this phase diagram and reported equations (note that metastable fakir drops could be observed also in the Wenzel region, dotted line, see [1]).

The capillary force between a hierarchical surface and a flat plane can also be derived, according to the well-known Laplace's law [16], as a function of the contact angle. Some insects, such as the beetle *Hemisphaerota cyanea*, use capillary to stick to their substrate, generating a force close to 1g (i.e. 60 times its body mass) for more than 2min [17], allowing them to resist attacking ants; tokay geckos use the same principle (in addition to van der Waals forces) to generate their tremendous adhesion [18], that could probably be scaled-up in order to produce a Spiderman Suit [19] (see also the related *New Scientist* story: Gecko inspired suit could have you climbing the wall, by J. Palmer, 28 April, 2007). Between a spherical surface (contact angle θ) of radius r_0 and a flat plate (contact angle θ_P), the capillary attractive or repulsive force is predicted to be $F_C = 2\pi r_0 \gamma_C (\cos\theta + \cos\theta_P)$ [20]. Thus, for a spherical pillar of size r_0 composed by N hierarchical levels the force is $F_C^{(N)} = n^N 2\pi r_N \gamma_C (\cos\theta + \cos\theta_P)$ and the nominal strength $\sigma_C^{(N)} = F_C^{(N)} / (\pi r_0^2)$ becomes:

$$\sigma_C^{(N)} = \frac{2(\varphi n)^{N/2}}{r_0} \gamma_C \left(\cos\theta_{W,F}^{(N)} + \cos\theta_P\right) \tag{7}$$

Note that for N=0 such a capillary strength corresponds to the previously discussed law. For N=1 the strength scales as $\sqrt{n}$, in agreement with a recent discussion [21]: splitting up the contact into n sub-contacts would result in a stronger interaction (with a cut-off at the theoretical strength): smaller is stronger [22]. This explains the observed miniaturized size of biological contacts. Introducing the previously computed contact angle related to the hierarchical surface allows one to evaluate the hierarchical capillary force, with or without activation of the Fakir state. Super-attraction/repulsion can be achieved due to hierarchy, as emphasized by $\sigma_C^{(N)} \approx \sigma_C^{(0)} (\varphi n)^{N/2}$.

3. Conclusions

Summarizing, the analysis demonstrates and quantifies that super-hydrophobic/hydrophilic and simultaneously super-attractive/repulsive surfaces can be realized, mimicking lotus leaves, thanks to hierarchical architectures. For example, assuming $\varphi = 0.5$, n=s=10 and $\theta \approx 120^\circ$ (as in lotus leaves, Figure 1), the analysis shows that fakir drops are activated and only two hierarchical levels are required to achieve super-hydrophobia ($\theta > \theta_{WF} = 95.2^\circ$, $N_{SHpho}^{(F)} = 1.9$; $\theta_F^{(1)} \approx 139^\circ$, $\theta_F^{(2)} \approx 151^\circ$), in agreement with direct observations on super-hydrophobic plants. Simultaneously, we deduce $\sigma_C^{(1)} \approx 2.2\sigma_C^{(0)}$, $\sigma_C^{(2)} \approx 5.0\sigma_C^{(0)}$ and $\sigma_C^{(3)} \approx 11.2\sigma_C^{(0)}$, i.e. just three hierarchical levels (or even two, if $\varphi \approx 1$ and $n \approx 10$) are sufficient to enhance the capillary strength by one order of magnitude, generating super-attractive ($\sigma_C^{(0)} > 0$) or super-repulsive ($\sigma_C^{(0)} < 0$) surfaces.

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