Tuning roughness to design robust superhydrophobic surfaces

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1. Introduction

Controlling the superhydrophobic/hydrophilic properties of surfaces is of great relevance in many applications. Examples are self-cleaning paints and surfaces, friction reduction, anti-icing and anti-fogging coatings, solar cells, stabilization of Leidenfrost vapor layers and microfluidics.

The contact angle of a water droplet on superhydrophobic surfaces typically exceeds 150°, whereas the roll-off angle is less than 10°, so the droplet can roll over the surface and even bounce on it, without sticking. Many examples of such surfaces are found in Nature, as for instance the sacred Lotus leaves [1], and many attempts have been done to fabricate bio-inspired self-cleaning surfaces [2].

The amazing super-hydrophobic behaviour is due to a combination of a mild chemical hydrophobicity, enhanced by a particular surface morphology.
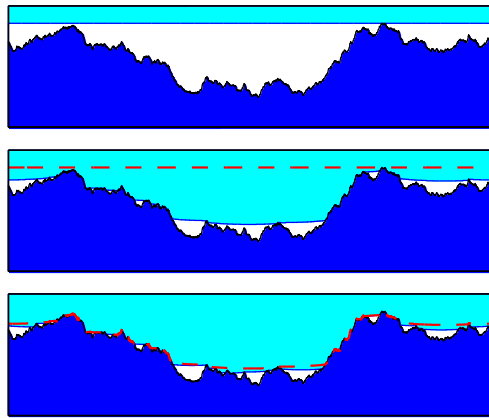

Figure 1: 1D rough substrate in contact with a liquid half plane. Liquid pressure is increased downwards from zero up to the threshold pressure p_W in the image sequence. Red dashed line represents the liquid profile at the previous pressure step to facilitate the comparison.

Typical super-hydrophobic surfaces have protrusions at the micro- or nano-scale, which cause the droplets to rest on the top of the asperities in what is called "fakir-carpet" state, so reducing the contact area and entrapping air. In this way, the adhesion with the underlying substrate is strongly reduced [3]. Super-hydrophobic surfaces can be obtained artificially with regular arrays of micro-pillars, hierarchical micro and nano-structures or even with random roughness [4].

In this paper the authors present a numerical procedure to simulate the composite interface between a liquid and a rigid rough substrate. The influence of the statistical properties of the roughness on the wettability of the solid surface have been investigated leading to the formulation of a simple criterion to design robust superhydrophobic randomly rough surfaces.

2. Numerical procedure

A numerical methodology to study the composite (Cassie state) contact between a drop and a self-affine randomly rough 1D profile $h(x)$ is presented. The advancing contact of a liquid on a rough surface is simulated [5], by gradually increasing the liquid pressure (Fig. 1).

The rough surface is generated as a 1-D rough profile given by the Fourier series:

$$h(x) = \sum_{k=1}^{M} h_k \cos(k q_L x + \phi_k) \qquad (1)$$

where q_L is the long-distance cut-off wave vector, equal to $2\pi/L$, where L is the size of the periodic domain, and ϕ_k is a random phase. The profile has been supposed to be a self-affine fractal and the coefficients of the series have been calculated accordingly [6]. Such a profile is completely described by only three independent statistical parameters: the mean squared height $\langle h^2 \rangle$ or, equivalently, the zero-*th* order moment of the power spectrum m_0, the mean squared slope $\langle h'^2 \rangle$, or the second moment of the power spectrum m_2, and the Hurst exponent H which is related to the fractal dimension D because $D = 2 - H$. It must be noticed that the mean squared slope of the profile is strictly related to the well-known Wenzel parameter r_W, which is defined as the ratio between the actual length of the profile and the projected length of the profile on the horizontal line.

The composite contact between the liquid and the solid phases has been simulated by a computer program which minimize the total energy of the system. The total energy of the liquid-solid interface with incompressible liquid, constant pressure and temperature is the Gibbs energy (per unit thickness) which can be calculated as the sum of the total interfacial energy (the Helmotz free energy) and the pressure potential. The effect of gravity is neglected. For one given value of the liquid pressure,

the expression of the Gibbs energy is the following:

$$G = \gamma_{LA} l_{LA} + \gamma_{SA} l_{SA} + \gamma_{LS} l_{LS} - p\Delta L = F - p\Delta L \qquad (2)$$

where $l_{LS,LA,SA}$ are the liquid-solid (LS), liquid-vapor (LA) and solid vapor (SA) interfacial lengths, $\gamma_{LS,LA,SA}$ are the liquid-solid (LS), liquid-vapor (LA) and solid vapor (SA) interfacial energies per unit area, Δ is the penetration of the solid substrate into the liquid, p is the liquid pressure and F is the Helmotz free energy (per unit thickness). The program starts with a pressure equal to zero, it finds the corresponding equilibrium configuration (local energy minimum); after that the pressure is increased of one small step and the new equilibrium configuration is found. The number and the size of the contact spots between the liquid and the solid phase can vary from one configuration to the other because new contact spots can be formed or pre-existent contact spots can coalesce. The procedure is repeated again and again until the program can not find any equilibrium configuration except the complete contact between the liquid and the solid phases (Wenzel state). At such point the simulation ends and the critical pressure p_W which destabilizes the Cassie state is recorded. More details about the simulation program can be found in [5].
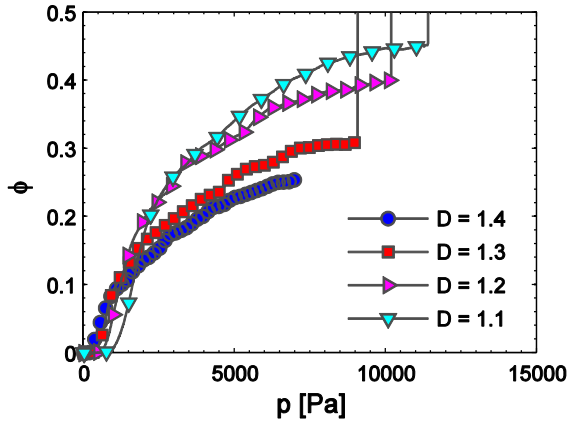
3. Most relevant numerical results

Figure 2 - The contact area fraction as a function of the liquid pressure with constant rms = 10 μm and $m_2 = 50$. For D = 1.4 the simulation has stopped before the occurrence of the transition to the Wenzel state.

The contact area fraction ϕ is shown as a function of the liquid pressure, with constant rms and m_2 and with different values of the fractal dimension D. The contact area fraction increases as the pressure is increased. At very low value of the contact area fraction, it increases very slowly with the pressure.
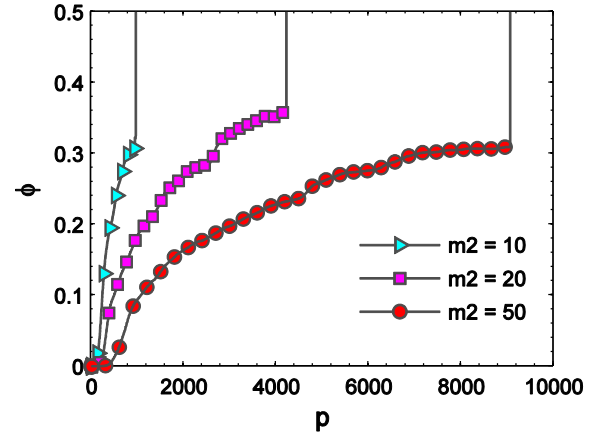

Figure 3 - The contact area fraction as a function of the liquid pressure with constant rms = 10 μm and D = 1.3.

In this phase, only the highest asperities are in contact. In a second phase, the contact area fraction increases sharply; then it reaches a sort of saturation regime. If the pressure is increased further, we observed that an abrupt transition to full contact (Wenzel state) is observed (in Figure 2 the transition is emphasized with a vertical grey line). The critical pressure p_W at which the transition to the Wenzel state occurs depends weakly on the fractal dimension and it reduces when the fractal dimension is increased with constant m_2 and rms. In self-affine fractal profiles with $H > 0.5$ as those investigated in this paper, if the fractal dimension is increased with constant m_2 and rms then the aspect ratio (height divided by length) of the longest wavelengths is reduced and the aspect ratio of the short wavelengths is increased. As already known in the case of a rough substrate made of one single sinusoidal wave [7], the aspect ratio of the sinusoid is crucial to determine the critical pressure p_W.

For this reason, the afore-mentioned result suggests that the long wavelength components are more important to define the Wenzel transition pressure than the short ones and that the transition firstly involves the short wavelengths of the roughness and, then, gradually moves to larger and larger scales.

As shown in Figure 3, the critical pressure p_W can be strongly enhanced by increasing the mean square slope of the surface, or equivalently the Wenzel roughness parameter r_W with constant rms and H. Moreover, it is clear that for any given value of the liquid pressure p, the contact area fraction is much smaller with higher m_2. We proof that r_W is the most crucial parameter in determining the super-hydrophobicity of the surface, also in the case of mixed contact with randomly rough surfaces.

4. A simple criterion for robust super-hydrophobicity

In a partial wetting regime, the surface free energy (per

unit thickness $F = \gamma_{LA}l_{LA} + \gamma_{SA}l_{SA} + \gamma_{LS}l_{LS}$ can be calculated as:

$$F = \left[-\cos\theta_Y \alpha\phi + \beta(1-\phi)\right]\gamma_{LA}L \qquad (3)$$

where a constant term $r_W L$ has been neglected. In the eq. (3), α is the fraction given by the contact length divided by the projected contact length, which differs from r_W unless the Wenzel state is reached, β is the actual length of the liquid-air interface divided by its projection on the horizontal line (hereafter $\beta \approx 1$ as also demonstrated with numerical simulations), θ_Y is the Young contact angle.

The parameter α depends on the actual contact area and, for this reason, it is a function of the pressure p. In Figure 4 the non dimensional surface free energy $F/(\gamma_{LA}L)$ is shown as a function of the contact area fraction for different values of the mean squared slope of the profile and fractal dimensions. It is clearly shown that the interfacial free energy follows a linear trend with the contact area fraction; moreover it is also shown that the fractal dimension does not affect the slope of such a linear trend, which depends only on the mean square slope m_2. If we assume that $\alpha \approx r_W$, and we write that:

$$r_W = \frac{1}{L}\int_0^L \sqrt{1+\left[h'(x)\right]^2}\,dx = \int_{-\infty}^{+\infty}\sqrt{1+h'^2}\,P(h')dh' \qquad (4)$$

where $P(h')$ is the probability density of h', which is given by:

$$P(h') = \frac{1}{\sqrt{2\pi m_2}}\exp\left(-\frac{h'^2}{2m_2}\right) \qquad (5)$$

it follows that $r_W = r_W(m_2)$. The eq. (3) can be re-written:

$$\frac{F}{\gamma_{LA}L} = 1 + \left[(-\cos\theta_Y)r_W - 1\right]\phi \qquad (6)$$

We also plotted eq. (6) in Figure 4 (dashed lines) to compare it with the numerical simulation results. A very good agreement is observed between the numerical results and the simple formula of eq. (6).

A criterion of super-hydrophobicity is formulated for hydrophobic ($\theta_Y > \pi/2$) substrates: if the surface free energy is an increasing function of ϕ, then the increase of ϕ is not energetically favorable and the surface is robust-superhydrophobic. According to eq. (6), the afore-mentioned condition gives:

$$r_W > (r_W)_{th} = -\frac{1}{\cos\theta_Y} \qquad (7)$$

which coincides with the Wenzel criterion to get an

apparent contact angle equal to 180° [8]. Because r_W is a single-valued function of m_2, then the threshold of m_2 can also be calculated using eq. (7) and inverting Eq. (4). A more strict but simple formula is obtained with a small approximation, defining the threshold value of m_2:

$$m_2 > (m_2)_{th} \approx \frac{\pi}{2\cos^2\theta_Y} \qquad (8)$$
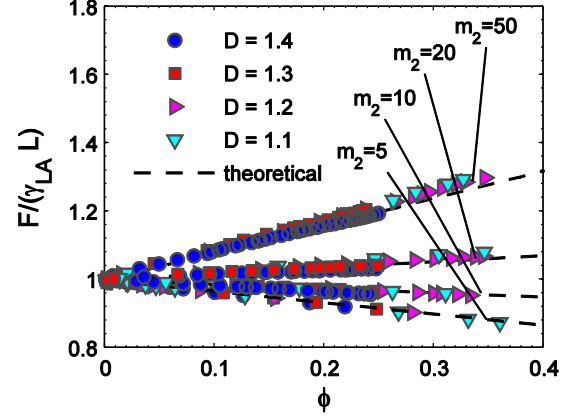

Figure 2 - The non-dimensional surface free energy per unit thickness as a function the contact area fraction with several values of m_2 and fractal dimension.

The simple criterion (eq. (8)) can be use to design randomly rough super-hydrophobic surfaces. Moreover, if similar considerations hold for 2D randomly rough surfaces, it can be demonstrated that a criterion can be also found in that case [5]:

$$m_2 > (m_2)_{th} \approx \frac{4}{\pi\cos^2\theta_Y} \qquad (9)$$

5. Conclusions

We present the results of a numerical methodology to study the wet contact between a drop and a self-affine randomly rough surface, with roughness in only one direction (1D rough surfaces), and propose a simple theoretical approach to assess the superhydrophobic properties of both 1D rough and 2D isotropic rough surfaces. The numerical methodology has been exploited to investigate the effect of statistical properties of the surface on the ability of the surface to stabilize the composite interface.

In particular, we focus on the liquid− solid contact area and how it evolves as the drop pressure is increased, and investigate how this evolution change depending on the statistical parameters of the rough surface. In particular, we find that, for Hurst exponent $H > 0.5$, the transition to the Wenzel state will first involve the short wavelengths and gradually the larger scales, although an abrupt transition occurs a certain point of the loading history.

The critical drop pressure p_W, which destabilize the interface causing the abrupt transition to the Wenzel state, is strongly increased as the mean square slope $\langle h'^2 \rangle$ of the surface is increased. Indeed, both the numerical approach and the theoretical calculation shows that $\langle h'^2 \rangle$ is the most crucial parameter affecting the superhydrophobicity of the surface.

By exploiting the proposed analytical model, given the Young contact angle θ_Y, we show that, if the mean square slope of the surface $\langle h'^2 \rangle$ exceeds the threshold value $\langle h'^2 \rangle \approx \pi/\left(2\cos^2 \theta_Y\right)$, the surface energy at the interface increases as the liquid−solid contact area is increased. When this happens, the fakir- carpet state is strongly stabilized and the drop cannot spread on the substrate, unless a significant amount of work is provided by an external force: a robust superhydrophobic surface is obtained. Interestingly, we show that $\langle h'^2 \rangle$ is related by a one-to-one relation to the Wenzel roughness parameter r_W, so that from a geometric point of view, both $\langle h'^2 \rangle$ and r_W measure the same statistical property of the surface. In terms of r_W, the criterion for robust superhydrophobicity becomes $r_W > \left(r_W\right)_{th} = 1/\left(-\cos\theta_Y\right)$ which is identical to the one that would be obtained in pure Wenzel regime to guarantee perfect superhydrophobicity (contact angle equal to 180°).

The criterion allows to tune the statistical properties of the roughness and to design very robust superhydrophobic randomly rough surfaces.

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