

Article

Predicting Wetting Properties for Surfaces with Stochastic Topography

Caroline Schmechel Schiavon ^{1,*}, Nadja Felde ^{2,†}, Sven Schröder ^{2,†}, Mario Lucio Moreira ^{3,†}
and Pedro Lovato Gomes Jardim ^{3,*}

¹ Instituto Federal de Educação, Ciência e Tecnologia Sul-rio-grandense, Bagé 96418-400, Brazil

² Fraunhofer Institute for Applied Optics and Precision Engineering IOF, 07745 Jena, Germany; nadja.felde@iof.fraunhofer.de (N.F.); sven.schroeder@iof.fraunhofer.de (S.S.)

³ Departamento de Física, Campus Capão do Leão, Universidade Federal de Pelotas, Pelotas 96010-610, Brazil; mlucio3001@gmail.com

* Correspondence: carol_schmechel@hotmail.com (C.S.S.); pedro.lovato@ufpel.edu.br (P.L.G.J.); Tel.: +55-53999584790 (C.S.S.)

† These authors contributed equally to this work.

Abstract: Understanding the influence of topography on wettability is essential for improving the modeling of superhydrophobic surfaces. Moreover, wetting predictions can foresee corrosion, biological contamination, self-cleaning properties, and all phenomena related to wetting. In this context, this research work reports the experimental corroboration of a novel theoretical model for stochastic surfaces that relates the static contact angle for the heterogeneous wetting of surfaces to the root mean square (RMS) slope of the surface structures, allowing wetting prediction through topography. For this study, hydrophobic and superhydrophobic alumina thin films with gradual roughness were constructed. The films were deposited on glass using the dip-coating technique, textured with boiling water, and functionalized to achieve low surface energy using Dynasylan F-8815. Surface wettability was characterized using the sessile drop technique, and the RMS slope of the alumina surfaces was quantified using the atomic force microscopy (AFM) technique. The model, presented here for the first time, fits the experimental data, allowing wetting prediction for hydrophobic and superhydrophobic surfaces considering static contact angles. As expected, topography plays a fundamental role in achieving superhydrophobicity. Therefore, defining a topographic criterion, as performed here, for obtaining superhydrophobic surfaces is highly relevant to reduce the production costs of these surfaces and also enable new production processes and designs.

Keywords: wettability; root mean square slope; superhydrophobicity



Academic Editor: Kirill A. Emelyanenko

Received: 20 December 2024

Revised: 5 February 2025

Accepted: 6 February 2025

Published: 7 February 2025

Citation: Schiavon, C.S.; Felde, N.; Schröder, S.; Moreira, M.L.; Jardim, P.L.G. Predicting Wetting Properties for Surfaces with Stochastic Topography. *Coatings* **2025**, *15*, 202. <https://doi.org/10.3390/coatings15020202>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Superhydrophobicity is the ability of some surfaces to highly repel water, meaning they are surfaces that, almost, do not get wet. In the textile industry, it is used to produce fabrics that do not absorb water [1]. In medicine, it is used in the production of materials such as prosthetics and surgical instruments that prevent pathogenic agent adhesion [2]. In the automotive and naval industry, it is used to produce anticorrosive materials. In the aerospace industry, it can be used with the intent of preventing or delaying icing over wings and turbine components [3,4]. Furthermore, superhydrophobicity can be applied to improve the generation of renewable energies. Solar panels coated with superhydrophobic layers can maintain efficiency due to the self-cleaning properties. When raindrops fall

on the photovoltaic device surfaces, they will immediately slide off, carrying away dust particles that scatter light, preventing efficiency reduction. This property is of great interest in various industries [5,6].

Hence, wetting is associated with crucial factors like contamination and corrosion, serving as a reference measure of species adhesion on the surface. Quantifying wetting can thus be used to anticipate the impact of these factors.

Surface wettability can be quantified by measuring the contact angle (CA) of a liquid drop [7], defined as the angle between the liquid–solid and liquid–gas interfaces, with the triple-phase line (solid, liquid, gas) as the vertex. For a surface to be considered superhydrophobic, the CA must be greater than 150° , and the hysteresis (H), which is the difference between the advancing and receding angles of a drop at the threshold of sliding on an inclined surface, must be less than 10° [8]. Two key factors are essential for increasing the contact angle and achieving superhydrophobicity: one is low surface energy, which reduces liquid adhesion over the surface, and the other is related to the topography, which should be nano- or micro-structured, or even both, forming hierarchical structures [9] and raising the water among surface structures. In the literature, three possible states of wettability are described. Young's wettability state describes the contact angle for perfectly smooth surfaces. Therefore, this angle depends exclusively on the surface tensions γ between the liquid–solid (LS), liquid–gas (LG), and solid–gas (SG) interfaces, as described by Equation (1), defining the Young angle, θ_y .

$$\cos\theta_y = \frac{\gamma_{SG} - \gamma_{LS}}{\gamma_{LG}}. \quad (1)$$

For surfaces with a certain roughness, which is the case for all surfaces in nature at some scale lengths, the Wenzel's wetting state [10,11] describes the contact angle in terms of surface tensions and the Wenzel roughness parameter (WRP). The WRP considers the influence of surface area on wettability, which always amplifies the surface wetting characteristic, whether hydrophobic or hydrophilic. The WRP is given by the ratio between the rough surface area and its horizontal projection, and it will always be greater than 1. This means that, for hydrophilic surfaces, when $\theta < 90^\circ$, the higher the WRP, the lower the θ_w , and the more hydrophilic the surface becomes. For hydrophobic surfaces, when $90^\circ \leq \theta < 150^\circ$, the higher the WRP, the bigger the θ_w , and the more hydrophobic the surface becomes, as shown in Equation (2), which defines the Wenzel angle, θ_w .

$$\cos\theta_w = r_w \cos\theta_y \quad (2)$$

Both previous cases reflect the Wenzel wetting state or homogeneous wetting, in which the liquid is in adhesion with the whole solid surface.

Superhydrophobic surfaces fall under Cassie's wetting state or heterogeneous wetting. This wetting state is characterized by the emergence of capillary forces generated by surface structures, causing water droplets to be elevated to the tops of the structures, forming pockets of air between the liquid and the solid. This results in partial water adhesion to the solid surface and increases the contact angle, now called the Cassie–Baxter angle, θ_{cb} .

The Cassie–Baxter equation takes into account the new LG interface present in this wetting state, as described in Equation (3).

$$\cos\theta_{cb} = r_{LS} f_{LS} \cos\theta_y - 1 + f_{LS} \quad (3)$$

The chemical influence on the wetting of the system can be represented by $\cos(\theta_y)$, as surface tensions depend on the chemical compounds of each phase. Meanwhile, the topographical influence is evident in the roughness parameter r_{LS} , calculated as the ratio

of the wetted rough area to its horizontal projection, and the term f_{LS} , which is the fraction of the area projected on the horizontal plane corresponding to the LS interface. It is also interesting to note that, in the limiting case where f_{LS} tends to one, we revert to the Wenzel model for wetting.

Pioneering authors in the study of CA relate wettability to the interfaces below the droplet. However, some authors show that it is the differential areas below the triple line (line that divides the solid, liquid, and gaseous phases) that influence the CA and not the total interface areas, which are related to the CA [12–15]. In the current literature, several works seek to relate surface wettability with topography [16]. However, the vast majority cite RMS roughness as the main factor influencing superhydrophobicity [17–19]. The tendency predicted in Wenzel's model for surface roughness to amplify its hydrophilic or hydrophobic property was corroborated through numerical simulations, but experimental results keep showing a certain divergence from the model [20]. As emphasized by Kaufman et al. [21] and Schiavon et al. [22], the slope of the local surface structures has a direct influence on their wettability. The slope of these structures is responsible for the capillary force that causes water droplets to rise to the top of the structures, in the hydrophobic case, resulting in superhydrophobicity for higher slope values. The surface area can also be expressed in terms of the root mean square slope for stochastic surfaces [22].

Obtaining the necessary structures to generate enough capillary force is a common concern when aiming to achieve superhydrophobic surfaces, as there is no general topographic criterion for obtaining superhydrophobicity. One focus of this study is on the surface structures' ability to promote superhydrophobic behavior. The lack of a well-established relationship between contact angle (CA) and any surface-related topographic parameter makes it impossible to predict wettability solely based on surface topography since CA cannot be estimated without considering surface topography [8,11]. Therefore, correlating surface topography with wettability can allow wetting prediction and, more specifically, for superhydrophobicity, can lead to the development of new modeling and manufacturing processes, thereby optimizing existing processes.

With this motivation, we describe for the first time the Cassie–Baxter (Equation (3)) equation in terms of the RMS slope of surface structures. This allows us, given the chemical composition of a given surface, to determine the necessary slope to achieve the minimum wetting angle for superhydrophobicity ($\theta \geq 150^\circ$) through wetting prediction. This equation, derived in the next section, was experimentally validated using hydrophobic and superhydrophobic nanostructured alumina surfaces, as described in Section 3.

2. Theoretical Model

In this section, we will present a new heterogeneous wetting model for isotropic Gaussian surfaces that allows us to express the Cassie–Baxter equation in terms of the root mean square (RMS) slope of the surface structures for Gaussian distribution of heights. The topography will be the main factor of interest, and therefore, from now on, we will consider the chemical composition of all surfaces as being the same, subtracting its influence. Thus, Young's contact angle (contact angle for smooth surfaces) will not be altered, as it is related to the chemical properties of the system through interface tensions (Equation (1)). The surface height, or surface profile, is a given function, $h(x, y)$, and h_x and h_y are the partial derivatives of $h(x, y)$ with respect to x and y , respectively. The RMS slope represents the root mean square of the surface's slopes. It is calculated as the square root of the sum of the squared slope values at each point on the surface. The RMS slope can be calculated by Equation (4).

$$\sigma^2 = \lim_{L \rightarrow \infty} \frac{1}{L^2} \int_{-\frac{L}{2}}^{\frac{L}{2}} \int_{-\frac{L}{2}}^{\frac{L}{2}} [h_x^2 + h_y^2] dx dy \quad (4)$$

where L represents the maximum length of integration in each direction of the area. This equation serves as a theoretical definition, but it can also be applied to real surfaces of finite dimensions, provided that sufficient sampling of the surface structures within the measured area is conducted [23].

We want to express the terms related to surface topography in Equation (3) in terms of the RMS slope. We will start by defining these terms. The modified WRP is defined as the ratio between the wetted area, A_w , and its plane projection, A_{pw} , denoted as $f_{LS} = \frac{A_w}{A_{pw}}$. The fraction of the wetted plane projection area is represented by $f_{LS} = \frac{A_{pw}}{A_{pt}}$, where A_{pt} is the total flat area. Therefore, the product of the modified WRP and the fraction of the wetted plane projection area can be expressed as:

$$r_{LS}f_{LS} = \frac{A_w}{A_{pw}} \frac{A_{pw}}{A_{pt}} = \frac{A_w}{A_{pt}} \quad (5)$$

The total area of the surface is given by the general Equation (6):

$$A = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sqrt{1 + h_x^2 + h_y^2} dx dy. \quad (6)$$

If we impose the condition that the area must be wet and divide by the total flat area, L^2 , we obtain the product $r_{LS}f_{LS}$. Therefore, we can write:

$$r_{LS}f_{LS} = \lim_{L \rightarrow \infty} \frac{1}{L^2} \int \int_{Wet} \sqrt{1 + h_x^2 + h_y^2} dx dy \quad (7)$$

Considering that $\frac{1}{L^2}$ represents the probability, $p(x, y)$, of simultaneously finding the positions x and y , the above formula can be seen as the expected value of the slope, $\langle \sqrt{h_x^2 + h_y^2} \rangle$. Statistically, we can change the integration variables to more convenient ones in the expected value calculation. It makes sense to work with the derivatives instead of the positions, as they are part of the integral's kernel. Therefore, we can write:

$$r_{LS}f_{LS} = \int \int_{Wet} p(h_x, h_y) \sqrt{1 + h_x^2 + h_y^2} dh_x dh_y \quad (8)$$

where the integration is performed over the wet components of the gradient. If we assume a Gaussian height distribution, the probability $p(h_x, h_y)$ follows a bivariate normal distribution, which can be expressed in terms of h_r , representing the magnitude, and ϕ , representing the direction of the surface gradient. The magnitude is defined as $h_r^2 = h_x^2 + h_y^2$ and represents the slopes in a given direction. When considering an isotropic Gaussian surface, $p(h_r, \phi)$ follows a Rayleigh distribution:

$$p(h_r, \phi) = \frac{h_r}{\pi\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \quad (9)$$

For an isotropic Gaussian surface, from Equations (8) and (9) we can achieve Equation (10), where the integration is performed over the wet slopes.

$$r_{LS}f_{LS} = \int_0^{2\pi} \int_{Wet} \frac{h_r}{\pi\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \sqrt{1 + h_r^2} dh_r d\phi \quad (10)$$

By integrating over ϕ , we obtain:

$$r_{LS}f_{LS} = \int_{Wet} \frac{2h_r}{\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \sqrt{1 + h_r^2} dh_r \quad (11)$$

First, we must estimate the amount of dry and wet slopes, taking into account that this is dictated by capillary force, and the intensity of the capillary force is determined by the curvature of the liquid–gas interface. We are now modeling the influence of capillary force that will be associated with the surface slope at specific points on the surface profile.

Considering a differential length over the surface profile in each direction and the water lying over the surface, which represents a small area of the water drop on a substrate, the local slope will determine the curvature of the LG interface near the solid surface. Looking at Figure 1, if $h_r > -\tan\theta_y$ (a), capillary forces will draw the water upward at these points, and their vicinity must be dry. If $h_r = -\tan\theta_y$ (b), the capillary force does not act and if $h_r < -\tan\theta_y$ (c), the capillary force acts in the opposite direction, lowering the water. In these cases, the vicinity of this point must be wet. Therefore, slopes steeper than $-\tan(\theta_y)$ on the surface cannot be wet. This delineates a range of slopes that can and cannot be wet on the surface (here, we assume that the surface structures are of micrometric or nanometric order, and so are the relative distances between these structures. This allows significant increases or decreases in height due to capillary force, as in Jurin's law, meaning that it is the local slope that determines whether that fraction of the surface area is wet or not). We can then write the limits of integration.

$$r_{LS}f_{LS} = \int_0^{-\tan\theta_y} \frac{2h_r}{\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \sqrt{1+h_r^2} dh_r \quad (12)$$

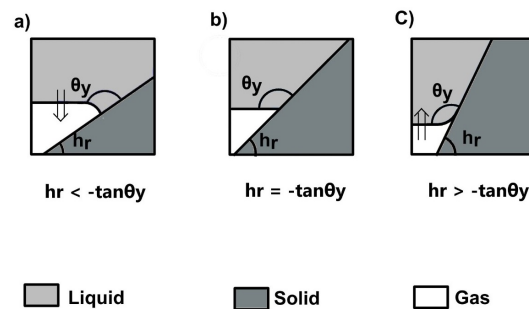


Figure 1. Expected curvature for three distinct slopes with θ_y fixed. The arrow represents the direction of the capillary force for each curvature. (a) For $h_r < -\tan\theta_y$, the curvature generates a downward capillary force. (b) For $h_r = -\tan\theta_y$, there is no capillary force. (c) For $h_r > -\tan\theta_y$, the curvature generates an upward capillary force.

Using partial integrals, we can rewrite the above expression as:

$$r_{LS}f_{LS} = \int_0^\infty \frac{2h_r}{\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \sqrt{1+h_r^2} dh_r - \int_{-\tan\theta_y}^\infty \frac{2h_r}{\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} \sqrt{1+h_r^2} dh_r \quad (13)$$

By making the substitution $g_r = \frac{1+h_r^2}{\sigma^2}$, we obtain:

$$r_{LS}f_{LS} = \sigma e^{\frac{1}{\sigma^2}} \int_{\frac{1}{\sigma^2}}^\infty g_r^{\frac{1}{2}} e^{-g_r} dg_r - \sigma e^{\frac{1}{\sigma^2}} \int_{\frac{1+\tan^2\theta_y}{\sigma^2}}^\infty g_r^{\frac{1}{2}} e^{-g_r} dg_r \quad (14)$$

In the equation above, it is possible to identify the incomplete Gamma function in both terms; we can then write:

$$r_{LS}f_{LS} = \sigma e^{\frac{1}{\sigma^2}} \left[\Gamma\left(\frac{3}{2}, \frac{1}{\sigma^2}\right) - \Gamma\left(\frac{3}{2}, \frac{1}{\cos^2\theta_y\sigma^2}\right) \right] \quad (15)$$

We now need to rewrite the fraction of the wet plane projection area, which can be calculated as the expected value of a straight horizontal profile, where the partial derivatives vanish.

$$f_{LS} = \int \int_{Wet} p(h_x, h_y) dh_x dh_y \quad (16)$$

In the case of isotropic Gaussian surfaces, it can be expressed as:

$$f_{LS} = \int_0^{-\tan \theta_y} \frac{2h_r}{\sigma^2} e^{-\frac{h_r^2}{\sigma^2}} dh_r \quad (17)$$

The expression above is the cumulative Rayleigh function. By making the substitution $g(r) = \frac{h_r^2}{\sigma^2}$, we obtain:

$$f_{LS} = 1 - e^{-\frac{\tan^2 \theta_y}{\sigma^2}} = 1 - e^{\frac{1}{\sigma^2}} e^{-\frac{1}{\cos^2 \theta_y \sigma^2}} \quad (18)$$

Using Equations (18) and (15) in Equation (3), all slopes within the range $h_r < -\tan(\theta_y)$ contribute to the CA, which is true for smooth surfaces; see Figure 2a. However, as the RMS slope increases, the (LS) interface rises between the structures towards the tops; see Figure 2b. Consequently, slopes in the range $h_r < -\tan(\theta_y)$ at the valleys do not contribute to the CA. Therefore, the LS fraction is overestimated at higher RMS slopes. To address this, we propose a correction factor to obtain the correct CA for cases with a high RMS slope.

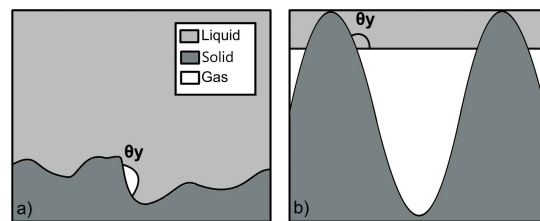


Figure 2. (a) Region containing LG interface on surface with low RMS slope. (b) Elevated LG interface between high RMS slope surface structures.

According to Longuet-Higgins [24], the density of maxima and minima (i.e., peaks and valleys) are equal on an isotropic Gaussian surface, and the number of extrema should equal the number of saddle points. In the limit of very high RMS slopes, only the tops of the structures are wet—specifically, only the maxima—which correspond to one-fourth of the equilibrium points that comprise the surface. On the other hand, statistically, the cumulative distribution reveals the amount of slopes that fall below a certain value. Here, the value of interest is $-\tan(\theta_y)$, as described in Equation (18), which represents the wet portion of the slopes. This portion decreases as we increase the RMS slope value. Based on this, we propose the following correction factor:

$$k = 1 - \frac{3}{4} e^{-\frac{\tan^2 \theta_y}{\sigma^2}} = 1 - \frac{3}{4} e^{\frac{1}{\sigma^2}} e^{-\frac{1}{\cos^2 \theta_y \sigma^2}} \quad (19)$$

The above fraction approaches 1 when the RMS slope tends to 0 and converges to 1/4 as the RMS slope tends to infinity. It represents the portion of the LS interface that contributes to the CA, with the liquid rising through the surface structures due to capillary forces as the RMS slope increases. Therefore, by using Equations (18), (19), and (15) in Equation (3), we obtain:

$$\cos\theta_{cb} = k\sigma e^{\frac{1}{\sigma^2}} \left[\Gamma\left(\frac{3}{2}, \frac{1}{\sigma^2}\right) - \Gamma\left(\frac{3}{2}, \frac{1}{\cos^2\theta_y \sigma^2}\right) \right] \cos\theta_y - 1 + k \left(1 - e^{\frac{1}{\sigma^2}} e^{\frac{-1}{\cos^2\theta_y \sigma^2}} \right) \quad (20)$$

It may be possible to predict CA through the topography and chemical composition of the system, and to determine the required value of the RMS slope needed to achieve superhydrophobicity, based on the static criterion ($\theta \geq 150^\circ$).

3. Materials and Methods

In order to experimentally validate this theoretical result, we constructed hydrophobic and superhydrophobic alumina films with graded nanostructured topographies.

The alumina was synthesized using a sol–gel process, following a well-established route described in the literature [25]. The molar ratio of the reagents used was 20:1:4:1, corresponding to $iPrOH:EAcAc:H_2O:Al(O - Al(O - Al - sec - Bu)_3)$. The specific reagents used are listed in Table 1. Further details about the synthesis can be found in a previously published work [22].

Table 1. Information about the used reagents in the alumina synthesis.

Reagent	Chemical Formula	Provider	Purity
Isopropyl alcohol	$iPrOH$	Sigma Aldrich	99.5%
Tri-sec-butyl-alumina	$Al(O - Al(O - Al - sec - Bu)_3)$	Sigma Aldrich	99.99%
Ethyl acetoacetate	$EAcAc$	Sigma Aldrich	99%

Sigma Aldrich Brasil Ltda, Cajamar 07790-330, Brazil.

The alumina films were deposited using the dip coating method with homemade equipment. It is moved by a stepper motor that moves a rack through a pulley system, generating movement at controlled speed. The substrate is attached to the equipment and follows its movement, submerging into the solution positioned just below. The immersion speed was set at 1 mm/s, and the immersion time was 10 s. The film thickness was controlled by the emersion speed, which was set at 2 mm/s. After deposition, the films underwent thermal treatment in a muffle furnace at a temperature of 400 °C for 10 min to perform hydrolysis and condensation, thereby improving film stability and adhesion. At this temperature, the boehmite sol does not yet transform into $\gamma - Al_2O_3$. The surface structures were formed through chemical etching using boiling water with varying exposure times (0 s, 6 s, 10 s, 16 s, 32 s, 64 s, 128 s, 512 s) to achieve different roughness levels, as varying topographies result in different wettability. After etching, the films were subjected to another thermal treatment in a muffle furnace at a temperature of 400 °C for 10 min.

Functionalization was performed to achieve low surface energy. A 1% solution of Dynasylan F8815 surfactant from Evonik in water was used, and it was deposited onto the films via dip coating with an immersion speed of 1 mm/s, an immersion time of 10 s, and an emersion speed of 2 mm/s. After surfactant deposition, the films were subjected to a thermal treatment at 120 °C in an oven for 15 min.

Two sets of samples were prepared using the same production parameters. However, characterization of wettability and characterization of topography were performed in different laboratories to verify reproducibility (we expect the AFM measurements to have a similar resolution so as not to significantly alter the value of the RMS slope). For the first group of samples produced, topography characterization was performed using atomic force microscopy (AFM) measurements. The equipment used was the Veeco Dimension 3100 from Veeco Digital Instruments Metrology Group, with a measurement area of $2 \times 2 \mu m^2$ to capture a representative sample of the entire surface with sufficient image resolution. The scanning probe used was the ScanAsyst-Air, with an elastic constant of 0.4 N/m.

The wettability characterization was performed by measuring the contact angle. The measurements were performed at room temperature and humidity (approx. 22 °C, 40%). Set 1 samples were measured using homemade equipment and a drop volume of 10 μL , while Set 2 samples were measured using a Kruss Goniometer (DSA 100S/2014) and a drop volume of 5 μL . A drop of distilled water was deposited in three distinct regions of each sample; a photo was taken of each drop. The contact angle was calculated for every drop and the average of the contact angles was calculated. The contact angle values were obtained by analyzing the images using ImageJ software (version v1.54k). The uncertainty was calculated from the standard deviation of the mean plus the instrumental accuracy. The hysteresis was calculated by the method of volume variation through subtracting the advance and retreat angle of the drop at the time when it is being inflated and deflated. The volume was varied from 5 μL to 20 μL and from 20 μL to 5 μL , with a variation of 1 $\mu\text{L/s}$. The hysteresis present in next section refers to the volume of 5 μL .

The topography of the second set of samples was measured using the Bruker Dimension Icon equipment, with the TAP150A probe having an elastic constant of 5 N/m. The measurement area was also $2 \times 2 \mu\text{m}^2$. Wettability was quantified using the same methodology as for the first set of samples; however, the drop size was 10 μL . The handmade equipment used was a contact angle measurement device (CAMD).

4. Results and Discussion

4.1. Topography

The following presents the AFM measurement images of the alumina films on glass substrates with graded roughness. Both the RMS roughness and RMS slope are expected to increase with increasing etching time as the chemical reaction with the alumina surface reaches deeper layers.

The topographies of the two sample sets are shown in Figures 3 and 4 (Set 1 and Set 2, respectively). The values of root mean square (RMS) roughness, $r_{r.m.s.}$, and RMS slope are presented for the respective surfaces. In general, it can be observed that these values increase with etching time, especially for the 16 s textured sample. In Figure 3, Sample 128 exhibits small measurement artifacts where the tops of the structures are not well resolved. In the same figure, Sample 512 appears well resolved in the upper part of the image; however, upon careful analysis, a loss of resolution can be noticed in the lower part. To confirm this suspicion, we selected the well-resolved area and calculated the RMS roughness, obtaining a value of $40.5 \pm 1.3 \text{ nm}$, which is higher than the value obtained for the entire measured area ($37.6 \pm 1.1 \text{ nm}$), thus supporting our hypothesis. This demonstrates that small measurement artifacts can significantly influence the measurable values of topography.

Figure 4 exhibits the same trend of increasing RMS roughness and RMS slope with longer etching times, except for the case of Sample 32, which shows a notably high value of RMS slope (2.480 ± 0.074) compared to Samples 128 and 512. Upon closer inspection of the topographic image for Sample 32, a drift in the AFM measurement, potentially causing a tilt in the surface structures image, may be responsible for an increase in the RMS slope. However, the RMS slope values obtained for Samples 128 and 512 closely align with those obtained for the sample set in Figure 3, despite the small variations between sets in the surface structures observed in the images, probably attributed to the use of different AFM tips.

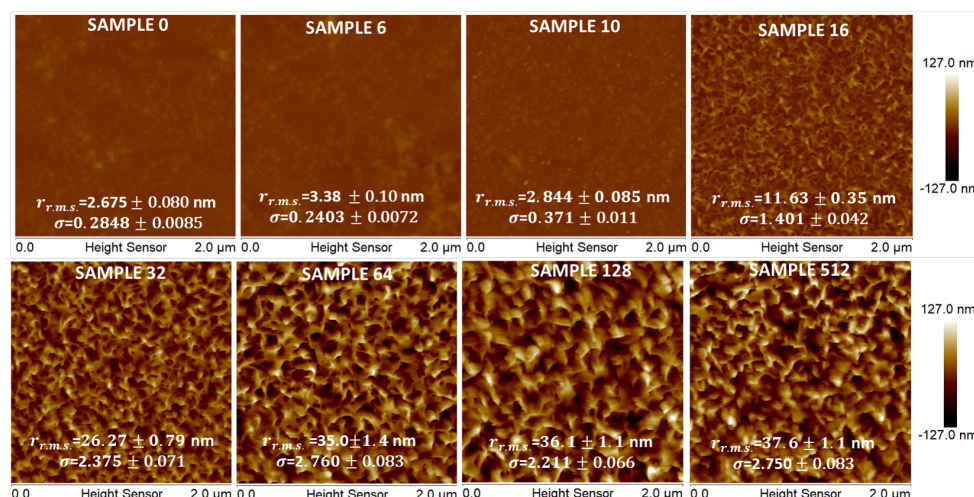


Figure 3. Representation of the topography of alumina films, textured for 0 s, 6 s, 10 s, 16 s, 32 s, 64 s, 128 s and 512 s, with a measuring area of $(2 \times 2) \mu\text{m}^2$.

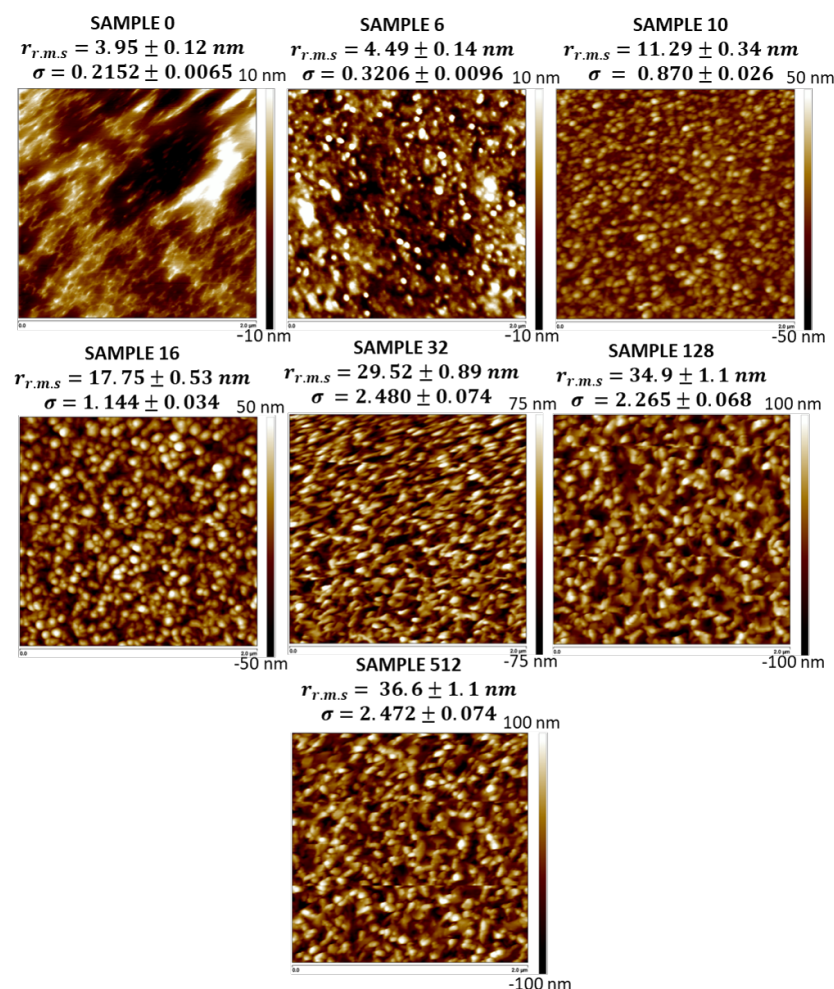


Figure 4. Representation of the topography of alumina films, textured for 0 s, 6 s, 10 s, 16 s, 32 s, 128 s, and 512 s, with a measuring area of $(2 \times 2) \mu\text{m}^2$.

Table 2 presents the results of RMS slope for the two sets of samples. One can observe an evolution in the topographical parameter with etching time. In the case of the first set of samples, the reduction of roughness between Samples 0 and 6 is attributed to the measurement position. The substrate and the deposition contain irregularities that may or

may not be included in the AFM measurement area. These irregularities tend to decrease with etching time. It is noteworthy that Sample 10 shows a more significant difference between the values of the two sets (0.371 ± 0.011 and 0.870 ± 0.026), showing that the first few seconds of etching significantly contribute to the increase in RMS roughness and slope.

Table 2. RMS slopes for both sets of samples.

Sample	σ Set 1	σ Set 2
Sample 0	0.2848 ± 0.0085	0.2152 ± 0.0065
Sample 6	0.2403 ± 0.0072	0.3206 ± 0.0096
Sample 10	0.371 ± 0.011	0.870 ± 0.026
Sample 16	1.401 ± 0.042	1.144 ± 0.034
Sample 32	2.375 ± 0.071	2.480 ± 0.074
Sample 64	2.760 ± 0.083	-
Sample 128	2.211 ± 0.066	2.265 ± 0.068
Sample 512	2.750 ± 0.083	2.472 ± 0.074

4.2. Wetting

Figures 5 and 6 show images of water droplets deposited on each surface, along with their respective average contact angles and errors. In general, it is evident that the contact angle increases with the RMS roughness and slope generated by the etching process. For both sample groups, starting from an etching time of 32 s, the static criterion for superhydrophobicity is achieved, within the error range. In Figure 6, in addition to the contact angle, the hysteresis values are also presented, indicating that the sample etched for 512 s satisfies the dynamic criterion for superhydrophobicity ($H < 10^\circ$).

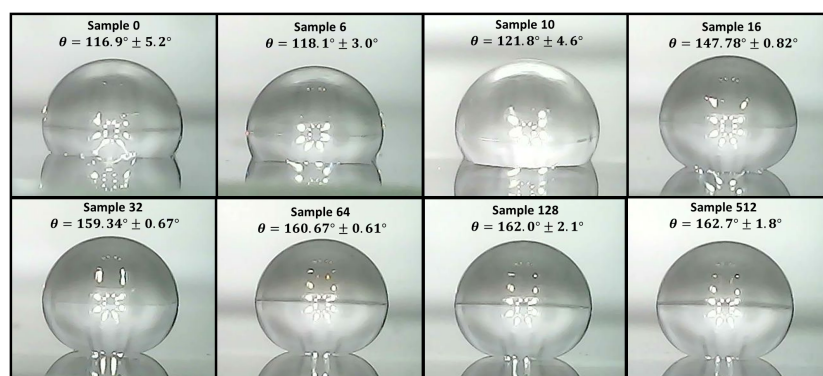


Figure 5. Contact angles for Set 1, Drop Volume = 10 μ L.

Figure 5 displays images of the 10 μ L droplet along with their corresponding average contact angles. Comparing these wettability values (Table 3) with the topographical data from Set 1 presented in Table 2, Samples 0 and 6 have near contact angle (CA) values ($116.9^\circ \pm 1.7^\circ$ and $118.12^\circ \pm 0.93^\circ$, respectively), and they also exhibit similar RMS slope values (0.2848 ± 0.0085 and 0.2403 ± 0.0072 , respectively). These CA values increase for Sample 10 and display even higher values for Sample 16, as well as the RMS slope values (Table 2). The latter presents a significant increase in CA, reaching $147.78^\circ \pm 0.27^\circ$, which is considerably higher than the CA limit (around 120°) for smooth surfaces determined by chemical composition [26]. The static criterion for superhydrophobicity is achieved with Sample 32, precisely where a noticeable increase in slope occurs (2.375 ± 0.071). The CA values continue to increase for Samples 64, 128, and 512, not following the variation of the RMS slope values. However, the RMS slope values for these samples are high when compared to the slope values of the samples that did not reach the minimum CA for superhydrophobicity (Samples 0, 6, 10, and 16). Furthermore, the uncertainty in the CA

values of Samples 128 and 512 suggests that these angles are almost the same. Comparing the slope values for these samples, it is possible to observe that these values are very close (2.211 ± 0.066 and 2.750 ± 0.083), further strengthening the direct relationship of CA with the RMS slope.

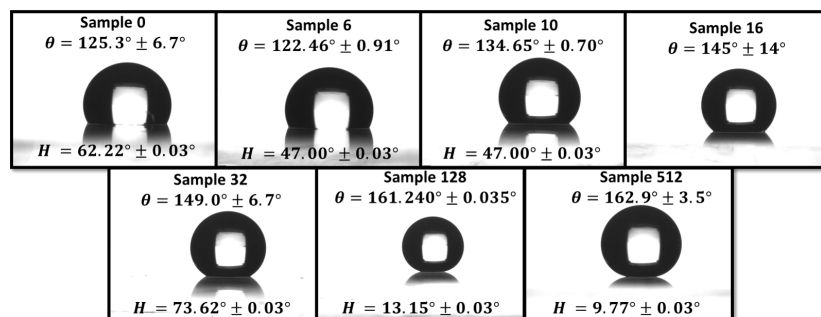


Figure 6. Contact angles for Set 2, Drop Volume = 5 μ L.

Figure 6 displays images of a 5 μ L droplet deposited on each surface of the Set 2 samples, along with their respective average contact angles (CAs). CA hysteresis values are presented at the bottom of the images. A slight reduction in CA can be observed between Samples 0 and 6, while the RMS slope slightly increases for these samples. The remaining samples show an increase in CA values with etching time. The RMS slope values (Table 2) increase up to Sample 32; Sample 64 was not available for this set. Samples 128 and 512 present a small reduction in RMS slope values compared to Sample 32, with Sample 512 having a value greater than that of Sample 128.

Sample 32, within a margin of error, achieves the static criterion for superhydrophobicity, while the dynamic criterion is achieved for Sample 512.

All these observations further reinforce the notion that the RMS slope is the primary factor influencing the surface wettability of these samples, assuming that all the samples possess the same chemical composition, as they undergo the same manufacturing procedure.

Table 3. Contact angles.

Sample	CA Set 1 (10 μ L)	CA Set 2 (5 μ L)
Sample 0	$116.9^\circ \pm 5.2^\circ$	$125.3^\circ \pm 6.7^\circ$
Sample 6	$118.1^\circ \pm 3.0^\circ$	$122.46^\circ \pm 0.91^\circ$
Sample 10	$121.8^\circ \pm 4.6^\circ$	$134.65^\circ \pm 0.70^\circ$
Sample 16	$147.78^\circ \pm 0.82^\circ$	$145^\circ \pm 14^\circ$
Sample 32	$159.34^\circ \pm 0.67^\circ$	$149.0^\circ \pm 6.7^\circ$
Sample 64	$160.67^\circ \pm 0.61^\circ$	-
Sample 128	$162.0^\circ \pm 2.1^\circ$	$161.240^\circ \pm 0.035^\circ$
Sample 512	$162.7^\circ \pm 1.8^\circ$	$162.9^\circ \pm 3.5^\circ$

4.3. Correlation Between Topography and Wetting

Figure 7 displays the fitting of the model proposed here for the contact angle (CA) as a function of the RMS slope and Young's angle (θ), according to Equation (20), represented by the solid curve. The experimental data points of the CA, along with their corresponding RMS slopes and associated errors, were plotted for both sets of samples. In this graph, Young's angle (θ_y) was determined by the fitting.

It is noticeable that the experimental points exhibit the same behavior as the theoretical curve and reasonably align with it, considering the inherent complexity of the proposed equation. The sample showing the greatest deviation is Sample 32 from Set 2. We have

two hypotheses for this: the RMS slope may be increased due to an artifact from the AFM measurement, or the functionalization process with the Dynasylan F8815 surfactant may have failed, resulting in a lower contact angle. The other observed deviations at low RMS slopes can be explained by the AFM measurement area's inability to capture the contribution of the undulations or agglomerates arising from substrate and deposition irregularities in the RMS slope calculation. Longer etching times tend to smooth out these irregularities.

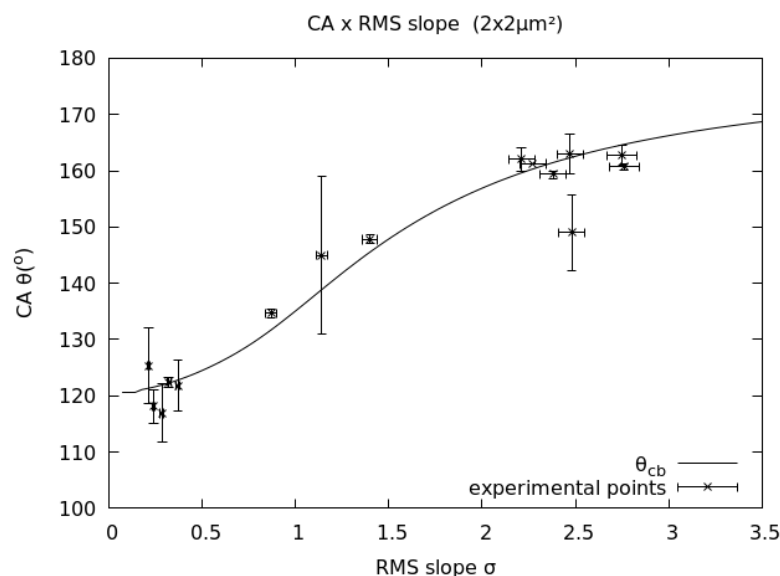


Figure 7. Fit of the theoretical curve (Equation (20)) to the experimental points. The obtained parameter was $\theta_y = 120.60^\circ \pm 0.54^\circ$.

Considering that the theoretical curve fits satisfactorily with the experimental data, and assuming the validity of our hypotheses regarding the deviations of the data points from the model, the CA can be predicted from topography and the chemical composition of the three phases. Furthermore, we can establish a static criterion for superhydrophobicity. In other words, we can determine the necessary RMS slope value for the surface to achieve a CA of 150° . According to the theoretical model proposed here, the topographical static criterion for superhydrophobicity, at the angle $\theta = 150^\circ$, is $\sigma = 1.60$.

The chemical composition of the system is incorporated into the model through θ_y . An increase in its value raises the beginning of the theoretical curve, increasing all values of CA on the curve and reducing the RMS slope value of the superhydrophobic criterion. Further studies exploring these possibilities are necessary.

The value of θ_y is above the 120° limit. Again, the explanation lies in the existence of clusters and undulations not detected by AFM measurements. This can underestimate the RMS slope values for low etching times. The aforementioned can shift the theoretical fit, leading to a higher θ_y value.

Theoretically, the model should encompass all isotropic Gaussian surfaces, provided that the gravitational force is negligible compared to the capillary force. As the dimensions of the structures and, specifically, the spacing between them increase, the gravitational force pulling the droplet downwards becomes more significant in relation to the capillary force pulling the droplet upwards. The wetted area would no longer be characterized solely by the local slope but dictated by the balance between these two forces in which the height, shape, and distance between the structures must be considered, falling outside the scope of our model. In our model, the wetted and non-wetted areas are entirely determined by the capillary force defined by the local slope of the surface structures. In this sense, we

expect that this model also applies to surface structures of micrometric order, in addition to nanometric order, because micrometric spacings between structures are capable of lifting the fluid to heights that often exceed the micrometric height of these structures due to the capillary force. However, this fact must be experimentally corroborated.

In relation to the application of the model on hierarchical surfaces, an extension of the model is necessary for this case. The calculations were based on a simple Gaussian distribution and not on the combination of slope distributions. For now, we can state that the evaluation of θ_y and σ is sufficient to predict the static contact angle for isotropic Gaussian structures of nanometric order.

5. Conclusions

A new theoretical model for calculating the CA in terms of the RMS slope and θ_y has been proposed using the modified Cassie–Baxter equation and considering isotropic Gaussian surfaces, i.e., surfaces with a Gaussian height distribution whose statistical moments exhibit isotropy. This is a relatively broad case since most deposited or abraded surfaces (such as those produced by wet bench processes, physical vapor deposition techniques, or chemical or physical etching) by processes that do not impose preferred directions or shapes (such as the use of masks in the previously mentioned techniques) possess this characteristic.

Two sets of alumina samples with graded topography were fabricated and functionalized, and their wettability and topography were quantified using the sessile drop method and AFM in two distinct laboratories. Superhydrophobicity under static criteria was achieved in both sets, while dynamic criteria were met in at least one of them.

The quantified data were plotted, and the theoretical curve was fitted to these data, showing reasonable agreement. We can say with relative confidence that the contact angle for the Cassie–Baxter model can be predicted if we know the RMS slope and Young's contact angle, which are related to the topography and the chemical composition of the involved phases, respectively. This allowed us to define the value of the RMS slope, given θ_y , at which the static superhydrophobic angle is achieved, establishing a superhydrophobic topographic criterion.

The establishment of a superhydrophobic criterion and the potential to predict the contact angle given chemical and physical factors, such as surface topography, allow for the optimization and creation of new processes for the construction of micro- and nano-structures aimed at applications where these are relevant, such as self-cleaning, anti-corrosive, anti-fogging, and anti-contaminant surfaces, which can combine these characteristics with other functionalities of interest.

As future perspectives, we aim to test the theoretical model for structures with varying orders of magnitude in dimensions and, if possible, determine the model's range of validity. To enhance the model's practical applicability, we plan to assess the behavior of the static topographic criterion for superhydrophobicity, namely, the RMS slope value for which the contact angle exceeds 150° , as a function of Young's contact angle. Finally, we intend to extend the model to hierarchical surfaces and to predict dynamic wettability, such as hysteresis.

Summary of conclusions:

1. A new model for predicting the wettability of hydrophobic surfaces in terms of the RMS slope and Young's contact angle for stochastic surfaces was presented.
2. To experimentally test this model, hydrophobic and superhydrophobic alumina surfaces with graded roughness were constructed.
3. The contact angle and RMS slope of these surfaces were experimentally measured.

4. The theoretical curve of the model adequately fitted the experimental data, confirming its validity.
5. The curve fitting allowed for the determination of a Young's angle-dependent topographic criterion for superhydrophobicity.

Author Contributions: Conceptualization, S.S., M.L.M., and P.L.G.J.; methodology, C.S.S., N.F., S.S., M.L.M., and P.L.G.J.; validation, C.S.S., N.F., S.S., M.L.M., and P.L.G.J.; formal analysis, C.S.S., N.F., and P.L.G.J.; investigation, C.S.S., N.F., S.S., M.L.M., and P.L.G.J.; resources, N.F., S.S., M.L.M., and P.L.G.J.; data curation, C.S.S.; writing—original draft preparation, C.S.S., and P.L.G.J.; writing—review and editing, C.S.S., N.F., and P.L.G.J.; visualization, C.S.S., N.F., and P.L.G.J.; supervision, C.S.S., N.F., S.S., M.L.M., and P.L.G.J.; resources, N.F., S.S., M.L.M., and P.L.G.J.; project administration, N.F., S.S., M.L.M., and P.L.G.J.; funding acquisition, C.S.S. All authors have read and agreed to the published version of the manuscript.

Funding: CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) granted a doctoral scholarship to make this study possible, finance code 001.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data for this article are available in the following repository: <https://drive.google.com/drive/folders/11M4B8w071iWQWdZx-OPEPUwiXEmHPkCf> (accessed on 30 October 2024).

Acknowledgments: We would like to thank Evonik for providing the Dynasylan F8815 functionalizing agent, Frederico L.G. Jardim for preparing the first two figures of the article, and Vinícius Becker for the design and assembly of the wettability measurement equipment and dip coater.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CA	contact angle
RMS	root mean square
WRP	Wenzel roughness parameter
H	hysteresis
AFM	atomic force microscopy
CAMD	contact angle measurement device
LS	liquid–solid
LG	liquid–gas
SG	solid–gas

References

1. Yetisen, A.K.; Qu, H.; Manbachi, A.; Butt, H.; Dokmeci, M.R.; Hinestroza, J.P.; Skorobogatiy, M.; Khademhosseini, A.; Yun, S.H. Nanotechnology in textiles. *ACS Nano* **2016**, *10*, 3042–3068. [CrossRef]
2. Bixler, G.D.; Bhushan, B. Rice-and butterfly-wing effect inspired self-cleaning and low drag micro/nanopatterned surfaces in water, oil, and air flow. *Nanoscale* **2014**, *6*, 76–96. [CrossRef] [PubMed]
3. Latthe, S.S.; Sutar, R.S.; Kodag, V.S.; Bhosale, A.; Kumar, A.M.; Sadasivuni, K.K.; Xing, R.; Liu, S. Self-cleaning superhydrophobic coatings: Potential industrial applications. *Prog. Org. Coat.* **2019**, *128*, 52–58. [CrossRef]
4. Zhang, D.; Wang, L.; Qian, H.; Li, X. Superhydrophobic surfaces for corrosion protection: A review of recent progresses and future directions. *J. Coat. Technol. Res.* **2016**, *13*, 11–29. [CrossRef]
5. Cherupurakal, N.; Mozumder, M.S.; Mourad, A.H.I.; Lalwani, S. Recent advances in superhydrophobic polymers for antireflective self-cleaning solar panels. *Renew. Sustain. Energy Rev.* **2021**, *151*, 111538. [CrossRef]
6. Mehmood, U.; Al-Sulaiman, F.A.; Yilbas, B.; Salhi, B.; Ahmed, S.; Hossain, M.K. Superhydrophobic surfaces with antireflection properties for solar applications: A critical review. *Sol. Energy Mater. Sol. Cells* **2016**, *157*, 604–623. [CrossRef]

7. Adam, N. *The Physics and Chemistry of Surfaces*; The Clarendon Press: Oxford, UK, 1930.
8. Cassie, A. Contact angles. *Discuss. Faraday Soc.* **1948**, *3*, 11–16. [[CrossRef](#)]
9. Barthlott, W.; Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **1997**, *202*, 1–8. [[CrossRef](#)]
10. Wenzel, R.N. Resistance of solid surfaces to wetting by water. *Ind. Eng. Chem.* **1936**, *28*, 988–994. [[CrossRef](#)]
11. Wenzel, R.N. Surface roughness and contact angle. *J. Phys. Chem.* **1949**, *53*, 1466–1467. [[CrossRef](#)]
12. Gao, L.; McCarthy, T.J. Contact angle hysteresis explained. *Langmuir* **2006**, *22*, 6234–6237. [[CrossRef](#)] [[PubMed](#)]
13. Gao, L.; McCarthy, T.J. How Wenzel and Cassie were wrong. *Langmuir* **2007**, *23*, 3762–3765. [[CrossRef](#)] [[PubMed](#)]
14. Choi, W.; Tuteja, A.; Mabry, J.M.; Cohen, R.E.; McKinley, G.H. A modified Cassie–Baxter relationship to explain contact angle hysteresis and anisotropy on non-wetting textured surfaces. *J. Colloid Interface Sci.* **2009**, *339*, 208–216. [[CrossRef](#)]
15. Xu, X. Modified Wenzel and Cassie equations for wetting on rough surfaces. *SIAM J. Appl. Math.* **2016**, *76*, 2353–2374. [[CrossRef](#)]
16. Löfflein, S.M.; Mücklich, F.; Grützmacher, P.G. Topography versus chemistry—How can we control surface wetting? *J. Colloid Interface Sci.* **2022**, *609*, 645–656. [[CrossRef](#)]
17. Du, Q.; Zhou, P.; Pan, Y.; Qu, X.; Liu, L.; Yu, H.; Hou, J. Influence of hydrophobicity and roughness on the wetting and flow resistance of water droplets on solid surface: A many-body dissipative particle dynamics study. *Chem. Eng. Sci.* **2022**, *249*, 117327. [[CrossRef](#)]
18. Wang, J.; Wu, Y.; Cao, Y.; Li, G.; Liao, Y. Influence of surface roughness on contact angle hysteresis and spreading work. *Colloid Polym. Sci.* **2020**, *298*, 1107–1112. [[CrossRef](#)]
19. Nguyen, H.N.G.; Zhao, C.F.; Millet, O.; Selvadurai, A. Effects of surface roughness on liquid bridge capillarity and droplet wetting. *Powder Technol.* **2021**, *378*, 487–496. [[CrossRef](#)]
20. Li, C.; Zhang, J.; Han, J.; Yao, B. A numerical solution to the effects of surface roughness on water–coal contact angle. *Sci. Rep.* **2021**, *11*, 459. [[CrossRef](#)]
21. Kaufman, Y.; Chen, S.Y.; Mishra, H.; Schrader, A.M.; Lee, D.W.; Das, S.; Donaldson, S.H., Jr.; Israelachvili, J.N. Simple-to-apply wetting model to predict thermodynamically stable and metastable contact angles on textured/rough/patterned surfaces. *J. Phys. Chem. C* **2017**, *121*, 5642–5656. [[CrossRef](#)]
22. Schiavon, C.S.; Moreira, M.L.; Cava, S.S.; Raubach, C.W.; Jardim, P.L. Wetting-state transition of random surfaces. *Thin Solid Film.* **2022**, *745*, 139102. [[CrossRef](#)]
23. Kamusewitz, H.; Possart, W. Wetting and scanning force microscopy on rough polymer surfaces: Wenzel’s roughness factor and the thermodynamic contact angle. *Appl. Phys. A* **2003**, *76*, 899–902.
24. Longuet-Higgins, M.S. The statistical analysis of a random, moving surface. *Philos. Trans. R. Soc. Lond. Ser. A Math. Phys. Sci.* **1957**, *249*, 321–387.
25. Tadanaga, K.; Katata, N.; Minami, T. Formation Process of Super-Water-Repellent Al₂O₃ Coating Films with High Transparency by the Sol–Gel Method. *J. Am. Ceram. Soc.* **1997**, *80*, 3213–3216. [[CrossRef](#)]
26. Nishino, T.; Meguro, M.; Nakamae, K.; Matsushita, M.; Ueda, Y. The lowest surface free energy based on- CF₃ alignment. *Langmuir* **1999**, *15*, 4321–4323. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.