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*Protocols for computing the contact angle on chemically- and
physically-patterned surfaces by numerical simulation*



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ABSTRACT

The study of the behavior of a drop of water, when it encounters a solid material, is certainly a phenomenon of great interest. In general, liquid and solid can interact in different ways and the material can demonstrate hydrophilic or hydrophobic properties depending on the cases analyzed. The parameter used for this study is the contact angle, i.e. the angle that forms between the drop of water and the solid surface when they come into contact; when the angle is greater than 90 degrees, it is possible to talk about hydrophobic material when the angle is less than 90 degrees the material is considered hydrophilic.

In this regard, it is worth mentioning those materials that have an angle of contact with water greater than 150 degrees and that are defined as superhydrophobic, they have numerous potential applications due to their great ability to repel water.

A factor that exerts an important influence on the wettability properties of a material is certainly the physical structure of its surface; in fact, numerous theoretical and experimental studies have shown that the roughness of the surface itself causes variations in the measured contact angle. The aim of the thesis is to predict with numerical simulations, carried out using a special tool (SE - FIT), the evolution of the water drop in contact with different surfaces with different roughness values, analyzing as said the contact angle. Specifically, simulations have been executed involving the contact of water with nanopatter surface, in particular they have been considered first pillar in 2D and after pillar in 3D.

The computational results obtained has been compared with the theoretical values that, all things being equal, it is possible to obtain using two fundamental models: the Wenzel model and the Cassie - Baxter model.

The simulated configurations show a better adaptation to certain situations rather than others, so we tried to explain the reasons for this situation.

In the final part, possible future developments are suggested in order to have a more complete understanding of the phenomenon.

1. INTRODUCTION

Water is a fundamental element on Earth, in fact it occupies about 71% of the Earth's surface. It is therefore reasonable to study its properties and the resulting applications. At the same time, it is fundamental to analyze the way other materials behave in relation to water itself, for this reason it is interesting to understand the way water and solid surfaces interact, without forgetting the interactions between water and air. In this context, particular interest was aroused by those materials that show a self-cleaning behavior, a phenomenon observed in nature on various plants and in particular on Lotus flowers, for this reason the name “Lotus effect” [1]. Similarly also in the animal world it is possible to find cases of this type, for example the skin of the shark, it is composed of diamond-shape dermal denticles that allow this animal to move faster in water [2].



Figure 1 - Drop of Water on lotus leaf

This behavior allows to introduce the concept of hydrophilic and hydrophobic material. A material is defined hydrophobic or hydrophilic according to its ability to absorb or retain water inside or on its surface [3]. In order to measure this property it is appropriate to consider the angle that a drop of water forms in contact with the surface of the material under analysis, if the contact angle is less than 90 degrees the material can be defined hydrophilic[4], consequently the materials that form an angle greater than 90 degrees on their surface can be described as hydrophobic. Also with reference to water, another two categories can be defined: superhydrophilic materials with a solid-liquid contact angle lower than 5 degrees and the

superhydrophobic materials, i.e. those that show an angle of contact greater or equal to 150 degrees when in contact with water [4]; these materials have a highly repellent behavior towards water, large static contact angle low resistance to water movement on their surface and their applications have been analyzed since the 1990s [5] . Superhydrophobic materials can be obtained by industrial processes, an example is the technique of placing a thin layer of polydimethylsiloxane (PDMS) on Nano metric SiO_2 particles using the Chemical Vapor Deposition (CVD) [6] .

With the idea of imitating what happens in nature and therefore find materials that have a strongly hydrophobic behavior to exploit their technological applications, the factors that could cause an increase in the contact angle have been investigated. In general, the wettability property concerns the interaction of three phases: one gaseous, one liquid and the usual. It is necessary to consider a chemical aspect, i.e. the bond between the water molecule and the solid, and a physical aspect influenced by various factors, to understand the behavior of a drop of water on a surface. One of the factors ,that certainly influences this aspect, is the roughness of the surface and this is evident when analyzing the wetting phenomena considering the area of the surfaces involved in the phenomenon and their energy values[7].

In this regard, it was particularly useful to analyze the behavior of a drop on a surface that has pillars of micrometric size, in fact according to the theory of Cassie-Baxter [8] and Wenzel [7] [9] in the contact angle will increases. The purpose of the following discussion is therefore to analyze from a numerical point of view the behavior of a drop of water on a surface with micrometric pillars in order to understand how it evolves. This type of analysis is particularly useful since the size of the drops is in the order of PicoLiters pL , i.e. $10^{-15}m^3$.

To evaluate the evolution of the drop to its equilibrium condition, an Open Source Software developed by Prof. Brakke and called Surface Evolver has been used. This software is based on a gradient descent method and in this way the software can find the configuration with the minimum value of the energy [10]

In order to evaluate the trend of the contact angle and surface tension, the behavior of the drop in different situations obtained by varying the size of the pillar, the volume of the drop and the contact angle was analyzed. The results obtained are mainly compared with the theoretical contact angle values that can be calculated using the Cassie - Baxter Theory that is particularly useful to describe the hydrophobic behavior of materials with a calculated roughness factor.

2. LITERATURE REVIEW

2.1 Surface Tension

The surface tension is one of the fundamental concepts to be considered and introduced for the following discussion. When a liquid is in contact with a non-miscible fluid an interface is created, obviously the formation of that interface requires a cost from the energy point of view, this energy cost per unit of area can be defined surface tension. This property depends mainly on the molecular bonds between the substances, in fact, considering a liquid in contact with another material, it is possible to notice that the molecules at the interface will have less probability to form chemical bonds and consequently will be at a higher energy level.

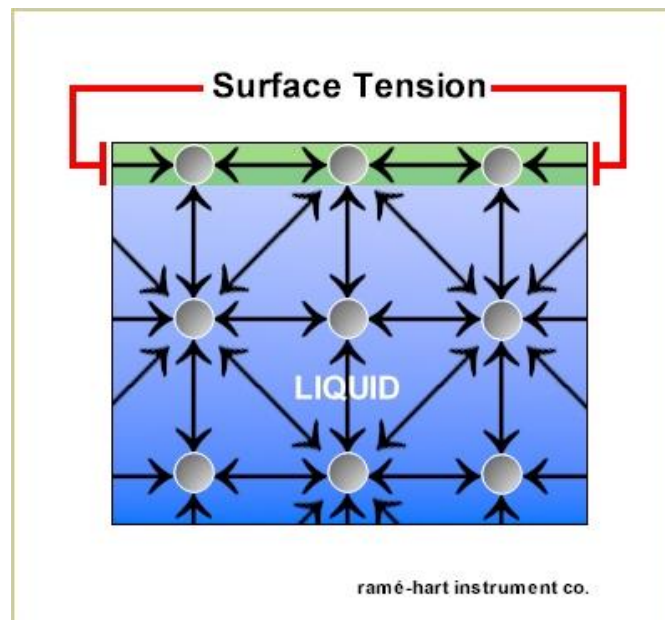


Figure 2 - Schematic explanation of the molecular interactions that cause the surface tension. Source: http://www.ramehart.com/surface_tension.htm

It is also possible to find a mathematical definition of γ , considering the Gibbs free energy (G) definition:

$$G = U + PV - TS \quad (2.1)$$

Where: U is the internal energy of the system P is the pressure, V is the Volume, T the temperature and S the entropy of the system.

In this case, considering an infinitesimal increasing and assuming the liquid incompressible and the system isothermal, the changes in Gibbs free energy are equal to Helmholtz free energy (df) [11]:

$$dG = df = dU = -\delta W \quad (2.2)$$

It also possible, to write from the definition of surface tension:

$$\delta W = -\gamma dA \quad (2.3)$$

Combining the equations (2.2) and (2.3):

$$\gamma = dG/dA \quad (2.4)$$

Consequently, from a dimensional point of view the surface tension can be measured using $[J/m^2]$ or $[N/m]$:

$$[\gamma] = \frac{E}{L * L} = \frac{F * L}{L^2} = \frac{F}{L}$$

In general the order of magnitude is mJ/m^2 , for example the value of the water-air surface tension is equal to $72 mJ/m^2$ at $25^\circ C$ [12].

2.2 Wettability

In general, wettability means the ability of a liquid to maintain its contact with a solid surface, the factors that influence this bond are to be found between the forces of molecular interaction and various physical factors such as impurities or surface defects. Wettability will therefore be given by the balance between adhesion and cohesion work [13]:

- Work of adhesion: it concerns the interaction between molecule of two different materials, as far as wettability is concerned the adhesion work concerns the liquid - solid interaction, as shown in Figure 3;

- Work of cohesion: it concerns instead the interaction between molecules of the same material, therefore with reference to Figure 3, the interactions solid - solid and that liquid – liquid

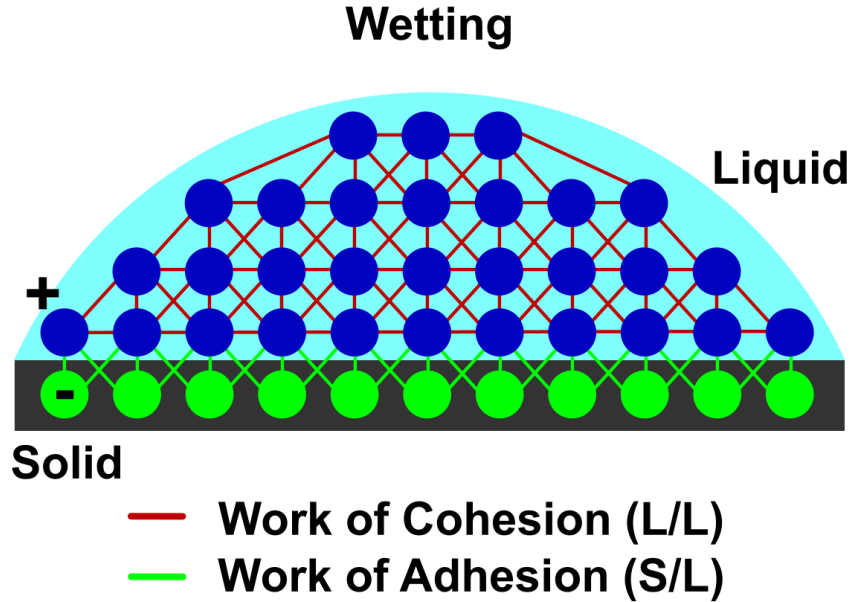


Figure 3 - Work of Cohesion and Work of Adhesion. Source:
<http://bioenzymerecovery.com/greenzymeoilreleasemechanism.html>

It is possible to quantify the wettability property by analyzing a parameter that is the spreading (S) [14] defined as the distance between the dry condition and the wet condition from the point of view of energy per unit area:

$$S = \gamma_{VS} - \gamma_{LS} - \gamma_{LV} \quad (2.5)$$

where: γ_{VS} is the surface tension between the interface vapor – solid, γ_{LS} is the surface tension between the interface liquid – solid, γ_{LV} is the surface tension between the interface liquid – vapor.

2.3 Young – Laplace equation

The presence of surface tension brings with it a series of implications, one of that is the difference in pressure between the drop of liquid and the surface with it is in contact. In order to maintain a spherical shape it is necessary that the internal pressure of the drop is greater than the external one; this pressure difference is called Laplace pressure. In general terms, it is possible to consider the Young – Laplace equation[15] which is applicable to any geometry interface, it states that the pressure is directly proportional to the curvature C of the interface under analysis and obviously to the surface tension:

$$\Delta p = \gamma C = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.6)$$

For the next discussion, it is appropriate to introduce a dimensionless number: the Bond Number (Bo). The Bond number express the relationship between the forces of gravity and the forces of surface tension, its mathematical expression is the following one:

$$Bo = \frac{\Delta \rho g L^2}{\gamma} \quad (2.7)$$

Where:

$\Delta \rho$: is the difference in density between the two phases [kg/m^3]

g : is the acceleration gravity [m/s^2]

L : is the characteristic length

Intuitively it can easily be said that the force of gravity affects the drops of a certain liquid but under certain conditions, it is possible that the drops are not affected by the effect of gravity. Conceptually it is possible to find a value for which the effect of gravity is negligible, this value is called capillarity length λ_c and its mathematical expression is the following:

$$\lambda_c = \sqrt{\left(\frac{\gamma}{\rho g} \right)} \quad (2.8)$$

For example considering the water at 20 °C $\lambda_c = 2.7 \text{ mm}$ [16]

Combining the expressions (2.6) and (2.7):

$$Bo = \left(\frac{L}{\lambda_c}\right)^2 \quad (2.9)$$

Therefore, a low Bond Number value ($Bo < 1$) indicates that the effects of surface tension prevail over those of gravity, whereas high Bond Number values indicate that the effects of gravity prevail over those of surface tension.

The concept of capillarity length is related to that of capillarity, i.e. the totality of phenomena caused by interactions between the molecules of a liquid and a solid due to cohesion and adhesion forces and surface tension.

The effect of capillarity strongly influences the shape of the surface in contact with a solid, it can lead to a raising of the surface when the adhesion forces are greater than the cohesion forces or, on the contrary, to a lowering when the cohesion forces prevail (Figure 4).

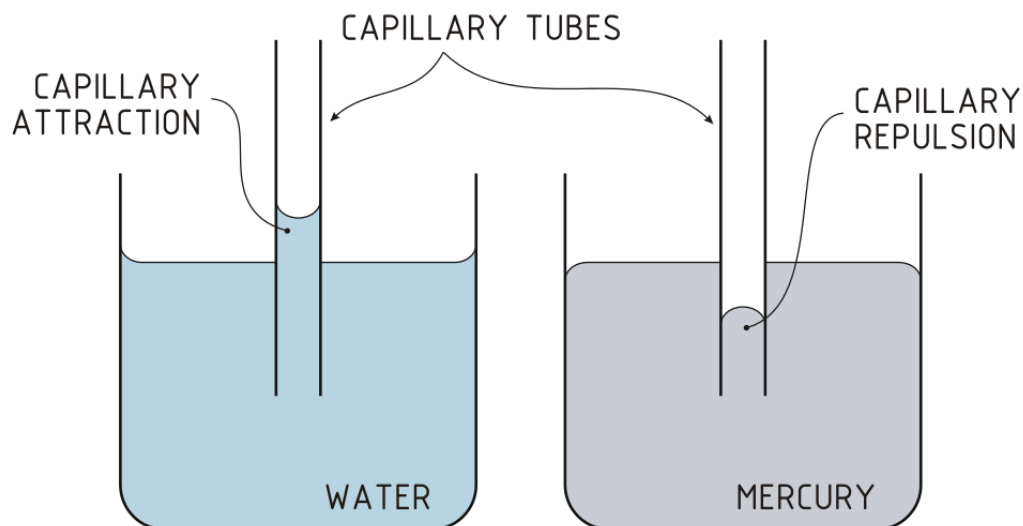


Figure 4 - Effect of the Capillarity. Source: www.wikipedia.org

2.4 Contact angle and Young Equation

When a drop comes into contact with a solid material, it is possible to define a contact line joining all three phases. In this situation it is possible to define an angle between the tangent to the liquid - solid interface and the horizontal plane of the surface, this angle is called contact angle θ_Y . From the physical point of view, it is used to quantify the wettability of a surface because it reflects the behavior of molecular interactions between the three phases: solid, liquid and vapor.

The value of the contact angle that water forms when in contact with a surface is a parameter used to classify materials according to their behavior (Figure 5):

- $\theta_Y < 90^\circ$ Hydrophilic behavior: indicates the tendency of some materials to bind with water and consequently to retain it on their surface;
- $\theta_Y > 90^\circ$ Hydrophobic behavior: indicates the tendency of some materials not to retain water on their surface;
- $\theta_Y > 150^\circ$ Superhydrophobic behavior;

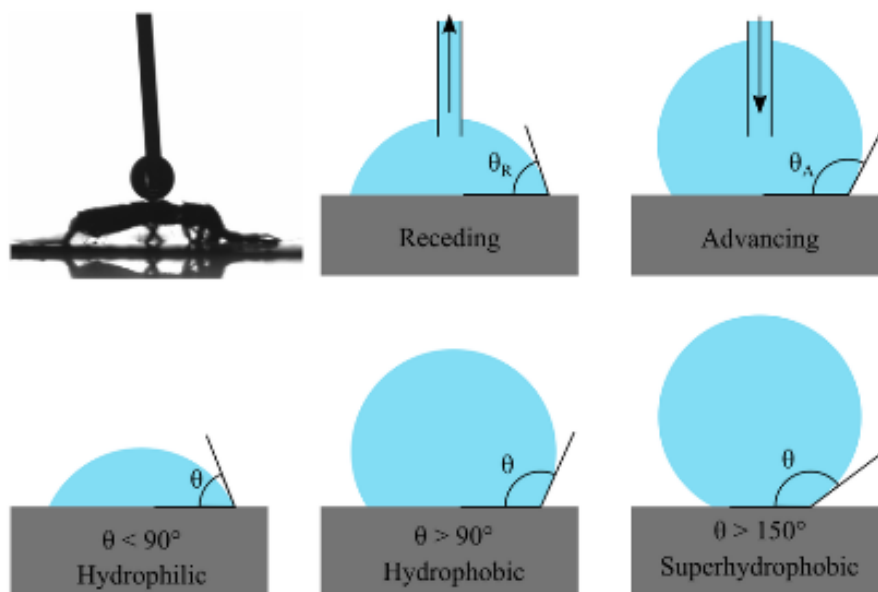


Figure 5 - Materials' classification using the value of equilibrium contact angle. Reproduced from [17]. Copyright © 2014 Gundersen et al. Appendix C for details.

When the drop reaches its equilibrium position it is possible to measure its equilibrium contact angle, from a mathematical point of view it can be considered a three-phase system characterized by three surface tensions γ_{VS} , γ_{LS} , γ_{LV} that act perpendicularly to the separation line between the three phases.

In the equilibrium situation, it is possible to write:

$$\gamma_{VS} + \gamma_{LS} + \gamma_{LV} = 0 \quad (2.10)$$

The expression (2.10) can be written as follow, considering the projection of γ_{LV} along the horizontal plane Figure 6):

$$\gamma_{VS} = \gamma_{LS} + \gamma_{LV} \cos \theta_Y \quad (2.11)$$

The equation (2.11) is called Young's Equation and it gives the possibility to calculate the equilibrium contact angle, balancing the different surface tension terms at the interface.

$$\cos \theta_Y = \frac{\gamma_{VS} - \gamma_{LS}}{\gamma_{LV}} \quad (2.12)$$

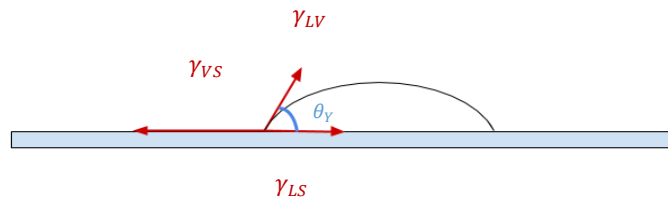


Figure 6 - Schematic view of surface tension and contact angle

The equilibrium contact angle is, as said, the value of the angle on the surface in a condition of equilibrium on a smooth surface in a static condition, in the reality a drop in contact with a surface can assume two different behaviors. In the first case, there is an increase in the contact area and it is possible to talk about advancing contact angle (θ_A), in the second case, there is a reduction in the contact angle and it is possible to talk of receding contact angle (θ_R).

It is also possible to define the hysteresis as the difference between the two previous angles:

$$\theta_H = \theta_A - \theta_R \quad (2.13)$$

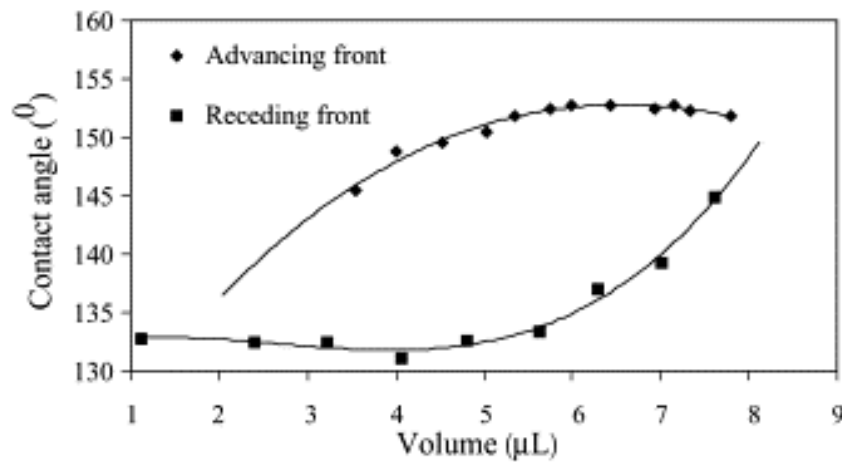


Figure 7 - Example of behavior of advancing contact angle, receding contact angle and hysteresis [18]. Reproduced with License Number: 4864271204336. Copyright © 2004 Elsevier B.V..

The value of the equilibrium contact angle is also linked to the concept of wettability mentioned above and to the value of the spreading coefficient. If $S > 0$ the liquid expands on the whole solid surface because of the favorable energy conditions, the contact angle

$\theta_Y = 0$ and it is possible to talk about of total wetting, if instead $S \leq 0$, the liquid does not expand well on the solid and tends to reach an equilibrium position, consequently the contact angle $\theta_Y \neq 0$ and in this case there is a partial wetting, in addition, the greater the contact angle, the lower the surface energy of the solid will be.

Suppose now to considerate a solid and a liquid layer with a contact area A and to want to separate them, this means putting them in contact with a third gaseous phase along the same area A , the work done to do this operation can be expressed with the following relationship, known as Dupré's equation [18]:

$$W_{LS} = (\gamma_L + \gamma_s - \gamma_{LS}) * A \quad (2.14)$$

Combining the Young's equation and the Duprè equation:

$$w_a = \frac{W_{LS}}{A} = \gamma_L(1 + \cos \theta_Y) \quad (2.15)$$

w_a is the work of adhesion and due to the fact that $(1 + \cos \theta_Y) \geq 1 \rightarrow w_a \geq 2 \gamma_L$, so recalling the equation (2.12), it is possible to obtain the condition of total wetting:

$$\gamma_s > \gamma_{LS} + \gamma_L \quad (2.16)$$

In this condition the solid is completely wetted by the liquid.

The equation (2.12) allows, however, the measurement of the surface tension of the liquid and of the contact angle, leaving, however, the surface energy of the solid unknown.

The value of the latter can be calculated experimentally based on several theories, the most used are [19]:

- Zisman Theory: the surface energy of the solid will be equal to the surface tension's value of the highest surface tension liquid that will completely wet the solid with a contact angle equal to 0° ;
- Owens/Wendt Theory: the surface energy of a solid is composed by two different components, a dispersive component and a polar component. The first one depends mainly on the Van der Waals interactions while the second one considers the dipole-dipole, the dipole-induced dipole interactions and hydrogen bonding;
- Fowkes Theory: it is also based on the fact that the surface energy of a solid is composed by two different components and it has two key properties: surface energies are additive and the geometric mean. The second one is used to calculate the adhesion work for each type of energy;
- Van Oss Theory: this theory separates the surface energy of a solid into three components: a dispersive component, an acid component and a base component.

2.5 Wetting and roughness

Until now we have referred to a contact angle considering the solid surface on which the drop of water rests without surface defects and therefore ideal, obviously in reality this does not occur because each surface has a certain roughness (r).

A suitable way to express r is the following one [14]:

$$r = \frac{A_{actual}}{A_{apparent}} \quad (2.17)$$

Where: A_{actual} is the area of the drop while $A_{apparent}$ is the project of the drop on the plane of the solid substrate.

It is therefore necessary to find a model that is able to describe the behavior just highlighted, currently there are two models for this purpose: that of Wenzel and that of Cassie -Baxter.

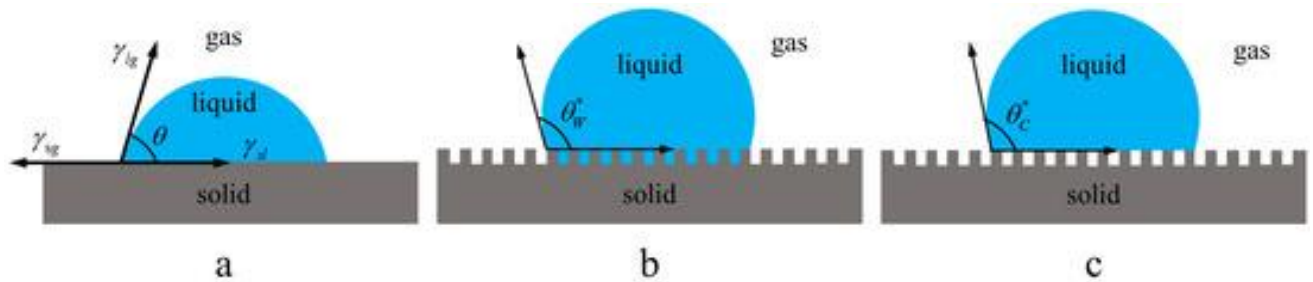


Figure 8 - Possible behavior of a drop on a roughness surface. (b) Wenzel model (c) Cassie - Baxter model. Reproduced from [20]. Copyright © 2012, American Chemical Society. Appendix D for details.

2.5.1 Wenzel State

Wenzel's model can be applied to both hydrophobic and hydrophilic surfaces and it is possible to notice that the presence of the roughness increase the coefficient of Spreading in each case [9].

Wenzel assumes that the material is chemically homogeneous and his model states that a surface with roughness tends to have a higher amount of surface free energy than a smooth

surface with the same area. This increase dE can be calculated by considering an infinitesimal increment dx :

$$dE = (\gamma_{LS} - \gamma_{VS})r dx + \gamma_{LV} \theta_{Wenzel} dx \quad (2.18)$$

r is the roughness factor calculated using (2.17).

Considering an equilibrium condition ($dE = 0$) the equation (2.18) becomes:

$$\gamma_{LV} \theta_{Wenzel} = (\gamma_{LS} - \gamma_{VS}) r \quad (2.19)$$

Applying the Young equation:

$$\cos \theta_{Wenzel} = r \cos \theta_Y \quad (2.20)$$

This relation, known as the Wenzel relation, highlights the following situation:

- If $\theta_Y < 90^\circ \rightarrow \theta_{Wenzel} < \theta_Y$
- If $\theta_Y > 90^\circ \rightarrow \theta_{Wenzel} > \theta_Y$

2.5.2 Cassie – Baxter Model

Unlike Wenzel's model, in Cassie - Baxter's model it is considered the chemical heterogeneity of the different species present. This model is based on the fact that the liquid does not fully penetrate the substrate [8], which is why this model is often used to describe phenomena related to superhydrophobicity. Considering also in this case an infinitesimal right increment dx , it is possible to write:

$$dE = f_1(\gamma_{LS} - \gamma_{VS}) dx + f_2(\gamma_{LS} - \gamma_{VS}) dx + \gamma_{LV} \theta_{Cassie-Baxter} dx \quad (2.21)$$

Where f_1 and f_2 are two different roughness factor referring two different chemical species and equal to:

$$\begin{cases} f_1 = \frac{A_1}{A_{total}} \\ f_2 = \frac{A_2}{A_{total}} \end{cases}$$

Imposing an equilibrium situation ($dE = 0$) to the equation (2.21) and considering the Young Equation:

$$\cos\theta_{Cassie-Baxter} = f_1 \cos\theta_{Y_1} + f_2 \cos\theta_{Y_2} \quad (2.22)$$

It should be noted that Cassie-Baxter's status is energetically favorable if

$$E_{Cassie-Baxter} < dE_{Wenzel} .$$

In addition, hydrophobic materials have an overall minimum state that corresponds to Cassie's, although Wenzel's state may have a favorable energy configuration. In these cases there is an energy barrier to switch from Cassie state to Wenzel state and therefore the drop tends to stay in the metastable Cassie state unless pressure is applied that forces it to switch to Wenzel state (Figure 7) [21].

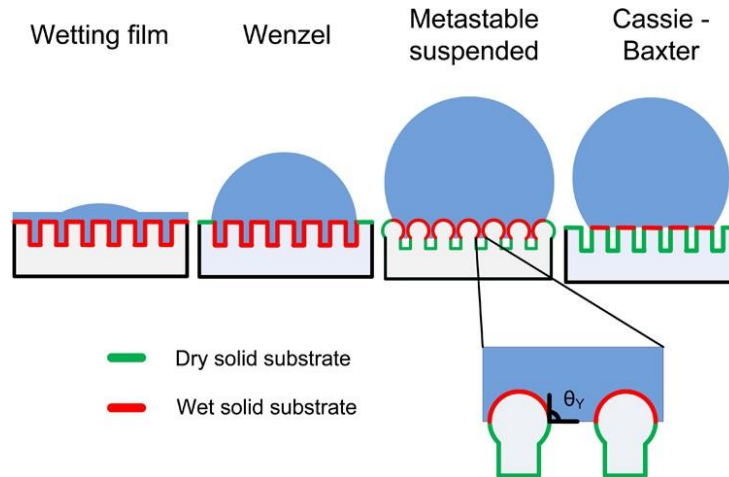


Figure 9 - Schematic view of possible equilibrium positions for a droplet on a textured surface. The inset shows a magnification of the idealized liquid-gas interface for the metastable configuration. Reproduced from [22]

3. METHODS

The purpose of this chapter is to describe the methods used and the steps for the definition the model, as well the parameters needed to run the simulations. In particular, three softwares have been used:

- Surface Evolver – Fluid Interface Tool (SE-FIT ®) for the simulations;
- MATLAB ® to create the input file for SE – FIT;
- ImageJ to measure the contact angle

3.1 Surface Evolver

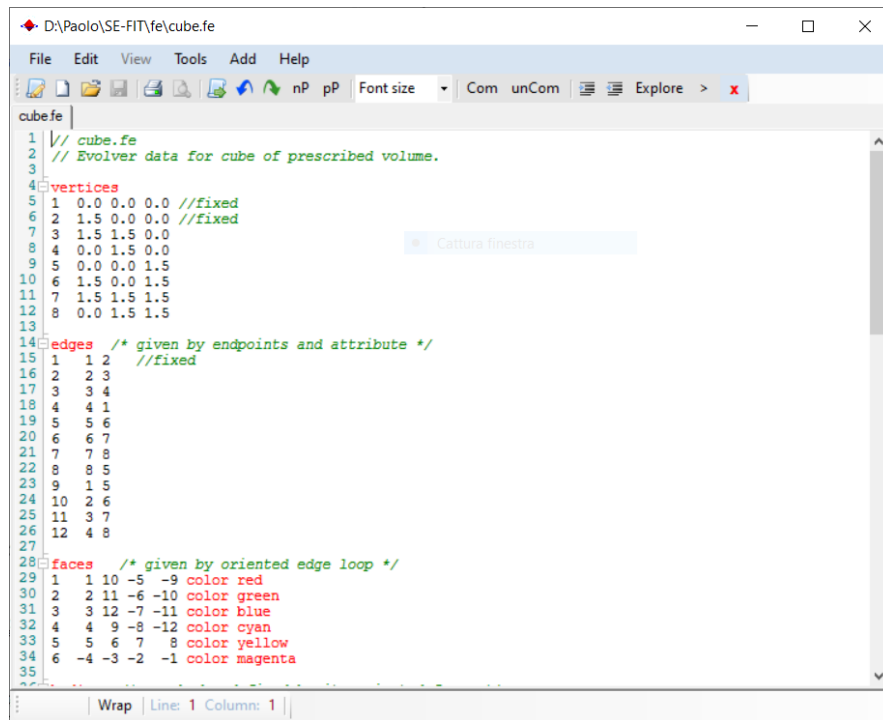
In order to simulate the behavior of a water drop on a surface, the software Surface Evolver – Fluid Interface Tool (SE-FIT ®) has been used, this application is the evolution of a previous software named Surface Evolver (SE). SE has not a graphical interface and consequently to User should launch the command form an appropriate Prompt of Command.

In latest version of SE-FIT (2.70) the frontend is composed by a graphical interface while the backend used Surface Evolver (SE) as the computational engine, in fact SE is a tool to calculate the evolution of a drop in order to find the equilibrium situation under specific conditions and constraints imposed by the User[23].

SE has been developed by Ken Brakke as a result of the author’s participation in The Geometry Center at the University of Minnesota[10], and its main function is to study the behavior of a body subject to surface tension and/or other energies under specified conditions and respecting certain parameters defined by the User.

The User also has the ability to build the initial geometry using a .fe format file (called *Data file*), which, as mentioned, will evolve during the simulation to achieve the minimum energy configuration using a gradient descent method or a Conjugate Gradient in case of quadratic functions. In particular, the core of SE is the iteration step that reduces energy respecting all the constraints, in fact, the software processes a mesh in such a way as to respect these constraints and being geometric in nature there are no variations in topology and triangulation. As said, SE – FIT provides various tools to set up and to perform the simulation:

- Text Editor: SE – FIT manage different formats file but the best choice is a .fe file, because this is the type of files that SE – FIT can manage. In this file the User must define the parameters, the geometry in a 3D domain (vertices, edges, facet, bodies), the boundaries and the constraints;



```

D:\Paolo\SE-FIT\fe\cube.fe
File Edit View Tools Add Help
Font size Com unCom Explore
cube.fe
1 // cube.fe
2 // Evolver data for cube of prescribed volume.
3
4 vertices
5 1 0.0 0.0 0.0 //fixed
6 2 1.5 0.0 0.0 //fixed
7 3 1.5 1.5 0.0
8 4 0.0 1.5 0.0
9 5 0.0 0.0 1.5
10 6 1.5 0.0 1.5
11 7 1.5 1.5 1.5
12 8 0.0 1.5 1.5
13
14 edges /* given by endpoints and attribute */
15 1 1 2 //fixed
16 2 2 3
17 3 3 4
18 4 4 1
19 5 5 6
20 6 6 7
21 7 7 8
22 8 8 5
23 9 1 5
24 10 2 6
25 11 3 7
26 12 4 8
27
28 faces /* given by oriented edge loop */
29 1 1 10 -5 -9 color red
30 2 2 11 -6 -10 color green
31 3 3 12 -7 -11 color blue
32 4 4 9 -8 -12 color cyan
33 5 5 6 7 8 color yellow
34 6 -4 -3 -2 -1 color magenta
35
Wrap Line: 1 Column: 1

```

Figure 10 - Text Editor inside SE – FIT

- Graphic window: In this window, the software graphically shows the initial geometry and its evolution during the simulation until the equilibrium situation or up to a certain condition set by the user in the .fe file. The User can choose a view, he can zoom in or zoom out and he can export a specific imagine using *PNG* command;
- Simulation control: the simulation can be managed using the buttons inside this part of SE – FIT. The user can choose the mesh between two options: *Fine Convergence* and *Rough Convergence* and then he can run the simulation. There is also the possibility to set manually the mesh using the *Re* command for refining or the *Ro* for roughening;

- Parameters control: in this tab, the User can manage the parameters defined in the .fe file and he can restart the simulation in order to find some changes or to perform analysis if necessary. In this window, the User can change the numerical values of the parameters defined in the .fe script without having to reopen the source file and he has also the possibility to define the maximum number of iterations;
- Summary results: In this tab, there are the main results of the simulation. In particular, the position of all vertices, edges and faces and their displacement from the initial condition is shown. It is also shown the total energy of the drop once the convergence situation has been reached and the value of the area

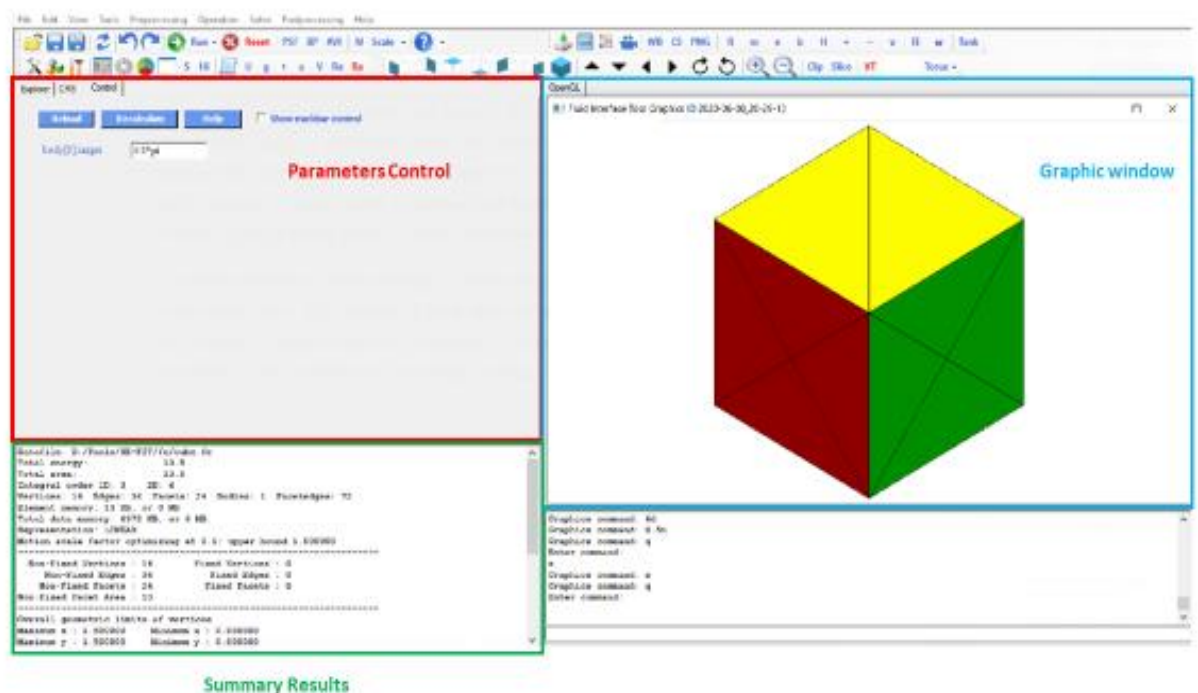


Figure 11 - Initial view of SE – FIT

3.1.1 Topology definition

First, it is necessary to define the position of the vertices that make up the simulation. To do so it is necessary to use the keyword *vertices* and then define the vertices in a consequential way indicating their position, then specifying the coordinates x, y, z.

Then, using the keyword *edges* it is necessary to define the edges using a consequential numbering and indicating for each one the starting vertices and the ending one.

Subsequently, it is necessary to define the faces using, also in this case, the keyword *faces*. The faces must be defined indicating the edges and in such a way that using the right hand rule the resulting vector is outgoing. It is necessary to consider the direction in which the edges are defined and therefore whether to use the minus sign if necessary.

The last step is the definition of the faces which compose the body under analysis. Here, it is also possible to impose the volume and density of the body using the keywords *volume* and *density*.

In the composition of the script, it is also possible to define numerical parameters that can then be called in the definition of geometric data. In this case, the following syntax must be used:

parameter *nameofparameter* = numerical value;

The user also has the possibility to define a variable according to different parameters; the following syntax must be used:

#define *nameoffunction* (numeralexpressionofthefunction);

SE- FIT also allows you to set some parameters for the simulation directly from the script, in fact it is possible to select the maximum number of iterations and the type of mesh to use.

3.1.2 Energy in SE – FIT

The main scope of SE – FIT is minimize the potential energy in order to reach an equilibrium condition. The total potential energy (E) consists of three main contributions and it can be expressed as follow:

$$E = E_I + E_G + E_K \quad (3.1)$$

where:

1. Interfacial Surface Energy or Work of adhesion (E_I)
2. Gravitational Energy (E_G)
3. Rotational Kinetic Energy (E_K)

3.1.3 Interfacial Energy (Work of Adhesion)

The interface energy occurs when a surface is used to separate two different phases (i.e. solid – liquid). It can be expressed by the following formulation:

$$E_I = \gamma_{SL} A_{SL} \quad (3.2)$$

where A_{SL} represent the contact area between the two different phases and γ_{SL} is the surface tension between the two surfaces under analysis.

Analyzing a drop on a surface it is reasonable to consider all three phases (liquid, solid, vapor) and therefore expression (3.2) can be reworded as follows:

$$E_I = \gamma_{VS} A_{VS} + \gamma_{VL} A_{VL} + \gamma_{LS} A_{LS} \quad (3.3)$$

3.1.4 Gravitational Energy

In classical mechanics, gravitational potential energy is the potential energy related to the gravitational attraction force between masses. It is an example of scalar potential. The starting point is the formulation that derives precisely from classical mechanics:

$$E_G = m * g * h \quad (3.4)$$

In which:

- m is the mass of the body considered
- g gravity acceleration equals to $9,81 \text{ m/s}^2$
- h body height in the reference system considered

In the analysis presented, it is necessary to consider the gravitational energy of the drop that will be given by the sum of the vapor phase and the liquid phase, and it has been done using the following formulation, coming from the rearrangement of the equation (3.4):

$$E_G = \rho_l V_l g \vec{C}_l + \rho_v V_v g \vec{C}_v \quad (3.5)$$

- ρ_l and ρ_v are the density, respectively of the liquid and the vapor,
- V_l and V_v are the volume, respectively of the liquid and the vapor,
- $\vec{C}_l$ and $\vec{C}_v$ are the displacement vectors linking the origin to the center, respectively of the liquid and vapor mass.

For subsequent analyses, the water density was considered equal to 1000 kg/m^3 .

3.1.5 Rotational Kinetic Energy

Rotational energy is a form energy related with the rotational motion of a rigid body. In the case of a rigid body with axial symmetry and rotating around the axis of symmetry, the rotational energy is equal to the product of the moment of inertia I of the body by the square of its angular velocity ω :

$$E_K = \frac{1}{2} I \omega^2 \quad (3.6)$$

In this case, since the drop is related only to a solid and rigid surface, it is reasonable to consider the rotational kinetic energy equals to 0.

3.1.6 Minimization of the Energy

As said before, Surface Evolver has the purpose of the minimization of the energy of the body in analysis, to do so it uses the Gradient descent method.

It is a first order iterative optimization algorithm for finding a local minimum of a differentiable function, it is based on the fact that, for a given function, the direction of maximum descent at an assigned point corresponds to the one determined by the opposite of its gradient at that point. In the specific SE- FIT the Conjugate Gradient method has been used, which is a variant of the descending gradient method and is particularly effective for linear and symmetric systems. This method makes it possible to achieve convergence in a smaller number of iterations for the case under consideration in certain situations.

3.2 Mathematical Reference

For the following discussion, it is appropriate to make some mathematical references concerning in particular the theorems of Gauss, Stokes and Green.

3.2.1 Gauss' theorem (Divergence Theorem)

Defined a Cartesian reference system xyz , considering a volume $V \subset R^3$ compact and bounded by a smooth surface ∂V , being $\vec{f}$ a vector field of class C^1 defined in a neighborhood of V and $\vec{n}$ the unit vector normal to V , it is possible to write:

$$\int_V \nabla \cdot \vec{f} \, dx dy dz = \int_{\partial V} \vec{f} \cdot \vec{n} \, dA \quad (3.7)$$

3.2.2 Stokes theorem

Defined still a Cartesian reference system xyz , given a cap surface $\Sigma \subset R^3$, for which $\vec{n}$ establishes a direction of travel of the cap's boundary, being $\vec{f}$ a vector field of class C^1 defined on an open set $A \subseteq R^3$ containing Σ , it is possible to write:

$$\int_{\Sigma} (\nabla \times \vec{f}) \cdot \vec{n} \, dS = \oint_{\partial \Sigma} \vec{f} \cdot d\vec{l} \quad (3.8)$$

3.2.3 Green's theorem

Green's theorem is a particular case of Stokes' theorem, in fact it is its application in two dimensions:

$$\int_{\Sigma} (\nabla \times \vec{f}) \cdot \vec{n} \, dS = \int_{\partial \Sigma} \vec{\omega} \cdot d\vec{l} \quad (3.9)$$

$\vec{\omega}$ is a vector field, defined as follow:

$$\vec{\omega}(x, y) = M(x, y)\vec{i} + N(x, y)\vec{j} \quad (3.10)$$

Where $\vec{i}, \vec{j}$ are the versors of the x-axis and y-axis respectively.

3.3 Model Formulation

Several steps have been taken to formulate the model. The first step provided for the parameterization of the drop actually resting on a material. The drop was parameterized as a cube in its initial situation and an initial contact angle was used to simulate the contact with the material.

The liquid/solid interface is given by the Stokes theorem:

$$A_{LS} = \iint_{A_{LS}} dA = \iint_{A_{LS}} (\nabla \times \vec{w}) \cdot \vec{n} dA \quad (3.11)$$

For the purposes of the simulation analyzed, the face of the drop in contact with the solid surface is omitted for computational reasons and therefore it is necessary to switch from a surface integral to a line integral. In order to do that, it is necessary to consider the Blue theorem:

$$A_{LS} = \iint_{A_{LS}} (\nabla \times \vec{w}) \cdot \vec{n} dA = \int_{\partial A_{LS}} \vec{w} \cdot d\vec{l} \quad (3.12)$$

$\vec{w}$ is a vector field and it is possible to define a suitable function $z = f(x, y)$ in order to have:

$$\nabla \times \vec{w} = f(x, y)$$

Considering all this and starting from the equation (3.11), it is possible to make some rearrangements.

In particular, considering that:

$$A_{vs} = A_S - A_{LS}$$

The equation (3.3) becomes:

$$E_I = \gamma_{VS}(A_S - A_{LS}) + \gamma_{VL}A_{VL} + \gamma_{LS}A_{LS} = \gamma_{VS}A_S - \gamma_{VS}A_{LS} + \gamma_{VL}A_{VL} + \gamma_{LS}A_{LS} \quad (3.13)$$

The contribution $\gamma_{VS}A_S$ can be considered negligible:

$$E_I = \gamma_{VL}A_{VL} + (\gamma_{LS} - \gamma_{VS}) A_{LS} \quad (3.14)$$

Considering now the Young Relation:

$$\cos \theta = \frac{\gamma_{LS} - \gamma_{VS}}{\gamma_{VL}} \rightarrow \gamma_{VS} = \gamma_{LS} - \gamma_{VL} \cos \theta$$

The equation (3.13) has now the following formulation:

$$E_I = \gamma_{VL}(A_{VL} + A_{LS} \cos \theta) \quad (3.15)$$

On the Interface:

$$E_I = \gamma_{VL} \left(\iint_{A_{VL}} dA + \iint_{A_{LS}} \cos \theta dA \right)$$

$$\frac{E_I}{\gamma_{VL}} = \iint_{A_{VL}} dA + \iint_{A_{LS}} \cos \theta dA \quad (3.16)$$

Since only solid liquid contact has been analyzed, the equation (3.16) has been rewriting as follow:

$$\frac{E_I}{\gamma_{VL}} = \iint_{A_{LS}} \cos \theta dA = w_{xe} \quad (3.17)$$

As said, to evaluate A_{LS} it is necessary to recall the Stokes theorem:

$$A_{LS} = \cos \theta \iint_{A_{LS}} dA = \cos \theta \iint_{A_{LS}} (\nabla \times \vec{w}) \cdot \vec{n} dA \quad (3.18)$$

Using the Green's theorem:

$$A_{LS} = \cos \theta \int_{\partial A_{LS}} \vec{w} \cdot d\vec{l} \quad (3.19)$$

It is necessary to define a function z in two variables: $z = f(x, y)$

$$\nabla \times \vec{w} = \sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \quad (3.20)$$

Substituting (3.20) into (3.19):

$$A_{LS} = \iint_{A_{xy}} \left(\sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \right) dx dy = \int_{\partial A_{xy}} \vec{w} \cdot d\vec{l} \quad (3.21)$$

It is now possible to write:

$$\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y} = \sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \quad (3.22)$$

Resolving the previous ODE:

$$\begin{cases} M(x, y) = 0 \\ N(x, y) = \int \left(\sqrt{1 + \left(\frac{\partial f}{\partial x} \right)^2 + \left(\frac{\partial f}{\partial y} \right)^2} \right) dx \end{cases}$$

Choosing $z = h \rightarrow N(x, y) = x \rightarrow w_{xe} = x \cos \theta$ (3.23)

Therefore, it is now possible to write:

$$\frac{E_I}{\gamma_{VL}} = x \cos \theta \quad (3.24)$$

This is in fact the constraint that must be imposed on the lower edge of the drop and this is done as follows:



Figure 12 - Constraint on the base's contour

It can be noted that it is also necessary to impose a constraint of the geometrical point of view; in this case, it was considered appropriate to impose the condition that does not allow the drop to fall below the contact plane.

The second step in the formulation of the model involves the imposition of a condition that considers the drop in contact with two different materials.

Specifically, we have tried to consider air as a second material and to find the contact angle between water and air, we started from the surface tension value equals to $(72 \text{ mJ}/\text{m}^2)$ at 25°C [12] and using the Young relation we have an angle $\theta = 86^\circ$. The formulation of the constraint changes in this way:

```

PARAMETER angle = 120 // interior angle between material and water
PARAMETER angle2 = 86 // interior angle between air and water
#define WALLT (-cos (angle*pi/180))
#define WALLTT (-cos (angle2*pi/180))
constraint 1
formula: z = 0
energy:
e1: 0
e2: (WALLT*x) *(x>0.5) +(WALLTT*x) *(x<=0.5)
e3: 0

```

In Figure 13 and Figure 14 the initial configuration of the drop. It should be noted that the reference system used is the Cartesian one, the x-axis is the red one, the y-axis is the blue one and the z-axis is the blue one.

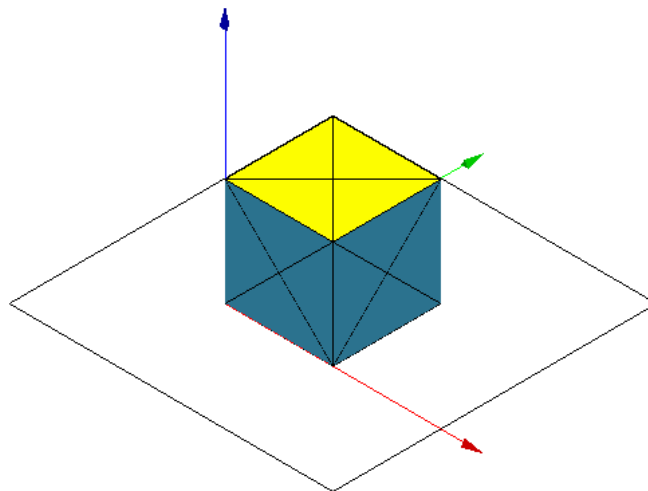


Figure 13 - Initial configuration of a drop in contact with two different materials (Isometric view)

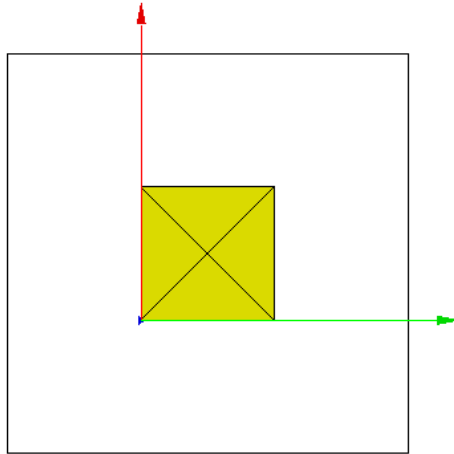


Figure 14 - Initial configuration of a drop in contact with two different materials (bottom view)

The Figure 13 is an isometric view while the Figure 14 is a bottom view. The drop has been parameterized, as a cube the upper face is the only yellow one in order to highlight the absence of the lower face in the bottom view.

By starting the simulation, the drop shows the following form when the energy is minimized.

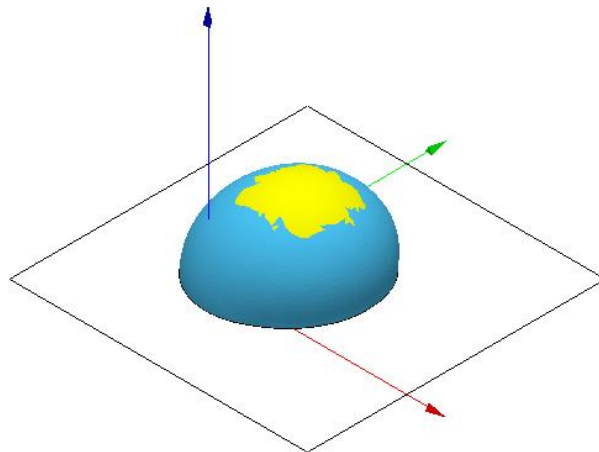


Figure 15 - Equilibrium configuration of a drop in contact with two different materials (Isometric view)

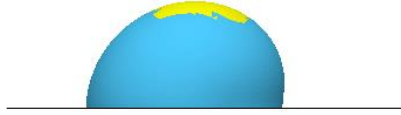


Figure 16 - Equilibrium configuration of a drop in contact with two different materials (bottom view)

Also in this case there are two different views of the final configuration (Figure 15 and Figure 16). Looking at the frontal view it is possible to see how the final configuration is strictly influenced by the contact angle. In fact, the side with an angle slightly lower than 90° , gives to solid a hydrophilic behavior while the other side, with an angle equals to 120° , gives to the solid an hydrophobic behavior. The next step was to simulate the contact between a material and the air, unlike the previous case, however, it was thought to simulate the contact between the drop and the air along a central strip. In the Figure 8 the initial configuration.

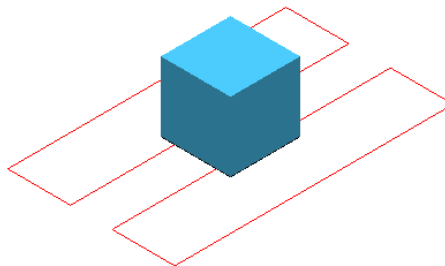


Figure 17 - Initial configuration of a drop in contact with air (central stripes) and two different material (lateral stripes)

In this case, it was considered appropriate to distribute the value of the water-air surface tension along the contour, similarly to what was done previously for water-material contact.

The following steps have been utilized:

$$\frac{E_I}{\gamma_{VL}} = \iint_{A_{VL}} dA = w_{xa} \quad (3.25)$$

Evaluating A_{VL} :

$$A_{VL} = \iint_{A_{VL}} dA = \cos \theta \iint_{A_{VL}} (\nabla \times \vec{w}) \cdot \vec{n} \, dA \quad (3.26)$$

Using the Green's theorem:

$$A_{VL} = \int_{\partial A_{VL}} \vec{w} \cdot \vec{dl} \quad (3.27)$$

It is necessary to define a function z in two variables: $z = f(x, y)$

$$\nabla \times \vec{w} = \sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \quad (3.28)$$

Substituting (3.28) into (3.27):

$$A_{VL} = \iint_{A_{xy}} \left(\sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \right) dx dy = \int_{\partial A_{xy}} \vec{w} \cdot \vec{dl} \quad (3.29)$$

It is now possible to write:

$$\frac{\partial N}{\partial x} - \frac{\partial M}{\partial y} = \sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \quad (3.30)$$

$$\begin{cases} M(x, y) = 0 \\ N(x, y) = \int \left(\sqrt{1 + \left(\frac{\partial f}{\partial x}\right)^2 + \left(\frac{\partial f}{\partial y}\right)^2} \right) dx \end{cases}$$

Choosing $z = h \rightarrow N(x, y) = x \rightarrow w_{xa} = x$

In this way, it is possible obtain the new constraint using the SE- FIT formulation:

```

PARAMETER angle = 120 // interior angle between material and water
#define WALLT (-cos (angle*pi/180))
constraint 1
formula: z=0
energy:
e1:0
e2:(x>-3 and x<3) ? (x+0.5*x):(WALLT*x+0.5*x)
e3:0

```

By starting the simulation and waiting for it to reach energy minimization, the following configuration is obtained (Figure 18):

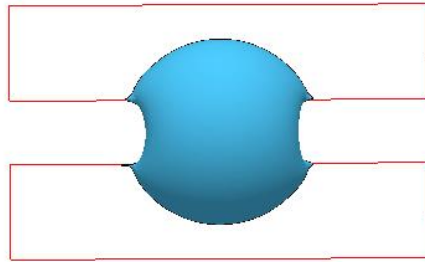


Figure 18 - Final configuration of a drop in contact with air (central stripes) and two different material (lateral stripes)

In the Figure 18 it is possible to identify a central meniscus in the area of contact between water and air and there is a discontinuity in the area of passage between the material and air. It is also possible to simulate the presence of two contact zones between air and water along the two different axes.

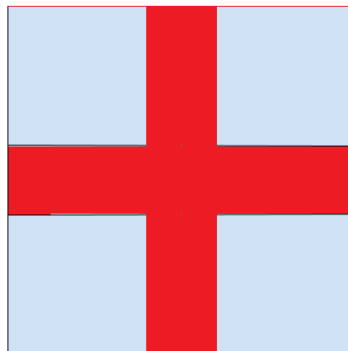


Figure 19 - Initial configuration of a drop in contact with a solid material (in the corners) and the air (central stripes)

In the Figure 19 the shape of the drop when it reaches a situation of equilibrium.

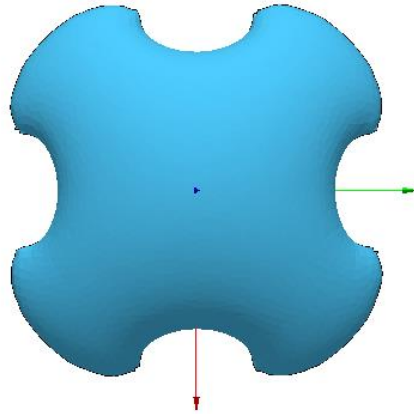


Figure 20 - Equilibrium condition of a drop in contact with a solid material (in the corners) and the air (central stripes)

This model shows limits, in fact, it is suitable for simulating drop contact with 2-dimensional pillars, and it is only possible to simulate the contact with the air along a whole strip but does not allow simulating the contact with the upper part of the pillars.

In order to simulate the behavior shown in the Figure 21, it is necessary to use another solution.

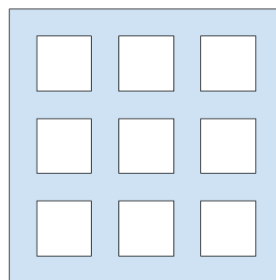


Figure 21 - Schematic view of a surface with Nano pillars (top view)

The solution chosen is not to parameterize the contact zones between water and material and apply the constraint seen in the initial step with the contact angle. On the contrary, the contact zones between water and air are parameterized and the surface tension value is used again. In all this the base is held fixed to allow the simulation to reach the configuration that minimizes energy. In the Figure 22 and Figure 23 the initial configuration, in two different views (isometric and bottom view):

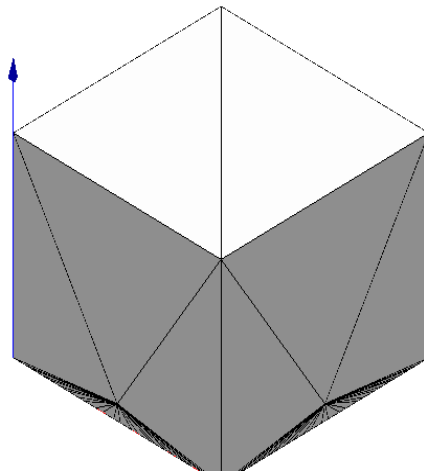


Figure 22 - Initial configuration of a drop in contact with a nanopattern surface (isometric view)

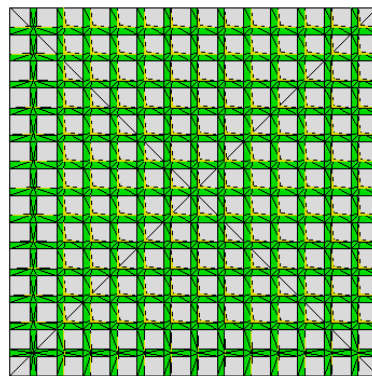


Figure 23 - Initial configuration of a drop in contact with a nanopattern surface (bottom view)

By starting the simulation, we obtain the following evolution (Figure 24) and then it is possible to measure the contact angle

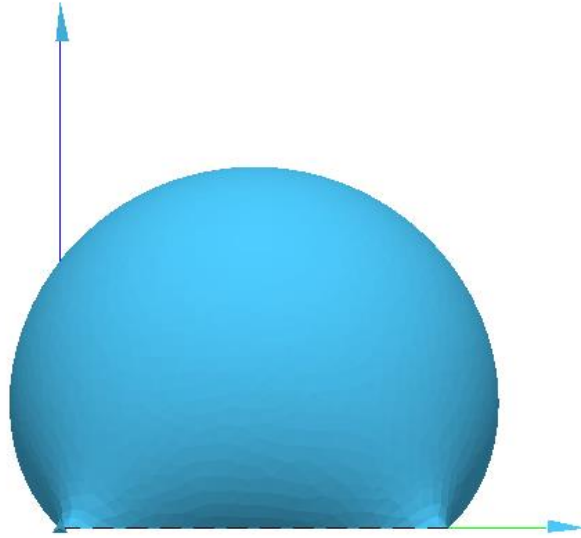


Figure 24 - Equilibrium condition of a drop in contact with a nanopattern surface

As a last step for the formulation of the step, it was thought to consider pillars in 3D dimensions. However, the model needs to consider some modifications and in particular, it was appropriate to consider the contribution of the wet wall volume and gravitational energy contribution of the wet wall.

The starting point for the evaluation of the volume contribution is the Gauss theorem:

$$V = \iiint 1 \, dx dy dz = \iiint \nabla \cdot (z\vec{k}) \, dx dy dz = \int_{\partial V_{LS}} z\vec{k} \cdot \vec{n} \, dA \quad (3.31)$$

Obviously it is necessary that $\nabla \cdot (z\vec{k}) = 1$.

For the evaluation of the integral in the equation (3.31), it is reasonable to consider a suitable function $z = f(x, y)$

$$\int_{\partial V_{LS}} z \vec{k} \cdot \vec{n} dA = \int_{\partial V_{LS}} f(x, y) \vec{k} \cdot \vec{n} dA \quad (3.32)$$

Considering now, the projection of the Volume under analysis on the plane x- y, it is possible to apply the Green's theorem:

$$\int_{A_{xy}} f(x, y) \vec{k} \cdot \vec{n} dxdy = \int_{A_{xy}} f(x, y) dxdy = \int_{\partial A_{xy}} \vec{\omega} \cdot d\vec{l} \quad (3.33)$$

As stated in the previous equations :

$$f(x, y) = \nabla x \vec{\omega} = \nabla x (M(x, y)\vec{i} + N(x, y)\vec{j}) = \frac{\partial N}{\partial x} - \frac{\partial M}{\partial y} \quad (3.34)$$

Solving the ODE:

$$\begin{cases} M(x, y) = 0 \\ N(x, y) = \int f(x, y) dx \end{cases}$$

Combing the ODE, the equation (3.33) and the equation (3.34) :

$$\omega_{volume}(x, y) = M(x, y)\vec{i} + N(x, y)\vec{j} = \int f(x, y) dx \vec{j} = v_{vol}\hat{j} \quad (3.35)$$

Looking at the geometry it is reasonable to write:

$$\omega_{volume}(x, y) = M(x, y)\hat{i} + N(x, y)\hat{j} = v_{vol}\hat{j} \quad (3.36)$$

The last step then provides for the choice of a reasonable z, given the geometry considered it is appropriate to choose z = h where h is the height of the pillar:

$$v_{vol} = h * x \quad (3.37)$$

The next step is to assess the contribution of gravitational energy. Theoretically, gravitational energy is given by the sum of three contributions: one on the x-axis, one on the y-axis and the z-axis. The first two contributions are equal to zero so the only contribution to be evaluated is the one on the z-axis:

$$E_{gz} = -\rho g_z \int_{A_{xy}} \frac{1}{2} f^2(x, y) dx dy \quad (3.38)$$

Considering the equation (3.10) and adapting it to the present case:

$$\frac{1}{2} f^2(x, y) = \frac{\partial N}{\partial x} - \frac{\partial M}{\partial y} \quad (3.39)$$

Solving the ODE:

$$\begin{cases} M(x, y) = 0 \\ N(x, y) = \int \frac{1}{2} f^2(x, y) dx \end{cases}$$

It is now possible to apply the Green's theorem:

$$\omega_{grav}(x, y) = M(x, y)\vec{i} + N(x, y)\vec{j} = \int \frac{1}{2} f^2(x, y) dx \vec{j} = g_z \hat{j} \quad (3.40)$$

In addition, in this case, it is appropriate to choose $z = h$, so the final contribution is:

$$g_z = \frac{1}{2} h^2 x \quad (3.41)$$

Now it is possible to rewrite the new constraint that we need to apply along the border of the contact face:

```
parameter angle = 120
#define WALLT (-cos(angle*pi/180))
constraint 1
formula: z=0.1
energy:
e1: 0
e2: -Tl*x - 0.5*h^2*x
e3: 0
content:
c1:0
c2:-h*x
c3:0
```

It is also necessary to impose a geometric condition (z =height of the pillar) in order to run the simulation. In the Figure 25 and Figure 26 the initial configuration, the pillars are the square in blue color.



Figure 25 - Initial configuration of a drop in contact with 3D pillars (front view)

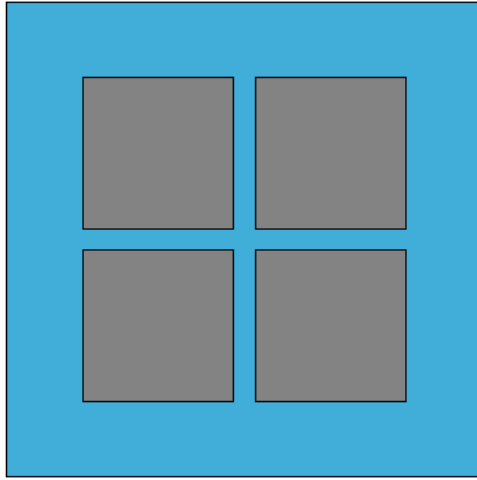


Figure 26 - Initial configuration of a drop in contact with 3D pillars (bottom view)

When the simulation is completed, the drop assume the shape in the Figure 27:

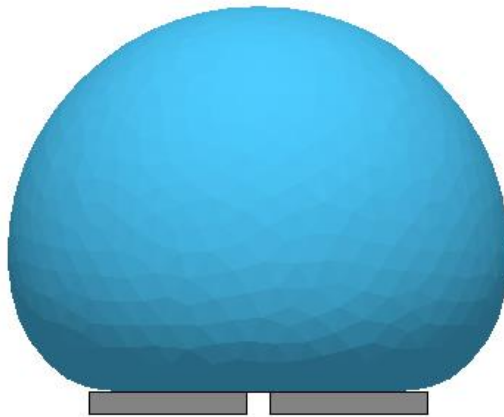
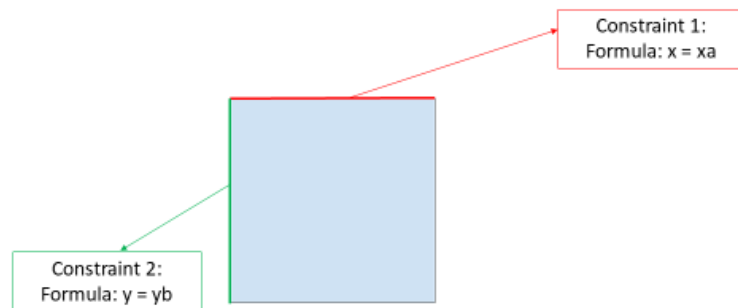


Figure 27 - Equilibrium condition of a drop in contact with 3D pillars

This configuration achieves convergence but to do that it is necessary to impose a geometric condition, the drop cannot go below the plane $z = \text{pillar height}$. This condition is quite strict because observing the reality it is possible to see that in the space between the pillars the drop tends to form a meniscus, because of the effect given by the lateral edge of the pillar and the gravity. It is therefore necessary to find a solution that allows simulating the behavior of the drop on the pillars in a more faithful way to reality,

It has been thought to divide the lower face of the drop and to parameterize the parts in contact with the air so that we can impose on these portions the condition that the surface tension is equal to 0.072 N/m. On the contrary, the portions of the lower face in contact with the pillars have not been parameterized as before and on each side of these portions a geometric condition has been set on the x-axis for the horizontal sides, on the y-axis for the vertical ones (Figure 28). On each side of the pillar must then be added additional conditions, either non-negative or non-positive. Such conditions impose to the function not to assume respectively negative or positive values[24], it is necessary to insert them because otherwise in the simulation the drop would collapse on itself.



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Figure 28 - Top view of the pillar with the geometric constraint

After setting all the vertices, sides, faces and geometric and energy conditions the initial configuration is the ones in the Figure 29.



Figure 29 - Initial configuration of a drop in contact with 3D pillars without constraint on z-axes

By starting the simulation and observing the situation when the simulation reaches convergence, it is possible to notice that in the space between two consecutive pillars the meniscus is created, as mentioned previously.

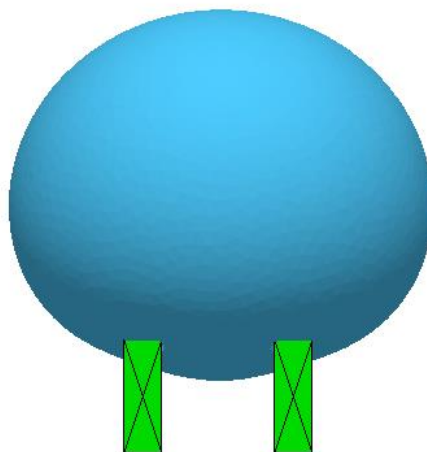


Figure 30 - Equilibrium condition of a drop in contact with 3D pillars without constraint along z-axes

In the Result chapter, the angles obtained with the 3D pillars with constraints on the z-axis and those without constraint along the z-axis will be compared. It is important to note that all the conditions imposed are necessary for the realization of the simulation itself and having defined them according to the volume it is necessary to note that they are valid only for certain ranges of volume.

3.4 Matlab

In order to automate the creation of the .fe file that is used for SE- FIT, scripts made with Matlab have been used.

Matlab is an environment for numerical calculation and statistical analysis written in C, which also includes the programming language of the same name created by Math Works[25].

Specifically, through the definition of appropriate vectors, cycles and functions, Matlab has been useful to calculate the number of vertices with their respective coordinates, the sides with the vertices that connect them, the faces with the sides that constitute them and the bodies with their respective faces. For example in the 2D model changed only the number of pillars it is possible to obtain the initial configuration. In the Figure 31, two examples:

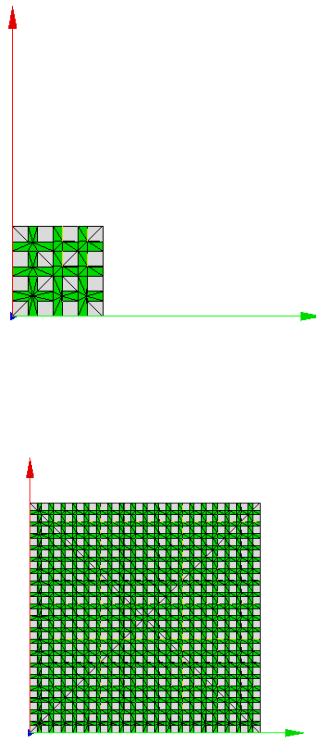


Figure 31 - Examples of configurations obtained by Matlab script

Matlab has also been used for the realization of appropriate graphs to show the results obtained in an appropriate way.

3.5 ImageJ

Completing the simulation with SE – FIT, it is necessary to measure the final contact angle in order to know how the drop has evolved. To do that an open source software, named ImageJ, has been used. ImageJ is a digital image processing computer program, developed by the National Institutes of Health of the United States, inspired by NIH Image or the Macintos[26].

Using this program, it is possible to edit and analyze color, greyscale, 8-bit, 16-bit and 32-bit images, different formats are supported. It is multithreaded, so different operation can performed in parallel with other operations. For this analysis, the version 1.46 has been used.

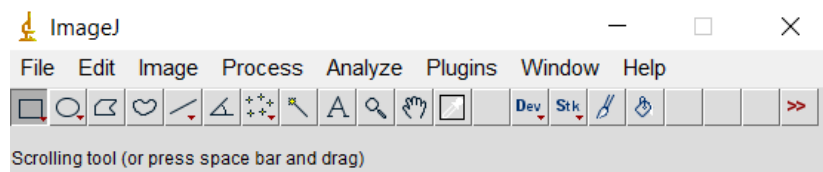


Figure 32 - ImageJ version 1.46

To install different plugins, most of them based on java, which give the possibility to perform different analyses. In this case, a plugin developed by Biomedical Imaging Group from the EPFL (Ecole polytechnique federal de Lausanne) has been installed to measure the contact angle. In particular, downloading the zip file (*drop_analysis.zip*) it is possible to use 2 different methodologies:

- 1) DropSnake[27] is based on B-spline snakes (active contours) to shape the drop.

Specifically you can draw a curve that follows the profile of the drop, it can be done both manually (blue curve, Figure 33) and automatically (red curve, Figure 34).

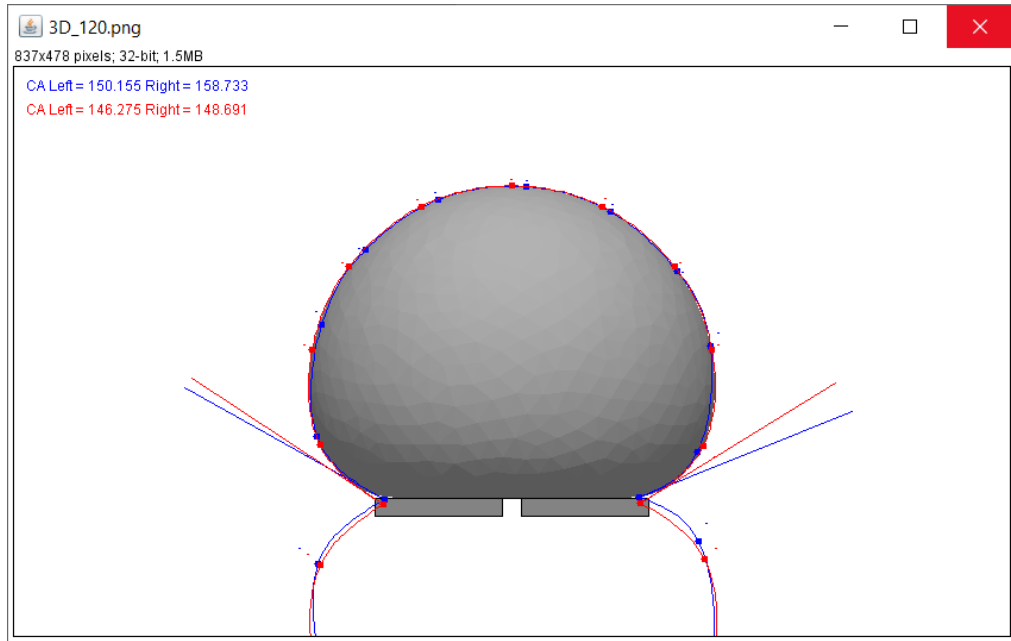


Figure 33 - Initial view of DropSnake plugin

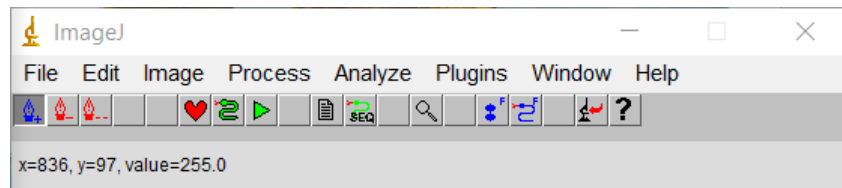


Figure 34 - DropSnake applied on ImageJ

2) LB-ADSA[27] is based on the fitting of the Young-Laplace equation to the image data.

The user can vary the following parameters:

b : radius of curvature of the drop in pixels

c : capillary constant of the liquid, in this case it is equal to the water's value,

x_0 : apex's abscissa,

y_0 : apex's ordinate,

h : drop's height in pixels,

d : reflection height in pixels.

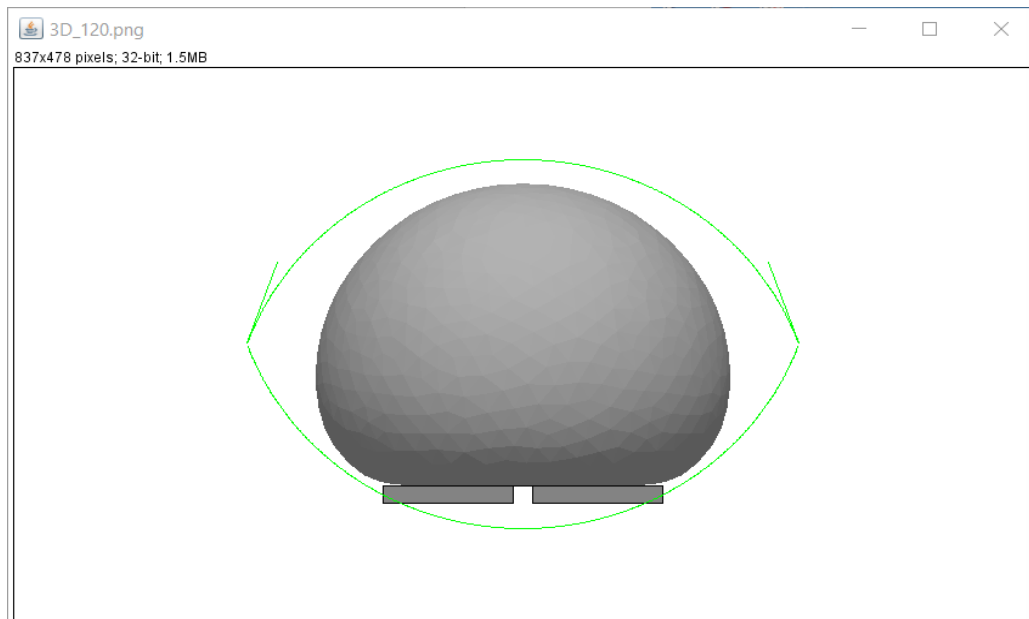


Figure 35 - Initial view of an image with the LBASDA plugin

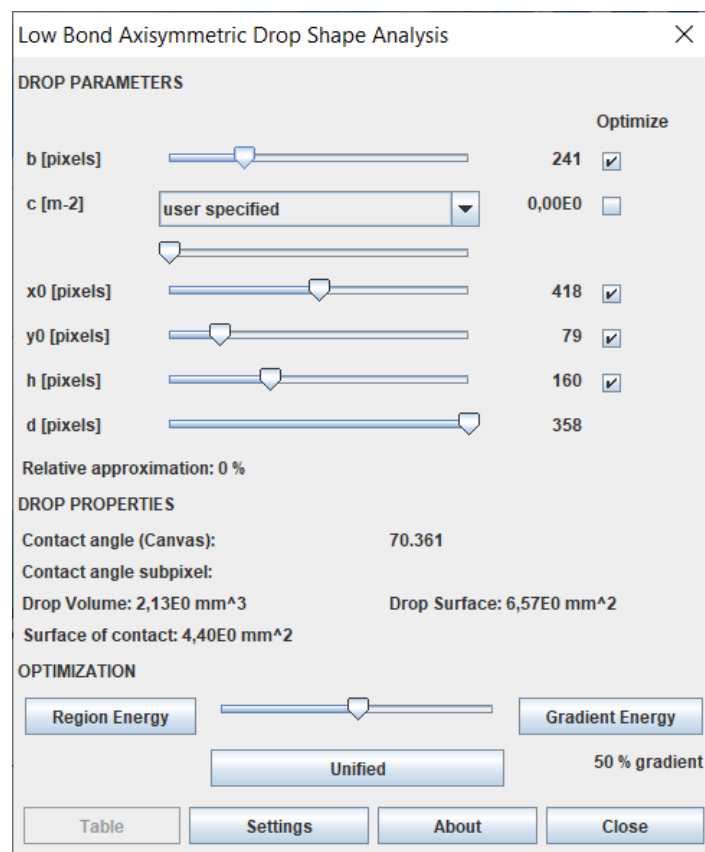


Figure 36 - Initial view of LBASDA plugin on ImageJ

The system shows the following results:

- Contact angle,
- Contact angle subpixel: this is the contact angle after an optimization,
- Drop volume,
- Drop surface,
- Surface of contact.

When using this methodology the system calculates and displays the relative error of the measurement in order to understand how probable and usable it is.

The results in Chapter 4, shown for contact angles, are obtained by averaging the values obtained with a manual curve, with an automatic curve and with the plugin LB-ADSA.

4. RESULTS

4.1 Analysis on 2D Pillars

As stated above, the contact angle is a fundamental parameter for measuring the hydrophobicity of a surface. The results obtained with numerical analysis are then compared with the theoretical values obtained using Cassie - Baxter's theory[8]. According to this theory the liquid does not enter completely into the substrate but does so only in part by remaining suspended between the various pillars, in this way it is possible to calculate the apparent contact angle with the following formula:

$$\cos\theta_{THE} = f_s \cos\theta_{initial} - (1 - f_s) \quad (4.1)$$

Where:

θ_{THE} = Value of apparent contact angle;

f_s = Roughness factor, i.e. the fraction of solid-liquid interface compared to the total base area;

$\theta_{initial}$ = Initial value of contact angle.

The value of $\theta_{initial}$ is set as a parameter for the simulation while it is reasonable to calculate f_s in this way:

$$f_s = \frac{\text{Area of solid liquid interface}}{\text{Total base area}} \quad (4.2)$$

4.1.1 Effect of size on the Contact Angle

The purpose of this section is to analyze the contact angle trend according to the size of the pillar, keeping constant the initial contact angle, the drop volume, the distance between pillars.

In the following figure the analysis is repeated with a base that contains from 14 x 14 to 7 x 7 or from 196 to 49 pillars on the base.

Analyzing the trend of angles measured with ImageJ plugins and reported in the Figure 29, it is already possible to see that the model seems to represent better certain configurations than others but additional analysis are needed to establish this.

It is therefore appropriate to report the trend of the angle measured keeping constant the number of pillars per side, the volume, the contact angle and varying their size, as a result will also vary the height of the drop. This value is related to the theoretical value obtained with the relationship of Cassie Baxter and in order to identify the distance between the two data is calculated the relative error. Fundamental step is the calculation of the roughness factor with the formula highlighted above.

The factor f_s , looking at the Figure 37, is calculated in the following way:

$$f_s = \frac{\text{area of pillar top surface} \times \text{number of pillars (white square)}}{\text{Total Area of the drop at the base}}$$

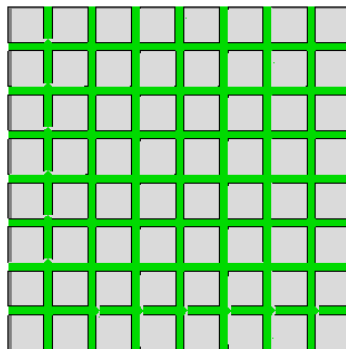


Figure 37 - Bottom view of the interface liquid solid. The top face of the pillars is in white.

The Table 1 show the values of the roughness factor, it is possible to note that the value of f_s decrease when the number of pillars increase but the size of the pillar is the same. Moreover, considering the same number of pillars the value of f_s increase with the sizing.

<i>Number of pillars</i>	Roughness factor				
	Size = 0.6 μm	Size = 0.7 μm	Size = 0.8 μm	Size = 0.9 μm	Size = 1 μm
196	0.578	0.64	0.693	0.740	0.780
169	0.498	0.552	0.598	0.638	0.673
144	0.425	0.470	0.509	0.543	0.573
121	0.357	0.395	0.428	0.457	0.482
100	0.295	0.327	0.354	0.377	0.398
81	0.239	0.264	0.287	0.306	0.322
64	0.189	0.209	0.226	0.242	0.255
49	0.144	0.16	0.173	0.185	0.195

Table 1 - Behavior of the roughness factor

As expressed by Cassie Baxter's formula illustrated above (4.1), using an initial contact angle equal to 120° , the theoretical angle decreases because it decreases the roughness factor, on the contrary the measured angle tends to increase up to a maximum of 121 pillars.

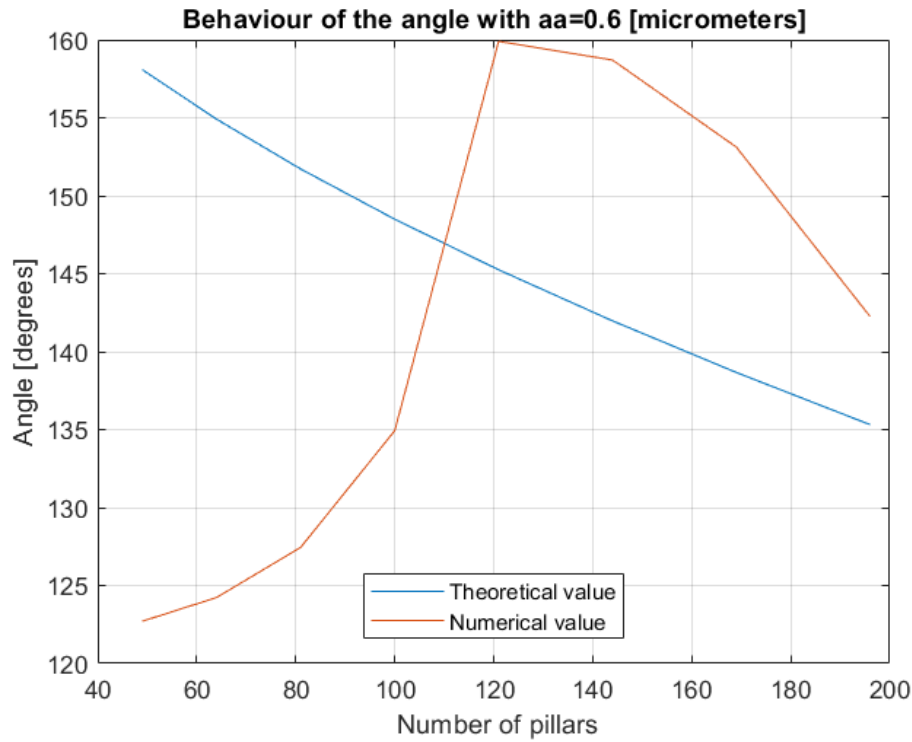


Figure 38 - Computational angle and Theoretical angle related to the number of pillars (size of pillar = 0.6 micrometers). The Theoretical value of the angle is obtained from Cassie-Baxter equation.

The first increasing trend until it reaches a maximum and then immediately decreasing, is also evident in the subsequent simulations carried out by increasing the size of the pillar and consequently also the size of the base. The maximum in this case will be reached with a lower number of pillars, for example with a pillar side length equal to 0.7 e $0.8 \mu m$, the maximum is reached with a total number of pillars equal to 100 (Figure 39 and Figure 40).

The motivation for this behavior could be found in the combination of the constructed geometry and above all the energy constraints dictated by the need to bring the simulation to convergence. One aspect to consider is the fact that the ratio between the area of the pillars at the base and the initial height of the drop, the latter in fact decreases with the increase of the base area being defined as the ratio between the volume that is kept constant ($1 pL$) and the base area that instead increases because it increases the side of the pillar. At this point it must be considered that the constraint imposed on the contour of the pillar depends on the volume and consequently

the z-coordinate has an important influence on the simulation. It is possible to highlight that the maximum is reached with a solid fraction at the base equal to 30 – 35 % .

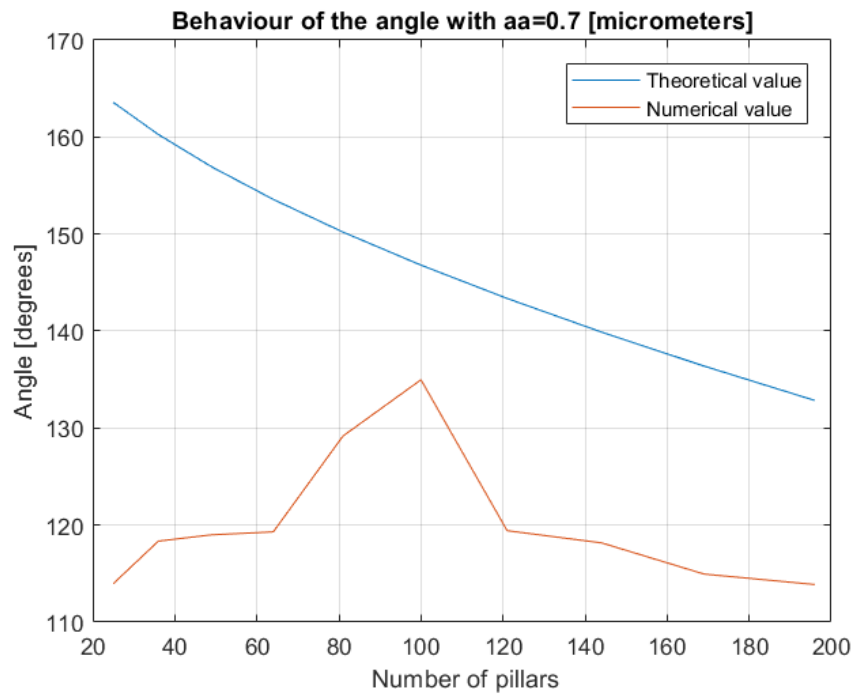


Figure 39 - Computational angle and Theoretical angle related to the number of pillars (size of pillar = 0.7 micrometers). The Theoretical value of the angle is obtained from Cassie-Baxter equation.

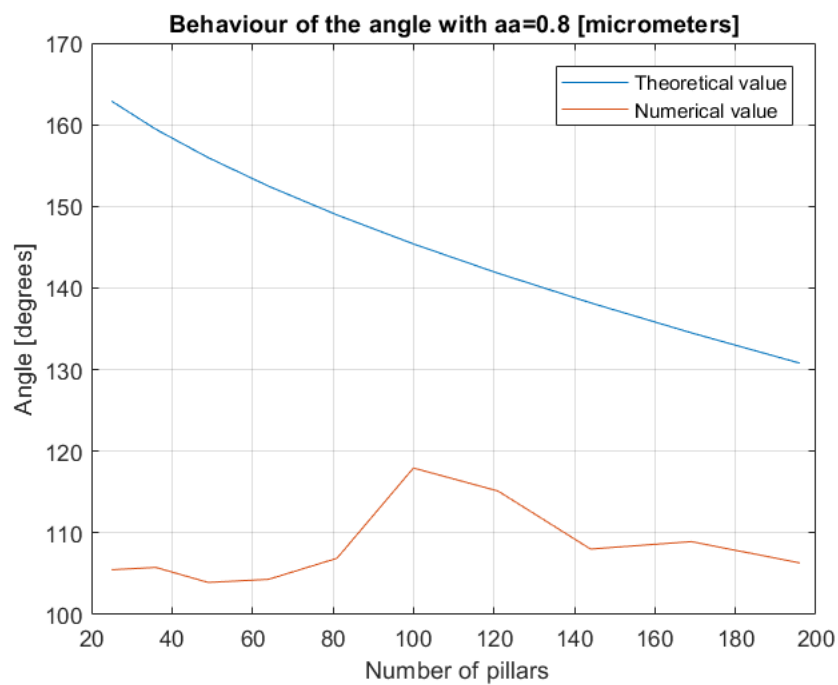


Figure 40 - Computational angle and Theoretical angle related to the number of pillars (size of pillar = 0.8 micrometers). The Theoretical value of the angle is obtained from Cassie-Baxter equation.

In order to have an indication on the validity of the simulation a factor to consider is the relative error necessary to understand how much the numerical model lends itself to simulate this situation (Figure 41). The following formulation is used:

$$R. Error [\%] = \frac{|\theta_{Cassie-Baxter} - \theta_{Simulation}|}{\theta_{Cassie-Baxter}} \quad (4.3)$$

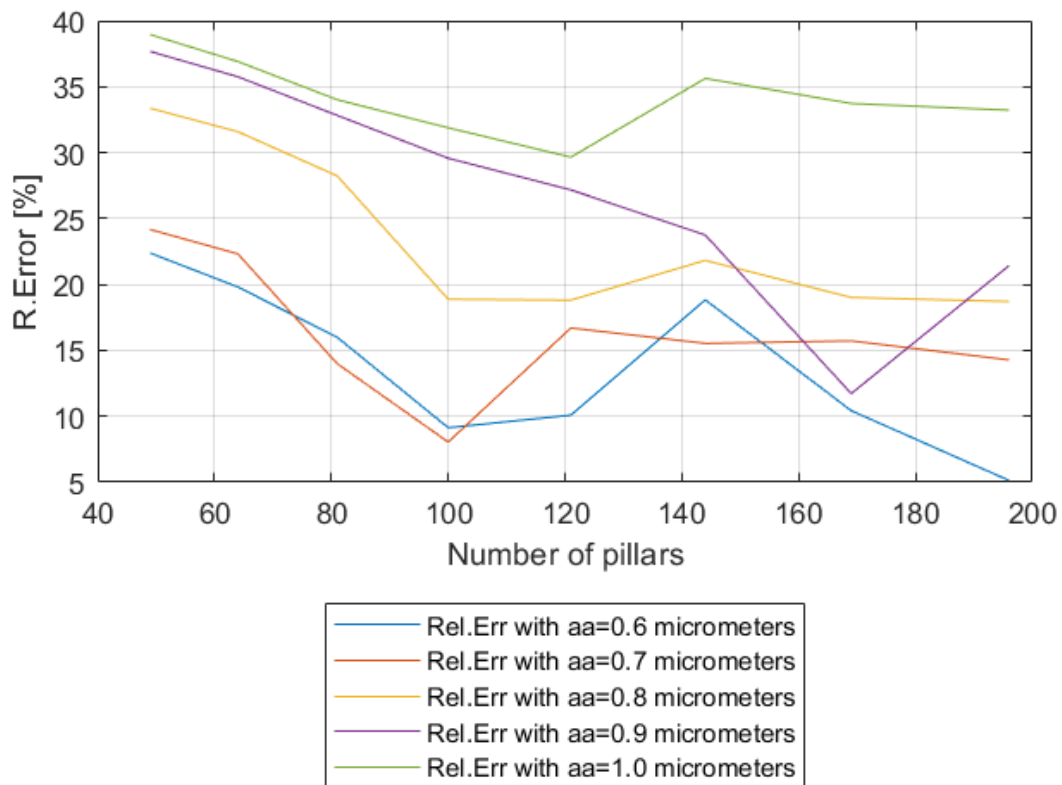


Figure 41 – Relative Error calculate for different values of pillar's edges vs number of pillars

The graph shows that the model used allows to have a relative variable error that is contained within 25% with regard to simulations with pillars with dimensions equal to 0.6 and 0.7 μm . While with increasing sides the error rises (except for some peaks to be attributed mainly to

the uncertainty in software measurement) and consequently the model does not describe reality at its best.

4.1.2 Effect of volume

Another analysis foresees the variation of the water volume, keeping constant the size of the pillars, the distance between them and the contact angle (120°). In particular, the volume varies from 600 to 2100 μm^3 , configurations with 144 and 64 pillars and they have two different values of side 0.7 and 1 μm .

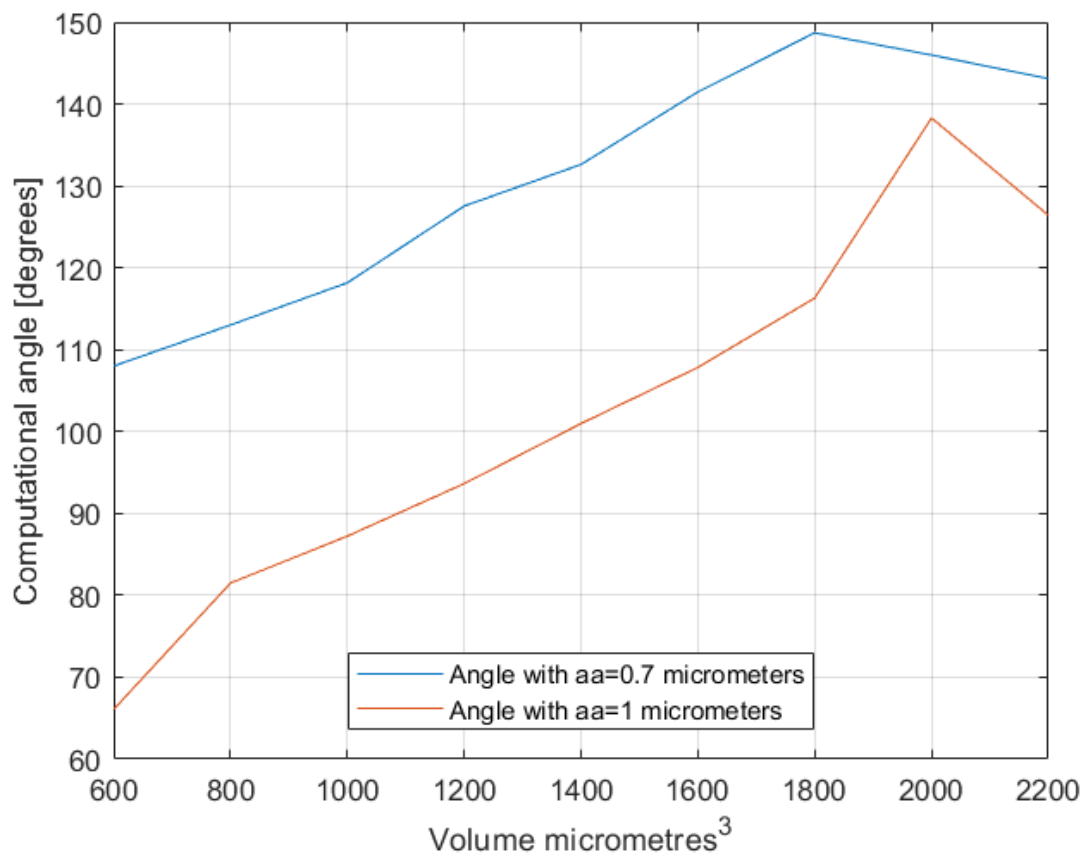


Figure 42 - Computational angle calculated using two different values for pillar's edges in function of the Volume (number of pillars = 144)

Before analyzing the trend of the graph, it should be noted that the volumes analyzed have been chosen because they allow convergence for both configurations analyzed (64 pillars and 144 pillars). For superior volumes the System does not reach the convergence and the motive is to

be found in the imposed constraint that as previously affirmed depend on the volume. Analyzing the trend of the graph, it is possible to see that as the volume increases the angle measured increases until it reaches a maximum. The maximum is reached earlier when the side of the pillar is smaller.

Also in this case the validity of the model is evaluated by comparing the value of the angle obtained with Cassie - Baxter's theoretical angle, which in fact is constant because it depends on the initial contact angle (120°) and the surface roughness. It is possible to make considerations, the simulated situation is close to the real one as the volume increases until a minimum condition is reached, which is set at $1600 \mu m^3$ with a $0.7 \mu m$ side and $2000 \mu m^3$ with a $1 \mu m$ side. The optimum condition corresponds to the right compromise between the percentage of solid at the base and the height of the drop, this is because the drop tends to reach a local balance near the pillar and this is reflected globally. Another aspect to be considered is the constraint imposed on the base, which not only keeps the surface of the pillar fixed, but also keeps the contour of the base of the drop fixed, influencing the interface energy and consequently also the final contact angle.

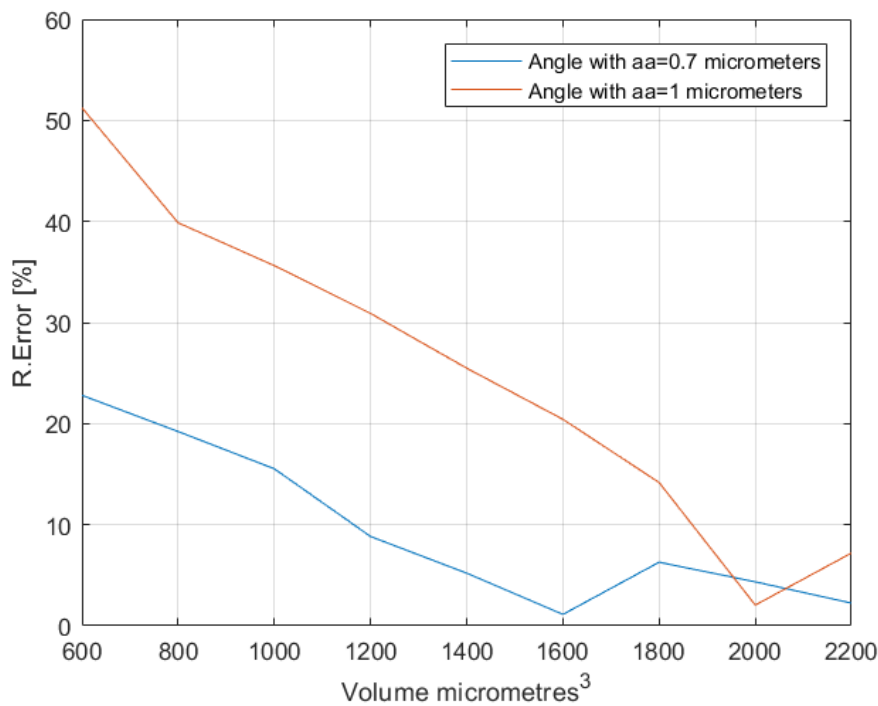


Figure 43 - Relative error calculated respect the Theoretical value obtained using the Cassie – Baxter theory in function of the Volume (number of pillars = 144)

A similar discussion is made when considering less pillars (64), analyzing two configurations corresponding to two different side measurements ($0.7 \mu m$ e $1 \mu m$). Also in this case the contact angle is equal to 120° and the volumes for which the simulation reaches convergence are between 600 to $2600 \mu m^3$. The angle measured in situations with a side equal to $1 \mu m$ is lower than the value of the angle measured with a side equal to $0.7 \mu m$, the reason for this behavior is mainly geometric because in the first case the base area is larger and therefore the drop tends to expand more on it.

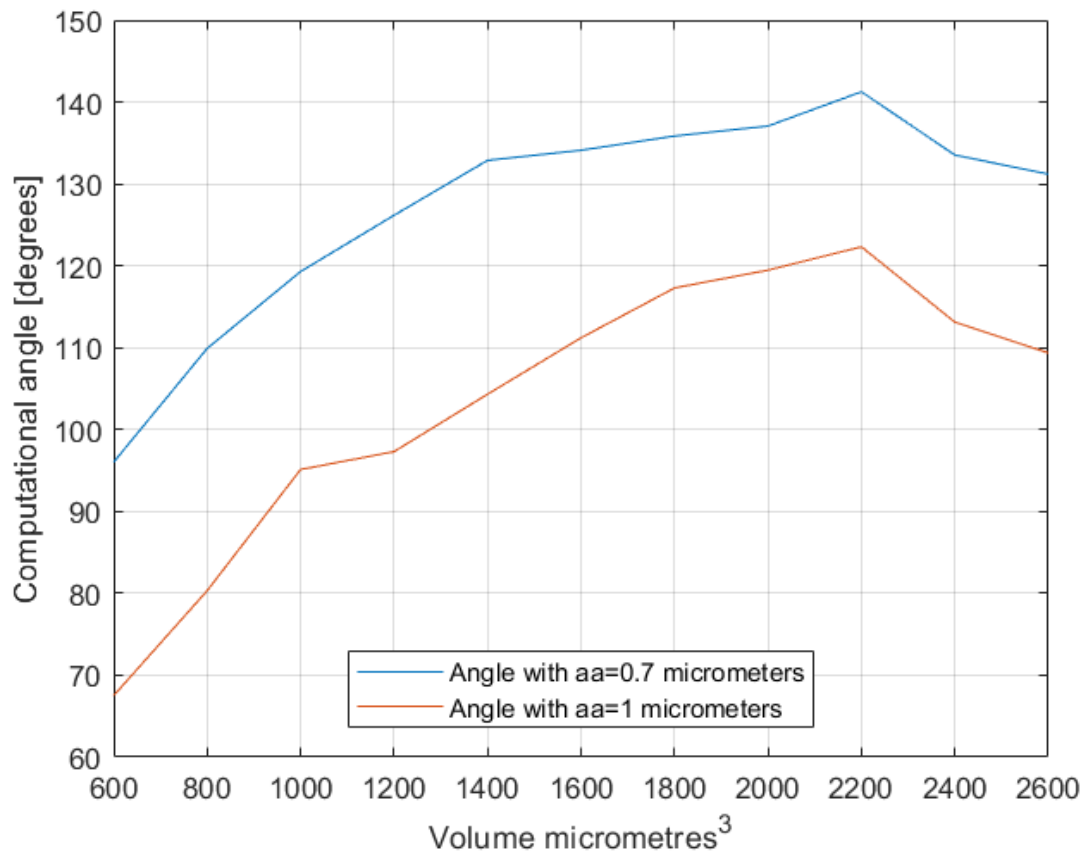


Figure 44 - Computational angle calculated using two different values for pillar's edges in function of the Volume (number of pillars =64)

In addition, in this case the angle value obtained was compared with the theoretical value calculated with Cassie - Baxter. The relative error shows a descending behavior until reaching a minimum where the simulation solution is closer to the theoretical value. Also in this case the motivation of this behavior has a geometric character related to the relationship between

base air and volume but also an energetic character, in fact the software tries to find the equilibrium condition in the light of the imposed constraints that have a significant influence.

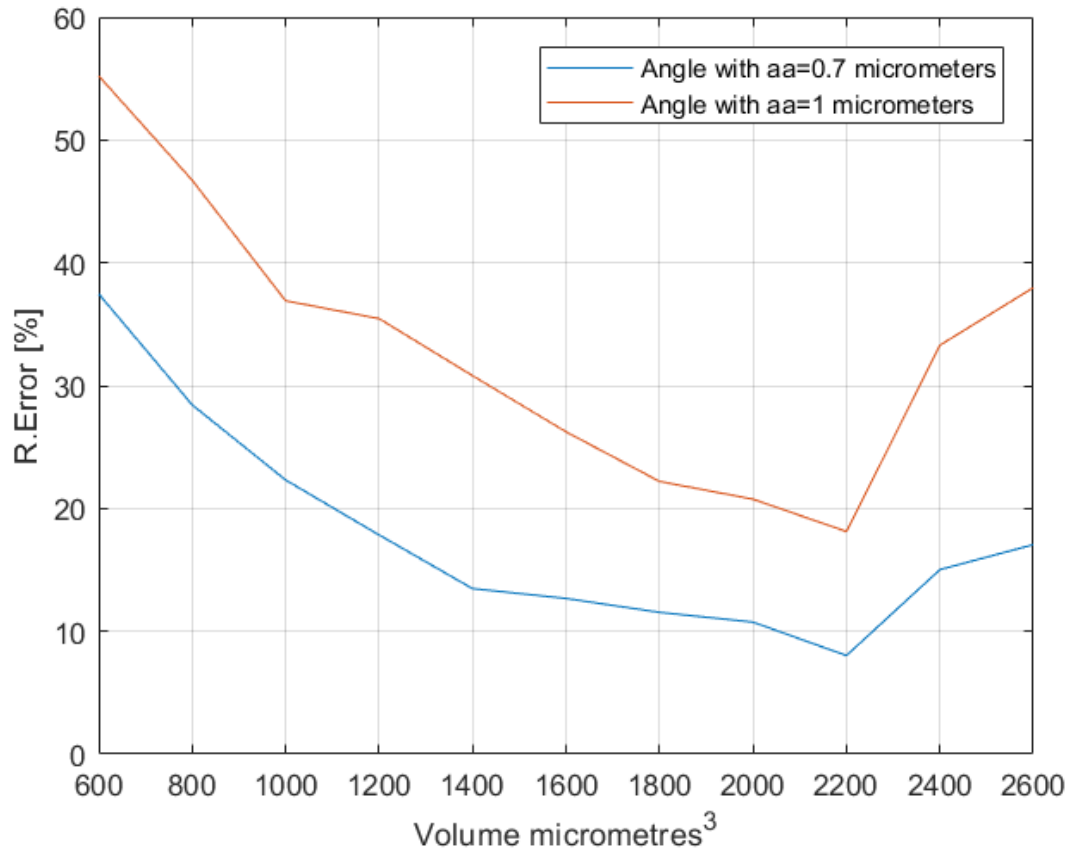


Figure 45- Relative error calculated respect the Theoretical value obtained using the Cassie – Baxter theory in function of the Volume (Number of pillars = 64)

4.1.3 Effect of contact angle

A further analysis has foreseen the variation of the contact angle, keeping constant the number of pillars (64 and 144), the volume (1000 and $2000 \mu m^3$) and the size of the pillars ($0.7 \mu m$) themselves.

Specifically, initial angles higher than 90° (from 100° to 180°) to simulate the behavior of hydrophobic and superhydrophobic material.

With reference to the Figures 46 and 47, it can be noted that as the initial imposed contact angle increases, so does the angle measured at the end of the simulation due to the effect of

roughness with regard to a fixed volume of $1000 \mu m^3$. In the case of a volume equals to $2000 \mu m^3$ the behaviour of the measured angle varies and this is determined by the fact that the software tries to reach a situation of equilibrium also dictated by the fact that on the basic contour there is a condition depending on the cosine.

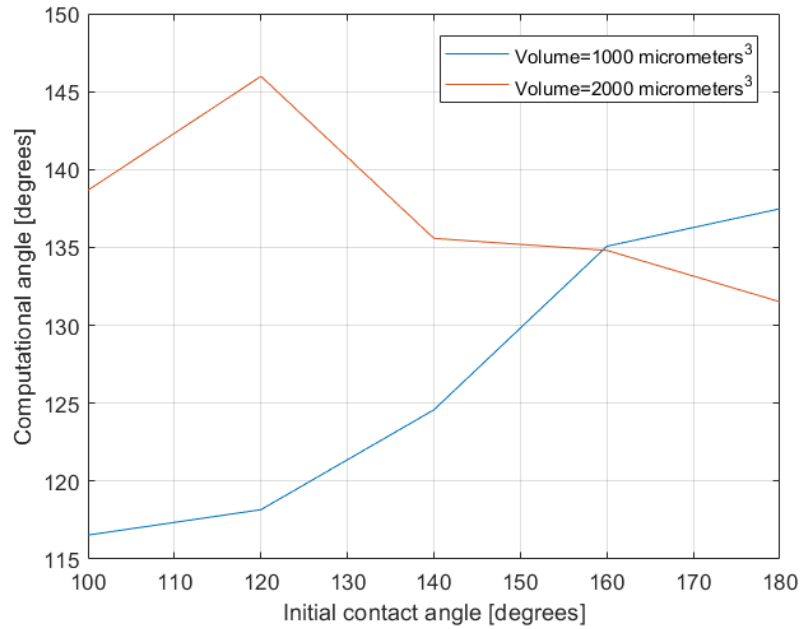


Figure 46 - Computational Angle calculating using two different Volumes for the water drop in function of the Initial Contact angle (number of pillars = 144)

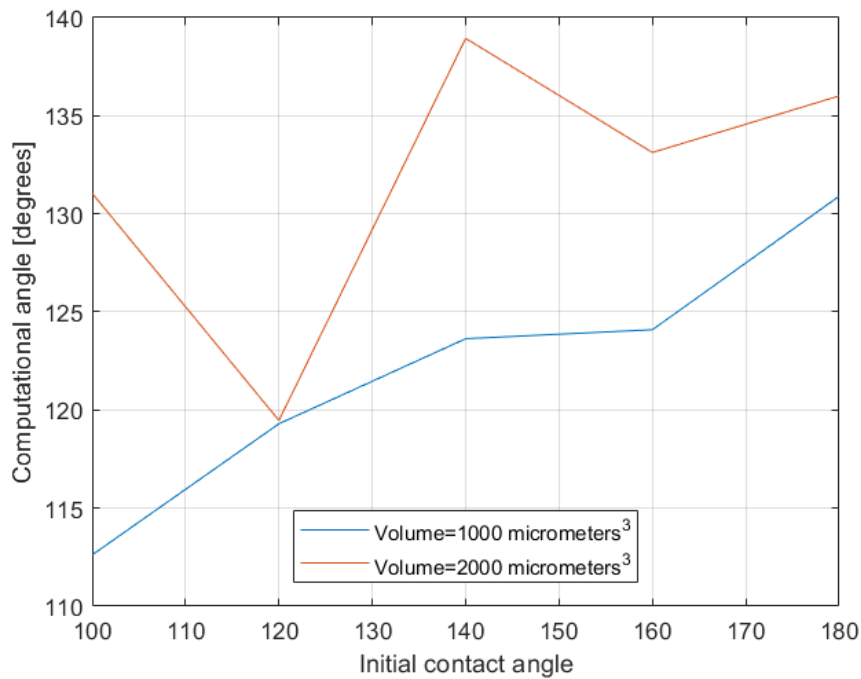


Figure 47 - Computational Angle calculating using two different Volumes for the water drop in function of the Initial Contact angle (Number of pillars = 64)

Also in this step the last step to carry out is the calculation of the relative error, what is evident is that the relative error increases with the increase of the angle and this is index of the fact that the model becomes less truthful when we approach angles of 180° that is to behaviors that could be defined of superhydrophobicity.

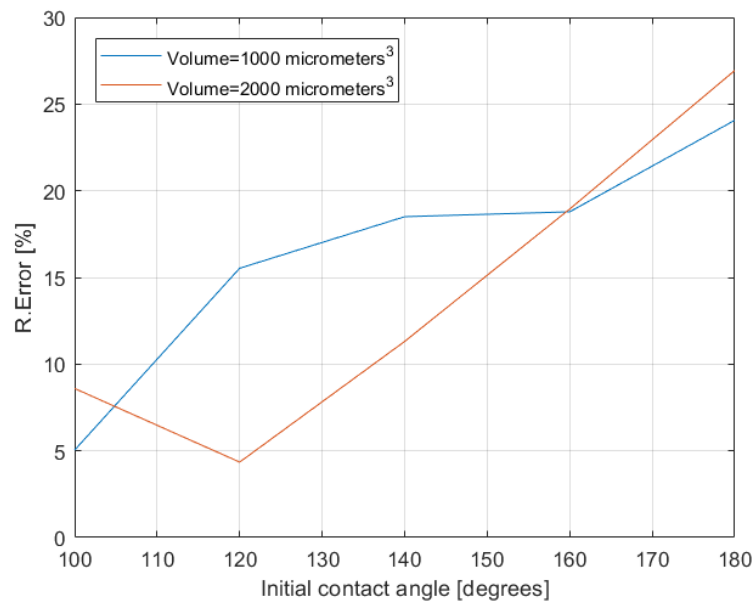


Figure 48 – Behavior of the relative error calculated respect the Theoretical value obtained by Cassie – Baxter in function of the contact angle (Number of pillars = 144)

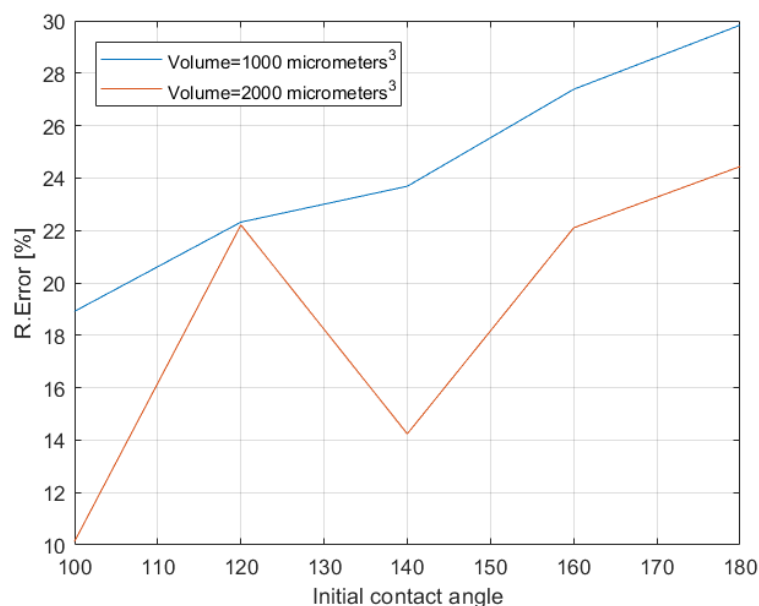


Figure 49 - Behavior of the relative error calculated respect the Theoretical value obtained by Cassie – Baxter in function of the contact angle (Number of pillars = 64)

4.2 Analysis on 3D Pillars

The next part of the simulation is based on simulations with pillars in 3D dimensions, specifically it has been simulated the behavior with 4 pillars at the base and the angle has been changed in a range from 70 to 180 degrees to analyze three different types of material: hydrophilic material, hydrophobic material and superhydrophobic material. In addition, different constraints have been set in order to simulate and analyze three different behavior states: Wenzel State, Cassie-Baxter model and Metastable model.

4.2.1 Wenzel state

In this case, to simulate a behavior like the one described by Wenzel, the drop was supposed to fill the spaces between the pillars. To do so, the drop was constructed by imposing three different types of geometric constraint on the lower sides of the drop according to their positions. The ones in contact with the top surface of the pillars will have a $z=h$ condition where h is the height of the pillar, the transversal ones will have a condition that forces them to follow the side of the pillar and finally the ones in contact with the bottom surface will have a $z = 0$ condition.



Figure 50 - Initial configuration for simulation Wenzel State

Using ImageJ the computational contact angle has been measured:

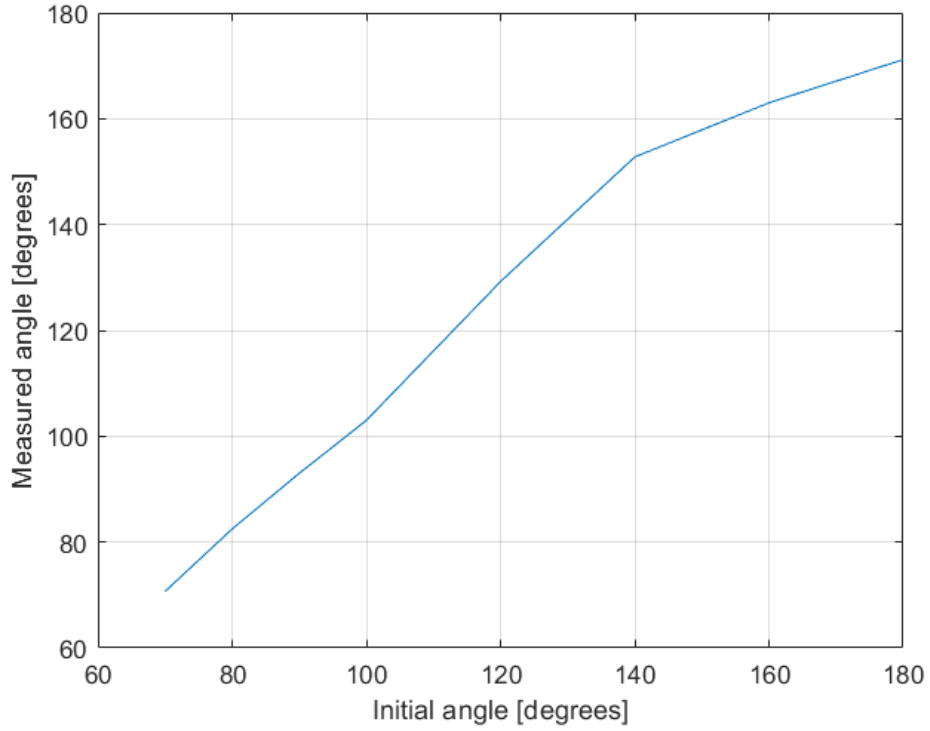


Figure 51 - Behavior of the computational angle vs value of initial contact angle

In order to quantify the validity of the model, it is appropriate to compare it with the theoretical value that can be obtained by means of the relationship assumed by Wenzel:

$$\cos \theta_{Wenzel} = r \cos \theta_{initial} \quad (4.4)$$

It is therefore necessary to determine the factor r to take into account the roughness calculated as follows:

$$r = \frac{A_{actual}}{A_{apparent}} \quad (4.5)$$

To calculate the Areas the proper function of AutoCad 2D has been used. After the calculation of r , using the equation (4.4), the corresponded angle has been founded (Figure 52)

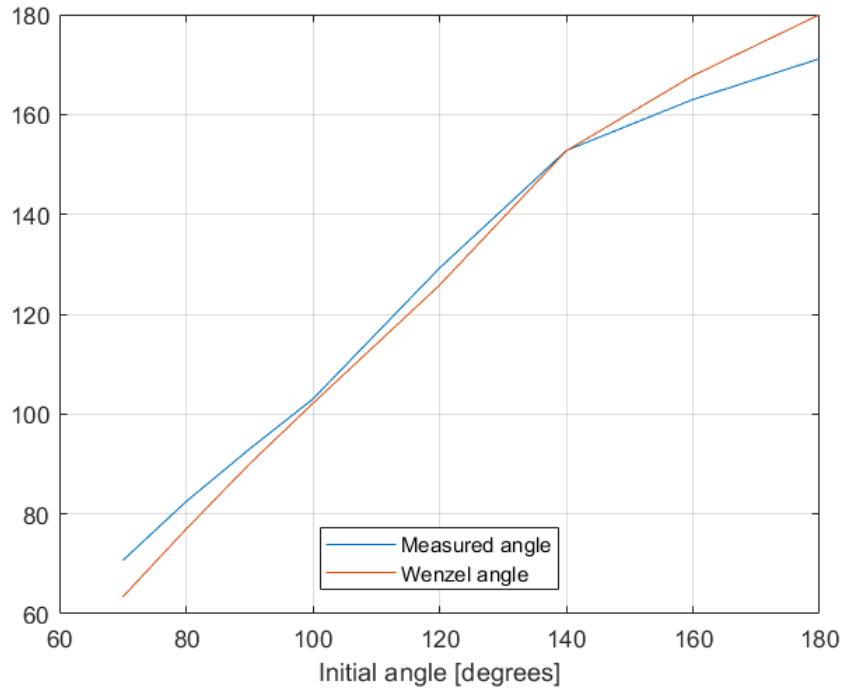


Figure 52 - Comparison between measured angle and Wenzel angle

In order to quantify the difference between the two angles it is appropriate to measure the distance between the two data by measuring the relative error as follows:

$$error [\%] = \frac{|\theta_{Wenzel} - \theta_{initial}|}{\theta_{Wenzel}} \quad (4.6)$$

Analyzing the resulting graph (Figure 53) it is highlighted the fact that the simulation returns values quite close to the theoretical value, in fact the R. error varies between 11% and <1%.

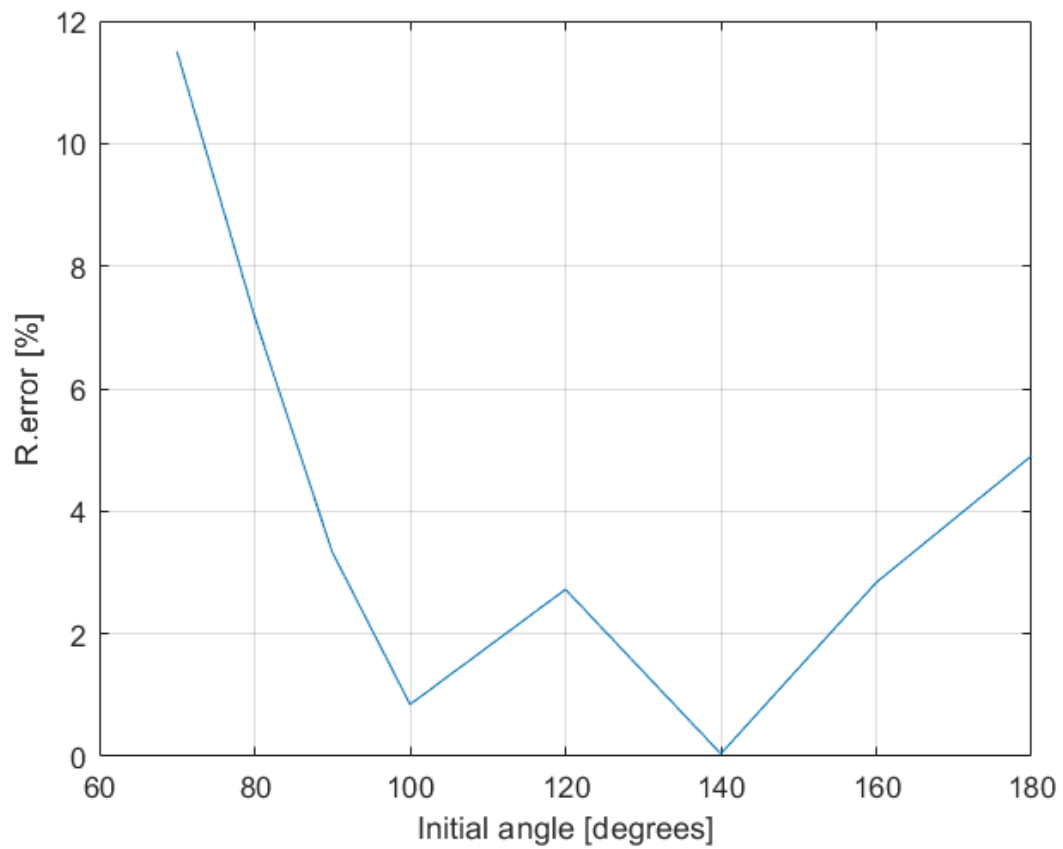


Figure 53 – Behavior of relative error for Wenzel model simulation

4.2.2 Cassie – Baxter model

In this situation, in order to simulate the Cassie – Baxter model only a geometrical condition has been imposed on the water edge, in particular the condition states cannot go below the plane with z corresponding to the height of the upper face of the pillar.



Figure 54 - Initial configuration for Cassie – Baxter model simulation

In addition, in this case, the angle obtained from the simulation is measured and it is then compared with the theoretical angle calculated with the formula (4.1) after having calculated the roughness factor as indicated by (4.2).

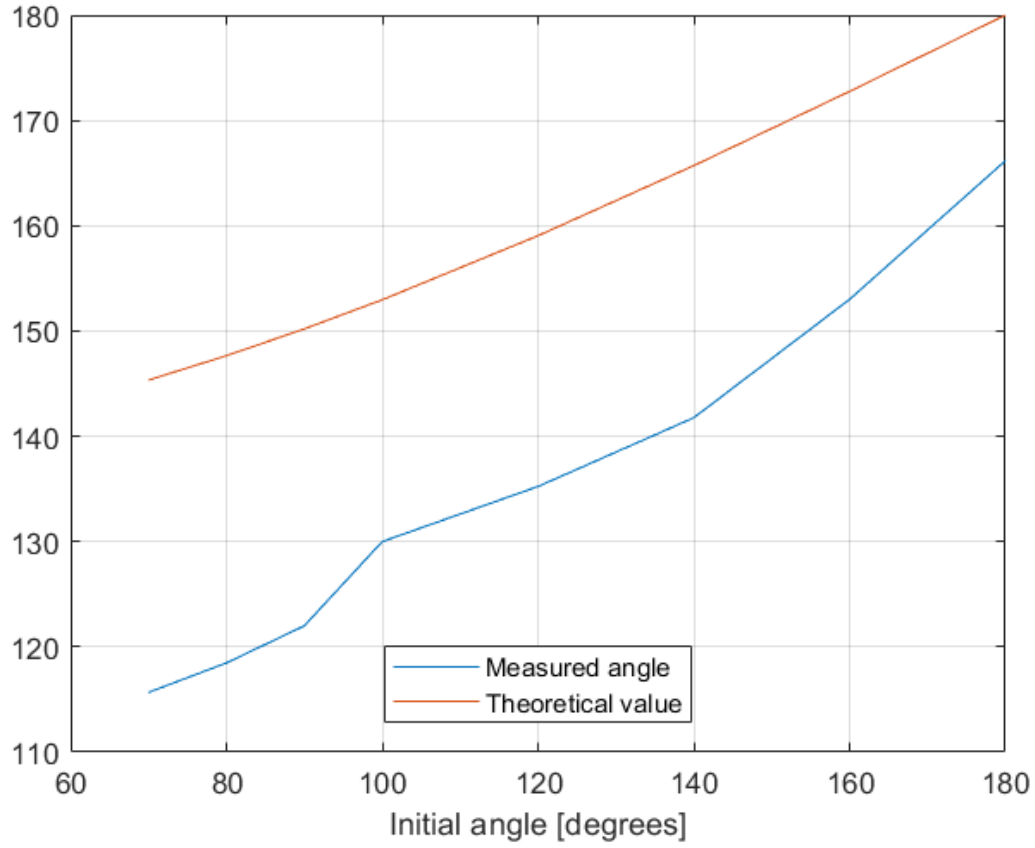


Figure 55 - Comparison between the measured angle and the theoretical angle for Cassie – Baxter simulation

Also in this case, it is possible to calculate the relative error as follow:

$$error [\%] = \frac{|\theta_{CB} - \theta_{initial}|}{\theta_{CB}} \quad (4.7)$$

In this case, compared to what we have seen before, the error presents higher values because the energy constraint on the base strongly influences the behavior of the drop that is forced to

find a minimum energy condition without modifying the imposed geometric conditions (Figure 56).

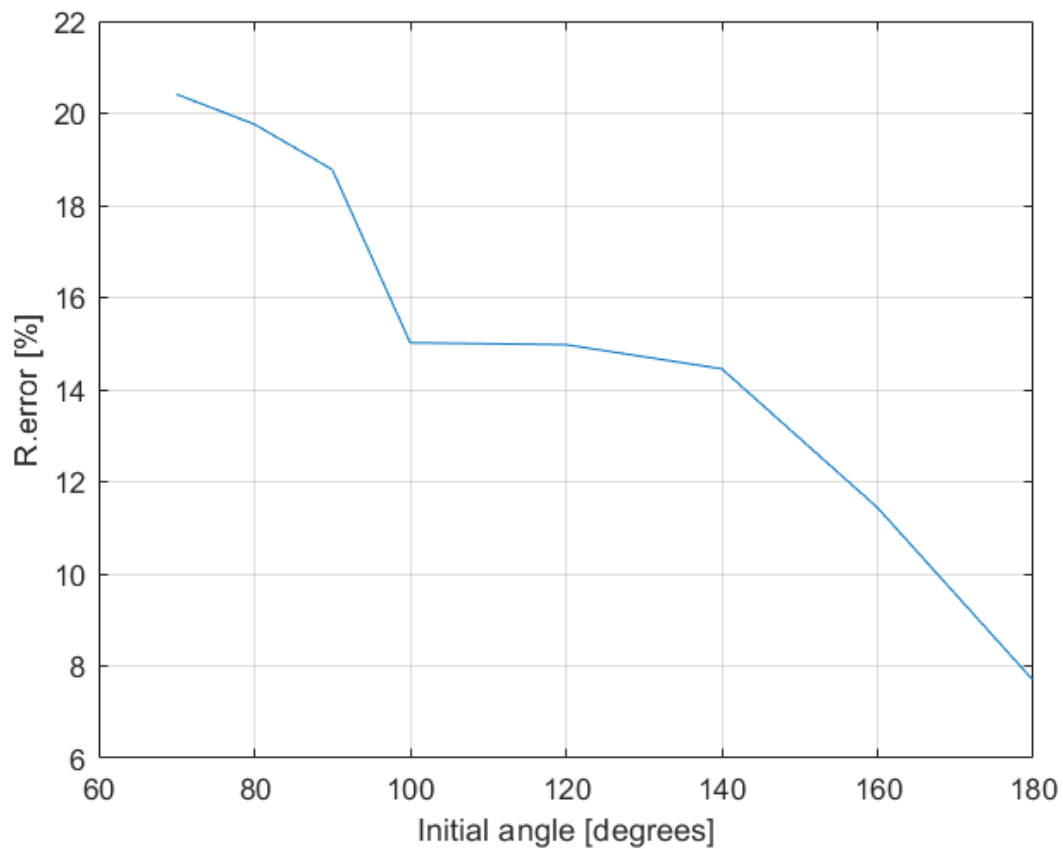


Figure 56 - Behavior of the relative error for Cassie - Baxter simulation

In any case it is possible to notice that as the angle and therefore the hydrophobicity increase, the relative error tends to go down because the energy constraint imposed tends to approach the real situation being defined in relation to the opposite of the cosine. Therefore the energetic value rises and also those of the contact angle measured by approaching the theoretical one.

4.2.3 Metastable state

The last configuration analyzed does not foresee the presence of any geometric constriction along the z coordinate (see Model Formulation for details).

In this case the drop tends to form menisci between the pillars in a state defined metastable. It can be seen that the model that best lends itself to the description of this situation is that of Cassie - Baxter, due to two main factors. The first is once again related to the software and the geometric constraints imposed on the upper face of the pillar. The second one is related to the fact that, hydrophobic materials have an overall minimum state that corresponds to Cassie's, although Wenzel's state may have a favorable energy configuration. In these cases there is an energy barrier to switch from Cassie state to Wenzel state and therefore the drop tends to stay in the metastable Cassie state unless pressure is applied that forces it to switch to Wenzel state (Figure 7) [21].

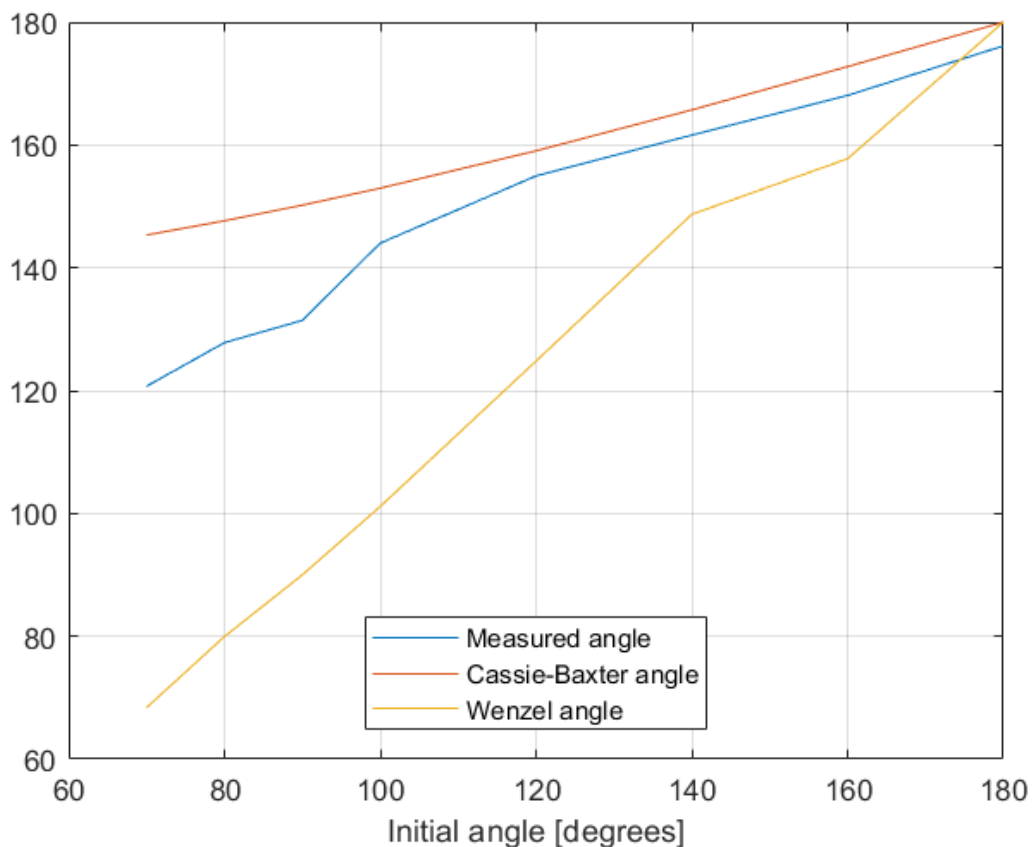


Figure 57 - Comparison between the computation angle, Cassie – Baxter angle and Wenzel angle for metastable state

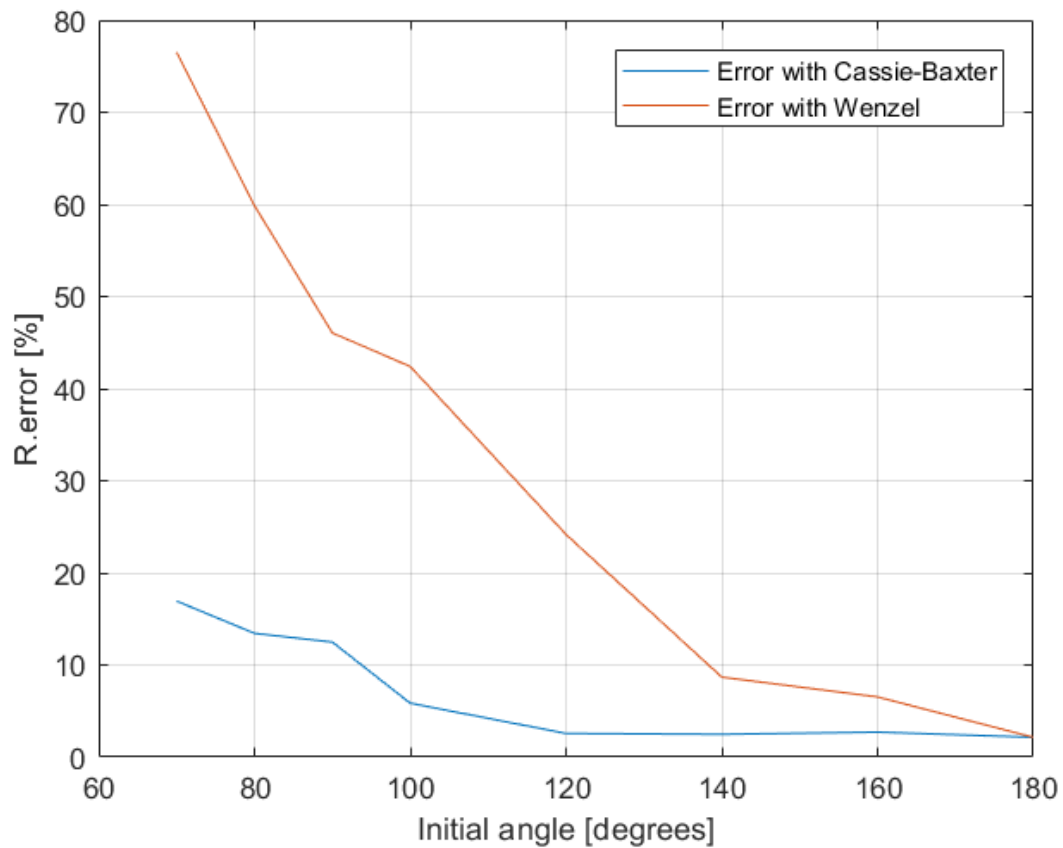


Figure 58 - Comparison between relative errors for Cassie Baxter State and Wenzel State

As anticipated, the relative error tends to be minor for minor angles using Cassie - Baxter model. The error tends to decrease as the angle considered increases, the error calculated with the Wenzel model also tends to decrease, with a greater slope until the two models are equivalent for an initial angle of 180 degrees.

4.2.4 Comparison of Metastable state with an experimental case

In order to validate the model, it is appropriate to do a comparison with some experimental data provided by Bhushan and Jung [28].

In the experimental data, the pillars have a cylindrical shape, so for having a proper comparison, the base area of pillar has been kept constant and consequently the side of the square pillar has been calculated:

$$l = \sqrt{\pi * r^2} \quad (4.8)$$

The other parameters considered are:

- h = height of pillar,
- s_p = distance between centres of two successive squares;
- Vol = volume of the drop = 5 μL
- a = dimension of the square base containing the pillars
- θ_i = initial contact angle = 120°

Table 2 - Parameters for the simulation

l [μm]	h [μm]	S_p [μm]	N° pillars	a [μm]
4.43	10	7	14	95.43
4.43	10	7.5	13	94.43
4.43	10	10	10	94.43
4.43	10	12.5	8	91.93
4.43	10	25	4	92.72
4.43	10	37.5	4	83.86
4.43	10	45	3	94.43
4.43	10	60	2	64.43
4.43	10	75	2	79.43

At this point, the computational values obtained are compared with the trend of the experimental data in order to understand how close the simulations are to reality (Figure 59 and Figure 60)

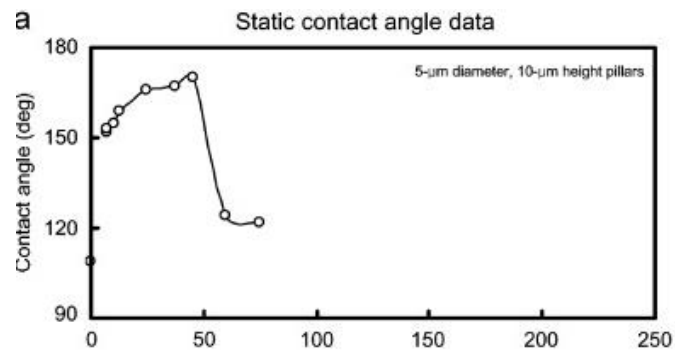


Figure 59 - Experimental values of static contact angle in function of the pitch [micrometers]. Copyright © 2007 Elsevier B.V.. License Number: 4864350259145.

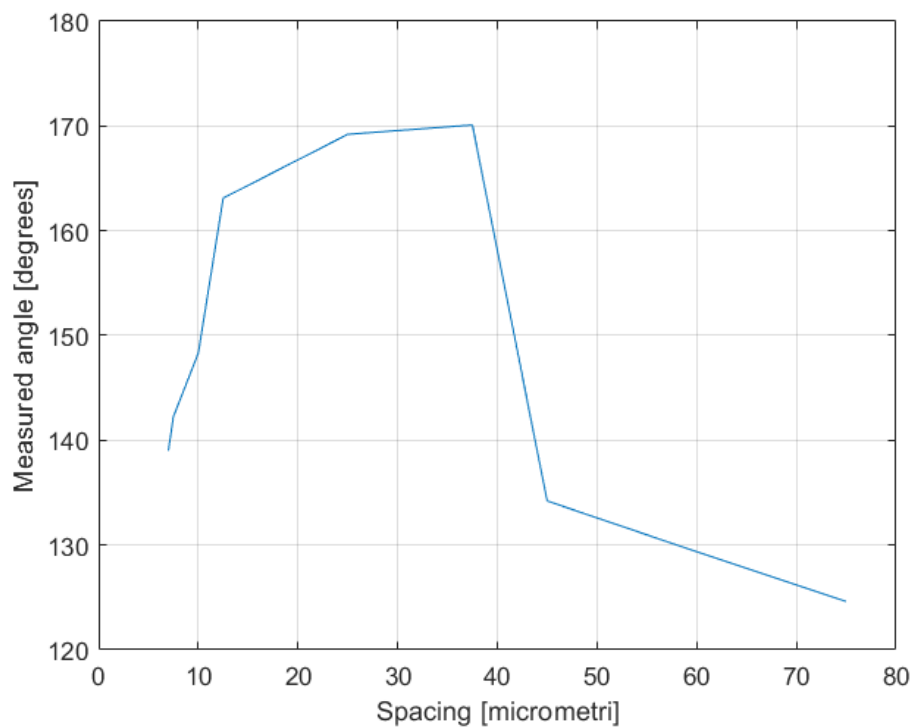


Figure 60 - Behavior of the value of the measured angle using ImageJ

The two graphs highlight the same trend showing a maximum spacing of $45 \mu m$ because, as previously highlighted, the volume of the drop allows to be distributed in an optimal way in consideration of the energy constraint at the base. Immediately after, this value begins to fall

also in consideration of the distance between the pillars that increases so the drop is in contact with a lot of air being the fraction of solid at the base reduced by a lot, the effect of the roughness is therefore very lower.

5. CONCLUSION

The main purpose of this thesis is to simulate the behavior of a drop in contact with surfaces that have a certain roughness due to the presence of pillars, such as surfaces subject to nanopattern. The simulations performed have been carried out with the help of SE – FIT.

The model analyzed lends itself to simulate, with good approximation, only a subset of situations where it is possible to define proper geometric and energetic constraints compatible with the SE - FIT optimization algorithm.

What is evident for the above-mentioned subset is a good approximation to the theoretical model of Cassie – Baxter, especially for the situation that considers the pillars flat neglecting the effect given by the volume of the pillars themselves.

Specifically it has been highlighted the fact that larger drop volumes require a greater number of pillars to achieve a situation that comes close to reality, also for angles that correspond to values of superhydrophobicity the model - while achieving convergence - shows instability.

What is appropriate to underline is that many misalignments with respect to reality are due to the need to impose reasonable approximations in order to allow numerical simulations to take place.

Furthermore, under certain assumptions, the proposed model adapts well to Wenzel's theoretical model if the situation is analyzed with 3D pillar dimensions.

In the same way, assuming you want to simulate a metastable configuration, you get relatively low errors compared to Cassie Baxter's.

Possible future analyses could focus on optimizing the topology of the pillars and their geometry (circular or hexagonal shape) with regard to 2D analysis.

As far as the 3D pillar analysis is concerned, high hydrophilicity conditions could be analyzed and also in this case we could think to modify the layout and formation of the pillars that in this study have been assimilated to parallelepipeds.

Finally, we would like to underline the usefulness of these simulations to identify superhydrophobic or superhydrophilic materials subject to self-cleaning that could be useful in many applications, for example self-cleaning surface (using the easy rolling of the water on the superhydrophobic surface), low-friction surface, anti-drop glasses and finally some types of outdoor paints.

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Appendix A - .fe Scripts

Script for the creation of a drop with 2D pillars

```
parameter angle = 120
parameter hh= 7.996668
parameter Vol = 1200.000000
parameter den = 1000*(10^(-9))
gravity_constant 0
#define T1 (-cos(angle*pi/180))
constraint 1
formula: z = 0
energy:
e1: -T1*z
e2: 0
e3: 0
vertices
1 0.000000 0.000000 0.000000 fixed
2 0.000000 0.700000 0.000000 fixed
3 0.000000 1.050000 0.000000 fixed
4 0.000000 1.750000 0.000000 fixed
5 0.000000 2.100000 0.000000 fixed
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551 564 563 constraint 1 fixed	602 128 129
552 563 539 constraint 1 fixed	603 130 131
553 541 542 constraint 1 fixed	604 132 133
554 542 566 constraint 1 fixed	605 134 135
555 566 565 constraint 1 fixed	606 136 137
556 565 541 constraint 1 fixed	607 138 139
557 543 544 constraint 1 fixed	608 140 141
558 544 568 constraint 1 fixed	609 142 143
559 568 567 constraint 1 fixed	610 170 171
560 567 543 constraint 1 fixed	611 172 173
561 545 546 constraint 1 fixed	612 174 175
562 546 570 constraint 1 fixed	613 176 177
563 570 569 constraint 1 fixed	614 178 179
564 569 545 constraint 1 fixed	615 180 181
565 547 548 constraint 1 fixed	616 182 183
566 548 572 constraint 1 fixed	617 184 185
567 572 571 constraint 1 fixed	618 186 187
568 571 547 constraint 1 fixed	619 188 189
569 549 550 constraint 1 fixed	620 190 191

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719 46 70
720 48 72
721 73 97
722 76 100

723 78 102	774 276 300
724 80 104	775 278 302
725 82 106	776 280 304
726 84 108	777 282 306
727 86 110	778 284 308
728 88 112	779 286 310
729 90 114	780 288 312
730 92 116	781 313 337
731 94 118	782 316 340
732 96 120	783 318 342
733 121 145	784 320 344
734 124 148	785 322 346
735 126 150	786 324 348
736 128 152	787 326 350
737 130 154	788 328 352
738 132 156	789 330 354
739 134 158	790 332 356
740 136 160	791 334 358
741 138 162	792 336 360
742 140 164	793 361 385
743 142 166	794 364 388
744 144 168	795 366 390
745 169 193	796 368 392
746 172 196	797 370 394
747 174 198	798 372 396
748 176 200	799 374 398
749 178 202	800 376 400
750 180 204	801 378 402
751 182 206	802 380 404
752 184 208	803 382 406
753 186 210	804 384 408
754 188 212	805 409 433
755 190 214	806 412 436
756 192 216	807 414 438
757 217 241	808 416 440
758 220 244	809 418 442
759 222 246	810 420 444
760 224 248	811 422 446
761 226 250	812 424 448
762 228 252	813 426 450
763 230 254	814 428 452
764 232 256	815 430 454
765 234 258	816 432 456
766 236 260	817 457 481
767 238 262	818 460 484
768 240 264	819 462 486
769 265 289	820 464 488
770 268 292	821 466 490
771 270 294	822 468 492
772 272 296	823 470 494
773 274 298	824 472 496

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 846 24 580
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 848 576 579
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 1 577 -8 -7 710 -53 -56 -588 -50 -49 -709 -3 -2
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 2 578 -12 -11 711 -57 -60 -589 -54 -710 -6
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 3 579 -16 -15 712 -61 -64 -590 -58 -711 -10
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 4 580 -20 -19 713 -65 -68 -591 -62 -712 -14
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 5 581 -24 -23 714 -69 -72 -592 -66 -713 -18
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 7 583 -32 -31 716 -77 -80 -594 -74 -715 -26
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 8 584 -36 -35 717 -81 -84 -595 -78 -716 -30
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 10 586 -44 -43 719 -89 -92 -597 -86 -718 -38
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 11 587 -48 -47 720 -93 -96 -598 -90 -719 -42
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 12 588 -55 722 -101 -104 -599 -98 -97 -721 -51
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 13 599 -103 734 -149 -152 -610 -146 -145 -733
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14 610 -151 746 -197 -200 -621 -194 -193 -745
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 15 621 -199 758 -245 -248 -632 -242 -241 -757
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 16 632 -247 770 -293 -296 -643 -290 -289 -769
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 17 643 -295 782 -341 -344 -654 -338 -337 -781
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 18 654 -343 794 -389 -392 -665 -386 -385 -793
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 19 665 -391 806 -437 -440 -676 -434 -433 -805
 -387 frontcolor blue backcolor yellow
 20 676 -439 818 -485 -488 -687 -482 -481 -817
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 21 687 -487 830 -533 -536 -698 -530 -529 -829
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 22 589 -59 723 -105 -108 -600 -102 -722
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 23 590 -63 724 -109 -112 -601 -106 -723
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 26 593 -75 727 -121 -124 -604 -118 -726
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 27 594 -79 728 -125 -128 -605 -122 -727
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 28 595 -83 729 -129 -132 -606 -126 -728
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 29 596 -87 730 -133 -136 -607 -130 -729
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 30 597 -91 731 -137 -140 -608 -134 -730
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 31 598 -95 732 -141 -144 -609 -138 -731
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 32 600 -107 735 -153 -156 -611 -150 -734
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 35 603 -119 738 -165 -168 -614 -162 -737
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 36 604 -123 739 -169 -172 -615 -166 -738
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 37 605 -127 740 -173 -176 -616 -170 -739
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 38 606 -131 741 -177 -180 -617 -174 -740
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43 612 -159 748 -205 -208 -623 -202 -747
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45 614 -167 750 -213 -216 -625 -210 -749
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53 623 -207 760 -253 -256 -634 -250 -759
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54 624 -211 761 -257 -260 -635 -254 -760
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55 625 -215 762 -261 -264 -636 -258 -761
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56 626 -219 763 -265 -268 -637 -262 -762
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58 628 -227 765 -273 -276 -639 -270 -764
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59 629 -231 766 -277 -280 -640 -274 -765
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61 631 -239 768 -285 -288 -642 -282 -767
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69 640 -279 778 -325 -328 -651 -322 -777
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70 641 -283 779 -329 -332 -652 -326 -778
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75 647 -311 786 -357 -360 -658 -354 -785
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78 650 -323 789 -369 -372 -661 -366 -788
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79 651 -327 790 -373 -376 -662 -370 -789
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80 652 -331 791 -377 -380 -663 -374 -790
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81 653 -335 792 -381 -384 -664 -378 -791
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83 656 -351 796 -397 -400 -667 -394 -795
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84 657 -355 797 -401 -404 -668 -398 -796
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87 660 -367 800 -413 -416 -671 -410 -799
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89 662 -375 802 -421 -424 -673 -418 -801
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 92 666 -395 807 -441 -444 -677 -438 -806
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 93 667 -399 808 -445 -448 -678 -442 -807
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 94 668 -403 809 -449 -452 -679 -446 -808
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 95 669 -407 810 -453 -456 -680 -450 -809
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 105 680 -455 822 -501 -504 -691 -498 -821
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 106 681 -459 823 -505 -508 -692 -502 -822
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112 688 -491 831 -537 -540 -699 -534 -830
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 113 689 -495 832 -541 -544 -700 -538 -831
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 114 690 -499 833 -545 -548 -701 -542 -832
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 116 692 -507 835 -553 -556 -703 -550 -834
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 120 696 -523 839 -569 -572 -707 -566 -838
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 121 697 -527 840 -573 -576 -708 -570 -839
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 122 844 841 842 843
 123 847 -841 -845 -4 709 -52 721 -100 733 -
 148 745 -196 757 -244 769 -292 781 -340 793
 -388 805 -436 817 -484 829 -532
 124 -844 -846 -45 -587 -41 -586 -37 -585 -33 -
 584 -29 -583 -25 -582 -21 -581 -17 -580 -13 -
 579 -9 -578 -5 -577 -1 845
 125 -574 -840 -526 -828 -478 -816 -430 -804 -
 382 -792 -334 -780 -286 -768 -238 -756 -190 -
 744 -142 -732 -94 -720 -46 846 -843 -848
 126 848 -842 -847 -531 698 -535 699 -539 700
 -543 701 -547 702 -551 703 -555 704 -559 705
 -563 706 -567 707 -571 708 -575
 bodies
 1 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33
 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48
 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63
 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78
 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93
 94 95 96 97 98 99 100 101 102 103 104 105
 106 107 108 109 110 111 112 113 114 115
 116 117 118 119 120 121 122 123 124 125
 126 volume Vol density den

Script for the creation of a drop with 3D pillars

```

parameter angle=80
parameter aa=40
parameter dd=220
parameter hh=40
parameter hp=hh/2
parameter bb=6*aa/2
parameter vol=dd*dd*4*dd-4*aa*aa*hh
parameter dens=1000*10^-9

#define T (-cos(angle*pi)/180)

constraint 1
formula: x=-bb/2

constraint 2
formula: x=-aa-bb/2

constraint 3
formula: y=-bb/2

constraint 4
formula: y=-aa-bb/2

constraint 5
formula: x=-bb/2
energy:
e1:0
e2:-T*z-1/2*hh^2*z
e3:0

content:
c1: 0
c2:-hh*z
c3:0

constraint in5con nonpositive
formula: x=-bb/2

constraint 6
formula: x=-aa-bb/2
energy:
e1:0
e2:T*z+1/2*hh^2*z
e3:0

content:
c1: 0
c2:hh*z

c3:0

constraint in6con nonnegative
formula: x=-aa-bb/2

constraint 7
formula: y=-bb/2
energy:
e1:T*z+1/2*hh^2*z
e2:0
e3:0

content:
c1: 0
c2:hh*z
c3:0

constraint in7con nonpositive
formula: y=-bb/2

constraint 8
formula: y=-aa-bb/2
energy:
e1:-T*z-1/2*hh^2*z
e2:0
e3:0

content:
c1: -hh*z
c2:0
c3:0

constraint in8con nonnegative
formula: y=-aa-bb/2

constraint 9
formula: x=bb/2

constraint 10
formula: x=aa + bb/2

constraint 11
formula: y=-bb/2

constraint 12
formula: y=-aa-bb/2

constraint 13

```

formula: $x=aa+bb/2$
 energy:
 e1:0
 e2: $-T*z-1/2*hh^2*z$
 e3:0

content:
 c1: 0
 c2: $-hh*z$
 c3:0

constraint in13con nonpositive
 formula: $x=aa+bb/2$

constraint 14
 formula: $x=bb/2$
 energy:
 e1:0
 e2: $T*z+1/2*hh^2*z$
 e3:0

content:
 c1: 0
 c2: $hh*z$
 c3:0

constraint in14con nonnegative
 formula: $x=bb/2$

constraint 15
 formula: $y=-bb/2$
 energy:
 e1: $T*z+1/2*hh^2*z$
 e2:0
 e3:0

content:
 c1: $hh*z$
 c2:0
 c3:0

constraint in15con nonpositive
 formula: $y=-bb/2$

constraint 16
 formula: $y=-aa-bb/2$
 energy:
 e1: $-T*z-1/2*hh^2*z$
 e2:0

e3:0

content:
 c1: $-hh*z$
 c2:0
 c3:0

constraint in16con nonnegative
 formula: $y=-aa-bb/2$

constraint 17
 formula: $x=-bb/2$

constraint 18
 formula: $x=-aa-bb/2$

constraint 19
 formula: $y=bb/2$

constraint 20
 formula: $y=aa+bb/2$

constraint 21
 formula: $x=-bb/2$
 energy:
 e1:0
 e2: $-T*z-1/2*hh^2*z$
 e3:0

content:
 c1: 0
 c2: $-hh*z$
 c3:0

constraint in21con nonpositive
 formula: $x=-bb/2$

constraint 22
 formula: $x=-aa-bb/2$
 energy:
 e1:0
 e2: $T*z+1/2*hh^2*z$
 e3:0

content:
 c1: 0
 c2: $hh*z$
 c3:0

constraint in22con nonnegative
formula: $x = -aa - bb/2$

constraint 23
formula: $y = aa + bb/2$
energy:
e1: $T \cdot z + 1/2 \cdot hh^2 \cdot z$
e2: 0
e3: 0

constraint in23con nonpositive
formula: $y = aa + bb/2$

constraint 24
formula: $y = bb/2$
energy:
e1: $-T \cdot z - 1/2 \cdot hh^2 \cdot z$
e2: 0
e3: 0

constraint in24con nonnegative
formula: $y = bb/2$

constraint 25
formula: $x = aa + bb/2$

constraint 26
formula: $x = bb/2$

constraint 27
formula: $y = aa + bb/2$

constraint 28
formula: $y = bb/2$

constraint 29
formula: $x = aa + bb/2$
energy:
e1: 0
e2: $-T \cdot z - 1/2 \cdot hh^2 \cdot z$
e3: 0

constraint in29con nonpositive
formula: $x = aa + bb/2$

constraint 30
formula: $x = bb/2$
energy:
e1: 0
e2: $T \cdot z + 1/2 \cdot hh^2 \cdot z$

e3: 0

constraint in30con nonnegative
formula: $x = bb/2$

constraint 31
formula: $y = aa + bb/2$
energy:
e1: $T \cdot z + 1/2 \cdot hh^2 \cdot z$
e2: 0
e3: 0

content:
c1: $hh \cdot z$
c2: 0
c3: 0

constraint in31con nonpositive
formula: $y = aa + bb/2$

constraint 32
formula: $y = bb/2$
energy:
e1: $-T \cdot z - 1/2 \cdot hh^2 \cdot z$
e2: 0
e3: 0

content:
c1: $-hh \cdot z$
c2: 0
c3: 0

constraint in32con nonnegative
formula: $y = bb/2$

constraint bottom nonnegative
formula: $z = -hp$

constraint top nonpositive
formula: $z = hh$

vertices
1 -aa-bb/2 -aa-bb/2 0 constraint 6, 8, bottom, top
2 -bb/2 -aa-bb/2 0 constraint 5, 8, bottom, top
3 -bb/2 -bb/2 0 constraint 5, 7, bottom, top
4 -aa-bb/2 -bb/2 0 constraint 6, 7, bottom, top
5 -aa-bb/2 -aa-bb/2 hh fixed

6 -bb/2 -aa-bb/2 hh fixed
 7 -bb/2 -bb/2 hh fixed
 8 -aa-bb/2 -bb/2 hh fixed

9 bb/2 -aa-bb/2 0 constraint 16, 14, bottom, top
 10 aa+bb/2 -aa-bb/2 0 constraint 13, 16, bottom, top
 11 aa+bb/2 -bb/2 0 constraint 15, 13, bottom, top
 12 bb/2 -bb/2 0 constraint 14, 15, bottom, top
 13 bb/2 -aa-bb/2 hh fixed
 14 aa+bb/2 -aa-bb/2 hh fixed
 15 aa+bb/2 -bb/2 hh fixed
 16 bb/2 -bb/2 hh fixed

17 -aa-bb/2 bb/2 0 constraint 24, 22, bottom, top
 18 -bb/2 bb/2 0 constraint 21, 24, bottom, top
 19 -bb/2 aa+bb/2 0 constraint 23, 21, bottom, top
 20 -aa-bb/2 aa+bb/2 0 constraint 22, 23, bottom, top
 21 -aa-bb/2 bb/2 hh fixed
 22 -bb/2 bb/2 hh fixed
 23 -bb/2 aa+bb/2 hh fixed
 24 -aa-bb/2 aa+bb/2 hh fixed

25 bb/2 bb/2 0 constraint 32, 30, bottom, top
 26 aa+bb/2 bb/2 0 constraint 29,32, bottom, top
 27 aa+bb/2 aa+bb/2 0 constraint 31, 29, bottom, top
 28 bb/2 aa+bb/2 0 constraint 30, 31, bottom, top
 29 bb/2 bb/2 hh fixed
 30 aa+bb/2 bb/2 hh fixed
 31 aa+bb/2 aa+bb/2 hh fixed
 32 bb/2 aa+bb/2 hh fixed

33 -aa-bb/2 -aa-bb/2 -hp fixed
 34 -bb/2 -aa-bb/2 -hp fixed
 35 -bb/2 -bb/2 -hp fixed
 36 -aa-bb/2 -bb/2 -hp fixed
 37 bb/2 -aa-bb/2 -hp fixed
 38 aa+bb/2 -aa-bb/2 -hp fixed
 39 aa+bb/2 -bb/2 -hp fixed
 40 bb/2 -bb/2 -hp fixed
 41 -aa-bb/2 bb/2 -hp fixed
 42 -bb/2 bb/2 -hp fixed
 43 -bb/2 aa+bb/2 -hp fixed

44 -aa-bb/2 aa+bb/2 -hp fixed
 45 bb/2 bb/2 -hp fixed
 46 aa+bb/2 bb/2 -hp fixed
 47 aa+bb/2 aa+bb/2 -hp fixed
 48 bb/2 aa+bb/2 -hp fixed

49 -dd/2 -dd/2 0
 50 dd/2 -dd/2 0
 51 dd/2 dd/2 0
 52 -dd/2 dd/2 0
 53 -dd/2 -dd/2 4*dd
 54 dd/2 -dd/2 4*dd
 55 dd/2 dd/2 4*dd
 56 -dd/2 dd/2 4*dd

edges

1 1 2 constraint 8, bottom, top, in5con, in6con
 2 2 3 constraint 5, bottom, top, in7con, in8con
 3 3 4 constraint 7, bottom, top, in5con, in6con
 4 4 1 constraint 6, bottom, top, in7con, in8con
 5 5 6 fixed
 6 6 7 fixed
 7 7 8 fixed
 8 8 5 fixed

9 9 10 constraint 16, bottom, top, in13con, in14con
 10 10 11 constraint 13, bottom, top, in15con, in16con
 11 11 12 constraint 15, bottom, top, in13con, in14con
 12 12 9 constraint 14, bottom, top, in15con, in16con
 13 13 14 fixed
 14 14 15 fixed
 15 15 16 fixed
 16 16 13 fixed

17 17 18 constraint 24, bottom, top, in21con, in22con
 18 18 19 constraint 21, bottom, top, in23con, in24con
 19 19 20 constraint 23, bottom, top, in21con, in22con
 20 20 17 constraint 22, bottom, top, in23con, in24con
 21 21 22 fixed

22 22 23 fixed	65 49 50
23 23 24 fixed	66 50 51
24 24 21 fixed	67 51 52
	68 52 49
	69 53 54
25 25 26 constraint 32, bottom, top, in29con,	70 54 55
in30con	71 55 56
26 26 27 constraint 29, bottom, top, in31con,	72 56 53
in32con	73 49 53
27 27 28 constraint 31, bottom, top, in29con,	74 50 54
in30con	75 51 55
28 28 25 constraint 30, bottom, top, in31con,	76 52 56
in32con	77 49 1
29 29 30 fixed	78 50 10
30 30 31 fixed	79 51 27
31 31 32 fixed	80 52 20
32 32 29 fixed	81 4 17
	82 11 26
33 33 34 fixed	83 2 9
34 34 35 fixed	84 3 12
35 35 36 fixed	85 18 25
36 36 33 fixed	86 19 28
37 37 38 fixed	
38 38 39 fixed	faces
39 39 40 fixed	1 2 84 12 -83 color lightblue
40 40 37 fixed	2 18 86 28 -85 color lightblue
41 41 42 fixed	3 81 17 85 25 -82 11 -84 3 color lightblue
42 42 43 fixed	4 -68 80 20 -81 4 -77 color lightblue
43 43 44 fixed	5 -65 77 1 83 9 -78 color lightblue
44 44 41 fixed	6 78 10 82 26 -79 -66 color lightblue
45 45 46 fixed	7 -80 -67 79 27 -86 19 color lightblue
46 46 47 fixed	8 -69 -73 65 74 color lightblue
47 47 48 fixed	9 76 -71 -75 67 color lightblue
48 48 45 fixed	10 73 -72 -76 68 color lightblue
49 33 5 fixed	11 75 -70 -74 66 color lightblue
50 34 6 fixed	12 69 70 71 72 color lightblue
51 35 7 fixed	13 -33 -36 -35 -34 tension 0 fixed color blue
52 36 8 fixed	no_refine
53 37 13 fixed	14 5 6 7 8 tension 0 fixed color blue no_refine
54 38 14 fixed	15 -5 -49 33 50 tension 0 fixed color blue
55 39 15 fixed	no_refine
56 40 16 fixed	16 52 -7 -51 35 tension 0 fixed color blue
57 41 21 fixed	no_refine
58 42 22 fixed	17 51 -6 -50 34 tension 0 fixed color blue
59 43 23 fixed	no_refine
60 44 24 fixed	18 49 -8 -52 36 tension 0 fixed color blue
61 45 29 fixed	no_refine
62 46 30 fixed	19 -37 -40 -39 -38 tension 0 fixed color blue
63 47 31 fixed	no_refine
64 48 32 fixed	20 13 14 15 16 tension 0 fixed color blue
	no_refine

21 -13 -53 37 54 tension 0 fixed color blue
no_refine
22 56 -15 -55 39 tension 0 fixed color blue
no_refine
23 53 -16 -56 40 tension 0 fixed color blue
no_refine
24 55 -14 -54 38 tension 0 fixed color blue
no_refine
25 -41 -44 -43 -42 tension 0 fixed color blue
no_refine
26 21 22 23 24 tension 0 fixed color blue
no_refine
27 -21 -57 41 58 tension 0 fixed color blue
no_refine
28 60 -23 -59 43 tension 0 fixed color blue
no_refine
29 57 -24 -60 44 tension 0 fixed color blue
no_refine
30 59 -22 -58 42 tension 0 fixed color blue
no_refine
31 -45 -48 -47 -46 tension 0 fixed color blue
no_refine
32 29 30 31 32 tension 0 fixed color blue
no_refine
33 -29 -61 45 62 tension 0 fixed color blue
no_refine
34 64 -31 -63 47 tension 0 fixed color blue
no_refine
35 61 -32 -64 48 tension 0 fixed color blue
no_refine
36 62 30 -63 -46 tension 0 fixed color blue
no_refine

bodies

1 1 2 3 4 5 6 7 8 9 10 11 12 volume vol density
dens

APPENDIX B

Example of Matlab script for the creation of .fe files

```
clear all
close all
clc

nn=13;
aa=1; %Dimension of the Pillar [micrometers]
bb=0.2375; %Distance between the Pillar [micrometers]

%% Vertex
%%Possible positions
position=zeros(2*nn,1);
jj=1;
kk=0;

for ii=1:(length(position)-1)
    position(ii+1)= aa*jj+bb*kk;
    if jj==kk
        jj=jj+1;
    else
        kk=kk+1;
    end
end

kk=1;
%Coordinates' construction
for ii=1:length(position)
    for jj=1:length(position)
        coor(kk,1)=kk;
        coor(kk,2)=position(ii);
        coor(kk,3)=position(jj);
        coor(kk,4)=0;
        kk=kk+1;
    end
end
vol=1000; %[micrometers^3]
hh=vol/(max(coor(:,2))*max(coor(:,3)));

%% Edges

for ii=1:(4*nn*nn)
    edge(ii,1)=ii;
```

end

for ii=1:nn

for jj=1:nn

edge(1+4*nn*(ii-1)+(jj-1)*4,2)= (1+2*(jj-1))+(nn*4*(ii-1));

edge(1+4*nn*(ii-1)+(jj-1)*4,3)= (2+2*(jj-1))+(nn*4*(ii-1));

edge(2+4*nn*(ii-1)+(jj-1)*4,2)= (2+2*(jj-1))+(nn*4*(ii-1));

edge(2+4*nn*(ii-1)+(jj-1)*4,3)= (2*nn+2*jj)+(nn*4*(ii-1));

edge(3+4*nn*(ii-1)+(jj-1)*4,2)= (2*nn+2*jj)+(nn*4*(ii-1));

edge(3+4*nn*(ii-1)+(jj-1)*4,3)= (2*nn+1+2*(jj-1))+(nn*4*(ii-1));

edge(4+4*nn*(ii-1)+(jj-1)*4,2)= (2*nn+1+2*(jj-1))+(nn*4*(ii-1));

edge(4+4*nn*(ii-1)+(jj-1)*4,3)= (1+2*(jj-1))+(nn*4*(ii-1));

end

end

%First Line

jj=0;

for ii=1:(nn-1)

edge(4*nn*nn+ii,1:3)=[edge(end,1)+1 2+2*jj 3+2*jj];

jj=jj+1;

end

%Other Lines

for ii=0:(nn-2)

for jj=0:(nn-2)

edge(end+1,1:3)=[edge(end,1)+1 (nn*2*3+2+2*jj)+nn*4*ii (nn*2*3+3+2*jj)+nn*4*ii];

end

end

for ii=1:nn

if ii==1

latstart(ii)=2*nn+1;

elseif ii==2

latstart(ii)=2*nn+4;

else

latstart(ii)=(2*nn+2)+2*(ii-1);

end

end

kk=0;

aa=1;

for ii=1:(nn-1)

for jj=1:nn

edge(end+1,1:3)=[edge(end,1)+1 latstart(jj)+2*nn*kk latstart(jj)+2*nn*aa];

end

kk=kk+2;

aa=aa+2;

end

%% Faces

```
face=[1 nn*nn*4+1 -8 -7 ((nn*nn*4)+nn*(nn-1)+2) -(nn*4+5) -(nn*4+8) -((nn*nn*4)+(nn-1)+1) -(nn*4+2) -
(nn*4+1) -((nn*nn*4)+(nn-1)*nn+1) -3 -2];
```

```
if nn>2
```

```
    for ii=2:(nn-1)
        face2(ii-1,:)= [ii (nn*nn*4+ii) -(4*ii+4) -(4*ii+3) (nn*nn*4)+(nn-1)*nn+(ii+1) -(nn*4+ii*4+1) -
        (nn*4+(ii+1)*4) -((nn*nn*4)+(nn-1)+ii) -(nn*4+(ii-1)*4+2) -((nn*nn*4)+(nn-1)*nn+ii) -(4*(ii-1)+2)];
    end
```

```
    for ii=1:(nn-2)
        face3(ii,:)= [face2(end,1)+ii ((nn*nn*4)+(nn-1)*ii+1) -(nn*ii*4+7) (nn*nn*4+(nn-1)*(nn)+nn*ii+2) -
        (nn*(ii+1)*4+5) -(nn*(ii+1)*4+8) -(nn*nn*4+(nn-1)*(ii+1)+1) -(nn*4*(ii+1)+2) -(nn*4*(ii+1)+1) -
        (nn*nn*4+(nn-1)*nn+nn*ii+1) -(nn*4*ii+3)];
    end
```

```
    for ii=1:(nn-2)
        for jj=1:(nn-2)
            face4(jj+((ii-1)*(nn-2)),:)= [face3(end,1)+jj+((ii-1)*(nn-2)) ((nn*nn*4)+(nn-1)*ii+jj+1) -
            (nn*4*ii+4+4*jj+3) (nn*nn*4+(nn-1)*nn+nn*ii+2+jj) -(nn*(ii+1)*4+4+4*jj+1) -(nn*(ii+1)*4+4+4*(jj+1)) -
            (nn*nn*4+(nn-1)*(ii+1)+1+jj) -(nn*4*(ii+1)+4*jj+2) -(nn*nn*4+(nn-1)*nn+nn*ii+1+jj) ];
        end
    end
end
```

```
coor(end+1,1:4)= [coor(end,1)+1 min(position) min(position) hh];
coor(end+1,1:4)= [coor(end,1)+1 max(position) min(position) hh];
coor(end+1,1:4)= [coor(end,1)+1 max(position) max(position) hh];
coor(end+1,1:4)= [coor(end,1)+1 min(position) max(position) hh];
```

```
edge(end+1,1:3)= [edge(end,1)+1 coor(end-3,1) coor(end-2,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(end-2,1) coor(end-1,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(end-1,1) coor(end,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(end,1) coor(end-3,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(1,1) coor(end-3,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(2*nn,1) coor(end,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(2*nn*(2*nn-1)+1,1) coor(end-2,1)];
edge(end+1,1:3)= [edge(end,1)+1 coor(2*nn*2*nn,1) coor(end-1,1)];
```

```
if nn>2
```

```
    face5(1,:)= [face4(end,1)+1 edge(end-4,1) edge(end-7,1) edge(end-6,1) edge(end-5,1)];
    index=1:2:(2*nn-1);
```

```
    for ii=1:length(index)
        lat1(1,index(ii):(index(ii)+1))= [-4*nn*(ii-1)+4 (4*nn*nn+(nn-1)*nn+nn*(ii-1)+1)];
    end
```

```
    face6(1,:)= [face4(end,1)+2 edge(end-1,1) -edge(end-7,1) -edge(end-3,1) lat1(1:(end-1))];
```

```
    for ii=1:length(index)
        lat2(1,index(ii):(index(ii)+1))= [-1+4*(ii-1) -(4*nn*nn+ii)];
    end
```

```

lat2b=flipr(lat2);
face7(1,:)=[face4(end,1)+3 -edge(end-4,1) -edge(end-2,1) lat2b(2:end) edge(end-3,1)];

for ii=1:length(index)
    lat3(1,index(ii):(index(ii)+1))=[-(4*nn*(ii-1)+4*(nn-1)+2) -(4*nn*nn+(nn-1)*nn+nn*ii)];
end
lat3b=flipr(lat3);
face8(1,:)=[face4(end,1)+4 lat3b(2:end) edge(end-2,1) -edge(end-5,1) -edge(end,1) ];

for ii=1:length(index)
    lat4(1,index(ii):(index(ii)+1))=[-(4*(nn-1)*nn+3+4*(ii-1)) (4*nn*nn+(nn-1)*(nn-1)+ii)];
end

face9(1,:)=[face4(end,1)+5 edge(end,1) -edge(end-6,1) -edge(end-1,1) lat4(1:(end-1))];
face_counter=1:face9(end,1);

else

face5(1,:)=[face(end,1)+1 edge(end-4,1) edge(end-7,1) edge(end-6,1) edge(end-5,1)];
index=1:2:(2*nn-1);
for ii=1:length(index)
    lat1(1,index(ii):(index(ii)+1))=[-(4*nn*(ii-1)+4) (4*nn*nn+(nn-1)*nn+nn*(ii-1)+1)];
end

face6(1,:)=[face(end,1)+2 edge(end-1,1) -edge(end-7,1) -edge(end-3,1) lat1(1:(end-1))];

for ii=1:length(index)
    lat2(1,index(ii):(index(ii)+1))=[-(1+4*(ii-1)) -(4*nn*nn+ii)];
end

face6(2,:)=[face(end,1)+3 -edge(end-4,1) -edge(end-2,1) lat2(1:(end-1)) edge(end-3,1)];

for ii=1:length(index)
    lat3(1,index(ii):(index(ii)+1))=[-(4*nn*(ii-1)+4*(nn-1)+2) -(4*nn*nn+(nn-1)*nn+nn*ii)];
end
lat3b=flipr(lat3);
face6(3,:)=[face(end,1)+4 lat3b(2:end) edge(end-2,1) -edge(end-5,1) -edge(end,1) ];

for ii=1:length(index)
    lat4(1,index(ii):(index(ii)+1))=[-(4*(nn-1)*nn+3+4*(ii-1)) (4*nn*nn+(nn-1)*(nn-1)+ii)];
end

face6(4,:)=[face(end,1)+5 edge(end,1) -edge(end-6,1) -edge(end-1,1) lat4(1:(end-1))];
face_counter=1:face6(end,1);
end

txt_parall

%% txt_parall, opening and writing the .fe file

fileID =fopen('exp13_volume1aa1.fe','w');

```


end

[illegible]

```
else
```

```
fprintf(fileID, '%d %d %d %d %d %d %d %d %d %d %d %d %d %d %d %d \r\n', face(1,:));
fprintf(fileID, '%d %d %d %d %d %d \r\n', face5(1,:));
for ii=1:length(face6(1:end,1))
    fprintf(fileID, '%d %d %d %d %d %d %d %d \r\n', face6(ii,:));
```

end

end

```
fprintf(fileID, 'bodies \r\n');
fprintf(fileID, '1 ');
fprintf(fileID, '%d ', face_counter);
fprintf(fileID, 'volume Vol density den');
```

APPENDIX C

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APPENDIX D



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Paolo Zupa ▾

Parametric Optimization of Inverse Trapezoid Oleophobic Surfaces

Author: Andrea Cavalli, Peter Bøggild, Fridolin Okkels

Publication: Langmuir

Publisher: American Chemical Society

Date: Dec 1, 2012



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BACK

CLOSE WINDOW

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Paolo

