February 2021

Design of High Stability Superhydrophobic Surfaces

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Recommended Citation

Wang, Shuo, "Design of High Stability Superhydrophobic Surfaces" (2021). *Major Papers*. 163.
https://scholar.uwindsor.ca/major-papers/163

Design of High Stability Superhydrophobic Surfaces

By

Shuo Wang

A Major Research Paper
Submitted to the Faculty of Graduate Studies
through the Department of Mechanical, Automotive & Materials Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science
at the University of Windsor

Windsor, Ontario, Canada

2021

Design of High Stability Superhydrophobic Surfaces

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January 25, 2021

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ABSTRACT

In the recent two decades, superhydrophobic surfaces' properties and their potential applications have attracted much attention. With the main advantages of self-cleaning, anti-icing, and drag-reduction, the superhydrophobic surfaces can be applied to many industry fields. But the traditional fabrication methods developed in the last twenty years for the superhydrophobic surfaces were focusing on mimicking nature. Specifically, most of the fabrication methods were based on the micro, and nano-scale structure of plants and animals, which came with the problems that such weeny structure on the surfaces would be damaged easily in the practical application without the self-healing capability like the creatures in nature and they are always with a high cost and strict requirements. Thus, people need to find another approach to fabricate superhydrophobic surfaces. The re-entrant angle model, which is basically wider on top and narrower at the bottom, and the most important thing is that this is a general structure that can be more durable in practical application. In this major research paper, we will emphasize the development of the fabrication of superhydrophobic surfaces and the newer design based on the re-entrant angle model.

Keywords: Superhydrophobic, Lotus leaf effect, Development, Self-cleaning, Water-repellent, Re-entrant angle model.

DEDICATION

To my beloved parents, Guoying Yang and Zhiyong Wang, and my fiancée, Yijun Wang, for their endless love and support.

ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my advisor, Dr. Vesselin Stoilov, for his continuous support and patient during my master’s studies. I always got into trouble during the research and literature review, and he can figure me out every time even he is very busy. Not only did he teach me the knowledge in the field of research and study, but also some important things in real life.

Then, I would like to acknowledge Dr. Vesselina Roussinova for her insightful comments and suggestions, which widened my horizon for more perspectives.

And finally, I would like to thank those who encouraged me during my studies and hard times. I wouldn’t finish my work without your help.

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LIST OF ABBREVIATIONS/SYMBOLS

θy	Contact angle
σ_s	Surface tension of solid-vapor interface
σ_{sl}	Surface tension of solid-liquid interface
σ_l	Surface tension of liquid-vapor interface
θw	Apparent contact angle
r	Roughness factor

CHAPTER 1

Introduction

This paper reviews the available literature to summarize the development of the property of superhydrophobicity and come up with the new trend for the design of structure for the superhydrophobic surfaces, which is the unique factor in enhancing the ability of water repellent for the surfaces.

Nature is always the best teacher of humanity. In nature, various kinds of organisms have developed over millions of years and evolved many unique and exceptional characteristics, especially superhydrophobicity[1-4]. The most important characterization for the superhydrophobic surfaces is that they have a high water contact angle, which is greater than 150 degrees, and a low sliding angle, which is less than 10 degrees.[5] Also, this property makes the surface with the abilities like self-cleaning, anti-icing, and drag-reduction, and any one of these abilities can make a great contribution to society.[6-9] As a result of this, the superhydrophobic surface structure had a rapid development, and this kind of phenomenon and its applications have attracted much attention in the past few decades.[10] Varies scientists have made significant advancements in the manufacture of superhydrophobic surface structures. Most of the methods are to make a rough surface structure by a complicated approach with a high cost and strict conditions required and then coat silane solution for the potential of self-cleaning and anti-corrosive applications.[11-14] However, these kinds of applications are temporary as the superhydrophobic coating will disappear with time going by, and the nano-scale structure can be easily destroyed as it cannot support that high pressure. According to Young's equation, only low surface energy material or high surface energy materials with coating the low surface energy materials can achieve the property of water-repellent.[15] This article briefly describes a new superhydrophobic surface structure on the substrate materials, which can make the choices of them without any restriction and allow the superhydrophobic surface to be used in more applications and fields. Besides, this paper provides some calculations to prove that this structure is with high stability by high enough extra pressure. Hopefully, this method could be beneficial for the scientists who are working in this field currently.

Outline of Paper

This paper is organized into chapters in order of the research process. It begins with the background introduction of our topic, superhydrophobic surfaces. It gives us a clear mind of the definition of it and some related parameters and characterizations. After a detailed understanding of the superhydrophobic surfaces, it introduces the advantages of this kind of surface and the actual applications in human life. Following this, it introduces the most used fabrication methods in the past two decades, like lithography, templating, etching, chemical vapor deposition and sol-gel method. It then explains the problem statement and the applications related to the superhydrophobic surfaces to be used in real life. Then, it introduces the theory and method for the new approach of design. Finally, it makes a conclusion and what people need to improve for the superhydrophobic surfaces in future work.

Chapter 2

Background

Lotus Effect

Nature is always full of magic, and different phenomena attract people to explore the unknown world. A poet from the Song Dynasty of Ancient China said, I only love the lotus leaves as they grow up from the mud and with the clean surfaces.[16] From this story, we can know that people have good habits of observing the environment we are interested in. Thus, have you ever thought about the question of how the lotus leaves keep them clean? To start with this question, we need to have a clear mind that not the lotus leaves themselves to make the movements to keep the dirt away from them, and it is the water droplets that matter. When it is a rainy day, some water droplets take the dirt away with themselves from the lotus leaves and roll-off without wetting it. This phenomenon keeps the leaves clean and without any contamination. With this doubt in our minds, people started the research work on this amazing phenomenon.[17]

In the twentieth century, Barthlott, the discoverer of the lotus effect, gave us the answer. He said it is the property of superhydrophobicity, which is the ability to be water-repellent, making the lotus leaves with that effect. And he claimed that there are two critical factors to make the surface of lotus leaves with the ability, which is the kind of waxy material and numerous micro and nano-scale bumps on the leaf. Both of these two factors are practical to superhydrophobicity, as they have different duties on them. A waxy material is always with the property of hydrophobic. It makes the water droplets stay a high distance from the surface of the leaf to minimize the contact area between the water droplets and leaves as much as possible. The microscopic bumps are to take a step further to decrease the contact area to make the air trapped in the room between the bumps. Only with the first factor, the lotus leaves may be hydrophobic, but with both these two factors, they can be superhydrophobic with a contact angle over 150 degrees. With an excellent contact angle over 150 degrees, it makes the water droplets nearly spherical, and they will roll-off from the lotus leaves with a small incline angle. In the meantime, the dirt and contamination are all away from the leaves.[18]

In nature, there is no doubt that lotus plants are not the only plants that exhibit the property of superhydrophobicity. This special ability of water-repellency can also be found in different species in the world, and we can realize that they may have some same points to make them with superhydrophobicity. And a part of them will be listed in Table 1.[19-20]

Table 1. Contact angles of some species

Name of the species	Contact angle (°)
Purple setcreasea	167
Perfoliate knotweed	162
Rice leaf	157
Diptera tabanus chrysurus	156
Ramee leaf	164
Chinese watermelon	159
Taro plant leaf	164
Leymus arenarius leaf	161

Homoptera	165
Water striders	167

Characterization

Not only the species listed in Table 1 can be with the property of water-repellent, but also some other species like the wings of the butterfly, the petals of the rose. The same point is that they have a great contact angle, so is there any other characterization for the surfaces to be superhydrophobic? As we know that, if the water droplets can roll-off from the surfaces, the contact angle hysteresis is another essential term to be used to determine the stickiness of the water droplets and the solid surface.[21] This property directly influences whether the droplets can roll-off or not. Usually, we can call a surface is superhydrophobic if the contact angle of it is greater than 150 degrees and with a contact angle hysteresis lower than 10 degrees, which is the difference between the advancing angle and the receding angle.

We often use the contact angle to determine whether the solid surface is with the ability of hydrophobicity or wettability.[22] So how should we measure the degrees of a contact angle? Usually, the contact angle should be measured at the contact line between the solid surface and the droplets. And there are four different types of wettability to describe the degree of it. They are superhydrophilicity, hydrophilicity, hydrophobicity, and superhydrophobicity, which are shown in Fig. 1.[23] From Fig. 1, we can easily find out where is the contact angle α, it is the angle between the contact line and the tangent line

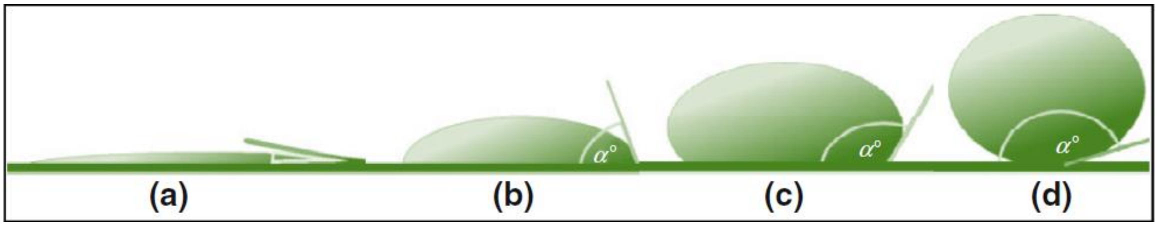

Fig. 1: (a) Superhydrophilicity, (b) hydrophilicity, (c)hydrophobicity, and (d) superhydrophobicity[15]

of the droplets. And there are four different types of wettability to describe the degree of it. They are superhydrophilicity, hydrophilicity, hydrophobicity, and superhydrophobicity, which are shown in Fig. 1. From Fig. 1, we can easily find out where is the contact angle α is the angle between the contact line and the tangent line of the droplets. And the four types of wettability are classified by the degrees of the contact angle. If the contact angle is less than 10 degrees, we call the solid surface is with the ability of superhydrophilicity. If the contact angle is between 10 degrees and 90 degrees, we call the solid surface is hydrophilic. If the contact angle is between 90 degrees and 150 degrees, we call the solid surface is hydrophobic. And the last one, if the contact angle is even greater than 150 degrees, this is a superhydrophobic surface with a 2% to 3% contact area of dew surface, and this is what we need in the actual application in our real life. In the past few decades, scientists were trying to build such superhydrophobic surfaces on our applications.[24] Normally, a hydrophobic surface in nature can be with a contact angle around 100 degrees to 120 degrees.[25] The methods from most of the scientists were adding the roughness on the surfaces to mimic the surfaces on the species from nature. As is well-known, superhydrophobicity has so many advantages in many applications in our lives, like self-cleaning, anti-icing, anti-fogging, oil-water separation, and anti-corrosion before we look into the deep side of superhydrophobicity, we need to understand the fundamentals of wettability.[26]

Chapter 3

Literature Review

To organize this chapter, I make it into sections of two. In the first part of this chapter, it discusses the fundamentals of wettability, starting with Young’s Equation, as the contact angle is the most important term to determine the degree of superhydrophobicity, and it is made by the water droplets with the contacting solid surface at the contact line to balance the surface tension between a total of three phases, which are the solid, liquid, and gas. Also, it emphasizes the two affecting factors to influence the wettability of the solid surfaces, which are the surface roughness depending on Young’s equation, Wenzel’s and Cassie’s theories, and the surface free energy, which is depending on the chemical composition. And the rest of this chapter introduces the most used fabrication methods in the past years. These are the important experience which make great contribution to our related research.

Fundamentals of Wettability

When the water droplets contact with a solid surface, the phenomenon of wettability appears. Different situations and surfaces show the different results on this phenomenon. Sometimes, the surfaces are wetted by the droplets as they spread and flow on the surfaces. So other times, the water droplets gather together to form a larger droplet and then roll off to the ground. This amazing difference attracted so many scientists to look into it. It is Thomas Young who made the summarize of this phenomenon and explained the concept of surface wettability to us. If a droplet is put on the solid surface and the perimeter of its contacts with the surface, there are three interfaces that will show up among the solid, liquid, and gas in Fig. 2.

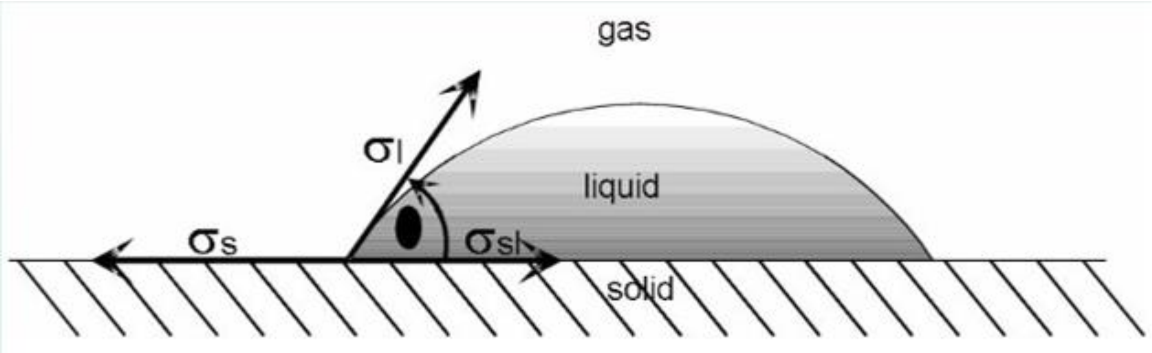

Fig. 2: Surface tensions and interfaces of a droplet on the solid surface[17]

In order to understand the rule of superhydrophobicity, we need to know that it is mainly based on the surface tensions from all three interfaces. Once the surface tensions got balanced, there would be an angle, which is the contact angle. As we can see from Fig. 2, there are no molecules in all directions at the liquid-vapor interface, so these molecules are pulled inwards to force all molecules in the droplet to gather together to minimize the contact area between the solid surface and the droplet. If the solid surface is a superhydrophobic one, we can find that it is just like a spherical droplet stands on it. Also, Thomas Young formulated the basic law from which the shape of a liquid droplet on a solid surface can be determined in Fig. 2, and it is called Young's Equation.

$$\cos\theta y = \frac{\sigma_s - \sigma_{sl}}{\sigma_l}$$

From this equation, we can know that the required condition for a droplet to spread out is that $(\sigma_s - \sigma_{sl}) > \sigma_l$, which means that the energy to create the solid-vapor interface should be great than that of liquid-vapor interface. If this condition is not satisfied, the droplet does not spread out and a contact angle exists.

But in reality, there is a problem that the solid surfaces are always with some roughness on them, and it makes Young's Equation does not fit the situation in our daily life. As a result of this, a relationship between roughness and contact angle was explained by Wenzel.[27] On the basis of Young's Equation, he modified it by adding a new term, which is the roughness factor, the ratio of actual surface to geometric surface. As the

$$cos\,\theta w = r * \frac{\sigma_s - \sigma_{sl}}{\sigma_l}$$

roughness factor is between the range of 0 to 1, so the roughness factor is equal to 1 if the surface is smooth, and this expression also satisfies Young's Equation. Besides, another important point is that the term contact angle can only be applied to the smooth surfaces, but the apparent contact angle is different, which should be applied to the rough surfaces. According to the research done by Wenzel, as the surface tensions at the solid-vapor interface and solid-vapor increase for the result of increased contact area, and the surface tension at the liquid-vapor interface stays the same. Thus, a greater apparent contact angle would appear to get the system balanced. It is an important point to let us know a rough solid surface will increase the contact angle between the droplets, and this may lead to the transition from hydrophobicity to superhydrophobicity.

The achievement finished by Wenzel was further extended by Cassie and Baxter for porous heterogeneous surfaces.[28] As they found that if the surface roughness is high enough, it is not necessary for the liquid to contact the solid surface to fill the entire space fully. As a result of this, the droplets would only contact the peak of the solid surfaces. And it has always shown a greater contact angle if the droplet and the solid surface have a state like that. This kind of contact is similar to the ones from the natural species, like the lotus leaves and wings of the butterfly. Including the two models discussed before, these three models are shown in Fig. 3. All of them give us a direction that if we want to achieve the higher contact angle to make the surface superhydrophobic, we need to mimic and build the structure just like what they are in nature.

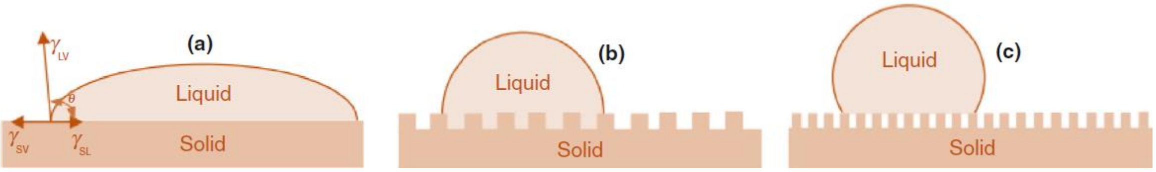

Fig. 3: Schematic illustration of (a) Young's Model, (b) Wenzel Model, and (c) Cassie-Baxter Model[15]

Fabrication Methods

Learning from nature, scientists started to mimic the superhydrophobic surfaces in this century with so many approaches.[29-32] Still, most of them are based on two types of category, one is from the top to etch the substrate surfaces, which is named by top-down approach, and another one is to add appropriate material to the base, which is named by bottom-up approach. The different category is always with different advantages, but both of them have the same point is that they need to follow the two important factors to build the superhydrophobic surfaces, which are low surface energy materials and suitable choices of roughness and surface texture. On the path of exploring the approach on the fabrication of the superhydrophobic surfaces, scientists found that no matter the lotus leaves or some other species, the surfaces were always with some micro-scale pillars, which were covered by some nanostructures. This kind of double-scale roughness ensured the water-repellent property on them. And this theory made the scientist reach the consensus at that time, and it is also a bright path for them to follow. For example, some approaches may be like modifying the micro-scale structure firstly and then coat with some mixture to make the ion on the micropillars and dry the whole surface at last.

Top-down Approach

For the top-down approach, the most practical part for the scientists is to figure out the appropriate material removal process for the chosen material. In the actual experiments, the most used processes are carving, machining, and lasers. And another important part is the fabrication methods. The main methods used are lithography, templating, micromachining, plasma treatments, etching, etc.[34]

Lithography is the most common method used in fabricating the micro-and nanoscale structure on superhydrophobic surfaces.[35] The most important advantage of this method is that it can ensure accurate control of the tiny structures for the aimed superhydrophobic surfaces. This method can build different patterns as what we want, no matter the size or the shape. What we need to do is to build a master pattern mask, and the machine will transfer and duplicate it on our prepared substrate. While the substrate material is exposed to the high-energy beam, the unexposed part will be removed, and we will get the aimed surface we want. This method is also called the photolithography method, which is really a useful technique for the fabrication of superhydrophobic surfaces. The main advantage is that the high-energy beam can ensure the accurate shape we want, but the problem is also on it, which is the high cost of the process, and the preparation of the master mask is complicated.

The second important top-down approach method is the templating method. For this method, it is a good choice for the fabrication of superhydrophobic surfaces with the polymer material. Firstly, we need to prepare a template for it and then use it to press on the substrate's surface to get the inverse shape of the template. Finally, we need to remove the template we pressed on it.[34]

And the third one introduced here is the etching method, which is the easiest one for us to think about. The main point is to etch the surfaces to get the shape we want by putting the surface at an appropriate place to be exposed to the etching medium, and the aimed surfaces will be formed by the chemical reactions. For this method, there is always a need for the post-treatment to dry it. The disadvantage of the etching method is that the reaction cannot be controlled, so it always reacts randomly. The suitable application to use the etching process is to use it in microscale fabrication.[36]

Bottom-up Approach

The bottom-up approach is in a totally different direction from the top-down approach. From Cassie-Baxter's theory, we know that the superhydrophobic surfaces can be built for two requirements. One is the low air fraction, and another one is the high contact angle. For here, the contact angle is Young’s contact angle, which means that it is connected with the choice of the material directly. If we want to build a superhydrophobic surface, the bottom-up is a better choice as not only can it build a suitable shape just like the top-down approach, also with a multiple choice of material when adding it to the base material to satisfy the different requirement for the formation of surfaces. Compared with the methods used for the top-down approach, the fabrication methods for the bottom-up approach are much more. Normally, scientists would like to use the methods of chemical vapor deposition, layer-by-layer deposition, electrochemical deposition, and sol-gel.

Different methods are always with different advantages. For the low overall cost and easy scalability, methods like ink-jet printing and dip-coating, this type of liquid-phase fabrication method is always too complicated for the use of solvents, which may lead the inaccuracy for the shape of surfaces as it may also remove the coating. But there is no worry about this if we take the method of chemical vapor deposition.[37] The advantages of this method are that not only can it build the rough structure for the surfaces, but it also can only make a hydrophobic film on the surfaces. The main disadvantage of this method is that the reaction time for the vapor-phase fabrication method is long, so we cannot use it in large-scale applications, like the cover of solar panels, the window on cars and buildings, which will lead the whole process to a long period.[38,39]

Another bottom-up approach that will be emphasized here is the layer-by-layer method, as it is a method that is independent of the substrate material.[40] This advantage will give scientists a lot of room to explore and use the aimed superhydrophobic surfaces in more applications. Just like the name of the method, the scientists are required to dip the solution on the substrate material layer by layer. Every time when the dipping for one layer is finished, the whole surface will be rinsed by water and then get it dried and ready for the next layer. This method can be used on different shapes and materials of the substrate, and it is not that strict for the experiment condition. For example, the whole process can be done at room temperature.[41]

The sol-gel method is another important one for the bottom-up approach, which broadens the horizon of scientists for more applications. This is also a method which is with the chemical reactions. But the difference is not there is no requirement for the post-treatment during the process, as it has already mixed the low surface energy materials inside.[42] And another advantage of this method is that it is a good choice for the fibre material to fabricate the structure on it to make the surface superhydrophobic. During the whole process of this method, as a result of the presence of a solvent, the sol will be produced at the hydrolysis reaction.[43] And then, due to the mixing of sol and solvent, the gel is formed. And finally, the thin layer will be formed on the substrate material while the shape and roughness are controlled by the reaction mixtures and conditions.[44,45]

There is also another type of fabrication method, which is the combined approach. This type of method combines both the top-down approach and the bottom-up approach in some special situations or some applications with higher requirements. For example, some superhydrophobic surfaces are with micro-and nanoscale structures on them. As we discussed before, scientists can take advantage of both two types of methods. For the microscale one, scientists can take the top-down approach to build the roughness at first. And they were then using the bottom-up approach to build the nanoscale structure on the micro one. This is a good match to use the advantages for both, and it is also a popular way for research nowadays. And this kind of approach is always making the aimed superhydrophobic surfaces with a better result on the measurement of apparent contact angle. If a new trend of approach of method can take us a better effect, it is worth to us to do more research on it.

Applications

There are a lot of good usages for the superhydrophobic surfaces. As is discussed before, the main point for this kind of property is that it can repel the water. Scientists followed the path of water-repellent to find the related applications, like anti-icing, self-cleaning, drag reduction, anti-corrosion, etc.

The most famous usage for the superhydrophobic surface is the property of self-cleaning. Learning from the lotus effect, the scientists got inspired by the amazing self-cleaning ability. This kind of property has always been used on the applications like outer windows of high buildings to keep the windows clean as it is so dangerous to get the cleaner outside of the building at that height with strong wind for a long time. With a vertical angle between the windows and ground, the rain or water droplets can take away the dirt and contamination easily. But sometimes, the superhydrophobic surfaces may not be that suitable to the windows of a high building as they are extremely dry and do not actually clean themselves at all. For now, this kind of property is more used in the application like solar panels. With a 45 degrees angle, the small particles can be taken away by the droplets successfully with the rolling effect. From this, we realize that the suitable inclined angle is also important to the self-cleaning applications.[46]

Anti-icing is another important application for superhydrophobic surfaces. This one is used in a special field as it can ensure the safety of people in the airplane. As it is always at so low a temperature at the height where the airplane is in the sky, water droplets will form into the ice easily there. To ensure the reliability of the airplane in the sky, we need to ensure the time duration of staying of water droplets on the outer surfaces of it.[47] This kind of property provides the safety to the human, but there is still a problem on it is that the strict environment at the condition makes it so hard to keep the micro-and nanoscale structure stable for a long time. Thus, it is a difficult point to overcome in future work.

The third application for superhydrophobic surfaces introduced here is the ability of drag-reduction.[48] This kind of ability is always applied to the largescale ships and submarines. It will be very significant for that largescale ships in the sea as the friction for them from water is too large, and it will lead to much more waste on the consumption of fuel. As we can think about from the Cassie-Baxter theory, as the air fraction is becoming bigger and bigger, the contact area between ships and water will be less. As a result of the reduction of contact area, the friction will be much smaller than before. And the trapped air in the rough structure will be like an air pillow to support the ships against the gravity from itself. Thus, it is very helpful and meaningful to the human, and it will save a lot of energy from the earth. Also, there is a big problem for this application as the weights of the ships and submarines are so big, so it is always too high a pressure to take for the micro-and nanostructure on the superhydrophobic surfaces. If the small space in the structure is filled by the water, there is no use for the surfaces anymore. This is also an important point we need to figure out in the future that how the superhydrophobic surfaces can support more extra pressure to avoid the transition from the Cassie-Baxter state to the Wenzel state.

And the last application introduced here is the property of anti-corrosion. In real anti-corrosive applications, people always use corrosion-resistant materials that contain chromium. As is well-known, chromium is a kind of toxic material, so we need to find another suitable one to take the position.[49] A water-repellent surface can keep the surface as dry as possible, and it will keep the moisture away from the important device.

Chapter 4

Problem Statement

In this chapter, the problem statement is explained here. As what is discussed and introduced before, I am clear about the development of fabrication of superhydrophobic surfaces nowadays, and I have realized that the technique of building the superhydrophobic surfaces is not hard for the technology we master now. With the two important factors, which are low surface energy material and suitable micro-and nanoscale structures, the scientists can build various kinds of superhydrophobic surfaces. But the problem is that this perfect water-repellent ability cannot be widely used in our life. The reasons for these applications cannot be widely used can be the high cost, robustness and surface fragility, mechanical durability, the difficulty of largescale production, and etc. For these reasons, I have a clear direction in my mind. First, I need to decrease the cost of the fabrication and keep the surface still with the ability, and then the surface is becoming more durable and robust. From these points, I realized that the existed two factors cannot satisfy the requirements anymore, and I need to seek the breakout to explore the new path to follow. The most important approach is to find an appropriate structure design to take the place of the existing concept, which is nanoscale bumps on the microscale pillars shape. To decrease the cost of it and make it more stable, I need to make the shape as general as it can be. Thus, the method I figure out is to generalize the structure model to satisfy the requirements as a generalized structure can be made at a lower cost, and if the shape can satisfy some rules, the whole system can still be stable to ensure it is not that easy to be inefficient. Starting from the analysis of forces is a good approach to think about it from the general situation. Based on the comparison of Wenzel state and Cassie-Baxter state, I found that the increase of air fraction between the roughness is related to the degrees of apparent contact angle. Does it mean that building the shape that can prevent the water droplets from contacting with the upper surface of the substrate will lead to high stability? Thus, we may not need a fixed shape to form the structure on the surfaces. Only the re-entrant structures are what we truly need, which are basically wider on top and narrower at the bottom. In our life, we can find this shape like fiber mats, micro-mushrooms, cylindrical pillars, and etc. In the next chapter, the detailed equation derivation will be discussed.

Chapter 5

Methodology

In this chapter, the detailed equation derivation is discussed firstly for the generalized model. Depending on the derivation we got from the equations, we realized that some unique shapes could be beneficial to the property of water-repellency to make the surfaces superhydrophobic. The shape of the micro-and nanostructure should be narrower at the top and wider on the bottom part, which is connected to the substrate material. Based on the shape of the structures, we offered two kinds of design to do the fabrication on the surface and to give an appropriate range to take the lengths of the structures. As there is no experiment set up for the design, only the thought of the designs and some calculations will be explained here.

Equation Derivation[50]

To think about the whole generalized system, we need to start from the analysis of force and energy. For the considered surface system, the Gibbs free energy can be expressed as

$$G = \sigma_l A_l + \sigma_s A_s + \sigma_{ls} A_{ls} \qquad (1)$$

Where σ stands for surface tension, A is the surface area and the subscripts s and l stand for the solid and liquid, respectively. According to the definition of Young's contact angle and the generalized structure of the whole system, we can express the equation

$$\cos\theta = \frac{\sigma_s - \sigma_{sl}}{\sigma_l} \qquad (2)$$

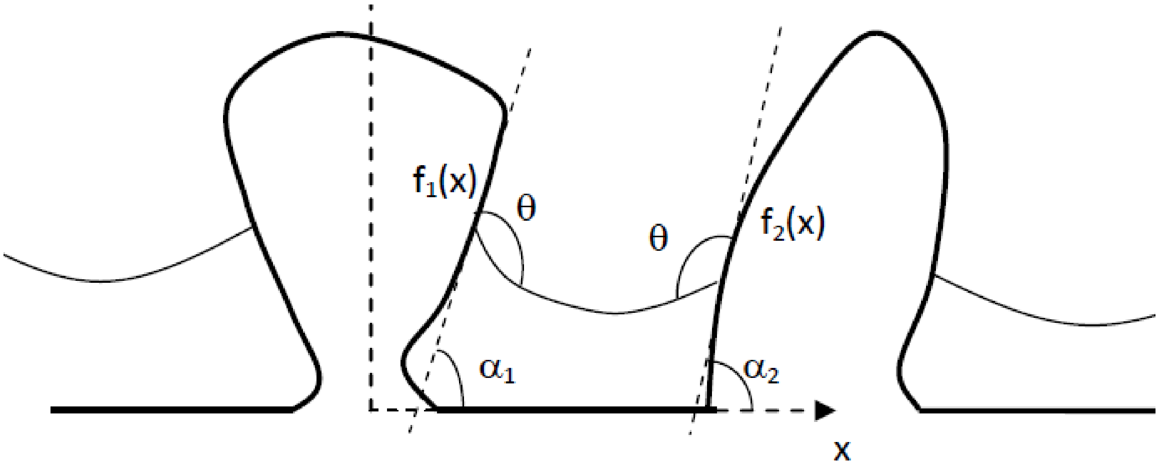

Fig. 4: Schematic of 2D pillars in generalized condition

Substituting Young's contact angle equation into the Gibbs free energy equation, it can be expressed as

$$G = \sigma_l (A_l - A_{ls} \cos\theta) + \sigma_s (A_s + A_{ls}) \tag{3}$$

Then the variation of the Gibbs free energy is

$$\delta G = \sigma_l (\delta A_l - \delta A_{ls} \cos\theta) \tag{4}$$

As the total area of the system, $A_{tot} = A_s + A_{ls}$ is always the same, so it has been considered in the derivation of equation 4. And then, we think about the variation of the location of the liquid surface δz. The change of the location of the liquid surface will make the changes in the corresponding contact areas A_l and A_{ls}.

$$\delta A_{ls} = -L\left(\sqrt{1+\frac{1}{f_1'^2(x)}} + \sqrt{1+\frac{1}{f_2'^2(x)}}\right)\delta z \tag{5}$$

$$\delta A_l = -L\left(\frac{1}{f_1'(x)} - \frac{1}{f_2'(x)}\right)\delta z \tag{6}$$

Substituting equation 5 and 6 into 4, the variation of the Gibbs free energy is

$$\frac{\delta G}{L\sigma_l \delta z} = -(\frac{1}{f_1'(x)} - \frac{1}{f_2'(x)}) + (\sqrt{1 + \frac{1}{f_1'^2(x)}} + \sqrt{1 + \frac{1}{f_2'^2(x)}}) \cos\theta \tag{7}$$

The equilibrium of the system will be achieved at the minimum of the Gibbs free energy where

$$\frac{\delta G}{L\sigma_l \delta z} = 0 \tag{8}$$

The contact angle equation will be reduced to

$$\cos\theta = \frac{\frac{1}{f_1'(x)} - \frac{1}{f_2'(x)}}{\sqrt{1+\frac{1}{f_1'^2(x)}} + \sqrt{1+\frac{1}{f_2'^2(x)}}} \tag{9}$$

The condition for reaching the equilibrium position of the liquid surface is equivalent to the equilibrium condition in equation 8, being the local minimum of the Gibbs free energy. Therefore, the second variation of the Gibbs free energy will be positive at the equilibrium.

$$\frac{\delta^2 G}{L\sigma_l \delta z \delta z} > 0 \tag{10}$$

Using equation 8 and do some transformations we can obtain that

$$\frac{\delta^2 G}{L\sigma_l \delta z \delta z} = \left(\frac{f_1''(x)}{f_1'^3(x)} - \frac{f_2''(x)}{f_2'^3(x)}\right) - \left(\frac{f_1''(x)}{f_1'^4(x)\sqrt{1+\frac{1}{f_1'^2(x)}}} + \frac{f_1''(x)}{f_1'^4(x)\sqrt{1+\frac{1}{f_1'^2(x)}}}\right) \cos\theta \tag{11}$$

Imposing the constrain in equation 10 on the equation 11, yields a condition for achieving heterogeneous wetting in a system with arbitrary pillar geometry.

$$\frac{1}{f_1'^2(x)}\frac{f_1''(x)}{f_1'(x)}\left(1-\frac{\cos\theta}{\sqrt{1+f_1'^2(x)}}\right)-\frac{1}{f_2'^2(x)}\frac{f_2''(x)}{f_2'(x)}\left(1-\frac{\cos\theta}{\sqrt{1+f_2'^2(x)}}\right)>0 \tag{12}$$

An obvious conclusion from equation 9 is that heterogeneous wetting can be achieved even if the solid surface is “hydrophilic”. For which the angles would be less than 90° with $\cos(\theta) > 0$. And then

$$\frac{1}{f_1'(x)}-\frac{1}{f_2'(x)}>0 \tag{13}$$

All in all, a nano structure pattern provides a stable heterogenous wetting on a naturally “hydrophilic” surface only if equation 9, 12 and 13 satisfied. And then we discuss what kind of design would satisfy these requirements.

In this section, we describe our design of the surface patterns that will provide heterogeneous wetting on naturally “hydrophilic” surfaces. To use the requirements for equation 9, 12 and 13, we can firstly simplify them by using $f_1'(x)=\tan\alpha_1$ and $f_2'(x)=\tan\alpha_2$. Here $\alpha_1$and α_2 are the angles of the tangents at the contact points with coordinates x_1 and x_2 in Figure 1. We can obtain the simpler forms of equation 9, 12 and 13.

$$\cos\theta=\frac{\sin(\alpha_2-\alpha_1)}{\sin\alpha_2+\sin\alpha_1} \tag{14}$$

$$\frac{\sin(\alpha_2-\alpha_1)}{\sin\alpha_2+\sin\alpha_1}>0 \tag{15}$$

$$\frac{f_1''(x)}{f_1'(x)}\left(\frac{1-\cos\theta|\cos\alpha_1|}{tan^2\alpha_1}\right)-\frac{f_2''(x)}{f_2'(x)}\left(\frac{1-\cos\theta|\cos\alpha_2|}{tan^2\alpha_2}\right)>0 \tag{16}$$

Because both of $\alpha_1$and α_2 are in the range of 0 to 180°, thus $sin\alpha_1$and $sin\alpha_2$ are greater than 0, so the equation 15 will be

$$\alpha_2>\alpha_1 \tag{17}$$

It can be simply proved that

$$K_1=\frac{1-\cos\theta|\cos\alpha_1|}{tan^2\alpha_1}>0 \tag{18}$$

$$K_2=\frac{1-\cos\theta|\cos\alpha_2|}{tan^2\alpha_2}>0 \tag{19}$$

Thus, the non-equality in equation 16 can be rewritten as

$$f_1'(x)f_2'(x)(f_1''(x)f_2'(x)K_1-f_2''(x)f_1'(x)K_2)>0 \tag{20}$$

For this kind of design, semi-cylindrical flat top pillars etc. We can easily find that $f_1'(x)$ ＞0，$f_2'(x)$ ＜0 and $f_1''(x)f_2'(x)K_1-f_2''(x)f_1'(x)K_2$＜0. Thus, the equation 20 can be satisfied. It is obvious that equation 17 satisfied, and there is a pair of angles $\alpha_1$and α_2 which satisfy equation 14 for θ＜90°. Thus, we verify that the proper nano structure can make the surface heterogenous wetting, which would make the surface superhydrophobic. This is one group of the general shape that can be built to make the superhydrophobic surfaces. Also, there are so other groups, like the horizontal flat-top pillars and the horizontal cylinders, and etc. All of them have a unique point that they are with the shape of narrow top and wide bottom contact with the surface of the substrate material. And this kind of shape is called the re-entrant angle model, which is the new design trend now for the structure fabrication of superhydrophobic surfaces.

Re-entrant angle model

For the techniques of fabrication of the superhydrophobic surfaces, it is well-known that the chemical composition and appropriate roughness of the surfaces are the main factors of wettability. It was in 2007, Tuteja et al. explained that there is another factor, which is the re-entrant angle geometry.[51] This factor can be greatly beneficial to the surface to be extremely water-repellent, and this kind of structure can make the aimed surfaces with less dependence on the chemical composition of the substrate surfaces. In other words, the scientists only need to consider the shape of the micro-and nanostructure of the re-entrant angle model. This kind of advantage gives the scientists more space for the research of structure design and the choice of material. Also, without the restriction of choices of material, there is a wider range of applications that can be built with the

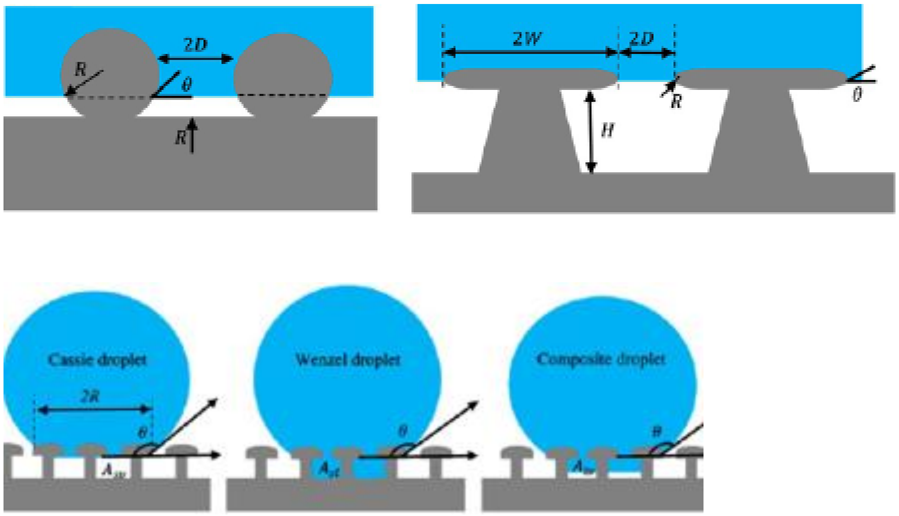

Fig. 5: Schematic of re-entrant angle model[10]

superhydrophobic surfaces. Not only is it a factor to determine the wettability of the surfaces, but also it takes the research of superhydrophobic surfaces to a higher level. As we know that the re-entrant angle structures are always with a long distance at the bottom, the shape of it can be like micro-mushrooms, micro-hoodoo arrays, fiber mats and etc. Normally, scientists would like to use the fabrication methods of photolithography, plasma texturing, chemical vapor deposition, and reactive ion etching to build the re-entrant angle structures. Compared with other structures used to build superhydrophobic surfaces, this kind of structure has a better ability to support the extra pressure, as a shape like this can generate an energy barrier to prevent the immediate contact between water droplets and the surface of the substrate. If they contact each other, there would be an irreversible transition from Cassie-Baxter state to Wenzel state. The theory of this energy, the barrier is that the capillary forces are acting on the liquid-air interface between the structures. This important force ensures higher stability compared with the used superhydrophobic surfaces. And if the whole system can take extra pressure of 1000Pa, it would be an appropriate setup for the degree of parameters.

Structure designs based on the re-entrant angle model

Based on the equation derivation we have and the theory of the re-entrant angle model, we have two designs for the structure of superhydrophobic surfaces. Because of the advantages of the re-entrant model, the applications can be built with lots of choices of material.

The first design is based on the shape of flat-top pillars, which is shown in Fig. 6. B is the distance between the centerlines of the adjacent two pillars, b is the half-length of the flat-top pillar, α is the angle we need to set up for the structure. For this structure, the fabrication method I choose is the low-speed wire electrical discharge machining

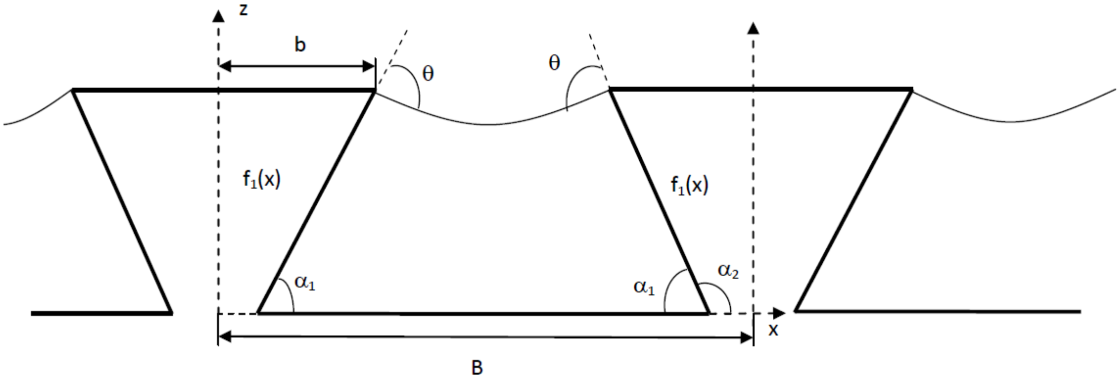

Fig. 6: Schematic of 2D flat-top pillars[50]

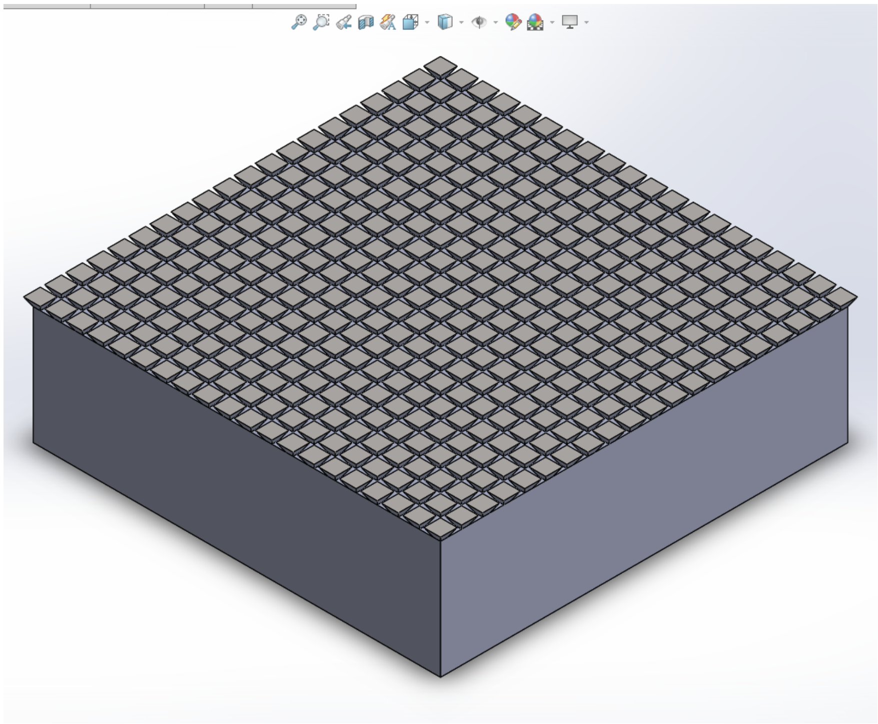

Fig. 7: Model of the aimed flat-top pillars surface

machinery, as the length for these parameters, can be in the range of micrometer, which is not that tiny. Using this fabrication method can ensure a better accuracy to keep the shape is what we truly need. For this model, we will calculate the extra pressure based on two kinds of material which are stainless steel and aluminum. The advantages of them are easy to be produced and with a low cost. Based on the fabrication method we chose and equation derivation, we will take the parameters b = 0.20mm with different B/b and α to calculate the extra pressure.

$$B > 2b(1 + \cos(\theta)\frac{\sin(\theta - \alpha)}{\theta - \alpha})$$

$$\Delta p \geq \frac{2\sigma}{(B - 2b)\sin(\alpha) - H\cos(\alpha)} * (\frac{\cos(\alpha)}{\cos(\theta - \alpha)} - \cos(\theta))$$

For the material of stainless steel, the apparent contact angle of it is 62.1 degrees.[52] Substitute θ =62.1° into the first equation with a range of α, we can get the minimum of B/b. And we can set B/b = 3, 3.5, 4, 4.5, 5 for the calculation of extra pressure with three different degree of α.

Table 2: Relationship between α and B/b_{min} for stainless steel

α	50	55	60
B/b_{min}	2.16239	2.27674	2.93565

Table 3: Relationship between B/b and ΔP_{min} for stainless steel at $\alpha = 50°$

α (°)	50	50	50	50	50
B/b	3	3.5	4	4.5	5
ΔP_{min} (Pa)	6037	361.0	179.8	118.5	89.47

Table 4: Relationship between B/b and ΔP_{min} for stainless steel at $\alpha = 55°$

α (°)	55	55	55	55	55
B/b	3	3.5	4	4.5	5
ΔP_{min} (Pa)	497.4	173.5	91.53	62.16	47.06

Table 5: Relationship between B/b and ΔP_{min} for stainless steel at $\alpha = 60°$

α (°)	60	60	60	60	60
B/b	3	3.5	4	4.5	5
ΔP_{min} (Pa)	87.84	51.08	26.95	18.30	13.86

For the material of aluminum, the apparent contact angle of it is 63.8 degrees.[52] Substitute $\theta = 63.8°$ into the first equation with a range of α, we can get the minimum of B/b. And we can set B/b = 3, 3.5, 4, 4.5, 5 for the calculation of extra pressure with three different degree of α.

Table 6: Relationship between α and B/b$_{min}$ for aluminum

α	50	55	60
B/b$_{min}$	2.24297	2.38102	2.88236

Table 7: Relationship between B/b and ΔP$_{min}$ for aluminum at α = 50°

α (°)	50	50	50	50	50
B/b	3	3.5	4	4.5	5
ΔP$_{min}$ (Pa)	5920	420.7	208.9	138.9	104.1

Table 8: Relationship between B/b and ΔP$_{min}$ for aluminum at α = 55°

α (°)	55	55	55	55	55
B/b	3	3.5	4	4.5	5
ΔP$_{min}$ (Pa)	765.3	185.3	105.4	73.66	56.61

Table 9: Relationship between B/b and ΔP$_{min}$ for aluminum at α = 60°

α (°)	60	60	60	60	60
B/b	3	3.5	4	4.5	5
ΔP$_{min}$ (Pa)	161.5	61.44	37.94	27.44	21.50

For most of metals, the apparent contact angles for them are between 60 to 70 degrees. For this range of apparent contact angle, the parameter α is better to be 50 degrees according to the calculations. The parameter H is going be 0.00023 which is less than b*tan50° as the deeper the depth, the more stable for the whole system. And an extra pressure above 5kPa is a satisfied result to be against most of conditions.

Another design is introduced here is the double horizontal cylinders. As we have done for the equation derivation, the cylindrical group makes me have thinking about the fiber filament. Both of them are of the same shape, which means that we don't need to use any fabrication method here anymore and reduce the cost so much.

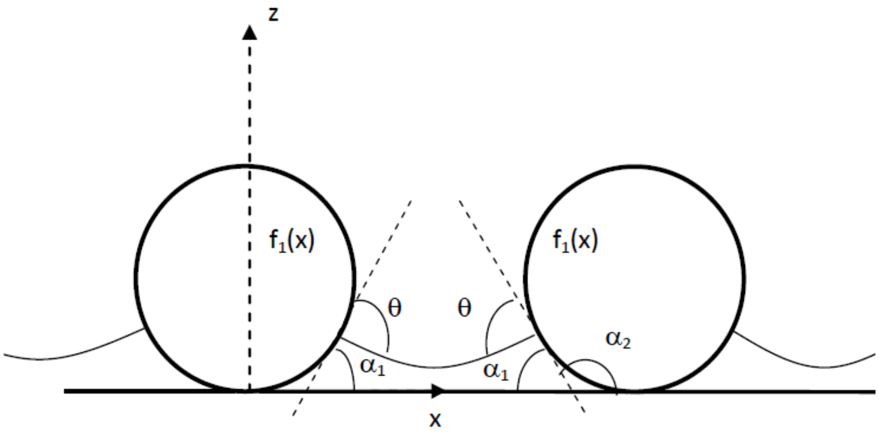

Fig. 8: Schematic of horizontal cylinders[50]

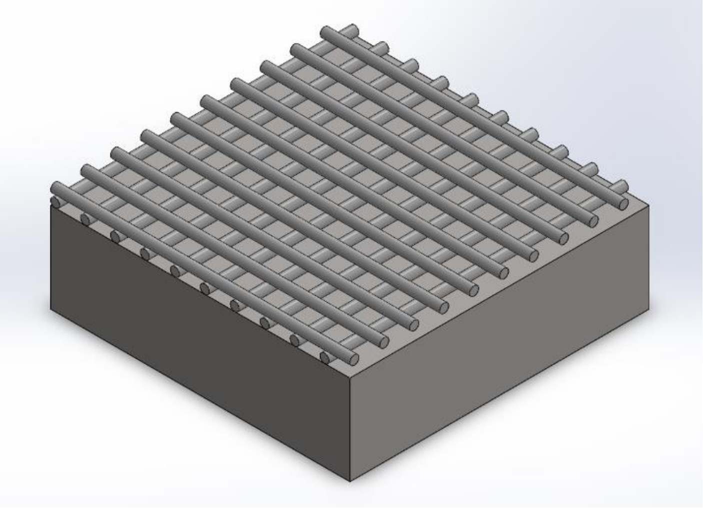

Fig. 9: Model of the double-horizontal cylinders surface

Compared to the first design, this cylinder one is with a smaller scale, the distance between the centerlines of the adjacent cylinders is related to the radium of fiber, and the radium of the fiberglass filament is 1.5μm. The apparent contact angle for the material of fiberglass is in the range of 24° to 36°, and the range is 60° to 65° for carbon fiber.[62] The advantage of this design of two layers of cylinders is that the increased depth from the liquid to the surface of the substrate ensures a harder transition for the system from Cassie-Baxter state to Wenzel state. Also, compared with other choices of fiber, fiberglass filament is at a low cost, and it will be convenient for people to do large-scale production. Another advantage for it is that there is no restriction to the material of substrate as there is no contact between the droplets and the substrate. We only need to think about the material used for the cylinders.

$$\frac{B}{2R} > \sin(\theta) + (\pi - \theta)\cos(\theta)$$

$$\Delta p \geq \frac{\sigma R(1 - \cos(\theta))}{B^2}\left(1 + \frac{17R}{2B}\sin(\theta)\right)$$

According to the two equations we have, we need to calculate the relationship between B and R firstly by using the apparent contact angles from the material. Then, using the relationship and known contact angle to get the minimum extra pressure. We will substitute the apparent contact angle of fiberglass to the equation first. With an apparent contact angle of 36°, we get the relationship for B/R is greater than 5.2421. Thus, we will take five different relationship between B and R like B/R is 5.3, 5.4, 5.5, 5.6, 5.7 to calculate the minimum extra pressure.

Table 10: Relationship between B/R and minimum extra pressure for fiberglass

θ (°)	36	36	36	36	36
B/R	5.3	5.4	5.5	5.6	5.7
ΔP_{min} (Pa)	634.9	606.1	579.1	553.9	530.2

For the second choice of material, carbon fiber is with a contact angle of 63°. From the first equation, we get that B/R should be greater than 3.6361. Thus, we will take the fraction B/R like 3.7, 3.8, 3.9, 4.0, and 4.1 to calculate the minimum extra pressure. The radium of carbon fiber filament is 6.9µm.

Table 11: Relationship between B/R and minimum extra pressure for carbon fiber

θ (°)	63	63	63	63	63
B/R	3.7	3.8	3.9	4.0	4.1
ΔP_{min} (Pa)	1270	1183	1104	1032	966.4

For these two kinds of design, they are starting from different directions. The flat-top pillars one is to use the substate to build the shape of the re-entrant angle model for its good advantages. But the horizontal cylinder one is to use the existed shape of the material to form the shape of the model, which is also with another advantage that the no restriction of the substrate material. And it can be used in more applications. In the cylinder design, it shows that the results for the material choice of carbon fiber are much better than fiberglass. And it is able to be against an extra pressure about 1270 Pa, which is really a good achievement.

Chapter 6

Improvement and Conclusion

In this paper, the fundamentals, development of superhydrophobic surfaces and the new design trend, the re-entrant angle model, are discussed and explained. From the existed applications, it is well-known that the superhydrophobic surface is of great future if it can be widely used in our life. Not only for the ability of water-repellency for the superhydrophobic surface, but also scientists have developed so many useful applications, for example, self-cleaning, drag reduction, anti-corrosion, anti-icing, antifogging, and etc. Also, mechanical durability is not the only concern in the actual application. Another factor we need to think about is that we can combine the advantages together. For a superhydrophobic surface, it can be self-cleaning, and can we make it with the transparency material. It means that the new generation superhydrophobic surface is multifunctional to get used to more conditions. Although the new model of design, the re-entrant angle model, is more stable than the used model for the reason that it can be in the transition state from Cassie-Baxter to Wenzel, but the problem of being abraded or eroded is still over there. The service life is always a problem for a surface modification application. And the last one which is also the most important one is the largescale production. To be widely used in actual life, the cost and the time consumption for fabrication are the most practical terms that scientists need to think about. The re-entrant angle model can save the cost, as it doesn't need the structure to stay the same without any broken. It only needs to be the shape wider at the bottom and narrower on the top side, and it can make the droplets away from the upper surface of the substrate. Thus, it is a good direction to go for the generalization. And it will achieve a lower cost and higher stability.

Finally, I wish that there is a wider platform from now on the fabrication of superhydrophobic surfaces and more and more applications will be developed in the coming days.

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