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Nanotechnologies for Synthetic Super Non-wetting Surfaces

Vincent Senez

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Contents

Chapter 1. Nanotechnologies for Synthetic Super Non-wetting Surfaces 1

1.1. Introduction 1
1.2. Modeling of liquid–solid interaction 3
1.3. Microscale and nanoscale coating processes 6
1.4. Experimental characterization 7
1.5. Emerging applications. 9
1.6. Conclusion 9
1.7. Bibliography 10

Chapter 2. Wetting on Heterogeneous Surfaces 13

2.1. Introduction 13
2.2. Wetting of an ideal surface: the Young contact angle 13
2.3. Real surfaces: apparent contact angle and contact angle hysteresis 15
2.4. Relationship between contact angle hysteresis and drop adhesion 17
2.5. Wetting of heterogeneous materials: the Wenzel and Cassie–Baxter models 18
2.5.1. Impact of roughness: the Wenzel wetting state. 19
2.5.2. Impact of chemical heterogeneities: the Cassie–Baxter wetting state 20
2.5.3. The lotus effect: toward super non-wetting surfaces. 22
2.6. Conclusion 24
2.7. Bibliography 24

Chapter 3. Engineering Super Non-wetting Materials 27

3.1. Introduction 27
3.2. Surface robustness 29
3.2.1. Stability of Cassie and Wenzel wetting states. 30

3.2.2. The contact line pinning criterion 32
3.2.3. The Cassie to Wenzel transition 34
3.2.4. Influence of sidewall angle. 38
3.2.5. Designing superoleophobic surfaces 40
3.2.6. Conclusion. 41
3.3. Contact angle hysteresis on super non-wetting materials. 43
3.3.1. Contact line pinning on dilute micropillars 45
3.3.2. Computing metastable states. 48
3.3.3. Contact angle hysteresis modeling: perspectives. 53
3.4. Conclusion 54
3.5. Bibliography 56

CHAPTER 4. FABRICATION OF SYNTHETIC SUPER NON-WETTING SURFACES 61

4.1. Introduction 61
4.2. Full substrate technologies 66
4.2.1. Thermal evaporation 68
4.2.2. Pulsed laser deposition 69
4.2.3. Sputtering deposition 69
4.2.4. Atomic layer deposition 70
4.2.5. Plasma-enhanced chemical vapor deposition. 71
4.2.6. Thermal spraying deposition. 72
4.2.7. Electrospray deposition. 73
4.2.8. Electrospinning 74
4.2.9. Electroless plating deposition 75
4.2.10. Electroplating 76
4.2.11. Chemical solution deposition (spin/dip/spray/blade coating) 77
4.2.12. Colloidal assembly 80
4.2.13. Hydrothermal synthesis 82
4.2.14. Catalyst-assisted growth 84
4.2.15. Controlled radical polymerizations 85
4.3. Direct writing technologies 89
4.3.1. Inkjet printing 89
4.3.2. Drop casting 91
4.3.3. Laser-assisted deposition. 91
4.3.4. Contact printing 92
4.3.5. Dip pen lithography. 93
4.3.6. Pneumatic dispensing. 94
4.3.7. Screen printing 94
4.4. Conclusion 95
4.5. Bibliography 95

CHAPTER 5. CHARACTERIZATION TECHNIQUES FOR SUPER NON-WETTING SURFACES 109

5.1. Introduction 109
5.2. The sessile drop method. 112
5.2.1. Equipment and experimental procedure. 113
5.2.2. Drop shape analysis. 113
5.2.3. The volume oscillation method 116
5.2.4. The tilted plate method 117
5.3. Wilhelmy method 118
5.4. Robustness measurement 120
5.4.1. Drop compression. 121
5.4.2. Drop evaporation 123
5.4.3. Hydrostatic pressure 125
5.4.4. Drop impact 126
5.4.5. Other methods (electrowetting and surface vibrations) 129
5.4.6. Conclusion on the robustness measurement techniques 132
5.5. Advanced techniques for better understanding of super non-wetting surfaces. 132
5.5.1. Imaging of the 3D geometry of the composite interface. 133
5.5.2. Imaging of the temporal evolution of the 3D composite interface 136
5.5.3. Conclusion. 142
5.6. Conclusion 142
5.7. Bibliography 143

CHAPTER 6. EMERGING APPLICATIONS. 149

6.1. Introduction 149
6.2. Lab-on-a-chip 150
6.2.1. Displacing liquid (continuous and digital) 150
6.2.2. Liquid confinement for detection (SERS and impedance spectroscopy) or analysis (mass spectrometry). 153
6.3. Drag reduction 156
6.4. Super non-wetting surfaces for the directed self-assembly of micro- and nano-objects 159
6.5. Super non-wetting materials for cell biology 162
6.6. Slippery liquid-infused porous surfaces 166
6.7. Conclusion 170
6.8. Bibliography 170

INDEX. 175

1

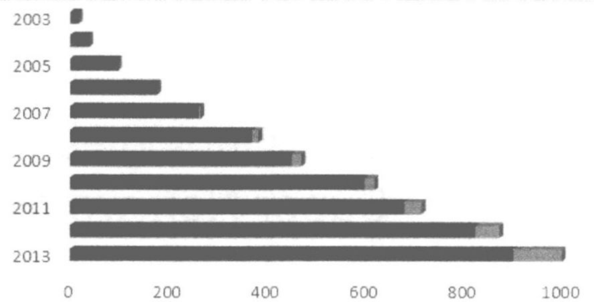
Nanotechnologies for Synthetic Super Non-wetting Surfaces

1.1. Introduction

Wetting forces are at play all around us. They have practical applications, such as controlling oil recovery mechanisms during water flooding of natural reservoirs [MOR 90], improving carbon dioxide storage in subsurface geologic formations to counter anthropogenic CO_2 emissions [BAC 00] or controlling rain penetration in soils which has a direct implication in agriculture, soil erosion or aquifer quality [DRD 07]. Wetting forces are also important for many biological processes. They provide a survival kit to microscale arthropods, protecting them against suffocation upon immersion into polluted water-flooded habitats [HEN 13]. They perform miracles for some classes of insects giving them the unique ability to walk on water [DSM 11]. They promote health among plants offering a self-cleaning property using water condensation on leaf [WWQ 13]. They are finally acting in our daily life. They bind sand grains to hold the shape of our child's sandcastle. They are involved in the formation of tears when we swirl our glass of wine. They control the colonization of our pleasure boat hull by thousands of marine microorganisms.

Wettability is a fundamental property of surfaces. It describes the tendency of one fluid to spread on, or adhere to, a solid surface in the presence of other immiscible fluids. Wettability is governed by the interfacial tension that is the energy per unit area (force per unit distance) at the surface between phases. It is commonly expressed in milli-Newtons/meter (mN/m). Water presents an interfacial tension with air equal to 72 mN/m while liquids such as oils and alkanes have an interfacial tension with air as low as 22 mN/m for ethanol. Wettability is modulated by the relief of the surface that can intensify the wetting or non-wetting behavior [JOD 64]. In particular, surface roughness enhances the intrinsic non-wetting chemistry of the surface, producing super non-wetting surfaces [CFH 99, QUE 05].

This book reviews the recent research works about the design and fabrication of highly liquid repellent surfaces, which is an exponentially growing topic over the last 20 years, whether in terms of fundamental studies, characterization techniques or applications (Figure 1.1).



	2013	2012	2011	2010	2009	2008	2007	2006	2005	2004	2003
■ Superhydrophobic	898	822	677	597	449	369	260	176	96	38	17
■ Superoleophobic	98	48	36	20	20	13	4	0	0	0	0

Figure 1.1. *Number of published scientific articles per year related to the design and characterization of super non-wetting surfaces called superhydrophobic (i.e. able to repel water) or superoleophobic (able to repel a wide range of liquids including non-polar solvents and hydrocarbons). Survey performed with the web of science software (statistics on 03.03.2014 with keyword "superhydrophobic" (dark gray) or "superoleophobic or superamphiphobic or superlyophobic or superomniphobic" (light gray))*

Due to the importance of water in many natural processes on Earth, studies of these surfaces started a long time ago [WEN 36], with the analysis of the interaction of pure water with a solid surface in gas (i.e. air). However, it is only recently that the term "superhydrophobic" appeared in the literature to qualify these surfaces [SOS 96].

Nowadays, these studies have been extended to a wide range of liquids, such as non-polar solvents or hydrocarbons. This generalization has been driven by both scientific and industrial interests, admitting that applications dealing with pure water are too restricted. However, as we will see throughout this book, super non-wetting surfaces efficient to a wide range of liquids are not easy to obtain. This new generation of super non-wetting materials came along with their share of new terms: "superlipophobic", "superlyophobic", "superamphiphobic", "superomniphobic", "superoleophobic", etc. As a matter of comparison, Figure 1.2 shows the occurrence of the main terms used in the literature, with a slight advantage for "superoleophobic". This term is used in this book in order to describe super non-wetting materials presenting an extended repellency to oil-like liquids.

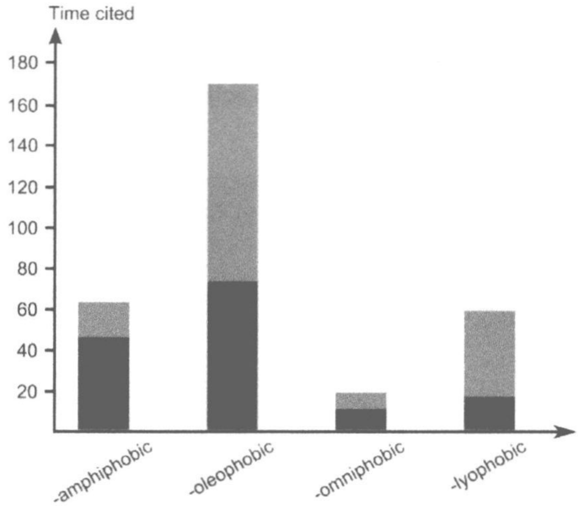
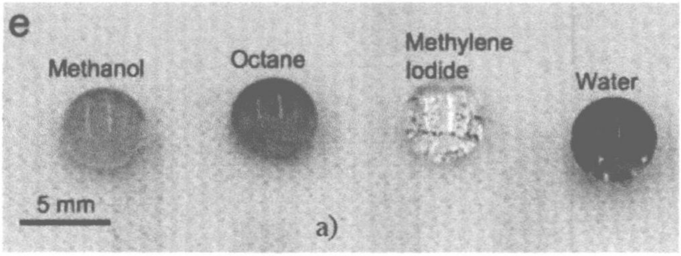


Figure 1.2. *Occurrence of the different terms used for surfaces exhibiting extended super non-wetting properties for a wide range of liquids (statistics: Web of knowledge, 05.09.2013, each term includes the prefix super- and ultra-). Dark gray: occurrence in light gray: occurrence in title or topic*

The scope of application of superoleophobicity is very broad. Macroscopic applications include anti-fingerprint and anti-reflective glasses for consumer electronics, anti-fouling surfaces for surgical tools [VAS 09], medical implants [PAV 08], textiles (see Figure 1.3(a)), food packaging [LI 09], marine equipment [SCA 11], drag reduction coatings for textile and ship industries [BHU 11], efficient membrane technologies for separation of oil–water emulsions [KOT 12], lubrication enhancement for all industrial processes on wet treatment of solid surfaces (e.g. semiconductor industry [VER 14]), anti-bouncing and anti-spreading surfaces for the printing industry [BRO 12]. Emerging applications are envisioned in micro- and nanotechnologies: self-assembly of colloidal objects for the microelectronic industry [KRA 13], energy scavenging [NOS 09], three-dimensional (3D) culture of biological cells [WAN 06], and microfluidics devices (Figure 1.3(b)).

1.2. Modeling of liquid–solid interaction

The study and modeling of wettability and capillarity phenomena started at the beginning of the 19th Century with Pierre Simon de Laplace [DE 47], Thomas Young [YOU 05] and, later, Henri Bouasse [BOU 24]. This topic developed rapidly in the middle of the 20th Century with the works of Wenzel [WEN 36], Cassie and Baxter [CAS 48, CAS 44], Zisman [FOX 52, ZIS 64], and then Derjaguin [DER 34], Landau [LAN 42], Cahn [CAH 77], De Gennes [GEN 04, GEN 85] and many others. Although the number of articles, reviews and books on this topic has grown exponentially in recent years, it is necessary to summarize the principal concepts of wettability in Chapter 2 of this book for the self-consistency of this document and the interest of non-expert readers.



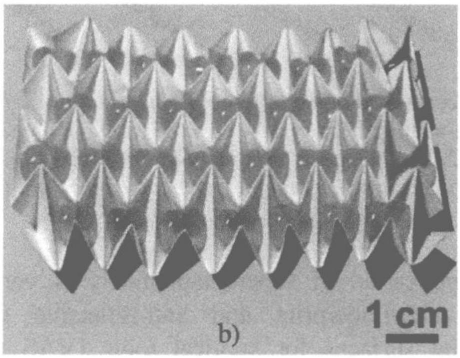


Figure 1.3. *a) Super repellency of fluorodecyl polyhedral oligomeric silsesquioxane (POSS) coated on a textile substrate against various polar and non-polar liquids (from 72 down to 21 mN/m) [CHO 09]. b) Oleophobic microtiter plates as an alternative to conventional material for microfluidics applications. It is fabricated by creasing and folding of fluoroalkylated paper coated by vapor-phase silanization with fluoroalkyl trichlorosilanes. The picture shows a square array of re-entrant honeycomb cells able to hold in each well 500 μl of organic liquids (toluene dyed with Sudan I, surface tension of 28 mN/m) [GLA 14]*

Chapter 2 is dedicated to the mathematical modeling of systems such as those shown in Figure 1.4. Without going into detail, but to give a flavor of this chapter, let us consider the case of a sessile liquid droplet sitting on a textured solid surface. Depending on the physical and chemical properties of the system, different behaviors can be observed: (1) super-wetting: drop spreads and forms a liquid film (Figure 1.4(a)), (2) partial wetting: drop retains a spherical shape while penetrating in the asperities and is definitely hanging to the surface (Figure 1.4(b)), (3) non-wetting: drop sits on the asperities with a sufficient surface of interaction with the solid to create a sticky droplet more or less easily detachable (Figure 1.4(c)) and (4) super non-wetting: drop also stands at the top of the asperities but is easily removable (Figure 1.4(d)). Each of these wetting states can target specific applications and we can aspire to obtain these properties individually. Nonetheless, for a unique surface, the obtained state is thermodynamically non-stable and a transition from one state to the other is possible. Furthermore, for a unique liquid, modifying the relief and roughness of the solid surface can either increase or decrease the surface wettability. In this book, our interest is focused on the last two non-wetting states, especially on the design of surfaces inducing repellent properties for a very wide range of liquids with low surface tension.

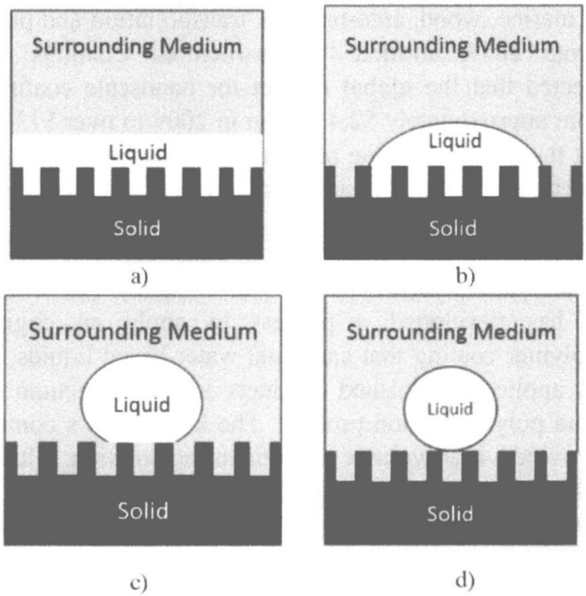


Figure 1.4. *Schematic representations of the different wetting states of a solid surface by a liquid in a surrounding medium: a) super-wetting, b) partial wetting, c) non-wetting and d) super non-wetting*

The first important characteristic when describing the interaction of a liquid with a non-planar solid surface is the adhesion property. The adhesion of a liquid to a surface represents the force required to move the liquid droplet in or out of the plane of the surface. The second important characteristic is called the robustness of the surface, which is the maximum internal drop pressure above which the liquid penetrates into the topography. Transition from the suspended to the impregnated state is critical for most of the aforementioned applications as it results in a loss of the super repellency property and is usually not reversible. Chapter 3 presents these two fundamental properties of a super non-wetting surface.

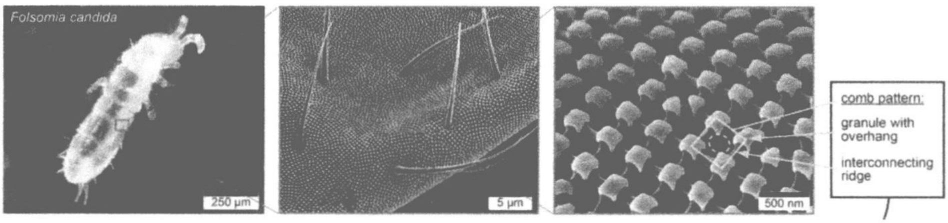
1.3. Microscale and nanoscale coating processes

Creating a synthetic super non-wetting surface has been proved to be extremely challenging. Nanotechnologies are playing an increasingly prominent role in introducing new coatings with specialized properties and enhanced performances. According to a recent market research report from Future Markets Research Inc. (Rockville, MD, www.marketresearch.com), these advanced coatings are likely to replace traditional coatings "in the medium to long-term in end-use segments such as packaging, anti-microbial coatings, architectural coatings, industrial manufacturing, marine, wood, auto-refinish, transportation and protective coatings". The report, from 2009, entitled "Nanostructured Coatings: Applications and Markets," projected that the global market for nanoscale coatings and thin films would grow from approximately $2.4 billion in 2009 to over $13 billion by 2016. It emphasizes that the fastest growing markets to 2016 will be in interior and exterior household protection, textiles and medical markets, driven by the increased demands for protective and repellent coatings.

Three examples are presented here. The company P2i Ltd. (Abingdon, UK, www.p2i.com) has developed a process to apply an engineered nanoscale fluorocarbon-polymer coating that can repel water-based liquids, oils and alcohols. The coating is applied to finished products inside a vacuum chamber using a two-stage plasma polymerization process. The key to P2i's commercial success is the ability to provide a high-volume manufacturing solution. Ultratech International Inc. (Jacksonville, FL, www.spillcontainment.com) has developed a process where a coating is deposited by air sprayers directly onto a wide range of surfaces, including steel, aluminum, plastic, fabric and wood, and makes them superoleophobic. The innovation lies in the abrasion resistance of the coating that is much higher than other commercialized solutions. Finally, Aculon Inc. (San Diego, CA, www.aculon.com) is another company that markets superoleophobic products. It uses a layer of self-assembled monolayer of phosphonates (SAMPs) to modify surface properties. The phosphonate head groups form covalent bonds with the substrate, while the tails are constructed with a number of chemical groups that face outward and give the surface the desired properties. However, although they bring better performances and functionalities, these coatings are quite basic as they are only based on chemical coating of low surface tension compounds. While they are far from being ideal, new concepts are studied in research laboratories in order to offer enhanced properties.

Nature is an abundant source of inspiration for the development of coatings leading to super non-wettability (Figure 1.5). The properties of natural surfaces result from a complex relationship between surface morphology [GAO 06] and physicochemical properties [NEI 97]. Major advantages of these surfaces are their tolerance to failure, their adaptation to the environment and their multifunctionality.

The major disadvantage is that they need to be run in mild environmental conditions (temperature, pressure and electromagnetic radiations on Earth). These natural surfaces are made of few chemical elements (i.e. carbon, hydrogen, oxygen and nitrogen) assembled in a hierarchical two length scales (from micro to nano) surface morphology giving advantageous properties [KOC 09]. On the contrary, engineered surfaces are most often homogeneous and their surfaces show simple hierarchical morphology at best. Over the past few years, many super non-wetting surfaces have been developed based on bio-inspired approaches and resulting in self-cleaning, drag reduction in fluid flow and anti-fouling [WON 13].



a) b) c)

Figure 1.5. *a) Lifeform of a springtail Folsomia candida. b) Scanning electron micrographs (SEMs) of the characteristically contained bristles, granules and ridges. The nanoscopic granules and interconnecting ridges form cavities, are arranged in a comb-like pattern, and provide a template for the fabrication of a polymer membrane [HEN 14]*

Despite over a decade of intense research, these bio-inspired surfaces are still restricted in their practical applications. Their robustness is not big enough for many applications under high liquid pressure. The adhesion of many liquids is still too important for many dynamic applications. Their synthesis is difficult and too expensive for application on large surfaces. Real breakthrough in this area will probably come from a better scientific understanding of the physicochemical mechanisms involved in synthesis of natural surfaces to design new fabrication processes of engineered surfaces [BIR 10] and by technological progresses in micro and nanoscale engineering. Chapter 4 presents state-of-the-art microscale and nanoscale fabrication technologies for the design of super non-wetting surfaces.

1.4. Experimental characterization

At thermodynamic equilibrium, the wettability of a smooth solid surface is typically quantified by the measurement of the so-called "Young contact angle" of a sessile liquid droplet (Figure 1.6). This static contact angle is the angle formed by the liquid with the solid surface at the three-phase contact line. The adhesion of the liquid to a smooth solid surface is quantified by the measurement of the contact angle hysteresis. Macroscopic techniques have also been developed to characterize the surface robustness through different dynamic forces (evaporation, compression, drop impact, etc.).

These parameters (static contact angle, contact angle hysteresis and robustness) are usually measured with macroscopic techniques (e.g. goniometry). The first part of Chapter 5 presents these classical characterization techniques giving their advantages and limitations.

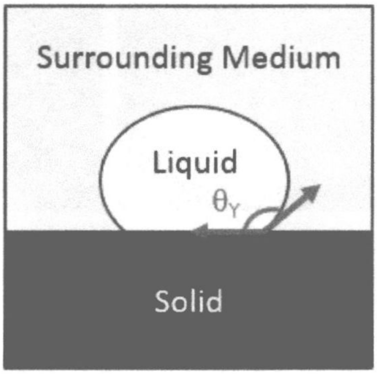


Figure 1.6. *Schematic representation of a liquid droplet sitting on a smooth solid surface in a surrounding medium (liquid or gas). At thermodynamic equilibrium, the wetting state is characterized by the measurement of the Young contact angle θ_Y, in reference to the work performed by Young [YOU 05]*

In the case of super non-wetting surfaces, these techniques usually give a different value of the contact angle due to their own limitations (e.g. reference to the in-plane solid surface) and they should be used with special care. Furthermore, they cannot access the complexity of the interactions in the vicinity of the triple contact line.

With these considerations, we can easily understand that the scientific community currently needs new characterization techniques to locally quantify the wetting state of a solid surface that can give dynamic information at the scale of the topography with two objectives: first objective aims at better understanding the physical mechanisms involved in the wetting process of these textured surfaces; second objective aims at developing in-situ characterization techniques (SEM, FIB, electric and acoustic methods) using the microsystem technologies to increase geometric and temporal resolutions of these measurements. This aspect is introduced in the second part of Chapter 5.