Chapter

Natural and Artificial Superwettable Surfaces-Superficial Phenomena: An Extreme Wettability Scenario

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Abstract

With the help of biomimetics, superficial characteristics were transposed, through various methods, onto artificially obtained materials. Many industrial fields applied surface architecture modifications as improvements of classic materials/methods. The medico-pharmaceutical, biochemical, transportation, and textile fields are few examples of industrial areas welcoming a “structural change.” Anti-bioadhesion was widely exploited by means of antibacterial or self-cleaning fabrics and cell culturing/screening/isolation. Anti-icing, antireflective, and anticorrosion materials/coatings gained attention in the transportation and optical device fields. Interdisciplinary approaches on extreme wettability include “solid-fluid” formations called liquid marbles, which will be further discussed as a superhydrophobic behavior exponent.

Keywords: superficial phenomena, extreme wettability, special surface architecture, liquid marble

1. Introduction

Since ancient times, humans observed special features which helped plants and animals survive in harsh environments. These properties were unraveled with the help of microscopical investigative techniques, which led to a more thorough understanding of superficial phenomena. Natural unique superficial architectures, like the lotus and rose petal effect, became iconic. Empirical models of wettability were developed (Young, Cassie, and Wenzel) to fully explain the behavior of liquids in contact with special surfaces.

Along with the fulminant expansion of technology during the last decades, a huge progress was also registered in surface sciences. Microscopical analysis techniques revealed surfaces’ special architectures and solved many mysteries regarding plants and animals’ adaptation to harsh environments (e.g., Namib beetles’ survival in the desert). Extreme wettability (superhydrophobicity/superhydrophilicity) was assigned to many natural phenomena, such as raindrops not collapsing while dropping onto ash-covered soil and moss storing the exact amount of water needed to survive. In particular, superhydrophobic surfaces which display a contact angle higher than 150°, a sliding angle smaller than 10°, and no hysteresis attracted researchers' attention. Apart from theoretical aspects on wettability, which are a part of the paper, natural extreme wettability models will be discussed (lotus leaf, rose petal, and insect wings).

Principles of biomimetics are included in this chapter, as special superficial properties were adapted to human necessities and used as a model in many industrial areas, including nanotechnologies. Biomimetics is, in this case, "the thread that makes the dress complete," or, in other words, "the scene that completes the movie." Applications related to superhydrophobicity will be presented: development of self-cleaning and low friction surfaces, satellite antennas, solar and photovoltaic panels, exterior glass, etc. Studies concerning superhydrophobic surfaces' applications in various domains will also be submitted: prevention of bacterial adhesion, of metal corrosion, of surface icing in humid atmosphere and low-temperature conditions, blood type determination techniques, etc. Efficient, cost-effective, ecological, and reproductible methods are still developing so that mass production of quality materials becomes a fact.

The chapter will also bring into attention an important exponent of superhydrophobicity: special structures called liquid marbles. The unique "solid-fluid" formations are regarded as soft objects, due to the microliter droplet encapsulated in hydrophobic particles. Practical uses include micro-reactors, miniature cell culturing, or screening devices, successfully replacing classical methods with cost- and reactive-efficient, low-toxicity analysis techniques. Other properties will be submitted along with applications in various fields.

2. Biomimetics: biology vs. technology

As human kind evolved, passing through the test of time, many necessities turned out as a result of convenience in everyday life activities. Thus, classical materials like wood, metal, and ceramic became no longer suitable and efficient, lacking performance in many domains (e.g., pharmaceutical, medical devices, weaponry, etc.). Aiming a more complex approach on artificial materials, the concept "materials by design" came to life (Bernadette Bensaude-Vincent, 1997) [1]. The concept refers to developing "composite" materials, which reunite properties of already known ones: heat resistance and time durability of ceramics, lightness of plastic, hardness, and breaking resistance of metals. Depending on quality requirements of the final product, many design possibilities came out, exhibiting improved sustainability, cost-effectiveness, durability, and an environmentally friendly character.

Undoubtedly, a much older concept, "biomimetics," also led to obtaining performant structural materials and is intricated to the "materials by design" concept. The term itself ("biomimetics") was firstly introduced by Otto Schmitt [1], but its principles are considered to be used since Leonardo da Vinci (1452–1519) while designing flying machines after analyzing bird's ability to fly [2].

According to some beliefs, biomimetics is a transfer of ideas between biology and technology, aiming to obtain superior device. A more complex approach refers to it as being "a study of the formation, structure or function of biologically produced substances, materials, biological mechanisms and processes especially for the purpose of synthetizing similar products by artificial mechanisms which mimic natural ones" [2].

As expected, a lot of controversial interpretations arise from different approaches of biology and engineering, considered "baselines" of biomimetics. On the one hand, biology relates to living organisms (cells, plants, and animals) which evolve following a natural DNA-embedded cycle. On the other hand, engineering

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relies on human intelligence which develops successive steps in order to obtain a final product [1].

Conflicts between biology and technology interpretations are classified through a Russian problem-solving system TRIZ (*Teorija Reshenija Izobretatel'skih Zadach*—"Theory of Inventive Problem Solving"), 40-standard features which offer solutions from both perspectives. For example, a few characteristics such as "keep poison out," "self-cleaning," "surface properties," and "waterproof" became conflict nr. 30-"external harm affects the object" [1].

Therefore, it became appropriate to say that "superficial properties" is a concept which can be regarded in the light of both "biology" and "technology." Structural investigation of natural (biological) surfaces is performed using microscopical techniques. Technical interpretations of these surfaces and empirical models arise. Examples include special wettable surfaces like the lotus leaf, rose petal, Salvinia leaf, insect eyes, wings, fish scales, etc. They provide templates in designing new engineered materials exhibiting improved properties compared to classical materials. Such artificially obtained materials and coatings can be considered results of "materials by design" and "biomimetics" concepts, as a reunion of biological inspiration and human engineering. Even though many contradictory assessments take place, it is important to state that biology and technology functioned perfectly together when inventing the Velcro closure system according to the way burdock (*Arctium* sp.) spreads its seeds, the helicopter inspired by the body of the dragonfly, the submarine resembling a whale, etc.

3. Extreme wettability: special patterns

3.1 Understanding wettability

As is well known, surface wettability characterizes interfacial phenomena between a liquid and a solid support. The liquid's behavior on the studied surface is in fact an indicator of wettability, a superficial property which helps evaluate hydrophilicity/hydrophobicity of a solid. The quantitative indicator of wettability is represented by the contact angle, given by Young's equation (Eq. (1)):

$$\cos\theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \tag{1}$$

where θ is the contact angle, γ_{SV} is the solid-vapor superficial energy, γ_{SL} is the solid-liquid superficial energy, and γ_{LV} is the liquid-vapor superficial energy [3].

The equation establishes an equilibrium between superficial energies at the solid-liquid-air interface. However, adaptations of Young's equation were proposed by Wenzel [4] and Cassie-Baxter [5], after it was proven that the original equation only applies to homogenous, smooth surfaces and that the contact angle is influenced by the support's rugosities, as a surface roughness indicator.

Wenzel's equation (Eq. (2)) applies to non-smooth surfaces. Surface rugosity is interpreted through the roughness factor r, defined as ratio of the actual rough surface area to the geometric area projected on a relatively smooth surface. This adapted equation refers to an apparent contact angle θ', as follows (Eq. (2)):

$$\cos\theta' = \frac{r(\gamma_{SV} - \gamma_{SL})}{\gamma_{LV}} = r\cos\theta \tag{2}$$

Another relationship defining an apparent contact angle θ' is similar to Wenzel's equation, with the difference that the surface's rugosities are separated by impenetrable air pockets (Cassie-Baxter wetting model). The surface f in direct contact with the liquid is considered, as follows (Eq. (3)):

$$f = \frac{\sum a}{\sum (a + b)} \tag{3}$$

where a and b are the contact areas with the drop (a) and, respectively, air (b). Considering (1 – f) the drop-air contact area and a contact angle of 180°, the calculation formula corresponding to the Cassie-Baxter wetting regime is shown in Eq. (4):

$$\cos\theta' = f\cos\theta + (1 - f)\cos 180^\circ = f\cos\theta + f - 1 \tag{4}$$

Empirical models of the Young, Wenzel, and Cassie-Baxter wetting states are presented in **Figure 1**.

Other interpretations by Quéré et al. [6, 7] consider the Wenzel wetting regime as an equilibrium state of the Cassie model: a critical value of the fraction f determines a critical contact angle θ_c, determined by the following equation (Eq. (5)):

$$\cos\theta_c = \frac{1 - f}{r - f} \tag{5}$$

Since wettability studies continue to unfold, researchers recently proved that Wenzel and Cassie wetting regimes actually co-occur on the same support surface. Hydrophobic surfaces with linear or pillar patterns exhibit both a Cassie levitating state corresponding to drops placed on the support and also a Wenzel pinned state for drops which come into contact with the surface after the impact. Transitions between these states were also reported as a result of external stimuli influence [8, 9]. Wenzel to Cassie and Cassie to Wenzel transitions were analyzed through sequential squeezing and releasing between texture surfaces of nonadhesive plate. Results indicate that both regimes exist at the same time on a double-scaled textured surface, resembling natural micro- and nano-surface architecture: the Wenzel state is characteristic for the larger texture and Cassie to the smaller one [9]. Further investigations consisted in exploiting these characteristics and developing super-repellent materials, also based on natural models, following the principles of biomimetics.

The "superwettability system," briefly presented in **Figure 2**, includes a much extensive approach on wetting states, depending on the liquid type, the solid support's architecture, and the environment in which the phenomenon is described. Thus, the terms discussed above (hydrophilicity/hydrophobicity) refer to water's behavior in air and upon flat surfaces. Regarding low-surface liquids, such as oils, the "oleophilic/oleophobic" concepts are defining. Moreover, if the support

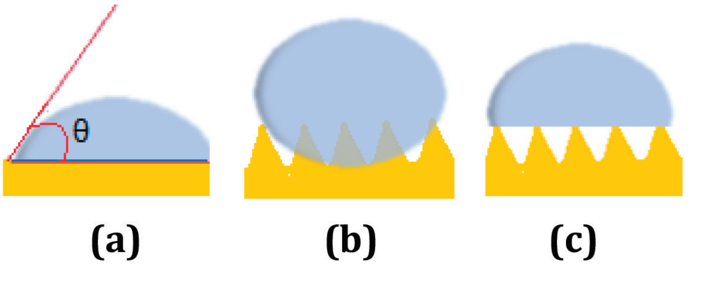

Figure 1.
Comparison between wetting regimes: (a) Young, (b) Wenzel, and (c) Cassie.

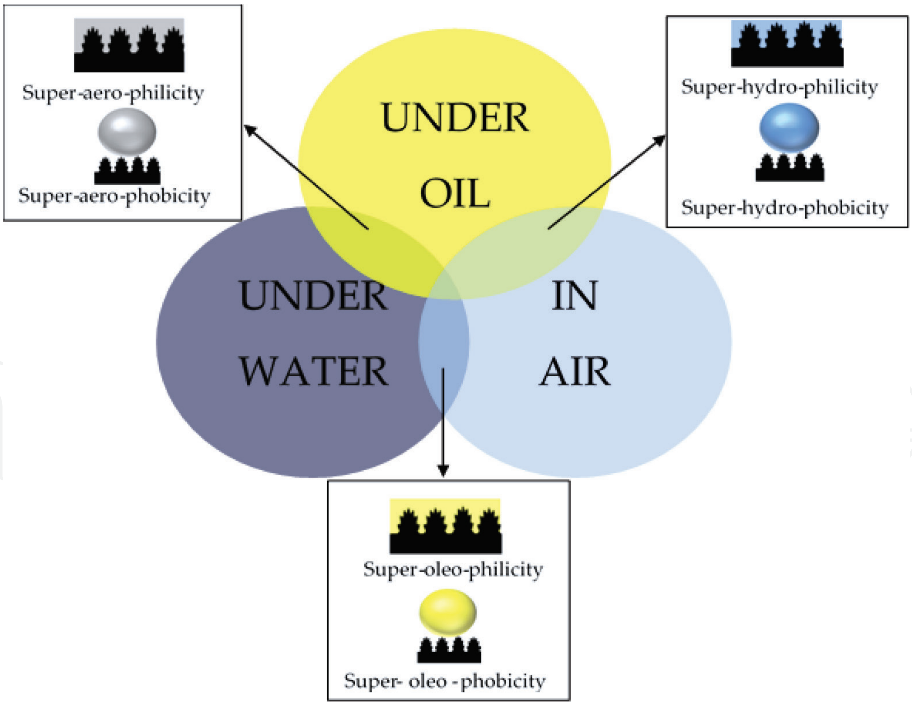

Figure 2.
The "superwettability" system.

exhibits a nano-/micro-rough architecture, then the behavior of liquids when contacting such a surface is known as "superhydrophobic/superhydrophilic" and "superoleophobic/superoleophilic." Corresponding wetting behaviors under water for structured rough supports are known as "superoleophobic/superoleophilic" and "superaerophobic/superaerophilic." If placed under oil, then the appropriate approach refers to "superhydrophobicity/superhydrophilicity" and also "superaerophobicity/superaerophilicity" [10].

3.2 Natural designs

Natural special surfaces transposed as survival skills in animals and plants captivated attention of researchers. They investigated and applied in practice what nature provided. Apart from scientists, novelists like Jules Verne were fascinated by certain elements from the environment and used them as inspirational sources to imagine innovative devices, mostly designed as transformational means and considered eccentrical in that era: the Nautilus submarine whose shape resembled a whale, the eponymous Steam House—a mechanical elephant, the helicopter imagined starting from insects' flight mechanisms and shapes, etc.

Apart from mechanical devices, natures' kingdom offered humans the possibility to improve artificial materials, based on the evolution of SEM analysis techniques in the 1960s. Detailed investigations of surface structure and properties were performed. As a result, surface architecture was held responsible for many phenomena which were not explained at that time: how plants maintain clean in marshy environments and how their water needs are satisfied during high-temperature exposure. From this category, two types of surface structures, designed as micro- and nano-scaled patterns, confer superhydrophobicity to the leaves of certain plant species: lotus, rice, and taro. Another model which confers water repellency was attributed to a unitary structure of 1–2 μm fibers (Chinese watermelon, Ramee leaves). Also, vertical/horizontal hairs were attributed in the property of water repellency in case of *Alchemilla vulgaris* and, respectively, *Populus* sp. [11–13].

The iconic plant superhydrophobic behavior belongs to the lotus leaf (*Nelumbo nucifera*). Surface wettability of the leaves is considered to be derived from the Cassie-Baxter wetting model: convex micrometric papillae along with nanometric wax needles determine water contact angles higher than 150°. This special architecture, also known as "The Lotus Effect," allows dust particles and other impurities to be collected by raindrops while rolling off (**Figure 3**) [14].

The other side of the lotus leaf presents no waxy crystals, but has tabular nano-groove convex lumps which confer inverse wettability [15].

An example of unique structural characteristics is the carnivorous plant *Nepenthes alata*. Its prey is caught due to oleophobic features which allow insects to slide down to the digestive cavity, capturing them [16]. Contributing to the survival of the *Cladonia chlorophaea* lichen are hydrophobic strains ending in cup-shaped structures which limit water storage, preventing excessive accumulation and further damage to the plant [17].

An exponent of plant adaptation to harsh environment conditions is represented by *Salvinia molesta*, the water fern, who gave rise to "The Salvinia Paradox": hydrophobic hairs ending in hydrophilic peaks retain an air film while submerged, allowing respiration [18]. The thin air film retained at the air-water interface also enables *Oryza sativa* (rice) to carry on photosynthesis, enhancing gas exchange and diminishing Na^+ and Cl^- intrusion through submerged leaves through salt-water floods [19, 20].

"The Rose Petal Effect" reveals how nano-folds covered with micro-papillae of rose petals confer contact angle values of 152°, resembling the Cassie impregnating model: water droplets maintain their spherical shape, adhere to the surface, and do not slip when turned upside down. Compared to the lotus leaf architecture, this wetting regime is characterized by a liquid film which impregnates the papillae, leaving only some dry areas. A dependence was observed between the drops' volume and surface tension: the equilibrium is ruined and the drop falls if it exceeds 10 μL in volume. Thus, smaller drops stay stable, while raindrops slide off, since they are bigger [21]. **Figure 4** illustrates a comparison between the rose petal (a) and the lotus leaf (b) surface structure [22].

Transitioning from the plant to the animal kingdom, it is important to state that apart from "slippery" surfaces discussed above, "adherent" superhydrophobic surfaces were also noted: the gecko lizard's finger structures confer them the ability to climb even perfectly vertical walls, due to micrometric lamellae divided into nanometric setae. A drop placed on this surface retains its shape even in an antigravity

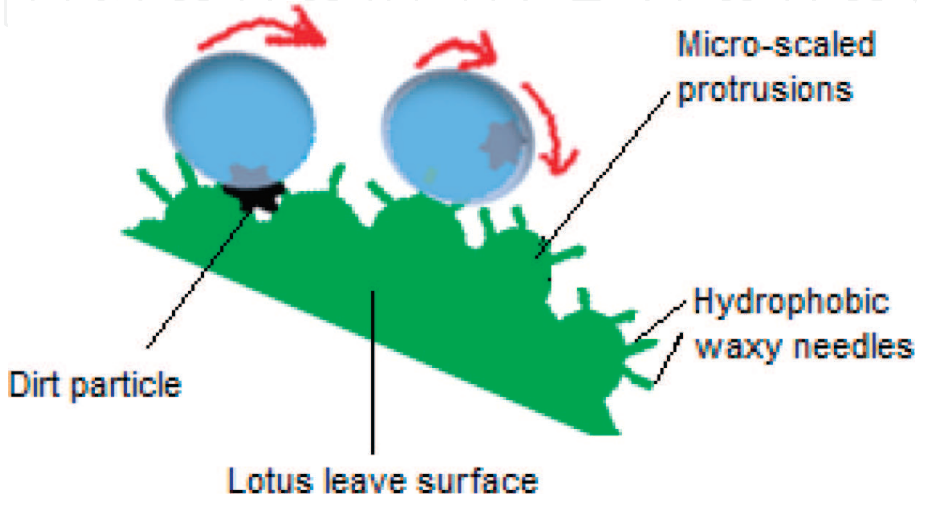

Figure 3.
Lotus leaf structure. Dirt particle removed by rain.

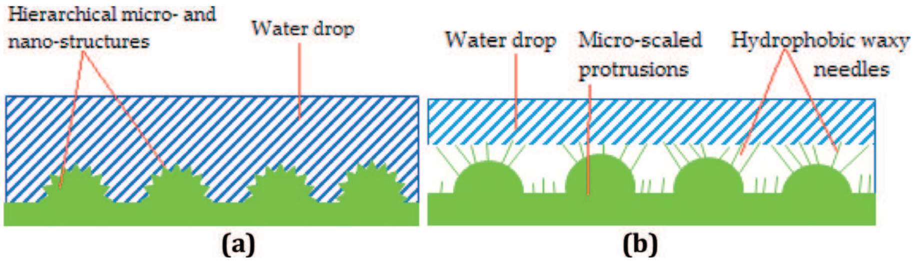

Figure 4.
(a) Rose petal surface structure (Cassie impregnating wetting state) and (b) lotus leaf surface structure (Cassie state) [22].

position [23, 24]. The gecko feet model inspired climbing a glass building using Kevlar and polyurethane special gloves [25]. The group of adhesive superhydrophobic natural surfaces includes also the rose petals, as previously discussed.

Regarded at first from a different angle, the insects' ability to fly, to maintain impurity and water-free wings, was later attributed to superhydrophobicity. Microscales hierarchically disposed on insect wings are responsible for maintaining them dry (**Figure 5**) and also exhibit, in some cases, antibacterial activity (cicada wings are bactericidal against Gram-negative bacteria) [26, 27].

For some insects, patterns joining superhydrophobicity in alternation with superhydrophilicity represent an adaptation to harsh environmental conditions: *Stenocara gracilipes* (the Namib desert beetle) shows on its back a real storage system which captures water from atmospheric humidity, due to superhydrophobic waxy edges and superhydrophilic peaks [17]. In relation with survival skills, *Argyroneta aquatica* (the diving spider) creates around itself a hydrophobic artificial lung, which is permeable to gases and allows underwater living [10].

3.3 Engineered superwettability—materials and coatings: practical applications

Moving on from the theoretical field, extreme wettability is regarded an open gate for numerous everyday life and also industrial applications.

Following biomimetic principles and varying surface templates, innovative materials are fabricated, depending on qualitative requirements. The first artificial superhydrophobic materials appeared in the early 1990s: the submicrometer-roughed glass plates hydrophobized with fluoroalkyl trichlorosilane (CA = 155°) [28], fractal surfaces covered in n-alkyl ketene (CA = 174°) [29, 30], and ion-plated polytetrafluorethylene (PTFE) coatings with nanometric rugosities [31]. In the 2000s, surface topography studies were correlated with surface chemistry, leading to patterned silicone surfaces with low wettability [32].

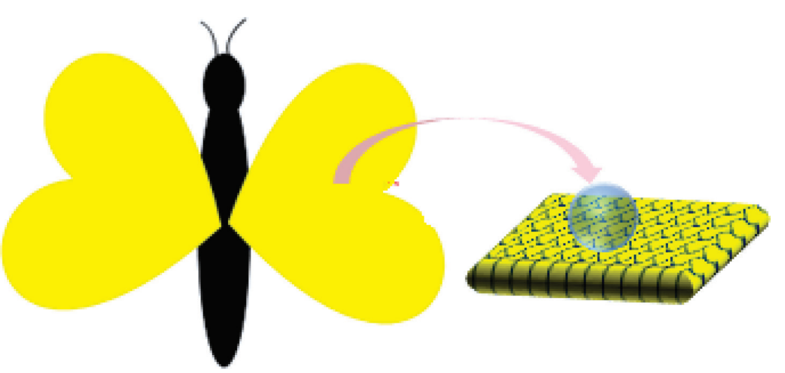

Figure 5.
Insect wing-microscaled superhydrophobicity.

Techniques used to confer surface roughness are still improving, along with transparency, permeability, resistance, and color change imparting methods [33–35]. Nature proved that hierarchical surface structures are responsible for surface special wettability, and not fluorocarbon derivatives, as it was considered at that time [36].

The most popular known procedures used to artificially obtain superhydrophobic surfaces include chemical reactions in a humid atmosphere [37], thermic reactions [38], electrochemical deposition [39], individual/layer-by-layer assembling [40], etching [41], chemical vapor deposition [42], and polymerization reactions [43]. Substrates include glass, metals (Cu, Ti, Zn), and cotton, and resulted structures exhibit CA > 150°, mimicking natural patterns [44]. For example, the rose petal was used as template in order to obtain polymeric coatings, resulting in "adhesive" superhydrophobicity [21]. Patterns resembling surface design of the lotus leaf were also fabricated through eco-friendly methods, without toxic solvents [45].

Fluorocarbon and silicone derivatives were preferred as substrates in fabricating superhydrophobic surfaces, assuming that the larger the number of flor atoms, the higher is the hydrophobicity [46]. Nowadays, these materials are replaced with biodegradable ones, such as agricultural residues [47]. Recent studies indicate that lignocellulose can be successfully used in obtaining fire-proof coatings [48]. Another example of eco-friendly superhydrophobic coatings includes waterborne resins from aqueous silanes and siloxane solutions with silica nanoparticles applied as protective coatings to cultural heritage (marble, sandstone, cotton, ceramic artifacts) [49].

The *Slippery Liquid-Infused Porous Surface* (SLIPS) technology includes smooth coatings applied onto military uniforms and medical gowns in order to avoid biological fluid contamination, due to surface fluids incorporated into a micro-/nano-porous substrate [50, 51]. The field of *anti-bioadhesion* also involves protein adsorption, bacterial adhesion, and cell culturing media, all of them wettability-dependent phenomena [52]. Thus, in vitro studies regarding platelet adhesion on implants reveal that no adhesion happens on TiO_2 nanotube-covered supports. Moreover, polydimethylsiloxane (PDMS) surfaces with various sized-rugosities, superposed scale plates, submicron structures, and nanostructured and smooth surfaces, proved the highest effectiveness against blood platelet adhesion in superposed scale plate surface [53]. Antibacterial cellulose fibers modified with siloxanes and silver nanoparticles show durable activity against *Escherichia coli* and *Staphylococcus aureus* [54], while bactericidal action against *Pseudomonas aeruginosa* was discovered for fluoroalkyl silane-hydrophobized glass [55].

The result of joining extreme wettability surfaces are patterns which promote development of cells planted as hydrogels/solutions in the hydrophilic zone. Advantages of the method include lack of lateral contamination risks due to hydrophobic separative borders, efficiency, economic analysis method, the possibility of real-time screening, and noninvasive diagnosis [56–58].

Other high-impact applications of superhydrophobic surfaces include *anti-icing*, *antireflective*, and *low friction* properties, mostly popular in the marine and aviation transportation fields, mirrors, and lens industry [59–62]. These properties along with a low adhesion degree, a high contact angle, and a low sliding angle allow impurity collection, while rolling off represent desired characteristics for windshields, exterior windows, and solar panels [63].

Since *metal corrosion* is a contemporary problem, superhydrophobic anticorrosion treatments were developed: coating techniques (microwave chemical vapor deposition, followed by immersion) with fluorochloride silanes of magnesium alloys and substrate modifications (Al with hydroxides, Zn immersed in superhydrophobic solutions), proving resistance against acids, alkaline, or saline solutions [64].

Closely following the corrosion issue is *friction reduction*, which is of interest in aeronautics and ships. The shark skin and the lotus leaf are models in designing continuous surface films with self-contained air bubbles, able to reduce laminar and turbulent liquid flow, lowering friction forces. Moreover, recent progress includes high-pressure-resistant special surfaces, with a high impact in the submarine industry [65]. Apart from enhancing classical transportation devices, inspirational novel ones were developed flowing the water strider's model. Prototypes of miniature robots which walk-in straight-line and function as water-pollutant monitors, displaying high transport capacities [66, 67]. Water collecting/storing systems are still developing as a solution for dry areas, starting from the Namib beetle's back special architecture [68].

Interdisciplinary researches on surface extreme wettability will be continued by discussing an intrinsically superhydrophobic behavior, characteristic for versatile structures entitled liquid marbles.

4. Small exponent—big impact: liquid marbles

4.1 State of the art

Liquid marbles are non-wettable structures, formed as a result of physical interactions between solid particles and a liquid drop. The formations are in fact represented by a liquid core covered in a particle shell (**Figure 6**) and exhibit a superhydrophobic-like behavior, without the intervention of surface modifications.

Among the first intents to obtain liquid marbles were carried out by Aussillous and Quéré [69], by rolling water droplets (1–10 mm^3) in a hydrophobic silica-covered *Lycopodium* powder bed (20 μm), as presented in **Figure 7**.

When compared to plain water drops, the manufactured liquid marbles did not wet the support, due to the fact that the liquid-solid interface (water-glass) is replaced with a solid-solid interface (*Lycopodium* particles-glass). They resemble raindrops falling on lotus leaves and collecting dust particles while rolling off, as previously discussed (The Lotus Effect) [70].

Liquid marbles' formulations are versatile, including various powders which differ in color, wetting degree, electrical charge, and even therapeutic activity.

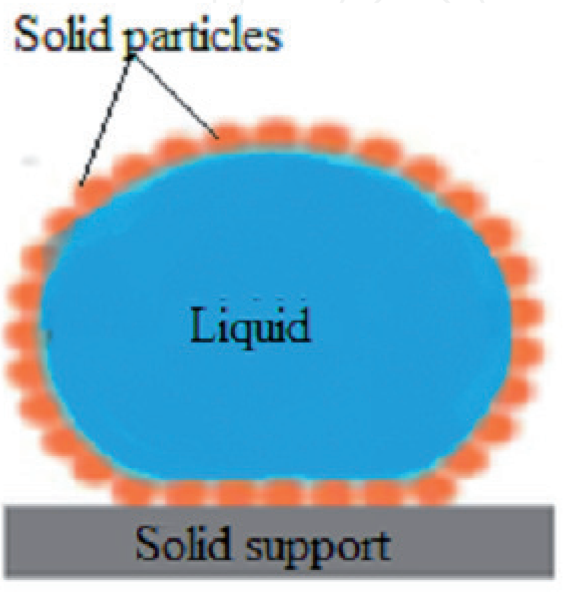

Figure 6.
Liquid marble structure.

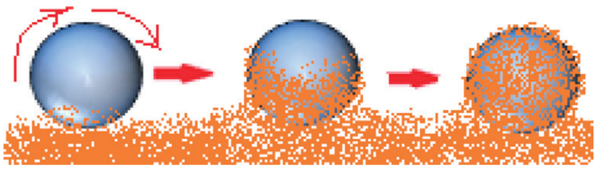

Figure 7.
Obtaining liquid marbles by rolling water drops into a Lycopodium powder bed.

Literature data indicates natural and synthetical powders such as *Lycopodium*, soot [71], respectively, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polyethylene (PE) [72], polymethyl methacrylate (PMMA) [73], and hydrophobic copper powder [74]. The hydrophobic particle wall thickness varies depending on the particles, which are linked by van der Waals forces and distribute as mono- or a multilayers. In time, the wall undergoes changes depending on environmental conditions: multilayered shells correspond to "long surviving marbles," due to the possibility to stretch of particles surrounding the circumference, maintaining the system's integrity. Moreover, since large particles do not provide liquid core's flexibility and protection, nanoparticles are recommended as shell formers which fill in the gaps formed through compression [75].

Similar to superhydrophobic surfaces, liquid marbles can also exhibit special structural architectures, depending on their components. Particular cases include porous shells made of hydrophobic poly-high internal phase emulsion (HIPE) polymer, with particles interconnected by "gigapores" of micronic dimensions, resembling natural organisms like radiolarians (protozoa-producing mineral microtubes) or diatoms (microalgae with cells interconnected by tubes) [76]. After the $CuSO_4$ solution (core) evaporates through the shell, a $CuSO_4$ shell remains. The method is proposed as the model in designing spherical objects. Among liquid marbles with curious properties are the ones guided using electric fields which resemble Janus particles. They are obtained by forcing together two marbles with different shells, resulting in a bigger marble: half covered in carbon black and the other in Teflon (**Figure 8**) [77].

Liquid marble's interior phase usually includes high-surface tension liquids like water or glycerol, but literature data also suggests low tension liquids such as ethanol, methanol, toluene, hexadecane, and 1,4-dioxane [78]. It is possible for the shells' particles to remain at the liquid-gas interface or to be engulfed by the liquid core, resulting in stable marbles [72]. Other particular liquid marbles include Galinstan (eutectic liquid mixture of gallium, indium, tin) covered in Teflon, isolators (SiO_2), or semiconductors (CuO, ZnO, WO_3). They are resistant to high temperatures, float on water, but must be obtained in a diluted hydrochloric acid solution, as an unwanted reduction reaction takes place in air [79].

Cases of hydrophilic particle-covered liquid marbles are possible due to air trapped between particles, resulting in aggregates which cover the droplets [80].

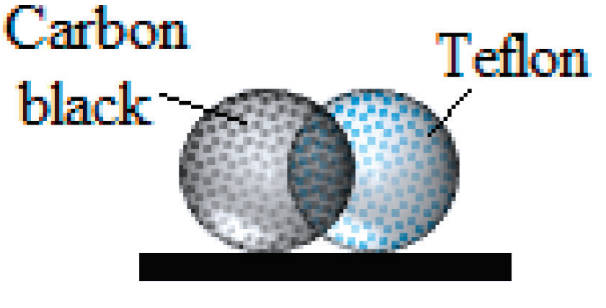

Figure 8.
Liquid marbles resembling Janus particles.

When discussing liquid marbles obtaining procedures, the most popular manufacturing method is the droplet rolling in a powder bed, as previously presented. Continuous research is developed concerning this domain since the proposed method is inefficient and time-consuming; irregularly covered marbles are formed and cannot be transposed at an industrial level. Methods including condensation and drop nucleation were recently reported: the liquid core is placed in a container, warmed by a heat source underneath. Hydrophobic particles (Cab-O-Sil fumed silica and micronic-sized Teflon) are distributed in a thin layer at the liquid-air interface. As the liquid boils, vapors condense and are covered by the particles. Micronic liquid marbles are formed. By heating these "parent-marbles," much smaller liquid droplets called "child-liquid marbles" are formed ("liquid marbles sweating"). The "child-marbles" roll off the "parent-marbles" and are more robust. Advantages of the method include industrially applicability of the technique and possibility to adapt conditions depending on the desired result [81]. Wrapping drops in transparent glass fibers, avoiding fluid evaporation, is a proposed design in developing new controlled drug release systems, water purification membranes [82]. Another automatized method is considered revolutionary by using instead of hydrophobic powders a superhydrophobic cloth of nanofibers. The drop is covered after impacting the cloth, resulting in highly resistant liquid marbles, with no internal phase loss [83].

Regarding their formulation, liquid marbles are versatile structures. The challenge is represented by choosing the appropriate components and experimental parameters of the fabrication/manufacturing process.

4.2 Liquid marbles: superhydrophobic entities with unique properties

Experimentally formed liquid marbles exhibit slightly different properties compared to naturally formed ones. Raindrops fall from big heights and get covered with particles due to internal currents and to kinetic energy [84]. Thus, the marbles exhibit *elastic-solid* and also *fluid* properties, known as a double "solid-fluid" character. The assumption that liquid marbles' elasticity is related to replacing liquid-solid (support) interface with solid (shell)-solid (support) interface is sustained by the absence of colored traces left by sodium hydroxide liquid marbles rolled on a phenolphthalein surface [85]. Moreover, shape changes occur for viscous marbles placed on an inclined plane: centrifugal forces determine marbles to slide off, while acceleration leads to the transformation of the spherical shape into "peanut," toroidal/"doughnut" shape [86], as presented in **Figure 9** [87].

Other experiments on liquid marbles' shape and elasticity proved how gradual compression of the marbles resulted in successive cracking and ultimately breaking of the shell, followed by collapse. Before the collapse, marbles allowed a compression up to 30% from the initial dimension [88].

Coalescence of the drops and possibility to engulf exterior objects may also be related to elasticity. As a result of applying exterior forces, two different liquid marbles connected through a glass bar undergo coalescence, forming a bigger structure and sharing a divided shell, as illustrated in **Figure 10(a)**. Regarding the possibility to "swallow" other objects, organic liquid covered in FD-POSS marbles is injected with another organic fluid. As long as the condition of immiscibility between the liquids is respected (proposed liquid pairs: toluene/DMSO, hexadecane/water), "encapsulating liquid marbles" are formed (**Figure 10 (b)**) [89].

Other liquid marbles' curious properties reside from freezing and drying in extreme temperature conditions. Experiments on PTFE-covered liquid marbles reveal surface aggregates, and multilayers are formed at the liquid-air interface, triggering wall thickening and shrinkage during *evaporation*. Thus, slow evaporation

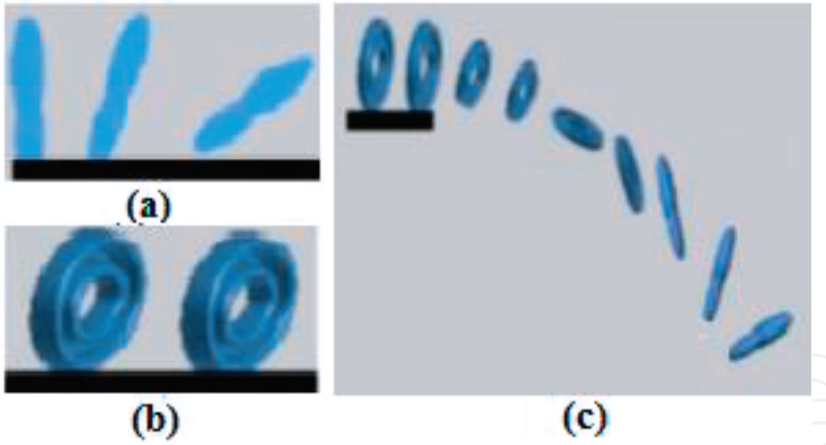

Figure 9.
Rolling liquid marbles: (a) "peanut" shape, (b) "doughnut" shape, and (c) transformation of "doughnut" into "peanut" shape, as the plane is removed [87].

Figure 10.
(a) Liquid marble coalescence: (b) FD-POSS liquid marble encapsulating DMSO.

of water results in prolonged resistance of the microparticle-covered marbles, with emerging applications in microfluidics [90]. The liquid marbles' shell layering raised curiosities: a mono-stratified shell determines the marbles to dry faster than a plain drop. The explanation lies in the fact that heat generates shrinkage at the liquid-air interface in case of the uncovered drop, while solid particles block interface compression during drying. Marbles covered in a multilayered shell dry harder than uncovered drops, depending on the thickness of the particle layer. Studies reveal the importance of environmental temperature and humidity in investigating evaporation: humid air delays evaporation of the liquid marble's internal phase [91, 92].

On the opposite pole of heating marbles are *freezing* ones, which were firstly reported as *Lycopodium*-covered water on a silicone support at −8°C. The marbles changed their shapes, as they flatten and extend sides: the "dome" shape evolves into a "flying saucer" shape, while the freezing process begins at the bottom and advances toward the top (**Figure 11**) [93].

Liquid marbles' behavior while *floating* on a liquid surface was also considered in recent experiments, since not only the liquid support surface deforms but also the marble itself. Particles covering the marble are packed between two fluids (liquid marble's core and carrier liquid) and change distribution leading to the marbles' collapse and release of the core into the support liquid. This phenomenon happens in normal conditions. In humid atmosphere, marbles maintain their shape many days while floating [94]. As expected, the deformation of the interface increases, consecutive to larger drops [95].

After floating investigations, *self-propelling* of liquid marbles became of interest, when an autonomous movement similar to Leidenfrost droplets was reported for water and alcohol marbles covered in extremely hydrophobic fumed silica. Supports include Petri dishes with water, and straight-line movement was observed. Taking into account the particles separating the core from the exterior, in the floating case,

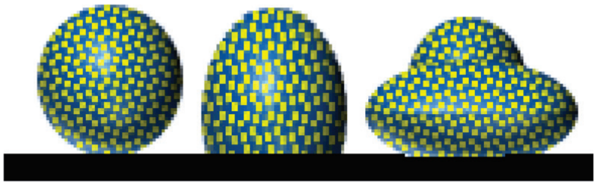

Figure 11.
Shape changes in freezing liquid marbles: Initial, "dome," and "flying saucer."

a vapor layer is responsible for marbles' support, similar to the Leidenfrost effect. The layer forms as ethanol evaporates (from the core). The Marangoni flow is triggered by ethanol condensation on the water support surface. Thus, the marbles begin to move without rolling. Fumed silica and Teflon-covered Janus marbles present no black traces while moving [96].

4.3 Small-scaled superhydrophobicity with innovative applications

Due to their versatile formulations and their special superhydrophobic-like properties, liquid marbles exhibit promising applications in various domains.

In the pharmaceutical domain, liquid marbles are known as precursors of hollow granules, microcapsules, and Pickering-like emulsions. Polytetrafluoroethylene (PTFE), aerosil, and Ballotini spheres as shells and binders (PVP, HPMC, HPC) are used to form liquid marbles which are dried through various methods: moist air at 24°C, freezing at −50°C, and dry air at 60°C, 80°C, 100°C). *Hollow granule* formation is promoted by high drying temperatures, nanometric particles, and high binder concentrations. Therefore, aerosil proved successful regarding spherical shape generation, when used together with HPMC and drying at 100°C forming ideal-shaped hollow granules [97], as presented in **Figure 12** [87].

Moreover, liquid marbles are able to include low solubility and hydrophobic active ingredients, representing formulation alternatives in case of substance incompatibilities and targeted release drugs (e.g., intestine and not stomach). The active ingredient's protection is mandatory against local acidity/enzymes and pathogens/other substances competing for binding sites and can be achieved by choosing the ideal development process while following Quality by Design Guidelines [87].

Microcapsules can also be obtained from liquid marbles: exposed to solvent vapors, submicrometer-sized polystyrene particles (PDEA-PS) covering

Figure 12.
Hollow granule [87].

poly(2(diethylamino)ethyl methacrylate) cores undergo a polymerization reaction, forming a filled capsule. After the core evaporates, the now empty microcapsule maintains its shape, representing an important idea for further design of modified drug release systems [98].

Liquid marbles have also been reported as precursors of *Pickering-like emulsions*. The difference between classical and Pickering emulsions stands in the lack of added stabilizing agents. Pickering emulsions are stabilized by solid particles adsorbed at the internal and external phase interface. These adsorbed particles are attached to the drop they cover and are wetted in both the watery and the oily phases, conferring integrity to the immersed drop [99, 100]. Stabilizer particles include clays, latexes, calcium carbonate, carbon black, magnetic particles, proteins, and even bacteria. Hydrophobic particles stabilize water/oil emulsions, and hydrophilic ones stabilize oi/water emulsions [99]. Stable Pickering like emulsions containing *Lycopodium*-covered liquid marbles were obtained in PDMS, as presented in **Figure 13**.

Experiments show good stability of marbles immersed in less polar liquids (silicone fluids, aromatic solvents), while collapse is a trigger in polar solvents. Pickering-like emulsions find their applicability in cosmetic formulations due to no allergenic, cytotoxic, or hemolytic stabilizers. Topical use of caffeine Pickering emulsions in controlled studies revealed higher absorption than the other pharmaceutical forms, due to silica-covered liquid marbles, which promote epidermal caffeine absorption from the aqueous phase of the emulsion [101]. Also, retinol included in the oily phase of a Pickering-like emulsion is stabilized against UV radiation and only penetrates the corneous layers of the epidermis [100].

Sticking to the field of topical application, liquid marble formulations represent a basis in foundation, antiperspirants/deodorants, solar protection products, and some drug formulation. Easy application is followed by a moisture and cooling sensation due to internal phase liberation. Among components, the most popular are deionized/floral water (50–90%) mixed with polymers/copolymers (PVP), wetting agents (hyaluronic acid), hydrosoluble vitamins, preservatives, and antioxidants. Such formulations are recommended for oily skins, due to a low oil content (<10%). Therapeutic agents may be added: antibacterial, antifungal, analgesic, keratolytic, corticosteroids, etc.

A novelty in blood typing is represented by liquid marbles as *biological microreactors*: hydrophobic-precipitated $CaCO_3$-covered blood drops are injected with antibody solutions (anti-A, anti-B, anti-D). If the color changes from red to dark

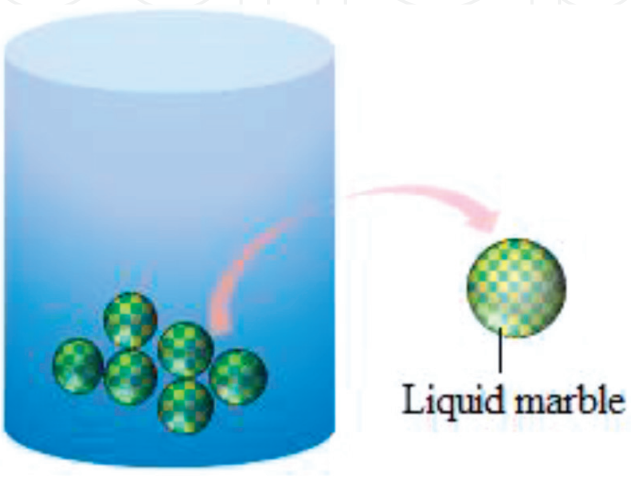

Figure 13.
Pickering-like emulsion.

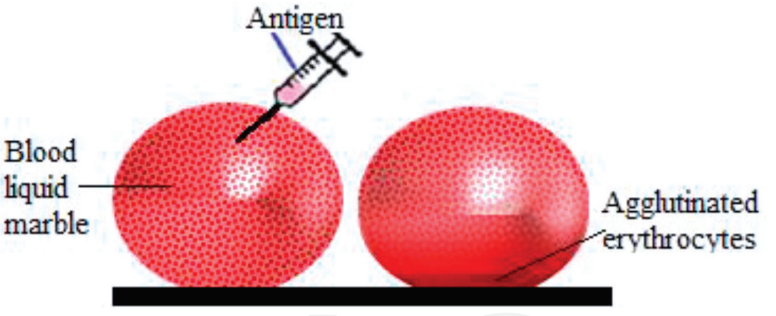

Figure 14.
Hemagglutination reaction inside a blood liquid marble [87].

red, the hemagglutination reaction is considered positive, as illustrated in **Figure 14**, and the blood type is immediately identified. If the color does not change, the reaction is negative, and another drop is tested using another antibody. The technique is considered innovative: low contamination risks and reagent costs and necessity of small blood samples, which is beneficial for patients [102].

PTFE liquid marbles were also used as *cell culturing medium*: spheroids successfully developed from $HepG_2$ hepatocellular cancer cells. Advantages include promoting cell aggregation due to restricted space and no human intervention. In order to screen cell development inside the marble, magnetic particles are proposed for shells, leaving an observation section open when a magnetic field is near. These methods are used in cell physiology screening or tissue engineering [103], stem cells evolution into embryoid bodies [104], and bacterial culturing especially for anaerobic species [105].

Liquid marbles are providers of 3D spherical space with adjustable volume and formulation and can also be regarded as *chemical micro-reactors*, hosting different chemical reactions resulting in toxic/explosive unwanted products, in small amounts, and isolated. Intervention from the outside is possible for "intelligent marbles" covered in magnetic particles, in order to inoculate a new reagent into the reaction, collect a product, identify, or quantitatively evaluate a certain compound. Indicators of core chemical reactions include color changes, chemiluminescence, and precipitation reactions [106]. Besides hosting chemical reactions, some marbles called "plasmonic liquid marbles" are covered in Ag/Au nanoparticles and represent special analytical platform precursors. They function as qualitative and also quantitative detectors for waste products resulted from industrial spills, being able to trace compounds in concentration of femto- or ato-molar concentrations (10^{-15}, 10^{-18}) [107]. "Cleaning agent stimuli-responsive liquid marbles" detect pollutants and signal their presence by shell breakage. The core eliminates a detoxifying agent (1 N-oxone covered in Cab-O-Sil T-530 shells) which cleans oil-contaminated water [108].

5. Conclusions

This chapter is an interdisciplinary approach on extreme wettability, granting particular attention to superhydrophobic natural and artificial surfaces and to liquid marbles, as exponent. Literature data is reunited in order to offer a unique and complex understanding of superficial properties from a theoretical point of view, in correlation with examples from the natural environment. An extensive picture illustrates how superhydrophobicity was initially interpreted, how its understanding evolved, becoming of large exploitation in many industrial fields. Superficial properties and liquid marbles are linked through conceptual similarities, as an opening gate to numerous applications.

Liquid marble exploration substantially advanced during the last years, from the phase of basic understanding through wetting models to more complex interpretations, obtaining methods and applications. Studies revealed a "non-wetting" contact with solid supports and many unexpected properties, such as versatility in choice of cores and shells, recoverable deformability, ability to float on water, low evaporation rate, and significant advantages derived from a well-confined compartment. Emerging applications discussed in this chapter are diverse and offer a rich variety of further exploitation possibilities, arising from complex structural designs.

Conflict of interest

We, the authors of this paper Cristina Elena Dinu-Pîrvu, Roxana-Elena Avrămescu, Mihaela Violeta Ghica, and Lăcrămioara Popa, declare no conflicts of interests.

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