

# The Quest for Extreme Water Repellency: Superhydrophobicity Made Easy

Graham C. Saunders

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton 3240  
(e-mail: g.saunders@waikato.ac.nz)

## The Interaction of Water with a Surface: An Introduction

In his seminal work *On Floating Bodies I* Archimedes of Syracuse provided an explanation of the action of solid bodies on water.<sup>1</sup> Although his thesis immediately benefitted King Heiro II<sup>2</sup> and has continued to serve mankind well, it ignores the effect of the interfacial interactions between the solid, water and air (surface tension). These interactions are negligible, or at least are considered negligible, compared to forces arising from the effect of gravity on large bodies. However, as the mass of the body decreases, the surface interactions become increasingly important leading to some unusual and potentially useful phenomena. The understanding and application of these effects is currently driving much fundamental research by physicists, chemical engineers, material scientists, and chemists into surfaces that display extreme properties, in particular extreme water repellency, or *superhydrophobicity*. It is only comparatively recently that detailed mathematical expressions for the interaction between a liquid, solid and gas at these extremes have been developed, making progress that parallels that for the fabrication of these surfaces.

When a drop of liquid comes into contact with a flat solid surface the outcome is determined by the interfacial free energies between surface and gas, between liquid and gas, and, most importantly, between surface and liquid. If the net interaction between liquid and solid is attractive then the drop will tend to spread out and increase the area of contact (or, more correctly, increase the length of the boundary between all three phases), and if it is repulsive then the drop will tend to bead up so as to decrease the area of contact (decrease the length of the boundary line between all three phases). Provided the volume of the drop is sufficiently small that the effect of gravity on its shape is negligible, then the liquid typically adopts the shape of a truncated sphere. This can be described by the contact angle ( $\theta$ ) which is the angle defined by the surface and the tangent of the liquid droplet at the point of contact of all three phases as shown in Fig. 1. The contact angle is related to the three interfacial free energies according Young's relation:<sup>3</sup>

$$\cos \theta = (\gamma_{\text{surface-gas}} - \gamma_{\text{surface-liquid}}) / \gamma_{\text{liquid-gas}}$$

where  $\gamma_{a-b}$  is the interfacial free energy per unit area (force per unit length) between two phases a and b.

This can be rewritten as the Young-Dupré equation:

$$\cos \theta = (\Delta W - \gamma_{\text{liquid-gas}}) / \gamma_{\text{liquid-gas}}$$

where  $\Delta W$  is the adhesion energy per unit area between

the solid and liquid, and  $\gamma_{\text{liquid-gas}}$  is the surface tension of the liquid. It is evident from this equation that, for surface-liquid combinations that are strongly attractive, the contact angle will be small: as  $\Delta W \rightarrow 2\gamma_{\text{liquid-gas}}$  and  $\cos \theta \rightarrow 1$ . Conversely, when the surface is *hostile*, *viz.* there is little attraction, the contact angle will be large as  $\Delta W \rightarrow 0$  and  $\cos \theta \rightarrow -1$ . It is also evident that for weakly attractive surface-liquid combinations, liquids with large surface tensions ( $\gamma_{\text{liquid-gas}}$ ) will tend to give larger contact angles, since, when  $\Delta W \ll \gamma_{\text{liquid-gas}}$  ( $\Delta W - \gamma_{\text{liquid-gas}} \approx -\gamma_{\text{liquid-gas}}$ ) Water has a high surface tension (*ca.* 0.072 Nm<sup>-1</sup>) in comparison to other common solvents such as hexane (*ca.* 0.018 Nm<sup>-1</sup>) and methanol (*ca.* 0.023 Nm<sup>-1</sup>), and so typically gives higher contact angles with hostile surfaces.

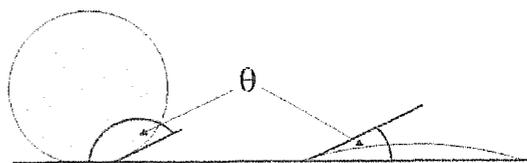


Fig. 1. Contact angles of a droplet on *phobic* and *philic* surfaces.

Most important liquid-surface phenomena and their applications, especially those in nature, involve water and air as the liquid and gas phases. The adjectives *hydrophobic* and *hydrophilic* have arisen to describe surfaces on which water beads up ( $\theta > 90^\circ$ ) and those on which it spreads ( $\theta < 90^\circ$ ). For more extreme contact angles the terms *superhydrophobic* and *superhydrophilic* have been introduced to describe surfaces that display contact angles of greater than  $150^\circ$  and less than  $5^\circ$ , respectively. These are arbitrary values that carry no special scientific significance, but they are universally accepted.

Nature provides us with some beautiful examples of superhydrophobicity. For example, pond skaters (genus *Gerriidae*), lotus leaves and the fog-harvesting Namib Desert beetles all show exceptionally high contact angles (Table 1). It is clear from these examples that a low surface energy coating is essential to generate superhydrophobicity; Nature uses waxy organic molecules to provide this coating. Although organic polymers, such as polythene (*ca.* 30 mN m<sup>-1</sup>), have lower surface energies than substrates such as metals and glass (*ca.* 45 mN m<sup>-1</sup>), they are not as low as those of polyfluoroalkyl organics. Consequently, it might be expected that a compound such as polytetrafluoroethylene (Teflon®), the archetypal non-stick material, which has a surface free energy of 22 mN m<sup>-1</sup> by virtue of the non-polar C—F bonds, would be at least as superhydrophobic as Nature's examples. However, the contact angle of polytetrafluoroethylene is meager in comparison (Table 1). Nature teaches us that roughness is also neces-

sary to generate superhydrophobicity. For example, pond skaters' legs have a hierarchical structure of nanogrooves in microsetae (tiny hairs), and it is this double roughness that dramatically enhances the contact angle.<sup>4</sup> The effect is also evident when polytetrafluoroethylene is roughened by treatment with oxygen plasma, although not to the same extent.<sup>5</sup>

Table 1. Representative contact angles

Material	$\theta / ^\circ$
Pond skater's leg	$167.6 \pm 4.4$
Lotus leaf	$\approx 160$
Namib Desert beetle	$\approx 160$
Polytetrafluoroethylene	$116 \pm 2$
Polytetrafluoroethylene after plasma treatment	$131 \pm 4$
Laser ablated polypropylene with sputtered polytetrafluoroethylene	up to 170
<i>n</i> -Perfluoroeicosane	$\approx 119$
Etched aluminium coated with polyfluoroalkylsiloxane	156
Etched copper coated with polyfluoroalkylsiloxane	153
Copper or zinc coated with silver or gold, coated with polyfluoroalkylthiol	$173 \pm 2$
Copper coated with silver, coated with dodecanoic acid	156
Silicon wafers treated with methyltrichlorosilane	up to 180

Although very probably simplistic and approximate, it is commonly considered that two regimes operate for water on a rough surface. In the Wenzel state, the water is in contact with all the surface,<sup>6</sup> whereas in the Cassie-Baxter state the water rests partly on cushions of air trapped in surface cavities and touches the surface only at promontories (Fig 2).<sup>7</sup> For the Wenzel state the relationship between the contact angle and surface roughness can be quantified by the expression:

$$\cos \theta = r \cos \theta',$$

where  $\theta'$  is the contact angle for a smooth surface of the same material and  $r$  is the roughness factor, *i.e.* actual surface area/planar projection. More correctly, this is the actual length of the boundary between all three phases/the projected length of the boundary between all three phases on a smooth surface.<sup>8</sup> Although in practice it is very difficult to measure 'r' directly, the equation clearly indicates that if  $\theta'$  is greater than  $90^\circ$  then hydrophobicity increases with the amount of roughness. Roughness also enhances hydrophilicity if  $\theta'$  is less than  $90^\circ$ .

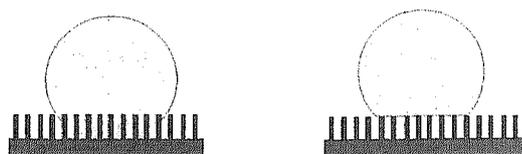


Fig. 2. Wenzel and Cassie-Baxter regimes.

For the Cassie-Baxter state the contact angle is given by:

$$\cos \theta = f_1 \cos \theta' - f_2,$$

where  $f_1$  is the fraction of liquid in contact with the surface and  $f_2$  is the fraction sitting on air ( $f_1 + f_2 = 1$ ). Although roughness is not explicit in this equation, it can be easily imagined that greater roughness will lead to more air trapped in surface cavities.

Although the contact angle is a useful parameter, it can be misleading and is difficult to measure at the extremes. It is calculated by line-fitting to photographs of the droplet and, as it is not always clear where the droplet touches the surface, a degree of subjective judgement is used. There is also often hysteresis in the contact angle for droplets as their size is altered. The difference between the advancing angle (that of a growing droplet) and receding angle (that of a shrinking droplet) also gives an indication of the degree of hydrophobicity. Another useful parameter is the roll off, or sliding angle. This is the angle through which the surface must be tilted before a sessile droplet will start to move and it is related to the contact angle hysteresis; a low hysteresis will give a low roll off angle and a large hysteresis will give a large one. The perfect hostile surface should display a contact angle of  $180^\circ$ , no contact angle hysteresis, and an immeasurably small roll off angle. Additionally, the surface should show no adhesion when it is lowered on to and lifted from a water droplet.<sup>9</sup>

Fabrication of extremely hydrophobic surfaces with  $\theta$  approaching  $180^\circ$  previously has been tricky and expensive: The substrates are difficult to prepare, the processing involves specialized equipment such as plasma generators, and reproducibility can be problematic.<sup>9,10</sup> Furthermore, the surfaces are fragile, easily damaged, and cannot be repaired or regenerated readily. Consequently, potential applications have been limited to small-scale high cost technologies, such as microfluidic and lab-on-a-chip devices. Large-scale industrial applications have also been limited severely by the lack of methods of preparing superhydrophobic surfaces on metals. There are a small number of methods for coating metals with *e.g.* polyfluoroalkylsilicones, but prior preparation of the metal surface is required, which for some metals involves lengthy acid treatment. The surfaces are only just superhydrophobic (Table 1) and are easily damaged.

## Easy Superhydrophobic Surfaces

The involvement of an inorganic chemist in this area arose when a colleague, Dr. Steven Bell, wished to use superhydrophobic surfaces for Raman spectroscopic experiments. Knowing of my background in fluorine chemistry, he approached me seeking assistance in making surfaces by etching a metal with hydrofluoric acid.<sup>11</sup> After etching, the metal was immersed in a solution of a polyfluoroalkylsiloxane formed *in situ* by aqueous methanol hydrolysis of a trialkoxysilane. Our results were disappointing. We wondered why this was the case, and we were particularly concerned that it was unclear how, or indeed if, the siloxane was chemically bonded to the metal. And so, with little knowledge of superhydrophobicity, or of other attempts to generate hostile surfaces, we naïvely set out to develop an alternative method.

It is well established that thioalcohols form self-assembled monolayers on gold and silver surfaces by way of covalent metal—sulfur bonds. Typically, past research focussed on well-defined smooth metal surfaces that are more amenable to study by a range of physical techniques, in particular ellipsometry. Indeed, a number of elegant studies have been performed to establish the packing of the thiols and structure-property relationships.<sup>12</sup> However, as these surfaces are smooth they do not display superhydrophobicity even if polyfluoroalkyl thiols are used. It is also well known that in the absence of a metal oxide coating, metals undergo spontaneous electrochemical oxidation with solutions of metal salts with more positive reduction potentials. In this way one metal may be galvanically deposited on another by simple immersion of the first in an aqueous solution of a salt of the other. For example, gold may be deposited on zinc [ $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.763 \text{ V}$ ] by dipping a piece of zinc in a solution of tetrachloroaurate(III) [ $E^\circ(\text{AuCl}_4^-/\text{Au}) = +0.994 \text{ V}$ ]. Thus, it occurred to us that depositing silver or gold on a metal and then coating that with a polyfluoroalkylthiol may be a good place to start our investigation. The results were astounding!<sup>13</sup>

Copper or zinc foil was immersed in an aqueous solution of silver nitrate or tetrachloroauric acid for *ca.* one minute, and then immersed in a dichloromethane solution of a thiol for five minutes. The contact angles of the surfaces were calculated conservatively as  $173 \pm 2^\circ$  (Fig. 3), but since the roll-off angles were only  $0.64 \pm 0.04^\circ$ , and no adhesion was observed when they were lowered onto and lifted from a water droplet, the surfaces can be regarded as almost perfectly hydrophobic. Furthermore, the surface free energies were calculated to be  $1.00 \pm 0.02 \text{ mN m}^{-1}$ , a value significantly lower than that of pure fluorocarbons such as *n*-perfluoroicosane ( $6.7 \text{ mN m}^{-1}$ ).<sup>14</sup> Scanning electron microscope studies showed that the surfaces had the necessary hierarchical structure. This resulted from the student, Iain Larmour, fortuitously selecting the correct combination of silver nitrate concentration and immersion time for the galvanic deposition; lower concentrations or shorter times would have given incomplete coverage of the metal or coatings too thin to give sufficient roughness, while higher concentrations or longer times would have given a thicker, but more uniform, smoother surface coatings.

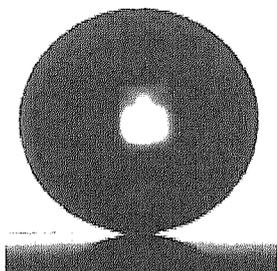


Fig. 3. An  $8 \text{ mm}^3$  water droplet on zinc coated with silver, coated with polyfluoroalkylthiol.

This double immersion method is cheap, simple and quick. It is applied to metals and, as the surfaces may be readily repaired by repeating the process, it represents a

technological leap in fabricating hostile surfaces. It is so simple that it has been adapted for a school experiment!<sup>15</sup> Subsequently, it was found that 1-decanethiol gives surfaces that are almost as superhydrophobic as those formed by polyfluoroalkylthiol, reducing the cost and alleviating concerns about the possible toxicological effects of polyfluoroalkyl compounds. And it is not limited solely to superhydrophobicity! For example, superhydrophilic surfaces may be generated by using 6-hydroxyhexanethiol in place of the polyfluoroalkylthiol. The method has allowed us, and others, to investigate a range of phenomena and develop possible industrial applications.

## Superhydrophobic Phenomena

Superhydrophobicity is responsible for a range of well-known phenomena, including self-cleaning by lotus leaves surfaces, meniscus-climbing by insects, and the combining of breathability and waterproofing in fabric. However, there are phenomena associated with superhydrophobicity that have been little studied because of the technical difficulties of preparing suitable surfaces. The double immersion method provides such surfaces, allowing the investigation of established and new phenomena, such as those described below.

### Underwater Mirror

Only as recently as 2006 was it predicted that underwater superhydrophobicity was possible and thermodynamically stable,<sup>16</sup> and the double immersion technique has provided surfaces that have confirmed this. Superhydrophobic metal surfaces appear matt black in air and maintain this when submerged and viewed at or close to the perpendicular. However, when viewed at an angle of *ca.*  $47^\circ$  or less to the plane of the surface, they have the appearance of a mirror (Fig. 4). This arises from reflection off an air-water interface (critical angle  $48.63^\circ$ ), as occurs with open areas of still water and bubbles of air trapped by aquatic insects, such as diving beetles. The presence of a layer of air over the surface is indicative of an extremely superhydrophobic surface in the Cassie-Baxter regime for which it is calculated that water touches less than 1% of the surface.

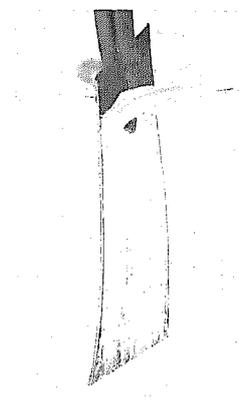


Fig. 4. Underwater mirror revealing blemishes (upwards from bottom left).

The mirror is useful for detecting defects in the surface, since these appear as dark spot or lines (Fig. 4). It might be expected that if the system is put under pressure the

surface will change from the Cassie-Baxter to the Wenzel regime, the onset of which will be evident from a disappearance of the mirror. It has yet to be established at what pressure this occurs, but the Cassie-Baxter regime is stable to at least 1.2 atm.

### Mesh Boats and Archimedes' Principle

Metal objects with superhydrophobic surfaces experience more buoyancy than those without these surfaces. This stems from the more repulsive surface-water interfacial interaction. As pointed out previously, the net force is dependent on the boundary line between the three phases rather than the surface area. Consequently, a superhydrophobic metal mesh should experience more force than a piece of foil of the same mass. Furthermore, below a certain hole size of the mesh the water repellency of the surface should prevent water from passing through the mesh, unless pressure is exerted. The double immersion method readily allows the fabrication of hostile metal meshes, and with a polyfluoroalkylthiol coating, water will not pass through holes smaller than *ca.* 2.5 mm in diameter. Thus, small boats may be constructed of mesh, rather than metal sheets. It has been reported that small rectangular boats (up to 4 x 5 cm) constructed of copper mesh with pore sizes up to 0.25 mm coated by the double immersion method, but treated with dodecanoic acid rather than polyfluoroaryl thiol, were able to support loads up to 30 times their mass.<sup>17</sup> Since dodecanoate generates a much smaller contact angle (Table 1), larger loads and larger pore sizes are possible with polyfluoroalkyl- or alkylthiols. Likewise containers for holding water may be constructed of mesh.

A related phenomenon concerns superhydrophobic sheets that float beneath the surface of the water. If a flat metal sheet is sufficiently light and floats in water, it will depress the water surface. If mass is added to the sheet the depression will increase until a point at which water will flow on to its upper surface and it will sink. For most metals the top surface would not be noticeably below the level of surrounding water before this occurred. However, if the sheet's top surface is hostile then it can actually be beneath the level of the surrounding water to a depth of *ca.* 4 mm (Fig. 5). A consequence of this is that the volume of water displaced by the object can be much greater than the volume of the object. At first it may appear that Archimedes' Principle is violated but it should be remembered that, rather than simply concerning equality of volumes, the principle states that the net upward force on a submerged object is equal to the weight of the water it displaces. Consequently, the upward force on the sheet will be much greater with a superhydrophobic coating than without one. It is interesting to note that it is only the top surface of the sheet that needs to be superhydrophobic. A superhydrophobic lower surface would provide a thin air layer, the volume of which would displace an equal volume of water, providing an additional upward force.

### The 'Cheerios' Effect

Metal powders can be conveniently coated by the double immersion method. Hostile powders are buoyant by virtue of the superhydrophobicity, and demonstrate a re-

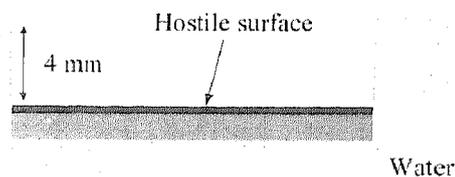


Fig. 5. Metal foil with a superhydrophobic top surface displacing more water than its volume.

markable effect, namely that when spread across the surface of water the particles congregate rapidly to form a raft: a dramatic demonstration of the *Cheerios Effect*.<sup>18</sup> This common phenomenon, named after the observation that the hoops of the well-known breakfast cereal tend to clump together in a bowl of milk, has been known for some time,<sup>19</sup> but it has only recently received a detailed mathematical treatment.<sup>20</sup> The reason the superhydrophobic metal powder shows the effect so well, is that since the attractive force between two particles is proportional to

$$[\frac{1}{3}\{2\rho_{\text{particle}}/\rho_{\text{water}} - 1\} - \frac{1}{2}\cos\theta + \frac{1}{6}\cos^3\theta]^2,$$

the more dense the particles the greater the force - and metals ( $\rho$ : 8.96 g/cm<sup>3</sup>) are considerably more dense than most floating objects, particularly cereal hoops. The strength of the force is reflected in the rapid formation of the raft, and its ability to support loads and wrap around objects when they are pushed downwards.<sup>21</sup>

### Applications

Superhydrophobicity provides a wealth of applications. To date, most have been developed with non-metal substrates, *e.g.* anti-mist glasses, self-cleaning surfaces, breathable waterproof fabrics, non-fouling medical implants, microfluidic devices, *etc.* The ability to provide a superhydrophobic surface that can be repaired on a metal, especially on a large scale, opens up further important possibilities.

It has been established that a layer of air between a surface and water has important consequences for the motion of one relative to the other, namely the reduction of drag. There have been some attempts to realize this for marine vessels by designing hulls with *cavity cushions* or by pumping air microbubbles over the hull.<sup>22</sup> Studies on the latter found that there was a net energy saving of 5–10% in a trial with a 120 m vessel. By virtue of providing an air layer, hostile metal surfaces may have an important application in marine transport, for which even a small energy saving has a large financial benefit. Additionally, such surfaces are expected to be more resistant to biofouling, which can increase drag by 50% and necessitate regular expensive treatment in dock. Use in metal pipes carrying water is another potential application. As well as reducing drag, the superhydrophobic surface can protect the metal pipe from corrosion. This latter property also suggests these surfaces will be useful in industrial heat exchangers and condensers. Fouling is also a huge problem with medical metal implants especially urethral stents. Mineral encrustation and bacterial colonization can cause life-threatening conditions, and regular replacement, requiring

expensive surgery, can be traumatic and dangerous. The lack of contact between water and a superhydrophobic surface significantly reduces both mineralization occurring on the stent and colonization by bacteria.

## Conclusions

Hostile, almost perfectly hydrophobic, metal surfaces can be prepared cheaply and quickly by a simple double immersion method. Imperfections can be readily identified using the underwater mirror and the surfaces can be readily repaired. It allows a range of phenomena to be investigated and opens up the possibility of large scale industrial applications that are being explored. It also provides some fun demonstrations, such as mesh boats and nets that can hold water. The method can be applied to provide other types of surface, e.g. superhydrophilic or reactive, by using an appropriate thiol. In conclusion, this innovation came from the collaboration of an inorganic and physical chemist to address a problem in surface science. Based on simple ideas, aided by some good fortune, the method has provided a welcome technological jump in the fabrication of hostile surfaces.

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## Acetonitrile Supplies

Late 2008 through to early 2009, acetonitrile supplies became another victim of the economic downturn currently being experienced globally. Companies looked after their big customers, but others were put on backorders or rationed with supplies.

Acetonitrile is widely used as a solvent in High Performance Liquid Chromatography (HPLC). The shortage now seems to be over but prices continue to be volatile and many users are finding the price much higher than a year ago.

The shortages were blamed on a combination of factors. Acetonitrile is a by-product of the process to form acrylonitrile, which is used in a range of materials for a variety of goods including car manufacture. The economic recession has meant these materials are not required as much as previously, hence less acetonitrile is being produced. In addition a big acrylonitrile plant in Texas was affected by hurricane Ike and one or more plants in China were shut down during the Beijing Olympics. Also, it was hard to know how much stockpiling added to the shortage.

The response to this shortage saw many companies heavily promoting products to either reduce acetonitrile usage or provide alternatives. Some laboratories began transitioning to using other solvents like methanol, while others began looking at whether recycled HPLC waste was a viable option. It seems even now the shortage appears to be passed, alternatives are still being worked on or methods changed.

It is interesting to note this response compared to the change in petrol pricing a year ago and what the general population did in response. While petrol was not in short supply, the significant price jump did not seem to greatly alter society's dependence or use of petrol. Yet when a sector of the scientific community was affected by shortage and price hikes, there seems to have been a great deal of action and change in behaviour, even after the crisis was largely over.