Immersed superhydrophobic surfaces: Gas exchange, slip and drag reduction properties

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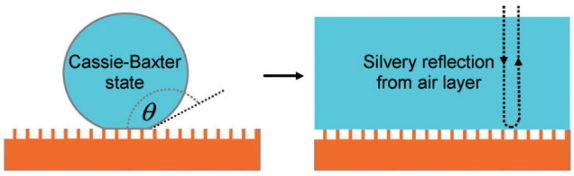
Immersion of some materials possessing superhydrophobic surfaces results in persistent surface-retained air-films. This provides a vapour-liquid interface allowing underwater respiration/gas exchange and modification of flow patterns inducing drag reduction.



Immersed Superhydrophobic Surfaces: Gas exchange, slip and drag reduction properties

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Abstract

Superhydrophobic surfaces combine high aspect ratio micro- or nano-topography and hydrophobic surface chemistry to create super water-repellent surfaces. Most studies consider their effect on droplets, which ball-up and roll-off. However, their properties are not restricted to modification of the behaviour of droplets, but potentially influence any process occurring at the solid-liquid interface. Here, we highlight three recent developments focussed on the theme of immersed superhydrophobic surfaces. The first illustrates the ability of a superhydrophobic surface to act as a gas exchange membrane, the second demonstrates a reduction in drag during flow through small tubes and the third considers a macroscopic experiment demonstrating an increase in the terminal velocity of settling spheres.

1. Introduction

Water and its interaction with solid surfaces are fundamental to both the core scientific subjects of biology, chemistry and physics and to the applied and technological subjects of materials science and engineering. To control that interaction, surface chemistry is used to alter the molecularly determined hydrophobic/hydrophilic properties of the surface.[1] Whilst surface chemistry can cause a droplet of water to spread into a film, there is no known surface chemistry that can cause a droplet to completely ball-up and roll off a surface. To achieve that, a surface must also possess an appropriate topography on a suitably small length scale. The modern era of research exploiting the interplay of surface chemistry and topography to create what are now known as superhydrophobic surfaces, began with research from two quite different areas: Materials Science and Plant Sciences. In 1996, Onda *et al.* demonstrated that a super-water-repellent surface could be made by controlling the crystallization of a paper-sizing wax so that a fractal-like surface structure formed.[2] A year later, Barthlott and Neinhuis highlighted how the microrelief of plant surfaces, mainly caused by epicuticular wax crystalloids, resulted in effective water repellency and also provided a self-cleaning mechanism (The Lotus Effect) for many biological surfaces.[3] In both cases, the focus was on the formation of droplets and the ease or function of their motion on the surfaces. Much of this focus has continued in the literature with many materials fabrication methods now available[4-6] and a well-developed understanding of the role of man-made and natural microtextures.[7]

The science of super-water-repellency predates that of the modern era with significant work in the 1940's and 1950's related to textiles[8-11] and to insect physiology.[12-15] For textiles to be fit for purpose, the production of a barrier to water penetration must often be accompanied by permeability for air and water vapour; the classic case being Gore-Tex®. For small insects, the surface of water presents a potential death trap. Surface tension is a force which scales with length, whilst gravitational force scales with length-cubed so that for sizes below the capillary length of water, κ^{-1}=2.73 mm, surface tension becomes dominant. Insects that do not have hydrophobic morphological adaptations to their bodies cannot escape the surface of ponds or other expanses of water. Some aquatic insects are even able to dive below the surface and use the hydrophobic structures to directly extract oxygen from water.[13-15] Thus, whilst much of the modern literature has considered superhydrophobic surfaces in the context of their droplet and water-shedding properties this remains a small part of their potential applications. A key feature of replacing a flat surface by a superhydrophobic surface is that, when in contact with water, a large area of the surface that would usually be a solid-water interface is replaced by two interfaces: solid-air and air-water.

In this paper, we highlight three of our recent experiments which have the common theme of investigating properties of immersed superhydrophobic surfaces. Our definition of a superhydrophobic surface is one on which a droplet of water has large contact angle, typically $\theta > 150^{o}$, and on which the droplet freely rolls, thus indicating low contact angle hysteresis. We start with a description of plastron respiration and its relationship to superhydrophobicity. We then consider whether a simple materials approach to superhydrophobic surfaces can reduce frictional drag during laminar flow of Newtonian liquids through small-bore tubes. Finally, we describe recent experiments reporting increases in terminal velocity when solid spheres with superhydrophobic surfaces settle in water.

2. Plastrons and gas exchange

When some superhydrophobic surfaces are dipped into water it is possible to observe a silvery mirror-like sheen at their submersed surfaces. This is due to the reflection of light from a sheathing layer of air retained at the surface (Fig. 1a) and is the underwater signature of a Cassie-Baxter state (Fig. 1b). A similar silvery sheen can be observed from some aquatic insects and spiders, and is due to a morphological adaptation that creates a superhydrophobic surface whose function is to allow underwater breathing without the need for a gill.[14] To understand plastron respiration first consider an insect carrying an air bubble as it submerges.[16] The bubble can act as an air store, but if that was all it was, the build up of carbon dioxide and the depletion of oxygen would soon terminate its dive. The effectiveness of bubble respiration is due to the extended bubble interface between the vapour and water allowing gaseous diffusion with carbon dioxide escaping into the water and oxygen from the water replenishing the bubble. However, an air bubble will shrink and eventually collapse, either due to changing size as nitrogen is slowly absorbed into the water or due to changing pressure as the insect dives deeper. The insect solution to the shrinking bubble problem is to fix the volume of the gas by creating a rigid set of hydrophobic hairs along a portion of their bodies to support a non-collapsible film of air (e.g. Fig. 1c) linked to their breathing holes; these plastron structures are similar to those used to create superhydrophobic surfaces (e.g. Fig. 1d). Any depletion of oxygen and increase of carbon dioxide in this layer results in a change in partial pressures across the gas-water interface which drives diffusion to restore the balance.[17]

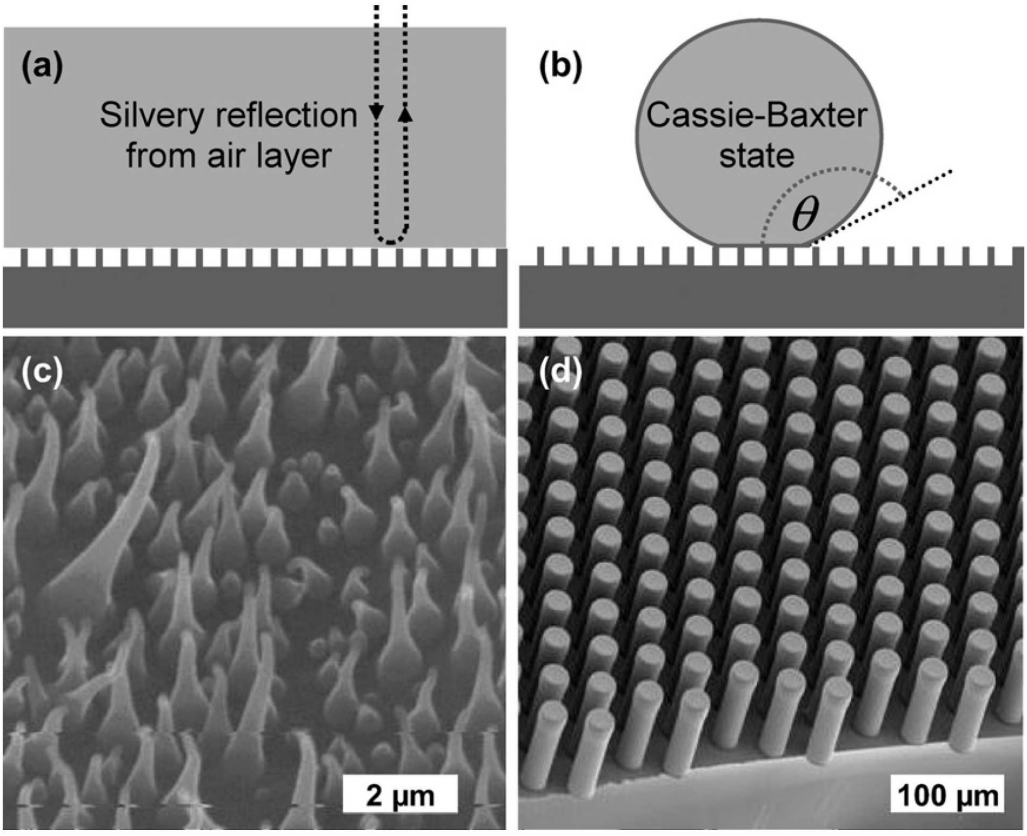

Fig. 1 Schematics of (a) an immersed superhydrophobic surface with a silvery reflection from a plastron, and (b) a droplet in a Cassie-Baxter state on a superhydrophobic surface in air. Electron micrographs of surface morphology of (c) plastron region of a Great Diving Beetle (*Dytiscus marginalis*), and (d) a superhydrophobic micro-post structure.

In the modern literature on superhydrophobicity the reports from insect physiology are rarely mentioned. Recently, Marmur discussed the theoretical feasibility of underwater superhydrophobicity and concluded that underwater superhydrophobicity "*is, in principle, feasible, and may be thermodynamically stable*."[18] Sixty years earlier, its existence had been recognised, a functional purpose identified and its theoretical relationship to the Cassie-Baxter equation, originating in textile research, examined.[12-14] More recently, the design and manufacture of technical superhydrophobic surfaces capable of withstanding significant fluid pressure heads and reducing fluid friction on the wetted portions of fluid handling systems has also been previously anticipated.[19,20] Nonetheless, Marmur's emphasis on focusing more widely than on droplets on surfaces in air is important and valuable. In our own work, we created a biomimic of a plastron using a hollow, superhydrophobic, sol-gel foam into which a fuel cell was inserted.[21] When operated with the foam immersed in oxygenated water, the internal cavity of the foam reaches an equilibrium oxygen level that can be maintained indefinitely. Subsequently, the mechanics of plastron respiration and its relationship to modern superhydrophobicity have been described in the review by Flynn and Bush.[22, 23] One of the conclusions from the original insect physiology literature was that an effective shape for the hydrophobic hairs forming the micro-topography is an inverted L shape using hairs of roughly circular cross-section. A matt of L-shape hairs is able to flex and so enable pressure to be better resisted, whilst the circular cross-section allows liquids to be supported even when the surface tension is lower and contact angle is far below 90^o (e.g. due to water contaminated by decomposing matter). With a horizontally oriented hair of circular cross-section, liquid can bridge between surface features even as the contact angle approaches zero. In recent work on superoleophobic surfaces this type of curvature has been termed re-entrant surface curvature.[24] We also repeated the plastron experiment using a superhydrophobic textile on a wire frame and observed higher equilibrium oxygen levels. It is therefore possible to speculate that some hydrophobic membranes may be acting as immersed superhydrophobic plastron retaining surfaces.

3. Slip and drag reduction

3.1 Super-channels and Slip

When a Newtonian liquid undergoes laminar flow across a solid surface it is commonly assumed that a no-slip boundary condition, requiring the velocity of the liquid to match that of the solid surface, applies.[25] The resulting velocity profile in a cross-section of a circular channel enclosed by a solid wall has a parabolic profile with a maximum flow rate at the mid-point between the walls as shown schematically in Fig. 2a. However, the fundamental boundary condition between two fluids, e.g. a liquid and a gas, is the continuity of the shear stress, and so when the upper half of the solid surface is replaced by an interface to air, the maximum in the velocity profile is close to the liquid-air interface (Fig. 2b). Effectively, the higher frictional drag experienced at the wall of the upper-half of the channel is replaced by a much lower frictional drag to air. Intuitively, it can be expected that when the entire wall of a circular channel is superhydrophobic, the situation is analogous to the flow of a liquid confined to retain its shape, but bounded on all sides by a layer of air – effectively the liquid flows as a tube of liquid through the air with little drag at its boundaries and having a plug velocity profile (Fig. 2c). This type of boundary condition is not true slip in the sense of liquid molecules sliding along the solid surface, but is apparent slip whereby the liquid-to-solid boundary has an intervening layer of gas of lower viscosity.[26, 27]

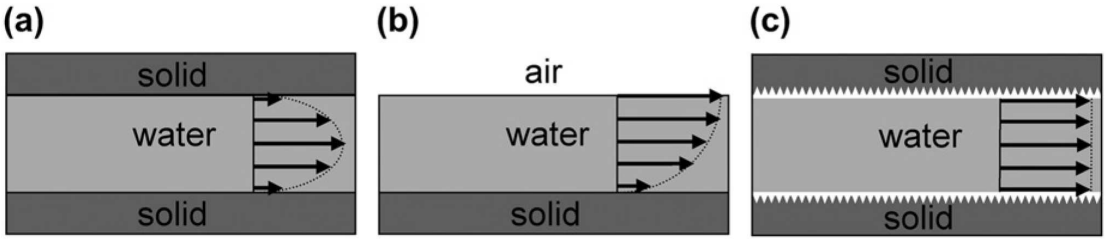

Fig. 2 Schematics of the cross-section of laminar flow through: (a) a tube with no-slip boundary conditions and high frictional drag at the walls, (b) a half-tube with a lower frictional drag at the air-water interface, and (c) a tube with a superhydrophobic interface providing a boundary with composite water-solid and water-air interfaces dominated by low frictional drag at the water-air interfaces.

The view of a superhydrophobic surface as providing an uninterrupted sheathing layer of air represents the extreme limit of vanishing Cassie solid surface fraction $\varphi_s \rightarrow 0$. A more realistic view is that the boundary condition varies locally across the solid surface with areas of no-slip and slip giving slip domains.[28,7] An effective slip length then provides a means to average flow over a composite surface.[27,28] These theoretical ideas developed and applied to superhydrophobic surfaces led Bocquet and Barrat[29] to conclude that "*very large slip lengths may be obtained only at the expense of important efforts to obtain nano-engineered surfaces with very small solid fraction.*" However, this conclusion seems to be strongly influenced by the micro-patterning approach to producing superhydrophobic surfaces and rather conservative given the many simple materials approaches to creating superhydrophobic surfaces[4] and the relatively early stage of development of related slip experiments.[30]

In our recent work, we developed a simple materials method to decorate the inside of copper tubes with nano-ribbons, whose surface chemistry could subsequently be converted to hydrophobic to create superhydrophobic walls.[31] When simultaneous experiments where performed to measure the pressure drop along four tubes, whose only difference was the type of surface finish of the internal walls, it was found that a significantly lower pressure drop occurred for the tubes with a superhydrophobic surface finish. The apparent slip lengths were a similar order of magnitude (100-200 μm) to those reported as giant slip on textured microstructures of posts and grates[32, 33], experiments confirming early reports on drag reduction by ultrahydrophobic surfaces.[34] The difference in resistance to flow was sufficient that it could be directly visualized by forcing water to a T-junction feeding one superhydrophobic tube and one ordinary tube and collecting the outflows in measuring cylinders.[35] The reduction in drag vanished at higher flow-rates, which could be due to a partial or full transition from the Cassie state to the Wenzel state so that the liquid conforms to the roughness[36-38] or a bubble mattress effect in which a curvature of the air-water interface can suppress slip or even increase drag.[39, 40, 7] Whilst the focus in the literature has generally been on ordered and well-defined topographic structures to allow testing of the predictions of slip models applied to superhydrophobic surfaces, it is probable that a more strongly oriented materials approach could deliver significant advances in practical systems.

3.2 Terminal Velocity and Non-Rigid Interfaces

It is well-known both experimentally and theoretically that the slow steady rise of a gas bubble involves significantly less drag than might be expected if it were a solid object of equivalent

radius and density.[25,41-44] This is because the solid-water interface of an immersed solid object satisfies a no-slip boundary condition (Fig. 3a), but an air-water interface of an air bubble satisfies a continuity of shear stress boundary condition that allows the tangential stress from the external flow to induce an internal circulation within the bubble (Fig. 3b). The effect of these different boundary conditions can be demonstrated experimentally simply by rigidifying the bubble surface using surfactants or impurities and so converting the bubble dynamics from one dominated by Hadamard-Rybzcynski drag into one dominated by Stokes drag. More recent work on fluid encapsulated droplets also indicates that internal circulation in both the shell and core can determine the drag (Fig 3c).[45] When the core is a solid and the encapsulating fluid is air (Fig 3d), the analytical solution for encapsulated spherical drops by Rushton and Davies[46] predicts a correction to Stokes' drag of 2/3 which gives the Hadamard-Rybzcynski bubble drag factor provided the thickness of the air shell does not become vanishingly small preventing circulation within the gas shell. This solution assumes that external flow does not distort the shape of the air-layer; an effect that could increase drag. In the literature relating to slip on superhydrophobic surfaces the possible importance of a non-rigid interface has rarely been mentioned, although the review by Neto *et al*,[27] which cites the experimental work in small air bubbles in water by Bachhuber and Sanford,[47] is one of the exceptions.

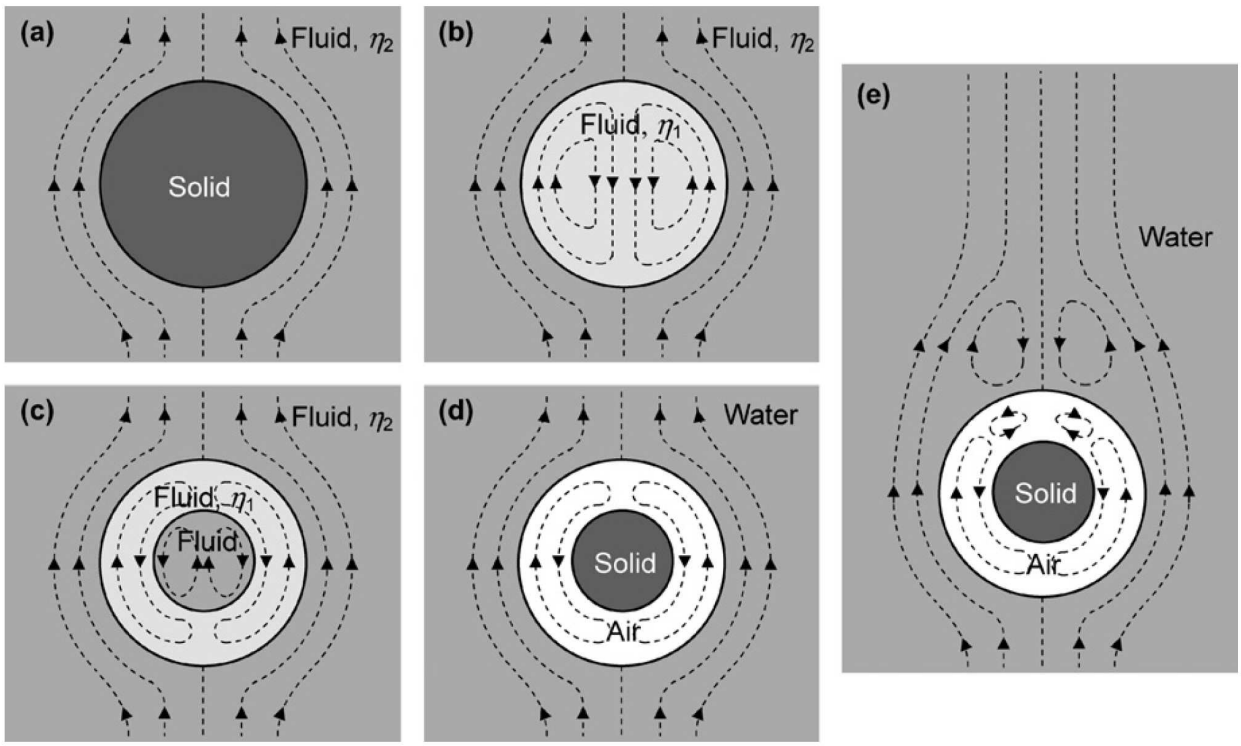

Fig. 3 Possible streamline patterns for spheres falling in a fluid of viscosity η_2: a) solid obeying Stokes drag, b) fluid of viscosity of η_1 obeying Hadamard-Rybczynski drag, c) fluid core encapsulated within a fluid sheath of viscosity η_1, d) solid core within an air sheath in water, and e) with a wake at higher Reynolds number.

In our work we investigated the terminal velocity of solid acrylic spheres (diameters in the range 2.533 cm to 5.071 cm) settling in large columns of water (2.2 m × 0.65 m) at intermediate Reynolds numbers Re=1×10^4-3×10^4.[48] The surface of each sphere was coated with sieved sand to create a rough coating and then further modified to provide a hydrophobic surface chemistry. On a flat surface this process creates a superhydrophobic surface with contact angles in excess of 150^o

and low contact angle hysteresis and when immersed in water the surfaces display a silvery sheen indicating that a layer of air (a plastron) is retained. To be able to make a direct comparison of the settling of a superhydrophobic sphere with and without a plastron, we also developed a wetting out procedure using ethanol so that a sphere could be immersed in water without retaining a plastron. This approach directly mimicked the methodology of early work in insect physiology examining the role of plastrons in underwater respiration. The results demonstrated that a settling acrylic sphere possessing a plastron had a higher terminal velocity than without a plastron, thus confounding what might be expected from the slight increase in buoyancy due to the air layer.[49] In our work we concluded that a persistent air layer, rather than just a superhydrophobic surface, is needed to achieve drag reduction. We also suggested that at these intermediate Reynolds numbers a sufficiently thick plastron would alter the flow patterns and wake separation and so could reduce drag (Fig. 3e). If it is the case that a superhydrophobic surface retaining an air layer when submersed can reduce drag, it is interesting to speculate whether the plastron observed on some aquatic insects might have a function relating to drag reduction and mobility rather than just underwater respiration.

4. Summary and Outlook

Superhydrophobic surfaces have a long history with the original studies spanning from textiles to insect and other biological surfaces. In the modern era, interest has been rekindled by the ability to fabricate or synthesize materials with micro- and nano-structured surfaces. It is not only the ability to create well-defined features on the smallest of scales that is of interest, but also the ability to shape those features. The height, size, spacing, curvature and orientation of surface features, controls the stability of droplets and the ease with which they move across the surface. There are many important aspects of droplet behaviour, such as directional shedding and asymmetric motion[50-52] and contact angle hysteresis[53], which can be further clarified. However, a fundamental characteristic of a superhydrophobic surface is the existence between the liquid and solid of both liquid-vapour and solid-vapour interfaces and the implications of this are far wider than simply the formation of a droplet shedding surface. For example, heat transfer[54], icing and frosting[55, 56] are all strongly influenced by the presence of the vapour phase.

The recognition that superhydrophobic surfaces can be designed to retain their Cassie state when completely immersed in water opens-up a range of possibilities. As shown in section 2, it is then possible to create a functional surface that acts as a gas exchange membrane extracting oxygen directly from water. In this mode of operation, the height, size, spacing, curvature and orientation determines the stability of the system with depth of immersion. However, the height of surface features and connectivity of the spaces between features will also determine the effectiveness of the diffusion of gas along the surface. This illustrates that the role of topography will be complemented by the effect of topology[57], an aspect that is also likely to become more important for droplet applications.[58]

The flow of liquids across surfaces or solids through liquids impacts upon a wide variety of applications and is not simply related to microfluidic systems where the solid surface area becomes large compared with the volume of liquid. Despite the widespread expectation that superhydrophobic surfaces lubricate flow, the number of experimental results supporting this remains relatively small, as indicated by the reviews cited in section 3.1. The claims of giant slip

have not been entirely free from controversy. Capillary flow experiments can be difficult to perform and durability of surfaces can present issues of reproducibility. The existence of both liquid-vapour and solid-vapour interfaces undoubtedly creates a heterogeneous boundary between a solid and the liquid in which it is immersed. However, the view of the boundary as possessing an effective or average slip may not be equivalent to viewing it as possessing an apparent slip due to a gas layer. In section 3.2, we have highlighted one type of macroscopic experiment with a possible interpretation (plastron drag reduction) that requires a non-rigid gas-liquid interface and the importance of circulation of the gas within all or part of the surface structure. Feature height and connectivity of the space between features may then be important beyond their influence on stability of the superhydrophobic state.

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