commentary

A smooth future?

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Research on superhydrophobic materials has mostly focused on their extreme non-wettability. However, the implications of superhydrophobicity beyond wetting, in particular for transport phenomena, remain largely unexplored.

When a water droplet rolls easily, retaining a nearly perfect spherical shape on a surface that remains essentially dry, such a surface is super-repellent or superhydrophobic. Common superhydrophobic materials include many plant leaves, duck feathers, and glass surfaces coated by black soot dispersed from a lighted candle (see Fig. 1a,b). By convention, for a surface to be superhydrophobic, the effective contact angle of the liquid droplet with the surface — a simple and robust characteristic — should exceed 150°.

The issue of the large contact angle of water droplets on plant leaves and animal surfaces was addressed over 80 years ago by Wenzel, Cassie and Baxter, who pointed out the two physical ingredients necessary for a surface to be superhydrophobic: a bare hydrophobic coating, such as wax crystalloids on plant leaves, and roughness at the micro-scale. Strong water repellency occurs because the roughness effectively increases the liquid–solid free energy. This is the consequence of either a larger real contact area between the two components, the case of the liquid impregnating the surface (the so-called Wenzel state[1]), or a replacement of the true liquid–solid contact by a highly energetic liquid–vapour interface — the case of the liquid interface suspended on an air cushion on top of the roughness peaks (the so-called Cassie[1] or fakir state). Although these early works spurred industrial interest in textile and glass coatings, the field of superhydrophobic materials remained essentially asleep for more than 50 years. In the late 1990s, as research in wetting reached maturity[2], publications by Onda and collaborators[3] and Neinhuis & Barthlott[4] demonstrated the possibility to reach nearly perfect non-wettability, far exceeding the performance of bare chemical coatings, such as Teflon (the contact angle of water on Teflon is about 120°). Subsequently, Bico & Quéré[5] laid out the basic physical picture for the transition between the Wenzel and Cassie states. This helped revive the enthusiasm for the field, and to attract scientists from physics, engineering, mathematics and chemistry.

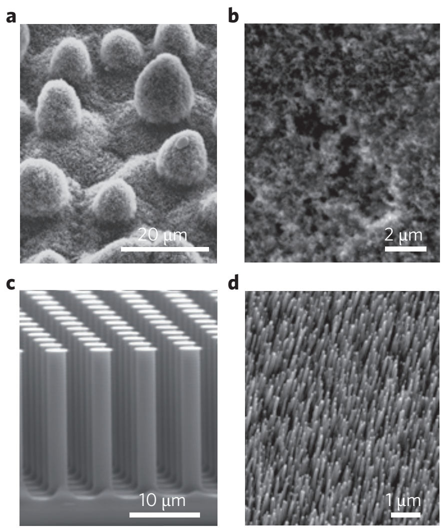

Figure 1 | Scanning electron microscopy images of four superhydrophobic materials with different structures. **a**, Hierarchical structure of the Lotus leaf (Nelumbo nucifera). Image adapted with permission from ref. 4, © 1997 Oxford Univ. Press. **b**, Black soot obtained from a lighted candle. Image courtesy of C. Duez. **c**, Patterned micro-pillars. Image courtesy of M. Reyssat. **d**, Carbon-nanotube carpet. Image courtesy of C. Journet.

What was behind this 'gold rush'? Taking a closer look at the literature on superhydrophobic materials over the past decade we see that, in response to the challenge of building cheap and scalable surfaces, research efforts have mainly focused on two questions: the design of new materials and the characterization of their wetting properties. Design-wise, imparting superhydrophobicity to a surface is not a difficult task. However, attaining robustness of the material over time and/or under external constraints has proved challenging, and much work has been dedicated to developing chemical recipes for superhydrophobic coatings[6]. Importantly, the popularization of nanofabrication tools has allowed well-controlled textured surfaces to be easily built (see Fig. 1c,d), thus providing ideal systems on which to test fundamental ideas. In parallel to the progress made in designing superhydrophobic materials, characterization of their wetting properties has been addressed with experiments, theory and computer simulations. For example, much insight has been gained into the relative stability of the Cassie and Wenzel states, the control of their stability by electric fields[7–9], and the transitions and hysteresis between these states.

Challenges in surface design

Notwithstanding significant theoretical and experimental progress, challenges remain in the material design of superhydrophobic surfaces for wetting purposes. First and foremost, there are the issues of robustness and surface fragility, both thermodynamic and mechanical. In fact, the fragility of the Cassie state is the main technological challenge for the use of superhydrophobic materials in underwater applications: at a depth of a few metres, the hydrostatic pressure is sufficient to balance the capillary pressure and thus destabilize the more desirable Cassie state in favour of a Wenzel state. This Cassie-to-Wenzel transition involves the impregnation of the roughness features of the surface with liquid, and it can occur for a number of reasons in addition to an increase in pressure, such as the presence of surface defects, evaporation, or the action of external forces. To avoid this problem, superhydrophobic materials can be designed with two length scales: a large scale governing the effective wetting properties of the surface, and a much smaller scale that prevents the final stage of impregnation[10] by increasing the critical transition pressure. Another method would involve a back-pressurization of the underlying gas layer, notwithstanding subtle geometric properties of the pressurized Cassie state with pressure-induced menisci curvature impacting both static and dynamic responses of the interface[11,12]. More work in this area will be needed, perhaps by taking clues from biology. The robustness of the superhydrophobic state in plant leaves or animal feathers originates from the self-healing of the surface, and similar biomimetic processes remain to be achieved in the lab. For instance, one could envision a systematic exploration of materials exhibiting self-organized disordered surfaces, such as alloy whiskers.

Second, even when the Cassie-to-Wenzel transition takes place, it is not at all clear how to induce a reversed Wenzel-to-Cassie route. The transition between the two states is strongly hysteretic. Proposed ideas have exploited Joule heating[7] or surface vibrations[13], but other practical approaches remain to be devised. A recent engineering breakthrough put forward a self-activating and self-limiting gas-restoration mechanism in the (wet) Wenzel state using electrolysis on surfaces with multiple length scales, which lead to a full transition to the (dry) Cassie state (Fig. 2), while preserving its superhydrophobic properties under high liquid pressure[14].

Finally, there is strong interest in the design of superoleophobic surfaces, able to repel organic liquids with very low surface tension. This is particularly relevant for applications in textiles and for screens in electronic devices. Recently, it has been shown that the use of re-entrant mushroom-like topologies for the surface roughness could lead to superhydrophobic behaviour for a large range of liquids[15], a result likely to spark off additional investigations.

New opportunities

Superhydrophobic materials have allowed the exploration of a wetting regime that is impossible to reach with chemical coatings. Many canonical capillarity concepts[2,16] have thus naturally been re-examined in the perfect non-wetting regime, both for statics (disjunction pressure, precursor films, wetting transition, critical wetting, role of defects) and dynamics (contact-line motion, forced wetting). However, we believe that the field should move beyond wetting, and should invest more effort into addressing how the unique properties of these materials can impact surface- and bulk-transport phenomena. For instance, the interface in the Cassie state consists of a majority of liquid–air contacts and very few direct solid–liquid contacts. Such an interface is thus essentially a flat bubble coating the solid, and it should strongly affect the transport of fluids, particles and heat, as well as phase-transition kinetics — such as dropwise condensation or boiling — acoustic impedance and optical reflection[17]. Another topic of interest is the drag-reducing ability of superhydrophobic surfaces. Indeed, the bubble cushion at the interface between the liquid and the solid in the Cassie state suggests a low viscous friction[18,19], as confirmed by a number of experiments[20].

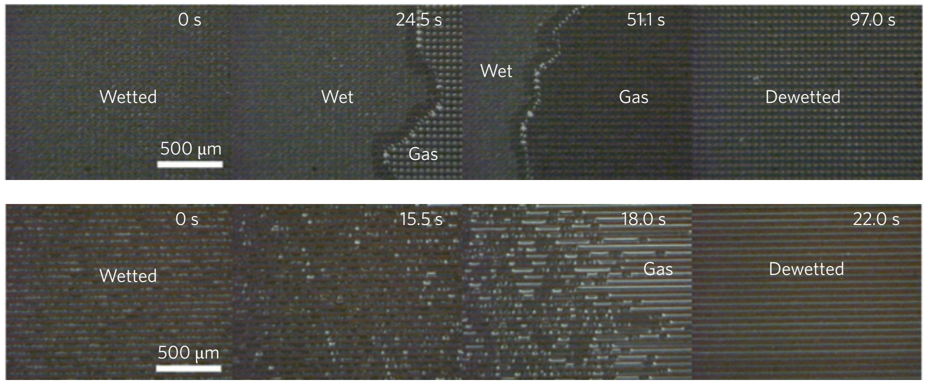

Figure 2 | Self-controlled Wenzel-to-Cassie transition induced using electrolysis. A superhydrophobic surface in contact with water is patterned with thin-film gold acting as the cathode, while an immersed thin wire acts as the anode. When the surface is in the Wenzel state (wetted), the circuit closes and gas is generated by electrolysis. The gas invades the topography of the surface causing the transition to the dry Cassie state (dewetted), at which point the chemical reaction stops. The geometry of the superhydrophobic surface can be a lattice of vertical posts (top) or a one-dimensional array of parallel grooves (bottom). Figure reproduced with permission from ref. 14, © 2010 APS.

New investigations will require new methods to quantify the effective properties of superhydrophobic surfaces. The traditional approach, which consists of characterizing superhydrophobic materials using solely their effective contact angles, will not necessarily lead to physical insight into transport phenomena. For example, the effective contact angle cannot be used as a parameter to characterize friction, for the simple reason that a geometrical (homothetic) scaling of the roughness features of a superhydrophobic surface will not modify its angle. Instead, a physical parameter that follows the scaling and quantifies drag reduction is an effective slip length, which is the ratio of the effective surface velocity to the surface shear rate (see Fig. 3). Slip lengths up to 400 µm have been attained[10], suggesting their potential applicability in ducts with diameters up to 1 mm. Indeed, a pipe 1 mm in diameter coated with a material with the aforementioned slip length would experience more than a 75% reduction in friction. Such a large reduction is of potential importance for laminar-flow fuel cells[21] and the dispersion of solutes in microfluidics, for example. However, it is unclear if fractal surfaces, such as the ones considered by Onda and co-authors[3], which show almost perfect non-wetting, would lead to a dramatic reduction in friction. Low friction requires a surface with a large no-shear (gaseous) region which, by definition, fractal surfaces do not possess.

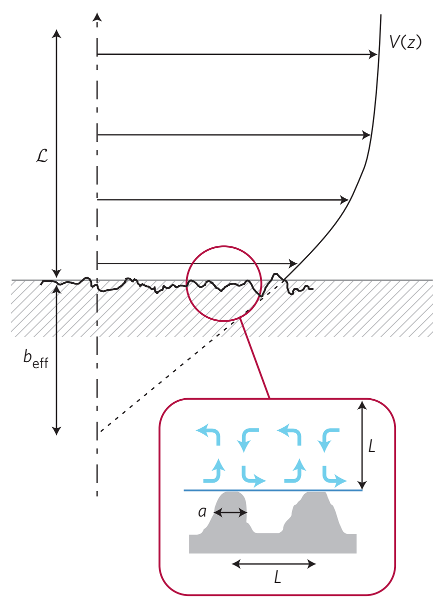

Figure 3 | Multiple length scales relevant to the fluid dynamics over a patterned superhydrophobic surface. $\mathcal{L}$ is the length scale of the macroscopic flow, characterized by a velocity profile $V(z)$, where z is the distance from the surface. b_{eff} is the effective slip length of the surface. A sketch of a typical roughness is shown in the inset, where L characterizes the feature-to-feature distance and a is the typical feature size. The blue arrows indicate the recirculating flow pattern occurring in the fluid over the roughness elements.

Multiple length scales

Extreme wetting in superhydrophobic surfaces is usually obtained at the expense of introducing many underlying microscopic length scales, which impact macroscopic properties and also lead to complex energy landscapes and contact-line dynamics. The two scales that characterize micro-machined surfaces are the typical size of the roughness features (usually in the micrometre or sub-micrometre scale) and the feature-to-feature distance (typically up to tens of micrometres). Disordered surfaces, instead, can display a broad spectrum of scales[6] (see Figs 1a,b and 3).

Yet the consequences of the presence of different length scales in superhydrophobic materials have been almost unexplored. This is the case for interfacially driven transport phenomena, the prototypical example of which is electro-osmosis — transport of fluid induced by an electric field. Electro-osmosis originates in the Debye layer, typically of nanometre thickness, where counterions in the bulk of an electrolyte screen electric charges present at the solid surface. By reducing viscous dissipation, slippage on a smooth surface was predicted to considerably enhance electro-osmotic transport[22]. However, the multi-scale nature of the superhydrophobic state precludes such amplification on a bare superhydrophobic surface[23]. In contrast, electrically polarized superhydrophobic surfaces, such as those developed for electrowetting, should considerably boost this transport, with an amplification predicted to scale proportionally to the (very large) ratio of the slip length to the Debye length. In the context of energy conversion devices, the dual phenomenon whereby an electric current is created by applying a pressure drop (the so-called streaming potential) is also expected to display strong enhancement, and thus be relevant for mechano-electric power conversion in microfluidics[24]. To give numbers, a microchannel (100 μm in width and 1 mm in length) polarized to a tension of 10 mV and working under 1 bar of pressure, with superhydrophobic walls characterized by a slip length of 1 μm, would produce a current of the order of 1 μA (for water with 100mM of salt). Accordingly, an A4-sized membrane with 10^6 channels working in parallel could theoretically produce a streaming current of several amperes. Such effects and their feasibility remain to be demonstrated experimentally.

Strong enhancement of transport on superhydrophobic surfaces was also predicted for diffusio-osmosis — the motion of fluid induced by solute gradients. The enhancement echoes Marangoni flow — transfer of mass as a result of a surface-tension gradient — but in the context of a liquid–air interface suspended on a solid carpet. Here again a superhydrophobic surface was predicted to amplify transport by the ratio of the slip length to the thickness of the diffuse interface[25]. This potentially large enhancement would provide opportunities to efficiently convert the free energy contained in salt gradients from natural environments into mechanical motion. Notwithstanding still-unexplored technological challenges related to scalability, as well as the robustness issues outlined earlier, these strong amplifications of surface phenomena show serious promise for energy-harvesting applications.

Similar issues arise in the context of heat transfer, where the Kapitza (or thermal surface) resistance plays the role of the slip length. Superhydrophobic surfaces are expected to act as strong thermal insulators, with the liquid interface supported by the tips of the roughness features acting as thermal bridges. Conversely, superhydrophobic materials could also be used as super-nucleating interfaces[26]. Indeed, superhydrophobicity favours dropwise condensation at the top of the underlying roughness, and the so-created droplets roll off easily, leading to strongly enhanced heat transfer. This is relevant for the design of more efficient heat exchangers and vapour cooling. Despite these and many other potential applications, such as the cooling of electronic devices, our fundamental understanding of heat transfer at superhydrophobic surfaces is still at its infancy.

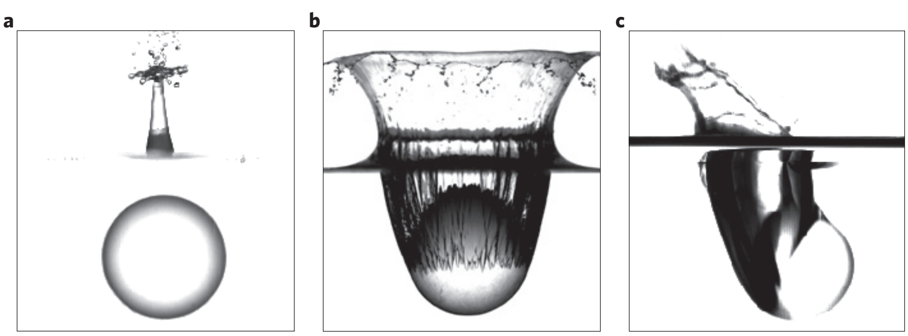

Figure 4 | Splash of a macroscopic bead impacting water at high velocity. Flow patterns differ owing to the coupling between the large-scale flow and the effective wettability of the bead's surface. **a**, A hydrophilic bead produces no splash; **b**, the splash of a hydrophobic bead; **c**, the partial splash of a Janus bead (half-hydrophilic and half-superhydrophobic). During the early stage of the impact the superhydrophobic coating of the Janus bead induces a forced-wetting dynamic instability at the contact line that deeply affects the large-scale flow pattern. Panels **a** and **b** courtesy of H. Lastakowski; panel **c** courtesy of C. Duez.

Bridging length scales

Can the intrinsically small-scale surface phenomena ever be relevant on large scales? For example, in the case of drag reduction through slippage at the wall, could superhydrophobic surfaces lead to an order-of-magnitude decrease in drag even for the most common turbulent flows? How do the length scales from the surface couple to the largest scales in the flow? Future work will have to tackle these and other problems. As fluid velocities increase beyond the creeping flow conditions, superhydrophobic surfaces are expected to affect the transition to unsteady flow for bluff bodies[27], as well as flow separation and the development of laminar boundary layers along streamlined bodies. Drag reduction, if present at all, would be most influential at the leading edge of the body, and would be expected to scale as the ratio of the slip length to the thickness of the boundary layer. As velocities increase even further, superhydrophobic walls could impact fully developed turbulent flow when the size of the viscous sublayer becomes of the order of the slip length. In this regard, Rothstein and collaborators demonstrated superhydrophobic drag reduction at high Reynolds numbers in laboratory conditions, confirming the pertinence of the couplings between small-scale roughness and large-scale flow[20]. However, further work is needed to explore the impact and feasibility of superhydrophobic drag reduction for high-speed flows, and this will require further interactions between researchers working in fluid dynamics and materials science.

Beyond the coupling of length scales, a different perspective may also be proposed. As an extreme interfacial property, the superhydrophobic state may alter the creation of macroscale features whenever they are generated by flow singularities, instabilities or the non-uniqueness of the flow pattern. In such cases, hydrodynamics naturally generates multi-scale structures, and the coupling with the small scales of superhydrophobic surfaces is thus expected to occur spontaneously. Some recently considered examples include the splashing of a superhydrophobic body on a fluid interface, which strongly depends on surface properties through a forced-wetting instability occurring during the early stages of impact[28] (Fig. 4); the teapot effect on superhydrophobic walls, where the non-uniqueness of the fluid-ejection problem in the inertial regime leads to a strong influence of boundary conditions[29]; and the influence of the symmetries of the underlying structure of a micro-textured surface on the formation and macroscopic geometry of hydraulic jumps[30].

Clearly, there is plenty to explore beyond wetting, as we have tried to outline here. In our view, a switch in focus from wetting to related areas — in particular to surface transport — may not be a smooth process, but it will probably be a rewarding one for the field as a whole. ❐

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