Self-cleaning surfaces — virtual realities

In the 19th century, Oscar Wilde stated "We live, I regret to say, in an age of surfaces". Today, we do so even more, and we do not regret it: key advances in the understanding and fabrication of surfaces with controlled wetting properties are about to make the dream of a contamination-free (or 'no-clean') surface come true. Two routes to self-cleaning are emerging, which work by the removal of dirt by either film or droplet flow. Although a detailed understanding of the mechanisms underlying the behaviour of liquids on such surfaces is still a basic research topic, the first commercial products in the household-commodity sector and for applications in biotechnology are coming within reach of the marketplace. This progress report describes the current status of understanding of the underlying mechanisms, the concepts for making such surfaces, and some of their first applications.

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The basic law determining the equilibrium shape of a liquid drop on a surface was formulated by Thomas Young, the eminent 19th-century scholar and (earlier) contemporary of Oscar Wilde's. The drop's shape is governed by the action of forces pulling at the three-phase contact line of the drop in the plane of the solid, which is where the solid/liquid, liquid/gas and solid/gas interfaces meet. The forces (per unit length) acting at this line are the surface tensions, and their balance yields the famous equation bearing Young's name, $\gamma_{sg} - \gamma_{sl} = \gamma_{lg}\cos\theta$, where the symbol γ denotes the surface tensions between the three phases indicated by the subscripts. If the drop is small enough such that gravity is negligible, which typically is the case for drops of millimetre size down to micrometres, the drop will have the shape of a spherical cap and the liquid/gas interface meets the solid surface at an angle θ, which is called the intrinsic contact angle of the drop.

Young's equation is the basis of all wetting phenomena. A drop fulfilling it is said to be partially wetting the substrate. But for small and large contact angles θ, distinctly different limiting cases arise. If the sum of the surface tensions of the liquid/solid and liquid/gas interfaces equals the tension of the solid/gas interface, θ vanishes, and the drop will flatten out to form a film. This is the case for a so-called high-energy surface, which is wetted easily. But if the solid/gas interface has a low surface energy, the contact angle will — in theory — increase almost until 180°, and the surface will remain dry.

The limit of a completely wetting surface can be achieved by tuning surface forces. This is shown by the existence of a thermodynamic wetting phase transition for some materials. In this transition, a surface state of partially wetting droplets exchanges its stability with a film-state at a characteristic temperature[1]. A similar situation does not generally arise for the dry surface state. The chemical modification of surface forces alone can typically lead to water contact angles of up to 120° by using fluoropolymeric coatings or silane layers (see, for example, ref. 2), but not more. To reach the extreme values of the contact angle near 180°, a second ingredient has to come into play: surface structure. This observation has been made and forgotten several times over the last century, and mathematical descriptions of various complexity devised to explain it.

The basic effect of surface structure is easily understood. It is usually described by the Wenzel equation[3], which states that the apparent contact angle θ^* of the drop on the rough surface is related to Young's intrinsic angle θ on the smooth surface by $\theta^* = r\cos\theta$. A value of $r > 1$ describes the solid roughness, given by the ratio of rough to planar surface areas. Wenzel's equation thus states that wettability is improved by roughness for a hydrophilic surface ($\theta^* < \theta$ for $\theta < 90°$), but gets worse for a hydrophobic one ($\theta^* > \theta$ for $\theta > 90°$). A drop on a rough high-energy surface will therefore appear to 'sink' into the surface.

For $\theta > 90°$, the free energy of the dry surface is lower than that of the wet solid, and hence it can be expected that the drop will recede from the roughest regions. To describe this situation mathematically, the rough surface can simply be assumed to be a heterogeneous surface composed of air pockets and the solid[4]. Cassie and Baxter[4] postulated that the cosine of the contact angle of a liquid drop on a heterogeneous surface then corresponds to the sum of the cosines of the contact angles on two homogeneous surfaces of the respective materials, weighted by the amount of available surface. If one of the surfaces is just air, the cosine of the contact angle on this surface is –1, and in this case the Cassie–Baxter equation reads $\cos\theta^* = -1 + \Phi_s(1 + \cos\theta)$. Here, Φ_s is the surface fraction of the solid. For 'very rough' surfaces, for which

Box 1

A LEAF OF CLEANLINESS

The Lotus leaf is the sign of purity — and two botanists, Barthlott and Neinhuis, from Bonn, Germany, found out why. In the course of their studies of plant leaf structures, performed to classify plant families, the two botanists noticed that structural features on the plant leaves, together with their waxy surface chemistry, render the leaves non-wettable (see Fig. 1). Water drips off these surfaces, taking powder-like contaminants along[9].

Rather than delving into fundamental research on the functional mechanisms of these surfaces, Barthlott and Neinhuis noticed the value of this natural cleaning mechanism for practical applications. Dubbing it the Lotus effect, they began to organize a wide-spread consortium of companies trying to develop products such as paints, roof tiles and others. (The Lotus effect consortium can be accessed by the webpage http://www.botanik.uni-bonn.de/system/bionik.htm.)

Although creating a big impetus in the business of self-cleaning surfaces, the simple combination of rough surfaces and non-wetting surface chemistry does not always hold up to its promise. Ageing and decay of the surface structures are a major problem that plants can avoid by either repairing or giving up damaged leaves. No wonder that biomimetic concepts are being sought to mimic leaf repair in industrial applications. RB

Figure 1 An almost ball-shaped water droplet on a non-wettable plant leaf.

Courtesy of S. Herminghaus.

Φ_s will tend to zero, θ^* will thus tend to 180°, and the drop will 'lift off' the solid surface.

This mechanism was first demonstrated mathematically for the simple case of a sinusoidally corrugated surface by Johnson and Dettre in 1964, for which the authors could compute the droplet free energy for various drop configurations on the surface[5]. They concluded that for surfaces with an intrinsically high contact angle, the uplifted configuration is the energetically most favourable one. We can thus summarize for the equilibrium configurations of liquids on rough surfaces: if the surface has a high interfacial free energy, roughness promotes wetting, and the liquid will accumulate within the corrugation (this is sometimes called surface wicking). But for a low-energy surface, roughness promotes drying: it becomes energetically too costly for the liquid to follow the surface corrugations, and the free-energy minimum for the configuration of a droplet is attained for a position on top of the corrugation. Literally, the drop behaves like a fakir would on his carpet (see Box 1 and Fig. 1).

These results are essentially phenomenological, as are more recent calculations concerned with specific surface structures[6]. But they are astonishingly successful, and have only recently been better founded within statistical mechanics[7,8]. Apart from some generalizations (concerning, for example, line-tension effects on nanometre-size droplets), the phenomenological laws survived this rigorous scrutiny quite well.

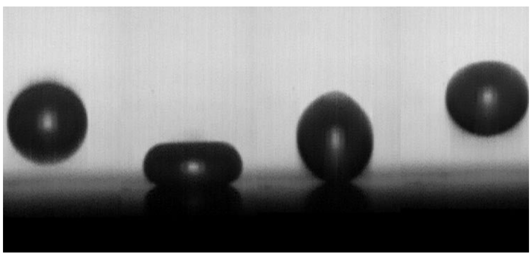

Figure 2 Impact of a millimetre-size drop (at a speed of impact of 30 cm s^{-1}) and full rebound from an ultraphobic surface.

Courtesy of D. Richard, C. Clanet and David Quéré[14].

ROUTES TO SELF-CLEANING

The equilibrium shapes of droplets or films on surfaces are only half the story: to clean a surface, material has to be transported along it — and best, off it. By tuning the wettability of the substrate, two basic options arise. The surface can be rendered very wettable, and the decontamination process is based on film flow. But, interestingly, biology hints at a different option. Non-wettable plant leaf surfaces, such as those of the famous Lotus plant, have a built-in elementary cleaning mechanism. This was noticed in the mid-nineties by botanists studying plant surfaces[9] (see Box 1). They observed that droplets running off the leaves can carry dry contaminants along — the origin for the Lotus leaf's status as a sacred object of purity[10].

The dynamic behaviour of droplets on such ultrahydrophobic (sometimes also called ultraphobic) surfaces was studied in most detail by David Quéré from the Collège de France and his collaborators who described their findings in a series of papers[6,11–15]. The first important effect of these surfaces on liquid drops concerns the contact line of the drop, that is, the one-dimensional line of intersection of the three interfaces. Because the contact area of the drop shrinks with the increase in contact angle, the contact line can be deformed less easily, and hence the hysteresis in contact angle between the advancing and receding angles is drastically reduced. The advancing angle θ_a is the front angle in direction of droplet motion, and the receding angle θ_r is the rear angle: both usually differ. A simple measure of this contact-angle hysteresis is the pinning force per unit length of the drop perimeter, $F = \gamma_{lg}(\cos\theta_r - \cos\theta_a)$.

It is this contact-angle hysteresis that accounts for droplet motion, because it has to be overcome by external forces (wind, gravity or other). If the hysteresis is too large, and the driving force is not big enough, the drop will stick or be smeared out across the surface[16]. Contaminations of surfaces by drying drops, a common nuisance on car paints, for example, are the consequence. If the contact angles are sufficiently high, that is, larger than 170°, viscous droplets indeed roll off the surfaces — they do not slide. This was proved by Richard and Quéré by monitoring the position of a gas bubble inside the drop and describing its arch-like trajectory as it stays attracted to the liquid interface[11,17].

The dynamic contact angles of a drop moving down a surface are affected by the size of structures creating the surface roughness[18]. If the surface structures are as big as several tens of micrometres, a droplet can still be deformed by them even if it is considerably larger than the structures themselves. Smaller structures than these are therefore generally needed for a good ultraphobic surface, but we will see below that from the point of view of applications, this alone is generally not specific enough due to other required functionalities of the materials.

The second dynamic feature of drops on ultraphobic surfaces concerns impact[12,14]. When a drop is thrown at such a surface, it rebounds elastically with a velocity almost equal to impact velocity (see Fig. 2). This behaviour is certainly useful for drying applications, but on the other hand creates problems in the precise positioning of drops on ultraphobic surfaces by conventional printing techniques. The ultraphobic effect can also be imparted on the drop. By coating the drop surface with water-repellent particles, the decorated drop can be made to roll on a smooth surface[14].

The self-cleaning mechanism of ultraphobic surfaces relies on the minuscule contact area of the drops with these surfaces. For the ultrahydrophilic (or, by analogy, ultraphilic) route to self-cleaning, the flow of the liquid film is essential. Ultraphilic surfaces are wetted easily with very low or vanishing contact angles: if the surface is inclined, it is the flowing liquid film that carries the material along. The usefulness of this concept thus depends on the rapidity with which a liquid film runs off a surface, and without producing a beading front or pinning of contact lines. For sufficiently thick films (of the order of hundreds of nanometres and above), flow is hydrodynamic, and beading of the film can be avoided[19]. For thinner films, however, the flow of the film will consist of a rapid equilibration by surface diffusion. But not all liquid will move: there will also be stagnant (solidified) layers on microscopic scales[20].

These static and dynamic properties of drops on ultraphobic surfaces and films on ultraphilic surfaces are the basic ingredients for droplet- and film-based self-cleaning or decontamination mechanisms. From a practical perspective, the first question to be answered now is how to fabricate surfaces with such controlled wettability.

MAKING SELF-CLEANING SURFACES

To characterize rough surfaces (which is, with the exception of mica and graphite, essentially every solid surface) it is useful to classify them into three separate sets. A rough surface can be a regular (that is, 'designer-made') surface or a random (irregular) rough surface. Hierarchical rough surfaces are an intermediate case, also of interest from the point of view of biology.

A regular rough surface is indeed a fakir carpet on the submicrometre scale (see Fig. 3). A classic way to make such fakir carpet surfaces with differently shaped protrusions is to etch them into masked silicon wafers using plasma-etching techniques. The required surface chemistry is then added. Hydrophobizing of the surface usually proceeds by exposing them to an organosilane atmosphere[18]. Such highly regular surfaces are very useful for quantitative studies of the equilibrium configurations of droplets on rough substrates, and their contact-line dynamics.

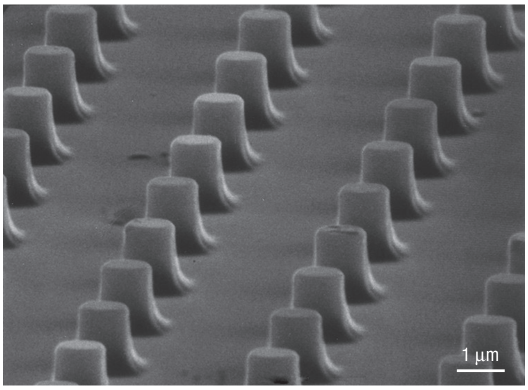

Figure 3 A designed rough surface — the similarity to a Fakir carpet is apparent.

Courtesy of J. Bico, C. Marzolin and David Quéré[6].

More advanced examples of regular rough surfaces are those with more complex structures, for example, hierarchical ones. Obvious cases are fractal or self-affine surfaces, the latter generalizing a fractal in which its lateral and vertical scaling behaviours are not identical but are themselves related by a scaling law. For such surfaces, Herminghaus derived an argument that a hierarchical structure of the roughness could render any surface (independent of contact angle) non-wettable (dry)[21]. Experiments on fractal surfaces made of alkylketene dimer on glass, yielded a contact angle of 174° for water[22]; the suggested behaviour has so far not been seen. The possible relevance of this argument for biological surfaces is evident: a biological surface may not be a true fractal, but the surface structures do have a hierarchical structuring owing to their biological design. This observation may also open an interesting path for new applications.

At present, random rough surfaces are much more relevant from a practical perspective, because they are cheaper to fabricate. Similar to the hierarchical rough surfaces, they also contain roughness on various length scales, which helps in the ultraphobic effect and makes the surfaces less vulnerable to damage. Furthermore, random rough surfaces can be made from large classes of materials, metallic and non-metallic. To increase and control the natural roughness of these surfaces, plasma-etching techniques are most often used; these can also be applied to polymer substrates. Another standard set of techniques is plasma-enhanced chemical vapour deposition[23–25]. Quite generally, as for the regular rough surfaces, a reduction of surface free-energy is performed afterwards by coating with organo- or fluorosilanes. An extended compilation of procedures to fabricate random ultrahydrophobic surfaces described in the literature can be found in a recent review[26] by Nakajima *et al.* There is also a large catalogue of further techniques and materials described in the patent literature[27].

The most detailed direct comparison of the wettability properties of different ultraphobic substrates and coatings to date was reported by Chen *et al.*[23] for both metallic and non-metallic surfaces. They also added a useful concept to describe the behaviour of droplets on these surfaces. They term a surface 'ultralyophobic' if drops move easily on it without pinning, irrespective of the value of their contact angle. Examples[23,28] of such (usually smooth) surfaces are provided by hydridosilane monolayers on SiO_2.

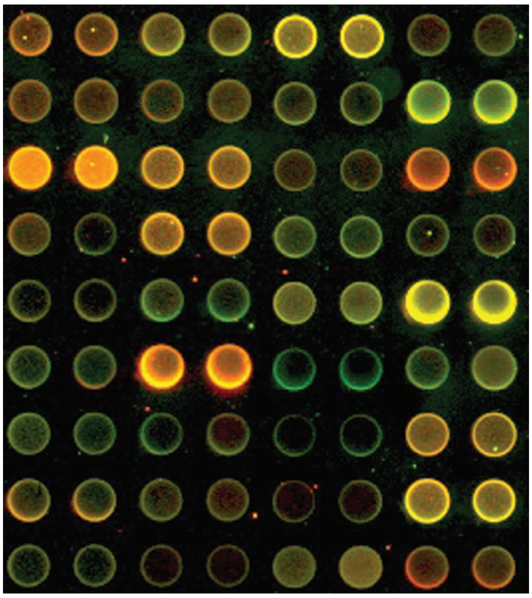

Figure 4 A Complementary DNA microarray on a silanized glass plate. The doughnut-like shapes of the deposits are clearly visible.

Courtesy of A. Bosio[39], MEMOREC.

Special classes of rough surfaces are those that embody some kind of biomimetic quality, that is, they are switchable in their wetting properties — and probably even renewable, like a plant leaf is. Of particular interest in this direction is the use of functional polymers in surface design. These materials display reversible behaviour on the change of a control parameter[29,30]. Even small amounts of reactive functional groups incorporated into polymers can be highly beneficial to improving surface characteristics and wettability. Oxygen-plasma treatment of polymers — for example, the simple and well-understood model system of polystyrene (PS) — yields a surface functionalized with various oxygen-containing groups (among them carbonyls). Therefore, plasma-oxidezed PS behaves as a polyelectrolyte that swells depending on pH[31].

Of particular interest for applications is the possibility to fabricate surface patterns out of a variation of hydrophobic/hydrophilic polymers, for example, by lithographic techniques. An example is provided by the work of Husemann *et al.*[32], who patterned polymer brushes of (wettable) poly(acrylic acid) and (non-wettable) poly(*t*-butyl-acrylate) onto SiO_2 wafers, generating a checkerboard surface with a wettability contrast of about 80° in the advancing contact angle of water.

Wettability, however, is not the only desired functionality: there are many additional requirements for surfaces in day-to-day use. For most glass applications, transparency or low scatter is essential. For self-cleaning transparent surfaces based on the ultraphilic route, the most interesting, and also with respect to applications the furthest developed route, has emerged by using TiO_2 as a surface coating[33]. TiO_2 is an example of a photocatalytically active metal oxide. Under exposure to ultraviolet light, it shows extremely small contact angles of less than 1°. The origin of this light-caused wettability enhancement is presumably the generation of a molecularly thin liquid water film on which mesoscopic water layers spread. Ultraviolet irradiation creates surface oxygen vacancies at bridging sites, converting Ti^{4+} to Ti^{3+}, favourable for dissociative water adsorption. Friction force microscopy reveals a submicrometre-size pattern of hydrophilic and oleophilic regions on these surfaces[33]. In addition to the enhanced hydrophilicity, the oxidizing capacity of the photocatalytic effect helps in degrading organic materials on the surface. Another system showing reversible wetting properties under ultraviolet irradiation are pyrimidine-terminated molecules attached to gold or quartz substrates. Contact angle changes of 20° and more are due to a decrease in surface charge caused by the dimerization of the thymine monomer[34].

The ultraphobic route to glass surfaces presents a fundamental problem: the substrate roughness may hinder transparency owing to scatter losses. To avoid this, the critical requirement is that the surface corrugations do not affect the light waves passing through them. Consequently, the light wavelengths of interest constitute an obvious upper limit for the spatial length scales of the surface corrugations. An example of a transparent rough surface is superhydrophobic boehmite (AlOOH) coated by a fluoroalkylsilane[35,36]. The combination of the oxidizing effect of TiO_2 with the ultraphobic route to self-cleaning was also achieved[37]. By adding about 2% of titanium acetylacetonate to aluminum acetylacetonate, contact angles of about 150° were achieved while maintaining low scatter. In this regime, the contact angle did not degrade under ultraviolet illumination, as it does significantly for higher TiO_2 content due to degradation of the fluoroalkylsilane by photocatalysis.

USING SELF-CLEANING SURFACES

Out of the broad areas of possible applications of self-cleaning surfaces, we focus here on two that are representative for very different target markets: the high-tech field of biotechnology, and the huge household-commodity sector. The first example is taken from microfluidic applications in biotechnology; the second self-cleaning surface is flat (window) glass.

In biotechnology, one is interested in controlling droplets containing biologically relevant molecules (DNA and proteins), minimizing contamination. Already the construction of complementary DNA (cDNA)-microarrays prepared by spotting techniques requires specific wetting properties of the substrates. Glass slides — the substrate most commonly used — are usually only mildly hydrophobized, such that the drops of drying cDNA-solution produce unwanted ring-like structures, a nuisance known in the field as the 'doughnut-effect'[38] (see Fig. 4). This effect is related to the well-studied 'coffee-stain effect': an evaporation-driven convection mechanism drives dissolved or dispersed particles inside the drop to the surface-pinned contact line, where evaporation is fastest[39]. Because this effect is strongly linked to the pinning of the contact line, which is much reduced for high contact angles, ultraphobicity is advantageous: the almost fully spherical drops on an ultraphobic surface can shrink exactly like a drop in free air[40].

The positioning and shape of spotted drops can be steered by combining hydrophilic and hydrophobic patternings. The usefulness of this idea is shown by a real biosystem: some desert beetles capture their drinking water by a hydrophobically–hydrophilically structured back[41]. On the technological side, several institutions and companies hold patents on the use of hydrophilically–hydrophobically structured surfaces for such applications[42–44]. By prepattering of a substrate, hydrophilic regions can help to contain small liquid volumes of DNA[45]. The combination of a hydrophilic prespotting (anchoring) on an otherwise hydrophobic or ultraphobic surface, results in new possibilities for improvements in spotting and analysing DNA and proteins by avoiding wall contact[46].

Beyond the possibility of improving deposit shapes on substrates, the possibility of a guided motion of droplets on ultraphobic surfaces offers the chance to develop a droplet-based microfluidics system, in contrast to the classical concept based on microfluidic channels[47]. Droplets moving freely on open surfaces and bulk liquids flowing in channels are indeed extreme technical solutions guided by the same goal, with bulk liquids moving in closed channels being the scenario that is still prevalent. Intermediate between these two is the possibility of using prepatterned surfaces, whereby complex topographic patterns can be generated[48]. Both liquid films and drops can move on such open structures.

Playing with patterned surfaces allows novel dynamic features to be brought in, such as morphological transitions from parallel liquid-filled stripes to configurations in which liquid bulges emerge that reach out from one channel across a hydrophilic region, and merge with another channel (see Fig. 5)[49–51]. The flow of liquid on the channel patterns is driven by the curvature of expanding liquid[52]. The advancement of the liquid front along a hydrophilic channel is — in the case of a newtonian fluid — well described by the standard lubrication equation derived from the Stokes equation, and shows a diffusion-like behaviour[53]. Driving the liquid along the channels and making them merge at predefined locations offers a novel way to mix reactants or steer biochemical reactions, defining the concept of a 'liquid microchip'[49] or 'surface-tension confined microfluidics'[50]. One advantage of the open structures over capillaries, in addition to their ease of cleaning, is that blocking of the capillary by unforeseen chemical reactions cannot occur.

Microfluidics can also be based on droplets on ultraphobic surfaces alone: because the drops have very low contact areas with the substrate, they are easy to move by external fields, for example, electrostatic forces or surface acoustic waves. Systems that make use of a droplet-based actuation mechanism are being developed by various researchers and companies[54–59]. The aim here is to control droplet positioning and motion on the substrates with as little surface contact as possible, and making the droplet-based system a programmable reactor, by which the liquid positions are prescribed and tuned externally.

Finally, we turn to the commodity applications of self-cleaning. Potential applications of self-cleaning surfaces in these market segments are wide-ranging, as a check with the projects running in the Lotus effect consortium proves[9]. Obviously — in Oscar Wilde's sense — we are surrounded by all too many surfaces that we want to keep clean, from roof tiles to bathroom surfaces to house walls that should be made graffiti-resistant.

The most obvious, and if successful, the most significant application is flat, glass windows. From a commercial point of view, cleaning of windows is expensive and cumbersome, especially if the windows are on a skyscraper. And apart from the business market, every housekeeper will just love the idea of a self-cleaning window.

The hydrophilic route to self-cleaning windows has meanwhile been realized by several companies (PPG, Pilkington, TOTO) and has just been released to market[60–62]. How far these windows will be a commercial success clearly remains to be seen; to some, the water film running off the glass may seem a nuisance. The main advantage of these surfaces is the combined hydrophilicity–photodegradation effect, which significantly aids in the cleaning process. And, the fact that a controlled roughness is not needed in this concept is a clear technological advantage. Although the ultraphilic effect is reversible in principle, the ageing of these surfaces under real conditions is not known.

The alternative, ultraphobic route, has not yet been realized in practice, but work in this direction is now under way. An ambitious attempt has been made by combining the basic elements of ultraphobicity with biomimesis. A system under development in industry contains a reservoir with a hydrophobic polymer that is intended to mimic the wax of the Lotus leaf: the outcome would be a self-cleaning surface that heals itself[27]. The concept relies on a replenishment layer embedded in the glass that serves as a surface-repairing reservoir, refuelling a hydrophobic cover layer when it has been depleted at the surface, and hence restores ultraphobicity in conjunction with the roughness of the surface.

To conclude, a final word must be said about the biggest problem facing all self-cleaning or contaminant-free surface applications: ageing and decay. For biotechnology applications, this is not so relevant; the surfaces will often be used for analytic purposes and hence designed as disposables. If one thinks of contaminant-free surfaces for use in medicine, the issues of reusability and hygiene are complex and not resolved. And yet a different matter is the use of self-cleaning surfaces in outdoor applications. Examples are known already in which an initially improved product lost its advertised self-cleaning property too rapidly, not justifying a higher initial investment. But failed products

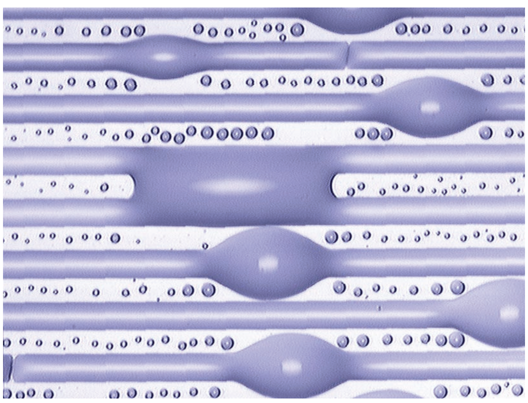

Figure 5 Liquid channels on a hydrophilically–hydrophobically patterned substrate: a possible pathway to surface-tension controlled microfludics.

Courtesy of S. Herminghaus[49].

bear the risk of discrediting a whole field of applications. Ageing will remain difficult to foresee — pure empiricism reigns in its description — but the benefits to investors and product users rest on keeping it under control.

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References

1. Cahn, J. W. Critical point wetting. *J. Chem. Phys.* **66,** 3667–3672 (1977).
2. Shafrin, E. G. & Zisman, W. A. in *Contact Angle, Wettability and Adhesion* Advances in Chemistry series, Vol. 43 (ed. Fowkes, F. M.) 145–167 (American Chemical Society, Washington D. C., 1964).
3. Wenzel, R. N. Surface roughness and contact angle. *Ind. Eng. Chem.* **28,** 988–994 (1936).
4. Cassie, A. B. D. & Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **40,** 546–551 (1944).
5. Johnson, Jr., R. E. & Dettre, R. H. in *Contact Angle, Wettability and Adhesion* Advances in Chemistry series, Vol. 43 (ed. Fowkes, F. M.) 112–135 (American Chemical Society, Washington D. C., 1964).
6. Bico, J., Marzolin, C. & Quéré, D. Pearl drops. *Europhys. Lett.* **47,** 220–226 (1999).
7. Swain, P. S. & Lipowsky, R. Contact angles on heterogeneous surfaces: A new look at Cassie's and Wenzel's laws. *Langmuir* **14,** 6772–6780 (1998).
8. Wolansky, G. & Marmur, A. The actual contact angle on a heterogeneous rough surface in three dimensions. *Langmuir* **14,** 5292–5297 (1998).
9. Barthlott, W. & Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **202,** 1–8 (1997).
10. Von Baeyer, H. C. The lotus effect. *The Sciences: Journal of The New York Academy of Sciences* 12–15 (January/February 2000).
11. Richard, D. & Quéré, D. Viscous drops rolling on a tilted non-wettable solid. *Europhys. Lett.* **48,** 286–291 (1999).
12. Richard, D. & Quéré, D. Bouncing water drops. *Europhys. Lett.* **50,** 769–775 (2000).
13. Aussillous, P. & Quéré, D. Liquid marbles. *Nature* **411,** 924–927 (2001).
14. Richard, D., Clanet, C. & Quéré, D. Contact time of a bouncing drop. *Nature* **417,** 811 (2002).
15. Bico, J., Tordeux, C. & Quéré, D. Rough wetting. *Europhys. Lett.* **55,** 214–220 (2001).
16. Miwa, M., Fujishima, A., Hashimoto, K. & Watanabe, T. Effects of the surface roughness on sliding angles of water droplets on superhydrophobic surfaces. *Langmuir* **16,** 5754–5760 (2000).
17. Mahadevan, L. & Pomeau, Y. Rolling droplets. *Phys. Fluids* **11,** 2499–2453 (1999).
18. Öner, D. & McCarthy, T. J. Ultrahydrophobic surfaces. Effects of topography length scales on wettability. *Langmuir* **16,** 7777–7782 (2000).
19. Huppert, H. E. Flow and instability of a viscous current running down a slope. *Nature* **300,** 427–429 (1982).
20. Seemann, R., Mönch, W. & Herminghaus, S. Liquid flow in wetting layers on rough substrates. *Europhys. Lett.* **55,** 698–704 (2001).
21. Herminghaus, S. Roughness-induced non-wetting. *Europhys. Lett.* **52,** 165–170 (2000).
22. Shibuchi, S., Onda, T., Satoh, N. & Tsuji, K. Super water-repellent surfaces resulting from fractal structure. *J. Phys. Chem.* **100,** 19512–19517 (1996).
23. Chen, W. *et al.* Ultrahydrophobic and ultralyophobic surfaces: Some comments and examples. *Langmuir* **15,** 3395–3399 (1999).
24. Youngblood, J. P. & McCarthy, T. J. Ultrahydrophobic polymer surfaces prepared by simultaneous ablation of polypropylene and sputtering of poly(tetrafluoroethylene) using radio frequency plasma. *Macromolecules* **32,** 6800–6806 (1999).
25. Wu, Y., Sugimura, H., Inoue, Y. & Takai, O. Thin films with nanotextures for transparent and ultra water-repellent coatings produced from trimethylmethoxysilane by microwave plasma CVD. *Chem. Vap. Depos.* **8,** 47–50 (2002).
26. Nakajima, A., Hashimoto, K. & Watanabe, T. Recent studies on super-hydrophobic films. *Monatsh. Chem.* **132,** 31–41 (2001).
27. Reihs, K., Duparré, A. & Notni, G. Substrate with a reduced light-scattering, ultraphobic surface and a method for the production of the same. World patent 01/92179 (2001).
28. McCarthy, T. J. & Fadeev, A. Y. Surface modification using hydridosilanes to prepare monolayers. World patent 00/069572 (2001).
29. Russell, T. P. Surface-responsive materials. *Science* **297,** 965–968 (2002).
30. Coupe, B., Evangelista, M. E., Yeung, R. M. & Chen, W. Surface modification of poly-(tetrafluoroethylene-co-hexafluorpropylene) by adsorption of functional polymers. *Langmuir* **17,** 1956–1960 (2001).
31. Dupont-Gaillain, Ch. C., Adriaensen, Y., Derclaye, S. & Rouxhet, P. G. Plasma-oxidized polystyrene: Wetting properties and surface reconstruction. *Langmuir* **16,** 8194–8200 (2000).
32. Husemann, M. *et al.* Manipulation of surface properties by patterning of covalently bound polymer brushes. *J. Am. Chem. Soc.* **122,** 1844–1845 (2000).
33. Wang, R. *et al.* Light-induced amphiphilic surfaces. *Nature* **388,** 431–432 (1997).
34. Abbott, S., Ralston, J., Reynolds, G. & Hayes, R. Reversible wettability of photoresponsive pyrimidine-coated surfaces. *Langmuir* **15,** 8923–8928 (1999).
35. Tadanaga, K., Katata, N. & Minami, T. Formation process of super-water-repellant Al_2O_3 coating films with high transparency by the sol-gel method. *J. Am. Ceram. Soc.* **80,** 3213–3229 (1997).
36. Nakajima, A., Fujishima, A., Hashimoto, K. & Watanabe, T. Preparation of transparent superhydrophobic boehmite and silica films by sublimation of aluminum acetylacetonate. *Adv. Mater.* **11,** 1365–1368 (1999).
37. Nakajima, A., Hashimoto, K., Watanabe, T., Takai, K, Yamauchi, G. & Fujishima, A. Transparent superhydrophobic thin films with self-cleaning properties. *Langmuir* **16,** 7044–7047 (2000).
38. Blossey, R. & Bosio, A. Contact line deposits on cDNA microarrays: A 'twin-spot effect'. *Langmuir* **18,** 2952–2954 (2002).
39. Deegan, R. D. *et al.* Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **389,** 827–829 (1997).
40. McHale, G., Rowan, S. M., Newton, M. I. & Banerjee, M. K. Evaporation and the wetting of a low-energy solid surface. *J. Phys. Chem. B* **102,** 1964–1967 (1998).
41. Parker, A. R. & Lawrence, C. R. Water capture by a desert beetle. *Nature* **414,** 33–34 (2001).
42. Huang, T.-L. J, Ko, J., Zhu, D.-W. & Fong, B. C. Patterned article having alternating hydrophilic and hydrophobic surface regions. World patent 99/57185 (2002).
43. Herminghaus, S., Gau, H. & Mönch, W. Element with extremely strong water-repellant dry zones on the surface thereof. World patent 99/23437 (1999).
44. Eickhoff, H., Nordhoff, E., Franzen, J. & Schürenberg, M. Processing of samples in solutions with a defined small wall contact surface. World patent 01/26797 (2001).
45. Gillmor, S. D., Thiel, A. J., Strother, T. C., Smith, L. M. & Lagally, M. G. Hydrophilic/hydrophobic patterned surfaces as templates for DNA arrays. *Langmuir* **16,** 7223–7228 (2000).
46. Eickhoff, H., Schürenberg, M. & Nordhoff, E. 2D/3D-biochips — neue werkzeuge für die funktionelle genom- und proteomanalyse. *Laborwelt III* (*transkript* suppl.), 30–33 (2001).
47. Whitesides, G. M. & Stroock, A. D. Flexible methods for microfluidics. *Phys. Today* 42–47 (2001).
48. Drelich, J., Wilbur, J. L., Miller, J. D. & Whitesides, G. M. Contact angles for liquid drops at a model heterogeneous surface consisting of alternating and parallel hydrophobic/hydrophilic strips. *Langmuir* **12,** 1913–1922 (1996).
49. Gau, H., Herminghaus, S., Lenz, P. & Lipowsky, R. Liquid morphologies on structured surfaces: from microchannels to microchips. *Science* **283,** 46–49 (1999).
50. Lam, P., Wynne, K. J. & Wnek, G. E. Surface-tension-confined microfluidics. *Langmuir* **18,** 948–951 (2002).
51. Darhuber, A. A., Troian, S. M. & Miller, S. M. Morphology of liquid microstructures on chemically patterned surfaces. *J. Appl. Phys.* **87,** 7768–7775 (2000).
52. Grunze, M. Driven liquids. *Science* **283,** 41–42 (1999).
53. Darhuber, A. A., Troian, S. M. & Reisner, W. W. Dynamics of capillary spreading along hydrophilic microstripes. *Phys. Rev. E* **64,** 031603 (2001).
54. Herminghaus, S. *et al.* Liquid microstructures at solid interfaces. *J. Phys. A* **11,** 57–74 (1999).
55. Washizu, M. Electrostatic actuation of liquid droplets for microreactor applications. *IEEE Trans. Ind. Appl.* **34,** 732–737 (1998).
56. Torkkeli, A. *et al.* Electrostatic transportation of water droplets on superhydrophobic surfaces. *Proc. IEEE MEMS 2001* 475–478 (2001).
57. Kim, J. & Kim, C. J. Nanostructured surfaces for dramatic reduction of flow resistance in droplet-based microfluidics. *Proc. IEEE MEMS* 2002 479–482 (2002).
58. Lehto, A., Kojola, H., Lövgren, T. & Lönnberg, H. Method and device for carrying out a chemical analysis in small amounts of liquid. World patent 99/54730 (1999).
59. Wixforth, A. Device and method for manipulating small quantities of materials. World patent 01/94017 (2001).
60. Greenberg, C. B. *et al.* Photocatalytically-activated self-cleaning article and method of making same. World patent 98/41480 (2000).
61. Ammerlaan, J. A. M., McCurdy, R. J. & Hurst, S. J. Process for the production of photocatalytic coatings on substrates. World patent 00/75087 (2000).
62. Kazuhito, H. *et al.* Self-cleaning member having photocatalytic hydrophilic surface. Japanese patent 1,152,051 (2001).

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