Super-hydrophobic and super-wetting surfaces: Analytical potential?

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Roughening or texturing surfaces provides super-liquid repellent or film forming properties without alteration of the surface chemistry. These surfaces are easy to produce, can amplify wetting properties and can be either “sticky” or “slippery” to liquids. Their use as water-repellent coatings is established, but their potential for use in microfluidics and sensor applications remains largely unfulfilled. This article explains several key ideas and suggests why there may be potential for analytical applications.

Introduction

Many scientific applications involve liquids and manipulation of liquids on or across surfaces. One obvious technological example is microfluidics, but others include liquid chromatography and any liquid phase sensor involving attachment or immobilization of biological molecules which alters hydrophobicity or hydrophilicity. The volume of liquid can be high or low with much interest in low volumes for on-chip assays. As the size of a liquid scales down the dominant force becomes the liquid-vapor surface tension, $\gamma_{lv}$. When the liquid is on a surface the balance between the surface tension and the solid-vapor and solid-liquid interfacial tensions determines both the equilibrium shape of the liquid surface and the driving force in moving the liquid.1,2 What determines these interfacial tensions at a microscopic level is solely the chemistry of the surface, but what determines how these forces act upon a liquid is the topography of the surface.3-5 An example of the importance of topography is shown by Fig. 1a-c of small (~ 2 mm diameter) droplets of water on various copper surfaces. On a flat copper surface the contact angle (the angle tangential to the liquid surface measured from the solid through the liquid) is less than 90°, a hydrophobic coating raises this into the range 115-120°, but texturing the surface and then treating it with the same hydrophobic coating increases it to around 160°. The specific surface used in fig. 1c was created using electrodeposition to produce a combination of slight roughness and a “chocolate chip cookie” texting with lateral sizes in the 20 µm range (Fig. 1d).

Super-hydrophobicity is defined as water contact angles greater than 150°, but then comes in two distinct flavours with one type providing a “sticky” surface on which liquid drops are difficult to move and the other a “slippery” surface where there is little resistance to drop motion.6 Since topography induced effects on contact angles are not limited to water we can refer to super-non-wetting when considering other liquids. On “slippy” super-hydrophobic surfaces water drops rolling off the surface also collect dust and so the surfaces are self-cleaning.7,8 For some liquids the effect of surface roughness or texture is not to create a rolled-up droplet, but is the opposite effect of super-wetting whereby a droplet is converted into a film. Super-hydrophobic surfaces can be created using roughness or texture at length scales from the sub-micron to the tens of micron and by techniques as diverse as vacuum deposition of PTFE thin films9,10 plasma polymerization11, tailoring sol-gel porous materials12,13 crystallizing wax14,15, electrochemical etching or deposition, and lithography16.

Topography Enhanced Wetting

The principles of super-hydrophobicity were outlined decades ago by Wenzel17 and by Cassie and Baxter.18 Wenzel noted that if a surface was rough and the contacting liquid followed the contours of the surface then the effect of roughness should be to emphasise the intrinsic wetting tendency of either film formation or of roll-up of the liquid. The observed contact angle on such a surface is given by Wenzel’s equation,

$$\cos \theta_e = r \cos \theta_w$$

where the roughness $r > 1$ is the ratio of the true surface area of the solid to its horizontal projection and $\theta_w$ is the equilibrium contact angle on a smooth flat surface of the same material. The chemistry lies within $\theta_e$ whilst controlling the effect of the chemistry on a liquid lies within $r$.

An analogy to Wenzel’s equation is an electronic amplifier whereby both a gain (analog electronics) and the possibility of saturation into one of two states (digital electronics) are possible. Wenzel’s equation predicts that the change in observed contact angle on a rough surface $\Delta \theta_w$ due to a change $\Delta \theta_e$ induced by surface chemistry is given by,

$$\Delta \theta_e = r \left[ \frac{\sin \theta_e}{\sin \theta_w} \right] \Delta \theta_w$$

Thus, the effect of a change in a contact angle due to a surface chemistry change is amplified by the rough surface into a larger change in the observed contact angle. For surface chemistry giving precisely $\theta_e=90°$ the amplification factor is equal to the...
roughness factor $r$ and this is also approximately true for a wide range of contact angles around 90°. For large enough roughness, Wenzel’s equation predicts saturation to either a film ($\theta^W=0°$) or a complete roll-up of the liquid ($\theta^W=180°$) should occur. The boundaries between the amplification and the saturation behaviours is given by $\cos \theta_e \approx 1/r$. From this perspective there is analytical potential for either transducing small changes in liquid properties by amplification of small effects on the surface tension or for producing simple yes/no threshold indicators using the saturation into either a film or a rolled-up droplet.

Due to capillary forces liquids can find it difficult to penetrate into the roughness or texture of a surface.\(^6\) Energetically it can be favourable for a liquid to break Wenzel’s assumption that the surface contours are followed and instead to bridge across the tops of surface protrusions so that the droplet sits upon a composite surface of the solid tops and the air gaps. The observed contact angle is then given by a weighted average of the cosines of the contact angles on the two types of surface (solid and air) using the Cassie-Baxter equation as,

$$\cos \theta^C = \phi_s \cos \theta_s - (1 - \phi_s) \cos \theta_e$$

where $\phi_s < 1$ is the fraction of the surface of the tops of the solids and $(1-\phi)$ is the fraction that corresponds to the air gaps; the liquid-air contact angle is 180° and the cosine of this gives the overall minus sign in the second term of the equation. Unlike the Wenzel form of topographic enhancement of hydrophobicity, a complete roll-up of a droplet cannot be achieved with surfaces whose chemistry provides $\theta_e < 180°$. In the Cassie-Baxter form of super-hydrophobicity, a remnant of the surface chemistry determined contact angle, $\theta_e$, is always present in the observed contact angle. Cassie-Baxter’s equation implies that contact angle enhancement towards super-hydrophobic can be created by surface roughness or texture, but the condition $\phi_s < 1$ means amplification of small changes in contact angle, $\Delta \theta_e$, does not occur.

Wenzel and Cassie-Baxter provide two alternative views of how a rough or textured surface may influence the wetting behaviour of a surface. The trend observed in experiments on superhydrophobicity is that as texturing or roughness is increased the contact angle is increased towards super-hydrophobic can be created by increasing the height of capillary rise equal to the roughness factor $r$ of the surface. The Cassie-Baxter form predicts either a reduced rise or even a depression of the trend of liquid.

The contact angle is also fundamental in determining the ease of generating drop motion. When pushing liquid into a drop resting on a surface the maximum contact angle achieved before the drop edge advances, $\theta_e$, is larger than the minimum contact angle achieved before the drop edge recedes, $\theta_r$, when withdrawing liquid from the drop. Because of contact angle hysteresis, a drop of rain on a window pane will cling without moving until its volume achieves a critical size. For the drop of rain clinging to a window pane there is a higher contact angle, $\theta_e$, at the lower side compared to the upper side, $\theta_r$. The net surface tension forces on the drop balancing its weight are proportional to $\gamma_s (\cos \theta_e - \cos \theta_r)$ and contact angle hysteresis prevents any motion of the drop until it reaches a critical size; the drop then runs down the window pane.\(^6\) A super-hydrophobic surface of the Cassie-Baxter type has low hysteresis and so drops can be moved on these surfaces by use of low tilt angles or low driving forces. Interestingly, as a drop rolls it collects dust and debris and so cleans the surface.

Another consideration is the effect of topography on the spreading of out of equilibrium droplets and liquids. During spreading the forces at the contact line are not in balance and the unresolved horizontal force $\gamma_s (\cos \theta_e - \cos \theta_r)$ drives the spreading. Wenzel type roughness or surface texture causes a modified force $\gamma_s (\cos \theta_e - \cos \theta_r)$ and the effect is to increase the speed with which a wetting liquid forms a film.\(^17\)\(^18\)

### Existing and Developing Applications

Most of the existing research on super-hydrophobic surfaces is materials oriented with a focus on combining super-water-repellent properties with good optical transparency and wear resistance.\(^19\) Exterior applications include coatings for radar domes, satellite dishes and glass. These coatings are water repellent, prevent adhesion of snow and provide self-cleaning.
under the action of rain; the mimicking of the self-cleaning action of the Lotus leaf is the so-called Lotus-Effect. Sol-gel based super-hydrophobic protective coatings are also being used to seal moisture sensitive electronic and optoelectronic components. A super-hydrophobic coated tip has also been suggested to enable accurate dispensing of droplets of low surface tension organic solvents. The difficulties with super-hydrophobic coatings are poor abrasion, chemical and UV resistance, clogging by dust and oil and optical clarity. There are few research publications on analytical applications of super-wetting and super-hydrophobicity, although there are a number of industrial interests. One theme is based on the idea that any mechanism that can act to change a contact angle at the three phase (solid-liquid-vapor) contact line or which can create a difference in contact angles between two sides of a droplet is a means to actuate motion of the liquid. A driving force can be generated at the edge of the liquid through electrostatic induced changes in the contact angle. Systems for both droplet actuation and for motion of a liquid in microcapillaries have been demonstrated. The basic principle in each case is that a driving force proportional to the change in cosθ, can be generated. A comprehensive microfluidics system based on this electrostatic principle and which includes droplet transport, separation and mixing is now commercially available (Nanolytics). A modification of this system using a super-hydrophobic surface for easier droplet actuation has been reported. Problems with this method include the electrostatic pressure causing droplets to convert to the Wenzel “sticky” form of super-hydrophobicity and so preventing motion, and attachment of biological moieties to the surface destroying the tailor made hydrophobic properties. Other applications include an intravenous super-hydrophobic filter to remove microorganisms and particles from emulsions and super-water-repellent membranes for the separation of pure liquids from microorganisms and particles from emulsions and super-water-repellent membranes for the separation of pure liquids from microorganisms and particles from emulsions. A variation on this theme could be identified which converts them into complete wetting liquids. A variation on this theme could involve measuring the enhancement of capillary rise caused by roughness or surface texture.

Conclusion
Understanding how surface topography or texture combines with surface chemistry to determine the wetting of surfaces by liquids is important in any application involving small volumes of liquids where capillary effects are dominant. The most spectacular example of this combination is the creation of super-hydrophobic surfaces from hydrophobic surfaces, but the principles are not restricted to water and are equally applicable to problems involving film formation and movement of liquids on surfaces. The major focus of research and applications development has been in the most obvious uses of super-hydrophobicity as water-repellent, self-cleaning and resistance/friction reducing coatings. However, it is probable that a wider range of analytical applications will exist based on the super-non-wetting and the super-wetting properties of topographically structured surfaces.

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