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Superhydrophobicity and Contact-Line Issues

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Abstract

The wettability of several superhydrophobic surfaces that were prepared recently by simple, mostly single-step methods is described and compared with the wettability of surfaces that are less hydrophobic. We explain why two length scales of topography can be important for controlling the hydrophobicity of some surfaces (the lotus effect). Contact-angle hysteresis (difference between the advancing, θ_A , and receding, θ_R , contact angles) is discussed and explained, particularly with regard to its contribution to water repellency. Perfect hydrophobicity ($\theta_A/\theta_R = 180^\circ/180^\circ$) and a method for distinguishing perfectly hydrophobic surfaces from those that are almost perfectly hydrophobic are described and discussed. The Wenzel and Cassie theories, both of which involve analysis of interfacial (solid/liquid) areas and not contact lines, are criticized. Each of these related topics is addressed from the perspective of the three-phase (solid/liquid/vapor) contact line and its dynamics. The energy barriers for movement of the three-phase contact line from one metastable state to another control contact-angle hysteresis and, thus, water repellency.

Introduction

When a raindrop falls on a horizontal surface, say, the hood of a car, a sessile water droplet forms in the shape of a sphere sectioned by the surface. There is a discrete contact angle between the surface and the tangent of the sphere at the three-phase (solid/liquid/vapor) contact line that can be measured. Measurement of the contact angle is the most common method for evaluating the property of wetting and is important in far-ranging processes such as pesticide application, adhesive joint formation, and heat transfer. Research that included contact-angle measurements became important and led to a large number of studies¹ in the 1950s. It became standard to report two different angles to describe the wettability of a surface, the advancing and receding angles, θ_A and θ_R , respectively. These angles can be measured if water is carefully withdrawn from (θ_R , Figure 1a) or carefully added to (θ_A , Figure 1b) a droplet. For a droplet to move on a tilted surface (Figure 1c), the droplet needs to both advance and recede, so it must distort from a section of a sphere to a complex shape with a changing radius of curvature, that is, different

contact angles around its entire perimeter. One suggested mechanism for hydrophobicity²⁻⁴ posits that hysteresis (difference between the advancing and receding angles) is more important than the maximum achievable or advancing contact angle.

Young first proposed that the contact angle formed between a sessile droplet and a solid surface is the result of the mechanical equilibrium between three surface tensions (Equation 1), solid-vapor (γ_{SV}), liquid-vapor (γ_{LV}), and solid-liquid (γ_{SL})

$$\cos \theta = (\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} \quad (1)$$

The units of γ in Equation 1 are erg/cm² (energy per unit area), and this is central to the classic view of wettability. Wenzel⁵ developed a theory for a droplet in contact with a rough surface that forms a sessile droplet with rough (higher-surface-area) liquid-solid and solid-vapor interfaces but a smooth liquid-vapor interface. He proposed that Young's equation (Equation 1) should be modified by multiplying the numerator (and not the denominator) of

the right side by a factor of r , which is the ratio of the contour area to the projected surface area of the sample (Equation 2).

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{smooth}} \quad (2)$$

The definition of the factor r in this equation clearly suggests that it is the area of contact between the liquid and solid that controls the contact angle. Cassie and Baxter⁶ considered surfaces made up of two (or more) components and proposed the equation

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (3)$$

to equate the contact angle of a binary composite surface (θ) containing area fractions f_1 and f_2 (where $f_1 + f_2 = 1$) of two components with contact angles of θ_1 and θ_2 , respectively. The idea that area is important is reinforced by this equation.

Superhydrophobic Surfaces

In the current decade, there has been an explosion of publications⁷ describing how topography can be used to control wettability. This is illustrated in Figure 1 of Reference 7, which shows a plot of citations to References 5 and 6. There are now a very large number of ways to produce superhydrophobic⁸ surfaces, some of which have been reviewed.⁹⁻¹² Essentially all of these reports include interpretations of data in terms of Wenzel's and Cassie's theories and Equations 1-3 discussed here.

The following sections describe seven superhydrophobic surfaces that have recently been prepared, studied, and reported. The first five of these surfaces are described here because they can be reproduced in any standard chemistry laboratory. The other two require processing by photolithography, and they are useful examples for explaining the lotus effect and how binary-length-scale topography can be used to enhance hydrophobicity. Indeed, some of these surfaces exhibit perfect hydrophobicity ($\theta_A/\theta_R = 180^\circ/180^\circ$, indicating that a drop touches the surface at a single point) and are thus the most hydrophobic surfaces possible.

A Commercially Available Perfectly Hydrophobic Surface

The starting materials of the first superhydrophobic surface example are submicron particles of oligomeric tetrafluoroethylene (OTFE) that are available commercially from Central Glass Company.¹³ This material can be compressed into monolithic supported samples that can be measured by contact-angle analysis.¹⁴ Figures 2a and 2b show consecutive frames from a videotape¹⁴ of a water

Figure 1. (a) Droplet of water receding (from 1 to 4) on a surface due to evaporation. The droplet is pinned at the three-phase contact line until the receding contact angle, θ_R , is reached at point 2, and θ_R remains constant during subsequent evaporation. (b) Droplet of water advancing (from 5 to 8) on a surface due to condensation. The droplet is pinned at the three-phase contact line until the advancing contact angle, θ_A , reaches point 6. (c) Droplet of water sliding on an inclined surface. The angle furthest downhill and the angle furthest uphill approximate, but are not the same as, θ_A and θ_R , respectively. (Reprinted from Reference 30 with permission of the American Chemical Society.)

droplet spontaneously detaching from this surface with an apparent receding contact angle of 180° . The contact/compression/release test (discussed further in the next section in relation to Figure 3) indicates that this surface is perfectly hydrophobic ($\theta_A/\theta_R = 180^\circ/180^\circ$).

Superhydrophobic Surfaces Based on Methylchlorosilane Chemistry

1940s patents first reported how to make generally hydrophilic surfaces hydrophobic using organosilanes.^{15–17} Recent studies have focused on reactions of silicon wafer surfaces with methylchlorosilanes both in solution and in the vapor phase. Two modification reactions are discussed here, one that forms a perfectly hydrophobic surface¹⁸ and one that forms a surface that is very close to perfect.¹⁹

In a solution synthesis procedure, cut sections of silicon wafers were submerged in toluene solutions of MeSiCl_3 at room temperature and under controlled humidity and were then rinsed with toluene, ethanol, and water.¹⁸ These conditions allow MeSiCl_3 to react with both water and surface silanols to form a cross-linked, covalently attached, toluene-swollen layer. Upon rinsing of the surface with ethanol, the toluene is extracted, and the methylsilicone phase separates to form a network of fibrils with diameters of ~ 40 nm. Figure 2c shows a scanning electron microscopy (SEM) image of this surface. This surface passes the contact/compression/release test (discussed further in relation to Figure 3) as perfectly hydrophobic ($\theta_A/\theta_R = 180^\circ/180^\circ$).

In a vapor-phase synthesis procedure, when silicon wafers are exposed, under controlled humidity, to the vapor of a 50:50 (vol/vol) mixture of Me_3SiCl and SiCl_4 (these two compounds form an azeotrope) for several minutes and then rinsed with water, extremely hydrophobic sur-

Figure 2. (a,b) Consecutive frames of a videotape of a water droplet detaching from a compressed sample of oligomeric tetrafluoroethylene (OTFE) at the bottom of the image. (c) Scanning electron microscopy (SEM) image of a surface prepared using MeSiCl_3 in toluene. (d) SEM image of a silicon surface exposed to a $(\text{CH}_3)_3\text{SiCl}/\text{SiCl}_4$ azeotrope for 6 min. (e) SEM micrograph of a hydrophobized conventional polyester fabric. (f) SEM micrograph of a hydrophobized microfiber polyester fabric. (g) SEM micrographs of a surface containing staggered $4\ \mu\text{m} \times 8\ \mu\text{m} \times 40\ \mu\text{m}$ rhombus posts. (h) Surface shown in image g after being modified using MeSiCl_3 in toluene. (Reprinted from References 14, 18, 19, 22, and 30 with permission of the American Chemical Society.)

Figure 3. Selected frames of a video of a $(\text{CH}_3)_3\text{SiCl}/\text{SiCl}_4$ azeotrope: derived surface (top) contacting, compressing, and being released from a sessile water droplet. The reflection of the sessile droplet defines the surface of the silicon wafer. (Reprinted from Reference 19 with permission of the American Chemical Society.)

faces are formed, and conventional water contact-angle analysis indicates that $\theta_A/\theta_R = >176^\circ/180^\circ$.¹⁹ SEM images of silicon surfaces as a function of reaction time indicate that contorted filaments with diameters of ~ 30 nm (Figure 2d) grow from nuclei and reach lengths of hundreds of nanometers. Two of us performed contact/compression/release tests many times on many surfaces prepared with this azeotrope.¹⁹ Figure 3 shows selected frames of a videotape of a test on a sample treated with $\text{Me}_3\text{SiCl}/\text{SiCl}_4$ vapor for 10 min. Defects cause the droplet to pin, stretch slightly, and vibrate during release. This surface is almost, but not perfectly, hydrophobic.

Superhydrophobic Surfaces Based on Textiles

Preparing water-repellent textiles by chemical modification and coating was a topic of significant interest in the 1940s.^{20,21} The topography that is imparted by the weaving of fibers can be exploited for hydrophobicity. Two of us recently reported²² the hydrophobization of two commercial textiles, conventional polyester and microfiber polyester, using a methylsilicone coating that was patented in 1945.²³

Figures 2e and 2f show SEM micrographs of silicone-coated polyester fabric samples. One is a conventional polyester fabric (CPF) and consists of ~ 1 -mm-scale woven bundles of ~ 40 - μm -diameter fibers. The other is a microfiber polyester fabric (μPF) and is made up of much finer (~ 2 - μm) individual fibers that are woven more finely (~ 50 μm in diameter). Water

θ_A/θ_R values for these materials are $151^\circ/140^\circ$ for CPF and $170^\circ/165^\circ$ for μPF . The origin for the difference in contact angles is discussed in the section on contact-line issues.

A Model Artificial Lotus Leaf

The surfaces described above were chosen for discussion here because they can be prepared from readily available materials in common laboratory settings. The McCarthy group at University of Massachusetts-Amherst has also studied more-difficult-to-prepare surfaces,^{2,4,24,25} and we describe one system here, that was chosen to mimic the lotus leaf, which has two length scales of topography.²⁴ A silicon surface containing staggered rhombus posts²⁵ was hydrophobized using a vapor-phase modification with dimethyldichlorosilane²⁶ that imparts no additional topography to the surface. An identical silicon sample was treated with methyltrichlorosilane in toluene using the same modification just described.¹⁸ Figures 2g and 2h show SEM micrographs of these two surfaces. One has a single (micronic) length scale of topography, and the other has two length scales, micronic and nanoscopic. The surface with the smooth coating exhibits water contact angles of $\theta_A/\theta_R = 176^\circ/156^\circ$, and that with nanoscopic roughness has $\theta_A/\theta_R = >176^\circ/>176^\circ$.

Contact-Line Issues

The water contact angles exhibited on superhydrophobic surfaces are usually interpreted using Equations 1–3 (Young, Wenzel, and Cassie equations), which are

in terms of interfacial free energies and interfacial areas. The works of Pease,²⁷ Bartell and Shepard,²⁸ and Extrand²⁹ also provide explanations of superhydrophobicity, in addition to the common Wenzel and Cassie theories.⁷ Two of us recently contended⁷ that interfacial area (the r in Equation 2 and f_1 and f_2 in Equation 3) does not affect the degree of hydrophobicity and that modeling contact angles one-dimensionally, from the perspective of the contact line, better explains surface behavior.

In a study to determine the influence of contact lines on hydrophobicity, we prepared surfaces containing single “spots” in surrounding fields: a hydrophilic spot in a hydrophobic field, a rough spot in a smooth field and smooth spot in a rough field. Spots with different diameters and droplets with different contact areas were studied. All of the data⁷ indicate that contact-angle behavior is determined by interactions of the solid and liquid at the three-phase contact line alone and that the interfacial area within the contact line is irrelevant.

Figure 4 provides an illustration of the contact line. Figure 4a is a two-dimensional representation of a droplet of water that has moved from one contact area to another; the droplet advances from point 6 to point 7 and recedes from point 2 to point 3. The solid circles in Figure 4a represent water molecules that do not move. In the case of a very small movement (~ 1 nm), the only interfacial water molecules that move are those on the contact line (~ 1 nm width).

The droplet needs to advance or recede along the entire three-phase contact line in order to move. Unless the hysteresis is zero, a change in shape of the droplet from a section of a sphere is required before it can move (Figure 4b). This necessary shape change can be regarded as an activation barrier to motion that can be quantified by the increase in liquid/vapor surface area, $E_a = \gamma_{LV}\Delta_{LV}$, where γ_{LV} is the liquid-vapor surface energy and Δ_{LV} is the change in liquid-vapor surface area. The difference between the advancing and receding contact angles, hysteresis, thus indicates (and controls) the activation energy for movement from one metastable state to another.³⁰

Now reconsider the seven example superhydrophobic surfaces discussed in the preceding section from the perspective of the contact line. Water droplets do not form contact lines with perfectly hydrophobic surfaces unless forced, as in a contact/compression/release test. The fibrillar structure of two of these surfaces (Figures 2c and 2d) causes the contact line (if it forms) to be contorted much more so

Figure 4. (a) Two-dimensional representation of a water droplet moving from one position to an equivalent one. The solid circles represent interfacial water molecules that do not move during this process. (b) A droplet must change shape from a section of a sphere increasing liquid-vapor interfacial area (and energy) in order to move. (c) Advancing and receding events on a superhydrophobic post-containing surface. (d) Structure of the tris(trimethylsiloxy)silyldimethylsilane monolayer. The umbrella shape represents the rotating siloxane functional group. (Reprinted from Reference 30 with permission of the American Chemical Society.)

than do surfaces with posts (Figure 2g). A contorted contact line increases the ground-state energy of metastable states, decreasing the activation energy for contact-line motion.

When water droplets move on fabric surfaces (Figures 2e and 2f) and staggered rhombus post surfaces (Figure 2g and 2h), the droplets roll. Droplets roll much more readily on microfiber polyester than on conventional polyester and on the posts with additional nanoscopic topography than on the smooth posts. These differences are readily explained from the perspective

of the contact line in both cases. Advancing events are not impeded on either type of fabric or on either type of post surface; in fact, the advancing contact line does not move. Instead, the liquid-vapor interface descends onto the next fibers or posts to be wet as the droplet rolls, and a new advancing contact line is formed. (This is shown for posts in Figure 4c.) Receding events are impeded by the smooth 40- μm fibers and smooth post tops. The post tops and fiber surfaces have (locally) lower receding contact angles than the macroscopic droplet, so the contact line cannot recede across the

tops of the posts or fibers and it must disjoin in concerted events as the droplet rolls. Introducing a second level of topography on the post tops or using bundles of 2- μm fibers as in the microfiber polyester allows recession across post tops or fiber weave by increasing the local receding contact angle.

We close by pointing out that smooth samples can also be extremely water-repellent even though they are not, by definition,⁸ superhydrophobic. This is best rationalized from the perspective of the three-phase contact line. Figure 4d shows a covalently attached monolayer of tris(trimethylsiloxy)silyldimethylsilane. This silicon-supported monolayer exhibits essentially no water contact-angle hysteresis ($\theta_A/\theta_R = 104^\circ/103^\circ$), and water droplets slide very easily on this surface. This supported monolayer is prepared by random covalent attachment of the groups, and nanoholes smaller than the groups are left vacant after complete reaction.³¹ The siloxane functionality rotates freely, and the surface can be regarded as liquidlike and able to move the three-phase contact line. When the three-phase contact line moves, it is either advancing or receding. The dynamic contact line is the reason for the absence of hysteresis.

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