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Contact Angle Hysteresis on Superhydrophobic Surfaces: An Ionic Liquid Probe Fluid Offers Mechanistic Insight

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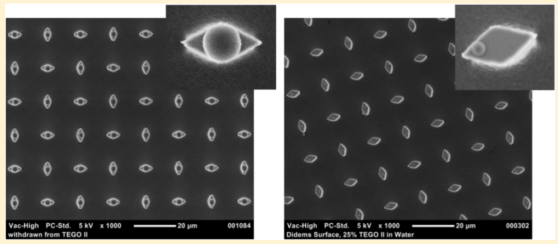
ABSTRACT: Silicon/silicon dioxide surfaces containing 3 μm (width) $\times$ 6 μm (length) $\times$ 40 μm (height) staggered rhombus posts were prepared using photolithography and hydrophobized using a perfluoroalkyl-containing monofunctional silane. These surfaces exhibit water contact angles of $\theta_A/\theta_R = 169°/156°$. Water drops come to rest on a carefully aligned horizontal sample but roll when the surface is tilted slightly. No visible trail or evidence of water "left behind" at the receding edge of the drop is apparent on surfaces that water drops have rolled on or on samples removed from water through the air—water interface. When dimethylbis(β-hydroxyethyl)ammonium methanesulfonate (N^+S^-, a nonvolatile ionic liquid) is used as the liquid probe fluid (instead of water), contact angles of $\theta_A/\theta_R = 164°/152°$ are observed and ~3-μm-diameter sessile drops are visible (by scanning electron microscopy - SEM) on the top of every post of a sample drawn out of this liquid. We interpret the formation of these sessile microdrops as arising from microcapillary bridge failure that occurs during receding events and emphasize that the capillary bridges rupture in primarily a tensile failure mode. Smaller sessile drops could be prepared using mixtures of water and N^+S^-. Microdroplets of N^+S^- were also observed to form selectively at particular features on surfaces containing square holes separated by ridges. This suggests that pinning sites can be identified using microscopy and this ionic liquid probe fluid.



When a sessile water drop moves on a solid surface, the drop must either advance or recede at every point on the three-phase solid/liquid/vapor contact line.[1] This motion almost always requires that a force be applied to either the drop or the surface, and the usual vantage of this process is one with a sessile drop on an inclined surface in a gravitational field (Figure 1a). When a surface with a stable sessile drop is tilted, the drop distorts from a section of a sphere to a shape that can be described as a section of a tapered ellipsoid. When the surface is tilted sufficiently to cause motion, the drop generally slides with a constant, reproducible shape. The 2D representations in Figure 1 trivialize the complex process because contact angle values vary around the entire perimeter of the drop; however, events at the downhill-most and uphill-most points on the contact line are very similar to those that occur during advancing and receding contact angle measurements, respectively.

When the appropriate topography is present on the surface that distorts and destabilizes the contact line, the contact angles can exceed ~150°, the surface can express behavior that is now commonly called "superhydrophobic,"[2−5] and the mechanisms of contact line events cause the drop to roll rather than slide (Figure 1b). The advancing contact line does not advance, rather a new contact line forms as the liquid—vapor interface descends on the next topographic features to be wet. Receding involves the disjoining of liquid from topographic features in concerted events. We have discussed[6,7] the rolling and sliding of moving sessile drops in some detail, have pointed out that these mechanisms are extremes of motion, and have emphasized that mixed mechanism rolling/sliding can occur and that events at the

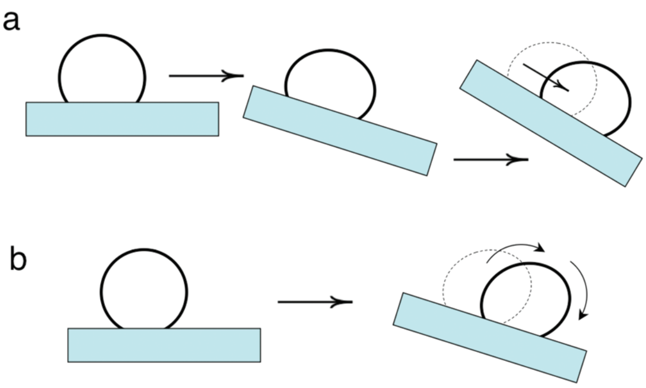


Figure 1. Two-dimensional representations of a drop (a) sliding and (b) rolling on surfaces.

contact line of a moving drop can be concerted, synchronous, or sequential. The difference between the advancing and receding contact angles is termed hysteresis, and this value determines both the force required to initiate drop movement and the degree to which the drop must distort in order to move. Contact angle hysteresis and its cause(s) were considered in detail ~70 years ago[8] and were quantitatively equated to the force required for drop motion ~50 years ago.[9,10] Without hysteresis ($\theta_A = \theta_R$), no force is required to move the drop, and it moves (slides or rolls)

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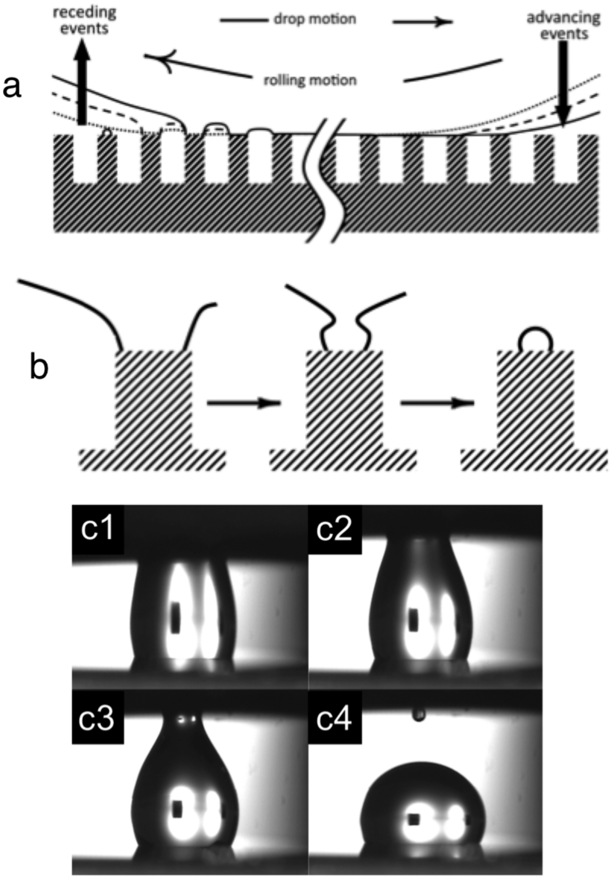

Figure 2. (a) Depiction of a drop exhibiting high advancing and receding contact angles and rolling on a surface containing posts. (b) Capillary bridge rupturing during a receding event at the contact line. (c) Selected frames from a movie of a capillary bridge rupturing as two smooth hydrophobic surfaces are separated. Portions of this Figure are reproduced with the permission of the Royal Society of Chemistry.

without distortion from the horizontal sessile shape. We have previously discussed our perspective on hysteresis in detail and in particular that it involves events that occur at the contact line.[6,7,11,12]

In a recent report,[13] we made the conjecture that when drops roll on certain superhydrophobic surfaces (containing hydrophobic posts) hysteresis is due to microcapillary bridges that form during dewetting at the receding contact line. Our argument that depicts water drop motion on a surface containing dimethylsilicone-modified posts[14] and exhibits water contact angles of θ_A/θ_R = 176°/156° (hysteresis of 20°) is reviewed in Figure 2. A smooth silicon surface with identical chemistry exhibits water contact angles of θ_A/θ_R = 104°/103°.[16] As the drop rolls, the advancing contact line continually reforms as the liquid−vapor interface spontaneously wets the smooth tops (θ_A = 104°) of the next posts that the drop encounters. These events are essentially vertical (perpendicular to the surface (θ_A = 176°)). The receding events are also quite vertical (θ_R = 156°), and the smooth post tops (θ_R = 103°) remain wetted during receding, which causes contact line pinning. Our insight into these simple events more than 10 years ago[15] was rather unsophisticated when we first wrestled with these contact angle data, and we did not consider that the disjoining mechanism at the receding contact line (that we described as involving "concerted events") must involve microcapillary bridge formation and rupture (Figure 2b) and that microdroplets must remain on post tops after dewetting. Indeed, a careful analysis of video recordings[17] of the separation of smooth perfluoroalkyl group-containing surfaces reveals that capillary bridge rupture and droplet formation occur during tensile dewetting (Figure 2c). We emphasize that Figure 2 uses a rolling drop as a visualization aid because this is the familiar perspective in the superhydrophobic literature. The events at the contact line, however, are local events that are independent of the rolling motion and also must occur during the withdrawal of a solid object from a liquid (see below) upon dragging a drop across a solid or at the meniscus of a liquid being withdrawn from a tube.

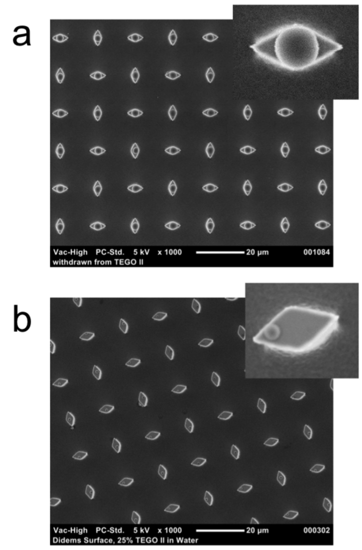

Figure 3. SEM micrographs of hydrophobized silicon surfaces containing staggered rhombus posts that were withdrawn from (a) N^+S^- and (b) a 3:1 mixture of water and N^+S^-.

We have not verified this conjecture concerning microcapillary bridge and microdroplet formation on posts during receding contact line events using water as a probe fluid; we have no direct evidence of microdroplets being "left behind" a receding contact line or a trail following a moving water droplet. We rationalize our lack of evidence by the assumption that the microdroplets evaporate too rapidly for observation. To capture these mechanistic intermediates, nonvolatile ionic liquid dimethylbis(β-hydroxyethyl)ammonium methanesulfonate (N^+S^-) was used as a probe fluid. This particular ionic liquid was chosen because it exhibits the highest surface tension (γ_{LV} = 66.4 dyn/cm) of the ionic liquids that we have measured.[18] The nonvolatility (absence of vapor pressure) of this liquid permits analysis using scanning electron microscopy (SEM). Figure 3a shows SEM data of a perfluoroalkyl group-modified silicon surface[19,20] containing staggered rhombus posts that was withdrawn from N^+S^- by hand using tweezers at ∼1 cm/s. This motion replicates the events that occur at a receding drop contact line (contact angles of θ_A/θ_R = 164°/152° are observed for this liquid on this surface) and is more laterally homogeneous.[21] The surface was removed in the direction that is upward in the micrograph. Microdroplets are formed on every post top, and our interpretation of these events is identical to the original conjecture described in Figure 2—microcapillary bridge formation and tensile failure. The forces required to rupture these capillary bridges decrease the macroscopic receding contact angle, thus

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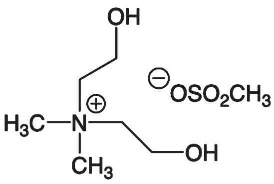
the capillary bridges can be implicated as the "cause" of hysteresis. Figure 3b shows the same surface after removal from a solution of 25 vol % N^+S^-/75 vol % water. The water evaporates, leaving microdroplets that are smaller than those formed by a pure ionic liquid. We note that the viscosity of this mixture is significantly lower than that of neat N^+S^- and that this difference is likely responsible for the greater decrease in droplet volume than is predicted using vol % N^+S^-. We have not examined viscosity effects, surface tension effects, or rate-of-evaporation effects independently or carefully and comment that ionic liquid mixtures and less volatile miscible liquids (perhaps glycerol) would be useful in sorting out this complex process.



N^+S^-

Reyssat and Quéré[22] and Mognetti and Yeomans[23] recently referred to pinning events as the cause of hysteresis and described possible shapes of menisci that may form at receding contact lines. The structures that they predict could be described as early stages of capillary bridge formation. Li, Ma, and Yan[24] reported high-speed video recordings of drops impacting post-containing surfaces. They comment on a "dark stripe" observed in the recordings that they attribute to a "liquid layer being left behind on the microposts" and propose that the mechanism of formation of this layer involves the "pinch-off of liquid threads." This qualitative description is consistent with the mechanism that we propose in Figure 2. Earlier, Patankar,[25] Chibowski,[26] and Fort[27] proposed that depressed receding contact angles (and hysteresis) are caused by a liquid film that is left behind on the surface but was not observed. Fort notes the lack of experimental support for this proposal, predicts that investigations attempting to observe this film will fail, and states that "it is difficult to understand why water should wet a hydrophobic solid surface (θ_S = 105.4°)." This view is incorrect as we explain in a paper[17] titled "Teflon is Hydrophilic," and we emphasize that curvature, particularly the sign of curvature of topographic elements, can cause receding contact line pinning on surfaces that, from a chemical perspective, should be "hydrophobic". The explanation for why concave curvature can inhibit water repellency is explained in Figure 4. The Figure shows two surface asperities (posts) of identical surface area and identical composition; a smooth surface of this substance would exhibit a receding contact angle of 90°. The only difference that distinguishes these asperities from one another is that the curvature of the two post tops is opposite in sign. The Cassie area fractions and Wenzel roughness ratios are identical for the two posts. A tensile force on the capillary bridge attached to the post top with positive curvature (Figure 4a) forces the contact angle to a lower value and the contact line to recede. The same tensile force on the post with negative curvature (Figure 4b) forces the contact angle to a higher value and opposes recession. Surfaces prepared with these features would exhibit, respectively, (a) high and (b) low receding contact angles.

Ionic liquid probe fluids should be useful in identifying pinning mechanisms and pinning sites (topographical features) on other, perhaps irregular superhydrophobic surfaces as well as on smooth, chemically heterogeneous surfaces. In the latter case, we expect that sessile capillary bridge rupture will occur because of the shear pinning of receding lines. The 2D curvature (and the sign of this value) will affect contact line pinning.

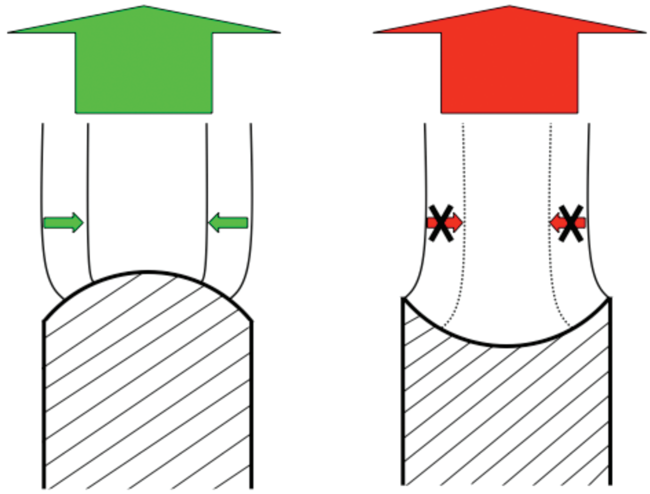


Figure 4. Capillary bridges on posts made of a material that exhibits θ_R = 90°. Tensile force (upward) on the capillary bridge attached to the post top with positive curvature (left) forces the contact angle to a lower value and the contact line to recede (it is not stable below 90°). An upward tensile force on the post with negative curvature (right) forces the contact angle to a higher value, at which angle it cannot recede, thus it remains pinned at the post edge.

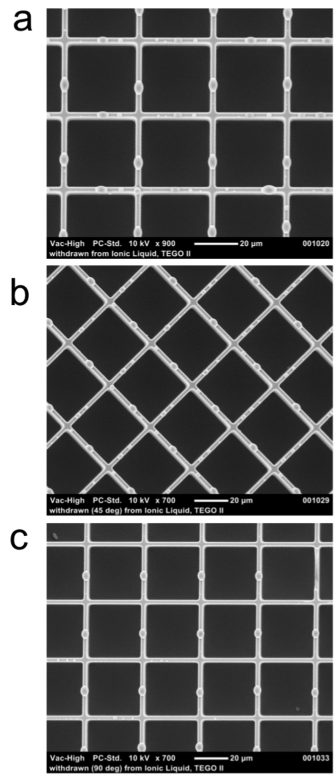


Figure 5. SEM micrographs of hydrophobized silicon surfaces containing square holes that were withdrawn from N^+S^- at (a) 0, (b) 45, and (c) 90° relative to an arbitrary (0°) direction.

Figure 5 shows SEM micrographs of a surface[28] containing square holes separated by ridges that was withdrawn from N^+S^- at three different (0, 45, and 90°) orientations from the surface of the liquid. In each case, the surface was removed in the direction oriented upward in the micrograph. It appears that capillary bridges tend to form on the ridges at the midpoint between intersections and not at the intersections. A simple surface area argument suggests that a capillary bridge at an intersection (X-shaped cross section) would move spontaneously from the intersection to a ridge to decrease the liquid−vapor surface area. We emphasize that these experiments were performed by hand with tweezers and hesitate to overanalyze these data. The differences between microdroplets on perpendicular ridges of the sample withdrawn at 45° from the square pattern (Figure 5b) suggest that there may be orientational defects in the surface (because the photolithography at 0° is different from that at 90°); however, comparing Figure 4a and c suggests that the withdrawal direction is important. In addition to the viscosity effect noted above, the rate of substrate removal from the liquid and the angle between the substrate and liquid surfaces (which is compound relative to the rhombus and square hole features) should affect the droplet volume and position on the features.

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