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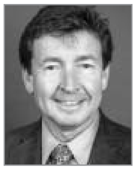

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Philippe Bourrianne and Gareth H. McKinley

Carbonated droplets deposited on a superhydrophobic surface float on a self-generated cushion of gas.

Liquids are defined by their ability to flow. In a river, water moves freely under the influence of even a tiny incline. At smaller scales, however, droplets can resist gravity and remain attached to a solid substrate—for example, when raindrops cling to window glass. That common observation emphasizes the important role that surface tension and three-phase contact lines at a liquid–solid interface (see the Quick Study by Laurent Courbin and Howard A. Stone, Physics Today, February 2007, page 84) play in overcoming the weight of a millimeter-scale droplet.

The main strategy for reducing liquid–solid adhesion is minimizing the contact area between a droplet and its substrate. In 1944 A. B. D. Cassie and S. Baxter, working at the Wool Industries Research Association in the UK, predicted a regime in which a water drop would sit above a textured and sufficiently hydrophobic solid. With its surface contact limited to a tiny fraction of the total basal area, a liquid in the so-called Cassie–Baxter regime adopts a quasi-spherical shape that is just slightly perturbed by the effects of gravity and appears to be predominantly surrounded by air, as displayed in figure 1a.

A droplet in the Cassie–Baxter state doesn't quite sit entirely above the surface. It still has small, localized contact points that lead to residual adhesion. More importantly, the surface repellency is fragile. An external perturbation can force the liquid to invade the textured surface's hydrophobic pores, thereby causing a dramatic increase in the contact area and, correspondingly, the adhesion. Ideal nonadhesion thus requires a droplet to levitate over a substrate, thereby avoiding any liquid–solid contact.

Leidenfrost droplets

The first levitating droplets were reported in 1756 by Johann Gottlob Leidenfrost, a German physician who described the rounded shape and extreme mobility of water drops deposited on a glowing-hot iron spoon. The volatile liquid was levitating on a thin cushion of its own vapor—the so-called Leidenfrost phenomenon observable in your own kitchen when liquid water droplets skitter across a sufficiently hot pan.

A droplet in the Leidenfrost regime experiences near-perfect insulation from the hot substrate below it. The insulation prevents boiling and enables zero adhesion and high mobility, and a droplet's motion can then be directed by, for example, surfaces with millimeter-scale textures (see Physics Today, June 2006, page 17). Still, the properties and applications of the levitating drops are limited by the high energetic cost of superheating the solid far above the liquid's boiling point. For water, the so-called Leidenfrost temperature above which droplets levitate is around 200 °C on common smooth solids, and it can be even higher for rough hydrophilic solids.

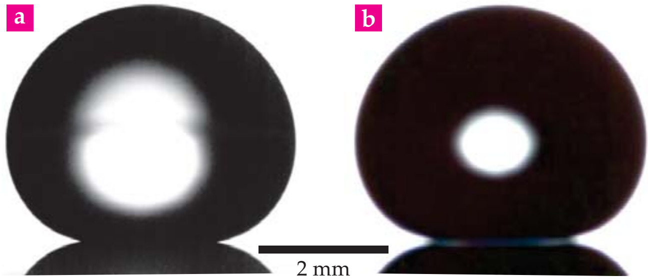

FIGURE 1. LEVITATION on a textured superhydrophobic solid. **(a)** A 30 µL drop of still water sits flush against the surface. **(b)** A thin ray of light passing between a 30 µL drop of carbonated water and its reflection on the solid indicates that the drop is levitating on a micrometer-scale gas cushion.

Recent studies have tried to lower the critical temperature above which droplets levitate. In 2012 Ivan Vakarelski and collaborators demonstrated that the use of a microtextured hydrophobic solid could extend the Leidenfrost regime all the way down to the boiling point of the liquid. The water-repellent solid stabilizes the vapor cushion, even as the temperature difference between the droplet and the solid shrinks and makes the cushion thinner. But that extension of the Leidenfrost domain still requires a substantial temperature difference between the liquid and the solid to maintain evaporation-driven levitation.

Fizzy droplets

Levitating a droplet at a temperature below its boiling point requires another strategy. A liquid that releases gas through a mechanism other than evaporation—for example, through a chemical reaction—can sustain its own cushion at ambient temperature in the absence of any external field. Here we illustrate the strategy using carbonated water made by pressurizing a bottle of deionized water with carbon dioxide gas.

The water-repellent solid in figure 1 features a so-called Glaco coating that consists of microscopic hydrophobic silica particles. It therefore combines hydrophobicity with submicrometrical roughness. Although similar hydrophobic surfaces can be readily made in the lab, the commercial Glaco

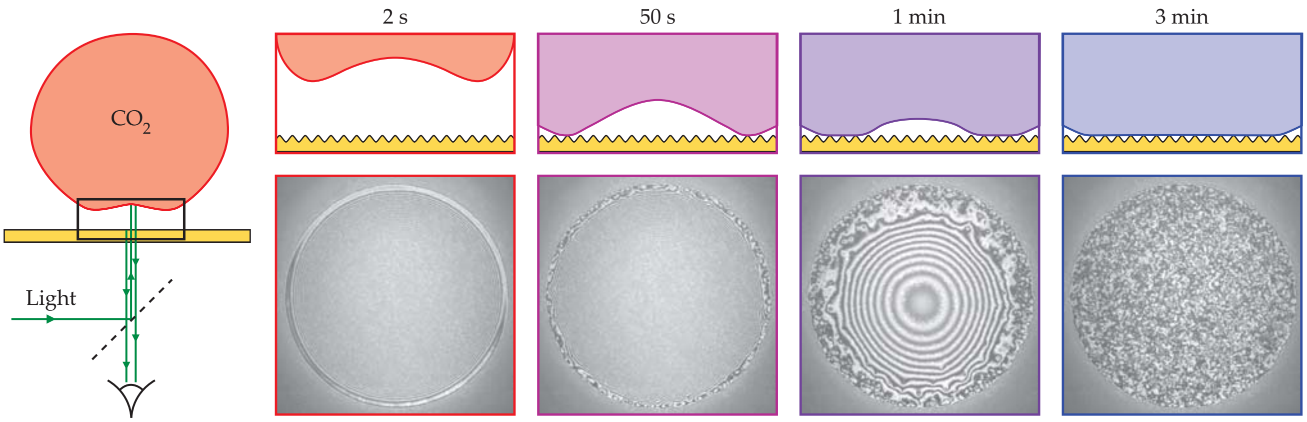

FIGURE 2. LIFE AND DEATH of a levitating fizzy water drop. In the experiment, a drop of sparkling water is placed on a transparent superhydrophobic substrate, and its basal area is imaged using interferometric microscopy with monochromatic light. Two seconds after deposition, the drop's base exhibits circular interference fringes, indicating the drop is entirely levitating over a thin gap of carbon dioxide gas. After 50 seconds, the first contacts between the solid and the liquid appear at the drop's edge. A central air bubble remains in the center. One minute into the experiment, the liquid–solid contacts spread inward as the central CO_2 bubble shrinks because gas is escaping through the porous solid. After three minutes, the remaining CO_2 concentration is too low to maintain levitation. The drop returns to a Cassie–Baxter regime, in which the liquid sits on the peaks of the surface's microtexture. (Note that the sketches in the upper row are not drawn to scale.)

coating developed by the Japanese company Soft99 has the added benefits of being mechanically robust and optically transparent.

After depositing a drop of carbonated water on the textured superhydrophobic surface, we indeed observed a subtle difference between it and a drop of still water. Although the drops' quasi-spherical shapes are roughly the same, a thin gap appears between the carbonated drop and the superhydrophobic substrate (figure 1b), thus indicating that the drop levitates at ambient temperature because of the continuous release of CO_2 gas under the drop and into the porous solid. A pressure difference builds up under the drop as the emitted gas is forced radially outward from under the drop's base.

Figure 2 shows interferometric microscopy images of a sparkling droplet's levitation. We imaged the drop's base from below through the transparent superhydrophobic solid. The monochromatic light used for imaging produced fringes as it interfered with the reflected light coming from the base of the liquid, and those fringes allowed us to reconstruct the topography of the liquid interface at the base of the drop.

When a drop of sparkling water is first deposited on the water-repellent solid, it produces axisymmetric fringes characteristic of a levitating liquid droplet. The dimpled liquid–air interface hovers a few microns above the solid. As the initially dissolved gas is progressively released, however, the gas-release rate decreases. After about 50 seconds, the gas-release rate is insufficient to generate enough of a pressure difference to sustain the drop's total levitation. Some liquid–solid contacts appear at the perimeter of the drop base. The drop enters a regime of partial levitation with a central bubble, or blister, trapped underneath. The contact patches spread progressively inward. Eventually, the liquid comes to rest on the random local peaks, or asperities, of the porous hydrophobic surface. The myriad dark and bright spots in the last image serve to emphasize the heterogeneous local nature of the Cassie–Baxter wetting regime.

The time between when the droplet is deposited and when it no longer retains sufficient CO_2 for levitation is just a few minutes. Despite that loss of levitation, carbonated water drops enjoy a better fate than their thermal equivalent: Leidenfrost drops eventually vanish because of their complete evaporation, whereas decarbonated fizzy water drops remain in the superhydrophobic regime. Similar levitation at ambient temperature can also be achieved with other liquids. For example, the same principle applies to a droplet of two mixed liquid chemicals whose reaction generates a gas. The procedure also paves the way for the levitation of nonvolatile liquids such as oils.

Fizzy levitating drops demonstrate that all the desired transport properties of Leidenfrost drops, including their high mobility, are now accessible at ambient temperature. They exhibit a reduced friction when sliding on a superhydrophobic solid and can be propelled by millimeter-scale textures. (See the online version of this article for videos of those behaviors.) Larger volumes of fizzy liquids also retain similar dynamic features: When poured into a superhydrophobic-coated glass, the bubbles in fizzy beverages can't cling to the inside of the glass and produce their usual sparkle. Instead, the liquid becomes encased in a thin continuous gas film that could cause bewilderment, and maybe disappointment, to an admirer of bubbly drinks.

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Additional resources

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