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Delayed Freezing on Water Repellent Materials

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Water drops on hydrophobic microtextured materials sit on a mixture of solid and air. In standard superhydrophobic situations, the drop contacts more air than solid, so that we can think of exploiting the insulating properties of this sublayer. We show here that its presence induces a significant delay in freezing, when depositing water on cold solids. If the substrate is slightly tilted, these drops can thus be removed without freezing and without accumulating on the substrate, a property of obvious practical interest.

A liquid deposited on a solid decorated with a hydrophobic microtexture has two main configurations.[1,2] Either it conforms to the contours of the solid surface (Wenzel state) or it rests on the crests of the roughness, leaving the cavities below filled with air. This latter condition, the Cassie state, is also referred to as the "fakir" state, since the drop then sits on a bed of micronails.[3,4] Comparing the surface energies of the two states indicates which one should be preferred, even if metastable Cassie states are often observed on dilute textures, despite a higher surface energy.[5,6] Owing to the presence of air below the liquid, the fakir situation generates remarkable properties, such as reduced adhesion (which prevents drops from sticking),[2,7,8] large slip (when water flows along the surface),[9,10] and antifogging properties for nanostructured materials.[11]

The substantial presence of air below the drop may also provide a thermal barrier between the solid and the liquid. Compare this configuration with the one reported long ago by Leidenfrost where water drops are observed to stay very long in hot spoons (temperature around 300 °C), due to the presence of a vapor film between the solid and the liquid.[12] This film prevents contact between both phases and thus the nucleation of bubbles (these drops indeed do not boil). Moreover, its insulating properties delay evaporation: water droplets of radius R = 1 mm can have lifetimes as high as 100 s on such hot solids![13]

The air sublayer in a superhydrophobic state is somewhat different from a Leidenfrost film. Its thickness is directly related to the texture height (often a few micrometers), which makes it generally much thinner than a Leidenfrost film, whose thickness typically is 100 μm.[13] In addition, only a small fraction of the surface area of a fakir drop directly contacts the solid, contrasting with a Leidenfrost drop, which literally floats on a vapor cushion. Nonetheless, as shown from contact angle measurements and from direct observations, the liquid/air surface area below a fakir drop is much larger than the solid/liquid surface area (by a factor of 10−100).[8,14] Therefore, it appears likely that these air sublayers can provide substantial thermal insulation, and we demonstrate here that freezing is indeed significantly delayed when depositing water on cold superhydrophobic materials.

We first fabricated rough surfaces, following the robust and convenient method proposed by Larmour et al.[15] Copper plates (dimensions 5 cm × 5 cm) are immersed in a 0.1 M solution of silver nitrate, which induces roughness at the scale of a few micrometers. Varying the immersion time, we showed that the desired wetting properties were reached after 1 min; a longer immersion does not provide any improvement. The relevant level of roughness is directly apparent from the darkening of the copper plates. The rough surfaces are then plunged 30 min in a bath of ethanol containing a (volumetric) proportion of 3×10^{-4} of fluorinated thiols. These HDFT molecules (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decanethiol) chemisorb onto the copper, forming a hydrophobic monolayer. Hence, we get rough (super-) hydrophobic surfaces, with advancing and receding contact angles of 165° and 155°, respectively. The corresponding low value of the hysteresis (10°) is consistent with the fakir state.

An aluminum plate is then brought in contact with a circulation of cryogenic liquid whose temperature is fixed for this study at −12 °C. The plate temperature is measured and found to be −8 °C. Both superhydrophobic and regular copper substrates are attached to this plate and quickly reach the same constant temperature. Without any precaution, the substrates are covered with frost within 30 min, due to condensation of water from the air. This phenomenon of course opposes any potential effect related to the presence of an air cushion, since this cushion is then replaced by ice. We have found that condensation can be avoided by simply covering the substrate with an inverted Petri dish.

The experiments consist of depositing a volume Ω of distilled deionized water (generally between 10 and 200 μL) of initial temperature T_0 = 25 °C on copper of temperature T = −8 °C, and then measuring the time τ when this drop starts to solidify.

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Performing this simple experiment with a given volume of water led to a very poor reproducibility: the measured times τ fluctuated by more than 1 order of magnitude. We realized that this is due to the low control we had on the content of impurities in the water. Distilled deionized water can be supercooled, to temperatures well below 0 °C before the onset of freezing. Freezing is a function of the particular (unknown) impurities present in the drop or on the solid surface. We solved this problem by using regular tap water, which contains enough impurities to trigger freezing at 0 °C, as checked by direct measurements of the temperature inside the drop. This change significantly improves the reproducibility of the measurements; specifically, the variability of the freezing time decreased from 1000% with "pure" water to 20−30% with tap water.

We show in Figure 1 the successive states of two drops on cold copper, either superhydrophobic or regular. Since a drop reflects the color of its substrate, the one on the left looks black and the second one looks orange. The first row shows the drops immediately after they are deposited on the substrates. Later (second row), the drop on flat copper has frozen, as revealed by its milky texture, but at a significant (and measurable) time later the left drop also solidifies (third row). We now try to quantify the delay between both solidifications.

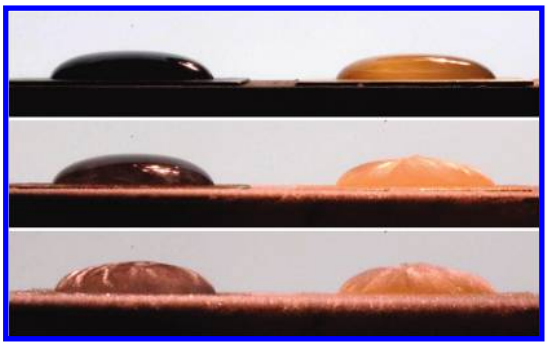

Figure 1. Comparison between two water drops (Ω = 1200 μL) deposited on microtextured superhydrophobic (black) copper (left) and flat (orange) copper (right), both at a temperature $T = -7$ °C. First row: the drops were just deposited; their colors reflect the substrates. Second row: the drop on flat copper has frozen. Third row: both drops are frozen. There is no difference in contact angle between the drops, because a thin ring (of radius R = 10 mm) has been etched in both plates, providing pinning for the contact line and allowing us to compare the freezing of drops of same volume and same surface area.

In a first series of experiments, we measured the freezing time τ as a function of the drop volume Ω on both surfaces. The corresponding results are displayed in Figure 2, with empty or full symbols when the plate is flat or microtextured, respectively. For the flat surface, we also reported data points obtained after treating the surface with the fluorinated thiol (squares), making it slightly more hydrophilic than the regular plate, with an advancing angle of 110° instead of 90° for the regular (oxidized) copper.

It is observed in Figure 2a that the presence of microtextures dramatically affects the freezing time of the drops, for all the considered volumes. Solidification is always delayed, by a factor between 3 and 5. Two effects can contribute to this difference. As mentioned above, the presence of a thin film of air may act as a barrier to thermal transfer. However, there is a more trivial reason, namely, the difference of surface area between both drops for a given volume Ω.

Our drops are larger than the capillary length a ($a = (\gamma/\rho g)^{1/2}$, denoting ρ as the liquid density and γ as its surface tension), so that their thicknesses are dictated by a balance between gravity (which tends to thin the drop) and capillarity (which tends to make it spherical).[13] For a puddle of thickness h, this balance can be written: $1/2\rho g h^2 = \gamma\,(1 - \cos\theta)$, where θ is the contact angle. The resulting thickness $h = 2a\sin(\theta/2)$ increases monotonically with the contact angle. Puddles are thicker on superhydrophobic surfaces than on regular copper, which implies a smaller (heat exchange) surface area S and thus a reduced thermal transfer and a slower freezing.

This argument can be made more precise. As emphasized earlier, the use of tap water induces freezing at 0 °C, so that the time τ is just the time needed for decreasing the drop temperature from its initial value T_0 to 0 °C. The equation of heat transfer can be written: $\Omega T_0/\tau = KS$, where K is a constant which captures the physical parameters of the problem (plate temperature, specific heat of the liquid, etc.). We thus expect the freezing time τ to vary as Ω/S and thus to be sensitive to the surface area S for a given volume of water. The latter relationship can be written: $\tau = (\Omega/S)/c$, which defines a freezing velocity c. We plotted in Figure 2b the data of Figure 2a (same symbols), as a function of the ratio Ω/S, which has the dimension of a length (roughly, the height of the drop). The two series of data are observed to be distinct, which suggests that the difference in surface area alone cannot explain the delay in freezing observed with the fakir substrate. Drawing a straight line through the origin for each series of data, as expected from the arguments above, we find that

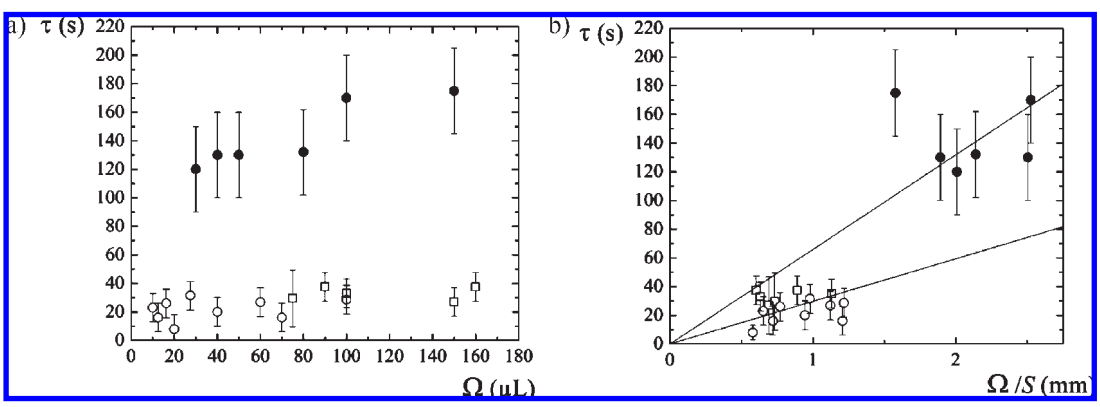

Figure 2. (a) Freezing time τ (in seconds) of water drops on flat copper (○), on copper treated with a fluorinated thiol (□), or on superhydrophobic copper (●), as a function of the drop volume Ω (in microliters). For all the data, the initial temperature T_0 of water is 25 °C, and the plate temperature T is −8 °C. The error bars express the standard deviations in the experiments. (b) Same data plotted as function of the ratio Ω/S (expressed in millimeters), where S is the (measured) (apparent) surface area between solid and liquid. The two families of data remain quite distinct.

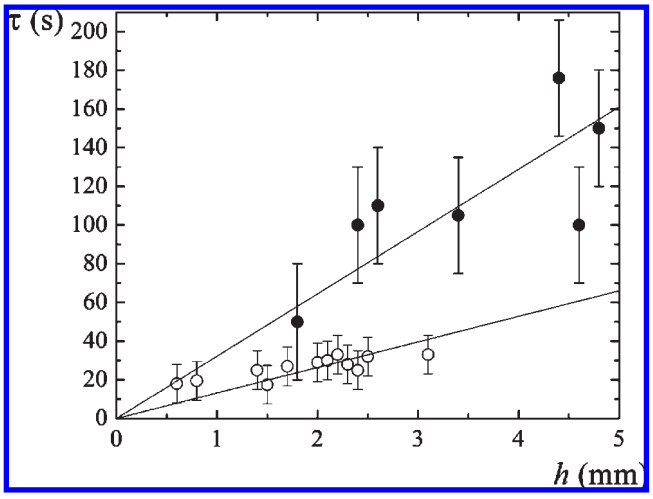

Figure 3. Freezing time τ (in seconds) as a function of the drop height h, for drops of the same surface area. A circular groove of radius $R = 10$ mm is first etched on the substrate in order to pin the contact line and to allow us to vary the drop volume (and thus the drop height) while keeping the surface area $S = \pi R^2$ constant. Data are reported for both regular copper (empty symbols) and superhydrophobic copper (full symbols), both at −8 °C. Freezing is again observed to be delayed in the latter case.

the slopes differ by a factor of about 2, which might imply a difference of the same order between the freezing velocities on both substrates.

The representation in Figure 2b is a useful step to decouple the geometrical effects (increasing the contact angles makes the puddle thicker and thus reduces the efficiency of thermal exchanges) from other possible causes of freezing delay, such as the presence of air below the fakir drop. In order to confirm this partial conclusion, we performed a second series of experiments, where both the volume *and* the surface area were kept constant, allowing us to compare the freezing kinetics independently of the puddle geometry. On both surfaces, we etched a thin circular line of radius $R = 10$ mm. As known since Gibbs, grooves efficiently pin contact lines, preventing drops from advancing or receding: on such "defects", the apparent contact angle is flexible. We placed a large volume of liquid inside the circle and suctioned it off until a prescribed volume Ω was reached. Whatever the nature of the solid (slightly hydrophobic for copper, or superhydrophobic for microtextured copper), we could thus prepare drops with the same shape, as shown in Figure 1 where this trick was used. We then measured the freezing time τ for different volumes Ω, keeping the surface area $S = \pi R^2$ constant. For centimeter-size drops, the ratio Ω/S is close to be the drop height h, and we plot in Figure 3 the solidification time τ as a function of h.

Once again, the two families of results are distinct, with slopes differing by a factor of the order of 2. This confirms the qualitative results of Figure 2b, namely, the significant difference in freezing kinetics between both substrates. The presence of an air film below the fakir drop might be responsible for its much slower solidification.

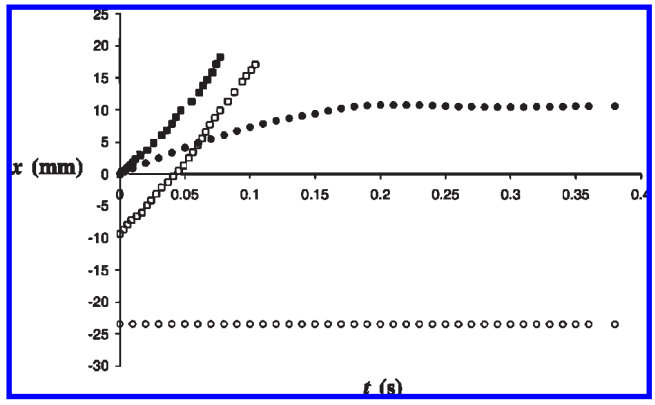

Figure 4. Positions of the leading and trailing edges (filled and empty symbols, respectively) of water drops of volume $\Omega = 100\,\mu$L deposited on cold substrates (at −8 °C) tilted by 40°. The substrate is either rough hydrophobic copper (squares) or flat copper (circles). In the first case, the drop quickly runs down without freezing, so that the solid remains dry. In the second case, the drop is slower. It leaves a film that immediately freezes (thus the trailing edge never moves), while the leading edge slows down, stops, and freezes.

This property can also be exploited dynamically. For drops larger than the capillary length, angle hysteresis cannot oppose the drop weight, so that we expect that the drops will run downward if the substrate is tilted. However, the descent velocities should be different on both substrates. On flat copper, the presence of a moving contact line slows down the liquid, while on superhydrophobic copper the high contact angle leads to much quicker descents. Together with the delayed freezing, we can thus anticipate very different behaviors on both solids. These differences are illustrated in Figure 4, where we follow the position x of drops on inclined substrates as a function of time t.

In the experiment of Figure 4, water drops of volume $\Omega = 100\,\mu$L are deposited on cold plates tilted by an angle $\alpha = 40°$. We follow the positions x_f and x_t of the leading and trailing edges of the drops, represented by full and empty symbols, respectively. The drop on the textured surface (squares) has a smaller initial diameter $x_f - x_t$ than the drop on flat copper (circles) due to a higher contact angle. It is observed that its velocity is larger but, more importantly, that it leaves the solid surface (at $x \approx 20$ mm) without depositing any film and without freezing. Conversely, the drop on flat copper spreads more and runs slower, so that it leaves a film that freezes immediately. For this drop, the trailing edge never moves (empty circles); on the other hand, the leading edge slows down and stops before the end of the plate and thus fully solidifies (full circles). The final states are thus completely different. In the first case, the solid is clean and dry. In the second case, the substrate is covered by a long patch of ice. This dynamic situation is directly applicable to rain running down solids in the field of gravity, and it helps to illustrate that water repellency is an excellent strategy to avoid formation of ice on cold solids.

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