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Dynamic Air Layer on Textured Superhydrophobic Surfaces

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Supporting Information

ABSTRACT: We provide an experimental demonstration that a novel macroscopic, dynamic continuous air layer or plastron can be sustained indefinitely on textured superhydrophobic surfaces in air-supersaturated water by a natural gas influx mechanism. This type of plastron is an intermediate state between Leidenfrost vapor layers on superheated surfaces and the equilibrium Cassie–Baxter wetting state on textured superhydrophobic surfaces. We show that such a plastron can be sustained on the surface of a centimeter-sized superhydrophobic sphere immersed in heated water and variations



of its dynamic behavior with air saturation of the water can be regulated by rapid changes of the water temperature. The simple experimental setup allows for quantification of the air flux into the plastron and identification of the air transport model of the plastron growth. Both the observed growth dynamics of such plastrons and millimeter-sized air bubbles seeded on the hydrophilic surface under identical air-supersaturated solution conditions are consistent with the predictions of a well-mixed gas transport model.

INTRODUCTION

Macroscopic gas films on surfaces or plastrons, a term coined by Brocher in 1912,¹ have been known for a long time to play a key role in enabling aquatic insects to breath under water. The physics of the process continues to attract broad interest,² for instance, in the spontaneous formation of bubbles in gassupersaturated liquids that are known to enhance the appreciation of aerated beverages.³ Interest in the apparent stability of nanobubbles in water on hydrophobic surfaces observed by atomic force microscopy^{4–6} has elicited a number of different theoretical models for the dynamic behavior of such gas bubbles.⁶⁻⁸ In a recent study of the cooling dynamics of very hot stainless-steel spheres held under water,⁹ the process begins with a dynamic Leidenfrost vapor film that isolates the sphere surface from the liquid $^{9-12}$ in the film boiling regime but, as the sphere cools, may subsequently transition to the nucleate boiling regime, depending upon the surface roughness and hydrophobicity.^{9,13-15} Our earlier experiments showed that, at a superhydrophobic surface with a rough texture of different length scales, cooling occurs entirely in the Leidenfrost regime without transition to nucleate boiling.⁹ When the hot sphere has finally equilibrated with the pool temperature, a Cassie–Baxter^{16–18} gas layer or plastron^{19–21} remains and covers the entire sphere surface, with the water in contact only with the roughness peaks of the textured superhydrophobic surface.

Prior studies have investigated various properties of the plastron on the superhydrophobic surface but mostly under air-

saturated conditions, under which the plastron will eventually dissolve over time. $^{21-24}$ Here, we report observations of the dynamic characteristics of such plastrons at varying degrees of air gas supersaturation, mostly nitrogen and oxygen, in the water. We demonstrate that a steady-state gas flux into the surface vapor layer drives plastron growth that results in periodic, buoyancy-driven pinch-off of bubbles from the top pole of steel spheres with radii of 5-15 mm with textured superhydrophobic surfaces, with a contact angle of $>160^{\circ}$. The generality of this gas flux driven mechanism is further illustrated with observations of the growth rate of small millimeter-sized bubbles that are seeded on hydrophilic surfaces. The growth rates of plastrons on superhydrophobic surfaces and small bubbles on hydrophilic surfaces exhibit the same dependence upon air gas supersaturation in the water. The growth of plastrons and small bubbles under gas-supersaturated conditions can be explained by a well-mixed transport model.

EXPERIMENTAL SECTION

Experimental Setup. The basic equipment setup used for the observation of the plastron growth dynamics on a steel sphere in water is illustrated schematically in Figure 1. Experiments are conducted in a 1 L Pyrex glass beaker filled with water and placed on a temperature-controlled hot plate. A steel sphere (radius of 5-15 mm) is mounted on a holding stake that is attached to an optical rail glider that

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Figure 1. Schematic of the experimental setup for observing plastrons on steel spheres held under temperature-controlled water.

facilitates the smooth immersion of the sphere into the water and the adjustment of the immersion depth. The water temperature and, hence, the degree of gas saturation can be adjusted by controlling the temperature of the hot plate. We used a K-type thermocouple probe connected to a thermocouple thermometer to monitor the temperature of the water in the beaker. A high-speed video camera (Photron Fastcam SA-S) was used to record the dynamics of the plastron on the superhydrophobic sphere surface.

Air Saturation Control of Heated Water. The gas content, air comprising mainly of nitrogen, N2, and oxygen, O2, in the water was controlled by a protocol of consecutive boiling, cooling, and heating of the water in the beaker. Initially, the water was degassed by boiling for 10-15 min. The hot plate temperature was then lowered to decrease the water temperature to about 85 °C and maintained at that level for about 20 min. This allows for some air to be reabsorbed and equilibrate in the water. The water temperature was then raised rapidly to above 90 °C. We found that, following this procedure, the water in the beaker could be maintained in an air-supersaturated state in the temperature range of 90-99 °C used in our experiment. When the heating and cooling temperatures and the duration of each of the temperature steps in this procedure were varied, it was possible to produce water with different degrees of gas concentration. A reference gas concentration can be identified with the water temperature at which we observed zero growth of the plastron on the superhydrophobic sphere. A lower temperature of zero growth corresponds to a higher gas concentration.

Preparation of Superhydrophobic Spheres. The spheres used were polished stainless-steel grinding balls (FRITSCH GmbH) of density $\rho_s = 7700 \text{ kg/m}^3$ and radii R = 5, 10, and 15 mm. The average surface roughness given by the manufacturer is $R_a < 0.06 \ \mu\text{m}$. Using an electrical discharge machine, we drilled 1.5 mm diameter holes radially into the top of the spheres down to the sphere center. This allowed us to mount a holding stake for easy handling of the spheres and surface modification without having to touch the sphere surface.

The spheres were made superhydrophobic by applying a commercial superhydrophobic coating, Cytronix PFC 1604V suspension liquid (Cytronix, LLS), described as a "FluoroPel copolymer solution containing dispersions of superhydrophobic nanoparticles", according to the manufacturer (http://www.cytonix.com). The superhydrophobic coating was applied on the clean surface steel spheres by pouring the suspension liquid over the spheres. A thin liquid film wets the sphere surfaces and dries in several minutes. After the first application, we heat-cure the spheres at 190 °C for 20 min and then repeat the suspension application and heat-cure procedure 2 more times. This procedure resulted in a surface layer with a translucent appearance that exhibits excellent superhydrophobicity properties with water contact angles of more than 160°, that is, an advancing contact angle of about 170° and a receding contact angle close to 160°. Scanning electron microscopy (SEM) images of the superhydrophobic coating reveal a coarse-scale rough surface topology

with 2–5 μ m structures (Figure 2a) and a nanoscale roughness topology with a characteristic particle size of about 200 nm (Figure 2b).



Figure 2. SEM images of Cytronix PFC 1604V coating on steel spheres: (a) coarse scale roughness of $\sim 2-5 \ \mu m$ at 3500× magnification and (b) nanoparticle scale roughness of $\sim 200 \ nm$ at 80000× magnification.

Spheres of Various Surface Modifications. To compare the dynamics of small gas bubble growth on a non-superhydrophobic surface to the behavior of the gas plastron on textured super-hydrophobic surfaces, we use spheres that we characterize as weakly hydrophilic, hydrophilic, and hydrophobic using the following surface modifications: (a) weakly hydrophilic steel spheres with a water contact angle of less than 30° are obtained by cleaning only with organic solvents (acetone and ethanol); (b) hydrophilic steel spheres with a contact angle of less than 10° were obtained using a plasmacleaner device (Harrick PDC-002), following cleaning with organic solvents; and (c) hydrophobic steel spheres were modified using a commercial hydrophobizing agent (Ultra Glaco, Soft 99 Co., http://www.soft99.co.jp) that gives a water contact angle of about 100°.

To make a quantitative comparison of the air flux into a single bubble and the air flux into the plastron on a superhydrophobic surface, we conducted experiments in which a superhydrophobic sphere was held in water under air-supersaturation conditions next to a hydrophilic sphere. We measure simultaneously the growth rates of the plastron on the superhydrophobic sphere and small bubbles (1–3 mm diameter) that form spontaneously at the apex of the hydrophilic sphere or were seeded using a needle attached to an air-filled microsyringe. The high-speed camera was used to capture the growth rate of the surface bubble and the pinch-off period. For improved resolution in some experiments, the microbubble growth was recorded using a micro-objective and back-light illumination to yield silhouetted images (panels a and b of Figure 11).

Velocity Field Visualization. To estimate the characteristic velocity of the convection flow around the sphere generated by the inherent thermal gradients in the beaker, we performed a simplified particle imaging velocimetry (PIV) experiment conducted under typical experimental conditions at a water temperature of 95 °C. The seeding particles used for flow visualization were standard fluorescent latex particles with a diameter range of 20–50 $\mu m.$ The particles are neutrally buoyant in water with true densities $\rho = 990-1020 \text{ kg/m}^3$. We use a 1× objective lens with a fully open aperture and back-lighting for silhouette imaging, and the field of view is restricted to 2 cm in both the horizontal and vertical directions. The high magnification and open aperture renders a very shallow depth of field, which essentially creates a pseudo-micro-PIV technique. The temporal evolution of the velocity field around the sphere was analyzed using PIV software (Davis 7.2, LaVision GmbH) by performing a time-series correlation between consecutive frames from the video sequences. A typical velocity profile measured near the sphere surface is shown in Figure 3. The typical measured velocity range from multiple trials was 6-14 mm/s; thus, we use a characteristic value of $U = 10^{-2}$ m/s for the purpose of estimating the Peclet number.



Figure 3. Instantaneous fluid velocity field measured by PIV near a 10 mm radius superhydrophobic sphere held in the beaker with the water temperature maintained at about 95 $^{\circ}$ C.

RESULTS AND DISCUSSION

Observation of Plastron Growth Dynamics. In most experiments discussed here, the spheres were heated to about 190 °C before immersion in water. As detailed in our prior study,⁹ when an overheated superhydrophobic sphere is dipped in water, the cooling of the sphere occurs entirely in the Leidenfrost regime, in which the sphere is surrounded by a thin vapor film. The sphere temperature, measured by a thermocouple inserted into the sphere, approaches the pool temperature smoothly, without transition to nucleate boiling that is observed for non-superhydrophobic spheres. During this process, the superhydrophobic sphere preserves a shiny appearance because of the vapor layer surrounding the sphere and bubbles pinch-off periodically from the vapor layer at the apex of the sphere (Figure 4a; see also ref 9 and supplementary videos to ref 9). The frequency of bubble pinching decreases as the sphere temperature decreases. To demonstrate the time scale of the equilibration process of a hot sphere in water, the time variation of the sphere temperature after immersion in



Figure 4. High-speed camera snapshots of a 10 mm radius superhydrophobic steel sphere in water at different phases of cooling: (a) during the sphere cooling phase in the Leidenfrost regime accompanied by periodic bubbles pinching off from the top of the sphere in water at 97 °C and the sphere temperature of about 150 °C, (b) same sphere during the later stage of steady gas dome growth after its temperature has equilibrated to the pool temperature of 97 °C, and (c) pool temperature being ramped down to 94 °C, which is below the zero growth temperature in that case. As a result, the dome growth stops and the plastron dissolves, changing the sphere appearance from shiny to matte.

water of 100 and 80 $^\circ C$ is shown in Figure 5. In the present work, all observations of plastron growth dynamics were made



Figure 5. Sphere temperature as a function of time for a 10 mm radius steel sphere coated with Cytronix superhydrophobic coating, with cooling water held at 80 or 100 $^{\circ}$ C. For details of these measurements, see ref 9.

at least 5 min (300 s) after immersing the sphere in the heated water, thus ensuring that the sphere temperature is in equilibrium with the surrounding water temperature. In control experiments, we compared the temperature reading of the thermocouple probe mounted inside the sphere and the thermocouple probe placed in the water close to the sphere surface. Such a comparative measurement confirmed a difference of less than 0.5 °C, which is within the limit of the temperature fluctuation with time.

Once the sphere temperature has equilibrated with the pool temperature, there are two possible scenarios. If the water is gas-supersaturated, the shiny appearance of the sphere is preserved, which is a signature of the presence of a thin air layer or plastron on the sphere surface (Figure 4b). At the same time, the gas dome at the top of the sphere continues to grow, with bubbles pinching off periodically from the gas dome, albeit at a much slower rate than during the sphere cooling in the Leidenfrost regime. If, however, the water is gas-undersaturated soon after the sphere temperature equilibrates with the pool temperature, the sphere loses its shiny appearance, indicating the dissolution of the plastron (Figure 4c). At the same time, the residual gas dome at the sphere apex starts to shrink and eventually dissolves completely.

A typical example of the stages of plastron growth on the superhydrophobic sphere held at equilibrium with heated air-supersaturated water is given in the high-speed video snapshot sequence in Figure 6 and Video 1 of the Supporting Information. The water temperature was maintained at about 95 °C, and the snapshots track a single cycle, lasting about 200 s, of the growth of the dome bubble because of gas influx into the plastron and ending with the bubble pinch-off. Several consecutive growth and pinch-off cycles under the same conditions are shown in Video 1 of the Supporting Information. Because the sphere temperature is in equilibrium with the pool temperature and below the boiling temperature of the water, the influx of dissolved air gas into the plastron surrounding the sphere drives the dome bubble growth.

Plastron Recovery. The plastron growth can also be observed using a "cold" superhydrophobic sphere with an initial temperature equal to the room temperature of 21 °C. Immediately following immersion into air-supersaturated



Figure 6. High-speed camera snapshots of a 10 mm radius superhydrophobic steel sphere held in 95 °C air-supersaturated water. The sphere was heated initially to 190 °C before immersion. The gas dome growth and pinch-off cycle shown is for a sphere that has already cooled to the pool temperature of 95 °C. Photos a–d are a time sequence of snapshots tracking a gas dome growth cycle from initiation to bubble pinch-off, lasting about 200 s. Several consecutive bubble pinch-off cycles under the same conditions are shown in Video 1 of the Supporting Information.

water held at 95 °C, the water surrounding the sphere cools and becomes gas-undersaturated locally. Thus, the sphere does not exhibit the shiny appearance immediately, as seen in Figure 7a. However, as the sphere warms and equilibrates with the pool temperature, the dynamic air layer passes through intermediate texture states (panels b and c of Figure 7 and Video 2 of the Supporting Information), before recovering to the steady-state plastron that covers the entire sphere (Figure 7d). Thereafter, it exhibits the same plastron growth and periodic bubble pinch-off dynamics as observed for the initially overheated sphere that cooled in water held at the same temperature as described earlier (see Figure 6). Such recovery of the gas layer on the superhydrophobic surface has been observed previously using electrolysis²⁴ or heating the superhydrophobic surface.⁹ Here, we demonstrate that, as long as the surface is in contact with air-supersaturated water, the surface air layer can self-recover to the steady state of plastron growth.

Quantification of the Gas Flux in the Plastron. Our experiments allow us to estimate the gas influx in the plastron as follows. The mean volumetric influx of gas into the plastron J can be estimated from the measured bubble pinch-off period $\tau_{\rm b}$ and the volume of the pinch-off bubble $V_{\rm b}$

$$J = V_{\rm b} / (4\pi R^2 \tau_{\rm b}) \tag{1}$$

for the sphere of radius *R*. The pinch-off bubble volume $V_{\rm b}$ is estimated by image-processing the pinched-off bubbles (for example, Figure 11d). Because the size of the pinched-off bubbles for spheres of a given sphere diameter was nearly constant for the temperature range investigated, the flux is therefore inversely proportional to the pinch-off period $\tau_{\rm b}$. In experiments in which the water temperature in the beaker is ramped up, we observed a gradual decrease of the pinch-off



Figure 7. High-speed camera snapshots of a 10 mm radius superhydrophobic steel sphere held in air-supersaturated water with a constant temperature of 95 °C. The sphere temperature was 21 °C before immersion. (a) Shiny gas layer is not immediately evident upon immersion, but as the sphere warms to the pool temperature, (b and c) intermediate air layer textures form during recovery to a (d) smooth plastron. The entire process is shown in Video 2 of the Supporting Information.

period, corresponding to an increase of the gas influx. Conversely, decreasing the water temperature will decrease the bubble pinch-off rate until a zero growth rate temperature is reached, below which the dome shrinks, and ultimately, the sphere will lose the shiny appearance, indicating dissolution of the gas layer.²¹ The increase of the gas influx with the water temperature is explained by the decrease of the air solubility with an increasing temperature,²⁵ that is, an increase of the air diffusion coefficient with the temperature increase.²⁶

The results in Figure 8a show examples for the variations in the pinch-off period, and the results in Figure 8b show the corresponding gas flux with temperature for two levels of water air supersaturation: lower gas concentration corresponds to the plastron zero growth (infinite pinch-off period) temperature of about 96 °C and the higher gas concentration corresponds to the plastron zero growth temperature of about 91 °C. In each case, the data were collected as the temperature was ramped up from the zero growth temperature. During the experiments, the sphere immersion depth was held constant by continual addition of small quantities of boiling water into the beaker, to compensate for water evaporation. During the experiment, the dissolved gas concentration in the water does change slowly, so that, if the temperature is ramped down from the maximum temperature, there will be some inherit hysteresis in the data compared to data collected by ramping up the temperature.

Comparison to Gas Diffusion Models. From the gas influx into the plastron estimated from data of bubble pinch-off experiments and eq 1, we can adduce a model to describe the mechanism of plastron growth. As detailed in the Experimental Section using PIV, we image the advection flow velocity profile in the vicinity of the sphere surface and deduced a characteristic fluid velocity $U \sim 10^{-2}$ m/s under present experimental



Figure 8. Temperature variations of the (a) dome pinch-off period and (b) respective air flux to the surface plastron for two levels of water gas supersaturation, where higher gas saturation (blue squares) corresponds to a zero growth rate at about 91 °C and lower gas saturation (red triangles) corresponds to a zero growth rate at about 96 °C. Each data set is collected by ramping up the temperature from the zero growth rate temperature of 91 or 96 °C.

conditions near the sphere surface. Taking a typical value of the diffusion coefficient $D \sim 10^{-8} \text{ m}^2/\text{s}$, we can estimate the ratio of advective to diffusive gas transport in terms of the Peclet number Pe = UL/D. For a typical length scale L = 1-10 mm, $Pe \sim 10^3-10^4$. This is sufficiently high to justify the use of a well-mixed model in which the gas concentration outside a transition zone near the plastron surface is constant because of the advection mixing of the solution. Accordingly, the gas flux into the plastron can be written as

$$J = \eta [c_{\rm m} - c_{\rm p}] \tag{2}$$

where $c_{\rm m}$ is the dissolved gas concentration in the water and $c_{\rm p}$ the saturation gas concentration in water corresponding to the gas pressure and temperature inside the plastron. The mass transfer coefficient $\eta = D/\delta$, where D is the gas diffusion coefficient and δ is the characteristic length of mixing, usually determined as a phenomenological parameter of the system.²⁷

This well-mixed model predicts that the flux should be independent of the sphere radius, and this can be tested using eq 1 by measuring the bubble pinch-off period τ_b and the volume of the pinch-off bubble V_b at spheres of three different radii R = 5, 10, and 15 mm. In this experiment, the three spheres are held together in the beaker to ensure that they are subjected to identical solution conditions, as shown in Figure 9. The bubble pinch-off periods and volumes were recorded at the same time during the solution temperature ramp up, and the flux on each sphere was estimated independently using eq 1. The data for the three spheres are compared in Figure 10 and



Figure 9. High-speed camera snapshots of 15, 10, and 5 mm radius superhydrophobic spheres held together in the same beaker for comparison of the gas flux dependence upon the sphere radius (see data in Figure 10).



Figure 10. Comparison of the air flux into the plastron on spheres of different radii: 5 mm (green squares), 10 mm (blue triangles), and 15 mm (red circles) measured under identical solution conditions. As shown in Figure 9, the three spheres are held together in the beaker to ensure identical conditions.

demonstrate clearly that the gas influx into the plastron is independent of the sphere radius over the 5–15 mm range. Therefore, this indicates that the well-mixed model gives a consistent description of the diffusion in the plastron for our experimental conditions. In contrast, a diffusion-controlled-type model^{28,29} would predict a flux that is inversely proportional to the sphere radius, e.g., $J = (D/R)[c_{\infty} - c_p]$. Simple derivations of the diffusion control and well-mixed models are given in the Appendix.

Comparison of the Air Flux into Plastron to the Air Flux into Bubbles. We also conducted experiments to study the dynamics of the growth of small gas bubbles that form on surfaces with different surface modifications and compared that to the behavior of the gas plastron on textured superhydrophobic surfaces. As detailed in the Experimental Section, we used a plasma-cleaned hydrophilic sphere, a chemically hydrophobized hydrophobic sphere, and an organic-solventcleaned weakly hydrophilic sphere. The observation of bubble growth on such differently modified sphere surfaces was made using the same experimental setup and sphere immersion protocol as for the superhydrophobic spheres. In Figure 11, we show snapshots that compare the appearance of stainless-steel spheres of various surface modifications held under identical conditions of water temperature of about 95 °C and level of gas concentration in the water resulting in zero plastron growth of about 91 °C. As expected, the density and morphology of the



Figure 11. High-speed camera snapshot of 10 mm radius steel spheres with various surface modifications held in 95 °C water of identical levels of air supersaturation: (a) plasma-cleaned hydrophilic sphere, (b) organic solvents only cleaned weakly hydrophilic sphere, (c) hydrophobic sphere (see Video 3 of the Supporting Information), and (d) superhydrophobic sphere (see Video 1 of the Supporting Information).

surface bubbles vary significantly with the surface properties.^{30,31} The plasma-cleaned hydrophilic sphere shown in Figure 11a is virtually bubble-free, which indicates that the pretreatment has eliminated most of the residual nucleation sites on the steel surface. In contrast, the hydrophobic surface sphere shown in Figure 11c provides a high density of bubble nucleation sites, resulting in a dense "bubble carpet" covering the surface. The intermediate case of the solvent-cleaned, weakly hydrophilic sphere shown in Figure 11b has a sparse collection of small bubbles formed over the surface.

We observed good qualitative correlation between the growth rate of bubbles on all non-superhydrophobic surfaces and the superhydrophobic surface sphere plastron growth. Both the bubble growth rate and plastron growth rate increase with an increasing temperature and the associated increase in the degree of gas supersaturation. Video 3 of the Supporting Information shows an example of the growth dynamics of bubbles on the hydrophobic sphere under conditions that are close to that for the case of plastron growth on the superhydrophobic sphere shown in Video 1 of the Supporting Information. On the other hand, if the water temperature is decreased to below the plastron zero growth temperature, the surface bubbles will start to shrink and dissolve under the same conditions in which the plastron dissolves.

For a quantitative comparison of the gas influx into a small air bubble and into the plastron, we measure the growth rate of single bubbles seeded at the top of a hydrophilic sphere, which was held at the same time in the beaker with a R = 10 mm superhydrophobic sphere. By image-processing of the highspeed video recording, we measure time variation of the bubble radius $R_{\rm b}$, and the gas flux can be estimated as $J = dR_{\rm b}/dt$. An example of the time dependence of the radius of growing bubbles $R_{\rm b}$ obtained by image-processing of the bubble growth video is given in Figure 12.



Figure 12. High-speed camera snapshots of a millimeter-sized bubble growing under gas supersaturation on the top of a hydrophilic steel sphere (a) at an earlier stage and (b) at just before pinch-off from the surface. The video is taken using a magnifying objective and backlit illumination. (c) Experimental data of the time dependence of the radius $R_{\rm b}$ of the growing used to estimate the bubble growth rates $J = dR_{\rm b}/dt$ (see Figure 13).

In Figure 13, we compare the millimeter-sized bubble flux with the plastron flux on a 10 mm radius superhydrophobic



Figure 13. Comparison of the air flux into the plastron on a superhydrophobic sphere of radius 10 mm (blue triangles) and into small air bubbles, with radii of 0.5-1.5 mm, on a hydrophilic sphere (red rhombi) measured under identical solution conditions.

sphere measured in a water temperature ramp-up experiment. Although the flux for the bubbles is slightly higher, there is very good agreement between results for the bubble and the plastron. This again suggests that a common physical mechanism sustains gas flux into millimeter-sized bubbles and plastron on a macroscopic superhydrophobic surface. The wellmixed model with a constant flux that depends only upon the gas supersaturation level provides a consistent explanation of the observations. We note in passing that the phenomena of continuous bubble pinching from the top of the superhydrophobic sphere held in air-supersaturated water considered here could be related to the phenomenon on the subcooled "boiling" on heated superhydrophobic surfaces reported by Takata et al.^{32,33}

Room-Temperature Plastron. Finally, we conducted a simple proof-of-concept experiment to demonstrate that the same process of steady plastron growth can be observed in room-temperature water provided that the water is air-supersaturated. Figure 14a is a high-speed camera snapshot



Figure 14. High-speed camera snapshot of a 10 mm radius superhydrophobic sphere at room temperature held in room-temperature water. (a) Shortly after immersion, the silver-mirror sheen of the immersed sphere is due to the thin air layer plastron present on the sphere surface. (b) At 4 h after immersion without water aeration, plastron dissolution is indicated by the change from shiny to matte appearance. (c) At 4 h after immersion when the water in the beaker was continually aerated by bubbling in compressed air, the shiny appearance is preserved and a gas dome slowly grows at the sphere apex.

image of a room-temperature superhydrophobic sphere freshly immersed in room-temperature water that exhibits the characteristic silver-sheen appearance. After about 4 h, the plastron on the sphere dissolved as indicated by the change from shiny to a matte appearance of the sphere (Figure 14b). On the other hand, if the water was kept aerated by passing compressed air through a stone bubbler mounted at the top of the beaker, the silver-sheen appearance will remain and a bubble dome will grow at the sphere apex (Figure 14c). The bubble dome growth rate increases with an increasing compressed air flow rate, and this experiment confirms that the state of constant growth of the plastron can be maintained at room temperature.

CONCLUSION

We have demonstrated that a macroscopic, stable air gas layer or plastron can be sustained on textured superhydrophobic surfaces with multi-scale roughness in water. The plastron exists in the Cassie-Baxter state with the characteristic silver-sheen appearance. Under air-supersaturation conditions, we quantified the plastron dynamics by measuring the gas influx rate into the plastron, whereby the plastron growth results in the continual periodic growth and pinch-off of bubbles at the top pole of such spheres. We further demonstrated that the gas influx rate into the plastron is comparable to the gas influx rate into single bubbles formed on non-superhydrophobic surfaces under identical air-saturation conditions. This confirms the common underlying physics of gas flux across the air-water interface that can be described by a well-mixed model of gas transport. We also showed that this gas flux mechanism could occur under laboratory conditions at room temperature, so that this is a general phenomenon that underlies the gas exchange

and aeration processes in oceans, lakes, and streams, in the biodigestion of effluents, and in facilitating the ability of aquatic insects to breath under water.

APPENDIX: MODELS OF THE PLASTRON ON THE SPHERE

Here, we outline the predictions of two growth models of the plastron on the superhydrophobic sphere that can be tested with our experimental measurements.

Diffusion-Control Model

This model is essentially the Epstein–Plesset²⁶ model, in which gas flux into the plastron on a surface of a sphere is governed by diffusion. The plastron thickness (~0.1 mm) is assumed to be much less than the sphere radius ($R \sim 10$ mm), and therefore, the plastron can be accounted for as a boundary condition for the diffusion equation of the gas concentration in water c(r,t)

$$\frac{\partial c(r, t)}{\partial t} = D\nabla^2 c(r, t) = D\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r, t)}{\partial r} \right)$$
(A1)

where we have assumed radial symmetry.

The gas concentration in plastron, where $c_p = \text{constant}$, is close to the gas saturation concentration in water for a given water temperature and atmospheric pressure. The gas concentration far from the sphere, where $c(r \rightarrow \infty, t) = c_{\infty} = \text{constant}$, set gas saturation in bulk.

The steady solution $(t \rightarrow \infty)$ that satisfies the above conditions is

$$c(r, \infty) = c_{\infty} - (R/r)[c_{\infty} - c_{p}]$$
(A2)

The steady state flux at the surface is

$$J(r = R) = -D \frac{\partial c(r = R, \infty)}{\partial r} = (D/R)[c_{\infty} - c_{p}]$$
(A3)

A consequence of this quasi-steady diffusion-controlled spherical model is that the flux is inversely proportional to the sphere radius, $J \sim 1/R$.

Well-Mixed Model

In this model, the water heated at a steady-state temperature \sim 95 °C is assumed to have a well-mixed average gas concentration $c_{\rm m}$ everywhere outside the sphere because of (gentle) convection and diffusion.

The steady-state flux at the surface is given by the phenomenological equation

$$J(r = R) = \eta [c_{\rm m} - c_{\rm p}] \tag{A4}$$

where η is the mass-transfer coefficient used in chemical engineering modeling. The mass-transfer coefficient $\eta = D/\delta$, where *D* is the gas diffusion coefficient and δ is a characteristic length related to the interfacial transition region or the thickness of the plastron. A similar model has been used to account for the exponential decay time of plastron films on flat hydrophobic surfaces.²¹ A consequence of the well-mixed model is that the gas flux on the sphere is independent upon the sphere radius.

ASSOCIATED CONTENT

S Supporting Information

Video 1: Plastron dynamics for a 20 mm diameter superhydrophobic sphere held in air-supersaturated water at a temperature T_w = 95 °C. Before immersion, the sphere was heated to 190 °C. The video tracks consecutive cycles of gas dome growth and pinch-off for sphere temperature, T_{st} in equilibrium with the water temperature; e.g., $T_s = T_w = 95$ °C. The video is played 24 times faster than real time. The video duration is 24 s, corresponding to a real time of 576 s. Video 2: Plastron recovery on a superhydrophobic sphere immersed in 95 °C air-supersaturated water (solution conditions are similar to those in Video 1). The sphere was initially at room temperature of about 21 °C before immersion into the water. The video is played 24 times faster than real time and is composed of two consecutive recordings. The first recording duration is of 23 s (real time of 552 s), and the second recording duration is of 18 s (real time of 432 s), with a real time lapse of about 50 s between the two parts. The total duration of the process in real time is about 1032 s. Video 3: Surface bubble growth dynamics on a 20 mm diameter hydrophobic sphere immersed in 95 °C air-supersaturated water (solution conditions are similar to those in Videos 1 and 2). The video is played 48 times faster than real time and is composed of two consecutive records. The first recording duration is of 12 s (real time of 576 s), and the second recording duration is of 11 s (real time of 528 s), with a real time lapse of about 80 s between the two parts. The total duration of the process in real time is about 1184 s. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Thorpe, W. H. Plastron respiration in aquatic insects. *Biol. Rev.* **1950**, *25*, 344.

(2) Flynn, M. R.; Bush, J. W. M. Underwater breathing: The mechanics of plastron respiration. J. Fluid Mech. 2008, 608, 275.

(3) Vignes-Adler, M. The fizzling foam of champagne. Angew. Chem., Int. Ed. 2013, 52, 187.

(4) Ishida, N.; Inoue, T.; Miyahara, M.; Higashitani, K. Nano bubbles on a hydrophobic surface in water observed by tapping-mode atomic force microscopy. *Langmuir* **2001**, *16*, 6377.

(5) Zhang, X. H.; Quinn, A.; Ducker, W. A. Nanobubbles at the interface between water and a hydrophobic solid. *Langmuir* **2008**, *24*, 4756.

(6) Zhang, X. H.; Chan, D. Y. C.; Wang, D.; Maeda, N. Stability of interfacial nanobubbles. *Langmuir* **2013**, *29*, 1017.

(7) Seddon, J. R. T; Zandvliet, H. J. W.; Lohse, D. Knudsen gas provides nanobubble stability. *Phys. Rev. Lett.* **2011**, *107*, 116101.

(8) Weijs, J. H.; Lohse, D. Why surface nanobubbles live for hours. *Phys. Rev. Lett.* **2013**, *110*, 054501.

(9) Vakarelski, I. U.; Patankar, N. A.; Marston, J. O.; Chan, D. Y. C.; Thoroddsen, S. T. Stabilization of Leidenfrost vapour layer by textured superhydrophobic surfaces. *Nature* **2012**, *489*, 274.

(10) Leidenfrost, J. G. On the fixation of water in diverse fire. Int. J. Heat Mass Transfer 1966, 9, 1153.

(11) Quéré, D. Leidenfrost dynamics. Annu. Rev. Fluid Mech. 2013, 45, 197.

(12) Vakarelski, I. U.; Marston, J. O.; Chan, D. Y. C.; Thoroddsen, S. T. Drag reduction by Leidenfrost vapor layers. *Phys. Rev. Lett.* **2011**, *106*, 214501.

(13) Takata, Y.; Hidaka, S.; Cao, J. M.; Nakamura, T.; Yamamoto, H.; Masuda, M.; Ito, T. Effect of surface wettability on boiling and evaporation. *Energy* **2005**, *30*, 209. (14) Patankar, N. A. Supernucleating surfaces for nucleate boiling and dropwise condensation heat transfer. *Soft Matter* 2010, *6*, 1613.
(15) Liu, G.; Fu, L.; Rode, A. V.; Craig, V. S. J. Water droplet motion

control on superhydrophobic surfaces: Exploiting the Wenzel-to-Cassie transition. *Langmuir* 2011, 27, 2595.

(16) Cassie, A. B. D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, 0546.

(17) Quere, D. Wetting and roughness. Annu. Rev. Mater. Res. 2008, 38, 71.

(18) Samaha, M. A.; Tafreshi, H. V.; Gad-el-Hak, M. Superhydrophobic surfaces: From the lotus leaf to the submarine. *C. R. Mec.* **2012**, *340*, 18.

(19) Shirtcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C.; Pyatt, F. B. Plastron properties of a superhydrophobic surface. *Appl. Phys. Lett.* **2006**, *89*, 104106.

(20) McHale, G.; Newton, M. I.; Shirtcliffe, N. J. Immersed superhydrophobic surfaces: Gas exchange, slip and drag reduction properties. *Soft Matter* **2010**, *6*, 714.

(21) Poetes, R.; Holtzmann, K.; Franze, K.; Steiner, U. Metastable underwater superhydrophobicity. *Phys. Rev. Lett.* **2010**, *105*, 166104.

(22) Verho, T.; Korhonen, J.; Sainiemi, T. L.; Jokinen, V.; Bower, C.; Franze, K.; Sami Franssila, S.; Andrew, P.; Ikkala, O.; Ras, R. H. A. Reversible switching between superhydrophobic states on a hierarchically structured surface. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, *109*, 10210. (23) Periklis Papadopoulos, P.; Mammen, L.; Deng, X.; Vollmer, D.; Butt, H.-J. How superhydrophobicity breaks down. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 3254.

(24) Lee, C.; Kim, C.-J. Underwater restoration and retention of gases on superhydrophobic surfaces for drag reduction. *Phys. Rev. Lett.* **2011**, *106*, 014502.

(25) Geng, M.; Duan, Z. Prediction of oxygen solubility in pure water and brines up to high temperatures and pressures. *Geochim. Cosmochim. Acta* **2010**, *74*, 5631.

(26) Han, P.; Bartels, D. M. Temperature dependence of oxygen diffusion in H₂O and D₂O. *J. Phys. Chem.* **1996**, *100*, 5597.

(27) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. Transport Phenomena, 2nd ed.; John Wiley and Sons: Hoboken, NJ, 2007.

(28) Epstein, P. S.; Plesset, M. S. On the stability of gas bubbles in liquid-gas solutions. J. Chem. Phys. 1950, 18, 1505.

(29) Scriven, L. E. On the dynamics of phase growth. *Chem. Eng. Sci.* **1959**, *10*, 1.

(30) Ryan, W. L.; Hemmingsen, E. A. Bubble formation in water at smooth hydrophobic surfaces. J. Colloid Interface Sci. 1993, 157, 312.

(31) Ryan, W. L.; Hemmingsen, E. A. Bubble formation at porous hydrophobic surfaces. J. Colloid Interface Sci. 1998, 197, 101.

(32) Takata, Y.; Hidaka, A.; Kohno, M. Boiling from a super-waterrepellent surface. Proceeding of the 5th International Conference on Enhanced, Compact and Ultra-compact Heat Exchangers: Science, Engineering and Technology; Whistler, British Columbia, Canada, Sept 11-16, 2005.

(33) Takata, Y.; Suroto, B. J.; Tashiro, M.; Hidaka, S.; Kohno, M. Wettability effects in boiling heat transfer. *Proceeding of the 8th International Conference of Multiphase Flow (ICMF)*; Jeju, Korea, May 26–31, 2013.