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Everlasting bubbles and liquid films resisting drainage, evaporation, and nuclei-induced bursting

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Soap bubbles are by essence fragile and ephemeral. Depending on their composition and environment, bubble bursting can be triggered by gravity-induced drainage and/or the evaporation of the liquid and/or the presence of nuclei. They can also shrink due to the diffusion of the inner gas in the outside atmosphere induced by Laplace overpressure. In this Letter, we design bubbles made of a composite liquid film able to neutralize all these effects and keep their integrity for more than 1 year in a standard atmosphere. The unique properties of this composite film are rationalized with a nonlinear model and used to design complex objects.

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Under a standard atmosphere, soap bubbles typically burst in minutes [Fig. 1(a)] due to the effect of gravity-induced drainage and/or liquid evaporation and/or nuclei-induced inception depending on their composition. "Bare" viscous bubble bursting follows gravity-induced drainage of the liquid, resulting in shell thinning down to a limit thickness of the order of tens of nanometers, wherein spontaneous breaking occurs [2]. The sliding condition of the liquid on air leads to plug flow in the shell and hence a characteristic lifetime $\tau = \mu/\rho_l gR$, which does not rely on the liquid shell thickness e but rather on the radius of curvature of the bubble R, with ρ_l the liquid density, g the gravitational acceleration, and μ the liquid dynamic viscosity. The addition of surfactants to produce soap bubbles can lead to completely different pictures depending on the concentration of surfactants [3,4]: At intermediate surfactant concentrations, bubble aging results from a complex interplay between gravity and capillary-induced drainage, Marangoni stresses due to gradients of surfactant concentration and bubble evaporation. At large surfactant concentrations, the surfactant rigidifies the film surface leading to a no-slip boundary condition, Poiseuille flow, and hence a considerably slowed down drainage. Nevertheless, while the surfactant drastically increases the lifetime of the soap bubbles, evaporation and/or the presence of nuclei will eventually lead to their rupture. Hence long bubble lifetimes are only reported in carefully controlled atmospheres [5], wherein dust is suppressed, the atmosphere is saturated to prevent evaporation, and the level of mechanical vibration is controlled. And even in these conditions, bubble shrinkage resulting from the diffusion of the inner air in the outside atmosphere due to Laplace overpressure still occurs [5].

Adding partially wetting particles to liquid/air interfaces [6] has been investigated as a means to strengthen their resistance to mechanical stresses providing a material with properties at the crossroads between solids and liquids [7]. When drops and bubbles are covered with such a composite interface, some extraordinary properties have been reported such as nonstick droplets [8–10] able to roll on solid surfaces, and "armored bubbles"[11] in a liquid stable to dissolution [12] and which

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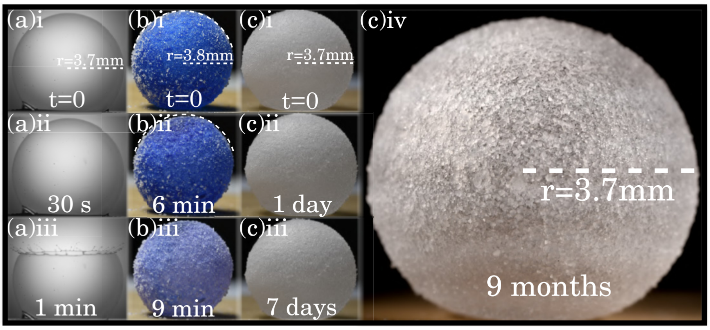

FIG. 1. Comparison of the lifetimes of three types of bubbles: (a) Soap bubble bursting after 1 min. (b) Water gas marble covered by partially wetting microparticles, whose shell rupture occurs after 6 min and complete drying after 9 min. The dashed line is used as a guide to visualize bubble opening and blue dye to visualize liquid drying. (c) Water/glycerol gas marble perfectly intact in a standard atmosphere after ~9 months (285 days). This bubble kept its integrity for more than 1 year (465 days) [1]. As can be seen in Fig. 2, the shell of a water gas marble once dried collapses as a sand pile (Movie M1), while the shell of the water/glycerol gas marble is still liquid and spherical and reacts as a liquid film when punctured (Movie M2).

can sustain metastable [13] nonspherical shapes [14,15] or "gas marbles" (air bubbles) [16,17] supporting positive and negative relative pressure one order of magnitude larger than the Laplace pressure. The addition of particles to an interface can also lead to some counterintuitive behaviors such as surface energy-driven fingering instability in a reversed Saffman-Taylor configuration [18] or films growing ahead of a liquid meniscus moving in a capillary tube [15].

Nevertheless, (i) the effect of such a composite interface on the lifetime of air bubbles has not been investigated and (ii) the single addition of particles to a bubble shell cannot prevent its evaporation [Fig. 1(b)] and hence its bursting. In this Letter [19], we show that covering a bubble water shell with microparticles inhibits gravity-induced drainage and that further adding glycerol leads to a stable state, wherein the evaporation of water is counterbalanced by the hygroscopicity of glycerol, which absorbs water molecules contained in the ambient air. This results in bubbles [Fig. 1(c)] which can keep their integrity in a standard atmosphere for more than 1 year, with no significant evolution of their radius [1]. This behavior is rationalized with a nonlinear model able to reproduce quantitatively the evolution of the mass of the bubble and predict their fate depending on the initial composition of the bubble and the surrounding atmosphere.

Neutralizing drainage. "Gas marbles" are by definition gas bubbles whose composite shell is made of liquid and partially wetting particles [16,17]. Here, we first study the mass evolution and lifetime of water gas marbles for different ambient humidities [Figs. 3(a) and 3(b)]. Gas marbles of radius 5.1 ± 0.1 mm are produced with the simple following process [see Movie M3 in the Supplemental Material (SM) [20]]: First, some partially wetting particles (polyamide-11 particles, average radius $r_p = 80 \pm 20$ μm, contact angle with water $71 \pm 3^\circ$ [15]), are spread at the surface of a water bath to form a jammed granular raft. Second, a controlled volume of air is injected with a syringe below the granular raft, leading to the formation of air bubbles whose upper interface is covered with particles. Third, the bubble is pushed with a spoon toward the surrounding particle raft and made to roll over it to cover its whole surface. Finally, the bubble is extracted and placed over a hydrophobic (Teflon) or superhydrophobic (nanopillar) substrate. The evolution of the gas marble mass and shape is respectively monitored with a FAS224 Fisherbrand high-precision balance and a Nikon D850 camera with a 25-mm ultra macro Laowa lens. The relative humidity is measured with an A+life TH1818 hygrometer. Figure 3(a) shows the evolution of the mass of a single water gas marble. Bubble drying is visualized with the addition of a blue dye and associated color change, while the bubble opening [marked with a yellow triangle in Fig. 3(a)] can be seen by the brutal change in the bubble shape when the bubble shell is no longer airtight (Movie M4). These data

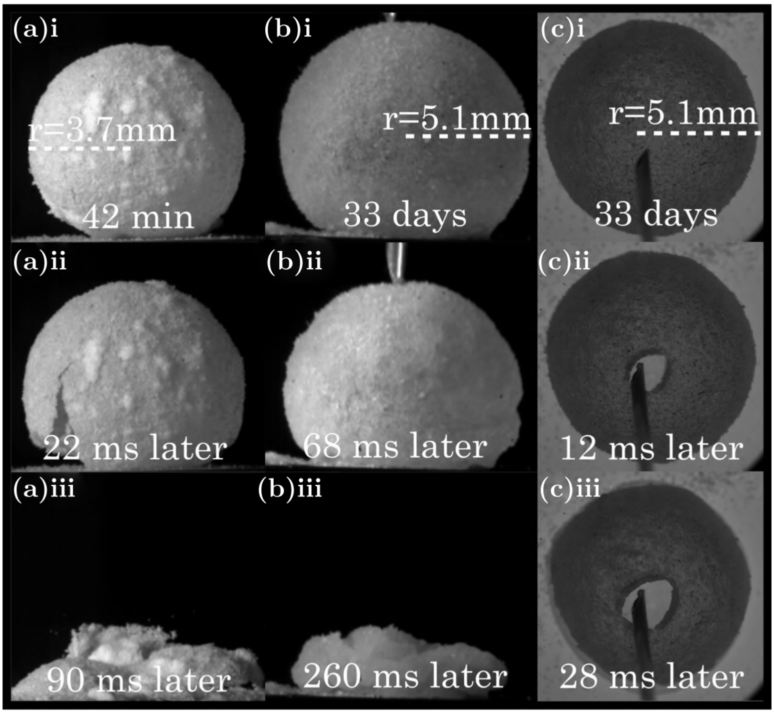

FIG. 2. (a) Lateral view of a water gas marble naturally collapsing after a few tens of minutes. (b) Top view and (c) lateral view of two 1-month-old water/glycerol gas marbles (initial glycerol mass ratio $\omega_{g0} = 0.60$) punctured with a needle.

show (i) that the bubble mass decreases linearly until its complete drying [plateau region after 54 min in Fig. 3(a)] and (ii) that the gas marble opening (yellow triangle) occurs a few minutes before its complete drying, thus underlying that the water gas marble lifetime is mainly determined by the evaporation process. This scenario is further confirmed by numerous experiments performed for different ambient humidities [Fig. 3(b)]. Hence, the presence of the particle shell inhibits the drainage of the liquid, which, in the absence of the particles, would provoke bubble bursting after a characteristic time of the order of $\tau = \mu/\rho_l g R \sim 20\ \mu\text{s}$ [2], with R the bubble radius, ρ_l the liquid density, g the gravitational acceleration, and μ the liquid viscosity. Note that the bubble lifetime variability in Fig. 3(b) at the same ambient humidity is due to the fact that the initial film thickness is not controlled during the gas marble formation process.

Neutralizing evaporation. Designing "everlasting" bubbles, i.e., bubbles with very long lifetimes, requires further neutralize evaporation. This problem is solved by adding glycerol to water. Indeed, glycerol is a liquid with a high concentration of hydroxyl groups, which have a strong affinity with water molecules with whom they create hydrogen bonds [21]. This mechanism is at the origin of glycerol's hygroscopicity (ability to absorb water molecules contained in air), which can compensate for water evaporation [22]. To test this hypothesis, bubbles were synthesized with the same process as described in the previous section but with a water/glycerol mixture. The evolution of the mass of these gas marbles for different initial glycerol mass ratios ω_{go} and different values of the ambient relative humidity h (given in SM [20]) is shown in Fig. 3(c). This figure shows that the shell of water/glycerol gas marbles with the lowest initial glycerol concentrations ($\omega_{go} \in [0, 0.15]$) rupture after lifetimes of the order of 50 min, while the bubbles with higher glycerol concentrations tend toward a steady state either by initially losing water ($\omega_{go} \in [0.30, 0.65]$), keeping a mass relatively constant ($\omega_{go} = 0.85$), or absorbing water from the humidity contained in the air ($\omega_{go} = 0.9$).

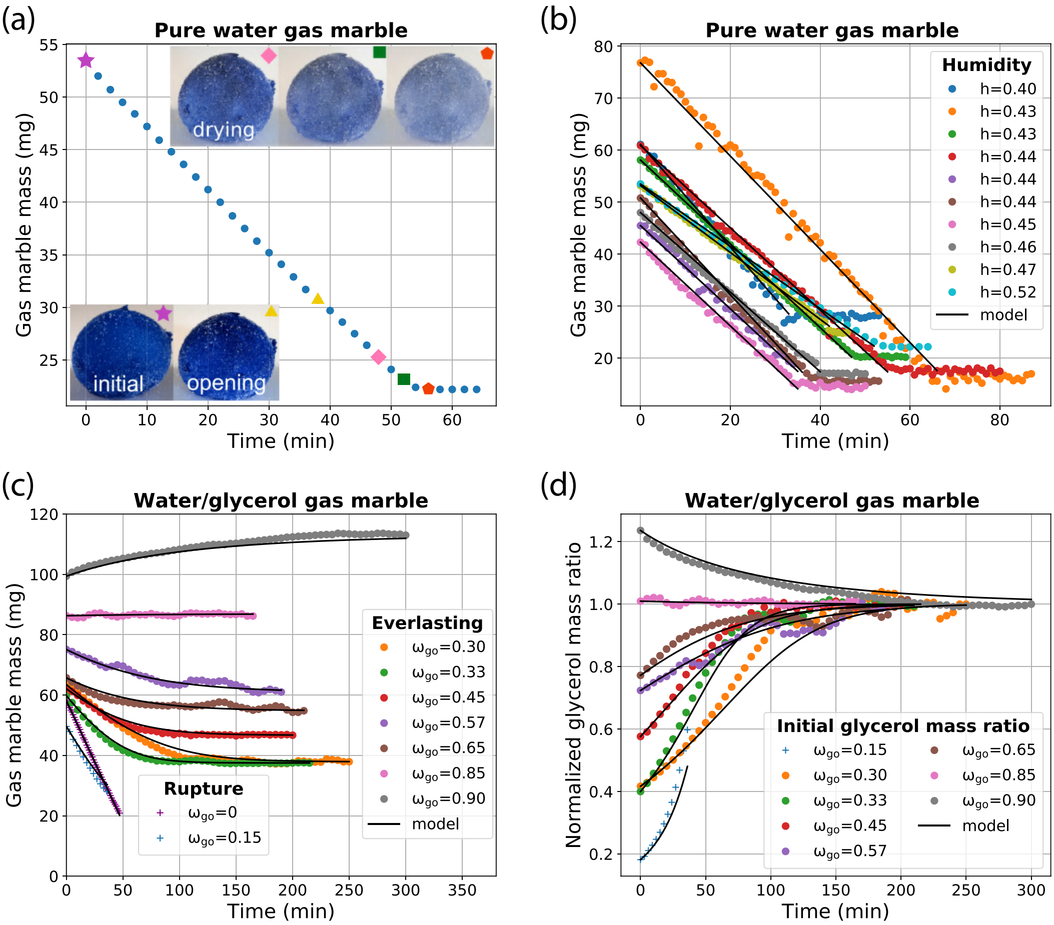

FIG. 3. Evolution of gas marbles in a standard atmosphere (temperature $T = 21.0 \pm 0.5\,^{\circ}\mathrm{C}$). (a) Evolution of the mass of a single water gas marble as a function of time at ambient humidity $h = 0.52 \pm 0.01$. Drying is reflected by the change in the bubble color and bubble opening (yellow triangle on the curve) by a brutal change in the bubble shape (Movie M4). The plateau region (after 54 min) occurs when the water is entirely evaporated. (b) Evolution of the mass of pure water gas marbles as a function of time at different relative humidities. (c) Evolution of the mass of water/glycerol gas marbles as a function of time for different initial glycerol mass ratios ω_{go}. (d) Normalized glycerol mass ratio ($\omega_g/\omega_{\mathrm{geq}}$) content of a gas marble as a function of time [same experimental data as in (c)]. Black curves: Evaporation/absorption model introduced in this Letter.

Since glycerol is a nonvolatile liquid, the mass variations of these gas marbles are solely due to water evaporation or absorption. The evolution toward a steady state with an equilibrium between the water and glycerol content is even clearer when we study the evolution of the normalized glycerol mass ratio [Fig. 3(d)], which tends toward a constant value (slight fluctuations are due to recorded fluctuations in the air humidity). We further studied the fate of gas marbles as a function of the initial glycerol mass ratio and relative humidity (Fig. 4). When a water/glycerol mixture is in contact with humid air with a relative humidity h, it will tend toward an equilibrium glycerol mass ratio ω_{geq} materialized by the blue dotted line in Fig. 4. The diagram shows that when the initial glycerol mass ratio ω_{go} is close to this equilibrium value, the gas marble evolves toward a stable equilibrium state (everlasting bubbles) either by losing some liquid (when $\omega_{go} < \omega_{\mathrm{geq}}$) or absorbing some liquid

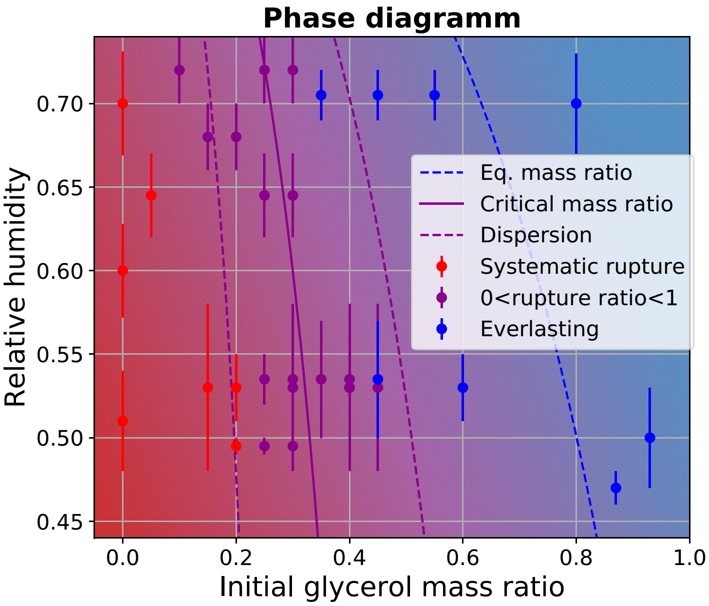

FIG. 4. Diagram of gas marble fate after 6 h as a function of the initial glycerol mass ratio and the relative humidity. Each point corresponds to statistics made on at least ten gas marbles. Red: Systematic rupture of the bubble. Purple: Part of the bubble sample rupture. Blue: All gas marbles keeping their integrity after 6 h. The vertical bar indicates the variation of the relative humidity for each set of experiments. The dashed blue curve entitled "Eq. mass ratio" represents the equilibrium glycerol mass ratio $\omega_{\text{geq}}(h)$ and the purple continuous line the critical glycerol mass ratio ω_{goc}.

(when $\omega_{go} > \omega_{\text{geq}}$) [23]. When the initial glycerol mass ratio is too far from this equilibrium value, the gas marble systematically ruptures.

Model. To rationalize this behavior, we introduce a model able to quantitatively reproduce the experimental trends described in Figs. 3 and 4 without any adjustable parameter. Since glycerol is a nonvolatile liquid, the liquid mass m_l evolution of a water/glycerol gas marble is set by an equilibrium between the flux of water evaporation and the flux of water absorption due to the hygroscopicity of glycerol: $dm_l/dt = \phi_{\text{abs}} - \phi_{\text{evap}}$. Water evaporation flux is driven by the vapor concentration gradient and hence is proportional to $(1 - h)$, with h the relative humidity of air far from the bubble [24,25]. Furthermore, since the shell liquid is a mixture of glycerol and water, the water evaporation flux will be proportional to the quantity of water molecules present at the bubble surface. Since the diffusion time $\tau_d = e^2/D_{wg} \lesssim 3$ min (with $e \sim 150\ \mu$m the thickness of the film estimated from the surface of the bubble and its mass and $D_{wg} \gtrsim 10^{-10}\ \text{m}^2\,\text{s}^{-1}$ [26] the diffusion coefficient of water molecules into the water/glycerol mixture) is short compared to the characteristic time $\tau_c \gtrsim 100$ min required for a bubble to reach its equilibrium state, the water/glycerol mixture in the film can be supposed to be homogeneous at the bubble mass evolution timescale. Hence, the water evaporation rate will be proportional to the concentration of water in the water/glycerol mixture $(1 - \omega_g)$ with ω_g the glycerol mass ratio. We thus obtain $\phi_{\text{evap}} = k_e(1 - h)(1 - \omega_g)$, with k_e a constant to be determined. Conversely the absorption of water through the formation of hydrogen bonds with glycerol molecules will be proportional to the concentration of water in the air h and to the concentration of glycerol in the liquid film ω_g, so that $\phi_{\text{abs}} = k_a h \omega_g$. The final equation, $dm_l/dt = k_a h \omega_g - k_e(1 - h)(1 - \omega_g)$, relies on two unknown coefficients k_e and k_a, which depend on the evaporation regime, absorption efficiency, and bubble geometry. The first coefficient can be determined by examining the case of a pure water gas marble. In this case $\phi_{\text{evap}} = k_e(1 - h)$. A first validation of this model is that the linear trend is well recovered in Fig. 3(b). The value of the coefficient $k_e = 2.3 \pm 0.2 \times 10^{-8}$ kg s^{-1} is obtained by taking the median value of the slopes in Fig. 3(b), which enables us to obtain good fits for all the curves. Note that this coefficient is not a universal parameter and depends on the complex physics behind the evaporation process and the bubble geometry. The second coefficient is determined by examining the equilibrium state $dm_l/dt = 0$. In this case, the mass concentration of glycerol in the water/glycerol mixture reaches a well-established equilibrium value [27], which depends on the relative humidity of the ambient air. Our model predicts a relation between the equilibrium glycerol mass ratio ω_{geq} and the relative humidity given by $\omega_{\text{geq}} = [1 + k_a h/k_e(1-h)]^{-1}$. A second validation of this model is that this law fits well the abacus available in the literature [27] (Fig. 2 in SM [20]), with $k_a/k_e = 0.248$, giving good confidence in the dependence of the evaporation and absorption fluxes on the glycerol concentration ω_g and relative humidity h. Now that the two coefficients k_a and k_e are determined we can compare the model predictions to the experimentally measured gas marble mass evolution. This model recovers quantitatively the trends observed in Figs. 3(c) and 3(d). From this model, we can also derive a criterion for the transition between ephemeral and everlasting bubbles (Fig. 4) depending on the initial glycerol concentration ω_{go} and relative humidity h. Assuming that bubble rupture occurs when the bubble shell liquid mass reaches a critical value m_{lc}, a bubble will be everlasting if its equilibrium liquid mass $m_{l\text{eq}}$ is larger than m_{lc} and ephemeral if $m_{l\text{eq}}$ is smaller than m_{lc}, with a transition between these regimes for $m_{l\text{eq}} = m_{lc}$. Since the mass of glycerol m_g is constant, we have $m_g = m_{l\text{eq}}\omega_{\text{geq}} = m_{lo}\omega_{go}$. Hence for $m_{l\text{eq}} = m_{lc}$, we obtain $\omega_{goc} = m_{lc}\omega_{\text{geq}}(h)/m_{lo}$ with $\omega_{\text{geq}}(h)$ determined previously. The critical liquid mass $m_{lc} = 14 \pm 4$ mg is determined by measuring the bubble total mass $m_c = 32 \pm 3$ when its rupture occurs (measured here for four different gas marbles) and subtracting the particle mass $m_p = 18 \pm 2$ mg [value extracted from Fig. 3(b) after total evaporation of water]. Since we cannot control the liquid content during the gas marble formation process, an ephemeral gas marble initial content m_{lo} varies typically between 22 and 57 mg. The plot of the equation $\omega_{goc} = m_{lc}\omega_{\text{geq}}(h)/m_{lo}$ in Fig. 4 shows that this model gives a good criterion for the transition between an ephemeral and everlasting bubble (the continuous purple line corresponds to the average value $m_{lo} = 34$ mg, while the purple dashed lines correspond to $m_{lo} = 22$ and 57 mg, respectively, and account for the dispersion of the initial state).

Perspectives: Composite films. In this Letter, we have shown that air bubbles keeping their integrity for more than 1 year can be produced in a simple way by replacing surfactants by partially wetting particles and water by a water/glycerol mixture. Indeed, partially wetting particles prevent drainage of the liquid due to gravity, while the hygroscopicity of glycerol-water mixtures counterbalances evaporation, which are the two main mechanisms at the origin of classical bubble bursting. In addition, (i) the neutralization of these two phenomena and the presence of the particle shell enables us to make the bubble insensitive to the nuclei contained in the air and (ii) no evolution of the bubble radius over the bubble life was observed, indicating that bubble shrinkage due to Laplace overpressure is also suppressed. Beyond bubbles, this work unveils a robust composite liquid film, which can be used to create a wealth of different objects. Indeed, when a metallic frame is dipped below a liquid surface covered with a layer of jammed particles and lifted slowly up to the surface, it captures the particle-covered film (see Fig. 5). While marginal pinching due to the presence of the frame and surfactants leads to soap films bursting near the edge after a few seconds [Fig. 5(a)], the replacement of surfactants by partially wetting particles leads to the apparition of evaporation-induced cracks after several minutes only [Fig. 5(b)], and a further addition of glycerol leads to a long-lasting liquid film stable for at least several months [Fig. 5(c)]. Following this process, complex objects such as everlasting pyramidal films with lifetimes of more than 1 year (378 days when these lines are written) can easily be manufactured [Fig. 5(d)] paving the way toward the design of new fluidic objects with unexplored physical and chemical properties. This work would be ideally completed with a study on a large set of parameters of the effect of the composition of the shell and of the ambient atmosphere on the bubble stability. Finally, a puzzling question remains: Does the Laplace overpressure inside the bubble vanish over time, and if it does,

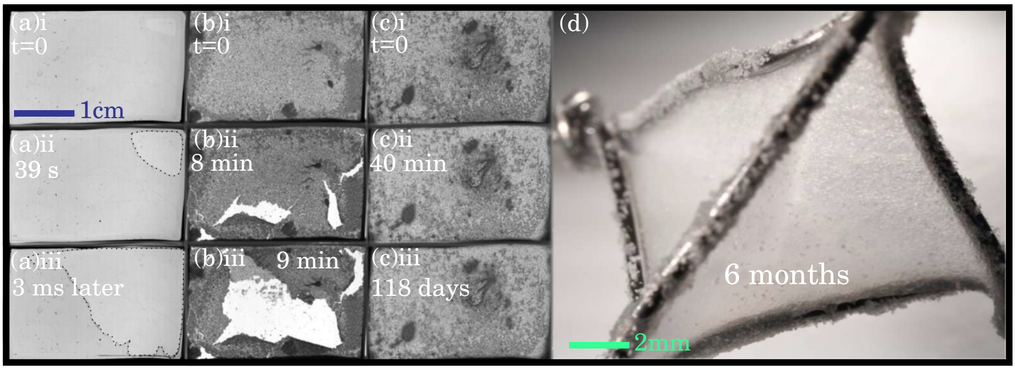

FIG. 5. Lifetimes of liquid films attached to a metallic frame [(a)–(c) horizontal frame, (d) pyramidal frame]. (a) Soap film made of water and surfactant. (b) Water film covered with partially wetting particles. (c) Water/glycerol liquid film (initial glycerol mass concentration $\omega_{go} = 0.80$) covered with particles. (d) Three-dimensional object created with a pyramidal frame supporting a water/glycerol liquid film covered with particles and perfectly intact after 203 days (∼6 months). When these lines are written the pyramidal film is still perfectly intact in our laboratory 378 days after its formation.

how does the bubble maintain its shape and size? We are currently trying to provide a convincing answer to this question.

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[1] Note that our oldest bubble ruptured after 465 days. We believe that this rupture can be attributed to the development of "life" in our bubble since the bubbles became slightly green during the last month, which would not be surprising since (i) the bubble is made of water and glycerol which is a favorable environment for the development of fungi and bacteria and (ii) we did not take any precaution to avoid the pollution of the bubble with living organisms.

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[23] Note that the evolutions of bubbles of different initial water glycerol mass ratios were followed over 6 h for more than 320 bubbles, 24 h for 36 of them, and more than 1 year for 6 of them. For all these bubbles no naturally occurring rupture event has been observed after the first 4 h of observation, indicating that a bubble which lasts more than 4 h will not break afterwards. This is consistent with Fig. 2(d) which shows that the time required to reach a stable state is less than 4 h. Hence, we have chosen a 50% longer time (6 h) than the last observed rupture (4 h) as a reference time to define “everlasting bubbles.”.

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