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Stable freestanding thin films of pure water

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Obtaining water microstructures is very difficult because of low viscosity and high surface tension. We produced stable freestanding thin films of pure water by x-ray bombardment of small liquid volumes in capillary tubes. A detailed characterization with phase-contrast radiology demonstrated a lifetime beyond 1 h with no chemical stabilizer for micron-thickness films with half-millimeter-level diameter. This can be attributed to the interplay of two x-ray effects: water evaporation and surface charging. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2892078]

In spite of the strong fundamental and applied interest in water microstructures,[1] so far, no technique[2,3] was able to produce stable freestanding pure-water thin films. The lifetime[4] was limited to <1 ms—unsuitable for most applications—due to rapid rupture caused by the very low viscosity (~ 1 mPa s) and high surface tension (~ 72 mN m^{-1}) of pure water in ambient conditions.[4–6] Water films have been stabilized by changing the hydrophilicity or the polarity with surfactants or electrolytes.[2,3,7] These, however, can cause deviations from the intrinsic water properties.

We present here an approach that produces large, micron-thick ultrapure-water films with excellent stability (see Fig. 1). The approach is schematically illustrated by Fig. 2. Using a micropipette, we injected through a plastic microneedle (diameter of <100 μm) an ~ 1 μl of 18 MΩ, Millipore ultrapure water in the middle of a horizontal hydrophilic Suprasil VitroCom capillary tube. The tube radii were $R_c = 290$, 500, or 680 μm and the length was ≈ 6 mm. Due to the hydrophilic character of the capillary tube, the injected water formed two concave menisci, as shown in Fig. 2.

Both ends of the tube were then sealed, and we bombarded the water volume with x-rays in the photon energy range of 10–60 keV from the PLS synchrotron source (7B2 beamline) in Pohang, Korea.[8–10] The x-ray beam direction (Fig. 2) was perpendicular to the tube and reached the side of the water volume. The beam cross section was 0.5×0.4 mm^2 and the dose rate was ≈ 970 Gy/s.

The process was carefully monitored (Fig. 3) by phase-contrast microradiology[8–10] using the same x-ray beam as for the bombardment. The x-rays caused water evaporation at a rate of ≈ 0.3 nl s^{-1} for the $R_c = 680$ μm tube. This progressively decreased the distance between the two menisci until a flat film was created—reminiscent of the liquid film between two adjoining gas-filled bubbles. The continuing x-ray bombardment then induced an increase of both the flat thin film radius and its thickness, as seen in Fig. 3.

The film so created had a very long lifetime, indicating that the x-rays play a stabilizing role in addition to producing the film by evaporation. Quantitatively, the freestanding flat-film diameter $2r_f$ in the $R_c = 680$ μm tube gradually evolved from ~ 10 μm after 0.5 min irradiation to ~ 0.4 mm after 54 min—whereas the thickness increased to a few microns.

Our interpretation in terms of electrostatic stabilization due to surface charging appears qualitatively and quantitatively plausible. The capillary pressure[3,7] $P_c = 2\gamma R_c/(R_c^2 - r_f^2)$ (where γ is the water surface tension) would by itself continue to thin the film until it ruptures. The electrostatic repulsion due to surface charging can counter this thinning effect leading to the observed thickness increase and to long-term stability even for large r_f values.

More precisely, the film thickness reaches equilibrium if P_c equals the disjoining pressure of the film. It is generally recognized[11–14] that the disjoining pressure is primarily determined by the sum of the attractive van der Waals force and repulsive double-layer electrostatic force. Charging by the x-ray bombardment enhances this second factor allowing film stability even for large capillary pressures.

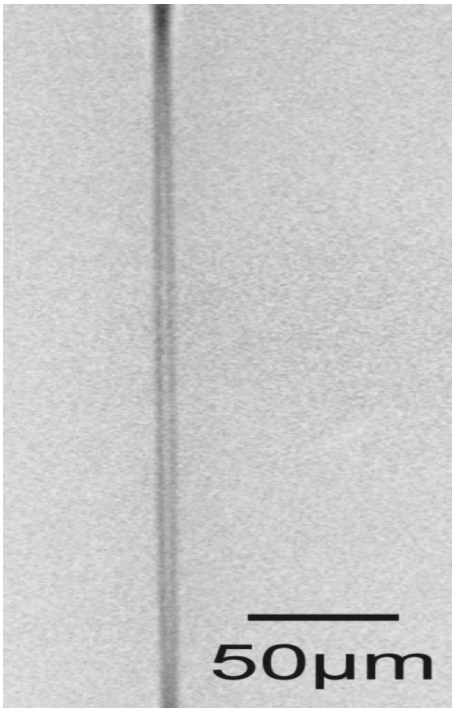

FIG. 1. Side image obtained by phase-contrast microradiology of a stable freestanding pure-water film produced with our approach inside a horizontal capillary tube (radius $R_c = 680$ μm).

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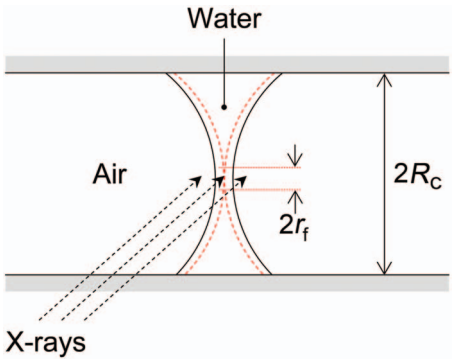

FIG. 2. (Color) Scheme of the experimental procedure. The x-ray bombardment occurs in the direction perpendicular to the capillary tube and reduces the distance between the two concave menisci—leading (red lines) to the formation of a thin flat film of radius r_f.

Note that $P_c=2\gamma R_c/(R_c^2-r_f^2)$ increases with r_f—so that avoiding rupture is more difficult for large-size films. Furthermore, P_c increases as R_c decreases; this explains why we could not obtain stable films for the $R_c=290$ and 500 μm capillary tubes. Even in those cases, however, the x-ray-induced charging effects were noticeable: we analyzed the power-law[4–6] time dependence of r_f and found a slow rupture dynamics.

Quantitatively, we can use the measured geometric parameters to evaluate $P_c=2\gamma R_c/(R_c^2-r_f^2)$. Assuming a constant γ, for the $2r_f=0.4$ mm film in the $R_c=680$ μm tube, we obtain $P_c\approx 320$ Pa—which is in the range (100–1000 Pa) of the disjoining pressure values of electrolyte-stabilized water.[13–15] This indicates that the x-rays act indeed as a surrogate for electrolytes in the film stabilization.

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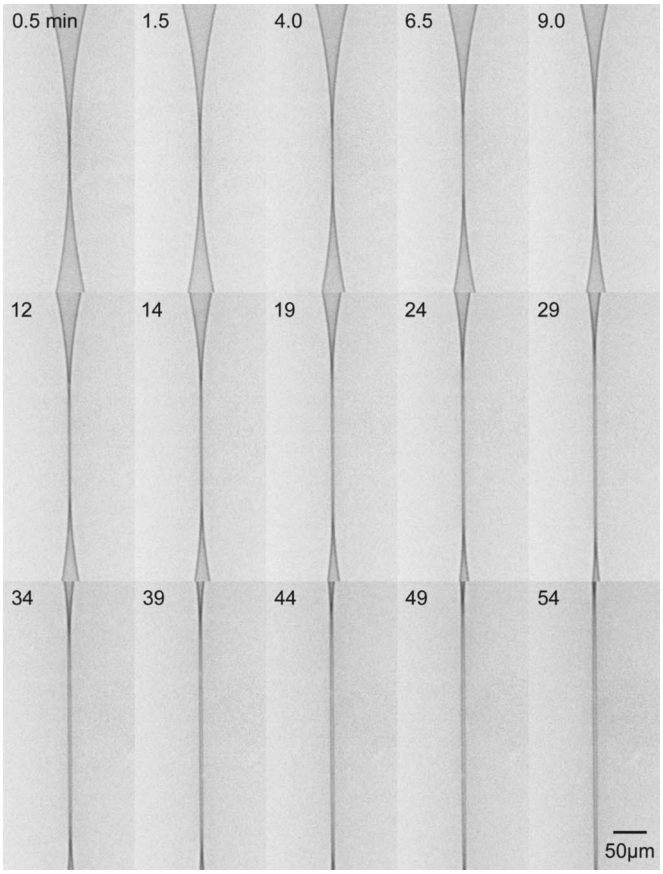

FIG. 3. Sequence of phase-contrast images revealing the evolution of the water film during x-ray bombardment. The two concave menisci evolve toward a flat region and a freestanding thin film. As the x-ray bombardment continues, the diameter $2r_f$ of this flat region gradually increases as well as its thickness. After the end of the bombardment (54 s), the freestanding water film remains stable for more than 1 h before rupturing, indicating that the x-rays play a stabilizing role in addition to causing water evaporation.

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