

Supplementary information for b922727j

Videos 1 to 4 show typical drying behaviour of different concentration droplets. The duration of each experiment was approximately 2 hours, and the size of each droplet initially around 75 μl and the distance across the image approximately 10 mm. Timings given in the captions below are given relative to the video files, to aid identification of the various stages and processes. It is also useful, if viewing the files in Quicktime (ver 7.5) to use the Jog/Shuttle control in A/V controls.

Video 1 shows drying of a sample with $c_0 = 5\%$ and exhibits pinned drying (stage 1) for around the first 5 seconds, before depinning when the contact angle becomes lower than the measured receding contact angle, θ_r . Stage 2 and bootstrap building do not take place.

Video 2 shows drying of a sample with $c_0 = 8\%$. This exhibits pinned drying (stage 1) for around the first 5 seconds, at which point the contact line depins and the droplet undergoes a dewetting transition (stage 2) until 9 seconds. At this time the contact angle remains constant at just over 90° , and the droplet climbs on top of the solid deposit, bootstrap building (stage 3). At 11 seconds the outer surface appears completely solid and the maximum height is reached. Stage 4 drying follows as the solid shape slowly shrinks. The base radius of the final cone is less than a quarter of that of the initial droplet.

Video 3 shows drying of a droplet with $c_0 = 25\%$ and again exhibits stage 1 pinned drying for the first 5 seconds. However, the solid deposit is already much thicker for this droplet. As the contact angle is increasing (stage 2) deposition occurs simultaneously (stage 3). The maximum height is reached at 10 seconds from which point, late stage drying (stage 4) accounts for the slow decrease in height. The final cone has half the base radius of the initial droplet.

Video 4 shows drying of a droplet with $c_0 = 40\%$ and has a very short stage 1, around 1 second. The contact angle increases until 3 seconds and bootstrap deposition (stage 3) continues until 4 seconds. However, there is still liquid inside the structure at this point, which is ejected as stage 4 begins. The base radius of the final cone is around three quarters that of the initial droplet.

Video 5 was recorded using an inverted microscope (Nikon Eclipse TE2000-S) with 2x objective lens. The images measure 5 mm across and the frame rate is increased by a factor of 300. The bright specks in the droplet are small clusters of polymer that would not dissolve, and help to visualise the flow within the droplet. Pinned drying (stage 1) occurs for the first 5 seconds, during which there is clear evidence for recirculation flow at the contact line, with the liquid near the base flowing radially outwards and moving inwards above. As the flow at the edge ceases, a bright region of solid deposit appears behind the retreating liquid droplet (stage 2). There is no longer evidence of recirculation flow within the droplet. At 14 seconds, the deposit has reached its maximum height at the end of stage 3 and final drying begins. A wide solid ring has been deposited with a liquid region in the centre. From around 18 seconds, darker lines appear in the bright deposit, indicating completely dry areas and at 24 seconds, the central liquid region begins to dry (darken) and by 40 seconds, the structure is hollow.