Hollow rims from water drop evaporation on salt substrates
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I. SCHEMATIC OF THE EXPERIMENT

Figure 1 shows the setup used in the experiments, with T1 and T2, platinum thermal probes, and H, a relative humidity probe.

II. EXPERIMENTAL VIDEO OF THE EVAPORATING DROP

A video (video1.mkv) of the evaporation of a pure water drop of volume 0.8 µl and initial sessile diameter 2 mm on a polished NaCl substrate heated at 65°C viewed from the top and from the side is provided. Time is accelerated three times.

III. DRYOUT PROFILE

Figure 2 shows an example of profile of a droplet dryout measured with vertical scanning interferometry (VSI). The red surface is the etched material and the green surface the grown one.

IV. COMPLEMENT ABOUT THE DEFECT PATTERN ON THE SHELL

Two zoom-ins of an example of the regular stripes observed on the shells are displayed in Fig. 3. The stripes are roughly oriented along the radius, with a slight anisotropy, possibly related to the crystallography of the salt.

V. COMPLEMENT ABOUT THE DROP EVAPORATION MODEL

We have considered two evaporation models for the third phase of the evaporation dynamics when the substrate is not covered by the drop in the center of the substrate. These models correspond to two opposite simplifications. The first model overestimates the increase of evaporation in the vicinity of the inner triple-line at \( r = r_{in} \), and considers that the uncovered surface in the middle is similar to an infinite dry surface, leading to a divergence at \( r = r_{in} \) which is similar to that occurring at \( r = r_{TL} \). The second model neglects the increase of evaporation in the vicinity of the inner triple line, and...
considers that the uncovered surface is still wet so that the evaporation rate profile is similar to that of the drop without hole in the middle.

The first model considered in the third phase of the evaporation is therefore:

\[
J^I_s(r) = \frac{J_0}{(1 - (r/r_D - r_S/r_D)^2)^{3/2}}
\]

where \( r_S = (r_{TL} + r_{in})/2 \), and \( r_D = (r_{TL} - r_{in})/2 \). In the second model, we simply choose \( J^II_s(r) = J_b(r) \), where \( J_b(r) = J_0/(1 - (r/r_{TL})^2)^{1/2} \) as in the main text.

The unknowns of the model are \( r_{TL} \), \( h_{TL} \), \( R \), and \( r_{in} \). To close the problem, we have 4 equations coming from the two mass conservation relations in Eqs. 1 and 2 of the main text, the condition of tangential contact \( \partial_r h = 0 \) at \( r = r_{in} \), and the condition of shell growth tangentially to the liquid-gas interface \( \partial_t h(r = r_{TL}) = \partial_t h_{TL}/\partial_r r_{TL} \).

The resulting system of equations has been integrated numerically.

The two models lead to slightly different results, mainly because the total evaporation rate is larger in model I as compared to model II. However, since the growth of the shell in the third phase of the dynamics is small, these differences are irrelevant for the main results discussed in the main text.

In order to go beyond the assumption of a flat substrate used in the model, one would need to replace \( h(t) \) by \( h(r) - h_{sub}(r) \) in Eqs. 1 and 2, where \( h_{sub}(r) \) is the substrate depth. This modified model could account for the lowering of the substrate surface under the drop caused by the initial dissolution. Since the salt solubility is about one third, this corresponds to an initial lowering of the substrate surface approximately equal to one third of the drop height. A quick investigation of a model with this modified initial condition revealed no qualitative novelty as compared to the model presented above. We therefore kept the simplest model that accounted for the observed shell morphologies, i.e., that with a flat substrate.

VI. NUMERICAL VIDEOS OF THE EVAPORATING DROP

Two videos of the modeling of the evaporation of a pure water drop on a dissolving salt substrate are provided. For both, we assume \( r_{TL0} = 1 \) mm, \( a = 1 \), \( \Omega_{c_a} = 0.26 \) and \( w = 20 \) mm. Video2.mkv displays the results using model I in the third phase of evaporation and Video3.mkv the results using model II.

VII. SHELL THICKNESS ESTIMATION

To estimate the shell thickness, Fig. 4 shows the salt dissolved volume \( V_{\text{diss}} \) as \( \pi^2 \Phi (2r_{TL0} - \Phi)/(2\sqrt{2}) \), with \( \Phi \) the width of the closed shell and \( r_{TL0} \) the initial solid-liquid interface radius. The quantities \( \Phi \) and \( V_{\text{diss}} \) have been measured with the VSI profilometry. We see that the experimental dots align roughly along a straight line. This leads us to consider as a first approximation the shell as a truncated torus of angle \( \theta = \pi/4 \) (see Fig. 5 in the main text), the volume of which is \( \pi^2 \Phi w (2r_{TL0} - \Phi)/(2\sqrt{2}) \), with \( w \) the thickness of the deposit. The thickness is given by the slope of the line. The best fit gives \( w \approx 17 \) \( \mu \)m.

We also observe no correlation between the temperature at which the experiments have been carried out and the slope of the dots representative of that temperature. Therefore no correlation between the shell thickness and the temperature is observable.

FIG. 4: Dissolved volume of salt as a function of \( \pi^2 \Phi (2r_{TL0} - \Phi)/(2\sqrt{2}) \) with \( \Phi \) the diameter of the truncated torus that the deposit forms and \( r_{TL0} \) the deposit external radius. The dashed line is a linear best-fit of the data. The color bar indicates the temperature (in °C) of each experiment.

VIII. MORPHOLOGY DIAGRAM

Fig. 5 displays the non-equilibrium morphology diagram displaying the domains of the closed and open hollow rim predicted using model I and model II in the third stage of evaporation.

IX. COMPLEMENT ABOUT SHELL THICKNESS SELECTION

As a first guess, the thickness of the shell could be selected by the trapping of the salt molecules in the vicinity of the interface due to the outward hydrodynamic flow created by evaporation. This trapping competes with diffusion, which tends to spread the concentration field to make it homogeneous. The balance between these two effects is described by the lengthscale \( \ell_a = D/J_s \), which is a first possible candidate for \( w \). Away from the triple
\[ J_s \approx J_0 \sim 10^{-7} \text{ m s}^{-1}, \] and using \[ D \sim 10^{-9} \text{ m}^2 \text{ s}^{-1}, \] we obtain \( \ell_s \approx 1 \text{ cm}. \) At distances of the order of \( w \) from the triple-line, we have \( J_s \approx J_0 (r_{\text{TL}}/2w)^{1/2}. \) Using \( w \sim 10 \mu\text{m} \) and \( r_{\text{TL}} \sim 1 \text{ mm}, \) we find that \( \ell_s \approx 1 \text{ mm}. \) Hence, the lengthscale \( \ell_s \) is too large and the balance between diffusion and evaporation cannot be invoked as a physical cutoff to account for the selection of the shell thickness.

In the main text, we have presented a discussion of shell thickness selection based on diffusion-limited kinetics. Another possibility is that dissolution dynamics are limited by detachment kinetics. Then, the dissolution rate is \( \sim k \Omega \gamma_{eq} (\Delta \mu/k_B T), \) where \( k \sim 10^{-3} \) to \( 10^{-4} \text{ m s}^{-1} \) is the attachment-detachment kinetic coefficient. This leads to

\[ w = \frac{8}{r_{\text{TL}}} \left( \frac{(1 - \Omega \gamma_{eq}) \Omega k_B T}{k_B T J_0} \right)^2 \] (2)

leading to \( w \sim 0.01 \) to \( 1 \mu\text{m}. \)

Even if this assumption provides slightly lower values than the diffusion-limited transport/surface tension competition, both regimes provide results of the same order of magnitude. This is related to the fact that the attachment-detachment length \( D/k \sim 1 \) to \( 10 \mu\text{m} \) is similar to \( w. \) However, the kinetic coefficient \( k \) is not known with a good accuracy.