Gallery of Fluid Motion

Shattered to pieces: Cracks in drying drops

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Mud cracks in dry regions and craquelures in pottery glaze are two examples of naturally occurring crack patterns. Similarly, a drop of a concentrated nanoparticle suspension creates a fascinating network of cracks as it dries. The progressive appearance and branching of cracks are remarkably ordered and reveal the hidden processes triggered by evaporation.

To study the crack dynamics, we deposit a millimetric drop of an aqueous suspension of 10% polystyrene nanoparticles (Magsphere Carboxylated PS Latex particles, diameter = 43 nm) on a horizontal glass slide. As water evaporates, the initial contact line remains pinned. The particles accumulate at the contact line and form a solid deposit of close-packed particles and water [1–3]. The deposit grows while the liquid region in the center of the drop recedes, as seen in the time-lapse reconstruction in Fig. 1. Continuous water evaporation at the top of the deposit prompts a flow of water and particles from the liquid region in the center of the drop to the deposit, fueling its growth [4]. The growth is accompanied by increasing stresses within the deposit, which are suddenly released by the formation of cracks [5].

The first cracks that appear are radial cracks, which start a few tens of microns from the deposit edge and extend to a distance of $95 \pm 10\,\mu$m away from the liquid region, as seen in Fig. 2. As the liquid region shrinks, the crack propagation front maintains approximately the same distance from the liquid region. Eventually though, a second generation of orthoradial cracks appear further away from the liquid region, at a distance greater than $217 \pm 18\,\mu$m. These cracks emerge from a multitude of independent branching events connecting two radial cracks, creating four-sided fragments and incrementally transforming the crack pattern into a complex tessellation that covers the entire deposit.

Why do cracks form? The evaporation at the top of the deposit induces a water flow inside the porous solid deposit from the boundary of the liquid region to the deposit edge. Viscous losses incurred by the flow lead to a pore pressure gradient, where the pore pressure is lower further away from the liquid region. The low pore pressure is balanced against atmospheric pressure via the Laplace capillary pressure at the water-air menisci that form at the top interface of the deposit [4].

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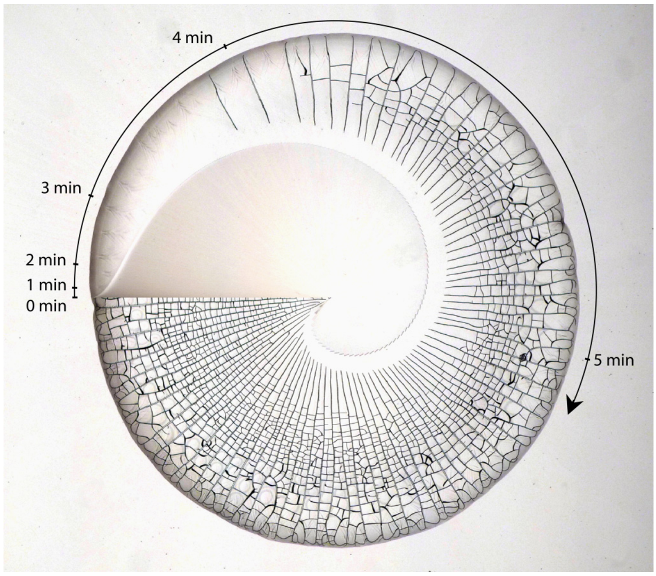

FIG. 1. Time-lapse reconstruction of the drying of a 0.3-μL drop of a nanoparticle suspension at a particle volume fraction of 10%. Adjacent sectors of consecutive images taken at one second intervals are combined to create the composite image. As water evaporates from the drop, the particles assemble into a thin solid deposit that grows from the edge of the drop and eventually cracks. The drop is imaged on an inverted microscope using an objective of magnification 4× (Eclipse TE2000-U, Nikon with Lumix GH5 camera). The deposit radius is 1.1 mm.

In response to the low pore pressure, the deposit wants to contract; but the contraction is prevented by the adhesion of the deposit to the substrate. This leads to the buildup of tensile stresses that are eventually released through the formation of cracks [6]. Since the stresses are set by the pore pressure, which is controlled by the flow, the stresses monotonically increase away from the liquid region [5]. Close to the liquid region, they are too low for the cracks to propagate, which defines the

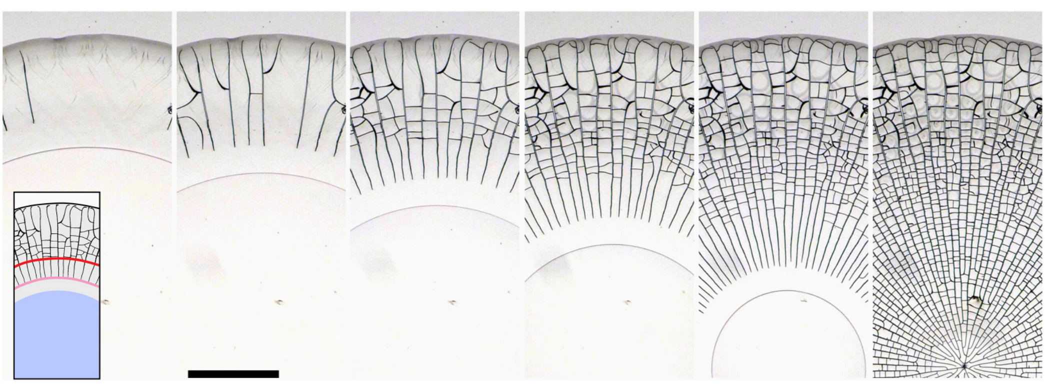

FIG. 2. Dynamics of crack propagation. Bottom-view images taken at 20-s intervals show that the tips of the radial cracks (pink line in inset) follow the retraction of the liquid region (blue region in inset). The formation of orthoradial cracks further away from the liquid cap defines a secondary propagating crack front (red line in inset). The scale bar represents 0.3 mm.

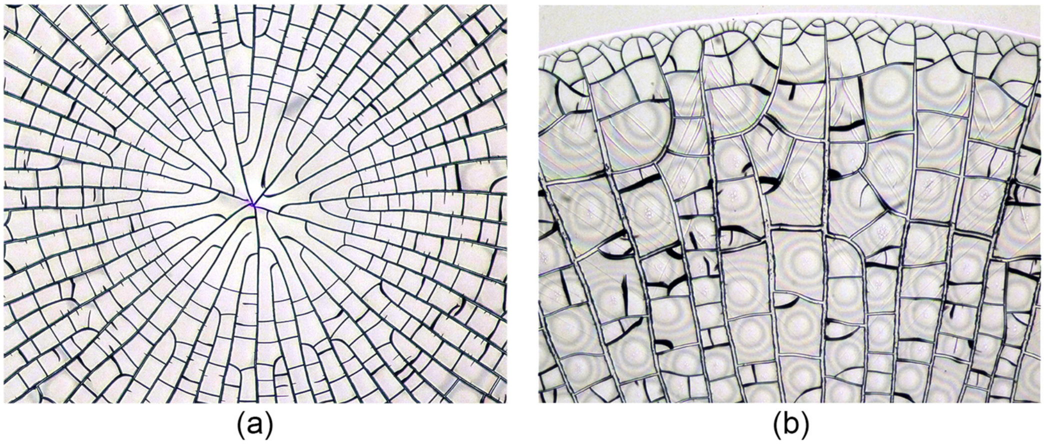

FIG. 3. Final crack pattern. (a) The radial cracks merge with each other in the center of the drop, maintaining an almost constant crack density. (b) The fringes in the deposit fragments are caused by a thin gap between the deposit and the substrate and reveal that individual fragments delaminate from the substrate and curl up. The image width is 560 μm.

first crack propagation front. Further into the deposit, the pore pressure continues to decrease and branching orthoradial cracks emerge.

The multitude of crack branching events throughout the life of the drop leads to a well-defined crack density in most of the deposit, which is visible in the last panel of Fig. 2 and reveals a remarkable order emerging from the stochastic process of crack formation. The lower crack density at the edge of the outer deposit reflects a locally larger deposit thickness, as the crack density is governed by the deposit thickness [3].

In the last few seconds of the drying process, the radial cracks merge with each other as they propagate toward the center of the drop, as shown in Fig. 3(a). Zooming closer and closer into the crack pattern exposes dizzying interference fringes in the larger fragments that indicate how the individual fragments curl up and delaminate from the substrate [Fig. 3(b)]. Deciphering nature's code of cracking allows one to read out the complex history of the drying dynamics and the processes triggered by evaporation from the final crack pattern, a lasting testament to the transient flows and hidden forces that have shaped its final form.

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