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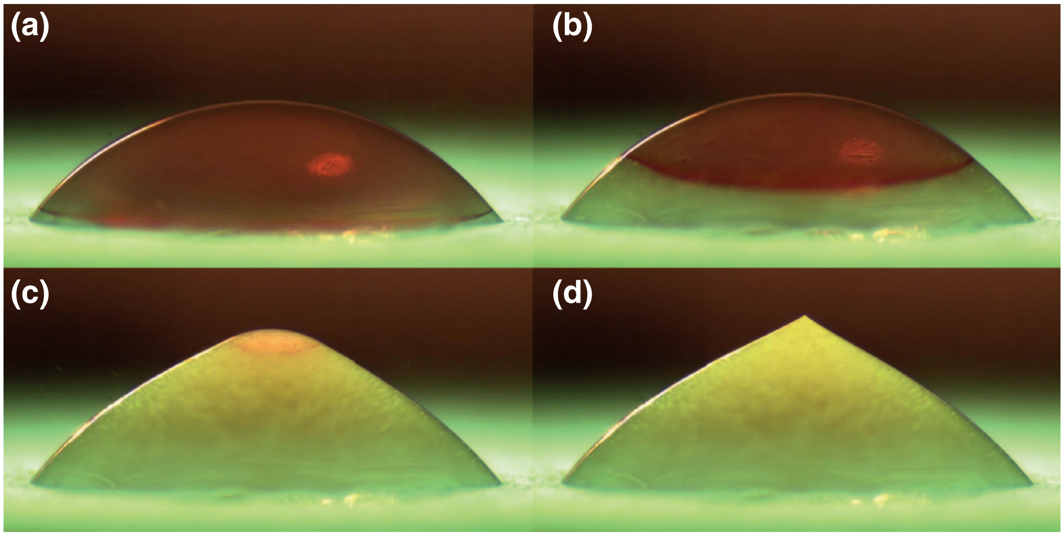

FIG. 1. Four snapshots of the freezing process of a drop of water on a cold plate ($T = -20\,^{\circ}$C). The freezing front travels from bottom to top in about 18 s. The time between the snapshots is 4.6 s (a) and (b), 11.42 s (b) and (c), and 1.28 s (c) and (d). The droplet radius at the base is approximately 2 mm. During the final stage of the freezing process, the ice drop develops a singular shape with a pointy tip (enhanced online) [URL: http://dx.doi.org/10.1063/1.4747185.1].

Freezing singularities in water drops

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When a drop of water is deposited on a very cold substrate, held well below the freezing temperature, the drop freezes into singular shape.[1] While just after deposition the liquid shape is a rounded sphere, the frozen ice drop exhibits a very distinct pointy tip (Figure 1, see video). We experimentally demonstrate how the freezing front propagates through the water drop and how the ice drop evolves towards its singular shape.

The experimental setup consists of a brass container filled with solid carbon dioxide (dry ice). A clean glass slide was placed over the brass container in contact with the dry ice, resulting in a temperature of approximately $T = -20\,^{\circ}$C. A drop of deionized and degassed water was deposited on the glass using a syringe pump. To increase contrast and observe the freezing front, red food dye was added to the water. In addition we used bottom light illumination provided by optic fiber lamps to achieve a nice visualization of the front. The process was recorded from the side using a long distance microscope (VZM1000 Edmund Optics) mounted on a color camera at a frame rate of 50 frames per second. The resolution obtained was 2048×1152 pixels with approximately 3 μm per pixel.

The process of solidification can be observed very clearly due to the change in refraction when water turns into ice. In Figure 1 the liquid water is red, but it turns bright after solidification.

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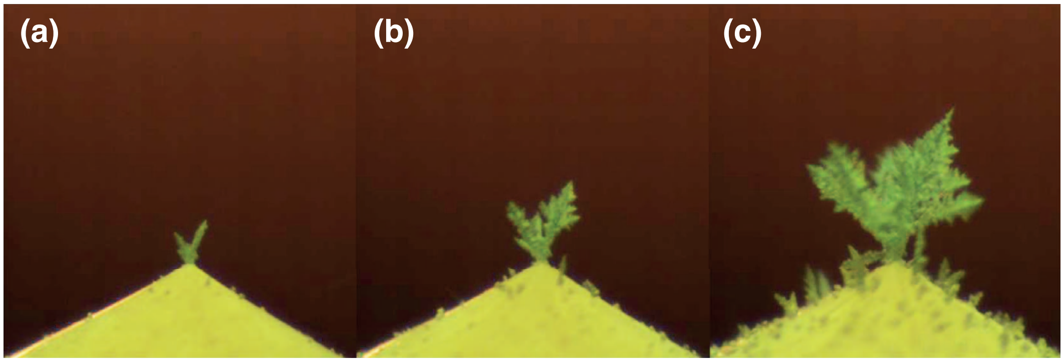

FIG. 2. Three snapshots of the "frozen tree" formation after the water drop has completely solidified. The singularity acts as a preferential site for deposition of water vapor from the surrounding air, and ice crystals grow at the tip of the ice drop. The width of each snapshot is approximately 1.5 mm. The times between frames (a) and (b) is 12 s, and between (b) and (c) is 27 s.

The snapshots at different times show that the freezing front moves upwards as it solidifies the water, starting from the bottom and moving towards the top of the drop. The unfrozen part of the drop remains spherical during the process, as is dictated by the liquid-vapor surface tension. A peculiar feature of water is that it expands upon solidification. As can be seen from the still images, the expansion does not occur in the radial direction. Instead, the ice expands vertically and pushes against the spherical cap of liquid. The vertical expansion of the ice in combination with the confining effect of surface tension leads to an interesting geometric problem: the result is a pointy tip.[2,3] Indeed, at the final stage of freezing (Figure 1(d)), when the last cap of liquid turns into ice, a singular tip develops spontaneously. The effect is very robust and is easily reproduced using ordinary tap water. By contrast, the tip formation is not observed for other liquids, which unlike water do not expand upon freezing.

Another unexpected phenomenon is observed once the liquid drop is completely frozen. The sharp tip of the ice drop acts as a preferential site for deposition of water vapor, and small ice crystals start to grow right at the tip (Figure 2). As a result, a beautiful "frozen tree" is formed on top of the singularity. This nucleation at the sharp tip can be understood from diffusion of water vapor towards the ice drop. The sharp tip naturally induces strong gradients of vapor concentration near the singularity. This locally gives a strong enhancement of the vapor flux, making the tip a preferential site for ice deposition (Figures 2(a)–2(c)). The physics behind the attraction of water molecules towards the tip is completely analogous to the attraction of electrical charges towards a sharp metallic lightning rod. Interestingly, the opposite effect extracts water molecules preferentially from the contact line of an evaporating drop[4] or from the sharp edge of potato wedges in the oven.[5]

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