Conical shape of frozen water droplets

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When a small water droplet is deposited on a cold surface, the freezing process transforms the droplet so that its upper portion attains a conical shape. Such a transformation occurs because the density of ice is lower than the density of water. Here, we assume that the freezing process in its final stage becomes self-similar, so the freezing front has a concave spherical shape, with a center that coincides with the vertex of the forming cone. This assumption gives a vertex angle of 65°, corresponding to a density ratio of 0.917, in a good agreement with experimental data.
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I. INTRODUCTION

If you cool a smooth plate with good thermal conductivity to a sufficiently low temperature and then place a small water droplet on the plate, the droplet will freeze in a relatively short time. During the freezing process, the upper part of the droplet takes a conical shape with a pointy tip at the top.[1–6] This shape appears because the final volume of the ice is larger than the initial volume of the water.

Several attempts have been made to describe this phenomenon quantitatively, allowing one to calculate the final shape of the frozen droplets.[1–4] The basic assumption of the simplest model[1–3] is that the freezing front remains flat and horizontal throughout the solidification process, just as it was at the beginning of the process. This assumption, while simple enough to account for the qualitative features observed experimentally, leads to the conclusion that a conical tip will only form if the density ratio of ice and water is less than 0.75. However, given that the density ratio of ice and water is 0.917, this model does not agree quantitatively with experimental data.

In a more realistic approach, the final shape of the frozen droplet is calculated numerically using the heat transfer equation. While the results obtained in such a way are in good agreement with experimental data,[4] the authors did not make any conclusions about the vertex angle of the cone.

In this paper, we propose a simple theoretical model that allows us to calculate this vertex angle. The main assumption of this model is that during the final stages of the freezing process the ice/water front is not flat but instead takes the shape of a concave sphere whose center coincides with the vertex of the forming cone. The fact that the freezing front is not flat has been previously observed,[4,6] but no theoretical explanation has been proposed to account for it. Below we explain this fact using arguments connecting the propagation velocity of the front with the rate of heat removal. We then calculate the vertex angle of the cone using a straightforward integration. Finally, we show that our theoretical results are in a good agreement with experimental data.

II. EXPERIMENTAL PROCEDURE

A massive steel plate with a smooth surface is cooled in a freezing chamber to a temperature of $-15\,^{\circ}$C. In our experiments, we use distilled water that is cooled to $0\,^{\circ}$C. At the beginning of the experiment, a water droplet is placed onto the plate using a syringe. The droplet diameters typically vary from 3–4 mm.

The role of gravity compared to surface tension is characterized by the Bond number

$$\mathrm{Bo} = \frac{\rho g a^2}{\gamma},$$

where a is the radius of a droplet, ρ and γ are density and surface tension of water, and g is the gravitational field strength. For the diameters cited above, the Bond number ranges from 0.3 to 0.6, showing that the influence of gravity is relatively small. Thus, the surface of an unfrozen droplet is approximately spherical.

The droplet begins to freeze from the bottom where it is in contact with the cold plate, and the freezing front moves upward. The freezing time ranges from 30 to 40 s, and the motion of the freezing front can be observed with the naked eye. During last few seconds of freezing the upper part of the droplet takes on a conical shape with a small pointy tip at the top (see Fig. 1).

The freezing droplet is photographed with a camera placed at the same level with the plate surface. Once completely frozen, the upper part of the droplet is quickly covered with tiny ice crystals. Therefore, to record the exact shape of the droplet, it is important to take a picture immediately after freezing.

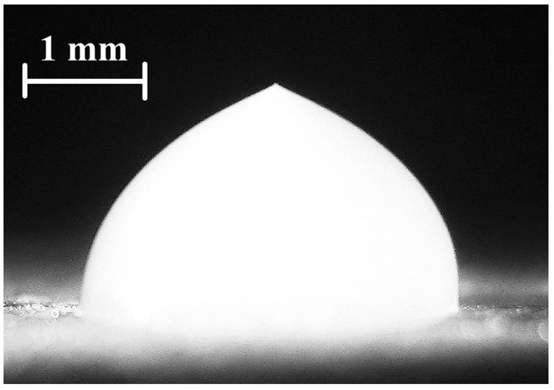

Fig. 1. Ice droplet frozen from distilled water on a cold surface. During last few seconds of freezing the upper part of the droplet acquires a conical shape.

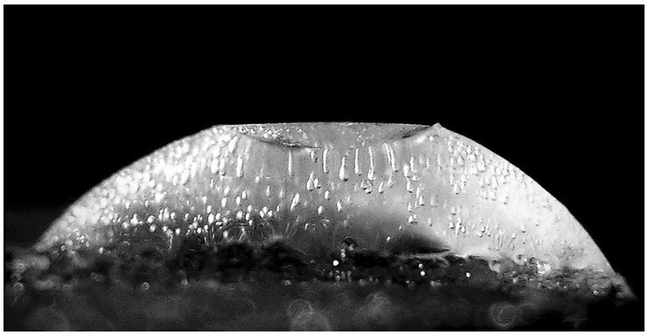

Fig. 2. When the ice/water front was near the top of a freezing droplet, the liquid water was removed with a syringe and the droplet cut in half with a sharp knife. At the top of the droplet a concave depression is seen.

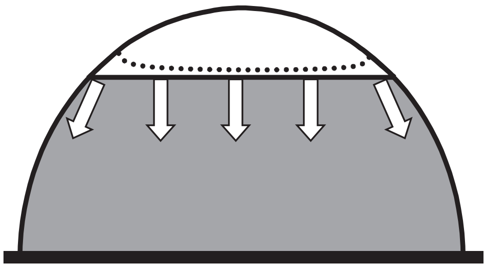

Fig. 3. If the freezing front is horizontal and flat, the heat flow (white arrows) at the periphery of the front will be greater than in the center. As a result, the front will move up at its periphery faster than in the center, resulting in a curved front (dotted).

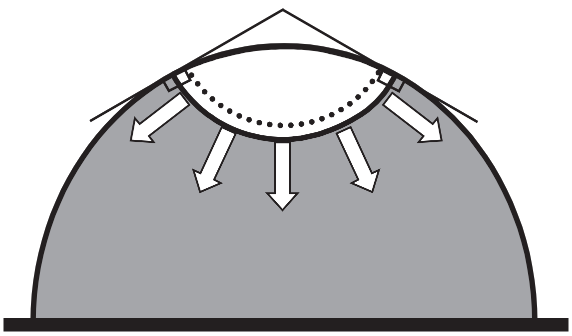

Fig. 4. During the final stages of freezing, the front takes the shape of concave sphere with the center at the vertex of the forming cone. In such a condition, the front moves forward with the same velocity at all points, and the freezing process is self-similar.

III. THE BASIS OF A THEORETICAL MODEL

A theoretical model a freezing droplet should explain the cone formation and predict the angle at the vertex of the cone. We know from direct observations that the upper part of the droplet acquires a conical shape, and that the free surface of (still unfrozen) water has the shape of a sphere inscribed in this cone. But it is also important to know the shape of the water/ice interface during solidification. To clarify this point, we followed the procedure of Nauenberg[6] and removed the water (using a syringe) when the front was close to the top of the droplet. Then we cut the droplet in half with a sharp knife to observe a noticeable concave crater (see Fig. 2).

Here, we provide a simple physical explanation for the non-flat nature of the freezing front. Assume that at a certain moment the front is flat. Then the heat flow on the periphery of the front will be greater than in the center—the latent heat of freezing water is transferred into the ice radially as well as vertically at the edges of the droplet (see Fig. 3). As a result, the front moves up at its periphery faster than in the center, and the flat surface became concave. Such a lifting of the periphery of the front at the first stages of solidification is clearly seen in the numerical calculations by Schultz *et al.*[4]

As the freezing front becomes more and more concave, it will reach a point at which all points of the front move forward with the same velocity; hence, the heat flux will be the same everywhere. Therefore, the front should be a part of the sphere whose center coincides with the vertex of the forming cone. Under this condition, the front will be perpendicular to the surface of the droplet (Fig. 4).

IV. THE VERTEX ANGLE OF THE CONICAL FROZEN DROPLET

Here, we consider the final stages of freezing and find the ratio of the current volume of (still unfrozen) water to the volume of ice that will arise from this water.

The volume of water is composed of volumes V_1 and V_2 (see Fig. 5); V_1 is the volume of the spherical cap that "fills in" the freezing-front crater, and V_2 is the volume of a different spherical cap sits on top of V_1. Meanwhile, the volume of ice is composed of volumes V_1 and V_C, where V_C is the volume of a cone that sits on top of V_1. These volumes can be expressed in terms of the angle α and radius r defined in Fig. 5 using standard techniques of trigonometry and calculus. The results are:

$$V_1(\alpha) = \frac{\pi r^3}{3} \frac{(1-\cos\alpha)^2(2+\cos\alpha)}{\sin^3\alpha}, \tag{1}$$

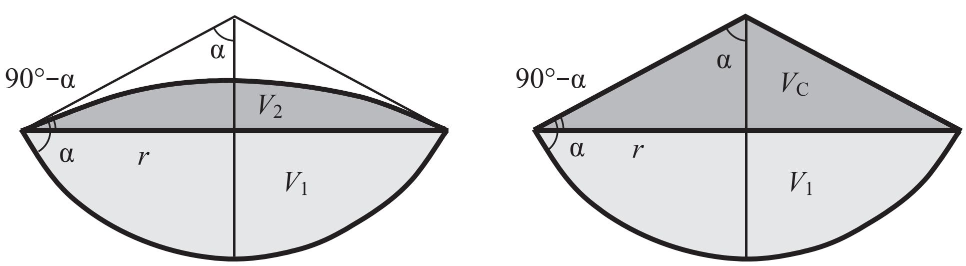

Fig. 5. The unfrozen portion of the droplet consists of two plane-convex sections with volumes V_1 and V_2. This water, when converted to ice, will occupy a volume given by V_1 plus the cone volume V_C.

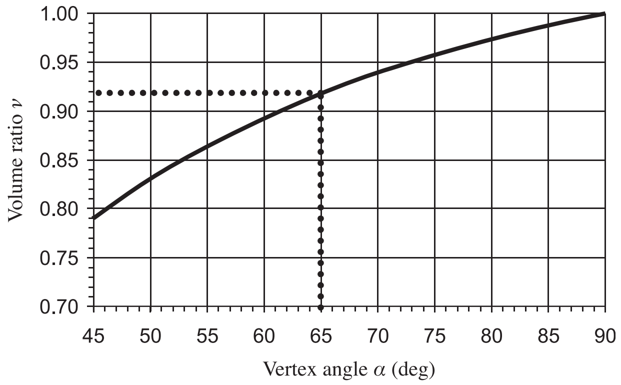

Fig. 6. The ratio of liquid to solid volumes ν, as given by Eq. (4), as a function of the vertex angle α. If the volume ratio is 0.917, as for water and ice, the vertex angle will be 65°.

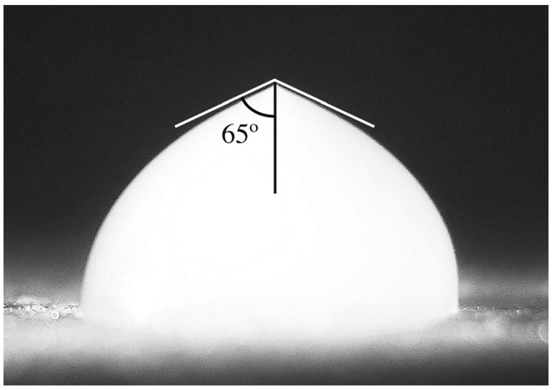

Fig. 7. The predicted vertex angle is superimposed on a photo of a frozen droplet. There is good agreement between the predicted and actual angle.

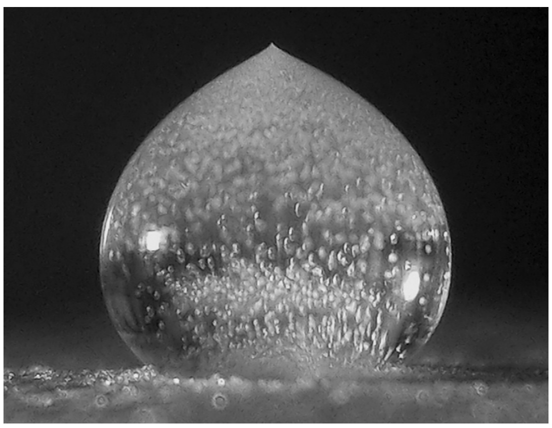

Fig. 8. In some experiments, we observe tiny air bubbles in the droplet. Their diameter is about 0.1 mm, so their rising speed in water due to Stokes law is about 5×10^{-9} m/s, which is 10^4 times slower than the freezing-front speed. Because of this difference in speed, these air bubbles become frozen in the ice.

$$V_2(\alpha) = \frac{\pi r^3}{3} \frac{(1-\sin\alpha)^2(2+\sin\alpha)}{\cos^3\alpha}, \tag{2}$$

$$V_C(\alpha) = \frac{\pi r^3}{3} \frac{\cos\alpha}{\sin\alpha}, \tag{3}$$

where the angle α and radius r are defined in Fig. 5.

Equations (1)–(3) demonstrate that the volume ratio of water to ice ν (or, equivalently, the density ratio of ice to water) is solely a function of the vertex angle α:

$$\nu = \frac{V_1(\alpha) + V_2(\alpha)}{V_1(\alpha) + V_C(\alpha)}. \tag{4}$$

Figure 6 shows a plot of Eq. (4) and shows that a volume ratio of $\nu = 0.917$ leads to a vertex angle of $\alpha = 65°$.

V. COMPARISON BETWEEN THEORY AND EXPERIMENT

Figure 7 shows a vertex angle of $\alpha = 65°$ superimposed onto the frozen droplet from Fig. 1. The agreement is quite good. To determine the vertex angle more accurately, we made measurement on 10 frozen droplets and found an average of $\alpha = 63.7° \pm 1.3°$. This angle corresponds to a volume ratio of $\nu = 0.911 \pm 0.006$, which is slightly less than the tabulated value 0.917. One possible explanation for this slight discrepancy is that when ice is frozen quickly enough, air bubbles can become trapped, as seen in Figs. 2 and 8. Such trapped air bubbles will result in a decrease in our ice density compared to the density of pure ice.

ACKNOWLEDGMENTS

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