Conical tip in frozen water drops

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Abstract

A theory is presented for the formation of a conical tip in water drops that are frozen on a flat surface below freezing temperature. For the known ice to water density ratio $r = .917$, the angle of aperture of this cone is found to be $\theta = 33.55^0$, consistent with observations.
FIG. 1. Four stages of a water drop freezing on dry ice. A) Shadow on drop shows the boundary of ice-water interface. B) Concave shape of the ice-water interface, made visible after the water is removed. C) and D) Later stage of the freezing process. E) Shape of drop just before the formation of cusp shown in F.

When a small drop of water is frozen on a flat surface below freezing temperature, a cusp appears at the tip of the drop; see Fig1 F. The origin of this cusp is attributed to the decrease in density when water freezes, but a quantitative understanding has not been achieved. D.M Anderson et al. studied this solidification process experimentally, and considered an analytic solution under the assumption that the solidification front is a planar surface[1].
Another theory for the formation of this tip was developed by Snoeijer and Brunet, but they also assumed that this front is flat, and for the known ice-water density ratio they did not find the formation of a cusp. Recently, however, I demonstrated experimentally that when this front approaches the tip of the drop, its shape becomes strongly concave; see Figs.1B,D. This behavior has been confirmed independently by O.R. Enríquez et al. In light of this evidence, I develop a theory that leads to the formation of a conical cusp at the tip of the frozen drop. During the freezing process, the surface of the front becomes increasingly concave, and the main assumption in this theory is that near the end of this process, the remaining liquid becomes a spherical drop which has the curvature of this front. This assumption is justified when the liquid phase remaining in the drop becomes very small, and then it might be expected that surface tension plays a dominant role that would confine it into a spherical shape.

**FIG. 2.** Supposing that the density of the liquid phase (grey), and the ice phase (blue) were equal, Fig.2 (a) illustrates the freezing process of a drop during a short time interval. Fig 2(b) corresponds to the real case that the density of ice is less than that of water, and the volume of the ice phase increases as shown, pushing the remaining liquid upwards.
The basic idea for this calculation is illustrated in Fig.2. Supposing that the density of water and ice were equal, the larger circle in Fig.2(a) with center at $C$ and radius $\rho$, represents a drop of water, that after a short time interval when a small portion of it freezes into ice (shown in blue), is represented by the smaller circle with center at $C'$, and radius $\rho - \delta \rho$. Since the freezing process occurs from below, the center of the smaller drop is displace vertically by an amount $\overline{CC'} = \delta \rho$. But actually the density of ice is less than the density of water, and therefore the increase in the volume of the frozen liquid implies that the center of the remaining drop of water is displaced upwards by an additional amount $\overline{CC'} - \delta \rho$ shown in Fig.2(b). The calculation then proceeds as follows:

Referring to Fig.2(b), let $\overline{PP'}$ be one of the two tangent lines common to both circles, and $\overline{CP}, \overline{C'P'}$ two perpendicular lines to this tangent from $C$ and $C'$, at an angle $\theta$ from the horizontal. Then the intersections of the two circles at the points $Q$ and $Q'$ shown in Fig.1(b), lie along the horizontal line $\overline{QQ'}$ that intersects the tangent line approximately half way between $P$ and $P'$. Hence, the difference in volume $\delta V$ between the segments of the larger drop and the smaller one that lies below their common disk with diameter $\overline{QQ'}$, consist of two parts: half the volume difference $2\pi \rho^2 \delta \rho$ between the two spheres (to first order in $\delta \rho$), and the corresponding difference in the volume of the segments contained between this common disk, and the disk through the middle of each sphere.

Let $x = \rho \cos \theta$. The volume of this segment for the larger sphere is

$$\pi \int_{0}^{\theta + \delta \theta} d\theta x^3 = \pi \rho^3 (\sin \theta - \frac{1}{3} \sin^3 \theta + \delta \theta \cos^3 \theta)$$

(1)

where $\delta \theta = \delta z \cos \theta / 2 \rho$, and $\delta z = \overline{CC'}$ is related to $\delta \rho$ by $\delta z = \delta \rho / \sin \theta$. The volume of the corresponding segment associated with the smaller drop is obtained by the replacements $\rho \rightarrow \rho - \delta \rho$, and $\delta \theta \rightarrow -\delta \theta$. Hence, the difference of the volumes of these two segments is $\pi \rho^2 (\delta \rho (3 \sin \theta - \sin^3 \theta) + 2 \rho \delta \theta \cos^3 \theta)$, and substituting $2 \rho \delta \theta = \delta \rho / \tan \theta$, and adding the difference in the volume of half of each of the two spheres, one obtains

$$\delta V = \pi \rho^2 \delta \rho (2 + 3 \sin \theta - \sin^3 \theta + \frac{\cos^4 \theta}{\sin \theta}).$$

(2)

After freezing, the water initially contained in the difference of volume $\delta V' = 4\pi \rho^2 \delta \rho$ between these two spherical drops, expands by a fraction $\xi = 1/r$, where $r$ is the ratio of the density of ice to water. Hence, setting $\xi \delta V' = \delta V$, we obtain a relation for the cone angle $\theta$ in terms
of $\xi$,
\[ \xi = \frac{1}{4}(2 + 3 \sin \theta - \sin^3 \theta + \frac{\cos^4 \theta}{\sin \theta}). \] (3)

An alternative method to obtain this relation is to assume that the volume of water in a spherical drop of radius $\rho$ in contact with the concave ice-water front eventually freezes into a cone of height $h$ and angle of aperture $\theta$, where $h = \rho \cos^2 \theta / \sin \theta$. The volume of such a cone is
\[ V_c = \pi \int_0^h dzz^2 \tan^2 \theta = \frac{\pi}{3} \rho^3 \frac{\cos^4 \theta}{\sin \theta}. \] (4)
The volume $V_s$ of the remaining segment of the drop of radius $\rho$ below this cone is
\[ V_s = \frac{2\pi}{3} \rho^3 + \pi \rho^3 (\sin \theta - \frac{1}{3} \sin^3 \theta). \] (5)

Hence, the water to ice volume expansion implies that
\[ \xi V = V_c + V_s, \] (6)
where $V = (4/3)\pi \rho^3$ is the initial volume of the drop, i.e. before freezing. Then substituting Eqs. 4 and 5 for $V_c$ and $V_s$, one recovers Eq. 3 for $\xi$. Notice, however, that in this derivation, the occurrence of a tip in the shape of a cone is an assumption that was previously deduced.

If the density of water and ice were the same, $\xi = 1$, and Eq. 3 yields $\theta = 90^0$ indicating, as expected, that a tip is not formed. But for the known density ratio $r = .917$, corresponding to $\xi = 1/r = 1.0905$, a conical tip is obtained with aperture $\theta = 33.55^0$ by solving Eq. 3. This cone aperture is in good agreement with the frozen drop tip shown in Fig.1 F. Observations of such frozen drops indicate that the conical tip is exceedingly small, implying that it appears only at the very last moment before the entire drop is frozen.

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1. D.M. Anderson, M.G. Worster, and S.H. Davis, “The case for a dynamic contact angle in containerless solidification,” Journal of Chrystal Growth 163 329-338 (1996).
2. J.H. Snoeijer and P. Brunet, “Pointy ice drops: How water freezes into a singular shape,” Am. J. Phys. 80, 764 (2012).
3. M. Nauenberg, “Comment on ‘Pointy ice drops: How water freezes into a singular shape,’” Am.J. Phys.81, 150 (2013).
4 O.R. Enríquez, A.G. Marín, K. G. Winkels, and J.H. Snoeijer, “Freezing singularities in water drops,” Phys. Fluids 24 09112 (2012).

5 J.H. Snoeijer and P. Brunet, “Response to Comment on Pointy ice drops: How water freezes into a singular shape,” Am. J. Phys. 81 151 (2013).