Theory and experiments on the ice–water front propagation in droplets freezing on a subzero surface

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Abstract

An approximate theory is presented that describes the propagation of the ice–water front that develops in droplets of water that are deposited on a planar surface at a temperature below the melting point of ice. This theory is compared with experimental observation of the time evolution of this front. These experiments were performed by freezing water droplets directly on a block of dry ice, and to examine the effects of the thermal conductivity of a substrate during the freezing process. Such droplets were also deposited on a glass plate and on a copper plate placed on dry ice. The temperature at the base of these droplets, and the dependence of the freezing time on their size were also obtained experimentally, and compared with our analytic theory. These experiments can be readily performed by physics undergraduate students, and reveal that the usual assumption of constant temperature at the base of the droplets cannot be implemented in practice.

Keywords: low temperature measurement, Stefan problem, ice–water front

(Some figures may appear in colour only in the online journal)

1. Introduction

Recently, there has been renewed interest in the properties of water droplets that are frozen on a planar surface at subzero temperatures [1–4, 6, 7, 9]. A theoretical analysis, and numerical solutions of the heat diffusion differential equations for the propagation of the ice–water front in spherical droplets have been carried out by Schultz et al [7], under the assumption that the temperature at the base of the droplet in direct contact with this surface is a constant. But up to the present time a comparison of the theory with observations of this propagation have not been reported. I present here the results of such observations with droplets deposited on a
block of dry ice, and on glass and copper plates placed on this block. It turns out that the thermal conductivity of these plates is very important in establishing the mean temperature at the base of the droplet, and the rate of freezing. To make the ice–water boundary easily observable, a drop of food coloring was added to a glass of tap water used in the experiment. While it is dark blue in the liquid phase, it becomes greenish in the frozen phase, see figure 1. The time-dependent height $h$ of this boundary, ending in a fully frozen droplet, figure 2, was recorded with a video camera, and the results are presented graphically in section 2, figure 6, where $h$ is plotted as a function of the time $t$. A curve fitting the experimental data on this plot, is based on an approximate theory of this freezing process discussed in section 1.

When the liquid phase is at the melting temperature of ice, the theory for the propagation of a planar ice–water front was given a long time ago by Stefan \cite{8}. Neglecting the heat capacity of ice, Stefan found that the height of the front as a function of time is $h(t) = \sqrt{c(t)t}$, where $c(t) = 2k_iT(t)/L$, $k_i$ is the thermal conductivity of ice, $L$ is the latent heat (per unit volume), and $T(t)$ is the average magnitude, during an interval of time $t$, of the temperature (in degree Celsius) below melting at the base of the droplet, $T(t) = (1/t) \int_0^t dT(t)$. For example, the data shown in figure 6 can be approximately fitted, for $t \leq 100$ s, with a constant value for $c \approx 0.003$ cm$^2$ s$^{-1}$, corresponding to $T \approx -21$ °C. The magnitude of this temperature appears to be surprisingly small because the temperature of dry ice is −78.5 °C, but due to the transfer of latent heat during the freezing process, it is expected that the droplet heats the dry ice surface underneath it. The effect of this heating can be observed, for example, in the appearance of a small cavity in the dry ice after the fully frozen droplet is removed. In section 2, direct measurements of the temperature at the base of several droplets are presented that verify this heating process, and its dependence on time. For $t \geq 100$ s, the height of the ice–water front increases more rapidly as a function of time than expected from Stefan’s relation. This increase in the velocity can be understood, because the

\footnote{1 For a modern presentation of Stefan’s theory, and a large bibliography on this subject, see \cite{10}. Stefan is well known for determining experimentally the fourth power temperature dependence of black-body radiation, that was established on theoretical grounds later by his student Ludwig Boltzmann.}
approximation that the ice–water front is nearly flat, required by the application of Stefan’s relation, ceases to be valid, and this front becomes concave. This change in shape has been observed experimentally \cite{4, 5, 9}, and it is also found in the numerical calculations of Schultz et al \cite{7}. Under the assumption that the shape of this front can be approximated by a spherical cap of constant curvature that is normal to the surface of the droplet, the top of the droplet takes the shape of a cone \cite{7, 9}. A novel feature in my theoretical approach, discussed in section 1, is to treat analytically the propagation of such a spherical ice–water front by an extension of Stefan’s relation for a planar front. In section 2 a calculation based on this approach is compared with an experimental observation of the front propagation in a droplet deposited on dry ice. In section 3, I present some time depended measurements of the temperature at the base of droplets of various sizes on dry ice, and also on a glass plate and on copper plate. Some of my conclusions are summarized in section 4.

2. Analytic approximation for the propagation of the ice–water front

In this section, I present an analytic calculation of the ice–water front propagation in a hemispherical droplet of water placed on a planar surface at a temperature below the melting point of ice. This calculation is based on the approximation that the propagation of this front can be split into two stages: (a) the front is planar until it reaches a critical height when the shape of the droplet evolves into a cone due to the expansion of the volume of water when it freezes into ice, and (b) afterwards, the front takes the shape of a spherical cap centered at the apex of this cone \cite{7, 9}, illustrated in figure 3. For simplicity we assume that the temperature $T_i$ at the base of the droplet is constant, but the theory can be readily generalized to account for the experimentally observed time dependence of $T_i$ presented in section 3.

Provided that the liquid phase of the droplet remains at the melting temperature $T_m$, the heat flux generated by the latent heat that emerges during freezing is conducted primarily by the ice phase of the droplet. Then the propagation velocity $v$ of a planar ice–water front moving along the positive $z$ axis is determined by the energy conservation relation \cite{8} (see footnote 1)

\[ v = \frac{h}{\frac{4}{3} \pi R^3} \]
where $T$ is the temperature at the front, $L$ is the latent heat per unit volume, and $k_i$ is the thermal conductivity of ice. Neglecting the heat capacity of ice, $\partial^2 T / \partial z^2 = 0$, and $T$ depends linearly on $z$, with $T = T_i$ at $z = 0$, where the drop is in contact with a subzero heat reservoir, and $T = T_m$ at the propagating ice–water front located at $z = z(t)$. Hence

$$T = T_i + (T_m - T_i)\frac{z}{z(t)},$$

and equation (1) becomes an equation of motion for the propagation of the ice–water front

$$\frac{dz(t)}{dt} = k_i(T_m - T_i) \frac{Lz(t)}{T_m - T_i}.$$ (3)

Setting $z'(t) = z(t)/\rho$, where $\rho$ is a length scale that we take to be the radius of the drop, and $t' = t/\tau_1$, where $\tau_1 = L\rho^2/(2k_i(T_m - T_i))$ is a time scale, one obtains Stefan’s relation in the dimensionless form

$$t' = z'^2.$$ (4)

The main approximation now is to assume that this relation holds until $z = z_o$, where $z_o$ is the location of the ice–water front when it attains the shape of a spherical cap. This cap is centered at the cusp of a cone with half opening angle $\theta$, and side length $r_o = \rho \cos \theta / \sin \theta$, and $z_o = \rho \sin \theta - \rho_o(1 - \cos \theta) = \rho \sin \theta / (1 + \cos \theta)$ (see figure 3). The angle $\theta$ is obtained by the requirement that upon freezing, the remaining volume of water expands into this cone and into the spherical cap $[7, 9]$. The ratio $\rho = 0.917$ of ice to water density determines $\theta \approx 65^\circ$, and corresponds to $z_0 \approx 0.64$. Assuming that for $z \geq z_o$ the ice–water front has the shape of a hemisphere centered at the cusp of the cone

$$v_iL = -k_i \frac{\partial T}{\partial z}.$$ (5)
where the origin of the radial distance $r$ is at the apex of the cone of length $r_o$, the radial velocity of the ice–water front is $v_t = \frac{dr}{dt}$, and the temperature $T$ satisfies the spherically symmetric Laplace equation

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} = 0.$$  \hspace{1cm} (6)

Hence $T = \frac{\alpha}{r} + \beta$, where $\alpha$ and $\beta$ are time dependent variables. I determine these variables by the condition that at $r = r(t)$, $T = T_m$, while at $r = r_o$, $T = T_o$, where according to equation 2, when $z(t) = z_o + r_o - r(t)$

$$T_o = T_i + \frac{(Tm - Ti)z_o}{z_o + r_o - r(t)}.$$  \hspace{1cm} (7)

Hence $\alpha = (Tm - To)r(t)r_o/(r_o - r(t))$, and the gradient of $T$ at the spherically shaped ice–water front at $r = r(t)$ is

$$\frac{\partial T}{\partial r} = -\frac{(Tm - Ti)r_o}{(z_o + r_o - r(t))r(t)}.$$  \hspace{1cm} (8)

As a bonus, one finds that when $r(t) = r_o$ the linear and the spherical gradient of the temperature $T$ are the same. Therefore, at this cross-over, the velocity of the front is continuous. Setting $x = r(t)/r_o$, and $\tau'' = t/t_2$, where $t_2 = r_o^2 L/(2k_i(T_m - T))$ is the relevant time scale for the propagation of the spherical ice–water front

$$\frac{dx}{d\tau''} = -\frac{1}{2(\eta + 1 - x)x},$$  \hspace{1cm} (9)

where $\eta = z_o/r_o = 1/\cos\theta - 1$. Integrating this equation of motion

$$\tau''(x) = \tau''(1) + (1/3 - x^2)(\eta + 1 - 2x/3),$$  \hspace{1cm} (10)

where $\tau''(1) = (t_i/t_2)\sin^2\theta/(1 + \cos\theta)^2$, and $t_i/t_2 = \rho^2/r_o^2 = \sin^2\theta/\cos^2\theta$. When $x = 0$, the ice–water front has reached the apex of the cone, and the freezing is completed, with the elapsed scaled time

$$t_t' = \frac{1}{1 + \cos\theta} + \frac{\cos^2\theta}{3\sin^2\theta}.$$  \hspace{1cm} (11)

For $\theta = 65^\circ$, $t_i' = 0.775$, figure 4 shows the time dependence of the height $z(t)$ of the ice–water front in scaled variables, and figure 5 shows the velocity $v(t)$ of this front. The transition from a planar to a spherical ice–water front occurs at about half the total freezing time $t_d = z_o^2 \approx 0.4$. The position and velocity of the front are continuous at this point, but in our approximation that at this time the ice–water front changes discontinuously from a planar to a spherical front, this effect can be seen as a small discontinuity in the acceleration of this front.

When the temperature at the base of the droplet is not a constant, but depends on the freezing time $t$, which in practice is the case, as shown in section 3, the scaling factors $t_i$ and $t_2$ become function of the time. Then $t_i(t) = L\rho^2/2k_i(T_m - T_i(t))$, and $t_2(t) = Lr_o^2/2k_i(T_o - T_i(t))$, where $T_i(t) = (1/t) \int_{t_0}^{t} dt' T_i(t')$ is the mean temperature at $t$ for $0 \leq t \leq t_0$, and $T_i(t) = (1/t) \int_{t_0}^{t} dt' T_i(t')$ is the mean temperature for $t_0 \leq t$. 

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3. Experimental results and comparison with the theory

The propagation of the ice–water front was observed in droplets of water deposited on a glass surface placed on a block of dry ice. An example is shown in figures 1 and 2, and the height of the ice–water front, recorded with a video camera (Canon Vixia HFS200), is plotted as a function of the time in figure 6. The curve shown on this plot is a fit to this data based on the theory discussed in the previous section. The bulk temperature of the dry ice is $-78.5^\circ C$, but in order to conduct the latent heat produced during the freezing process, the temperature at the contact between the base of the drop and the glass plate must be higher. Direct evidence for this heating was observed by depositing the drop directly on the surface of the dry ice. After the freezing process was completed, removal of the frozen drop left a small hole due to the heating of the dry ice under the base of the drop. In the next section, it will be shown that this temperature is not a constant as has been assumed in all the theoretical work up to the present time, but for large size droplets its value can be approximated by an average temperature during the freezing process. For example, in the fit of the analytic approximation discussed in section 1 to the experimental data in figure 6, the only unknown parameter is the mean value of the temperature, given by $T_i = -0.39\rho^2L/k_i t_i$. For the effective radius of the droplet, $\rho \approx 0.7$ cm, and the observed time to complete the freezing process, $t_i = 120$ s, $T_i = -22^\circ C$. Unfortunately, this data cannot be compared also with the numerical calculations of

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2 Near the top of the droplet, the theoretical curve gives the height $z$ at the base of the assumed spherically shaped ice-water front, while the height of the front can be observed only at the surface of the drop. Therefore, there is an offset which, however, vanishes at the top of the droplet. The approximate agreement of the data shown in figure 6 with the theoretical curve confirms that elsewhere this offset is small.
Schultz et al [7], because their time dependent results were given only for the velocity of the ice–water front.

4. Temperature measurements

During the freezing process, the temperature was measured at the base of several droplets of different sizes deposited on a block of dry ice, figure 7, and on a copper plate 0.1 cm thick, placed on this block, figure 8. These measurements were made with a thermistor 0.2 cm in diameter from the Keystone Carbon Company, St. Marys, PA. It is shown that in an extremely short time after these droplets were deposited on these subzero surfaces, the temperature increased very rapidly to higher values that depended on the size of the droplet, and afterwards it decreased at a rate that was slower with increasing size of the droplet. For the smallest droplet (0.1 cm in radius) deposited on dry ice, the decrease in temperature was very sharp, but for the larger droplets the assumption of a nearly constant temperature during the freezing process made in the numerical calculations of Schultz et al [7], and in my analytical calculations in section 1, should be applicable. The inflection that appears at longer times in the temperature versus time curve, figure 7, occurred when the freezing of the droplet was nearly completed, and the release of latent energy had ended. But as expected, the temperature of the frozen droplet continues to fall until it came into thermal equilibrium with the dry ice. A similar behavior was observed with droplets on the copper plate, figure 8, but in this case the rate of freezing was approximately 10 times faster.
The time $t_f$ to complete the freezing of droplets of different sizes deposited on dry ice, and on copper and glass plates placed on dry ice, is shown in the tables below. According to the theoretical analysis, if the temperature $T_i$ at the base of the droplet were constant, the ratio $\rho^2/t_f$ should be a constant. Although the observed temperature varies during the freezing process, this constancy is approximately valid in the examples given in the tables below. According to the numerical calculations of Schultz et al [7], $T_i = -0.12L/k_i(\rho^2/t_f)$, where $L$ is the latent heat and $k_i$ is the thermal conductivity of ice. For droplets freezing on the copper plate, $\rho^2/t_f = 0.015$, and taking $L = 333 \text{ J cm}^{-3}$, and $k_i = 0.024 \text{ J cm s}^{-1} \text{ K}$, $T_i = -25 \text{ C}$. This value of $T_i$ is considerably higher than the mean value (between $-45 \text{ C}$ and $-50 \text{ C}$) of the time dependent temperature during the freezing process shown in figure 8, while my analytic approximation gives $T_i = -80.5 \text{ C}$, which is too low. For droplets freezing directly on dry ice, $\rho^2/t_f \approx 0.002$, and the calculation of Schultz et al gives $T_i = -3 \text{ C}$, which also is much higher than the mean value of the experimentally observed temperature in figure 7, while my analytic approximation yields $T_i = -10.4 \text{ C}$.

Another problem with the comparisons of theory and experiment is that only the smallest size droplets—with a radius $\rho \approx 0.1 \text{ cm}$—have a spherical shape, while larger droplets are flattened by the effect of gravity. This effect can be seen in the droplet shown in figures 1 and 2. For these droplets, I have taken for the value of $\rho$ one half of the diameter measured at the base of the droplet.

In tables 1, 2 and 3 below, the freezing times $t_f$ and the ratio $\rho^2/t_f$ are shown for droplets of different radius $\rho$. In particular, this ratio is shown to be approximately independent of the droplet radius, as predicted by my theory.
Figure 7. The temperature at the base of droplets of water of different sizes deposited on a block of dry ice, as a function of time: $\rho = 0.23$ (crosses), $\rho = 0.5$ (squares) and $\rho = 0.63$ (hexagons).

Figure 8. The temperature at the base of two droplets of water of different sizes deposited on a copper plate placed on block of dry ice, as a function of time: $\rho = 0.4$ (crosses), $\rho = 0.8$ (hexagons).
5. Conclusions

I have shown that the main features of the time dependent propagation of the ice–water front of water droplets deposited on a surface at subzero temperatures can be understood by Stefan’s relation for planar surfaces, together with an extension of this relation when this front becomes concave. Previous calculations of Schultz et al [7], based on the numerical integration of the heat diffusion differential equations for this propagation, assume that the temperature at the base of these droplets is a constant, while my analytic approximation can also be applied to time varying temperatures. My measurements, presented in section 3, indicate that during the freezing process this temperature is not constant, and for small drops, \( \rho \approx 0.1 \text{ cm} \), it varies rapidly. The assumption that the theory can be applied by taking the mean value of the temperature leads to some of the observed results, e.g. the approximate constancy of the ratio \( \rho^2/t_f \) for a range of values of drop sizes and freezing times, shown in the tables presented in section 3.

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References

[1] Anderson D M, Worster M G and Davis S H 1996 The case for a dynamic contact angle in containerless solidification J. Cryst. Growth 163 329–38
[2] Snoeijer J H and Brunet P 2012 Pointy ice drops: how water freezes into a singular shape Am. J. Phys. 80 764
[3] Enríquez O R, Marín A G, Winkels K G and Snoeijer J H 2012 Freezing singularities in water drops Phys. Fluids 24 091102
[4] Nauenberg M 2013 Comment on “Pointy ice drops: how water freezes into a singular shape” [Am. J. Phys. 80, 764–771 (2012)] Am. J. Phys. 81 150
[5] Snoeijer J H and Brunet P 2013 Response to “Comment on ‘Pointy ice drops: how water freezes into a singular shape’” [Am. J. Phys. 80, 764–771 (2012)] Am. J. Phys. 81 151
[6] Nauenberg M 2014 Conical tip in frozen water drops arXiv:1404.4425v1 [physics.flu-dyn]
[7] Schultz W W, Worster M G and Anderson D M 2001 Solidifying sessile water droplets Interactive Dynamics of Convection and Solidification ed P Ehrhard et al (Dordrecht: Kluwer) pp 209–26
[8] Stefan J 1889 Über die Theorie der Eisbildung insbesonder über die Eisbildung im Polarmeere, S.-B Wien Akad. Mat. Natur. 98 965–83
[9] Marín A G, Enríquez O R, Brunet P, Colinet P and Snoeijer J H 2014 Universality of tip singularity formation in freezing water drops Phys. Rev. Lett. 113 054301
[10] Rubenstein L I 1971 The Stefan Problem (Translations of Mathematical Monographs vol 27) (Providence, RI: American Mathematical Society)