Indian J Phys
https://doi.org/10.1007/s12648-018-1265-6

ORIGINAL PAPER

Origin of the infra-red emission peak in freezing water

R Stahlberg*, H Yoo and G H Pollack

Department of Bioengineering, University of Washington, Box 355061, Seattle, WA 98195, USA

Received: 22 December 2017 / Accepted: 08 May 2018

Abstract: When droplets of purified water (1–5 µl) were cooled from the bottom, they slowly and continuously supercooled before releasing latent heat as a transient burst of infra-red (IR) radiation. In order to determine the role of this IR emission, a thin rectangular water layer was cooled unilaterally while imaged from above by an infrared (FLIR) camera. The first noticeable event was an IR burst that rapidly (< 0.1 s) moved through a 5-mm-long path of water. Final solidification of the water layer was recognized by an increase in volume, as the meniscus at the air interface changed from concave to convex. The propagation of the IR burst through the water layer preceded the first visible onset of volume increase and solidification by more than one second. The transient and early appearance of the IR burst belongs to what is called the first stage of freezing. This stage has been linked to the formation of so-called spongy ice. Both IR burst and pinnately shaped spongy ice appear at the same time and share a short transient existence. It is only this early type of ice that is associated with the IR burst. By contrast, the later-occurring solid ice formation parallels a diminishing IR emission.

Keywords: Ice formation; Phase transition; Spongy ice formation; Dendritic ice; Peak in infra-red emission; IR heat dissipation

PACS Nos.: 44.40.+a; 64.70.-p; 64.60. My

1. Introduction

Ice is the most abundant crystal on earth and the largest resource of fresh water on the planet. The phase transition from water to ice affects a wide variety of natural processes on earth, in the atmosphere, and in space. Accordingly, freezing is a fundamental process under investigation by biologists, meteorologists, chemists, physicists and engineers. Ice formation is responsible for processes ranging from the electrification of thunder clouds [1] to the frost sensitivity of living organisms. Many living organisms lose viability near − 10 °C, a temperature that falls within the range of freezing temperatures of water [2].

A puzzling aspect of the freezing mechanism is the latent heat release. As a water droplet is cooled continuously to subzero temperatures (i.e. it supercools), it suddenly heats up to 0 °C, the droplet then further cools and finally forms ice [3, 4]. It has been asserted that the heat release is coincident with ice formation, while the subsequent temperature drop represents the rapid cooling of ice itself [3, 5].

It is believed that the heat release derives from the strengthening of hydrogen bonds between water molecules, which stops translational and rotation movements [6, 7]. This loss of kinetic energy slows the water molecules sufficiently to be locked into their new positions within the forming ice lattice. On the other hand, the production of heat should be counterproductive to freezing. Its quick removal is a crucial step, which limits the amount of water that can be frozen [8].

When water is supercooled from the outside, large concentric temperature gradients form, which trigger exceptionally fast-growing (> 1 cm/s) spongy ice in the "first phase of freezing" [8]. The ice grows rapidly and by multiple branching, creating a network of dendritic structures that retains considerable amounts of water [8–10]. As in a sponge, both liquid and solid states coexist, and this ice form is therefore referred to as spongy, skeletal or dendritic [8–10]. Upon continued cooling, a second phase of much slower ice formation follows, which consolidates the remaining water [4]. While the heat released during the first stage could be quickly passed on to the neighboring

*Corresponding author, E-mail: raista@u.washington.edu

Published online: 11 August 2018

supercooled water, it now has left only IR radiation through the air interface to dissipate [8].

We investigated the freezing of water using CCD (charge-coupled device) and IR imaging, and found that the burst of IR (heat) occurs up to twelve seconds before the slowly occurring volume expansion—the formation of a solid ice lattice. Therefore, solid ice formation cannot be the cause of the heat release.

2. Methods

Ultra-pure water with a resistivity of 18.2 MΩ cm^{-1} was collected from a Barnstead Nanopure water purification system and used for all experiments.

2.1. Freezing chambers

Droplets of purified water were cooled from the bottom, while imaged from the top and side by CCD and IR cameras (Fig. 1). The bottom of the droplet was in direct contact with the cold side of a Peltier device. The warm side, beneath, contacted an aluminum jacket with cold (− 5 °C) ethylene glycol circulating through a refrigerating circulator (VWR International). A thermocouple was placed between the aluminum bottom and Peltier device to feed back to the temperature control module (Omegaette PV) of the Peltier device. For the freezing runs, we set the target temperature to − 30 °C.

To better resolve the timing of the IR emission relative to the first appearance of ice, we designed an alternative chamber (Fig. 2). This design converted a 2-µl water drop into a 0.2 mm shallow layer in the shape of a 2 × 5 mm rectangle.

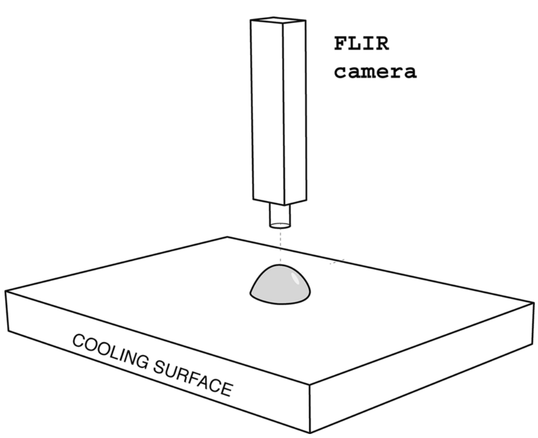

Fig. 1 A FLIR infrared recording camera takes a series of birds-eye images of a freezing water drop, which is cooled from the bottom by a Peltier device

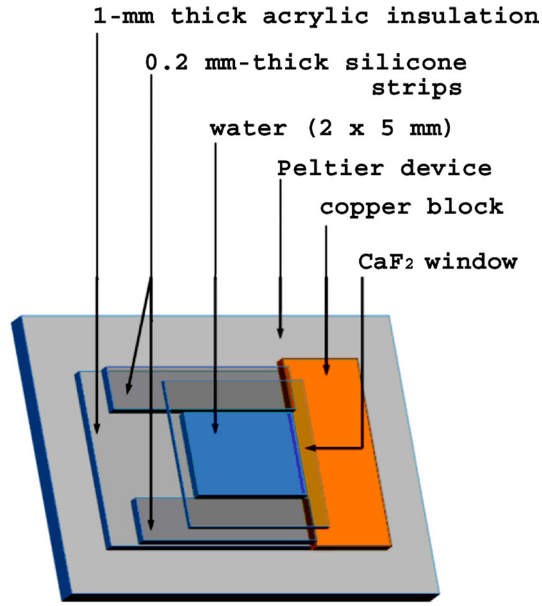

Fig. 2 Schematic view of the chamber used to cool and observe the IR emission from a thin water layer. Insertion of 0.2 mm thick silicone strips sandwiched the water between the acrylic bottom and an IR-transmitting CaF_2 window on top. The thin rectangular water layer (blue) was cooled by a copper sheath (orange) in contact with the cold side of a liquid-cooled Peltier device (grey). The other side of the water layer remained open to air (left side) (color figure online)

2.2. Freezing procedures for shallow water layers

A 2-µl droplet of ultra-pure water was dispensed onto an acrylic surface between two parallel, 0.2 mm thick silicone strips and then confined into a shallow rectangular shape by the weight of an IR-transparent CaF_2 window on top (Specac Ltd, Slough, Great Britain). While the longer sides bordered thin silicone strips, one short side formed a meniscus interfacing with air (Fig. 2). The opposite short side contacted a piece of copper that was cooled by the Peltier device. Except for this copper block, the chamber was insulated by a 0.5 mm-thick, transparent acrylic layer. This setup imposed unilateral cooling of the shallow water layer.

2.3. IR imaging

The progress in IR emission and ice formation over a span of 5 mm from the cooling copper block to the air interface was recorded by an IR camera in a bird's eye view. The Thermo-Vision infrared camera (SC 600, FLIR systems, Inc.) is equipped with an InSb sensor, which detects photons within a bandwidth range of 3–5 µm. The camera had 50 mK sensitivity and acquired images with 640 × 512 pixel resolution. The maximal frame rate was 100 Hz. For improved spatial resolution, a 4 × IR microscope lens was attached to the camera. The collected IR images were analyzed using FTIR ExaminIR software for quantification and data extraction. To check for IR emission beyond the limited range of the SC 600 camera, another camera was employed (FLIR, Model A 655sc; sensor 7.5–15 μm) as well as a CCD machine-vision camera system (CFW-1612, Scion Corporation, Frederick, MD, USA), which recorded in the visible and near IR range.

2.4. Ice imaging under polarized light

Spongy ice images were taken with a CCD camera under polarized illumination. Ice differs from water by its birefringence [e.g. 11]. Due to its hexagonal crystal symmetry, ice has a uniaxial birefringence [6]. Under crossed linear polarizers, the birefringent ice is easy to differentiate from water. To identify the first appearance of ice structures in water we therefore used imaging by a CCD camera under visible polarized light.

2.5. IR imaging with external IR source

For certain experiments, it was advantageous to use an external infrared source, directed at a shallow angle to the water surface. The IR source was a Ceramic Infrared Heat emitter (Zoo Med Laboratories, Inc., San Luis Obispo, CA, USA).

2.6. Spongy or skeletal ice

We used a chamber consisting of a strong U-shaped aluminum frame, which sandwiched a 4 mm-thick water layer between two thick acrylic windows. The chamber was filled with 0.5 μl of purified water, to which a trace of methylene blue was added for improved contrast. Accordingly, the water body measured 50 mm high × 25 mm wide and 4 mm deep. Freezing was initiated by inserting the chamber into a freezer, which was set to − 36 °C. The freezer (SCFU386 Compact Display Freezer, Summit, USA) featured a clear glass window, which permitted real-time, direct observation from the outside.

3. Results and discussion

3.1. IR emission shows a distinct peak

The starting point for this study was the observation of a distinct and sudden emission of an IR burst from a freezing drop (Fig. 3). By confining the region of interest (ROI) to the droplet area and averaging pixel values, we could track the IR emission from the entire droplet over time. An IR pulse appeared abruptly as a reversal in the trend of slowly cooling drop. At this point, the drop changed from the coldest spot in the IR image to the warmest one (Fig. 3, bottom, panel II). The emission peak rose steeply and then declined steadily in intensity over the course of 1–3 s, persisting the longest time in the center of the droplet. It was not confined to the 3–5 μm-wavelength range detectable by the main FLIR camera but extended into the range from 7.5 to 15 μm detected by a different type of FLIR camera. The use of a CCD camera showed that no visible light was emitted.

The IR flash in Fig. 3 illustrates that the heat release of the phase transition is not a continuous process, but one with a discrete peak. This distinct peak opens the possibility of determining the timing and role of the IR burst in the freezing process with great accuracy. From the existing literature, it is not clear whether IR emission coincides or precedes ice crystallization [3, 12].

3.2. The IR peak precedes solid ice formation

To clarify this issue, we designed a thin chamber (see Fig. 2) that allowed the simultaneous and precise measurement of IR emission and volume expansion. This chamber housed a horizontally oriented, rectangular-shaped layer of water, which was cooled from one side. Both IR emission and ice solidification were directly observed in real-time during their progress from one side of the chamber to the other (Fig. 4).

IR emission began in frame 2 at the bottom of the image, where the cooling copper sheath was located. The emission advanced from the cooled side to the air-interface within 0.12 s (reaching the interface between frames 3 and 4) with a propagation velocity of approximately 40 ± 2 mm/s (SEM, $n = 4$). After reaching the meniscus, the emission lasted only five more seconds (0.12 s to 5.5 s) before contracting to a small spot at the air interface (frames 5–7), and disappearing altogether after 13 s (frame 8).

Ice lattice formation is indicated by a volume expansion [6]. In the shallow water layer of this chamber, any volume change will affect the meniscus. The meniscus did not change during the propagation of the IR burst (Fig. 4; frames 2–4), but required another 1.4 s before shifting from concave to convex (frames 5–8). Hence the lattice formation started more than a second after the IR emission, and cannot therefore be the cause of it.

The final step in the freezing sequence was a dimming of the IR emission, which coincided with the formation of a convex meniscus that signaled the volume expansion of consolidated ice (frames 5–8). The volume increase began after more than one second (frame 5) and continued for another 12 s (frames 5–7). Accordingly, the computed speed of crystallization approximates 0.4 ± 0.01 mm/s (SEM, $n = 4$). This is an order of magnitude slower than the velocity of the IR wave (40 mm/s; see above). Thus,

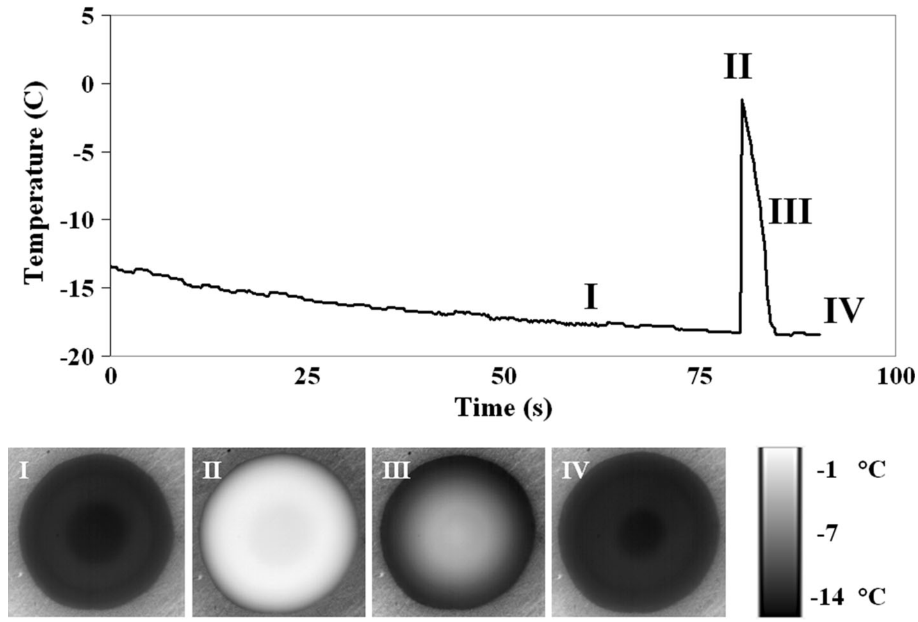

Fig. 3 Time course of IR emission during the freezing of a 4-μL water droplet, which was cooled from below and imaged from above. Selected IR images are pasted at corresponding points along the curve (I, II, III and IV). Each image provides a gray-scale distribution of the IR irradiance, which is plotted as equivalent temperature (see scale, bottom right). The average temperature within the droplet was used to plot the time course above the images. The time course shows a sudden burst in IR emission, disrupting a previously steady drop in temperature. The figure shows one representative example of an experimental series of 10 similar repetitions

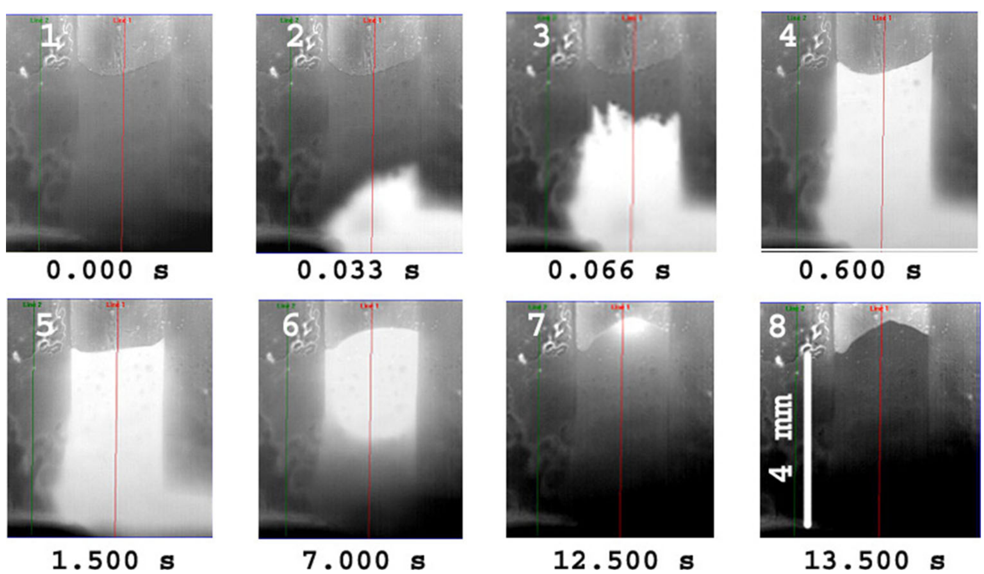

Fig. 4 Sequence of IR images taken during the freezing of a shallow water layer, which is cooled through a copper sheath located at the bottom of the images. Images of the horizontal chamber are taken from the top. The water layer is situated between the copper sheath at the bottom and the air interface on the top. Emission began at the copper sheath and moved rapidly through the entire layer of water (frames 2–4). By contrast, volume expansion started later, as the meniscus turned convex (frames 5–8). The red line is the axis along which the advance of the IR wave was measured. Shown is one example out of an experimental series of four repetitions

freezing- induced IR emission propagated much faster than bulk ice formation, and do not therefore appear directly related.

3.3. Dendritic ice feathers appear synchronously with the IR emission peak

A comparison of the timing of the IR burst with that of the events recorded in other studies, implies that the IR burst may coincide with the first or stage-one phase of freezing [10], and may involve the formation of skeletal or spongy ice [8, 10]. To test this hypothesis, we searched for the occurrence of spongy ice under our experimental conditions. Since ice is a birefringent material and water is not [6, 11], any ice formation becomes instantly visible under crossed polarizers.

Indeed, the transparent image of clear water (frame 1) gave way to the appearance of two types of colored, birefringent structures. The first type is dendritic ice feathers filling half a millimeter of the image in panel 2.

The second type appears as a thickening of the solid dark band at the bottom of panels 1 to 3. This is due to the formation of solid ice on the copper sheath. It appears black because the brightness level was set low to visualize the main target: the fine ice feathers. With increased brightness, the thickening band of ice next to the copper sheath could be visualized.

Another approach to visualizing feathery ice used IR reflection (Fig. 6). In this approach, we cooled a 1-mm deep copper cylinder of water from the bottom, while illuminating the water surface from a shallow angle of 30 degrees with an IR source, and recorded the IR emission from above. Despite some induced surface heating, freezing temperatures were reached. The IR bursts occurred at approximately − 3.5 °C, while at the same time, through reflection of the external IR beam, we could visualize the transient appearance of surface structures (Fig. 6). These structures vanished within 0.4 s of their appearance. The coincident timing of the IR burst and appearance of surface structuring demonstrates that a transient ice form appears during the IR emission.

3.4. Can spongy ice survive the IR burst?

Under the conditions of the preceding experiments, dendritic ice feathers of the spongy ice occurred as ephemeral structures that disappeared within 0.5 s of their appearance (Figs. 5, 6). One could imagine that stronger cooling might overcome the generated heat emission and keep the temperature low enough for spongy ice to survive. Such a scenario was found when water (containing traces of methylene blue for better visualization) was frozen between heat-conducting aluminum blocks within a chamber placed inside a freezer set to − 36 °C (Fig. 7). While solid ice columns were slowly forming next to the aluminum surface (visible as a bluish layer), the center of the chamber was demarcated with a crisscross pattern of ice daggers that coexisted with liquid water (Fig. 7). This became visible after decanting the liquid water from the chamber (right panel). Spongy ice persisted much longer than under the conditions shown in Fig. 5.

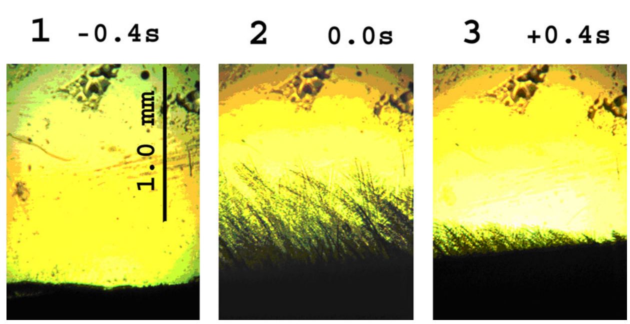

Fig. 5 Sequence of images taken at 0.4 s-intervals under polarized light during the freezing of a rectangular, 0.2 mm shallow water layer. The water was cooled from the left side by a copper plate appearing as a dark band in frame 1. Conditions were similar to those of Fig. 4 and images were acquired from above. The first frame illustrates unfrozen water next to the cooling copper plate (frame 1, dark strip at bottom). The shapes visible in upper right corner of the frame are scratch marks at the acrylic bottom of the chamber. The second frame shows the sudden appearance of birefringent structures in the form of dendritically branching feathers. These pinnate structures extended into the water for 0.3–0.4 mm from the copper plate (frame 2). The third frame was taken 0.4 s later and shows that most of the ice feathers have melted. Shown is one example out of four similar sequences

3.5. Time-disparity between IR emission and solid ice formation

During the course of freezing, a water droplet releases latent heat, not only continuously but also prominently as a distinct peak in IR emission. Using the clear timing of this peak, we reinvestigated the process of freezing in drops and shallow layers of water. The results clarified the role of the IR emission in the freezing process. When judged by volume expansion, ice consolidation started more than one second after the IR burst and could not therefore cause the burst.

3.6. The potential role of the IR emission

It has long been known that the removal of the heat of phase transition determines the rate of ice formation [14, 17, 19]. Our results show that heat release is not a lengthy and continuous process, but that a major amount of heat leaves in a distinct, short burst of IR emission (Fig. 3).

A sudden burst in IR irradiance provides a convenient time marker for determining the onset of freezing, a feature that is used conveniently in the operation of freezing-point osmometers. However, our data show that this point does not coincide with, but substantially precedes the solidification of water into ice. Freezing of a shallow, 5-mm-long water layer (Fig. 4), demonstrated the IR flash as the first fleeting step in a sequence of discrete events in a freezing process. The consistency of the appearance of this IR burst implies that it is a necessary step in the events towards ice formation. Without it, there is no ice formation despite the water being at sub-zero temperatures. IR radiation may affect ice formation in different ways. These are suggested by X-ray diffraction measurements [13], the Mpemba effect (warm water freezes faster and earlier than cold one [14, 15], and direct IR effects on the crystallization of proteins [16].

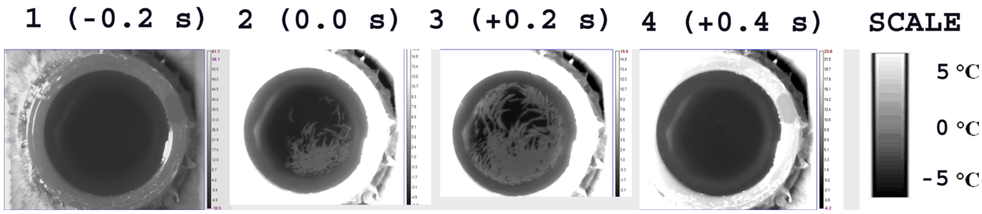

Fig. 6 Sequence of IR images taken at 0.2 s intervals from the upper surface of a 1-mm deep water layer that is cooled from the bottom inside a round copper dish (d = 20 mm). The right panel shows the gray-scale distribution of the IR irradiance plotted as equivalent temperature. The first frame shows the surface of liquid water at − 3.5 °C. The next two frames show the IR burst, which raised the temperature of the water surface to 1 °C. It is during this event that ice-like structures at the water surface appear transiently. This figure shows the synchronicity of IR emission and spongy ice formation. Shown is one example out of a series of 5 similar repetitions

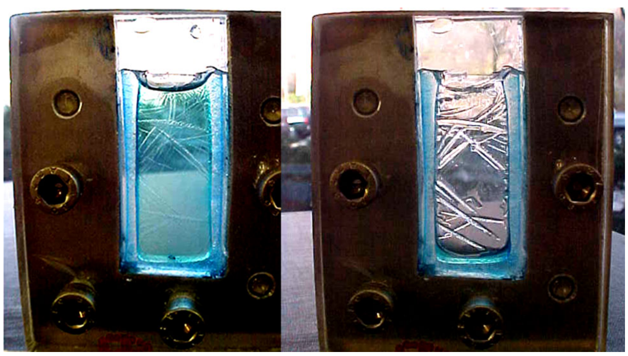

Fig. 7 Two images of freezing water inside a chamber with a u-shaped aluminum frame. When set in a freezer at − 36 °C, U-shaped solid ice columns were found next to the aluminum. Note, however, that the liquid bulk water between these ice columns is crisscrossed by dagger-shaped skeletal ice. While barely visible in the left panel, the right panel shows the skeletal ice after all liquid water had been decanted. Under this freezing regime, solid and liquid states of water coexist for many minutes. Shown is one example out of six similar series

3.7. The cause of the IR burst

Our conclusion that freezing involves separate events follows the logic of previous studies [8, 10]. A study of levitated droplets demonstrated two phases in the freezing process: a fast, stage-one freezing phase, and a 100-1000 times slower matrix solidification phase [4]. Since these distinct stages could not have arisen from nucleation points on the cooling surface, the two-step process appears as a general feature of freezing water. These findings confirm the classic result of Macklin and Ryan (1962; 1965) that bulk water freezes first in skeletal spears crossing through a bulk of liquid water and creating what is called spongy ice [10], stage-one ice [4], or dendritic ice [16]. A comparison of this rapid and transient stage-one phase of freezing [9] with the timing of the IR peak suggests that these early, rapid and transient events coincide.

There were three reasons for this suggestion. First, both features appear in the same short time window, and would therefore represent different aspects of the same process. A second argument for the association of the IR burst with spongy ice comes from the image of the IR-burst progression (Fig. 4, frame 3). The image shows leading-edge emanations that resemble the structure of spongy ice seen under polarized light (Fig. 5, frame 2). Third, those structures could be visualized by the reflection of an external IR beam at the water surface (Fig. 6). This allowed us to see their transient appearance at just the same moment as the IR burst.

3.8. Is spongy ice always short-lived?

Under the conditions of the previously discussed experiments, the spongy-ice needles vanished within 0.5 s of their appearance. However, with lower temperatures, conditions seem to exist under which the feathery ice can survive and grow. Such ice has been found to survive in freezing containers and water pipes, where they can cause a blockage and destruction [17, 18]. We also observed a surviving form of spongy ice when we cooled water in a rectangular chamber inside a freezer set at − 30 °C (Fig. 7). Under these conditions, solid and liquid states of water appeared to coexist until solidification had been completed.

3.9. Implication for the freezing mechanism

Dendritic ice may have implication for biology as well. Multiple freezing-induced IR bursts were found to occur in animal and plant tissues [3, 5]. The association of IR emission with the formation of dendritic ice provides reason to test for potential effects and possible damage by this rapidly advancing and disappearing ice type. At the least, one should test whether feathery ice formation is one of the unexplored factors encountered in the cryopreservation of cells and tissues [19].

The current study strongly supports the view that the phase transition from water to ice involves multiple steps [3, 4, 8, 10]. First, the water supercools to well below 0 °C without noticeable change; then, there is an explosive formation of feathery ice that has the speed to potentially take over the entire bulk volume.

The build-up of this ice type releases latent heat in the form of a rapid IR burst, which sometimes results in its own self-destruction by rapid melting (Figs. 5, 6). The released IR readjusts the temperature of the liquid bulk water right back to where it had had been some time before this event. This newly liquid water, however, may differ from the water before the burst. Although at a similar temperature, the water molecules have less kinetic energy [20], and are now in a state that readily and irreversibly converts to ice, which could be due to created nucleation sites and/or exposure to IR. This state could be tested by various spectroscopic methods [6, 20–22].

By contrast, a recently-proposed two-stage freezing process suggests the formation of a zone of ordered water as the first step, followed by the subsequent conversion into solid ice [23]. Evidence shows that these two stages appear as well during the melting of ice [22]. Many features of the findings reported here fit this proposed ice-formation mechanism: the "feathery ice" may be the same as the ordered (crystalline) water; the sharp IR burst may arise from the massive proton displacement required to initiate ice formation; and, solid-ice formation finally occurs from subtle shifts of structure, which should have little or no consequence for IR emission.

4. Conclusions

IR images confirm that the freezing of supercooled water involves at least two stages. The first stage was the heat release, which produced a distinct peak of IR emission. It preceded the start of ice lattice formation by more than a second, its completion by 12 s. The peak coincided, however, with the short-lived appearance of dendritic needles inside a spongy ice mixture. Depending on the cooling regime, this ice form can rapidly melt or survive.

References

[1] T Takahashi *J. Atmos. Sci.* **35** 1536 (1978).

[2] P Mazur *Science* **168** 939 (1970)

[3] M S Brown, E S B Pereira, B J Finkle *Plant Physiol.* **53** 709 (1974)

[4] Bauerecker, P Ulbig, V Buch, L Vrbka, P Jungwirth *J. Phys. Chem.* **C 112** 7631 (2008)

[5] D B Idle *Ann. Bot.* **30** 199 (1966).

[6] V F Petrenko, R W Whitworth *Physics of ice* (London: Oxford University Press) (1999).

[7] B M Weckhuysen *Chem. Soc. Rev.* **39** 4802 (2010).

[8] W C Macklin, B F Ryan *J. Atmos. Sci.* **22** 452 (1965) https://journals.ametsoc.org/doi/pdf/https://doi.org/10.1175/1520-0469(1965)022%3c0452:tsoigi%e2.0.co%382

[9] Y Furukawa, W Shimada *J. Cryst. Growth* **1128** 234 (1993)

[10] W C Macklin, B F Ryan (1962) *Q. J. R. Meteorol. Soc.* **88(378)** 548 (1962)

[11] J Palca J Scientists keep water below zero liquid far below zero degree. *NPR, Science*, Morning Edition, Article #1233376191(2010)

[12] Fuller, M P, Wisniewski, M (1998) *J. Therm. Biol.* **23**: 81 (1998)

[13] S Shimokawa, T Yokono, T Mizuno, H Tamura, T Erata, T Araiso (2004) *Jpn. J. Appl. Phys.* **43** L545 (2004).

[14] J D Brownridge (2011) *Am. J. Phys.* **79** 78 (2011)

[15] Y Tao, W Zou, J Jia, W Li, D Cremer *J. Chem. Theory Comput.* **13** 55 (2017)

[16] M Kowacs, M Marchel, L Juknaite, J M S Esperanca, M R Romao, A L Carvalho, L P Rebelo (2017) *J. Cryst. Growth* **457** 362 (2017)

[17] R R Gilpin *Int. J. Heat Mass Transf.* **20(6)** 693 (1977) https://doi.org/10.1016/0017-9310(77)90057-6.

[18] J J M Guzman, S L Braga *Int. J. Thermophys.* (2005) **26** 1781.(2005). https://doi.org/10.1007/s10765-005-8596-1.

[19] D E Pegg *Methods Mol. Biol.* **368** 39 (2007)

[20] T G Nunes, E W Randall, G Guillot *Solid State Nuclear Magn. Reson.* **32** 59 (2007)

[21] A A Shibkov, Y I Golovin, M A Zheltov, A A Korolev, AA Leonov *J. Cryst. Growth* **236** 434 (2002)

[22] E So, R Stahlberg, G H Pollack (*eds.*) D W Pepper and C A Brebbia *Water Soc.,* p 3 (2012)

[23] G H Pollack *The Fourth Phase of Water: Beyond Solid, Liquid and Vapor* (USA, Seattle: Ebner & Sons) p 135 (2013) www.ebnerandsons.com.