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Frozen waterfall and a video of supercooled water turning into frazil ice

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Abstract

In early January 2018, after days of subfreezing temperatures, a 20-metre waterfall became mostly frozen with supercooled water pouring over the top of the frozen parts of the fall. A video was taken of the waterfalls and supercooled turbulent water flowing on the frozen surface as it turned into frazil ice right before our eyes. Frazil ice consists of random crystal orientations and can be considered as a quasi-solid substance, a slush. The majestic *Looking Glass Falls* is located in Pisgah National Forest, Transylvania County, in western North Carolina, USA. One of the authors (CC) made the trip in very adverse weather of -15 °C to take the video of turbulent supercooled water flowing and turning into frazil slush ice. For background material and context, an interesting chart of metastable water states, which includes supercooled water, is compared to the stable states of water with which students are familiar. Nucleation is briefly discussed so students can understand how supercooled water crystallises. Finally, a discussion of danger is included with video footage of a young lady being rescued after she fell in up to her waist.

Introduction

Water is an extremely important substance discussed in all natural science courses. Its properties have been extensively studied and continue to be the subject of research. To appreciate the wealth of

publications on water science, see the more than 4,000 references compiled by Martin Chaplin, a Chartered Chemist of the Royal Society of Chemistry [1]. One fascinating property of water known for centuries was rediscovered by Erasto B Mpemba, a high-school student in Tanzania, and published in this journal in 1969 [2]. He observed that hot milk froze faster than cold milk in making ice cream one day. He had skipped the usual cooling to room temperature after boiling so he could get the last available ice-tray [2]. This observation led to the paper in *Physics Education* on the freezing of water [2]. The phenomenon that there are occasions when hot water freezes faster than cold water¹ is called the Mpemba Effect [1]. The story also has a moral since the high-school teacher's response to Mpemba's insistence that hot milk freezes first was: 'Well, all I can say is that that is Mpemba's physics and not the universal physics' [2]. The high-school teacher was later proven wrong; Mpemba's physics is the 'universal physics'. Mpemba was taken seriously by the British physicist and later diplomat, Professor Denis Gordon Osborne [3], who was then teaching at the University of Dar es Salaam in Tanzania and invited as a guest speaker to Mpemba's high school one day [2]. Osborne listened attentively to Mpemba's experimental observations, had lab work done, and published with Mpemba in *Physics Education* [2].

Auerbach points out that though the Mpemba effect was 'first recorded in school and higher educational journals in recent times, the Mpemba effect was born with Aristotle, grew up with Bacon and Descartes, and has been recorded and discussed in both research journals as well as popular scientific journals' [4]. Auerbach gives an analysis of the Mpemba effect within the context of supercooling, the latter being the subject of this paper. Supercooling is another fascinating property of water and discussed in the next section.

¹ Years of ago one of the authors (MJR) found his freezing hot water pipes bursting before the cold water pipes when his house lost its heating during a winter storm.

Supercooling and the metastable states of water

Water exists in its stable form between 0 °C and 100 °C. Usually, below 0 °C water becomes ice (a solid) and above 100 °C water becomes vapour (a gas). However, in 1721 Fahrenheit discovered that water can exist in liquid form below the 0 °C freezing point [5] in a supercooled state. The supercooled water is in a thermodynamic metastable state, one that is stable under small disturbances but unstable 'when the disturbance exceeds a certain magnitude' [6]. Supercooled water freezes when molecules start 'to join together to form a solidification nucleus to which other molecules can be added,' a process called nucleation [7]. However, significant uniform homogeneous nucleation requires temperatures near -40 °C [8]. For ice formation at typical weather freezing temperatures the nucleation process is initiated by impurity particles in the liquid, heterogeneous nucleation [8].

The stable forms of H₂O are shown in figure 1a. These forms are the usual ones students encounter in introductory science: ice (solid); water (liquid); and steam (gas). However, water can exist in metastable forms such as the supercooled state discovered by Fahrenheit. Figure 1b indicates all forms of amorphous (liquid) water, both stable and metastable. Figure 1b is adapted from figures credited to Osamu Mishima [9-13] and used with permission from Mishima. At the highest-temperature end water can exist above 100 °C in a superheated metastable state. The upper limit for superheated liquid water is roughly 553 K [280 °C] at atmospheric pressure [11]. The well-known stable region of water is bounded by the temperatures 0 °C and 100 °C.

From 0 °C to -40 °C water can exist in the metastable supercooled state. The limit of approximately -40 °C 'below which pure liquid water cannot be subcooled ... is sometimes called the *Schaefer point* to honor Vincent Schaefer, who first established this temperature experimentally' [14] in the 20th century. 'Below the Schaefer point, pure water freezes by *homogeneous nucleation* of the ice phase' [14]. Beyond the approximate -40 °C barrier 'is a "no man's land" where water exists only in the

solid, crystalline phase' [10]. However, in this 'no man's land' water may briefly exist as liquid just before crystallisation occurs.

Below the crystallisation region lies a relatively narrow region of 'presumably highly viscous water' [11] and finally the lowest region of 'low-density amorphous ice (LDA)' [13]. Amorphous ice lacks the crystallisation of a solid and therefore can change 'shape over very long time periods, like decades. They are a type of glass, and glasses are really more like frozen liquids.' [15]. See reference 12 for a more general version of figure 1b that includes higher pressures and a high-density amorphous (HDA) ice state.

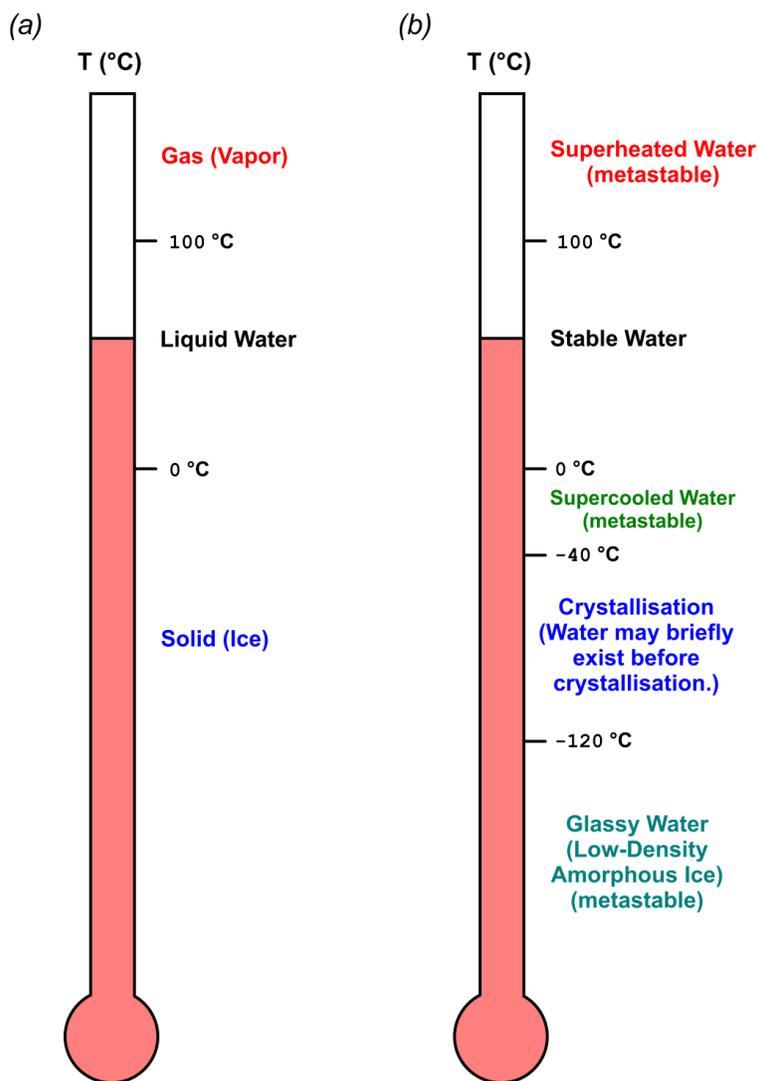


Figure 1. (a) At atmospheric pressure, the stable forms of H₂O as solid, liquid, and gas. (b) The amorphous (liquid) forms of water, both stable and metastable with approximate temperatures, adapted from figures [9-13] credited to Osamu Mishima. The authors have received permission from Mishima to adapt his figures.

Supercooled water and frazil ice

In January 2018, residents in western North Carolina, USA experienced eight days of freezing temperatures, one of the longest stretches of 'dangerously cold weather on record' [16]. One of the authors (CC) visited a nearby waterfall during the freezing cold spell and shot some video. The waterfall was Looking Glass Falls in Pisgah National Forest, Transylvania County, North Carolina, USA, with a waterfall drop of 18 metres. At the weather station in Brevard, roughly 7 kilometres from the Waterfalls, from 4 January 2018 through 7 January 2018 temperatures at midnight were recorded between -15 °C and -10 °C. The temperatures dropped even further until the morning daylight appeared. Then, temperatures climbed, reaching about 1 °C from noon to 3 pm. Later in the day the temperatures dropped back down for the cycle to repeat [17]. A plot of temperature data [17] against hours since midnight on the day the video was shot (7 January 2018) is shown in figure 2.

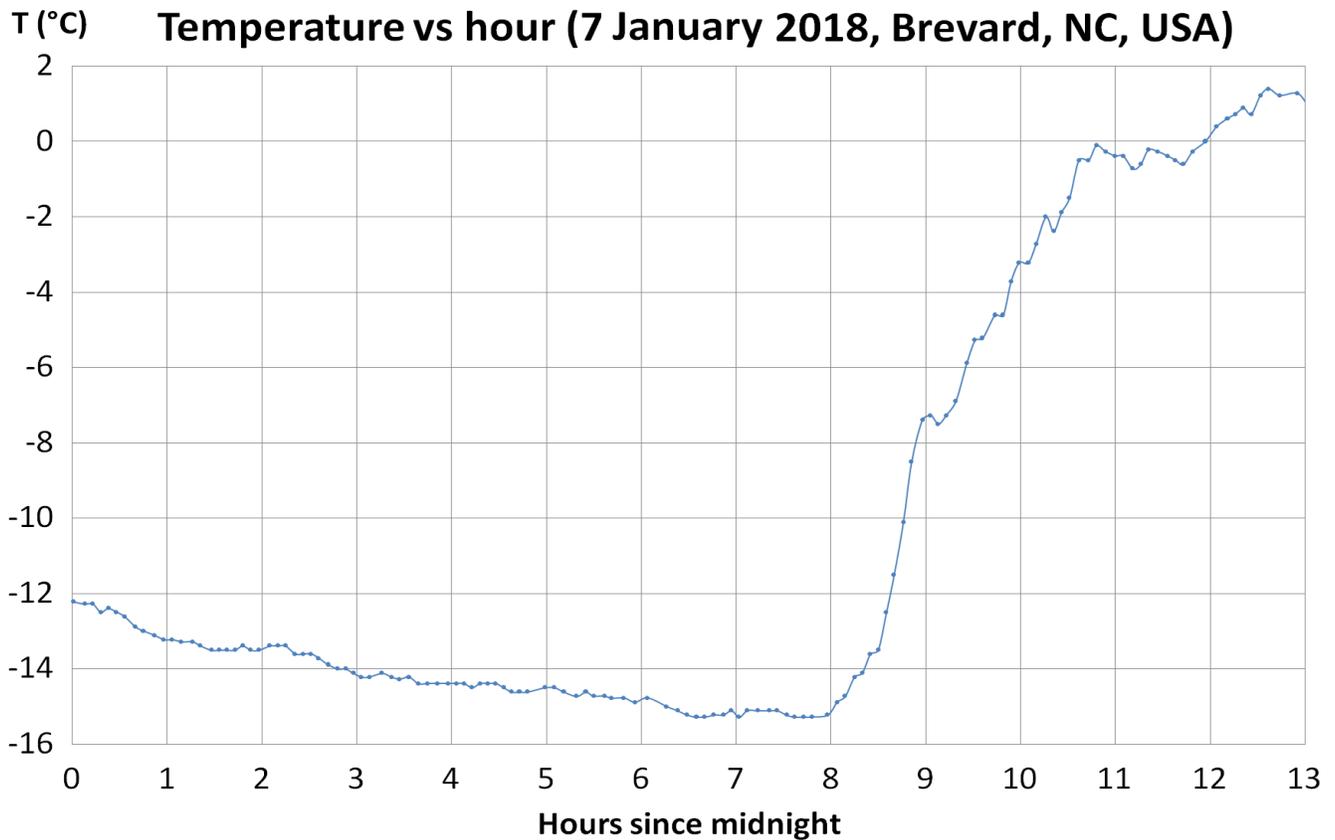


Figure 2. A plot of temperature against hours since midnight in Brevard, NC, USA on 7 January 2018.

The several days of freezing temperatures caused most of the waterfall and water below the falls to freeze. The reader can watch our video abstract [18] and the full version of the frozen waterfalls video [19].

See figure 3 for a photo of Looking Glass Falls taken in 20 °C weather (a) and the frozen waterfall in -15 °C temperature. Note the significant accumulation of snow and ice raising up to about halfway on the left side of the roughly 20-metre falls in figure 3a. In figure 3a the full 20 metres from the top to the bottom can be seen in the warm weather. Also note the accumulated breadth of ice in figure 3b as the water navigated other pathways when encountering ice.

(a)



(b)



Figure 3. (a) Looking Glass Falls (18 metres) at about 20 °C. Photo Credit: Co-author Michael Ruiz. (b) Looking Glass Falls at about -15 °C. Photo Credit: Co-author Charles Cranford.

During the freezing weather, water was still flowing, water that was supercooled due to the days with temperatures below freezing. As the flowing water reached the surface of ice, it moved along a stream-like path with portions turning to ice as it flowed. Our videos are easily accessed by the links [18, 19] provided to that teachers and students can witness the freezing of water before their very eyes. The frozen result is called frazil ice. See figure 4 for a screenshot from our video taken at 7:30 am on 7 January 2018, when the temperature was -15 °C, as found on the graph in figure 2.

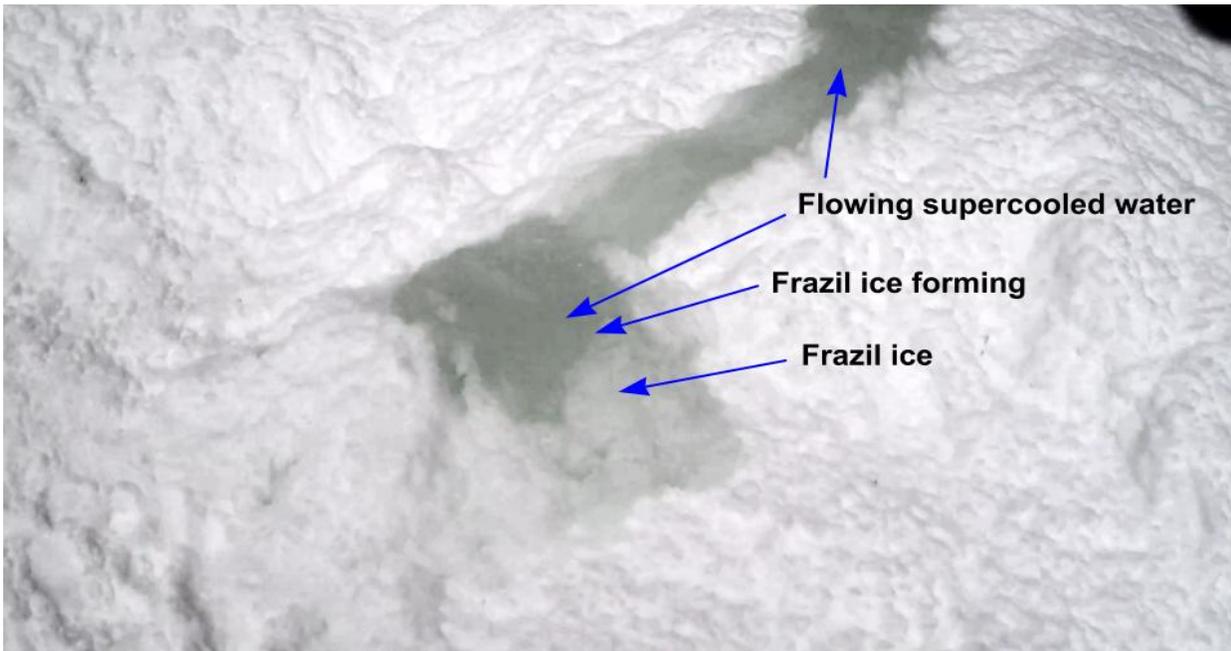


Figure 4. Supercooled water flowing where the ambient weather temperature is $-15\text{ }^{\circ}\text{C}$. There are sections of flowing supercooled water, water turning to frazil ice, and newly-formed frazil ice. Photo Credit: Co-author Charles Cranford.

Frazil ice is 'created and develops only in water that is turbulent' [20], illustrated in figure 4, a screenshot from our videos [18, 19]. The crystallisation of the frazil ice is initiated by nucleation as discussed earlier. The resulting crystal formation is random, making its texture a congealed slush [21]. Therefore, frazil can be considered a semi-solid. Frazil ice 'is observed to consist of roughly disk-shaped crystals' and research continues on the details of 'crystal nucleation' [22]. Frazil ice poses many environmental challenges and problems such as flooding, blocking 'water supply intakes,' interfering with hydroelectric power plants, and disrupting 'ship and barge transportation' [23].

Dangers and a young lady falling through gets rescued

Students should be advised not to try to take photos or videos of frazil ice formation due to several dangers. First, the necessary weather temperatures are subfreezing. Second, one can fall through frazil slush into ice-cold water on a lake. Even if the water is not very deep, coming into contact with ice water is extremely hazardous in a cold, outside environment. Third, if it is windy, the wind-chill factor brings the already-cold temperature even lower. One can easily get frostbite.

In the portion of our video taken later in the day, around 12:30 pm, you will see that a young lady had fallen into the mixture of snow, ice, and water. From the graph in figure 2, the temperature had risen to 1 °C by midday. Two gentlemen pulled her out eventually, but with some difficulty. At first, it looked like she wouldn't budge, so they used their hands to dig some of the ice away from her and give her some wiggle room. It took about three minutes to finally pull her out. The two guys lifted her by her arms and she wiggled her legs to free them from the ice. The rescuers, with trousers similar to those that firefighters wear, may indeed have been firefighters.

The ice was probably around 2 to 3 metres above the ground where the young lady fell in. Comparing the photos in figure 3, the ice near the falls itself on the left was about halfway or more up the 20-metre falls. The ice on the right was about a third of the way up. From the falls, the snow and ice sloped gradually away and down towards the stream. In warm weather, the pool on the side that the young lady fell through is usually only about 50 centimetres deep. However, in the freezing weather, the exact nature of the mix of snow, ice, and water beneath the surface is uncertain.

Co-author Cranford's right leg sunk into snow during his video shoot. Luckily, it was dry snow. He is an experienced camper and took proper precautions for dressing. That day he was wearing a wool base layer, cotton trousers, with a water resistant pair of cover trousers (similar to ski trousers that zip up the sides). He was also wearing wool socks and water-resistant hiking boots. Students should never attempt to put themselves in dangerously cold environments. They should consult with their teachers and camping experts for acquiring proper gear and supervision. Teachers and students are encouraged to consult references on staying safe on ice, e.g. the excellent safety pages posted by the British Swim School [24] and Nature Travels (Specialists for Outdoor & Adventure Holidays in the Nordic Countries) [25].

Conclusion

The fascinating properties of water existing in metastable liquid states were introduced as background information. Students may be aware of the stable states of water as depicted in figure 1(a). They will be surprised to learn that this stable diagram is not the whole story. Supercooling, shown in figure 1(b), is interesting in itself. The concept of nucleation in conjunction with supercooled water can lead to a discussion on the crystallisation of freezing. Crystallisation in frazil ice is random and the ice appears as a slush. Furthermore, frazil ice has many interdisciplinary connections. The science of frazil ice includes thermodynamics, condensed matter physics, atmospheric science, chemistry, environmental science, and engineering challenges to address problems that frazil ice can cause. Our short video abstract [18] of supercooled water turning into frazil slush will enhance student fascination with science. Our full video taken on that extremely cold, wintry morning can be watched on YouTube [19]. Students will find the videos fascinating and memorable.

Acknowledgements

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Charles Cranford is an outdoorsman who likes camping, hiking, canoeing, backpacking, cycling, and pretty much anything outdoors. His love of the outdoors was instilled by his father. He also likes taking things apart, sometimes with the intentions to put them back together, and sometimes not. Charles is American by birth and a naturalised Australian citizen.