

# When does hot water freeze faster than cold water? A search for the Mpemba effect

James D. Brownridge<sup>a)</sup>

*Department of Physics, Applied Physics, and Astronomy, State University of New York at Binghamton, P.O. Box 6000, Binghamton, New York 13902-6000*

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It is possible to consistently observe hot water freezing faster than cold water under certain conditions. All conditions except the initial temperature of water specimens must be the same and remain so during cooling, and the cold water must supercool to a temperature significantly lower than the temperature to which the hot water supercools. For hot water at an initial temperature of  $> \approx 80$  °C and cold water at  $< \approx 20$  °C, the cold water must supercool to a temperature of at least  $\approx 5.5$  °C, lower than the temperature to which hot water supercools. With these conditions satisfied, we observed initially hot water freezing before the initially cold water 28 times in 28 attempts. If the cold water does not supercool, it will freeze before the hot water because it always cools to 0 °C first regardless of the initial temperatures. © 2011 American Association of Physics Teachers.

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## I. INTRODUCTION

Two identical containers with the same amount of water at different temperatures are placed in a freezer, and the hot water freezes first. Did you observe the Mpemba effect?<sup>1</sup> Since around 300 BCE, the idea that hot water sometimes freezes before cold water has been studied and debated.<sup>2,3</sup> The reasons why hot water can freeze before cold water when all conditions are equal are still discussed in the popular and scientific literature.<sup>4-9</sup>

In 1948, Dorsey published data that suggest an answer to this question.<sup>10</sup> Although he did not specifically address the question, the answer is in his data, and my results have confirmed several of his findings. Key among them includes that “for each sample there are one or more preferred temperatures at which spontaneous freezing occurs” and “preheating the melt produces no certain effect upon it.”<sup>10</sup> In other words, if water in a sealed container is heated and then cooled again, it may freeze at a higher, lower, or the same temperature as it would have if it had not been heated. Heating a container of water does not ensure that it will freeze before a cold sample.

There is no generally accepted mechanism for the Mpemba effect. Jeng stated, “Because there are so many factors that can be varied and the results of the experiments can depend sensitively on any of these factors, experimental results are varied and difficult to organize into a consistent picture.”<sup>3</sup> An important factor is the characterization of freezing—is it the occurrence of the first ice crystal or is it when all the liquid is solid? Other factors include the position of the temperature-measuring device in the water (see Fig. 1), the type of container and its shape, and the possible loss of water by evaporation. Are all conditions except the initial temperature identical and remain so during cooling? Does a hot container cause a change in the cooling rate?

The aim of this paper is to address each of these factors and questions and identify the conditions under which hot water freezes before cold water. Because the question of why hot water sometime freezes faster than cold water has remained unanswered for over 2000 years, we will describe in detail the experiments that led to the identification of the conditions under which hot water freezes before cold water.

A primary reason why researchers have not been able to

obtain reproducible results is because the position of the temperature-measuring device is critical to an accurate determination of when all of the water in a container is frozen. Imagine that we have combined the results from many laboratories in which everything was identical except for the positions of the thermocouples in the containers of water, and we had agreed that when the temperature reached  $-4$  °C, we would consider the water frozen (see Fig. 1). In this case, each laboratory would likely report a different time of freezing. These differences were a major barrier in obtaining reproducible results during the early phase of this study, and I suggest that it is a universal problem. A difference in position of only a few millimeters can be significant. The time to complete solidification varies with the depth of supercooling.

To avoid this problem, we will define the time of freezing as the time when the latent heat of freezing is released. An abrupt change in the temperature of the water signals that latent heat has been released. Small volumes of very pure water with no foreign particles in it can be supercooled to as low as  $\approx -41$  °C,<sup>11</sup> at this temperature, it is homogeneous nucleation that initiates freezing.<sup>11,12</sup> Hereafter, we will refer to foreign particles as “ice nucleation sites.”

If drinking water is placed in a subzero environment and not disturbed, it will usually not freeze when its temperature falls to 0 °C. It will supercool to below 0 °C before heterogeneous nucleation initiates freezing.<sup>11</sup> When freezing is initiated by heterogeneous nucleation, the water will not freeze until its temperature falls to what we call the “ice nucleation temperature.” We define the latter as the temperature at which latent heat is released. This temperature varies from sample to sample and may vary for the same sample. Our experiments show that many foreign particles are present in every sample of water and that the temperature at which a particular foreign particle initiates heterogeneous nucleation may be at any temperature between 0 and  $\approx -25$  °C. None of the water samples we used supercooled below  $\approx -25$  °C.

## II. DATA ACQUISITION

The apparatus consisted of one Omega OMB-DAQ-3000 Series 1-MHz, 16-bit USB Data Acquisition module, two National Instruments PIC-6034E interface cards configured to accept eight Type K thermocouples each, two PASCO

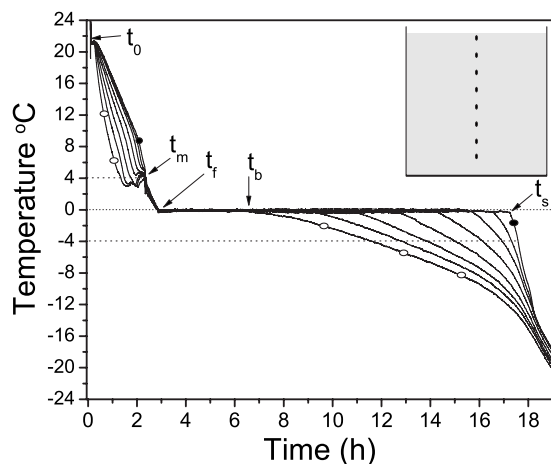


Fig. 1. Illustration of the importance of the position of the temperature-measuring device to accurately determine the time it takes for the water to completely freeze. The curve with the solid circles represents the temperature at the top of the container and the curve with the open circles represents the temperature at the bottom of the container. The unlabeled curves show the temperature gradient from bottom to top as the water cools from time  $t_0$  and then freezes to solid ice. At time  $t_m$ , the water has cooled to  $\approx 4^\circ\text{C}$ , the temperature of maximum density, and all eight thermocouples show that the water in the container is at a uniform temperature for the first time since cooling began. The water remains at uniform temperature until solid ice begins to form at the bottom of the container at time  $t_b \approx 7$  h. Latent heat was released after time  $t_f \approx 3$  h. If we had used only one thermocouple near the bottom, we would have erroneously concluded that the water had frozen at time  $t_b$ . The water did not completely become solid until time  $t_s \approx 17$  h after cooling began. The correct location for a single temperature-measuring device is just below the surface of the water in the center of the container as depicted in the inset.

Xplorer GLX with eight temperature probes, two Keithley Instrument Model 155 Null Detector micro voltmeters, three freezers, and a Lauda RM6-RMS Brinkmann Refrigerating Circulating Bath. The temperature and time data were recorded by a computer usually at a rate of 1 Hz but more slowly for cooling rates less than  $1^\circ\text{C}/\text{min}$ . We collected data for several thousand freeze/thaw cycles because it took this many cycles to discover all of the factors that could and did go wrong and to design a set of experiments that met our objectives.

### III. DOES HEATING WATER CAUSE IT TO FREEZE FASTER?

To answer this question we flame-sealed 1 ml of distilled water in a small Pyrex test tube, hereafter referred to as a vial. A type K thermocouple was affixed with epoxy to the outside of the vial below the water line. The vial was suspended in the center of a copper box that was affixed to a thermoelectric heater/cooler inside a vacuum chamber (see Fig. 2), which was pumped to less than 1 mTorr. The vial was supported by the thermocouple wires and was heated and cooled by radiation. The side of the thermoelectric heater/cooler in contact with the copper box was heated or cooled depending on the polarity of the applied voltage. The idea was to heat and cool the vial and water without contact or physical disturbance.

The data in Fig. 3 were collected from a single sample of de-ionized, distilled water that was randomly heated to temperatures between  $\approx 8$  and  $\approx 103^\circ\text{C}$  and then cooled until it froze. This cycle was performed 138 times without disturb-

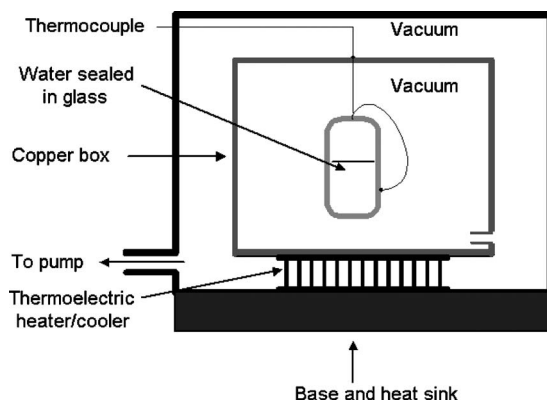


Fig. 2. Apparatus used to measure the time to freeze.

ing the vial. The mean freezing temperature was  $-11.80 \pm 0.17^\circ\text{C}$ , with a maximum freezing temperature of  $-11.2 \pm 0.4^\circ\text{C}$  and a minimum of  $-12.8 \pm 0.1^\circ\text{C}$ . Heating this sample of water did not reduce the time of freezing. The hotter the water, the longer it took to cool to  $0^\circ\text{C}$  and ultimately freeze from a supercooled state. This experiment was repeated in a completely different setup using hard tap water, and no Mpemba effect was observed. These data show that each sample of water had a narrow range of ice nucleation temperatures—the temperature at which latent heat was released. The mean ice nucleation temperature of  $-11.80 \pm 0.17^\circ\text{C}$  was unaffected by heating the water to a temperature of  $\approx 103^\circ\text{C}$  as was done 18 times out of the 138 freeze/thaw cycles. We conclude that heating water does not cause it to freeze faster.

### IV. WHY HOT WATER MAY SOMETIMES FREEZE FASTER

In some cases, hot water freezes sooner because of the higher thermal conductivity between the water container and the surface of the subzero environment. Two identical copper cups were placed in a freezer on a bed of frost. The hot cup caused the frost underneath it to melt forming a pool of liquid water that soon froze. The cooling conditions were

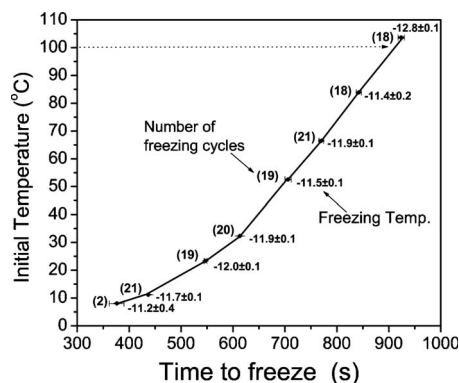


Fig. 3. Initial temperature of de-ionized, distilled water versus the time to freezing for 138 freeze/thaw cycles of the same water sample. The temperature and time were recorded every second until the latent heat of freezing was released. The lines connecting the data points are a guide to the eye. The error bars represent standard errors. The numbers in parentheses represent the number of freezing cycles. The mean ice nucleation temperature of this water sample was  $-11.80 \pm 0.17^\circ\text{C}$ .

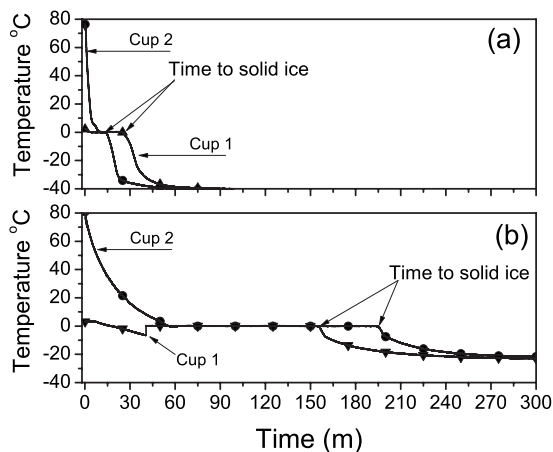


Fig. 4. The dramatic difference in the cooling rates when (a) cup 2, a cup of hot tap water, and cup 1, a cup of cold tap water, are placed in a freezer on a bed of freezer frost. In (b), the same two cups are placed on an insulator and then put into the same freezer on the same bed of freezer frost. When the cups were on an insulator, the cold water froze solid first.

changed because the thermal conductivity of water is higher than ice and the thermal conductivity of ice is higher than freezer frost. Hence, the hot water container was in better thermal contact with the freezer floor, which caused energy to be transferred from the hot water container to the freezer at a faster rate. For this reason, the hot water froze first, as shown in Fig. 4(a), where the hot water froze about 15 min before the cold water. This result is not an example of the Mpemba effect because the cooling conditions were not identical. If we prevent the hot water container from melting more frost than the cold water container, we should be able to maintain nearly identical conditions for the two containers. In Fig. 4(b), we show the results when the two containers were placed on an insulator rather than directly on the frost; in this case, the initially cold water froze first.

### V. DOES HEATING WATER CAUSE IT TO COOL FASTER?

To determine if heating water causes it to cool faster, two hot and two cold samples of hard tap water from the same source were placed in a subzero environment. The four samples were held in separate compartments of a copper container. The container had a mass of 400 g, far exceeding the 48 g of water it held, and was made of oxygen-free, highly thermally conducting copper. Four shallow holes were milled into the solid copper. Type K thermocouples were positioned in the center of each hole to record the temperature near the surface of the water. A copper lid covered the water to prevent ice crystals from falling into the water and initiating spontaneous freezing at 0 °C. Fresh water was added to the four holes for each freeze cycle to ensure that each run had the same initial volume of water. The experiment was repeated many times over several weeks. In Fig. 5, we show typical results. The temperature of the cool water initially rises as the temperature of the hot water falls. Once all four samples reach thermal equilibrium with the container, they cooled to 0 °C at the same rate.

We conclude that the time to cool to 0 °C is the same for hot and cool water when all other conditions are the same. Heating water does not cause it to cool to 0 °C faster than

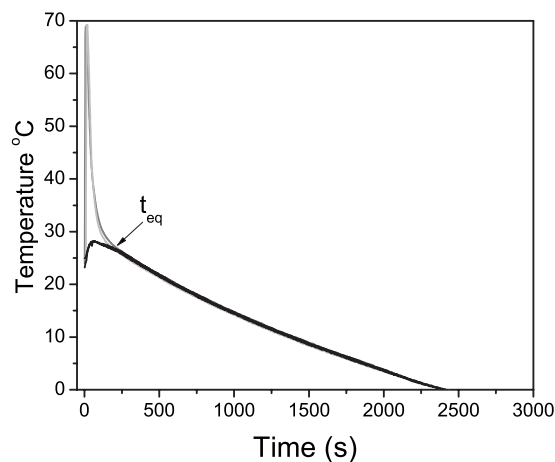


Fig. 5. The temperature versus time for four samples of tap water. Two samples were initially at  $\approx 69$  °C (gray curves) and two were initially at  $\approx 23$  °C (black curves). All conditions were identical, except for the initial temperatures. The hot and cool water initially cool at different rates, but after they reached thermal equilibrium with the copper container at  $t_{eq}$ , all four cooled at the same rate. Heating water does not cause it to cool to 0 °C faster. When cooling conditions are identical, the cooling curves are identical and superimposed on each other.

cool water. We saw no difference between soft water, hard water, very hard water, or de-ionized distilled water. They all cooled at the same rate once they were in thermal equilibrium with the copper container.

### VI. THE EFFECT OF SOLUTES, MINERALS, GASES, AND SUGARED MILK

We have shown that when all conditions except the initial temperature are equal, hot water will not cool to 0 °C before cold water. It has been proposed that heating hard water changes its properties in ways that could cause it to freeze before unheated water.<sup>4</sup> To test this hypothesis, we placed four samples of hard well water from the same source into the cooling chambers used to collect the data, as shown in Fig. 5. Prior to adding equal volumes of water to each chamber, the water was divided equally into two containers. One was boiled until its original volume was reduced by about 50%. Then, an equal volume of water was added to each chamber. The purpose of boiling was to induce a chemical reaction that produces calcium bicarbonate and remove dissolved gases. Both factors are believed to play a role in hot water freezing faster than cold water.<sup>3,4,11,12</sup> We saw no difference in the cooling rates after thermal equilibrium was achieved at time  $t_{eq}$  between the water and the container for any of the samples to reach 0 °C (see Fig. 5).

The rate of cooling of water with high concentrations of minerals such as calcium bicarbonate (hard water) was likewise not affected by heating the water, as seen in Fig. 5. We also determined that dissolved CO<sub>2</sub> in water does not affect the cooling rate or the time to freeze. To confirm that the equipment was sensitive to subtle differences such as the presence of CO<sub>2</sub>, calcium bicarbonate, or mixing, we removed 0.3 ml of water and then added 0.3 ml heavy water (D<sub>2</sub>O) to two 12 ml samples of water. All four chambers had equal volumes of water. We stirred one of the heavy water samples to ensure that the D<sub>2</sub>O was well mixed in the water. The other was not stirred, thus leaving the D<sub>2</sub>O not evenly

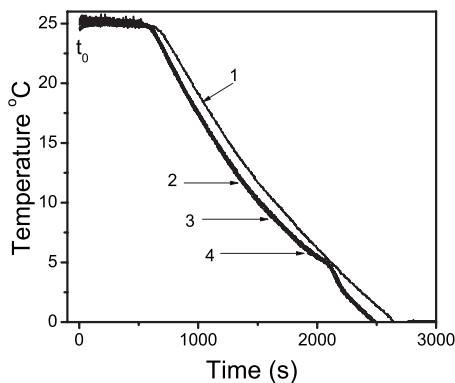


Fig. 6. Although the cooling conditions may be identical, the cooling rate of water can be changed by a slight change in the nature of the water. Just prior to time  $t_0$ , 12 ml of water from the same source was added to each of the four chambers of the 400 g copper container. Then 0.3 ml of water was removed from chambers 1 and 2 and replaced with 0.3 ml of heavy water. Chamber 1 was not stirred, and chamber 2 was. The other two, chambers 3 and 4, served as controls. Notice that the cooling curves of chambers 2–4 reached 0 °C at the same time (2500 s), and chamber 1 with unmixed heavy water reached 0 °C in 2640 s. There was a clear difference in the time it took equal volumes of water cooling under identical conditions to cool to 0 °C. The only difference was not stirring and therefore not having a homogeneous mixture of heavy water in light water in chamber 1.

mixed in the water. It has been shown that unstirred water with added  $D_2O$  cools at a slower rate than water that was thoroughly mixed with the same amount of added  $D_2O$ .<sup>13</sup> Milk-sugar mixtures (the essence of ice cream) also cools to 0 °C at a slower rate than water. A typical result of these experiments is presented in Fig. 6 and shows that a subtle change in cooling rate was detectable and the unmixed heavy water reached 0 °C more slowly.

## VII. EVAPORATION AND ORTHR VARIABLES

We investigated the effect of evaporation by flame-sealing 5 ml samples of water in six Pyrex test tubes. Three contained tap water, and three contained de-ionized, distilled water. The intent was to reduce the number of variables and to cool six vials at the same time in the same environment. The vials were not in contact with each other, and air was used as the cooling medium. The holder and vials were placed into and removed from the freezer at the same time. Care was taken not to shake or otherwise agitate the vials, except when that was the object of an experiment. The freeze/thaw cycle was repeated several times per day over many weeks. With this arrangement, the vials could be shaken, heated, or turned upside down to possibly affect the ice nucleation temperature.

The first objective was to determine the temperature at which latent heat is released in each vial. The ice nucleation temperature was extracted from the cooling curves as the lowest temperature recorded before the temperature of the supercooled water began to increase. The vials were cycled through 27 freeze/thaw cycles to determine the ice nucleation temperatures. The results from each vial are presented in Fig. 7. Note that the ice nucleation temperatures of the water in each vial range from  $-8.3 \pm 0.1$  to  $-14.4 \pm .01$  °C for the first 27 freeze/thaw cycles. After 5 min of vigorous shaking, there were no significant changes in these samples. In Fig. 7, vigorous shaking took place between times  $t_1$  and  $t_2$ . In other samples, we observed major changes produced by

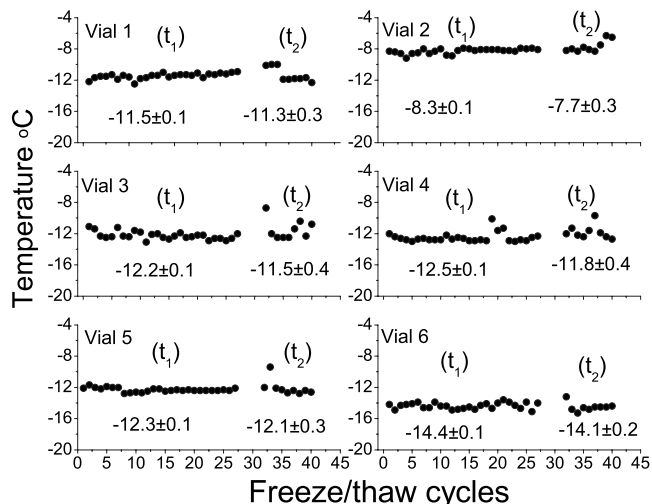


Fig. 7. Vigorously shaking water in a glass vial does not change the ice nucleation temperature.  $t_1$  denotes the data points corresponding to the first 27 freeze cycles, and  $t_2$  denotes the data from the nine freeze cycles performed after the vials were vigorously shaken for 5 min. The numbers under each set of data points are the mean temperatures and the standard errors at which latent heat was released. The water in each vial was collected at the same time from the same source, yet each specimen had a unique ice nucleation temperature that varied from  $-8.3$  °C (vial 2) to  $-14.4$  °C (vial 6) for 27 consecutive freeze/thaw cycles. If vial 2 were initially hot, it would freeze before an initial cold vial, vial 6, because it would cool to  $-8.3$  °C before vial 6 cooled to  $-14.4$  °C.

shaking. When shaking causes the ice nucleation temperature to change significantly, it was difficult to obtain the kind reproducible results shown in Fig. 7 from freeze cycle to freeze cycle. It is unknown why shaking will sometime cause a change in the ice nucleation temperature. Heating can also cause the ice nucleation temperature to change as shown in Fig. 8, where sample (a) was heated after the first set of freeze/thaw cycles and (b) was not. Notice that in this case, heating this sample to  $\approx 100$  °C caused the ice nucleation temperature to change from  $\approx -6$  °C in (a), set 1, to  $-11$  °C at (a), set 4. There was no change in the ice nucleation temperature in the control [Fig. 8(b)] between set 1 and set 5. The water in the control was not heated, and therefore its ice nucleation temperature did not change. Between sets 5 and 6, the control sample was replaced with new water, and the ice nucleation temperature changed.

## VIII. NUCLEATION SITES WITH HIGH ICE NUCLEATION TEMPERATURES

It is well known that biological materials are involved in the freezing of water in the atmosphere.<sup>14</sup> We collected fresh snow and let it melt at room temperature to obtain water with ice nucleation sites in it. The intent of this experiment was to test the hypothesis that the ice nucleation temperature can be changed by heating.

Fourteen screw-cap vials were placed into a plastic vial holder that allowed us to change several variables in addition to the temperature. Snow water, tap water, de-ionized water, and distilled water were used. Some vials were heated, while some were left unheated as controls. To produce the typical data shown in Fig. 8, 10 ml samples of fresh snow water was added to six vials. Vials 1, 3, and 5 were the test vials, and vials 2, 4, and 6 were controls and were not opened or heated



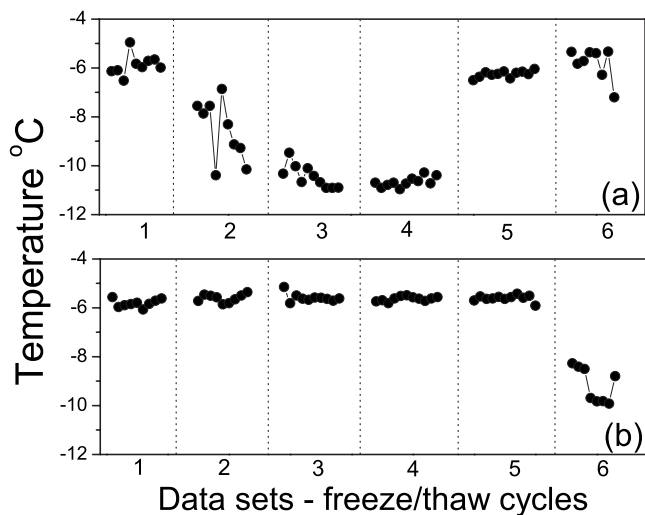


Fig. 8. A typical example of how heating water can change its ice nucleation temperature. (a) Test water and (b) a vial of the same water that serves as a control. After cycling both samples through nine freeze/thaw cycles (set 1), we heated the test water to  $\approx 100^\circ\text{C}$  and then cycled both vials through nine additional freeze/thaw cycles (set 2). This process was repeated twice more, giving sets 3 and 4. Notice that the average temperature at which the control sample froze did not change between freeze/thaw cycles 1 and 5, while the test sample temperature changed from  $\approx -6$  to  $\approx -11^\circ\text{C}$ . At the end of set 4, we opened the test water and added fresh ice nucleation sites from the original stock of snow water, and the ice nucleation temperature was returned to  $\approx -6^\circ\text{C}$ . At the end of set 5 for the control sample, we removed the snow water and added distilled water. Notice that the ice nucleation temperature fell to  $\approx -10^\circ\text{C}$ . This set of experiments demonstrates that the ice nucleation sites were in the water.

for the first five experiments. Each experiment consisted of nine or more freeze/thaw cycles over several days. Was the mean ice nucleation temperatures changed by heating, and if so, can they be restored by adding ice nucleation sites from the original stock of snow water? All six vials were initially put through nine freeze/thaw cycles; a typical result is presented in Fig. 8, data set 1. Between data sets 1 and 2 in Fig. 8(a), the test vial was placed in a bath of boiling water for 1 h and then allowed to return to room temperature, after which both vials were cycled nine more times; see data set 2. The result was a decrease in the ice nucleation temperature from  $\approx -6^\circ\text{C}$  to a mean of  $\approx -9^\circ\text{C}$ . This process was repeated two more times. The data are presented in Fig. 8, data sets 3 and 4. Between data sets 4 and 5, the test vial was opened, 0.5 ml of water was removed, and 0.5 ml of snow water from the original stock was added. After the addition of unheated snow water, the ice nucleation temperature was returned to the original ice nucleation temperature of  $\approx -6^\circ\text{C}$ , Fig. 8(a), data set 5.

Between data sets 5 and 6 in Fig. 8(a), the vial was opened and the water was temporarily removed and returned to the same vial. The purpose was to determine if removing the water from the vial would change the ice nucleation temperature. Following this action, the ice nucleation temperature was more variable, but its mean was not significantly changed. This result is consistent with changes that shaking sometime produces. Why shaking or pouring water sometimes causes a change in the nucleation temperature is unknown. At this time, the control vial in Fig. 8(b) was disturbed for the first time between data sets 5 and 6. The snow water was removed, and 10 ml of de-ionized water was

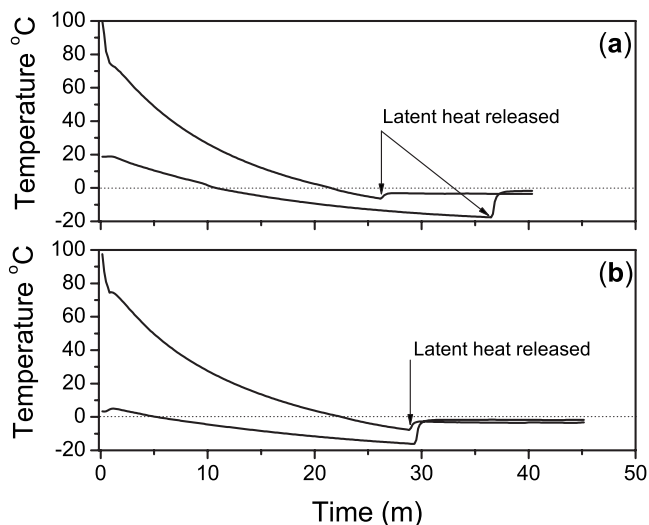


Fig. 9. Examples of water initially at  $\approx 100^\circ\text{C}$  that freezes before water initially at  $\approx 20^\circ\text{C}$  as well as water initially below  $5^\circ\text{C}$ . Notice the time difference between the release of latent heat of freezing in (a) was  $\approx 10$  min and in (b) was  $< 1$  min. The cold water in (b) was  $\approx 15^\circ\text{C}$  closer to its ice nucleation temperature, and therefore it took less time to cool to its nucleation temperature. If the cold water's ice nucleation temperature in (b) had been  $\approx -15.2^\circ\text{C}$  rather than  $\approx -16.2^\circ\text{C}$ , it would have frozen first and the Mpemba effect would not have been observed. The ice nucleation temperature of the hot water in (b) was  $\approx -7.8^\circ\text{C}$ . The Mpemba effect occurs only when the initial hot water cools to its ice nucleation temperature before the initial cold water does. In (a), the ice nucleation temperature of the hot water was  $\approx -6.5^\circ\text{C}$ , and the cold water was  $\approx -17.5^\circ\text{C}$ . The time difference between the release of latent heat in (a) and (b) is due to the difference in the initial temperatures of the two cold waters.

added. This change of water caused the ice nucleation temperature to go from  $\approx -6$  to  $\approx -10^\circ\text{C}$ . From the results presented in Fig. 8, we conclude that the ice nucleation sites were in the water and not associated with the vials. We also conclude that heating fresh snow water can significantly change its ice nucleation temperature.

This data confirm that a sample of water freezes when its temperature has fallen to the temperature of the ice nucleation site with the highest ice nucleation temperature. Although not discussed in this paper, silver iodide crystals are also high temperature (from  $-2$  to  $-5^\circ\text{C}$ ) ice nucleation sites.<sup>11,12</sup>

## IX. HOT WATER CONSISTENTLY FREEZES FASTER THAN COLD WATER

To create conditions in which hot water froze before cold water 28 times in 28 attempts, we selected two vials with ice nucleation temperature differences greater than  $\approx 5.5^\circ\text{C}$ . One was tap water and the other was distilled water. We heated the tap water vial to  $\approx 100^\circ\text{C}$  in a boiling water bath, while the other vial remained at  $25^\circ\text{C}$  or lower. We then quickly placed both vials in the freezer. This process was repeated 28 consecutive times over 9 days. We show two typical cooling curves in Fig. 9. Note that the latent heat of freezing was released by the hot water first and at a higher temperature than the cold water. The release of latent heat in the hot water at much higher temperature than in the cold water is the key to hot water freezing before cold water.

These results suggest that it should be possible to observe initial  $\approx 100^\circ\text{C}$  water freezing before initial  $\approx 0^\circ\text{C}$  water.

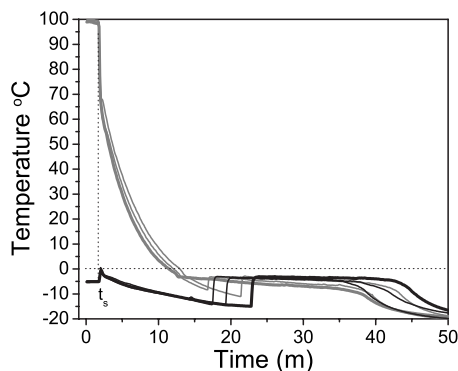


Fig. 10. Fresh melted snow water in three vials initially at  $\approx 100^\circ\text{C}$  (gray curves) and de-ionized water initially at  $\approx 0^\circ\text{C}$  (black curves) in three vials was placed in a freezer at time  $t_s$ . Two of the three hot water samples (gray curves) froze before any of the cold water samples (black curves). This phenomenon occurs with water from the same source but at a much lower frequency because the ice nucleation temperatures are usually too close in most samples from the same source. See Fig. 7 for a typical example of how close the ice nucleation temperatures can be.

To demonstrate this possibility, we used fresh snow water and de-ionized water. Snow water was selected because it previously froze at higher temperatures than de-ionized water. 10 ml of each water sample were flame-sealed in six Pyrex test tubes, three of which contained snow water and three of which contained de-ionized water. The six vials were cycled to  $\approx 100^\circ\text{C}$  several times before the data presented in Fig. 10 were collected. Prior to cooling the vials in the freezer, the three snow water vials sat in boiling water until their temperatures reached  $\approx 100^\circ\text{C}$ , while the three de-ionized water vials sat in a salt/water ice bath. Note that two of the hot water vials shown in Fig. 10 froze (released latent heat) before any of the cold water vials. The temperature probes did not read  $0^\circ\text{C}$  when the latent heat of freezing was released because they were located on the outside of the vials, and there was just enough latent heat to raise the water temperature to  $\approx 0^\circ\text{C}$ , while the vials remained cooler.

This experiment confirms that it is not the initial temperature of the water that determines the time of freezing but rather the ice nucleation temperature of the ice nucleation site in the water. Similar results have been obtained with water from the same source; considerable time was spent selecting samples with sufficient differences in the ice nucleation temperatures for the hot water to freeze first (see Fig. 7).

## X. HOW LONG WILL WATER REMAIN SUPERCOOLED JUST ABOVE ITS ICE NUCLEATION TEMPERATURE?

Four small Pyrex test tubes, each containing 2 ml of tap water, were flame-sealed. The vials were repeatedly heated to  $\approx 100^\circ\text{C}$  and then cooled until the water in each vial froze. The process was repeated until the ice nucleation temperatures varied by less than  $1^\circ\text{C}$  over five or more consecutive freeze/heat/freeze cycles. Heating the water does not necessarily cause its nucleation temperature to vary less; however, it usually results in the water supercooling to a lower temperature as reported by Dorsey<sup>10</sup> and as shown in Fig. 8(a).

We wanted to conduct this test at the lowest temperature obtainable with our equipment. The four vials were then

placed in a constant temperature bath at  $-15^\circ\text{C}$ ,  $\approx 1^\circ\text{C}$  above the mean ice nucleation temperature of the vial that exhibited the highest nucleation temperature. The purpose of this experiment was to test how long undisturbed tap water will remain liquid at  $-15^\circ\text{C}$ . The bath's stability is assumed to be  $\pm 0.5^\circ\text{C}$ . If the ice nucleation temperature, not the initial temperature, determines when a sample of water freezes, then the water in these vials will remain liquid until their temperatures fall below their previously determined mean spontaneous freezing temperatures. Vial 3, which was the one whose ice nucleation temperature was closest to  $-15^\circ\text{C}$ , froze on day 72 after being placed in the  $-15^\circ\text{C}$  constant temperature bath. It froze first because the temperature of the bath most likely fell below the ice nucleation temperature of the site with the highest ice nucleation temperature in this sample of water. The other three samples are still liquid after 339 days and counting. We hypothesize that the other three will freeze when the temperature of the bath is lowered to the previous determined ice nucleation temperature of each vial.

## XI. CONCLUSIONS

Ordinary drinking water contain many harmless impurities, which can act as ice nucleation sites, each of which have an ice nucleation temperature, that is, the temperature at which that site will imitate heterogeneous freezing. Still water in a closed container will almost always supercool and will therefore not begin freeze until its temperature falls to the temperature of the ice nucleation site with the highest ice nucleation temperature. Consequently, if a container of hot water has ice nucleation sites with an ice nucleation temperature  $\approx 5.5^\circ\text{C}$  or higher than the ice nucleation site with the highest ice nucleation temperature in the cold water, then the hot water will freeze first. If this is not the case, the cooler water will freeze first, and the Mpemba effect will not be observed.

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<sup>a</sup>Electronic mail: jdbjdb@binghamton.edu

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