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The Mpemba effect is the assertion that it is quicker to cool or freeze water when the initial temperature is high. We define the Mpemba effect to have been observed when two samples of water, one initially warmer than the other, are cooled and the initially hotter sample freezes or cools to a prescribed temperature in less time; providing that the samples are of the same mass, are at least as pure as drinking water, the cooling is delivered to both samples in the same manner, and the same level of insulation is applied to both. Under this definition, we enable repeatable observations of the Mpemba effect by systematically introducing increased nucleation sites (in our case by roughening the container walls with sandpaper) within the cooling environment of the initially warmer sample. We remain able to observe the Mpemba effect when the enthalpy of cooling and freezing the initially warmer sample exceeds that of the initially cooler sample by over 50%, corresponding to a difference in the initial temperatures of around 50°C. The context of this study, initiated by a high-school student who then carried out all of the experiments, highlights the value of the Mpemba effect as a tool for scientific learning and engagement.

1. Introduction

The assertion that it is quicker to cool or freeze water that is initially hotter is commonly termed the ‘Mpemba effect’. Under the strictest definition of the Mpemba effect, two equal masses of water with different initial temperatures, must be cooled in identical conditions. If the initially warmer sample cools to a given temperature, or freezes, in less time than the initially cooler sample then an observation of the Mpemba effect has been made. The adoption of the term ‘Mpemba effect’ is owed to the curiosity of a Tanzanian school boy, Mpemba, thanks to the open-minded scientist Dr Osborne¹. The origin of the present study is the curiosity of a Swedish high-school student, Oscar Hallstadius, and his communications with Dr Burridge.

The experiments by Mpemba & Osborne¹ sought to record the time taken for two notionally identical volumes of water, one initially warmer than the other, to cool and start freezing. They plotted results for “the time to start freezing” — a notoriously difficult observation to make scientifically — recording some extraordinary results, e.g. water initially at 80 °C started to freeze in less than a third of the time of that of water initially at 20 °C. Since then studies have tended to either examine the time taken to cool to 0 °C, e.g.^{2,3}, or the point in time at which the latent heat is released⁴, or the time taken for complete freezing to occur, e.g.^{5,6,7,8,9} — all of which are easier to rigorously observe. Conclusions are mixed with certain studies reporting positive observations of the Mpemba effect e.g.^{1,10} and others reporting no positive observations could be made e.g.^{3,6,11}. This lack of certainty regarding the effect is, in large part, due to the lack of a clear, universally accepted definition of the Mpemba effect. Using the strictest definition of the effect, Burridge & Linden³ analysed the data of numerous experimental studies ultimately concluding that “the Mpemba effect is not observable in any meaningful way” with ‘meaningful’ therein defined to refer to repeatable observations of the effect that were beyond the scope of experimental uncertainty. Herein, we review the pertinent literature in order to inform a rigorous, yet more inclusive, definition of the Mpemba effect that allows for controlled variations in the conditions within prescribed limits.

The history of the Mpemba effect is rich and interesting, dating back to at least the time of Aristotle^{12,13}. In the same year that Mpemba & Osborne¹ reported the results of their experiments, Kell¹⁴ documented centuries-old Canadian ‘folklore’ of wooden pails containing initially warm water being known to freeze faster than those containing initially cooler water. He concluded that evaporative effects could be sufficient to give rise to the Mpemba effect. Scientific investigations of the effect have been ongoing ever since with both Jeng¹³ and Burridge & Linden³ providing particularly thorough reviews of the historical literature. A noteworthy contribution to understanding and resolving the controversy regarding the effect, took place in 2012 when a competition was organised by the Royal Society of Chemistry (RSC) seeking explanations of the effect. The winning entry¹⁰; concluded that supercooling and convection are the most likely candidates for giving rise to the Mpemba effect.

The role of convection in the Mpemba effect has formed the focus of a number of recent studies. For example, Ibekwe & Cullerne¹⁵ reported observations of the Mpemba effect attributed to differences in the convective currents within initially warmer and cooler samples. However, the Mpemba effect was only observed therein when the initial temperatures differed by just a few degrees Celsius. Vynnycky & Kimura⁹ carried out experiments designed to maximise the role of convection within the cooling process and concluded that the vigour of convection was primarily important in determining the extent to which supercooling actually occurs. Moreover, Burridge & Linden³ reported that they were unable to experimentally produce the Mpemba effect even for limiting high Rayleigh number (strong) convection.

The effects of supercooling have been investigated in the context of the Mpemba effect but with mixed conclusions. For example, Auerbach⁵ reports less supercooling (and therefore potentially faster freezing) in initially hot water whilst both Brown¹⁶ and Dorsey¹⁷ report the opposite results. Brownridge⁴ observed the Mpemba effect by consistently freezing initially hot tap water in less time than initially cooler distilled water. He concluded that changes in the ‘ice nucleation

temperature' between the sample of tap water and the sample of distilled water were dominant in determining the time to freeze rather than their initial temperature. We carry out experiments designed to systematically alter the nucleation process during freezing and investigate the time taken for complete freezing to occur.

There is much interesting work investigating molecular effects in water, that had been motivated by the Mpemba effect^{18,19,20,21,22}. However, such motivation requires validation, or otherwise, of the effect at the continuum scale. We seek to provide that validation.

In addition to studies concerning the Mpemba effect in water, similar effects have been reported based on experiments in other mediums. For tetrahydrofuran hydrate, Ahn *et al.*²³ report that the formation kinetics might depend on the initial temperature of the material. Moreover, for polymers Hu *et al.*²⁴ observed that the thermal history of a specimen affected the crystallisation process within polylactide. They reported that samples which were quenched from initially higher temperatures crystallised faster than those quenched from initially lower temperatures.

Indeed, Mpemba-like effects have also been simulated for more generic systems. Lasanta *et al.*²⁵ and Torrente *et al.*²⁶ examined the thermal behaviour of fluid-like systems by considering the kinetics of inelastic hard spheres. Initially hot systems could be observed to cool more quickly than initially cooler systems when the difference in "the deviation of the velocity distribution function from the Maxwellian shape at the lowest order"²⁶ was sufficiently large between the two systems. Nava & Fabrizio²⁷ carried out simulations using the Ising model, which they describe as 'the prototype of quantum first-order phase transitions' — first-order phase transitions being those which involve a latent heat, as exhibited by water. They quenched the system from two different initial temperatures, in both cases the system entered a metastable state (akin to a supercooled state). However, the initially hotter system passed through the metastable state more quickly and reached thermal equilibrium first, thereby exhibiting behaviour akin to the Mpemba effect. The Ising model was also used by Lu & Raz²⁸, in addition to diffusion dynamics and a three-state model, to observe what they describe as the 'Markovian Mpemba effect'. They conclude that in initially warmer systems "most of the probability is spread across the high-energy microstates, which flow into the global minimum through a fast relaxation" whilst for initially cooler systems a significant portion of the corresponding equilibrium probability is temporarily 'trapped' in a metastable state during cooling. Klich *et al.*²⁹ also use Markovian dynamics and observe what they described as "the strong Mpemba effect" in which the effect is 'substantially enhanced' only for a discrete set of 'special' initial temperatures. All of these studies suggest that Mpemba-like effects should be observable in a variety of systems.

(a) Defining the Mpemba effect

The inception of the present investigation was an email written by a high-school student (who is the co-author of this study):

"Dear Mr. Burridge, My friend and I are students at Katedralskolan Lund and are currently working on a physics project regarding the mpemba effect. Having come across your paper 'Questioning the Mpemba effect: hot water does not cool more quickly than cold' (Published online 2016 Nov 24.) we were greatly impressed and are therefore wondering if it would be possible for you to share the data used in figures 1 - 3. This would be highly appreciated and helpful. Yours sincerely, Oscar Hallstadius".

The first thought following receipt of this email was to share the data with pleasure and leave it at that. However, there was also a desire to encourage scientific experimentation while not wanting these high-school students to be put off by the expected negative results. So began further consideration.

With such a rich scientific history^{30,31,32}, and a continuing interest (see above), a rigorous definition of the Mpemba effect should be agreed upon. We attempt to provide such a definition. It has been shown that under the strictest definition, i.e. that for “observation of the Mpemba effect, one must compare two experiments which are identical in every manner except for a difference in the initial temperatures of the water samples”, the Mpemba effect has not been repeatably observed³. However, such a definition has attracted criticism for being overly restrictive since, by its very nature, the definition precludes a number of the physical processes which have been proposed to give rise to the effect. We attempt to provide a more inclusive definition of the Mpemba effect that permits prescribed variations in the experimental conditions, we hope that this might be more universally acceptable.

To begin defining the Mpemba effect, we consider the various physical mechanisms that have been proposed to give rise to it and how differences in these mechanisms might be promoted and inhibited by systematic changes within scientifically justifiable boundaries. The winning entry to the RSC competition¹⁰, for example, cites four factors as possibly contributing to the Mpemba effect, namely: (a) evaporation, (b) dissolved gases, (c) mixing by convective currents, and (d) supercooling. We discuss these, and other pertinent factors, in turn.

The occurrence of evaporation necessarily results in a lessened mass of water remaining. It is obvious that a lesser mass of water will take less energy, and therefore less time, to cool (or heat) and one would not wish to include this within the Mpemba effect. All else being equal, hot water evaporates at a greater rate than cold and so keeping the hotter sample warm for a long period of time prior to cooling could result in significant and undesirable differences in the mass lost from the two samples. Hence, wherever this might occur we recommend that the water vapour produced is captured, for example, by simply sealing a region of air above the liquid water. Thus, should the effects of evaporation be significant in causing the Mpemba effect, they are not restricted from inclusion but crucially the evaporation does not result in significant differences in the mass of water being cooled.

Potable water contains a variety of dissolved gases, and for that matter dissolved minerals and salts, at relatively low concentrations. At sufficiently high concentration these significantly alter the freezing point of water (e.g. the lower freezing temperature of water when salt is added is why salt is put on roads during winter in an attempt to prevent ice forming). Concentrations of dissolved gases, minerals and salts which materially alter the freezing point of water should be excluded from the Mpemba effect. We therefore restrict the effect to only include investigations with water that is at least as pure as water that has been deemed safe to drink. In so doing we permit systematic variations in the levels of dissolved gases, minerals and salts, within reasonable limits without imposing the need for the precise chemical composition to be determined for each and every experiment — one only has to show that the water being experimented upon is as least as pure as, for example, the local tap water providing that it can be deemed drinkable.

Convection (the transfer of heat by fluid motion) plays a significant role in enhancing heat transfer in many scenarios. Forced convection, where mechanically energy is input to drive fluid motion, should be excluded from the Mpemba effect as it should be no surprise that water cools faster if it is constantly stirred. However, natural convection arises when differences in (temperature dependent) density within a sample of water are unstable under gravity (e.g. when cold water sits above warmer water). The extent to which these convective currents arise should be expected to differ between those within colder and those within warmer samples of water. These differences should be included within any definition of the Mpemba effect. However, it is not reasonable to include within the Mpemba effect a comparison of the cooling rate when convection is promoted (e.g. cooling a water sample at its upper surface) to that when it is inhibited (e.g. when a sample is cooled by below) since it is already known that the two will differ significantly. As such, we recommend that for meaningful observation of the Mpemba effect the cooling must be delivered to both samples in the same manner. Moreover, the heat transfer by conduction via the sample’s container and its contact with any surface should also not

be artificially biased. As such, the Mpemba effect should only be deemed to have been observed when both samples have been insulated in the same manner.

Water can exist in a supercooled state, i.e. it can remain liquid below its freezing point (more strictly its melting point of 0°C). The extent to which supercooling arises depends on its purity and the presence of nucleation sites, i.e. locations where ice crystals might first form (e.g. at imperfections within the container walls). We have already discussed constraints which we deem reasonable regarding systematic variations in the purity of water that are permitted to contribute to the Mpemba effect — should these alter the time over which the freezing process occurs, via the extent to which supercooling arises, then we also permit these effects to be included. Moreover, we deem it reasonable to allow the presence of nucleation sites to be systemically varied, via these or other means, within our definition of the Mpemba effect provided that such variations do not alter the heat transfer properties of the container nor its contact with any surface.

In summary, we define the Mpemba effect to have been observed when two samples of water, one initially warmer than the other, are cooled to a given temperature and/or frozen and the initially hotter samples cools in less time; providing that the samples are of the same mass, are at least as pure as drinking water, the cooling is delivered to both samples in the same manner, and that both samples are exposed to the same level of insulation — moreover, the observation must be repeatable and the initial temperatures and respective cooling times must differ beyond the extent of experimental uncertainty. We apply this more inclusive definition to our present study and we hope that it proves more widely useful.

2. Experiments and analysis

(a) Experimental set-up and procedures

For all experiments temperatures were digitally recorded (with an accuracy to within 0.1°C) and stored with a data-logger connected to a computer running LoggerPro. In total, three identical rigid plastic beakers of diameter $D = 4.7$ cm weighing 12.43 g with relatively smooth insides were first chosen. The inside of one of the containers was then roughened using sandpaper (a coarse ‘60-grit’ aluminium oxide paper) and weighed 12.14 g after the procedure. The outside of the other two containers was then roughened with sandpaper until they weighed the same as the beaker with the roughened inside. In so doing, we ensured that all beakers contained the same thermal mass and that their walls were rough on one side and smooth on the other. Hence, no difference in the thermal conductivity of the beakers could be expected, and the beakers were notionally identical except that one had roughened inside walls, herein the ‘roughened’ beaker, whilst the other two had relatively smooth inside walls, herein the ‘smooth’ beaker. Before each experiment, two beakers were selected and both were cleaned using deionised water, allowed to dry and thereafter filled with either tap water or deionised water, of mass 60 g, filling the beakers to a water depth of approximately $H = 3.6$ cm. In most experiments one or both of the water samples were then either heated or cooled to some desired initial temperature. To heat the water samples, the containing beaker was partially submerged in a warm water bath and let to sit for varying amounts of time. In order to extend the range of initial temperature differences explored, for certain experiments initial cooling of one water sample was carried out. To cool the water samples, the containing beaker was partially submerged in a cold water bath and let to sit until the desired initial temperature had been reached. Once the desired initial temperatures had been obtained the samples were placed on a 2 cm thick plastic plate within a standard domestic freezer. Both containers were placed inside the freezer at the same time in order to ensure that the samples were exposed to the same cooling from the thermostatically controlled freezer. The thermostat on the freezer was set to -18°C . Prior to being placed inside the freezer a temperature probe with a low thermal mass was fitted to an adjustable laboratory stand. The probe was then lowered into position and carefully fixed centrally within each sample of water. The temperature of the thermometer within each water sample was recorded at 2 second intervals throughout the experiment until ‘complete freezing’ had occurred.

The term “complete freezing” was determined to be the moment that the temperature started decreasing after the freezing process had completed. Due to the freezing process being a first-order thermodynamic phase transition, the temperature will remain almost equal to its melting point as long as crystallization takes place. When solid and liquid ceases to coexist i.e. the entire volume of water has become a solid block of ice, the temperature will start to drop. See the following section for a complete discussion.

To establish the repeatability of the experimental measurements a number of notionally identical experiments were carried out, in which two water samples of the same initial temperature were both contained within a smooth beaker. The time for complete freezing was recorded and a measure of the experimental uncertainty and repeatability was determined — the scale of which is reflected by the size of the markers in figures 1, and 3–7.

In order to investigate the potential for dissolved minerals within the water to affect its cooling and freezing, a set of experiments using tap water (drawn from the mains water supply in Lund, Sweden) was carried out. For these experiments, two samples of tap water were set to freeze from the same initial temperature — one of the samples was placed inside a smooth walled beaker the other in a roughened wall beaker. For all other experiments, deionised water was used. Throughout the experimental campaign that followed the initial temperatures of the samples, along with whether the initially hotter or cooler sample was placed in a roughened wall or smooth walled beaker, were systematically varied. A summary of all experiments is presented in section 3 whilst details of selected experiments are presented in appendix A.

(b) Analysis of the data

To analyse the data, we first took the time series of temperature for each sample during freezing (see figures 3–7). For each time series a period of approximately constant temperature is observed – evidence of the phase-change process being ongoing for the first-order thermodynamic phase transition from liquid water into ice. Examining the gradients of the time series of temperature enables the start and end of this approximately ‘constant temperature regime’ to be identified. The start and end of the constant-temperature-regime for each sample is highlighted by the vertical lines plotted within figures 3–7. The constant-temperature-regime highlighted within the figures is then utilised in order to calculate a mean temperature of the sample during the phase transition, i.e. freezing process. We, however, are interested in robustly quantifying the time at which ‘complete freezing’ has occurred. During the freezing process heat transfer to the freezer is still occurring but this heat transfer is of latent heat, rather than sensible heat. Once complete freezing has occurred the heat transfer reverts to being one of sensible heat and the sample of, then, ice begins to cool further. In order to rigorously identify the onset of complete freezing, we wish to identify the point at which the sample commences cooling beyond the occurrence of the phase transition. To do so, we utilise two independent methods to identify complete freezing, a method based on absolute temperatures and another based on the rate of change of temperature with time, the gradient-based method. We identify complete freezing via the absolute temperature method by calculating when the temperature of the sample first falls below the mean temperature of the sample during the phase transition minus some threshold temperature. We plot results taking the threshold temperature to be 1°C , however, our findings are insensitive to the precise choice of threshold temperature within the range 0.5°C to 3°C . We identify complete freezing via the gradient-based method by calculating when the rate of change of temperature with time first falls below some threshold gradient. We plot results taking the threshold temperature gradient to be $-10^{-3}^{\circ}\text{C/s}$, however, our findings are insensitive to the precise choice of threshold temperature within the range $-10^{-2}^{\circ}\text{C/s}$ to $-10^{-4}^{\circ}\text{C/s}$. In all plots, squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.

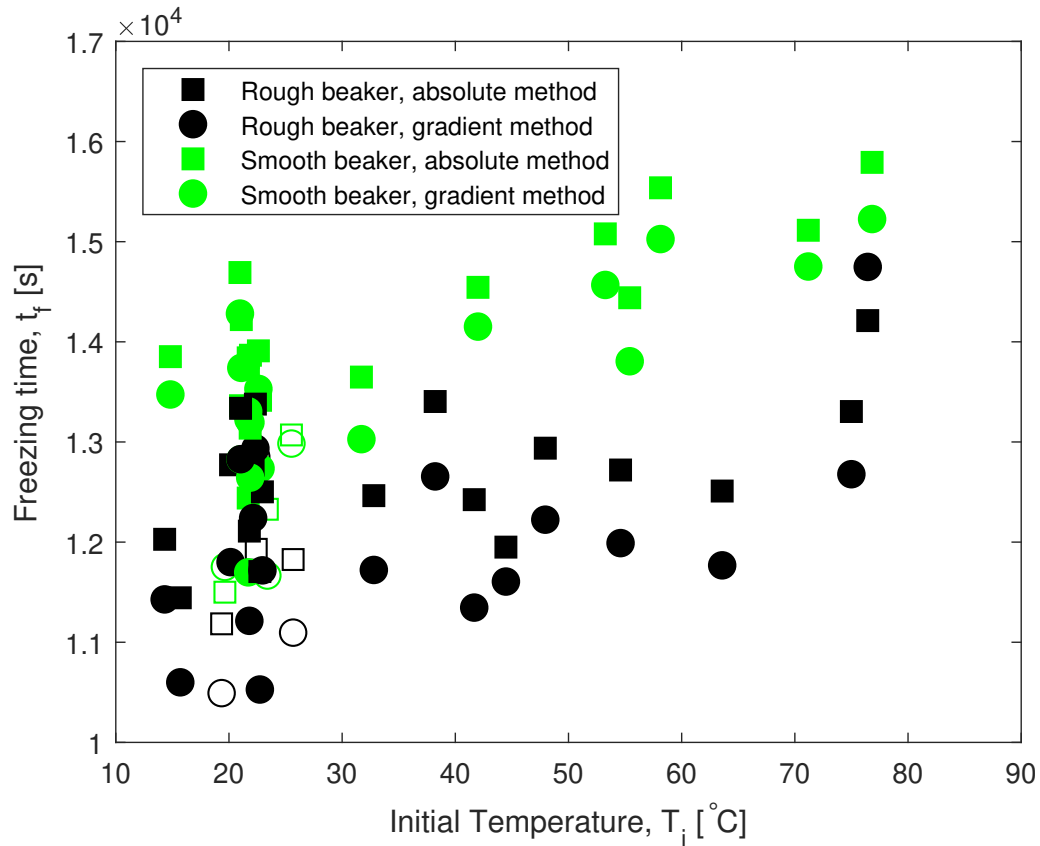


Figure 1. Variation in the time to achieve complete freezing, t_f , with initial temperature for all experiments carried out. Empty symbols denote tap water, filled symbols deionised water.

3. Results

We present and analyse experimental results concerning the cooling and freezing of pairs of water samples. The experiments were kept deliberately simple so as enable them to be easily repeated elsewhere and were in our case carried out at Katedralskolan Lund high-school. Each pair of water samples were simultaneously placed on an insulated base within a standard domestic freezer. The temperatures of both water samples were recorded using a thermocouple carefully positioned and fixed centrally within the water sample. The time taken for complete freezing to occur was then determined using two independent methods (see §2 for full details). Moreover, we include systematic presentation of the cooling curves for selected pairs of experiments in the appendix A.

Data showing the variation in the complete freezing time with initial temperature for all experiments carried out is shown in figure 1. The size of the markers within the figure indicate estimates of our experimental uncertainty and repeatability. Over the relatively narrow band of initial temperatures $20^\circ\text{C} \leq T_i \leq 25^\circ\text{C}$ the data shows a relatively wide spread in the time t_f to attain complete freezing. This highlights the differences that can occur when samples are cooled by the same freezer but on different occasions, i.e. differences due to the cooling imposed by the thermostatically controlled freezer. The data show a consistent spread around a certain trend; namely, that the freezing time increases with increased initial temperature. Moreover, the data show that samples contained within a roughened walled beaker (black) consistently froze faster

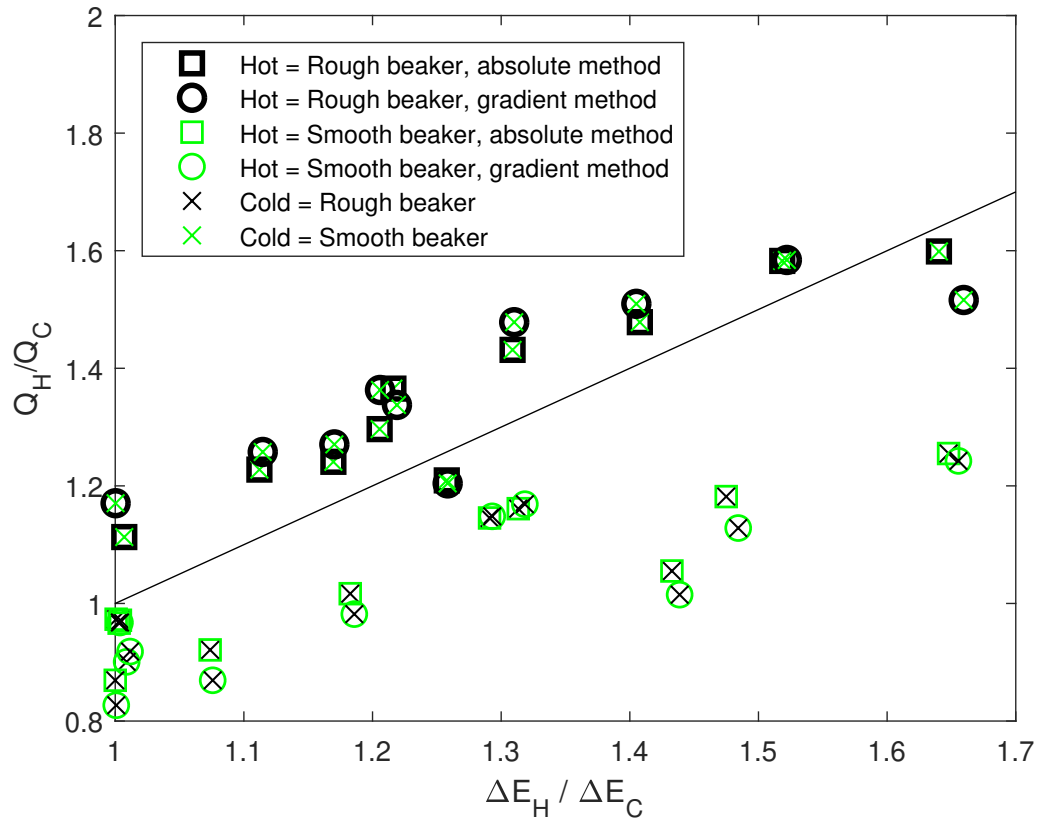


Figure 2. The variation in the ratio of mean heat transfer rates with initial temperature for pairs of hot and cold water placed in the freezer at the same time. The black solid-line marks the ‘Mpemba line’ defining the region (above the line) in which data can be said to have exhibited the Mpemba effect.

than those contained within a smooth walled beaker (green). This marked difference is evidence of more timely formation of ice crystallisation when in the presence of enhanced nucleation sites, i.e. the rough wall of the beaker.

In order to establish a single observation of the Mpemba effect, one must compare two experiments which differ only by the initial temperatures of the water samples. Following Burridge & Linden³, to illustrate when the Mpemba effect may be reported to have been observed we consider the average rate at which heat is transferred Q from the initially hot Q_H and initially cold Q_C samples. Herein, since we consider the freezing process one must include the transfer of latent heat during the freezing process. For a given sample $Q = \Delta E/t_f$ where ΔE denotes the change in specific enthalpy between the initial and final states and t_f is the time to achieve complete freezing. The Mpemba effect can be reported as having been observed when the inequality $Q_H/Q_C > \Delta E_H/\Delta E_C$ is satisfied, since $Q_H/Q_C > \Delta E_H/\Delta E_C \implies t_C > t_H$, where t_C and t_H denote the time for complete freezing of the cold and hot samples, respectively. Figure 2 shows the variation in the ratio of mean heat transfer rates with the ratio of enthalpy drops, $\Delta E_H/\Delta E_C$, for pairs of hot and cold water placed in the freezer at the same time. The black solid-line marks the ‘Mpemba line’ defining the region (above the line) in which data can be said to have exhibited the Mpemba effect. What is noteworthy is that pairs for which the initially hot sample was contained within a beaker with a roughened wall the Mpemba effect can be consistently and systematically observed. This is clear evidence that the increased presence of nucleation sites reduces the occurrence of supercooling and promotes the more timely formation

of ice-crystals which ultimately enables clear observation of the Mpemba effect in the freezing of water. Moreover, we have been able to make repeatable successful observations of the Mpemba effect when the enthalpy of cooling and freezing the initially warmer sample exceeds that of the cooler sample by 50%.

4. Conclusions

We provide and justify a rigorous, yet inclusive, definition of the Mpemba effect that permits variations of the experimental conditions within prescribed limits. We have made repeatable observations of the Mpemba effect in water by making systematic alterations to the cooling environment within these limits. Without systematically imposing a bias we were unable to make any observations of the Mpemba effect.

In our experiments, we introduced additional nucleation sites to the initially warmer sample by roughening the container walls (with sandpaper) and comparing the freezing time to that of an initially cooler sample in a relatively smooth walled container (with the same insulating properties). Using this approach we have been able to repeatedly cool and freeze initially warmer samples of deionised water in less time than the initially cooler samples. We were successful in doing so even when the enthalpy required to induce complete freezing within the warmer sample was greater than that of the initially cooler sample by 50%, in our case this corresponded to initial temperatures of 75°C and 22°C for the initially warmer and cooler samples, respectively, or an initial temperature difference of 53°C.

We conclude that one can observe the Mpemba effect in water by making systematic changes to the cooling environment, herein roughened container walls. However, in the absence of any bias in the cooling (i.e. a strict definition of the Mpemba effect) then warmer water was always observed to take longer to freeze than cooler water, in accordance with the conclusions of Burridge & Linden³. Observing that, with the same cooling applied and by simply roughening the container walls, 50% more internal energy could be removed from water in a lesser time is noteworthy — perhaps this provides justification for our more inclusive definition of the Mpemba effect. However, it is important to note that observations of the Mpemba effect under the present definition are not groundbreaking, e.g.⁴, and their application is more limited than if observations of the Mpemba effect could be made under a strict definition. Put simply, if one wishes to make ice quickly then one should put cold water in the freezer and not hot water.

Crucially, this project was initiated, inspired and the experiments carried out by a scientifically curious high-school student. This once again serves to remind us that the Mpemba effect is an excellent challenge with which to pique scientific interest and engage broader society in scientific investigations. Moreover, this article is evidence that with the right amount of curiosity and determination anyone can make a meaningful contribution to scientific knowledge and understanding.

Data Accessibility. All data presented here is available as supplementary material.

Authors' Contributions. OH inspired the study, HCB conceived and led the research, OH carried out the experiments, HCB analysed the data, wrote the main manuscript text and prepared the figures. OH reviewed and edited the manuscript.

Competing Interests. The authors declare that they have no competing interests.

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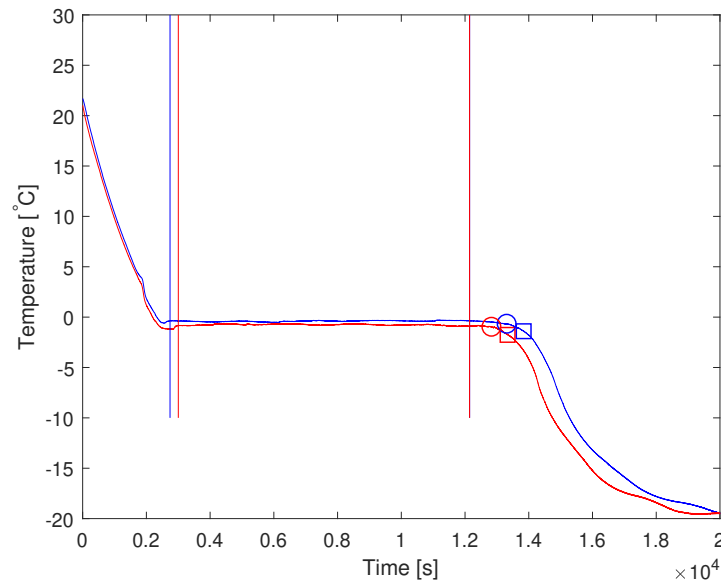


Figure 3. Typical cooling curve of two notionally identical samples of deionised water placed in the freezer at the same time. Vertical bars mark the start and end of the constant-temperature-regime. Squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.

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A. Cooling curves

Figure 3 shows typical cooling curves for two notionally identical samples of water, placed in the freezer at the same time, one marked by a red curve and the other blue. The vertical bars in all plots of cooling curves mark the start and end of the constant-temperature-regime identified for each sample. In all plots, squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method. The data show that for identical samples, under identical cooling conditions the time for complete freezing, t_f , were similar to within 3% and 4% for the absolute temperature and gradient-based methods, respectively. This degree of uncertainty is comparable with our estimates for the experimental uncertainty which is represented by the size of the circular and square markers in each of figures 1–7.

Figure 4 shows typical cooling curves for two notionally identical samples of tap water, placed in the freezer at the same time. The blue curve marks the cooling data for the sample contained within a smooth walled beaker and the red curve marks that of the sample contained within a beaker with roughened walls. The data show that for identical samples, placed in beakers that differ only by their wall roughness there is a marked difference in the time for complete freezing — with the water in the rough beaker completing freezing first. Note that during both the cooling phase and the constant-temperature-regime the evolution of the temperatures of the specimens remain notionally identical providing reassurance that the roughening of the beaker wall did not significantly affect its thermal properties. The fact that the water sample within the rough walled beaker froze first suggests that the increased presence of nucleation sites resulted in more timely

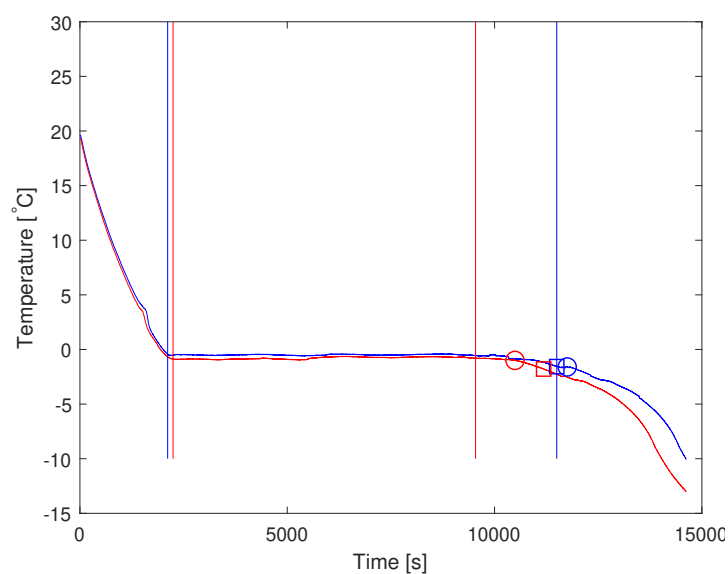


Figure 4. Typical cooling curve for two samples of tap water placed in the freezer at the same time. Both samples were notionally identical, one sample (blue) was placed in a smooth wall beaker and the other sample (red) was placed in a beaker with roughened walls. Vertical bars mark the start and end of the constant-temperature-regime. Squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.

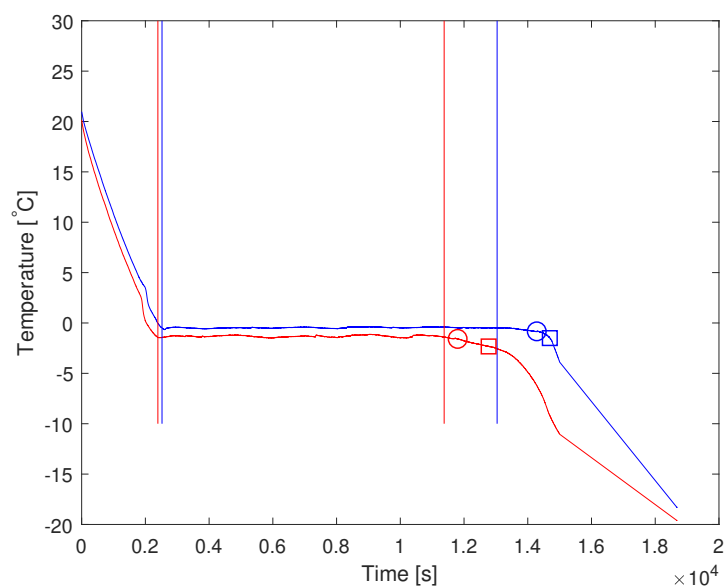


Figure 5. Typical cooling curve for two samples of deionised water placed in the freezer at the same time. Both samples were notionally identical, one sample (blue) was placed in a smooth wall beaker and the other sample (red) was placed in a beaker with roughened walls. Vertical bars mark the start and end of the constant-temperature-regime. Squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.

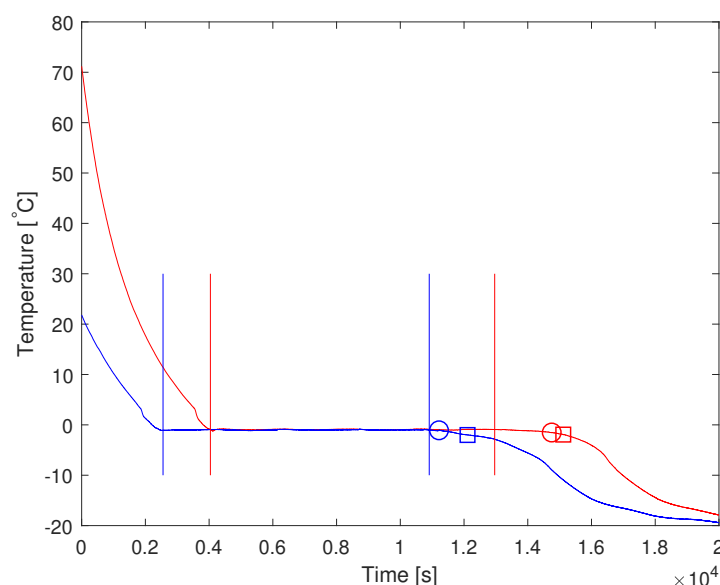


Figure 6. Typical cooling curve for two samples of deionised water placed in the freezer at the same time. Both samples were taken from the same batch of water and were the same mass, one sample (red) was initially hotter. In addition, one sample (red) was placed in a smooth wall beaker and the other sample (blue) was placed in a beaker with roughened walls. Vertical bars mark the start and end of the constant-temperature-regime. Squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.

ice-crystal formation. The data plotted in figure 5 supports this assertion. The figure shows typical cooling curves for notionally identical samples of deionised water and highlights that the effects are more marked. The water sample contained within the rough walled beaker reaches complete freezing in around 85% of the time of the sample contained within the smooth walled beaker.

Figure 6 shows cooling curves for two samples of deionised water taken from the same batch of water and of the same mass, one had an initial temperature of 21.80°C (blue data) and the other 71.79°C (red data). Notably, the initially cooler sample was placed in a rough walled beaker whilst the initially warmer sample was placed in a smooth walled beaker. As expected the initially cooler sample both reaches 0°C first and also attains complete freezing first in about 65% of the time of the initially warmer sample. Hence, one does not observe the Mpemba effect.

Figure 7 shows cooling curves for two samples of deionised water taken from the same batch of water and of the same mass, one has an initial temperature of 22.6°C (blue data) and the other 54.6°C (red data). Moreover, the initially warmer sample was placed in a rough walled beaker whilst the initially cooler sample was placed in a smooth walled beaker. As expected (for example from the study of Burrige & Linden³) the initially cooler sample (blue) reaches 0°C first and hence one does not observe the Mpemba effect in the cooling phase. However, despite this the initially warmer sample (red) is observed to achieve complete freezing in a significantly shorter time than the initially cooler sample. Hence, one can state that we have observed the Mpemba effect when observing the complete freezing of water. We note that to observe the Mpemba effect it was necessary to bias the cooling environment of the warmer sample and we hypothesise that the presence of additional nucleation sites leads to more timely ice-crystal formation and hence enables the initially warmer sample to attain complete freezing first.

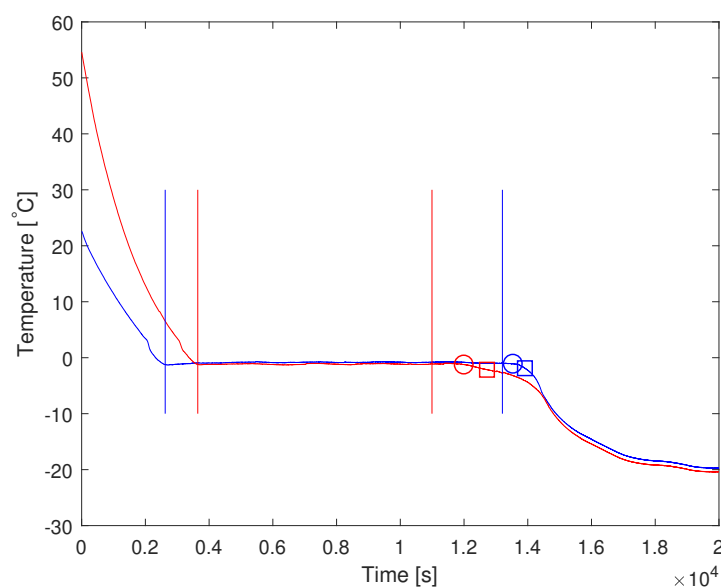


Figure 7. Typical cooling curve for two samples of deionised water placed in the freezer at the same time. Both samples were taken from the same batch of water and of the same mass, one sample (red) was initially hotter. In addition, one sample (blue) was placed in a smooth wall beaker and the other sample (red) was placed in a beaker with roughened walls. Vertical bars mark the start and end of the constant-temperature-regime. Squares mark the point of complete freezing determined via the absolute temperature method, circles mark the point of complete freezing determined via the gradient-based method.