The Mpemba effect: When can hot water freeze faster than cold?

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We review the Mpemba effect, where initially hot water freezes faster than initially cold water. Although the effect might appear impossible, it has been observed in numerous experiments and was discussed by Aristotle, Francis Bacon, Roger Bacon, and Descartes. It has a rich and fascinating history, including the story of the secondary school student, Erasto Mpemba, who reintroduced the effect to the twentieth century scientific community. The phenomenon is simple to describe and illustrates numerous important issues about the scientific method: the role of skepticism in scientific inquiry, the influence of theory on experiment and observation, the need for precision in the statement of a scientific hypothesis, and the nature of falsifiability. Proposed theoretical mechanisms for the Mpemba effect and the results of contemporary experiments on the phenomenon are surveyed. The observation that hot water pipes are more likely to burst than cold water pipes is also discussed.
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I. INTRODUCTION

The Mpemba effect occurs when two bodies of water, identical in every way, except that one is at a higher temperature than the other, are exposed to identical subzero surroundings, and the initially hotter water freezes first. The effect appears theoretically impossible, but has been observed in numerous experiments,[1–7] and we will see that the effect is possible.

Readers who are certain that the effect is forbidden by the laws of thermodynamics should first try to explain as precisely as possible why it is impossible. Then think about how to respond to a non-scientist who insists that they have observed the Mpemba effect. Whether or not the effect is real, these tasks will raise a wealth of important issues about the scientific method that can be understood and discussed by students without any knowledge of advanced physics.

In Sec. II we describe early observations and experiments on this phenomenon. The effect was discussed by Aristotle, Roger Bacon, Francis Bacon, and Descartes among others.[8–11] The effect was repeatedly discussed in support of an incorrect theory of heat and was forgotten once more modern conceptions of heat were developed, which appeared to indicate that the effect was impossible. In fact, Kuhn incorrectly claimed that modern experiments cannot replicate these early observations.[12] In Sec. III we describe the reintroduction of this phenomenon to the modern scientific community by a secondary school student, Erasto Mpemba. Mpemba's story cautions us against dismissing the observations of non-scientists and raises questions about the degree to which our theoretical understanding can and should bias our acceptance and interpretation of experiments.

In Sec. IV we will see that the Mpemba effect, as it is now called, also provides a good illustration of the need to formulate a scientific hypothesis carefully, and the need for theory in the design of an experiment. We see that the Mpemba effect is much more difficult to study experimentally than might be expected, and we discuss some common problems with household experiments on the Mpemba effect. An analysis of the experiments naturally brings up Popper's thesis that a scientific hypothesis must be falsifiable.[13]

The discussions in Secs. II–IV should be comprehensible regardless of whether the Mpemba effect is real or not. In Sec. V we discuss possible theoretical mechanisms for the effect, and readers uninterested in the history may jump straight to Sec. V. We explain why a common proof that the Mpemba effect is impossible is flawed. Multiple explanations have been proposed for the effect. Evaporative cooling is one of the better explanations, but the effects of convection, dissolved gases, and the surrounding environment may also be important. We discuss the results of contemporary experiments on the effect, which are confusing, but for interesting reasons.

It has sometimes been reported that hot water pipes are more likely to burst from freezing than adjacent cold water pipes. Experiments on this phenomenon, which we discuss in Sec. VI have been more conclusive than those on the Mpemba effect and target supercooling as the cause. The experiments on pipes are closely related to the Mpemba effect, because they provide a clear situation where the water can "remember" what has happened to it. In Sec. VII we look at the possible importance of supercooling in the Mpemba effect, ultimately concluding that its role is unclear. Finally, in Sec. VIII we discuss the possibilities for future experiments that can be done by students.

II. EXPERIMENTS BEFORE THE SCIENTIFIC REVOLUTION

The Mpemba effect has long been known in the Western world (although not by this name until fairly recently). Around 350 B.C., Aristotle wrote[8]

> "If water has been previously heated, this contributes to the rapidity with which it freezes: for it cools more quickly. (Thus so many people when they want to cool water quickly first stand it in the sun: and the inhabitants of Pontus when they encamp on the ice to fish…pour hot water on their rods because it freezes quicker, using the ice like solder to fix their rods.) And water that condenses in the air in warm districts and seasons gets hot quickly."

Aristotle used this observation in support of antiperistasis, which is the "sudden increase in the intensity of a quality as a result of being surrounded by its contrary quality, for instance, the sudden heating of a warm body when surrounded by a cold.[14,15]

Although the idea of antiperistasis now sounds ridiculous with the hindsight of our understanding of heat transfer, energy, and temperature, it should be remembered that Aristotle was working without these paradigms and without a thermometer. The fact that ice requires cold temperatures, yet hail comes in the summer, rather than the winter, requires an explanation—Aristotle's explanation was antiperistasis. Later, several medieval scientists used antiperistasis to explain the (apparent) facts that bodies of water are colder in the summer and that human bodies are hotter in the winter.[14] Although we can now explain these observations with our modern theory of heat transfer, the explanations are not obvious. The concept of temperature and the zeroth law of thermodynamics are counterintuitive to anyone who has touched metal and wood on a cold day.

In the 13th century, well before the scientific revolution, Roger Bacon argued repeatedly for the importance of experiments in science. He wrote[9]

> "Moreover, it is generally believed that hot water freezes more quickly than cold water in vessels, and the argument in support of this is advanced that contrary is excited by contrary, just like enemies meeting each other. But it is certain that cold water freezes more quickly for any one who makes the experiment. People attribute this to Aristotle in the second book of Meteorologics; but he certainly does not make this statement, but he does make one like it, by which they have been deceived, namely, that if cold water and hot water are poured on a cold place, as upon ice, the hot water freezes more quickly, and this is true. But if hot water and cold are placed in two vessels, the cold will freeze more quickly. Therefore all things must be verified by experience."

What is particularly interesting about this quote is that Roger Bacon agrees that hot water can under some circumstances freeze faster than cold water, but argues that specification of the precise experimental conditions is important. We will see that this observation is crucial and is equally important in discussions about contemporary experiments on the Mpemba effect.

In the Middle Ages, debates raged over whether objects could only be cooled by extrinsic sources or whether some objects might be able to cool themselves. In the middle of this debate, Giovanni Marliani reported around 1461 on experiments described here by Clagett:[16]

> "…To support his contention that heated water freezes more rapidly [than cold], Marliani first points to a passage in Aristotle's *Meteorologica* affirming it. However, [Marliani] does not depend on Aristotle's statement alone. He claims that not only has he often tested its truth during a very cold winter night, but that anyone may do so. You take four ounces of boiling water and four ounces of nonheated water and place them in similar containers. Then the containers are exposed to the air on a cold winter's morning at the same time. The result is that the boiling water will freeze the faster."

Belief in the Mpemba effect continued strong into the 17th century. Francis Bacon and Descartes both wrote extensive works on the scientific method and experiments, and both wrote about the Mpemba effect. Bacon wrote that "…water a little warmed is more easily frozen than that which is quite cold… ."[10] In 1637 Descartes wrote about this phenomenon in *Les Meteores*, a work that was published as an attachment to his more famous *Discourse on Method*.[11] He emphasized the importance of experiment, described how to analyze the density-dependence of water, and stated results about the freezing times:

> "We can see this by experiment, if we fill a beaker—or some other such container having a long, straight neck—with hot water, and expose it to freezing cold air; for the water level will go down visibly, little by little, until the water reaches a certain level of coldness, after which it will gradually swell and rise, until it is completely frozen. Thus the same cold which will have condensed or shrunk it in the beginning will rarefy it afterwards. *And we can also see by experiment that water which has been kept hot for a long time freezes faster than any other sort*, because those of its parts which can least cease to bend evaporate while it is being heated (emphasis added)."

A modern writer on Descartes has commented on the italicized statement: "This statement, which the simplest of experiments could have refuted, was repeated with elaborate details in a letter to Mersenne, and it emphasizes Descartes' readiness to rely on *à priori* conclusions."[17] But this writer's position is contradicted by Descartes' letter to Mersenne in which Descartes makes clear that he has done this experiment. In this 1638 letter Descrates wrote that[18,19]

> "… I dare to assure you that there is nothing incorrect, because I did these experiments myself, and particularly the one which you commented on of the *hot* water that freezes more quickly than *cold*; where I said not *hot* and *cold*, but that *water that one has held for a long time over the fire freezes more quickly than the other*; because in order to correctly do this experiment, one must first have boiled the water, then let it cool off, until it has the same degree of coolness as that in a fountain, and having tested it with a thermometer, then draw water from that fountain, and put the two waters in the same quantity in same vases. But there are few people who are capable of correctly doing these experiments, and often, in doing them poorly, one finds the complete opposite of what one should find (emphasis in original)."

As with Roger Bacon's earlier experiment, we see that the details of the experiment are crucial. Descartes did not measure the time for the hot water to freeze, but wrote that when water has been heated, it is somehow changed so that it cools more easily, even after being brought back to room temperature. Although this observation described is different from our statement of the Mpemba effect, it is similar in that it implies some sort of history-dependence (memory) of the water. Descartes' letter also indicates that both he and others had done this experiment and that the results are contradictory, a problem that we will also see in more modern experiments.

With the advent of the modern theory of heat transfer, these earlier observations were forgotten. Because these experiments appear to contradict what we know about heat, it is natural to dismiss them as mistakes.

Presentations in textbooks typically show the progress of science as a simple, straight-line progression, with experiments pointing in a straightforward and unambiguous manner to new scientific theories. But, as Kuhn has pointed out, the development of scientific theories is not so simple.[12] Most of the time scientists are engaged in what Kuhn calls "normal science," during which research "…is a strenuous and devoted attempt to force nature into the conceptual boxes supplied by professional education … ."[20] When scientists are working under a given paradigm, results that cannot be forced into the existing paradigm might be ignored, as attention is focused on experiments that appear more promising for advancing knowledge. To give one of Kuhn's examples:[21]

> "In the eighteenth century, for example, little attention was paid to the experiments that measured electrical attraction with devices like the pan balance. Because they yielded neither consistent nor simple results, they could not be used to articulate the paradigm from which they derived. Therefore, they remained mere facts, unrelated and unrelatable to the continuing progress of electrical research. Only in retrospect, posessed of a subsequent paradigm, can we see what characteristics of electrical phenomena they display."

The Mpemba effect illustrates the points raised by Kuhn. Because the Mpemba effect appears to contradict modern theories of heat, scientists are more skeptical, or even dismissive, of experiments that show the Mpemba effect. Furthermore, like the eighteenth century experiments with pan balances, experiments on the Mpemba effect, for reasons we will discuss, yield "neither consistent nor simple results." Thus, the Mpemba effect, although interesting, is a factual curiosity, and is not fundamental to our modern understanding of heat.

Kuhn briefly mentions the experiments by Marliani and Bacon: "…the natural histories often juxtapose [correct] descriptions…with others, say, heating by antiperistasis (or by cooling), that we are now quite unable to confirm."[22] Kuhn did not cite any experimental evidence that we are unable to confirm these older results.[23] We will see that at the time that Kuhn wrote this, there were multiple papers confirming the existence of the Mpemba effect. Kuhn thus unintentionally, and ironically, demonstrates how our theoretical expectations can color our experimental beliefs.

III. ERASTO MPEMBA AND 20th CENTURY KNOWLEDGE

Erasto Mpemba was a secondary school student in Tanzania.[1] In 1963 Mpemba and his fellow students were making ice cream using a mixture that included boiled milk. Because excessively hot objects could damage the refrigerator, they were supposed to let their mixture cool before putting it in the refrigerator. However, space in the refrigerator was scarce, and when another student put his mixture in without boiling the milk, Mpemba decided to put his hot mixture in without waiting for it to cool. Later, Mpemba found that his hot mixture froze first.

Mpemba asked his teacher for an explanation, but his teacher said that Mpemba must have been confused. When the teacher later covered Newton's law of cooling, Mpemba persisted in his questioning. The teacher's response was "Well, all I can say is that is Mpemba physics and not the universal physics." From then on the teacher and the class would mock Mpemba's mistakes by saying "That is Mpemba's mathematics," or "That is Mpemba's physics."[1]

Mpemba ran more experiments, both with water and with milk and obtained similar results. When Dr. Osborne, a professor at a nearby university, visited Mpemba's school, Mpemba asked him why water at 100 °C froze faster than water at 35 °C. After returning to his university, Osborne asked a technician to test Mpemba's question. "The technician reported that the water that started hot did indeed freeze first and added in a moment of unscientific enthusiasm 'But we'll keep on repeating the experiment until we get the right result'."[24] More experiments gave similar results, and Mpemba and Osborne later published their results.[1] In the same year, Dr. Kell of Canada independently reported the phenomenon, along with a theoretical explanation that we will consider later.[25]

Subsequent publications showed that the effect was already known and believed by non-scientists in diverse regions of the world. Kell stated that it was widely believed in Canada, and that "Some will say that a car should not be washed with hot water because the water will freeze on it more quickly than cold water will, or that a skating rink should be flooded with hot water because it will freeze more quickly."[25] Mpemba reported that he found that ice cream makers in Tanga City, Tanzania used hot liquids to make the ice cream faster.[1] Letters to the New Scientist reveal a wealth of lay observations. One writer stated that it was well known that in the winter, hot water pipes were more likely to freeze than cold water pipes.[26] Another stated that the phenomenon was well known in the food freezing industry.[27] Several letters reported that their (non-scientist) friends and family had known of this effect even in the 1920s.[28–30] One writer was a science teacher, who described his experiences with a student who asked him why hot water froze faster than cold:[31]

> "…I told him that it was most unlikely, but he replied that he had seen it happen when his mother threw out her washing water onto the path. I explained to him that the particles in the hot liquid would be escaping more readily to the atmosphere due to evaporation and that this would leave a thinner layer of liquid to freeze than in the colder one where the particles would be escaping more slowly. He was not, however, convinced, and a few

> days later he reported that he had placed two cans, one containing hot water, and the other cold water, outside and that the hot one was still the first to freeze…Still in no doubt I criticized his experiment …[He then] obtained two identical specimen jars and placed hot water ($\approx 50\ ^\circ\mathrm{C}$) in one and colder water ($\approx 20\ ^\circ\mathrm{C}$) in the other; both tops were left off and they were placed in the freezing compartment of a refrigerator. To my disbelief, and his delight, the hotter one was indeed the first to form a layer of ice on the surface… ."

The skepticism with which scientists react to the Mpemba effect is quite common.

Mpemba's story provides a parable about dismissing the observations of non-scientists. But his story is particularly interesting because it is more than just a story of close-minded scientists. There is no excuse for the Tanzanian teacher's mockery of Mpemba. But is it "unscientific" for scientists to immediately suspect errors in the experiment upon hearing of the Mpemba effect? Kuhn emphasizes that scientists interpret experiments in light of the reigning paradigm; that is, with their preexisting theoretical understanding.[12]

What is interesting about the Mpemba effect is that unlike the examples commonly given in science textbooks, where theory and experiment march hand-in-hand, always leading to further progress, theory here (rightly or wrongly) prevents acceptance of experimental results. We are not arguing that the reaction of the scientific community to surprising experimental results is arbitrary or necessarily hostile. Our point is that the reaction to an experiment depends significantly on how well the experiment matches accepted theoretical preconceptions. Because experimental claims can be in error, scientists do not accept all published claims. Although few scientists would find this statement controversial, it is quite different than the impression one obtains from science textbooks and from what appears in certain positivistic views of science. The Mpemba effect provides a lovely case for considering these issues, because although it provokes skepticism, it has been observed in multiple experiments; yet, in support of the skeptical position, we will see that the experimental results are not consistent and that the theoretical situation is still unsettled.

IV. WHAT IS THE QUESTION AND IS IT SCIENTIFIC?

To analyze the Mpemba effect, we first need to precisely state what we are trying to test. At first sight, the question is simple: "Does hot water freeze faster than cold?" However, this formulation is not adequate. Clearly, a small drop of hot water can freeze faster than a cold ocean. Hot water in a freezer will freeze faster than cold water on a warm day (the latter will not freeze at all). These examples are silly, but illustrate the need to state the question clearly.

A better statement of the problem might be "Given two bodies of water, which are identical in all respects (for example, mass, shape, surroundings, …), except that one is initially at a higher uniform temperature than the other, the hotter water will freeze first." But this statement cannot be correct. If the initially hotter water is at $99.9999\ ^\circ\mathrm{C}$ and the initially colder water is at $0.0001\ ^\circ\mathrm{C}$, then the initially cold water is just seconds away from freezing, and the hot water cannot possibly overtake it. Furthermore, there is no reason to expect the Mpemba effect to occur for all possible initial parameters.

So a better phrasing might be "There exists a set of initial parameters and a pair of initial temperatures such that given two bodies of water identical in these parameters, and differing only in their initial uniform temperatures, the hot one will freeze sooner." This statement is much better, although we will see later that deficiencies remain.

Once the Mpemba effect is properly stated, it is clear that we are only looking for some set of parameters, such that if we plot the freezing time versus the initial temperature, there is some range of initial temperatures for which the effect holds. Restriction of the effect to a specific class of parameters is logically necessary for the problem to be at all reasonable, but this point is not always appreciated in popular discussions. Consider the discussion of the Mpemba effect in Ann Landers' column:[32]

> …Ann Landers addressed [the question of whether warm water freezes faster than cold water], as well as the related cosmic issue of whether cold water boils faster than hot water. She…consulted Dr. Jermore Weisner, chancellor of the Massachusetts Institute of Technology, who kicked the problem over to the MIT Dean of Science, Dr. John W. Deutch. Landers never recorded what Deutch thought of being given such a problem by an advice column, but the eminent scientist reported 'Neither statement was true.' Whereupon 'Self-Reliant in Riverdale'…upbraided her for using 'argument by authority' rather than doing her own experiment. 'Self-reliant' said she reached the same conclusion as Deutch by using a pan of hot water, a thermometer, a stove, a refrigerator, and a watch with a second hand."

Cecil Adams also discussed the Mpemba effect in his popular column:[33]

> "…I carefully measured a whole passel of water into the Straight Dope tea kettle and boiled it for about five minutes. This was so I could compare the freezing rate of boiled H_2O with that of regular hot water from the tap. (Somehow I had the idea that water that had been boiled would freeze faster.)
>
> Finally I put equal quantities of each type into trays in the freezer, checked the temp ($125\ ^\circ\mathrm{F}$ all around), and sat back to wait, timing the process with my brand new Swatch watch, whose precision and smart styling have made it the number one choice of scientists the world over.
>
> I subsequently did the same with two trays of cold water, which had been chilled down to a starting temperature of [$38\ ^\circ\mathrm{F}$].
>
> The results? The cold water froze about 10 or 15 minutes faster than the hot water, and there was

> no detectable difference between the boiled water and the other kind. Another old wives' tale thus emphatically bites the dust. Science marches on."

These discussions fail to appreciate that a single test cannot show that the effect never occurs for any parameters and initial temperatures.

Further consideration of this point brings up another issue. Logically, our statement about the Mpemba effect can never be proven false. Regardless of the number of experiments that fail to see the effect, a believer in the Mpemba effect can always claim that the effect occurs for other sets of initial parameters that differ slightly from the ones used. Popper has argued that the hallmark of a scientific hypothesis is that it be falsifiable, meaning that it could possibly be proven false.[13] Is our most recent statement of the Mpemba effect unscientific?

It is not unusual that a scientific phenomenon cannot be proven impossible, because the parameter space in which it might occur is, in principle, infinite. If we search a representative sample of the parameter space over which the phenomenon might be thought to occur, and the phenomenon is not observed, that would be fairly convincing evidence against it. We thus need a list of parameters that we might vary when studying the Mpemba effect. We might include the mass of the water, the shape of the container, whether the container has a lid, the surrounding environment, and the gas content of the water. Note that several items on this list are not single parameters. For example, the shape of the container requires multiple parameters. We might also want to include the color of the container, or the electrical conductivity of the walls of the refrigerator. If we list all the parameters we might consider, the list would be infinite, and we would be at a loss as to how to proceed. Without a theoretical framework in which to design and conduct an experiment, we are reduced to randomly collecting facts, such as the color of the container. However, we have strong theoretical reasons for ignoring parameters such as the color of the container and the electrical conductivity of the walls of the refrigerator.

As we will see in Sec. V, the first several parameters can plausibly be considered important. Furthermore, their effects are not independent of one another. But an experimenter cannot be expected to establish a vast multidimensional array of containers with different dimensions and shapes, independently varying masses, gas contents, and refrigeration methods. We do not claim that a scientific investigation of the Mpemba effect is impossible. But a common response upon first hearing about the Mpemba effect is that it should be straightforward to study experimentally. To the contrary, even for this deceptively simple problem, productive experimental design requires at least some theoretical understanding of why the effect might occur—otherwise we will not know whether we should consider, for example, the gas content of the water. We will see that because the time to freezing is sensitive to many parameters, the experimental results become very confusing.

Our statement of the Mpemba effect now reads "There exists a set of initial parameters (mass and gas content of the water, container shape and type, and refrigeration method), such that given two bodies of water identical in these parameters, and differing only in their temperatures, the hot body will freeze sooner." One final difficulty that must be considered is how to define the time of freezing—do we consider it to be frozen when ice crystals first appear or only when the entire body of water is frozen? Or, to simplify the experiment, we might just measure the time until some specified part of the water reaches 0 °C. This issue might seem minor, but we will see in Sec. VII that it is potentially crucial.

V. HOW COULD THE MPEMBA EFFECT OCCUR?

We have deliberately avoided discussing the theoretical explanations for the Mpemba effect until now. We have done so because the historical reaction to the Mpemba effect is only comprehensible in light of the effect's apparent inconsistency with modern conceptions of heat transfer and to emphasize the need for a theoretical framework when designing experiments on the effect. We now discuss some proposed mechanisms for the Mpemba effect, but we will not attempt to analyze their relative plausibility in depth.

To see how the effect might occur, it is useful to think about why the effect appears impossible. Suppose that the initial temperatures for the hot and cold water are 70 and 30 °C. Then the 70 °C must first cool to 30 °C, after which it must do everything the 30 °C water must do. Hence the 70 °C water must take longer to freeze.

A good way of analyzing the Mpemba effect is to think about why this argument is incorrect. The problem with this argument is that it implicitly assumes that the water is completely characterized by a single parameter—the temperature. We need to think of a parameter that might change during the course of the experiment so that the 70 °C water cooled to 30 °C would not be the same as the water initially at 30 °C.

One possible parameter is the mass of the water. Both bodies of water initially have the same mass. But if the initially hotter water loses mass to evaporation, then the 70 °C water cooled to 30 °C will have less mass and be easier to freeze; that is, less energy will need to be removed to cool and freeze it. This argument is one of the strongest explanations for the Mpemba effect. Kell numerically integrated the heat loss equations assuming that the cooling was by evaporation alone and that the mass lost to evaporation never recondensed and found that there were initial temperatures for which the hot water would freeze faster than the cold water.[25] But this explanation does not prove that evaporative cooling is the only factor behind the Mpemba effect. Several experimenters have claimed that the amount of mass lost to evaporation was insufficient to explain their results.[2,34,35] And Wojciechowski *et al.* observed the Mpemba effect in a closed container, which suggests that evaporative cooling is not the sole cause of the effect.[3]

A more complex parameter is the temperature distribution of the water. As the water cools it will develop convection currents, and the temperature will become nonuniform so that the water is no longer characterized by a single number. The analysis is now much more complex because we have to consider a scalar field. Nevertheless, we can say that for temperatures above 4 °C, hot water is less dense than cold water and will thus rise to the top. So we can generally expect that when the 70 °C water has cooled to an average temperature of 30 °C, the top of the water will be hotter than 30 °C and the bottom of the water will be below 30 °C. If the water primarily cools at its surface, the nonuniform distribution with an average temperature of 30 °C will thus lose heat faster than water at a uniform 30 °C. Consistent with this idea is that Deeson found that gentle stirring substantially increased the time to freezing.[7] Convection could work in concert with other factors such as evaporative cooling. Convection currents are sensitive to the shape and dimensions of the container, so this explanation may play very different roles for different container shapes.

Parameters also need to be associated with the surrounding air. Modeling the cooling process should take into account the convection currents of the air, which will depend on the shape of the refrigerator. Firth's studies of the Mpemba effect found that the cooling environment was of as much importance as any aspect of the container itself.[5]

It has also been suggested that the Mpemba effect could be explained if the containers of water were sitting on layers of frost. Frost conducts heat poorly and the hot water causes the layer of frost to melt, thus establishing better thermal conduct with the refrigerator floor.[36] The melting of frost might explain some everyday observations of the effect, but the published experiments generally used containers on thermal insulators.

Another possibility is that the hot and cold water differs in their gas content. Hot water can hold less dissolved gas than cold water, and the gas content affects the properties of the water. Mpemba and Osborne's original experiments were done with recently boiled water to remove dissolved air,[1] as were the experiments by Walker.[4] These experiments suggest that dissolved gasses are not necessary to the Mpemba effect. (To confuse matters, under typical conditions the degassed water will slowly regain dissolved gasses from the atmosphere.) However, Freeman only observed the Mpemba effect when carbon dioxide was dissolved in the water.[2] Similarly, Wojciechowski *et al.* only saw the effect for non-degassed water.[3] A number of explanations have been proposed for how the amount of dissolved gas could affect the properties of the water and cause the Mpemba effect, although they remain largely speculative. One of the few quantitative findings is that for water saturated with carbon dioxide, the enthalpy of freezing was smaller for the initially warmer water (but that preheating is irrelevant to the enthalpy if dissolved gasses are absent).[3] We will return to the effects of dissolved gases and other impurities when we discuss supercooling.

All the factors we have discussed are at least potentially important in explaining the Mpemba effect. What makes the situation particularly difficult to analyze is that the factors are not independent of each other. For example, the rate of evaporative cooling depends on the shape of the container. The experimental results we have described do not point to a single, clear, conclusion.[1–7] 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. (Recall Kuhn's statement about 18th century pan balance experiments.) As Firth wrote,[5] "There is a wealth of experimental variation in the problem so that any laboratory undertaking such investigations is guaranteed different results from all others." It is not even clear whether it makes sense to look for a single explanatory factor, isolated from all others.

In Fig. 1 we show the experimental results by Walker of the dependence of the time of freezing on the initial temperature for various initial conditions. Some graphs show a strong Mpemba effect, some only show a weak one, and some show no Mpemba effect at all. These results indicate that the cooling is sensitive to a number of parameters. Furthermore, Walker reported that although his results were mostly repeatable, he "still obtained strange large deviations on some of the results."[4]

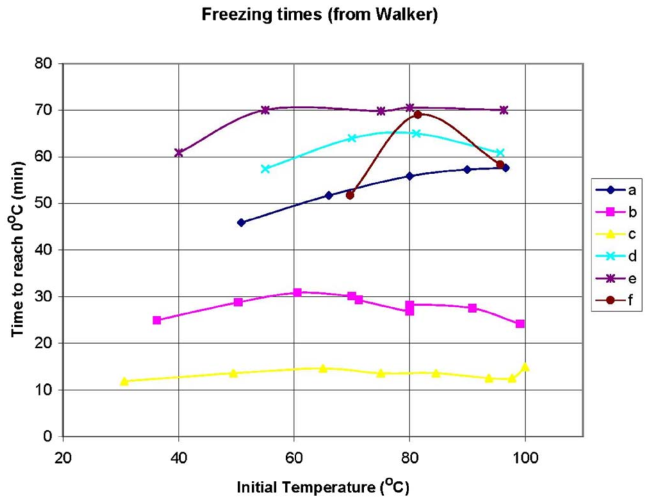

Fig. 1. Dependence of the time of freezing on the initial temperature for various experimental conditions: (a) 50 ml in small beaker, (b) 50 ml in large beaker, (c) 50 ml in large beaker in frost-free freezer, (d) 100 ml in large beaker, thermocouple near bottom, (e) 100 ml in large beaker, covered with plastic wrap, thermocouple near bottom, and (f) 100 ml in large beaker, thermocouple near top. Graph produced from data obtained by Walker (Ref. 4).

VI. SUPERCOOLING AND BURSTING WATER PIPES

It has often been said that hot water pipes burst from freezing more often than adjacent cold water pipes.[26,37–39] This effect is different from the Mpemba effect, but it is similar because it requires the water to have a memory. The mechanism behind the bursting water pipes is better understood than that behind the Mpemba effect.

The water pipe claim was first investigated by Brown in 1916.[37] He confirmed the claim by taking 100 glass test tubes and filling 50 with tap water and 50 with tap water that had been boiled. After allowing all the tubes to first reach room temperature, he placed them outside in subzero temperatures. He found that 44 of the tubes with the boiled water burst, while only 4 of the tubes with non-boiled water burst. Because all the water was at the same temperature when placed outside (as with Descartes' experiment) and he looked for the occurrence of bursting rather than the time until freezing, this observation is not a test of the Mpemba effect.

Freezing water will generally supercool. Supercooling to −4 to −6 °C is common, and much greater supercooling can occur for small samples.[38,40] Once freezing starts, the ice-water mixture must go to 0 °C. So when freezing begins, a finite fraction of the water must lose energy and turn to ice, transferring energy to the remaining subzero water, whose temperature will rise to 0 °C. Thus, the more supercooling occurs (that is, the lower the temperature at which freezing begins), the larger the volume fraction of water that will freeze initially. In other words, the larger the fraction of H_2O molecules that will be in ice structures. Also, a certain volume fraction of ice will not always correspond to the same volume of the region spanned by the ice. The ice will form a dendritic structure interspersed with liquid. If more super-

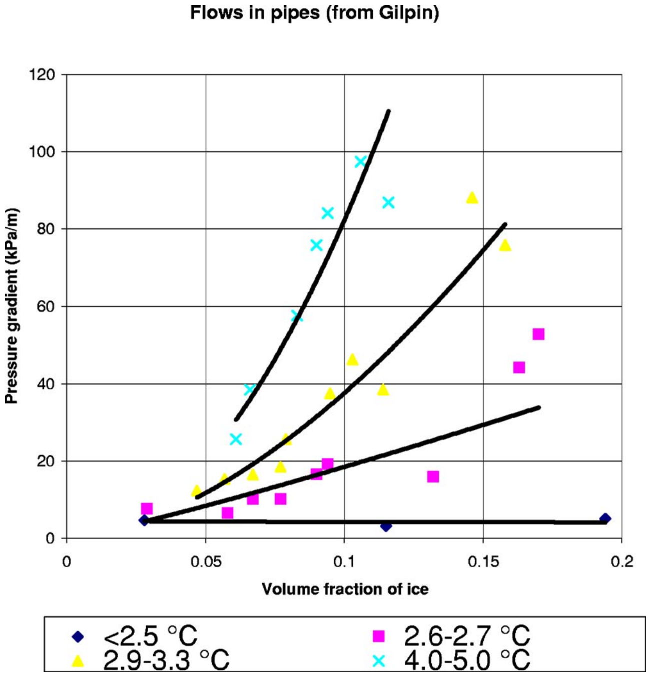

Fig. 2. Effect of the amount of supercooling on the pressure gradient required to start flow through the pipe. The four sets of data points are for different amounts of supercooling. Graph produced from data obtained by Gilpin (Ref. 39). The curves are power law fits and are guides to the eye only.

cooling has occurred, more of the water will have reached subzero temperatures, and the dendritic structure will span a larger region for a fixed volume fraction of ice.[38,39]

Brown observed that the water that had been boiled first, later supercooled, while the nonboiled water did not, and argued that this difference was responsible for the difference in bursting behavior.[37] He argued as follows: If water in a pipe freezes near 0 °C, only a small amount of ice will be formed initially. This ice will be localized to the coldest regions, the sides of the pipes, leaving a hole in the center. With further cooling the hole will shrink, but until all the water has frozen, liquid water will still be able to flow through the hole. Furthermore, the water flow can break away the ice on the sides, relieving pressure. In contrast, if the water supercools significantly before freezing, a larger structure of dendritic ice will form throughout the pipe. This dendritic ice will span more of the pipe, possibly leaving no hole, and thus blocking the flow of water, resulting in a burst pipe. Consistent with this explanation, Brown found that the ice rose higher from expansion in the tubes with non-boiled water, indicating the existence of a central region in which the water was mobile, and the ice able to move up.

In 1977 Gilpin performed quantitative experiments that confirmed Brown's qualitative explanation.[39] Gilpin exposed pipes to subzero temperatures and measured the pressure gradient necessary to induce the flow of water at various times after the ice had formed. He found that the more supercooling, the greater the pressure gradient needed for the same amount of total ice formed (see Fig. 2). He concluded, as did Brown, that with more supercooling, the ice formed would be more likely to form a dendritic structure spanning the pipe and causing blockage. He confirmed this picture with photographs of the cross section of the pipe during the freezing process.

These experiments convincingly demonstrate that greater supercooling leads to burst pipes, leading to the question of why initially hot water supercools more than initially cold water. Brown argued that it is because boiled water has less dissolved gas and the dissolved gas prevents supercooling.[37] However, Dorsey did an extensive series of experiments on the factors affecting supercooling and found that dissolved gasses were not a significant barrier to supercooling; he also pointed out that, unlike boiled water, the water in hot water pipes contains significant amounts of dissolved gas.[38,41] Dorsey agreed that heated water supercooled more and this supercooling would result in burst pipes, but argued that the greater supercooling occurred because heating served to prevent nucleation sites.[38] Both explanations agree that the formation of nucleation sites is prevented by heating the water, but disagree as to the cause.

Gilpin not only confirmed that hot tap water supercooled more than cold tap water, but that tap water left in an open container supercooled least of all. This observation can be explained by the fact that water in an open container will absorb impurities from the air and these impurities can act as nucleation sites.[39]

VII. SUPERCOOLING AND THE MPEMBA EFFECT

The results discussed in Sec. VI are in the wrong direction to explain the Mpemba effect. If initially hot water supercools more, then it has to reach an even lower temperature to freeze than initially cold water, which will increase the time that it takes to freeze. Consideration of supercooling greatly complicates the Mpemba effect, and it is not clear how or whether it helps to explain it. We first need to decide precisely how we measure the time to freezing. If we wait until the first appearance of ice, then the experimental situation is complicated by the randomness of supercooling, and multiple trials are needed to obtain accurate average times to freezing. For simplicity, many experiments have studied the time for some specified location in the water to reach 0 °C.[2,4,5] Supercooling is irrelevant for these experiments if the specified location is one of the first to reach 0 °C.

Auerbach considered the relevance of supercooling to the Mpemba effect.[6] He found that initially hot water would supercool less (measuring the time to the first appearance of ice crystals) than initially cold water. Auerbach did not determine the reason, but pointed out that the initially hotter water should have greater temperature gradients, and that the presence of a gradient is known to trigger crystallization.[42] However, his observation that heated water supercools less than nonheated water is opposite to the findings of Brown and Dorsey.[37,38] Auerbach did a relatively small number of trials so the significance of his results is unclear.

Although Auerbach's result is in the correct direction to explain the Mpemba effect (because if the hot water supercools less, it will freeze sooner), he found that the initially hot water took longer to freeze on average, due to the greater time the hot water took to reach 0 °C.[6] Thus it is unclear whether Auerbach's experiments should even be described as observations of the Mpemba effect. Due to the random fluctuations in the times until freezing, Auerbach found that the hot water might freeze first by chance. He found that when the ambient temperature T_a was $-5\,^\circ\mathrm{C} > T_a > -8\,^\circ\mathrm{C}$, the probability of a randomly chosen container of initially hotter water freezing before a randomly chosen container of initially colder water was 53%.[6] For $-8\,^\circ\mathrm{C} > T_a > -11\,^\circ\mathrm{C}$, the probability was 24%. If the hot water, on average, takes longer to freeze, but only freezes first in some samples due to random fluctuations, it is not clear that this observation should be called a Mpemba effect. (Given Auerbach's small number of samples, 53% is not significantly greater than 50%.) Although the experiments on pipes show that supercooling can induce significant memory effects, the role of supercooling in the Mpemba effect remains uncertain.

VIII. PROSPECTS

It is clear that evaporative cooling can play an important role in the Mpemba effect, and that the history of the water can affect the amount of supercooling. But beyond these conclusions, experiments paint a very muddled picture. More experiments are needed to solve this 2000+year-old puzzle. Despite the theoretical complexity of the Mpemba effect, the experiments needed to probe it can be done at the K–12 and undergraduate level. Indeed, simple experiments on the Mpemba effect are a common science fair project.

Much thought needs to go into the experimental design. Walker has discussed the basic setup and reading Walker's article[4] is a good way to appreciate some of the subtle complexities in the experiment. For example, Walker pointed out that the container should be heated along with the water, because if hot water is poured into a cold container, the sudden change in the water's temperature causes problems. To make sure that all samples of water have the same mass, masses need to be measured after heating, rather than before, as a fair amount of mass is lost during heating. The environment surrounding the container is important, and it can make a difference whether the water is in the middle of an empty freezer or jammed between a frozen pizza and a frost-covered bucket of ice cream. The temperature can be read with a common thermometer, but a device that can more quickly and accurately register changes in temperature is better.

A series of measurements will produce a graph of freezing time versus initial temperature of the sort shown in Fig. 1. A single curve may or may not show a Mpemba effect, but is not particularly useful for probing the cause(s) of this phenomenon. To see how the Mpemba effect depends on the various parameters of interest, several curves need to be produced for different parameter settings. In practice, you will have to decide which factors are of most interest to you and design your experiment accordingly. I give some suggestions in the following, but there are many reasonable experimental designs.

Kell claimed that because the Mpemba effect relies on surface cooling, it is more likely to be observed in wooden pails than in metal ones, because in metal pails much heat is lost through the sides.[25] This claim can be tested by producing a series of curves of freezing time versus: initial temperature for containers with differing degrees of thermal insulation on the sides. Alternatively, varying the height of the water, while keeping the base fixed, would provide another way of varying the importance of evaporation.

The importance of evaporation can be largely eliminated by putting the water in a closed container or by putting a layer of oil over the surface of the water. Such experiments would be extremely useful in assessing claims that evaporation is the sole cause of the Mpemba effect. I know of only one published paper observing the Mpemba effect in a closed container.[3] Confirming that the Mpemba effect can occur in closed containers would show that it can occur without evaporation.

Rather than looking at freezing times versus initial temperature, you could investigate supercooling. Simply reproducing earlier experiments would be valuable in resolving the discrepancy between the recent results of Auerbach[6] and the older results of Brown and Dorsey.[37,38] A repeat of Descartes' experiment would also be interesting.

More systematic studies of how the history of the water affects its properties would be helpful. For example, if you find that pre-boiled tap water has different properties than water straight out of the tap, you could investigate why it differs (dissolved oxygen? impurities?) by looking at how long it takes pre-boiled water's properties to return to those of tap water and under what conditions.

An estimate of the errors is crucial, because if a graph of freezing time versus initial temperature shows only a weak local maximum, it would be unclear if this maximum corresponds to the Mpemba effect or is just the result of fluctuations. As with any experiment, you need to make sure that your results are repeatable. It is better to have a small amount of reliable data than a large amount of unreliable data.

What would constitute experimental success? You do not need to observe the Mpemba effect for your experiment to be a success. Finding that the Mpemba effect does not occur under certain conditions is a good experimental result. But it is more dramatic and psychologically satisfying if you can find conditions under which the effect occurs. And if you do, you can then study what changes destroy the effect, which provides a potentially valuable probe of the phenomenon. You may want to do some preliminary testing to find parameters where the Mpemba effect occurs and then decide how to proceed. If enough experiments are done, perhaps this 2000+year-old problem can be resolved.

Finally, those who like the counterintuitive nature of the Mpemba effect might be interested in a similar phenomenon: water drops will last longer on a skillet well above 100 °C than on one only a little above 100 °C. This effect is easier to explain than the Mpemba effect.[43]

ACKNOWLEDGMENTS

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Disk Electrostatic Machine. This electrostatic machine with a forty-inch glass disk is in the collection of Vassar College in Poughkeepsie, New York. Standing behind the machine is Sonia Greenslade. The machine is unmarked, but it is almost certainly by Edward S. Ritchie of Boston. Vassar was founded in 1861, and the 1860 catalogue of E. S. Ritchie of Boston shows a similar machine for $160. Originally this had a silk "pillow case" covering up the lower half of the glass disk to prevent the loss of the electrical charge. Ritchie's largest electrostatic machine had a six-foot diameter plate, used for many years at the University of Mississippi. (Photograph and Notes by Thomas B. Greenslade, Jr., Kenyon College)

The following twelve questions should only be read after reading the paper

1. Is it true that hot water can freeze faster than cold water?

2. What is the purpose of the author in this paper?

3. What's the home institution of the author?

4. Name one possible explanation for the Mpemba effect.

5. Does the article have a conclusion? If so, what is it?

6. Who is Mpemba?

7. Name other physicists who studied the effect.

8. How many figures does the article have?

9. Can you say what the meaning of the horizontal and vertical axes represent in at least one of the figures?

10. Does the author acknowledge financial support from a funding agency?

11. How many references does the paper list?

12. Were they published in reputable journals?