The Mpemba Effect: Studying the effects of initial temperature, evaporation, and dissolved gasses on the freezing of water.

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An investigation into the Mpemba Effect was performed by studying the effects of initial temperature, evaporation, and dissolved gasses on the freezing of water. Precision thermistors were used to measure the temperature of three different samples of water in a freezer held at $-12.0 \pm 0.5°$C. The time it took the sample to completely change to ice was measured, using the latent heat of fusion. Data was collected for both water that is initially warm, and water that had been previously heated and then allowed to cool. It was determined that the Mpemba effect is widely reproducible, and the evaporation of mass from the samples was negligible. The conclusion was reached that the expulsion of dissolved gasses from the sample during the heating process resulted in the appearance of the Mpemba effect.

I. INTRODUCTION

As early as the fourth century BCE, scientists and observers puzzled over the fact that, in some cases, initially warmer water appears to freeze faster than initially colder water. The first known observation of this effect was documented by Aristotle around 300 BCE when he said "The fact that water has previously been warmed contributes to its freezing quickly; for so it cools sooner."[1]

In 1963, a Tanzanian secondary school student by the name of Mpemba observed the effect when making ice cream. Mpemba boiled milk to make ice cream and placed it, still hot, into the freezer. It was placed alongside the mixture of another student who, in haste, neglected to boil his concoction. When checking on the two mixtures "an hour and a half later [I] found that my tray had frozen into ice cream, while his was still only a thick liquid, not yet frozen."[2] It was this astonishing observation and documentation that gave the effect its name.

Since Mpemba reintroduced the subject in the 1960s, there has been significant research and investigation done on the phenomena, with widely varying results. Firth even went so far as to say that "any laboratory undertaking such investigations is guaranteed different results from all the others."[3] In order to understand, and eventually shed light on these inconsistencies, previous studies and their results must be considered.

In a 1971 study, Freeman concluded that "the experimental evidence obtained strongly suggests that dissolved carbon dioxide causes the Mpemba effect."[4] He says that tap water has some concentration of dissolved CO^2, and heating the water decreases the solubility of carbon dioxide. This would explain the effect, as long as the assumption that dissolved gasses affect the cooling of water is true.

More recently, David Auerbach studied the effect of supercooling on the freezing of water in his 1995 study. He concluded that supercooling took place in almost all samples. He said that the Mpemba effect is observed when "The hot water supercools, but only slightly, before spontaneously freezing. Superficially, it looks completely frozen."[5] His study says that the hot water will freeze at warmer temperatures, but not necessarily earlier times, because the colder water will supercool more than the hot.

All previous studies, with the exception of Auerbach, measured the time it took samples of water to reach 0° C. While this is widely accepted as the freezing point of water, this measurement does not shed light on the time it takes water to completely turn to ice.

Based on previous work, it is clear that there are wide number of factors that could potentially contribute to an effect that at first glance appears simple to test. In order to bring new information to the study of the Mpemba effect, it was decided that an investigation combining new and old theories would be appropriate. Similar to previous experiments, the contribution of dissolved gasses in the water, the effect of evaporation, and the effect of supercooling would be investigated. This experiment, however, would focus on when water was completely turned to ice, not simply when the sample reached 0° C.

II. THEORY & BACKGROUND INFORMATION

There are several fundamental thermodynamic concepts that relate to the freezing of water. First, the principle known as Newton's Law of Cooling is important to the study of water freezing. This law states that the heat loss of an object is proportional to the difference in the temperatures of the object and its environment. This can be shown by the fact that the change in temperature is proportional to the change in thermal energy,

$$\Delta Q = mC_P \Delta T \tag{1}$$

where m is the mass of the object, and C_P is the heat capacity of the substance. Using this law, it can be inferred that

$$\frac{dT(t)}{dt} = -K(T - T_e) \tag{2}$$

where T_e is the temperature of the objects environment and K is some experimental constant. This states that the bigger the difference in temperature is between the object and its environment, the faster the objects temperature will change. This does not support the effect, however, because every temperature that the cooler sample goes through, must also be transversed by the warmer sample.

Another principle that is critical to the investigation of the Mpemba effect is the enthalpy of fusion (directly related to the latent heat of fusion). The enthalpy of fusion is defined by the change in entropy that must occur for a substance to change from a solid to a liquid (or vice-versa). This principle is important because it illustrates how one can determined when the water is completely turned to ice.

Enthalpy is defined as

$$H = U + pV \tag{3}$$

where U is the energy of the system, p is the pressure, and V is the volume.[7] For the purposes of this experiment it can be assumed to good approximation that the changes in pressure and volume are small compared to the change in thermodynamic energy.

The change in enthalpy between the initial and the final state requires some amount of heat to be transfered. This heat is called the latent heat of fusion, and can be written as

$$dQ = \tau(s_f - s_i) \tag{4}$$

where dQ is the heat transferred, τ is the thermodynamic temperature (kT), and s_f and s_i are the final and initial entropies of the system, respectively.[7] This shows that some finite change in heat that occurs in the phase transition between liquid and solid. If we define this heat of fusion to be L, and assume the sample to have mass m, the energy that must be transferred for the phase transition to occur can be written as [9]

$$\Delta Q = Lm. \tag{5}$$

This heat of fusion for water at standard temperature and pressure is known to be L =333 J/g.[9]

In this experiment, it can be reasonably assumed that the rate at which thermal energy is being lost is constant. This is reasonable for several reasons. First, the temperature of the reservoir is held constant. Second, the Enthalpy of Fusion states that the amount of energy that is required for the phase transition must be transferred in order for the particles to be ordered into solid form, which will take some time. Only once this heat of fusion has been transferred can the temperature begin to change again, eventually cooling to the temperature of the reservoir. Therefore, during the phase transition the temperature of the sample will remain constant. If temperature is plotted as a function of time, a nearly flat plateau should be visible during the phase transition.

The effects of evaporation must also be considered when determining a theoretical understanding of the freezing of water. Based on the first law of thermodynamics, it is not sufficient to simply consider the mass of the sample when determining the effects of evaporation. The molecules in the water exhibit the classic energy distribution shown in Figure 1. The molecules in the long, tapering tail of the plot have significantly higher energy than the majority of the molecules. It is these higher energy molecules that are more likely to evaporate. Because of this the percentage of the mass lost does not directly correlate to the thermal energy transferred.

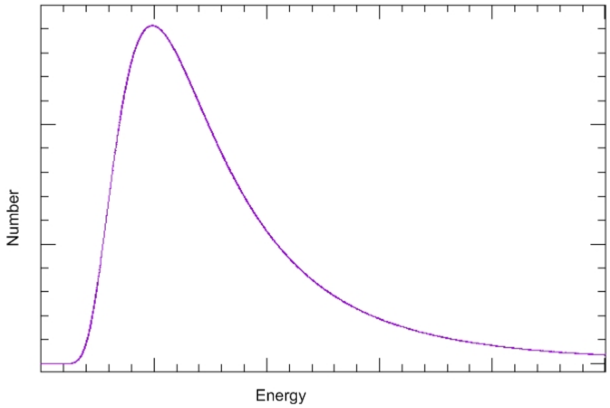

Figure 1: The energy of the water molecules is distributed as shown above. The ones with the highest energy are the most likely to evaporate, causing a large exchange of thermal energy.

The last factor that must be considered is the effect of dissolved gasses on the freezing of water. Because it is known that higher water temperature corresponds to lower dissolved gas content,[8] changing the gas content by heating the water will hopefully shed some insight into the impact of dissolved gas on freezing.

III. EXPERIMENTAL SET-UP

In this experiment, three samples at different temperatures were placed into 100ml Pyrex beakers. The samples were known to be the same size, as the mass of the water inside each container was held to 50 ± 0.5g. Submerged near the middle of each of these beakers was a YSI-44004 Precision Thermistor. These thermistors were used because they are interchangeable to ±0.2°C.

A constant current was generated in the circuit by a 100 μA TRI Research constant current source. By measuring the voltage across each thermistor (V1, V2, or V3), the resistance can be found using Ohm's law, because the current through the system is constant. The experiment was then wired as shown in Figure 2.

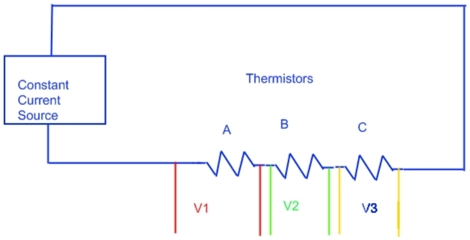

Figure 2: A wiring diagram of the circuit, including the constant current source, all three thermistors, and the wires for measuring the voltage across them.

The wires connected to measure the voltage across the thermistors were all connected to analog differential channels on a National Instruments USB-6009 DAQ. This device allowed the computer, using National Instruments LabVIEW software to read the difference in voltage, and record it as data. A virtual instrument (vi) was created that polled the USB device for the voltage information, and wrote it to a file.

The reservoir used in the experiment was the freezer compartment of an ordinary refrigerator. The temperature of the reservoir was precisely controlled using a Ranco ETC-11100 Electronic Temperature Controller. This device used a thermocouple wire to record the temperature inside the freezer compartment, and turn the power to the chilling device on and off to maintain a set temperature. For the purposes of this experiment, the freezer compartment was held at -12 ± 0.5°C.

IV. PROCEDURE & EXPERIMENTATION

In order to determine if the Mpemba effect is evident in samples that are completely frozen, it was first necessary to determine if it could be easily estimated when the water was completely frozen. In order to check this, a sample of tap water was placed into one of the containers and then placed in the freezer. Data was taken using the LabVIEW program, and the resulting curve is shown in Figure 3.

The water begins to freeze at about 0° C, which is reached in about 2200 seconds. The temperature (in this case represented as a voltage difference) of the water is then unchanging for almost 8000 seconds. This period of time where the voltage difference is unchanging is where the phase transition is occurring, and the water is crystallizing into ice. This is known from the principle of the Enthalpy of Fusion, discussed earlier. After about 10500 seconds, the temperature begins to drop again. When this occurs, it can be assumed that the water is completely frozen. It then cools to the temperature of the reservoir. The oscillations near the end of the plot are due to the slight temperature fluctuations in the reservoir.

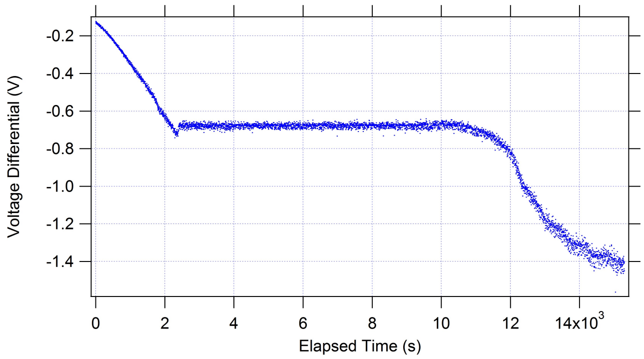

Figure 3: Voltage difference versus Time plot for one sample. The phase transition can clearly be seen as the area where the plot has slope of 0. The total time for this data run was about 14000 seconds, or roughly 4 hours.

In order to investigate the Mpemba effect, different samples of water were heated to different initial temperatures using a coiled immersion heater. After these samples had been raised to the desired initial temperature, they were placed in the freezer and hooked up to the circuit, which would provide a current and measure the voltage across the thermistors. These data were taken to determine the reproducibility of the Mpemba effect, and for what temperature ranges it held true. It would also determine whether or not supercooling is a significant factor in the Mpemba effect.

After several data runs, the samples were heated slowly on a hot plate rather than with an immersion heater. By using the hot plate, data could be taken with water that was heated slowly, where no part of it was brought near the boiling point. This was done to determine the effect of dissolved gasses in the existence of the Mpemba effect.

Finally, water was boiled, and then allowed to cool to room temperature. This was then compared to a sample of room temperature water that had not been boiled. In this case, the water would have the same initial temperature, but the sample that had been boiled would have had nearly all of its dissolved gasses expelled. This final set of data should determine if the effect is in fact caused by initial temperature, or the history and dissolved gas content of the sample.

In all cases, it was important that the samples be massed both before and after freezing. If the masses differed by too much initially, it would change the results, and possibly falsely produce the effect. Also, if any of the samples lost a significant amount of mass during the data collection, evaporation could be considered a primary cause of the effect.

V. RESULTS & ANALYSIS

In the first set of data runs, samples were heated by submerging a coiled immersion heater into them for different amounts of time. In almost every case, the hottest sample was completely frozen first, followed by the middle sample, with the coldest sample freezing last. It was determined from these data runs that supercooling has little effect in this scenario. In no case did any sample cool below -1° C before beginning the phase transition to ice. Sample data are shown in Figure 4.

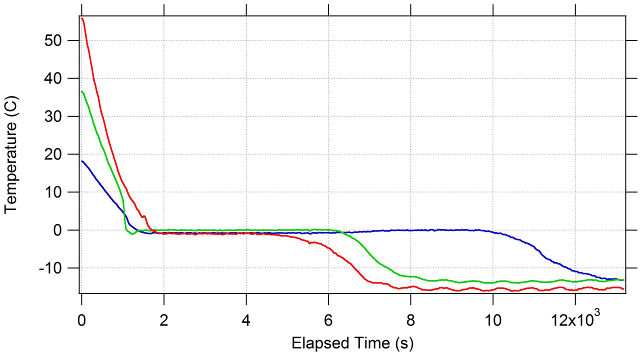

Figure 4: A sample data run with initial temperatures of 56°C, 38°C, and 17°C. The coolest sample is the first to reach 0°C, consistent with Newton's Law of Cooling, but the hottest sample is completely frozen first.

Several conclusions can be drawn from the results shown in Figure 4. First, the Mpemba effect in this experimental set up is relatively reproducible. This means that there is perhaps something more fundamental to the effect than spontaneous crystallization of the samples. Secondly, these results could support the theory that dissolved gasses have an effect on the freezing pattern of the samples.

In the second set of data runs, the water samples were heated to different initial temperatures slowly using a hot plate. This was done so that no portion of the samples would ever be brought close to the boiling point, which would theoretically result in less expulsion of dissolved gasses. These runs all clearly exhibited the Mpemba effect, in that the warmer the sample, the faster it was turned to ice.

The results from data runs such as the one in Figure 4 yield strong support for the reproducibility of the Mpemba effect in a wide variety of initial conditions. The analysis of these dramatic results can lead to a dramatic conclusion. The assumption can be made the increase in the temperature of water decreases the solubility of carbon dioxide[4]. Therefore, it can be assumed that water at a higher temperature has less dissolved carbon dioxide, which could change its freezing properties.

After all data was collected, each sample in each data run was carefully analyzed. The initial temperature of each sample was carefully measured and recorded for each sample, as well as the time it took the sample to reach 0° C, and the time it took for the sample to become completely frozen. Finally, the time it took for the sample to be completely frozen was measured as the time at which a new minimum temperature for the sample was achieved, and was followed by consistent, subsequent new minima.

Using the data collected, the trends among all data runs could be investigated. First, the time it took the sample to reach 0° C was plotted as a function of the initial temperature of the water, and is shown in Figure 5. The data differ greatly than those gathered by Mpemba. Mpemba's data indicated a nearly linear inverse relationship between initial temperature and time to start freezing, provided the water is heated to at least approximatly 10° C. Mpemba's data, however, was based on visual observation of the samples, and not of accurate temperature measurements. The curve Mpemba showed is the time it took for ice to become visible in a sample, not the time it took to reach the freezing point. This could possible explain the difference in the data, because the samples might reach 0° , but not begin freezing right away.

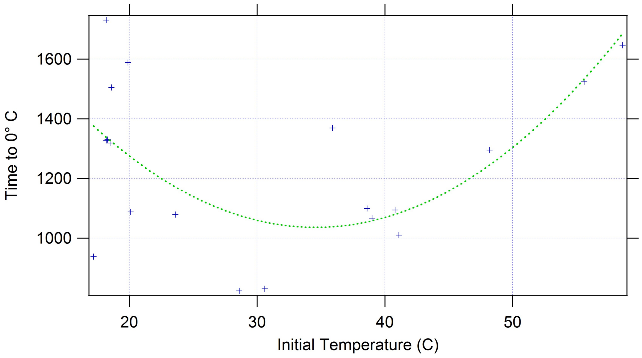

Figure 5: The time it took each sample to reach 0° C plotted as a function of the initial temperature. Slightly warmer water appears to reach the point faster, but then significantly warmer water begins to take longer.

It appears that water that has not been heated above room temperature takes longer to reach the freezing point than water that has been heated, with the exception of water that has been heated to fairly extreme temperatures. The fact that a sample heated to nearly 60° C takes about the same time to reach 0° C as a sample that starts at 18° C is quite startling. This shows that the heating of the sample does indeed change the way it behaves, and shows that Newton's Law of Cooling (Equation 2) does not apply consistantly to these samples.

Next, the time it took the sample to completely freeze, shown in Figure 6, was investigated. The results of this analysis yielded very strong support for both the Mpemba effect and Freeman's prediction on the effect of dissolved gasses. The data appear in two distinct groups, as shown in the figure, heated and non-heated. The average time for a non-heated sample to freeze was 9289 s, almost 3 hours. The average time for a heated sample to freeze was 4913 s, less than 2 hours. These results clearly show that the exposure to heat has a significant effect on the waters freezing pattern. The most likely explanation for this is the reduced solubility of gasses at warmer temperatures [6].

Finally, the time spent in the phase transition as a function of initial temperature, was investigated similar

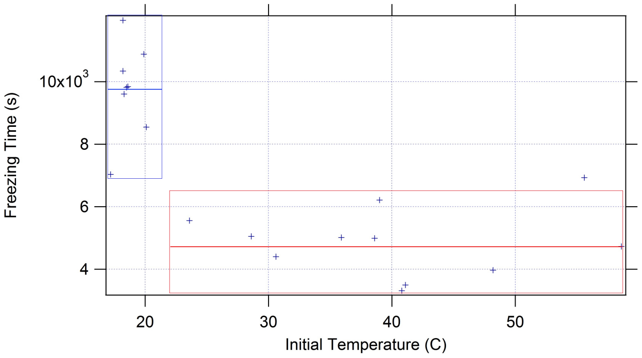

Figure 6: Time to freeze plotted as a function of initial temperature. The data is clearly grouped into heated (red) and non-heated (blue) samples. The average time to freeze for each is indicated as a solid line.

to the previous analysis. The freezing time for heated samples was markedly less than unheated samples. This is what would be expected, since the majority of the time in each data run is spent in the phase transition. While there is some data to indicate that heating affects the rate of cooling to the freezing point, it is the speed at which the water turns to ice that creates the true difference. The heating of the water changes some property of the water that causes it to undergo the phase transition much faster. This would imply that either the heat of fusion, discussed earlier, is less for these pre-heated samples, or the thermal energy is transferred faster.

One might assume that the evaporation of the water in the warmer samples caused a change in the mass of water, leading to less energy being required for the crystallization. This does not, however, appear to be an adequate conclusion based on experimental results. In this experiment, no sample changed mass during the freezing process by more than 3.0%, regardless of initial temperature. The difference in freezing time is on the order of thousands of seconds, implying a very large difference in the thermal energy transfer, and thus cannot be explained by such small evaporation.

The final verification for the impact of dissolved gasses on the Mpemba effect came in the last sets of data collected. The first sample was simply room temperature tap water, while the second was tap water that was boiled, and then allowed to cool to room temperature. Therefore, both samples start with roughly the same initial temperature.

It was found that the water that had previously been boiled froze much faster than the non-boiled water, as was predicted based on previous data. The boiling of the water would expel nearly all the dissolved gas. Since this water froze first, this is strong support for the assumption that the Mpemba effect is dependent on the dissolved gas in the substance. Also, since these samples had the same initial temperature, this data shows the the Mpemba effect is in fact not a function of the initial temperature, but of the history of the sample, and its contents.

VI. CONCLUSIONS

The investigation into the Mpemba effect performed in this experiment determined that the effect does exist, and is in fact widely reproducible for water with different initial temperatures. The spectrum of initial temperatures varies widely as well. Supercooling was not evident in any of the samples, as Auerbach predicted.

The effect is not, however, related to the initial temperature of the water, as Mpemba inferred. It is in fact a function of the dissolved gas in the water, which is removed by the heating process. Because the heating process removes the dissolved gas, the water was able to freeze faster. This conclusion is verified by the final set of data presented. The previously heated water froze significantly faster than the non-heated water, even though they had the same initial temperatures when the data was collected. The data shed significant light on the mechanism of the Mpemba effect.

VII. ACKNOWLEDGMENTS

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