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Article

Examination of the underlying chemical physics of the Mpemba effect in water and other liquids

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SUMMARY
With all other conditions identical, hot liquid freezes faster than cold liquid, which might seem impossible according to Newton's law of cooling. The primary goal of this paper was to find out the reasons behind this phenomenon, known as the Mpemba effect. We hypothesized that the physical properties and hydrogen bonds of liquids could be the reason behind this phenomenon. In addition to water, four other liquids were tested in this study. Interestingly, liquids with hydrogen bonds showed the Mpemba effect. Apart from hydrogen bonds, physical properties like density, supercooling, and thermal conductivity showed their importance behind the Mpemba effect. These results demonstrated the significance of physical properties and chemical bonds behind this effect, agreeing with our hypothesis. Also, liquids like glycerol and ethanoic acid showed a strong Mpemba effect because of their initial temperature. We believe the findings we predicted in this study can help physicists create a more comprehensive model of how substances emit or absorb heat.

INTRODUCTION
Liquid is a state of matter that flows freely but contains a constant volume. The atoms inside liquids attract each other because of interatomic energy and create different interactions, such as hydrogen bonds, dipole-dipole interactions, and van der Waals interactions. The interatomic energy can be represented as a negative number where the addition of other energy, such as heat, makes the number less negative, and when it becomes zero, the bond breaks. On the contrary, subtraction of energy makes the interatomic energy more negative which results in a stronger bond. As the molecules get closer, the volume decreases, and the matter starts to turn into a solid, a process is known as freezing. Water is an exception to this rule since its molecules are hexagonal; it expands and increases in volume when it turns into a solid.

In specific circumstances, if the only difference between two liquids is their initial temperature, then the liquid with a higher initial temperature will freeze sooner than the other liquid (1). This effect, also known as the Mpemba effect, was considered by Aristotle, Francis Bacon, and René Descartes in their writings (2-4). Many theories have been proposed trying to explain this phenomenon. Kell's research suggests that surface evaporation could be the reason behind the Mpemba effect (5). However, later on, it was shown that his theory was insufficient to explain this effect. In 1971, Deeson tried to explain the Mpemba effect through convection current (6). Dissolved gas was another parameter that was believed to be the reason behind the Mpemba effect. However, Auerbach showed an explanation that suggests dissolved gas doesn't have any high influence on the Mpemba effect (7).

Our research is another attempt to answer the question of why the Mpemba effect occurs. Even though the Mpemba effect was first observed at least 2,500 years ago, the exact explanation behind this phenomenon is still not clear. We hypothesized that physical properties (supercooling, thermal conductivity, density) and the hydrogen bonds (H-bonds) inside cold and hot liquids could be the reason for this effect, as those are the properties responsible for different states of matter (8). H-bonds are a strong intermolecular force, so having strong hydrogen bonds accelerates the solidifying process. In solids, when temperature increases, lattice vibration increases, and due to this, more heat conduction takes place. Therefore, faster thermal conductivity of containers quickens the freezing process. Additionally, density decreases the heat transfer average distance, which is why density is disproportionate to solidifying. Most liquids have a lot of similarities, such as no specific shape, limited volume, limited space between molecules, and similar intermolecular forces (9). The secondary goal of our study was to observe the Mpemba effect on other types of liquids.

We looked for the Mpemba effect in five different liquids: water (H_2O, freezing point (f.p.) = 0°C), candle wax (C_nH_{2n+2}, f.p. = 52°C), coconut oil ($C_nH_{2n}O_2$, f.p. = 21°C), glycerol ($C_3H_8O_3$, f.p. = 18°C), and ethanoic acid (CH_3COOH, f.p. = 16.5°C). Our results showed that hydrogen bonds could be one of the prime reasons behind the Mpemba effect, which agreed with our first hypothesis. Additionally, we saw that the supercooling phase, surface temperature of containers, as well as liquid density, may play a vital role in the Mpemba effect (10). We were able to see the Mpemba effect in water, glycerol, and ethanoic acid, but were unable to see it when using candle wax and coconut oil. This suggests that most liquids with H-bonds will show the Mpemba effect.

RESULTS
All liquids were monitored for temperature until they become solid. Temperature readings were collected in five-

minute intervals for water and one-minute intervals for the other liquids.

Water

We saw that with a higher initial temperature, water had a higher decay constant (**Figure 1**, **Table 1**). The decay constant is proportional between the initial temperature and the rate at which the temperature decreases. Our results also indicate that hot water has a fast cooling rate than cold water. The hot water (75°C) caught up with the cold water (27°C) between 110-115 minutes and around 12°C (**Figure 1**). The cold water took less time to reach the freezing point (-1°C) than the hot water, but the cold water took 15 minutes more than the hot water to become solid (i.e., the hot water froze before the cold water). The shape of both curves was similar after the hot water temperature caught up with the cold water and both had extended periods of time (280+ min) where the temperature was lower than the freezing point.

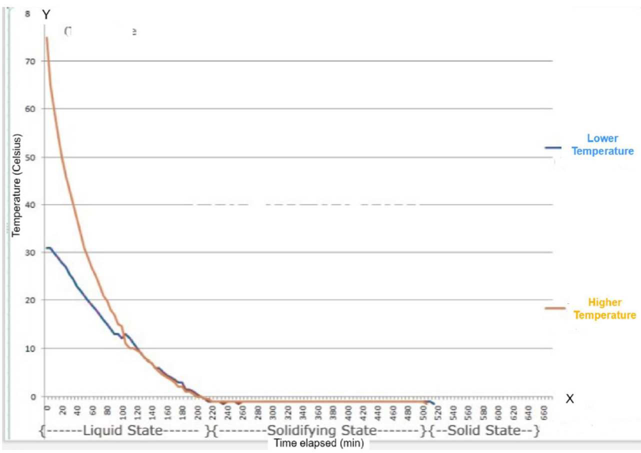

Figure 1: Water shows the Mpemba effect. Liquid State: 0-215 min (cold), 0-220 min (hot); Solidifying state: 215-515 min (cold), 220-505 min (hot). The solid-state was reached after 515 min (cold) and 505 min (hot). The red line went lower than the freezing point (-1°C) before the green line, so the Mpemba effect was observed.

	Initial Temp	Exponential decay constant (λ)	Freezing point	Cooling time (min)	Freezing time (min)	Total time (min)
Water	27°C	0.0198	-1°C	215	300	515
	75°C	0.0222	-1°C	220	285	505
Candle Wax	80°C	0.0069	52°C	15	47	62
	100°C	0.0096	52°C	22	46	68
Coconut Oil	27°C	0.0033	21°C	62	14	76
	50°C	0.0104	21°C	59	24	83
Glycerol	27°C	0.0041	18°C	32	65	97
	50°C	0.0107	18°C	33	62	95
Ethanoic Acid	27°C	0.0055	16.5°C	31	58	89
	50°C	0.0130	16.5°C	34	51	85

Table 1: Time elapsed for cooling and freezing of different liquids. Blue indicates cold samples and orange indicates hot samples. Cooling time: the time liquids took to reach the freezing point from the initial temperature. Freezing time: the time liquids took to become solid after reaching the freezing point. The decay constant denotes the cooling rate, where a higher decay constant means a faster cooling rate.

Candle Wax

We saw that the cold wax (80°C) reached the freezing point (52°C) sooner than the hot wax (100°C), but the hot wax had a higher decay constant, indicating that hot wax has a higher cooling rate (**Figure 2**, **Table 1**). But in total, the cold wax became solid sooner. Also, both waxes had similar curves after the hot wax reached a temperature of 80°C (Figure 2).

Coconut Oil

The coconut oil results were unique from the other liquids in this research (**Figure 2**). We found that the hot oil had a higher decay constant, but that the cold oil froze first (**Table 1**). The curves for hot and cold oil were not as identical as they were for the wax. The hot oil started freezing earlier, but the cold oil became solid first (**Figure 2**). We also observed a phase where the temperature is lower than the freezing point. This phase was longer in the cooler sample.

Glycerol

We saw that the hot glycerol had a higher decay constant, meaning a higher cooling rate (**Figure 3**, **Table 1**). The hot glycerol caught up to the cold glycerol between 18 and 22 minutes and around the temperature of 21°C. Both samples reached the freezing point almost at the same time, but the cold glycerol took three more minutes to become solid after reaching the freezing point. Therefore, the glycerol that started hot became solid sooner.

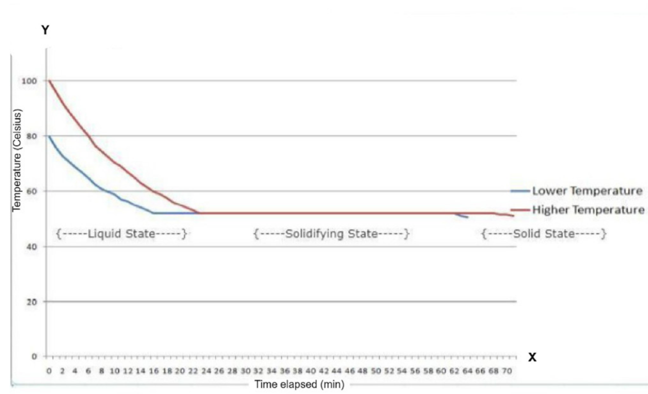

Figure 2: Candle wax does not show the Mpemba effect. Liquid State: 0-15 min (cold), 0-22 min (hot); Solidifying state: 15-62 min (cold), 22-68 min (hot). The solid state was reached after 62 min (cold) and 68 min (hot). The blue line went lower than the freezing point (52°C) before the red line, so the Mpemba effect was not observed.

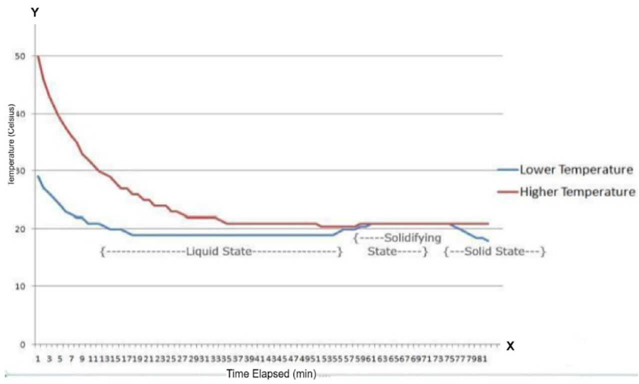

Figure 3: Coconut oil does not show the Mpemba effect. Liquid State: 0-62 min (cold), 0-59 min (hot); Solidifying state: 62-76 min (cold), 59-83 min (hot). The solid-state was reached after 76 min (cold) and 83 min (hot). The blue line went lower than the freezing point (21°C) before the red line, so the Mpemba effect was not observed.

Ethanoic Acid

We saw that the hot ethanoic acid had a higher decay constant and the cold ethanoic acid started freezing three minutes earlier than the hot ethanoic acid (**Figure 4**, **Table 1**). However, the hot acid surpassed the cold acid where it took four minutes less to freeze, becoming a solid sooner. The graphs were also similarly shaped after the hot acid reached the initial temperature of the cold acid.

DISCUSSION

For three out of our five chosen liquids, the hot sample froze sooner than the cold sample (**Table 1**). The initial temperature had a high impact on the freezing rate of water, ethanoic acid, and glycerol. We saw the effect of initial temperature on coconut oil, too, but it was not strong enough to show the Mpemba effect (**Figure 3**). The reason behind this could be that the cold coconut oil was only eight degrees higher than the freezing point, which could have negatively impacted the result. Even so, ethanoic acid and glycerol showed a strong Mpemba effect.

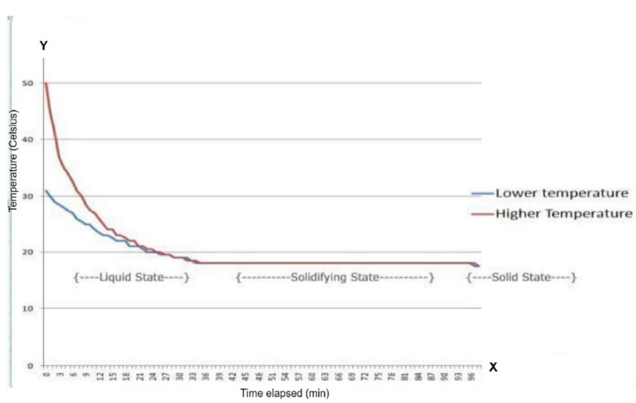

Figure 4: Glycerol shows the Mpemba effect. Liquid State: 0-32 min (cold), 0-33 min (hot); Solidifying state: 32-97 min (cold), 33-95 min (hot). The solid-state was reached after 97 min (cold) and 95 min (hot). The red line went lower than the freezing point (18°C) before the blue line, so the Mpemba effect was observed.

Candle wax was the only liquid where the initial temperature had no effect on the cooling or freezing process (**Figure 1**). One reason for this could be that the wax is made of hydrocarbons and so it was the only liquid without any H-bonds present (11). Coconut oil is made of fatty acids containing H-bonds. Water, glycerol, and ethanoic acid, all have strong H-bonds. A short H-bond length is stronger than a long H-bond because the atoms are closer to each other (12). Both short and long H-bonds can be present within the same liquid (12). Stronger H-bonds help liquids solidify faster as stronger bonds can pull the molecules more quickly together and form crystals. When we increased the temperature, the weak H-bonds were broken because of the lower bond energy, and only the strong H-bonds remained in the liquid (13). That's why the big clusters of atoms within the liquids paired with weak H-bonds were broken and became small clusters in warm liquid. When only strong H-bonds are present in the warm liquid, the small clusters quickly start to transition to a solid (13). In the case of cold liquids, the weak H-bonds become stable and form strong H-bonds with the decrease in temperature. This is due to the molecular movement becoming slower allowing for stronger interatomic attraction. And only after forming the strong H-bonds, the cold liquid starts to freeze as these strong H-bonds get stronger with the temperature continuing to decrease, thus turning the substance into a solid. This could be why the cold liquid took more time to freeze, suggesting the H-bond is a crucial parameter for the Mpemba effect (10).

We noticed a special phase in the curves of water and coconut oil. In the cold sample graph of the coconut oil where the graph was below the freezing point and then jumped back up (**Figure 3**). This phase was also present in the ethanoic acid and glycerol, but it was not identical compared to the water and coconut oil. We called it "the supercooling phase" (1, 10). In this phase, the temperature was lower than the freezing point, but the matter was still liquid. The supercooling phase was longer in the cold liquid. The reason behind this could be that the nucleation agents (dissolved gasses, silver iodide, sand, etc.) in hot liquid are more active than in cold liquid. So the initial hot liquid tends to have a shorter supercooling phase than the cold liquid (14). As supercooling is disproportionate to solidifying, the longer the supercooling phase lasts, the more it takes time to solidify (10). That is why even after reaching the freezing point, we noticed the solidifying phase of cold samples was longer than the hot samples for water, glycerol, and ethanoic acid (**Figures 1, 4, 5**). If there was no supercooling, then both the hot and cold samples should have taken about the same amount of time to solidify. Thus, supercooling may be a vital reason behind the Mpemba effect.

The surface temperature of all hot liquid containers was higher than the cold liquid containers. Even though we did not directly observe any frost on any of the liquid

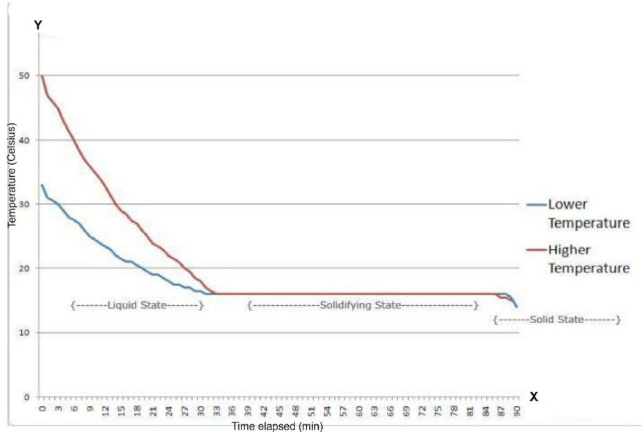

Figure 5: Ethanoic acid shows the Mpemba effect. Liquid State: 0-31 min (cold), 0-34 min (hot); Solidifying state: 31-89 min (cold), 34-85 min (hot). The solid-state was reached after 89 min (cold) and 85 min (hot). The red line went lower than the freezing point (16.5°C) before the blue line, so the Mpemba effect was observed.

containers, there is a possibility that the containers of the hot liquids melted through a layer of frost (10). This layer could work as a conductor helping the hot liquid to contact much colder surfaces, such as refrigerator ice or coal (10). With the presence of a much colder surface, the hot liquid could emit heat faster than the cold liquid and this may be another reason behind the Mpemba effect observed.

The density of the liquids could be another reason behind the Mpemba effect. Density decreases with the increase in temperature and denser substances have a lower cooling rate (15-16). All of the hot liquids had lower densities than the cold liquids. With a lower density, the heat could easily flow inside the hot liquid at a much higher rate than the cold liquid (10). This high heat transfer rate could help the ice crystals to spread around faster and form ice more quickly than the cold liquid (10).

Surprisingly we saw with coconut oil, which had the longest supercooling period, that it did not show the Mpemba effect. This could be an experimental error as well because the other liquids with supercooling phase in this study showed the Mpemba effect. Performing additional trials would help to confirm this result. Therefore, the approximation error could vary with more trials of this experiment. Additional sources of error include using a digital thermometer to collect our data, which can produce reading errors or visual errors, and the additional heat added at each interval in the refrigerator could also influence the result as well.

There are some other parameters that could be the reason behind the Mpemba effect, such as the effect of different nucleation agents such as dissolved air, salt, or clay. We did not check the impact of these parameters as we eliminated these unwanted substances before the experiment. Also, the evaporation rate of hot water could decrease the volume and affect the Mbemba effect. Another concern is that we identified the potential impact of H-bonds on the Mpemba effect, but the candle wax is a mixture of different substances, so, there could be other reasons for not showing the Mpemba effect apart from H-bonds. Also, all the H-bonds in this research were between oxygen and hydrogen. To clearly state the impact of H-bonds, we would need to conduct more experiments with liquids that have H-bonds between hydrogen and other atoms, such as nitrogen or fluorine. Further experiments to see the impacts of these parameters are necessary to strengthen our assumptions of the reasons behind the Mpemba effect.

In conclusion, based on the results of this experiment, we can suggest that the H-bonds, supercooling, thermal conductivity, and density could be some potential reasons behind the Mpemba effect.

MATERIALS AND METHODS

General Sample Preparation and Data Analysis

Proper management, such as the use of chemistry lab filter paper, was taken to eliminate unwanted influences like salts, solids, and other byproducts. All the liquids were kept at 1 atm pressure. The room temperature was 27°C. The thermometer used was a digital thermometer manufactured by TechnoHealth. The test tubes were closed with cork sheets to eliminate unwanted evaporation which could decrease the volume of the liquids. The liquids were determined as solid according to the temperature we noted from our digital thermometer. When the temperature started to get lower than freezing point, we declared them as solid. The data collection process for wax, glycerol and ethanoic acid inside the refrigerator took 20-30 seconds each time, so, a small amount of heat was added each time. The temperature inside the refrigerator was monitored through a transparent glass the whole time and the reading was taken twice: first before putting the test tubes and flasks inside the refrigerator and then after the liquids of the tubes and flasks became solid.

We noted the first temperature as the refrigerator temperature (-20°C) and the second temperature (collected after the liquid turned into a solid) gave an approximation of the error in this experiment, which was ± 0.125°C. This approximation error was denoted by the digit temperature we got from our digital thermometer.

The exponential decay constants were calculated using **Equation 1:**

$$N(t) = N_0 e^{-\lambda t} \qquad [1]$$

Where N(t) is the final temperature after time, t; N_0 is the initial temperature; λ is the decay constant; t is the time elapsed.

Water

200 mL of water was collected from Water Supply and Sewerage Authority, Bangladesh. We used filter paper to filter unwanted solids from water samples. The high starting temperature sample was heated to 75°C using a Bunsen burner and then both water samples were placed inside a

refrigerator with a thermometer in them. Temperatures were collected after every five minutes by watching through the transparent glass until they became ice.

Candle Wax

Candle wax (Paraffin wax) was collected from Milton Candle Company. 30 mL of melted wax was added to two test tubes. The first test tube was heated up to 100°C (the hot sample) and the second one was heated up to 80°C (the cold sample). As the freezing point of wax is higher than room temperature, both test tubes were kept at room temperature and a thermometer was inserted. The temperature was collected every minute until the wax became solid again.

Coconut Oil, Glycerol, and Ethanoic Acid

The coconut oil used in this experiment was 100% refined oil and manufactured by Cute Bangladesh. The Glycerol used in this experiment was collected from BD & Co company and it was 99% pure. Ethanoic acid was collected from Desertcart which was also 100% pure. For coconut oil, glycerol, and ethanoic acid the experimental procedure was the same. We added 30 mL of a liquid to two conical flasks. The first flask was kept at room temperature and the second flask was heated up to 50°C in a water bath, then a thermometer was added to both flasks before putting the flasks in a refrigerator. The temperature was collected every minute until the liquids became solid again.

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