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'Mechanism of Mpemba Effect'

Atin Shanker

Abstract
The purpose of this study is to find the extent to which Mpemba effect is possible and provide a collected sum of reasons that produce it. When hot water freezes faster than cold water then the phenomenon is known as Mpemba effect. Three major reasons which can help to understand the Mpemba effect are supercooling, Newton's law of cooling, and entropy. It is a topic which has been largely debated and till date no specific explanation has been there as to say why this phenomenon occurs. This research will help to provide a better understanding and showcase that there are several factors behind this effect (named above). Some physical conditions like evaporation and frosting also play a part. It is to be noted that Mpemba effect usually occurs under specific conditions of temperature, surroundings, and type of liquid used.

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I. Introduction

It is a warm summer evening and a few friends have come over. Everyone is thirsty and craving for a cold beverage. You open the freezer and realize there is no ice, not even in the nearby supermarket. So what do you do? Your first move would be to take the cold water from the fridge and keep it in the freezer, but is it the right move? Or boiling the cold water first and then keeping it in the freezer would be a better play? Theoretically, and sometimes practically, the latter would be more beneficial. The process in which hot water freezes faster than cold water is known as Mpemba effect.

In 1963, Erasto Mpemba experienced this phenomenon while making ice cream in his school with his classmates. The standard procedure was to boil milk, add sugar and ingredients to it, and then leave it for cooling at room temperature. Then when the mixture cooled down they used to keep it in the refrigerator to convert into solid form. There was always a hassle for refrigerating spots. So, one day Mpemba decided to skip the cooling part (at room temperature) and directly placed the milk in the refrigerator. To his surprise it took relatively less time to make ice cream, which according to common knowledge was not possible. He asked his teacher but he refuted the claim and said there must be a mistake. But he came across some other ice cream makers who also kept boiled milk in the freezer first and got the same results as Mpemba. He finally had the chance to talk to Dr. Denis Osborne, a university professor, but Dr. Osborne did not know if this effect was possible. So, he went back to his university and performed a few experiments. In those tests the results matched Mpemba's claim.

A concrete explanation for this phenomenon is yet to be discovered, some even say there is no such effect, but there are some factors which prove its existence like super cooling, evaporation, entropy, Newton's law of cooling and frosting.

Supercooling

Although the concept of supercooling has not been ideal for understanding the Mpemba effect, there have been instances in which supercooling was observed during Mpemba experiments. Dr. Daniel Auerbach demonstrated in experiments that cold water supercools down to a lower temperature than hot water, and then freezes. As a result hot water freezes first. He predicted that suitable temperature for this simulated condition would be -6°C to -12°C. Dr. J Brownridge also did similar experiments and said two samples will always freeze at different times due to different spontaneous freezing temperatures. In all the experiments, although identical samples were taken under same conditions, the samples had different highest temperature nucleation sites (HTNS) - temperature at which they are supposed to freeze. The samples were identical, so they should have had same HTNS value, but the value ranged from 0°C to -45°C. Heating may also have an impact on the HTNS value. Brownridge did the experiment 28 times and at all instances hot water froze faster than cold water because after supercooling the spontaneous freezing temperature of hot water was higher than cold water.

Newton's law of cooling

The equation of Newton's law of cooling is:

$$\frac{dT}{dt} = -k(T - T0\ )$$

Where t is time, T is the temperature of the substance at time t, dT/dt is the rate of cooling, k is the constant heat transfer coefficient, and $(T - T0)$ is the difference between the temperature of the substance and its surroundings at time. This equation cannot model the Mpemba effect.
This law clearly contradicts the Mpemba effect because the temperature difference between hot water and surrounding is large compared to cold water and surrounding. So, hot water should take more time to freeze but the opposite happens.
Dr. Vladan Pankovic and Dr. Darko V. Kapor produced a modified model of Newton's law, and introduced a term which was proportional to the quadrate of the geometrical average value of the initial and later difference between liquid and surrounding (cooling) temperature.
It after simple transformations yields usual Newton's linear differential equation but with a different cooling parameter.

Note: there are lot different modifications of the Newton's law of cooling.
Pankovic and Kapor's modifications produced a simple equation which is in compliance with the Mpemba effect.
I was also able to produce a similar equation by using logarithms and integration, calculations are followed

$$\frac{dT}{dt} = -k(T - T0)$$

$$dT/(T - T0) = -kdt$$

Integrating both sides of the equation and taking log gives

$$\ln(T - T0) = -kt + \ln C$$

Further solving

$$\ln(T - T0) = \ln(e^{-kt}) + \ln C$$

$$\ln(T - T0) = \ln(Ce^{-kt})$$

$$T - T0 = Ce^{-kt}$$

To find C, consider the equation at time $t = 0$. Here, $T = T'$

Substituting into the equation gives $C = T' - T0$

$$T - T0 = (T' - T0)\, e^{-kt}$$

And finally, rearranging the equation gives us

$$T = T0 + (T' - T0)\, e^{-kt}$$

This is a modified form of Newton's law of cooling with a slight change in the cooling parameter. This equation is also in compliance with the Mpemba effect. We can also substitute experimental values in the final equation to see the functioning of Newton's law. The results are in accordance with the effect. The equation proves that a liquid with higher temperature, after a certain time interval, cools faster than a liquid with a lower temperature.

Entropy
Entropy is a measure of the availability of energy which cannot be used or in simple terms useless energy. It basically tells the randomness or disorderly arrangement of particles in a system.
There are two ways to calculate entropy:

$$S = k_b \ln W$$

S = entropy
k_b = Boltzmann constant
ln = logarithm
W = number of microscopic configurations
And

$$dS = \frac{dQ}{T}$$

dS = change in entropy
dQ = change in heat
T = absolute temperature

Ilias J. Tyrovolas conducted experiments to check the effect of entropy in Mpemba effect.
In the first test he took two water samples, A and B, at same temperature and volume but the entropy of A was more than B. Since, A has more entropy its particles will have more random motion/collisions than B. As a result, particles in A will lose more kinetic energy.

$$E = (3/2)bT$$

According to the above relation, loss in energy decreases temperature. So A will cool down faster as compared to B. This shows that entropy plays a role in cooling.

Remember both the bodies were at the same temperature initially. Heat transfer coefficient (HTC), h, of the body also plays a key role. More the value of HTC greater is the cooling effect and higher the chances of Mpemba effect.

In his second experiment he took three water samples – A at 50℃, B at 25℃, and C first preheated to 50℃ then cooled down to 25℃. He kept all three samples for freezing at -18℃. A and C froze almost at the same time and before B. A cooled down to 25℃ and then followed the same cooling curve as C. HTC for both A and C was same whereas it was greater for B. The half life period was also less for A and C. This experiment was conducted at the laboratory of the Nafplio Regional Quality Control Centre. As a result warm water cools faster than cold because it has more entropy.

Physical aspects

There is also a simple theory of evaporation. Common sense tells us that hot water will have more evaporation as compared cold water. It will decrease the temperature and mass of the hot water. Eventually less mass of water will be available to cool hence, Mpemba effect may be possible. So, in order to check this theory few scientists weighed two water samples before heating one of them and after cooling found out that the weight difference was not very significant. There was a 3% mass difference between water samples which does not really cause any change in freezing time.

Another popular theory is of frosting. Let's say two water samples are taken, one hot and one cold, in a material which is a good conductor of heat. These two samples are then put in a freezer. The ice around the hot sample will melt quickly in the freezer and then due to the cold temperature quickly refreeze. This will make a good connection for conduction of cold from the freezer to the hot water as compared to the cold sample. As a result the hot water sample will freeze quickly.

Since water become less dense from 4℃ to 0℃, a layer of water will come on the top and convert into ice in the cold sample. This layer of ice will act as an insulating layer and lower the freezing time for rest of the sample (cold water). Hence, hot water will again be able to freeze faster than the cold sample.

II. Discussion

Ancient scientists such as Aristotle, Francis Bacon, and René Descartes all observed this phenomenon during their respective periods, but none of them could provide a definitive reason for its occurrence. Majority of modern researches and experts around the world consider the Mpemba effect a paradox. There is lot of skepticism regarding the functioning of the effect. It is clear from the above explanations that certain conditions and settings are required for the Mpemba effect to occur. Slight differences like the presence of dissolved gases or the presence of impurities may produce different results. If the Mpemba effect is possible then theoretically an inverse condition of the effect should also be feasible, where a cold object will heat up faster than a hot body. I did an experiment in which I took two water samples, A and B, and heated them at around 530℃. Sample A consisted of ice and sample B consisted of water at room temperature. I was not able to develop conditions required to prove the inverse, but both the samples started boiling at the same time, after 4 minutes. It proves the possibility of an inverse and ultimately the Mpemba effect. Dr. Zhiyue Lu and Dr. Oren Raz had previously proved this phenomenon by using theory of non-equilibrium thermodynamics and mechanisms of anomalous heating and cooling of water and named it inverse Markovian Mpemba effect.

I believe frosting (mentioned above under physical conditions), along with supercooling, is a very good reason for Mpemba effect. It is also found naturally in cold countries. When the temperature drops below 0℃ the top layer of ponds and lakes freeze. This layer then prevents the cooling of rest of the lake, by acting as an insulating layer, and helps sustain aquatic life. In some video demonstrations when boiling water is thrown in air at -17℃ the vapors quickly crystallize and convert into frost (natural process). This is a clear demonstration of the effect. Evaporation can be considered a logical reason for the effect but experimentally it does not hold up.

III. Conclusion

Let me first answer the question in the introduction. No, you will not get ice faster if you boil the water first in normal housing conditions. Experimentally I have found out that the time taken to freeze cold water and hot water is very close. That being said Mpemba effect does occur. It is just that there is no one specific reason that may state the cause. Another major reason is that scientists have never been able to repeat the results of same tests. Mpemba effect is a collection of various factors like supercooling, frosting, Newton's law of cooling, entropy working under specific conditions that make the effect possible. There are some reasons which also contribute to the effect like hydrogen bonding, latent heat, crystallization etc but I don't have the resources to check them. I believe further laboratory experiments to check the above stated factors under specific circumstances will help understand the Mpemba effect better and give a concrete explanation. If the exact conditions can be found out in which the Mpemba effect occurs then it could be very useful to save time in manufacturing liquefied products. The data I have collected prove the occurrence of Mpemba effect, but the fact that something so simple like freezing takes place in an opposite way than expected is enough to keep us digging for more.

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