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Revisiting the Mysterious Mpemba Effect

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ABSTRACT

The effect of hot water freezing faster than cold water is mentioned in Greek literature. However, it came out as a scientific phenomenon during the last few decades and is known as Mpemba effect since 1969. But there is an inadequacy of explanation which was a challenge to the modern science. Hence, it is an important issue to revisit this mysterious effect.

In this research work it is attempted to justify the Mpemba effect in terms of the heat loss through a number of experiments. A newly introduced technique was used to explore the influence of evaporation on the effect using a thin oil layer. Moreover it was noticed that higher the length of time duration, greater the chance of observing the effect.

Finally the Mpemba effect is classified into two, based on cooling curves known as High Cooling Rate (HCR) and Quick Freeze (QF). Then they were analyzed and justified by means of relevant simulations and logical interpretations. Finally it was concluded that the evaporation and nature of ice due to convection current are the main reasons for the effect. A new observation around 4^oC is also found in the research.

1. INTRODUCTION

1.1 What is Mpemba Effect

The effect of hot water freezing faster than cold water is known as Mpemba effect. But this is in adequate as a scientific definition [1]. There are two quantities, initial temperature and freezing which are very important to define correctly because they are the main parameters of the effect. Maximum temperature that reaches in the heating process is known as initial temperature in these experiments. Every liquid in the freezing process absorbs some heat known as latent heat of fusion. Cooling curves can be used to identify this event as a straight line. But dissolving some compounds in water decreases the freezing point.

Considering the given two samples of water, if one of them first reaches zero or depart from zero after absorbing latent heat, then it can be considered as the first frozen sample. The first one is responsible for high cooling rate (HQR[1]) and the second is quick freezing (QF[1]). But it is difficult to separate these two since literature examples show one of these or both may happen. Later these two phenomena will be deeply and separately considered.

[1] HCR & QF are first introduced in this research for reference purposes.

1.2 Why is it Mysterious?

Normally cooling of two bodies is described by Newton's law of cooling (since 1688). According to Newton's law two samples of water with the same conditions take equal time duration (t) to pass certain temperature range. Although time taken for hot water to reach the temperature of the cold water should be lesser (δt), but it cannot be zero and never minus. But first mystery is;

$$t, \delta t > 0 \Rightarrow t + \delta t < t$$

But some graphs mentioned in literature shows that the problem is around the freezing point (QF).second mystery is how the same amount of water has a different latent heat of fusion. Unlike in other scientific phenomena, difficulty of reproducing is the third mystery.

2. LITERATURE REVISITING

2.1 History

The Mpemba effect has long been known in the western world due to wintry weather but not in this name until the previous century. It also mentioned by Greek philosophers, medieval physicist and philosophers. In time, a modern theory of heat was developed, and the earlier observations were forgotten. The first two decades of twentieth century was very important for physics Especially Boltzmann introduced the modern understandings of thermodynamics and Statistical Physics. However, by this time no one had knowledge on this effect. Mpemba stands for Tanzanian school student Erasto B. Mpemba. He was a secondary school student in Tanzania, and found this effect when he was making ice cream, Mpemba and Osborne later published their results. In the same year, Dr. Kell of Canada independently reported the phenomenon, along with a theoretical explanation.

2.2 Modern Research and explanation

Modern researches on this effect are trying to model the effect mathematically and investigate it through the gas concentration; the research previously done in Sri Lanka has investigated the effect through ion concentration. It is extremely useful to mention the following currently use suggestions.

Evaporation - When initially warmer water lose significant amounts of water through evaporation. The reduced mass will make it easier for the water to cool and freeze. Evaporation cannot explain experiments which were done in closed containers, where no mass was lost to evaporation. And many scientists have claimed that evaporation alone is insufficient to explain their results. Other suggestions are dissolved gasses, convection, surroundings and supercooling.

3. METHODOLOGY

3.1 Temperatures Measuring System

The system contains temperature sensors (DS18S20), Microcontroller (PIC 16F877A), PC, SSD display and a Cooling oven (Temperature range is -60^{0}C to 80^{0}C). They are arranged as follows. This system was used precisely for the research previously done in Sri Lanka [4].

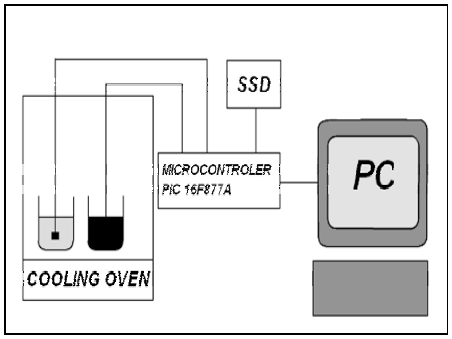


Figure 1a: Temperatures measuring system. **Figure 1b: Final experiments apparatus.**

Temperature sensor (DS18S20) has 0.5^{0}C accuracy. Then the collected data point has ± 0.5^{o}C accuracy but cooling curves have been gone through interpolation process to have a smooth nature using MATLAB *smooth( )* command.

3.2 Possible Experiments

There are lots of experiments to investigate this but it is important to mention that these experiments are based on ion consecration rather than heat loss. Moreover, an experiment with an oil layer is first introduced in this experiment. It is reliable an accurate than the experiment in closed container, since in a container with a lid it is difficult to say that it does not absorb the energy of evaporated molecules but here evaporation never occurs. But it does not completely remove the heat loss from the surface. Then it is reasonable to assume that this trick mainly halts evaporation. And oil layer does not change the outer pressure as well.

3.3 Scientific Path of the Method

Scientific method would be applied in two ways for this experiment. If effect can be found, then try to reduce the effect by changing some parameters. The progress of this reduction is responsible for dependency on the changed parameter. If the effect cannot be found, then the path will get the counter way with the same argument. One example is given here.

Ex: - Oil layer experiment:-Effect can be found: - Oil layer insert on the hot water.
Effect cannot be found: - Oil layer insert on the cool water.

4. NEW HYPOTHESIS

4.1 Evaporation Based Model

Dr. Kell of Canada gave the explanation based on evaporation .That explanation has two main problems, mass loss is not enough to explain the effect and sometimes experiment with a closed container shows the effect. But we know that evaporation is a random process and also in this process particles with high energy are lost. Then the probability of choosing an escaping practical from the left of the Gaussian distribution is high. Then new calculation should be modified as below.

$$E = m \int_{cooling\ curve} c_e T dt \ , c_e = evoporative\ heat\ capacity\ (c_e >> c\ \&\ c_e\ \alpha\ T)$$

The new heat capacity introduced here is a function of temperature. It is the energy lost from certain amount of liquid to reduce its temperature by 1^{o}C due to evaporation and other processes such as conduction, convection and radiation. But evaporation can be applied only for liquid and it's the predominate factor for liquids. It is known as evaporative heat capacity.

As further suggestions, hot water continues the convection current after 4^{0}C because hot water has high speed particles than cold water which helps to freeze. This phenomenon has very chaotic nature that may be responsible for randomness. Hot water molecules may have higher rotational motion which may increase the probability for connecting the molecules for freezing process.

5. EXPERIMENT RESULTS I

When we are studying these data (graphs) it is important to observe both events considered in section 1.1 i.e. QF & HCR .This section contains the experiments which are directed to find out depending parameters of the effect and distilled water was used for experiments to avoid ion concentration, but it was unable to show the effect even with carbonated water.

5.1 Time Measurements.

This section contains time measurement of the cooling curve. Objectives of this analysis were to find out the dominant phenomena from the two previously introduced effects (QF, HQR) and identify the initial temperatures which show effect clearly. Following three time periods were measured from the cooling curve to achieve above objectives.

Time taken to reach initial temperature to 0^{0}C - Cooling time
Time taken from initial temperature to end of freezing - Freezing time
Time taken to absorb latent heat

Figure 2 shows the cooling times for all distilled water samples. The curve fitting to these data is done by neglecting exceptional values. Then shape of the fitting shows the effect for high cooling rate (HCR). For an example if we consider 55^{0}C and 75^{0}C the effect is there but it is difficult to observe (~6s).Equation of this fit is

$$Time = -0.282x^2 + 36.361x + 37.317 \quad \rightarrow (Eq\ 5.1)$$

$$x = initial\ \ Temperature,$$

$$55^oC \ \Rightarrow 1184.067s\ ,75^oC \ \Rightarrow 1178.067s$$

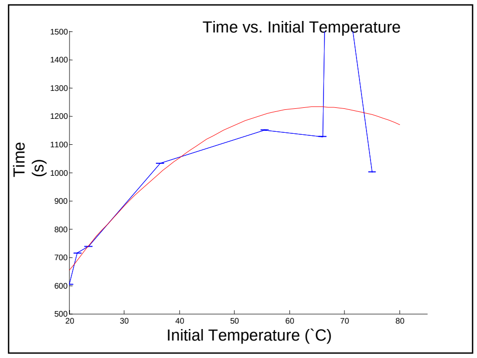


Figure 2: Cooling time vs. initial temperature

5.2 Current Observations and Planning Next Experiments

Randomness of effect and difficulty of repeating were the main observations, High cooling rate cannot be clearly observed but some samples of water has shown low latent heat. Although carbonated cool water should increase the effect as current suggestions it is same as distilled water however Carbonated water has made soft ice., Oil layer has an influence on cooling but not enough to give the effect, Then experiments are done with different cooling rates and normal water until the effect of high cooling rate is observed. The literature also shows the randomness of this effect [2].

6. EXPERIMENT RESULTS II

As mentioned in previous section we used normal water but here the ambient temperature was gradually increased for experiments. Experiments were very time consuming however it was possible to find the effect at ambient temperature -20^{o}C.

6.1 Experiments at -20^{o}C Ambient Temperature.

This was the first time where the HCR could be observed and here it shows the low latent heat as well. Repeating of above experiment also gave the same results. A doted line shown in next graph is responsible for oil layer on hot water which has removed HCR.

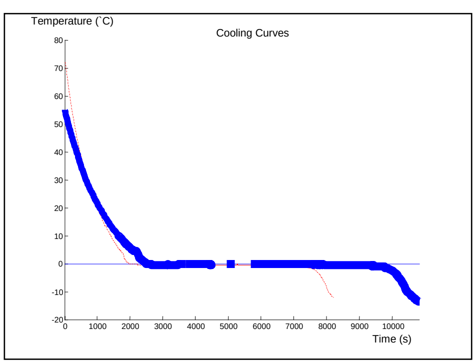


Figure 3a: Experiment at -20oC ambient temperature

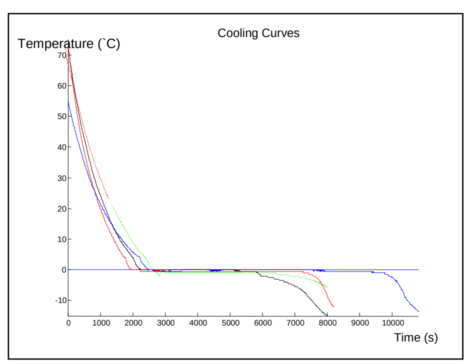


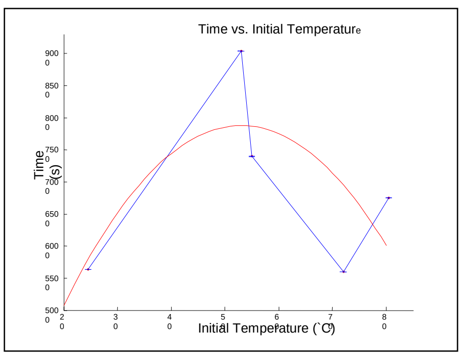
Figure 3b: At -20^{o}C Repeating and oil layer

Thereafter the results are verified to ceramic container as well.

Variables of the curve	Fitted equation and time Deference
Cooling Time vs. Temperature at -20°C	$\text{Time} = -675.05+92.548x-0.6476x^2 \rightarrow (Eq\ 7.1)$ $x = Initial\ Temperature, then,$ $72^oC \quad \Rightarrow 2494.39s\ , 54.5^oC \Rightarrow 2366.87s$ $\Delta t = 127.52s \approx 2\min$
Freezing Time (-35°C & -20°C)	$\text{Time} = 2210+68.88x-0.64x^2 \rightarrow (Eq\ 7.3)$ $x = Initial\ Temperature, then\ 72^oC \quad \Rightarrow 3776s\ , 55^oC \Rightarrow 4062.4s$ $\Delta t = 286.4s \approx 5\min$

6.2 Time taken to absorb latten heat (-35 °C & -20 °C)

Time taken to absorb latent heat vs. initial temperature was plotted for both -35°C and -20°C to identify the differences in the latent heat with the initial temperature. Highest curvature was found ad -35 °C.



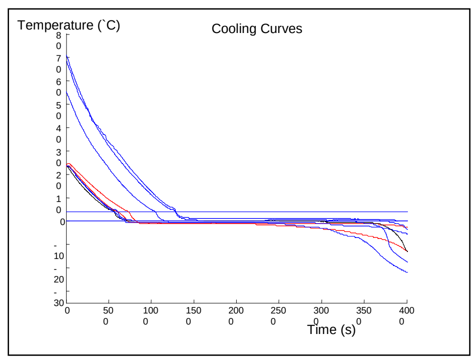


Figure 4: Observations

6.3 Observations

Possibility of repeating is high for this ambient temperature (-20°C),high cooling rate (HCR) can be observed, some samples of water show low latent heat, carbonated water makes soft ice, oil layer has an influence on cooling and remove the effect, observations can clearly be done with considerable time difference, the container has no considerable influence.

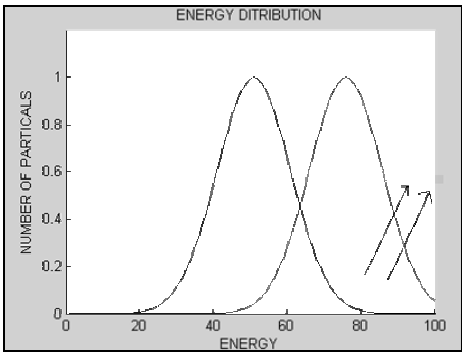
6.4 Special Observation

This section includes a special observation, which seems to be related with the effect. In all cooling curves a small distortion is observed on the 4°C line. This is a special observation which can be related with other suggestions in section 4 as well.

7. NEW EXPLANATIONS

7.1 Development of evaporation based model

Suggestions in section 4 and results of the oil layer experiment shows evaporation is the main reason for the effect. This model suggests that a small mass loss can remove higher amount of energy from water because the particles are removed from the left of the Gaussian distribution.



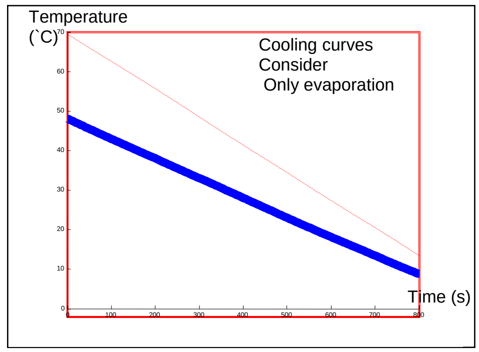


Figure 5a: Removing particles from a left of Gaussian distribution. **Figure 5b: Results of the simulation.**

Then a computer simulation was written according to equation $T = \frac{2\overline{E}}{3k}$ to exhibit this using the Monticalo methods.

$$\overline{E} = \frac{3}{2}kT \quad \Rightarrow \quad T = \frac{2\overline{E}}{3k} \quad \Rightarrow T \;\alpha\; \overline{E}, k = Boltsman's\ constent$$

Steps of the computer simulation are as follow

STEP	RESPONSIBLE PHYSICAL PHINOMINA
Generate two sets of random numbers having thousand random numbers each.	Temperature distribution of particles
Set the mean as 70 and 50 by multiplying the set by 70 and 50.Ordering them in ascending order and put them in to an array (*array1*).	Cool and hot water sample
Remove last number.	Evaporate particle with high energy
Get the new mean and put in to new array	New temperature
Repeat last two steps several times & Plot *arry2*	Cooling curve only with only considering evaporation

The result are shown in Figure 5, Hot water curve has the highest slope. But the fact that this is a random process and will not happen always is useful to explain the effect. Thereafter combining this with Newton's law of cooling will help to explain the effect.

8. CONCLUSION AND DISCUSSION

8.1 Conclusion

Results were helpful to draw the following conclusions;

- The Mpemba effect can be classified into two, HCR and QF. The fact that hot water freezes soon is a consequence of those two events.
- Evaporation is the main reason for HCR.
- The nature of ice is the main reason for QF.
- Ambient temperature is important to observe effect.

Equations of fitted curve give two temperature values where the effect occurs. But still generalization of those equations is needed; that is for any container, any ambient temperature and for any amount of water etc.

8.2 Discussion

Section 8 gives the explanation to observation except for how the ambient temperature influences the effect. But it can be described as follows. Consider the following question. “Who will win the match between great sprint athlete and the normal young man?” With the common sense, the answer is “sprint athlete” but that is when we consider a short distance. But what happen when the question is about twenty kilometer race. Now “sprint athlete” may not be the exact answer. This means that the expected results are only achieved in small space or small time. That is why the effect is observed more times when the ambient temperature is increased since it gives a longer time for the process. This is the main reason for the difference between section 6 and 7. Using 500ml of water at ambient temperature -20^{o}C will give 1 hour difference (section 7.6:12x5=1 hour) in time as Mpemba observed. Then it seems important to turn towards the thermodynamic explanation than the ion concentration or molecular base approaches. As a future development fitted curve should be corrected for low temperatures as well and experiment should be carried out with low ambient temperature.

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