Mpemba effect from a viewpoint of an experimental physical chemist

by Nikola Bregović

Introduction

Checking my email a few weeks ago, I found a message from my close friend with the title "This seams like something you could work out". The link for this contest was all that the body of the message contained. Whether I was able to "work out" Mpemba effect I am still not sure, but I was intrigued by the matter the same instance I realized the nature of the problem.

Initial results

An empty icebox of the refrigerator in my lab, a 2.5 litre bottle of deionised water, numerous beakers, and a 6 digit multimeter with a calibrated thermistor already plugged into it were at my glance and I couldn't resist setting up an experiment and giving it a try. Although I have heard the saying: "Several months in laboratory can save you a few hours in laboratory" some time ago, I immediately put a beaker containing 30 ml of water at room temperature with immersed thermistor into the icebox. After it was frozen, the experiment was repeated with all the parameters kept the same, but the water was preheated to roughly 35 °C. The temperature was measured and collected every second. The following data were obtained;

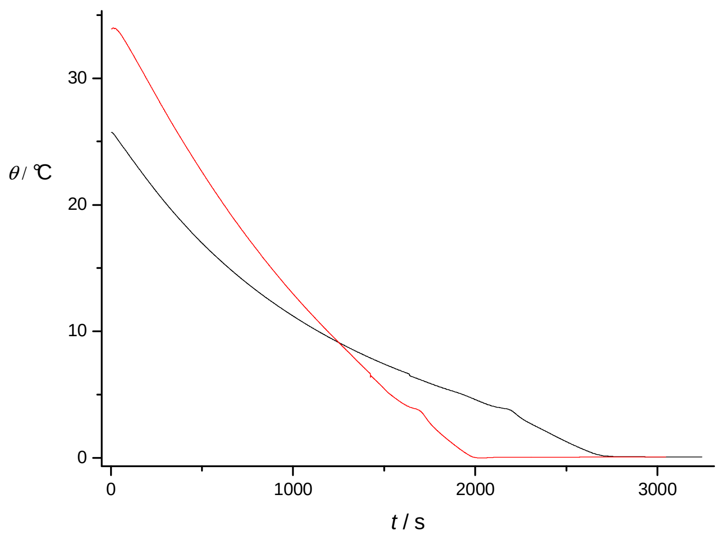

Fig. 1. Cooling and freezing of deionised water (V = 30 ml) at ≈ 25 and 35 °C in a glass beaker with no cover, without mixing.

During the time the experiments were conducted I have read several reports on the hot water freezing more rapidly than a cold one, and even found a "Mpemba effect experiment kit" sold on a website.[1] The results shown in Fig 1 (obvious case of the Mpemba effect) were thus expected. Taking into account some conclusions drawn from reports I read, I feel that some details of the experiment should be pointed out. Both experiments were done in the same beaker (one at the time), the water was changed after first freezing, the thermistor was placed in the centre of the sample, the beaker holding the sample was placed on a metal surface of a magnetic stirrer which was not covered in frost but was not stirred. Since the experiments were done in a subsequent manner it was important to make sure that the conditions (temperature) inside the icebox were more or less constant during both measurements. By measuring the temperature in the empty icebox, I found that the conditions in the icebox were far from constant, and that the temperature drifted between -18 and -10 °C with about hour and a half period. Although it is not likely that in all reported cases of hot water freezing prior to a cold one the difference in the temperature of the iceboxes was the cause, it is possible that the matter derived confusions and misinterpretations of the results in some cases. Therefore, all further experiments done in the icebox were started at the minimum of the temperature and thus conducted in the conditions uniformed as possible. Some of the obtained results are shown in Fig 2.

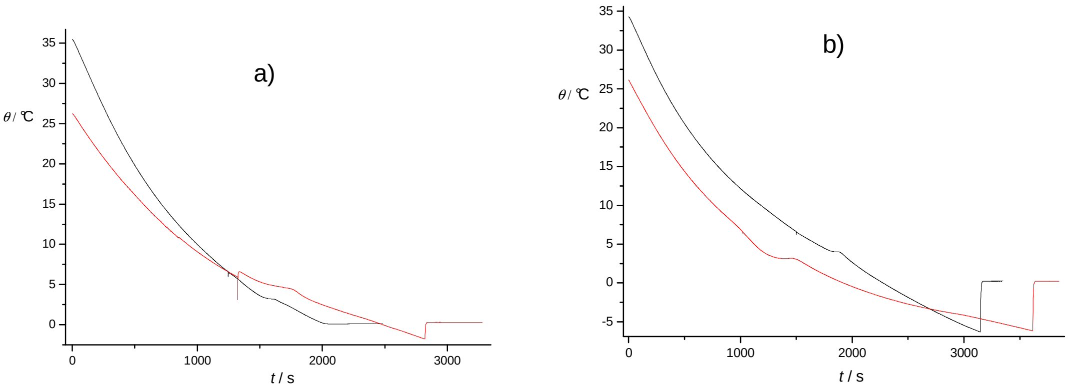

Fig 2. Cooling of 30 ml of deionised water in an icebox with controlled conditions, without mixing.

By inspecting the data presented in Fig 2 superficially, the conclusion that Mpemba effect is observed in both cases (a and b) may be drawn. However, if the curves from a and b are compared, significant differences become obvious, along with the fact that the warmer water does not always take the shortest time to freeze. The differences of the supercooling temperature in the a and b curves are also more than obvious, but the explanation of this results is far from it, since the same beaker, same batch of water and the same icebox were used in all experiments.

Although not very informative and definitely not explaining the Mpemba effect, these results emphasize the problem all scientists that researched freezing of water dealt with; poor reproducibility.[2, 3, 4] Whether freezing of water is indeed a phenomenon defined partly by chance as some authors claim, or these "hard to explain differences" are caused by the lack of control of the experimental conditions I am not able to say. However, the fact that a process so common and important as water freezing is not fully resolved and understood, is astonishing.

The explanation

Since the results of the first few experiments allowed almost no conclusions, a more detailed literature search was needed in order to continue my investigations. I encountered a number of theories on why hot water freezes more quickly than the colder one, and the phenomena most often accused of causing it are:

1. evaporation of the water
2. dissolved gasses
3. heat gradient induced convection
4. supercooling

The nature and properties of contact between the sample and the surface of the cooler, i.e. melting of the frost enabling better thermal conduction, are also often mentioned but this aspect will not be given further attention in this paper, since enough data is provided to show that Mpemba effect occurs even when melting of the frost in icebox is hampered or completely excluded. [1a]

By stating this, the task of my research, this elaboration and the contest in general becomes resolving which of the stated phenomena is the most important and which could possibly be disregarded.

A careful consideration of the Mpemba effect allows us to define one single necessary condition for the effect to occur: As the initially warmer water (at temperature θ_h) reaches the temperature of the initially colder water (θ_c) it's properties must be changed in the way that the rate of further cooling (from θ_c to freezing) is increased or the temperature of freezing (supercooling) is significantly lowered. This differentiation may occur during the process of heating the sample to θ_h or cooling it from θ_h to θ_c. If this is not achieved, Newton's law of cooling and not to mention common sense, tell us Mpemba effect is not possible.

Let me now pay attention to each of the four phenomena stated above and discuss their possible impact on the cooling of water.

1. Evaporation of the water

Some authors believe that the increase of vaporization rate of the water at higher temperatures is responsible for the Mpemba effect. However, several scientists weighed the samples prior and after the freezing. The differences in mass never exceeded 3 %. Although there is undoubtedly less water to be frozen after hot water reaches θ_c, such a minor change couldn't have significantly changed the time needed for water to freeze. The heat consumed by the vaporization process is not negligible ($\Delta_{vap}H$ = 43.99 kJ mol^{-1} at 25 °C) but again, as the θ_c is reached, the cooling curve should be continued more or less the same as the cold water curve. Therefore, I find that the vaporization phenomenon is not a relevant cause of the Mpemba effect. Unfortunately this claim is not simple to prove experimentally, since it would request a comparison of cooling curves for a closed and open sample. By sealing a sample, not only the vaporization, but also thermal conduction would be hindered making impossible to examine each effect separately.

2. Dissolved gasses

It is known that the equilibrium constant for the process of gas dissolving in water decreases with an increase in temperature. This means that there is more gas dissolved in cooler water, but also that the process of dissolving gasses is exothermic. Thomas, one of the authors claiming gas dissolution is the main factor responsible for Mpemba effect, gives a number of experimental data indicating that this claim stands.[5] In his research he noticed great differences in the time needed to freeze the whole amount of water depending on the initial temperature. However, the dependence of time needed for the formation of the first ice nuclei on the initial temperature was far less expressed. No mechanism of the effect of dissolved gasses was given by Thomas.

An attempt to explain the phenomenon that degassed water (by boiling it for a while) freezes quicker than non-degassed one was given by Wojciechowski et al.[6] According to their theory, gas molecules stiffen the arrangement of the water around them reducing convection in the sample. This means that the viscosity of the water should be significantly increased as gasses dissolution is favoured. In 1903. Ostwald showed this was not true in the case of any air contained gas. Namely, saturating water with carbon dioxide, oxygen or nitrogen, did not change the viscosity of the sample in reference to pure water.[7]

A few other possibilities might come to mind considering the mechanism by which gasses could affect the time of water freezing;

a) by lowering the temperature of phase transition
b) by inducing a negative heat flow

We can dismiss the point under a) since all the data in Thomas' research show that the freezing temperature is very close to 0 °C. This is expected if we take the concentration of the dissolved gasses and the cryoscopic constant of water into account. On the other hand, as warmer water contains less gas it is logical to assume that during cooling more and more gas is being dissolved in it. As already stated, this process is exothermic which means that it "produces" heat, which should slow down the process of cooling, not speed it up. Additionally, such a fast establishing equilibrium would cause the warm and cold water to be exactly the same as initially warmer sample reaches the cold water temperature. Hence, this couldn't cause the Mpemba effect. However, it is possible that the process of dissolving (and expelling) gasses was much slower. If this was the case differences in gas concentration in degassed and saturated water could cause significantly different behaviour of degassed and saturated samples during cooling (letting the mechanism aside). In that case I don't see how a significant difference in the concentration, sufficient to increase the cooling rate, could be induced by quickly heating the water by 10 or 15 °C. It is worth noting that Mpemba effect was observed even in such cases. Auerbach gave an estimation of 5 min needed to saturate 1 cm water column with gases under normal conditions, which indicates that, as Aurebach put it, "...degassed water does not remain so." In addition, Auerbach investigated the influence of dissolved gases on supercooling temperature and found no correlation between these variables.

3. Heat gradient induced convection

An extensive review regarding thermally driven flows was given by Kowalewski.[8] In this paper the experimental and theoretical approaches to the problem of convection in fluid during cooling and phase change are described in detail. The propagation of the ice front formed in supercooled water and the flows induced thereby, as well as flows occurring in fluid placed in differentially heated cavities are shown.

I believe that an explanation on how this is related to the Mpemba effect is needed. Namely, heat flows depend on the temperature gradient. When a warm sample of water is placed in a cold environment, the part of it next to the walls of the container gets cooled quickly while the inner part remains its temperature. A temperature gradient is thereby induced inside of the sample which causes convective heat transport. The greater heat gradient gets, the convection is more expressed, and the overall cooling of the sample is faster, since the heat gradient on the container walls is maintained. It is now important to point out that convection has both properties required to cause Mpemba effect; the flow induced during the cooling from θ_h to θ_c continues throughout the cooling, undoubtedly enhancing the heat transfer from the water sample. In other words, the hotter water initially is, the more convective flow is induced in it, which makes the cooling to the freezing point faster. As was already mentioned, the convective flows depend on the viscosity of the media. As viscosity of the water increases exponentially with decrease in temperature (Fig. 3) the convective flow is much easier to induce at higher temperatures.[9] Although convection is reduced during cooling, it is reasonable to assume that this effect is sustained throughout the cooling process, accelerating cooling of the initially hotter water even after it reaches θ_c.

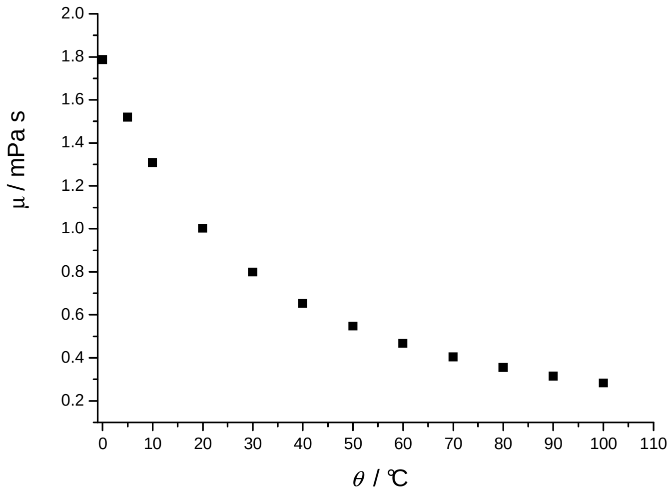

Fig. 3. Dependency of absolute viscosity of pure water on temperature.[8]

If we examine the cooling curves given in Figs. 1 and 2, it is easy to notice a plateau as temperature reaches 4 °C. Auerbach explained this observation by keeping in mind that this is the temperature where colder water becomes less dense than warmer water.[3] As it reaches this temperature, the convection is hindered, since the density gradient becomes zero (at the maximum of the function). After that, as colder water is becoming less dense, it rises through the column of water inducing probably the greatest convective flow during the whole cooling process. This causes the sample to be cooled very quickly right after 4 °C is reached. It can also be seen that the plateau is less expressed in the cooling curve of initially warmer water, since in those samples "usual" convective flows are greater even at 4 °C.

Additional confirmation for the importance of convective flow is the fact that, Mpemba effect was significantly reduced when the sample was vigorously mixed throughout the cooling process using a magnetic stirrer (Fig 4).

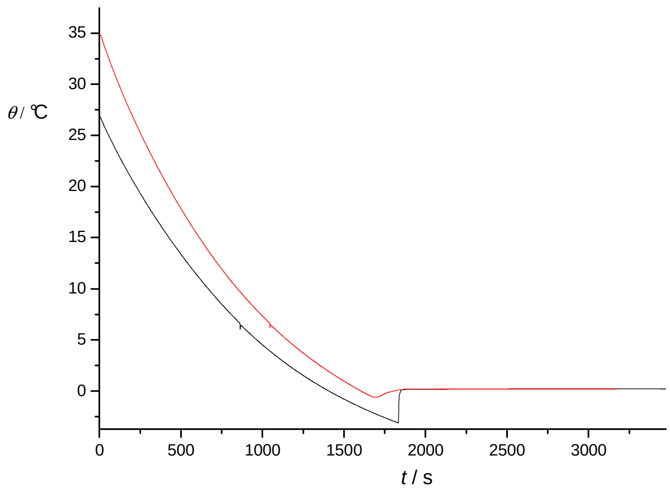

Fig 4. Cooling and freezing of deionised water (V = 30 ml) at ≈ 25 and 35 °C in a glass beaker with mixing.

To summarize, the convective flows induced by heat gradients during cooling are most certainly responsible for the Mpemba effect. Although more experimental confirmation is needed, the shape of the cooling curve caused by the anomaly of water corroborates this statement, along with several investigations summarized by Kowalewski. However we can't ignore the fact that Mpemba effect still exists, even when the sample is mixed (although reduced). This fact brings us to the final point in this elaboration, supercooling.

4. Supercooling

This phenomenon is probably one that causes most "problems" *i.e.* lack of reproducibility in the investigations of water freezing. Even throughout my humble set of experiments great differences in the temperature of supercooling were observed and in some cases it even appeared to be absent. It is important to bare in mind that complete absence of supercooling prior to a phase transition is not possible, since supercooling is necessary in order to form initial ice crystal. However, in some cases supercooling is simply not noticed during the experiment because it is localized on the walls of the container. Although the temperature is significantly lower than 0 °C at the site where ice crystals starts to grow (on the walls of the beaker) in the middle of the sample this may not be notable. Hence the significant differences in conclusions drawn by Auerbach and Thomas.[3, 5] Namely Auerbach measured the temperature just a few millimetres from the wall of the vial and observed supercooling in all cases, whereas Thomas placed the temperature sensor in the middle of the sample and commented that no significant supercooling was observed.

I feel that the effect supercooling has on the time needed to freeze a sample of water should be briefly addressed. As I stated earlier, the rate of cooling depends on the temperature gradient between the sample and the surrounding. As freezing (supercooling) temperature is lowered, the time needed to achieve this temperature increases, since the cooling rate for that last few degrees diminishes drastically. This is why even a slight change in the supercooling could prolong freezing notably.

The main problem however is not to explain how supercooling could affect freezing time, but how supercooling itself could be influenced by initial temperature. In his work Dorsey gave attention to almost every thinkable factor defining supercooling temperature. As a result, a new theory of phase transition, which we could call a “general heterogeneous theory” was born.[2] According to this theory, the temperature of supercooling may be lowered or increased by preheating, depending on the nature of the sample and its container. It may also vary by subsequent freezing and melting. The heterogeneity this theory supposes allows that even two samples of water taken from the same bottle may differ significantly in supercooling properties. Applying this knowledge to the problem of Mpemba effect gives us no simple an unambiguous explanation. It however allows that the effect may or may not occur under the same conditions.

Conclusion

The statement by J. D. Brownridge, “Hot water will freeze before cooler water only when the cooler water supercools, and then, only if the nucleation temperature of the cooler water is several degrees lower than that of the hot water. Heating water may lower, raise or not change the spontaneous freezing temperature,**”** summarizes in great part the conclusions that may be drawn from almost all the data I have collected myself and others presented earlier. However, the effect of convection, which enhances the probability of warmer water freezing first should be emphasized in order to express a more complete explanation of the effect.

The fact that this effect is not fully resolved to this day, was an indication to me that fundamental problems lie underneath it, but still I did not expect to find that water could behave in such a different manner under so similar conditions. Once again this small, simple molecule amazes and intrigues us with it’s magic.

Literature

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