FRONT MATTER: LETTER TO THE EDITOR

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Paradox of temperature decreasing without unique explanation

Marek Balážovič[1,*] and Boris Tomášik[2,*]

[1]Constantine the Philosopher University in Nitra; Nitra, Slovakia; [2]Matej Bel University in Banská Bystrica; Banská Bystrica, Slovakia

Dear Editor-in-Chief,

The question, why warm water freezes faster than cold water is not new. In fact, it has been here for hundreds of years.[1] In 1969 Erasto Mpemba observed the effect of paradoxical freezing in the preparation of ice cream. This phenomenon we today call Mpemba effect, but Mpemba is actually not its first explorer. First notices we find in Aristotle's work Meteorologica from 350 B.C.[2] Despite more than 2000 y of history, Mpemba phenomenon hasn't got its uniform explanation. How is it possible, that we couldn't get right explanation of this effect?

Unanswered questions lead us to searching and inquiring. From time to time we can find articles about this unexpected behavior. We can read many different explanations by different authors, who examined Mpemba effect. Two years ago, the Royal Society of Chemistry offered £1,000 to the person or team producing the best and most creative explanation of the phenomenon and they received explanations from 22,000 respondents.[3] The reason is that the question, why does hot water freeze faster than cold water, is not well formulated. It contains too many variables which affect the freezing process. It does not specify the amount of water, temperature difference between hot and cold water, the source of water used in experiment, the method of cooling and we don't define freezing. Many experimenters focused their observation on different phenomena. Some of them measured the time until the temperature of water reached 0 °C. Other measured the time to the point at which water forms a visible surface layer of ice, yet another the point at which the entire volume of water becomes a solid block of ice, and so on. This causes divergence among the authors' conclusions. Hot water can freeze faster than cold water for a wide range of experimental conditions. We can only give the specific explanation for certain specific conditions, when we observe the effect. The common or general answer does not exist. It can look original or interesting, but it cannot be used as a universal reason.

According to the plethora of published results Mpemba effect has no definitive explanation. Thus it is an appropriate candidate to experimentation and inquiring. The phenomenon doesn't occur regularly, therefore it is interesting to search conditions when it may arise. It provides a wide option of various parameters, which provides a plenty of space for the discussion of different results from similar initial conditions. Importance of individual explanation and mechanism is affected by different conditions. We list here some explanations that have appeared throughout the literature. Many of them refer to practical realization of the process with water put in usual home freezer.

Ice coating in freezer. If the containers are cooled in a freezer with ice coating, the container with hot water can melt ice under itself. Ice is not a good heat conductor. If it is melted below the jar more, the jar will be closer to the freezer. The heat will then be transported faster. Mpemba himself considered this the most likely interpretation for his first observation of the phenomenon.

Temperature gradient. Unless we mix the water, temperature will not be the same in all its volume. Heat transfer is proportional to temperature gradient, i.e. to the steepness of temperature change with position. The gradient is larger in hot water. When we mix the water it prolongs the cooling process.[4]

Evaporation. Warmer water evaporates faster than cold water. Because of that it reduces its volume faster. Since the time needed for freezing is directly proportional to the amount of water, it can be easy to explain the observations. This explanation was one of the first after the rediscovery of the phenomenon. It is discussed in more detail by G. P. Kell.[5] Evaporation is well applicable as the cause of the Mpemba phenomenon in cases where free liquid surface is too large.

Microstructure of water. Water molecules are not completely isolated from one another and they often merge, creating more complex structures called clusters. Such clusters effectively hinder ice forming. When you heat the water, molecules are separated out of clusters. Much effort has been devoted recently to investigations with the help of advanced measurement and computational techniques (see also the discovery paper by Chang Qing Sun[6]).

Effective freezing system in freezer. The fridges or freezers have often a thermostat. A thermostat is a component of a control system which senses the temperature of a system so that the system's temperature is maintained near a desired set point. When you put something hot inside your freezer the thermostat indicates it, and it amplifies cooling inside. This could make differences between cooling process with different

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*Correspondence to: Marek Balážovič; Email: marek.balazovic@ukf.sk; Boris TomášIK; Email: physics,boris.tomasik@umb.sk

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samples unless we use the same refrigerator at the same time.

Convection. In warmer water there are stronger streams. The water circulates and the heat is transferred toward the walls of the container more quickly. The inertia can provide significant flow of water during its entire cooling. For hot water, this means faster cooling and the water can catch up the advantage of cool water.[4]

Chemical composition. Heating process of water change the quantity of dissolved gases and solid substances contained in water. By decreasing the amount of gases and solids in water, its thermal conductivity can increase. Its freezing point may also shift. Finally, the change in composition can improve water circulation in the vessel.

Temperature of freezing. The freezing temperature of water at normal pressure is often identified with the temperature of 0 °C. Freezing process, however, usually starts at a lower temperature. Water may remain in the liquid state sometimes even at much lower temperatures, and we call it supercooled water. One of the explanations of the phenomenon is that initially warmer water is supercooled less than initially cooler water. The first to come up with this explanation was D. Auerbach.[7]

Hot water does freeze faster than cold water. It has been seen to occur in a number of experiments. However, despite claims often made by one source or another, there is currently no universaly accepted explanation for how this phenomenon occurs.

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