Reply to Burridge & Linden: Hot water may freeze sooner than cold

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In a recent paper in Scientific Reports, Burridge & Linden misinterpret the Mpemba effect as a statement about the rate of cooling of liquid water, when it is in fact a statement about the rate of freezing of water. Debunking an obviously absurd claim about cooling, they miss the significant effect, its only quantitative experimental study and a theoretical argument that explains the effect and predicts that it occurs only for “hard” water (water with significant dissolved Mg and Ca bicarbonates). This prediction remains to be tested.

Keywords: Mpemba effect

Introduction

Burridge & Linden review experiments and perform a new experiment on the cooling of hot and cold water. Unsurprisingly, they find, both in their new careful experiments and in the extensive but very heterogeneous earlier literature, that in the same thermal environment (cold air) it takes longer for hot water to cool to 0°C than for cold water. However, the “Mpemba effect” is usually taken to be the observation, reported since ancient times and a matter of folklore, but hardly studied quantitatively, that initially hot water freezes sooner than initially cold water when placed in the same environment. This is a quite different assertion.

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Cooling Water

It is evident from elementary thermodynamics that the version of the “Mpemba effect” that Burridge & Linden are at pains to refute must be wrong. As long as water is in thermodynamic equilibrium (if it were not, a temperature could not be meaningfully defined; see, however, 2 who suggest that the Mpemba effect is intrinsically a nonequilibrium phenomenon, requiring macroscopic relaxation times) and all the water in a container is at the same temperature (usually a good approximation because of natural buoyancy-driven convection), initially warm water must pass through all lower temperatures on its way to $0^\circ C$. Heat flows from the warmer water to a colder external temperature $T_{ext} < 0^\circ C$ and specific heats are positive (required for thermodynamic stability). If the heat flow is determined by the instantaneous temperature difference (requiring that fluid flows in the water and the environment relax rapidly to the instantaneous temperature difference, retaining no memory of earlier conditions), then the time to cool from an initial temperature $T_i > 0^\circ C$ to $0^\circ C$ is

$$t_i = \int_{T_i}^{0^\circ C} \frac{F(T_{ext} - T)}{C_P} dT,$$

where $F(T_{ext} - T) < 0$ is the rate of heat flow out of the water and $C_P > 0$ (a weak function of temperature) is the heat capacity of the water and its container. $dT$ is negative, integrating from a higher $T_i$ to $0^\circ C$, and the integral is positive. Then the time $t_w$ to cool to $0^\circ C$ from a warm temperature $T_w$ is related to the time $t_c$ required to cool to $0^\circ C$ from an initially cooler temperature $T_c$, where $0^\circ C < T_c < T_w$:

$$t_w = \int_{T_w}^{0^\circ C} \frac{F(T_{ext} - T)}{C_P} dT$$

$$= \int_{T_w}^{T_c} \frac{F(T_{ext} - T)}{C_P} dT + \int_{T_c}^{0^\circ C} \frac{F(T_{ext} - T)}{C_P} dT$$

$$= \int_{T_w}^{T_c} \frac{F(T_{ext} - T)}{C_P} dT + t_c$$

$$> t_c.$$

It is hardly surprising that experimental results satisfy this inequality.

The Mpemba effect

The Mpemba effect 3, 4 is usually considered to refer to the freezing of water. Because of the large latent heat of freezing, removal of latent heat accounts for more of the time
required to freeze than removal of internal energy in the liquid phase. In most experiments this is the case even if the “hot” water is initially at temperatures close to 100°C because at high temperatures in unsaturated atmospheres evaporative cooling is rapid. Most of the cooling time is spent at temperatures comparatively close to 0°C where evaporative cooling is unimportant and the remaining internal energy that must be removed before the onset of freezing is small compared to the latent heat of freezing.

There appears to be only one quantitative experimental study of the Mpemba effect in freezing, that of Wojciechowski, Owczarek and Bednarz [5], not cited by Burridge and Linden [1]. These authors found that initially warmer water froze before cooler.

**Discussion**

A theoretical explanation was offered by Katz [6]. The explanation involves both concentration of solutes by zone refining and freezing point depression; the reader is referred to the original paper for details. Contrary to an assertion in Burridge & Linden [1], this paper successfully explained the effect, at least qualitatively. It also predicts that an Mpemba effect will be observed in “hard” water containing bicarbonates of Mg and Ca. Heating the water removes CO₂, turning bicarbonates into carbonates that precipitate [7] and “softening” hard water. This gives specific form to earlier suggestions that heating somehow changes the nature of the water, so that water that has once been heated differs from water that has not been heated, or not heated recently (water exposed to air recaptures CO₂ from the atmosphere). Burridge & Linden [1] boiled all their water samples before cooling them, so it is predicted that they would not have observed hot water to freeze before cold water, even if they had searched for this.

Unfortunately, authors of papers of the Mpemba effect have not described the composition or hardness of the water they used. Many natural waters are hard because they are obtained from aquifers in carbonate rock. It remains for further experiments to compare rates of freezing of warm and cold water, soft and hard.

**Author contributions**

This paper is entirely the work of the sole author, J.I.K.
Additional information

**Competing financial interests:** The author declares no competing financial interests.

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