New explanation for the Mpemba effect

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Abstract: The purpose of this study is to check out the involvement of entropy in Mpemba effect. Several water samples were cooled down to frozen in order to probe if preheat affects the cooling duration time. We found out that preheating of the water sample the cooling duration was reduced. Given this, we theoretically show that water gains more entropy when warmed and re-cooled to the original temperature.

1. Introduction

This case study proposes an explanation for the Mpemba effect, which is considered as the phenomenon wherein, under uncertain conditions, hot water freezes faster than cold water. The fact that the water has been warmed previously contributes to its rapid freezing. Hence many people, when they want to cool water quickly, begin by placing it in the sun. Named after Erasto Mpemba in 1963 [1], the Mpemba effect was reported by Aristotle, Bacon, and Descartes and has been discussed widely in both research as well as popular scientific journals [2]. Auerbach claims that it is different from the supercooling effect [2], but Brownridge argues that it is actually the same [3]. A latest (2016) study [4] disputes the phenomenon at all, although a more recent study [5] shows that the effect is present in granular fluids. Lu and Raz had a generic theory on the Mpemba effect but was not specific applied to water [6]. The explanations have been suggested, can be divided in two general categories. The first one, which for ease can called "physicals", includes theories like these: evaporation [7], frost [8], conduction [9], solutes [10], and supercooling [11]. Second category, called for ease "chemicals", includes theories involving hydrogen bonds such these: crystallization [12], hydrogen bonding [13] and hydrogen bond memory [14]. But, a main query remains unanswered: Why the effect is not always occurs?

In this study, this unique effect is defined as the phenomenon wherein, under certain conditions, it takes a shorter time to cool hot water than to cool cold water: this perspective is adopted by Lu and Raz [6], and described based on macroscopic variables. Further, the underlying mechanism responsible for the effect is proposed and the low repeatability of the phenomenon is explained.

Let us consider two same jars, A and B, with each containing an equal quantity of water at the same temperature (T), such that the water in A has more entropy than that in B. This means that the water molecules of both jars have the same energy; however, those in jar A are moving randomly in all directions, whereas the thermal motion of those in jar B is restricted by the structure mentioned above. Therefore, in the case of the water sample in jar A, random collisions are more likely to occur than in the case of the sample in jar B, resulting in the water molecules losing more kinetic energy (E) on average. This results in a reduction in the temperature according to the relationship $E = (3/2)bT$, where b is the Boltzmann constant. Therefore, the water in jar A cools faster than that in jar B.

Convection is the dominant form of heat transfer in liquids. According to Newton's law of cooling, during the cooling of a material body, the rate of temperature decrease (cooling rate=q) is proportional to the temperature (T):

$$q = dT/dt = -hT => T = T_0 e^{\wedge}(-ht) \qquad (1)$$

where t is the time, h is the heat transfer coefficient, and T_0 is the initial temperature. The half-time period (HTP) is equal to ln2/h. The greater the value of h, the higher is the cooling rate, q so more likely to occur Mpemba effect: this is my aspect discussed below in Discussion section. Heat

transfer coefficient is dependent upon the physical properties of the water and the physical situation. However, h is affected by much many factors such as the container's shape and material and the air circulation within the freezer, among others. For example, equation (2) applies to a PET bottle assuming a planar geometry [15]:

$$h=1/(1/h_1 +1/h_2 +\delta/k) \tag{2}$$

h : overall heat transfer coefficient
h_1: heat transfer coefficient inside the bottle
h_2: heat transfer coefficient outside the bottle
δ : PET layer thickness
k : PET thermal conductivity

Thus, the Mpemba effect is hard to predict and is not observed in every instance. We restrict ourselves to the study of the thermodynamics in the single bottle representing a closed thermodynamic system, namely a system that exchanges energy with the environment represented by the cooling chamber. Since we are dealing with phenomena taking place locally and under conditions of local equilibrium inside and outside a typical bottle, all intensive and extensive thermodynamic variables have a space and time dependence [16].

2. Materials and Methods

An experiment was performed to elucidate the effect of preheating on the cooling duration, wherein three bottles, A, B, and C, each containing the same quantity of water, were placed in a freezer with an internal temperature of -18 °C. The temperature of the water in bottle C was 50 °C while that of the water samples in B and A was 25 °C. The water in bottle B was first heated to 50 °C and then cooled to 25 °C. After one hour and ten minutes, it was observed that the temperature of the water samples in bottles B and C reached 0°C sooner than that for the water in A. It is likely that samples B and C followed the same cooling process; that is to say, the coefficient h was the same for both B and C, while it was larger for A. The HTP for both B and C was the same and lower than that of A. This experiment was conducted at the laboratory of the Nafplio Regional Quality Control Centre, which had met the requirements of the standard ISO/IEC 17025:2005 since 2009 (accreditation body: ESYD S.A., certificate number: 609).

Commercial PET bottles with a volume of 500 mL were filled with 500.00 g of degased distilled water produced by a distiller (Bibby Sterilin, model: A 4000D, conductivity of water: 1–2 µS/cm). The ambient temperature within the laboratory was adjusted to 25 °C. The water in bottle B was heated to 50 °C in a Pyrex glass using a hot plate and then left to cool to 25 °C. The water in bottle C was heated to 50 °C. The water was poured immediately into the bottles, which were at the ambient temperature. The sensors (pins) of the digital alert thermometers used for the temperature measurements were inserted from the top to the middle of the bottles. With no relaxation time, the bottles were capped then immediately placed in a freezer and cooled to 2 °C (**Figure 1**).
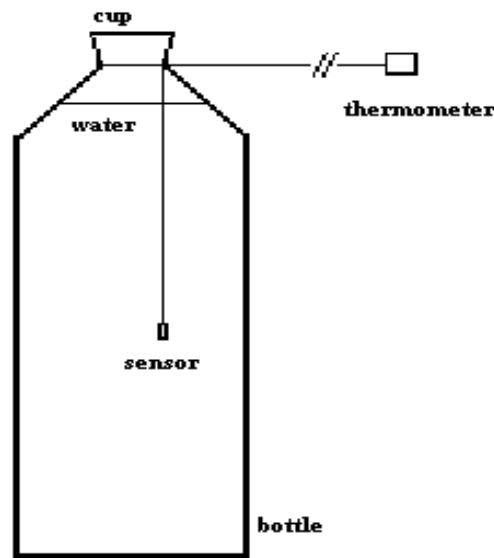
Figure 1. Experimental layout

Digital alert timers were used to measure the duration time. Measurements were carried out under the plan one bottle per day. Initial conditions are kept the same in the different repeated runs.

3. Results

The experimental results are shown in **Table 1** arranged in descending order:

Table 1. Cooling duration

Process	Time (min)										Average	S.D.
A	101	100	100	100	100	100	100	100	100	99	100	0.5
B	99	99	98	98	97	97	97	97	96	96	97.4	1.1
C	98	98	97	97	97	97	97	97	96	96	97	0.7

Data are illustrated in **Figure 2.** The average values were compared using the F test. First, the average value of the A samples (Aav) was compared with those of samples B and C ([Bav + Cav]/2), in order to check whether preheating affected the duration of cooling. Next, Bav and Cav were compared to determine whether they were equal within the limits of experimental uncertainty. In the first case, the F value, F1, was calculated to be 86.0. Further, the F tables with a significance level of 0.1% gave F = 13.6 << F1, showing that the preheating of the water strongly affected the cooling duration. In the second case, F2 was calculated to be 1.3, which is significantly less than 13.6 (F1). This meant that Bav = Cav.
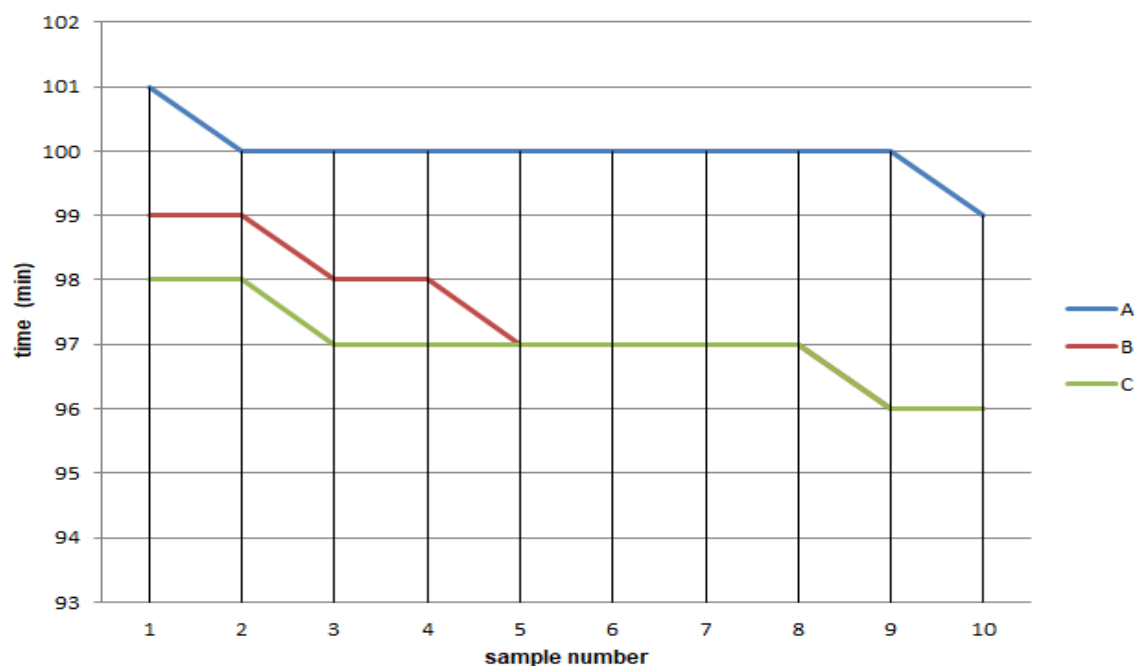
Figure 2. The three processes

4. Discussion

Water molecules are V-shaped electric dipoles. Cold water has a rudimentary structure, hereinafter referred to as simply the "structure." The structure consists of intermolecular cyclic associates (clusters) of water with the general formula $(H_2O)n$ [17]. The ordering of water molecules into associates corresponds to a decrease in their entropy (randomness) [17]. Each water molecule can form two hydrogen bonds involving their hydrogen atoms plus two further hydrogen bonds utilizing the hydrogen atoms attached to neighboring water molecules. These four hydrogen bonds optimally arrange themselves in a tetrahedral structure around each water molecule, as observed in ordinary ice [18]. In liquid water, thermal energy can cause these hydrogen bonds to bend and stretch and even break. However, the average structure of a water molecule is similar to this tetrahedral arrangement [18]. Today, this tetrahedrally coordinated water structure is generally accepted; however, the arrangement of most hydrogen-bonded molecules is not symmetrical. At room temperature, 80% of the molecules of liquid water have one strongly hydrogen-bonded O-H group and one non- or only weakly bonded O-H group at any instant. The remaining 20% of the molecules are made up of four-hydrogen-bonded tetrahedrally coordinated clusters [18]. The average energy of the hydrogen bonds between the H_2O molecules during the process of cluster formation is 0.1067 ± 0.0011 eV. As the energy of the hydrogen bonds between the H_2O molecules increases to 0.14 eV, the water clusters are destroyed [17]. A typical cluster consists of five water molecules. In ice, this tetrahedral clustering is extensive, producing crystalline structures [18]. In liquid water, tetrahedral clustering is only observed locally and its extent reduces with an increase in the temperature. When decreasing the temperature, the liquid undergoes a structural transformation coinciding with the onset of an extended hydrogen bond network [19]. In bulk water, at any instant, it is expected that strongly tetrahedrally oriented hydrogen bonds form a network (lattice), with a small number of isolated pockets of water molecules with weak or broken hydrogen bonds also being present [18]. Most of the interesting properties of water come from this three-dimensional hydrogen-bonding network [19]. The hydrogen bond energy is 5–10 kcal/mole, while the energy of O–H covalent bond in the H_2O molecule is 109 kcal/mole. The average energy (ΔE H...O) of the hydrogen H…O bonds between H_2O molecules is 0.1067 ± 0.0011 eV. With

fluctuations in the temperature of water, the average energy of the hydrogen H...O bonds in the water molecule clusters changes [17]. This is the reason that the hydrogen bonds in the liquid state are relatively weak and unstable: it is thought that they form and break readily with changes in the temperature. It is known that thermal oscillations (fluctuations) lead to the bending and breaking of hydrogen bonds [17,18]. When water is heated, the hydrogen bonds break, and the molecules move further apart and get repositioned randomly, resulting in extensive collapse of the structure. Hence, the fraction of water molecules joined by hydrogen bonds decreases. According to theoretical calculations, heating to 40 °C breaks approximately half the hydrogen bonds in water associates [17]. The breaking of these bonds and the resulting increase in the degree of disorder of the water molecules leads to increased entropy (S). The increase in the internal entropy (dS) when water is heated from a lower temperature T_1 to a higher temperature T_2 can be calculated as follows [16]:

$$dS_1{}^2 = mc\ln(T_2/T_1) \qquad\qquad (3)$$

where m is the mass of water and c is the specific heat. My aspect is that the lattice does not extensively re-form immediately upon cooling, as the reconstruction process requires time. If the cooling process is very fast and performed using a freezer, the water molecules do not get sufficient time to restructure. There is a strong possibility for surpassing network formation and going directly to the ice crystallization. In contrast, when water remains for a long time in a fridge, wherein a stable temperature of 5 °C is maintained, the water molecules have sufficient time to reorder. Entropy is the measure of the disorder. When the water is cooled to an initial low temperature, the structure does not form instantaneously, that is, its internal entropy does not decrease immediately: the disordering process requires some time to totally reversed. Supposed $T_1 < T_2$, only for a reversed process or cycle can be $dS_1{}^2 = dS_2{}^1$, while for an unreversed process it is always $dS_1{}^2 > dS_2{}^1$ [16]: during the cooling process, the water structure does not instantaneously return to the ordered state, as hydrogen bonds do not form instantly.

Considering a cycle $T_1 \rightarrow T_2 \rightarrow T_1$ (Figure 3) (in our experiment T_1=25 °C, T_2 = 50 °C) it is:

$$dS_1{}^2 \geq dS_2{}^1 \quad \text{or} \quad dS_h\,(\text{heating}) \geq dS_c\,(\text{cooling})$$

- If $dS_h = dS_c$ the Mpemba effect does not happen

- If $dS_h > dS_c$ the Mpemba effect occurs

Entropy for a defined body is a state variable and i.e. for T_1 is given by integration of (3) thus: $S = mc\ln T_1$, but here they are two different water bodies with different "structures": this before heating and the same one after re-cooling. The different "structure" implies different specific heats. The last inequality above combined with (3) results to inequality of the specific heats:

$$dS_h > dS_c \Leftrightarrow mc_h\ln(T_2/T_1) > mc_c\ln(T_1/T_2) = -mc_c\ln(T_2/T_1) => c_c > c_h$$

Specific heat is not a constant but varies with temperature [16] which affects the network's extent [19]. Specific heat of water is in average 1 cal/gr °C = 4,18 J/gr °C in the range 25 ºC – 60 ºC [20]. Anyhow specific heat is affected by the network's extent [18]. This thermodynamic process or cycle can be visualized in a "temperature vs entropy diagram" or T-S diagram [21]. The curve for entropy reduction as a function of the temperature, $S_c = f(T)$, lags relative to the entropy growth curve $S_h = f(T)$:

$$c_h < c_c => mc_h\ln T < mc_c\ln T \Leftrightarrow S_h < S_c$$
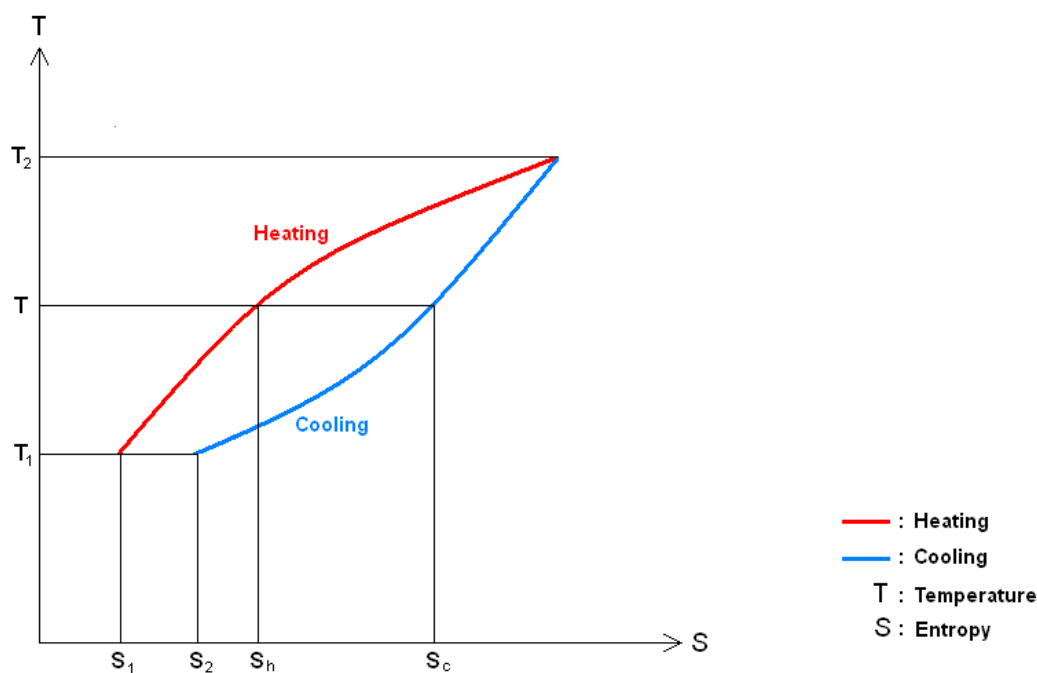
Figure 3. Curves of entropy as function of temperature

As we see in Figure 3, at any temperature T, the entropy during heating, S_h, is less than the entropy during cooling, S_c. After being heated and then cooled to the starting temperature, the water now has greater entropy and fewer hydrogen bonds than it did immediately prior to being heated, even though the temperature is now the same i.e. for T_1 it is $S_1 < S_2$.

5. Conclusions

Warm water is cooling faster than cold because it contains more entropy when it comes to its temperature. The lattice structure is more extended in cold water. Any dissolved salts present in the water change the structure of the water molecules because ions are hydrated [18]. Consequently, in the case of water containing dissolved ions, the water network is smaller, and the molecules are less organized than in pure water. Thereby, the effect of preheating is expected to be weaker.

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