Explaining the Mpemba effect

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1. Introduction:

The Mpemba effect goes back a long way; apparently, philosophers like Aristotle already knew about it, [1, 2] in ancient times. Nearer to us, Bacon and Descartes also knew of it and tried to explain it. It has been rediscovered and brought back to prominence in the modern era by a schoolboy in Tanzania, in the 60's, [3]. It is the observation that warmer water may freeze quicker that colder water. Two things make it interesting and, to many rather irresistible:

1. It is counter-intuitive since cold water should be closer in state to frozen water (ice), than hot water; it, therefore, should freeze quicker.
2. Experiments do not show the effect every time.

So, those who observed it want to explain it and those who did not, despite experimenting, think it is a hoax and want to debunk it.

2. The theory

Water, in its liquid state, is a collection of H_2O molecules that can move freely with respect to each other. This freedom of movement is removed when the water is in its solid (frozen) state as the molecules are interlocked to form some crystalline structure. There are many crystalline structures of frozen water. However, the most common one is the hexagonal structure. Before developing our theory, we give the following definitions.

Definition 1: A Solid State Inducing Position (SSIP) within the liquid water under consideration is a position (location) that favours the formation of ice. Equivalently, it is the position of one of the vertices (nodes) of a crystalline structure of frozen water.

Definition 2: A Transient Solid State Position (TSSP) within the liquid water under consideration is a position occupied temporarily by a molecule with minimum energy, surrounded by other molecules which are excited enough not to bond with it to start forming a crystalline structure. Equivalently, it is the position that the molecule, having lost its energy, occupies for some time (very short time, one should reasonably assume) before it is hit by another molecule and regains energy. Therefore, it will not yet be the node of a crystalline structure.

When a molecule of water is in an SSIP, it will tend to stay there because its energy state is low (possibly minimal) and it has bonded with other molecules surrounding it. When it is in a TSSP, it will not stay there, or remain in that state of minimum energy for too long.

2.1 The freezing process:

Water reaches its frozen state when all its molecules are in SSIP's. A molecule H_2O will reach an SSIP as a result of one of the following steps:

> **Step 1.** Losing its energy suddenly after a shock with one or more molecules to which it transfers this energy;
>
> **Step 2.** Gradual 'nudging' of a molecule which has little energy, through attraction and/or repulsion, into an SSIP by other molecules.

Remark 1: Crystalline structures of frozen water are achieved through Steps 1 and 2 above, i.e. when the water molecules are in SSIP's with respect to each other, and in states of minimum energy giving the structure its great stability.

Remark 2: In cold water, freezing occurs mostly as a result of Step 2 of the freezing process above.

Remark 3: Step 2 of the freezing process above is potentially slower than Step 1.

Remark 4: The cooling process, by gradually reducing the temperature of the vessel containing the water, reduces that of the molecules too, but not all of them by the same amount; those nearer to the surface and to the sides of the vessel will lose more energy than the ones in the middle of the vessel. This reduction in temperature 'encourages' the H_2O molecules to move into SSIP's, the positions of great stability.

2.2 Explaining the Mpemba effect

Because the molecules of hot water move about more than those of cold water, they hit each other in such a way that some stop in their tracks, as a snooker ball may do when it hits another one at high speed. This happens because in the process they transfer their (kinetic) energy to the other molecules. Consequently, they reach a state of minimum energy, which, if in an SSIP, will help form the crystalline structure of the frozen water. This phenomenon is much less likely to happen in cold water, as the molecules move slowly just as a snooker ball when moving slowly would not stop when it hits another one. So, in hot water, the high energy of the molecules and their fast movement contribute to the freezing process, but, importantly, only when the molecules that lose their energy happen to be in SSIP's corresponding to those of the crystalline structure of the frozen water.

Propostion: As a consequence of Remarks 2 and 3 above, hot water may freeze faster than cold water.

Remark 5: If a molecule loses its energy, but is not in a SSIP, it will not contribute to the formation of the crystalline structure, and therefore to the frozen state of water. In other words it is in a TSSP. This could happen when the molecule after losing its energy happens to be in the middle of other molecules that have enough energy (or are excited enough) not to be ready to settle down and bond with it (see Definition 2).

3 Other consequences of the above theory

3.1 The Mpemba effect may not be observed in every experiment

If a molecule loses its energy, but is not in a SSIP, it will not contribute to the formation of the crystalline structure, and therefore to the frozen state of water. In other words it is in a TSSP. This could happen when the molecule having lost its energy is in the middle of other molecules that have enough energy (or excited enough) not to be ready to settle down and bond with it (see Definition 2). This means hot water may or may not freeze quicker than the cold water, which explains why the Mpemba effect is not observed every time the experiment is attempted. Supercooling, on the other hand, may occur instead.

3.2 Supercooling

In warm water or colder water, it must be possible to have suddenly most molecules in TSSP positions. The water cools quickly but does not freeze although its molecules have minimum energy. The temperature of the water may be lowered well below the freezing point of water (0^{o} Celsius), but as long as its molecules are in TSSP's, it will not freeze. We conjecture, therefore, that:

Remark 6: Supercooling is the process of keeping most molecules in TSSP's.

3.3 Water with impurities

Impurities in water may hinder the freezing process by having their molecules or atoms bond with water molecules, thus increasing the chances that the water molecules which have lost their energy find themselves in TSSP's. The formation of the stable crystalline structure of ice is therefore less likely.

3.4 Similarity with annealing

SSIP's may be equivalent to the positions attained by atoms through the annealing process in some metals [4].

4 Conclusion

We have given an intuitive explanation to the Mpemba effect which also accounts for it not being observed in some experiments, supercooling and experiments with water containing impurities. We have ignored factors such as the shape of the vessel, its position in the freezing device, its colour and others because we believe that although some of them may have an effect, they would not explain the fundamental Mpemba effect.

Bibliography:

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