Supercooling and the Mpemba effect: When hot water freezes quicker than cold

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(Received 2 November 1994; accepted 28 March 1995)

Temperature measurements taken near vessel walls show that initially hot water may well begin to freeze quicker than cold. This is not, as previously surmised, due to the cooling history of the water (e.g., air expulsion during heating). Rather, supercooling virtually always takes place. On those occasions where the cold water supercools sufficiently more than the hot the Mpemba scenario is the following: The hot water supercools, but only slightly, before spontaneously freezing. Superficially it looks completely frozen. The cold water (in larger volume than that of the hot sample) supercools to a lower local temperature than the hot before it spontaneously freezes. This scenario can occur more often for ambient cooling temperatures between $-6\,^\circ\mathrm{C}$ and $-12\,^\circ\mathrm{C}$. © *1995 American Association of Physics Teachers.*

Although first recorded in school[1–7] and higher educational journals in recent times,[8] the Mpemba effect was born with Aristotle,[9] grew up with Bacon[10] and Descartes,[11] and has been recorded and discussed in both research journals[12] as well as popular scientific journals.[13–15] The effect is that on cooling, initially hot water freezes more quickly than initially cold (we will drop the word "initially"). How has this effect been understood? The effect itself has been explained away in some cases where either evaporation of the hotter vessel reduced the amount of water remaining to cool[8] or where the hot vessel's thermal contact was augmented due to melting ice[6] (although the original experiment[1] accounted for both of these effects). For experiments where these two effects were accounted for and hot water still either cooled to zero,[13] began freezing,[2,6] or froze completely more quickly than did cold,[12] explanations were sought in changes in material constants due to the fact that heated water ejects dissolved air. This seems to be the only mechanism bringing memory into the system, something which has been considered a prerequisite for the effect. No quantitative analysis was given for these explanations and detailed measurements and calculations indicate that these explanations are unlikely.[16]

Strangely enough, although supercooling has been recorded in Mpemba experiments,[2,12] it has never been considered pertinent to the understanding of the effect. On the other hand there is a growing amount of literature recording significant supercooling in systems similar to those used for studying the Mpemba effect. Here not only is supercooling beneath -5° (centigrade[17]) well known, but it has also been found that even for large volumes supercooling generally takes place[18] before freezing, for example, $T_f=-5^\circ$ for 75 l of water.[19] In phase change literature, the phenomenon of supercooling and subsequent freezing in water has been extensively studied,[20] in particular the dendritic form and scaling relations during its growth.[21] Factors indicted in influencing the mean supercooling temperature before spontaneous freezing occurs include the volume of fluid[22,23] ($T_f=-34.5^\circ$ for small volumes in capillaries); time[24] (increased for large times at very low temperatures), roughness[24] (decreased by smooth walls), or the degree of tilt[25] (minimum at an angle of 60°) of the vessel; rubbing of solids[26] (induces it); the existence of electric[27] or magnetic[28] fields; fluid motion (increased by shear[29,30] and turbulence;[26,31–33] ambient temperature; purity of the water[34] and the amount of dissolved gas.[12] One of the main results of these studies (in particular[23,24,26,29]) is that neither the time taken nor the freezing temperature are predictable.[22] It is the statistical nature of these two quantities which we examine in order to see whether they could explain the Mpemba effect.

In our experiments 100 ml standard Schott pyrex glass beakers (see "cooling curves for the second range" for details on cleaning) were plunged into a 10 l Julabo cryostat (tempering bath). The working fluid of the cryostat was ethanol which was constantly agitated by a magnetic stirrer and kept at a constant temperature whose value could be varied between 0° and -50° (to within $\pm 0.2^\circ$), no lid being used in order to facilitate quick transfer from the heat source.[35] The "hot" beakers had 50 ml of double distilled degassed water at $T_i=90^\circ$ when they reached the cooling bath, the "cold" beakers, water at $T_i=18^\circ$. Since freezing began at the walls, a thermistor (FP07 thermometrics, response $>2^\circ/\mathrm{s}$) was glued to the inner (sensor distance from the wall: 0.5 mm) wall a few mm from the water surface. The placement of the thermistor near the wall seems to be a novel aspect. All in all, we carried out 103 runs, 52 with hot and 51 with cold water. We shall first describe the *general results* which lead to a categorization of the cooling phenomena based on the ambient temperature T_a of the cryostat, then look at details of typical *cooling curves*, and finally discuss the *visual appearance*. As we shall see, there is a vast difference between *spontaneous freezing while supercooling*—whose occurrence we refer to as the "beginning of freezing"—and the (subsequent) *slow motion of a freezing front*, which is not the subject of this article and which we shall only discuss briefly in the section on the visual appearance.

GENERAL RESULTS AND THE EFFECT OF THE AMBIENT TEMPERATURE

The main parameter which we varied was the ambient temperature of the cryostat T_a. This was varied between 0° and -30°. The first result is that in all 103 experiments the water supercooled prior to freezing. Three ranges may be distinguished, depending on the ambient temperature T_a: $0^\circ>T_a>-6^\circ$; $-6^\circ>T_a>-18^\circ$ and $T_a<-18^\circ$. For the *first* range, the water seldom freezes at all (where necessary we gave up to 12 min). In the *third* range the gradients are so strong that only the water directly adjacent to the walls supercools before freezing. Here and in the first range we find the expected behavior in which the hot water's cooling curve trails that of the cold water throughout the pure liquid and mixed phases. In fact we were never able to corroborate experiments where the (average) cooling curve of hot water overtook that of the cold water when both samples were in the same phase[12] although the thermal conductivity might conceivably be slightly dependent on the temperature rate of change.[36] Our temperature measurements, however, were restricted to the immediate vicinity of the walls, a place where no other data on the Mpemba effect seems to have been gathered. It is in the second range, $-6° > T_a > -19°$, that the Mpemba effect can take place due to the statistical nature of spontaneous freezing. One ought to note that the ranges are not sharply defined, for there was one case where water with $T_a = -4°$ froze. Further all three cooling phases typical of the second range which we shall presently discuss could (and did sometimes) take place, even at $T_a = -20°$. The information which they gave, however, was so restricted to the near-wall region (see under "Appearance" later) that the occurrences there hardly reflected what was happening in the bulk of the sample. We now discuss the cooling curves and general appearance of the samples, giving a detailed description of the second range, and only mentioning the other ranges where necessary.

COOLING CURVES FOR THE SECOND RANGE

Figure 1 shows four typical cooling curves taken near the air/water interface, two for initially hot water and two for initially cold water, both with $T_a = -12°$. The curves were chosen from ten runs at this ambient temperature and represent the earliest and the latest times at which hot (cold) water began freezing. The abrupt upward jump in the temperature represents the instant of freezing, after which the recordings were stopped. In the abovementioned temperature range, cooling goes through two or more of three possible *phases* before spontaneous freezing takes place, each characterized by a different slope. The hot late (taking longest to freeze: $t = 560$ s) sample went through all three phases, so we discuss this curve in detail. The first Newtonian type cooling phase (time scale: heat capacity/heat transfer coefficient), taking until 160 s, is followed by a phase where the temperature decreases more slowly (from a degree per 2 s to around a degree per minute) due to buoyancy induced convection coming from the density anomaly of water: Rising cold water at the walls induces a ring vortex flow, thus augmenting heat transfer.[19] This phase took until some 400 s. The three dips at 200, 300, and 360 s were caused by the sample being willfully bumped to see whether this might cause spontaneous freezing (which did not occur in this case). Both this aspect as well as the sinuosity of the curve indicate the tendency to stable stratification beginning to show itself: propagation of gravity waves becomes possible. During this period the local (in a temporal sense) convective cooling time scale is $\nu/(\beta g \Delta T^2 d)$ with β the coefficient of expansion; ΔT, the temperature difference; d, the characteristic length and ν, the kinematic viscosity.[37] Velocities of maximally a few mm/s occur during this phase. The convection time scale becomes infinite at 4° ($\beta \to 0$): Cooling again becomes Newtonian as convection ceases and the temperature decreases more rapidly at the wall. For ambient temperatures above −6° (first range) where freezing seldom takes place, the exponential nature of this phase becomes more apparent. Note in particular the different forms which the cooling curves take on during the convective phase, the most radical differences occurring between the hot early and the hot late curves. This behavior is largely due to the fact that the number, typical velocities and the spatial distribution of the convection cells are generally sensitive to initial and boundary conditions.[38]

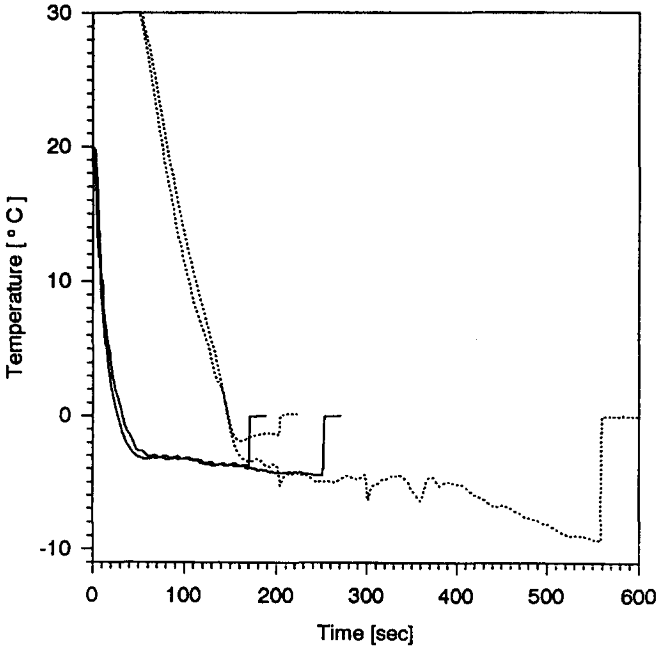

Fig. 1. Temperature traces near the junction between wall and the water surface for the four extremes measured for $T_f = -12$ °C. The dotted lines are the extremes for the hot samples, the continuous, for the cold.

Table I. Probabilities for freezing at a particular temperature.

Freezing temp. T_f	Probability	
	Hot	Cold
0°−−2°	0.41	0.03
−2°−−4°	0.15	0.22
−4°−−6°	0.13	0.56
−6°−−8°	0.10	0.19
−8°−−10°	0.21	0.00

Table I shows the probability for the hot and cold samples to reach a particular supercooling temperature before freezing. The most probable temperature for the hot samples to freeze was between $0° > T_f > -2°$, that for the cold sample, $-4° > T_f > -6°$ (supercooling below −9° never occurred). Why should the probabilities be different? Four possibilities come to mind. The first possibility is that the history of the water is important in the cooling process, a claim made by some authors.[6,12] Their explanation is that heating degasses the water which will in turn affect the cooling behavior.[22] However, according to the above authors heated water with consequently fewer nuclei would tend to reach a lower temperature before spontaneously freezing, whereas we found the opposite tendency. We thus tried to determine a dependence of the consistency of the water on its cooling behavior.

One of the main problems is that once degassed water is left in the open air, it absorbs gas, the time scale (in this case, as "half life") being $\sqrt{l2/D}$ (l, typical length, D, coefficient of diffusion between air and water—typically 10^{-5} cm^2/s: some 5 min for a length of 1 cm). In other words degassed water does not remain so. We took already commercially degassed distilled water (flow methods) and degassed it in two ways, first by boiling, second, by alternately freezing and then melting the water several times and then heating (where necessary) and cooling it immediately afterwards. All samples cooled in effectively the same manner. In fact even water which was supersaturated with CO_2 gas by letting it bubble through the sample for half an hour preceding a run before cooling showed no significantly decreased tendency to supercool. We also took moderately dirty river water (from the Swan river estuary in Perth) and generally found no significant differences between cooling curves.

A second possibility is that the experiments will always have slightly different initial conditions due to the way in which the beakers are treated after each run. For example, simply refilling beakers after each run may be seen as a gradual rinsing process (done by the water of each new run). If they are wittingly rinsed each time (with or without detergents) they also become progressively cleaner. Such rinsing may affect both the chemical (surfactants) as well as the physical (particles sticking to the edge) initial conditions. Although we did not carry out a systematic investigation, even the manner in which the beakers were washed and rinsed seemed to make no significant difference to the results. For example, washing the beaker with detergent prior to an hour's rinsing appeared to have no effect. However, due to the total number of samples, the above statements must be treated with care. I was always surprised to see how a number of runs with almost identical freezing times were followed by runs with significantly shorter or longer freezing times.

A third explanation for the maximum probability for the hot sample lying at a larger ambient temperature is the increase in the freezing temperature on increasing shear:[29] Temperature gradients, and thus the resulting shear in the anomalous temperature regime, are generally larger in the hot samples. At least the direction for this prediction is correct. The final possibility is that the 103 experiments were not a representative sample. This might well be the case. We carried out only 12 experiments for $-5° > T_a > -8°$ and 29 for $-9° > T_a > -12°$. The remainder of the experiments were carried out for colder ambient temperatures for I only stumbled onto this effect toward the end of the stay in Australia, first looking at the cooling and freezing regimes in an attempt to repeat reports of overtaking as discussed earlier. The anomaly, that the hot sample has its second maximum for the in the 8°–10° interval, is even more unusual and we can offer no explanation for this. However, even if the maxima lay elsewhere, this would make no difference to the mechanism for the Mpemba effect.

Due primarily to the sensitivity of the form of the convective phase to initial and boundary conditions mentioned earlier, the above probability does not allow us to predict probabilities for the time taken to freezing and hence, the probability for the Mpemba effect occurring. In Fig. 1 the hot early sample began freezing after 200 s and the cold late sample began freezing some 50 s later. If these two runs had been carried out simultaneously the Mpemba effect would have occurred. For the 103 experiments carried out, the probability for the Mpemba effect occurring was 0.53 for ambient temperatures $-5° > T_a > -8°$ (19 times out of 36 runs) and 0.24 for $-8° > T_a > -11°$ (7 out of 29 runs). For our experiments the Mpemba effect could not have occurred for temperatures either above or below this range (0 out of 38 runs).

APPEARANCE

Until now we have discussed only the cooling curves. What do the samples look like? As mentioned before, we must clearly distinguish two kinds of freezing,[20] spontaneous freezing (times of the order of a second)[39] and the subsequent motion of the freezing front from the wall toward the center as Stefan type cooling takes place (order of an hour). When the supercooled water freezes, a fraction $C_w \Delta T / L_i$ (where C_w is the specific heat of water, ΔT, the supercool temperature and L_i, the latent heat of fusion for water)—1/16 for a supercool temperature of 5°—of the water turns to ice. The structure of the spontaneously formed ice is dendritic, either as a thin layer along the walls for early samples where only the wall near water is supercooled, or stretching from the walls to the center for late samples where the entire volume is supercooled. For moderate supercooling this radial pattern is restricted to the region adjacent to the air/water interface. For more extreme supercooling, dendrites are so densely packed and extend throughout the entire volume that the entire ice/water matrix superficially looks frozen solid, then taking on an opaque appearance—the so-called mushy zone.[40] One recognizes the difference between hot and cold samples most clearly when the Stefan type freezing front begins moving: Cold samples eject air in the form of small bubbles as the freezing front moves, so that the whole takes on a gray opaque appearance.[41] On the other hand hot samples, having ejected their air on heating, form whitish (initially almost transparent) ice. Observers of the Mpemba effect may often be deluded into believing that a just spontaneously frozen hot late water sample (supercooled water throughout the sample and thus a completely frozen appearance but where the actual freezing front is still at the walls) is further advanced than a cold early frozen sample (supercooling restricted to the wall neighborhood and thus a predominantly watery volume with the freezing front located near the wall). It is often not easy to distinguish between this effect and the true Mpemba effect without watching the walls of the hot vessel very closely. This effect occurs far more often than the true Mpemba effect. The fact that Mpemba and some of the others mentioned at the outset invariably found this effect may partly be due to their being insensitive to the difference between the two types of freezing described above, the probability for the true Mpemba effect to occur in normal refrigerators $(-4° > T_a > -8°)$ being only a little more than one half. As a final point we should emphasize that the above results were carried out with 50 ml of water. As mentioned, smaller amounts of water allow a generally lower supercooling temperature whereas larger amounts (lakes) will tend hardly to supercool any longer. We know of no systematic work done on this valuable aspect.

ACKNOWLEDGMENT

The experiments were carried out during my 1992 sabbatical at the Centre for Water research at the University of Western Australia. I wish to thank the director, Professor Jorg Imberger, for his support.

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COMPARE PHYS REV B

On leaving Princeton in 1935, I had the good fortune to receive a position in the physics department of the University of Rochester, then under the enlightened leadership of Lee DuBridge who did so much for the renaissance of the California Institute of Technology in the period after World War II. There was complete freedom for research and teaching and I decided to take the opportunity to attempt to write a consolidated account of the various aspects of solid state physics in order to give the field the kind of unity it deserved and which was now possible with the unifying outlook that the development of quantum mechanics offered. The result, *The Modern Theory of Solids*, published by McGraw-Hill, emerged five years later. It has since been reissued by Dover and presumably possesses at least archaeological value. I think it is safe to say that I became familiar with every paper related to the field during the period of writing. The literature obviously was far smaller then.

Frederick Seitz, "The Princeton Years and Beyond: 1930–1940," paper delivered at the March, 1992 meeting of the American Physical Society.