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Mpemba Effect Revisited: Background Oriented Schlieren Measurements and Simplified Models

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***Abstract* -** Evaporative cooling of water in open tanks is investigated. The paradox of Mpemba effect implies that water with higher initial temperature can be cooled down to 0°C more quickly. Two major factors responsible for this counterintuitive phenomenon are evaporation and convection. It is shown by extending the known 0D engineering model that evaporation alone can explain the Mpemba effect. However, even under the most favorable conditions, with insulated side walls and air temperature -20°C, the effect is very weak: water, which is initially hotter, is never colder for more than 0.5 K. Therefore, convection contribution is essential for observations of Mpemba effect. Experimental measurements of instantaneous temperature fields, performed by Background Oriented Schlieren, confirm higher cooling rate in initially hot water at the same average temperature, i.e. the memory effect. They also demonstrate that, excluding thin boundary layers at the walls, temperature fields are essentially 1D with vertical variations dominating over horizontal ones. This is explained by cold liquid sinking along the walls, thus transforming the side walls heat flux into a bottom one. Two different regimes of cooling are discovered, with stable and unstable stratification. The choice between these two regimes is determined by the ratio of the surface and side walls heat fluxes. The transition due to evaporation intensity decrease during cooling can contribute to the Mpemba effect. 1D engineering model is developed, which takes into account temperature distribution along the vertical coordinate. The forthcoming comparison of 1D model results with experimental data should clarify the importance of different factors in the Mpemba effect. It should be noted that common 0D engineering models do not take into account spatial variations of temperature and, if convection is important, have to be used with precautions in modeling such problems as unsteady cooling of the molten pool during nuclear reactor failure.

***Keywords*:** Mpemba effect**,** Cooling, Evaporation, Convection, Background Oriented Schlieren.

1. Introduction

Almost 50 years ago a Tanzanian schoolboy Erasto Mpemba obtained an unusual result, trying to make ice-cream. He took two identical beakers, filled them with the same amount of liquid, but with different temperatures, and put into refrigerator. He observed that the liquid with higher initial temperature froze earlier. After the first publication (Mpemba and Osborne, 1969) Mpemba experiment was repeated by several groups and most of them managed to reproduce the effect, though the details (temperature difference within the liquid, evaporated mass, location of ice formation) and conclusions varied greatly among different groups. Most of the researchers used the following problem formulation: two identical uncovered beakers, thermally insulated at the bottom, were filled with distilled water of the same mass, but with different temperatures, and allowed to cool down in refrigerator due to heat removal through the free surface and the side walls. Some of the experimentalists recognized ice formation anywhere within a beaker as a stop-watch criterion, others preferred the moment when water temperature, measured by a thermocouple, reached 0°C. The latter approach excludes possible supercooling and freezing kinetics out of consideration, so we will follow it to make the problem more clear. In all the experiments water temperature was measured by one or several thermocouples, installed within a beaker. Since water level decreases during the process, the exact location of thermocouples with respect to the surface is meaningless and is usually described as “near the surface” or “in the middle”.

The Mpemba effect is a paradox if the state of cooling water in a beaker is assumed to be characterized by the average temperature only. Then it is obvious that water with higher initial temperature will cool down to the initial temperature of colder water and repeat its state trajectory completely. So, in this model hot water cannot beat the colder one in their race towards 0°C. The situation can be different if any additional “hidden” variable exists, characterizing the state of cooling water. Several candidates were proposed. First, water mass is decreasing due to evaporation, which is more intense in the beginning, when temperature difference between the water surface and the ambient air is large. Therefore, water, which is initially hotter, will reach the initial temperature of cold water, having lower mass and lower total heat capacity. This leads to higher cooling rate, which can compensate the time handicap at the start. A 0D numerical model was proposed by Kell (1969), describing evaporation contribution to the Mpemba effect. The effect was obtained, but the mass of evaporated water appeared much larger than observed in the experiments: according to Kell’s model 16% of water will evaporate from a beaker with thermally insulated walls during cooling from 100°C to 0°C, whereas the mass loss in experiments by Mpemba and Osborne (1969), Firth (1971) and Freeman (1979) was 6%, 5% and 10% respectively. This discrepancy, as well as ignoring the heat removal by radiation and through the side walls and unclear origin of the empirical relation for the evaporation rate, led to some distrust for Kell’s explanation. Another “hidden” variable is temperature difference within water volume, which can change the cooling rate because the heat fluxes are related to water temperature at the surface and near the walls, rather than the average one, and because the convective flow enhances the heat transfer between the walls and the bulk if stratification is unstable. Strictly, it is always unstable, because the thin surface layer (cool skin), which is cooled by evaporation, is colder than water layer beneath it. It has thickness about 3-5 mm only, hence temperature measurements “near the surface” are to be attributed to lower layers. However, even for these upper layers of the bulk water contradictory results were reported by different authors. Most of the researchers reported large temperature difference between water near the top and near the bottom of the container with top water being hotter (hot top). Maximal temperature difference was 27 K, 15 K and 14 K in experiments by Deeson (1971), Freeman (1979) and Mpemba and Osborne (1969), respectively. On the other hand, Firth (1971) did not find any hot top, highest temperature values were obtained by thermocouple located in the middle of the beaker and the difference was about 6 K.

Even with modern computational resources the Mpemba problem is too costly to allow direct numerical simulation. One has to solve coupled unsteady 3D hydrodynamics equations in water and air (the air-side convection determines evaporation rate) with moving boundary, as well as heat conduction equation inside the walls. A recent attempt by Vynnycky and Maeno (2012) involved such simplifications as axisymmetric problem formulation for a cylindrical beaker, insulated side walls and, which is more sad, neglect of convection in liquid. Thus, though two main factors responsible for the Mpemba effect were outlined in 1970s, the problem still lacks quantitative model, which would take into account both evaporation and convection. Experimental data are sometimes controversial too, and the temperature field inside cooling water, which determines the convection intensity, has never been fully observed. The goal of the present research was to measure instantaneous temperature fields in cooling water by Background Oriented Schlieren (BOS) and to elaborate 0D or 1D simplified models of the phenomenon, taking into account more factors than the model developed by Kell (1969). It should be noted that 0D engineering models are utilized to describe the behavior of large variety of systems involving heat exchange, from cooling of the circuit boards to cooling of nuclear reactors, and if they yield inappropriate result under some conditions, this is important for the whole heat transfer community. Thus, the Mpemba effect is not merely an interesting hocus-pocus, but a test case for commonly accepted models.

It should also be noted that more explanations were proposed for Mpemba effect, including the influence of the dissolved gases (see Freeman, 1979) and modification of thermal contact between the bottom of the beaker and refrigerator. The dissolved gases are not considered in the present paper, because they can affect only freezing kinetics, but cooling down to 0°C, which is considered here, depends on temperature field and thermodynamic properties of water, unaffected by small addition of gas. The formation of ice layer under the beaker bottom and the resultant change of the bottom heat flux can probably explain the original Mpemba results. But further experiments were all performed with insulated bottom and still the effect was reproduced.

2. Experiment

Experimental setup is diagrammed in Fig. 1. BOS, introduced by Meier (2002), is quantitative visualization technique, based on refraction. Two images of the same background pattern are taken by the camera, first through medium with constant refractive index (the reference image), second through the flow being investigated (distorted image). If the flow contains refractive index variations, the elements of the second image are shifted with respect to the first one due to refraction. The displacement field is evaluated by digital comparison of two images using cross-correlation interrogation similar to Particle Image Velocimetry. The displacement is proportional to spatial derivatives of the refractive index, so it can be used to reconstruct 2D refractive index field (averaged over line of sight) if the refractive index value at some point is known. Then, for liquids it is possible to derive temperature and density fields by solving algebraic system composed of equation of state under constant pressure assumption and Lorentz-Lorenz formula. More information about BOS and its application to temperature measurements in liquids can be found in Vinnichenko et al. (2013).

BOS sensitivity requires the distance between the background pattern and water tanks to be large enough, about 70-80 cm, and the optical access should be provided. The experiments were performed in an unheated building during winter in Moscow, so the air temperature was determined by the weather. Background pattern composed of square black dots with size about 2-3 pixels in the final image, randomly distributed over a white paper sheet, was used. The images were taken automatically once every minute for 1.5-2.5 hours during cooling of the water. The camera was installed at the level of water tanks centres, hence the boundary layers close to the walls and to the free surface were lost due to perspective. Since it is impossible in this case to obtain an image through water tank with constant refractive index (i.e. with constant temperature), the last image taken before ice formation is treated as a reference one because thermal gradients in the end are much lower than in the beginning of cooling process. This assumption, as well as the limited field of view, probably leads to underestimation of temperature difference within each tank. Every image was compared to the next one in time sequence in order to decrease the displacement gradient and corresponding error of cross-correlation algorithm. Reference temperature values, required for refractive index field reconstruction, were measured by two thermocouples, installed in lower corners of the tanks. The background pattern and thermometers were illuminated by energy-saving lamps.

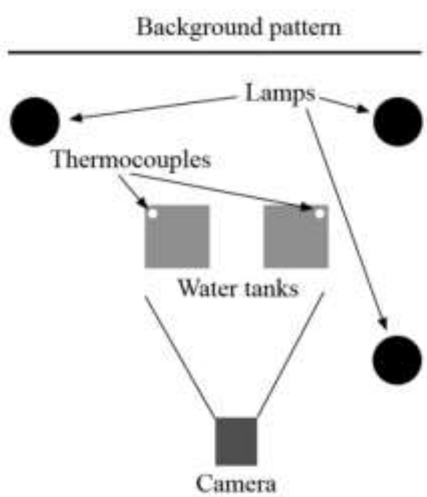

Fig. 1. Experimental setup (not in scale).

Rectangular water tanks 56×56×30 mm with flat walls, made of 3-mm thick glass, were employed. The initial mass of water was controlled by digital scale with total accuracy about 1 g. Initial temperature was not strictly controlled, because weighing and placing water tanks at their positions take up to 3-4 minutes, during which water temperature is significantly decreased. Special care was taken to find systematic error for each thermometer over the whole temperature range. This is probably one of the major sources of error, leading to controversial results found in literature.

Typical temperature field, obtained by BOS, is shown in Fig. 2. It is almost 1D with vertical temperature variation being much larger than horizontal one. Unstable stratification is observed, i.e. lower layers are hotter. However, it must be kept in mind that the presented field corresponds to the middle part of the tank. Regions adjacent to the surface and to the bottom with thickness about 1 cm had to be removed from the original images. More experiments with camera aligned for the lower or upper part of the tank are required to resolve these layers.

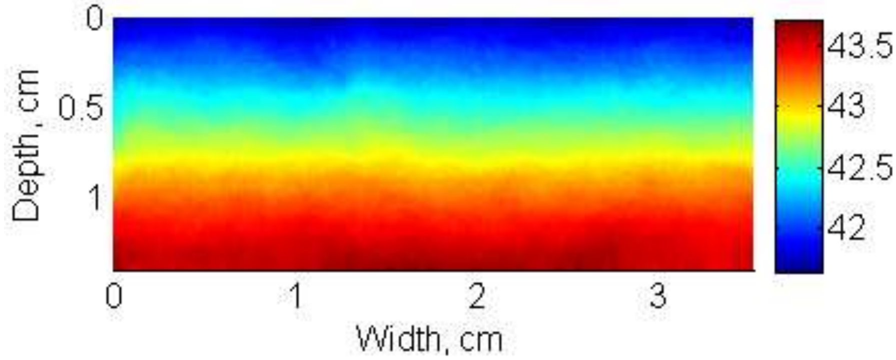

Fig. 2. Temperature field (°C) measured by BOS.

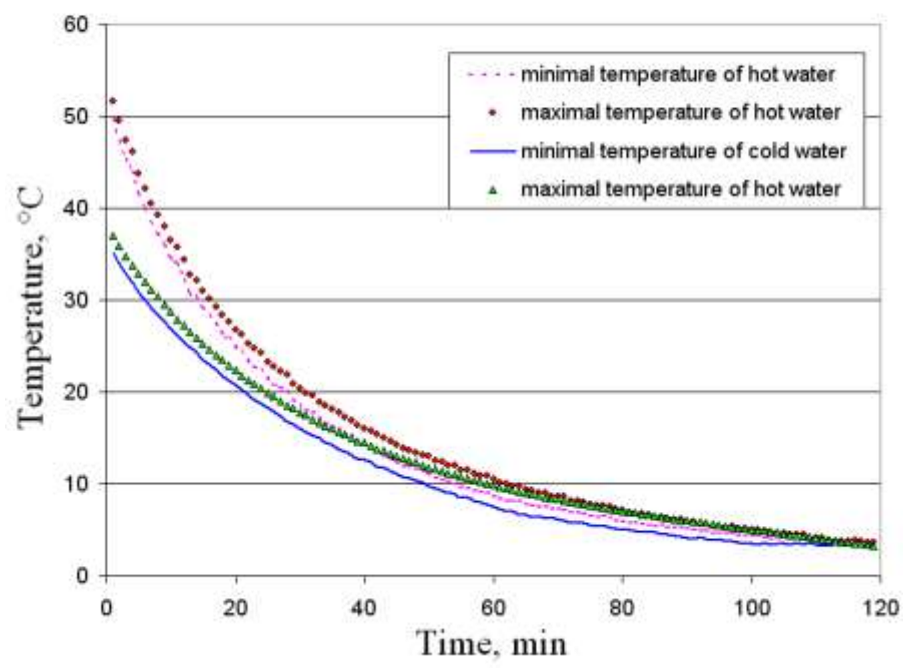

Fig. 3. Minimal and maximal temperatures in both tanks as functions of time.

Temporal evolution of minimal and maximal temperatures in each tank, as determined from BOS measurements, is presented in Fig. 3. Water with higher initial temperature cools down more quickly at the same average temperature, indicating the presence of memory effect in the flow. The temperature difference inside each tank is about 2 K for most of the time, decreasing to zero in the vicinity of 4°C. Similar result was obtained by Firth (1971) and, as discussed in Sect. 3.1, it has theoretical explanation. In a separate set of experiments with evaporation limited by covering part of the free surface with a lid the hot top stratification was observed. Also, in some experiments transition from cold top to hot top was discovered at temperature about 6-7°C, though temperature difference is quite small close to 4°C and this effect is weak. No Mpemba effect was found so far. However, the number of performed experiments was limited because of unusually warm weather. The research will be continued using a refrigerator with glass windows embedded into two opposite walls to provide optical access.

3. Modeling

3.1. Simplified Hydrodynamic Simulation

The observed 1D structure of the temperature field can be explained by a model 2D hydrodynamic simulation of water in a square cavity cooled by isothermal (0°C) top and side walls. This problem formulation is oversimplified for quantitative assessment of the Mpemba effect: it does not take into account temporal evolution of the walls and surface temperature or mass loss due to evaporation, and simulation is 2D. Nevertheless, since the complete empirical equation of state is used for water, the convection effect on the temperature field is captured.

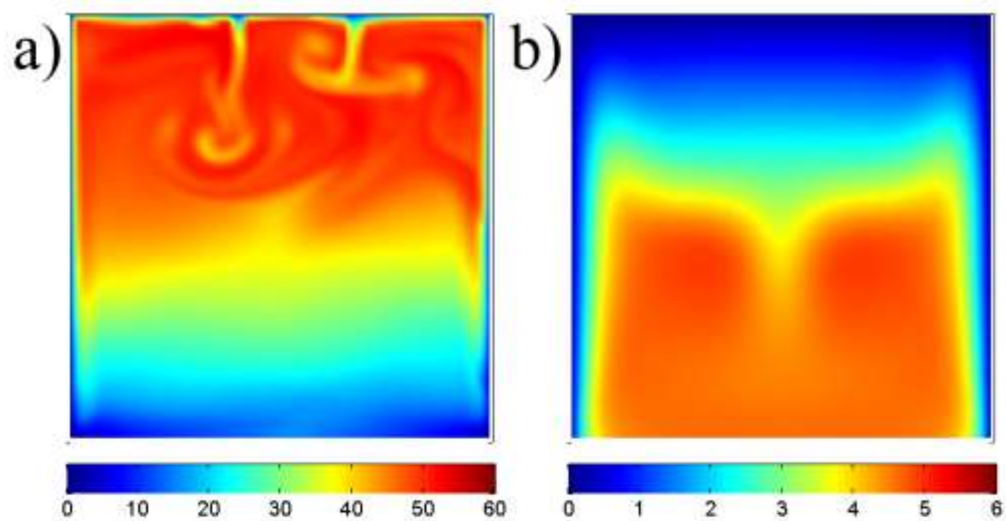

Fig. 4. Temperature fields (°C) obtained by simplified hydrodynamic simulation: a) in the beginning of cooling process, b) in the end.

It can be seen from the simulated temperature field in the beginning of cooling (Fig. 4a) that thermal boundary layers at the surface and the side walls are very thin. As long as water temperature exceeds 4°C, cooled water sinks along the side walls, forming a cold layer at the bottom. Randomly located plumes of cold water, plunging from the surface due to unstable stratification, in 3D case are averaged over the line of sight and therefore cannot be seen in BOS images. Thus, 1D structure is formed, taking into account that BOS experiment yields only the central part of the field and thin boundary layers are not resolved. However, Firth (1971) could probably install the surface thermocouple within the boundary layer, so cold top and bottom were observed with maximal temperature value recorded by the middle thermocouple. Though a global hot top stratification can be seen in Fig. 4a, the direction of temperature gradient in the bulk water is determined by the ratio of heat removal at the surface (both latent and contact) and at the side walls. In wide tanks with hot water or in tanks with insulated walls evaporative cooling dominates over the side walls heat flux and cold top stratification must be observed. For narrow tanks heat removal through the side walls can prevail, forming a cold bottom layer as in Fig. 4a. The ratio of the heat fluxes is also changed during the cooling process, because evaporation rate depends strongly on the temperature difference between water surface and the ambient air. Thus, the observed transition from cold top to hot top at temperature about 6-7°C can be qualitatively explained. Since the effective heat transfer coefficient can be quite different for these two configurations, the transition can contribute to the Mpemba effect. When temperature drops below 4°C (Fig. 4b), flow direction along the walls reverses. Most dense water with temperature about 4°C stays at the bottom, whereas both the surface and the side walls heat fluxes begin to contribute to cooling of the upper layers. Cold top configuration is expected to be observed below 4°C with the thickness of the surface boundary layer rapidly increasing. Indeed, it was observed by Firth (1971). Hot top remained until 0°C in experiments by Mpemba and Osborne (1969), which can be an artefact caused by improper thermocouples calibration in their work. Also, it can be concluded that for temperature measurements using thermocouples the result, including the presence or absence of Mpemba effect, depends strongly on exact location of the probes.

3.2. Extended 0D model

Since the problem is too complex for direct numerical simulation, simplified engineering approaches are to be employed. In this section the model by Kell (1969) is extended to take into account heat losses by radiation and through the side walls. The whole liquid volume is assumed to have the same average temperature, so the problem is 0D and convection in water is not taken into account. Temporal evolution of water mass and temperature is governed by the balance equations

$$\frac{dm}{dt} = -J\, S_{surf} \tag{1}$$

$$cm\frac{dT}{dt} = -q_{surf}S_{surf} - q_{walls}S_{walls} \tag{2}$$

with evaporation rate J calculated from the empirical Sherwood-Rayleigh relation and q_{walls} based on heat transfer coefficients for convection near the walls in air and water, thermal conductivity inside the walls and radiation at the walls outer surface. q_{surf} includes convection in air, radiation and latent heat of evaporation. The well-known empirical Nusselt-Rayleigh relations for convection near the vertical and horizontal heated plates (Çengel, 2007) were used to calculate heat transfer coefficients. Sherwood number was found from Chilton-Colburn analogy between heat and mass transfer. All temperature-dependent material properties (density, specific heat, thermal conductivity, viscosity, thermal expansion coefficient) for water and air were modeled by polynomial approximations of experimental data found in literature. Additionally, the difference between the temperature of the thin surface layer (cool skin) and the bulk temperature can be taken into account, introducing heat balance for the surface layer with negligible heat capacity

$$h_{bs}\left(T - T_{surf}\right) = q_{surf} \tag{3}$$

Heat transfer coefficient for heat exchange between the bulk liquid and the surface layer h_{bs} is determined from empirical Nusselt-Rayleigh relation proposed by Katsaros et al. (1977).

Mpemba effect implies that dependence of time required for water to cool down to 0°C on initial water temperature has a local maximum. The dependence shown in Fig. 5 was calculated for insulated side walls of the tank (Kell's problem formulation) and ambient air temperature -20°C. Local maximum is observed about 63°C, so evaporation alone can really explain the Mpemba effect. However, the maximum is very shallow: cooling time for 100 g of water in a tank with surface area 6×6 cm is 76.4 min for initial temperature 63°C and 73.8 min for 100°C. The temperature difference between the water starting from 100°C and the water starting from 63°C is never less than -0.52 K, which is about the overall error of temperature measurements in experiment. The mass loss for cooling from 100°C is about

13.2%, which is little less than reported by Kell (1969). On the other hand, cooling from 80°C with conductive walls, which is closer to typical experimental conditions, results in 8% of mass being evaporated. Taking into account heat removal through the walls and specifying higher ambient air temperature both lead to even more shallow maximum. Thus, though evaporation could be the only source of the Mpemba effect, the latter would be very weak and hardly observable. The convection contribution is essential if significant effect exists.

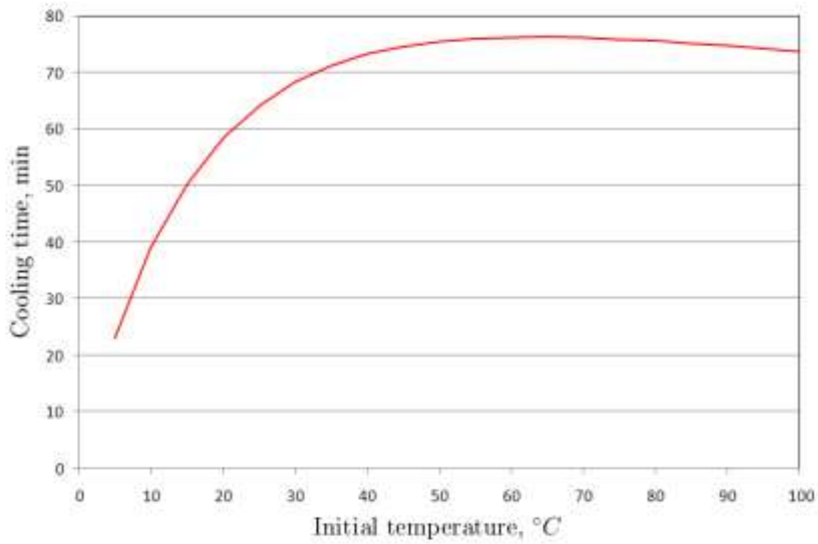

Fig. 5. Cooling time calculated by 0D model. Side walls are thermally insulated.

3.3. 1D model

Nearly 1D structure of experimentally observed temperature field, supported by model hydrodynamic simulations, allows elaborating more detailed model, which takes into account convection in water. Assume the temperature is above 4°C, hence cold water sinks along the side walls. Then the side walls heat removal can be associated with bottom. The problem becomes 1D, governed by the heat conductivity equation

$$c\rho \frac{\partial T}{\partial t} = \lambda_{eff}(z) \frac{\partial^2 T}{\partial z^2} \tag{4}$$

with boundary conditions

$$\left(\lambda_{eff} \frac{\partial T}{\partial z} \right) \bigg|_{z=H(t)} = q_{surf}, \left(\lambda_{eff} \frac{\partial T}{\partial z} \right) \bigg|_{z=0} = q_{walls} \frac{S_{walls}}{S_{surf}} \tag{5}$$

The mass loss is simulated by Eq. (1) as for 0D model. The key element of the model is the effective thermal conductivity coefficient λ_{eff}, which takes into account convection. An expression relating it to instantaneous temperature distribution was derived by Cheung (1977). Results show that it severely overestimates temperature gradient in the bottom layer, where stable stratification is realized. However, it can be used in case of insulated walls.

4. Conclusion

Experimental measurements of temperature fields during evaporative cooling of water in the context of Mpemba effect have been performed. Unlike all the previous studies, where temperature was measured by several thermocouples, 2D temperature fields averaged over the third axis were obtained by BOS. They appeared to be nearly 1D, which is explained by the cold water flowing down along the walls and forming a cold layer at the bottom of the tank. The side walls heat flux is thus transformed into a bottom one, which allows formulation of 1D model, taking into account both evaporation and convection. Above 4°C water in thin boundary layers near the surface, at the walls and near the bottom is always colder than the bulk water. Temperature stratification in the bulk is determined by the ratio of heat removal at the surface and at the side walls. Hot water in wide vessels is expected to exhibit cold top. This can be changed to hot top stratification during cooling due to decrease of evaporation rate. Another transition occurs at 4°C, when flow direction along the walls is reversed. Then, both heat fluxes through the walls and from the surface contribute to cooling of the upper layers and cold top stratification settles. So far, the Mpemba effect was not found. However, it was shown by extending 0D model developed by Kell (1969) that evaporation alone can lead to Mpemba effect, but then it is very weak and cannot be confirmed with thermocouple measurements. Thus, convection contribution to cooling, which is not described by 0D models, seems essential for observing a significant Mpemba effect. This makes the latter an interesting example of limited applicability of 0D models, which are widely used in engineering practice.

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