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Tested Demonstrations

Thermodynamics of Water Superheated in the Microwave Oven

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The beauty of classical thermodynamics is that heat transfers can be accounted for without a detailed description of the physical systems considered, but the concepts are rather abstract and concrete examples are welcome. A simple visual demonstration is proposed, which provokes thinking about the elementary chemical thermodynamics of heating and boiling. Water is made to boil in a microwave oven, heating is interrupted and boiling stops, but subsequent addition of a few rough particles can still cause a brief, spectacular burst of steam bubbles. Elementary notions of chemical thermodynamics are sufficient to conclude that water must have been heated a few degrees above its normal boiling point.

Experimental Procedure

The water can be regular drinking water but should not contain many undissolved particles. It can be heated in any domestic microwave oven; a research-grade microwave oven such as used by Kennedy (*1*) to determine the enthalpy of vaporization of liquids is unnecessary here. The recommended heating vessel is a glass teapot sold to be used in the microwave oven (no metal parts). Using such a teapot generally has several advantages: its walls have relatively few nucleation sites for bubble formation, yet enough to put a reasonable limit on superheating; it has a plastic lid to prevent boiling water from splashing out of it; and it has a plastic handle so that it can easily be removed from the microwave oven once the water is boiling.

Before the demonstration, it helps to wipe the glass walls with cleaning paper and vinegar to remove lime deposits. Using
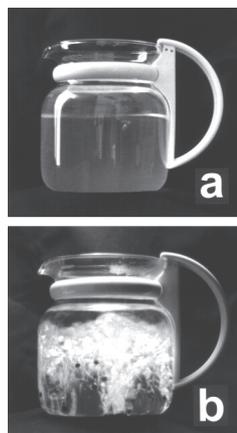

Figure 1. (a) Water-filled glass teapot with a plastic handle within 3 seconds after boiling for 5 minutes in a microwave oven (1 liter of water, nominal power: 900 W). Boiling has stopped. (b) Effect of subsequently adding 20 grains of dry peppercorn (the black dots). Boiling briefly starts again. The photos were taken in separate experimental runs, to optimize lighting conditions.

a microwave oven allows one to superheat water relatively homogeneously throughout the entire volume, as opposed to using a stove or a Bunsen burner, in which case superheating is highest in a thin water layer near the heating source. Heating should be continued for a few minutes after boiling starts, to raise the water temperature above 100 °C and to remove dissolved gas. When the teapot is removed from the microwave oven, boiling stops (Fig. 1a), but subsequent addition of a few rough particles within a few seconds causes a brief, spectacular burst of steam bubbles (Fig. 1b). The rough particles can be porous boiling stones, Carborundum anti-bumping granules, small pieces of glass, peppercorn, or even a tea bag.

The heating time required for a convincing demonstration partly depends on microwave oven power and water volume. To save time, one can fill the teapot with hot tap water. The proposed approach with a microwave oven and a teapot designed to be used in it is relatively safe, but the experiment should nevertheless be carried out with caution, because glass teapots can break, boiling water can cause severe skin burns, and the burst of steam bubbles can be violent if many rough particles are added at once.

Using Thermodynamics to Explain the Observations

Unprepared observers of the demonstration should be able to find an explanation for the sudden burst of steam bubbles on the basis of the following elementary notions of thermodynamics. Heat is required to raise water temperature to its boiling point and further heat is required to sustain boiling. In the experiment, one observes that when the rough particles are added, water starts to boil again, which means that heat is available despite the absence of an external heating source. This heat must come from the water itself, whose temperature necessarily decreases in the process. One must conclude that before the rough particles were added, the temperature must have been above that required for boiling.

In additional experiments, superheating was confirmed with a digital thermometer preheated in water boiling at 100.0 °C in a pan on a stove (atmospheric pressure was close to 1.00 atm). After boiling in a 900-W microwave oven for about 5 minutes, 1 liter of water in the teapot shown in Figure 1 reached a steady-state temperature of 103.0 °C. When heating was interrupted and rough particles were added, the temperature dropped to 100 °C simultaneously with the release of steam bubbles. It is remarked that during such measurements, precise temperature readings may vary depending on the response time of the thermometer and on

the extent of steam bubble formation at the surface of the temperature probe.

Without a thermometer, superheating can be estimated on the basis of the volume of steam suddenly released within seconds, a few times the volume of the teapot. For example, making 5 L of steam requires 6770 J, calculated from the latent heat of boiling of 2260 J g^{-1} and from 1 g of water yielding 1670 mL of steam (*2*). Withdrawing 6770 J from 1 L of water decreases its temperature by 1.6 °C, calculated from the heat capacity of 4.2 J per °C per gram of boiling water (*2*). From this, one calculates an initial temperature of 101.6 °C, of the same order as measured with the thermometer.

Background on Steam Bubble Formation

According to thermodynamics, boiling cannot occur below the temperature at which vapor pressure equals external pressure (i.e., the boiling point). Superheating occurs because this temperature is still insufficient for bubble formation. A growing steam bubble fights not only against the external pressure on the liquid but also against the tension on its curved surface. Owing to surface energy, the vapor pressure inside a bubble is lower than at the flat free surface of the liquid and is therefore lower than external pressure at the boiling point. Temperature must therefore be raised further before steam bubbles can grow. It can be shown that the vapor pressure inside the bubble must exceed external pressure by more than $2\gamma/r$, where γ is surface tension and r the bubble radius (*3–5*). In the extreme case of homogeneous steam bubble nucleation, in the absence of rough particles and nucleation sites on the walls of the heating vessel, water must be heated to about 300 °C at 1 atm (*3*).

Generally, the temperature required to make water boil at 1 atm is much closer to 100 °C. The walls of the vessel are not perfectly smooth, and gas can be trapped in pits or crevices of the scale of a few micrometers at the moment when the vessel is filled with water, yielding nucleation sites for bubble formation. Once boiling has started, such cavities always remain filled with gas or steam, and the size of the cavities puts a lower limit on the radius of the bubbles growing from them and thus an upper limit on the superheating required for bubble growth (*3, 4*). In the demonstration, when water has boiled for a sufficiently long time to remove dissolved gas, steam-filled cavities fill up with water soon after heating is interrupted and boiling stops right away; in contrast, when water has boiled for a shorter time and dissolved gas remains, boiling takes longer to stop, because gas-filled nucleation sites remain active.

In the chemical laboratory, superheating is a phenomenon to be prevented for safety reasons, since an uncontrolled release of vapor can cause a liquid to leave the heating vessel. To increase the number of nucleation sites for bubble growth, porous boiling stones, Carborundum anti-bumping granules, or small pieces of glass are sometimes added. Most of the vapor is not formed at the nucleation sites but while bubbles rise through the superheated liquid toward the flat free surface (*4*). Superheating can therefore also be prevented by flowing gas through the liquid using a capillary tube, in which case vapor is released into the gas bubbles.

Conclusions

The proposed demonstration visually illustrates the elementary thermodynamics of heating and boiling and also has other pedagogical applications. It involves the formation of bubbles at preferential nucleation sites on the walls of a vessel or at rough particles, an effect also observed in daily life: in a glass of carbonated beverage such as champagne, columns of bubbles also emanate from a limited number of nucleation sites. It shows why, for safety reasons, precautions are taken to prevent superheating in the laboratory, where smooth-walled glass vessels are generally used; in the kitchen, such precautions are unnecessary, since cooking pans and their contents are sufficiently (micro)rough that superheating is seldom a problem. An analogy can be made between the rough particles in the demonstration and catalysts, since the particles facilitate bubble formation without being changed in the process. Finally, the demonstration gives a tangible example of thermodynamic metastability, perhaps more convenient to carry out than demonstrating supercooled water and certainly less abstract than the metastability of diamond with respect to graphite.

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