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The myth of the boiling point

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ABSTRACT

Around 1800, many reputable scientists reported significant variations in the temperature of pure water boiling under normal atmospheric pressure. The reported variations included a difference of over 1°C between boiling in metallic and glass vessels (Gay-Lussac), and “superheating” up to 112°C on extracting dissolved air out of water (De Luc). I have confirmed most of these observations in my own experiments, many of which are described in this paper. Water boils at the “boiling point” only under very particular circumstances. Our common-sense intuition about the fixedness of the boiling point is only sustained by our limited experience.

Keywords: *boiling point, replications of historical experiments, superheating, water, De Luc, Gay-Lussac*

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Introduction

We all learn at school that pure water always boils at 100°C (212°F), under normal atmospheric pressure. Like surprisingly many things that “everybody knows”, this is a myth. We ought to stop perpetuating this myth in schools and universities and in everyday life: not only is it incorrect, but it also conveys misleading ideas about the nature of scientific knowledge. And unlike some other myths, it does not serve sufficiently useful functions.

There are actually all sorts of variations in the boiling temperature of water. For example, there are differences of several degrees depending on the material of the container in which the boiling takes place. Removing dissolved air from water can easily raise its boiling temperature by about 10 degrees centigrade.

The fickleness of the boiling point is something that was once widely known among scientists. It is quite easy to verify, as I have learned in the simple experiments that I discuss below. And it is still known by many of today’s experts. So actually the strange thing is: why don’t we all hear about it? Not only that, but why do most people believe the opposite of what is the case, and maintain it with such confidence? How has a clear falsehood become scientific common sense?

History

History of science provides the most convenient entry to the constellation of issues discussed in this paper. The old thermometer shown in Figure 1 is emblematic. This instrument, dating from the 1750s, is preserved at the Science Museum in London; the glass stems have broken off, so all we have is the frame, which shows four different scales on it. The third one is the familiar Fahrenheit scale. (The second one, due to Delisle, is “upside down”, with 0° at the boiling point and increasing numbers as it gets colder¹.) There are two boiling points marked on this thermometer. At the familiar 212°F it says “water boyles vehemently”. Down at about 204°F it says “begins to boyle”. What is going on here? You may think that the artisan who made this thermometer must have been pretty incompetent on scientific matters. But it turns out that this thermometer was the work of George Adams, official scientific instrument-maker to King George III. And the idea of two boiling points actually came straight from Isaac Newton, whose temperature scale published in 1701 was indeed the first of Adams’s four scales².



Fig. 1. George Adams's thermometric scale, showing two boiling points (inventory no. 1927–1745). Science Museum/Science & Society Picture Library.

Stimulated by such oddities from the 18th century, I looked more deeply into the history, to see what people really knew and thought about the boiling point in those early days. In fact there was so much uncertainty about it that in 1776 the Royal Society of London appointed a special committee charged with making definite

recommendations about the “fixed points” of thermometers. The Royal Society Committee recorded various types of variations in the boiling temperature of water³. Henry Cavendish, who chaired the committee, left us a rather enigmatic statement in one of his unpublished manuscripts: “The excess of the heat of water above the boiling point is influenced by a great variety of circumstances”⁴.



Fig. 2. Henry Cavendish (1731–1810).

Another key member of the committee was Jean-André De Luc, Genevan geologist, physicist, meteorologist, theologian and businessman. By this time he was living in England, installed in Windsor as “Reader” to Queen Charlotte. Around 1770 De Luc had made extensive investigations into boiling⁵. He reasoned that in an ordinary boiling situation the layer of water touching the heated surface, where the vapour bubbles form, must be much hotter than the rest of the water. He wanted to find out the temperature of that

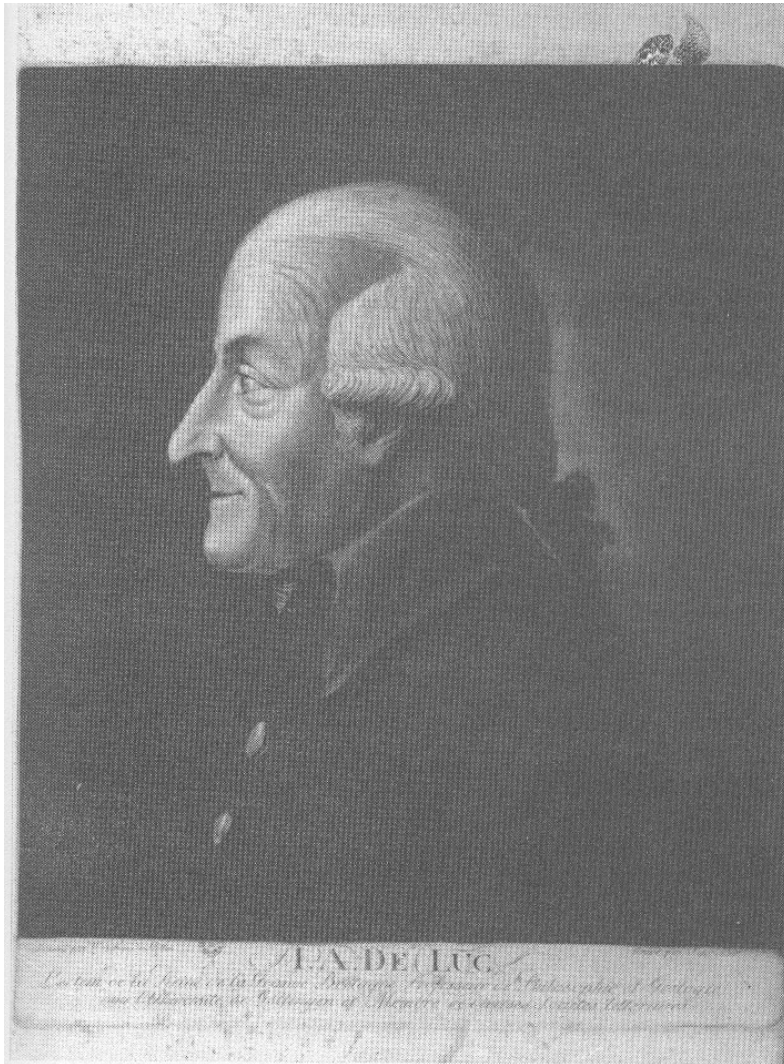


Fig. 3. Jean-André De Luc (1727–1817). Geneva, Bibliothèque publique et universitaire, Collections iconographiques.

“first layer”, which would be the temperature of “true ebullition”. So he put water into a narrow-necked flask and heated it in a bath of oil (rather than on an open flame), trying to bring the whole body of the water to the same temperature by slow heating with minimal loss of heat at the open surface. But when he did this, De Luc found that the water would not boil normally at all. The bubbles were infrequent and very large, sometimes explosive; the temperature was high and unsteady, sometimes reaching up to 103°C.

A further puzzle awaited De Luc. He noticed that the presence of dissolved air in water induced what seemed like premature boiling. He tried to take the air out by various methods, but concluded that for sufficient results he needed to put previously boiled water in a sealed container and shake it for a long time (remember how shaking a bottle of fizzy drink releases bubbles of gas). He reported: “This operation lasted four weeks, during which I hardly ever put down my flask, except to sleep, to do business in town, and to do things that required both hands. I ate, I read, I wrote, I saw my friends, I took my walks, all the while shaking my water.” Four mad weeks of shaking had its rewards. De Luc’s precious airless water reached 112.2°C before boiling off explosively.

In the course of the 19th century, further study revealed boiling to be an even more complex and unruly phenomenon than De Luc had glimpsed. For example, in the 1810s Joseph-Louis Gay-Lussac in Paris reported that water boiled at 101.2°C in a glass vessel, while it boiled at exactly 100°C in a metallic vessel^{6,7}. This result became fairly well known, but there was no definitive explanation of it available for a long while. In 1842 François Marcet in Geneva extended Gay-Lussac’s work and reported that water could reach over 105°C in a glass vessel treated with hot sulfuric acid⁸. Superheating became a clearly recognized object of study after Marcet’s work, stimulating a string of virtuoso experimental performances vying for record temperatures. François Marie Louis Donny, chemist at the University of Ghent, combined Marcet’s ideas with a revival of De Luc’s ideas about the role of air, and produced a stunning 137°C using airless water in his own special instrument⁹. Donny declared:

“The faculty to produce ordinary ebullition cannot in reality be considered as an inherent property of liquids, because they show it only when they contain a gaseous substance in solution, which is to say only when they are not in a state of purity.”



Fig. 4. Joseph-Louis Gay-Lussac (1778–1850).

In 1861 the work of Louis Dufour, professor of physics at the Academy of Lausanne, added yet another major factor for consideration¹⁰. He argued that contact with a solid surface was the crucial factor in the production of ebullition, and demonstrated the soundness of his idea by bringing drops of water floating in other liquids up to 178°C, without even purging the air out of the water. Even Dufour was outdone, when Georg Krebs in 1869 achieved an estimated 200°C with an improvement of Donny's technique¹¹.

Experiments

I was very surprised to read these reports. Having put a detailed account of them in the first chapter of my book on the history and philosophy of thermometry¹, I was still left with a problem of incredulity. Were the 18th- and 19th-century scientists right? Or was this an error like the infamous recent case of "cold fusion", or the older case of "N-rays"? I decided that there was only one way to find out: see for myself, in the lab.

In six sets of experiments, I confirmed and extended the seemingly anomalous results that I found in the scientific literature from the late 18th century and the early 19th century. (Video clips showing some highlights of these experiments are available online¹².) These experiments were initially carried out in the summer of 2004, and repeated with very similar results in the summer of 2007, in the Graham Laboratory at the Department of Chemistry at University College London. The basic setup was very simple: distilled water boiled in various containers, with various heat sources. The temperature was monitored by three types of thermometers: (a) ordinary mercury thermometers, graduated down to one degree (centigrade); (b) Beckmann thermometers, which are very large mercury thermometers with a very fine scale (graduated down to one-hundredth of a degree), whose zero can be set at any point in a wide temperature range; (c) a platinum electric-resistance thermometer, with a digital display, reading down to one-tenth of a degree.

Experiment 1. The indefiniteness of the boiling point

It is easily seen that ordinary boiling is a very complicated and quite indefinite phenomenon, as witnessed by the Adams thermometer discussed above. If water is heated in an ordinary glass beaker with a Bunsen burner, vapour bubbles can be seen forming at the base of the beaker from very early on in the process. When the temperature

of the main body of the water is much below 100°C , these bubbles get collapsed before making it through to the surface. This is called “subcooled” boiling by modern engineers. In older terminology, what we have is “hissing” (*sifflement* in French), in which the vapour bubbles are collapsed, with a characteristic noise, before reaching the surface of the water. It was also known as the “singing of the kettle” to serious tea-drinkers – the peculiar noise heard just before full boiling sets in.

What exactly is boiling, then? If one considers that boiling begins when the bubbles start breaking the surface, then it seems that water “begins to boyle” around 96°C (204.8°F), in fact just around where Adams had marked it (Figure 1)! There is quite active boiling from around 98°C . After “vehement boiling” starts, the temperature does seem to settle around 100°C (with expected slight variations linked to atmospheric pressure). But in fact the temperature creeps up slowly, often reaching around 101°C , consistent with Gay-Lussac’s report. The maximum attainable temperature after prolonged vehement boiling is quite a stable point in each instance, but it is not constant across different circumstances, even under fixed pressure.

Experiment 2. Different temperatures in different vessels

After observing the very ordinary boiling of water with some care, the next obvious thing to do was to test Gay-Lussac’s claim that the boiling temperature was affected by the material of the vessel in which the boiling took place. In the glass vessels I used (Pyrex), the temperature of prolonged vehement boiling was always over the standard boiling point, easily reaching 101°C . Even higher temperatures, up to 102.4°C , were observed in a beaker previously treated with high heat. In metallic vessels, the temperature of vehement boiling can be as low as 99°C . It was always lower than in glass vessels, whenever back-to-back trials were made. Among metallic vessels, great variation was observed depending on the quality of the inner surface: the temperature can be near that in glass beakers in a smooth-surfaced stainless pot, but usually lower in a rough-surfaced stainless pot; the temperature was much lower in a rough-surfaced aluminium pot (maximum of 99.3°C); Teflon-coated pots produced the lowest boiling temperatures. The results of my experiment are easily consistent with the glass-versus-metal difference of 1.232°C reported by Gay-Lussac.

Generally, it seems quite clear that the maximum attainable temperature of vehement boiling is different in different types of vessels. I have easily observed differences of over 4°C in the

temperature of boiling water in quite ordinary glass, metal and ceramic vessels. The temperature variations do not seem to be a straightforward function of vessel size and shape (except as the shape affects the surface area of the water, as discussed in Experiment 5 below). Rather, it seems that a crucial factor is the smoothness of the surface, as predicted by the standard modern theory of bubble-nucleation, discussed below. The differences observed in different vessels are not only in temperature, but also in the shape, size and number of bubbles. The variability of boiling behaviour is illustrated most strikingly in a comparison between ceramic mugs and Teflon-coated pots. On a Teflon-coated surface, bubbles form very eagerly and can be seen sticking to the surface from very low temperatures; the temperature of both the onset and the peak of boiling is significantly lower compared to boiling in a glass beaker. In the opposite direction, the trial with some ordinary ceramic mugs showed very high temperatures, sometimes exceeding 102°C , with bubbles forming and detaching themselves with great difficulty and a peculiar noise. With bubbles not forming at a high enough rate, the water cannot lose heat quickly enough, and ends up in a superheated state. In one case (observed on 2 August 2004) the water temperature reached 106°C without boiling, at which point I terminated the heating for fear of explosion. When boiling takes place in a ceramic container, the bubbles are clearly larger and less frequent than in other types of vessels, with some completely quiet periods.

Experiment 3. Lower temperature in a hydrophobic vessel

Gay-Lussac's explanation for the effect of surface quality was that the boiling temperature was higher when water adhered to the surface of the vessel more strongly. When Marcet developed Gay-Lussac's work further, he noted that a glass beaker covered in a layer of sulfur, which was water-repellent, showed a boiling temperature of 99.7°C . I tried a modern version of the experiment suggested by Andrea Sella, in which the inside of an ordinary glass beaker was made hydrophobic by treatment with Me_3SiCl (trimethylsilyl chloride). The boiling temperature in this "silanized" beaker was much lower than in an untreated beaker; in the silanized beaker, good boiling was possible from around 99°C , and the maximum temperature attainable was just around 100°C . The qualitative behaviour was very similar to boiling in the Teflon-covered pot, with numerous bubbles forming easily from a very low temperature and crowding around at the bottom surface. To confirm

that nothing had happened to the water chemically, I poured out the same water to an ordinary beaker and boiled it again; normal boiling behaviour was observed, with a higher temperature and only a few spots of active bubble-formation at the bottom surface.

Experiment 4. The action of boiling chips

Gay-Lussac also reported that throwing in metal filings or even powdered glass into water boiling in a glass vessel lowered the temperature, bringing it closer to 100°C. In fact this idea was later developed into the use of “boiling chips” to avoid superheating and facilitate smooth boiling, a common practice in chemistry labs to this day. Initially I experimented with relatively old-style boiling chips, namely “anti-bumping granules” made of marble. These granules clearly lower the temperature of vehement boiling in glass and ceramic vessels and bring it close to 100°C, also making the bubbles smaller and more frequent. In metallic vessels the granules had much less effect; in one case (2 August 2004), the addition of the granules to a Teflon-coated pot was even seen to raise the temperature by about 0.3°C.

With the use of PTFE (Teflon) “boiling stones”, the lowering of the boiling point is more significant. Inserting these boiling stones into water boiling in a glass beaker at about 101°C produces extremely vigorous bubbling. The surface of the water breaks violently, and the boiling stones are continually covered in a film of vapour. This vigorous boiling brings the temperature down below 100°C. In trials in ceramic mugs, the boiling temperature can be brought down by over 3°C. If the boiling stones are placed in the water before heating (in glass beakers), very active bubbling starts from around 91°C, and vehement boiling from around 98°C. The maximum attainable temperature is only around 99°C.

Experiment 5. Superheated boiling by slow heating

I carried out a long series of experiments in an attempt to replicate De Luc’s work published in 1772, to examine what happens when water is boiled using a gentle source of heat while minimizing heat loss at the surface. De Luc had used a round flask with a long, thin neck for this purpose, and I was able to approximate that quite easily by using chemists’ volumetric flasks. For the source of heat, it was convenient to use a hotplate, which is very hot but still much gentler than a naked flame. The boiling behaviour in this setup is very different from boiling driven by an open flame. As the

temperature approaches 100°C, the water starts to boil in a normal way. As boiling continues, however, the temperature continues to rise, easily exceeding 102°C, while the bubbles increase in size and decrease in number and frequency. During this phase the bubbles tend to come in bursts, making what 19th-century observers termed “bumping” (which is prevented by the use of boiling chips). Later in the process we can observe the “puffing” behaviour: long quiet periods punctuated by isolated large bubbles; sometimes the puffs are explosive, throwing some water out of the flask. The temperature can easily exceed 104°C during puffing. After trying De Luc’s method of gentle heating with a bath of hot oil, I switched to a bath of graphite heated on a hotplate for safety and convenience.

The boiling behaviour in a graphite or oil bath is quite similar to that seen in the hotplate setting. Sometimes there is one spot (or two) on the inner surface of the flask, or on the thermometer bulb, from which a continuous stream of bubbles arise (I will call this “streaming”). The boiling temperature can be quite steady if there is continual streaming, and tends to get only up to 102°–103°C. If there is no streaming and the boiling is unsteady, the temperature is quite variable. During bumping, the temperature dips visibly with the production of a burst of bubbles, and climbs slowly back up during periods of no activity. During puffing, the temperature usually creeps up in the long run (despite noticeable dips when large bubbles are produced), going up to 104–105°C. When water is boiled in this way, even the use of anti-bumping granules fails to bring down the temperature near 100°C. The granules do facilitate smooth boiling rather than bumping or puffing; however, even while smooth boiling takes place, the temperature creeps up appreciably.

I must emphasise that the superheating observed here is not a state of unstable equilibrium that is reduced to the “normal” stable equilibrium on some stimulus. Boiling by streaming can be sustained, apparently indefinitely, at 102–103°C. During bumping and puffing, the production of a burst of bubbles or a large puff does bring down the temperature, but never close to 100°C. There are various stable temperatures depending on the particular circumstances, and from my experiments there is no evidence that 100°C is generally speaking any more stable than any other point.

Experiment 6. Superheating facilitated by de-gassing

Finally, I tried to replicate De Luc’s result on taking dissolved air out of the water. But unlike De Luc I was not willing to commit to

four weeks of shaking, so I found an alternative method. My procedure begins with the recognition that heating water to 100°C already removes much of the dissolved air, since the solubility of air in water decreases sharply with temperature. And then the water is boiled for a long time in a loosely covered pot, to sweep out as much of the remaining air as possible through the bubbling process. Then the boiled water is poured carefully into a long-necked flask, and placed on a hotplate. Boiling in this partially degassed water is very bumpy, and the temperature goes well beyond 100°C, almost certainly resulting in further degassing (I say “almost certainly” because I have not been able to find data for the solubility of atmospheric gases for water beyond 100°C). After a while the flask is removed from the hotplate, and allowed to cool slightly. And then it is inserted into a graphite bath for gentler heating, with the graphite temperature at only about 250°C.

At high degrees of superheating the insertion of an ordinary mercury thermometer excites violent boiling, as the roughness at the tip of the thermometer serves as a site for nucleation (bubble-formation). Therefore the temperature of the water in the graphite bath can only be monitored intermittently. For the most part the water is absolutely still, although its temperature is very high. Inserting the thermometer prompts very active boiling, bringing the temperature down; temperatures of 107–109°C are easily recorded. At high degrees of superheating, the water will explode on contact with the thermometer, or sometimes spontaneously. The Beckmann thermometer, whose bulb is very large and smooth, does not provide effective nucleation sites, so that a continuous monitoring of temperature is possible. However, as the instrument I was using only had a 6-degree scale, and the zero was calibrated near 100°C, the water temperature went well off the scale at higher degrees of superheating. Using a Beckmann thermometer in the degassed water, the result is often quite remarkable: nothing visible at all happens for a long while, and then suddenly the water explodes; this happens at estimated temperatures of 105–108°C. In either setup, after an explosion the water may settle into bumpy boiling at a relatively low temperature (still well over 100°C), or return to a still state at a higher temperature punctuated with puffing and explosions. The latter is the likely outcome when the initial de-gassing is sufficient. If the surface area of the water is relatively large (which happens when the water level goes down sufficiently below the neck of the flask), the fast evaporation that happens at the surface of the superheated water must cause a rate of heat loss matching the rate

of heat input from the graphite. In that equilibrium situation, it is easy to have water superheated to 105–106°C sitting there indefinitely with no bubbling.

The following (27 August 2004) is a typical run of this experiment, with fairly good de-gassing, with a Beckmann thermometer: initial explosion at 105.50°C, about 4 minutes after passing 100°C; post-explosion temperature down to 103.4°C; afterwards temperature climbing back up quite steadily, despite a couple of small sharp puffs; 4 minutes after the initial explosion, another explosion, at about 106.3°C; for 2.5 minutes afterwards, puffing at around 105.5°C; thermometer removed for the next 4.5 minutes, resulting in no significant difference in the behaviour of the water; on re-insertion of the thermometer, temperature found to be steadily over 106°C, with occasional puffs accompanied by a hissing noise. All in all, De Luc's reports on the boiling behaviour of de-gassed water are amply confirmed, although I have never been able to record temperatures reaching 112°C as he reported in one trial.

If the boiling point is indefinite, how can thermometers be made?

The results of these experiments leave a puzzle regarding the very possibility of thermometry: if there were such unmanageable and ill-understood variations in the temperatures of boiling water, how could the boiling point have served as a fixed point of thermometry at all? It seems that the variations would have threatened the notion of a definite “boiling point”, but the very thermometers used for the investigation of these variations in the 18th century were graduated with sharp boiling points. We can only conjecture that there must have been an identifiable class of boiling phenomena with sufficiently stable and uniform temperatures, which allowed the calibration of thermometers with which scientists could then go on to study the more exotic instances. Happily, a closer look at the history bears out that conjecture. There were three main factors that allowed the boiling point to be used as a fixed point despite its vagaries.

First of all, an immediate relief comes in realizing the difference between the temperature that water can withstand without boiling, and the temperature that water maintains while boiling. All observers of superheating from De Luc onward had noted that the temperature of superheated water went down as soon as steady boiling was induced, or each time a large bubble was released. Extreme temperatures were reached only before boiling set in, and

could be disregarded for the purpose of fixing the boiling point. De Luc got as far as 112°C without boiling, but the highest temperature he recorded while the water was boiling was 103°C (a figure quite consistent with my own results). Still, the latter is 3°C higher than the “normal” boiling temperature, and there was also Gay-Lussac’s observation that the temperature of boiling water was over 101°C in a glass vessel. Marcet investigated this question with more care than anyone else. In ordinary glass vessels, he observed the temperature of boiling water to range from 100.4° to 101.25°C . In glass treated with hot sulfuric acid, the temperature while boiling went easily up to 103° or 104°C , and was very unsteady in each case due to bumping⁸.

The second factor helping to stabilize the boiling point was in fact a whole set of miscellaneous factors, which might cause embarrassment to misguided purists. The spirit here was to do whatever happened to prevent superheating. The Royal Society Committee avoided superheating by using metallic vessels instead of glass. Gay-Lussac showed how to prevent superheating in glass vessels by throwing in metal chippings or filings (or even powdered glass). Other investigators found other methods, including the insertion of solid objects (especially porous things like charcoal and chalk), sudden localized heating, and mechanical shocks. But in many practical situations the prevention of superheating simply came down to not bothering too much. If one left naturally occurring water in its usual state full of dissolved air (rather than taking the trouble to purge air out of it), and if one left the container vessels just slightly rough (instead of smoothing it off with something like hot sulfuric acid), and if one did not do anything else strange like isolating the water from solid surfaces, then common boiling did take place. Serious theoretical arguments about the factors that facilitate ebullition continued into the 20th century, but all investigators agreed sufficiently on how to break superheating and prevent bumping in practice. Marcel Verdet observed that under “ordinary conditions,” there would be dissolved air in the water and the water would be in contact with solid walls, and hence boiling would “normally” set in at the normal boiling point¹¹. It was a great blessing for early thermometry that the temperature of boiling was quite fixed under the sort of circumstances in which water tended to be boiled by humans living in ordinary European-civilization conditions near the surface of the earth without overly advanced purification technologies.

However, happy-go-lucky sloppiness is not the most robust strategy of building scientific knowledge in the end, as the Royal

Society Committee realized quite well. The committee's lasting contribution, the last of our three factors contributing to the fixity of the boiling point, was to find one clear method of reducing the variations of the boiling point due to miscellaneous causes: "The most accurate way of adjusting the boiling point is, not to dip the thermometer into the water, but to expose it only to the steam"³. Somehow, using the boiled-off steam rather than the boiling water itself seemed to eliminate many of the most intractable variations in the temperature:

"The heat of the steam therefore appears to be not sensibly different in different parts of the same pot; neither does there appear to be any sensible difference in its heat, whether the water boil fast or slow; whether there be a greater or less depth of water in the pot; or whether there be a greater or less distance between the surface of the water and the top of the pot; so that the height of a thermometer tried in steam, in vessels properly closed, seems to be scarce sensibly affected by the different manner of trying the experiment"³.

The recommendation to use steam came most strongly from Cavendish, who had already made the same proposal in his review of the instruments used at the Royal Society. Marcet later confirmed that even steam resulting from highly superheated boiling was only a fraction of a degree above 100°C⁸.

Why don't we all know about the variations?

Even after we understand how the accurate graduation of thermometers was possible despite the variability of the boiling point, a question remains as to why most people are not aware of that variability, even though most of us boil water on a daily basis. The main reason is that in everyday life we tend to boil water always in the same sort of manner: in broad vessels with heating from the bottom, which requires intense heat sources because of the high rate at which heat is lost at the open surface and the sides. (In the graphite bath used in Experiment 6, I could not make water boil at all in any wide-open vessels, despite urging the graphite temperature to over 250°C.) In order to see that the "standard" act of boiling could be different for people with different ways of life, consider the following three situations, one fictitious and two real.

- (a) Imagine a civilization with no access to open flames, but only to hot stones or sand; there, boiling would be done in narrow-necked flasks, routinely producing the kind of superheated boiling that I have observed in volumetric flasks heated with a graphite bath or a hotplate. Such people would not dream of drawing a sharp line between the “liquid” and “gas” regions in a temperature-pressure phase diagram.
- (b) Coming back to real life in the 20th/21st century, note widespread reports of the superheating of water in microwave ovens, which heat water directly and evenly, not by means of a hot solid surface. This phenomenon is often noticed because the superheated water is apt to boil over violently when instant coffee is dropped into it. (Try putting “superheated water” into an internet search engine; Joe Wolfe of the University of New South Wales has a particularly good online discussion¹³.) Some recent researchers on boiling have employed laser pulses as a heating mechanism.
- (c) In the 19th century, the age of the steam engine, boiler explosions resulting from superheating created a real concern, and various methods of preventing superheating were devised successfully. I have not seen a good theoretical or historical account of this business, but I suspect that the water in the steam-engine setup is prone to de-gassing, and that the explosive force would have been quite considerable in high-pressure engines. In the 20th century, mechanical and chemical engineers encountered a wide variety of situations in which boiling takes place, and have been accumulating experimental and theoretical knowledge of various different types of boiling that take place in different situations, as I will explain briefly in the next section^{14,15,16}.

Modern theories of boiling

In the traditional theory of boiling in physics and physical chemistry, the boundary between the liquid state and the gas state is sharply defined as the line on which the vapor pressure (as a function of temperature) reaches the level of the external pressure. This is as shown in a typical phase diagram (Figure 5). The assumption of the sharpness of the liquid-gas boundary theoretically precludes any variability in the boiling temperature under fixed external pressure; this means that there is no obvious way of accommodating the observed variations within the traditional physical theory. In modern treatises on boiling in mechanical and chemical engineering, we do not find the standard thermodynamic

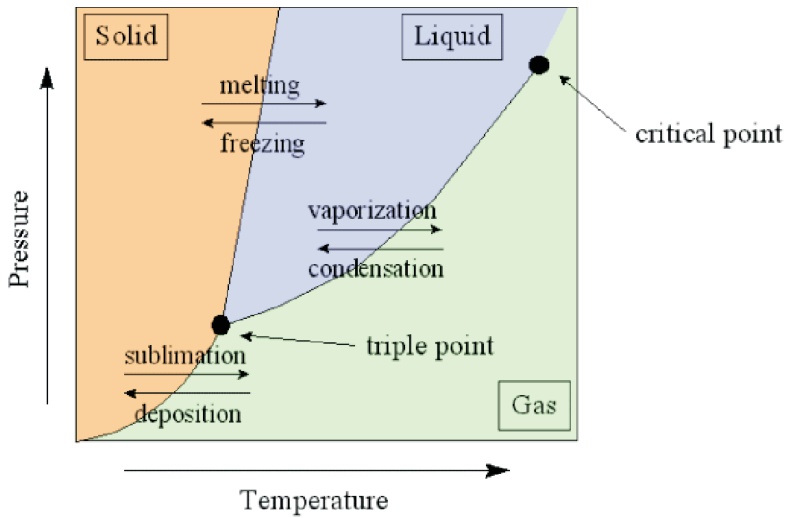


Fig. 5. A standard phase diagram.

phase diagrams. Instead, the engineers' paradigmatic representation of boiling is the "boiling curve", which plots the rate of heat transfer against the degree of the "surface superheat" or the "excess temperature". Figure 6 shows a typical boiling curve. The contrast between the phase diagram and the boiling curve reveals a fundamental difference in physicists' and engineers' understanding of boiling. In fact it is impossible to translate straightforwardly between the two discourses, so the situation here warrants the use of Thomas Kuhn's concept of incommensurability¹⁷.

The main independent variable in the engineering discourse is how much the temperature of the heating element exceeds the "normal" boiling point. I assume that the water in immediate contact with the heating element (what De Luc called the "first layer" of water) is also heated beyond the normal boiling point – by how much, we cannot really say. It would be extremely difficult to measure such a thing and, presumably, the engineers are more interested in variables that they can measure and control, like the temperature of the heating element. Therefore, in the best modern theory of boiling we have, the temperature of the water itself has no role to play! And if we do assume that there is some degree of superheating in the first layer of water, and seek to say something about the effect of that superheating, we find that there is no theory that can be applied easily. The question cannot even be articulated in standard thermodynamic discourse, because the basic theory

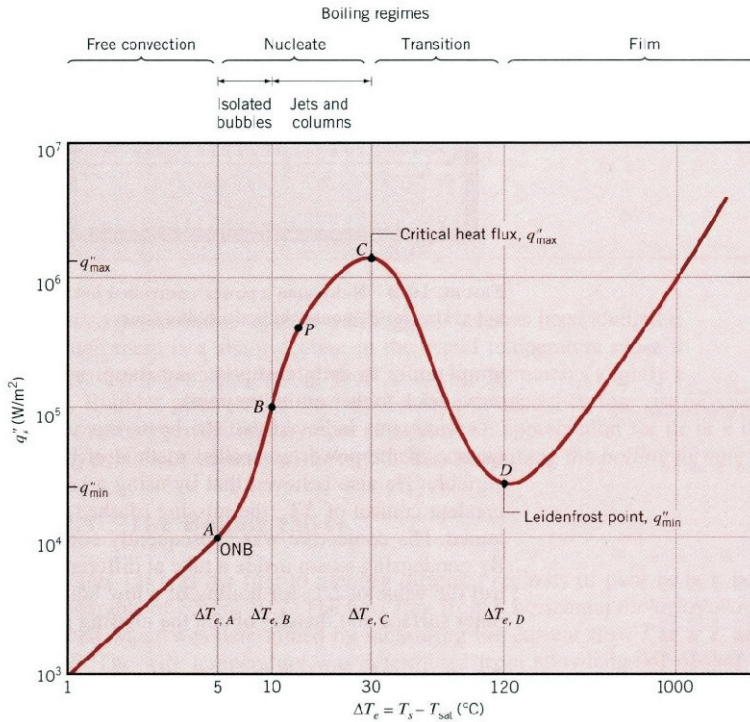


Fig. 6. A standard boiling curve, from Incropera and DeWitt (1996), p. 502 (figure 10.4). Courtesy of John Wiley and Sons.

there rests on the idealized assumption that superheating never occurs. Instead, we would need to give a microphysical treatment of the chemical bonds among the water molecules, and the interaction of water molecules with solid surfaces (and with molecules of dissolved gases).

The other main thing to note about the engineers' boiling curve is that the main dependent variable is the rate of heat transfer. These engineers are mainly interested in boiling as a method of carrying heat away from hot places (one can easily imagine the consequences of not understanding this correctly, in trying to keep a nuclear reactor from overheating, for example). In that context, the temperature of the liquid water, especially well above the first layer, is distinctly of secondary interest, and is freely admitted to be quite variable depending of the situation. The engineering treatises on heat transfer give a detailed classification of boiling behaviour, largely determined by the degree of surface superheat and the configuration of the boiling setup. A great deal of experimental work is also going on.

Particularly pertinent for current purposes is the modern theory of nucleation (bubble-formation), which gives excellent and detailed explanations of the effect of vessel-surface quality on boiling behaviour (shown in Experiment 2 and Experiment 4). Surface tension emerges as the basic reason why water is prone to superheating; in order for boiling to take place, vapour bubbles need to form within the body of the water, and grow sufficiently to be visible as they come up through the water. Now, the basic condition for a bubble to sustain itself is that the vapour pressure should match (or exceed) the external pressure. However, there is a complication here because the water molecules forming the surface of the vapour bubble attract each other. This attraction manifests itself in the form of surface tension, which tends to close up the bubble. Therefore an additional force of vapour is required to sustain the bubble, which means the water temperature has to be higher than the boiling point indicated by the simple balance between the vapour pressure and the external atmospheric pressure.

Standard theory says that the additional pressure created by surface tension is inversely proportional to the radius of the bubble. In other words, the additional pressure to be overcome becomes infinite when the radius is 0, which means that it would be impossible to grow vapour bubbles without starting from finite-sized spaces. This is why the precise quality of the solid surface becomes so important for the facilitation of boiling. If the surface has micro-pores and it is sufficiently water-repellent, then there would be pockets of vacuum or trapped air that can serve as the site of bubble-formation (nucleation). This is why bubbles only arise from specific places in ordinary boiling situations, especially as the water gets more and more de-gassed with the progress of boiling.

Some questions arising from my experiments are more difficult, and they are not satisfactorily resolved by an elementary knowledge of the modern engineering theory of boiling that I have so far acquired. First, it is difficult to understand the role of dissolved air in facilitating boiling; this may require some detailed molecular modelling, which the engineering theory does not provide. Second, the lowering of the boiling temperature below the thermodynamically defined boiling point is difficult to understand. The only explanation I can currently offer is that the “first layer” of water in those situations must be heated well beyond the normal boiling point although the main body of the water is much cooler, and that the bubbles rise to the surface before they have enough time to be collapsed in coming through the cooler water.

Concluding remarks

My investigation has revealed some significant gaps in the common knowledge of boiling in standard physics and chemistry, especially in the way these subjects are taught, even in higher education. These gaps exist not because science is incapable of filling them, but because science needs to set aside many questions and facts in order to allow its focus on the current cutting-edge of research. History and philosophy of science can serve the function of preserving and developing aspects of scientific knowledge that are lost and neglected in the process of scientific progress. I would have not learned all the good things about boiling that I have presented in this paper, if I had not started by learning from historical sources. And I would not have looked into that history if I had not been investigating philosophical questions about how we can know whether our thermometers are reliable. Using history and philosophy of science to improve our knowledge of nature is a program of research that I call “complementary science” because it supplements current specialist science without disputing its legitimacy¹. I hope that this brief presentation of a concrete question has given you a glimpse of the potential of this research programme.

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