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The History of the Cooling Law: When the Search for Simplicity can be an Obstacle

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Abstract This paper presents an historical overview of the research on the cooling law, from Newton until the beginning of 20th century, and provides some suggestions for the use of this history as a resource for teaching. This history begins with a description and an interpretation of Newton's earlier work in 1701 and an overview of studies confirming or confuting Newton's law during the 18th century. Subsequently, it presents the early studies on cooling due to radiant heat, the fundamental work of Dulong and Petit published in 1817, and a brief overview of the research conducted after 1850 on the laws of thermal radiation and of natural and forced convection. It is shown that many scientists persisted in maintaining Newton's law, despite numerous evidence to the contrary, by attributing the found discrepancies to empirical errors or to other disturbance factors. Many scientists considered this law as a fundamental principle rather than a conjecture to be tested by means of experiments, while others were searching for a different but general and unique cooling law. The faith in the simplicity of natural laws and the spontaneous idea of proportionality between cause and effect seem to have strongly influenced Newton and many later scientists. A discussion of epistemological, methodological and pedagogical implications is offered.

1 Introduction

The role of the history of science in teaching has been studied and debated at great length (see Matthews 1994). It has been considered as something that gives cultural value to learning, favouring a more critical attitude and a conception of science as an evolving human activity. Moreover, the history of science could contribute to give sense to physics learning. In fact, the didactic transposition (Chevallard 1991) constrains to isolate and restructure physics subjects in order to adapt them to the school context. As a consequence, usual teaching tends to hide the cultural and social references that defined the problems in answer for which scientific theories have been formed. This can produce a fragmentary,

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algorithmic more than conceptual, knowledge. Studying "case histories" involving significant historical or philosophical aspects can contribute to giving back the atmosphere of debates, controversies and technical and economic backgrounds that constituted the context of science development (Stinner et al. 2003). This can give students examples of *science in making* (Conant 1957).

Research on common sense conceptions has renewed this debate from another standpoint because it has found that many of these conceptions are similar to ancient ideas or theories historically abandoned (Viennot 1979; McCloskey 1983). It has been supposed that, confronted with such ideas and theories, students would have recognized their own conceptions, discussing and reviewing them, with conceptual change sequences similar to the historical ones (Benseghir and Closset 1996). Resuming the theory according to which ontogeny recapitulates phylogeny, it was supposed that individual cognitive development could recapitulate in some way the historical development of science. Such proposals have been criticized of their often too simplistic analogy between ancient theories and common thought and because of the strong differences in the context, the meaning of concepts and ideas used and the mental and logical processes involved (Nersessian 1995; Carey 1988). Nonetheless, some analogies exist even if in a limited form, for example Piaget and Garcia (1983) emphasized it strongly.

It is argued that history of science can contribute to improve science understanding in its conceptual, procedural and contextual aspects (Wang and Marsh 2002; Teixeira et al. 2009), can positively contribute to a better understanding of scientific methods, of the nature of science, of the relationships between science, technique and society, and to metacognitive learning (Matthews 1994). History of science can provide a repository of strategic knowledge of how to construct, change and communicate scientific representations and science educators could choose, integrate and transform these resources into instructional procedures (Nersessian 1995; Seroglou and Koumaras 2001; Holton 2003; De Berg 2008). Moreover, many problems, models and explanatory frameworks utilised in the early historical development of a scientific topic are more in resonance with the preferences of student and common reasoning, often centred on dynamical, causal, qualitative and analogical reasoning (Besson 2010a). The USA National Science Education Standards (1996) "recommend the use of history of science in school programs to clarify the different aspects of scientific inquiry, the human aspects of science and the role that science has played in the development of various cultures".[1]

In this paper, I present a history of research on the cooling law and I will show how this history can be the support of interesting cases histories useful for teaching. In fact, the history of cooling law is interesting for its epistemological implications and its possible didactical utilisations. Its treatment involves only simple mathematics and can be easily understood by secondary school or first university years students. It involves concepts and phenomena which are well known and usually treated in normal school practice and syllabus, but on which there exist diffuse difficulties, misconceptions and conceptual ambiguities. For example, the following are typical of conceptions found in literature (see Stavy and Berkovitz 1980; Shayer and Wylam 1981; Erickson and Tiberghien 1985; Arnold and Millar 1996; Cotignola et al. 2002; Besson et al. 2010): confusion between temperature, heat and internal energy; temperature considered as a extensive quantity; reasoning in terms of objects properties instead of processes; quality of being or doing warm or cold attributed to materials (an ice cube melts quicker if wrapped in a wool cloth);

[1] See: http://www.nap.edu/catalog/4962.html, Chap. 6a, p. 107.

the existence of a maximum possible temperature for a given material; a lacking or incorrect consideration of the infrared radiation in processes of thermal energy exchange.

Concerning the beneficial role of history for the teaching and learning of this specific topic, for example Cotignola et al. (2002) showed "the parallel, in the intermixed use of the internal energy and heat concepts, between the first historical steps in the use of the First Law of Thermodynamics and current students' interpretations" (p. 288), and De Berg (2008) proposed the use of analogies based on the historical caloric theory for "helping students draw a distinction between heat and temperature even though the analogy draws upon an outdated concept of heat" (p. 88).

Moreover, even if it does not concern fundamental theories or problems, the history of cooling law implies valuable epistemological issues, as the relationship between theory and experiments, the field of validity of empirical laws, the role of philosophical ideas of scientists (e.g. what counts as "simplicity") in scientific research, the under-determination of mathematical models of empirical phenomena.

2 The Development of Research on the Cooling Law

The cooling law of objects in a colder environment has been the object of numerous studies since the beginning of the 18th century. The search for such a law was neither linear nor simple, because the cooling process embeds two different phenomena, thermal radiation and heat transfer by contact (convection and conduction), which have different properties. Moreover, these phenomena, especially convection, are not very regular and in certain aspects they appear to be "dirty phenomena", which challenge attempts of finding simple and general laws. This is a case in which the reliance on the simplicity of natural laws has constituted an obstacle for many scientists. The resistance opposed to the abandon of Newton's law is probably due to this reliance and to the spontaneous idea of a proportionality between cause and effect, beyond that to the scientific authority of the great scientist. Moreover, research on cooling processes was connected with the problem of defining a good scale of temperatures, and for the thermal radiation with the definition of the absolute zero of temperature.

Section 3 presents a description and an interpretation of Newton's early work and Sect. 4 provides an overview of the studies confirming or confuting Newton's law during the 18th century. The early studies on cooling due to radiant heat at the beginning of 19th century are described in Sect. 5, and the fundamental work of Dulong and Petit published in 1817 in Sect. 6. Sections 7 and 8 offer a brief overview of the research conducted after 1850 on the laws of thermal radiation and of natural and forced convection. Section 9 provides conclusive observations and offers some suggestions for teaching.

3 Newton's Work

In 1701, Newton published (in Latin and anonymously) in the Phil. Trans. of the Royal Society a short article (*Scala graduum Caloris*), in which he established a relationship between the temperatures T and the time t in cooling processes. He did not write any formula but expressed verbally his cooling law:

> the excess of the degrees of the heat … were in geometrical progression when the times are in an arithmetical progression (by "degree of heat" Newton meant what we now call "temperature", so that "excess of the degrees of the heat" means "temperature difference").

This relationship is equivalent to an exponential or logarithmic law (T_o and T_a are the initial and the ambient temperature, respectively, and γ is a time constant):

$$(T - T_a) = (T_o - T_a)\exp(-t/\gamma) \tag{1a}$$

$$t = -\gamma \ln \frac{(T - T_a)}{(T_o - T_a)} \tag{1b}$$

Newton noted that his law can be deduced mathematically from a linear relationship between temperature change rate and temperature difference between the object and the environment:

$$\frac{dT}{dt} \propto -(T - T_a) \tag{2}$$

He wrote:

> the heat which hot iron, in a determinate time, communicates to cold bodies near it, that is, the heat which the iron loses in a certain time is as the whole heat of the iron; and therefore (*ideoque* in Latin), if equal time of cooling be taken, the degrees of heat will be in geometrical proportion.

The mathematical connection between Eqs. 1 and 2 was clear to Newton, who had already studied in his *Principia* (Book II, Section I, Proposition II) a similar relationship in the case of an object moving in a fluid opposing a resistance proportional to the object velocity, so that $a = \frac{dv}{dt} \propto -v$.

Even though Newton's article is very short (5 pages) and not well supported by data, it has had a strong influence on later studies on the same topic and it has been the object of many historical studies.[2] Currently, Newton's cooling law is usually given in terms of heat flux q, i.e., the rate of heat loss from a body $q = dQ/dt$:

$$q = \frac{dQ}{dt} \propto -(T - T_a) \tag{3}$$

In the formulation of his law, Newton shows his confusion, which was normal in his days, between heat and temperature. He spoke of *heat loss* and *degree of heat* and this means that for him a loss of heat was always proportionally accompanied by a decrease of "degree of heat", i.e., of temperature, so that according to him Eqs. 2 and 3 would be equivalent, and similar expressions have been used by many other scientists for a number of decades after 1701[3]

[2] See: Ruffner J. A. (1963); Molnar G. W. (1969); Grigull U. (1984); Winterton R. H. S. (1999); Simms D. L. (2004); Cheng K. C. (2009).

[3] The Scotsman Joseph Black (1728–1799) was the first to clearly understand, around 1760, the distinction between heat and temperature, but his ideas only diffused slowly after 1770 and his *Lectures* were published after his death in 1803. In his *Lectures on the Elements of Chemistry* (1803), he wrote that in a situation of thermal equilibrium usually scientists imagined that "there is an equal quantity of heat in every equal measure of space, however filled up with different bodies. The reason they give for this opinion is that to whichever of those bodies the thermometer be applied, it points to the same degree. But this is taking a very hasty view of the subject. It is confounding the quantity of heat in different bodies with its general strength or intensity, though it is plain that these are two different things, and should always be distinguished … The quantities of heat which different kinds of matter must receive, … to raise their temperature by an equal number of degrees, are not in proportion to the quantity of matter in each, but in proportions widely different from this, and for which no general principle or reason can yet be assigned… different bodies, although they be … of the same weight, when they are reduced to the same temperature or degree of heat, … may contain very different quantities of the matter of heat".

Newton gave only few data and experimental specifications to support his conclusions (further indications and data are reported in some unpublished manuscripts[4]). He wrote that he used a linseed oil thermometer, but he gave no further descriptions.

Desaguliers repeated Newton's experiment in 1714 and in his *Course* (1744, pp. 293–294) he described the kind of thermometers used by Newton:

> as I mention Sir Isaac Newton's thermometer, I think it will not be improper to give an account of the manner of making it, as I made three of them once by Sir Isaac's direction. I took a tube of half an inch bore 3 feet long, with a ball of two inches diameter at one end of it, and to the tube pasted a list of paper in order to mark a scale upon it. … linseed-oil was poured into it up to the 10th or 12th division on the scale of the tube … He [Newton] also told me that his most general linseed-oil thermometer, for lower degrees of heat began at the freezing point and that the distance between that and boiling water made 34 of his divisions.

The study on the cooling process was connected with the problem of defining a good scale of temperatures, because practically these experiments consisted in measuring variations of fluid volumes, from which to deduce the temperature changes. These two problems were entangled in Newton's paper. In fact, Newton (1701) was mainly interested in defining a thermometric scale (*scala graduum caloris*) also for high temperatures and more than half of his article is occupied by a list of values of measured temperatures and descriptions of corresponding situations (*calorum descriptiones et signa*). He established some fixed-points (human body temperature, melting or boiling points of various substances[5] and mixtures of substances…) and took (*ponendo*) degrees zero and 12 for freezing water and for human body, respectively. He used the oil thermometer to measure the temperatures from the freezing-point up to tin melting point (232°C), assuming temperature changes proportional to oil volume changes ("putting (*ponendo*) the degrees of the heat of the oil proportional to its rarefaction"). He found 34°N for boiling water, so that his scale is in a ratio 100/34 with the Celsius scale: $T(°C) \cong 3 \cdot T(°N)$. Then, in order to discover the higher temperatures, he measured the time of cooling of a piece of hot iron, taken out of the fire, down to the temperature of the human body,

> supposing (*ponendo*) that the excess of the degrees of heat of the iron above the heat of the atmosphere, found by the thermometer, were in geometrical progression when the time are in an arithmetical progression.

This means that Newton did not consider the exponential law of cooling as an experimental result but rather as a general hypothesis, which is a mathematical consequence of a law of proportionality similar to Eq. 2 and which allows to build a temperature scale.[6] In other words, he found the temperatures of his scale by using two different kinds of thermometers, one based on the property of thermal dilatation of fluids (linseed oil), and the other based on the time of cooling of a piece of iron, by assuming two simple laws for the thermal dilatation of linseed oil and for the cooling time. But he considered this last law more reliable and fundamental than the former, in fact he concluded that

[4] See Jones (1991).

[5] To be more precise, Newton did not consider that phase changes of pure substances take place at constant temperature, but rather over a small temperature interval. For example, he wrote: "Water begins to boil with a degree of heat of 33 parts, and by boiling scarcely acquires any greater degree than that of 34½ (*Incipit aqua ebullire calore partium 33 & calorem partium plusquam* 34½ *ebulliendo vix concipit*)"; and "96. Least degree of heat that melts lead; lead, by growing hot, is melted with the heat of 96 or 97 parts, and cooling it hardens with 95 parts.".

[6] Ruffner (1963) had already remarked this aspect: "he [Newton] intends, ultimately, to define a scale of heat by means of his cooling law" (p. 149). Previously, E. Mach (1896) sustained that Newton's argument was circular (Mach 1896, p. 60).

> the several degrees of heat thus found [assuming the exponential law of cooling of iron] had the same ratio among themselves with those found by the thermometer: and therefore (*propterea*) the rarefactions of the oil were properly (*recte*) assumed proportional to its degrees of heat.

This quotation show that, according to Newton, the exponential law of cooling was able to confirm the correctness of a linseed oil thermometer and not vice versa. Newton seems to have a strong confidence in a law like Eq. 2, which probably appeared to him as an example of a general property of proportionality between the cause (here the temperature difference) and the effect (the rate of the decrease of the object temperature), so that it became a fundamental principle rather than a conjecture to be tested by means of experiments. The *discreet charm of the proportionality* and the confidence in the simplicity of natural laws seem to have strongly influenced Newton and will influence many later scientists.

4 Confirmations and Invalidations of Newton's Law in the 18th Century

Later on, other scientists confirmed the Newton's law of cooling, such as the Russian G. W. Richmann, and Johann Heinrich Lambert (1755).

Richmann (1747)[7] reports the results of ten experiments that he made using warm (64–67°F) or hot (141–182°F) water in glass containers cooling in air, also changing the water mass, the surface area and the air temperature. He concluded that the rate of temperature decrease is directly proportional to the temperature difference with air and to the surface area and inversely proportional to the water mass. He found several discrepancies from an exact exponential trend, till 1–2°F and in one case till 4.8°F, but he attributed these discrepancies to the inconstancy of air temperature and incertitude of measures (*inconstantiae temperiei aëris vel observandi difficultati*), even if he could consider as a valuable clue the fact that the calculated values were always in excess at higher temperatures. But he seemed to be attracted by the wish of confirming

> "the admirable harmony between calculations and observations" which "demonstrates the truth of the found law" (*admiranda harmonia calculi et observationum … demonstrat legis inventae veritatem*).[8]

However, very soon after other scientists found discrepancies from Newton's law, such as the Scotsman George Martine and the German I. C. P. Erxleben.

G. Martine (1738) resumed the law of Newton according to which

> the quantities of heat lost [from a body] in given small times would always be proportional to the heats subsisting in it,

and considered that it means that

> the diminution of heat in such a body is like the retardation of a projected body … moving [horizontally] in a medium with a resistance proportional to its velocity (p. 53).

But he added that

> this hypothesis is more mathematical than physical, it gives a fine and beautiful, but not a true view of nature. The heat of a body does not really decrease exactly in that proportion.

[7] The works of Richmann were considered very authoritative, so that some authors made reference to the cooling law (1–2) as Richmann's law.

[8] Unless different indications are given, all quotations that were in Latin, in French or in German in the original were translated in English by the author of the present paper.

Fig. 1 Cooling experiment of G. Martine (1738–1740), p. 60

In a little Mercurial Thermometer, heated to *gr.* 108, and expoſed to the open air, I found the heat decreaſe in this order.

The Times.	Degrees of Heat loſt, by obſervation.	Degrees of Heat loſt, by the firſt conſideration.	Degrees of Heat loſt, by the 2d conſideration.	Degrees of Heat loſt, according to calculation	The Differences.
′					
0½	13	13'6	0'4	14	+1
1	25	24'1	0'8	24'9	—0'1
1½	34	32	1'2	33'2	—0'8
2	40	38'1	1'6	39'7	—0'3
2½	45'5	42'8	2	44'8	—0'7
3	49'5	46'4	2'4	48'8	—0'7
3½	52'5	49'1	2'8	51'9	—0'6
4	55	51'2	3'2	54'4	—0'6
4½	56'5	52'8	3'6	56'4	—0'1
5	58	54	4	58	0

He was looking for the correct law and he wrote (p. 55) that:

> as results of many observations, I find that the decrements of heat [temperature] may be looked on as partly equable, and partly in proportion to … the excesses whereby the heat of the body is warmer than the ambient air [the temperature difference]. And consequently, taking the times in an arithmetical progression, those decrements may be resolved into two series. In the one… they are in a geometrical progression… while in the other … the decrements are as the times, that is equal quantity of heat lost in equal times. And so the law of this decrease of heat coincides with the law of the retardation of a heavy body ascending perpendicularly in a medium which resists it in proportion to its velocity

This problem was studied by Newton in his *Principia* (Book II Section I, Proposition III, Problem I). In formulas, posing $v = \Delta T = (T - T_a)$, this leads to equation $\dot{v} = -av - g$ which solution is $v = \left(v_o + \frac{g}{a}\right)\exp(-at) - \frac{g}{a}$. It is worth to point out that, according to this equation, $v = \Delta T$ becomes zero in a finite time $t = \frac{1}{a}\ln\left(\frac{a}{g}v_o + 1\right)$ and Martine stressed that this is in agreement with what actually happens in the experiments, in contrast with the infinite time previewed by the exponential law:

> For were that truly the case, the body, though continually cooling, would take an infinite time to arrive at the temperature of the surrounding medium. Which however, in fact, we find to be accomplished in a very moderate space of time. (p. 54)

Martine provided a number of data and tables, which would confirm his law but show that the term correcting Newton's law was a small fraction of the observed values of temperature, almost always 1–5% till a maximum of 8% (see Fig. 1).

Nevertheless, he admitted (p. 62) that his law "will not always hold exactly in all circumstances", especially if the heated body is "very large and without a free ventilation of air. … In those circumstances it is difficult, if not impossible, to reduce the decrease of heat to a regular series of number". For these cases he drew the graph of the relationship $(T - T_a) = f(t)$, by reporting on the ordinates the time t and on the abscises $(T - T_a)$ (Fig. 2); he found that the obtained curve is an hyperbola[9] and by founding the parameters of the

[9] Mackenzie (1989) develops an interesting presentation of the Martine's life and works, but he writes erroneously (p. 1829) that Martine argued that the cooling law coincides with "that obeyed by a heavy body *descending perpendicularly* in a medium…" whilst it is matter of a body *ascending vertically*. Moreover, he specifies that this law "according to Newton's *Principia* is a hyperbolic curve" represented by the Fig. 2. On

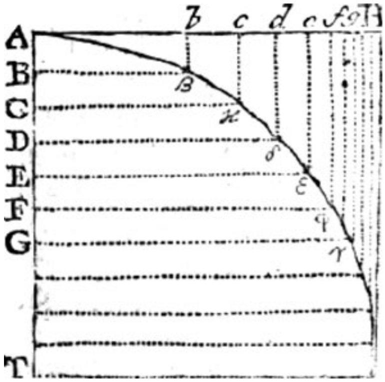

Fig. 2 A figure of G. Martine (1738–1740, p. 63) representing the graph of the relationship between temperature difference and time $(T - T_a) = f(t)$, in the cases of an object "very large and without a free ventilation of air". "Let the time the body takes in cooling be expressed by the line AT, the quantity of heat lost (being its excess above the heat of the ambient medium) by AH … this curve will be the curve of the decrease of heat… I find this curve to be a sort of hyperbola"

hyperbola fitting with a series of data it would be possible to calculate other data (p. 64).At the end of his study, he concluded that

> this doctrine of the heating and cooling of bodies … should be carried on by a variety of experiments … so that I must leave it to others … for establishing and perfecting that doctrine, to which I have only been able to furnish some helps (p. 87).

Erxleben (1777) showed with careful measures that the discrepancies from Newton's law increase with the increasing of the temperature difference with the air. He used the Réaumur scale and a mercurial thermometer with a sensibility of 0.1°R to study the warming (by means of an alcohol lamp) and cooling processes of water in air. He found that the cooling rate is not exactly proportional to the temperature difference with the air, and that at higher temperatures the cooling process is quicker than an exponential law. He also observed that some results of Richmann seem to indicate a similar result. He concluded that Newton's classical law is certainly false (*falsam in se esse legem vulgarem*, p. 92) but he was not able to find another precise law. He added that in any case it is an important result for science to avoid false natural laws (*qui falsas naturae leges abrogat*, p. 92).

5 Early Studies on Cooling Due to Radiant Heat, at the Beginning of 19th Century

The first studies on radiant heat began in the 17th century (see Cornell 1936). The existence of invisible heat rays that can be concentrated by using mirrors was proven by F. Bacon (1620, *Novum Organum*, Liber secundus, XII, 4–7, pp. 126–127). Experiments realizing the separation of the radiant heat from the light by a glass were performed by E. Mariotte (1679) and confirmed by R. Hooke (1682). Newton himself suggested ether vibrations as a way of heat propagation:

Footnote 9 continued
the contrary, this law is not represented by a hyperbola, because it is an exponential function, and in the Martine's paper Fig. 2 did not represent this law, but the cases in which this law is not valid.

> Is not the Heat of the warm Room convey'd through the *Vacuum* by the Vibrations of a much subtiler Medium than Air, which after the Air was drawn out remained in the *Vacuum*? … And do not hot Bodies communicate their Heat to contiguous cold ones, by the Vibrations of this Medium propagated from them into the cold ones? *Optiks* (1712), Query 18.

and he described some experiments made by Desaguliers on the heat transmission in a vacuum.[10]

But the first systematic experiments well distinguishing the different properties of light, radiant heat and heat convection were described by C.W. Scheele (1777), who also introduced the term "radiant heat". Other terms used were "invisible heat", "obscure heat", "free heat" or "free fire". In 1790 M-A. Pictet wrote that "free fire is an invisible emanation which moves according to certain laws and with a certain velocity", P. Prévost (1791) sustained that "free radiant heat is a very rare fluid, the particles of which almost never collide with one another and do not disturb sensibly their mutual movements" (translated in Brace 1901, p. 5), and J. Hutton (1794) suggested that it was an "invisible light", "which is reflexible by metallic surfaces, and which has great power in exiting heat" (pp. 86–88). Finally, in 1800 W. Herschel (1800) discovered the infrared radiation in the solar spectrum, but the debate about the nature of radiant heat will yet continue for decades.

Benjamin Thompson 'Count Rumford' (1804),[11] reported that he discovered in 1785 that heat could be transmitted through a vacuum, by means of several experiments performed by using a device made of a "globular bulb of a mercurial thermometer, half an inch in diameter, in the centre of another glass bulb an inch and a half in diameter", in which a vacuum was made, by a barometric method, in the "the space between the outer surface of the thermometer bulb and the inner surface of the outside ball" (p. 193). He immerged the device in water at different temperatures and observed that the heat is transmitted "nearly twice as fast when the bulb is surrounded by air as when it is in a vacuum." (p. 196).

Rumford strongly supported his conception of heat as a vibratory motion of constituent particles of bodies, against the idea of caloric fluid. In his conception the heat transmission, both for conduction and radiation, is due to the propagation of sound-like undulations in the ethereal fluid filling the entire space, caused by the vibrations of body particles:

> Some regard it [heat] as a *substance*, others as a *vibratory motion* of the particles of matter of which a body is composed. Those who have adopted the hypothesis of a peculiar calorific substance which they call *caloric* suppose that the heating of a body is always the result of an *accumulation* of this substance in the body; on the other hand, those who regard heat as a vibratory motion which is conceived to exist always with greater or less rapidity among the particles of all bodies, consider heat as an *acceleration* of this motion. (p. 167)
>
> I have discovered, first, that all bodies at all temperatures (cold bodies as well as warm ones) emit continually from their surfaces rays, or rather, as I believe, *undulations*, similar to the undulations which sonorous bodies send out into the air in all directions, and that these rays or undulations influence and change, little by little, the temperature of all bodies upon which they fall without being reflected, in case the bodies upon which they fall are either warmer or colder than the body from the surface of which the rays or undulations proceed (p. 178).

In order to sustain his ideas, Rumford described many experiments performed using a special instrument, the *thermoscope* (see Fig. 3), which he described as following:

[10] Manuscripts Copy of Journal Book of the Royal Society of London, 15 November 1716, quoted by Simms (2010), pp. 73–74.

[11] The quotations in the text make references to the book Rumford (1873) *The Complete Works of Count Rumford*, Vol. 2, which contains also a *Historical Review Of The Various Experiments Of The Author On The Subject Of Heat*, at pp. 188–240.

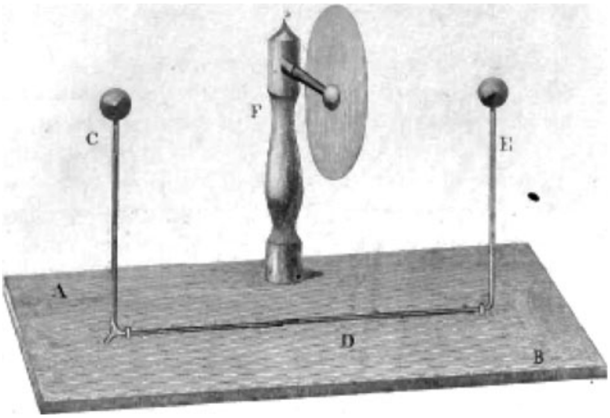

Fig. 3 The Rumford's *thermoscope* (from Rumford 1804, Fig. II)

> AB is a board, 27 inches long, 9 inches wide, and 1 inch thick, which serves as a support for the bent tube CDE, at the two extremities of which the two balls are fixed. The two projecting ends of the tube, C and E, which are in a vertical position, are each 10 inches long; and the horizontal part D of the tube, which is fastened down on the board, is 17 inches in length. The balls are each 1.625 inches in diameter … The pillar F, which, by means of a horizontal arm projecting from it, serves for supporting the circular vertical screen … This circular screen (which is made of pasteboard, covered on both sides with gilt paper) serves for preventing one of the balls of the instrument from being affected by the calorific rays proceeding from a hot body which is presented to the opposite ball. (p. 50)

All the device contained air and "a very small quantity of spirit of wine, tinged of a red colour, is introduced into the instrument":

> A small *bubble* of the spirit of wine … is now made to pass out of the short tube into the long connecting tube; and the operation is so managed that this bubble (which is about ¾ of an inch in length) remains stationary, at or near the middle of the horizontal part of the tube, *when the temperature (and consequently the elasticity) of the air in the two balls, at the two extremities of the tube, is precisely the same*. (p. 48).

The heating or cooling of only one of the balls forces the alcohol bubble "to move out of its place and to take its station nearer to the colder ball" (p. 49). He wrote:

> the result of the foregoing experiment appeared to me to afford the most indisputable proof of the radiation of cold bodies, and that the rays which proceed from them have a power of generating cold in warmer bodies which are exposed to their influence (p. 61)

As this quotation shows, he considered that both calorific and frigorific radiations[12] exist, in the sense that the radiation emitted by a body will have a heating effect on a colder body and a cooling effect on a warmer body, and this latter is a real effect, due to the undulations of lower frequency, which produce a deceleration of the particle's vibration of the warmer body that they invest.

[12] The ideas of frigorific rays and of reflection and focusing of cold were previously sustained by G. Della Porta (1589) and confirmed by the *Accademia del Cimento* of Florence, in Italy (*Saggi di Naturali Esperienze fatte nell'Accademia del Cimento* (1667), p. 176, English translation in: *Essayes of Natural Experiments made in the Academia del Cimento,* trans. by R. Waller, London, 1684, p. 103). By contrast, Marc-Auguste Pictet, Pierre Prevost and other sustainers of material nature of heat interpreted these phenomena as a result of a peculiar arrangement of caloric transmission. An interesting controversy took place between Rumford and Prévost about the existence of cold radiation and the nature of heat. In fact, Rumford considered the existence of frigorific radiation as a strong argument against the caloric theory (see also Chang 2002).

> From these facts we might conclude a priori, that those bodies which, when warm, give off many calorific rays would, when colder than the surrounding objects, give off to them many frigorific rays. This is exactly what my experiments have made evident to me. … the frigorific influences of cold bodies have always appeared as real and effective as the calorific influences of warm bodies. (p. 179)

He provided some practical examples of phenomena that he considered proving the existence of frigorific rays:

> The excessive cold which is known to reign, in all seasons, on the tops of very high mountains and in the higher regions of the atmosphere, … seem to indicate that frigorific rays arrive continually at the surface of the earth from every part of the heavens. May it not be by the action of these rays that our planet is cooled continually, and enabled to preserve the same mean temperature for ages, notwithstanding the immense quantities of heat that are generated at its surface, by the continual action of the solar rays ? (p. 130).

Moreover, Rumford considered that the cooling or warming effects depend on colour and roughness of body surfaces, because these characteristics can modify the absorption, reflection and emission of radiation. "Desirous of finding out what effect colour would produce" he measured the cooling time of the same brass vessel, filled with hot water, using various kinds of surfaces: naked brass; covered with clothing, fur or glue; painted black or white. He found that the time employed in cooling through a given interval of temperature was longer for naked brass surface than for white and black painted surfaces ($\sim$55, 36 and 35 min, respectively, pp. 40–41). He considered the effect of the body surfaces colour and roughness both for calorific and frigorific rays:

> Finding reason to conclude that frigorific rays are always emitted by cold bodies, and that these emanations are very analogous to the rays which hot bodies emit, I was impatient to discover whether all cold bodies, at the same temperature, emit the same quantity of rays, or whether (as I had found to be the case with respect to the calorific rays emitted by hot bodies) some substances emit more of them and some less. With a view to the ascertaining of this important point, I made the following experiments. … I repeated it several times, and always with the same results; the motion of the bubble, which constituted the index of the instrument, constantly showing that the frigorific rays from the blackened surface were more powerful in generating cold than those which proceeded from the naked metal. (pp. 63–64)
> It has been shown that the warmth of clothing depends much on the *polish* of the surface of the substance of which it is made. … The fine fur of beasts, being a highly polished substance, is well calculated to reflect those rays which fall on it; and if the body were kept warm by the rays which proceed from it being reflected back upon it, there is reason to think that a fur garment would be warmest when worn with the hair inwards; but if it be by reflecting and turning away the frigorific rays from external (colder) bodies that we are kept warm by our clothes in cold weather, we might naturally expect that a pelisse would be warmest when worn with the hair outwards, as I have found it to be in fact. (pp. 128–129)

After 1800, the existence of invisible radiant heat was well established and clearly distinguished from the heat convection. Many researches were conducted on these subjects in the first decades of 19th century, also in the frame of the debate on the nature of invisible radiant heat and in particular its relation with light, whether they have an identical or a distinct nature.

Consequently, after 1800, researches on the cooling law hold an account of radiant heat explicitly and try to distinguish the effects due to convection and those due to radiation.

The Scotsman John Leslie, Benjamin Thompson 'Count Rumford', John Dalton and the Swiss Pierre Prévost once again confirmed Newton's law also for the cooling processes due to radiant heat.

Leslie (1804) wrote:

> It is *assumed* as a *general principle*, that the decrements of heat are proportional to the difference of temperature of the conterminous surfaces. On this supposition, the successive temperatures of a substance exposed to cool, would, at equal periods, form a descending geometrical progression (p. 263–264).

Moreover, Leslie performed very accurate experiments showing the dependence of cooling times on the surfaces colour and nature, due to the different properties of radiation emission and absorption.

Rumford (1804) performed some measures involving hot water in the temperature range 126–140°F, and concluded that the temperature difference ΔT decreased with time t according to a logarithmic curve (pp. 32–33), even if the data reported in a table provided few pages before (p. 29) do not fit well with that law. He appealed to the authority of Newton ("a very great philosopher and mathematician") to present as more probably true the law of proportionality between the rate of heat loss and the temperature difference with the environment and he supposed that the observed discrepancies should be attributed to the imperfections of the thermometer divisions. He added that it could be possible to modify the thermometer divisions so that they could produce the regular law precisely, but he did not do this work:

> it is not impossible to divide the scale of a thermometer in such a manner as to indicate with certainty *equal increments of heat*, as thermometers ought to do; but this is not the proper place to enlarge on this subject. I may perhaps return to it hereafter (p. 35).

He seemed to consider the exponential cooling as an exactly true principle on which to adapt the thermometric scale more than an empirically testable relationship.

A similar attitude was taken by Dalton (1808), who developed thoroughly this program. He remarked that the exponential law of cooling was not exactly valid, if the common [Fahrenheit] thermometric scale was used:

> if a body were 1000° above the medium, the times in cooling from 1000° to 100, from 100 to 10, and from 10 to 1°, ought all to be the same. This, though nearly, is not accurately true, if we adopt the common scale, as is well known: the time in the lower intervals of temperature are found longer than in the upper (p. 12).

Then, he decided to construct a new scale of temperatures (Fig. 4), so that by adopting this new scale such law ("one remarkable trait of temperature derived from experiments [!] on the heating and cooling of bodies, which does not accord with the received scale, and which, nevertheless, claims special consideration") would turn out valid, together with other three simple physical laws concerning the thermal dilatation of liquids and of gases and the change with temperature of steam pressure.

> A mercury thermometer graduated according to this principle will differ from the ordinary one… by having its lower degrees smaller and the upper ones larger. (p. 13)

Correspondences of the Thermometric Scales.

old scale.	new scale.	old scale.	new scale.
212°	212°	409°.8	342°
225	222	427. 3	352
238.6	232	445. 3	362
252.6	242	463. 6	372
266.8	252	482. 2	382
281.2	262	501.	392
296.2	272	520. 3	402
311.5	282	539. 7	412
327.	292	559. 8	422
342.7	302	580. 1	432
359.2	312	600. 7	442
375.8	322	621. 6	452
392.7	332	642	462

Fig. 4 The new Dalton's thermometric scale, compared to the "old" Fahrenheit scale. (Dalton 1808, p. 108). In another table, at p. 14, he indicated other temperature correspondences, for example, 754.7, 1,000, 1,285°F became 512, 612, 712°D, and −14, −68°F became −40, −175°D

These quotations show that Dalton considered Newton's cooling law as a defining principle rather than as a falsifiable empirical generalization. He was looking for a phenomenon which depends on temperature according to a precise simple law, so likely connected to fundamental properties of heat and consequently being a good measure of degrees of heat in a body. He considered a phenomenon following *almost exactly* a simple general law, then he assumed it as a precise law and changed the temperature scale according to this law. He considered the agreement that he found among four simple laws of four different phenomena as a confirmation of the new temperature scale. In fact, it appears very unlikely that such a multiple agreement could be a mere coincidence. Dalton's reasoning is quite sophisticated but his experimental data were not so accurate and ample, especially at high temperatures (this weakness of Dalton's conclusions will be remarked by Dulong and Petit, see next section).

For a long time scientists with a similar epistemological attitude thought too easily that they were finding an exact general law. It acted probably, in these cases, the spontaneous tendency of human minds to attribute to things more order and regularity than they actually observe, a tendency that F. Bacon (1620) pointed put as one of *idola tribus* hindering the formation of a correct knowledge:

> The human understanding, from its peculiar nature, easily supposes a greater degree of order and equality in things than it really finds (*Intellectus humanus ex proprietate sua facile supponit majorem ordinem et aequalitatem in rebus quam inveni*) (p. 20, prop. XLV).

Pierre Prévost published in 1809 a long study on heat radiation, providing many theoretical and experimental observations, and quoting many previous studies of other scientists (such as Richmann, Biot, Dalton, Rumford…), but he again confirmed Newton's law. He wrote almost exactly the same words of Newton:

> In a medium of constant temperature, a body that is hotter or colder requires this temperature according to the law that the periods of time being in arithmetical progression, the differences of temperature are in geometrical progression (translated in Brace 1901, p. 19).[13]

Nevertheless, he remarked that some Dalton's measures at high temperatures (till 600°F) did not follow a regular geometrical progression, so posing the question (p. 48) whether "some causes disturb the law beyond certain limits of temperature".[14]

On the contrary, the Frenchman F. Delaroche (1812 and 1813) clearly stated that:

> The quantity of heat which a hot body yields in a given time by radiation to a cold body situated at a distance, increases, caeteris paribus, in a greater ratio than the excess of temperature of the first body above the second. This proposition being at variance with the opinion of Mr. Leslie, and of several other philosophers, it necessary to establish it by a great variety of experiments. These experiments leave no doubt of the fact; though they are not sufficient to enable us to deduce the rate at which the increase takes place.[15] (Delaroche 1813, p. 102)

[13] «Dans un milieu de température constant, un corps s'échauffe ou se refroidit, de sorte que les différences de sa chaleur à celle du milieu sont en progression géométrique, tandis que les tems de l'échauffement ou du refroidissement sont en progression arithmétique» (Prévost 1809, pp. 46–47).

[14] "Quelque cause trouble-t-elle la loi au-delà de certaines limites ?".

[15] He wrote in French (Delaroche 1812, pp. 215 et 220) : «La quantité de chaleur qu'un corps chaud cède dans un temps donné par voie de rayonnement à un corps froid situé à distance, croît, toutes choses égales d'ailleurs, suivant une progression plus rapide que l'excès de la température du premier sur celle du second. Cette proposition n'est pas d'accord avec les opinions reçues. M. Leslie a même fait des expériences dont le résultat semble lui être directement contraire. Aussi ai-je cru devoir répéter plusieurs fois les expériences qui établissent sa justesse, et les varier de plusieurs manières… Je crois qu'en général la quantité de chaleur reçue est d'autant plus éloignée d'être proportionnelle à l'excès de la température du corps chaud sur celle du corps froid, que la température du premier devient plus élevée ; mais je n'ai pas multiplié assez mes

Fig. 5 Delaroche's table showing the results of his experiments on thermal radiation (Delaroche 1812, p. 219). The first column gives only a name for each measures. The second column provides the temperature excesses of the copper ingot over the thermometer temperature when this last has become stationary, and the third column gives, at the same time, the temperature differences between the thermometer and the surrounding air. It is clear from the table that the ratios between the values of the second and third columns are not constant, in fact they decrease roughly from 40 to 9

Indication des expériences.	Excès de la température du lingot de cuivre sur celle du thermomètre au moment où celui-ci est devenu stationnaire.	Elevation de la températur. du thermomèt. au-dessus de celle de l'air environnant.
a	68,7	1,5
b	93,5	2, 5
c	95,4	2,45
d	103,3	2,65
e	138,0	4,05
f	155,6	4,85
g	207,7	7,35
h	208,8	7,50
i	272,7	12,20
k	284,5	13,85
l	292,0	12,80
m	399,1	25,50
n	423,0	25,70
o	486,3	38,55
p	531,4	42,50
q	590,9	56,55
r	592,0	57,85
s	604,4	62,60
t	643,8	65,9
v	713,8	80,55

He considered a very warm body A, at temperature T_A (an iron crucible filled with mercury, up to 250°C, and a spherical ingot of red copper, up to around 900°C), another body B (a mercury thermometer) and the cold ambient air C at constant temperatures T_c. In a stationary situation, at equilibrium, the amount of heat that B receives from A must be equal to that it gives to ambient air C. If the heat flow is proportional to the temperature difference, then for the same experimental situations the ratio $(T_A - T_B)/(T_B - T_C)$ between the temperature differences would have to remain constant by varying the initial temperature T_A. On the contrary, he found that this ratio was not constant (see Fig. 5), both in the case of radiation concentration by means of concave mirrors, and in the case of directed transmission of thermal radiation between A and B. Moreover, he compared the radiating heat emitted in a given time by bodies at different temperatures (a copper ingot at 427°C and 960°C), by measuring the mass of ice fused by such heat (the ice and the ingot were placed in the focuses of two concave mirrors), and he found that radiated heat is not proportional to the temperature; indeed the ratio between the fused ice masses is more than double of the ratio between the corresponding temperatures (by converting in kelvin the temperatures given by Delaroche, I have obtained a relationship $q \propto T^{2.8}$).

Biot (1816) resumed the Delaroche's experiments and proposed a mathematical formula for representing the data: instead of a proportionality $(T_B - T_C) = a(T_A - T_B)$, a formula also containing a cubic term $(T_B - T_C) = a(T_A - T_B) + b(T_A - T_B)^3$. He found this formula well verified in all cases he considered and concluded that

Footnote 15 continued
observations, pour établir avec quelque précision, la loi suivant laquelle se fait l'accroissement de cette quantité de chaleur.».

> the radiant heat that a body B receives from a hotter body A is not simply proportional to the excess of temperature of A above B, but it increases according to a more rapid law, expressed by the first two odd powers of the temperature.[16]

The above quotations show that different attitudes were activated by scientists to face the discrepancy between law and experiments. The more empiricist scientists prefer to conclude that the cooling law is not exactly true and eventually to look for a new less simple different law (e.g. Martine, Erxleben, Delaroche, Biot). The more theoretical scientists, on the contrary, try to maintain the beautiful simple law by considering the effect of various disturbance factors (e.g. Richmann, Prévost, Leslie) or by revising the common temperature scale in order to re-obtain the agreement between theory and experiments (e.g. Rumford, Dalton). It is worth to point out that this difference of attitude seems to have no connection with the theory of heat supported by the scientists. In fact, among those who tried to maintain the Newton's law there were supporters of kinetic theories of heat (like Rumford and Newton), as well as supporters of material caloric theories (like Lambert, Prévost, Pictet, Dalton, Leslie), in the both versions of discrete fluid made up of point-like particles or of continuous elastic fluid, whose "tension" corresponds to the temperature. The difference seems to reside rather in a different epistemological attitude, i.e., whether they were mainly interested in defining and validating a physical theory or in finding accurate empirical relationships.

6 The Work of Dulong and Petit

In 1817, the Frenchmen Pierre Dulong and Alexis Petit published a very accurate and large experimental research on the measure of temperatures and on the law of cooling (Dulong and Petit 1817). They studied first the cooling processes in a vacuum, therefore due to radiation. They used two mercury thermometer with bulbs of 6 and 2 cm of diameter placed in a spherical copper chamber of 3 dm of diameter, in which the air was pumped off and which was immerged in a large cylindrical vessel filled with water (Fig. 6).

They established that (p. 248) "the cooling of a body in a vacuum is given by the excess of its own emitted radiation over that of the surrounding bodies (*le refroidissement d'un corps dans le vide n'est que l'excès de son rayonnement sur celui des corps environnans*)", elsewhere (p. 258) they write "quantity of heat sent by the chamber (*la quantité de chaleur envoyée à chaque instant par l'enceinte*)". Consequently, the cooling velocity or the rate of temperature decrease by radiation $V_{\mathrm{rad}} = dT/dt$ equals the difference $F(T) - F(T_a)$ between the functions representing the law of emitted radiation for the temperature T of the warm object and for the temperature T_{a} of the surrounding ambient. From their measures (Fig. 7) they obtain the function:

$$F(T) \propto a^T + \mathrm{const} \tag{4}$$

where $a = 1.0077$ and consequently (m is a constant):

$$V_{\mathrm{rad}} = \frac{dT}{dt} = m(a^T - a^{T_a}) = ma^{T_a}(a^{(T-T_a)} - 1) \tag{4a}$$

[16] «lorsqu'un corps chaud A agit sur un autre corps B à distance et à travers l'air, la quantité de calorique rayonnant que celui-ci reçoit à chaque instant infiniment petit, n'est pas simplement proportionnelle à l'excès de la température de A sur la sienne, mais croit suivant une loi plus rapide, qui, dans les expériences citées, est exprimée par les deux premières puissances impaires de la température» (p. 24).

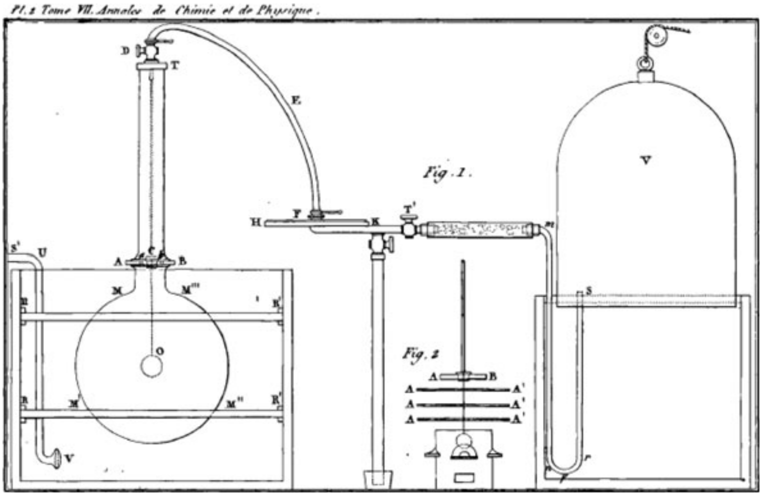

Fig. 6 The experimental apparatus of Dulong and Petit (1817) to study the cooling process due to thermal radiation in a vacuum

Fig. 7 A table of measures of Dulong and Petit (1817, p. 253–254) for the cooling process due to thermal radiation in a vacuum. The external copper chamber was at 20°C with a residual air pressure of 2 mmHg. The first column gives the temperature differences between the thermometer and the external copper chamber, the second columns reports the measured cooling velocities in °C/min, and the third one provides the cooling velocities calculated by using Eq. 4a where $m = 2.037$ and $T_a = 20$°C

Excès de température, ou valeurs de *t*.	Valeurs observées de *V*.	Valeurs calculées de *V*.
240°;	12°,40;	12°,46;
220;	10,41;	10,36;
200°;	8°,58;	8°,56;
180;	7,04,	7,01;
160;	5,67;	5,68;
140;	4,57;	4,54;
120;	3,56;	3,56;
100;	2,74;	2,72;
80;	1,99;	2,00;
60;	1,40;	1,38;
40;	0,86;	0,85;
20.	0,39.	0,39.

They found also that V_{rad} depends on the nature of the body surface (they compared the behaviour of a glass bulb and of the same bulb but silver-plated). Because the value of a in Eq. 4 is found to be the same in all cases, they conclude, erroneously, that the radiative emission of a substance is the same at all temperatures (p. 259). Finally, they found from Eq. 4a the relationship between temperature and time:

$$t = \frac{1}{M \log a}\left(\log \frac{a^{\Delta T} - 1}{a^{\Delta T}}\right) + \text{const} \qquad (5)$$

where the constants $M = ma^{T_a}$ and *const* can be determined from two experimental data. They specify that for little values of ΔT, by developing the exponential only at first degree, Eq. 5 reduces itself to Newton's law.

It is interesting that Dulong and Petit stress that their laws are valid only considering a scale of temperatures based on the air thermometer. They remarked (pp. 114–115) that almost all previous studies had the default of considering an excessively limited range of temperatures, which has been the source of many erroneous inferences, because phenomena obeying different laws can show very similar behaviours in a narrow temperature interval. They criticized Dalton, because

> M. Dalton … tried to establish general laws applicable to the measurement of all the temperatures. These laws constitute for their regularity and simplicity a remarkable group … but he unduly hastened to generalize some outlines … which were based only on dubious evaluations: in fact almost all his assertions will be disproved by the results of our present research.[17]

Moreover, they specify (p. 260), perhaps for the first time, that the law of cooling velocity does not necessarily coincide with the law of heat loss, because the heat capacities of a body can vary with the temperature (so, finally the laws (2) and (3) can effectively be seen as different): to obtain the law of heat loss one should multiply the law of cooling velocity (Eq. 5) for the thermal capacity. Even though they specify that the changes of the thermal capacity with the temperature are very slight and become clearly observable only for temperatures over 500°C.

Once established the cooling law due to radiation, they studied the cooling processes inside the air or other gases. They considered the total cooling velocity V_{tot} as the sum of the cooling velocities due to radiation V_{rad} and to convection V_{con}: $V_{\mathrm{tot}} = V_{\mathrm{rad}} + V_{\mathrm{con}}$. Having previously measured and calculated the term V_{rad}, by measuring V_{tot} they can calculate $V_{\mathrm{con}} = V_{\mathrm{tot}} - V_{\mathrm{rad}}$. They found:

$$V_{\mathrm{con}} = m \cdot p^c \cdot (T - T_a)^b \tag{6}$$

where p = pressure of gas, $b = 1.233$ for all gas and bodies, c depends on the gas, m is a constant depending on the nature of gas and on the dimension of the body (Fig. 8).

Note that the maximum temperature they used in all these experiments was only 280°C. Dulong and Petit criticizes the results obtained by Leslie and by Dalton, because these latter did not understand that the cooling velocity due to radiation depends not only on the temperature difference ($T{-}T_{\mathrm{a}}$) but also on the absolute value of the ambient temperature T_{a}. They concluded (pp. 366–367) by noting that the cooling law must be very complicated and

> perhaps its extreme complication has been the cause of the very little successes obtained until now in the attempts made to discover it.[18]

7 After 1850: The Laws of Thermal Radiation

After the middle of the 19th century, the cooling process is treated mainly in terms of energy losses from the body, including a convective term dE_{con} and a radiative term dE_{rad}:

$$\frac{dE}{dt} = C\frac{dT}{dt} = \frac{dE_{\mathrm{con}}}{dt} + \frac{dE_{\mathrm{rad}}}{dt} \tag{7}$$

(C is the thermal capacity of the body) and the laws of each term are investigated.

[17] «M. Dalton, en considérant la même question sous un point de vue beaucoup plus élevé, a essayé d'établir des lois générales applicables à la mesure de toutes les températures. Ces lois, il faut en convenir, forment un ensemble imposant par leur régularité et leur simplicité. Malheureusement cet habile physicien s'est trop empressé de généraliser des aperçus fort ingénieux, il est vrai, mais qui ne reposaient que sur des évaluations incertaines : aussi n'est-il presqu'aucune de ses assertions qui ne se trouve contredite par les résultats des recherches que nous allons faire connaître», p. 15.

[18] «c'est sans doute à l'extrême complication de cette loi qu'il faut attribuer le peu de succès des tentatives faites jusqu'à ce jour pour la découvrir. On ne pouvait évidemment y parvenir qu'en étudiant à part chacune des causes qui contribuent à l'effet total», p.367.

Excès de température du thermomètre à surface vitreuse.	Vitesses totales de refroidissement de ce thermomètre.	Vitesses de refroidissement qui auraient lieu dans le vide.	Différences, ou vitesses de refroidissem. dues à l'air seul.
200° ;	14°,04 ;	8°,56 ;	5°,48 ;
180 ;	11,76 ;	7,01 ;	4,75 ;
160 ;	9,85 ;	5,68 ;	4,17 ;
140 ;	8,05 ;	4,54 ;	3,51 ;
120 ;	6,46 ;	3,56 ;	2,90 ;
100.	4,99.	2,72.	2,27.

Fig. 8 A table of measures of Dulong and Petit (1817, p. 338) for the cooling process in air of a mercury thermometer having a glass bulb of 6 cm of diameter. Temperature and pressure of air were 20°C and 72 cmHg. Apart from the air pressure in the chamber, the experimental setting was the same as the data in Fig. 7. The first column gives the temperature differences between the thermometer and the external air, the second column reports the observed cooling velocity in °C/min, the third provides the calculated cooling velocity that would be in a vacuum (by Eq. 4a, see Fig. 7), and the fourth column gives the difference between the second and third column, i.e. the cooling velocity due to air only

Concerning the radiative term, J. Ericsson (1872) affirmed that "the deviation from the Newtonian doctrine assumed by Dulong and Petit is groundless" (p. 106) and described an experiment similar to that of the two French scientists, conducted with a spherical radiator, composed of very thin copper, inserted in a spherical enclosure from which the air is exhausted. He concluded that data showed that

> the rate of cooling is proportional to the differential temperatures, thus establishing the correctness of the Newtonian law,

except for a little discrepancy at low temperatures, which Ericsson interpreted as an effect of a change of the emissive power with the temperature, which would not question the correctness of the law for bodies of definite radiant properties:

> Regarding the discrepancy indicated by the slight irregularity of the curve, the writer attributes the same to the difference of emissive power of the radiator at different temperatures… Let us be careful not confound this increase of emissive power with the increase of radiant energy resulting from mere augmentation of temperature… Nor are we justified in questioning the correctness of Sir Isaac Newton's assumption that heated bodies of definite radiant properties develop energies proportional to their excess of temperature over the surrounding media (pp. 106 and 108).

The problem was that the considered temperatures were in a too limited range of 43–133°F (6–56°C), even if he reported Dulong and Petit's data up to $\Delta T = 240$°C and he criticized as erroneous their law on radiant power by considering some of his data on metals at very high temperatures (till 3,000°F). It is interesting to note his attitude of strong attempt to save Newton's law by introducing other factors as a protection belt of his theoretical conviction:

> Newton, as our experiments prove, is incomparably nearer the truth than the French experimenters; and possibly future research will prove that his law, when properly applied, will be found absolutely correct (p. 507).

On the other hand, without using an absolute temperature scale, like that introduced by Kelvin in 1848, it was impossible to find a correct law for thermal radiation.

On the contrary, the Irish scientist John Tyndall (1865) considered much higher temperatures, up till 1,200°C. He accurately measured the radiation emitted from a platinum wire heated by means of electric current:

> A spiral of platinum wire was surrounded by a small glass globe to protect it from currents of air; through an orifice in the globe the rays could pass from the spiral and fall afterwards upon a thermo-electric pile. …the platinum was gradually raised from a low dark heat to the fullest incandescence, with the following results [Fig. 9]. Thus the augmentation of the electric current, which raises the wire from its primitive dark condition to an intense white heat, exalts at the same time the energy of the obscure radiation, until at the end it is fully 440 times what it was at the beginning. (pp. 27–28)

In 1879, starting from the experimental measurements made by Tyndall and by Dulong and Petit, the Slovene-Austrian scientist Josef Stefan proposed the famous empirical relationship asserting that the total radiant energy emitted by a body per unit time is proportional to the fourth power of the absolute temperature of the body (Stefan 1879). He did not feel comfortable with the formulas of Dulong and Petit, then investigated in detail their experimental set-up and realized that there were significant losses due to conduction in the spherical bulbs that they used (see also Crepeau 2007). After making adjustments in the data, he proposed the formula (using his own symbols) $H = AT^4$, which fitted the data quite well. Nevertheless, the temperature used by Dulong and Petit was relatively low, whilst an effective test of the formula would come at higher temperatures, but Stefan found a good confirmation looking at the results given by Tyndall, which gave radiant energy data for platinum wire over a wide temperature range (up to 1,200°C):

> From weak red heat (about 525°C) to complete white heat (about 1200°C) the intensity of radiation increases from 10.4 to 122, thus nearly 12-fold (more precisely 11.7). This observation caused me to take the heat radiation as proportional to the fourth power of the absolute temperature. The ratio of the absolute temperature 273+1200 and 273+525 raised to the fourth power gives 11.6 (Stefan 1879, p. 421).

Stefan's formula was not immediately accepted by the scientific community, until L. Boltzmann did not derive it theoretically in two article published in 1884. In his first article Boltzmann demonstrated from thermodynamic considerations a relationship between the radiation energy density ψ and the radiation pressure f as functions of absolute temperature t:

$$tdf(t) - f(t)dt = \psi(t)dt \tag{8}$$

In his second article, he recalled the Maxwell's formula of the pressure of radiation

$$f = \frac{1}{3}\psi \tag{9}$$

and by inserting Eq. 9 into Eq. 8 he obtained the Stefan's formula:

Fig. 9 A table of Tyndall's measures (1865, p. 28) of heat radiation. The "appearances of spiral" of platinum correspond to different temperatures, e.g. Intense white ≅ 1,200°C, Red ≅ 525°C, Dark ≅ 45–50°C

Appearance of Spiral.	Energy of Obscure Radiation.
Dark	1
Dark, but hotter	3
Dark, but still hotter	5
Dark, but still hotter	10
Feeble red	19
Dull red	25
Red	37
Full red	62
Orange	89
Bright Orange	144
Yellow	202
White	276
Intense White	440

> In my article about a relationship discovered by Bartoli between heat radiation and the second principle, I showed that a relationship exists between the two functions ψ and f : $f = t \int \psi dt/t^2$, whose differential gives: $tdf - fdt = \psi dt$; thus, as from the electromagnetic light theory it follows that $f = 1/3\psi$, one obtains: $t \cdot d\psi/3 = 4\psi \cdot dt/3$ and by integration $\psi = ct^4$, a law which, as well known, was already empirically established by Stefan since longer time and found in good agreement with the observations.[19] (Boltzmann 1884, p. 292)

Moreover, in the same article Boltzmann gave a new demonstration of Eq. 9, in which the radiation was treated in analogy with a gas, and a new derivation of Eq. 8 based on thermodynamic considerations about a thought experiment concerning a transformation applied to a cylinder with a piston containing heat radiation.

Since 1884 the law of the fourth power of the absolute temperature was to become the starting point for all studies concerning thermal radiation, and the net energy loss by radiation from a hot body in a colder environment is considered as the net result of the emitted and absorbed radiation, according to the equation:

$$\frac{dE_{\mathrm{rad}}}{dt} \propto \left(T^4 - T_a^4\right) \tag{10}$$

Consequently, by inserting Eq. 10 in Eq. 7 and supposing a simple law of proportionality for convection $\frac{dE_{\mathrm{con}}}{dt} \propto (T - T_a)$ (which is not obvious, see next section), the cooling processes were studied by considering a first order differential equation like this one below

$$\frac{dT}{dt} = c_1(T - T_a) + c_2\left(T^4 - T_a^4\right) \tag{11}$$

Even if one considers parameters c_1 and c_2 as constant, Eq. 11 does not provide a simple analytical solution, like an exponential or logarithmic function (see O'Sullivan C. T. 1990; Besson 2010b), so the idea of simplicity was waning.

8 Forced and Natural Convection

The heat convection is a very complicated phenomenon. Langmuir (1912, p. 1) wrote:

> The loss of heat by convection from a heated body has apparently always been looked upon as a phenomenon essentially so complicated that a true knowledge of its laws seemed nearly impossible … The phenomenon of the convection of heat at the surface of a body immersed in a cooling fluid is one which does not lend itself readily to mathematical calculation. If the fluid be a gas the variations of the pressure, density, and velocity at different points of the gas so complicate the problem that little progress towards a complete solution has yet been made.

Concerning the convective cooling, it is necessary to distinguish between the case of natural convection, in which the motion of air is only due to the temperature gradient near the hot object, and the case of forced convection, in which a significant current of air or fluid is produced by external causes. In the case of forced convection, the Eq. 3 is well satisfied. In this regard, it is interesting that in his article of 1701 Newton specifies that "the

[19] In the original article in German, Boltzmann wrote: "In meinem Aufsatze über eine von Bartoli entdeckte Beziehung der strahlenden Wärme zum zweiten Hauptsatze habe ich gezeigt, dass sich zwischen den beiden Funktionen ψ und f aus dem zweiten Hauptsatze die Beziehung ergibt $f = t \int \psi dt/t^2$, deren Differential lautet: $tdf - fdt = \psi dt$, wenn also, wie aus der elektromagnetischen Lichttheorie folgt, $f = 1/3\psi$ gesetzt wird, so erhält man: $t \cdot d\psi/3 = 4\psi dt/3$ und durch Integration $\psi = ct^4$, ein Gesetz, welches bekanntlich schon vor längerer Zeit von Stefan empirisch aufgestellt und in guter Übereinstimmung mit den Beobachtungen gefunden wurde".

iron was laid not in a calm air, but in a wind that blew uniformly upon it", Martine (1738) wrote that his law "will not always hold exactly in all circumstances … without a free ventilation of air", and Delaroche (1812, p. 216) reported that "this law is not perfectly exact in still air (cette loi n'est pas parfaitement exacte dans un air tranquille)". In open air and also in ordinary laboratory experiments this condition is often well verified, if the temperature differences are not very high, because a slight stream of air is sufficient to stay in this kind of regime. The case of natural convection is more complicated and depends on the geometry of bodies involved and on the characteristics of the fluid and of its motion. The problem was studied experimentally and theoretically during the last decades of the 19th century (Oberbeck A. 1879; Lorenz L. 1881) in the cases of vertical or horizontal planes in a fluid under the influence of buoyancy and for other simple geometries (cylinder, sphere), leading to a relationship

$$q = \frac{dQ}{dt} \propto (T - T_a)^n \tag{12}$$

where the exponent n is found equal to $5/4 = 1.25$ for a laminar motion of the fluid, whilst in the case of turbulent motion the value $n = 4/3$ is usully considered (see McAdams 1933; Thomas 1980). Researchers in heat transmission, instead of equations like Eq. 12, prefer to use a linear relationship $q = h_c \Delta T$ and then to search for the dependence of the parameter h_c on ΔT and on other quantities, so that the relationships for the cases of laminar and turbulent fluid motion become $h \propto \Delta T^{1/4}$ and $h \propto \Delta T^{1/3}$, respectively (see Fig. 10).

It is interesting that the law found by Dulong and Petit for cooling process by convection in gas (Eq. 6, Sect. 6) agrees quite well with the modern law for natural convection in laminar motion, as they found an exponent $n = 1.233$ very near to that of 1.25. Note that these relationships, which were mainly proposed in the framework of engineering research, according to their authors and users had an epistemological status quite different from that one conceived by earlier scientists studying the cooling law. It is not now a matter of considering general fundamental laws, but rather useful rules having practical meanings and purposes, and even when they were based on theoretical rigorous calculations, they were considered valid only under specific conditions and physical hypotheses.

9 Conclusions

As shown in this historical narrative, the search for a law of cooling was neither linear nor simple. This was because the cooling process embeds two very different phenomena, emission and absorption of thermal radiation and heat transfer by convection and conduction, which have different properties and obey different laws. Moreover these phenomena are not very regular since they depend strongly on the features of the considered materials and situations.

Scientists activated different attitudes in front of the found discrepancies between Newton's law and experiments. The more empiricist scientists preferred to conclude that Newton's cooling law was not entirely true and eventually to look for new different laws (e.g. Martine, Erxleben, Delaroche, Biot, Dulong and Petit). The more theoretical scientists, on the contrary, tried to keep the simple remarkable law, by considering the effect of various disturbance factors (e.g. Richmann, Prévost, Leslie) or by revising the common temperature scales in order to re-obtain the agreement between theory and experiments (e.g. Rumford, Dalton). As shown in Sect. 3, these two problems were already entangled in Newton's paper of 1701: in fact, Newton was mainly interested in defining a thermometric

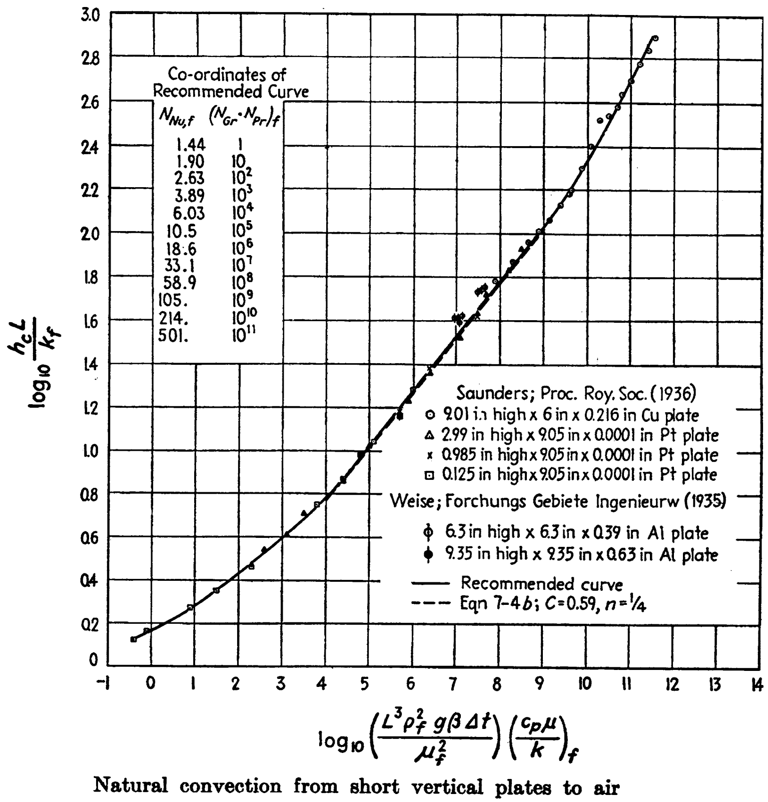

Fig. 10 Natural convection in laminar and turbulent air movement (McAdams 1933, p. 173). Apart from other parameters, on y-axis and x-axis there are, respectively, a quantity proportional to $\log_{10}h_c$, where $h_c = q/\Delta T$, and a quantity proportional to $\log_{10}\Delta T$. In the laminar range, for $4 < x < 9$, data fit with a relationship $h_c \propto \Delta T^{1/4}$; in the turbulent range, for $9 < x < 12$, data fit with a relationship $h_c \propto \Delta T^{1/3}$. In ordinary air ambient, the values $x < 4$ correspond to very low temperature differences (for a plate having $L \sim 1$ m, $\Delta T < 1$°C)

scale for high temperatures and considered his cooling law as a general property of heat, on which to build a temperature scale and which was able to confirm the correctness of linseed oil thermometer rather than vice versa.

Other scientists were searching for a different but unique and general law ("I cannot by any means imagine how heat can be communicated in two ways entirely different from each other", Rumford wrote). Probably, they were impressed by the success of general laws found in mechanics and electricity, without considering that these latter are fundamental physics phenomena whilst heat transmission is the result of complicated processes which are the result of different basic phenomena.

The law of thermal radiation was only discovered in 1879–1884 and until this date scientists tried to establish new laws reproducing the experimental results, but without any real success, also because of the inadequacy of the available temperature scales. In fact, without using an absolute temperature scale, like that introduced by Kelvin in 1848, it was impossible to find a correct law for thermal radiation.

Later on, convection also revealed to be a complicated phenomenon which did not obey a unique simple law, but showed different behaviours according to the cases of forced or natural convection, and to laminar or turbulent fluid movement.

The tenacity of many scientists in keeping Newton's law, despite numerous contrary evidence, beyond the fact that a similar law was very well verified for the heat conduction between solids, seems due to the belief in the simplicity of natural laws and to the spontaneous idea of a proportionality between cause and effect. Many scientists have shown to have a strong confidence in this law, which they considered as a general property or a fundamental principle, rather than a conjecture to be tested by means of experiments. The *discreet charm of the proportionality* and the confidence in the simplicity of natural laws seem to have strongly influenced Newton and many later scientists.

10 Suggestions for Teaching

The above developed history offers the occasion for treating various interesting epistemological and methodological issues, as for example:

– The relationship between experimental data and mathematical models, and the possibility of interpreting the data concerning a same phenomenon by using different empirical models (the under-determination problem).
– The problem of the field of validity of empirical laws, and the possible need of changing the model when the range of values of the involved physical quantities is enlarged.
– The role of philosophical ideas and preferences of scientists in their scientific research, for example, the faith in the simplicity of natural laws or the confidence in the existence of a unique law and a sole cause for an empirical phenomenon.
– The interpretation of discrepancies between empirical laws and experimental data, in order to decide when they can be interpreted as the effect of casual errors and of disturbance factors or as a clue or a proof that the used law is not valid.
– The definition of quantities as temperature, which cannot be defined simply by means of a sentence as "temperature is …" but need a progressive construction starting from thermal sensations towards the choice of thermometric substances and quantities, and the search for a universal property independent from a specific substance.

The history of cooling law can be used in teaching as a unique great *case history* or as the resource from which to extract various shorter *cases histories*, as for example:

– The relationship between the cooling law and the definition of a good temperature scale, from Newton to Dalton.
– The progressive distinction between heat convection and thermal radiation exchange, as radically different phenomena involving different laws and properties.
– The discovery of thermal radiation, the hypothesis of the existence of both heat and cold radiation (Dalla Porta, Rumford …) and the debate on the nature of invisible radiant heat in relation with light, whether they have identical or distinct nature.
– The analysis and reproduction of the Delaroche's historical experiments, as experiments that refute a theory but that do not support a new theory.
– The laws of convection, from Dulong and Petit to the distinction between the laws of forced and free convection.

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