Blackbody Radiation and the Carbon Particle

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Since the days of Kirchhoff, blackbody radiation has been considered to be a universal process, independent of the nature and shape of the emitter. Nonetheless, in promoting this concept, Kirchhoff did require, at the minimum, thermal equilibrium with an enclosure. Recently, the author stated (P.-M. Robitaille, *IEEE Trans. Plasma Sci.*, 2003, v. 31(6), 1263–1267; P.-M. Robitaille, *Progr. in Phys.*, 2006, v. 2, 22–23), that blackbody radiation is not universal and has called for a return to Stewart's law (P.-M. Robitaille, *Progr. in Phys.*, 2008, v. 3, 30–35). In this work, a historical analysis of thermal radiation is presented. It is demonstrated that soot, or lampblack, was the standard for blackbody experiments throughout the 1800s. Furthermore, graphite and carbon black continue to play a central role in the construction of blackbody cavities. The advent of universality is reviewed through the writings of Pierre Prévost, Pierre Louis Dulong, Alexis Thérèse Petit, Jean Baptiste Joseph Fourier, Siméon Denis Poisson, Frédérick Hervé de la Provostaye, Paul Quentin Desain, Balfour Stewart, Gustav Robert Kirchhoff, and Max Karl Ernst Ludwig Planck. These writings illustrate that blackbody radiation, as experimentally produced in cavities and as discussed theoretically, has remained dependent on thermal equilibrium with at least the smallest carbon particle. Finally, Planck's treatment of Kirchhoff's law is examined in detail and the shortcomings of his derivation are outlined. It is shown once again, that universality does not exist. Only Stewart's law of thermal emission, not Kirchhoff's, is fully valid.

1 Introduction

If real knowledge is to be derived from an equation, it is often necessary to reassess the experiments that gave it life. A thorough evaluation of these developments, relative to Planck's equation [1, 2], can be found in Hans Kangro's *Early History of Planck's Radiation Law* [3]. Kangro reminds us of the need to study important milestones relative to physical ideas: "*Only concern with details appearing in sources reveals — often unexpectedly — what has really happened historically, and allowed something to be divined from that history as to 'how it really happened'*" [3; p. 3]. He then sets forth a fascinating account of the history of the law [1, 2] which gave birth to modern physics. Kangro's work [3] is unique for its balance relative to experimental methods and theoretical foundations. It covers, in considerable detail, the period from Kirchhoff to Planck [3]. Hoffmann's work [4] is also valuable since it is short, well written, and reviews the experiments from which Planck formulated his equation [1, 2]. Kuhn's text [5] centers on the theoretical basis of Planck's law. It has been the subject of substantial justified criticism, primarily for advancing that Planck was not the first to introduce quantized processes [6–8]. It is by using such works, and the collection of the scientific literature, that we may revisit the days of Planck [9–16] and judge, with perhaps greater insight than our forefathers, the soundness of the claims on which universality in blackbody radiation rests.

At the onset, it should be emphasized that the validity of Planck's equation [1, 2], as a mathematical solution to the blackbody problem, is not being disputed in any way. The accuracy and merit of Planck's equation [1, 2] has been established beyond question. Nonetheless, two aspects of Planck's formulation are being brought to the forefront. First, that Planck [1, 2, 9–16], Einstein [17, 18], and all of physics have yet to ascribe a direct physical process for the production of blackbody radiation [19]. That is to say, blackbody radiation remains unlinked to a specific and identifiable physical entity (such as the nucleus, the electron, etc). Second, that blackbody radiation is not universal, contrary to what Kirchhoff has concluded [20–22] and Planck believed [1, 2, 9].

I have previously stated that Kirchhoff's law [20–22], and, as a necessary result, Planck's law [1, 2] and blackbody radiation, are not universal in nature [23–25]. Kirchhoff's conclusions hold only for objects in thermal equilibrium with a perfectly absorbing enclosure [23]. Under these conditions, Kirchhoff's cavities act, in essence, as transformers of light [23]. Any object placed within them will give a total emission which is the sum of its own emission and the reflection of the emission from the cavity wall. Consequently, the entire cavity appears black [23, 25]. Outside the restrictions imposed by such a cavity, universality does not exist [23–25]. As for Kirchhoff's law, it holds only under very limited experimental conditions: the walls of these cavities, or the objects they contain, must be perfectly absorbing (see [25] for a proof).

Otherwise, Kirchhoff's law in its widest sense (i.e. universality) does not hold [23]. However, that section of Kirchhoff's law specifically addressing the equality between emissivity and absorptivity at equilibrium is valid. This is Stewart's law [26], not Kirchhoff's [20–22], as will be seen below.

In Planck's words (see [9; §44]), Kirchhoff's law of thermal emission holds that: "*With these assumptions, according to equations (46), (45), and (43), Kirchhoff's law holds,* $E/A = I = d\sigma \cos\theta \, d\Omega \, K_\nu \, d\nu$, *i.e., the ratio of the emissive power to the absorbing power of any body is independent of the nature of the body*". The implications of Kirchhoff's law are best summarized in the words of its originator: "*When a space is surrounded by bodies of the same temperature, and no rays can penetrate through these bodies, every pencil in the interior of the space is so constituted, with respect to its quality and intensity, as if it proceeded from a perfectly black body of the same temperature, and is therefore independent of the nature and form of the bodies, and only determined by the temperature… In the interior of an opaque glowing hollow body of given temperature there is, consequently, always the same brightness whatever its nature may be in other respects*" [22; §17]. Kirchhoff's law states that, for all bodies, the ratio of emissive to absorbing power is a function of only wavelength and temperature, given thermal equilibrium with an enclosure. All that Kirchhoff knew about his universal function, in 1859, was that its value was zero in the visible range at low temperatures, non-zero at high temperatures, and non-zero at the longer wavelengths at all temperatures [3; p. 7]. Planck [1, 2], in 1900, eventually defined the function on the right side of Kirchhoff's law [20–22].

Given thermal equilibrium within an enclosure, Kirchhoff's law [20–22] states that the ability of an object to emit a photon is equal to its ability to absorb one. This aspect of Kirchhoff's work [20–22], properly called Stewart's law [25, 26], is not being questioned. If equilibrium holds, the equality between emissivity and absorptivity has been experimentally demonstrated (see [25] for a complete discussion). It is only when objects are permitted to radiate freely, that equality may fail. Discussions on this issue have been published [27–29]. It has been argued that the equality between absorptivity and emissivity may, in fact, still be applicable for freely radiating bodies, provided that "*the distribution over material states is the equilibrium condition*" [27]. At the same time, it should be realized that, under all non-equilibrium conditions, these laws collapse [20–22, 25, 26].

The vast experimental knowledge relative to thermal emission reveals that virtually all materials fall far short of exhibiting blackbody behavior. Yet, Max Thiesen, a pupil of Kirchhoff, in 1900 stated that: "*we have become accustomed to treat radiation independently of the emitting body*" and therefore, this radiation should "*be designated simply as black radiation*" [3; p. 184]. Experimental reality illustrates that nothing in nature behaves like a blackbody. Kirchhoff's statement that: "*In the interior of an opaque glowing hollow body of given temperature there is, consequently, always the same brightness whatever its nature may be in other respects*" [22; Brace, p. 97] is incorrect without much further consideration. Even graphite and soot produce the desired result only over a limited range of conditions. It remains true that "*different bodies … radiate different kinds of heat*" as published in the first issue of *Nature* in 1869 [30]. An examination of thermal emissivity plots is sufficient to confirm these statements [31]. Not a single object in nature is a blackbody. Hence, it is reasonable to wonder why this concept has so captivated physics. In studying blackbody radiation, it will be demonstrated that radiation within an enclosed body is not necessarily black [25], as Kirchhoff's law erroneously dictates [20–22].

If this subject matter remains important after all these years [1, 2, 20–22], it is because so much of physics, and more specifically astrophysics, is tied to the concept of universality in blackbody radiation. Agassi highlights the importance of Kirchhoff's law for astrophysics: "*Browsing through the literature, one may find an occasional use of Kirchhoff's law in some experimental physics, but the only place where it is treated at all seriously today is in the astrophysical literature*" [32]. As a result, in astrophysics, if a thermal spectrum is observed which displays, or even approximates, a Planckian (or normal) distribution, temperatures are immediately inferred. For this reason, the fall of universality heralds, in the most profound and far-reaching manner, a new dawn in this sub-discipline. Should universality be reconsidered, there are significant consequences for our models of the Sun and relative to the temperatures of the stars [33–35]. The validity of the ~ 3 K microwave background temperature would be questioned [36–41] and with it, perhaps, the entire framework of cosmology [33, 42]. Kirchhoff's law of thermal emission [20–22] may well be the simplest law in physics, but it is clear that, upon its validity, rests the very foundation of modern astrophysics.

Given these facts, it is unusual that Planck has advanced an equation [1, 2] which remains unlinked to any real physical process or object. Sadly, it is somewhat as a result of Kirchhoff's law that Planck remained unable to link his equation to a physical cause. The problem was an extremely serious one for Planck, and the fact that his hands were tied by universality is no more evident than in the helplessness he displays in the following quotation: "*On the contrary, it may just as correctly be said that in all nature there is no process more complicated than the vibrations of black radiation. In particular, these vibrations do not depend in any characteristic manner on the special processes that take place in the centers of emission of the rays, say on the period or the damping of emitting particles; for the normal spectrum is distinguished from all other spectra by the very fact that all individual differences caused by the special nature of the emitting substances are perfectly equalized and effaced. Therefore to attempt to draw conclusions concerning the special properties of the parti-*

cles emitting the rays from the elementary vibrations in the rays of the normal spectrum would be a hopeless undertaking" [9; §111].

Yet, it is primarily universality that makes this task a "hopeless undertaking". Planck, in fact, realized that vibrating atoms, electrons, or particles of some sort, must be responsible for the process of thermal emission. He specifically believed that the answer might be found by studying the electron and devoted much of his life to this topic [5; pp. 133–134, 198–199, 245]. But, unfortunately, Planck never makes the link to a real physical species, and the electron itself is not the proper lone candidate. Planck's belief that the answer lay in electron theory is explicitly contained in his letter to Paul Ehrenfest on July 6, 1905 in which he states: "*But perhaps it is not out of the question to make progress in the following way. If one assumes that resonator oscillations are produced by the motion of electrons...*" [5; p. 132]. Lorenz had already been successful, in deriving the radiation equation for long wavelengths (the Rayleigh-Jeans solution), using the analysis of electrons [5; p. 190].

Surprisingly, the real solution to the blackbody radiation problem has never been discovered [19]. Even Albert Einstein, in 1909, expressed frustration in this regard in a letter to H. A. Lorentz: "*I cherish the hope that you can find the right way, if indeed you find the reasons given in the paper for the untenability of the current foundations to be at all valid. But if you should deem those reasons to be invalid, then your counterarguments could perhaps furnish the key to the real solution of the radiation problem*" [18; p. 105]. The problem was never solved. As late as 1911, Einstein continues to express his frustration to Lorentz: "*I am working on the case of damped resonators; it involves quite a lot of calculation. The case of the electrons in the magnetic field, which I already mentioned in Brussels, is interesting, but not as much as I had thought in Brussels. Electrons in a spatially variable magnetic field are oscillators with variable frequency. If one neglects the radiation, then statistical mechanics yields the distribution law at every location if it is known at one location. If that location is field-free, then Maxwell's distribution holds there; from this one concludes it must hold everywhere. This leads of course to Jean's formula. Nevertheless, to me the thing seems to show that mechanics does not hold even in the case of the electron moving in the magnetic field. I am telling you this as an argument against the view that mechanics ceases to hold at the point where more than two things interact with each other. Anyway, the h-disease looks ever more hopeless*" [18; p. 228]. Blackbody radiation was never linked to a direct physical process. Yet, according to Kuhn, Einstein pointed out that "*not only the vibrations of electrons but also those of charged ions must, contribute to the blackbody problem*" [5; p. 210]. Nonetheless, Kuhn goes on to write that by the early 1910s "*while the nature of Planck's oscillators and of the corresponding emission process remained a mystery, the black-body problem could provide no further clues to physics*" [5; p. 209]. In 1910, Peter Debye, derives Planck's law by quantizing the vibration modes of the electromagnetic field without recourse to oscillators [5; p. 210]. Albert Einstein would soon obtain it using his coefficients [17]. But the nature of the emitter was not identified [19]. In fact, in both cases, physics moved increasingly outside the realm of physical reality and causality.

Astrophysics believes that nothing of known physical origin is needed to obtain a blackbody spectrum. All that is required is a mathematical construct involving photons in thermal equilibrium and this, well outside the confines of a solid enclosure, as demanded by the experimental constraints surrounding blackbody radiation. Astrophysics has no need of the physical lattice, of some physical species vibrating within the confines of a structural physical assembly. But, if a thermal spectrum is to be produced, it is precisely this kind of physical restriction which must exist [19, 23]. However, as long as the idea that blackbody radiation is independent of the nature of the walls prevails, there can be no correction of this situation. It is the very formation of Kirchhoff's law [20–22] which must be brought into question, if any progress is to be made toward linking Planck's equation [1, 2] to the physical world and if astrophysics is to reform the manner in which it treats data. For these reasons, we now embark on the review of the findings which led to the concept of universality. Overwhelming evidence will emerge (see also [23–25]) that this concept is erroneous and should be reconsidered.

2 Experimental production of black radiation

2.1 The 19th century and the lampblack standard

Wedgwood published his delightful analysis on the production of light from heated substances in 1792 [43]. The works are noteworthy and pleasant to read because 1) they define the "state of the art" just prior to the 19th century, 2) they examine a plethora of substances, and 3) they possess wonderful historical descriptions of antecedent works. The experiments contained therein are nothing short of elegant for the period. Even at this time, the emission within a cylinder, either polished or blackened (presumably covered with lampblack), had already gained the attention of science [43]. Wedgwood realized that it did not matter, if heat entered the substance of interest through light, or through friction [43]. Much was already known about thermal radiation, but confusion remained.

The experimental aspects of the science of thermal radiation really began with the release of Leslie's *An Experimental Inquiry into the Nature and Propagation of Heat* [44]. In this classic work, Leslie describes how all objects emit light, but also that they have very different emissive powers, even at the same temperature [44; pp. 81, 90, 110]. This was well understood throughout the 19th century [45, 46]. Leslie opens his work as follows: "*The object I chiefly proposed, was to discover the nature, and ascertain the properties of* *what is termed Radiant Heat. No part of physical science appeared so dark, so dubious and neglected*" [44; p. X]. Ironically, Leslie's last sentence rings somewhat true, even 200 years later.

Using reflectors made of tin, Leslie analyzed radiation emitted from the sides of a cube made of "block tin". At least one side was kept polished, one side was often coated with lampblack, and the other two were used to place miscellaneous substances, like tin foil, colored papers, or pigments [44; p. 8]. In order to maintain a constant temperature, the cubes were filled with water. The key to Leslie's experiments was a differential thermometer. By positioning various faces of the cube towards the reflector and placing his thermometer at the focal point, he soon discovered that polished metals give much less radiant heat than soot. He also realizes that the power to absorb or emit heat is somehow conjoined [44; p. 24]. It is interesting that, in his very first experiment, Leslie examines lampblack. It would become, for the rest of the 1800s, the means by which radiation would be calibrated.

Lampblack, the oxidation product of oil lamps, was not only a suitable material for coating surfaces and generating blackbodies over the course of the 1800s, it rapidly became the standard of radiation. By 1833, the Reverend Baden Powell, whose son was to form the Scouting movement, already writes that: "*all experimenters have usually blackened their thermometer*" [47; p. 276]. In 1848, G. Bird notes how lampblack has become a reference standard in the study of emission [48; p. 516]. Stewart refers repeatedly to lampblack invoking that soot had become the standard by which all radiation was to be measured: "*The reason why lampblack was chosen as the standard is obvious; for, it is known from Leslie's observations, that the radiating power of a surface is proportional to its absorbing power. Lampblack, which absorbs all the rays that fall upon it, and therefore possesses the greatest possible absorbing power, will possess also the greatest possible radiating power*" [26; §4]. He directly refers to lampblack heat [49; p. 191]. His experiments with lampblack are covered below in the context of the theoretical formulation of the law of radiation. Silliman's work is particularly valuable in that it was completed in 1861 [50]. It not only gives a well written and thorough account of the current state of knowledge in heat radiation, but it restates the central role of lampblack: "*Lampblack is the only substance which absorbs all the thermal rays, whatever be the source of heat*" [50; p. 442].

Langley re-emphasizes the extensive use of lampblack in his paper on solar and lunar spectra: "*I may reply that we have lately found an admirable check upon the efficiency of our optical devices in the behavior of that familiar substance lampblack, which all physicists use either on thermometers, thermopiles, or bolometers*" [51]. In 1893, Clerke writes of the "*lampblack standard*" in her tremendous work on the history of Astronomy [52; p. 271]. Tillman, in the 4th edition of his *Elementary Lessons in Heat*, summarizes well the belief that prevailed throughout the 1800s: "*Lampblack is the most perfect absorber and radiator, it being devoid of both reflecting and diffusive power. Its absorbing power is also most nearly independent of the source of heat. It absorbs all rays nearly alike, the luminous as well as the dark ones. Lampblack is accordingly taken as the standard surface of absorption, absorbing in the greatest degree every variety of ray which fall upon it. It is consequently, also , when hot, the typical radiator, giving out the maximum amount of heat which any substance at the same temperature could possibly give out; moreover, it gives out the maximum amount of each kind of heat that can be given out by any body at that temperature*" [46; p. 92]. Tillman does recall Langley's discovery that, in the infrared, lampblack was nearly transparent [51]. In any event, the role of lampblack in thermal radiation was well established by the end of the 19th century.

In his textbook on physics, published for the 7th time in 1920, Watson provides an elaborate description of the use of lampblack in coating both thermometers and surfaces for the study of comparative emission between objects [53]. He describes the lampblack standard as follows: "*Lampblack, although it does not absorb quite the whole of the incident radiation, yet possesses the property of absorbing very nearly, if not quite, the same proportion of the incident radiation whatever the wave-length, and so this substance is taken as a standard*" [53; p. 301].

A review of the blackbody literature for the 19th century reveals that blackbodies were produced either from graphite itself or from objects covered with lampblack (soot) or paints, which contained soot or bone black [54]. That is not to say that other substances were not used. Kangro [3] outlines an array of studies where experimentalists, over a small region of the spectrum, used different materials (platinum black, copper oxide, iron oxide, thorium oxide, etc). Nonetheless, graphite and soot take precedence over all other materials, precisely because their absorbance extends over such a wide range of wavelengths. Conversely, all other materials exhibit disadvantages, either because of their suboptimal emissivity, or due to their limited frequency ranges [31]. There are problems in visualizing the infrared, even with platinum black. Kangro explains: "*They (Lummer and Kurlbaum) changed to a platinum box as being more easily heated electrically and better suited to exact temperature measurement, then they used a platinum roll and finally a platinum cylinder the interior of which was blackened with iron oxide, and also divided by diaphragms the whole enclosed in a large asbestos cylinder*" [3; p. 159]. They also report "*the defective absorption of long wavelengths by Platinum black with which their bolometers were coated*" as a possible source of error [3; p. 159]. Lummer and Kurlbaum made their 1898 cavity from platinum blackened with a mixture of chromium, nickel, and cobalt oxide [4]. Nonetheless, in order to properly visualize the longest wavelengths, the method of residual rays, developed by Rubens, was utilized [4]. These were critical experiments for Planck. Yet, since platinum black could not reach elevated temperatures, in 1903, Lummer and Pringsheim would design a new blackbody with graphite walls [4]. This design has endured, essentially unchanged, until the present day [4].

2.2 The 19th century and the general state of knowledge

In 1833, Powell gave his excellent report on radiant heat [47]. By this time, the amount of radiation was known to be inversely related to conductive power [47; p. 266]. The more an object conducted thermal radiation, the better it acted as a reflector and the worst it was as an emitter/absorber. Based on the experiments of William Ritchie [55], it was also known that the absorptive power of a substance was directly related to its emissive power [47, p. 265]. Prévost's theory on thermal equilibrium, the famous *Theory of Exchanges* [56–58] was understood [47; p. 261]. Herschel's studies with infrared radiation were complete and the blocking action of glass was established [47; pp. 269–272]. While Herschel had discovered infrared radiation in 1800 [59], it was not until Langley, that infrared radiation could be accurately monitored [51]. At the time, Langley observed that lampblack was very nearly transparent to infrared radiation. Using prisms, it was also known that, on opposite sides of the spectrum, there existed "isothermal points" [47; p. 296]. Prisms played an important role in the early classification of the quality of light and heat by separation into colors [47; pp. 291–296]. Interestingly, Powell takes a sidestep relative to liquids and writes in his conclusion: "*In liquids, it has been disputed whether there can be radiation; and they are worse conductors than solids*" [47; p. 300]. Silliman notes that, even at the time of Kirchhoff, there remained some debate as to the relation between absorptive and emissive powers [50; p. 441], with de la Provostaye, Desains, and Melloni highlighting that these were not always equivalent. Given this general state of knowledge during the 19th century, we now move to the most important areas of experimentation, Prévost's *Theory of Exchanges* [56–58] and cavity radiation at thermal equilibrium.

2.3 The 19th century and cavity radiation

Pierre Prévost advanced his powerful *Theory of Exchanges* just as the 19th century came to life [56–58]. In formulating his law, Prévost invokes the enclosure: "*... I will suppose the two portions to be enclosed in an empty space, terminated on all sides by impenetrable walls*" [56; in Brace, p. 5]. He then moves to develop his *Theory of Exchanges* [56–58]. This theory was critical to Kirchhoff's thinking when the concept of universality was formulated [20–22]. As such, it is important to understand how Prévost's theory was viewed, not simply at the time of its formulation, but in the days of Kirchhoff. This knowledge can be gained by examining Balfour Stewart's summary of Prévost's theory. Stewart recounts the central ideas of equilibrium with an enclosure in his *Treatise* [49]. He summarizes Prévost's findings as follows: "*1. If an enclosure be kept at a uniform temperature, any substance surrounded by it on all sides will ultimately attain that temperature. 2. All bodies are constantly giving out radiant heat, at a rate depending upon their substance and temperature, but independent of the substance or temperature of the bodies that surround them. 3. Consequently when a body is kept at uniform temperature it receives back just as much heat as it gives out*" [49; p. 215].

With Prévost, nearly 70 years before Kirchhoff, the real study of cavity radiation began. At the same time, the understanding of cavity radiation really grew near the 1820s. This was when the experimental work of Dulong and Petit [60] with cavities took place. Simultaneously, theoretical studies of heat were being forged by Fourier [61–67] and Poisson [68, 69]. Fourier's works are particularly important in that they represent the most far-reaching theoretical analysis of heat and cavities in this time frame.

The paper by Dulong and Petit [60] is a major milestone in experimental science and it is difficult to do it justice in a brief treatment. Thus, let us concentrate not on the first section dealing with the measurements of temperatures, the dilatation of solids, and the specific heats of materials, but rather on the second section. This section addresses the laws of cooling derived within an enclosure. Of course, Kirchhoff's law of thermal emission [20–22] deals with radiation under equilibrium conditions. Conversely, the results of Dulong and Petit examine a dynamic process [60]. While they do not directly apply, the studies by Dulong and Petit form the experimental basis for the works that follow and are crucial to understanding cavity radiation. Dulong and Petit recognized the importance of distinguishing the effects of gas particles and radiative emission in cooling [60]. By examining the cooling of water and liquids in enclosures of varying shapes, they conclude that the rate of cooling is independent of the shape of the walls of the enclosure, on its size, and on the nature of the liquid [60; p. 245]. Note how this conclusion is reminiscent of Kirchhoff's law [20–22]. Importantly, they observe that the rate of cooling is dependent on the state of the surface of the enclosure [60; p. 245].

Dulong and Petit continue their inquiry into the laws of cooling by building a copper enclosure, the inner surface of which they cover with lampblack [60; p. 247]. They place a thermometer at the center of the enclosure. The outer surface of the thermometer is either silvered or left in its glassy state [60; p. 250]. Using a pump, a balloon (containing various gases of interest), and a barometer attached to the enclosure, they deduce the law of cooling. Dulong and Petit accomplished their goal by varying the gas pressure within the enclosure while monitoring the drop in temperature of the previously heated thermometer. Initially, ignoring the effect of gases and working near vacuum, they quickly realize that the rate of cooling depends on the nature of the thermometer surface, and this even within the blackened cavity [60; p. 260]. The rates of cooling of the two thermometers were proportional to one another, not equal [60; p. 260]. They arrive at a simple general law of cooling that applies to all bodies [60; p. 263]. Finally, by repeating the same experiments with gases at different pressures, they derive a law of cooling with two terms depending on radiation and the effect of the gas. They infer that the first term depends on the nature, the size, and the absolute temperature of the enclosure, while the second term depends only on the characteristics of the gas [60; p. 288]. Dulong and Petit's work is not revisited in a substantial manner until de la Provostaye and Desain publish their Mémoires [70–75].

De la Provostaye and Desain published their second *Memoir on the Radiation of Heat* in 1848, more than 10 years before the formulation of Kirchhoff's law of thermal emission [71]. The authors open their work by stating (all translations from French were made by the author): "*We must know how the quantity of heat emitted by a surface of a determined size depends on its temperature, its proper nature, its state, on the direction of the emission*" [71; p. 358]. They then highlight: "*but that we (scientists) have not, up to this day, introduced into the solution questions of equilibrium and of movement of the heat*" [71; p. 358].

The authors revisit Dulong and Petit's experiments with gases using a half liter cylinder, blackened interiorly with lampblack (*noir de fumée*), in which they can introduce gases. They were never able to confirm the exact relation of Dulong and Petit and, therefore, present a more elaborate equation to describe the law of cooling [71; p. 369]. The paper contains a relevant caveat in that the authors report that it is not always easy to obtain a black surface, even with lampblack paste. They resort to the flame of a lamp to resurface the object of interest in order that its emission becomes truly independent of angle of observation [71; p. 398]. However, the bulk of our concern is relative to their work on the approach towards thermal equilibrium within an enclosure [71; pp. 406–431].

They recall that Fourier has proved: "*1) that within a blackened enclosure without reflective power, equilibrium is established from element to element, 2) that the equilibrium is maintained in the same manner if we restore to one of the elements a reflective power, as long as we admit, in the first instance, that the absorbing and reflecting powers are complementary; and in the second place, that the emissive power is equal to the absorptive power, 3) that the same will hold, if we restore a certain reflective power to all the elements*" [71; p. 406].

De la Provostaye and Desain highlight that the enclosure must be blackened for Fourier's conclusions to hold, but the latter does not always specifically state if his cavity is blackened interiorly. Nonetheless, Fourier's derivations make the assumption that the wall of the enclosure follows Lambert's law [66]. As such, the objects can be viewed as placed within a perfectly absorbing cavity. De la Provostaye and Desain make the point as follows: "*The demonstration supposes, what the author* (Fourier) *seems in fact to have recognized for himself (Annales de Chimie et de Physiques, tome XXVII, page 247* (see [66]) *in his last Memoires, that the radiating body is stripped of all reflective power. It would therefore be not at all general. . .* " [71; p. 408].

De la Provostaye and Desain begin their studies by placing a hypothetical thermometer in a spherical cavity and make no assumptions other than stating that diffuse reflection does not occur. They permit, therefore, that both the cavity and the thermometer can sustain normal reflection and emission. Assuming that reflective power does not depend on the angle of incidence, they permit the rays to travel throughout the cavity and follow the progression of the rays over time, until equilibrium is reached. The authors conclude that the radiation inside such a cavity will not follow Lambert's law [71; p. 414]. The result is important because it directly contradicts Kirchhoff's assertion that the radiation inside all cavities must be black [20–22]. They then restrict their treatment to the consideration of angles below 60° or 70°, in order to reach a simplified form for the laws of cooling.

Like Dulong and Petit [60], de la Provostaye and Desain [70–75] are not concerned exclusively with thermal equilibrium, but rather, they are examining the velocity of cooling, the path to equilibrium. They provide important insight into the problem, as the following excerpt reveals: "*When in an blackened enclosure with an invariable temperature t, we introduce a thermometer at the same temperature and a body either warmer or colder, but maintained always at the same degree T, the thermometer will warm or cool, and, following the reciprocal exchanges of heat, it will attain a final temperature θ, whose value, function of T and t, depends also on the emissive power E' of its surface, of that E of the source, and of their forms, sizes and reciprocal distances*" [71; p. 424].

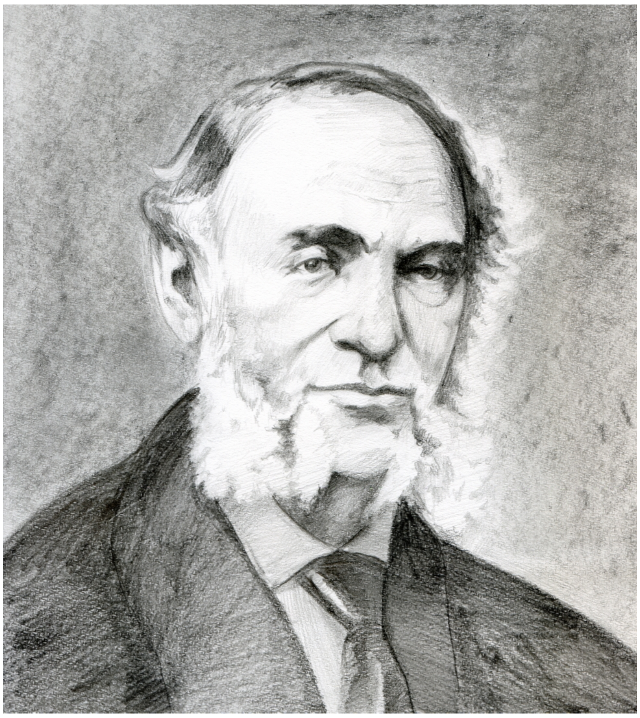
Siegel [76] highlights appropriately that de la Provostaye and Desains defined the emissive power E of a body as a fraction of the radiant emission of the blackbody where $f(t)$ is the emission of the blackbody, and the emission of the body is $Ef(t)$ [74; p. 431]. In contrast, Kirchhoff defines emission simply as E, which, in fact, corresponds to de la Provostaye and Desain's $Ef(t)$ [76]. Consequently, the universal function $f(t)$ is incorporated into Kirchhoff's law, even when it does not seem to be the case [76].

3 Cavity radiation

3.1 The Stewart-Kirchhoff dispute

Balfour Stewart [26] preceded Kirchhoff [20–22] by at least 2 years in the treatment of radiation at thermal equilibrium. Both Kirchhoff and Stewart built on the idea, initially advanced by Prévost [56–58], and expanded upon by Fourier [61–67], Poisson [68, 69], Dulong [60], Petit [60], de la Provostaye [70–75], Desains [70–75], and surely others, that thermal equilibrium existed between objects at the same temperature in the presence of confinement [49; p. 196]. The Stewart-Kirchhoff conflict is one of the darkest moments in

Gustav Robert Kirchhoff (12 March 1824 – 17 October 1887)



Balfour Stewart (1 November 1828 – 19 December 1887)

the history of science and it has been the subject of an excellent review [76]. This public quarrel is worth revisiting, not only because it is a powerful example of how science must not be performed, but also because it is very likely that the dispute between these men, and the international involvement of their collaborators [76] was directly responsible for the persistence of universality. If Stewart and Kirchhoff had better communicated, Kirchhoff might have yielded and the erroneous concept of universality, might have been retracted.

However, nationalistic passions were inflamed to such a measure that reason and scientific truth were moved to secondary positions. The animosity between Germany and British scientists would eventually reach the boiling point when, in 1914, Planck and 92 other learned men signed the *Appeal to the Cultured Peoples of the World* [16; pp. 70–ff]. Planck apparently signed the *Appeal* without examining its contents. Wien, for his part, insisted that British scientists "*appropriated discoveries made in Germany, confused truth and falsehood, argued in bad faith, and . . . that England was the worst enemy of the Reich*" [16; p. 72]. He urged that German scientists avoid, as much as possible, publication in British journals [16; p. 72]. Planck, for his part, refused to sign Wien's manifesto [16; pp. 70–ff]. While the Stewart-Kirchhoff affair cannot bear all the responsibility for these tragic developments, and while other scientific battles also raged [76], it is relatively certain that the situation played an early role in the building of such misconceptions.

The papers from Stewart and Kirchhoff which caused this conflict were all published in *The London, Edindurgh, and Dublin Philosophical Magazine and Journal of Science*. Kirchhoff was able to have access to the English literature, primarily through the assistance of F. Guthrie and Henry E. Roscoe. The latter translated many of Kirchhoff's works into English for *Philosophical Magazine*. Roscoe had studied and published with Bunsen who, in turn, eventually became Kirchhoff's key collaborator.

Stewart opens the discourse by publishing, in 1858, "*An account of some experiments on radiant heat, involving an extension of Prévost's Theory of Exchanges*" [26]. It will be discovered below that, in fact, it is Stewart's work which reached the proper conclusion, not Kirchhoff's [25]. Yet, Stewart's *Account* [26] has been forgotten, in large part, because, unlike Kirchhoff's papers [20–22], it did not arrive at universality as Seigel emphasizes [76].

The battle really begins when F. Guthrie translates Kirchhoff's paper and places it in *Philosophical Magazine* [21], the journal where Stewart's work had appeared just two years earlier. Kirchhoff is rapidly criticized for failure to cite prior work, not only relative to Stewart, but relative to other seminal discoveries [76]. With the aid of Roscoe [77–80], he publishes in 1863, "*Contributions towards the history of spectrum analysis and of the analysis of the solar atmosphere*" [81] in which he seems to dismiss the importance of Stewart's contributions. Kirchhoff writes: "*This proof cannot be a strict one, because experiments which have only taught us concerning more and less, cannot strictly teach us concerning equality*" [81]. Kirchhoff highlights that Stewart is not treating an enclosure in his experiments, but extends his conclusions to these objects [81]. In the end, Kirchhoff's *Contributions* [81] is not impolite... but it is tough.

For Stewart, Kirchhoff's *Contributions* [81] is viewed as an attack which must be immediately countered [82]. Stewart opens his rebuttal by stating: "*In the course of his remarks the learned author has reviewed in a somewhat disparaging manner some researches of mine on radiant heat, in consequence of which I am forced to reply, although very unwillingly, and desiring much to avoid a scientific controversy, especially with Professor Kirchhoff as an opponent*" [82]. In his own defense, Stewart then adds: "*nor did I omit to obtain the best possible experimental verification of my views, or to present this to men of science as the chief feature, grounding theory upon the experiments, rather than deducing the experiments from the theory*" [82]. This powerful charge by Stewart, in the end, forms the entire argument against Kirchhoff's proof [82]. Kirchhoff's results can never be validated by experiments, and Stewart, as an expert in heat radiation, must have recognized this to be the case [82].

Stewart closes his defense as follows: "*Although I preceded Kirchhoff nearly two years in my demonstration, I did not hesitate to acknowledge that his solution had been independently obtained; but, as a general principle, I cannot consent to admit that when a man of science has proved a new law and is followed by another who from the same premises deduces the same conclusions, the latter is justified in depreciating the labours of the former because he conceives that his solution is more complete. Will Kirchhoff himself willingly forego his own claims in favour of any one who shall in the future ages devise (if this be possible) a simpler and more convincing demonstration than that which has been given us by the Hiedelberg Professor? I feel, Sir, that, as an historian of science, you will acknowledge the justice of these remarks, and join me in regretting that one who has so eminently distinguished himself in original investigation should have chosen to superadd to his functions as a discoverer those of a severe and hostile critic upon the labours of those men who have worked at the same subject with himself, and by all of whom he has been treated with the utmost possible consideration*" [82].

The Stewart-Kirchhoff dispute reached such a magnitude that Kirchhoff, it seems, never again publishes in *Philosophical Magazine*, even though Bunsen, for his part, continues to utilize the journal. Stewart remained at a profound disadvantage, as he did not benefit from a relationship similar to that between Kirchhoff, Bunsen, and Roscoe. Roscoe would reprint Kirchhoff's infamous *Contributions* [81] in his *Spectrum Analysis* [80; pp. 115–122]. However, in this version [80; pp. 115–122], all text referring to Stewart has been removed without comment. It is impossible to understand Roscoe's motivation for the attenuated version. Roscoe may have suffered for having translated the letter. Alternatively, Kirchhoff's *Contributions* [81] might not fit in its entirety within the context of the other lectures. In any event, Roscoe's *Spectrum Analysis* is a strange ode to Kirchhoff, which lacks broad scientific review. Regrettably, it seems that Roscoe made no attempt to reconcile the Kirchhoff-Stewart matter through proper and continuing scientific discourse.

In the end, Kirchhoff and Stewart each fell short of the mark. However, Kirchhoff's error was more serious [20–22], since it has theoretical consequences to this day. As for Balfour Stewart, had he presented a better theoretical case [26], the course of physics may have followed a different path. Kirchhoff, for example, correctly highlighted that Stewart's proof should not use the index of refraction, but rather, the square of the index [81]. Stewart conceded the point [76, 82]. For Kirchhoff, Stewart's proof was possibly true, not necessarily true [81]. Siegel elegantly clarified Kirchhoff's concerns [76]. These shortcomings in Stewart's derivation hinder the search for truth. Finally, had nationalistic sentiments not been aroused [76], it might have been easier to resolve the conflict.

3.2 Balfour Stewart

In examining Stewart's writings [26, 49, 82–85], we discover, as Brace highlights, "*the comprehensiveness of his mind and the originality of his genius*" [83; p. 72]. Many of Stewart's [26, 82–85] ideas are contained in his *Elementary Treatise on Heat* [49] and the later reflects his positions at the end of his life. As such, our discussion will begin first with the examination of this work and close with the review of his 1858 and 1859 papers [26, 83].

By the time Stewart writes his *Treatise*, he clearly recognizes that all substances display at least selective absorption of light [49; p. 191]. He comments on the probable identity of heat and light and writes: "*The facts detailed in this chapter all tend to shew that radiant light and heat are only varieties of the same physical agent, and also that when once the spectrum of a luminous object has been obtained, the separation of the different rays from one another is physically complete; so that if we take any region of the visible spectrum, its illuminating and heating effect are caused by precisely the same rays*" [49; p. 195]. He continues: "*Furthermore, we have reason to suppose that the physical distinction between different parts of the spectrum is one of wave length, and that rays of great wave length are in general less refracted than those of small wave length*" [49; p. 196].

Stewart's thoughts with respect to radiation within a cavity are important, not only because they provide us insight into the proper analysis of the enclosures, but also because they clearly outline what was known just prior to Planck. Stewart's comments relative to these experiments are summarized once again in his *Treatise*: "*... let us for our present purpose imagine to ourselves a chamber of the following kind. Let the walls which surround this chamber be kept at a constant temperature, say 100°C, and let them be covered with lampblack — a substance which reflects no heat, or at least* *very little; — also let there be a thermometer in the enclosure. It is well known that this thermometer will ultimately indicate the temperature of the surrounding walls... Suppose that the outside of the bulb of the thermometer of last article is covered with tinfoil, so that its reflecting power is considerable. Now according to the Theory of Exchanges this thermometer is constantly radiating heat towards the lampblack, but it is receiving just as much heat as it radiates. Let us call radiation of lampblack 100, and suppose that 80 of these 100 rays which strike the thermometer are reflected back from its tinfoil surface, while the remaining 20 are absorbed. Since therefore the thermometer is absorbing 20 rays, and since nevertheless its temperature is not rising, it is clear that it must be also radiating 20 rays, that is to say, under such circumstances its absorption and radiation must be equal to one another. If we now suppose the outside of the bulb to be blackened instead of being covered with tinfoil, the thermometer will absorb nearly all the 100 rays that fall upon it, and just as in the previous case, since its temperature is not rising, it must be radiating 100 rays. Thus we see that when covered with tinfoil it only radiated 20 rays, but when blackened it radiates 100. The radiation from a reflecting metallic surface ought therefore, if our theory be true, to be much less than from a blackened one. This has been proved experimentally by Leslie, who shewed that good reflectors of heat are bad radiators. Again, we have seen that in the case of the bulb covered with tinfoil 80 of the 100 rays which fell upon it were reflected back, and we have also seen that 20 were radiated by the bulb. Hence the heat reflected plus the heat radiated by this thermometer in the imaginary enclosure (author underscoring text) will be equal to 100, that is to say, it will be equal to the lampblack radiation from the walls of the enclosure. We may generalize this statement by saying that in an enclosure of constant temperature the heat reflected plus the heat radiated by any substance will be equal to the total lampblack radiation of that temperature, and this will be the case whether the reflecting substance be placed inside the enclosure or whether it form a part of the walls of the enclosure*" [49; pp. 199–201].

Stewart reaches this conclusion for an enclosure whose walls have been covered with lampblack [49]. In that case, the heat inside the enclosure will correspond to that from lampblack, as I have shown [25]. In the pages which follow [49], Stewart goes on to explain that his law holds, in a manner which is independent of the nature of the walls, provided that both radiation and reflection are included. He also illustrates independence relative to wall shape. Importantly, he invokes the work of de la Provostaye and Desains with silver and lampblack to demonstrate that the total radiation inside an enclosure containing a silver surface will also be equal to 100, where 2.2 parts arise from the emission of silver itself and 97 parts from the reflection of lampblack. Stewart realizes that the value of 100 is only achieved in the presence of lampblack. The nature of the wall was immaterial simply because lampblack was always present. In fact, it appears that Stewart was actually contemplating enclosures which contain both reflective surfaces and absorbing ones, as seen in his section 227: "*It has already been stated (Art. 204) that the stream of radiant heat continually proceeding through an enclosure of which the walls are kept at a constant temperature depends only on the temperature of the walls, and not on the nature of the various substances of which they are composed; the only difference being that for metals this stream is composed partly of radiated and partly also of reflected heat, while for lampblack it is composed wholly of radiated heat. This may be expressed by saying that this stream depends upon or is a function of the temperature, and of it alone; but there is the following very important difference between a reflecting and lampblack surface, as representing this stream of radiant heat. It is only when a reflecting surface forms part of a complete enclosure of the same temperature as itself, that the radiated and reflected heat from this surface together represent the whole stream of heat; for if we bring it for a moment into another enclosure of lower temperature, the reflected heat is altered, and although the radiation will for a short time continue nearly constant, yet this radiation will not represent the whole stream of heat due to the temperature of the surface. On the other hand, if a lampblack surface be placed in the above position, since the stream of heat which flows from it is entirely independent of the reflexion due to neighboring bodies, the heat which it radiates when brought for a moment into an enclosure of lower temperature than itself will truly represent the stream of radiant heat due to the temperature of the lampblack*" [49; pp. 221–222]. One can see that reflecting materials provide very different conditions than lampblack within enclosures. That is, within an enclosure under dynamic conditions, objects which are partially or fully reflecting cannot indefinitely support black radiation. They simply emit their own radiation and reflect the heat incident upon their surface. Through this discussion, Stewart demonstrates that thermal equilibrium would be disturbed when a perfect absorber is replaced with a reflector, bringing about dynamic rather than equilibrium conditions. This was an important insight relative to the analysis which I recently provided [25] of Kirchhoff's second proof [21, 22].

In order to examine the velocity of temperature change, Stewart invokes a thin copper globe lined with lampblack: "*Having now considered the law of cooling as representing with much accuracy the quantity of heat given out by a black substance at different temperatures, we come next to the relation between the temperature and the quality or nature of the heat given out. And here we may remark that the laws which connect the radiation of a black body with its temperature, both as regards to the quantity and the quality of the heat given out, hold approximately for bodies of indefinite thickness which are not black, — thus, for instance, they would hold for a metallic surface, which would represent very nearly a lampblack surface, with the radiation diminished a certain number of times. These laws would not, however, hold* *exactly for a white surface, such as chalk; for this substance behaves like lampblack with respect to rays of low temperature, while it is white for rays of high temperature, and the consequence of this will be that its radiation will increase less rapidly than that of a lampblack surface. In like manner, these laws will not hold exactly for coloured surfaces*" [49; p. 230]. Note how these statements are directly contradictory to what Kirchhoff requires. For Stewart, there is no universality and this is a major distinction between his work and that of his adversary [25].

With regards *specifically* to a black surface, Stewart writes (see page 231): "*1. The spectrum of the radiant heat and light given out by a lampblack surface is continuous, embracing rays of all refrangibilities between certain limits on either side… 2. We have reason to think that as the temperature rises, the spectrum of a black substance is extended in the direction of greatest refrangibility, so as to embrace more and more of the violet and photographic rays*" [49; p.231]. Stewart goes on to discuss thin plates of glass and explains how they cannot be compared to lampblack, as their radiation with increasing temperature will be substantially different [49; p. 232].

It is clear that if scientists of the period coated the walls of their enclosure with lampblack, that emission would be independent of the nature of the walls themselves, precisely because lampblack was coating these walls. After all, Stewart fully realizes that silver, for instance, has a total emission much below lampblack [49; pp. 201–206]. Stewart used an enclosure coated with lampblack to arrive at the following laws: "*1. The stream of radiant heat is the same throughout, both in quantity and quality; and while it depends on the temperature it is entirely independent of the materials or shape of the enclosure. 2. This stream is unpolarized. 3. The absorption of a surface in such an enclosure is equal to its radiation and this holds for every kind of heat*" [49; p. 206]. That is how the concept of independence of the nature of the walls entered the literature. Nothing, in fact, was independent. The walls were simply coated with lampblack [49; pp. 201–206]. This was such an obvious part of these experiments, during the 19th century, that it is likely that most scientists, unlike Balfour Stewart, simply neglected to report their common practice. As a result, future generations who followed the theoretical avenues of Kirchhoff, actually came to believe that the nature of the walls was unimportant and the vital role of the soot coating was forgotten.

Stewart's law stated that absorption was equal to radiation for every kind of heat [26, 49, 76, 82]. This was true under equilibrium conditions. However, Kirchhoff objected [81] to this formulation by Stewart [26], since he believed that Stewart had inappropriately extended the results of his experimental finding to include equality whereas proportionality was all that had been proven [76, 81]. In any event, the fact remains that Stewart's conclusion [26, 49, 82], not Kirchhoff's [20–22], was correct. It alone was supported by the experimental findings and, unlike Kirchhoff's law [20–22], made no claims of universality [76].

The central portion of Stewart's proof considers a continuous plate of rock salt positioned between two plates covered with lampblack [26; §12]. The idea is both simple and powerful. Stewart immediately reaches the result that "*the absorption of a plate equals, its radiation, and that for every description of heat*" [26; §19]. Then, Stewart considers radiation internal to a substance: "*Let AB, and BC be two contiguous, equal, and similar plates in the interior of a substance of indefinite extent, kept at a uniform temperature*" [26; §20]. Stewart is invoking the same restriction found for thermal equilibrium with an enclosure. However, he moves to the interior of a body, apparently in order to avoid dealing with surface reflection [82]. Seigel [76] highlights this point. Kirchhoff believes that Stewart has not properly treated the enclosure [81]. The point is weak as Stewart's entire treatment is based on the ideas of Prévost [55–57].

Stewart is clearly working within the confines of Prévost's *Theory of Exchanges* [26, 56–58]. Considering the equilibrium between lampblack and an arbitrary surface at thermal equilibrium, he writes "*… hence the total quantity of heat radiated and reflected which leaves the surface… (is) the same as if the substance had been lampblack, the only difference being, that, in the case of lampblack, all this heat is radiated, whereas in other substances only part is radiated, the remainder being reflected heat*" [26; §31]. He continues: "*Although we have considered only one particular case, yet this is quite sufficient to make the general principle plain. Let us suppose we have an enclosure whose walls are of any shape, or any variety of substances (all at a uniform temperature), the normal or statical condition will be, that the heat radiated and reflected together, which leaves any portion of the surface, shall be equal to the radiated heat which would have left that same portion of the surface, if it had been composed of lampblack… Let us suppose, for instance, that the walls of this enclosure were of polished metal, then only a very small quantity of heat would be radiated; but this heat would be bandied backwards and forwards between the surfaces, until the total amount of radiated and reflected heat together became equal to the radiation of lampblack*" [26; §32]. These passages are quite similar to Kirchhoff's with the distinction that universality is never invoked. Stewart realizes that the lampblack surface within the enclosure is essential.

Stewart's manner of addressing the problem is lacking, as Siegel highlights [76], especially for Kirchhoff [81]. A review of this work [76] provides a sufficient discussion. Stewart advances an initial attempt at the correct solution to the radiation puzzle, but the presentation was not sufficient, at least for his adversary. Surprisingly, in his *Reply* to Kirchhoff in 1863, Stewart seems embarrassed [76] relative to reflection writing: "*I shall only add that it was attempted, as far as possible, to disengage the proof, theoretical and experimental, from the embarrassment of considering surface reflexion*"

[82]. If reflection is neglected, however, almost by definition, the radiation must be black [25]. Consequently, all attempts to address the issue devoid of surface reflection can never yield the proper conclusion relative to the existence of universality. Stewart reaches the proper answer because he does include reflection in his papers [26, 83] and within his *Treatise* [49]. Within an enclosure containing a lampblack surface and another object, he reminds us that "*the reflection plus the radiation of the body at any temperature equals the lampblack radiation at that temperature*" [83; §44]. The proper consideration of reflection is key [25] and though Stewart may have had weaknesses in his presentation, he did ascertain the truth.

3.3 Gustav Kirchhoff and his law

It can be said that Kirchhoff's law of thermal emission [20–22], through its claims of the universal nature of radiation within enclosures, represents one of the most profound dismissals of experimental science in the history of physics. The great mass of experimental evidence speaks against universality of radiation within cavities. Cavity radiation only assumes the normal distribution (i.e. that of the blackbody) when either the walls of the cavity, or at least one of the objects it contains, are perfectly absorbing [23, 25]. In fact, the proof that Kirchhoff's law does not hold, in its universal form, does not require extensive mathematical or experimental arguments, only simple ones [23–25].

Schirrmacher [86] emphasizes that, at the time Planck formulated his law, a solid proof of Kirchhoff's remained absent. Furthermore, he highlights that, as late as 1912, Hilbert was arguing that Kirchhoff's law still lacked proof [86]. Hilbert makes this statement in spite of Planck's attempt to prove the law in his *Theory of Heat Radiation* [9]. Schirrmacher also outlines that nearly all attempts to advance universality were met with a refutation [86; p. 16]. Sadly, these corrections never prevailed.

De la Provostaye was one of the first to offer an analysis of cavity radiation following Kirchhoff, in 1863 [87]. In his work, de la Provostaye deduces that the radiation within a perfectly absorbing cavity must be black [87]. He also infers that a cavity, a portion of whose walls are perfectly absorbing, and which contains an object of arbitrary emittance and reflectance, must also contain normal (or blackbody) radiation [87]. Like Kirchhoff, he attempts to extend his findings to a perfectly reflecting cavity. At first, he concedes that a fully reflecting cavity must be devoid of radiation. At this point, de la Provostaye should have ceased as the question was resolved; but strangely . . . he continues. Prompted perhaps by the quest for Kirchhoff's universality [20–22], he permits radiation to enter the perfectly reflecting cavity and immediately moves to show that such radiation must be black [87]. As a result, de la Provostaye stumbles in a manner quite similar to Kirchhoff and his paper does not, in fact, form a refutation of Kirchhoff's law [87]. De la Provostaye simply objected that Kirchhoff, by introducing perfect reflectors, essentially dictated the result which he sought [86].

De la Provostaye's analysis of cavity radiation is particularly important, because he was an expert in the subject. He had dealt with enclosures on an experimental basis and must have known from the work of his own hands, that Kirchhoff's law could not hold, in its universal form. This is why he presents the second case discussed above where at least a portion of the cavity walls remained perfectly absorbing. De la Provostaye did overreach in his conclusions [87] in a manner not dissimilar from Kirchhoff [20–22].

In any event, de la Provostaye's theoretical objections relative to the absence of a perfectly reflecting mirror was not the central problem for Kirchhoff [25]. While many followed de la Provostaye's initial objection, refutations always seemed to be based on arguments such as perfectly reflecting mirrors do not exist, neither do perfectly diathermanous (or transparent) bodies, or bodies which can only absorb one wavelength. Such idealized substances are utilized in various proofs of Kirchhoff's law [86]. Unfortunately, since Kirchhoff's law is based on a theoretical extension of experimental reality, the fact that idealized objects do not exist is not sufficient to overturn Kirchhoff's position [25]. Hence, the law has prevailed, even though experimental reality is well established against its claims as de la Provostaye and Stewart must have realized.

The only way to refute Kirchhoff's law is to show that some section of its treatment either fails to consider an essential aspect of physical reality or that, through its derivation, Kirchhoff himself violates the thermal equilibrium, which he required as a precondition [25]. Both of these complications have been brought to the forefront [25]. Kirchhoff's law is not valid for two reasons: first, the importance of reflection is not properly included and second, Kirchhoff's model gives rise, under certain conditions, to a violation of thermal equilibrium [25].

Physics is in a difficult position relative to Kirchhoff's law, since the modern relationship between radiation and absorption, under equilibrium conditions, is based upon this work. At the same time, Kirchhoff's claims of universality given enclosure are strictly invalid [25]. A perfect absorber must be present. The only means of rectifying this situation is to finally acknowledge the merit of Stewart's contributions [26, 49, 83].

3.4 Max Planck and cavity radiation

3.4.1 Whence the carbon particle

In the first preface of his book *The Theory of Heat Radiation* Planck mentions that he has "*deviated frequently from the customary methods of treatment, wherever the matter presented or considerations regarding the form of presentation seems to call for it, especially in deriving Kirchhoff's laws. . .*" [9; p. xi]. Yet, when one reads Planck's text, the precise nature of the deviations cannot be ascertained and the origin of the carbon particle remains a mystery. Since the exposition deals with Kirchhoff, one could be led to assume that the idea came from Kirchhoff [23]. Planck, after all, was a strict theoretician. He relied on experimentalists to give him insight in the particle used for the generation of blackbody radiation. Still, we are never told specifically that Kirchhoff invoked the carbon particle [23]. It is certain that, at the time of Kirchhoff, virtually all blackbodies were covered with lampblack. Hence, radiation in a cavity whose inner walls were coated with lampblack would have been observed to be independent of the nature of the walls. This simple observation may well have prompted Kirchhoff and Planck to reach for physically profound statements relative to universality while minimizing the role of soot.

The origin of the carbon particle is surely of historical interest. However, with regards to physics, its existence causes concern, not its historical origin. How a particle of carbon entered the perfectly reflecting cavity and involved the actions of Kirchhoff, Planck, or another scientist, alters nothing relative to the consequences for universality [23]. What remain critical are Kirchhoff's claims that blackbody radiation was independent of the nature of the walls of the cavity, whether these were absorbing, transparent or reflecting to radiation, provided that thermal equilibrium was maintained [21, 22]. Planck's invocation of the carbon particle [9] shatters all these arguments [23, 25] and, as such, it is important to repeat the many words of Planck relative to the need for a tiny piece of carbon.

We begin by recalling how Planck himself was well aware that real blackbodies are formed using lampblack. Nothing here is independent of the nature of the walls: "*Now, since smooth non-reflecting surfaces do not exist … it follows that all approximately black surfaces which may be realized in practice (lampblack, platinum black)…*" [9; §11]. Relative to the carbon particle itself, the first key passages come at the end of Part I: "*Thus far all the laws derived in the preceding sections for diathermanous media hold for a definite frequency, and it is to be kept in mind that a substance may be diathermanous for one color and adiathermanous for another. Hence the radiation of a medium completely enclosed by absolutely reflecting walls is, when thermodynamic equilibrium has been established for all colors for which the medium has a finite coefficient of absorption, always the stable radiation corresponding to the temperature of the medium such as is represented by the emission of a black body. Hence this is briefly called "black" radiation. On the other hand, the intensity of colors for which the medium is diathermanous is not necessarily the stable black radiation, unless the medium is in a state of stationary exchange of radiation with an absorbing substance*" [9; §50]. Planck recognizes that the presence of a perfectly absorbing substance is required within the perfect reflector. If this condition is not fulfilled, Planck reminds us immediately that: "*… in a vacuum bounded by totally reflecting walls any state of radiation may persist*" [9; §51]. As such, Planck is fully aware that the perfect reflector can never produce blackbody radiation in the absence of a perfect absorber. It is not simply a matter of waiting a sufficient amount of time, but rather, the radiation will *persist* in a non-blackbody or arbitrary state. He re-emphasizes this aspect clearly "*Every state of radiation brought about by such a process is perfectly stationary and can continue infinitely long, subject, however, to the condition that no trace of an emitting or absorbing substance exists in the radiation space. For otherwise, according to Sec. 51, the distribution of energy would, in the course of time, change through the releasing action of the substance irreversibly, i.e., with an increase of the total entropy, into the stable distribution corresponding to black radiation*" [9; §91].

Planck soon brings the carbon particle front and center: "*But as soon as an arbitrarily small quantity of matter is introduced into the vacuum, a stationary state of radiation is gradually established. In this the radiation of every color which is appreciably absorbed by the substance has intensity K_ν corresponding to the temperature of the substance and determined by the universal function (42) for $q = c$, the intensity of radiation of the other colors remaining intermediate. If the substance introduced is not diathermanous for any color, e.g., a piece of carbon however small, there exists at the stationary state of radiation in the whole vacuum for all colors the intensity K_ν of black radiation corresponding to the temperature of the substance. The magnitude of K_ν regarded as a function of ν gives the spectral distribution of black radiation in a vacuum, or the so-called normal energy spectrum, which depends on nothing but the temperature. In the normal spectrum, since it is the spectrum of emission of a black body, the intensity of radiation of every color is the largest which a body can emit at that temperature at all*" [9; §51].

"*It is therefore possible to change a perfectly arbitrary radiation, which exists at the start in the evacuated cavity with perfectly reflecting walls under consideration, into black radiation by the introduction of a minute particle of carbon. The characteristic feature of this process is that the heat of the carbon particle may be just as small as we please, compared with the energy of radiation contained in the cavity of arbitrary magnitude. Hence, according to the principle of conservation of energy, the total energy of radiation remains essentially constant during the change that takes place, because the changes in the heat of the carbon particle may be entire neglected, even if its changes in temperature would be finite. Herein the carbon particle exerts only a releasing (auslösend) action. Thereafter the intensities of the pencils of different frequencies originally present and having different frequencies, directions, and different states of polarization change at the expense of one another, corresponding to the passage of the system from a less to a more stable state of radiation or from a state of smaller to a state of larger entropy. From a thermodynamic point of view this process is perfectly analogous, since the time necessary for the process is not essential,* *to the change produced by a minute spark in a quantity of oxy-hydrogen gas or by a small drop of liquid in a quantity of supersaturated vapor. In all these cases the magnitude of the disturbance is exceedingly small and cannot be compared with the magnitude of the energies undergoing the resultant changes, so that in applying the two principles of thermodynamics the cause of the disturbance of equilibrium, viz., the carbon particle, the spark, or the drop, need not be considered. It is always a case of a system passing from a more or less unstable into a more stable state, wherein, according to the first principle of thermodynamics, the energy of the system remains constant, and, according to the second principle, the entropy of the system increases*" [9; §52]. Planck views the carbon particle simply as a catalyst. He does not recognize that it has a vital function as a perfect absorber. This is a critical oversight, as demonstrated in my review of thermal equilibrium within a perfectly reflecting cavity containing a carbon particle [25].

Planck invokes the carbon particle repeatedly throughout his text. This issue is so central to the discussion at hand that all these sections must be brought forth. He writes: "*For the following we imagine a perfectly evacuated hollow cylinder with an absolutely tight-fitting piston free to move in a vertical direction with no friction. A part of the walls of the cylinder, say the rigid bottom, should consist of a black body, which temperature T may be regulated arbitrarily from the outside. The rest of the walls including the inner surface of the piston may be assumed to be totally reflecting. Then, if the piston remains stationary and the temperature, T, constant, the radiation in the vacuum will, after a certain time, assume the character of black radiation (Sec. 50) uniform in all directions. The specific intensity, K, and the volume density, u, depend only on the temperature, T, and are independent of the volume, V, of the vacuum and hence the position of the piston*" [9; §61].

"*Let us also consider a reversible adiabatic process. For this it is necessary not merely that the piston and the mantle but also that the bottom of the cylinder be assumed as completely reflecting, e.g., as white. Then the heat furnished on compression or expansion of the volume of radiation is $Q = 0$ and the energy of radiation changes only by the value pdV of the external work. To insure, however, that in a finite adiabatic process the radiation shall be perfectly stable at every instant, i.e., shall have the character of black radiation, we may assume that inside the evacuated cavity there is a carbon particle of minute size. This particle, which may be assumed to possess an absorbing power differing from zero for all kinds of rays, serves merely to produce stable equilibrium of the radiation in the cavity (Sec. 51 et seq.) and thereby to ensure the reversibility of the process, while its heat contents may be taken as so small compared with the energy of radiation, U, that the addition of heat required for an appreciable temperature change of the particle is perfectly negligible. Then at every instant in the process there exists absolutely stable equilibrium of radiation and the radiation has the temperature of the particle in the cavity. The volume, energy, and entropy of the particle may be entirely neglected*" [9; §68].

"*Let us finally, as a further example, consider a simple case of an irreversible process. Let the cavity of volume V, which is elsewhere enclosed by absolutely reflecting walls, be uniformly filled with black radiation. Now let us make a small hole through any part of the walls, e.g., by opening of a stopcock, so that the radiation may escape into another completely evacuated space, which may also be surrounded by rigid, absolutely reflecting walls. The radiation will at first be of a very irregular character; after some time, however, it will assume a stationary condition and will fill both communicating spaces uniformly, its total volume being, say, V'. The presence of a carbon particle will cause all conditions of black radiation to be satisfied in the new state*" [9; §69].

"*If the process of irreversible adiabatic expansion of the radiation from the volume V to the volume V' takes place as just described with the single difference that there is no carbon particle present in the vacuum, after the stationary state of radiation is established, as will be the case after a certain time on account of the diffuse reflection from the walls of the cavity, the radiation in the new volume V' will not any longer have the character of black radiation, and hence no definite temperature … If a carbon particle is afterwards introduced into the vacuum, absolutely stable equilibrium is established by a second irreversible process, and, the total energy as well as the total volume remaining constant, the radiation assumes the normal energy distribution of black radiation and the entropy increases to the maximum value S'…*" [9; §70].

"*Hence, on subsequent introduction of a carbon particle into the cavity, a finite change of the distribution of energy is obtained, and simultaneously the entropy increases further to the value S' calculated in (82)*" [9; §103].

Throughout *The Theory of Heat Radiation*, Planck invokes the carbon particle as a vital determinant of blackbody radiation. Only in the section of the derivation of Wien's law does he try to minimize the importance of his catalyst. However, in this case, the derivation starts with the presence of a blackbody spectrum *a priori*. One could argue that Planck goes through great pains to explain that he does not need the particle when, in fact, he has already invoked it to produce the radiation he requires as a starting point. The discussion is well worth reading precisely for the number of times that the carbon particle is utilized: "*The starting point of Wien's displacement law is the following theorem. If the black radiation contained in a perfectly evacuated cavity with absolutely reflecting walls is compressed or expanded adiabatically and infinitely slowly, as described above in Sec. 68, the radiation always retains the character of black radiation, even without the presence of a carbon particle. Hence the process takes place in an absolute vacuum just as was calculated in Sec. 68 and the introduction, as a precaution, of a carbon particle is shown to be superfluous. But this is true only in this special* *case, not at all in the case described in Sec. 70...*" [9; §71].

"*Let the completely evacuated hollow cylinder, which is at the start filled with black radiation, be compressed adiabatically and infinitely slowly to a finite fraction of the original volume. If, now, the compression being completed, the radiation were no longer black, there would be no stable thermodynamic equilibrium of the radiation (Sec. 51). It would then be possible to produce a finite change at constant volume and constant total energy of radiation, namely, the change to the absolutely stable state of radiation, which would cause a finite increase of entropy. This change could be brought about by the introduction of a carbon particle, containing a negligible amount of heat as compared with the energy of radiation. This change, of course, refers only to the spectral density of the radiation u_v, whereas the total density of the energy u remains constant. After this has been accomplished, we could, leaving the carbon particle in the space, allow the cylinder to return adiabatically and infinitely slowly to its original volume and then remove the carbon particle. The system will then have passed through a cycle without any external changes remaining. For heat has been neither added nor removed, and the mechanical work done on compression has been regained on expansion, because the latter, like the radiation pressure, depends only on the total density u of the energy of radiation, not on its spectral distribution. Therefore, according to the first principle of thermodynamics, the total energy of radiation is at the end just the same as at the beginning, and hence also the temperature of the black radiation is again the same. The carbon particle and its changes do not enter into the calculation, for its energy and entropy are vanishingly small compared with the corresponding quantities of the system. The process has therefore been reversed in all details; it may be repeated any number of times without any permanent change occurring in nature. This contradicts the assumption, made above, that a finite increase in entropy occurs; for such a finite increase, once having taken place, cannot in any way be completely reversed. Therefore no finite increase in entropy can have been produced by the introduction of the carbon particle in the space of radiation, but the radiation was, before the introduction and always, in the state of stable equilibrium*" [9; §71].

In reading these sections, it is almost as if Planck has entered into a duel with the carbon particle. He tries to minimize its role, even though it is strictly necessary to his success. In any event, as I have shown [25], when Planck (or Kirchhoff) places the carbon particle inside the perfectly reflecting cavity, it is as if the entire cavity had been lined with soot [23]. Thermal equilibrium arguments are powerful, and one of their interesting aspects is that equilibrium does not depend on the extent of the interacting surfaces. This affects only the amount of time required to reach equilibrium, not the nature of the radiation present under equilibrium conditions. Planck's catalyst is a perfect absorber, and therefore, given equilibrium, it controls the entire situation. The carbon particle does not simply lead to a distribution of radiation which would have occurred even in its absence.

3.4.2 Planck's derivation of Kirchhoff's law

Planck's derivation of Kirchhoff's law, as presented in *The Theory of Heat Radiation* [9; pp. 1–45], brings the reader to universality, precisely because reflection is not fully considered. Planck's exposition is elegant and involves two distinct parts. The first deals with radiation within an object [9; §4–26] and is eerily similar to Stewart's formulation [26, 82]. The second examines radiation between "*two different homogeneous isotropic substances contiguous to each other ... and enclosed in a rigid cover impermeable to heat*" [9; §35–39]. By combining these two parts, Planck arrives at a relationship which is independent of the nature of the materials in a manner consistent with his belief in universality.

A cursory examination of this derivation [9; pp. 1–45], suggests that universality must be valid. Planck seems to properly include reflection, at least when discussing the interface between two separate materials [9; §35–39]. He arrives with ease at Kirchhoff's law, $q^2(\varepsilon_v/\alpha_v) = q^2 K_v$, [9; Eq. 42], involving the square of the velocity of propagation, q, the coefficient of emission, ε_v, the coefficient of absorption, α_v, and the universal function, K_v. This relationship simplifies to the familiar form $\varepsilon_v/\alpha_v = K_v$. *The Theory of Heat Radiation* focuses, later, on the definition of the universal function, which of course, is the right side of Planck's famous equation [1, 2]:

$$\frac{\varepsilon_v}{\alpha_v} = \frac{2hv^3}{c^2}\,\frac{1}{e^{hv/kT}-1}\,.$$

Unfortunately, there is a difficulty at the very beginning of the Planck's elucidation of Kirchhoff's law.

In order to arrive at universality [20–22], Planck first examines the equilibrium of radiation within an object. He begins by considering only the emission from a single element $d\tau$ internal to the object and in so doing, is deliberately ignoring reflection. Planck writes, in deriving Eq. (1), that the "*total energy in a range of frequency from v to $v+dv$ emitted in the time dt in the direction of the conical element $d\Omega$ by a volume element $d\tau$*" [9; §6] is equal to $dt\,d\tau\,d\Omega\,dv 2\varepsilon_v$. This will lead directly to Kirchhoff's law. If Planck had properly weighed that the total radiation coming from the element $d\tau$ was equal to the *sum* of its emission and reflection, he would have started with $dt\,d\tau\,d\Omega\,dv\,2(\varepsilon_v+\rho_v)$, which would not lead to universality.

Planck moves on to examine absorption, by imagining two elements $d\sigma$ and $d\sigma'$ which are exchanging radiation within the same substance [9; §20]. Finally, he views the total "*space density of radiation*" in a sphere at the center of which is a volume element, v, receiving radiation from a small surface element, $d\sigma$ [9; §22]. In the end, by combining his results for emission and absorption, Planck demonstrates that within an individual substance, $K_v = \varepsilon_v/\alpha_v$. He writes the powerful conclusion that "*in the interior of a medium in a state of thermodynamic equilibrium the specific intensity of radiation of a certain frequency is equal to the coefficient of emission divided by the coefficient of absorption of the medium for this frequency*" [9; §26]. This was the flaw in his presentation. Had Planck fully included reflection, he would have obtained $K_v = (\varepsilon_v + \rho_v)/(\alpha_v + \rho_v)$.

Yet, this is only the first portion of Planck's walk to universality. In order to extend his deduction to all substances, he must first bring two differing materials in contact with one another. He accomplishes this correctly in §35–38. Properly treating reflection in this case, he is led, as was seen above, to $q^2(\varepsilon_v/\alpha_v) = q^2 K_v$ [9; §38], a statement of universality. The equation becomes completely independent of the nature of the substance. But if Planck had properly executed the first portion of his proof [9; §1–26], he would have been led, for every substance, once again to $K_v = (\varepsilon_v + \rho_v)/(\alpha_v + \rho_v)$.

In hindsight, there are many problems with Planck's derivation. In the first section of his proof, he moves to the inside of an object. He advances that thermal equilibrium is achieved internally, not through conduction and the vibration of atoms, but rather through radiation. While it is true, as Planck believes, that in a state of thermal equilibrium there can be no net conduction, it cannot be said that there can be no conduction. In fact, modern condensed matter physics would surely argue that thermal equilibrium within objects is sustained through conduction, not radiation. Planck like Stewart before him [26, 76, 82] invokes internal radiation as a central component of his proof. He does so precisely to avoid dealing with reflection. He assumes that the volume elements $d\tau$, $d\sigma$ and $d\sigma'$ can sustain only emission, not reflection. In so doing, he predetermines the outcome he seeks, beginning as we have seen with his equation (1) [9; §6].

3.5 Graphite, carbon-black, and the modern age

Graphite and soot, whose commercial forms include carbon black [88] and black carbon [89], continue to be at the center of nearly all blackbody experiments conducted by the National Bureau of Standards and other laboratories. Nonetheless, certain metal blacks [88], namely platinum black and gold black [90–92], have a narrow range of uses as absorbers, especially at long wavelengths. Platinum black is usually prepared by electroplating the surface with platinum. Gold black is particularly interesting as a material. It is produced, by vaporizing the metal onto a substrate until thin gold films are generated. In this sense, the conductivity of gold is being structurally limited and the resulting material is black. In the end, the metal blacks are used primarily in the infrared, and their applications, while important, even in the days following Planck, are somewhat limited.

It remains the overwhelming case that the walls of many cavities are still made from graphite [93–97]. However, if they are made of alternate materials (i.e. brass [98], copper [99], clay [93]), they are either blackened, or smoked with soot [98], or they are covered with black paint [93, 96, 98–104]. Some of these paints have proprietary contents. Nonetheless, it is relatively certain that they all contain the carbon black pigment [105, 106]. For instance, the author has been able to verify that Aeroglaze Z306 and Z302 both contain carbon black (private communication, Robert Hetzell, Lord Corporation, Erie, PA). The same can be ascertained relative to Nextel Velvet coating P/N101-C10 black. It is true that carbon black, with its extremely high carbon content remains the premium black pigment [105]. Graphite and soot (carbon black, black carbon) continue to absolutely dominate all work with experimental blackbodies.

Even fixed point blackbodies [95] which operate at the freezing points of elements such as gold [95], aluminum, zinc, and tin [100] rely either on graphite [107] walls or cavities coated with black paints. In these fixed point blackbodies, the metal freezing/melting point ensures that the entire surface of the emitter can be temporarily maintained at a unique temperature. Interestingly, the metals themselves appear to be relatively innocuous or transparent to emission by the graphitic, or carbon lined, surfaces of the cavity.

There are restrictions on the quality of freezing point blackbody cavities, and these have been outlined by Geist [108]: "*How well the actual radiance approaches the ideal radiance in a given blackbody is often referred to in a qualitative manner as the quality of the blackbody...The principle restriction on the concept of quality...is that it can only be defined for radiation from blackbodies with wall materials whose thermal radiative parameters are independent of wavelength. One important class of freezing point blackbody for which this is not a serious restriction is the class whose cavity walls are constructed from graphite.*" A mathematical treatment of laboratory blackbodies reveals that the production of a cavity whose performance will yield a high quality blackbody is not a trivial task [109].

In any event, it remains clear that whether a blackbody is designed to operate at the freezing point of an element or not, graphite [31, 107], or soot (carbon black [105, 106], or black carbon [89]) continue to dominate this field.

4 Conclusion

Through the exposition of Kirchhoff's law, we have been able to highlight that universality does not hold in cavity radiation. The great bulk of experimental evidence leads to this conclusion. Indeed, if blackbody radiation was universal, there would be no need for the National Bureau of Standards to utilize graphite or soot in order to study such processes. The absence of cavities made of arbitrary walls (without any trace of a perfect absorber) is the best physical proof that universality does not hold. Our laboratories require carbon. Nothing further is needed to shatter Kirchhoff's belief. Nonetheless, even the simplest of mathematical considerations suffices to illustrate the point [25]. Perfectly reflecting cavities, containing no objects, emit no radiation [25]. Perfectly reflecting cavities which contain objects emit radiation which is characteristic of these objects [25]. Thus, if a carbon particle is placed within a perfectly reflecting cavity, the cavity will be black, irrespective of the size of the particle. This is a testament to the power of thermal equilibrium; but if the particle is small, it may take some time to reach this equilibrium. Perfectly absorbing cavities emit normal, or blackbody radiation [23, 25]. In such a cavity, the proper description of the radiation from an arbitrary object is $(\varepsilon_v + \rho_v)/(\alpha_v + \rho_v) = f(T, v)$ [25]. This equation echoes Stewart [26, 49, 82]. Conversely, Kirchhoff incorrectly advanced $\varepsilon_v/\alpha_v = f(T, v)$, leading to universality [20–22].

Consequently, when examining blackbody radiation, we are not dealing with a phenomenon of universal significance. Rather, we are dealing with a physical process which is extremely limited in its applications. Blackbodies are made of solids, and specifically relative to practical blackbodies, they are made of graphite. Nature knows no equivalent as is well demonstrated by the review of thermal emissivity tables [31]. Yet, even in the case of radiation from graphite, the physical cause of the process remains remarkably unknown to modern science. The physical species producing blackbody emission has not been concretely identified [19, 23].

If Planck's law [1, 2] has not been linked to a physical species, it is in part certain that the formulation of Kirchhoff's law [20–22], in its creation of universality, hindered the process. At the same time, there is a fundamental difficulty in providing a complete physical picture relative to thermal emission. This is because the nature of the oscillators, at the heart of thermal radiation, can change depending on the physical nature of the material being examined. The thermal emission profiles of metals are highly affected by their conduction electrons, at least in the sense that their presence acts to prevent emission and favor reflection. For each opaque material, a unique emission profile exists [31] and the answer to these problems will most likely involve the use of computational tools, not simple algebraic solutions. It may well be that entire lattices will have to be represented and processed in digital forms, in order to yield meaningful results. Yet, some thermal emission profiles, which provide Planck-like behavior, such as graphite, the microwave background (only apparent Planckian behavior), and the emission of the photosphere (only apparent Planckian behavior), may be capable of being solved analytically. A solution for one of these is likely to have broad implications for the others. At the same time, only graphite will remain truly Planckian in nature, as it is the only one restricted to a solid. The microwave background and the photosphere produce only apparent Planckian spectra. Since their physical sources are not solids, their relevant internal bonds (if any) are weak, and they support convection processes which alter the validity of the temperatures they report [33].

For graphite or soot

$$\frac{\varepsilon_v}{\alpha_v} \sim \frac{2hv^3}{c^2}\,\frac{1}{e^{hv/kT}-1}$$

as Planck derived [1, 2]. Conversely, for the Sun and the microwave background, we can write that

$$\frac{\varepsilon_v}{\alpha_v} \sim \frac{2hv^3}{c^2}\,\frac{1}{e^{hv/kTapp}-1}\,,$$

where T_{app} is constant. $T_{app} = T/\iota$, where T is the real temperature of the source and ι is a variable, with temperature dependence, whose value is $\sim$1,000 for the photosphere and $\sim$100 for the microwave background [33]. Thus, the real temperature of the photosphere is $\sim$1,000 times higher than the currently accepted temperature [34, 35]. Similarly, the temperature for the source of the microwave background is $\sim$100 times higher than the measured value [33, 39, 40]. These complications arise because we are dealing with non-solids outside the confines of enclosure [23, 33].

If a Planckian approach is used to analyze graphite, the carbon nucleus can be viewed as the mass and the carbon-carbon bond as the spring in an oscillator scenario [1, 2]. If the microwave background is confirmed to be from an oceanic source [33, 36–42], then the oscillators might be entire water molecules, linked through weak hydrogen bonding, vibrating within a fleeting lattice. In this regard, it remains interesting that water can become completely black. This occurs, for instance, when shock waves from nuclear explosions propagate in the sea. For the photosphere, if a hydrogen-based condensed Sun is contemplated [34, 35], the vibration of protons within a fleeting lattice field will have to be considered. In this case, the electrons might simply occupy conduction bands. Nonetheless, the nuclei should be viewed as being confined to a distinct condensed structure which, though fleeting, is being maintained, perhaps only by the need to sustain the quantum mechanical requirements to produce the conduction bands. Physicists versed in the properties of condensed liquid metallic hydrogen might consider these questions. Only the future can reveal how mankind moves forward on linking a given physical species to a center of emission.

With the loss of the universal function, the proper treatment of materials will involve the long recognized fact that the ratio of the emission, e, of an object to its absorption, a, is equal to a complex function dependent on its temperature, T, its nature, N, (its shape, the roughness of its surface, its specific heat, etc.), and the wavelengths of interest, namely $e/a = f(T, N, \lambda)$. Also, e and a, individually, are functions of these parameters, otherwise, as Agassi highlights [30], spectroscopy would be impossible. The aforementioned equation can be simplified to Kirchhoff's formulation $e/a = f(T, \lambda)$ only within a perfectly absorbing enclosure or within an enclosure where a perfect absorber is also present. In all these cases, the object never truly becomes a blackbody. Along with its own emission, it simply reflects radiation in the cavity and appears to hold blackbody properties. It is difficult to envision how this scenario is of any use in modern physics.

The physics community has persisted in upholding Kirchhoff's law of thermal emission even though it has been refuted both recently [23–25] and in the past (see [86] for a discussion of the controversy surrounding Kirchhoff's law). This has occurred despite the fact that graphite and soot are uniquely positioned in all blackbody work with cavities. Nonetheless, some of this hesitance may be due to a certain respect, even reverence, for Kirchhoff and his work. In part, there is also the proximity to Planck himself. Such concerns are unjustified, in that even if Kirchhoff's law loses its universal status, nothing changes relative to Planck's derivation. Planck's law [1, 2] simply becomes devoid of universal significance. It maintains its value relative to the treatment of radiation within perfectly absorbing enclosures and within perfectly reflecting enclosures which contain a perfect absorber. Of course, Planck's equation will no longer extend to simple perfectly reflecting enclosures.

At the same time, the merit of k and h, at the heart of Planck's law, is not altered. The great changes simply involve the interdict of extending the laws of thermal emission [1, 2, 110, 111], without modification, to objects which are not solids [33–42] or enclosed within perfectly absorbing cavities [23–25].

Despite these facts, it may well be that physics remains unwilling to pronounce itself relative to the invalidity of Kirchhoff's treatment until the consequences of the error become so great that society demands retraction. The reassignment of the microwave background to the Earth [33, 36–42] should eventually provide sufficient motivation to act. On that day, a new age in astrophysics will spring forth [34, 35] and we may finally begin to write the long-awaited ode to Balfour Stewart.

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Dedication

This work is dedicated to my sister Hélène, her husband Gervais Bédard, their children (Sonia, Karl, and Geneviève) and their grandchildren (Megan Gagné, Raphaël Turcotte†, and Théogènes Turcotte) on this, their 30th wedding anniversary (May 22, 1978).

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References

1. Planck M. Über eine Verbesserung der Wien'schen Spectralgleichung. *Verhandlungen der Deutschen Physikalischen Gesellschaft*, 1900, v. 2, 202–204. (This is Planck's famous October 19, 1900 lecture. It can also be found in either German, or English, in: Kangro H. Classic papers in physics: Planck's original papers in quantum physics. Taylor & Francis, London, 1972, 3–5 or 35–37.)
2. Planck M. Über das Gesetz der Energieverteilung im Normalspektrum. *Annalen der Physik*, 1901, v. 4, 553–563. (English translation by ter Haar D.: Planck M. On the theory of the energy distribution law in the normal spectrum. The old quantum theory. Pergamon Press, 1967, 82–90; also Planck's December 14, 1900 lecture *Zur Theorie des Gesetzes der Energieverteilung in Normalspectrum*, which stems from this paper, can be found in either German, or English, in: Kangro H. Classic papers in physics: Planck's original papers in quantum physics. Taylor & Francis, London, 1972, 6–14 or 38–45.)
3. Kangro H. Early history of Planck's radiation law. Taylor & Francis Ltd., London, U.K., 1976.
4. Hoffmann D. On the experimental context of Planck's foundation of quantum theory. In: *Revisiting the Quantum Discontinuity*, Max Planck Institute for the History of Science, Preprint 150, 2000, 47–68. http://www.mpiwg-berlin.mpg.de/Preprints/P150.PDF
5. Kuhn T.S. Black-body theory and the quantum discontinuity, 1894–1912. The Univ. of Chicago Press, Chicago, IL, 1978.
6. Buttner J., Renn J., Schemmel M. Exploring the limits of classical physics — Planck, Einstein, and the structure of a scientific revolution. *Studies in History and Philosophy of Modern Physics*, 2003, v. 1(34B), 37–59. (Also in: *Revisiting the Quantum Discontinuity*, Max Planck Institute for the History of Science, Preprint 150, 2000, 23–46. http://www.mpiwg-berlin.mpg.de/Preprints/P150.PDF).
7. Darrigol O. The historians' disagreements over the meaning of Planck's quantum. *Centaurus*, 2001, v. 43(3–4), 219–239. (Also in: *Revisiting the Quantum Discontinuity*, Max Planck Institute for the History of Science, Preprint 150, 2000, 3–21. http://www.mpiwg-berlin.mpg.de/Preprints/P150.PDF)
8. Landsmann N.P. Between classical and quantum. In: *Handbook of Philosophy and Science: Philosophy of Physics*. J. Butterfield, J. Earman, D.M. Gabbay, P. Thagard, J. Woods (eds), Elsevier, Oxford, 2007, v. 2, 417–554.
9. Planck M. The theory of heat radiation. P. Blakiston's Son & Co., Philadelphia, PA, 1914.
10. Planck M. Eight lectures on theoretical physics originally delivered at Columbia University, 1909. Translated by A. P. Wills, Columbia University Press, New York, 1915.
11. Planck M. Treatise on thermodynamics. Dover Publications, Inc., New York, 1905.
12. Planck M. A survey of physical theory. Dover Publications, Inc., New York, 1993. (Also under the title: A survey of physics. Methuen and Co., Ltd., London, 1925.)
13. Planck M. Scientific autobiography and other papers. Philosophical Library, New York, 1949.

14. Planck M. The new science. Meridian Books, Inc. New York, 1959. (This issue contains three essays: 1. Where is science going? 2. The universe in the light of modern physics. 3. The philosophy of physics.)
15. Robitaille P.M.L. Max Karl Ernst Ludwig Planck (1858–1947). *Prog. in Phys.*, 2007, v. 4, 117–120; a bibliographic list of Planck works online: http://bibliothek.bbaw.de/bibliothek/kataloge/literaturnachweise/planck/literatur.pdf
16. Heilbron J. L. The dilemmas of an upright man: Max Planck and the fortunes of German science. Harvard University Press, Cambridge, MA, 1996.
17. Einstein A. Strahlungs-emission und absorption nach der quantentheorie. *Verhandlunger der Deutschen Physikalischen Gesellschaft*, 1916, v. 18, 318; Einstein A. *Phys. Zs.*, 1917, v. 18, 121. (English translation by ter Haar D: Einstein A. On the quantum theory of radiation. The old quantum theory, Pergamon Press, 1967, 167–183.)
18. Einstein A. The collected papers of Albert Einstein (Vol. 5). The Swiss years: Correspondence 1902–1914. Princeton University Press, Princeton, N.J., 1995, 105.
19. Robitaille P.M.L. Comment to the NRC committee on condensed matter and material physics. January 20, 2005. Available online: http://www7.nationalacademies.org/bpa/CMMP2010_Robitaille.pdf
20. Kirchhoff G. Über den Zusammenhang Zwischen Emission und Absorption von Licht und Wärme. *Monatsberichte der Akademie der Wissenschaften zu Berlin*, sessions of Dec. 1859, 1860, 783–787.
21. Kirchhoff G. Über das Verhältnis Zwischen dem Emissionsvermögen und dem Absorptionsvermögen. der Körper für Wärme und Licht. *Poggendorfs Annalen der Physik und Chemie*, 1860, v. 109, 275–301. (English translation by F. Guthrie — Kirchhoff G. On the relation between the radiating and the absorbing powers of different bodies for light and heat. *Phil. Mag.*, 1860, ser. 4, v. 20, 1–21.)
22. Kirchhoff G. On the relation between the emissive and the absorptive power of bodies for light and heat. (Reprinted from *Investigations of the solar spectrum and the spectra of the chemical elements*, 2nd edition, Berlin, Ferd. Dummler's Publishing House, 1866, Gesammelte Abhandlungen, 571–598, Liepzig, 1882 as found in Harper's Scientific Memoirs (J.S. Ames, Ed.) — The laws of radiation and absorption: memoirs of Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen (translated and edited by D.B. Brace), American Book Company, New York, 1901, 73–97.)
23. Robitaille P.M.L. On the validity of Kirchhoff's law of thermal emission. *IEEE Trans. Plasma Sci.*, 2003, v. 31(6), 1263–1267.
24. Robitaille P.M.L. An analysis of universality in blackbody radiation. *Prog. in Phys.*, 2006, v. 2, 22–23 (also in arXiv: physics/0507007).
25. Robitaille P.M.L. A critical analysis of universality and Kirchhoff's Law: a return to Stewart's law of thermal emission. *Prog. in Phys.*, 2008, v. 3, 30–35 (also in arXiv: 0805.1625).
26. Stewart B. An account of some experiments on radiant heat, involving an extension of Prevost's Theory of Exchanges. *Trans. Royal Soc. Edinburgh.*, 1858, v. 22(1), 1–20. (Also found in Harper's Scientific Memoirs (J.S. Ames, Ed.) — The laws of radiation and absorption: memoirs of Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen (translated and edited by D.B. Brace), American Book Company, New York, 1901, 21–50.)
27. Weinstein M.A. On the validity of Kirchhoff's law for a freely radiating body. *Am. J. Phys.*, 1960, v. 28, 123–125.
28. Bates H.P. On the validity of Kirchhoff's law of heat radiation for a body in nonequilibrium environments. *Progress in Optics XIII* (E. Wolf, ed.), North-Holland, 1976.
29. Kraabel B., Shiffmann M., Gravisse P. On the validity of Kirchhoff's law. *Laboratoire de physique et du rayonnement de la lumière*. Available online: http://lprl.org/technology/Kirchhoffs_law.pdf
30. News Physics-Professor Magnus on heat spectra. *Nature*, 1869, v. 1(1), 28.
31. Touloukian Y.S., DeWitt D.P. Thermal radiative properties of nonmetallic solids. Vol. 8 in: *Thermophysical Properties of Matter*, IFI/Plenum, New York, 1972.
32. Agassi J. The Kirchhoff-Planck radiation law. *Science*, 1967, v. 156(3771), 30–37.
33. Robitaille P.M.L. The collapse of the Big Bang and the gaseous Sun. New York Times, March 17, 2002, page A10 (available online: http://thermalphysics.org/pdf/times.pdf).
34. Robitaille P.M.L. The solar photosphere: evidence for condensed matter. *Prog. in Phys.*, 2006, v. 2, 17–21.
35. Robitaille P.M.L. A high temperature liquid plasma model of the Sun. *Prog. in Phys.*, 2007, v. 1, 70–81 (also in arXiv: astro-ph/0410075)
36. Robitaille P.-M. WMAP: A radiological analysis. *Progr. in Phys.*, 2007, v. 1, 3–18.
37. Robitaille, P.M.L. NMR and the age of the Universe. *American Phys. Soc. Centenial Meeting*, BC19.14, March 21, 1999.
38. Robitaille P.M.L. On the origins of the CMB: insight from the COBE, WMAP, and Relikt-1 satellites. *Progr. in Phys.*, 2007, v. 1, 19–23.
39. Robitaille P.M.L. On the Earth microwave background: absorption and scattering by the atmosphere. *Prog. in Phys.*, 2007, v. 3, 3–4.
40. Robitaille P.M.L. The Earth microwave background (EMB), atmospheric scattering and the generation of isotropy. *Progr. in Phys.*, 2008, v. 2, L7–L8.
41. Rabounski D. The relativistic effect of the deviation between the CMB temperatures obtained by the COBE satellite. *Progr. in Phys.*, 2007, v. 1, 24–26.
42. Borissova L., Rabounski D. PLANCK, the satellite: a new experimental test of General Relativity. *Progr. in Phys.*, 2008, v. 2, 3–14.
43. Wedgwood T. Experiments and observations on the production of light from different bodies, by heat and by attrition. *Phil. Trans. Roy. Soc. Lond.*, 1792, v. 82, 28–47; Wedgwood T. Continuation of a paper on the production of light and heat from different bodies. *Phil. Trans. Roy. Soc. Lond.*, 1792, v. 82, 270–282.

44. Leslie J. An experimental inquiry into the nature and propagation of heat. T. Gillet, Salisbury Square, 1804 (online: http://books.google.com).
45. Tillman S.E. Elementary lessons in heat. J.B Lippincott Company, Philadelphia, 1889 (online: http://books.google.com).
46. Tillman S.E. Elementary lessons in heat. 4th Edition, John Wiley & Sons, London, 1911 (online: http://books.google.com).
47. Powell B. Report on the present state of our knowledge of the science of radiant heat. *Report of the first and second meeting of the British Association for the Advancement of Science*, London, 1833, 259–301 (online: http://books.google.com).
48. Bird G. Elements of natural philosophy: being an experimental introduction to the study of the physical sciences. John Churchill, London, 1848 (online: http://books.google.com).
49. Stewart B. An elementary treatise on heat. Clarendon Press, Oxford, U.K., 1888 (online: http://books.google.com).
50. Silliman B. Principles of physics, or, natural philosophy; designed for the use of colleges and schools. H.C. Peck and Theo. Bliss., Philadelphia, 1861, 437–447 (available online: http://books.google.com).
51. Langley S.P. The invisible solar and lunar spectrum. *Am. J. Science*, 1888, v. 36(216), 397–410.
52. Clerke A.M. A popular history of astronomy during the nineteenth century. Adam and Charles Black, London, 1893.
53. Watson W. A textbook of physics: including a collection of examples and questions (7th Ed.). Longmans, Green and Co., New York, 1920 (online: http://books.google.com).
54. Ebonex Corporation. Product history of bone black. (Available online: www.ebonex.com/hist.html).
55. Ritchie W. Experimental illustration of the equality between the radiation and absorbing power of the same surface. *J. Royal Institution*, 1831, v. 2, 305–307.
56. Prévost P. Mémoire sur l'equilibre du feu. *Journal de Physique*, 1791, v. 38, 314–322 (translated in Harper's Scientific Memoirs (J.S. Ames, Ed.) — The Laws of Radiation and Absorption: Memoirs of Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen (translated and edited by D.B. Brace), American Book Company, New York, 1901, 1–13).
57. Prévost P., Du calorique rayonnant. JJ Paschoud, Geneva & Paris 1809 (Sections are translated in Harper's Scientific Memoirs (J.S. Ames, Ed.) — The Laws of Radiation and Absorption: Memoirs of Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen (translated and edited by D.B. Brace), American book company, New York, 1901, 15–20).
58. Prévost P., Recherches physico-mécaniques sur la chaleur. Barde, Manget, Geneve: Mérigot, Paris, 1792.
59. Herschel W. Investigation of the powers of the prismatic colors to heat and illuminate objects; with remarks, that prove the different refrangibility of radiant heat. To which is added, an inquiry into the method of viewing the Sun advantageously, with telescopes of large apertures and high magnifying powers. *Phil. Trans.*, 1800, v. 90, 255–283.
60. Dulong P.L., Petit A.T. Recherches sur la mesure des températures et sur les lois de la communication de la chaleur. *Journal de L'École Polytechnique*, 1820, v. 11(18), 189–294.
61. Fourier J. Mémoire sur la Propagation de la Chaleur dans les Corps Solides. *Nouveau Bulletin des Sciences par la Société Philomathique de Paris*, 1808, v. 1, 112–116.
62. Fourier J. Théorie de la chaleur. *Annales de Chimie et de Physique*, 1816, v. 3, 350–375.
63. Fourier J. Questions sur la théorie-physique de la chaleur rayonnante. *Annales de Chimie et de Physique*, 1817, v. 6, 259–303.
64. Fourier J. Théorie du movement de la chaleur dans les corps solides. *Mémoires de l'Académie Royale des Sciences*, 1819–1820, v. 4, 185–555 (section VII deals with the solution for the spherical enclosure).
65. Fourier J. Théorie du movement de la chaleur dans les corps solides (suite). *Mémoires de l'Académie Royale des Sciences*, 1821–1822, v. 5, 153–246.
66. Fourier J. Résumé théorique des propriétés de la chaleur rayonnante. *Annales de Chimie et de Physique* 1824, v. 27, 236–287.
67. Fourier J. Mémoire sur la théorie analytique de la chaleur. *Mémoires de l'Académie Royale des Sciences*, 1825, v. 8, 581–622.
68. Poisson S.D. Mémoire sur la distribution de la chaleur dans les corps solides. *Journal de l'École Polytechnique. Paris*, 1823, v. 12, 249–403.
69. Poisson S.D. Sur la chaleur rayonnante. *Annales de Chimie et de Physique*, 1824, v. 26, 225–245.
70. de la Provostaye F., Desains P. Mémoire sur le rayonnement de la chaleur. *Annales de Chimie et de Physique*, 1846, v. 16, 337–425.
71. de la Provostaye F., Desains P. Mémoire sur le rayonnement de la chaleur. *Annales de Chimie et de Physique*, 1848, v. 18, 358–431.
72. de la Provostaye F., Desains P. Mémoire sur la détermination du pouvoir absorbant des corps pour la chaleur rayonnante, *Annales de Chimie et de Physique*, 1850, v. 30, 431–443.
73. de la Provostaye F., Desains P. Mémoire sur la reflexion de la chaleur. *Annales de Chimie et de Physique*, 1850, v. 30, 276–286.
74. de la Provostaye F., Desains P. Mémoire sur la polarisation de la chaleur par réfraction simple. *Annales de Chimie et de Physique*, 1850, v. 30, 159–178.
75. de la Provostaye F., Desains P. Mémoire sur la diffusion de la chaleur, *Annales de Chimie et de Physique*, 1852, v. 34, 192–225.
76. Siegel D.M. Balfour Stewart and Gustav Robert Kirchhoff: two independent approaches to Kirchhoff's Law. *Isis*, 1976, v. 67(4), 565–600.
77. Roscoe H.E. Letter from Prof. Kirchhoff on the chemical analysis of the solar atmosphere. *Phil. Mag.*, 1861, v. 21, 185–188.
78. Roscoe H.E. On the solar spectrum, and the spectra of the chemical elements (an extract of Kirchhoff). *Phil. Mag.*, 1862, ser. 4., v. 23, 63–64.
79. Roscoe H.E., Bunsen R. Photochemical researches: the optical and chemical extinction of the chemical rays. *Phil. Mag.*, 1858, ser. 4, v. 15, 230–233.

80. Roscoe H.E. Spectrum analysis. D. Appleton and Co., New York, 1869.
81. Kirchhoff G. Contributions towards the history of spectrum analysis and of the analysis of the solar atmosphere. *Phil. Mag.*, 1863, ser. 4, v. 25, 250–262 (also found in part within Roscoe's Spectrum Analysis, see [80], 115–122).
82. Stewart B. Reply to some remarks by G. Kirchhoff in his paper "On the history of spectrum analysis". *Phil. Mag.*, 1863, ser. 4, v. 25, 354–360.
83. Stewart B. Researches on radiant heat. *Trans. Royal Soc. Edinburgh.*, 1859, v. 22(I), 59–73 (also found in Harper's Scientific Memoirs (J.S. Ames, Ed.) — The laws of radiation and absorption: memoirs of Prévost, Stewart, Kirchhoff, and Kirchhoff and Bunsen (translated and edited by D.B. Brace), American Book Company, New York, 1901, 51–73).
84. Stewart B. On the radiative powers of bodies with regard to the dark or heat-producing rays of the spectrum. *Phil. Mag.*, 1860, ser. 4, v. 20, 169–173.
85. Stewart B. On the light radiated by heated bodies (with supplements added). *Phil. Mag.*, 1860, ser. 4, v. 20, 534–540.
86. Schirrmacher A. Experimenting theory: the proofs of Kirchhoff's radiation law before and after Planck. *Munich Center for the History of Science and Technology*, 2001 (available online: http://www.mzwtg.mwn.de/arbeitspapiere/Schirrmacher_2001_1.pdf).
87. de la Provostaye F. Considérations théoriques sur la chaleur rayonnante. *Annales de Chimie et de Physique*, 1863, v. 67, 5–51.
88. Harris L. The optical properties of metal blacks and carbon blacks. *MIT and The Eppley Foundation for Research, Monograph Ser.*, 1, New Port, R.I., Dec. 1967.
89. Smith D.M., Chughtai A.R. The surface structure and reactivity of black carbon. *Colloids and Surfaces A*, 1995, v. 105, 47–77.
90. Nelms N., Dowson J. Goldblack coating for thermal infrared detectors. *Sensors and Actuators*, 2005, v. A120, 403–407.
91. O'Neill P., Ignatiev A, Doland C. The dependence of optical properties on the structural composition of solar absorbers: Gold black. *Solar Energy*, 1978, v. 21, 465–478.
92. Harris L., McGuiness R.T., Siegel B.M. The preparation and optical properties of gold black. *J. Opt. Soc. Am.*, 1948, v. 38, 582.
93. Murphy A.V., Tsai B.K., Saunders R.D. Comparative calibration of heat flux sensors in two blackbody facilities. *J. Res. Nat. Inst. Stand. Technol.*, 1999, v. 104, 487–494.
94. Murphy A.V., Tsai B.K., Saunders R.D. Transfer calibration validation tests on a heat flux sensor in the 51 mm high-temperature blackbody. *J. Res. Nat. Inst. Stand. Technol.*, 2001, v. 106, 823–831.
95. Navarro N., Bruce S.S., Carol Johnson B., Murphy A.V, Saunders R.D.. Vacuum processing techniques for development of primary standard blackbodies. *J. Res. Nat. Inst. Stand. Technol.*, 1999, v. 104, 253–259.
96. Chahine K., Ballico M., Reizes J., Madadnia J. Optimization of a graphite tube blackbody heater for a thermogage furnace. *Int. J. Thermophys.*, 2008, v. 29, 386–394.
97. Hanssen L.M., Mekhontsev S.N., Zeng J., Prokhorov A.V. Evaluation of blackbody cavity emissivity in the infrared using total integrated scatter measurements. *Int. J. Thermophys.*, 2008, v. 29, 352–369.
98. Birkebak R.C. A technique for measuring spectral emittance. *Rev. Scient. Instr.*, 1972, v. 43 (7), 1027–1030.
99. Fowler J.B. A third generation water bath based blackbody source. *J. Res. Nat. Inst. Stand. Technol.*, 1995, v. 100, 591–599.
100. Schalles M., Bernhard F. Triple-fixed-point blackbody for the calibration of radiation thermometers. *Int. J. Thermophys.*, 2007, v. 28, 2049–2058.
101. Bauch A., Schroder R. Experimental verification of the shift of the cesium hyperfine transition frequency due to black radiation. *Phys. Rev. Let.*, 1997, v. 78(4), 622–625.
102. Best F.A., Revercomb H.E., Knueson R.O., Tobin D.C., Ellington S.D., Werner M.W., Adler D.P., Garcia R.K., Taylor J.K., Ciganovich N.N., Smith W.L., Bingham G.E., Elwell J.D., Scott D.K. The geosynchronous imaging Fourier transform spectrometer (GIFTS) on-board blackbody calibration system. *Proc. Soc. Photo-Optical Instrum. Eng.*, Fourth Int. Asia-Pacific Environmental Remote Sensing Symposium, 8 November, 2004 (available online: http://www.ssec.wisc.edu/gifts/blackbody/bibliography/SPIE_2004_5655-10_Best.pdf)
103. Fowler J.B., Carol Johnson B., Rice J.P., Lorenz S.R. The new cryogenic vacuum chamber and black-body source for infrared calibrations at the NIST's FARCAL facility. *Metrologia*, 1998, v. 35, 323–327.
104. Fowler J.B. An oil-bath-based 293 K to 473 K blackbody source. *J. Res. Natl. Inst. Stand. Technol.*, 1996, v. 101, 629–637.
105. Buxbaum C. Industrial inorganic pigments. 2nd Edition, Wiley-Interscience, New York, 1998
106. International Carbon Black Association. Carbon black user's Guide (online: http://carbon-black.org/user_guide.html).
107. Burchell T.D. Thermal properties and nuclear energy applications. In: *Graphite and Precursors*, Gordon and Breach Science Publishers, Amsterdam, The Netherlands, 2001, 87–109.
108. Geist J. Note on the quality of freezing point blackbodies. *Applied Optics*, 1971, v. 10(9), 2188–2190.
109. Geist J. Theoretical analysis of laboratory blackbodies 1: a generalized integral equation. *Applied Optics*, 1973, v. 12(6), 1325–1330.
110. Wien W. Über die Energieverteilung in Emissionspektrum eines schwarzen Körpers. *Ann. Phys.*, 1896, v. 58, 662–669.
111. Stefan J. Über die Beziehung zwischen der Warmestrahlung und der Temperature. *Sitzungsberichte der mathematischnaturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften, Wien* 1879, v. 79, 391–428.