"The Theory of Heat Radiation" Revisited: A Commentary on the Validity of Kirchhoff's Law of Thermal Emission and Max Planck's Claim of Universality

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Affirming Kirchhoff's Law of thermal emission, Max Planck conferred upon his own equation and its constants, h and k, universal significance. All arbitrary cavities were said to behave as blackbodies. They were thought to contain black, or normal radiation, which depended only upon temperature and frequency of observation, irrespective of the nature of the cavity walls. Today, laboratory blackbodies are specialized, heated devices whose interior walls are lined with highly absorptive surfaces, such as graphite, soot, or other sophisticated materials. Such evidence repeatedly calls into question Kirchhoff's Law, as nothing in the laboratory is independent of the nature of the walls. By focusing on Max Planck's classic text, "*The Theory of Heat Radiation*', it can be demonstrated that the German physicist was unable to properly justify Kirchhoff's Law. At every turn, he was confronted with the fact that materials possess frequency dependent reflectivity and absorptivity, but he often chose to sidestep these realities. He used polarized light to derive Kirchhoff's Law, when it is well known that blackbody radiation is never polarized. Through the use of an element, $d\sigma$, at the bounding surface between two media, he reached the untenable position that arbitrary materials have the same reflective properties. His Eq. 40 ($\rho = \rho'$), constituted a dismissal of experimental reality. It is evident that if one neglects reflection, then all cavities must be black. Unable to ensure that perfectly reflecting cavities can be filled with black radiation, Planck inserted a minute carbon particle, which he qualified as a "catalyst". In fact, it was acting as a perfect absorber, fully able to provide, on its own, the radiation sought. In 1858, Balfour Stewart had outlined that the proper treatment of cavity radiation must include reflection. Yet, Max Planck did not cite the Scottish scientist. He also did not correctly address real materials, especially metals, from which reflectors would be constructed. These shortcomings led to universality, an incorrect conclusion. Arbitrary cavities do not contain black radiation. Kirchhoff's formulation is invalid. As a direct consequence, the constants h and k do not have fundamental meaning and along with "Planck length", "Planck time", "Planck mass", and "Planck temperature", lose the privileged position they once held in physics.

. . . That the absorption of a particle is equal to its radiation, and that for every description of heat.

Balfour Stewart, 1858 [1]

1 Introduction

Seldom does discovery bring forth scientific revolution [2]. In this regard, there can be no greater exception than Max Planck's [3] introduction of the quantum of action, at the beginning of the twentieth century [4, 5]. Within "*The Theory of Heat Radiation*" [5] Planck outlined the ideas which gave life both to this revolution and to the concept that fundamental constants existed which had universal significance throughout nature. The pillars which supported his ideas included: 1) Kirchhoff's Law of thermal emission [6, 7], 2) the irreversability of heat radiation, and 3) the adoption of discrete states.* He utilized Kirchhoff's Law not only to assist in the derivation of his equation, but to infer universality. Max Planck concluded that all cavities, irrespective of experimental evidence, would eventually become filled with blackbody, or normal, radiation. He argued that, if a cavity did not contain black radiation, the cause was a lack of thermal equilibrium, which could be easily rectified by the introduction of a minute particle of carbon [8]. For Max Planck, as for his teacher Gustav Kirchhoff [9], cavity radiation was independent of the nature of the enclosure. In reality, such ideas were not supported by experiment, as arbitrary cavities do not contain black, or normal, radiation. By applying his law to all cavities, the father of quantum theory detached his equation from physical reality itself. In truth, Planck's equation was only valid for laboratory blackbodies constructed from highly

**The Theory of Heat Radiation* is readily available online [5].

absorbing materials.

As a direct consequence, Planck's equation was never linked to a particular physical process and he did not provide physics with a cause for thermal emission. In fact, Kirchhoff's Law prevented him from advancing such a link [8, 10]. The exact nature of the oscillators responsible for thermal radiation could not be identified. Planck emphasized that [5, § 111],

> "...*to attempt to draw conclusions concerning the special properties of the particles emitting the rays from the elementary vibrations in the rays of the normal spectrum would be a hopeless undertaking*".

Studying Planck's classic text, the reader is eventually brought to the equation which governs spectral energy density **u** [5, Eq. 275],

$$\mathbf{u} = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}}-1}, \qquad (1)$$

wherein ν, c, h, k and T represent the frequency of interest, the speed of light,* Planck's constant, Boltzmann's constant, and absolute temperature, respectively. The validity of this equation appears to have been established for blackbodies; namely those specialized heated cavities whose interior is always lined with good absorbers over the frequency of interest, such as graphite, soot, carbon black, or other specialized materials (see [8] and references therein). Max Planck recognized that blackbodies were complex devices, as the data provided for his analysis had been obtained by some of the premier experimentalists in Germany [11–13].

He relied on the work of Rubens and Kurlbaum [11, 13] to secure the data which led to Eq. 1. In this regard, it is important to note the elaborate experimental setup used [11, 13]. It was very far from a simple cavity. These results made use of "the method of residual rays", a process which actually took place well beyond the confines of the cavity [11, 13]. Repeated reflections were supported by using crystals of quartz, fluorite, rocksalt, and sylvine, each for a given frequency of interest [11, 13]. The desired data points could only be obtained with an apparatus used to select the frequency of interest at the proper intensity.

In themselves, such extreme experimental methods confirmed that not all enclosures were filled with black radiation. Surely, if arbitrary cavities contained black radiation, there should have been no need for the use of these sophisticated approaches [13].

In this regard, it is also interesting to note that when faced with non-compliant experimental facts, scientists often invoke the inability to reach thermal equilibrium. This is especially true when cavities are constructed from materials with a low emissivity. Such arguments are not reasonable, given the speed of light and the relative ease of maintaining temperature equilibrium in metallic objects through conductive processes. Laboratory findings do not support Planck's position relative to Kirchhoff's Law.

Clearly, real blackbodies were much more than simple arbitrary cavities [11–13]. Yet, Max Planck believed with certainty in the universality of Kirchhoff's Law. It is this aspect of Planck's work which must be carefully considered. For if it holds true, then Eq. 1 continues to have far-reaching consequences. It can be applied to any thermal spectrum, whether on Earth in the laboratory, or within any astrophysical context, provided of course, that thermal equilibrium can be demonstrated.† However, if Kirchhoff's Law can be shown to be false, then Planck's equation, while still valid for laboratory blackbodies, loses all universal significance [8, 10, 14–19].

It could no longer be used indiscriminately outside of the laboratory, at least if the observer could not ensure that the source of the observed spectrum originated from a known solid. Hence, all applications of Planck's law in astronomy would very likely constitute violations of its required setting. In addition, the fundamental nature of Planck's constant, Boltzmann's constant, and of "Planck length", "Planck time", "Planck mass", and "Planck temperature" would forever be lost. All would have ordinary significance. They would be no more fundamental for physics than the mile versus the kilometer. Everything simply becomes a question of the scale physics chooses to select, rather than scales being imposed upon mankind by nature itself. Consequently, Max Planck's conclusion that Eq. 1 could be applied to all arbitrary cavities had great implications.

It remains an experimental fact that good reflectors, such as silver, are never utilized to construct blackbodies, in direct contradiction to Kirchhoff's claim that cavity radiation is independent of the nature of the walls from which it is comprised. Silver walls would prefer to increase their temperature when confronted with an influx of heat, such as that typically used to drive blackbodies in the laboratory (see [8] and references therein). They would not easily maintain their temperature while building a radiation field within a cavity using reflection (see [19] for a discussion). It has also not been established that cavities constructed from walls of low emissivity can contain Lambertian emission. These are some of the reasons why Kirchhoff's Law fails.

As such, how could this law have survived for so long? In order to answer this question, it is important to revisit both the experimental and theoretical foundations which brought forth Kirchhoff's Law. For this exposition, the journey will begin with the experiments of Balfour Stewart [1] in keeping with the reality that experiments [10], not solely theory, govern the laws of physics. At this point, the work of Gus-

*The United Nations has declared that 2015 will be the "Year of Light".

†There must be radiative equilibrium, no temperature changes, and no conduction or convection taking place in the system of interest.

tav Kirchhoff [6, 7] must be discussed, especially as related to his treatment of reflection. Then, finally, a detailed analysis of Max Planck's derivation of Kirchhoff's Law, as outlined in "*The Theory of Heat Radiation*" [5], will be presented. It will be demonstrated that Planck's derivation suffers, not only with minor problems, but with significant departures from experimental reality.

2 Balfour Stewart and the Law of Equivalence

Balfour Stewart was a Scottish physicist. In 1858, one year before Kirchhoff's Law was proposed [6, 7], Stewart published what can be considered one of the most important works in the history of thermal emission [1]. His analysis of radiation was entirely based on experimental grounds. Hence, he never claimed, as law, principles which could not be proven experimentally [1]. Using actual measurements with material plates made of various substances, Stewart formulated the Law of Equivalence, first in §19 of his work [1],

> "*The absorption of a plate equals its radiation, and that for every description of heat*",

and then in §33 [1],

> *"That the absorption of a particle is equal to its radiation, and that for every description of heat*".

At the same time, he addressed cavity radiation, arriving at a general principle by considering a single theoretical argument. For Stewart, this principle did not rise to the level of a law, precisely because the conclusion had not been experimentally verified. He treated cavity radiation purely from a theoretical perspective and highlighted that the radiation which should come to fill the cavity resulted from the radiation emitted, in addition to the radiation which had been built up by reflection. The arguments advanced, being theoretical and not experimental, prevented him from formally proposing a new law with respect to cavity radiation. Rather, he spoke of a general principle [1],

> "*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 surfaces, until the total amount of radiated and reflected heat together became equal to the radiation of lampblack*".

The problem is that good reflectors do not readily emit radiation. As such, in order to drive the reflection term, one must try to inject heat into the walls of these cavities, while hoping that additional photons will be produced. But, if one attempts to pump heat into their walls using conduction, for instance, the temperature of the walls can simply increase [18, 19]. Nothing dictates that new photons can become available for the buildup of the reflective term, while maintaining the cavity at the same temperature. One can infer that good reflectors can easily move away from the temperature of interest and fall out of thermal equilibrium. As a result, they cannot easily be filled with the desired radiation, even if theoretical arguments suggest otherwise. In the real world, nothing is independent of the nature of the materials utilized.

Stewart recognized that, if one could "drive the radiation" in a cavity made from arbitrary materials, by permitting the slow buildup of reflected radiation, the interior could eventually contain black radiation. The argument was true in theory, but not demonstrated in practice. Stewart remained constrained by experimental evidence. The situation could not be fully extended in the laboratory.

From Balfour Stewart, we gain three important lessons. First, he correctly supplied the Law of Equivalence: *Given thermal equilibrium, the emission of an object is equal to its absorption*. Second, he outlined the principle that cavity radiation can become black, in theory, in the event that the reflective term can be driven. Third, and most importantly, he did not advance a new law of physics without experimental confirmation.

3 Gustav Kirchhoff: Physics from Theory Alone

Soon after Balfour Stewart formulated the Law of Equivalence [1], Gustav Kirchhoff published his law of thermal emission [6, 7]. Almost immediately, the work was translated into English by F. Guthrie [7] and Kirchhoff's paper was then re-published in the same journal where Stewart had presented his law the year before. At this point, a battle ensued between Kirchhoff and Stewart.* The problem centered on Kirchhoff's attempt to dismiss Stewart's priority claims for the Law of Equivalence. Kirchhoff did so by arguing that Stewart had not brought forth sufficient theoretical support for his law. As for Stewart, he believed that the law had been experimentally proven, even if his mathematical treatment might have lacked sophistication.

In any event, Kirchhoff's paper went much beyond the Law of Equivalence. Thus, Stewart, who had outlined the principle that arbitrary cavities might come to hold black radiation, did not insist that this was always true [1]. Conversely, Kirchhoff formulated this conclusion as a law of physics, but

*An excellent treatment of this incident has already been published [20] and one of the authors has also addressed the issue [8].

he did so without recourse to a single experiment. Both of his proofs were theoretical [6, 7].

To begin his investigation, Kirchhoff, in the first section of his text, defined a blackbody as follows [7, § 1]:

> "*This investigation will be much simplified if we imagine the enclosure to be composed, wholly or in great part, of bodies which, for infinitely small thickness, completely absorb all rays which fall upon them*".

Note the emphasis on the absorption by an element of infinitely small thickness. The contrast between Kirchhoff's definition of a blackbody and that adopted by Max Planck was profound [5], as will be discovered below. In any event, in §3 of his classic paper [7] Kirchhoff presented his law as follows,

> "*The ratio between the emissive power and the absorptive power is the same for all bodies at the same temperature*".

In § 13, he explicitly wrote the following form,

$$\frac{E}{A} = e. \tag{2}$$

Kirchhoff eventually set $A = 1$ [7, § 3]. In modern notation,* one could express Kirchhoff's Law as follows:

$$\frac{E_\nu}{\alpha_\nu} = f(T, \nu), \tag{3}$$

where $f(T,\ \nu)$ corresponds to the right side of Eq. 1 above, as first defined by Max Planck [4, 5]. In §17 of his classic paper [7], Kirchhoff outlined his law as follows,

> "*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. The truth of this statement is evident if we consider that a pencil of rays, which has the same form but the reverse direction to that chosen, is completely absorbed by the infinite number of reflections which it successively experiences at the assumed bodies. 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.*"

Relative to Kirchhoff's formulation, three important concerns must be raised. First, the law becomes undefined in the perfect reflector, as $\alpha_\nu = 0$ under that condition. Planck himself recognized this fact [5, § 48], but might not have exercised proper care relative to its consequences. Second, it is clear that Kirchhoff lacked an accurate understanding of what was happening within his cavity, as an "infinite number" of reflections will never amount to absorption. An "infinite number" of reflections does not involve the exchange of energy. Conversely, when absorption occurs, energy is exchanged between the field in the interior of the cavity and the walls. Third, and the most serious objection to Kirchhoff's Law, centers upon his improper treatment of reflection. One of the authors has previously addressed these problems in detail [16].

In brief, within his first proof, Kirchhoff utilized transmissive plates to accomplish the proof, even if blackbody cavities must always be opaque. He addressed transmission by positioning mirrors behind his plates. In so doing, it appeared that Kirchhoff had properly treated reflection, because the mirrors did, in fact, reflect radiation. However, he had dismissed the possibility that the plates considered could possess differing surface reflection [16]. As shall be discovered below, Max Planck committed the same error, when he attempted to formulate Kirchhoff's Law [5, § 36–38]. In his second proof, Kirchhoff unknowingly permitted the cavity to fall out of thermal equilibrium, depending on the order in which operations were performed (see [16] for a detailed presentation).

It is evident that no valid theoretical proof of Kirchhoff's Law existed before Max Planck formulated his law of emission (see [21] for an excellent presentation). In fact, physicists continued to argue about a proper theoretical proof for Kirchhoff's Law until well after Planck's ideas became accepted [21]. Thus, in search of a proof, those provided by Planck, Hilbert, or Pringsheim may be the most relevant [21]. Yet, the proofs provided by Pringsheim and Hilbert have their own shortcomings [21].† It has even been claimed that, by applying Einstein coefficients to arrive at Planck's law, physics could dispense with the proof of Kirchhoff's Law [21]. However, Einstein's derivation utilized the energy density associated with a Wien radiation field, something which could only be found within a blackbody. Surely, Wien had not dispensed with Kirchhoff. In truth, it appears that those concerned with bringing forth a proper proof for Kirchhoff's Law were never able to reach their goal. The problem of finding a valid proof, seems to have simply been displaced by "more exciting physics", as the long sought definitive formulation of Kirchhoff's Law could no longer provide sufficient interest. The entire issue appears to have come to a slow death, without proper resolution.

It is certain that all theoretical proofs of Kirchhoff's Law

*Though Kirchhoff speaks of absorptive power, A, he was actually referring to the unitless absorptivity, α_ν. Conversely, when referring to emissive power, E, he was, in fact, referring to this quantity, even in modern terms. That is, Kirchhoff's "E" has the same units as his "e" and neither is equal to 1. Kirchhoff, stated that "e" was a universal function and believed that its elucidation was a matter of great scientific importance.

†The authors have not been able to locate an analysis of the proof advanced by Max Planck within "*The Theory of Heat Radiation*".

will be found to contain significant misapplications of experimental facts. The inability to provide a proper proof before the days of Planck [21], has not been easily overcome by some new insight into the nature of materials, after Planck. It remains true that all theoretical proofs of Kirchhoff's Law suffer from one or more of the following: 1) an improper treatment of reflection, absorption, or transmission; 2) the invocation of polarized light, when heat radiation is always unpolarized; 3) the use of transmissive materials, when Kirchhoff's Law refers to opaque enclosures; and 4) the existence of hypothetical objects which can have no place in the physical world.

However, the central proof of Kirchhoff's Law must always be the one outlined by Max Planck himself (see [5, § 1–51]), forty years after Kirchhoff [6,7]. For it is upon this proof (see [5, § 1–51]) that Eq. 1 was derived and through which Planck would ultimately attempt to lay the foundation for universality. Hence, it is best to forgo Kirchhoff's own derivations, as the theoretical validity of Kirchhoff's Law now rests with Max Planck [5, § 1–51].

4 Max Planck and Departure from Objective Reality

Having held such reverence for Max Planck over the years [3], it is with some regret that the following sections must be composed, outlining his sidestep of known experimental physics in the derivation of Kirchhoff's Law. Fortunately, in Planck's case, the validity of his equation is preserved, but only within the strict confines of the laboratory blackbody. The quantum of action continues to hold an important place in physics. Yet, the loss of universality cannot be taken lightly, as this aspect of Planck's work was the pinnacle of his career. In fact, above all else, it was universality which Planck sought, believing that he had discovered some great hidden treasure in nature [5, § 164],

> "*Hence it is quite conceivable that at some other time, under changed external conditions, every one of the systems of units which have so far been adopted for use might lose, in part or wholly, its original natural significance. In contrast with this it might be of interest to note that, with the aid of the two constants h and k which appear in the universal law of radiation, we have the means of establishing units of length, mass, time, and temperature, which are independent of special bodies or substances, which necessarily retain their significance for all times and for all environments, terrestrial and human or otherwise, and which may, therefore, be described as 'natural units'* ".

This was an illusion. With the collapse of Kirchhoff's Law, there are no "natural units" and all the constants of physics become a manifestation of the scales which the scientific community chooses.

4.1 Planck's Derivation of Kirchhoff's Law: Part I

Throughout his derivation of Kirchhoff's Law (see [5, § 1–51]), Max Planck sub-optimally addressed reflection, transmission, and absorption. This can be seen in the manner in which he redefined a blackbody, in an array of quotations [5, § 4],

> "*Strictly speaking, the surface of a body never emits rays, but rather it allows part of the rays coming from the interior to pass through. The other part is reflected inward and according as the fraction transmitted is larger or smaller, the surface seems to emit more or less intense radiation*".

For Planck, photons were being released from an object, not because they were emitted by its surface, but simply because they managed to be transmitted throughout, or beyond, its interior. The blackbody became a sieve. Planck stated [5, § 10],

> "*A rough surface having the property of completely transmitting the incident radiation is described as 'black'* ".

Planck continued [5, § 12],

> "*Thus only material particles can absorb heat rays, not elements of surfaces, although sometimes for the sake of brevity, the expression absorbing surfaces is used.*

Note the contrast, with Kirchhoff, which can be repeated for convenience [7, § 1],

> "*This investigation will be much simplified if we imagine the enclosure to be composed, wholly or in great part, of bodies which, for infinitely small thickness, completely absorb all rays which fall upon them*".

Planck acknowledged in a footnote that Kirchhoff considered a blackbody as absorbing over an infinitely thin element. He stated [5, § 10],

> "*In defining a blackbody Kirchhoff also assumes that the absorption of incident rays takes place in a layer 'infinitely thin'. We do not include this in our definition.*"

With his words, Planck redefined the meaning of a blackbody. The step, once again, was vital to his derivation of Kirchhoff's Law, as he relied on transmissive arguments to arrive at its proof. Yet, blackbody radiation relates to opaque objects and this is the first indication that the proofs of Kirchhoff's Law must not be centered on arguments which rely upon transmission. Planck ignored that real surface elements must possess absorption, in apparent contrast with Kirchhoff and without any experimental justification. Planck would expand on his new concept for a blackbody with these words [5, § 10],

"*... the blackbody must have a certain minimum thickness depending on its absorbing power, in order to insure that the rays after passing into the body shall not be able to leave it again at a different point of the surface. The more absorbing a body is, the smaller the value of this minimum thickness, while in the case of bodies with vanishingly small absorbing power only a layer of infinite thickness may be regarded as black.*"

Now, he explicitly stated that bodies which are poor absorbers can still be blackbodies. Yet, we do not make blackbodies from materials which have low absorptivities, because these objects have elevated reflectivities, not because they are not infinite. Planck had neglected the important effects of absorption and reflection when formulating his new definition for a blackbody. This may have consequences throughout physics and astronomy [8, 17, 22].

In the end, Planck's surface elements must be composed of material particles. Since Planck was a theoretical physicist, he cannot work solely in the vacuum of a mathematical world. His derivations and conclusions must be related to physical reality. Yet, Planck's treatment had moved away from laboratory experiments with thin plates. These experiments were vital to the development of blackbody radiation science from the days long before Balfour Stewart [1]. Planck stated that [5, § 12],

"*Whenever absorption takes place, the heat ray passing through the medium under consideration is weakened by a certain fraction of its intensity for every element of path traversed.*"

Clearly, Planck's element at the "bounding surface", as will soon be discovered, was an "element of path traversed". He therefore cannot neglect its absorption. Planck was well aware of this fact [5, § 12]:

"*We shall, however, consider only homogeneous isotropic substances, and shall therefore suppose that α_ν has the same value at all points and in all directions in the medium, and depends on nothing but the frequency ν, the temperature T, and the nature of the medium.*"

and again [5, § 32],

"*Consider then any ray coming from the surface of the medium and directed inward; it must have the same intensity as the opposite ray coming from the interior. A further immediate consequence of this is that the total state of radiation of the medium is the same on the surface as in the interior.*"

Still, at every turn, he attempted to include the effect of transmission, when it had no proper place in the treatment of blackbody radiation, as found in opaque bodies [5, § 14],

"*Let $d\sigma$ be an arbitrarily chosen, infinitely small element of area in the interior of a medium through which radiation passes.*"

Planck thereby included the transmissive properties of the element, $d\sigma$, though he should have avoided such an extension. In the end, his definition of a blackbody was opposed to all that was known in the laboratory. Blackbodies are opaque objects without transmission, by definition. By focusing on transmission, Planck prepared for his move to universality, as will now be discussed in detail.

4.2 Planck's Derivation of Kirchhoff's Law: Part II

In the first section of his text, leading to his Eq. 27, [5, Eq. 27], Planck chose to formally neglect reflection, even though the total energy of the system included those rays which are both emitted/absorbed and those which would have been maintained by driving reflection [18, 19]. Such an approach was suboptimal. Planck must have recognized that the reflective contributions could eventually be canceled. Perhaps, that is why he simply neglected these terms, but the consequence was that insight was lost. In addition, by adopting this approach, Max Planck explicitly prevented the newcomer to the field of thermal radiation from appreciating the crucial importance of reflection within cavity radiation, as Balfour Stewart had well demonstrated [1, 18, 19].

In order to properly follow Planck's work, it is important to recognize his unusual conventions with respect to symbols. Dimensional analysis reveals that even though he spoke of a coefficient of emission (Emissionskoeffizienten) and utilized the symbol now reserved for emissivity, ϵ_ν, he was not referring to the emissivity in this instance. Rather, he was invoking the emissive power, **E**, an entity with units. Conversely, when he spoke of the coefficient of absorption (Absorptionkoeffizienten), α_ν, he was truly referring to the dimensionless absorptivity, as we know it today. Insufficient attention relative to Planck's notation has, in fact, caused one of the authors to revise some of his previous works [18, 19]. Suffice it to note for the time being that, in order to remain consistent with Planck's notation, the following conventions will now be adopted: The symbol ϵ_ν, will represent emissive power, **E**, and not emissivity. The symbols α_ν and ρ_ν will retain their modern meaning and represent dimensionless absorptivity and reflectivity, respectively. This is in keeping with Planck's notation. At the same time, we shall add the symbol η_ν, in order to deal with dimensionless emissivity, since Max Planck had already utilized the needed symbol when expressing emissive power.*

*In § 44, Planck presented Kirchhoff's Law in the following form [5, Eq. 48],

$$\frac{E}{A} = I = d\sigma \cos\theta \, d\Omega \, \mathbf{K}_\nu \, d\nu,$$

where A is actually the unitless absorptivity. Then, in § 45, Planck set $A = 1$. But, he also set, $E = A$. In so doing, he removed dimensionality from the emissive power, E.

At the outset, Max Planck considered the radiation within the interior of an isotropic medium. Inside this material, the total energy emitted from a volume element, $d\tau$, in frequency range of interest, $\nu + d\nu$, and in time, dt, in the direction of a conical element, $d\Omega$, was given by [5, Eq. 1],

$$dt\, d\tau\, d\Omega\, d\nu\, 2\epsilon_\nu, \tag{4}$$

from which Planck immediately surmised, by integrating over all directions and frequencies, that the total energy emitted corresponded to [5, Eq. 2],

$$dt\, d\tau\, 8\pi \int_0^\infty \epsilon_\nu\, d\nu. \tag{5}$$

He then moved to present the same equation, in slightly modified form in § 25 as,

$$dt\, \upsilon\, 8\pi \int_0^\infty \epsilon_\nu\, d\nu, \tag{6}$$

where υ now corresponded to the volume element.

But since this element was contained within the medium of interest, it must also be reflecting radiation from other elements within the medium. That is because, as Balfour Stewart correctly highlighted, the total radiated power measured from a particle is to that portion which was emitted by the particle itself and that portion which it reflected [1]. This reflective component corresponds to the reflection coefficient, ρ_ν, multiplied by the specific intensity, $\mathbf{K}_\nu$, of the radiation leaving the second element, $d\tau'$, positioned at the end of Planck's conical section. The proper form of Eq. 4 [5, Eq. 1], including all of the radiation which leaves the particle, becomes,

$$dt\, d\tau\, d\Omega\, d\nu\, 2\left(\epsilon_\nu + \rho_\nu \mathbf{K}_\nu\right). \tag{7}$$

This expression, rather than leading to Eq. 6, results in,

$$dt\, \upsilon\, 8\pi \int_0^\infty \left(\epsilon_\nu + \rho_\nu \mathbf{K}_\nu\right)\, d\nu. \tag{8}$$

Similarly, Planck characterized the fate of the radiation which strikes the volume element, by including only absorption [5, Eq. 25],

$$dt\, \upsilon\, 8\pi \int_0^\infty \alpha_\nu\, \mathbf{K}_\nu\, d\nu. \tag{9}$$

If however, one considers that the radiation incident to the volume element, υ, can be either absorbed or reflected, then Eq. 9 [5, Eq. 25] becomes,

$$dt\, \upsilon\, 8\pi \int_0^\infty \left(\alpha_\nu + \rho_\nu\right)\, \mathbf{K}_\nu\, d\nu. \tag{10}$$

Equating Eqs. 6 and 9, Planck obtained,

$$dt\, \upsilon\, 8\pi \int_0^\infty \epsilon_\nu\, d\nu = dt\, \upsilon\, 8\pi \int_0^\infty \alpha_\nu\, \mathbf{K}_\nu\, d\nu, \tag{11}$$

which led to [5, Eq. 27],

$$\mathbf{K}_\nu = \frac{\epsilon_\nu}{\alpha_\nu}. \tag{12}$$

Note that in this expression, Planck, like Kirchhoff, removed all consideration of reflection. Conversely, by combining Eqs. 8 and 10, we obtain that,

$$dt\, \upsilon\, 8\pi \int_0^\infty \left(\epsilon_\nu + \rho_\nu \mathbf{K}_\nu\right) d\nu = dt\, \upsilon\, 8\pi \int_0^\infty \left(\alpha_\nu + \rho_\nu\right) \mathbf{K}_\nu d\nu. \tag{13}$$

This expression leads to the following relation,

$$\epsilon_\nu + \rho_\nu \mathbf{K}_\nu = \alpha_\nu \mathbf{K}_\nu + \rho_\nu \mathbf{K}_\nu. \tag{14}$$

If one eliminates the terms involving reflection, this expression immediately leads to Eq. 12 [5, Eq. 27]. More importantly, since $\alpha_\nu + \rho_\nu = 1$ at thermal equilibrium, then a second expression, which retains the importance of reflectivity, is obtained,

$$\epsilon_\nu = \left(1 - \rho_\nu\right) \mathbf{K}_\nu. \tag{15}$$

Since Eq. 14 leads directly to Eq. 12, it now becomes clear why Max Planck chose to ignore the contribution of reflection in his derivation. He adopted a physically incomplete picture, but without mathematical consequence, at least in this instance. It could also be argued that Eq. 12 and Eq. 15 do not differ from one another, since at thermal equilibrium $1 - \rho_\nu = \alpha_\nu$. However, mathematically this is not the case. Eq. 12 becomes undefined when the absorptivity, α_ν, is set to zero. This is precisely what happens in the perfect reflector. Conversely, Eq. 15 is never undefined, as long as the reflective term is retained. As such, the prudent course of action for Max Planck might have been to adopt Eq. 15.

At this point, a trivial observation can be easily advanced. As mentioned above, given thermal equilibrium, then $1 - \rho_\nu = \alpha_\nu$. But at the same time, $\alpha_\nu = \eta_\nu$. This is the Law of Equivalence, first presented by Balfour Stewart [1]. As a result, it can be readily noted that Eq. 15 can be expressed as,

$$\epsilon_\nu = \eta_\nu\, \mathbf{K}_\nu \quad \text{or} \quad \mathbf{E}_\nu = \eta_\nu\, \mathbf{K}_\nu, \tag{16}$$

which is similar to Planck's Eq. 26 [5, Eq. 26]. In this case, $\mathbf{K}_\nu$ is given by Planck [5, Eq. 300]. It corresponds to a Planck function multiplied by the square of the index of refraction of the medium. Note what Eq. 16 is stating: *The emissive power of an arbitrary cavity at thermal equilibrium is equal to the emissivity of the material which makes up the cavity multiplied by a function.* This constitutes a proper and direct contradiction of universality. The nature of the radiation within the cavity becomes dependent on the nature of the cavity itself.

Thus, if the derivation is accomplished while including reflection, additional insight is gained. If given the choice, a function which is never undefined, like Eq. 15, must always take precedence over a function which can become undefined, like Eq. 12. Then, consider Eq. 16. This relationship is important, because, like the form presented by Kirchhoff (Eq. 2) and Planck (Eq. 12), it is devoid of the consideration of reflection. But, when confronted with Eq. 16, it is impossible to conclude that arbitrary cavities contain black radiation.

In this initial treatment, Planck had not yet formally introduced Kirchhoff's Law. In order to accomplish this feat, he had to explore more than one medium at a time. Nonetheless, in this initial exposition of Planck's derivation, an important lesson has been learned: it is vital to recognize that the manner in which a result is presented can have a great deal of influence on its interpretation. Nowhere is this more applicable than in Planck's formal presentation of Kirchhoff's Law, as he leads the reader from Eq. 27 to Eq. 42 [5, Eq. 27–42]. It is here that Planck sidestepped experimental reality.

4.3 Planck's Derivation of Kirchhoff's Law: Part III

Heat radiation is unpolarized, by definition [23, p. 450]. In § 4 of *The Theory of Heat Radiation* [5], Planck considered a homogeneous isotropic emitting substance. Any volume element of such a material necessarily emits heat radiation uniformly in all directions. In § 5 Planck admitted that homogeneous isotropic media emit only natural or normal, i.e. unpolarized, radiation [5, § 5]:

> "*Since the medium was assumed to be isotropic the emitted rays are unpolarized.*"

This statement alone, was sufficient to counter all of the arguments which Planck later utilized to arrive at Kirchhoff's Law [5, Eq. 42]. That is because the important sections of Planck's derivation, namely § 35–37 make use of plane-polarized light. These steps were detached from experimental reality, relative to heat radiation [5, § 35],

> "*Let the specific intensity of radiation of frequency ν polarized in an arbitrary plane be $\mathbf{K}_\nu$ in the first substance … and $\mathbf{K'}_\nu$ in the second substance …*"

Planck also stated [5, § 36],

> "*… we have for the monochromatic plane-polarized radiation…*"

As such, to prepare for his use of polarized light in later sections, Planck resolved, in § 17, the radiation into its two polarized components. However, note that he could have arrived at Eq. 12 [5, Eq. 27] without ever resolving the radiation into its components. Nonetheless, his proof for the universality of Kirchhoff's Law [5, Eqs. 27–42] depended upon the use of polarized light [5, § 35–37]. Planck utilized polarized light in an isotropic medium, even though he had already recognized in § 5, that such radiation must be unpolarized. He clearly remarked in § 107,

> "*For a plane wave, even though it be periodic with a wave lying within the optical or thermal spectrum, can never be interpreted as heat radiation.*"

In order to arrive at Kirchhoff's Law, in § 35–37, Planck placed two different homogeneous isotropic media in contact with one another, as illustrated in Figure 1. The whole system was "*enclosed by a rigid cover impermeable to heat*". He then considered two arbitrary plane-polarized waves, one from each of the media, incident upon an element of area $d\sigma$ at the *bounding surface* of the two media. It can be seen in § 38, that Planck initially endowed this element with differing reflectivities, depending on whether the incident rays approached from medium 1 or medium 2. For Planck, both waves underwent reflection and refraction. He sidestepped that the ray could be absorbed, a decision vital to his ability to derive Kirchhoff's law [5, § 9],

> "*… a discontinuous change in both the direction and the intensity of a ray occurs when it reaches the boundary of a medium and meets the surface of a second medium. The latter, like the former, will be assumed to be homogeneous and isotropic. In this case, the ray is in general partly reflected and partly transmitted.*"

Planck invoked a small element of area $d\sigma$ at the boundary of his two contiguous media. This element had no consistent meaning in Planck's analysis. First, in § 36 and § 42 Planck placed this element in the *bounding surface* and, in so doing, allocated it properties characteristic of medium 1 on one half and medium 2 on the other. However, in § 43, he placed the element firmly within the surface of medium 2,

> "*… and falls on the surface element $d\sigma$ of the second medium.*"

Note that Planck had already introduced three causes for objection. First, what exactly was the location of $d\sigma$? In reality it must rest in one of the two media. Second, Planck neglected the fact that real materials can possess finite and differing absorptivities. While these can be ignored within the medium when treating propagation, because of the counter effect of emissivity, they cannot be dismissed at the boundary. Third, the simplest means of nullifying the proof leading to Planck's Eq. 42, is to use a perfect reflector as the second medium. In that case, a refractive wave could never enter the second medium and Planck's proof fails. The same objection can be raised using any fully opaque material for the second medium (i.e. $\alpha_\nu + \rho_\nu = 1$), as for all of them, τ_ν=0. This would include many materials typically used to construct real blackbodies in the laboratory. Consequently, for his proof of Kirchhoff's Law, Planck eliminated, by definition, virtually all materials of interest. In fact, he even excluded the perfect reflector, the very material he had chosen to consider throughout much of his text [5].

In § 36 Planck considered a monochromatic plane-polarized ray of frequency ν, emitted in time dt. In order to

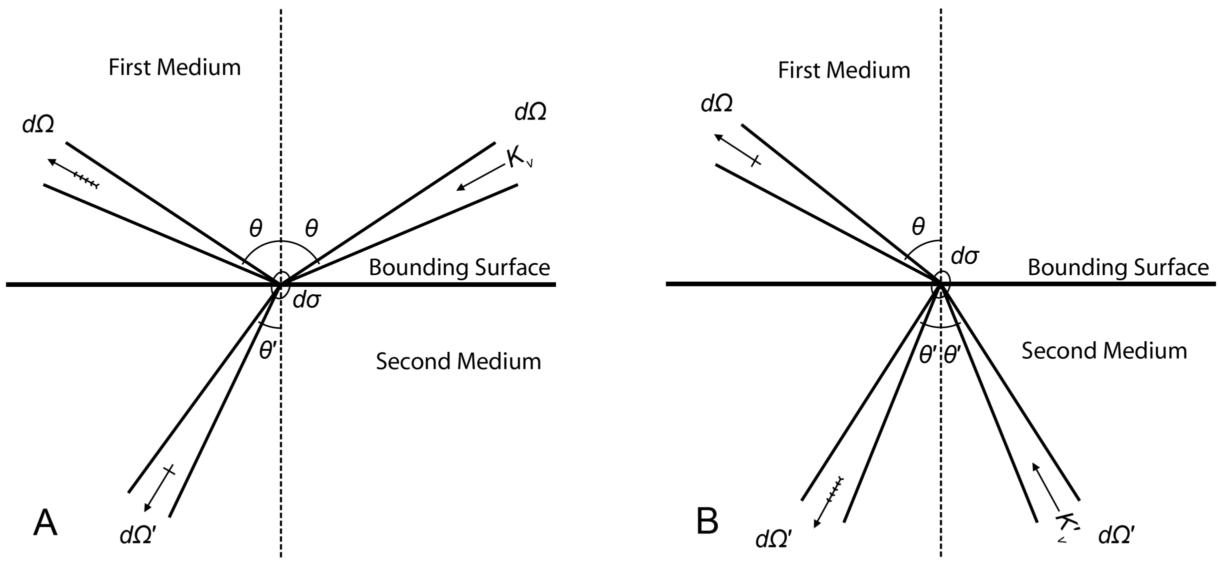

Fig. 1: Expansion of Figure 3 in "The Theory of Heat Radiation" [5] depicting the full complement of rays involved in treating the interaction between two media separated by a "bounding surface" which contained a hypothetical element of interest, $d\sigma$. Planck considered the reflective nature of $d\sigma$ to ascertain whether its reflection coefficients were identical depending on whether the incident ray originated from medium 1, (A), or medium 2, (B). A) Schematic representation of the incident specific intensity, $\mathbf{K}_\nu$ (plain arrow), at an angle θ, contained in the conical section, $d\Omega$, of the first medium (upper right quadrant) which is reflected by the bounding surface into the conical section $d\Omega$ in the upper left quadrant and refracted into the conical section $d\Omega'$ of the second medium, at an angle θ', in the lower left quadrant. Note that in order to preserve the proper specific intensities, $\mathbf{K}_\nu$, in the upper left quadrant, Planck must sum the reflected portion of the incident specific intensity of medium 1, $\rho_\nu \mathbf{K}_\nu$, with the refracted portion of the incident specific intensity of medium 2, $(1 - \alpha'_\nu - \rho'_\nu)\mathbf{K}'_\nu$, depicted in B. This fact is represented by the feathered arrow. However, he neglected to include that part of the specific intensity in the upper left quadrant was being produced by emission in that direction, η_ν, by $d\sigma$. B) Schematic representation of the incident specific intensity, $\mathbf{K}'_\nu$ (plain arrow), at an angle θ',contained in the conical section, $d\Omega'$, of the second medium (lower right quadrant) which is reflected by the bounding surface into the conical section, $d\Omega'$, in the lower left quadrant and refracted into the conical section, $d\Omega$, of the first medium, at an angle θ, in the upper left quadrant. Note that, in order to preserve the proper specific intensities, $\mathbf{K}'_\nu$, in the lower left quadrant, Planck must sum the reflected portion of the incident specific intensity of medium 2, $\rho'_\nu \mathbf{K}'_\nu$, with the refracted portion of the incident specific intensity of medium 1, $(1 - \alpha_\nu - \rho_\nu)\mathbf{K}_\nu$, as depicted in A. This fact is represented by the feathered arrow. However, he neglected to include that part of the specific intensity in the lower left quadrant was being produced by emission in that direction, η'_ν, by $d\sigma$.

address absorption at the "bounding surface", as mentioned under the second objection above, the total radiation which was both emitted and reflected by an element within the medium of interest (i.e. the incident ray) towards the "bounding surface" must be considered, as illustrated in Figure 2.

Note in this case, that the ray which is approaching the bounding surface will be transformed into three components: 1) that which will be absorbed at the "bounding surface" and then re-emitted in the direction of reflection; 2) that which will be reflected into the same medium; and 3) that which will be refracted into the other medium. The distinction is important, for Planck inferred that $\rho_\nu + \tau_\nu = 1$, whereas the correct expression involves $\rho_\nu + \tau_\nu + \alpha_\nu = 1$.* Planck permitted himself to state that $\tau_\nu = 1 - \rho_\nu$, whereas he should have obtained $\tau_\nu = 1 - \rho_\nu - \alpha_\nu$. Again, this completely prevents further progress towards Kirchhoff's Law [5, Eq. 42].

Planck considered the reflected rays in the first medium, of specific intensity $\mathbf{K}_\nu$ at incidence [5, Eq. 38],

$$\rho_\nu \, dt \, d\sigma \, \cos\theta \, d\Omega \, \mathbf{K}_\nu \, d\nu, \tag{17}$$

which were augmented by rays of incident specific intensity $\mathbf{K}'_\nu$ refracted from the second medium [5, Eq. 39],

$$(1 - \rho'_\nu) \, dt \, d\sigma \, \cos\theta' \, d\Omega' \, \mathbf{K}'_\nu \, d\nu. \tag{18}$$

In this setting, the resultant rays in medium 1 consist of components from both media, the reflected and the refracted rays. Planck then obtained the following equation, at the end of his § 36,

$$\frac{\mathbf{K}_\nu}{\mathbf{K}'_\nu} \cdot \frac{q^2}{q'^2} = \frac{1 - \rho'_\nu}{1 - \rho_\nu}, \tag{19}$$

where q and q' correspond to speeds of light in first and second media, respectively. He rapidly moved to [5, Eq. 40],

$$\rho_\nu = \rho'_\nu, \tag{20}$$

*Note that in §36 Planck referred to frequency dependent reflectivity, ρ_ν, but chose to write it simply as ρ. In this case, since he was dealing with the frequency dependent value, the subscripted form will be utilized throughout the presentation which follows. As such, the equations presented by Max Planck will be modified such that ρ is replaced with ρ_ν in accordance with his description that the term was frequency dependent.

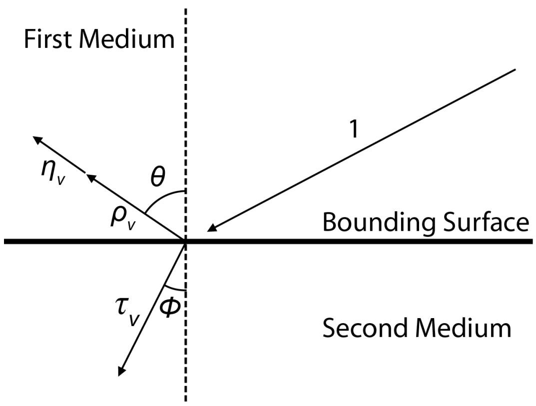

Fig. 2: Schematic representation of the fate of an incident ray, 1, which strikes a bounding surface. The ray will be split into three components: 1) the reflected ray, ρ_ν; 2) the refracted ray, τ_ν; and 3) that portion of the ray which is first absorbed, α_ν, then immediately re-emitted, η_ν, in order to preserve energy balance, in the direction of the reflected ray ($\alpha_\nu = \eta_\nu$). Thus, it is possible to describe this problem mathematically as $1 = \rho_\nu + \tau_\nu + \alpha_\nu$.

The result was stunning. Max Planck had determined that the reflectivities of all arbitrary media were equal. Yet, he attempted to dismiss such a conclusion by stating relative to Eq. 20 [5, Eq. 40]:

> "*The first of these two relations, which states that the coefficient of reflection of the bounding surface is the same on both sides, is a special case of a general rule of reciprocity first stated by Helmholtz.*"

Planck provided for the element of the bounding surface two separate coefficients of reflection. These must, in fact, correspond to those of the media utilized. Planck has already stated in § 35 that

> "*. . . let all quantities referring to the second substance be indicated by the addition of an accent.*"

Consequently, ρ and ρ' can only take meaning with respect to the media under consideration. Thus, how did Planck possibly reach the conclusion that these values must be equal? At the onset in Eq. 19 [5, § 35], Planck sought to force $\rho_\nu = \rho'_\nu$, in general, by first making $\rho_\nu = \rho'_\nu = 0$, in particular. To accomplish this feat, he considered rays that were,

> "*polarized at right angles to the plane of incidence and strike the bounding surface at the angle of polarization*" [5, § 37].

Again, such rays could never exist in the context of heat radiation [23, p. 450].

The "plane of incidence" is that containing the unit normal vector from the surface of incidence and the direction of the incident ray. There are two natural ways by which the orientation of an electromagnetic wave can be fixed; by the electric vector $\overline{\mathbf{E}}$ or the magnetic vector $\overline{\mathbf{B}}$. Contemporary convention is to use the electric vector $\overline{\mathbf{E}}$ [24, § 1.4.2]. Planck used the erstwhile magnetic vector convention.

The "angle of polarization" is Brewster's angle [23, p. 450]. The angle between reflected and refracted rays resulting from a given incident ray is then 90°. The reflected wave is entirely plane-polarized*, as shown in Figure 3,

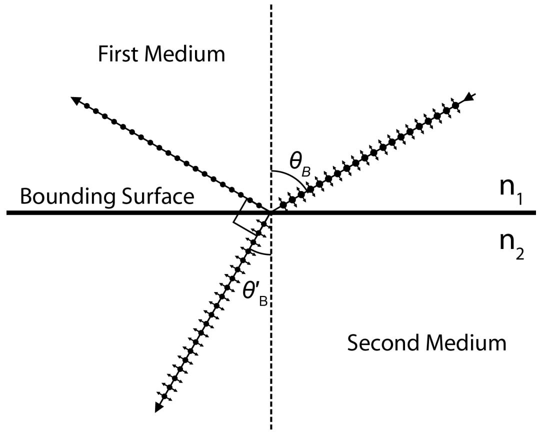

Fig. 3: Schematic representation of Brewster's Law. The dots correspond to the electric vector perpendicular to the page, whereas the double-headed arrows represent the electric vector in the plane of the page. An unpolarized, or arbitrarily plane-polarized, incident ray (upper right quadrant), strikes a surface at an angle of incidence, θ_B, corresponding to the Brewster's angle, or the angle of polarization. The reflected ray, depicted in the upper left quadrant will be entirely plane-polarized in such a way that it has no component of its electric vector in the plane of incidence. The transmitted ray produced at the angle of refraction, θ'_B, depicted in the lower left quadrant, will be partially polarized. The angle between the reflected and refracted rays is 90°. The angles, θ_B and θ'_B are complementary $\left(\theta + \theta'_B = 90^\circ\right)$. This process depends on the refractive indices of the two media involved, n_1 and n_2, such that the process is defined by Snell's Law, $n_1 \sin\theta_B = n_2 \sin(90^\circ - \theta_B)$, which in turn becomes $n_1 \sin\theta_B = n_2 \cos\theta_B$, or $\tan\theta_B = n_2/n_1$.

Planck's medium 2 has a Brewster's angle complementary to the Brewster's angle of his medium 1 ($\theta_B + \theta'_B = 90^\circ$). Brewster's angle is defined in terms of a reflected and a refracted beam. Unpolarized light, and plane-polarized light that is not "*at right angles to the plane of incidence*", produce reflected and refracted beams, in accordance with Brewster's Law. Planck invoked Brewster's Law [23, p. 450] with the special condition that incident rays are orthogonal to the plane of incidence. In this case, there could be no reflection, but only refraction, in accordance with Snell's Law. He simultaneously applied these same restricted conditions to medium 2.

> "*Now in the special case when the rays are polarized at right angles to the plane of incidence and strike the bounding surface at the angle of polarization, $\rho = 0$, and $\rho' = 0$.*"

*The reflected ray has no $\overline{\mathbf{E}}$ component in the plane of incidence.

However, Planck's two contiguous media were homogeneous and isotropic. They could only emit unpolarized light and not plane-polarized light. Since the entire system was enclosed by a barrier impermeable to heat, there was no external source of any incident plane-polarized rays. All incident rays considered must be unpolarized and all resultant composite rays, at best, partially polarized. This implied that the reflectivities of both media were never zero. Yet, Planck made all rays plane-polarized and, in this special case, orthogonal to the plane of incidence (magnetic vector convention). Since plane-polarized rays in both media were chosen orthogonal to their common plane of incidence, they had no components which could be reflected. The conclusion that the reflectivities were equal was therefore never properly tested, as Planck had offered no possibility of any reflection taking place. Consequently, Planck's conclusion, that $\rho_\nu = 0$, and $\rho'_\nu = 0$ cannot be true. Thus, Planck becomes unable to move to Kirchhoff's Law, as presented in his Eq. 42 [5, Eq. 42].

The situation was actually more complex, as Planck did not provide the proper form for Eqs. 17, 18, and 19. In reality, he neglected the contribution from emission or absorption in Eqs. 17 and 18. He had already redefined the blackbody as possessing a purely transmissive surface, in contradiction to Kirchhoff, as seen above. This was a critical error. The proper form of Eq. 17 [5, Eq. 38] must also include a term for emissivity, η_ν, in the direction of the conical element,

$$(\eta_\nu + \rho_\nu)\, dt\, d\sigma\, \cos\theta\, d\Omega\, \mathbf{K}_\nu\, d\nu. \tag{21}$$

The proper form of Eq. 18 [5, Eq. 39] must also include a term for absorptivity of the second medium, α'_ν,

$$(1 - \rho'_\nu - \alpha'_\nu)\, dt\, d\sigma\, \cos\theta'\, d\Omega'\, \mathbf{K}'_\nu\, d\nu. \tag{22}$$

That is because the intensity of the ray from medium 2 which is refracted into medium 1 corresponds to the transmissivity ($\tau'_\nu = 1 - \rho'_\nu - \alpha'_\nu$). Clearly, the intensity of the transmitted ray must account for the reduction of the incident ray within medium 2 as a result of *both* reflection and absorption. Planck cannot ignore the absorption of the surface. Consequently, Eq. 19 should have included the emissivity of the first medium, η_ν, and the absorptivity of the second medium, α'_ν. If one considers that the emissivity of the first medium, η_ν, is equal to its absorptivity, α_ν, then Eq. 19 becomes,

$$\frac{\mathbf{K}_\nu}{\mathbf{K}'_\nu} \cdot \frac{q^2}{q'^2} = \frac{1 - \rho'_\nu - \alpha'_\nu}{1 - \rho_\nu - \alpha_\nu}. \tag{23}$$

This equation can never lead to Kirchhoff's Law [5, Eq. 42].

As a consequence, it is readily apparent that Planck, through Eqs. 17-20, adopted a presentation which selectively applied the rules of reflection and refraction to polarized rays, irrelevant to the discussion of heat radiation. Furthermore, he then arbitrarily chose the plane of polarization such that when the waves were incident at Brewster's angle, there would be no reflection. Nonetheless, if there could be no reflection, then Brewster's angle, or the angle of polarization, could have no meaning. That is because such an angle depends on the reflected and refracted rays being at 90° to one another. But since Planck insisted that no reflection occurred, then clearly the reflected and refracted rays could not form a 90° angle. Importantly, not only did Planck advance Eq. 20 (i.e. Planck's Eq. 40) by neglecting absorptivity and emissivity, he thereby selected materials which have little or no relevance to heat radiation. Planck could not neglect absorption and emission, treating only transmission and reflection, if he wished to have any relevance to actual blackbodies. In addition, he hypothesized a *bounding surface* without any true physical meaning. Given this array of shortcomings, this derivation of Kirchhoff's law can never be salvaged. Planck's claims for universality were without proper theoretical confirmation.

5 Planck's Perfectly Reflecting Cavities and the Carbon Particle

Throughout "*The Theory of Heat Radiation*", Planck had recourse to a perfectly reflecting cavity, in which he placed a minute carbon particle (see [8] for a detailed treatment). Obviously, cavities comprised solely of perfectly reflecting surfaces, can never contain black radiation, as such materials cannot emit photons [16]. Nonetheless, Planck believed that these cavities contained radiation. He was careful however, not to state that this radiation was black [5, § 51],

> "*... in a vacuum bounded by totally reflecting walls any state of radiation may persist.*"

This statement, by itself, was a violation of Kirchhoff's Law. Nonetheless, Planck believed that he could transform the radiation contained in all cavities into the thermodynamically stable radiation by inserting a carbon particle [5, § 51],

> "*If the substance introduced is not diathermanous for any color, e.g., a piece of carbon however small, there exists at the stationary state in the whole vacuum for all colors the intensity* $\mathbf{K}_\nu$ *of black radiation corresponding to the temperature of the substance*".

and later [5, § 52],

> "*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 the 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 can be entirely neglected, even if its changes in temperature should be finite. Herein the carbon particle exerts only a releasing (auslösend) action*" .

Recall however, that Stewart's law insisted that [1],

> "*... That the absorption of a particle is equal to its radiation, and that for every description of heat.*"

When Planck moved the carbon particle into the cavity, clearly the emissive field of the particle also entered the cavity provided the former had some real temperature. However, if one assumes that the particle was at T=0K, then no radiation from the carbon particle could enter the cavity. At the same time, if the particle was allowed to come into physical contact with the walls of the cavity, then energy could flow from the walls into the particle by conduction. Hence the particle, being perfectly emitting, would fill the entire cavity with black radiation. Alternatively, if the carbon particle could be suspended within the cavity, with no thermal contact to its walls, then the only radiation entering the system, would be that which accompanied the carbon particle itself [16]. That is because the walls of the cavity would not be able to "drive" the carbon particle, since they could emit no radiation. In that case, the radiation density within the cavity would remain too low and characterized only by the carbon particle. Unlike what Planck believed, the carbon particle could never be a simple catalyst, as this would constitute a violation of Stewart's law [1]. Catalysts cannot generate, by themselves, the product sought in a reaction. They require the reactants. Yet, the carbon particle was always able to produce black radiation, in accordance with Stewart's findings [1]. This was evidence that it could not be treated as a catalyst.

6 Planck's Treatment of Two Cavities

Planck's suboptimal treatment of the laws of emission continued [5, § 69],

> "*Let us finally, as a further example, consider a simple case of a irreversible process. Let the cavity of volume V, which is everywhere 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 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. Then, since there is neither external work nor addition of heat from the outside, the energy of the new state is, according to the first principle, equal to that of the original one, or U′ = U and hence from (78)*
>
> $$T'^4 V' = T^4 V$$
>
> $$\frac{T'}{T} = \sqrt[4]{\frac{V}{V'}}$$
>
> *which defines completely the new state of equilibrium. Since V′ > V the temperature of the radiation has been lowered by the process.*"

This thought experiment was unsound. First, both cavities were made of perfectly reflecting walls. As such, Planck could not assume that the second cavity contained no radiation. To do so, constituted a violation of the very law he wished to prove. Kirchhoff's Law stated that the second cavity could not be empty. Therefore, Planck could not surmise that the temperature had dropped.

If one accepted that Kirchhoff's Law was false, as has been demonstrated above, then both cavities must be viewed as empty, other than the minute contribution made by the carbon particle. Here again, Max Planck had moved beyond the confines of reality, for he advanced a result which could not be correct, whether or not Kirchhoff's Law was true. The cavities were either both empty (i.e. Kirchhoff's Law was not valid), or both filled with radiation (i.e. Kirchhoff's Law was valid). One could not be filled, while the other was empty. Planck's equation, in the quote above, was incorrect.

7 Conclusion

Throughout "*The Theory of Heat Radiation*' [5] Planck employed extreme measures to arrive at Kirchhoff's Law. First, he redefined the nature of blackbodies, by adopting transmission as a central element of his derivation. Second, he neglected the role of absorption at the surface of such objects, in direct contradiction to experimental findings and Kirchhoff's understanding of blackbodies. While it could be argued that absorption does not take place entirely at the surface, Planck could not assume that no absorption took place in this region. He was bound to include its contribution, but failed to meet this requirement. Third, he sidestepped reflection, by neglecting its presence in arriving at Eq. 12 [5, Eq. 27]. Nonetheless, the energy of the system under investigation included both that which was involved in emission/ absorption and that associated with the reflection terms. Stewart has well highlighted that such terms are central to the nature of the radiation within arbitrary cavities [1] and the concept has recently been re-emphasized [18, 19]. Fourth, Planck had recourse to plane-polarized light, whereas blackbody radiation is never polarized.

In the end, Planck's presentation of Kirchhoff's Law did not properly account for the behavior of nature. Arbitrary cavities are not always black and blackbodies are highly specialized heated objects. Planck's characterization of the carbon particle as a simple "catalyst" constituted a dismissal of Stewart's Law [1]:

> ". . . *That the absorption of a particle is equal to its radiation, and that for every description of heat.*"

Planck could not transform a perfect absorber into a catalyst. Yet, without the carbon particle [8], the perfectly reflecting cavities, which he utilized throughout "*The Theory of Heat Radiation*" for the derivation of his famous Eq. 1 [4, 5], remained devoid of radiation. Perfectly reflecting cavities are incapable of producing radiation, precisely because their emissivity is 0 by definition. Planck can only properly arrive at Eq. 1 by having recourse to perfectly absorbing materials, a truth which he did not acknowledge. The presence of reflection must always be viewed as suboptimal to the creation of a blackbody, since significant reflection acts as a hindrance to the generation of photons through emission. It is never clear that the reflection term can easily be driven to arrive at the desired radiation, since thermal equilibrium, under these circumstances, can easily be violated, as the temperature of the cavity increases.

Planck's detachment from experimental findings relative to Kirchhoff's Law was evident in his presentation of Eq. 20 [5, Eq. 40]. His conclusion, with respect to the equivalence of the reflection in arbitrary materials, was false. Obviously, if reflection was always the same, then all opaque cavities would become identical. Eq. 20 [5, Eq. 40] became the vital result in Planck's derivation of Kirchhoff's Law. Unfortunately, the conclusion that $\rho=\rho'$ [5, Eq. 40] constituted a distortion of known physics and, by extension, so did Kirchhoff's formulation.

Without a proper proof of Kirchhoff's Law, Planck's claim for universality loses the role it plays in science. This has significant consequences in both physics and astronomy [8, 17, 24]. The constants h and k do not have fundamental meaning. Along with "Planck length", "Planck time", "Planck mass", and "Planck temperature", they are to be relegated to the role of ordinary and arbitrary constants. Their value has been defined by our own selection of scales, not by nature itself.

Dedication

This work is dedicated to the memory of Balfour Stewart [1].

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