On the Validity of Kirchhoff's Law of Thermal Emission

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Abstract—**In this paper, Kirchhoff's law is discussed in the context of two extremes: the perfect absorber and the perfect reflector. It is argued that Kirchhoff's extension of his law to the perfect reflector is not justified based on experimental evidence. This greatly limits the universality of the formulations advanced by Kirchhoff and Planck in that blackbody radiation becomes dependent on the nature of the radiating object. In this regard, it is emphasized that graphite is unique in its ability to act as a nearly perfect absorber. The consequences are important in our analysis of all temperatures based on radiative emission.**

Index Terms—**Liquids, plasmas, solar energy, solar radiation, solids, temperature measurements.**

I. Introduction

KIRCHHOFF'S law [8], [9] represents one of the first mathematical extensions of experimental reality. The law considers the emission of radiation from bodies at rest and in thermal equilibrium with an enclosure. Advanced in 1859 [8], [9], Kirchhoff's law remains one of the most important and far reaching laws in physics. Kirchhoff himself struggled with his law as did numerous others, for more than 50 years after its formulation [26]. There has been clear controversy regarding Kirchhoff's law and its proofs have come under significant attack [26]. The mathematical formulation of Kirchhoff's law was based on blackbodies, nonexistent ideal objects which "strictly speaking…cannot exist…" [7]. Nonetheless, it is clear that certain solids, namely graphite, can approach blackbody behavior in the laboratory.

Kirchhoff's theoretical treatment rested heavily on experimental findings with cavities producing nearly ideal blackbody spectra. Kirchhoff believed that not only perfectly absorbing cavities could produce the desired thermal spectrum. He observed that any object placed in thermal equilibrium within an absorbing cavity would eventually emit a blackbody spectrum. Kirchhoff set forth to bring universality to these findings. In seeking to extend these results, he moved from a perfectly absorbing cavity to one which was perfectly reflecting. It is this extension, by Kirchhoff, which is responsible for the concerns presented in this work.

Eventually, Planck [21] provided the mathematical form for the function contained in Kirchhoff's law. Consequently, Kirchhoff's law is imbedded within Planck's equation itself. It is for this reason that Planck believed in the universality of his own law. This universality rested on the validity of Kirchhoff's formulation. If Kirchhoff's law involving perfectly reflecting walls were valid, Planck's law would apply in the broadest sense. Planck stated that "According to the Kirchhoff law, this radiant energy is independent of the nature of the radiating substance and therefore has a universal significance" [22]. Further, from Kirchhoff's findings Planck argues that "…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" [23]. In this respect, one can see how the universality of Planck's equation became inherently linked to the validity of Kirchhoff's formulation for the perfect reflector.

Scientists have often utilized thermal formulations to assign temperatures to spectra which, though thermal in appearance, do not appear to have met the requirements set forth by Kirchhoff for treatment as blackbodies. Thus, the laws of thermal emission have been used to assign temperatures without knowledge that the requirements for thermal equilibrium had been met [13], [14], [20].

Perhaps in order to justify such extensions of laboratory reality, it has been imprudently argued [26] that Kirchhoff's law has been superseded by Einstein's derivation of Planck's equation in 1916 [4]. Einstein's work relies on energy levels with discrete separation [4]. Einstein coefficients are used to extract the correct equation once transitions are assumed between quantized energy levels separated by an energy $h\nu$. As a result, some assume [26] that Einstein's derivation have moved us beyond Kirchhoff's law and the confines of the enclosure. Interestingly, it could be argued that by making use of energy levels separated by discrete values, Einstein confined the system and indirectly invoked the same mathematical ideas as Kirchhoff. Suffice it to note that, for Planck, the oscillator treatment led to the discovery of the quantum of action $h\nu$, by necessity. This is something which Einstein assumes *a priori* in his formulation. What Planck derives from first principles, Einstein introduces as a given $(\Delta E = h\nu)$. This may help explain, in part, the underlying cause for the more elegant treatment by Einstein.

Despite these mathematical arguments, careful analysis of earthly emission spectra reveals that Kirchhoff's law describes an experimental setting which cannot be ignored. As stated by A.J. Chapman, "It must be noted that Kirchhoff's law is subjected to the restrictions of thermal equilibrium within an isothermal enclosure. Extensions of (Kirchhoff's law), as attractive as they may be, to other situations must be made with caution" [3]. In this regard, it is important to note that Einstein

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never addresses the physical species making the transition or the physical setting. Nonetheless, beyond the mathematical treatment, the underlying physical cause of a process is always important, as Chapman reminds us [3].

In any case, through the formulation of Kirchhoff's law, many believe that the conclusions Planck reached relative to blackbody radiation could be extended to all phases of matter. However, to be properly applied, Planck's formulation requires that the body in question be in equilibrium with an enclosure. Notwithstanding these restrictions, thermal arguments have been used to set the temperature of the photosphere [13], [14] and of the universe [20]. The accuracy of these temperatures depends strongly on the ability of the emitting object to meet the requirements set forth in Kirchhoff's formulation. More broadly, the universality of blackbody radiation also depends on the validity of Kirchhoff's own formulation. As such, a review of the physical basis for Kirchhoff's law is likely to shed important light on the assignment of temperatures based on radiative emission.

II. Perfect Absorbers and Reflectors of Radiation

Kirchhoff's law of thermal or blackbody emission deals with the transfer of heat through space. Formulated in 1859 [8], [9], this law is central to modern astrophysics since it enables the study of the temperature of objects through the analysis of the photons they emit. In its simplest formulation, Kirchhoff's law can be represented as follows: $\varepsilon_\nu/\kappa_\nu = f(T,\nu)$, where ε_ν, κ_ν, T, and ν denote emission, absorbance, temperature, and frequency, respectively. It asserts that for an object in thermal equilibrium with a rigid enclosure, the ratio of the emission and absorption is simply a function of temperature and frequency. Kirchhoff's law considers two operational settings: the perfect absorber and the perfect reflector. Based on these two extremes, the perfect absorber $(\kappa_\nu = 1)$ and the perfect reflector $(\varepsilon_\nu = 0, \kappa_\nu = 0)$, it appears that Kirchhoff's law can be stated as follows: "The ratio of emissive and absorptive power of any body is independent of the nature of the body" [23]. This is provided, of course, that the object is in thermal equilibrium with an enclosure. Unfortunately, the situation is more complex.

If the enclosure is made from graphite, an almost perfectly absorbing $(\kappa_\nu = 1)$ cavity, or blackbody, is obtained. In defining a blackbody, it is asserted that the absorption of incident rays must take place in a layer which is infinitely thin [23]. At the same time, as a contradiction, a blackbody must also have a minimum thickness as to ensure complete absorption [23]. It must possess a vanishingly small coefficient of scattering. Most importantly, *a blackbody must not sustain either net conduction or convection* since these destroy local thermal equilibrium [23].

In the mid-1800s, scientists produced blackbodies either from graphite plates or by covering objects with black paint often containing soot. Since the paint was black, the body became a nearly perfect absorber/emitter of radiation. In either case, these blackbodies were limited to solids. Currently, blackbodies are still made either from graphite [15]–[17] or from cavities covered with black paint often containing graphite particles [5], [6].

Thus, Kirchhoff studied objects with widely varying thermal signatures. He then placed the objects within graphite-based blackbody cavities. In doing so, he noticed that the spectra, which previously manifested the nature and temperature of the object were being transformed into blackbody spectra which varied only according to the equilibrium temperature of the entire system. Through the use of graphite cavities and thermal equilibrium, Kirchhoff was thus able to determine the temperature of any object in a manner which was independent of its nature. This, however, was critically dependent on the presence of the graphite cavity. Soon, Kirchhoff sought to further extend his formulation and move beyond the graphite enclosure.

Thus, Kirchhoff also considered the perfectly reflecting enclosure $(\varepsilon_\nu = 0, \kappa_\nu = 0)$. Planck defines a perfectly reflecting surface as one of "an absolute conductor (metal) of infinitely large conductivity" [23]. The situation with the perfectly reflecting enclosure is highly interesting. It has become the basis of the universality evoked by Planck and the basis for the overwhelming power of thermal arguments.

In reading Planck's account of the formulation of the theory of radiation [23], it becomes clear that neither Kirchhoff or Planck were ever able to obtain a blackbody radiation spectrum under conditions of perfectly reflecting walls. In fact, if an object is placed within such walls, an equilibrium will be established, but it will not correspond to that of a blackbody [23]. Indeed, the radiation contained within such a device will reflect purely the emission profile of the object it contains. For instance, if the enclosed object is a heteronuclear diatomic molecular gas, a series of vibrational-rotational lines would be observed. The equilibrium in theory could hold indefinitely if the walls were indeed perfectly reflecting both to radiation and to collisions. Unfortunately, a perfectly reflecting enclosure, by itself, is unable to yield the desired blackbody spectrum. On the surface, Kirchhoff's desire to reach universality had failed. The perfect reflector could never replicate the findings of the perfect absorber. However, there was something more to the experiment.

When dealing with the perfectly reflecting wall scenario, the experimentalists always added a small particle of graphite or thermalyzer [23] within the cavity. When this small particle of graphite [2] was added, the spectrum rapidly converted to that of a blackbody. Yet, Kirchhoff and Planck only saw the addition of the graphite particle as trivial disturbance of the system. Planck refers to this addition as similar to adding a "catalyst" [23]. This same interpretation has persisted to this day [12].

However, catalysts act solely to lower the activation energy of a reaction. As a rule, they facilitate reactions that lead to dissimilar products if originating from dissimilar reactants. Yet, the graphite particle facilitated the production of a blackbody spectrum in a manner which was completely independent of the nature of the initial body or of the initial radiation. Catalysts, on the other hand, tend to be very sensitive to the nature of the reactants and products.

At the time when Kirchhoff and Planck had hypothesized that graphite was merely a catalyst, they had little idea of the structural requirements associated with catalysts in chemical reactions. In fact, Kirchhoff lived well before formulation of modern atomic theory. As such, it is reasonable that both Kirchhoff and Planck erroneously viewed the graphite particle as a catalyst rather than as a central and vital component in producing the required thermal radiation profile. Kirchhoff and Planck observed that the blackbody radiation spectrum could be obtained by inserting even the smallest particle of graphite within a perfectly reflecting cavity. It mattered little how large a piece of graphite was inserted.

Modern insight can be gained by viewing the graphite particle not as a catalyst, but as a perfectly absorbing medium $(\kappa_\nu = 1)$. When Kirchhoff added the graphite particle to the perfectly reflecting cavity, *it was as if he had coated the entire walls of the cavity with graphite*. It is clear that, given thermal equilibrium, all of the radiation within the cavity would eventually become incident on the graphite particle. There it would be absorbed. The graphite particle would then transfer this energy to its vibrational states. With equilibrium maintained, graphite would eventually re-emit the photons in a manner reflecting its densities of states [10], [12], [18], [25], [28]. In so doing, the spectrum was slowly altered from that of the object initially contained within the box, to the spectrum of graphite. It did not matter that only a small piece of graphite was provided. Indeed, within the context of perfectly reflecting walls, the smallest piece of graphite $(\kappa_\nu \sim 1)$ was more than sufficient to produce the blackbody spectrum.

Whether only a small piece of graphite was present or an entire cavity was constructed from graphite, the result was the same: a condition with *perfectly absorbing material* had been created. Conversely, perfectly reflecting walls, by themselves, could never produce a blackbody spectrum. Graphite was required. In fact, the entire process of producing the blackbody spectrum relied heavily on the density of states contained within the graphite particle or the graphite walls.

The graphite particle had brought Kirchhoff unknowingly back to the perfectly absorbing scenario. In reality, there can be no extensions to the perfectly reflecting wall and blackbody radiation is, in fact, highly linked to the nature of the enclosure. As a result, the belief that blackbody radiation is independent of the nature of the emitter is erroneous. A blackbody spectrum is only obtained when $\kappa_\nu = 1$ either for the entire cavity or for the graphite particle. This condition depends directly on the nature of the medium. The situation with perfectly reflecting walls does not lead to the production of a blackbody spectrum. In fact, it leads to radiative equilibrium which is not that of a blackbody unless a blackbody source is provided. As such, of the two situations described by Kirchhoff, only that with a perfect absorber leads to a blackbody spectrum. The reevaluation of the role of the graphite particle within the perfect reflector constitutes a major reshaping of Kirchhoff's law of thermal emission.

III. The Nature of Thermal Emission

Experimental analysis of thermal emission in solids, liquids, gases, and plasmas yield the following general observations.

1) Solids tend to emit in continuous bands of radiation the intensity of which, at any given frequency, varies with temperature and is *directly affected by the nature of the particular solid* [27], [30]. No solid displays a true blackbody radiation spectrum. Some forms of graphite, however, approach this behavior with deviations primarily in the low frequency region of the spectrum. Few solids actually are able to fully follow Stephan's law [27] across a broad range of temperatures. Metals can deviate very significantly from blackbody behavior and tend to display peak emissivities near the visible region at room temperature [27]. Polished metals tend to have low emissivities. Metal oxides can have reasonable normalized emittance values but these occur over very limited frequency ranges [30]. All solids eventually deviate from expected thermal behavior near the phase transitions to liquids and to gases [30].
2) Liquids, like solids, tend to emit radiation in a continuous manner, although fewer examples have been studied (usually over narrow ranges of frequency). As expected, most experimental studies concentrated on molten metals [27]. Unlike solid metals, their emissivity tends to remain relatively constant with temperature. Water and sea water have been extensively studied both in the infrared and microwave regions of the spectrum [27], [31]. Water is a strong emitter of infrared radiation particularly in certain bands, most notably around 3 μm [27]. Presumably, this is related to absorption and emission by the hydrogen–oxygen bond itself. Water, of course, is nearly transparent in the visible range. Many organic solvents are transparent to infrared radiation at least in some frequency bands. Notable cases include CCl_4 and CS_2. Liquids can sustain convection currents. When this occurs, they are unable to follow Kirchhoff's law [23]. Convection currents can lead to interesting redistributions of energy with profound thermal consequences.
3) Gases, provided they have a dipole moment, tend to produce discrete vibrational-rotational emission spectra in the microwave region whose complexity increases in accordance with changes in molecular structure [19]. Gaseous spectra are highly dependent on both temperature and pressure. No free gas is capable of emitting a blackbody spectrum. Sparse atmospheric gases, such as CO_2 and H_2O, can lower their total emission in association with increased temperatures [11] in direct contradiction of Stephan's law [29].
4) Molecular plasma can produce vibrational-rotational spectra in addition to electronic spectra. Nonmolecular ionic plasmas cannot produce vibrational-rotational spectra. All plasmas are characterized by either discrete or continuous electronic spectra. Under no circumstances has an isolated plasma, not in a thermolyzing enclosure $(\kappa_\nu \sim 1)$, ever produced a blackbody radiation spectrum. In this regard, it is important to highlight that Tokamak reactors are often lined with graphite [2].

The production of a blackbody spectrum of analytical quality has required either graphite [15]–[17], or speculated black paint usually containing soot (graphite) [5], [6]. As Kirchhoff observed experimentally in the mid-1800s, very few objects are able to produce true blackbody spectra. In fact, graphite alone dominates solids as the closest example of blackbody radiation. Other solids vary widely in their ability to produce such spectra and indeed many fail completely to produce the required pattern over a reasonable temperature range [30]. In solids, continuous spectra are obtained, but in all but graphite, these lack true blackbody characteristics [30].

However, when an object is placed within a graphite enclosure and permitted to come to thermal equilibrium, the radiation emitted from the blackbody will eventually report the correct temperature of the object independent of its nature, phase, and composition. Such an experiment forms the experimental justification of Kirchhoff's law for the perfect absorber ($\kappa_\nu = 1$) [15]–[17]. Thus, a graphite enclosure is able to fully absorb the radiation emitted by the enclosed object. The graphite wall then "transforms" this radiation into the blackbody spectrum. This transformation is made possible by the structure of graphite itself. In this view, Kirchhoff's blackbody is best seen as a transformer of light. This is a phonon [25], [28] and density of states problem [10], [12], wherein individual states within the graphite absorb the emitted radiation and transfer this energy to other states. Once equilibrium is achieved, the graphite is able to produce a blackbody spectrum reflecting thermal equilibrium and a proper blackbody behavior.

Kirchhoff's requirement for an enclosure reflects his experimental knowledge of blackbodies and the transforming nature of graphite. Only solids can approach meeting the requirements set forth in Kirchhoff's law of thermal emission since only solids can provide a rigid environment for enclosure. Liquids, gases, and plasmas are unable to provide rigid self-enclosure and therefore cannot, in isolation, produce blackbody radiation spectra reporting the correct temperature. The situation for liquids, gases, and plasmas is further complicated by the possible presence of convection currents. The implications are important since the assumption of blackbody behavior enables scientists to predict the extent of emission at a given frequency.

Interestingly, Planck never sought to bring full physical meaning to his own law by linking it to a specific physical process, undertaken by a specific physical species, in a specific physical setting. In this sense, Planckian thermal emission remains unique in physics to this day. Scientists have yet to link the production of a thermal photon in blackbody radiation to a direct physical cause. Planck speaks of oscillators, but does not move to the atomic scale [21], [23]. His oscillators are finite segments of matter, not atoms or nuclei. In this regard, blackbody radiation remains quite different than all other physical processes wherein light is either emitted or absorbed. During every other process, a physical species (for instance, an electron) undergoes transitions between known energy states in a certain setting (for instance, within an atom). However, in Planckian thermal emission neither the physical species nor the nature of the energy levels nor the physical setting is defined. Surely, the situation can be corrected if true blackbody emission is viewed as a consequence of the vibration of atomic nuclei within the confines of a lattice structure. In this regard, the theorist must pay close attention to the characteristics of graphite itself.

IV. Conclusion

Throughout his career, Planck assumed the full validity of Kirchhoff's law even in the context of the perfect reflector [23]. He saw the graphite particle simply as a catalyst [23]. However, it was nothing more than a nearly perfect absorber. Had Planck emphasized this distinction, the extension of Kirchhoff's law in a manner independent of the nature of the walls might have been reconsidered.

The universality of blackbody radiation has been overstated. It is imprudent to speak in terms of "blackbodies" without noting, as Kirchhoff did, the constraints of the enclosure [13], [14], [20]. It is also imprudent to ignore the realities of the "graphite particle" and extend the formulation of blackbody radiation to perfectly reflecting enclosures. Such enclosures fail to produce the required result without the addition of graphite (or a similar thermalyzer). Kirchhoff's law holds only when $\kappa_\nu \sim 1$.

The underlying physical cause of thermal radiation must not be ignored and this includes the internal structure of matter. Yet Einstein's derivation of Planck's law, though masterful, has led some to ignore Kirchhoff, thermal equilibrium, and the physical realities involved in thermal emission. After more than a century since their formulation, both Kirchhoff's law and Planck's law remain imperfectly understood and unlinked to the physical world. Einstein never addresses either the physical species making the transition or the physical setting.

Our inability to link Planck's equation to physical reality is based in large part on the assumption that the perfect reflector was able to produce blackbody radiation. This erroneous assumption has reinforced the belief that virtually any object can produce a blackbody spectrum. Planck's equation lacks physical constraints as a direct result. Consequently, astrophysics can currently have recourse to Planckian arguments without being limited by the experimental realities of the laboratory. Everything, it seems, hinges on the role of the graphite particle. A new role for this particle (as an absorber, not a catalyst) will bring a new physical reality in thermal emission. This reality is likely to have profound implications in the study of space and the cosmos.

For instance, the sun cannot be in thermal equilibrium with an enclosure and clearly does not meet the requirements for setting a temperature based on Planckian arguments. Unlike experimental blackbody cavities, the solar surface is not in equilibrium with a rigid graphite based cavity. The sun is operating far out of thermal equilibrium. Its convection currents alone tell us that the solar surface cannot be considered to be a blackbody. Planck realized the complicating aspects of convection and this is why he held that such bodies could not follow Kirchhoff's law [23].

Thus, when Langley measured the solar emission spectrum [13], [14], it was improper for him to assign a temperature of ~6000 K to the photosphere. Given the continuous nature of the solar spectrum and its blackbody appearance, such a conclusion at first seems unavoidable. Yet, the assignment of a temperature from Planckian spectra requires additional considerations. The fact that a spectrum has a thermal appearance does not automatically imply that a valid temperature can be extracted. A spectrum may well appear to be valid, but the object producing it may be supporting other processes beyond thermal emission. For instance, the energy sustaining solar convection may not be available for thermal emission. For a temperature to be valid, the experimentalist must ensure that the object in question is devoid of all convection currents and is in strict thermal equilibrium with an enclosure. In this manner, all of the energy contained within the object is directly coupled to the thermal emission.

The current belief that blackbody radiation is independent of the nature of the medium, a belief that has survived for 150 years, is based on assigning to a graphite particle a strictly catalytic role and ignoring its absorptive characteristics $(\kappa_\nu \sim 1)$. However, given the nature of graphite and its importance in the blackbody problem, such an assumption simply can no longer be supported by experimental fact. Kirchhoff's argument for a catalytic role would have been much stronger if a solid other than graphite had been introduced into the perfect reflector.

Consequently, blackbody radiation reporting an accurate temperature is absolutely dependent on the nature of the walls forming Kirchhoff's enclosure. This experimental constraint is reflected in Kirchhoff's law of thermal emission [8], [9] when $(\kappa_\nu = 1)$, as properly addressed herein. The mathematical extension of Kirchhoff's law from the perfect absorber $(\kappa_\nu = 1)$ to the perfect reflector $(\varepsilon_\nu = 0, \kappa_\nu = 0)$ does not hold. Kirchhoff's law, in fact, remains valid only for the perfect absorber. Blackbody radiation is not universal and is critically dependent on the nature of the emitting body.

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