Kirchhoff's Law of Thermal Emission: 150 Years

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In this work, Kirchhoff's law (Kirchhoff G. *Monatsberichte der Akademie der Wissenschaften zu Berlin*, sessions of Dec. 1859, 1860, 783–787) is being revisited not only to mark its 150th anniversary but, most importantly, to highlight serious overreaching in its formulation. At the onset, Kirchhoff's law correctly outlines the equivalence between emission and absorption for an opaque object under thermal equilibrium. This same conclusion had been established earlier by Balfour Stewart (Stewart B. *Trans. Royal Soc. Edinburgh*, 1858, v. 22(1), 1–20). However, Kirchhoff extends the treatment beyond his counterpart, stating that cavity radiation must always be black, or normal: depending only on the temperature and the frequency of observation. This universal aspect of Kirchhoff's law is without proper basis and constitutes a grave distortion of experimental reality. It is readily apparent that cavities made from arbitrary materials ($\varepsilon < 1$) are never black. Their approach to such behavior is being driven either by the blackness of the detector, or by black materials placed near the cavity. Ample evidence exists that radiation in arbitrary cavities is sensitive to the relative position of the detectors. In order to fully address these issues, cavity radiation and the generalization of Kirchhoff's law are discussed. An example is then taken from electromagnetics, at microwave frequencies, to link results in the resonant cavity with those inferred from the consequences of generalization.

1 Introduction

Kirchhoff's law is one of the simplest and most misunderstood in thermodynamics [1, 2]. It is widely considered to be the first of the laws of thermal emission [3–7]. In simple mathematical terms, Kirchhoff's law can take on several formulations, which stem from the equivalence between the coefficients of emission, ε, and absorption, α, at thermal equilibrium. The most general expression of Kirchhoff's law for opaque objects is, in fact, a statement of Stewart's law [6], namely, $\varepsilon = 1 - \rho$, where ρ corresponds to the coefficient of reflection. However, Kirchhoff's law [1, 2] is much farther reaching than Stewart's [6], in requiring that radiation within an enclosure, or cavity, must always be black, or normal [5]. Kirchhoff conceives that the ratio of emissive power, e, to absorptive power, a, of all bodies can be described by a universal function, f, common to all radiation within enclosures: $e/a = f(T, \lambda)$. Furthermore, this must be the case in a manner which is independent of the nature and shape of the enclosure, and which depends only on the temperature, T, of the system and the wavelength, λ, of observation [1, 2, 5, 7].

Kirchhoff's law constitutes an attempt to summarize the state of knowledge in radiative heat transfer during the mid-1800's. At the time, physicists created blackbodies from graphite plates, by lining the interior of cavities with soot, or by coating objects with black paint containing soot [8]. Contrary to Gustav Kirchhoff [1, 2], Balfour Stewart, in 1858 [6], stated that radiation in thermal equilibrium depends on the constituents involved and his treatment did not lead to a universal function. If Kirchhoff's law can be expressed as $e/a = f(T, \lambda)$, then Stewart's would be $e/a = f'(T, \lambda, N)$, where N represents all factors linked to the nature of the emitter itself and f' is not universal. Like Kirchhoff, Stewart based his ideas on Prévost's theory of exchanges [9, 10], which was ultimately linked to the study of radiation within enclosures. The distinctions between Stewart's formulation and Kirchhoff's are profound [11, 12]. Kirchhoff's ideas advocate a universal function [5]. Stewart's do not [6, 11, 12].

Today, 150 years after its formulation [1, 2], the foundation of Kirchhoff's law still rests on condensed matter physics. Blackbodies continue to be highly specialized objects [13–25] constructed from absorbers which are nearly perfect over the frequency range of interest. Yet, if Kirchhoff was correct about the nature of radiation within cavities, it should be possible to assemble a blackbody from any material. Surely, the presence of the universal function, f, dictates that cavity radiation must always be black, or normal [5]. All that should be theoretically required is thermal equilibrium with the walls of an enclosure. The attributes of the walls, or its contents, should be inconsequential. However, the body of experimental knowledge, relative to the assembly of blackbodies in the laboratory, stands firmly opposed to this concept [13–25]. True blackbodies [13–25] are extremely difficult to produce and testify against Kirchhoff's universal formulation [1, 2, 5]. Stewart's law [6] alone, not Kirchhoff's [1, 2], is supported by a careful consideration of experimental reality [8, 12–41]. Still, a cursory review of the literature, relative to cavity emission, would suggest that arbitrary cavities can appear black. Furthermore, the trend towards blackness appears to increase as "truer" cavities are produced. This seems to be the case, irrespective of the emissivity of the cavity walls. The subject is a fascinating problem in physics.

2 Cavity radiation

While ideal blackbodies do not exist in nature, laboratory examples approach theoretical performances, especially when narrow frequency and temperature ranges are considered [8, 13–25]. Typically, the best laboratory blackbodies are constructed from highly absorbing walls ($\alpha \approx 1$) usually containing soot, carbon black, or graphite [8, 13–25]. Cavities which operate in the far infrared may also be lined with metals, metal blacks, or metal oxides [35–41]. Blackbody enclosures are often made isothermal using water, oil, or molten metal baths. Alternatively, metal freezing point techniques or electrical heating elements may ensure isothermal operation. The vast body of the laboratory evidence supports the idea that standard blackbodies are always made from highly absorbing materials set to function in an isothermal state.

Nonetheless, in treating cavity radiation from a theoretical standpoint, Planck invokes the perfectly reflecting enclosure [7, 8]. This is an interesting approach, since perfectly reflecting enclosures are adiabatic by definition and cannot therefore participate in the exchange of heat, either through emission or absorption. Planck, though, requires that the interior of such cavities contains black radiation [7; §51–52], in conformity with Kirchhoff's law [1, 2]. In so insisting, Planck makes constant recourse [8] to a minute particle of carbon [7; §51–52]. He inserts the particle into the cavity, in order to ensure that the latter appropriately holds black radiation. Planck invokes carbon, despite the fact that Kirchhoff's law should have ensured the presence of the radiation sought. In the end, and though carbon particles are perfect absorbers, Planck treats them simply as catalysts, and ignores their importance to the blackbody problem [7, 8].

It remains commonly acknowledged that all cavity radiation must be black. This is the case even though cavities with arbitrary walls of low emissivity are never used as laboratory blackbody standards [13–25]. Clearly, there is more to the understanding of arbitrary cavities than the belief that they are black [1, 2, 5]. In any case, when arbitrary cavities are analyzed with radiometric detectors, they do appear to become black, as seen in classic texts [i.e. 28] and the references they contain [29–34, 42–48]. Ample theoretical work reinforces this position [i.e. 42–48]. Monte Carlo calculations on lambertian spherical arbitrary cavities constructed from walls of low emissivity provide a good example [28]. Such calculations lead to apparent cavity emissivities approaching 1 [28]. These amazing results hint at proof, at least on the surface, that Kirchhoff's law is fully valid. Unfortunately, it can be shown that such conclusions are erroneous.

Let us return for a moment to Planck's treatment [7] and the perfectly reflecting cavity containing a carbon particle [8]. A schematic representation of this situation is presented in Figure 1A. Since the cavity wall is perfectly reflecting, one can treat it as an adiabatic boundary producing no radiation of its own. All of the radiation which comes to fill the cavity is being produced by the carbon particle [12]. As a result, if one examines the contents of the cavity through a small hole, the radiation it contains will obviously be black. Now, let us displace the carbon particle, such that it is located just outside the aperture leading to the cavity (see Fig. 1B). From this position, the particle will once again be able to fill the cavity with photons, and the observer will find that its interior contains black radiation. Finally, let us place the carbon particle well outside the cavity itself, such that its radiation can still penetrate the cavity (see Fig. 1C). In this instance, the observer will record that the cavity is black, but not because it was able to become black on its own. It is black simply because the carbon particle has filled the cavity with radiation.

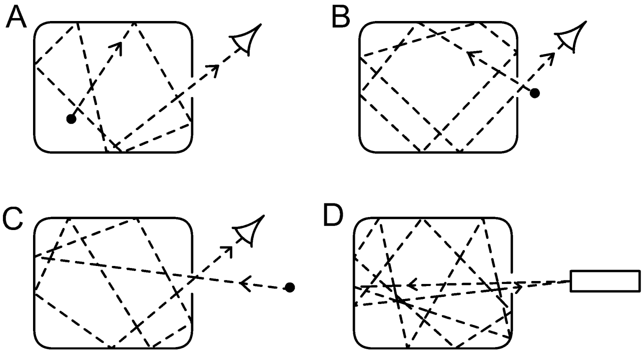

Fig. 1: Schematic representation of a perfectly reflecting cavity A) containing a carbon particle, B) with a carbon particle near the aperture, C) with a carbon particle farther from the aperture, and D) with the carbon particle replaced by a physical detector. The eye represents a point of detection. Note that if perfectly reflecting cavities contain any radiation whatsoever, it is solely because they have been filled with photons either from the carbon particle or the detector.

Returning to the days of Kirchhoff, it is evident that limited experimental means existed. As a result, cavity radiation was monitored through a combination of prisms, for frequency differentiation, and thermometers, for energy detection. These thermometers were always blackened with soot, as Langley reminds us in 1888: "*I may reply that we have lately found an admirable check on the efficiency of our optical devices in the behavior of that familiar substance lampblack, which all physicists use either on the thermometers, thermopiles, or bolometers*" [49]. Consequently, by sampling the cavity with a thermometer coated with lampblack, every experimentalist brought about for himself the result which he sought. All cavities appeared black, because all cavities were being filled unintentionally with black radiation. Adding the carbon particle directly to the interior of the cavity simply helped to bring about the desired experimental scenario.

In Fig. 1D, a cavity is represented along with a radiometric detector. In order to maintain a logical progression, let us assume that the cavity is perfectly reflecting in its interior.

In this case, the cavity itself cannot emit any photons [12]. A small hole is made into the cavity, and the radiation contained within it can be sampled with the radiometer. The cavity will be found to contain black radiation [12]. Yet, if the cavity was a perfect reflector, then how could its interior be black? The answer, of course, is similar to what Planck had done with the small carbon particle. A carbon particle, no matter how tiny [8, 12], will instantly fill an experimental cavity with black radiation. Planck, in fact, relies on this reality [7; §51–52]. Now, consider our radiometric detector. This instrument must have high photon capture rates. That is to say, it must possess an elevated absorptivity. As a result, by Stewart's law [6], it must also possess a high emissivity. Thus, if the cavity appears black, it is only because it has been filled with black radiation by the detector. Again, the experimentalist inadvertently produced the expected result.

In order to more fully appreciate the role of the detector in generating black radiation within cavities, let us consider the classic works by De Vos [32, 33] and Ono [28, 34]. Even though he is addressing arbitrary cavities, De Vos emphasizes that: "*The radiation emerging from the hole of observation in the blackbody should be an approximation, as well as possible, to the theoretical blackbody radiation*" [32]. A cursory examination of these studies would lead one to believe that all arbitrary cavities are indeed black. However, upon closer analysis, these investigators have not distinguished themselves from their predecessors. De Vos elegantly links mathematical and experimental results obtained from cavities [32]. If the cavities appear black under certain viewing conditions, it is simply because black radiation has been injected into them using detectors. De Vos notes that in order to sample black radiation in a spherical cavity of arbitrary construction: "*It is necessary to take care that the surface element observed is not perpendicular to the direction of observation*" [32]. The reason for this statement is evident. If the surface element was perpendicular, most of the radiation introduced by the detector into the cavity would undergo normal specular reflection back out of the cavity and the latter would not appear black. In subsequently describing the tubular blackbody (see Figure 2A), De Vos states that: "*The actual value of the quality will be better than calculated in this way but only slightly better since the radiant intensity decreases rapidly towards the ends of the tube*" [32]. Of course, the detector is pumping radiation into the hole at the center of the tube. It is, therefore, simple to understand why radiation must fall rapidly towards the ends of the tube. Clearly, the tubular cavity is manifesting the performance of the detector. In fact, De Vos himself unintentionally makes the point: "*Owing to the small hole in the tungsten tube a small quantity of energy was available only. Hence it was necessary to use radiation receivers of high sensitivity*" [33]. De Vos might have more appropriately written that it was important for the detector to provide an ample supply of photons. For his part, Ono has demonstrated that the apparent emission of the tubular cavity depends on the position of the detector itself. Ono writes: "*The apparent emissivity has deep minima around $\theta = 0°$ at which specularly reflected radiation escapes through the lateral hole. The shallow minima around 30° are also due to specular reflection effects where incident radiation escapes after two successive specular reflections*" [28, p. 605]. This situation is reproduced schematically in Fig. 2B. Of course, the incident radiation arises from the detector. It alone is filling the cavity with black radiation. The cavity itself is not producing this radiation for, if it did, the position of the detector would be immaterial. This is certain proof that Kirchhoff's law does not hold. Much depends on the detector, not on the cavity.

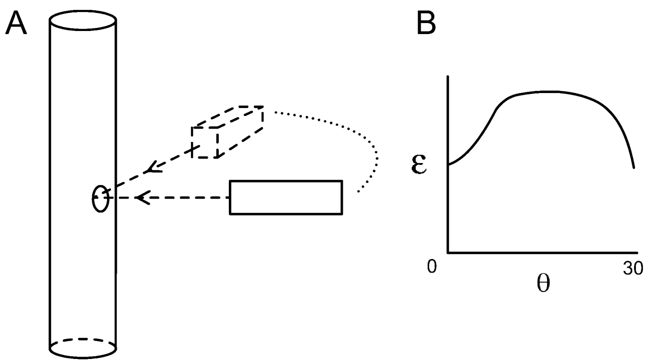

Fig. 2: A) Schematic representation of a tubular cavity and a detector. B) Illustration of the type of result seen with the detector as a function of angle from the normal. Note how there is less emission measured at 0° and 30°.

The point is further amplified by considering the work of Sparrow and Heinisch [30]. The authors demonstrate that the normal emission from a cylindrical cavity is absolutely dependent on the distance of the detector from the cavity. They fail to examine the cavity as a function of detector angle. Still, it is obvious that distance variations should not be occurring. Again, the detector is critically important in flooding the cavity with radiation.

Vollmer's studies [29] help us to understand that arbitrary cavities are not black, despite the fact that, at least on the surface, they point to the contrary. His work is particularly interesting, as it aims to reconcile theoretical foundations, stemming from Buckley's classic paper [42], with experimental data. Surprising agreement is obtained between theory and experiment. In the limit, these results appear to re-emphasize that cylindrical cavities of sufficient size, made from arbitrary materials, will indeed behave as blackbodies. Everything seems to rest on solid footing, until the experimental setup is carefully examined. In order to reach agreement with theory, the apparatus used not only supplied the typical detector radiation, but also a black bellows, a black water cooled shutter, and a black water cooled cylinder [42]. Given these many possible sources of black radiation in front of the cavity opening, there can be little wonder that the cavity begins to appear black. In reality, the contrary position should have been adopted. How surprising that, bombarded with black radiation, some cavities still fail to be able to appear fully black.

R. E. Bedford, though he believes in the validity of Kirchhoff's law, re-emphasizes the point that arbitrary cavities are simply not black [28; p. 678]: "*A blackbody is a lambertian emitter; with the exception of a spherical cavity, none of the blackbody simulators we will discuss will radiate directionally as does a blackbody*". Yet, as seen above for the spherical cavity, "*It is necessary to take care that the surface element observed is not perpendicular to the direction of observation*" [32]. Consequently, when these two excerpts are taken together, Bedford's statement constitutes a direct refutation of Kirchhoff's law. The situation deteriorates further: "*At some angle of view away from the normal to the cavity aperture (the angle depending on the particular cavity shape), the cavity radiance will begin to drop sharply from its axial value as that part of the wall becomes visible where $\varepsilon_a(y)$ near the aperture is much lower than $\varepsilon_a(x)$ deep within the cavity. In most cases this deficiency in emitted energy will be significant only at angles of view larger than are subtended by most pyrometers*" [28; p. 678]. In any event, the point is made. None of the cavities modeled can ever truly be considered blackbodies. Arbitrary materials are not lambertian and their emissivity can never be black [5]. Spherical cavities must be monitored with careful attention to the angle of observation. This should not occur if they were truly blackbodies.

If Monte Carlo simulations and other calculations reveal that arbitrary cavities move to blackness independent of wall emissivities, it is strictly because such methods fill the cavities with black radiation [42–48]. Once again, blackbodies are unique in possessing lambertian surfaces. Thus, models which utilize lambertian surfaces of low emissivity represent situations which have no counterparts in nature. In addition, there can be no difference between placing a carbon particle in a cavity, in order to ensure the presence of black radiation, and simply filling the cavity with black radiation without physically making recourse to carbon. Monte Carlo simulations introduce black photons into cavities. Hence, they become black. The process is identical to placing a highly emitting carbon particle, or radiometer, at the opening of a cavity. No proof is provided by computational methods that arbitrary cavities contain black radiation.

It can be stated that Monte Carlo simulations obtain similar answers by modeling the repeated emission of photons directly from the cavity walls. In this case, computational analysis relies on internal reflection to arrive at a cavity filled with black radiation. The problem is that this scenario violates the first law of thermodynamics and the conservation of energy. It is not mathematically possible to maintain an isothermal cavity while, at the same time, enabling its walls to lose a continual stream of photons. Such approaches build up the photon density in the cavity at the expense of wall cooling. These methods must therefore be forbidden on grounds that they violate the 1st law of thermodynamics.

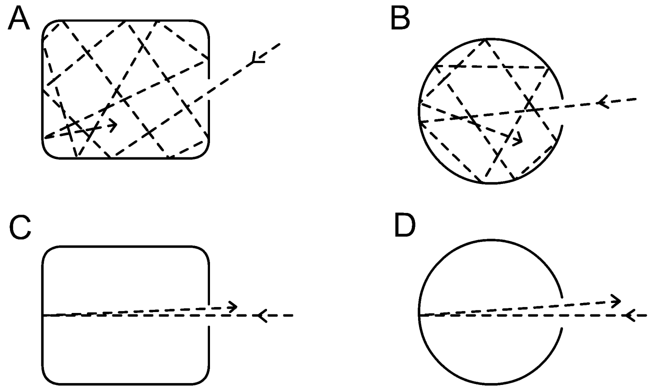

Fig. 3: Schematic representations typically used to argue that cavity radiation is always black. Figure A is similar to Figure 6.1 in [50]. Figure B is similar to 5.6 in [51]. Note that figures illustrating immediate reflection back out of the cavity (C and D) are never invoked. This is precisely because they represent direct physical proof that arbitrary cavities are not black.

It is commonly argued [50, 51] that a cavity with a sufficiently small hole contains black radiation. For example, in his classic text on the photosphere D. F. Gray writes: "*Let us begin with a container that is completely closed except for a small hole in one wall. Any light entering the hole has a very small probability of finding its way out again, and eventually will be absorbed by the walls of the container or the gas inside the container. . . We have constructed a perfect absorber*" [50; p. 100]. In reality, the maintenance of thermal equilibrium requires that if a photon enters the cavity, another photon must exit. The experimentalist will never be able to discern whether the exiting photon was 1) the same, 2) a photon that was newly emitted without reflection, 3) a photon that had previously undergone several reflections before exiting the cavity, or 4) a photon that had undergone a nearly infinite number of internal reflections before exiting the cavity. Each of these cases corresponds to different types of cavities, made either from arbitrary walls, perfectly absorbing walls, or perfectly reflecting walls. In any case, a photon must exit to maintain thermal equilibrium and nothing has been learned about the internal nature of the cavity. Clearly, given thermal equilibrium and the first law of thermodynamics, we cannot be sure that the radiation inside the cavity was black. Such arguments [50; p. 100–101] are unsound *a priori*. Notice, for instance, the types of figures typically associated with such rhetoric: the photon is usually drawn such that normal and immediate specular reflection back out of the cavity is discounted (see Figure 3A–B). This is precisely because immediate specular reflection of the photon back out of the cavity provides a sound logical defeat of such arguments (see Figure 3C–D).

In summary, the radiation contained inside arbitrary cavities is not black and depends exclusively on 1) the nature of the cavity, and 2) the nature of the radiation which is permitted to enter. If excellent radiometers are used, they will be good emitters, and will act to fill the cavities with black radiation. As such, it seems logical, although counterintuitive, that the sampling of cavity radiation should be performed with suboptimal radiometers. Radiometers for these studies should not have high photon capture rates. Such devices would provide lower photon emission towards the cavity. In so doing, they would minimally alter the true nature of the radiation they seek to measure. Perhaps, by using cryogenic devices, it might be possible to build detectors which retain adequate sensitivity. By maintaining lower detector emissions, the true nature of radiation within cavities might be ascertained. The proper result should echo Stewart, as previously demonstrated mathematically [12].

3 The generalization of Kirchhoff's law

The proofs of Kirchhoff's law are usually limited to the realm of geometrical optics. In his classic paper [2], Kirchhoff states in a footnote: "*The effect of the diffraction of the rays by the edges of opening 1 is here neglected. This is allowable if openings 1 and 2, though infinitely small in comparison with their distance apart, be considered as very great in comparison with the length of a wave*." Since Planck's treatment of Kirchhoff's law is also based on geometric optics, Planck writes: "*Only the phenomena of diffraction, so far at least as they take place in space of considerable dimensions, we shall exclude on account of their rather complicated nature. We are therefore obliged to introduce right at the start a certain restriction with respect to the size of the parts of space to be considered. Throughout the following discussion it will be assumed that the linear dimensions of all parts of space considered, as well as the radii of curvature of all surfaces under consideration, are large compared to the wave lengths of the rays considered. With this assumption we may, without appreciable error, entirely neglect the influence of diffraction caused by the bounding surfaces, and everywhere apply the ordinary laws of reflection and refraction of light. To sum up: We distinguish once for all between two kinds of lengths of entirely different orders of magnitudes — dimensions of bodies and wave lengths. Moreover, even the differentials of the former, i.e., elements of length, area and volume, will be regarded as large compared with the corresponding powers of wave lengths. The greater, therefore, the wave length of the rays we wish to consider, the larger must be the parts of space considered. But, inasmuch as there is no other restriction on our choice of size of the parts of space to be considered, this assumption will not give rise to any particular difficulty*" [7; §2]. Kirchhoff and Planck specifically excluded diffraction. They do so as a matter of mathematical practicality. The problem of diffraction greatly increases the mathematical challenges involved. As a result, Kirchhoff and Planck adapt a physical setting where its effects could be ignored. This is not a question of fundamental physical limitation.

Nonetheless, the first section of Kirchhoff's law, namely the equivalence between the absorption and emission of energy by an opaque material at thermal equilibrium, has been generalized to include diffraction. Correctly speaking, this constitutes an extension of Stewart's law, as will be discussed below.

Much of the effort in generalizing Kirchhoff's (Stewart's) law can be attributed to Sergi M. Rytov, the Russian physicist. Indeed, it appears that efforts to generalize Kirchhoff's law were largely centered in Russia [52–55], but did receive attention in the West [56, 57]. Though Rytov's classic work appears initially in Russian [52], later works have been translated into English [53]. In describing their theoretical results relative to the generalization of Kirchhoff's law, Rytov and his associates [53; §3.5] write: "*Equations (3.37-39) can be termed Kirchhoff's form of the FDT (fluctuation-dissipation theorem), as they are a direct generalization of Kirchhoff's law in the classical theory of thermal radiation. This law is known to relate the intensity of the thermal radiation of a body in any direction to the absorption in that body when exposed to a plane wave propagating in the opposite direction...*" The authors continue: "*and most important, (3.37–39) contain no constraints on the relationships between the wavelength λ and characteristic scale l of the problem (the size of the bodies, the curvature radii of their surfaces, the distances from the body to an observation point, etc.). In other words, unlike the classical theory of thermal radiation, which is bound by the constraints of geometrical optics, we can now calculate the second moments of the fluctuational field, that is to say both the wave part (taking into account all the diffraction phenomena), and the nonwave (quasistationary) part for any λ vs l ratio*" [53; §3.5].

A discussion of the fluctuation-dissipation theorem (FTD), as it applies to thermal radiation, can also be found in the book by Klyshko [54]. This text provides a detailed presentation of the generalization of Kirchhoff's law [54; §4.4 and 4.5]. Apresyan and Kravtsov also address generalization in their work on radiative heat transfer [55]. They summarize the point as follows: "*In this formulation, the Kirchhoff statement — that the radiating and absorbing powers of a body are proportional to each other — as was initially derived in the limit of geometrical optics, is valid also for bodies with dimension below or about the wavelength*" [55; p. 406].

It appears that the generalized form of Kirchhoff's law has been adapted by the astrophysical community [57]. Like the Russians before them, Linsky and Mount [56] assume that the equality between emissivity and absorptivity at thermal equilibrium is a sufficient statement of Kirchhoff's law [1, 2]. They refer to a Generalized Kirchhoff's Law (GKL) as $E(\mu_0) = 1 - \rho(\mu_0)$, where $E(\mu_0)$ is the directional spectral emissivity and $\rho(\mu_0)$ corresponds to the directional hemispherical reflectivity [56]. This statement should properly be referred to as Stewart's law [6], since Stewart was the first to argue for the equality between the emissivity and absorptivity of an opaque material under conditions of thermal equilibrium. Furthermore, Stewart's law makes no claim that the radiation within opaque cavities must be black, or normal [5]. Seigel [11] speaks for physics when he outlines the important distinction between Stewart's law [6] and Kirchhoff's [1, 2]. He writes: "*Stewart's conclusion was correspondingly restricted and did not embrace the sort of connection between the emissive and absorptive powers of different materials, through a universal function of wavelength and temperature which Kirchhoff established*" [11; p. 584]. Herein, we find the central difference between Stewart and Kirchhoff. It is also the reason why Kirchhoff's law must be abandoned. In fact, since universality is not valid, there can be no more room for Kirchhoff's law in physics.

Returning to Rytov and his colleagues, following their presentation of the generalization of Kirchhoff's law [53; §3.5], they move rapidly to present a few examples of its use [53; §3.6] and even apply the treatment to the waveguide [53; §3.7]. Interestingly, though the authors fail to discuss the microwave cavity, from their treatment of the waveguide, it is certain that the radiation within the cavity cannot be black. It must depend on the dimensions of the cavity itself. Such a result is a direct confirmation of Stewart's findings [6], not Kirchhoff's [1, 2]. As a consequence, the generalization of Kirchhoff's law brings us to the conclusion that the radiation within cavities is not black, and the second portion of Kirchhoff's law is not valid.

These questions now extend to ultra high field magnetic resonance imaging [58, 59], and hence the problem of radiation within cavities should be reexamined in the context of the generalization of Kirchhoff's law [52–55]. Since generalization extends to situations where cavity size is on the order of wavelength, it is appropriate to turn to this setting in magnetic resonance imaging. In fact, this constitutes a fitting end to nearly 10 years of searching to understand why microwave cavities are not black, as required by Kirchhoff's law.

4 Cavity radiation in magnetic resonance imaging

Prior to treating the resonant microwave cavity, it is important to revisit Kirchhoff's claims. In his derivation, Kirchhoff initially insists that his treatment is restricted to the study of heat radiation. He reminds the reader that: "*All bodies emit rays, the quality and intensity of which depend on the nature and temperature of the body themselves*" [2]. Then, he immediately eliminates all other types of radiation from consideration: "*In addition to these, however, there may, under certain circumstances, be rays of other kinds, — as, for example, when a body is sufficiently charged with electricity, or when it is phosphorescent or fluorescent. Such cases are, however, here excluded*" [2]. Kirchhoff then proceeds to provide a mathematical proof for his law. Surprisingly, he then reintroduces fluorescence. This is precisely to make the point that, within cavities, all radiation must be of a universal nature. Moreover, this occurs in a manner which is completely independent of the objects they contain, even if fluorescent, or any other processes. Kirchhoff writes: "*The equation $E/A = e$ cannot generally be true of such a body, but it is true if the body is enclosed in a black covering of the same temperature as itself, since the same considerations that led to the equation in question on the hypothesis that the body C was not fluorescent, avail in this case even if the body C be supposed to be fluorescent*" [2]. Kirchhoff deliberately invokes the all encompassing power of universality and its independence from all processes, provided enclosure is maintained.

Consequently, two important extensions exist. First, given the generalization of Kirchhoff's law [52–55], it is appropriate to extend these arguments to the microwave cavity. In this experimental setting, the wavelengths and the size of the object are on the same order. Furthermore, assuming thermal equilibrium, it is proper to consider steady state processes beyond thermal radiation. This is provided that a cavity be maintained. In any event, it is established that thermal loses exist within microwave devices. Thus, we can examine the electromagnetic resonant cavity in light of Kirchhoff's law.

When the use of the blackbody resonator in UHFMRI was advanced [60], it was not possible to reconcile the behavior of such a coil, given the conflict between Kirchhoff's law [1, 2] and the known performance of cavities in electromagnetics [61, 62]. A photograph of a sealed blackbody resonator for UHFMRI [60] is presented in Figure 4. In the simplest sense, this resonant cavity is an enclosure in which radiation can solely enter, or exit through, at a single drive point. The radiation within such cavities should be black, according to Kirchhoff [1, 2]. Nonetheless, measurements of the real cavity show that it does not contain black radiation, as demonstrated experimentally in Figure 5. Resonant cavities are well known devices in electromagnetics [61, 62]. Their radiation is determined purely by the constituent properties of the cavity and its dimensions [61, 62]. This point is affirmed in Figure 5. In its current form, Kirchhoff's law [1, 2] stands at odds against practical microwave techniques [61, 62]. Since this knowledge should not be discounted, something must be incorrect within Kirchhoff's law. Everything about the blackbody resonator presented in Figure 4 echoes Planck, yet the radiation it contains is not black [5]. The type of radiation within this cavity is being determined by electromagnetics [61, 62], not by Kirchhoff's law. Only the attributes of any substance present and that of the enclosed resonant elements, along with the size and shape of the enclosure itself, govern the type of radiation. For example, as seen in Figs. 4 and 5, the simple addition of echosorb acts to significantly alter the resonances within such cavities. The associated loses are thermal. Of course, at these frequencies, echosorb is not a perfect absorber and the radiation inside the cavity cannot easily be made black. Still, in partial deference to Kirchhoff, if a perfect absorber could be found, the radiation within cav-

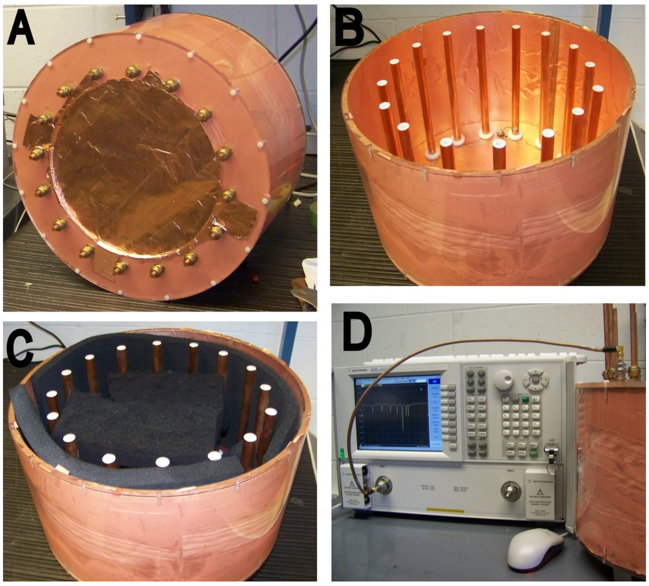

Fig. 4: A) End-view photograph of a sealed blackbody resonator [60] for use in UHFMRI studies. This device behaves as a resonant cavity [61, 62] and is constructed by sealing both ends of the well-known TEM resonator [63, 64]. In this particular case, one of the ends of the resonator was made by sealing an acrylic ring with a thin copper sheet which was then re-enforced with copper tape on the inner and outer surfaces. All other assembly details are as previously reported [60]. When a resonator is sealed at both ends to make a cavity [61, 62], radiation can solely enter or leave the device through a single drive port. As such, the blackbody resonator can be regarded as the electromagnetic equivalent of Kirchhoff's blackbody [1, 2, 5, 7], with the important difference, of course, that the radiation inside such a device is never black. This constitutes a direct refutation of Kirchhoff's law of thermal emission as demonstrated experimentally in Fig. 5. B) Photograph of the interior of the blackbody coil illustrating the TEM rods, the interior lined with copper, and the drive point. Note that for these studies, a matching capacitor [60] was not utilized, as the measurement of interest does not depend on matching a given resonance to 50 ohms. It is the resonant nature of the coil itself which is of interest, not the impedance matching of an individual resonant frequency. C) Photograph of the blackbody coil filled with pieces of Echosorb. D) Photograph of the blackbody coil connected to an Agilent Technologies N5230C 300kHz – 6 GHz PNA-L Network Analyzer using an RG400 cable and SMA connectors. Since the RF coil was assembled with a BNC connector, an SMA/BNC adaptor was utilized to close the RF chain. The calibration of the analyzer was verified from 200–400 MHz using a matched load of 50 ohms placed directly on the network analyzer port. In this case, the return loss (S11) was less than −40 dB over the frequency range of interest. The matched load was also placed on the end of the test cable used for these studies and in this case the return loss (S11) was less than −25 dB from 200–400 MHz. The network analyzer provides a continuous steady state coherent source of radiation into the cavity. The coherence of this radiation is critical to the proper analysis of the returned radiation by the network analyzer. This does not alter the conclusions reached. Only the ability to properly monitor cavity behavior is affected by the use of incoherent radiation. The cavity, of course, is indifferent to whether or not the radiation incident upon it is coherent.

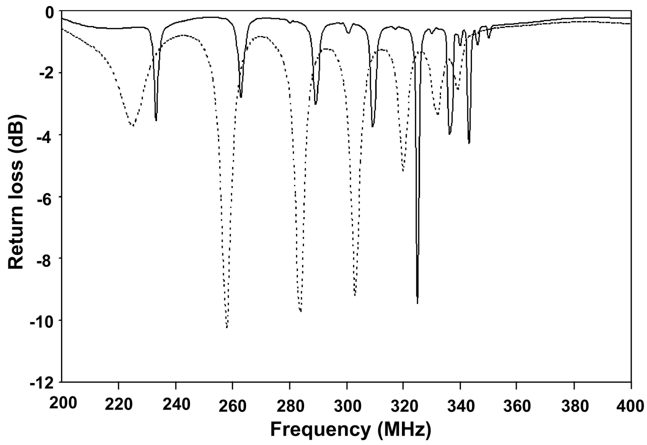

Fig. 5: Plot of the return loss (S11) for the blackbody coil (solid line) as measured from 200–400 MHz. Note that even though this cavity is completely closed, the radiation within this device is not black. Several sharp resonances are observed whose resonant position depend on the nature of the resonant cavity itself (dimension of the cavity, quality of the inner copper lining, dimensions of the TEM resonant elements, degree of insertion of the struts into the TEM elements, etc.). It is the presence of such resonances within cavities that forms the basis of practical electromagnetics and enables the use of resonant cavities in both EPR and MRI [61, 62]. If Kirchhoff's law of thermal emission had been correct, such a resonant device would not exist. The problem is easily rectified if one adopts Stewart's formulation for the treatment of thermal emission [6]. The dashed line displays the return loss (S11) for the blackbody coil filled with the carbon-foam Echosorb as measured from 200–400 MHz. Note that Echosorb is not a perfect absorber of radiation at these frequencies. But since this foam is somewhat absorbing, the resonance lines are broadened substantially. The return losses at several frequencies are lower, as is to be expected from the introduction of an absorbing object within a resonant cavity. If a perfect absorber could be found at these frequencies, the return loses would become extremely low across the entire frequency range of interest. Given these measurements and access to resonant devices, network analyzers and microwave technology, it is likely that Kirchhoff would have reconsidered the formulation of his law of thermal emission.

ities containing such objects would be black. Nonetheless, only Stewart's law [6] is formulated in such a way as to conform with results from electromagnetics [61, 62].

5 Conclusions

Tragically, if Kirchhoff believed in universality, it was because he did not properly treat both reflection and absorption, as previously highlighted [12]. The correct treatment of radiation at thermal equilibrium was first performed by Stewart, in 1858 [6]. Stewart properly addresses reflection [6, 8, 12], and does not arrive at universality. Unfortunately, Stewart's formulation lacked mathematical rigor [6, 12] and this did not help in drafting a central law of thermal emission. At the same time, in deriving Kirchhoff's law in his treatise, Planck fails to fully treat reflection [7; §6]. Like Kirchhoff his teacher, Planck is thereby lead erroneously to the concept that all enclosures contain black radiation. Planck begins his derivation of Kirchhoff's law by considering elements $d\tau$ within an extended substance. He then analyzes the radiation emitted by these elements, but ignores the coefficient of reflection, ρ_ν. He writes: "*total energy in a range of frequency from ν to $\nu + d\nu$ emitted in the time dt in the direction of the conical element $d\Omega$ by a volume element $d\tau$*" [7; §6] is equal to $dt\, d\tau\, d\Omega\, d\nu\, 2\varepsilon_\nu$. As a result, he is brought to a universal function, which is independent of the nature of the object, and affirms the validity of Kirchhoff's law: $\varepsilon_\nu / a_\nu = f(T, \nu)$. In this equation, the coefficient of emission, ε_ν, the coefficient of absorbance, a_ν, the temperature, T, and the frequency, ν, alone are considered. Had Planck properly addressed the coefficient of reflection, ρ_ν, and recognized that the total radiation which leaves an element is the sum produced by the coefficients of emission, ε_ν, and reflection, ρ_ν, he would have obtained $(\varepsilon_\nu + \rho_\nu)/(a_\nu + \rho_\nu) = f'(T, \nu, N)$, where the nature of the object, N, determined the relative magnitudes of ε_ν, a_ν, and ρ_ν. By moving to the interior of an object and neglecting reflection, Planck arrives at Kirchhoff's law, but the consequence is that his derivation ignores the known truth that opaque objects possess reflection.

Given thermal equilibrium, the equivalence between the absorptivity, a_ν, and emissivity, ε_ν, of an object was first recognized by Stewart [6]. Stewart's formulation preserves this central equivalence. Only, it does not advance the universality invoked by Kirchhoff [1, 2]. At the same time, it remains fortunate for human medicine that Kirchhoff's law of thermal emission does not hold. If it did, MRI within cavities [60] would not be possible. Devices containing solely black radiation would be of no use, either as microwave components, or as antenna for human imaging. Physics and medicine should return thereby, by necessity, to Stewart's formulation [6] and the realization that radiation within cavities depends not uniquely on frequency and temperature, as stated by Kirchhoff [1, 2], but also on the attributes of the cavity itself and the materials it contains. This contribution was first brought to physics by Balfour Stewart [6]. Stewart's law, not Kirchhoff's, properly describes physical reality as observed in the laboratory across all subdisciplines of physics and over the entire span of the electromagnetic spectrum.

Practical blackbodies are always made from specialized substances which are nearly perfect absorbers over the frequency range of interest [13–25]. Accordingly, the nature of the enclosure is important, in opposition to Kirchhoff's law which claims independence from the properties of the walls and its contents. Through the formulation of his law of thermal emission, Balfour Stewart [6], unlike Kirchhoff, recognized the individualized behavior of materials in thermal equilibrium. In addition, it is well-established that the radiation within microwave cavities is not necessarily black. Rather, it depends on the nature, shape, contents, and dimensions of the enclosure itself. This is in accordance with Stewart's law. Alternatively, if Kirchhoff's law was correct, cavities should strictly contain blackbody radiation and their use in radio and microwave circuitry would be pointless. Network analyzer measurements of return losses for a sealed enclosure, or blackbody resonator [60], from 200–400 MHz, confirm that Kirchhoff's law of thermal emission does not hold within arbitrary resonant cavities.

At the same time, the physics community is justified in taking a cautious approach in these matters. After all, it was Planck [5] who provided the functional form contained in Kirchhoff's law [1, 2]. As a result, there is an understandable concern, that revisiting Kirchhoff's law will affect the results of Planck himself and the foundation of quantum physics [5]. There is cause for concern. The loss of the universal function brings about substantial changes not only in astrophysics, but also in statistical thermodynamics.

Relative to Planck's equation itself, the solution remains valid. It does however, become strictly limited to the problem of radiation within cavities which are known to be black (i.e. made of graphite, lined with soot, etc). Universality is lost. As for the mathematical value of Planck's formulation for the perfectly absorbing cavity, it is preserved. In describing blackbody radiation, Planck consistently invokes the presence of a perfect absorber. In his treatise [7], he repeatedly calls for a minute particle of carbon [8]. Planck views this particle as a simple catalyst, although it can be readily demonstrated that this is not the case: the carbon particle acted as a perfect absorber [12]. As a result, I have stated that Kirchhoff's law is not universal [8, 12, 26, 27] and is restricted to the study of cavities which are either made from, or contain, perfect absorbers. Arbitrary cavity radiation is not black [12]. There can be no universal function. Planck's equation presents a functional form which, far from being universal, is highly restricted to the emission of bodies, best represented on Earth by materials such as graphite, soot, and carbon black [8].

In closing, though 150 years have now elapsed since Kirchhoff and Stewart dueled over the proper form of the law of thermal emission [11, 12], little progress has been made in bringing closure to this issue. Experimentalists continue to unknowingly pump black radiation into arbitrary cavities using their detectors. Theorists replicate the approach with Monte Carlo simulations. At the same time, astrophysicists apply with impunity the laws of thermal emission [1–7] to the stars and the universe. Little pause is given relative to the formulation of these laws [1–7] using condensed matter. The fact that all of electromagnetics stands in firm opposition to the universality, instilled in Kirchhoff's law, is easily dismissed as science unrelated to thermal emission [61, 62]. Losses in electromagnetics are usually thermal in origin. Nonetheless, electromagnetics is treated almost as an unrelated discipline. This occurs despite the reality that Kirchhoff himself specifically included other processes, such as fluorescence, provided enclosures were maintained. Though the generalization of Kirchhoff's law is widely recognized as valid [52–55], its application to the microwave cavity has been strangely omitted [52], even though it is used in treating the waveguide. This is the case, even though waveguides and cavities are often treated in the same chapters in texts on electromagnetics. All too frequently, the simple equivalence between apparent spectral absorbance and emission is viewed as a full statement of Kirchhoff's law [57, 65], adding further confusion to the problem. Kirchhoff's law must always be regarded as extending much beyond this equivalence. It states that the radiation within all true cavities made from arbitrary walls is black [1, 2]. The law of equivalence [57, 65] is Stewart's [6].

Most troubling is the realization that the physical cause of blackbody radiation remains as elusive today as in the days of Kirchhoff. Physicists speak of mathematics, of Planck's equation, but nowhere is the physical mechanism mentioned. Planck's frustration remains: "*Therefore to attempt to draw conclusions concerning the special properties of the particles emitting rays from the elementary vibrations in the rays of the normal spectrum would be a hopeless undertaking*" [7; §111]. In 1911, Einstein echoes Planck's inability to link thermal radiation to a physical cause: "*Anyway, the h-disease looks ever more hopeless*" [66; p. 228]. Though he would be able to bring a ready derivation of Planck's theorem using his coefficients [67], Einstein would never be able to extract a proper physical link [68]. In reality, we are no closer to understanding the complexities of blackbody radiation than scientists were 150 years ago.

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Dedication

This work is dedicated to my eldest sister, Christine.

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