Kirchhoff's Law of Thermal Emission: Blackbody and Cavity Radiation Reconsidered

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Kirchhoff's law of thermal emission asserts that, given sufficient dimensions to neglect diffraction, the radiation contained within arbitrary cavities must always be black, or normal, dependent only upon the frequency of observation and the temperature, while independent of the nature of the walls. In this regard, it is readily apparent that all cavities appear black at room temperature within the laboratory. However, two different causes are responsible: 1) cavities made from nearly ideal emitters self-generate the appropriate radiation, while 2) cavities made from nearly ideal reflectors are filled with radiation contained in their surroundings, completely independent of their own temperature. Unlike Kirchhoff's claims, it can be demonstrated that the radiation contained within a cavity is absolutely dependent on the nature of its walls. Real blackbodies can do work, converting any incoming radiation or heat to an emission profile corresponding to the Planckian spectrum associated with the temperature of their walls. Conversely, rigid cavities made from perfect reflectors cannot do work. The radiation they contain will not be black but, rather, will reflect any radiation which was previously incident from the surroundings in a manner independent of the temperature of their walls.

1 Introduction

Kirchhoff's law of thermal emission was formulated in 1859 [1, 2]. It is often presented as stating that, at thermal equilibrium, the emissivity of an object, ϵ_ν, is equal its absorptivity, α_ν. However, this should properly be considered as 'the law of equivalence', first proposed by Balfour Stewart [3] in 1858.

Kirchhoff's law extended much beyond Stewart's [3] and stated that, given thermal equilibrium, the radiation contained within an arbitrary cavity was depended only on the temperature of the enclosure and on the frequency of observation [1, 2]. Such radiation was completely independent of the nature of the walls [1, 2]. It was because of Kirchhoff's law that blackbody, or normal, radiation has always been viewed as independent of the lattice and unlinked to a physical cause [4]. Clearly, if Kirchhoff was correct and blackbody radiation was independent of the nature the walls, then such radiation could not be ascribed causality in the emitting structure.

Yet, it has been known for over 200 years that the radiation emitted from objects was highly variable [5]. In 1804, Leslie reported that the emission of surfaces depended on their nature and established the primacy of lampblack as a blackbody surface [6]. As a result, lampblack or soot, along with graphite, soon gained a dominant role in the construction of laboratory blackbodies (see [7] and references contained therein). The nature of the surface producing a thermal spectrum clearly did matter, in stark contrast to Kirchhoff's claims relative to cavity radiation [1, 2].

In the early 19^{th} century, blackbodies were simply objects made from graphite or coated with materials such as soot and lampblack. Carbon black was also employed, a pigment used in paints since pre-historic times [8]. Eventually, blackbodies became increasingly sophisticated devices, typically cavities. Other good absorbers of radiation slowly moved onto the scene relative to the construction of laboratory blackbodies [9–11], but graphite, soot, and carbon black retained their pre-eminent role [12]. Max Planck soon benefited from the construction of advanced cavities [9–11], when he formulated the blackbody solution [13, 14]. Contrary to Kirchhoff law [1, 2] the nature of the walls was thereby proven to be important on a practical level. It governed the quality of a blackbody. The quest for ever blacker surfaces [15–22] has now turned to novel structural absorbance approaches guided by samples as diverse as butterflies [23, 24] and birds [25]. Yet still today, many blackbodies in national laboratories are based upon the use of graphite (e.g. [26, 27]).

It remains true that blackbodies are specialized cavities which depend entirely on the nature of their walls [7, 9–12, 26, 27]. Laboratory blackbodies are made from materials that have an elevated emissivity over the range of interest, as is widely known throughout metrology. This fact alone is sufficient to illustrate that Kirchhoff's law cannot be valid.

As such, it is surprising that many still believe that any arbitrary cavity can produce a blackbody spectrum. In the laboratory, this was never the case. Planck himself [13] was dependent on the work of leading scientists in order to obtain a spectrum with the blackbody frequency distribution [9–11]. If Kirchhoff law had been correct [1, 2], this should not have been necessary.

The author has previously stated that Kirchhoff's law was not valid (see [4, 7, 12] and references therein), as it has no proper theoretical [28] or experimental proof. Planck's equation [13, 14] remained unlinked to a physical mechanism [4] because of Kirchhoff's law [1, 2]. As a result, physics was prevented from accounting for the production of a thermal photon from a simple cavity made from a block of graphite. Blackbody radiation remained, according to Kirchhoff, independent of the nature of the walls [1, 2]. In this respect, Planck's equation [13] was unique in spectroscopy. This has enabled scientists, in disciplines other than condensed matter physics, to infer that thermal photons could be produced without having recourse to a physical lattice, as was clearly required when emitted from graphite [4]. This has also enabled Max Planck to claim that his equation had universal significance [14, §164]. But in reality, Planck's solution was strictly limited to actual blackbodies (e.g. [7, 9–11, 26, 27]) and not to all cavities.

Thus, cavity radiation is reconsidered herein as to refute Kirchhoff's law [1, 2] and place a proper perspective on cavity radiation. In order to do so, cavities were constructed from materials which acted as nearly perfect absorbers or reflectors of radiation in the infrared. The results are discussed in terms of the work required to convert incident energy into normal radiation within the blackbody cavity. Conversely, the existence of nearly perfectly reflecting cavities is discussed in the context of resonant cavities used in magnetic resonance imaging [29], microwave cavities [30, 31], and lasers [32]. The findings demonstrate that cavity radiation is absolutely dependent on the nature of the walls. Consequently, Kirchhoff's law was never valid [4, 7, 12] and Planck's equation is not universal, as confirmed by a wide array of experimental results [29–32].

For the sake of brevity, the challenge to Kirchhoff's law presented herein can be limited to the study of a single approach without any loss in content. In 1954, de Vos published his *Evaluation of the Quality of a Blackbody* in the journal *Physica* [33]. This article has become a classic in blackbody radiation. de Vos [33] examined the quality of cavities constructed from materials with varying emissivity by noting the change upon incident radiation. This radiation was allowed to enter a cavity, exit, and be monitored with a detector placed at various angles. For cylindrical cavities, de Vos was concerned with the ratio of the length of the cavity to its diameter. He demonstrated that the radiation within cavities appeared to become increasingly isotropic as this ratio was increased [33]. However, de Vos had not demonstrated that all cavities will be black, independent of incident radiation. In fact, de Vos was concerned with the degree to which the surface of the cavity was either specular or white [33]. He did not evaluate whether a cavity could actually emit photons at the correct temperature. Thus, his work provided only limited insight into blackbody radiation [33]. He did analyze to what extent the surface property of a cavity affected the change of incoming light into fully diffuse reflection [33]. However, if a cavity was not constructed of a near ideal absorber, it was not necessarily black unless it was able to receive the proper incident radiation from its surroundings.

At the same time, if a cylindrical hole of sufficient depth was placed in a material with an elevated emissivity, the findings from de Vos suggest that the resulting cavity should indeed be black [33]. This approach was therefore implemented in this work in order to construct a simple blackbody cavity from small blocks of graphite. In parallel fashion, nearly perfectly reflecting cavities were constructed from blocks of brass, copper, and aluminum.

2 Materials and methods

Infrared images were obtained using a CompactPro thermal imaging camera (Seek Thermal, Inc., Santa Barbara, CA 93117; Thermal.com) interfaced with an Android (version 4.4.2) cell phone, as shown in Fig. 1A.

The camera had a focusable lens and a 32° field of view. It was equipped with a 320×240 thermal sensor, had a temperature range of -40 to 330°C, and was capable of obtaining ei-

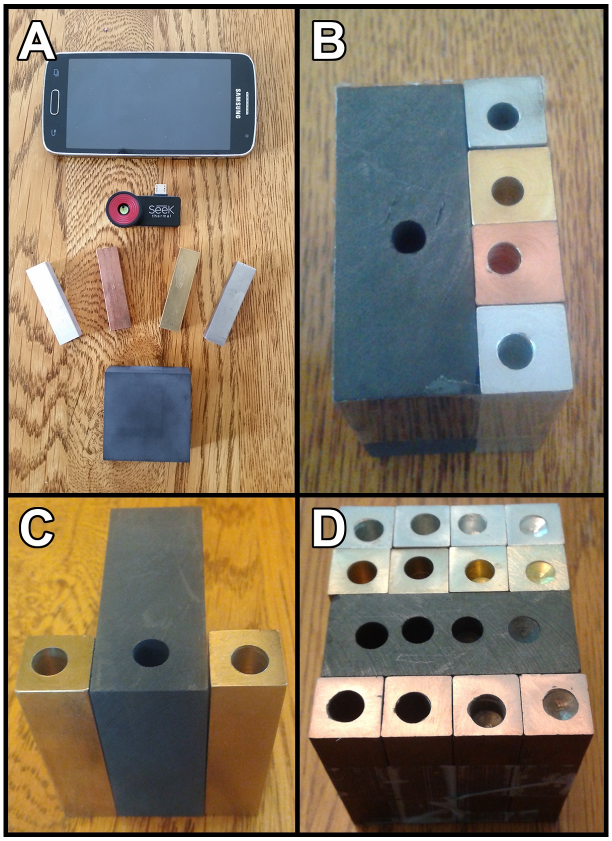

Fig. 1: A) Photograph of the Android phone, Seek Thermal camera, and aluminum, copper, brass, steel, and graphite blocks; B) Block assembly I (graphite on the left, then on the right from top to bottom: steel, brass, copper, aluminum). Note that two small scratches are visible near the graphite cavity. C) Block assembly II (brass, graphite, brass). D) Block assembly III (horizontal rows from top to bottom: aluminum, brass, graphite, copper).

ther still images or video. All images were obtained with the camera operating in white mode, except for Fig. 2A, where black mode was utilized.

Cylindrical cavities where constructed by drilling a small hole into 12.5 × 12.5 × 50 mm blocks of copper, aluminum, brass, and steel (Specific Gravity Metal Blocks, EISCO, Haryana 133001, India). The expected emissivity of the copper, brass, and steel holes should be on the order of 0.03-0.1 [34]. The type of steel was unknown. A 20 × 50 × 50 mm 99.9% Purity Graphite Ingot Block EDM Graphite Plate Milling Surface (Otoolworld, China) was used to build the reference blackbody using the same approach.

Cavities were produced with a drill press using either standard $\frac{3}{16}''$ or $\frac{1}{4}''$ diameter drill bits or a DeWalt Pilot Point $\frac{1}{4}''$ diameter drill bit to the depth described in the figure legends. Cavities were examined at room temperature or after having reached steady state while being heated on a hotplate (Cuisinart, East Windsor, NJ) to a temperature of approximately ∼304°C. Small graphite particles were made from 2 mm mechanical pencil refills (Menards, Eau Claire, WI) cut to a length of 0.5 cm and inserted into the cavities of interest.

Experiments were initiated at room temperature, by placing the camera at a distance of ∼20 cm above the table surface and therefore ∼15 cm above the surface of the block assembly. The eye of the camera was positioned directly over the center of this assembly. In order to document the effect of ambient radiation on the cavities, a galvanized steel rod was placed in an oven, heated to ∼232°C, and then brought near the cavities, as described in the figures.

3 Results

Thermal images are presented in Fig. 2 with the corresponding schematic representations outlining the position of the rod in Fig. 3. In Fig. 2A, a thermal image is presented in black mode, revealing that all the cavities appeared nearly the same at room temperature. In this image, there was also reflection of thermal radiation from the body of the observer onto the block assembly. Thus, on cursory examination, Kirchhoff's law appeared valid as all cavities essentially contained the same radiation. Still, the block was positioned within a room filled with radiation at the same temperature. Therefore, it was important to determine whether the cavities were generating radiation on their own or simply manifesting the radiation in their surroundings.

For other studies, the camera was switched to white mode and the cavities all appeared black, as seen in Fig. 2B. Next, in Fig. 2C-F (see schematics in Fig. 3C-F), a heated galvanized steel rod was placed above their surface. The rod had been heated to ∼232°C. In Fig. 2C, the rod was positioned to the right of the steel cavity (see schematic Fig. 3C). With the heated rod in this position, the graphite and steel cavities could not be filled with its radiation. These two remain pretty much as they were with just a tiny spec of reflection at the graphite cavity. Thus, radiation from the rod was reaching this cavity as well, as expected. At the same time, the aluminum, copper, and brass cavities were immediately filled with radiation from the rod.

The rod was then moved to the left in Fig. 2D, as shown in Fig. 3D. Notice, once again, that there was no effect on the graphite cavity and that only a slight reflection was observed at the top of the steel cavity. However, all the others were filled with radiation from the rod. In particular, note the pattern in the brass cavity revealing that it was still not able to fully convert incoming radiation into isotropic ejected radiation. This indicated this cavity should be deeper to render the radiation fully isotropic, as suggested in de Vos' classic work [33].

In Fig. 2E, the rod was placed near the center of the block as represented in Fig. 3E. The three cavities from aluminum, copper and brass were again filled with rod radiation, but the graphite cavity remained unaffected and the steel cavity almost unaffected. However, reflection of rod radiation could be observed in the scratches on each side of the graphite cavity. As such, radiation from the rod was clearly reaching this cavity. Finally, in Fig. 2F, the rod was positioned just to the right of the steel cavity as shown in Fig. 3F. In this position, the steel cavity was no longer black. Now, it could be observed that rod radiation was able to partially fill the steel cavity. Nonetheless, the bottom of this cavity was darker, thereby indicating that steel had a much higher emissivity than the aluminum, copper, or brass cavities, but was not on par with graphite. The aluminum, copper, and brass cavities all appeared filled with radiation from the rod.

Next, the effect of inserting a small piece of graphite into the cavities was examined as shown in Fig. 4. In Fig. 4A (see schematic 4D), the graphite cavity was indistinguishable from the surface of the block at thermal equilibrium. Both cavities within the brass blocks were clearly visible.

When the heated steel rod was brought in close proximity to the cavities, its radiation was reflected off the surfaces and the signal to noise of the resulting image increased, as shown in Fig. 4B (schematic 4E). However, the central graphite cavity appeared black and both of the brass cavities became filled with rod radiation. This revealed that real blackbodies do work and convert any incident radiation to that corresponding to the temperature of their walls. Conversely, the two brass cavities on each side became filled with radiation originating from the steel rod. Again, the reflecting cavities were not black, as they manifested the radiation present in their surroundings in a manner independent of the temperature of their own walls. When the graphite particle was introduced into each of the cavities, it was unable to make the brass cavities fully black, as clear signs of radiation from the heated rod remained, as shown in Fig. 4C (schematic 4F).

Next, consider the findings from block assembly III, as displayed in Fig. 5. Initially, this assembly was monitored at room temperature, in equilibrium with its surroundings, as

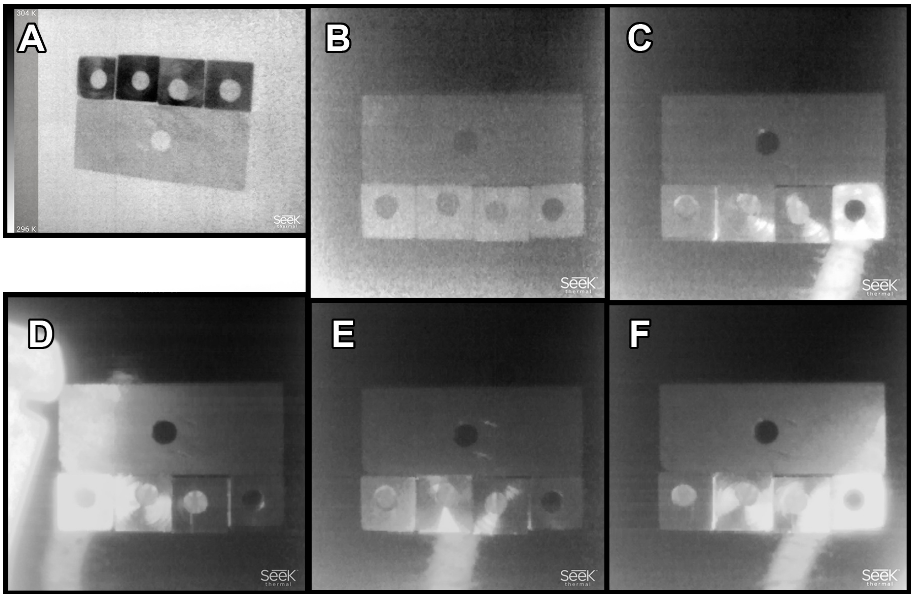

Fig. 2: A) Infrared image obtained from the Block Assembly I (see Fig. 1B) with the camera operating in black mode. For this image the camera was hand held. All the cavities were made using a standard $\frac{3}{16}''$ drill bit to a depth of $1''$ and appeared to contain the same radiation; B-F) Infrared images obtained from the block assembly with the camera in white mode. The lens of the camera was exactly 15 cm directly above the top of the block assembly or 20 cm above the top of the table. In these images, photons emitted from the heated rod and reflected prior to detection are observed as a white streaks on the images. B) The galvanized steel rod was not near the block assembly. Thermal radiation from the observer was likely to account for the good signal to noise on this image; C) The heated galvanized steel rod was placed on the right near the steel cavity; D) The heated galvanized steel rod was placed on the left side near the aluminum cavity. In this case, both the rod and its reflection are clearly visible; E) The heated galvanized steel rod was placed at the center of the block assembly. The two small scratches near the graphite cavity reflected radiation, demonstrating that radiation from the rod was reaching this cavity as well; F) The heated galvanized steel rod was placed just to the right of the steel cavity.

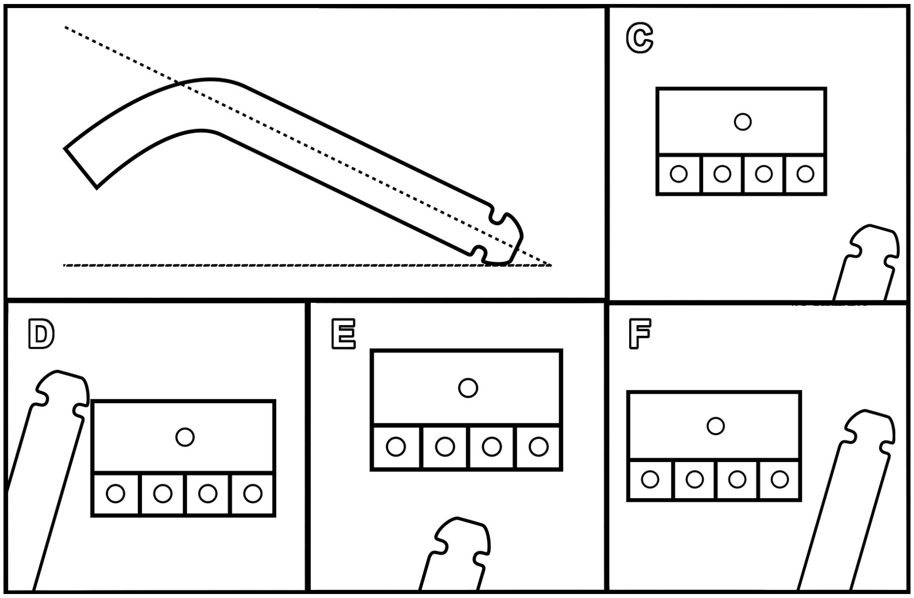

Fig. 3: Schematic representation illustrating the position of the heated rod relative to the block assembly. In the upper left, a vertical cross section is presented. For Fig. 2C-F, the rod was held using locking pliers at an angle of ~25-30^o relative to the table. C-F) top view illustrating the rod position in Figs. 2C-F, respectively.

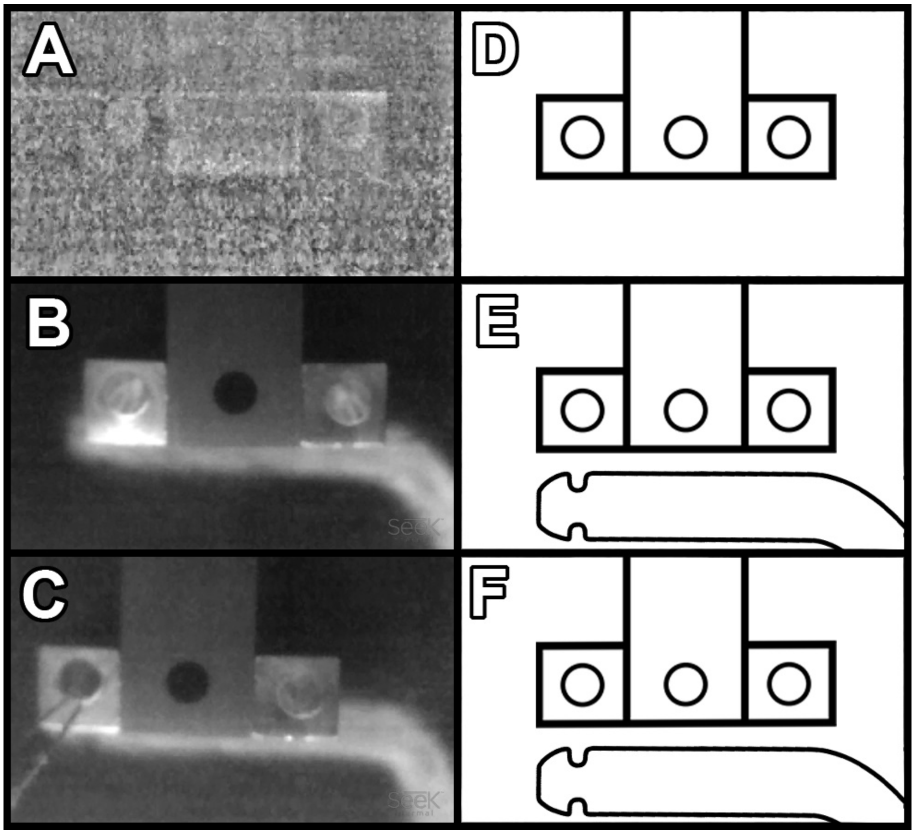

Fig. 4: Infrared images (A-C) and their schematic representations (D-F). The cavities were drilled with a DeWalt Pilot Point $\frac{1}{4}''$ diameter drill bit to the depth $1\frac{1}{4}''$. A) Infrared image obtained from the Block Assembly II (see Fig. 1C) at room temperature without any heated rod present (schematic in D). B) Image obtained while placing a heated steel rod in close proximity to the cavities (schematic in E). C) Repeat of B, but this time, a graphite particle was suspended from two strings into the left brass cavity such that the center of the particle was exactly 1 cm from the top of the block (schematic in F). Graphite particles were also inserted at the bottom of the other two cavities. In B and C, the stem of the rod was parallel to and about 7 cm above, the top of the table (or a height of about 2 cm above the top of the block). In schematics E and F, the rod was illustrated such that its position from left to right could be accurately represented relative to the block. However, in the plane of the image, the rod was actually positioned just below the field of view considered by the schematic, or about one rod width from the block.

shown in Fig. 5A (corresponding schematic, 5C).

Once again the infrared camera was positioned a distance of ∼15 cm from the top of the block. The cavities within the graphite portion of the block under those conditions were indistinguishable from the graphite surface. The image was noisy, as expected, since the observer was well removed from the block during data acquisition. At the same time, the cavities made within the aluminum, brass, and copper blocks were clearly visible and distinct from one another, demonstrating that they did not contain identical radiation. Since these cavities were made from highly reflective materials, this implied that the space surroundings of the block contained some anisotropic radiation.

In Fig. 5B, the same block was examined (schematic 5D). This time, the hands of the investigator were positioned on each side of the block, such that thermal equilibrium was not maintained and the associated radiation could be observed filling the aluminum, brass, and copper cavities. Clearly, these nearly perfectly reflecting cavities were not black, but contained radiation emitted by their surroundings. Conversely, under these conditions, the three deepest graphite cavities, located on the left of the third row, remained essentially unaffected. At the same time, the shallowest cavity, made from the tip of the drill bit and located on the right of the third row, was sensitive to this challenge (Fig. 5B, D). There were reflections of thermal photons off the surfaces of each block which altered the appearance of the images as well. This study served to exemplify, once again, that real blackbodies could do work converting radiation incident upon their walls to black radiation manifesting their temperature. Conversely, rigid perfectly reflecting cavities could not do work. They contained the radiation present in their surroundings in a manner independent of their own temperature and such radiation was clearly observed in the aluminum, brass, and copper

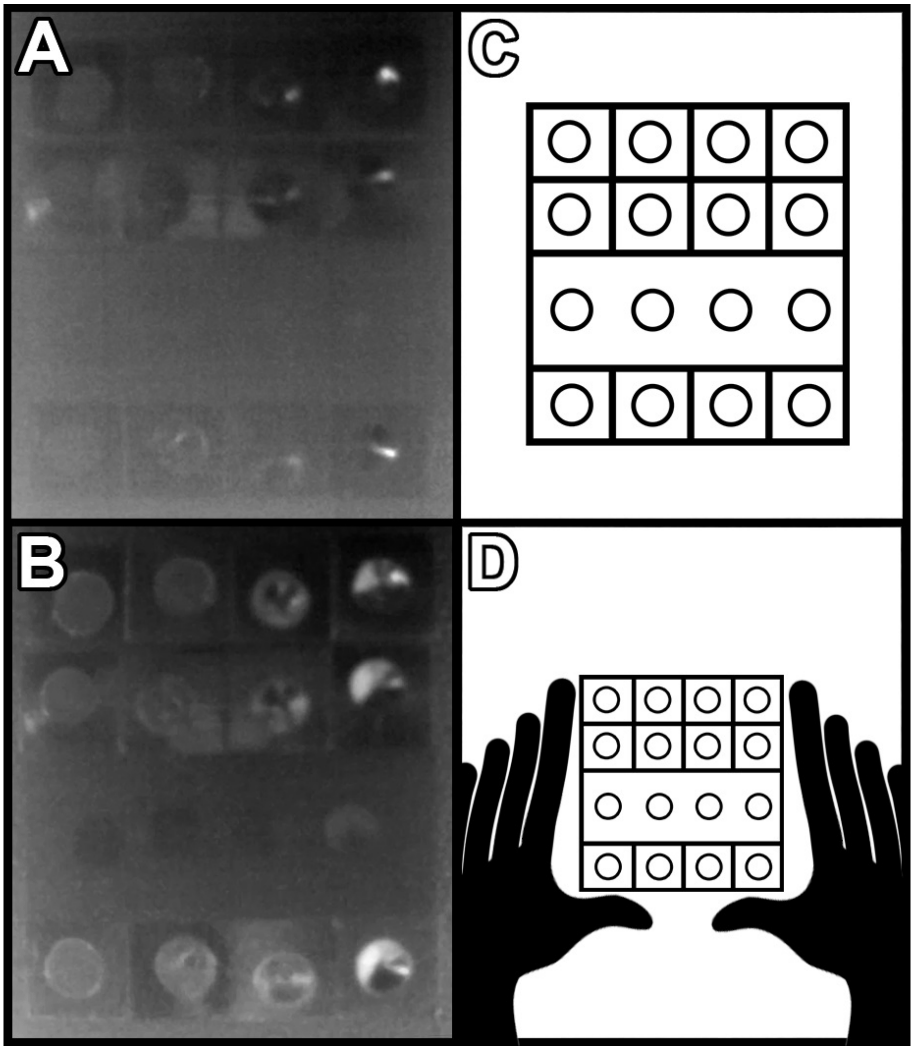

Fig. 5: A) Infrared image obtained from the Block Assembly III (see Fig. 1D) at room temperature. The corresponding schematic is displayed in C (reduced by 25%). B) Same as in A, but this time the hands of the investigator were placed near the sides of the block such that thermal photons from the first two fingers of each hand could challenge the cavities, as seen in the schematic representation D (reduced by ~50%). The horizontal rows from top to bottom correspond to aluminum, brass, graphite, copper. These cylindrical cavities were made using a standard $\frac{1}{4}''$ drill bit to different depths (from right to left: 1) depth corresponding to just the cone of the drill bit, 2) depth to $\frac{1}{4}''$, 3) $\frac{3}{4}''$ and 4) $1\frac{1}{4}''$).

cavities.

At this point Block Assembly III was placed onto the surface of a hotplate brought to a temperature of ~304°C, as shown in Fig. 6.

Under these conditions, the graphite cavities located on the third row all appeared to contain isotropic radiation closely manifesting their equilibrium temperature. This indicated that these cavities were able to convert heat energy located in their walls to blackbody radiation. Even the cavity produced with only the tip of the drill bit, on the right, contains isotropic radiation. Conversely, the cavities constructed from aluminum, brass, and copper did not all contain such radiation. Rather, they showed clear signs that their radiation originated from the hotplate and was a property of the surroundings, not the cavity itself.

While the $1\frac{1}{4}''$ aluminum (top row, left most) and copper (bottom row, left most) cavities appeared to contain isotropic radiation, the brass cavity of the same depth (second row, left most) clearly did not. In addition, careful examination revealed that crescents were visible in the aluminum, brass, and copper $\frac{3}{4}''$ cavities (second column) as well. With the exception of graphite, the $\frac{1}{4}''$ cavities (third column) did not contain isotropic radiation at the appropriate temperature and neither did the corresponding conical cavities made from just the tip

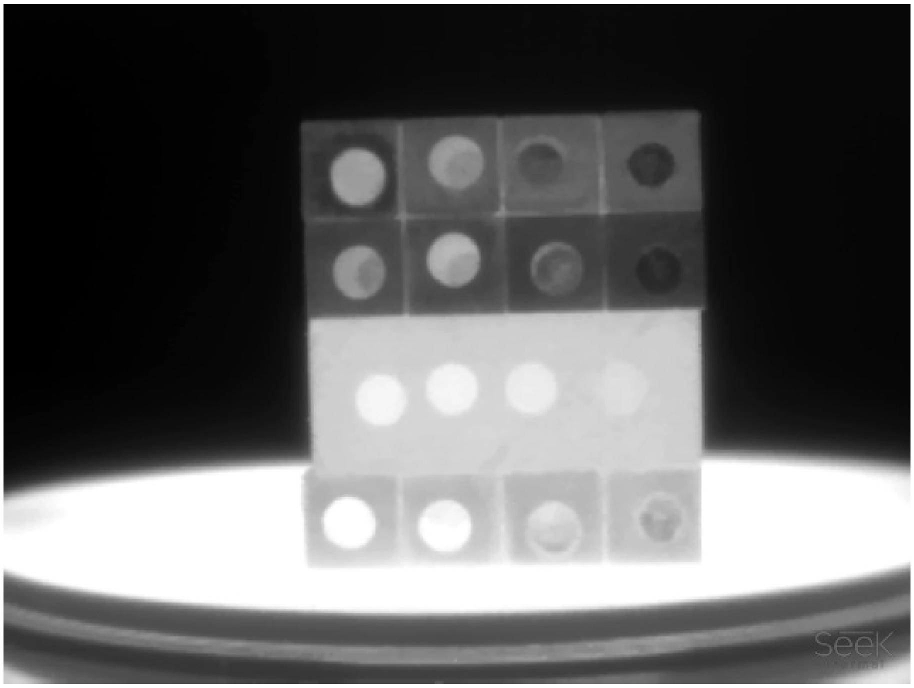

Fig. 6: Infrared image obtained from the Block Assembly III (see Fig. 1D) positioned on a hotplate surface at a temperature estimated at ~304°C using the thermal camera. In order to acquire this image, the camera was mounted on a tripod such that its lens was ~20 cm from the face of the block.

of the drill bit (fourth column). For instance, note the inability of any of the smallest cavities, made from these materials, to sustain radiation at the proper temperature. Crescent patterns also appeared in cavities constructed from aluminum, brass, and copper, even at a depth of $\frac{3}{4}''$ (second column), despite the fact that the radiation in the graphite cavity at the same depth was clearly isotropic. At a depth of $1\frac{1}{4}''$, the brass cavity (second row, first column) still displayed such patterns.

When the block assembly was cooled, it was apparent that the copper blocks had become highly oxidized and this, in addition to their proximity to the hotplate, might help explain their superior performance when compared to aluminum and brass.

Still, these results revealed that real blackbodies, represented herein by the graphite cavities, could do work and manifested the radiation appropriate to the temperature of their own walls. Conversely, the aluminum, brass, and copper cavities illustrate that nearly ideal reflectors could not do work, but contained the radiation present in their surroundings which was independent of the nature of their walls.

4 Discussion

The approach to, and departure from, thermal equilibrium has been the subject of countless studies by Fourier [35], Dulong [36], Petit [36], de la Provostaye [37], and Desains [37] (see [38] for a full review). In similar fashion, through the studies presented herein, a greater understanding has been sought about the nature of the radiation within cavities. This was accomplished both under conditions of thermal equilibrium and also by considering challenges which represent small departures from equilibrium. However, these challenges were important because they served to highlight the nature of the radiation which filled a cavity and thereby help to establish the identity of those objects which properly constituted blackbodies.

4.1 Blackbodies defined

Prior to formulating his law, Kirchhoff first defined a blackbody by stating that *"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"* [2, §7]. Kirchhoff therefore recognized the importance of surface absorptivity in the blackbody problem.

Surprisingly however, when Max Planck would later define the blackbody in his classic text [14], he completely rejected Kirchhoff's approach writing: *"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"* [14, §10]. Planck then changed the characteristics of a blackbody surface: *"A rough surface having the property of completely transmitting the incident radiation is described as 'black"'* [14, §10]. With this definition, Planck removed absorbance of the surface itself from the requirements for creating a blackbody and inappropriately placed the focus on transmittance. Planck adopted this new definition because he was preparing to advance a proof of Kirchhoff's law which ignored absorbance at the boundary of two materials [14, §35-37]. But in doing so, Planck moved away from physical reality. His approach proved invalid [39]. Nearly ideal absorbance for thin surfaces remains the hallmark of all materials used to construct quality blackbodies [7, 9–11, 25, 27].

4.2 The mathematical form of Kirchhoff's Law

In advancing his law [2], Kirchhoff did not have recourse to experimental verification. He first stated that the emissive power of an object, E, divided by its absorptive power, A, was equal to a universal function which depended only upon temperature, T, and frequency, ν (E/A= e where e = $f\{T,\nu\}$). He then immediately replaced absorptive power, A, with absorptivity, α_ν, such that E/α_ν=$f\{T,\nu\}$. For actual blackbodies, it is clear that α_ν can be set to 1 and E=$f\{T,\nu\}$. However, Kirchhoff's expression becomes undefined when α_ν is set to zero, as would occur if the cavity was constructed from a perfect reflector. Planck himself recognized the undefined nature of Kirchhoff's law under those conditions (see §48, §51, §52 in [14]).

Thus, relative to Kirchhoff's relationship, two limits are involved. The first, addresses cavities constructed from perfect absorbers, such that α_ν can be set to 1. The second, involves cavities constructed from perfect reflectors, such that α_ν can be set to zero and the law becomes undefined. Perfectly reflecting cavities never followed Kirchhoff's law. They are important however as they form the basis for many resonant devices [29–32]. In any event, Kirchhoff had no mathematical basis for arguing that all cavities must contain black radiation which is dependent only upon temperature and frequency.

4.3 Laboratory blackbodies

Clearly, laboratory blackbodies [4, 7, 12, 26, 27], including those utilized to provide Planck with data [9–11], were specialized cavities constructed from highly absorbing materials. This observation alone was sufficient to conclude that Kirchhoff's law was invalid.

In the infrared, it was evident that the graphite cavities used in this study were able to maintain their internal radiation in a manner which was essentially independent of any radiative challenge. They acted as real blackbodies and could do work. They could ensure that the radiation they contained was governed by the nature and the temperature of their own walls. They converted incoming energy, whether in the form of incident radiation or heat, into normal radiation with the correct frequency distribution.

Conversely, cavities constructed from aluminum, brass, and copper acted as nearly ideal reflectors. They contained the radiation which was incident from their surroundings and showed no ability to convert this radiation to black radiation corresponding to the temperature of their own walls. In this regard, it was evident that perfect reflectors could not do work. They were unable to effect any change upon incident radiation other than that which would occur given specular or diffuse reflection.

de Vos noted the extent to which cavities could make radiation isotropic as a function of the ratio of their diameter and depth [33]. However, perfectly reflecting cavities, by definition, could not emit radiation. As such, the radiation which they contained must remain completely independent of the temperature of their walls and dependent solely on the radiation contained in their surroundings. de Vos's analysis of the quality of a cavity in terms of its ability to convert incoming radiation into ejected isotropic radiation, while of interest, actually had little baring on the behavior of real blackbodies. This was because real blackbodies depended on the nature of their surfaces, not on the dimension of a cavity, in order to ensure that the emitted radiation would be both isotropic and black. A cavity in fact, should not be required, provided that the surface material was black and that no external radiation was able to contaminate this emission. This explained in part the interest in materials with elevated emissivity values [9–11, 26, 27] and highly absorbing surfaces [15–22]. Cavities did enable blackbody radiation to be contained, but they were not necessary for its production.

4.4 Cavities and work

Perhaps the central feature of all actual blackbodies was that they must have the ability to do work and convert any incident energy into the frequency distribution corresponding to the temperature of their own walls. In this sense, the work performed by a blackbody conformed to the standard definition whereby energy was converted from one form to another. Blackbodies accomplished this task in two ways. First, they were able to alter the frequency of incoming radiation and re-emit it with the blackbody frequency distribution corresponding to the temperature of their walls. Secondly, they could convert heat energy located in their own walls into thermal radiation associated with this temperature. In either case, only absorbers of radiation could act as blackbodies, as only they could serve as emitters. Radiation was absorbed by the walls and re-emitted in a manner which depended on the density of states and thereby upon temperature.

Conversely, rigid perfect reflectors could only redirect incoming radiation in a specular or diffuse manner. A change in phase occurred without any change in frequency. Therefore, no work was done, as a change in the energy distribution of the incoming radiation did not occur. Furthermore, perfect reflectors could not harness the energy contained in their walls and thereby emit radiation. Unable to absorb, they could not emit.

The reality that rigid perfectly reflecting cavities cannot do work is the basis for resonant cavities in ultra high field magnetic resonance imaging (UHFMRI) [29], electron paramagnetic resonance (EPR) [30], microwave communications [31] and the resonant cavities used for building coherent radiation following stimulated emission in lasers [32]. All of these disciplines strive to build highly reflective resonant cavities with optimal quality factors, $Q = f/\delta f$, where f is the frequency of interest and δf full width at half maximum of the resonance. Q-factors are inversely proportional to surface resistance echoing Planck's desire for infinitely large conductivity.

In clinical MRI, dielectric loses in the human body will dominate Q-factors for any resonator [26]. As a result, little can be gained in this discipline from building resonators from materials more sophisticated than copper or silver.

However, lasers do not experience these limitations. As a result, resonant cavities in lasers can benefit from the construction of highly reflective Bragg super-mirrors, which can have reflectance values of 99.9999% [40–42]. Ion-beam interference coating mirrors [43] are associated with LIGO [44]. Specialized mirrors are also used in high precision atomic clocks to generate optical cavities with low thermal noise in that setting [45]. Laser cavities can thus achieve Q-factors of 10^{10}, or more [46].

The use of resonant cavities in UHFMRI [29], EPR [30], microwave technology [31], and lasers [32] proves that Kirchhoff's law is not valid. These cavities critically depend on their nearly perfectly reflecting nature which allows them to serve as resonant devices, unable to alter incoming radiation by making it black. It is evident that the radiation in these cavities is absolutely dependent upon the radiation which was incident upon them and completely independent of the temperature of their walls. Absorption of incident photons, transformation into thermal vibrations, and re-emission into thermal photons does not occur in perfectly reflecting cavities. Kirchhoff and Planck cannot claim otherwise, when they assert that all cavities contain black radiation [1, 2, 14].

4.5 Max Planck and Kirchhoff's law

Max Planck attempted to prove the validity of Kirchhoff's law in the opening sections of *The Theory of Heat Radiation* [14, §1-52]. Upon close examination, the derivation was discovered to be unsound [39]. In order to construct his proof, Planck actually redefined the very nature of a blackbody and no longer required, as did Kirchhoff, the ability to absorb radiation over an *infinitely small thickness* [2, §1]. In contrast to Kirchhoff, Planck permitted radiation to enter a medium without absorption/emission at its surface [14, §36-37]. When considering a medium with a vanishingly small absorptivity, he allowed for their use as blackbodies by invoking infinite thickness [14, §10]. Thus, Planck's proof of Kirchhoff's law used transmission and, at times, improperly ignored absorption. Additionally, his proof relied on the use of polarized light [14, §35-37] and the use of Brewster's angle, when heat radiation is never polarized [47].

In this regard, it is noteworthy that in order to address the blackbody problem Max Planck actually focused his attention on the perfectly reflecting, rather than the perfectly absorbing, wall [14]. Planck had defined the reflector as: *"the surface of an absolute conductor (metal) of infinitely large conductivity"* [14, §55]. Planck's focused on perfectly reflecting cavities despite the fact that such cavities cannot function as proper blackbodies.

Indeed, Planck understood that *"In a vacuum bounded by perfectly reflecting walls, any state of radiation may persist"* [14, §51]. However, he advanced that such radiation could be converted to blackbody radiation at the correct temperature with the simple addition of a small particle of carbon [14, §51]. He believed that this particle acted as a catalyst and provided no heat energy of its own [14, §51]. However, Fig. 3 demonstrated that the addition of a carbon particle alone was not sufficient to produce the desired radiation. In fact, it was doubtful that Planck or his contemporaries ever tested the concept, as a small particle of graphite could never do enough work to fully convert the radiation, incident upon a cavity, into fully black radiation. The second law has always restricted what the carbon particle could achieve. In addition, Planck's use of the carbon particle [14, §51] could easily lead to a violation of the 1st law.

Using a thought experiment, it could be demonstrated that the catalyst argument violated the 1st and 2nd laws of thermodynamics [48]. Planck himself recognized that the radiation contained in a perfectly reflecting cavity was undefined [14, §48, §51, §52]. As such, the energy contained in these radiation fields could not be transformed to the proper frequency distribution, unless it exactly matched the energy required at the temperature of interest. Since the radiation was undefined, any attempt to transform radiation of arbitrary energy content to that with the proper frequency distribution for a given temperature risked violating the 1st law of thermodynamics. Planck could not be assured that the energy density within the cavity enabled the carbon particle to make the radiation black at the correct temperature. Only when the correct energy density was initially present in the cavity, could Planck avoid violating the 1st law. Furthermore, the carbon particle must do work to transform heat energy into radiation and fill the cavity. It could never act as a catalyst. Planck's attempt to address the undefined nature of the radiation in a perfectly reflecting cavity, by the insertion of a carbon particle, stood in opposition to the laws of thermodynamics [48].

Throughout his text on *The Theory of Heat Radiation* [14], Max Planck attributed all of the energy to the radiation field and included none in the walls of the cavity. Obviously, if this was done, the solution could not depend on the nature of the walls. However, the approach was not justified. Real cavities have energy in their walls. The most important example is the perfectly reflecting cavity, wherein thermal equilibrium is governed by the conduction of energy in the walls, not within a radiation field. By definition, such walls have no means of interacting with radiation and, therefore, a radiation field cannot be used to set equilibrium in a perfectly reflecting cavity. Perfectly reflecting cavities are responsive to the radiation incident upon their openings only through reflection. The reflection can be either specular, white, or a mixture. However, any effect on the incoming light in a perfectly reflecting cavity will occur in a manner completely devoid of any relationship to the temperature of its walls. The radiation within perfectly reflecting cavities is determined by history and environment, not temperature.

5 Conclusions

For more than 150 years [12], Kirchhoff's law of thermal emission [1, 2] has governed much of scientific thought in physics and astronomy, despite the fact that it lacked proper theoretical [28] and experimental proof [4, 7, 12, 28, 38, 39, 48]. Now it is clear that cavities do not all contain the same radiation, independent of the nature of their walls. Perfect reflectors are unable to convert incoming radiation into the Planckian distribution corresponding to their wall temperature. In the absence of wall motion, they are unable to do any work and merely sustain the radiation in their surroundings. If this incident radiation is phase coherent, then perfect reflectors can even sustain standing waves, as required in UHFMRI [29], EPR [30], microwave telecommunication [31] and lasers [32]. Had Kirchhoff's law been valid, then none of these modalities would exist, as no cavity would become resonant and all incident radiation would become destined to adopt the blackbody profile.

Kirchhoff's law is demonstrably false. Real blackbodies can do work on any incoming radiation and, as shown herein, they appear to do so instantly. They exclusively contain radiation which reflects the temperature of their walls, not the presence of the radiation in their surroundings. It is this ability to do work in the ideal blackbody, and the inability to do work in the perfect reflector, which determines the real behavior of cavities. That is also why laboratory blackbodies are always constructed from materials which possess relatively elevated emissivity values over the frequencies of interest [4, 7, 9–12, 26, 27]. The production of a blackbody spectrum absolutely requires the presence of a vibrating lattice and is intrinsically tied to the nature of the walls [4], contrary to Kirchhoff's claim [1, 2].

As a result, Max Planck's long advocated universality [14, §164] as to time, length, mass, and temperature was never valid. The concept was entirely dependent on the notion that Kirchhoff's law was correct, but this was never the case. As a consequence, the units of measure remain a product of humanity's definitions and science constrained by this fact. Though Planck's equation remains correct for actual blackbodies, it is no longer reasonable to proclaim that black radiation can be produced simply through arbitrary cavities in thermal equilibrium. Such assertions are incorrect as evidenced by the preeminent role of graphite and soot in the construction of actual blackbodies [4] and as modern technology readily demonstrates [29–32].

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Dedication

This work is dedicated to Joseph Benoît Martin Robitaille.

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