Further Insight Relative to Cavity Radiation II: Gedanken Experiments and Kirchhoff's Law

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Kirchhoff's law of thermal emission states that cavity radiation must always be black, or normal, irrespective of the nature of the walls. Arbitrary cavity radiation must be solely dependent upon the equilibrium temperature and the frequency of observation. Despite such theoretical claims, it is well established that laboratory blackbodies are not constructed from arbitrary materials, but rather from nearly perfect absorbers of radiation over the frequency of interest. In the laboratory, arbitrary cavities do not contain black radiation. This experimental fact stands in direct conflict with Kirchhoff's formulation. Nonetheless, Kirchhoff's law of thermal emission endures, in part, due to Gedanken experiments whose errors in logic are difficult to ascertain. In this work, thought experiments are discussed in order to expose some logical shortcomings. It will be demonstrated that Kirchhoff's law cannot be supported in this context.

If a space be entirely surrounded by bodies of the same temperature, so that no rays can penetrate through them, every pencil in the interior of the space must be so constituted, in regard to its quality and intensity, as if it had proceeded from a perfectly black body of the same temperature, and must therefore be independent of the form and nature of the bodies, being determined by temperature alone... In the interior therefore of an opake red-hot body of any temperature, the illumination is always the same, whatever be the constitution of the body in other respects.

Gustav Robert Kirchhoff, 1860 [1]

1 Introduction

Recently, the validity of Kirchhoff's law [1, 2] and the universality of the laws of thermal emission [3–6] have been brought into question [7–13]. This reformulation of an established thermodynamic principle has repercussions throughout the fields of physics and astronomy. The issues at hand not only concern our understanding of the nature of the stars [14] and the microwave background [15], but also the universality endowed upon Boltzmann's and Planck's constants [12]. Thus, although 150 years have passed since Kirchhoff's law was formulated [1,2], it is appropriate to carefully reconsider its authenticity. In this respect, the author has argued against the validity of this law of thermal emission [7–13].

Stewart's law [16], not Kirchhoff's [1, 2], properly accounts for the equivalence between emissivity and absorptivity in thermal equilibrium. Unlike his contemporaries [1,2,6], Stewart [16] does not require that all radiation within cavities be black, or normal. In this work, the variable nature of cavity radiation is affirmed by addressing a Gedanken experiment which is often invoked to justify Kirchhoff's law, either in the classroom or within textbooks.

2 Experiment I: Two ideal cavities

In this experiment, two cavities of the same dimensions are imagined to exist in an empty universe at the same temperature (see Fig. 1A). In order to ensure that the heat contained within each cavity cannot escape, let us surround the exterior of these enclosures with an adiabatic wall. The interior of each cavity is then placed under vacuum to prevent convective processes. The inner surface of the first enclosure (cavity 1) is comprised of an ideal, or perfect, emitter (Emissivity (ϵ) = 1, Reflectivity (ρ) = 0; at the frequency of interest). The interior of cavity 2 is constructed from an ideal, or perfect, reflector ($\epsilon = 0$, $\rho = 1$; at the frequency of interest). For pedagogical purposes, a perfectly adiabatic structure is selected for the inner wall of cavity 2. The cavities are in temperature equilibrium with a third object in the same universe, which is also surrounded by an adiabatic wall.

The physics community currently maintains that, under these conditions, both cavities must contain black radiation, in accordance with Kirchhoff's law [1,2], despite the fact that the second cavity, being fully adiabatic, acts as a perfect reflector and, hence, is unable to emit a single photon. How can it be argued that cavity 2 is filled with black radiation?

Let the two cavities come into contact with one another and place a small hole between them, as displayed in Fig. 1B. When this occurs, photons must cross from cavity 1 (perfectly emitting) into cavity 2 (perfectly reflective). Yet, if cavity 2 is devoid of black radiation, it will not be able to transfer a photon back into the first cavity. As a result, since the first cavity would be losing net photons into the second cavity, its energy content or temperature would drop. Conversely, the energy content of the second cavity would rise. This cannot be permitted according to the zeroth law of thermodynamics, since all three objects are already at the same temperature. Consequently, it is argued that the perfectly reflecting cavity

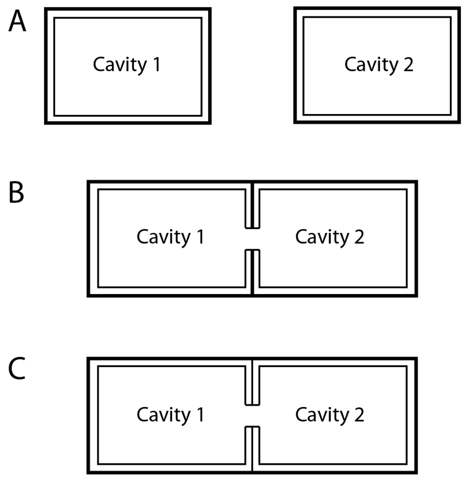

Fig. 1: Schematic representation of our thought experiments. A) Two cavities are presented. Cavity 1 is constructed from a perfect emitter ($\epsilon = 1$, $\rho = 0$) surrounded by an adiabatic wall. Cavity 2 represents a perfect reflector ($\epsilon = 0$, $\rho = 1$). In this case, we assume that both the inner lining and the outer wall are fully adiabatic. B) The cavities displayed in A are brought together and a small hole is made between them in order to permit radiation to flow from one enclosure into the other. C) Two cavities are presented which again have been brought in contact with one another. The inner surface of cavity 1 is constructed from graphite, or soot, and is assumed to act as a perfect emitter ($\epsilon = 1$, $\rho = 0$). The inner surface of cavity 2 is constructed from silver which is assumed to act as a perfectly reflector ($\epsilon = 0$, $\rho = 1$). Both cavities are surrounded by adiabatic walls. However, when the two cavities are brought together, the adiabatic walls between them are removed. This allows for direct thermal contact of the two inner surfaces. A small hole is included to permit radiation to move from one enclosure into the other.

must have contained black radiation all along, such that radiative equilibrium could always be maintained and that the temperature of the cavities can remain intact.

The error in such arguments must be found in permitting net energy to be transferred from cavity 1 into cavity 2. This cannot be allowed, simply based on the zeroth law of thermodynamics, if both cavities are said to be at the same temperature. A logical misstep must have been made in this thought experiment. The two cavities must not have been properly conceived.

The problem can be attributed to the inner surface of the second cavity and in the fact that both cavities must be surrounded by an adiabatic wall to prevent the emission of photons into the surrounding empty universe. This was central to maintaining the energy/temperature stability of each subsystem.

In designing the second cavity from a perfectly adiabatic wall, a physical regimen has been adopted which has no relationship to the best reflectors. Adiabatic walls are immune to all thermal processes. As a consequence, scientists who invoke their use in this setting, fail to recognize that such walls cannot be characterized with a temperature. Thus, if Kirchhoff's law is invalid and there are actually no photons within cavity 2, one cannot even set a temperature for the second system. By default, adiabatic walls cannot store energy within themselves. Namely, in addition to being perfectly reflective, they cannot support thermal conduction or electron flow. This stands in direct opposition to the known properties of the best reflectors and real heat shields.*

In reality, all good reflectors are also good conductors. As a case in point, silver constitutes a very efficient reflector in the infrared, but it is also one of the best electrical and thermal conductors.†

Since the formulation of a law of physics must depend upon the proper characterization of the physical world, one must be careful not to invoke a mathematical or physical regimen which has lost all relation to reality. The use of a fully adiabatic perfectly reflecting cavity has not allowed for sufficient degrees of freedom in which to store energy, as it cannot sustain any phonons within its walls. The only degree of freedom which might be available to such a cavity would rest in its ability to contain a radiation field. However, can cavity 2 actually have the ability to spontaneously generate such a field, despite its complete lack of phonons and perfect reflection, simply driven by a law of physics which is currently under question?

As cavity 2 is perfectly reflecting, the proper conclusion remains that it cannot self-generate a single photon. Thus, it should initially be devoid of a radiation field. Because it also cannot hold any energy in its adiabatic walls, cavity 2 cannot be characterized by *any* temperature.

Consequently, at the beginning of the experiment, cavity 2 cannot be in thermal equilibrium with cavity 1. Therefore, cavity 1 is allowed to transfer photons into cavity 2, simply because there is no thermal equilibrium initially. The temperature of cavity 1 must drop, as it pumps photons into cavity 2. Thus, cavity 1 falls out of thermal equilibrium with the third object, and Kirchhoff's law has not been proven.

Obviously, there are shortcomings in cavity 2. As such, the cavities should be redesigned, such that the validity of Kirchhoff's law can be assessed from a slightly different perspective.

*Superconducting magnets for MRI utilize heat shields in their interior that may well represent the closest example of an adiabatic shield in nature. Such shields are typically made from a highly reflective and conductive metal. They are suspended in the interior of the cryostat using very thin and insulating fiberglass rods which act to help eliminate all conductive thermal contact between the shield and other portions of the magnet system (i.e. the liquid helium Dewar containing the magnet windings, other heat shields, the liquid nitrogen Dewar, the outer casing of the magnet, etc.). These heat shields are typically suspended in a vacuum environment. This is done in order to minimize any convective contact between the shield and the rest of the magnet.

†Silver is amongst the best conductors with a resistivity of only $\sim 1.6 \times 10^{-8}$ Ω m at 300 K and of $\sim 0.001 \times 10^{-8}$ Ω m at 4 K [17]. It is also an excellent reflector in the infrared, our frequency range of interest.

3 Experiment II: Two cavities in thermal contact

Once again, each cavity is surrounded, under vacuum, with an adiabatic wall such that heat radiation cannot be lost into the universe and the temperature of each cavity can be maintained. As before, these two cavities are in temperature equilibrium with a third object in the same universe, which is also surrounded by an adiabatic wall.

The inner surface of cavity 1, the perfectly emitting cavity, will be constructed from graphite, or soot. These materials are known to be very good physical examples of blackbodies in the laboratory [18–21]. Departure from physical reality will consist solely in assuming that the emissivity of the inner surface is perfect ($\epsilon = 1, \rho = 0$).

Silver will be used to line the inner surface of cavity 2. This metal is perhaps the best known reflector in the laboratory. In parallel fashion, a single departure is made from physical reality, namely in assuming that the reflectivity of the silver interior will be perfect ($\epsilon = 0, \rho = 1$), much like the second cavity in section 2.

Each cavity has a total energy which is now equal to the sum of the energy it contains in the photons it encloses and in the phonons which exists in its walls.* In this sense, each cavity is given access to only two possible degrees of freedom: 1) the vibrational/phonon system in its walls and 2) the radiation field.

Since the systems must be in thermal equilibrium, net conduction is forbidden in accordance with the requirements set forth by Max Planck [6, p. 23].

Let us now bring the two cavities together. But this time, before making the small hole, let us remove the adiabatic outer wall from that section of the cavities which come into direct contact. In this manner, thermal conduction can occur between the two cavities, if necessary. Finally, let us make the small hole and permit cavity 1 to transfer a photon into cavity 2 (see Fig. 1C).

Under these conditions, if a photon from cavity 1 enters cavity 2, an identical quantum of energy instantly propagates from the second perfectly reflecting cavity, through conduction and phonon action, into the walls of the first cavity. In a sense, cavity 1 has instantly converted this phonon into the photon it just expelled. As a result, cavity 1 has simply acted as a transformer of energy. It has taken phonon energy from cavity 2, created a photon, and sent energy back into cavity 2. Cavity 1 has not lost any net photons. The total energy of each system does not change and the zeroth law is not violated.

Thus, when a small hole is made between the two enclosures, each cavity eventually becomes filled with blackbody radiation when thermal equilibrium is reestablished. This conclusion has previously been demonstrated mathematically [9] and was recognized long ago in the laboratory. The net result is that no net energy has been exchanged. The temperature does not change, and no laws of thermodynamics have been violated. Yet, for the period of time when photon and phonon transfer was occurring, the entire system fell out of thermal equilibrium, even if temperature equilibrium was being maintained. Eventually however, thermal equilibrium is re-established and both cavities are filled with black radiation.

Over the course of this experiment, something very important has occurred in cavity 2. The energy which this cavity contained has been redistributed amongst its two degrees of freedom. Although the net temperature of cavity 2 has not changed, phonon energy has been lost to the radiation field. This simple observation has consequences in physics, as it signifies that the law of equipartition which characterizes so much of statistical thermodynamics cannot hold. The energy of a system is not necessarily distributed equally between all of its available degrees of freedom.

It could be argued, of course, that a behavior has been demanded from real materials which can never exist. This is a question of how closely physical reality can be modeled. Is it a more grievous error to assume 1) that a perfectly adiabatic cavity can exist, a material which cannot emit photons, cannot sustain conduction in any form, or be associated with any temperature, or 2) that graphite and silver come to represent two 'perfect' examples of emissivity and reflectivity, respectively?

Relative to this question, it is clear that the construction of a perfectly reflecting cavity from an ideally adiabatic wall (Experiment I) constitutes the greater departure from physical reality. Adiabatic surfaces, with their inability to emit any photons and their incapability of sustaining thermal or electrical conduction simply are not approached by anything in nature. It is impossible to state that a truly adiabatic wall is at any given temperature, as temperature in the physical world must be associated with energy content and adiabatic walls contain none. They represent a convenient intellectual concept and offer very little relative to properly modeling physical reality. For this reason, their use results in the finding that all cavities must be filled with blackbody radiation, even if their walls lack the physical ability to emit a single photon. Obviously, a logical conflict has been produced which highlights that our model has deviated too far from physical reality. As a result, it is unlikely that such a model (Experiment I) provides a proper proving ground relative to the validity of Kirchhoff's formulation.

Conversely, it is known that laboratory blackbodies constructed from graphite, or soot (carbon black, lampblack), can reach rather high emissivities over certain frequencies [18–21]. The requirement that these materials can come to have an emissivity of 1 is very close to reality. At the same time, silver can manifest an excellent reflectivity over certain frequencies. Silver surfaces are the best reflectors known. As a result, the assumption that silver can exhibit a reflectivity of 1, is not very far from experimental fact. In this regard,

*For the purpose of this discussion, the energy associated with the electrons in conduction bands, or any other degree of freedom, can be neglected, as these do not provide additional insight into this problem.

it must be concluded that Experiment II constitutes a much better representation of nature. It is known that laboratory blackbodies are always made from near perfect emitters of radiation, like graphite or soot [10, 11]. They are never made of excellent reflectors, such as silver [10, 11].

The silver cavity was initially devoid of any radiation, precisely because it can emit none. It is only when it is placed in contact with a perfectly absorbing cavity, that the energy contained in its vibrational degrees of freedom can be transformed into a radiation field. This directly highlights that Kirchhoff's formulation cannot be correct. We do not find an equal ability to construct blackbody cavities in the laboratory irrespective of the nature of the walls. Silver cavities cannot hold black radiation unless they have been subjected to the action of a perfect absorber [9].

4 Conclusions

When properly analyzed, Gedanken experiments reveal that Kirchhoff's law of the thermal emission cannot be valid. The proper analysis of cavity radiation must be open to realistic treatments of energy balance within real materials. When this is correctly accomplished, cavity radiation becomes absolutely dependent on the nature of the enclosure. Phonon transfer can balance photon transfer. As such, Kirchhoff's law holds no validity, either mathematically, in the experimental setting, or in the context of thought experiments [7–13]. Cavity radiation is not always black, but is absolutely dependent on the nature of the enclosure. As demonstrated in Experiment II, two cavities can be at the same temperature, but not contain identical radiation. The introduction of black radiation into opaque enclosures absolutely depends on the presence, or action, of a perfect emitter. Based on this presentation, the constants of Planck and Boltzmann are not universal [12].

Beyond Kirchhoff's law, the analysis of cavity radiation leads to the conclusion that the equipartition theorem cannot be valid across all systems. The amount of energy associated with a given degree of freedom at temperature equilibrium is not necessarily equal to that contained in all other degrees of freedom. The zeroth law of thermodynamics, by which temperature is defined, is not concerned with radiation fields, but simply temperature equilibrium. If two objects are at the same temperature, they are by definition in thermal equilibrium, provided that their is no net emission, conduction, and convection taking place in the systems of interest.

In Experiment II, a system is initially placed under temperature and thermal equilibrium. It then is allowed to remain under temperature equilibrium, while it temporarily falls out of thermal equilibrium, as the small hole is created to enable the exchange of phonons and photons. At any time, if the two cavities are physically separated and the hole filled, they would immediately regain both temperature and thermal equilibrium. At that point, the second cavity would contain an arbitrary number of photons and not black radiation. It is only if cavity 1 is given sufficient time to act that cavity II will contain black radiation. However, the action of the first cavity was absolutely critical to this transformation. A perfect emitter had to be present. It is not simply a question of time, but of physical action by a perfect emitter.

Experiment II is indicating that it is not necessarily possible to equilibrate the energy contained within the degrees of freedom within real materials. Under these conditions, equipartition cannot hold. Equipartition requires that all degrees of freedom have the same ability to contain energy. This cannot be correct. The most compelling example is illustrated by the hydrogen and hydroxyl bonding systems within water [14]. The force constants in these two systems are drastically different. As a result, the hydrogen bonding system is likely to be filled with energy at temperatures just above absolute zero (~3K). This is the reason, in fact, why the microwave background which surrounds the Earth does not vary in intensity in response to seasonal changes [14]. Equipartition is also invalid in the photosphere, where dramatic differences in the energy content of the translational and vibrational degrees of freedom are likely to exist [22].

Throughout his treatise on heat radiation [6], Max Planck invoked a carbon particle, which he surmised to act as a simple catalyst (see [10] for a detailed review). However, he inserted a perfect emitter into his cavity. This particle could then fill the cavity with black radiation, provided that it was placed in physical contact with the energy source to be converted. It did not matter how much carbon was inserted, as this only governs the time involved. For this reason, when Planck introduced the carbon particle into his cavity [6], it was as if he had lined it completely with carbon [10]. He had not demonstrated that all cavities contained black radiation, only that all perfectly emitting cavities are black.

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Dedication

This work is dedicated to my father, Noel Antoine Robitaille (born on December 22, 1929). He devoted his life to the practice of family and emergency medicine, delivering over 800 babies and tending the medical needs of the communities in which he resided, both in Canada and Iowa. He retired on August 30, 2013, at the age of nearly 84, after having, for many years, served at his small clinic in LaPorte City and making visits to the local nursing home. A few years ago, as he walked with nostalgia in the cemetery of his village, he recalled how so many buried there were once his patients and friends. His daughter-in-law, to help lighten the atmosphere, had inquired: "So Noel, do you think you were a good doctor?"

In February 2014, he passed the 50 year anniversary of receiving the rare privilege, as a white man, to be named an honorary Indian Chief — "Kitchitouagegki". He was the first named by any of the Three First Nations: The Council of Three Fires (Ojibway, Odawa, and Potawatomi). In describing the honor conferred upon him, Allen Toulouse recalled, *"His presence contributed to reducing the infant mortality rate of the Sagamok First Nation (Reducing the number of deaths during pregnancy for both the mothers and their babies). He also made many actions to improve the conditions of the people of Sagamok — including having running water and wells installed in the reserve in the early 1960s"* [23]. It appears that his elevation to Chief represents *"the first official case of a First Nation bestowing this honor upon a Caucasian medical doctor in North-American history"* [23].

Fig. 2: Noel Antoine Robitaille, honorary chief "Kitchitouagegki". Photo courtesy of Allen Toulouse and Christine Robitaille.

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