LETTERS TO PROGRESS IN PHYSICS

Further Insight Relative to Cavity Radiation: A Thought Experiment Refuting Kirchhoff's Law

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Kirchhoff's law of thermal emission demands that all cavities contain blackbody, or normal, radiation which is dependent solely on the temperature and the frequency of observation, while remaining independent of the nature of the enclosure. For over 150 years, this law has stood as a great pillar for those who believe that gaseous stars could emit a blackbody spectrum. However, it is well-known that, under laboratory conditions, gases emit in bands and cannot produce a thermal spectrum. Furthermore, all laboratory blackbodies are constructed from nearly ideal absorbers. This fact strongly opposes the validity of Kirchhoff's formulation. Clearly, if Kirchhoff had been correct, then laboratory blackbodies could be constructed of any arbitrary material. Through the use of two cavities in temperature equilibrium with one another, a thought experiment is presented herein which soundly refutes Kirchhoff's law of thermal emission.

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

Kirchhoff's law [1, 2] is generally considered to be the first amongst the laws governing thermal emission [3–6]. With its formulation, blackbody radiation achieved a magical presence within every cavity. Based on Kirchhoff's law, Planck believed that blackbody radiation had universal significance [6]. It is because of Kirchhoff that Boltzmann's and Planck's constants are viewed as sharing the same quality [5–10]. As such, the collapse of Kirchhoff's law [7–10] has great implication throughout physics. It touches not only condensed matter, but also the very makeup of the stars and our understanding of the microwave background (see [11–13] and references therein). Consequently, many refuse to accept that there can be problems with Kirchhoff's formulation. In so doing, they deny Balfour Stewart proper credit for correctly noting that the emissivity of a material is equal to its absorptivity at thermal equilibrium [14]. Furthermore, *cavity radiation is actually dependent on the nature of the enclosure* [7–10]. As such, a simple thought experiment is now presented which elegantly exposes the error in Kirchhoff's claims.

Cavity radiation revisited

Let us begin with a large perfectly absorbing enclosure - an ideal blackbody (Emissivity (ϵ) = 1, Reflectivity (ρ) = 0; at all temperatures and frequencies), as depicted in Fig. 1. The contents of this cavity are kept under vacuum. Within this outer cavity, let us place a somewhat smaller perfectly reflecting enclosure with 5 sides closed and 1 open ($\epsilon = 0$, $\rho = 1$; at all temperatures and frequencies). Guided by Max Planck [6], both cavities will be large compared to those dimensions which would require the consideration of diffraction. Since the inner cavity is perfectly reflecting, it will also be highly conducting, as good reflectors tend to be good conductors.*

Throughout his classic text on heat radiation [6], Planck makes use of perfectly reflecting enclosures. Therefore, it is appropriate to consider both the perfect emitter ($\epsilon = 1$) and the perfect reflector ($\epsilon = 0$) in this exercise.

At the onset, the experiment requires a mechanical means of closing the inner enclosure. This can be achieved with a mechanism which crosses the walls of the outer cavity while preserving the vacuum. The mechanism is allowed, because laboratory blackbodies are known to possess a small hole in their outer walls through which radiation is typically sampled.

Once this has been accomplished, place the perfectly absorbing enclosure ($\epsilon = 1$, $\rho = 0$), which contains the inner perfectly reflecting cavity ($\epsilon = 0$, $\rho = 1$), in a large helium bath at 4 K. The inner open cavity, is permitted to rest directly on the floor of the outer perfectly absorbing cavity (see Fig. 1). Under these conditions, the inner cavity will achieve temperature equilibrium with the outer cavity using conduction. Radiation inside the perfectly absorbing cavity will correspond

*For example, silver is amongst the best conductors with a resistivity of only ~1.6 x 10^{-8} Ω m at 300 K and of ~0.001 x 10^{-8} Ω m at 4 K [15]. It is also an excellent reflector in the infrared, our frequency range of interest.

Fig. 1: Schematic representation of our thought experiment. A large outer cavity acts as an ideal blackbody ($\epsilon = 1$, $\rho = 0$) and is initially immersed in a helium bath at 4 K. Within this cavity, a perfectly reflecting enclosure ($\epsilon = 0$, $\rho = 1$) rests of the floor with one of its sides initially remaining open.

to black radiation at 4 K. It will fill both the large cavity and the smaller open cavity.

When temperature equilibrium has been reached, permit the inner cavity to be sealed mechanically. At that moment, 4 K blackbody radiation has been trapped inside the smaller perfectly reflecting enclosure.

One can then permit the outer perfectly absorbing enclosure to rise in temperature to 300 K. It will now contain black radiation at that temperature. As for the perfectly reflecting enclosure, it will also move to 300 K, because it can reach temperature equilibrium through conduction (we can use any of 3 mechanisms to reach equilibrium - radiation, conduction, and convection). The inner cavity walls are thus also brought to 300 K. However, unlike the outer cavity which is filled with blackbody radiation at 300 K, the inner cavity remains filled with blackbody radiation at 4 K. Thereby, Kirchhoff's law is proven to be false.

Under these conditions, the only way to enable the inner cavity to hold 300 K blackbody radiation would be to permit a violation of the first and zeroth laws of thermodynamics. Namely, once temperature equilibrium has been reached through conduction, the inner cavity will not be allowed to spontaneously emit photons in search of a new radiative condition, while denying the zeroth law. Photons will not be created where no mechanism exists for their generation.*

In addition, the zeroth law of thermodynamics defines the conditions under which temperature equilibrium exists. These conditions refer to real objects. As long as the outer cavity is in temperature equilibrium with the bath/room and is in temperature equilibrium with the inner cavity; then by definition, the inner cavity is in temperature equilibrium with the bath/room. The nature of the field contained within the inner cavity is not covered by the zeroth law of thermodynamics. As is appropriate, the zeroth and first laws of thermodynamics must guide our judgment relative to Kirchhoff's formulation. Thermal equilibrium is defined as that condition which prevails in the absence of all net changes in conduction, convection, and radiation. Thus, thermal equilibrium has been met when the inner cavity reaches 300 K, despite the fact that it contains 4 K radiation, as there can no longer be any change in net conduction, convection, or radiation, across cavity walls. To argue otherwise implies that the temperature of an object depends on the radiation field it contains. This constitutes a direct violation of the zeroth law of thermodynamics which is independent of radiation fields.

Summary

In this thought experiment, two cavities have been considered and temperature equilibrium between them ensured using conduction. The perfectly absorbing cavity ends up holding perfectly black radiation at all temperatures because its emissivity is 1. But the situation is not the same for the inner cavity, as its emissivity is 0 at all temperatures.

Max Planck previously noted in his classic text on heat radiation that: *"... in a vacuum bounded by totally reflecting walls any state of radiation may persist"* [6, § 51]. In order to ensure that a perfectly reflecting cavity could contain black radiation, he inserted a small particle of carbon (see [9] for a detailed discussion). However, when Planck does so, it is as if he had lined the entire cavity with an excellent absorber, because the carbon particle was identical to graphite, a *nearly perfect absorber*, almost by definition [9]. Planck remains incapable of demonstrating that cavity radiation will always be black, independent of the nature of the walls [7–10].

When the temperature was brought to 300 K, the two cavities responded in different ways as a result of their inherent emissivities. The outer cavity has a perfect emissivity ($\epsilon = 1$) and is able to pump out additional photons, as required by Stefan's law [4]. Since Stefan's law has a fourth power dependence on temperature (T^4), the outer cavity now contains 3.2 x 10^7 times more photons than it did when its temperature was a 4 K. However, the radiation within the inner cavity *persists*, just as Max Planck stated. That is because this cavity lacks the physical mechanism to emit a photon. Until it is opened, it will forever contain black radiation which had cor-

*The emissivity of a material is defined relative to the emissivity of a blackbody at the temperature in question. Selecting an emissivity value for the surface of a cavity therefore implies thermal equilibrium by definition. Yet, in modeling the blackbody problem, computer simulations often perpetually pump photons into cavities, invoke reflection, and build up radiation until they achieve the blackbody spectrum. But real materials cannot act as perpetual sources of photons without dropping in temperature. Obviously, the temperature of a cavity which is already at equilibrium, by definition, cannot be allowed to drop. The pumping of ever more photons into an arbitrary cavity while invoking reflection as a means to justify the buildup of the blackbody spectrum is forbidden by the first law of thermodynamics [10].

responded to that initially produced by the outer cavity when it was at 4 K.

The perfectly absorbing cavity ends up holding perfect black radiation at all temperatures because its emissivity is 1. The perfectly reflecting cavity maintains 4 K radiation, because its emissivity is zero. There is no violation of the first law and the zeroth law guarantees the equilibrium arguments. It is permitted to utilize a perfectly reflecting ($\epsilon = 0$) cavity in this work using the same logic which allows the physics community to hypothesize that perfectly absorbing cavities ($\epsilon = 1$) exist. In reality, both objects cannot be found either in nature, or in the laboratory, over the range of frequencies and temperatures which might be of interest.

The discussion can be extended further to hypothesize, of course, that initial conditions (before the inner cavity was sealed) were at absolute zero. In that case, the inner cavity will always be devoid of radiation once it is closed. Should another initial condition be selected, then, when it is sealed, the inner cavity will contain black radiation at that temperature.

What becomes clear is that the radiation contained in the inner cavity can be made to be absolutely dependent on initial conditions (unrelated to final temperature) and dependent on the nature of the cavity walls. Stewart's law [8, 14] and not Kirchhoff's [1, 2] properly describes the relationship between emission and absorption under conditions of thermal equilibrium.

At the same time, it should be recognized that temperature equilibrium can be achieved without a detailed balance between emission and absorption. This can occur if there is net conduction, convection, or radiation into, or out of, an object whose temperature does not change. For instance, heat could enter through radiation and leave through conduction, while the temperature remains constant. Under these conditions, the object is under temperature equilibrium, but not under thermal equilibrium. Namely, its emission can be much less than its absorption, even if the temperature is not changing. When considering thermal equilibrium and the laws of emission *there must be no net conduction, convection, or radiation*.

This should sufficiently address, in the simplest form, the truth of Kirchhoff's formulation. Based on this presentation, Kirchhoff's law is not valid and the constants of Planck and Boltzmann are not universal.

Acknowledgment

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Dedication

This work is dedicated to my first grandchild, Simone, as this thought experiment was envisioned on the day of her birth while I was driving alone from my home in Columbus to the hospital in Indiana.

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