Further Insight Relative to Cavity Radiation III: Gedanken Experiments, Irreversibility, and Kirchhoff's Law

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Recently, gedanken experiments have been proposed in order to examine the validity of Kirchhoff's Law of Thermal Emission (*P.-M. Robitaille, Further Insight Relative to Cavity Radiation: A Thought Experiment Refuting Kirchhoff's Law, Prog. Phys., 2014, v. 10, no. 1, 38–40; P.-M. Robitaille, Further Insight Relative to Cavity Radiation II: Gedanken Experiments and Kirchhoff's Law, Prog. Phys., 2014, v. 10, no. 2, 116–120*). In the second of these works, real materials (i.e. graphite and silver) were utilized in order to construct two separate cavities at the same temperature which are then placed in thermal contact with one another. It was hypothesized that the graphite cavity initially contained blackbody radiation and that the silver cavity was devoid of radiation. In the case of the silver cavity, all of the energy of the system was assigned to the phonons in its walls. When the cavities were brought together and a small hole introduced between the cavities, it was hypothesized that thermal contact between the cavity walls would enable the transformation of phonon energy into photon energy, eventually resulting in filling the silver cavity with black radiation. Energy contained within the wall of the silver cavity was believed to be *reversibly* trapped. However, in allowing energy to flow reversibly out of the walls of the silver cavity in this context, it has been assumed that the silver conduction bands could be neglected and that only phonon energy need be considered. However, the reflectivity attributed to the silver cavity should be considered uniquely as a result of energy associated with the formation of its conduction bands. Such formation must be considered *irreversible*. It will be demonstrated that under these conditions Kirchhoff's law, once again, does not hold. The lack of thermal radiation within the silver cavity does not lead to a violation of the second law of thermodynamics.

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

Gedanken experiments have played a major role in building support for Kirchhoff's Law of Thermal Emission [1, 2]. If this is the case, it is because Kirchhoff proposed his law without any experimental verification [1,2]. This remains a significant departure from the other laws of thermal emission [3–6] which have been confirmed through the construction of laboratory blackbodies. In addition, The Law of Equivalence, first formulated by Balfour Stewart [7], has also been confirmed experimentally. However, Kirchhoff's law, namely the belief that the radiation contained within an arbitrary cavity will always be black, or normal, independent of the nature of the cavity wall, has never been demonstrated experimentally [8–12]. Furthermore, Kirchhoff's law knows no proper theoretical proof [13]. Even Max Planck's theoretical proof of Kirchhoff's law can be shown to be invalid [14]. As such, the real justification for Kirchhoff's law falls on thought experiments, all of which can be shown to contain logical omissions and errors.

A powerful sentiment remains in the physics community that should Kirchhoff's law be invalid, then a violation of the second law of thermodynamics would exist and perpetual motion machines of the second kind could be constructed. The arguments typically involve the consideration of two cavities isolated from the outside world by exterior adiabatic walls. The inner walls of the first cavity are then constructed from a perfect absorber (emissivity $\epsilon = 1$ and reflectivity $\rho = 0$) and should therefore contain black radiation. The inner walls of the second cavity are constructed from a perfect reflector (emissivity, $\epsilon = 0$ and reflectivity, $\rho = 1$). Both cavities are theorized to be at the same temperature. It is then argued that if the second cavity is empty of radiation, that the second law of thermodynamics would be violated as photons could travel from the first cavity into the second cavity and do net work, even if the temperatures of the two cavities were equal. As such, the conclusion is immediately made that the second cavity cannot be devoid of radiation and indeed must contain black radiation, even if a perfect reflector has no means of generating such radiation. Obviously, a logical error exists in such arguments. The question remains to identify the error.

2 Cavity radiation revisited — reversibility

Recently, the author has proposed two gedanken experiments in order to revisit Kirchhoff's law [15, 16].

In the first of these works, two cavities are considered, wherein a perfectly reflecting cavity is placed within a perfectly absorbing cavity (see Figure 1 in [15]). The experiment demonstrates that arbitrary cavities can indeed be permanently filled with arbitrary radiation [15]. This reinforces Max Planck's statement: *"... in a vacuum bounded by totally reflecting walls any state of radiation may persist"* [6, § 51]. This gedanken experiment and Planck's statement point to a direct contradiction of Kirchhoff's law, as the radiation within all cavities is supposed to be black, independent of the nature of the walls.

In the second of these works, two cavities are once again considered (see Figure 1 in [16]). This time however, the concern is centered on the nature of the cavities themselves. Of particular significance is the realization that the perfectly reflecting cavity cannot be made solely from a theoretical adiabatic wall. That is because such a wall cannot be characterized by any temperature [16]. As such, the author moved to create the second cavity from silver, although importantly, within a footnote, he emphasized that he had neglected the conduction bands of the metal. The idea was that all of the energy of the second cavity could be placed reversibly within its walls and phonons. Thus, the interior of the second cavity would be devoid of any photons. Thermal contact could then be made with the perfectly absorbing first cavity, and the energy contained within the phonons from the second cavity could be released, such that the second cavity becomes eventually filled with black radiation through the action of the first cavity [16].

The idea of this thought experiment was to consider what would happen within the perfectly reflecting cavity, if all of the energy within this system was initially reversibly contained within the phonons of its walls. No energy was permitted to be trapped in the conduction bands.

It could be argued that this was not a proper representation of the silver cavity. As such, it is also possible to build the second perfectly reflecting cavity from a material devoid of conduction bands, but now, to enclose both its inner and outer surfaces with adiabatic walls. In this case, all of the energy of the perfectly reflecting cavity can indeed be contained within its phonons. When the second cavity is placed in thermal contact with the first cavity, by removing part of the outer adiabatic walls, the energy will flow reversibly out of its phonons. This energy would move into the walls of the first cavity, enabling a photon to be produced and then to cross through a small opening into the second cavity. Both cavities end up being filled with black radiation. No net work is done as the displacement of phonons out of the second cavity, is exactly balanced by the entry of photons into its interior space. No net temperature change is experienced by the second cavity or by the first. All that has happened is that energy initially trapped in the walls of the second cavity has been released into the radiation field. Both cavities still possess the same energy as they did initially.

In hindsight, the reversible experiment was probably not well suited to represent a perfectly reflecting cavity. In fact, it could be imagined that if one removed the inner adiabatic lining from the second cavity, that the phonons could have been used to fill the cavity directly with photons. The first cavity was not even required in this case. This serves to emphasize Max Planck's approach, in that the energy of the system could be accounted for simply through the generation of the radiation field [6]. This has now been shown to be correct when the process involved in creating the field was reversible and no other processes are involved. However, not all processes in materials are reversible and this is why Kirchhoff and Planck have stumbled. Given the state of knowledge at the time, they were unable to properly consider the effect of conduction bands.

3 Cavity radiation revisited — irreversibility

This bring us to the question of what happens when the energy of the second cavity is irreversibly trapped within the conduction bands of the silver.* Let us once again state that the exterior of the first and second cavities are surrounded by adiabatic walls. The first cavity, constructed from graphite acting as a perfect absorber [16], is assumed to be filled with black radiation. The second cavity, constructed from silver acting as a perfect reflector [16], will be assumed to be devoid of any radiation. Then, let us place the cavities in contact, but this time permitting only a small hole to link the interior of the two cavities.

It is often argued that, under these circumstances, photons can flow from the first cavity into the second cavity. However, such a proposal in itself violates the second law. The problem is evident when one considers what happens to a photon which would enter the second cavity. It is clear that at some point, such a photon would interact with the wall of the second cavity. Since a photon contains both energy and momentum, it would impart momentum and energy momentarily to

*This is a structural question, as the presence of conduction bands becomes critical to the structure of silver. It is not possible to manipulate the energy associated with the formation of these bands without destroying the very nature of the metal. Hence, the existence of the conduction bands will be considered irreversible. As for the phonons, they are now assumed, within silver acting as a perfect reflector, to contain no energy.

the wall of the silver cavity. This is strictly forbidden by the second law, because heat would be moving into the wall of the second cavity, not only within the cavity void. Alternatively, consider the entry of the second photon from cavity 1 into cavity 2. This presents a substantial problem now, since cavity 2, having already gained the first photon, has a higher energy content than cavity 1. This is because *both* the cavity wall and the radiation field are used to define the system. Movement of the second photon into cavity 2 must be strictly forbidden by the second law, because heat would be moving from a cavity with a lower temperature to a cavity with a new higher temperature.

Still, our instinct desires that photons can enter the second cavity without violating the second law. The secret to resolving this problem involves the natures of the walls themselves. Let us divide the walls of each cavity into many elements. Within the perfectly absorbing cavity, each of the elements selected possessed at one time the energy contained in the photon at the frequency of interest. However, this energy has now flowed to the interior of cavity 1, as required by Max Planck [6]. The wall elements of the first cavity can be thought of as devoid of energy, but able to absorb the energy of the photon of interest. Conversely, the elements in the silver cavity can be thought of as containing the same amount of energy as the photon of interest. That is because for the silver cavity, all of the energy is initially confined to the wall elements.

Now, the only way to permit a photon to enter the second cavity without violating the laws of thermodynamics is to simultaneously permit an element from cavity 1 to interchange with an element from cavity 2. In this way, when the photon hits the wall of the second cavity, it will actually momentarily impart its momentum and energy to a wall which has now a reduced energy by the value contained in one element of the silver cavity. The photon can enter, but the net result is that the emissivity of the second cavity has begun to rise. Simultaneously, the emissivity of the first cavity, now short one photon and with one perfectly emitting element replaced with a perfectly reflecting element, has begun to fall. Should the cavities be of equal dimensions and contain equal numbers of elements, the net result would be that the total emissivity of both cavities becomes a weighted average of the joint emissivities. Both cavities now contain gray radiation and the second law was never violated.

It is evident that when the small hole was made between the two cavities, that their walls, from a thermodynamic point of view, became one. It is in neglecting this important fact that some physicists attempt to state that the second law of thermodynamics has been violated. In fact, the law is violated only when the experiment is not fully presented. The truth is that the net emissivity of the total cavity simply becomes gray. Photons can exist anywhere within this new cavity, but their net density will not be black.

At the same time, if it is possible to drive additional heat into this system, one can built up black radiation in these two cavities, as highlighted long ago by Stewart [7] and as re-emphasized recently by the author [17, 18].

4 Summary

In the end, arbitrary cavities are not necessarily filled with black radiation. Laboratory blackbodies are specialized objects always made from relatively good emitters of radiation over the frequency range of interest, as well illustrated by the facts (see references within [8–12]). No valid theoretical proof of Kirchhoff's law has been formulated and no gedanken experiments can properly account for the existence of this law.

Dedication

This work is dedicated to my second grandchild, Daniel.

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