

On the Equation which Governs Cavity Radiation II

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In this work, the equation which properly governs cavity radiation is addressed once again, while presenting a generalized form. A contrast is made between the approach recently taken (P. M. Robitaille. On the equation which governs cavity radiation. *Progr. Phys.*, v. 2, no. 2, 126–127) and a course of action adopted earlier by Max Planck. The two approaches give dramatically differing conclusions, highlighting that the derivation of a relationship can have far reaching consequences. In Planck's case, all cavities contain black radiation. In Robitaille's case, only cavities permitted to temporarily fall out of thermal equilibrium, or which have been subjected to the action of a perfect absorber, contain black radiation. Arbitrary cavities do not emit as blackbodies. A proper evaluation of this equation reveals that cavity radiation is absolutely dependent on the nature of the enclosure and its contents. Recent results demonstrating super-Planckian thermal emission from hyperbolic metamaterials in the near field and emission enhancements in the far field are briefly examined. Such findings highlight that cavity radiation is absolutely dependent on the nature of the cavity and its walls. As previously stated, the constants of Planck and Boltzmann can no longer be viewed as universal.

Science enhances the moral value of life, because it furthers a love of truth and reverence...

Max Planck, Where is Science Going? 1932 [1]

1 Introduction

Recently [2], the equation which governs radiation in an arbitrary cavity, Eq. 1, has been derived by combining Kirchhoff's law of thermal emission [3, 4] with Stewart law [5, 6]:

$$\epsilon_\nu = f(T, \nu) - \rho_\nu, \quad (1)$$

where ϵ_ν corresponds to the frequency dependent emissivity, ρ_ν to the frequency dependent reflectivity, and $f(T, \nu)$ to the function defined by Max Planck [7, 8].* This expression is valid under assumptions made by the German scientist in neglecting the effects of diffraction and scattering [8, §2]. At the same time, it implies that all materials used to assemble blackbodies will act as Lambertian emitters/reflectors. The total emission will vary with the cosine of the polar angle in accordance with Lambert's Law (see e.g. [9, p. 19] and [11, p. 22–23]). Planck assumes that white reflectors, which are Lambertian in nature, can be utilized in the construction of blackbodies (e.g. [8, §61 §68 §73 §78]). But very few materials, if any, are truly Lambertian emitters/reflectors.

*The emissivity of an object is equal to its emissive power, E , divided by the emissive power of a blackbody of the same shape and dimension. Similarly, the reflectivity can be taken as the reflected portion of the incoming radiation, divided by the total incoming radiation, as often provided by a blackbody [9, 10]. Like emissivity, the reflectivity of an object is an intrinsic property of the material itself. Once measured, its value does not depend on the presence of incident radiation. As a result, Eq. 1 can never be undefined, since ρ_ν can only assume values between 0 and 1. For a perfect blackbody, $\rho_\nu = 0$ and $\epsilon_\nu = 1$. In that case, the Planck function is normalized.

Consequently, a fully generalized form of Eq. 1 must take into account that all of these conditions might not necessarily be met:

$$\epsilon_{\nu,\theta,\phi} = f(T, \nu, \theta, \phi, s, d, N) - \rho_{\nu,\theta,\phi}, \quad (2)$$

where θ and ϕ account for the angular dependence of the emission and reflection in real materials, s and d account for the presence of scattering and diffraction, respectively, and N denotes the nature of the materials involved.

Since laboratory blackbodies must be Lambertian emitters [11, p. 22–23], they are never made from materials whose emissivity is strongly directional. This explains why strong specular reflectors, such as silver, are not used to construct blackbodies. It is not solely that this material is a poor emitter. Rather, it is because all reflection within blackbodies must be diffuse or Lambertian, a property which cannot be achieved with polished silver.

It should also be noted that when Eq. 1 was presented in this form [2], the reflectivity term was viewed as reducing the emissive power from arbitrary cavities. There was nothing within this approach which acted to drive the reflection. Within the cavity, the absorptivity must equal the emissivity. Hence, any photon which left a surface element to arrive at another must have been absorbed, not reflected. The overall probability of emission within the cavity must equal the probability of absorption under thermal equilibrium. This precludes the buildup of reflective power and, thereby, prevents a violation of the 1st law of thermodynamics.

However, are there any circumstances when the reflection term can be driven? In order to answer this question, it is valuable to return to the work of Max Planck [8].

2 Max Planck's treatment of reflection

In his derivation of Eq. 1,* Max Planck had also sought to remove the undefined nature of Kirchhoff's law, when expressed in term of emission and absorption [8, §45–49]. However, in order to address the problem, he actively placed the surface of interest in contact with a perfect emitter [8, §45–49]. In so doing, Planck permitted a perfectly emitting body to drive the reflection and, thereby, build the radiation within his cavities, noting in §49 that “*the amount lacking in the intensity of the rays actually emitted by the walls as compared with the emission of a black body is supplied by rays which fall on the wall and are reflected there*”. In §45, he had informed the reader that the second medium was a blackbody. It is for this reason that Planck insists that all cavities must contain black radiation.

Thus, despite the advantage of expressing Eq. 1 in terms of reflection, Planck abandoned the relationship he had presented in §49 [8], as reflection became inconsequential if it could be driven by a carbon particle. He subsequently summarized “*If we now make a hole in one of the walls of a size $d\sigma$, so small that the intensity of the radiation directed towards the hole is not changed thereby, then radiation passes through the hole to the exterior where we shall suppose there is the same diathermanous medium as within. This radiation has exactly the same properties as if $d\sigma$ were the surface of a black body, and this radiation may be measured for every color together with the temperature T* ” [8, §49].

The problem of radiation emitted by an arbitrary cavity had not been solved, because Planck ensured, throughout his *Theory of Heat Radiation* [8], that he could place a minute particle of carbon within his perfectly reflecting cavities in order to release the ‘stable radiation’ which he sought [12]. He advanced that the carbon particle simply had a catalytic role [8, 12]. In fact, since he was placing a perfect emitter within his cavities at every opportunity [8, 12], he had never left the confines of the perfectly absorbing cavity, as represented by materials such as graphite or soot. His cavities all contained black radiation as a direct result. Perhaps this explains why he did not even number Eq. 1 in his derivation. Since he was driving reflection, all cavities contained the same radiation and Eq. 1 had no far reaching consequences.

Planck's approach stands in contrast to the derivation of Eq. 1 presented recently [2]. In that case, particles of carbon are never inserted within the arbitrary cavities. Instead, the emissivity of an object is first linked by Stewart's law [5, 6] to its reflectivity, before a cavity is ever constructed

$$\epsilon_v + \rho_v = \kappa_v + \rho_v = 1. \quad (3)$$

*Planck obtains $I = E + (1-A)I = E + RI$, where E corresponds to emitted power, $R (=e)$ is the fraction of light reflected and $I (=f(T, \nu))$ is the blackbody power which, in Planck's case, also drives the reflection [8, §49]. This is because he places a carbon particle inside the cavity to produce the black radiation.

This is how the emissivity of a real material is often measured in the laboratory. The experimentalist will irradiate the substance of interest with a blackbody source and note its reflectivity. From Stewart's law (Eq. 3), the emissivity can then be easily determined.

It is only following the determination of the emissivity and reflectivity of a material that the author constructs his arbitrary cavity. As such, the recent derivation of Eq. 1 [2], does not require that materials inside the cavity can drive the reflectivity term to eventually ‘build up’ a blackbody spectrum. This is a fundamental distinction with the derivation provided by Max Planck [8, §49].

The emissivity of a material is defined relative to the emissivity of a blackbody at the same temperature. To allow, therefore, that reflectivity would ‘build up’ black radiation, within an arbitrary cavity in the absence of a perfect emitter, constitutes a violation of the first law of thermodynamics (see [2] and references therein). Planck himself must have recognized the point, as he noted in §51 of his text that “*Hence in a vacuum bounded by perfectly reflecting walls any state of radiation may persist*” [8].

Consequently, one can see a distinction in the manner in which Eq. 1 has been applied. This leads to important differences in the interpretation of this relationship. For Planck, all cavities contain black radiation, because he has insisted on placing a small carbon particle within all cavities. The particle then actively drives the reflection term to produce black radiation.

In contrast, in the author's approach, arbitrary cavity radiation will never be black, because a carbon particle was not placed within the cavity. Emissivity and reflectivity are first determined in the laboratory and then the cavity is constructed. That cavity will, therefore, emit a radiation which will be distinguished from that of a blackbody by the presence of reflectivity. This term, unlike the case advocated by Max Planck, acts to decrease the net emission relative to that expected from a blackbody.

In this regard, how must one view arbitrary cavities and which approach should guide physics? Answers to such questions can only be found by considering the manner in which blackbodies are constructed and utilized in the laboratory.

3 Laboratory blackbodies

Laboratory blackbodies are complex objects whose interior surfaces are always manufactured, at least in part, from nearly ideal absorbers of radiation over the frequency of interest (see [13], [14, p. 747–759], and references therein). This fact alone highlights that Kirchhoff's law cannot be correct. Arbitrary cavities are not filled with blackbody radiation. If this was the case, the use of specialized surfaces and components would be inconsequential. Blackbodies could be made from any opaque material. In practice, they are never constructed from surfaces whose emissive properties are poor and whose

emissivity/reflectivity are far from Lambertian.

Sixty years ago, De Vos summarized black body science as follows: ‘Resuming, it must be concluded that the formulae given in the literature for the quality of a blackbody can be applied only when the inner walls are reflecting diffusely to a high degree and are heated quite uniformly’ [15]. De Vos was explicitly stating that mathematical rules only apply when a cavity is properly constructed. Even if the temperature was uniform, the walls must have been diffusely reflecting. Everything was absolutely dependent on the nature of the walls. Lambertian emitters/reflectors had to be utilized. Specialized materials were adopted in the laboratory, in sharp contrast to Kirchoff’s claims (see [2] and references therein).

At the same time, there is another feature of laboratory blackbodies which appears to have been overlooked by those who accept universality and Planck’s use of reflection to produce black radiation.

Laboratory blackbodies (see [13], [14, p.747–759], and references therein) are heated devices: “In photometry and pyrometry often use is made of blackbodies i.e. opaque hollow bodies which are provided with one or more small holes and whose walls are heated uniformly” [15]. They tend to be cylindrical or spherical objects heated in a furnace, by immersion in a bath of liquid (water, oil, molten metal), through electrical means like conduction (where resistive elements are placed in the walls of the cavity) and induction (where electromagnetic fields are varied), and even by electron bombardment [13–15].

The question becomes, when does the heating in a laboratory blackbody stop? For most experiments, the answer is never. Once the desired temperature is achieved, additional heat continues to be transferred to the blackbody with the intent of maintaining its temperature at the desired value. The consequences of this continual infusion of energy into the system are ignored. Since temperature equilibrium has been achieved, scientists believe that they have now also reached the conditions for thermal equilibrium. The two, however, are completely unrelated conditions.

4 Theoretical considerations

As an example, an object can maintain its temperature, if it is heated by conduction, or convection, and then radiates an equivalent amount of heat away by emission. In that case, it will be in temperature equilibrium, but completely out of thermal equilibrium. For this reason, it is clear that heated cavities cannot be in thermal equilibrium during the measurements, as this condition demands the complete absence of *net* conduction, convection, or radiation (neglecting the amount of radiation leaving from the small hole for discussion purposes).

Planck touched briefly on the subject of thermal equilibrium in stating, “Now the condition of thermodynamic equilibrium required that the temperature shall be everywhere the

same and shall not vary with time. Therefore in any given arbitrary time just as much radiant heat must be absorbed as is emitted in each volume-element of the medium. For the heat of the body depends only on the heat radiation, since, on account of the uniformity in temperature, no conduction of heat takes place” [8, §25]. Clearly, if the experimentalists were adding energy into the system in order to maintain its temperature, they could not be in thermal equilibrium, and they could not judge what the effect of this continual influx of energy might be having on the radiation in the cavity.

4.1 Consequences of preserving thermal equilibrium

Consider an idealized isothermal cavity in thermal equilibrium whose reflection has not been driven by adding a carbon particle. Under those conditions, the emissivity and absorptivity of all of its surface elements will be equal. Then, one can increase the temperature of this cavity, by adding an infinitesimal amount of heat. If it can be assumed that the walls of the cavity all reach the new temperature simultaneously, then the emissivity of every element, ϵ_v , must equal the absorptivity of every element, κ_v , at that instant. The process can be continued until a much higher temperature is eventually achieved, but with large numbers of infinitesimal steps. Under these conditions, reflection can play no part, as no energy has been converted to photons which could drive the process. All of the energy simply cycles between emission and absorption. The cavity will now possess an emissive power, E , which might differ substantially from that set forth by Kirchoff for all cavities. In fact, at the moment when the desired temperature has just been reached, it will simply correspond to

$$E = \epsilon_v \cdot f(T, \nu), \quad (4)$$

because the emissivity of a material remains a fundamental property at a given temperature. This relationship will deviate from the Planckian solution by the extent to which ϵ_v deviates from 1.

4.2 Consequences of violating thermal equilibrium

At this stage, an alternative visualization can be examined. It is possible to assume that the influx of energy which enters the system is not infinitesimal, but rather, causes the emissivity of the cavity to temporarily become larger than its absorptivity. The cavity is permitted to move out of thermal equilibrium, if only for an instant. Under these conditions, the temperature does not necessarily increase. The additional energy can simply be converted, through emission, to create a reflective component. Thermal equilibrium is violated. Emissivity becomes greater than absorptivity and the difference between these two values enters a reflected pool of photons. A condition analogous to

$$\epsilon_v = \kappa_v + \delta\rho_v \quad (5)$$

has been reached, where $\delta\rho_v$ is that fraction of the reflectivity which has actually been driven.

The emissive power might still not be equal to the Kirchhoff function in this case, depending on the amount of photons that are available from reflection. If one assumes that the radiation inside the cavity must be governed in the limiting case by the Planck function, then the emissive power under these circumstances will be equal to the following:

$$E = (\epsilon_v + \delta\rho_v) \cdot f(T, \nu). \quad (6)$$

The cavity is still not filled with blackbody radiation, as the reflective term has not yet been fully driven. Nonetheless, the process can be continued until $\delta\rho_v = \rho_v$ and the reflective component has been fully accessed. At the end of the process, Eq. 3 becomes valid in accordance to Stewart's Law [5, 6]. The temperature has not yet increased, but the energy which was thought to heat the cavity has been transformed to drive the reflective component.

Finally, thermal equilibrium can be re-established by limiting any excess heat entering the system. The reflected photons will bounce back and forth within the cavity. Balfour Stewart referred to these photons as 'banded' [5] and, for historical reasons, the term could be adopted. Thus, given enough transfer of energy into the system, and assuming that the material is able to continue to place excess emitted photons into the reflected pool, then eventually, the cavity might become filled with black radiation, provided that emission and reflection are Lambertian. In that case, the Planckian result is finally obtained:

$$E = (\epsilon_v + \rho_v) \cdot f(T, \nu). \quad (7)$$

In practice, when a blackbody is being heated, some reflected photons will always be produced at every temperature, as the entire process is typically slow and never in thermal equilibrium. However, for most materials, the introduction of photons into the reflected pool will be inefficient, and the temperature of the system will simply increase. That is the primary reason that arbitrary cavities can never contain black radiation. Only certain materials, such as soot, graphite, carbon black, gold black, platinum black, etc. will be efficient in populating the reflected pool over the range of temperatures of interest. That is why they are easily demonstrated to behave as blackbodies. Blackbodies are not made from polished silver, not only because it is a specular instead of a diffuse reflector, but because that material is inefficient in pumping photons into the reflected pool. With silver, it is not possible to adequately drive the reflection through *excessive* heating. The desired black radiation cannot be produced.

In order to adequately account for all these effects, it is best to divide the reflectivity between that which eventually becomes banded, $\delta\rho_{v,b}$, and that which must be viewed as unbanded, $\delta\rho_{v,ub}$:

$$\rho_v = \delta\rho_{v,b} + \delta\rho_{v,ub}. \quad (8)$$

The unbanded reflection is that component which was never driven. As such, it must always be viewed as subtracting from the maximum emission theoretically available, given applicability of the Planck function. With this in mind, Eq. 1 can be expressed in terms of emissive power in the following form:

$$E = (1 - \delta\rho_{v,ub}) \cdot f(T, \nu), \quad (9)$$

where one assumes that the Planckian conditions can still apply in part, even if not all the reflectivity could be banded. In a more general sense, then the expression which governs the radiation in arbitrary cavities can be expressed as:

$$E = (1 - \delta\rho_{v,\theta,\phi,ub}) \cdot f(T, \nu, \theta, \phi, s, d, N). \quad (10)$$

In this case, note that $f(T, \nu, \theta, \phi, s, d, N)$ can enable thermal emission to exceed that defined by Max Planck. The specialized nature of the materials utilized and the manner in which the cavity is physically assembled, becomes important. In this regard, Eqs. 1, 9, and 10, do not simply remove the undefined nature of Kirchhoff's formulation when considering a perfect reflector, but they also properly highlight the central role played by reflectivity in characterizing the radiation contained within an arbitrary cavity.

5 Discussion

Claims that cavity radiation must always be black or normal [7,8] have very far reaching consequences in physics. Should such statements be true, then the constants of Planck and Boltzmann carry a universal significance which provide transcendent knowledge with respect to matter. Planck length, mass, time, and temperature take on real physical meaning throughout nature [8, §164]. The advantages of universality appear so tremendous that it would be intuitive to protect such findings. Yet, universality brings with it drawbacks in a real sense, namely the inability to properly discern the true properties of real materials.

Moreover, because of Kirchhoff's law and the associated insistence that the radiation within a cavity must be independent of the nature of the walls, a tremendous void is created in the understanding of thermal emission. In this respect, Planckian radiation remains the only process in physics which has not been linked to a direct physical cause. Why is it that a thermal photon is actually emitted from a material like graphite or soot?

This question has not yet been answered, due to the belief that Kirchhoff's law was valid. Thus, Kirchhoff's law has enabled some to hope for the production of black radiation in *any* setting and in a manner completely unrelated to real processes taking place within graphite or soot. It is for this reason that astronomers can hold that a gaseous Sun can produce a thermal spectrum. Such unwarranted extensions of physical reality are a direct result of accepting the validity of Kirchhoff's formulation. Real materials must invoke the same mechanism to produce thermal photons. Whatever happens

within graphite and soot to generate a blackbody spectrum must also happen on the surface of the Sun.

The belief that arbitrary materials can sustain black radiation always results from an improper treatment of reflection and energy influx. In Max Planck's case, this involved the mandatory insertion of a carbon particle within his cavities. This acted to drive reflection. In the construction of laboratory blackbodies, it involves departure from thermal equilibrium as the inflow of energy enables the emissivity to drive the reflection. In the belief that optically thick gases can emit blackbody radiation [16], it centers upon the complete dismissal of reflection and a misunderstanding with respect to energy inflow in gases [17].

Relative to the validity of Kirchhoff's Law, it is also possible to gain insight from modern laboratory findings. Recent experiments with metamaterials indicate that super-Planckian emission can be produced in the near field [18–20]. Such emissions can exceed the Stefan-Boltzmann law by orders of magnitude [18–20].

Guo et al. summarize the results as follows: “*The usual upper limit to the black-body emission is not fundamental and arises since energy is carried to the far-field only by propagating waves emanating from the heated source. If one allows for energy transport in the near-field using evanescent waves, this limit can be overcome*” [18]. Beihls et al. states that, “*Accordingly, thermal emission is in that case also called super-Planckian emission emphasizing the possibility to go beyond the classical black-body theory*” [19].

Similar results have been obtained, even in the far-field, using a thermal extraction device [21, 22]. In that case, the spatial extent of the blackbody is enhanced by adding a transparent material above the site of thermal emission. A four-fold enhancement of the far-field emission could thus be produced. In their *Nature Communications* article, the authors argue that this does not constitute a violation of the Stefan-Boltzmann law, because the effective ‘emitting surface’ is now governed by the transmitter, which is essentially transparent [21]. However, this was not the position advanced when the results were first announced and the authors wrote: “*The aim of our paper here is to show that a macroscopic blackbody in fact can emit more thermal radiation to far field vacuum than $P=\sigma T^4 S$* ” [22].

In the end, the conclusion that these devices do not violate the Stefan-Boltzmann relationship [21] should be carefully reviewed. It is the opaque surface of an object which must be viewed as the area which controls emission. Kirchhoff's law, after all, refers to opaque bodies [3, 4]. It is an extension of Kirchhoff's law beyond that previously advanced to now claim that transparent surface areas must now be considered to prevent a violation of the laws of emission.

In this regard, Nefedov and Milnikov have also claimed that super-Planckian emission can be produced in the far-field [23]. In that case, they emphasize that Kirchhoff's law is not violated, as energy must constantly flow into these sys-

tems. There is much truth in these statements. Obviously, modern experiments [18–23] fall short of the requirements for thermal equilibrium, as the cavities involved are heated to the temperature of operation. But given that all laboratory blackbodies suffer the same shortcomings, the production of super-Planckian emission in the near and far fields [18–23] cannot be easily dismissed. After all, in order for Planck to obtain a blackbody spectrum in every arbitrary cavity, he had to drive the reflection term, either by injecting a carbon particle or by permitting additional heat to enter the system, beyond that required at the onset of thermal equilibrium.

An interesting crossroads has been reached. If one assumes that modern experiments cannot be invoked, as they require an influx of conductive energy once temperature equilibrium has been reached, then the same restriction must be applied to all laboratory blackbodies. Yet, in the absence of banded reflection, very few cavities indeed would adhere to Kirchhoff's law. In fact, many cavities can never be filled with black radiation, even if one attempts to drive the reflection term. That is because certain materials are not conducive to emission and prefer to increase their temperature rather than drive reflection. Arbitrary cavities do not contain black radiation, and that is the measure of the downfall of Kirchhoff's law.

Taken in unison, all of these observations, even dating back to the days of Kirchhoff himself, highlight that the universality of blackbody radiation has simply been overstated. The emissive characteristics of a cavity are absolutely dependent on the nature of the cavity walls (see [13], [14, p. 747–759], and references therein). This has broad implications throughout physics and astronomy.

Dedication

This work is dedicated to our mothers on whose knees we learn the most important lesson: love.

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