LETTERS TO PROGRESS IN PHYSICS

A Re-examination of Kirchhoff's Law of Thermal Radiation in Relation to Recent Criticisms

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This paper investigates claims made by Pierre-Marie Robitaille in a series of papers from 2003 to 2015 that Kirchhoff's Law of thermal radiation does not apply to cavities made of arbitrary materials, and that Planck's theoretical derivation and apparent proof of this law in these cases is faulty. Robitaille's claims are compared to statements in the original papers by Kirchhoff and Planck. The present paper concludes that Robitaille's claims are not sustainable and that Kirchhoff's Law and Planck's proof remain valid in the situations for which they were intended to apply, including in cavities with walls of any arbitrary materials in thermal equilibrium.

1 Introduction

In a series of papers from 2003 to 2015 [1–10], Pierre-Maire Robitaille has challenged the validity of Kirchhoff's Law of thermal emission and Planck's derivation of the mathematical form of the universal function of spectral radiance absorbed and emitted by a black body. As the consequences of a failure of Kirchhoff's Law would, if proven, include the loss of universality of application of various fundamental physical constants including '*Planck's constant, Boltzmann's constant, ... "Planck length", "Planck time", "Planck mass", and "Planck temperature"* [10, p. 121], Robitaille's claims deserve serious consideration.

In this paper, Robitaille's claims will be compared to the original works by Kirchhoff [11] and Planck [12] in order to determine whether his criticisms of these earlier works are valid. The present paper focuses initially on the arguments contained in the series of papers by Robitaille from 2003 to 2014 [1–9]; the second part will address the recent paper authored jointly by Robitaille and Crothers [10].

2 Robitaille's earlier papers [1–9]

2.1 Kirchhoff's law and Planck's proof

Kirchhoff's Law of thermal radiation dating from 1859-1860 may be stated as follows: "For an arbitrary body radiating and emitting thermal radiation, the ratio E / A between the emissive spectral radiance, E, and the dimensionless absorptive ratio, A, is one and the same for all bodies at a given temperature. That ratio E / A is equal to the emissive spectral radiance I of a perfect black body, a universal function only of wavelength and temperature". This radiance, I, is often referred to simply as black radiation.

The form of the universal function was not known until Planck derived it theoretically in 1914 in what is now known as Planck's Law. Planck's derivation is seen as proof of Kirchhoff's Law. However, Robitaille points out that the above definition of Kirchhoff's Law is not complete and furthermore Robitaille maintains that the statement above should be called Stewart's Law as it was originally propounded by Stewart in 1858 [13]: "All too frequently, the simple equivalence between apparent spectral absorbance and emission is viewed as a full statement of Kirchhoff's law, ... Kirchhoff's law must always be regarded as extending much beyond this equivalence. It states that the radiation within all true cavities made from arbitrary walls is black. The law of equivalence is Stewart's" [5, p. 11].

According to Robitaille, in deriving his law of equivalence Stewart had considered the case of a cavity made from perfectly absorbing (i.e. black) material; he had shown that the radiation in such a cavity at thermal equilibrium must also be black, of an intensity appropriate to the equilibrium temperature.

Whilst Robitaille agrees with Stewart, he profoundly disagrees with Kirchhoff's extension of this finding to cavities made of arbitrary materials, and therefore with Planck's proof of Kirchhoff's result. Planck had based his proof on a consideration of perfectly reflecting cavities containing "an arbitrarily small quantity of matter" [12, § 51], arriving at the same result that Kirchhoff had obtained for perfectly absorbing cavities. Planck had thereby demonstrated that all cavities either containing some arbitrary matter, or equivalently having walls made of some arbitrary matter, must also contain black radiation when at thermal equilibrium.

2.2 Black radiation in a perfectly reflecting cavity

In following the reasoning of both sides of this disagreement, it is important to distinguish between a perfectly reflecting cavity containing a vacuum and one containing an opaque object or a partially-absorbing medium.

In the first case, Planck writes that "Hence in a vacuum

bounded by totally reflecting walls any state of radiation may persist" [12, § 51]; Robitaille claims that this statement is a violation of Kirchhoff's Law [10, p. 130]. However, Planck's statement should perhaps be more properly be viewed as a situation to which Kirchhoff's Law does not apply because there is no matter present which either absorbs or emits radiation.

When considering the case of a perfectly reflecting cavity containing an arbitrary object, again it is important to distinguish between two situations. The first is that the object absorbs and emits some fraction of all frequencies of radiation; this situation may be further subdivided into the special case where the object is itself a black body such as Planck's particle of carbon which is a perfect absorber and emitter at all frequencies; and the general case where the object only absorbs and emits some fraction above zero but less than unity of every frequency. The second situation is that the object only absorbs and emits over part of the spectrum i.e. there are some frequencies for which the object itself is a perfect reflector, neither absorbing nor emitting at those frequencies.

The question in both situations is, what is the nature of the radiation in the perfectly reflecting cavity at thermal equilibrium?

Starting with the special case of a black body, Robitaille, Kirchhoff and Planck all agree that the radiation is necessarily black. The disagreements start over the general case of an object imperfectly absorbing at all frequencies.

Planck maintains that "... the radiation of a medium completely enclosed by absolutely reflecting walls is, when thermodynamic equilibrium has been established for all colors for which the medium has a finite coefficient of absorption, always the stable radiation corresponding to the temperature of the medium such as is represented by the emission of a black body" [12, § 51], quoted in [1, p. 1263]. Note that the quoted statement covers both the situation where the object absorbs and emits over all frequencies, and the situation where some frequencies are not absorbed or emitted at all.

In contrast, Robitaille claims that "In fact, if an object is placed within [perfectly reflecting] walls, an equilibrium will be established, but it will not correspond to that of a blackbody. Indeed, the radiation contained within such a device will reflect purely the emission profile of the object it contains" [1, p. 1264].

This is Robitaille's central argument against the universality claimed by Kirchhoff and Planck i.e. that all cavities containing an object must, at equilibrium, come to contain black radiation at all frequencies absorbed and emitted by the object.

2.3 The approach to equilibrium

In effect, the argument comes down to the quantity of the radiation in the cavity at equilibrium. Both sides agree that there is some radiation at all frequencies absorbed and emitted by the object; the disagreement is over the intensity of that radiation. Does it, as Kirchhoff and Planck maintain, equal the intensity of black radiation which we can now quantify according to Planck's Law of 1914; or does the radiation density in the cavity fall short of the black body level at some or all frequencies because of the imperfect absorption and emission of the object in the cavity, as Robitaille claims?

The role played by the reflected radiation, i.e. that fraction of incident radiation which is not fully absorbed by the object, is the key. Robitaille maintains that the radiation density in the cavity cannot be increased to black body levels by what he terms "driving the reflection" because this would imply a departure from thermal equilibrium which, Robitaille argues, contravenes the initial assumption that thermal equilibrium exists.

A simplified numerical example may be helpful here in order to crystallise the arguments. Suppose an opaque object in a perfectly reflecting cavity is in thermal equilibrium at a certain temperature and has a coefficient of absorption of 0.8 (i.e. 80%) of all incident radiation at all frequencies. The remaining 20% of any incident radiation will be reflected. Suppose further that the radiation density in the cavity is already at the level at which a black body at the same temperature would be in thermal equilibrium with it, say100 units. This will represent the incident radiation on the opaque object which will then absorb 80 units and reflect 20 units. The object will also re-emit the same 80 units into the cavity. The total radiation coming off the surface of the object, consisting of the emitted and reflected components, is 100, therefore thermal equilibrium will be maintained with the radiation in the cavity. What's more, the radiation density is and remains black according to the initial assumption. This represents the situation described by Kirchhoff's Law.

Consider now the situation where the same object at the same initial temperature is introduced into the perfectly reflecting but otherwise empty cavity, i.e. there is no radiation density in the cavity initially. In this case, the object will emit 80 units appropriate to its temperature; these will be reflected off the walls and become "incident" radiation on the object. The object will now absorb 80%, or 64 units, and reflect 16 units. But it is bound by its initial temperature to continue emitting 80 units. There is therefore a shortfall between the amount absorbed and the amount emitted and the object will cool down. The energy lost by the object will be converted to additional radiation density in the cavity which will increase until equilibrium is achieved between the object and the radiation density at some new, lower, temperature. At this point, the radiation will again be black, but at the level appropriate to the lower temperature, not the initial temperature of the object.

Robitaille would object to this second example on the grounds that thermal equilibrium has not been maintained. This is correct. But Robitaille goes further and maintains that this proves that the cavity cannot contain black radiation because it is not allowable to "drive the reflection" until a new equilibrium is reached – the object must be maintained at the original temperature throughout and therefore there is no spare energy available to "drive the reflection" up to black body densities.

In essence, Robitaille disallows the approach to thermal equilibrium between the object and the radiation density in the cavity by the mechanism outlined in the second numerical example above. As a result, Robitaille maintains that the cavity cannot contain the black radiation required by Kirchhoff's Law and therefore the law fails.

In support of his argument, Robitaille quotes Stewart [13] as follows: "Let us suppose we have an enclosure whose walls are of any shape, or any variety of substances (all at a uniform temperature), the normal or statical condition will be, that the heat radiated and reflected together, which leaves any portion of the surface, shall be equal to the radiated heat which would have left that same portion of the surface, if it had been composed of lampblack ... Let us suppose, for instance, that the walls of this enclosure were of polished metal then only a very small quantity of heat would be radiated; but this heat would be bandied backwards and forwards between the surfaces, until the total amount of radiated and reflected heat together became equal to the radiation of lampblack" [13, § 32] quoted in [4, p. 45].

Robitaille comments: "These passages are quite similar to Kirchhoff's with the distinction that universality is never invoked. Stewart realizes that the lampblack surface within the enclosure is essential" [4, p. 45]. But Stewart is quite specific – the walls may be of any variety of substance including polished metal. This implies that Robitaille's objection to what he refers to as Kirchhoff's extension of Stewart's result to cavities made of arbitrary material is unfounded; Stewart had already made the theoretical leap.

How then did Stewart conclude as he did that "the sum of the radiated and reflected heat together became equal to the radiation of lampblack?"

2.4 Stewart's treatment of reflection

In Stewart's original paper there is a footnote to the section quoted above which explains the calculation by which he arrived at this conclusion. Stewart considers "two parallel plates of polished metal of the same description radiating to one another" [13, § 32-footnote] and investigates what happens to an initial amount r of radiation emitted by each opposing plate and falling perpendicularly on the other plate, where a proportion is reflected back to the first plate. As an ever-decreasing part of the original radiation r is "bandied about" by repeated reflection between the plates, with a proportion $\alpha(< 1)^*$ of the incident radiation being reflected each

time, Stewart shows that the total amount falling on one of the plates is

$$r(1 + \alpha + \alpha^2 + \alpha^3 + \alpha^4 \dots) = \frac{r}{1 - \alpha}$$

which, Stewart explains, is the same formula as results from the case where one of the plates is a black body in thermal equilibrium with the other plate.

The question then arises, can this calculation also be applied to a situation where thermal equilibrium has not yet been achieved? It turns out that it can. Note that, in modern parlance, Stewart's calculation sums the repeated reflections of the two initial pulses (one from each plate) emitted in the first interval of time δt over subsequent intervals of time. It may be supposed without loss of generality that the interval of time δt corresponds to the transmission time of radiation between the plates. Then the same sum would result from considering what proportion of a series of identical initial pulses each of emission duration δt fell on one plate in a single (later) interval of time δt . This second case represents continuous emission of radiation in thermal equilibrium. One of the plates may then be replaced with a black body at the same equilibrium temperature which emits exactly the same amount of radiation that it absorbs, or alternatively with a perfect reflector. Again, the same sum emerges from the calculation, as Stewart explained.

What's more, exactly the same result is obtained when one plate is perfectly reflecting and there is no radiation in the gap between the plates initially, i.e. there is no initial thermal equilibrium to supply the series of constant pulses prior to the arrival interval δt under consideration. In this case, all the radiation is emitted by just one of the plates; therefore double the time is required to achieve the same result that Stewart obtained but, in effect, this result shows that once a steady state has been achieved then the radiation arriving on the single partially-absorbing plate is equivalent to that coming from a black body. The only difference in this case is that during the initial period the partially-absorbing plate is absorbing less radiation than it is emitting; it is therefore cooling down and part of its initial thermal energy is being used to increase the radiation density between the plates, or, in Robitaille's terms, in "driving the reflection". However, when thermal equilibrium is established then the calculation shows that the radiation reflected back on to the emitting plate will be equivalent to black radiation at the equilibrium temperature.

What this demonstrates is that Stewart's method of calculation of the reflection being "bandied about" can also be applied to the approach to equilibrium provided that time is allowed for a sufficient number of reflections to build up the radiation density in the cavity to equilibrium levels. The total time necessary to fill the space with black radiation is likely to be short because of the extremely short transmission time δt and the limited number of reflections necessary to achieve near-perfect black body radiation in most normal situations.

^{*}Stewart uses α to represent the proportion of reflected radiation; in Planck's usage, α represents the coefficient of absorption. To comply with Planck's usage, α should be replaced with ρ in the above equation. The derivation of the equation is unaffected.

Only in cases where the plate is nearly a perfect reflector might an appreciable time be required.

Thus "Stewart's mechanism", if we may so call it, should be interpreted as indicated in the second numerical example given above, with the walls themselves taking the part of the opaque object. Stewart's words "bandied about" can be applied to the reflected proportions of the continuing emission which build up the radiation density in the cavity until thermal equilibrium is achieved. Robitaille calls this "driving the reflection"; it may be clearer to think of the effect as "increasing the radiation energy density in the cavity" at the expense of the thermal energy of the walls. The important point, though, is that it occurs on the approach to thermal equilibrium between the walls and the radiation density in the cavity, not at the stage where equilibrium has already been achieved. However, once thermal equilibrium has been established then the radiation in the cavity will be black.

If an object in a perfectly reflecting cavity absorbs and emits some radiation at all frequencies it is clear that Stewart, Planck and Kirchhoff all held that the full black body spectrum will by achieved by the mechanism outlined numerically above and described by Stewart in the passage quoted. In contrast, Robitaille maintains throughout his series of papers [1–9] that it is necessary to include a black body in the cavity, whether by making part of the walls black or by inclusion of a black object, in order to achieve black radiation in accordance with Kirchhoff's Law.

2.5 Planck's particle of carbon

Robitaille claims that this is precisely why Planck insisted on including a carbon particle in his analysis and why Kirchhoff included one in his experiments. Robitaille dismisses Planck's assertion that the particle merely acts as a catalyst and insists that the carbon particle is responsible for producing the black radiation that Kirchhoff's Law requires. For example, as recently as 2014 Robitaille stated "[Planck's] *cavities all contained black radiation as a direct result* [of placing a carbon particle in the cavity] ... *Since he was driving reflection, all cavities contained the same radiation* ... " [9, p. 158].

However, it is important to distinguish between the *nature* of the black radiation emitted and the *quantity* of it. Planck is perfectly clear that the reason for assuming that the carbon particle is merely a catalyst is that it may be made as small as one likes and, most importantly, its thermal energy can be made so small as to not significantly change the total energy in the cavity [12, § 52]. By definition, therefore, the carbon particle cannot increase the radiation density in the cavity to the level commensurate with the black body temperature; in Robitaille's terms, the particle cannot "drive the reflection", and therefore this cannot be the reason why Planck included it.

Furthermore, if the radiation density is being increased

at all frequencies by Stewart's mechanism then there is no need for the particle at all; all one needs to do is wait until thermal equilibrium has been achieved. If the object is a very poor absorber and emitter then this could take some time. In adding a carbon particle to his experiments, Kirchhoff may simply have wanted to accelerate the process.

The situation is somewhat different in the case when the object is a perfect reflector at one or more frequencies. In that case, as Planck stated, the spectrum is black for all frequencies at which the object absorbs and emits but it is indeterminate at the frequencies for which the object is a perfect reflector: "Hence in a vacuum bounded by totally reflecting walls any state of radiation may persist. But as soon as an arbitrarily small quantity of matter is introduced into the vacuum, a stationary state of radiation is gradually established. In this the radiation of every color which is appreciably absorbed by the substance has the intensity K_v corresponding to the temperature of the substance and determined by the universal function ..., the intensity of radiation of the other colors remaining indeterminate" [12, § 51].

However, if the spectrum is indeterminate at any frequencies then it is not possible to properly determine a temperature which is defined in terms of the black body spectrum. See for example "... the radiation in the new volume V' will not any longer have the character of black radiation, and hence no definite temperature ... " [12, § 70]. It is apparently in order to avoid this situation that Planck included a particle of carbon which guaranteed that the intensity of radiation was determinate at all frequencies. Why Planck considered that this precaution was necessary is apparent from earlier sections of his work.

Planck had previously discussed the relationship between surface roughness and reflection, pointing out that whether a surface reflected or not was a function of roughness in relation to the wavelength: "All the distinctions and definitions mentioned in the two preceding paragraphs refer to rays of one definite color only. It might very well happen that, e.g., a surface which is rough for a certain kind of rays must be regarded as smooth for a different kind of rays. It is readily seen that, in general, a surface shows decreasing degrees of roughness for increasing wave lengths. Now, since smooth non-reflecting surfaces do not exist (Sec. 10), it follows that all approximately black surfaces which may be realized in practice (lamp black, platinum black) show appreciable reflection for rays of sufficiently long wave lengths" [12, § 11].

Thus all objects except perfect black bodies will become reflective at long enough wavelengths. It is apparently in order to avoid this situation that Planck insisted on including a particle of carbon which ensured that all frequencies were present in the equilibrium spectrum. The total radiation energy would not be affected because the particle would not have sufficient energy to do so, by definition. Thus the particle merely acted as a catalyst, as Planck insisted, to convert the spectrum emitted by the object into a black spectrum as necessary for a proper temperature measurement to be made in accordance with the definition.

Interestingly, despite numerous repetitions in Robitaille's papers [1-8] of his claim that Planck's carbon particle was essential in order to increase the radiation density to the required black body level, Robitaille [9] hints at a change of stance, admitting that eventually, the cavity might become filled with black radiation, provided that emission and reflection are Lambertian" [9, p. 160] but then he negates the possibility by stating "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" [9, p. 160]. In 2015, Robitaille & Crothers [10] return to this theme, stating "Stewart recognized that, if one could "drive the radiation" in a cavity made from arbitrary materials, by permitting the slow buildup of reflected radiation, the interior could eventually contain black radiation. The argument was true in theory, but not demonstrated in practice" [10, p. 122].

It appears that Robitaille and Crothers now accept Stewart's mechanism for building up the radiation density by *"bandying about"* the reflection, at least in principle. The authors do not give any explanation for this remarkable *volteface* from Robitaille's earlier works [1–8], but it now appears that his previous objections to Planck's particle of carbon are unfounded: the particle cannot, by definition, increase the total radiation density in the cavity, and Robitaille & Crothers apparently now accept that it is not necessary for the validity of Kirchhoff's Law that it does so.

2.6 Experimental evidence against Kirchhoff's law

Robitaille bases many of his arguments against the validity of Kirchhoff's Law on the fact that black body cavities are never constructed of arbitrary materials; on the contrary, Robitaille insists that manufacturers go to great lengths to construct cavities from special materials to ensure that the radiation is black. Equally, Robitaille points out that resonant microwave cavities cannot contain black radiation. Both these counter-examples are held to demonstrate that Kirchhoff's Law must be incorrect.

However, there appear to be alternative explanations available. In the former case, it may well be that users are concerned about the efficiency of the approach to equilibrium and therefore require black materials in order to speed up the process. It is also likely that manufacturers are concerned, as Planck himself apparently was, to ensure that there are no frequencies at which the cavity is a perfect reflector, which would preclude a proper measurement of temperature.

In the case of microwaves, the cavity is being electromagnetically forced to resonate at a particular frequency and so the radiation cannot be black. Such cases of non-thermal emission were specifically excluded by Plank in deriving his proof: "A necessary consequence of this is that the coefficient of emission ϵ depends, apart from the frequency v and the nature of the medium, only on the temperature T. The last statement excludes from our consideration a number of radiation phenomena, such as fluorescence, phosphorescence, electrical and chemical luminosity, ..." [12, § 7].

Thus it is not logical to conclude that Kirchhoff's Law must necessarily fail because of these supposed counter-examples.

2.7 Challenges to Monte Carlo simulations

Robitaille states that Monte Carlo simulations apparently support Kirchhoff's Law but then he objects on the grounds that: "Monte Carlo simulations introduce black photons into cavities. Hence, they become black. The process is identical to placing a highly emitting carbon particle, or radiometer, at the opening of a cavity. No proof is provided by computational methods that arbitrary cavities contain black radiation. It can be stated that Monte Carlo simulations obtain similar answers by modeling the repeated emission of photons directly from the cavity walls. In this case, computational analysis relies on internal reflection to arrive at a cavity filled with black radiation" [5, p. 6].

Apparently, Robitaille's objection to the Monte Carlo simulations is that they rely on Stewart's mechanism for building up the radiation by internal reflection. As Robitaille and Crothers [10] now accept that this mechanism is valid in principle, Robitaille's previous objections to Monte Carlo simulations supporting Kirchhoff's Law should also drop away.

2.8 Super-Planckian emission

Robitaille suggests that recent research into metamaterials supports his arguments. For example, he states: "Recent results demonstrating super-Planckian thermal emission from hyperbolic metamaterials (HMM) 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" [9, p. 157].

In relation to the near field emissions, Robitaille refers to three examples from the recent literature [14–16]. All three papers refer to experiments involving bodies with separation distances smaller than the thermal wavelength. However, experimental distances below the thermal wavelength were expressly excluded by Planck: *"Throughout the following discussion it will be assumed that the linear dimensions of all parts of space considered, as well as the radii of curvature of all surfaces under consideration, are large compared with the wave lengths of the rays considered"* [12, § 2].

Planck was concerned about the effects of diffraction at

small scales, in effect limiting his analysis to what are now known as far field effects. Near-field effects are not covered by Kirchhoff's Law and so these three papers cited by Robitaille cannot be used as examples of contraventions of the law. In fact, Guo et al point out that Kirchhoff's Law still suffices to calculate the thermal emission in the far-field and that *"the high-k waves which are thermally excited in the HMM are trapped inside and will be evanescent in vacuum (not reach the far field)"* [14, p. 2]. After comparing the behavior of HMM to other near-field phenomena of surface electromagnetic excitations and photonic crystal structures, Guo et al *"emphasize that in all the above cases including hyperbolic metamaterials, the presence of an interface is enough to guarantee that the far-field emissivity is limited to unity"* [14, p. 5], i.e. that it is Planckian.

The evidence for super-Planckian far-field emissions is not convincing either. Robitaille cites two papers by Yu et al [17, 18] and Nefedov & Melnikov [19] but he notes that Yu et al's claim of emissions in excess of the Stefan-Boltzmann Law made in their arXiv preprint were withdrawn in the published version, and that Nefedov & Melnikov's experiment was not in thermal equilibrium as required by Kirchhoff's Law.

Robitaille's conclusion that "the universality of blackbody radiation has simply been overstated" [9, p. 161] does not appear to be warranted on the basis of these recent experiments into metamaterials.

2.9 Robtaille's thought experiment

In [7], Robitaille postulates a thought experiment which he claims disproves Kirchhoff's Law: "Through the use of two cavities in temperature equilibrium with one another, a thought experiment is presented ... which soundly refutes Kirchhoff's law of thermal emission" [7, p. 38]. In this thought experiment, the outer cavity is perfectly absorbing and emitting; the second cavity, which is contained entirely within the outer cavity, has perfectly reflecting walls and one side which can be closed remotely. Starting with this inner side open, the two cavities are brought to 4 K; the inner side is then closed; the outer cavity is then heated to 300 K. Robitaille continues: "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" [7, p. 39].

But by making the inner cavity walls perfectly reflecting and closing the last side, Robitaille has created two entirely separate cavities; by definition, the inner cavity walls cannot emit radiation in either direction, whatever their temperature. They therefore act as boundary walls to what has become a "hollow" outer cavity. The outer cavity no longer contains the inner cavity within itself in the thermal sense; Kirchhoff's Law therefore survives this thought experiment.

3 Robitaille and Crothers 2015 paper

Robitaille & Crothers' paper [10] represents a significant departure from the previous works by Robitaille alone [1–9]. Robitaille and Crothers' *volte-face* on the viability of Stewart's mechanism for filling any cavity with black radiation has been discussed above. However, apart from a re-statement of many of Robitaille's previous objections which have also been discussed above, the thrust of the 2015 jointly-authored paper is to concentrate on criticising Planck's proof of Kirchhoff's Law, a matter only touched on briefly in previous works. Section 4 is titled "*Max Planck and Departure from Objective Reality*" and contains the authors' principal objections to Planck's proof. These will now be examined in detail.

3.1 The meaning of Planck's term "surface"

A number of Robitaille and Crothers' objections hinge on their interpretation of Planck's term "surface" which Planck himself had been careful to distinguish from Kirchhoff's earlier definition. Robitaille and Crothers quote from Planck: "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" [10, p. 124] quoting a footnote from [12, § 10]. In the original text, Planck later explains why he is diverging from Kirchhoff on this point: "Heat rays are destroyed by absorption. According to the principle of the conservation of energy the energy of heat radiation is thereby changed into other forms of energy (heat, chemical energy). Thus only material particles can absorb heat rays, not elements of surfaces, although sometimes for the sake of brevity the expression absorbing surfaces is used" [12, §12]. It appears that Planck could not accept Kirchhoff's "infinitely thin" absorbing layer because it could not include any material particles.

In § 12, Planck is simply being consistent with his earlier discussion of emission: "The creation of a heat ray is generally denoted by the word emission. According to the principle of the conservation of energy, emission always takes place at the expense of other forms of energy (heat, chemical or electric energy, etc.) and hence it follows that only material particles, not geometrical volumes or surfaces, can emit heat rays. It is true that for the sake of brevity we frequently speak of the surface of a body as radiating heat to the surroundings, but this form of expression does not imply that the surface actually emits heat rays. Strictly speaking, the surface of a body never emits rays, but rather it allows part of the rays coming from the interior to pass through. The other part is reflected inward and according as the fraction transmitted is larger or smaller the surface seems to emit more or less intense radiations" [12, §2].

In both § 10 and § 12, it is clear that Planck's use of the term "surface" refers to a geometrical surface dividing two media; the material effects of emission and absorption take

place within the adjoining media. Planck's reference to the surface radiating or absorbing heat is clearly stated as being no more than a convenient shorthand. In contrast, Robitaille and Crothers interpret Planck's term "surface" as being one composed of material particles; it appears that this misinterpretation has led them to a number of erroneous conclusions.

For example, Robitaille and Crothers ask in relation to an element $d\sigma$ of the bounding surface: "First, what exactly was the location of $\delta\sigma$? In reality it must rest in one of the two media" [10, p. 127]. This is contrary to Planck's own description of the bounding surface σ as a "surface separating the two media" [12, § 35]. Thus Robitaille and Crothers' first objection, that Planck is being inconsistent as to the location of the bounding surface, is unfounded. Similarly, Robitaille and Crothers' second objection to Planck's treatment of the bounding surface, namely "Planck neglected the fact that real materials can possess finite and differing absorptivities" [10, p. 127] cannot be maintained.

Robitaille and Crothers raise a third objection to the analysis of an element $d\sigma$ of the bounding surface, namely: "Third, the simplest means of nullifying the proof leading to Planck's Eq. 42, is to use a perfect reflector as the second medium. In that case, a refractive wave could never enter the second medium and Planck's proof fails" [10, p. 127]. However, if the surface separating the two media is itself a perfect reflector then the reflectivity on the side of the first medium is obviously equal to 1 but so is the reflectivity for any rays coming from the other side. Thus, $\rho = \rho'$ in accordance with Planck's Eq. 40 leading to his Eq. 42 (see also below) and the proof remains valid. In fact, Planck had already considered this theoretical possibility as occurring for an instant: "Since the equilibrium is nowise disturbed, if we think of the surface separating the two media as being replaced for an instant by an area entirely impermeable to heat radiation, the laws of the last paragraphs must hold for each of the two substances separately" [12, §35]. Obviously the instantaneous nature of this theoretical replacement is necessary to preserve the single system being analysed; a more permanent separation would create two separate systems to which the analysis did not apply. Once again it seems that Robitaille and Crothers' objection is unsustainable.

3.2 Absorption and transmission

Following their quote from Planck's footnote departing from Kirchhoff's definition of an infinitely thin surface in which all the absorption occurred (see above), Robitaille and Crothers commented as follows: "With his words, Planck redefined the meaning of a blackbody. The step, once again, was vital to his derivation of Kirchhoff's Law, as he relied on transmissive arguments to arrive at its proof. Yet, blackbody radiation relates to opaque objects and this is the first indication that the proofs of Kirchhoff's Law must not be centered on arguments which rely upon transmission. Planck ignored that

real surface elements must possess absorption, in apparent contrast with Kirchhoff and without any experimental justification" [10, p. 124].

However, as is obvious from the passages quoted above, Planck did recognize that absorption must be related to material particles. Once again, the apparent problem arises from the fact that Planck's surface is a geometrical one, whilst Robitaille and Crothers are obviously referring to a surface layer in which, they maintain, all absorption must take place because transmission is not permitted through a black body.

However, Planck also allows for the possibility that absorption in an opaque medium may take place at some unspecified depth below the geometrical surface, i.e. not necessarily in the particles immediately adjacent to the surface. Robitaille and Crothers quote from Planck's description in § 10 of the dependence of the absorbing power on the thickness of the black body material which ends "The more absorbing a body is, the smaller the value of this minimum thickness, while in the case of bodies with vanishingly small absorbing power only a layer of infinite thickness may be regarded as black". Robitaille & Crothers object to this sentence stating that "Now, [Planck] explicitly stated that bodies which are poor absorbers can still be blackbodies. Yet, we do not make blackbodies from materials which have low absorptivities, because these objects have elevated reflectivities, not because they are not infinite" [10, p. 125] quoting [12, §10].

But these two objections, about absorptivity and reflectivity respectively, seem to be missing the points that Planck is making: firstly, some absorption may take place by particles situated below the surface. Secondly, Planck had previously stated: "When a smooth surface completely reflects all incident rays, as is approximately the case with many metallic surfaces, it is termed "reflecting". When a rough surface reflects all incident rays completely and uniformly in all directions, it is called "white". A rough surface having the property of completely transmitting the incident radiation is described as "black" [12, § 10]. Note that Planck defines black materials as those with a rough surface which does not reflect; all rays falling on a black material pass through Planck's geometrical surface and are subsequently absorbed at some depth in the interior of the black body. No rays are reflected from the body even if the material is, in Planck's terms, a poor absorber. This immediately undermines Robitaille and Crothers' second objection.

Robitaille and Crothers also argue that Planck incorrectly includes transmission within the material of the black body when in fact, Robitaille and Crothers claim, absorption must all occur at the surface: *"Blackbodies are opaque objects without transmission, by definition"* [10, p. 125]. Once again, they are apparently overlooking Planck's definition of a geometrical surface and his careful consideration of where any absorption of radiation passing through that geometrical surface subsequently takes place.

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3.3 Reflection

Robitaille and Crothers' § 4.2 deals further with Planck's treatment of reflection. The authors state: "In the first section of his text, leading to his Eq. 27, ... Planck chose to formally neglect reflection, even though the total energy of the system included those rays which are both emitted/absorbed and those which would have been maintained by driving reflection. Such an approach was suboptimal" [10, p. 125].

However in the first section of his text, Planck is expressly dealing with the situation within a medium, not with surface effects. His § 25 begins: "We shall now, as in the previous chapter, assume that we are dealing with homogeneous isotropic media whose condition depends only on the temperature, and we shall inquire what laws the radiation phenomena in them must obey in order to be consistent with the deduction from the second principle mentioned in the preceding section ... Let us consider, first, points of the medium that are far away from the surface" [12, §25]. A mathematical treatment then follows, leading to Planck's Eq. 27 towards the end of § 26 which Planck follows with the words "i.e.: in the interior of a medium in a state of thermodynamic equilibrium the specific intensity of radiation of a certain frequency is equal to the coefficient of emission divided by the coefficient of absorption of the medium for this frequency" [12, § 26].

Note that Planck is still talking about the interior of the medium where reflection is not applicable because there is no surface; therefore Robitaille and Crothers' objection cannot be maintained.

3.4 Polarization and equality of reflection

Robitaille and Crothers then object to Planck's analysis based initially on a plane-polarised ray, stating: "In § 5 Planck admitted that homogeneous isotropic media emit only natural or normal, i.e. unpolarized, radiation: "Since the medium was assumed to be isotropic the emitted rays are unpolarized". This statement alone, was sufficient to counter all of the arguments which Planck later utilized to arrive at Kirchhoff's Law [Eq. 42]. That is because the important sections of Planck's derivation, namely § 35–37 make use of plane-polarized light. These steps were detached from experimental reality, relative to heat radiation [Planck, § 35]..." [10, p. 127] quoting [12, § 35].

Yet Robitaille and Crothers themselves admit that there was method in Planck's approach, quoting Planck again: "to prepare for his use of polarized light in later sections, Planck resolved, in § 17, the radiation into its two polarized components" [10, p. 127], which in itself is unobjectionable. However, Robitaille and Crothers later state that "such rays could never exist in the context of heat radiation" [10, p. 129] and this appears to be their principal objection to this means of analysis from which Planck derives the equality of the reflectivity on either side of a geometrical surface separating two different media in his Eq. 40.

But Planck made it clear that an analysis of the special case of polarised light under consideration leads to a valid general conclusion because, as he explained at the end of § 36, the intensity of radiation K_{ν} , the velocity of propagation q, and the coefficient of reflection ρ at a surface dividing two different media are related by the equation

$$\frac{K_{\nu}}{K'_{\nu}}\frac{q^2}{q'^2} = \frac{1-\rho'}{1-\rho}$$

where the accented quantities refer to the second medium. Planck continued in §37: "In the last equation the quantity on the left side is independent of the angle of incidence and of the particular kind of polarization; hence the same must be true for the right side. Hence, whenever the value of this quantity is known for a single angle of incidence and any definite kind of polarization, this value will remain valid for all angles of incidence and all kinds of polarization. Now in the special case when the rays are polarized at right angles to the plane of incidence and strike the bounding surface at the angle of polarization, $\rho = 0$, and $\rho' = 0$. The expression on the right side of the last equation then becomes 1; hence it must always be 1 and we have the general relations:

and

$$q^2 K_{\nu} = q'^2 K'_{\nu}$$
 (41)".

(40)

 $\rho = \rho'$

Regarding Planck's Eq. 40, Robitaille and Crothers state bluntly that "The result was stunning. Max Planck had determined that the reflectivities of all arbitrary media were equal" [10, p. 129]. On the contrary, what Planck had in fact demonstrated is that the reflectivities on each side of a geometrical surface bounding two different media are equal. Clearly if a different pair of media are chosen, the value of the reflectivity of the bounding surface may be different as well. Planck had previously addressed this point in § 10: "Since, in general, the properties of a surface depend on both of the bodies which are in contact, this condition shows that the property of blackness as applied to a body depends not only on the nature of the body but also on that of the contiguous medium. A body which is black relatively to air need not be so relatively to glass, and vice versa" [12, § 10]. Robitaille & Crothers' interpretation that Planck had determined that the reflectivities of all media were equal is unwarranted.

4 Summary and conclusions

Stewart [13] had shown that the radiation in a cavity made from perfectly absorbing material at thermal equilibrium must be black, of an intensity appropriate to the equilibrium temperature. According to Robitaille, Kirchhoff [11] extended this finding to cavities made of arbitrary materials. In a series of papers [1–10], Robitaille has raised various objections to Kirchhoff's extension of Stewart's finding to arbitrary cavities, and to Planck's proof of Kirchhoff's Law [12]. Robitaille concludes that the Law can only be applied validly to cavities containing a black body.

The present paper has investigated Robitaille's claims in depth and compared them to the original papers by Stewart [13], Kirchhoff [11] and Planck [12]. In no instances have Robitaille's objections been found to be sustainable. Furthermore, is has been noted that one of Robitaille's key and oftenrepeated objections to the build-up of black radiation in an arbitrary cavity according to a mechanism first proposed by Stewart [13] has now been effectively withdrawn in the recent paper by Robitaille and Crothers [10].

Robitaille is obviously correct to point out that black body cavities are never made from reflective materials. However, this fact appears to be more a question of practicality and the need to ensure that the walls are not perfectly reflective at any wavelength so that proper measurements of temperature can be made. It does not seem to amount to a demonstration that Kirchhoff's Law necessarily fails, as Robitaille claims.

This investigation suggests that Kirchhoff's Law and Planck's proof of it remain valid in the situations for which they were intended to apply, including in cavities with walls of any arbitrary materials in thermal equilibrium, unless some other more sustainable objections can be raised in the future.

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