Plausible Fundamental Origins of Emissivity (I)

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Emissivity is a fundamental property of matter that measures the ratio of the thermal radiation emanating from a thermodynamic surface to the radiation from an ideal black-body surface at the same temperature and it takes values from 0 to 1. This property is not a theoretically derived thermodynamic property of matter, but a *posteriori justified* property that is derived from experiments after its need was found necessary in order to balance up the theoretically expected radiation of a black-body at the same temperature to that actually measured in the laboratory for a material body at the same temperature. From a fundamental theoretical stand-point, we argue herein that emissivity may arise due perhaps to the *existence of non-zero finite lower and upper cut-off frequencies* in the thermal radiation of matter, thus leading to material bodies emitting not all the radiation expected from them when compared to equivalent black-body surfaces. We demonstrate that a non-zero lower limiting frequency is implied by the refractive index of materials, while an upper limit frequency is adopted from Debye's (1912) ingenious idea of an upper limiting cut-off frequency which arises from the fact that the number of modes of vibrations of a finite number of oscillators must be finite.

1 Introduction

Emissivity is a fundamental, intrinsic and inherent property of all known materials. Commonly, one talks of the emissivity of solid materials and as such, emissivity is a property typically associated with solids. In reality, all forms (solid, liquid, gas) of matter exhibit this property. In general, the emissivity of a given material is defined as the ratio of the thermal radiation from a surface to the radiation of an ideal black surface at the same temperature. As presently obtaining, this important property of matter – *emissivity* – has no fundamental theoretical justification – it is an experimentally derived property of matter. This article seeks to lay down a theoretical framework and basis that not only justifies the existence of this property of matter, but to investigate this from a purely theoretical standpoint.

To that end, in the present article, we conduct an *initial forensic analysis* of the modern derivation of the Planck Radiation Law (PRL) [1–3]. In this analysis, we identify two *loopholes* in the derivation of the PRL, and these are:

1. **Dispersion Relation Problem:** The dispersion relation assumed in the PRL is that of a photon in a *vacuo*, i.e.:

$$E = pc_0, \quad (1)$$

where: (E, p) are the (kinetic) energy and momentum of the photon in question, and: $c_0 = 2.99792458 \times 10^8 \text{ m s}^{-1}$ is the speed of light in *vacuo* (2018 CODATA[*]). This Eq. (1), is what is used in the derivation of the PRL in relation to the energy and momentum of the photon in the interior of material bodies. Without an iota of doubt, the interior of material

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[*]https://physics.nist.gov/cgi-bin/cuu/Value?c

bodies is certainly not a *vacuo*. This means that the dispersion relation (1) is not the appropriate dispersion relation to describe these photons generated therein material bodies. We need to use the correct equation – i.e. by replacing (1) with:

$$E = pc, \quad (2)$$

where: $c = c_0/n$; and here: c, is the speed of light in the material (medium) whose refractive index is n and n: $0 < n < 1$. This is the first correction to the PRL that we shall conduct.

2. **Limits Problem:** The second correction has to do with the lower and upper limits in the integral leading to the PRL. As one will notice (and most probably ignore) is that the derivation leading to the PRL does not have a finite upper limit (i.e. $\nu_H = \infty$) and at the same time, this same integral has a lower bound limit of zero (i.e. $\nu_L = 0$). What this means is that the photons emitted by material bodies have wavelengths in the range – zero ($\nu_L = 0$) to infinity ($\nu_H = \infty$). A zero frequency photon implies zero kinetic energy and an infinite frequency photon implies an infinite kinetic energy of the photon. The lower bound frequency ($\nu_L = 0$) has serious problems with Heisenberg's uncertainty principle [4], while the upper infinite frequency ($\nu_H = \infty$) has obvious *topological defects* with physical and natural reality as we know it.

Using the above *two points of critique* in the derivation of the PRL, we shall advance a thesis which seeks to demonstrate that, it is possible *in principle* to justify from a physical and fundamental theoretical level the existence and the need of the emissivity function of a material. There is no such effort in the present literature where such an endeavour has been attempted – this, at least is our view point derived from the wider literature that we have managed to lay our hands on.

Now, in closing this introductory section, we shall give a synopsis of the remainder of this article. In §2 and §3, for self-containment, instructive and completeness purposes, we present an exposition of the Planck radiation theory and the derivation of the Stefan-Boltzmann Law respectively, where emphasis is made on the two points of critique to the Planck theory that we made above. In §4, we present our derivation. In §5, a general discussion is presented. Lastly, in §6, in a rather succinct manner, the conclusion drawn from the present work is laid down.

2 Planck radiation theory

As was presented in the first article of this series [5], we shall make the derivation of the PRL our point of departure. We know that the number of quantum states dN in the momentum volume space d^3p and physical volume space V, is given by:

$$dN = \frac{2V d^3 p}{h^3}, \tag{3}$$

where: $h = 6.62607015 \times 10^{-34}$ J s is Planck's constant (2018 CODATA[*]). The factor 2 in (3) comes in because of the number of degrees of freedom of the photon: one for traverse and the other for longitudinal polarisation – i.e. the photon has two polarization states. Now, given that: $d^3p = 4p^2 dp$, it follows that:

$$dN = \frac{8\pi V p^2 dp}{h^3}, \tag{4}$$

and further, given that for a photon of momentum p_γ, energy E_γ and frequency ν, its energy-momentum is such that: $p_\gamma = E_\gamma/c_0 = h\nu/c_0$, it follows from this, that the number of modes in the frequency interval: ν to $\nu + d\nu$ is:

$$dN = \left(\frac{8\pi V}{c_0^3}\right) \nu^2 d\nu. \tag{5}$$

The actual number of occupied states dn is such that $dn = f_{BE}(\nu, \mathcal{T}) \, dN$ where:

$$f_{BE}(\nu, \mathcal{T}) = \frac{1}{e^{h\nu/k_B T} - 1}, \tag{6}$$

is the Bose-Einstein probability function which for a temperature $\mathcal{T}$, gives the probability of occupation of a quantum state whose energy is $E_\gamma = h\nu$ and: $k_B = 1.38064852(79) \times 10^{-23}$ J K^{-1} is the Boltzmann constant (2018 CODATA[†]). From the foregoing:

$$dn_* = \frac{8\pi V}{c_0^3} \frac{\nu^2 d\nu}{e^{h\nu/c_0 h_B T} - 1}, \tag{7}$$

leading to the energy density: $B_\nu(\nu, T)d\nu = E_\gamma dn_*/V$, now being given by:

$$B_\nu(\nu, T)d\nu = \frac{8\pi h}{c_0^3} \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1}, \tag{8}$$

where: $B_\nu(\nu, T)$ is the spectral irradiance given in terms of ν: (8) is our sought-for PRL.

3 Stephan-Boltzmann law

Now, to derive the Stefan-Boltzmann Law (SBL) from (8), we start by setting: $x = h\nu/k_B T$. This setting implies that: $d\nu = k_B T dx/h$, thus substituting this into (8), we then have:

$$B_\nu(\nu, T)d\nu = \frac{8\pi k_B^4 \mathcal{T}^4}{h^3 c_0^3} \frac{x^3 dx}{e^x - 1}. \tag{9}$$

From the foregoing theory, the total energy density $\mathscr{E}_{theo}$ radiated per unit time by a radiating body is such that:

$$\begin{aligned} \mathscr{E}_{theo} &= \frac{c_0}{4} \int_{\nu_L=0}^{\nu_H=\infty} B_\nu(\nu, T)d\nu, \\ &= \frac{2\pi k_B^4 \mathcal{T}^4}{h^3 c_0^2} \int_0^\infty \frac{x^3 dx}{e^x - 1}, \end{aligned} \tag{10}$$

and given that: $\int_0^\infty x^2 dx/(e^x - 1) = \pi^4/15$, it follows that the SBL will thus be given by:

$$\mathscr{E}_{theo} = \sigma_0 \mathcal{T}^4, \tag{11}$$

where one can most easily deduce that the fundamental and universal constant – the *Stefan-Boltzmann constant*: $\sigma_0 = 2\pi^2 k_B^4/15h^3 c_0^2$. In terms of its actually experimentally measured value: $\sigma_0 = 5.670374419 \times 10^{-8}$ W m^{-2} K^{-4} (2018 CODATA[‡]).

Written as it appears in (11), the SBL is not compatible with physical and natural reality as it needs to be supplemented with a new term – namely the emissivity ϵ, i.e.:

$$\mathscr{E}_{exp} = \epsilon \sigma_0 \mathcal{T}^4. \tag{12}$$

The above result is what one gets from experiments. We shall derive the emissivity function: $\epsilon = \epsilon(\nu, \mathcal{T})$ from the fundamental soils of theory.

4 Derivation

In this section, we shall in two parts, i.e. §4.1 and §4.2, derive a relation that connects the emissivity function with the refractive index of the given material and both the upper and lower limits in the energy of the photon.

4.1 Dispersion relation problem

In the derivation of the PRL, i.e. (8), and as well as the SBL, i.e. (11), we have used the *vacuo* dispersion relation (1) for the photon. As stated in the introductory section, this is *not correct* as one is supposed to use the correct non-*vacuo* photon dispersion relation (2). If we do the *correct* thing and

instead use (2) in the derivation of the PRL, instead of the PRL given in (8), we will obtain the new revised PRL:

$$
\begin{aligned}
B_\nu(\nu, T)d\nu &= \frac{8\pi h}{c^3}\frac{\nu^3 d\nu}{e^{h\nu/k_B T}-1}, \\
&= \frac{8\pi h}{c_0^3}\frac{n^3\nu^3 d\nu}{e^{h\nu/k_B T}-1}.
\end{aligned}
\tag{13}
$$

The difference between (13) and (8), is the introduction of the refractive index, n.

Now, from this new PRL (13) together with the correct non-*vacuo* photon dispersion relation (2), one obtains the following refractive index modified SBL:

$$
\mathscr{E}_{\exp} = \frac{c_0}{4}\int_{\nu_L}^{\nu_H}\frac{cB_\nu(\nu, T)d\nu}{c_0} = \frac{c_0}{4}\int_{\nu_L}^{\nu_H}\frac{B_\nu(\nu, T)d\nu}{n},
\tag{14}
$$

where in (14), we have not set the limits ($\nu_H = \infty$; $\nu_L = 0$), but have left this as a task to be dealt with in §4.2.

Now – proceeding to institute in (14) the substitution: $x = h\nu/k_B T$, and remembering that the refractive index n is a function of ν and possibly $\mathcal{T}$ as well (i.e. $n = n(\nu, \mathcal{T}) = n(x)$), it follows that (14) will reduce to:

$$
\mathscr{E}_{\exp} = \sigma_0\mathcal{T}^4\int_{x_L}^{x_H}\frac{15}{\pi^4}\frac{x^3 n^2(x)dx}{e^x - 1}.
\tag{15}
$$

With $\mathscr{E}_{\exp}$ now written as it has been written in (15), one can reasonably identify the emissivity function as:

$$
\epsilon = \frac{15}{\pi^4}\int_{x_L}^{x_H}\frac{x^3 n^2(x)dx}{e^x - 1} = \epsilon(x) = \epsilon(\nu, \mathcal{T}).
\tag{16}
$$

In this way, the emissivity has not been introduced as a result of an experimental requirement, but foisted by subtle theoretical requirements to do with the (obvious *but* neglected) shortcomings stated in the introduction section.

Our intention in the present article is not to investigate this newly-derived emissivity function (16), but merely to make a statement to the effect that the emissivity function can be derived from the fundamental soils of theoretical physics. We shall slate for the next installation, the task to test the emissivity function (16) against real data. In the subsequent subsection, we will now deal with the issue of the limits in the integral (16).

4.2 Limits problem

As stated previously, a photon frequency of zero (i.e. photon with zero energy) does not make sense especially in the face of Heisenberg's [4] uncertainty limit. To obtain a reasonable estimate of this, one can appeal to logical reasoning by simply asking the question: *What is the largest wavelength of a photon that can travel in a medium with a mean inter-molecular spacing: $\ell = \ell(T)$?* We know that the speed of our photon is c and that this speed is such that it is equal to: $\lambda\nu$, where λ is the

wavelength of our photon. In order for the smooth passage of the photon in such a medium, it is reasonable to assume that the wavelength of the photon be at most equal to one half of the mean spacing of the given medium, i.e. $\lambda_{\max} = \ell/2$. Given that: $c = \lambda\nu$, it follows that we must have: $\nu_L = 2c_0/n\ell$.

Now, in establishing the upper limiting frequency that must enter the integral leading to the PRL, we will use the reasoning already laid down by Debye [9]. As is well known, in November of 1907, Einstein [10] proposed the first reasonably good model of the *Heat Capacity of a Solid* that employed the then nascent concept of quantization of energy. Einstein's [10] motivation was really not to propose a rigorous working model of a solid but to promote the then strange *Quanta Hypothesis* that had been promulgated earlier by Planck [1–3] and had been *given breath to* by him in his landmark and *1921 Nobel Prize* winning 1905 explanation of the *Photoelectric Effect* [11].

In his model of a solid, Einstein [10] made three fundamental assumptions: (1) Each atom in the lattice is an independent 3D quantum harmonic oscillator and the energy of this oscillator is quantized, (2) All atoms oscillate with the same fundamental frequency of vibration and (3) The probability of occupation of any given microstate is given by the Boltzmann thermodynamic probability. In summing up (integrating) all the energies of these oscillators, Einstein's oscillators have a minimum of zero frequency and an infinity frequency for a maximum frequency. While Einstein's [10] model gave a reasonably good fit to data, Debye [9] realized that Einstein's limits of integration where non-physical, especially the upper limiting frequency: $\nu_H = \infty$. So, in constructing a revised (modified) version of Einstein's [10] model, Debye [9] had to correct this by limiting the upper frequency ν_H.

Debye [9] required that for the N oscillators – each with three degrees of freedom – the sum total of the modes of vibration must equal $3N$. That is to say, if $g(\nu)$ is the density of states, then:

$$
\int_{\nu_L}^{\nu_H} g(\nu)d\nu = 3N.
\tag{17}
$$

Debye [9] set: $\nu_L = 0$ because in reality: $\nu_L \simeq 0$ and keeping ν_L as non-zero in his model did not bring in any significant improvement to the model, so he simply set this equal zero. Thus from (17), Debye [9] could calculate ν_H, and this maximum frequency one obtains from this calculation is known as the *Debye frequency* and symbolized ν_D.

For the photons under probe (in the present article), the density of states: $g(\nu) = dN/d\nu$ can be calculated from (5)*, and so doing one obtains: $g(\nu) = 8\pi V\nu^2/c^3$. Since a photon has two degrees of freedom, accordingly, N photons will have

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*The reader must remember to substitute c in place of c_0 because in the foregoing calculation, we have disposed of the *vacuo* dispersion relation (1), and adopted the non-*vacuo* dispersion relation (2).

2N degrees of freedom, hence:

$$\int_{\nu_{\mathrm{L}}}^{\nu_{\mathrm{H}}} \frac{8\pi V \nu^2 d\nu}{c^3} = \frac{8\pi V}{c_0^3} \int_{\nu_{\mathrm{L}}}^{\nu_{\mathrm{H}}} n^3(\nu, \mathcal{T})\nu^2 d\nu = 2N. \qquad (18)$$

Since ν_{L} is known, ν_{H} can be known if $n(\nu, \mathcal{T})$ is known. In the present article, we have no intention of evaluating the model, i.e. (16) and (18), that we have just set because we are yet to make further modifications where we shall include possible *non-zero photon mass effects*. For now, all we want to do is to show that one can demonstrate from a most fundamental level, that the emissivity function ϵ can be furnished with solid theoretical foundations rather than have this function as an experimental construct with no solid fundamental theoretical basis.

5 Discussion

The main aim of this paper has been to seek a fundamental and foundational basis and justification for the existence of the emissivity property of matter from the soils of fundamental theoretical physics. We are of the view that the grounds for such an endeavour have herein been set. Our final theoretically derived expression for the emissivity is given in (16). This expression we arrived at by revising the traditional derivation of the PRL as articulated in the introduction section. This emissivity function, i.e. (16), here derived has three free parameters associated with it and these parameters are:

1. The lower cut-off frequency: ν_{L}. The meaning of which is that there exists in this material medium in question, a *Lower Cutoff Frequency* (ν_{L}) below which frequency the body does not emit.

2. The upper frequency: ν_{H}. The meaning of which is that there exists in this material medium in question, an *Upper Cutoff Frequency* (ν_{H}) above which frequency the body does not emit.

3. The refractive index: n of the given material.

Of these three free adjustable parameters, the refractive index is less free as an adjustable parameter as there are already experimentally verified models of this quantity (see e.g. [12–14]). However, the lower (ν_{L}) and upper (ν_{H}) frequencies can be fixed to suit the given material, thus one can *in principle* fit the emissivity function (16) to the experimentally measured emissivity of a given material medium. When we say *one can in principle fit the emissivity function (16) to the experimentally measured emissivity of a given material medium*, we do not mean in an arbitrary manner, but that one will have to work out a realistic model that leads to a theory that fits to the data. In closing, allow us to say that in our next instalment, an attempt to fit the herein derived emissivity function, i.e. (16), to real data will be made.

6 Conclusion

Without the dictation of experience, it is possible in principle to justify by way of solid physical arguments and from a *bona fide* fundamental theoretic level, the existence and the need of the emissivity function for natural material.

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