Developments on the Entropy of Thermal Radiation

by

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We accept this thesis as conforming to the required standard

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ABSTRACT

The objectives of this work are to improve the understanding and also to simplify the calculation of the entropy transferred by thermal radiation (TR). Thermal radiation plays an important role in the thermodynamic analysis of many systems. For example consider the Earth. Thermal radiation exchange is frequently the dominant form of energy and entropy transfer within the Earth system and is the only significant form of exchange between the Earth and the universe ([15], p. 38,39). Moreover, radiation-matter interaction is responsible for most of the entropy produced by the Earth system.

With respect to the energy of TR there has been extensive research and application in engineering analysis. The entropy of TR with an arbitrary spectrum can be calculated by numerical integration using Planck's [1] fundamental spectral entropy radiance (L_ν) expression. This requires the knowledge of the spectral energy radiance (K_ν) spectrum with position and direction. Exclusive use of numerical integration is straightforward but laborious and from an analytical perspective the entropy of non-blackbody radiation (NBR) is not well understood. Heat transfer textbooks usually exclude entropy altogether. Furthermore, most thermodynamic texts are misleading because they state that the entropy flux of 'heat' transfer is the ratio of the energy flux to the local temperature (q/T) with no restriction for TR (e.g. Moran and Shapiro [2], p. 220 and 230; Reynolds and Perkins [3], p. 223; and McGovern [4], p. 177).

In this work simple closed form expressions for the entropy flux of NBR are presented. Entropy-to-energy ratios, entropy balance at a material surface, and the nature and significance of the family of black body curves are developed and discussed. The entropy flux of heat conduction and TR are compared and the error introduced in taking the entropy flux of TR as q/T is evaluated for BR and NBR. The results of this research are then used in a preliminary discussion of Stephens and Obrien [5] paper on the total entropy production rate of Earth and the role of TR in climate modelling.

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LIST OF SYMBOLS

Energy:

U Internal Energy (J)
u Internal energy per unit volume (J/m^3)
$\dot{E}$ Energy flow rate (W)
H Energy irradiance or flux (W/m^2)
H_ν Spectral energy irradiance (J/m^2)
K Energy radiance (W/m^2·sr)
K_ν Spectral energy radiance (J/m^2·sr)

Entropy:

S Internal Entropy (J/K)
s Entropy per volume (J/m^3·K)
$\dot{S}$ Entropy flow rate (W/K)
J Entropy irradiance or flux (W/m^2·K)
J_ν Spectral entropy irradiance (J/m^2·K)
L Entropy radiance (W/m^2·sr·K)
L_ν Spectral entropy radiance (J/m^2·sr·K)

Entropy Production:

$\dot{\pi}$ Entropy production rate per unit volume (W/m^3·K)
$\dot{\Pi}$ Total entropy production rate (W/K)

Table S-1: Energy and Entropy Quantities

	Energy		Entropy	
	Symbol	Units	Symbol	Units
Internal	U	J	S	J/K
Flow Rate	$\dot{E}$	W	$\dot{S}$	W/K
Irradiance or Flux	H	W/m^2	J	W/m^2·K
Spectral Irradiance	H_ν	J/m^2	J_ν	J/m^2·K
Radiance	K	W/m^2·sr	L	W/m^2·sr·K
Spectral Radiance	K_ν	J/m^2·sr	L_ν	J/m^2·sr·K
Non-Dimensional Spectral Radiance	y_ν	none	z_ν	none

a BR constant = $4\sigma/c = (7.61)10^{-16}$ J/m^3·K^4
A Area (m^2)
c Speed of light = $(2.9979)10^8$ m/s
$C(\varepsilon)$ Function introduced in equation (4.16)
C_L, C_K Constants introduced in section 4.2, equation (4.11)
k Boltzman's constant = $(1.38)10^{-23}$ J/K
h Planck's constant = $(6.626)10^{-34}$ J·s
$I(\varepsilon), m$ Functions introduced in equations (3.8) and (4.1)
n Constant introduced in equation (4.28)
N Number of moles

p	State of polarization, p =2 for unpolarized, p =1 for plane polarized (section A.3)
$p(\varepsilon)$	Function introduced in equation (4.22)
P	Pressure
q	Heat flux (W/m^2)
$\dot{Q}$	Heat Transfer Rate (W)
$R\theta\phi$	Spherical Coordinates
T	Temperature (K)
T_ν	Spectral temperature (K)
V	Volume (m^3)
x	Dimensionless frequency ($h\nu/kT$)
x_K	Dimensionless frequency (K_ν fixed)
y_{BB}	Dimensionless spectral energy radiance for blackbody radiation
z_{BB}	Dimensionless spectral entropy radiance for blackbody radiation
z_K	Dimensionless spectral entropy radiance (K_ν fixed)
α	Constant = $1+2^{-4}+3^{-4}+\ldots.. = \pi^4/90 \approx 1.0823$
ε	Emissivity for gray radiation (GR): also denoted e in some figures
ν	Frequency (s^{-1})
σ	Steffan-Boltzman constant = $(5.67)10^{-8}$ W/m^2·K^4= $\frac{2\pi^5}{15}\frac{k^4}{c^2 \cdot h^3}$
Ω	Solid angle (sr)

Subscripts:

Abs	Absorbed	i	initial
B	Blackbody	Inc	Incident
BR	Blackbody radiation	NBR	Non-Blackbody radiation
c	conduction	r	radiation
ch	characteristic location	Ref	Reflected
Emi	Emission	RM	Radiation-matter
f	final	T	at temperature T
G	Gray	ν	frequency

Notes:

- The following abbreviations and acronyms are used throughout:

BB , BR	Blackbody, Blackbody radiation
GR, DBR	Gray Radiation or Diluted blackbody radiation
MR	Monochromatic Radiation
NB, NBR	Non-Blackbody, Non-Blackbody thermal radiation
TR	Thermal Radiation

- Planck used the word intensity in place of radiance. The units of energy and entropy intensity are W/sr and W/sr·K. Also, Planck used the symbol I for energy flow rate.
- Landsberg and Tonge [6] used the radiance notation K and L.
- Stephens and Obrien [5] used the irradiance notation H and J.
- Note that although the BR and GR spectrums are mathematically smooth functions they are depicted as rough in some figures because of word processing difficulties.

ACKNOWLEDGMENTS

I owe many thanks to Dr. David Scott and Dr. Marc Rosen for their contributions of knowledge and time that they provided in supervising this work. I would also like to thank to Dr. James Haddow for his ongoing discussions and thoughtful input to this research.

I wish to acknowledge that the credit for realizing that there was a need to improve the understanding of the entropy transferred by TR goes to Dr. Scott. The motivation for this research arose from analyzing the entropy transfer and production rates within the Earth system where TR plays a very important role. And I am thankful for working on such an enjoyable and rewarding research topic.

Lastly, I wish to recognize and thank Dr. Scott for financial support drawn from his research funds, and the department of Mechanical Engineering for financial support through the teaching assistant program.

CHAPTER 1 INTRODUCTION

1.1 Motivation

The motivation for this research arose from the task of quantifying the entropy produced within Earth's various domains and the entropy transport mechanisms that sustain approximately constant entropy within these domains. The domains of particular interest to our group's research include those of: the Earth as a whole*, the atmosphere, the hydrosphere, the biosphere, and civilization's energy system.

Thermal radiation exchange is the only significant form of energy and entropy transfer between the Earth and the surrounding universe. Consequently the total entropy produced by Earth reduces to the entropy balance between in-coming (low entropy sunlight) and out-going (high entropy) thermal radiation fluxes. Thermal radiation is also an important energy and entropy transfer mechanism between the atmosphere and the other domains of the Earth system.

Radiation exchange is also important for the biosphere. The exergy flux** of low entropy sunlight supports all life on Earth. Flora on the Earth receives sunlight and the fauna is in turn supported by consuming the flora. Thermal radiation emission carries away a significant portion of the entropy produced by fauna on the Earth. Consequently, radiation is an important energy and entropy exchange mechanism between the biosphere and its surroundings.

Moreover radiation-matter interaction is responsible for the majority of the entropy produced by the Earth system. Stephens and Obrien [5] state that "the production of global entropy is dominated entirely by radiative processes". This entropy production is

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* The " Earth" refers to the total system including the lithosphere, hydrospere, and the atmosphere.

** The exergy flow rate is the maximum work production rate obtainable from TR in a given environment.

caused by absorption of sunlight emitted from a source with a temperature near 6000 K by material in the Earth system that is near 300 K. Other entropy producing processes such as mass transfer and convection within the atmosphere or processes in the biosphere are secondary because the driving force is incoming sunlight that must first be absorbed by 'low' temperature material on Earth.

Clearly the thermodynamics of thermal radiation has a very important role in the analysis of the Earth and its subsystems. With respect to the energy of radiation there has been extensive research and application in engineering analysis. However an understanding of the entropy of thermal radiation is not fully developed.

Integration of the spectral entropy radiance (L_ν) spectrum of arbitrary thermal radiation over frequency gives the entropy radiance L in a certain direction at a fixed location in space. For blackbody radiation (BR) a simple analytical solution results. However, for non-blackbody thermal radiation (NBR) numerical integration is required. As a result, calculating the entropy flux is straightforward but laborious. Furthermore, from an analytical perspective the entropy of NBR is not well understood. Thermodynamic texts are often misleading because they state that the entropy flux of 'heat' transfer is the ratio of the energy flux to the local temperature (q/T) with no restriction for TR. For example see the system analysis of Moran and Shapiro ([2], p. 220 and 230), Reynolds and Perkins ([3], p. 223), and McGovern ([4], p. 177).

1.2 Objectives and Scope

The objectives of this work are to (1) improve the understanding and to simplify the calculation of the entropy of non-blackbody thermal radiation (NBR), and with this knowledge (2) to review the work of Stephens and Obrien [5] on the total entropy production rate of Earth based on satellite measurements. Processes such as scattering are not considered here.

This research can help us to better model, analyze, design, and optimize systems where thermal radiation is important. It can also help in analyzing the accuracy of assumptions and simplifications made in thermal radiation entropy calculations. The following are three examples of situations in which this research could play an important role:

(1) Heat transfer including TR: In thermodynamic analysis the entropy of TR is often taken as that of conduction or convection. In doing so the entropy production within the material system is incorrectly calculated (section 4.6).

(2) Global Climate Modeling: The majority of current Global Climate Models (GCM's) use the principles of energy, momentum, and mass conservation, but typically do not utilize fully the insights available via thermodynamic analysis. Specifically they do not incorporate the second law of thermodynamics, and the principle of entropy non-conservation [5]. An improved understanding of the entropy of non-blackbody thermal radiation will support the development of improved climate modeling.

(3) Entropy Production Rate of the Earth System: Stephens and Obrien [5] have estimated the total entropy production of the Earth based on satellite measurements of the radiation field at the outer atmosphere. They simplified their analysis by approximating the radiation as isotropic with a black body spectrum over relatively large space and time intervals. It is difficult to analyze the accuracy of the simplifications in their calculations without having a good understanding of the entropy of TR.

CHAPTER 2 THE FUNDAMENTAL EXPRESSIONS FOR THE ENERGY AND ENTROPY OF ELECTROMAGNETIC RADIATION

2.1 Origin of Planck's Blackbody Spectral Radiance Formulas

Before the 20th century scientists could not explain the observed blackbody (BB) emission spectrum of "heat" radiation. Objects, regardless of their physical or chemical character, were observed to begin glowing "red hot" at the same temperature. The radiation emitted was continuous, rather than in bands or lines, and was determined completely by one parameter, the temperature T. At the time, the frequency (10^{12} to 10^{15} hz) of heat radiation tested the limits of physical measurements.

At the turn of the century, Maxwell introduced the general electromagnetic equations describing the current oscillations in wires. He stated that the frequency of the current oscillations was equal to that of the electromagnetic waves generated, and the electromagnetic waves behaved in every way like light. This lead to the understanding that light was a type of electromagnetic wave created by extremely high frequency electric oscillators in matter. The success of Maxwell's theory motivated scientists to apply it to the long standing puzzle of explaining the blackbody radiation (BR) spectrum emitted by a "glowing" solid.

Wien's exponential law was as far as one could get using Maxwell's equations and thermodynamics. This law was loosely based on Maxwell's velocity distribution for gas molecules and agreed very well with experimental results at high frequency. This was because Wien's law actually stated the limiting form

$$K_v \propto \upsilon^3 e^{\frac{-B\upsilon}{T}} \tag{2.1}$$

of the BB formula for high frequency where B is a constant later found equal to h/k. When Max Planck learnt that the other limiting form of the BB formula at low frequencies

was $K_\nu \propto \nu^2 T$, he used mathematical interpolation between the two limiting forms to obtain the blackbody (BB) spectral energy radiance formula [1]

$$K_\upsilon(\upsilon,T) = \frac{ph\upsilon^3}{c^2}\frac{1}{e^{\frac{h\upsilon}{kT}}-1} \tag{2.2}$$

where:

K_ν = Spectral energy radiance (J/m^2• sr)
ν = frequency (s^{-1})
T = thermodynamic temperature of the emitting body (K)
p : represents the state of polarization of the radiation
h = Planck's constant = (6.626)10^{-34} J • s
c = the speed of light = (2.9979)10^8 m/s
k = Boltzman's constant = (1.38)10^{-23} J/K

Planck then proceeded to explain his results from an equilibrium statistical thermodynamics perspective. The thermally agitated resonators have a distribution of vibrational frequencies. To establish agreement with experiment Planck postulated that the vibrational energy of each oscillator in a solid was confined to discrete energy levels (quantized)

$$E_{vib} = n h \nu \tag{2.3}$$

where n is a positive integer, h is Planck's constant, and ν is the vibrational frequency. Note that it was later realized that the vibrational energy of any system (pendulum, springs, complex systems, etc.) is quantized but for most systems the frequency is such that the smallest quanta of vibrational energy ($h\nu$) is too small to observe or measure. Planck further postulated that the radiation emitted from a resonator has energy $h\nu$.

As a result, Planck arrived at the monochromatic entropy radiance L_ν formula [1] (p. 169) :

$$L_\upsilon(\upsilon,K_\upsilon) = \frac{pk\upsilon^2}{c^2}\left\{\left(1+\frac{c^2K_\upsilon}{ph\upsilon^3}\right)\ln\left[1+\frac{c^2K_\upsilon}{ph\upsilon^3}\right]-\left(\frac{c^2K_\upsilon}{ph\upsilon^3}\right)\ln\left[\frac{c^2K_\upsilon}{ph\upsilon^3}\right]\right\} \tag{2.4}$$

The K_ν formula (2.2) could then be derived using the definition of temperature (section C.1). The monochromatic entropy flux L_ν is dependent on the energy flux K_ν and the frequency ν only. Monochromatic radiation is referred to by a single frequency but exists in a finite frequency interval ([1], p. 16). As a result, radiation with an arbitrary spectrum is a superposition of monochromatic rays that do not interact with each other. The L_ν spectrum of arbitrary thermal radiation is found by substituting measured or estimated K_ν data into (2.4), and the entropy radiance L is calculated by integration of L_ν over frequency ([1], p. 87 and 93). For BR the L_ν entropy spectrum is found by substituting equation (2.2) into (2.4).

Recently, Landsberg and Tonge [6] used a non-equilibrium statistical mechanics approach to obtain the same result as Planck. They concluded* "This result, usually obtained from equilibrium statistical mechanics, is therefore of wider significance and represents a non-equilibrium entropy." Non-equilibrium radiation is thermal radiation (TR) that does not have a blackbody (BB) spectrum (section C.3).

* Two assumptions were specified for this result to be exact: (1) the probabilities $p_j(N_j)$ are independent in the probability sense where $p_j(N_j)$ is the probability of finding N_j bosons in quantum state j whatever the occupation number of the other quantum states, and (2) the probability of an additional particle occupying a state j is independent of the number already in that state.

2.2 Monochromatic Radiation (MR)

Planck showed that the laws derived for the energy and entropy radiance of BR can be applied to monochromatic radiation and thus to radiation with any arbitrary spectrum whatsoever. This can be done if the temperature T_ν (section 2.2.1) is interpreted as the temperature of a hypothetical blackbody that would radiate the same spectral energy radiance K_ν at the frequency ν. Thus we have:

$$\frac{1}{T_\nu} \equiv \frac{dL_\upsilon}{dK_\upsilon} \qquad \text{and} \qquad K_\upsilon(\upsilon,T) = \frac{ph\upsilon^3}{c^2}\frac{1}{e^{\frac{h\upsilon}{kT_\nu}}-1} \tag{2.5}$$

For BR T_ν is independent of frequency, $T_\nu = T$.

2.2.1 The Concept of Temperature for Monochromatic Radiation (MR)

Bejan [8] p. 469 provides a good presentation of the temperature of monochromatic radiation. Consider an isolated and evacuated enclosure initially devoid of radiation with perfectly reflecting walls (Figure 2-1). Body A is made of a material that only emits and absorbs monochromatic radiation of frequency ν_A, and body B is a blackbody.

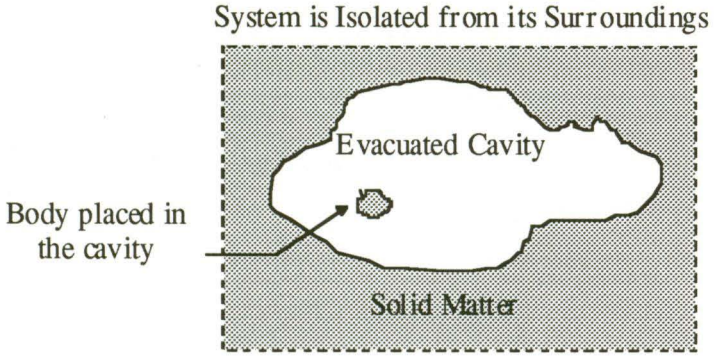

Figure 2-1: An evacuated cavity in an isolated solid.

When body A or body B is placed in the enclosure an equilibrium state will be established after a sufficiently long time. From the zeroth law the temperature of the body is measurable and equal to the temperature of the radiation in the enclosure. If body A is placed in the cavity then the equilibrium state will be monochromatic radiation at some

temperature T_A. If body B is placed in the cavity then the equilibrium state will be BR at some temperature T_B .

If instead both body A and B are placed in the cavity we would again have BR when equilibrium was reached. Bejan states that at equilibrium we will have the same temperature for bodies A and B which means "that A and B will be in equilibrium, and that the temperature of the monochromatic radiation with which A is in equilibrium with will be the same as the temperature of the BR sustained by body B. The monochromatic radiation is, therefore, the same as that sample of photons that occupy the narrow frequency band (ν_A) to ($\nu_A + d\nu_A$) in the frequency diverse population of photons that make up the BR of the same temperature". And note that since the choice of frequency is arbitrary, the BR spectrum temperature is independent of frequency and can therefore be defined for the spectrum itself.

Thus, it is correct to speak of the temperature of monochromatic radiation: this is the temperature of a black body that would emit radiation at that frequency and spectral energy radiance (K_ν). Planck's [1] spectral energy and entropy radiance equations are applicable to monochromatic radiation. Thus, the entropy radiance spectrum for arbitrary non-blackbody thermal radiation (NBR) can be determined and the energy and entropy radiance can be calculated using numerical integration.

CHAPTER 3 THE ENTROPY FLUX OF THERMAL RADIATION (TR)

The character of thermal radiation (TR) emitted from a solid depends on the nature of the emitting material and its temperature. Some materials can be approximated as blackbody (BB). This means that the material absorbs all incident radiation and emits the maximum possible energy for a given temperature, according to Planck's formula (2.2). Other materials can be approximated as gray. A Gray material absorbs a fraction (ε) of the incident radiation at each frequency and emits the same fraction (ε) of the radiation emitted by a BB. On the other hand, some materials may have a unique emission spectrum that cannot be adequately modeled as BB or graybody.

3.1 Blackbody Radiation (BR)

The energy radiance K (in W/m^2•sr) of TR is calculated by integrating the spectral energy radiance K_ν (in J/m^2•sr) spectrum over frequency. In simple terms the radiance is the area under the spectral radiance spectrum, see section A.1. For BR a simple analytical solution results

$$K_B = \frac{\sigma}{\pi} T^4 \tag{3.1}$$

where σ is the Steffan-Boltzman constant. This result can also be obtained from the analysis of enclosed equilibrium BR (section C.2). Similarly, the entropy radiance L (in W/ m^2•K•sr) is:

$$L_B = \frac{4}{3}\frac{\sigma}{\pi} T^3 \tag{3.2}$$

The energy irradiance H (W/m^2) is the integration of the energy radiance K over solid angle:

$$H = \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta \; K \, d\theta \tag{3.3}$$

For the BR model the radiation is isotropic so K can be removed from the integrand. Thus the energy irradiance H for BR is:

$$H_B = K_B \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta \, d\theta = \pi K_B = \sigma T^4 \tag{3.4}$$

Similarly the entropy irradiance J (W/m^2•K) is:

$$J_B = \pi L_B = \frac{4}{3}\sigma T^3 \tag{3.5}$$

For further discussion on the entropy of BR see Bejan [8].

3.2 Gray Radiation (GR)

By definition the spectral energy radiance and the energy radiance for GR* is:

$$K_{\nu G} = \varepsilon K_{\nu BR} \qquad \text{and} \qquad K_G = \varepsilon \frac{\sigma}{\pi} T^4 \tag{3.6}$$

The entropy is not as easily calculated** because L_ν is not a linear function of K_ν. By substituting equation (3.6) into equation (2.4) and integrating over frequency we find that the entropy radiance of GR is

$$L_G = \frac{2k^4}{c^2h^3} T^3 \int_0^\infty x^2 \left\{ \left(1 + \frac{\varepsilon}{e^x - 1}\right) \ln\left(1 + \frac{\varepsilon}{e^x - 1}\right) - \left(\frac{\varepsilon}{e^x - 1}\right) \ln\left(\frac{\varepsilon}{e^x - 1}\right) \right\} dx \tag{3.7}$$

where $x = h\nu/kT$. The definite integral in equation (3.7) is a function of ε only named $I(\varepsilon)$ here but first recognized by Landsberg and Tonge [7] as $\varepsilon X(\varepsilon) 4\pi^4/45$. Thus, we have

$$L_G = \frac{45}{4\pi^4} I(\varepsilon) \; \frac{4}{3}\frac{\sigma}{\pi} T^3 = \frac{45}{4\pi^4} I(\varepsilon) \; L_B = \varepsilon X(\varepsilon) L_B \tag{3.8}$$

The integral $I(\varepsilon)$ has not been solved in closed form, but Stephens and Obrien [5] presented an infinite series solution

$$I_s(\varepsilon) = \varepsilon\left(\frac{4\pi^4}{45} - 2\alpha\right) - 2\varepsilon \ln(\varepsilon) - 2\varepsilon \sum_{n=1}^{\infty} \frac{\ln\varepsilon + \sum_{i=1}^{n} \frac{(1-\varepsilon)^i}{i}}{(n+1)^3} + 2\sum_{n=1}^{\infty} \frac{1-(1-\varepsilon)^n}{n^4} \tag{3.9}$$

and Landsberg and Tonge [7] presented the approximate limiting solution for $\varepsilon < 0.10$:

$$X(\varepsilon) \approx 0.9652 - 0.2777 \ln(\varepsilon) + 0.0511(\varepsilon) \tag{3.10}$$

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* Note that Landsberg and Tonge [7] refer to gray radiation (GR) as diluted blackbody radiation (DBR).

** Petela [9] stated that $L_G = \varepsilon L_B$ for the same emission T.

CHAPTER 4 THE DEVELOPMENT OF SIMPLE CLOSED FORM EXPRESSIONS FOR THE ENTROPY OF NON-BLACKBODY RADIATION (NBR)

4.1 Approximations for the Entropy of Gray Radiation (GR)

The entropy of GR is a cubic function of the emission temperature (3.8) where the integral $I(\varepsilon)$ can be numerically calculated given the emissivity (ε). However, attempts at finding a closed-form solution for $I(\varepsilon)$ suggest using the approximation

$$I(\varepsilon) \approx \varepsilon\left\{\frac{4\pi^4}{45} - m \ln \varepsilon \right\} \tag{4.1}$$

where m is optimized for a specific emissivity range, $I(1)$ gives $L_G=L_B$, and $I(0)$ gives $L_G=0$. Thus, we have from equation (3.8):

$$L_G \approx \varepsilon\left\{1 - m\frac{45}{4\pi^4}\ln(\varepsilon)\right\}\frac{4}{3}\frac{\sigma}{\pi}T^3 = \varepsilon\left\{1 - m\frac{45}{4\pi^4}\ln(\varepsilon)\right\}L_B \tag{4.2}$$

The integral $I(\varepsilon)$ was calculated numerically for two hundred emissivity values over the range $0.005 \le \varepsilon \le 1$, in equally spaced steps of 0.005. Using this numerical $I(\varepsilon)$ data the corresponding $m(\varepsilon)$ data is calculated. By finding the "best" fit to the $m(\varepsilon)$ data we obtain accurate approximations for the entropy of GR. The percentage error caused by using (4.2) is calculated as a function of emissivity. Best fit refers to the solution that results in the lowest maximum percent error in $I(\varepsilon)$ over the specified emissivity range. If m is approximated as a constant the resulting expressions are within 0.8% of the numerical integration result over the emissivity range $0.005 \le \varepsilon \le 1$ (Table 4-1).

Table 4-1: Accuracy of the Approximation for the Entropy of GR (4.2) with: $m = C_1$ and $m=C_2 - C_3(\varepsilon)$.

Emissivity Range	C_1	Max. % error	C_2	C_3	Max.% error
.005 to.200	2.319	0.72	2.336	0.260	0.33
0.005 to 1.0	2.317	0.77	2.336	0.260	0.33
0.010 to 1.0	2.310	0.71	2.328	0.200	0.33
0.050 to 1.0	2.285	0.49	2.311	0.175	0.16
0.200 to 1.0	2.319	0.23	2.292	0.150	0.03

The accuracy of the approximation is increased if m is approximated as a linear or higher order function of emissivity. Table 4-1 shows the maximum percent error in the entropy calculation for various emissivity ranges, for both $m = C_1$ and $m = C_2 - C_3(\varepsilon)$. Note that the accuracy of the approximation is strongly dependent on the lower limit of the emissivity range.

Figure 4-1 shows the numerical m data and an example approximation for the emissivity range $0.050 \leq \varepsilon$; that is $m(\varepsilon) = -0.175\varepsilon + 2.311$, the fourth entry in Table 4-1.

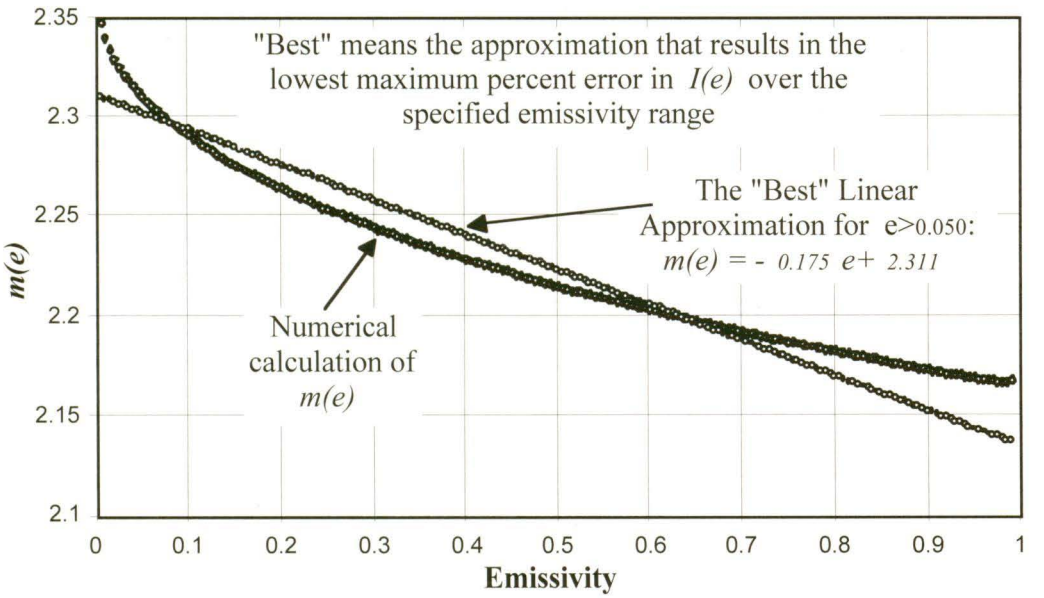

Figure 4-1: The function m(ε) for the entropy of gray radiation in eqn. (4.1). Note that *e* is sometimes used to denote emissivity (ε) in some figures.

Figure 4-2 shows that the approximation is very accurate. Specifically, it is within 0.16% over the emissivity range. Note that on the graph the $I(\varepsilon)$ data and its approximation cannot be visibly distinguished from one another.

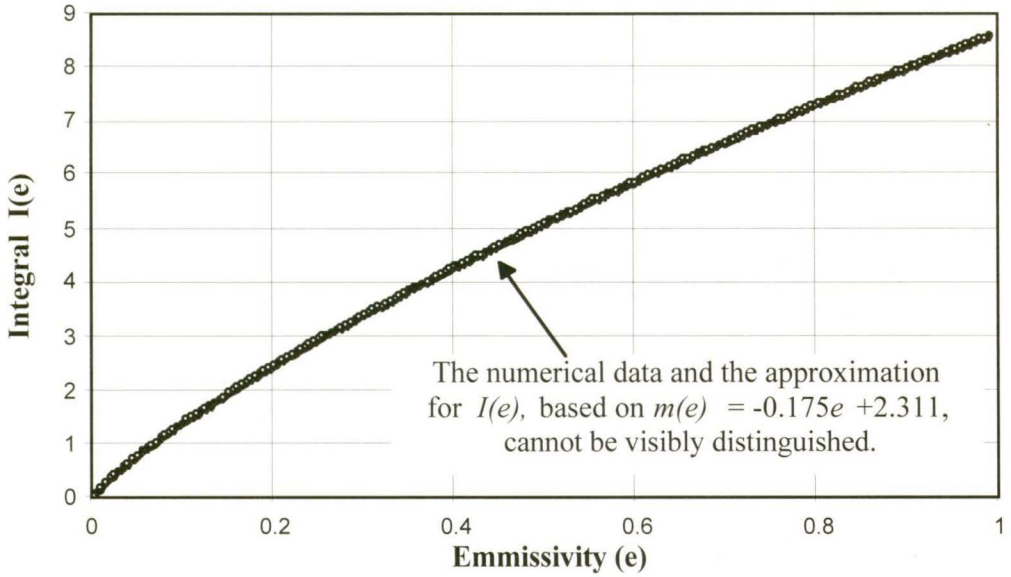

Figure 4-2: The function $I(\varepsilon)$ for the entropy of gray radiation in eqn. (4.1).

The K_G expression for GR (3.6) and the L_G expression (4.2) give the energy and entropy fluxes as a function of emission temperature. For example, if the emissivity of a surface is 1/2 then we have $K = (9.0241\text{x}10^{-9}\ \frac{W}{m^2 \cdot sr \cdot K^4}\ )T^4$ and $L \approx (1.4168\text{x}10^{-9}\ \frac{W}{m^2 \cdot sr \cdot K^4}\ )T^3$, where the entropy is within 0.03% using $m = 2.292 - 0.075\varepsilon$ in equation (4.2).

4.2 Model for Materials with a Unique Emission Spectrum ($L=C_L T^3$ and $K=C_K T^4$)

It is common for materials to be modeled as gray by calculating the effective emissivity based on measured energy fluxes. The K_G (3.6) and the L_G expression (4.2) can then be used to estimate the entropy flux as a function of emission temperature. Similarly, we can do the same for materials with a unique energy emission spectrum that cannot be adequately modeled as BR or GR.

This is done by approximating the energy spectrum, as is done for the gray model, as having a fixed (1) polarization, and (2) shape and relative size with respect to BR over the temperature range of interest.

By definition of the shape of the energy spectrum in section C.5

$$\varphi(\hat{\upsilon}) \equiv \frac{K_\nu(\nu)}{K_\nu(\nu_{ch})} \tag{4.3}$$

the spectral energy radiance can be expressed as

$$K_\upsilon(\nu) = \varphi(\hat{\upsilon})\ K_\upsilon(\nu_{ch}) \tag{4.4}$$

From the definition of the relative size of the unique spectrum (NBR) with respect to the blackbody spectrum (BR) in section C.5

$$b = \frac{K_\upsilon(\upsilon_{ch})}{K_{\upsilon BR}(\upsilon_{ch})} \tag{\$.5}$$

we have:

$$K_\upsilon(\nu) = \varphi(\hat{\upsilon})\ b\ K_{\upsilon BR}(\nu_c) \tag{4.6}$$

The frequency of the characteristic location in the spectrum can be expressed as $\nu_{ch} = g_{ch}T$ (section C.4). Using equation 2.2 the BR spectral energy radiance $K_{\nu BR}(\nu_{ch})$ reduces to a constant times the temperature cubed:

$$K_\upsilon(\nu) = b\ \varphi(\hat{\upsilon}) \cdot K_{\upsilon,BR}(g_{ch}T) = \frac{phbg_{ch}^3}{c^2\left(e^{hg_{ch}/k}-1\right)} T^3 \varphi(\hat{\upsilon}) \tag{4.7}$$

The energy radiance is thus

$$K = \int_0^\infty K_\upsilon(\nu)\, d\nu = \frac{phbg_{ch}^3}{c^2\left(e^{hg_{ch}/k} - 1\right)} T^3 \int_0^\infty \varphi\left(\frac{\nu}{g_{ch}T}\right) d\nu \qquad \textbf{(4.8)}$$

and after changing variables

$$x = \frac{h\upsilon}{kT} \quad or \quad \upsilon = \frac{kTx}{h} \quad and \quad \hat{\upsilon} = \frac{kxd}{h} \qquad \textbf{(4.9)}$$

we have

$$K \propto T^4 \int_0^\infty \varphi(fx)\, dx \qquad \textbf{(4.10)}$$

where $f = k/hg_{ch}$. The definite integral is fixed for any spectrum with a shape and relative size that are independent of temperature. Then just as for BR and GR $K \propto T^4$ and it can be shown that $L \propto T^3$. By introducing constants of proportionality we have:

$$K = C_K T^4 \qquad \text{and} \qquad L = C_L T^3 \qquad \textbf{(4.11)}$$

Knowledge of the K_ν spectrum at a single temperature allows K and L to be calculated by numerical integration, and consequently C_K and C_L to be found. The above expressions can then be used to estimate the energy and entropy emissions over the temperature range of interest.

This result can be explained as follows. For a characteristic location in the spectrum the frequency $\nu \propto T$, $K_\nu \propto T^3$, and $L_\nu \propto T^2$. Thus, the energy radiance $K \propto T^4$ because it is the integration of K_ν over frequency. Similarly, the entropy radiance $L \propto T^3$ because it is the integration of L_ν over frequency.

This approach can also be used to determine the absorption or reflection fluxes at different temperatures. By Kirchoff's principle the absorptivity coefficient and emissivity are equal. With knowledge of the energy spectrum of the incident radiation we can determine the constants C_K and C_L for absorption and reflection. These constants are different from the emission constants and are unique to the combination of the surface material and incident radiation characteristics. For example see equation (5.3) for GR.

4.3 Entropy-to-Energy Radiance Ratios for Thermal Radiation

4.3.1 General considerations

The mathematical form of the spectral entropy radiance L_ν function provides us with a qualitative understanding of the entropy-to-energy ratios for thermal radiation. The L_ν function is concave and monotonically increasing function of K_ν (appendix B). Monotonically increasing means that the slope of entropy versus energy is positive and concave means that the slope is decreasing with increasing energy (the second derivative is negative). This is to be expected from stability requirements for a BR system in equilibrium with a material enclosure (section B.2). In other words, the slope of entropy versus energy is the inverse of temperature, the temperature is always positive, and thus the slope is as well (higher energy means higher entropy). Furthermore, as energy increases the temperature increases and thus the slope decreases.

To clearly see the functional dependence of L_ν on K_ν consider the dimensionless form of equation (2.4)

$$z_\nu = (1+y_\upsilon)\ln(1+y_\upsilon) - y_\upsilon \ln(y_\upsilon) \tag{4.12}$$

where the dimensionless spectral entropy and energy radiances are,

$$z_\nu = \frac{c^2}{pk\upsilon^2} L_\nu \qquad \text{and} \qquad y_\nu = \frac{c^2}{ph\upsilon^3} K_\nu \tag{4.13}$$

respectively.

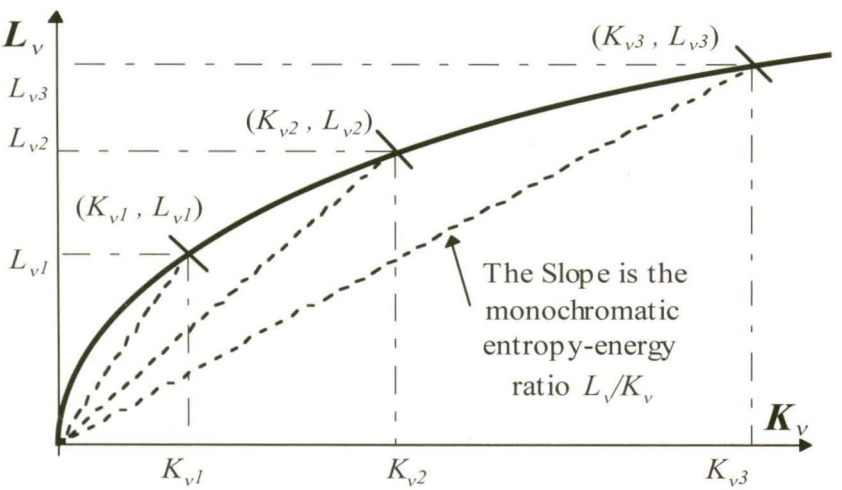

Fig. 4-3: Spectral entropy radiance L_ν versus energy radiance K_ν.

The derivative $dz_\nu/dy_\nu = \ln(1+1/y_\nu)$ is positive for all values of y_ν and the derivative $d^2z_\nu/dy^2_\nu = -1/(y^2_\nu + y_\nu)$ is negative for all values of y_ν. Thus, the function $z_\nu = z_\nu(y_\nu)$, and likewise the function $L_\nu = L_\nu(K_\nu)$, are monotonically increasing and concave. This means that the slope of $L_\nu = L_\nu(K_\nu)$ is always positive, but decreasing in magnitude, as shown in the figure 4-3. Note that for thermal radiation $0 < y_\nu < 1.4$.

As shown in figure 4-3, the entropy-to-energy ratio L_ν / K_ν is the slope of the line from the origin to the point (K_ν, L_ν) and the slope increases as K_ν decreases. Thus, the entropy-to-energy ratio L_ν / K_ν increases as K_ν decreases. For example, if K_ν is decreased by 1/2 then L_ν decreases by less than a half; $(L_\nu)_{new} > 1/2\ (L_\nu)_{old}$.

For a given material emission temperature a blackbody emits the maximum energy (K_ν) at each frequency. Thus the blackbody curve encloses all other thermal emission spectrums emitted from materials with the same temperature. This means L_ν / K_ν is lower at each frequency and thus L/K is a minimum for BR:

$$\left.\frac{L_{NBR}}{K_{NBR}}\right|_T > \left.\frac{L_{BR}}{K_{BR}}\right|_T \qquad \text{For the same emission temperature.} \qquad \textbf{(4.14)}$$

Figure 4-4 illustrates BR and NBR emitted from materials with the same T.

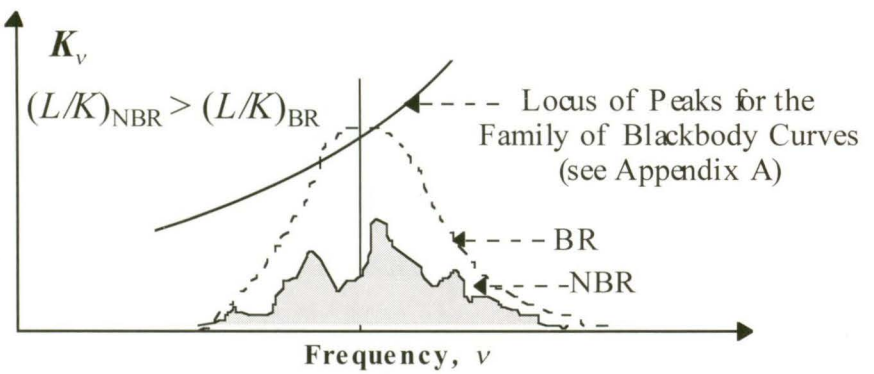

Fig. 4-4: Illustration of the energy spectrum $K_\nu(\nu)$ for BR and NBR with the same emission temperature.

For a given material emission temperature a BB emits the maximum possible energy and entropy but the minimum ratio of entropy-to-energy. This may seem to violate the second law of thermodynamics because we think of BR as having the maximum disorder or entropy. The equilibrium condition for an enclosed TR system is that of BR at the temperature of the enclosure (section C.3). Further, Planck [1] p.80 stated that "the normal spectral distribution of energy or that of BR is distinguished from all others by the fact that it has the maximum entropy of radiation". But this statement is referring to the spectral distribution of a fixed amount of energy rather than comparing the entropy-to-energy ratio of TR emission from materials with the same temperature (4.14).

The addition of a particle of real matter to a perfectly isolated* enclosed NBR system will cause it to spontaneously equilibriate to BR with the same energy, thereby producing entropy. In section 4.4 we show quantitatively that there is entropy produced during the transition of GR to BR. Thus, the entropy-to-energy radiance ratio of BR is greater than that of GR or other NBR with the same energy radiance K:

$$\left.\frac{L_{NBR}}{K_{NBR}}\right|_K < \left.\frac{L_{BR}}{K_{BR}}\right|_K \qquad \text{For the same } K. \qquad \textbf{(4.15)}$$

Following this argument, Figure 4-5 illustrates the redistribution of energy from an initial NBR spectrum at T_i to a final BR spectrum at T_f. Energy radiance K is unchanged while entropy radiance L increases.

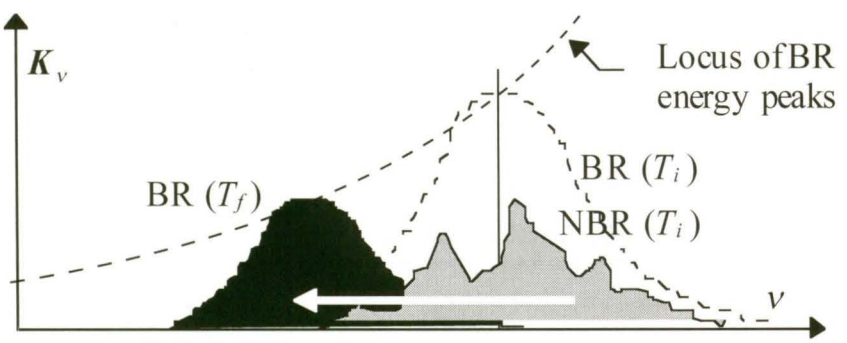

Fig. 4-5: Isolated transition of NBR to BR: K = cst. while L increases.

It is important to note that equation (4.14) is a comparison of TR emitted from material with the same temperature while equation (4.15) and figure 4-5 represent a spontaneous process that produces entropy.

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* See section C.3.1 regarding perfectly isolating enclosures.

4.3.2 The entropy-to-energy radiance ratio for gray radiation (GR)

In this section we will show quantitatively that the entropy-to-energy ratio of GR is greater than that of BR emitted from a material with the same temperature. Using equation 3.8 and $K_G = \varepsilon K_B$ the entropy-to-energy ratio for GR is

$$\frac{L_G}{K_G} = \frac{45}{4\pi^4}\frac{I(\varepsilon)}{\varepsilon}\frac{L_B}{K_B} \equiv C(\varepsilon)\frac{L_B}{K_B} \tag{4.16}$$

where $C(\varepsilon)$ is defined as the coefficient to L_B/K_B; where $L_B/K_B = \frac{4}{3}\frac{1}{T}$ from equation (3.1) and (3.2). By utilizing the approximate solution for the entropy of GR, equation (4.1), we can quantitatively find the ratio of entropy to energy:

$$C(\varepsilon) = \frac{45}{4\pi^4}\frac{I(\varepsilon)}{\varepsilon} = 1 - \frac{45}{4\pi^4} m \ln(\varepsilon) \tag{4.17}$$

The logarithm $ln\ (\varepsilon)$ is always negative because $0 \leq \varepsilon < 1$ and since m is positive the coefficient function $C(\varepsilon)$ is greater than one for all emissivities. That is, the entropy-to-energy ratio for GR is greater than that for BR at the same emission temperature, i.e.

$$\frac{L_G}{K_G} = C(\varepsilon)\frac{L_B}{K_B} \geq \frac{L_B}{K_B} \tag{4.18}$$

Figure 4-6 illustrates the functional dependence of $C(\varepsilon)$ on ε based on the approximation used previously; $m = 2.311\text{-}0.175\varepsilon$.

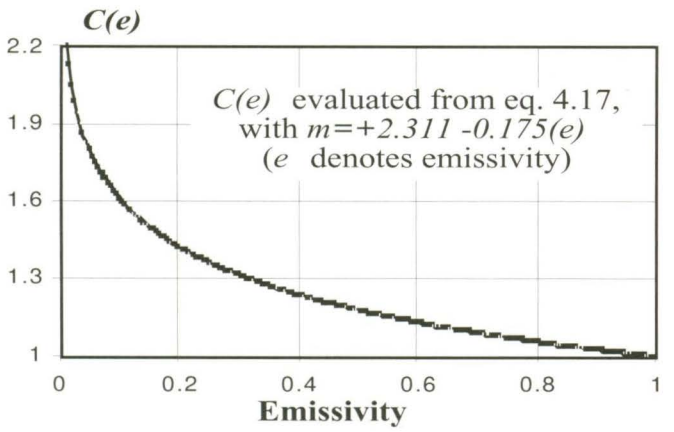

Fig. 4-6: Coefficient to *L/K* ratio in equation (4.16) for GR.

The entropy-to-energy ratio is 20% higher than that of BR for $\varepsilon = 0.5$ and 40% higher for $\varepsilon = 0.2$. Thus, the error introduced is large when the entropy of GR is taken as the emissivity times that of BR, $L_G = \varepsilon L_B$. Petela made this mistake in his paper which was first pointed out by Landsberg and Tonge [6].

However, the error is much less if the entropy of the GR is approximated as that of BR with the same energy radiance (section 4.4). For example the error is within 1% for $\varepsilon > 0.5$. This is also true for any NBR that has spectral emissivities greater than 1/2 for all frequencies.

4.4 The Entropy Radiance *L* of BR and GR with the Same Energy Radiance *K*

In this section we show that equation (4.15) can be numerically verified, as was done with equation (4.14) in section 4.3.2, using the approximate solution for the entropy of GR (4.2). Consider an isotropic GR system with an initial temperature of T_i that is enclosed by an isolated evacuated enclosure with perfectly reflecting internal walls. Upon the addition of a small particle of real matter the radiation will equilibriate to BR at some final temperature T_f. The system is isolated during the process so the internal energy is fixed.

BR at temperature T_i has a higher energy radiance than the original GR emitted from material with temperature T_i. Consequently, the GR must equilibriate to BR of a lower temperature $T_f < T_i$. The transition is spontaneous so entropy must be produced*. In the previous section the approximate solution for the entropy of GR resulted in $(L/K)_G > (L/K)_B$ for emission from materials with the same temperature. We will use this same approximation here to show that there is entropy produced when an isolated GR system equilibriates to BR.

The initial energy U_i is $U_i = aT_i^4 V(\varepsilon)$. Using eqn. (4.2), the geometric relationship for isotropic radiation $S = 4\pi VL/c$, and $a = 4\frac{\sigma}{c}$, we find that the initial entropy of the GR is:

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* First recognized by Planck ([1], p. 45) for NBR.

$$S_i = \frac{45}{4\pi^4}\,\frac{4}{3}aT_i^3V\;\;I(\varepsilon) \tag{4.19}$$

Since the initial and final energy are the same

$$U_f = aT_f^4V = aT_i^4V\;(\varepsilon) \tag{4.20}$$

and solving for T_f we have $T_f = \varepsilon^{1/4}T_i$. Thus, the final entropy is

$$S_f = \tfrac{4}{3}\,aT_f^3V = \tfrac{4}{3}\,aT_i^3V\;(\varepsilon)^{3/4} \tag{4.21}$$

and the entropy produced in the process is

$$\Delta S = S_f - S_i = \frac{4}{3}aT_i^3V\;\;p(\varepsilon) \tag{4.22}$$

where the function $p(\varepsilon)$ is defined as follows:

$$p(\varepsilon) = (\varepsilon)^{3/4} - \frac{45}{4\pi^4}I(\varepsilon) \tag{4.23}$$

The percent increase in the entropy during the process is given by:

$$100\%\frac{\Delta S}{S_i} = 100\%\frac{4\pi^4}{45}\frac{p(\varepsilon)}{I(\varepsilon)} = 100\%\;\frac{(\varepsilon)^{3/4} - \dfrac{45}{4\pi^4}I(\varepsilon)}{\dfrac{45}{4\pi^4}I(\varepsilon)} \tag{4.24}$$

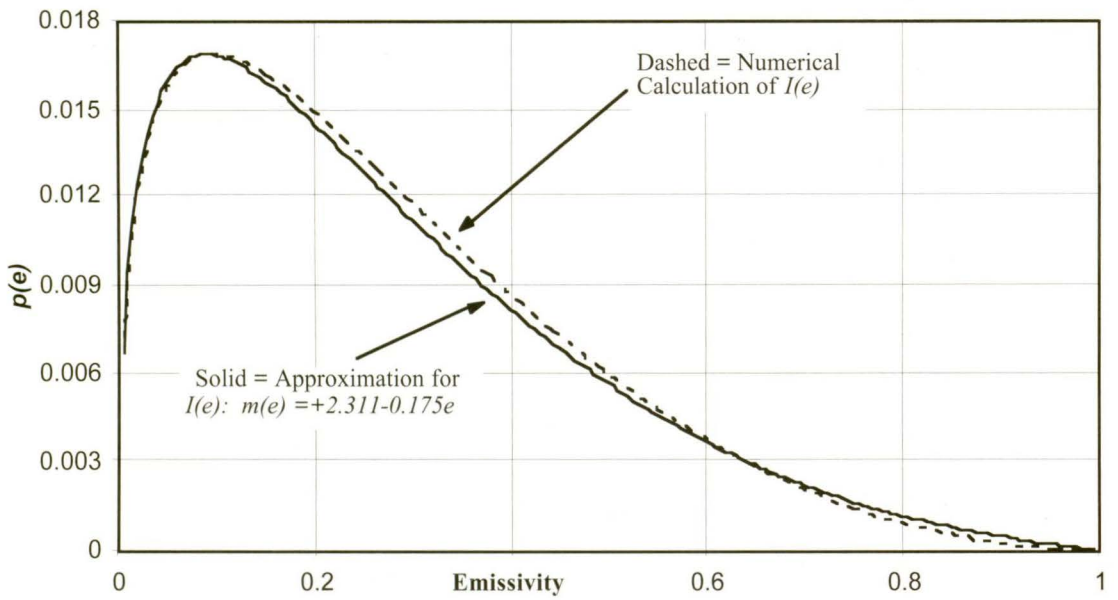

Fig. 4-7: Dependence on emissivity of the function *p(e)* in eqn. (4.23).

The dependence on emissivity ε is illustrated in Fig. 4-7 for $p(\varepsilon)$ and in Fig. 4-8 for the percent increase in entropy. Curves are shown in both figures for the cases where the integral $I(\varepsilon)$ is (1) numerically calculated, and (2) evaluated with the approximation $m = 2.311 - 0.175(\varepsilon)$. Figure 4-7 shows that the entropy produced is always positive and thus there is no violation of the second law.

Figure 4-8 shows that for GR with an emissivity greater than 1/2, the percent increase in entropy is very small, less than 1%. At $\varepsilon = 0.20$ the increase is about 5 % and at $\varepsilon = 0.10$ it is 10.5%. This means that for any NBR that has spectral emissivities greater than 1/2 over the whole spectrum the percent difference in entropy is within 1% as well. Thus, the error is usually relatively low in approximating the entropy of NBR as that of BR with the same energy radiance K. Stephens and Obrien ([5], p. 134) use this simplification when calculating the total entropy production rate of the Earth.

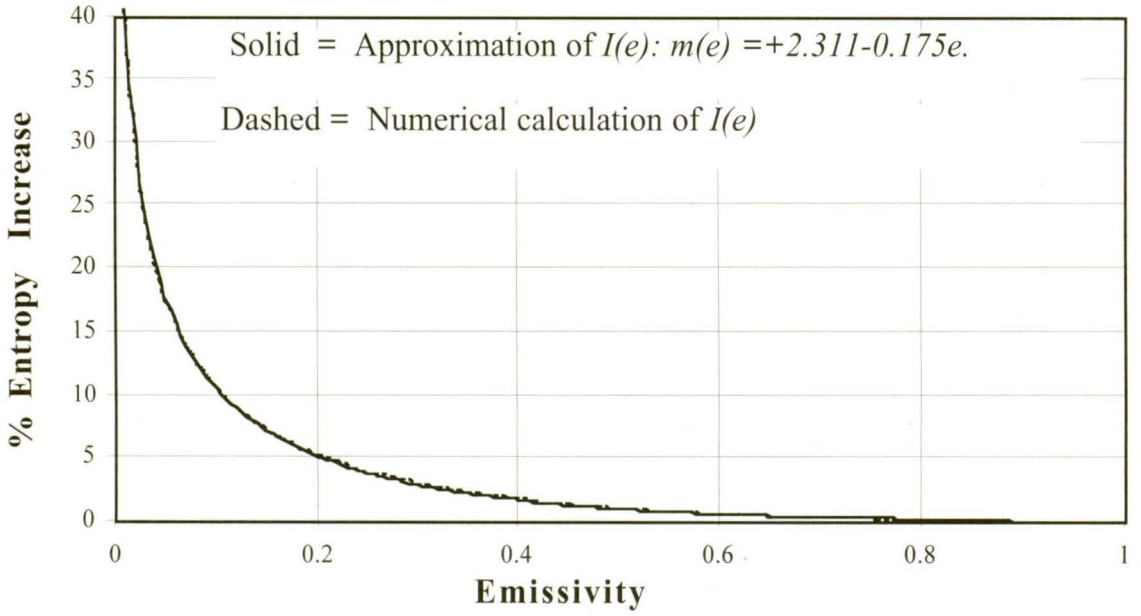

Fig. 4-8: Percent Increase in Entropy for an Isolated Transition of GR to BR (4.24).

4.5 The Variation of the Entropy-to-Energy Radiance Ratio *L/K* with Temperature

For BR, GR, and NBR described in section 4.2 the energy and entropy radiances are $K = C_K T^4$ and $L = C_L T^3$ where C_K and C_L are positive constants particular to each type of energy spectrum. By eliminating temperature we have

$$L = (C_L C_K^{-3/4}) K^{3/4} \tag{4.25}$$

The signs of the first and second derivatives with respect to K

$$\frac{dL}{dK} = \frac{3}{4}\frac{C_L}{C_K^{3/4}} K^{-1/4} > 0 \qquad \text{for all K} \tag{4.26}$$

and

$$\frac{d^2L}{dK^2} = -\frac{3}{16}\frac{C_L}{C_K^{3/4}} K^{-5/4} < 0 \qquad \text{for all K} \tag{4.27}$$

show that the entropy L is a monotonically increasing concave function of the energy K. Following the argument in section 4.3.1 for L_ν / K_ν the mathematical form of $L=L(K)$ implies that the entropy-to-energy ratio L/K increases as K and thus temperature T decreases. Figure 4-9 illustrates this result using BR and GR as examples.

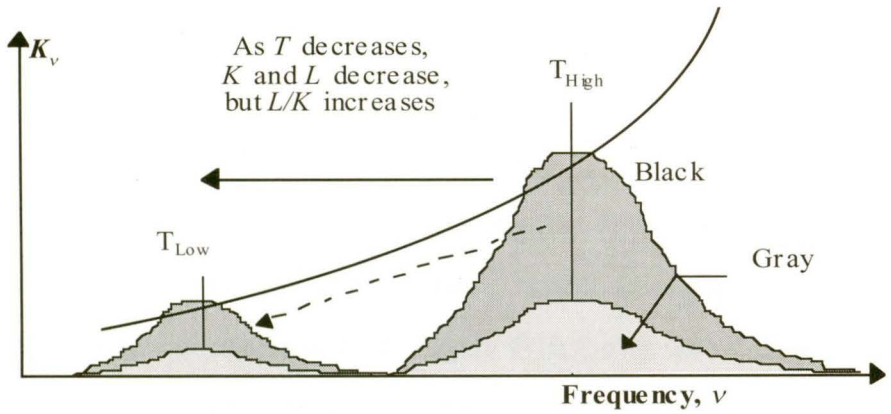

Figure 4-9: Entropy-to-Energy ratio *L/K* variation with temperature.

Note that although the BR and GR spectrums are mathematically smooth functions they appear rough in some figures because of word processing difficulties.

4.6 Comparison of the Entropy Flux for Thermal Radiation Emission and Heat Conduction

For heat conduction the entropy flux is the ratio of the energy flux and the local temperature ($\dot{S} = q/T$). For thermal radiation this relationship does not hold. Most thermodynamic texts are misleading in this regard because they state that the entropy flux of 'heat' transfer is q/T without any restriction for TR. For example see the open system analysis in Moran and Shapiro ([2], p. 220 and 230); Reynolds and Perkins ([3], p. 223); and McGovern ([4], p. 177).

To compare the entropy of TR to that of heat conduction we can express the entropy-to-energy ratio in terms of the emission temperature T. For BR, GR, and other NBR emission described in section 4.2 that is isotropic we have*

$$J_{Emi} = n\left(\frac{H_{Emi}}{T}\right) \tag{4.28}$$

where n is dependent on the character of the TR and the subscript Emi denotes emission. For BR $n = 4/3$ and for NBR $n > 4/3$. For GR with $\varepsilon > 0.05$ the upper bound for n is about 2.5 ($n < 2.5$), see figure 4-6. Researchers^ have stated that BR is not heat because $\dot{s} \neq q/T$, but there is no indication in the literature that the ratio of entropy-to-energy for NBR is higher than that for BR with the same emission temperature.

The error introduced can be large when the entropy flux of thermal radiation is incorrectly assumed to be q/T. For example consider heat transfer from the external surface of an energy conversion device at steady state. Figure 4-10 shows both cases where the device is hot and when it is cold relative to its immediate surroundings. The boundary of the system encloses the device and is located immediately adjacent to its outer surface. For simplicity the thermal conductivity of the material is large so that the temperature in the

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* Note that in general the entropy flux of the emitted and reflected TR cannot be calculated independently, see chapter 5.

^ For example see Beretta and Gyftopoulos [10].

interaction region is approximately uniform and entropy production due to heat conduction is negligible. Now consider an area on the surface of the device that is an opaque* solid and where the surroundings are in the gaseous state.

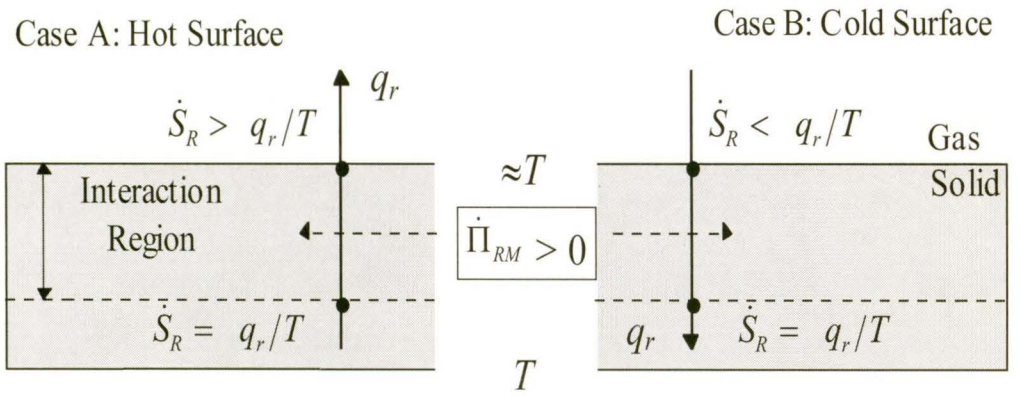

Fig. 4-10: Net thermal radiation entropy flux at a solid surface.

Both convection (q_c) and thermal radiation transfer (q_r) occur at the system boundary. Whenever** $q_r \neq 0$ there is entropy production due to radiation-matter interaction ($\dot{\Pi}_{RM}$) as determined by an entropy balance using Planck's spectral entropy radiance equation (2.4). This entropy production occurs in a thin layer of material at the surface. This layer, referred to here as the interaction region, is defined as the region of material that contains TR that has or will travel into/from the region exterior to the solid material. This distinction between exterior and interior is required because all atoms including those within a solid continuously emit thermal radiation.

In both hot and cold cases the entropy flux q_r/T occurs at the lower boundary of the interaction region. When the entropy flux of the TR is taken as q_r/T the entropy production $\dot{\Pi}_{RM}$ within the system is neglected. Thus, the irreversibility of the device is underestimated whenever q_r is a significant portion of the total q. Significant TR transfer

* Opaque to the particular incident thermal radiation.

is most likely to occur when there are gases involved; gas flow across the system boundary or a solid-gas interface at the system boundary.

As an example consider emission from a solid surface in the absence of incident radiation. Referring to equation (4.28), the thermal radiation entropy flux at the system boundary is $33\frac{1}{3}\%$ higher than q_r/T for BR and up to about 150% higher for NBR.

** Note that it is possible to have $\dot{\Pi}_{RM} > 0$ even when $q_r = 0$. This occurs when the net incoming and outgoing energy spectrums are not the same.

CHAPTER 5 ENTROPY BALANCE AT THE SURFACE OF A SOLID

The net entropy flux from a surface can be calculated by numerical integration over frequency, solid angle, and position. This is a laborious task because it requires knowledge of the K_ν spectrum in all propagation directions at each position on the surface. Alternatively we can estimate the entropy flux from a surface using the relationships discussed in sections 4.1 and 4.2 but we must use caution.

The radiation emitted from the solid depends on the temperature and the radiative characteristics of the material only, not on external conditions. The fraction of incident radiation absorbed by the surface is given by Kirchoff's principle: emissivity is equal to the absorptivity. This principle allows us to determine the absorbed energy spectrum and the net flux of energy is simply the difference between the absorbed and emitted fluxes.

In contrast, the net entropy flux cannot be calculated in this way. The absorbed entropy spectrum cannot be used to calculate the difference between the incident and reflected entropy. Furthermore, the emitted and reflected fluxes occupy the same directional hemisphere so their entropy flux cannot be calculated independently unless their K_ν energy spectrums do not overlap. For example consider a gray surface at temperature T with incident BR at 300 K. Table 5-1 gives the percent error in the *net* entropy flux calculation if the reflected and emitted radiation are treated independently.

Table 5-1: Percent Error in the net entropy flux calculation due to overlap of emitted and reflected energy spectrums: A gray surface with incident BR at $T = 300$ K.

Emission Temperature (K)	**Emissivity** 0.2	0.5	0.8
400	26.3 %	10.3 %	3.14 %
800	5.74 %	2.08 %	0.61 %
1200	2.11 %	0.73 %	0.21 %

Thus, to evaluate the net entropy flux we must consider the following: (a) the outgoing entropy flux is that of the combined emitted and reflected energy spectrums, (b) the incoming entropy flux is that of the incident radiation, and (c) the net flux is the difference between the outgoing and incoming radiation entropy fluxes. To apply this method we need to specify or estimate (a) the radiative characteristics of the material, (b) the temperature of the material, and (c) the characteristics of the incident radiation.

5.1 Net Entropy Flux from a Surface when the Incident Radiation is BR at T_i

Consider as an example the situation shown in Figure 5-1 where:

1) The incoming radiation is BR at T_i.
2) The surface has a temperature T and has a unique emission spectrum.
3) The reflected and emitted energy spectrums do not overlap significantly.
4) All radiation considered is unpolarized (p=2) and isotropic over the appropriate hemisphere of directions.
5) The energy emission spectrum retains relative size and geometric similarity with temperature.

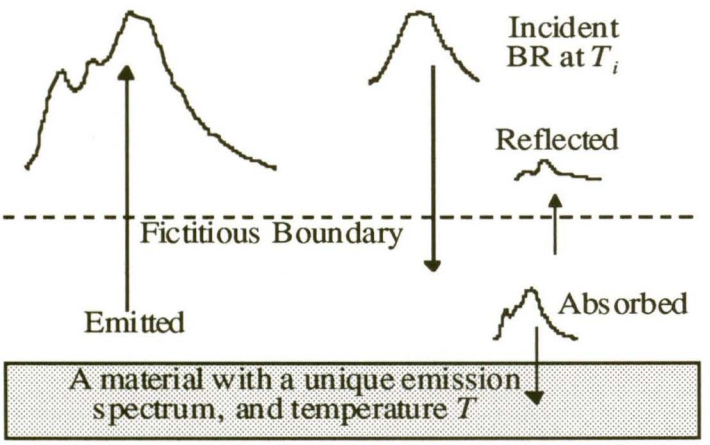

Fig. 5-1: Example of radiation energy balance at a solid surface.

The energy and entropy fluxes are evaluated at a fictitious boundary. The boundary can be arbitrarily close to the surface but it should not pass through any material of the surface. The energy and entropy fluxes of the emitted radiation are $H_{Emi} = \pi C_K T^4$ and

$J_{Emi} = \pi C_L T^3$, and for the incident radiation $H_{Inc} = \sigma T_i^4$ and $J_{Inc} = (4\sigma/3)\ T_i^3$. The portion of the incident BR that is absorbed is the same as the radiation that would be emitted from the arbitrary surface if it had the temperature T_i, that is $H_{Abs} = \pi C_K\ T_i^4$.

The energy spectrum of the reflected radiation has a different shape than the emitted and absorbed spectrums. But we can define a new constant C_L* such that the energy and entropy of the reflected radiation are $H_{Ref} = (\sigma - \pi C_K) T_i^4$ and $J_{Ref} = \pi\ (C_L^*)\ T_i^3$. Thus, the constant C_L is for the entropy of the emitted and absorbed energy spectrum shape, and the constant C_L* is for the reflected energy spectrum shape. Thus the net flux of entropy away from the surface is

$$J = J_{Emi} + J_{Ref} - J_{Inc} = \pi C_L T^3 - (\tfrac{4}{3}\sigma - \pi\, C_L^*) T_i^3 \qquad (5.1)$$

while the net energy flux away from the surface is:

$$H = H_{Emi} + H_{Abs} = \pi C_K (T^4 - T_i^4) \qquad (5.2)$$

Note that if the surface is a gray body $C_{KG} = \sigma\varepsilon/\pi$, and the constants C_L and C_L* can be estimated as

$$C_{LG} \approx \frac{4\sigma}{3\pi}(\varepsilon)\left[1 - \frac{45}{4\pi^4} m \ln\varepsilon\right] \quad \text{and} \quad C_{LG}^* \approx \frac{4\sigma}{3\pi}(1-\varepsilon)\left[1 - \frac{45}{4\pi^4} m \ln(1-\varepsilon)\right] \qquad (5.3)$$

CHAPTER 6 SUMMARY OF RESULTS

6.1 On the Entropy of Thermal Radiation (TR)

The entropy flux of any TR can be calculated by numerical integration of Planck's spectral entropy radiance (2.4) over frequency and solid angle. The exclusive use of numerical integration is straightforward but laborious and does not lend itself to understanding the entropy of TR. In this thesis some basic characteristics of TR were uncovered and expressions were presented that make the calculation of the entropy of TR easier.

The entropy of gray radiation (GR) can be approximated by (section 4.1)

$$L_G \approx \varepsilon\left\{1 - m\frac{45}{4\pi^4}\ln(\varepsilon)\right\}\frac{4}{3}\frac{\sigma}{\pi}T^3 = \varepsilon\left\{1 - m\frac{45}{4\pi^4}\ln(\varepsilon)\right\}L_B \qquad \textbf{(4.2)}$$

where m is a constant that is optimized for each emissivity range (tables 4-1 and 4-2). This approximation is within 0.8% of the numerical integration result when m is a constant (table 4-1) for any emissivity range where the lower limit is greater than 0.005.

For any TR that retains geometric similarity and relative size with respect to BR the energy and entropy are quadric and cubic functions of the emission temperature

$$K = C_K T^4 \qquad \text{and} \qquad L = C_L T^3 \qquad \textbf{(4.11)}$$

where C_K and C_L are constants dependent on the spectrum of the TR (section 4.2). For this type of NBR, GR, and BR the entropy-to-energy ratio L/K increases as temperature T decreases and thus K decreases (section 4.5 and figure 4-9):

$$\frac{L}{K} \text{ increases as } T \text{ decreases and also } K \text{ decreases because } K \propto T^4$$

As a result of the mathematical form of the L_ν function (appendix B), the monochromatic entropy-to-energy ratio (L_ν / K_ν) increases as the spectral energy radiance (K_ν) decreases (section 4.3.1 and figure 4-3):

$$\frac{L_\nu}{K_\upsilon} \text{ increases as } K_\nu \text{ decreases}$$

This implies that the entropy-to-energy radiance ratio for BR is a minimum for any TR at the same emission temperature (figure 4-4):

$$\left.\frac{L_{NBR}}{K_{NBR}}\right|_T > \left.\frac{L_{BR}}{K_{BR}}\right|_T \qquad \text{For the same emission temperature.} \qquad \textbf{(4.14)}$$

This is a surprising result because we think of BR as "equilibrium" radiation with the maximum disorder and entropy. However, equation (4.14) is a comparison of TR emitted from materials with the same temperature while it is true that BR has the highest entropy of TR with the same energy radiance. Thus, the spontaneous transition of an enclosed NBR system to BR produces entropy and there is no violation of the second law.

Consider GR as an example of NBR. Using the approximation for the entropy of GR (equation 4.1), the entropy-to-energy radiance ratio is quantitatively given by (section 4.3.2 and figure 4-6):

$$\frac{L_G}{K_G} = \frac{45}{4\pi^4}\frac{I(\varepsilon)}{\varepsilon}\frac{L_B}{K_B} = \left[1 - \frac{45}{4\pi^4}\, m\, \ln(\varepsilon)\right]\frac{4}{3}\frac{1}{T} \qquad \textbf{(4.16)}$$

The entropy-to-energy ratio is 20% higher than that for BR for $\varepsilon = 0.5$ and 40% higher for $\varepsilon = 0.2$. Thus, the error introduced is large when the entropy of GR is taken as the emissivity times that of BR. In his paper Petela made this mistake which was first pointed out by Landsberg and Tonge [6].

Many thermodynamic texts can be misleading with regard to TR entropy because they state that the entropy flux of 'heat' transfer is q/T without any restriction for TR (section 4.6). For example see the system analysis of Moran and Shapiro ([2], p. 220 and 230), Reynolds and Perkins ([3], p. 223), and McGovern ([4], p. 177). If the entropy flux of TR transfer at a solid surface is taken as q/T the irreversibility of the device is underestimated whenever q_r is a significant portion of the total q (figure 4-10). This is

most likely to occur when there are gases involved; gas flow across the system boundary or a solid-gas interface.

To compare the entropy of TR to that of heat conduction we can express the entropy-to-energy ratio in terms of the emission temperature T. For BR, GR, and other NBR emission described in section 4.2 that is isotropic we have*:

$$J_{Emi} = n\left(\frac{H_{Emi}}{T}\right) \tag{4.28}$$

For BR $n = 4/3$ and for NBR $n > 4/3$. For GR with $\varepsilon > 0.05$ the upper bound for n is about 2.5 ($n < 2.5$), see figure 4-6. In percentages the TR entropy flux is $33\frac{1}{3}\%$ higher than q_r/T for BR and up to about 150% higher for NBR. Some researchers have concluded that BR exchange is not heat [9] because $\dot{s} \neq q/T$, but there is no indication in the literature that the ratio of entropy to energy for NBR is higher than that for BR with the same emission temperature.

An isolated NBR system has a spontaneous tendency to equilibriate to BR. As Planck expected, this means that BR has a higher entropy than NBR with the same energy, or in other words the entropy-to-energy ratio of BR is a maximum for any TR with the same energy (section 4.4 and figure 4-5):

$$\left.\frac{L_{NBR}}{K_{NBR}}\right|_K < \left.\frac{L_{BR}}{K_{BR}}\right|_K \qquad \text{for the same energy } K \tag{4.15}$$

This result has been shown quantitatively for GR and is consistent with (1) equation (4.14) for the entropy-to-energy ratio at the same temperature, and (2) the second law of thermodynamics. For GR the percent increase in entropy during a fixed energy transition to BR is given by (figure 4-7):

$$\text{Percent increase in entropy} = 100\% \frac{(\varepsilon)^{3/4} - \frac{45}{4\pi^4} I(\varepsilon)}{\frac{45}{4\pi^4} I(\varepsilon)} \tag{4.24}$$

---

* Note that in general the entropy flux of the reflected and emitted TR cannot be calculated independently.

For emissivity values greater than 1/2 the percent increase in entropy is very small, less than 1%. Thus, the error can be relatively low in approximating the entropy of GR or NBR as that of BR with the same energy. Stephens and Obrien ([5], p. 134) used this simplification when calculating the total entropy production rate of the Earth.

6.2 On the Entropy Balance at a Solid Surface

The fraction of incident TR that is absorbed by a surface can be determined using Kirchoff's law if the radiative emission characteristics of the material are known. The net energy flux from the surface is simply the difference between the absorbed and emitted energy fluxes. However, the net entropy flux cannot be calculated in this way. Instead, the outgoing entropy flux is calculated from the combined emitted and reflected energy spectrum. The net entropy flux is the difference between this combined emitted and reflected entropy flux and the incident flux. This method of calculation is necessary for TR because the spectral entropy radiance is not a linear function of the energy.

The net fluxes from a material depend on the TR that is incident. For incident BR we have presented net energy and entropy from a surface for blackbody, graybody, and NBR materials modeled in section 4.2.

6.3 New Contributions in Appendix B on Stability Requirements

The mathematical form of the spectral entropy radiance (L_ν) function presented by Planck [1] is in agreement with stability requirements for equilibrium between TR and a material enclosure. This directly implies that the entropy-to-energy ratio of BR is a minimum for all TR at the same emission temperature (section 4.3.1).

Other material covered in appendix B that we believe is a new contribution is the dimensionless plot of the spectral entropy radiance versus frequency for spectral energy radiance fixed.

6.4 New Contributions in Appendix C On the Family of BB Curves

Although TR does not interact with itself the equilibrium BR condition inside an isothermal cavity is established because (1) emission of radiation by the enclosure is dependent on its temperature only while (2) absorption depends on the character of the incident radiation as well.

At equilibrium the radiative character of the enclosure dictates the equal and opposite energy and entropy exchange rates between the enclosure and the radiation system. The exchange rates are maximum for BB material, but the ratio of entropy-to-energy rate is a minimum. Also the character of the material enclosure dictates how quickly equilibrium is established; with BB materials equilibrium is established the fastest, almost instantaneously because TR travels at the speed of light. In appendix C we also discuss the concept of equilibrium with regard to perfectly reflecting enclosures.

The frequency (C.23) and spectral energy radiance (C.24) of the BR entropy peak are linear and cubic functions of the emission temperature, respectively. Furthermore, from these relationships we arrive at the locus of energy and entropy peaks for BR (equations C.22 and C.25).

When considering spectrum overlap it is useful to define cutoff points for the BR energy spectrum because it asymptotically approaches zero at the high and low frequency sides of the spectrum (equation C.26). The high and low cutoff frequencies are proportional to the emission temperature. The proportionality constants depend on the cutoff limit; the fraction of the peak value at the cutoff points (table C-1).

The shape of any NBR energy spectrum can be non-dimensionalised with respect to BR at the same emission temperature (equation C.29). Assuming that the shape and relative size of the NBR is fixed within the temperature range of interest, this allows us to calculate the energy and entropy radiance as a function of emission temperature (section 4.2).

CHAPTER 7 THE ENTROPY PRODUCTION RATE OF EARTH: A PRELIMINARY DISCUSSION OF STEPHENS AND OBRIEN [5]

TR exchange is essentially the only form of energy and thus entropy transfer between the Earth and the rest of the universe ([15], p. 38,39). Thus, the total entropy production rate of the Earth is simply the difference between the entropy of incoming (sunlight) and outgoing (emitted and reflected) TR fluxes.

To obtain the actual instantaneous entropy production rate of Earth the energy radiance spectrum as a function of position and direction is required. However, in a practical measurement the radiation transfer has to be discretized over time, frequency, position, and direction. This simplification of the data collection introduces error into the analysis.

Stephens and Obrien [5] estimated the total entropy production rate of Earth based on satellite thermal radiation energy measurements. These measurements were carried out in the Earth Radiation Budget Experiment (ERBE) by satellites orbiting at the top of the atmosphere (TOA). Barkstrom [11] provides an overall description of the ERBE experiment. Stephens and Obrien found that the monthly entropy production of Earth is approximately constant at $(6.8)10^{14}$ W/K with an annual cycle variation of 1 to 2%. Also, they found that the entropy flux of TR emitted from the Earth system is much greater than that of reflected sunlight.

7.1 Sources of Error in the Entropy Production Rate of Earth Calculation

In the ERBE three satellites were used [11]; two were in sun-synchronous orbits and the other was at a 600 km altitude with an inclination of 57° and a westerly precession of 4.95°/day. The position at the TOA was discretized into a 2.5° grid of longitude and latitude. Error is introduced in the analysis due to (1) discretization, (2) incomplete data collection over the grid (orbital coverage at the TOA), and (3) the fact that the altitudes of the three satellites were not exactly the same.

The ERBE fluxes derived from irradiance data of the longwave (5 to 200 μm wavelengths) TR scanners were averaged over time. Stephens and Obrien used the monthly averages of daily averages for their entropy calculations. This averaging introduces error because the TR exchange changes with the time; time-of-day, time-of-month, weather conditions, etc.

The outgoing (longwave) TR fluxes are greatest in the direction normal to the Earth's surface and decrease in directions approaching the horizon. For simplicity Stephens and Obrien estimated the outgoing TR as isotropic. Note that the thinness of the atmosphere (about 5% of the diameter of the Earth) reduces the error introduced by this simplification. Stephens and Obrien stated that it was more important to resolve the spectral character of the TR rather than the directional distribution.

The ERBE scanners measure the energy irradiance of longwave TR with wavelengths between 5 and 200 μm [12] and thus the spectral distribution of the TR is not measured. Stephens and Obrien use TR transfer models for the atmosphere to estimate the spectral distribution of the TR for different scene or land surface types and weather conditions. In comparing the NBR entropy to that of BR with the same energy they conclude that the error introduced in estimating the entropy in this way is low, probably within 1% ([5], p. 133). This is not surprising because the NBR emitted from Earth with an overall albedo (reflectivity) of about 0.29 is likely to have spectral emissivities greater than 1/2 and thus the error is within 1%, as discussed in section 4.4.

In their conclusion Stephens and Obrien state that the "entropy fluxes calculated from the ERBE measurements are estimated to be accurate to 2-3% and this uncertainty arises primarily from the measurement error of the ERBE longwave fluxes." Note that Harrison [13] provides a detailed account of the uncertainties in the ERBE fluxes. At this point we have not determined how accurate this overall error estimate of their analysis is.

7.2 Extremum Principle for Climate Modeling

Thermodynamic modeling and analysis of the Earth's atmosphere is an alternative approach to conventional energy, momentum, and mass balance models. The thermodynamic approach is attractive because of its intrinsic simplicity while the responses of the conventional models are difficult to unravel.

Stephens and Obrien state that the fundamental question is whether the climate system is at a maximum or minimum entropy production rate ([5], p.147). They conclude that "we present an analysis that suggests the earth is near a maximum entropy production for the given observed albedo of the planet. This arises from the fact that the long-wave entropy flux to space is very closely approximated by the *equivalent* black-body entropy flux."

The phrase "for the given observed albedo" or overall reflectivity of the Earth is important because specifying the albedo determines:

(1) By definition the energy flow rate absorbed by the Earth system.

(2) The approximate temperature of the planet based on a gray body model of the Earth system with emissivity equal to unity minus the albedo ($\varepsilon = 1 - a$), and the energy emission rate approximated by the absorption rate (steady state).

(3) How accurately the emitted entropy flux can be approximated by that of BR with the same energy (section 4.4). This is true because a low albedo means that in general the NBR emitted from the Earth will have spectral emissivities greater than 1/2.

Thus, by fixing the planetary albedo it appears they have arrived at the conclusion that the Earth's entropy production rate is near its maximum. Note that if the albedo of the earth was lower then the entropy production rate would be greater.

In their conclusion we believe it might be misleading to say the "equivalent" black-body entropy flux. The entropy of NBR emitted from Earth is approximated by that of BR at the same energy and thus lower emission temperature. How the accuracy of this approximation is relevant with regards to finding an extremum principle is not clear to us.

At this time our view is that the magnitude of the total entropy production rate of Earth is not relevant in supporting a principle that governs the behavior of the system. There is a continual tendency for the Earth system to reach equilibrium while the system is constantly being disturbed by the interaction with sunlight and minor* processes such as volcanism. This drive towards equilibrium (maximum disorder) or uniformity constantly produces entropy. But, how much entropy the system is producing is not relevant in the context of supporting a governing principle. The tendency to establish equilibrium in the atmosphere governs circulation. TR processes change the state of the material in the atmosphere and are, in this indirect way, the primary cause of circulation.

7.3 Sources of Entropy Production within the Earth System

Stephens and Obrien stated that the entropy production of Earth is dominated entirely by radiative processes ([5] p. 147). This is directly due to the absorption of sunlight emitted from a source near 6000 K by material on Earth with temperatures near 300 K. Atmospheric and ocean processes such as fluid flow and non-radiative heat transfer have little influence on the total entropy production rate of Earth [5]. They are secondary entropy producing processes because the exergy of low entropy sunlight drives these processes but the sunlight must first be absorbed. In other words, a small portion of the exergy of sunlight supports the biosphere and circulation of the atmosphere and oceans.

7.4 The Role of the Biosphere in Climate Change Modeling

The radiative character of the atmosphere and the Earth's surface determines the overall albedo of the planet and thus its approximate temperature and total entropy production rate. In turn, the biosphere effects the composition and thus the radiative character of the atmosphere (especially CO_2, O_2, and H_2O), land surfaces and hydrosphere. Thus, a thermodynamic model for studying climate change should include the role of the biosphere. However, for strictly modeling the circulation of the present atmosphere and ocean system the biosphere would likely be viewed as invariant.

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* See the energy balance diagram for the Earth system on page 39 of [15].

CHAPTER 8 CONCLUDING REMARKS

Plancks spectral entropy radiance (L_ν) expression (2.4) is the basis for determining the entropy of TR. The spectral entropy radiance (L_ν) spectrum is determined from the spectral energy (K_ν) spectrum. The entropy flow rate ($\dot{S}$) through a surface is the integration of L_ν over frequency, solid angle, and surface area. The exclusive use of numerical integration is a straightforward but laborious task that does not lend itself well to understanding the entropy of TR.

In this thesis approximate methods suitable for engineering applications have been developed for *evaluating the entropy flux of NBR*:

- The approximate expression for the entropy radiance (4.2) of GR is within 0.8% of the numerical integration result for emissivities greater than 0.005. Expressions (4.2) and (3.6) give the entropy and energy emission rate from a gray surface as a function of temperature. Further, in engineering analysis materials are commonly modelled as gray by calculating an effective emissivity. The approximation for the entropy of GR allows the corresponding entropy flux to be calculated in a quick and simple manner.
- For TR that cannot be adequately modelled as BR or GR the relationships presented in section 4.2 can be used to estimate the energy and entropy emission rates as a function of temperature (4.11).
- Alternatively, the entropy radiance L of NBR can be estimated as that of BR with the same energy radiance K and accordingly different emission temperature (section 4.4 and 4.3.1). For GR this approximation is within 1% for emissivities greater than 1/2, and likewise for any NBR with spectral emissivities greater than 1/2 over the whole spectrum.

Further, the object of this work is to improve the *understanding of the entropy of TR*:

- As recognized by Planck, BR has the highest entropy of all TR with the same energy. In this work we qualitatively evaluate the entropy production rate for the isolated transition of GR to BR with the same energy (section 4.4).
- NBR has a higher entropy-to-energy ratio than BR at the same emission temperature (sect. 4.3.1) as shown quantitatively for GR (sect. 4.3.2). The validity and implications of this result are discussed and a clarification is made from comparing NBR and BR at the same energy radiance rather than the same emission temperature. This result is a direct implication of the mathematical form of the L_ν expression (2.4). Further, the validity of the mathematical form of Planck's expression (2.4) is supported by stability requirements for a TR system in equilibrium with its material enclosure (sect. B.2).
- The evaluation of the net entropy flux of TR at the surface of a material is not as straightforward as calculating the net energy flux. The calculation of the net entropy flux from a solid surface is clarified in chapter 5.
- The entropy-to-energy ratio L/K for BR , GR, and other NBR described in section 4.2 increases as temperature decreases (sect. 4.5).
- In appendix C we review and present some new results on the characteristics of the family of BR curves, including: the location of the entropy peaks, locus of peaks, and cutoff frequencies.

TR is a significant energy/entropy transfer process in many thermodynamic systems especially where high or very low temperatures relative to the environment are involved. Significant errors are introduced when the entropy flux of TR is incorrectly assumed to be q/T (section 4.6). If this error is made when analyzing a gas-solid boundary of a thermodynamic device then the irreversibility of the device is underestimated regardless of whether the device is hot or cold relative to its surroundings. Further, the higher entropy-

to-energy ratio for NBR means that the error introduced is even greater for NBR than for BR exchange.

The results in this work have various applications but a preliminary application to the Earth was chosen because it was the motivation for this research (chapter 7). TR transfer is a very important in the analysis of the Earth and radiation-matter interaction is responsible for the majority of the entropy produced by the Earth system. Stephens and Obrien's [5] conclusion that the Earth is near its maximum entropy production rate may be misleading and its relevance to finding an extrenum principle for climate modelling is not clear to us. The results from this work also provide a basis for analyzing and estimating the magnitude of the sources of error in Stephens and Obrien's calculation of the total entropy production rate of Earth.

8.1 Recommendations for Future Work

The following are some *recommendations for future work*:

- Improve the physical understanding of the current results; especially regarding the fact that (1) the entropy-to-energy ratio for BR is exactly 1/3 higher than q/T, and (2) for NBR it is more than 1/3 higher than q/T.
- Investigate further the role of TR in thermodynamic climate modeling. Conduct an error analysis of Stephens and Obrien's [5] calculation of the total entropy production rate of the Earth system based on the sources of error described in section 7.1.
- Estimate the entropy production rates within various domains of the Earth system; such as the atmosphere, lithosphere, biosphere, and hydrosphere.
- Extend this work into the domain of exergy analysis by utilizing the present results to assist in evaluating the exergy flux of TR.

- Investigate the temperature dependence of the radiative character of common engineering materials used in applications were TR exchange is important. Use this information to test the approximate methods for the variation of entropy emission with temperature presented in sections 4.1 and 4.2.
- Find an analytical solution for the entropy of GR or prove that it does not exist.
- Determine the equations of the energy and entropy envelops that enclose all TR.

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APPENDIX A: GEOMETRIC CONSIDERATIONS

A.1 Description of the Radiation Field

The description of a radiation field is laborious but straightforward. In general the field is non-uniform with position and at any position in the field the frequency distribution (K_ν spectrum), the energy radiance K (area enclosed by the K_ν spectrum), and the polarization can vary with direction and time.

Figure A-1 shows the variation of the frequency distribution (K_ν spectrum), and the energy radiance K with direction at a particular position in the radiation field.

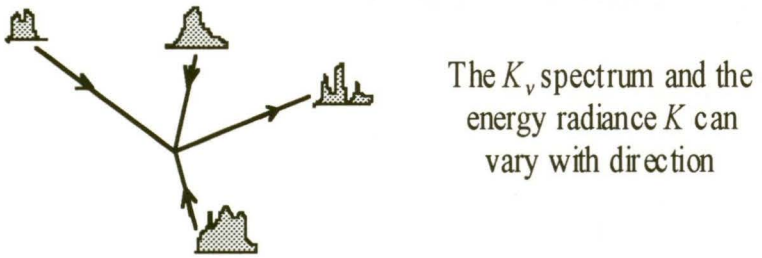


Figure A-1: The radiation field at a particular position and time.

The orientation of radiation propogation is usually described by a single direction, but in actuality it is never confined to a single direction, in contrast it diverges as a cone of directions (pencil of rays). The fraction of possible directions subtended by the cone, multiplied by 4π, is called the solid angle of the pencil of rays.

The solid angle is the 3D quantity corresponding to the 2D angle. Like the radian (rad) measure of an angle, the steradian (sr) measure of a solid angle has no physical units of time, space, or mass. Consider an infinitesimal pencil of the rays that pass through a point in a radiation field, as shown in figure A-2. And imagine a fictitious sphere, of radius R, centered at the point in question.

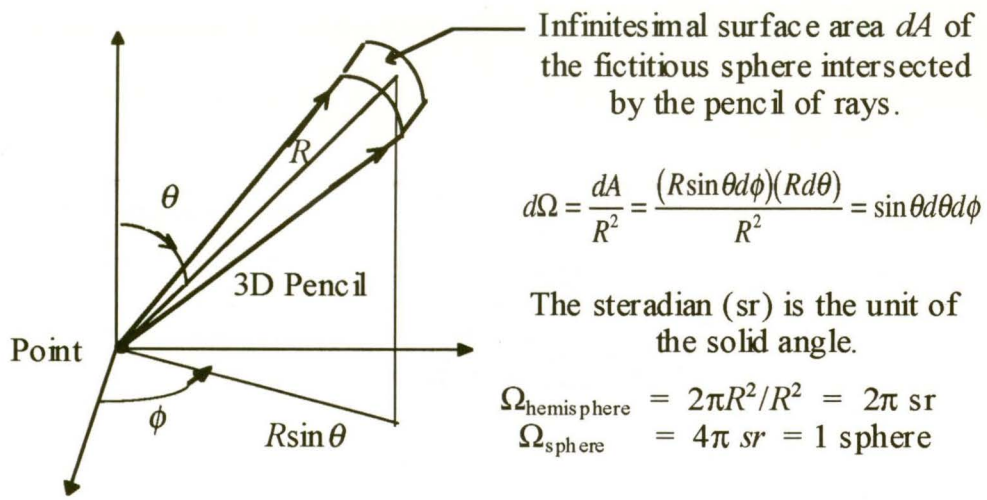


Figure A-2: Infinitesimal pencil of rays.

The solid angle is the fraction of the surface area of the fictitious sphere that is intersected by the pencil of rays, times 4π.

Consider the emission of thermal radiation from a solid surface. The energy irradiance H in W/m^2 is the flux of energy from the surface at a particular location on the surface per unit surface area. The flow rate of energy $\dot{E}$ in W from the surface is:

$$\dot{E} = \int_{Surface} H\ dA \qquad \textbf{(A.1)}$$

The irradiance H is calculated by integrating the radiance K ($W/m^2 \cdot sr$) over all possible propagation directions,

$$H = \int_{\phi_1}^{\phi_2} d\phi \int_{\theta_1}^{\theta_2} (K\cos\theta)\sin\theta d\theta \qquad \textbf{(A.2)}$$

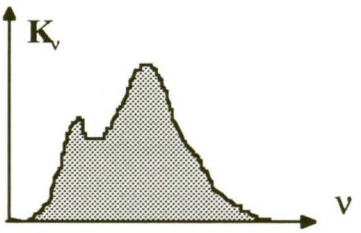
where $K\cos\theta$ is component of K perpendicular to the surface, and the infinitesimal solid angle is $d\Omega = \sin\theta\ d\theta\ d\phi$. If the emission is isotropic the radiance K does not depend on direction and the irradiance H is

$$H = K\int_0^{2\pi} d\phi \int_{-\pi/2}^{\pi/2} (\cos\theta)\sin\theta\ d\theta = \pi K \qquad \textbf{(A.3)}$$

The energy radiance K is the area under the spectral energy radiance K_ν ($J/m^2 \cdot sr$) spectrum, as shown in figure A-3.

K is the area under the K_ν spectrum

$$K = \int_0^\infty K_\upsilon \, d\upsilon$$



UNITS

K_ν: $J / m^2 sr$

K: $W / m^2 sr$

Figure A-3: The energy radiance K is the area under the K_ν spectrum.

Moving on from radiation emission, consider the radiation system inside an evacuated isothermal cavity. The internal energy U of the radiation is the energy that is contained in the volume V of the cavity. The specific internal energy u is the internal energy U of the radiation per unit volume.

If the radiation is uniform in position and isotropic, then the energy radiance K of the radiation is geometrically related to the specific internal energy u of the radiation

$$K = \frac{c}{4\pi}\frac{U}{V} = \frac{uc}{4\pi} \qquad \textbf{(A.4)}$$

The fundamental expression for the entropy of monochromatic radiation, the spectral entropy radiance L_ν, is a function of frequency (ν) and spectral energy radiance (K_ν) alone

$$L_\nu = L_\nu(\nu, K_\nu) \qquad \textbf{(A.5)}$$

The entropy variables of the radiation field are analogous to the energy variables. The entropy radiance L is the area under the spectral entropy radiance L_ν spectrum, the entropy irradiance J is the integration of the entropy radiance L over all directions, and similarly for the entropy equivalent of (A.4).

A.2 The Energy and Entropy Flow Through a Surface

The energy and entropy flows through a surface in a radiation field are calculated in the same manner. The energy flow is arbitrarily chosen here, but the procedure is analogous for the entropy flow calculation. The net energy flow rate $\dot{E}$ through the a surface located in an arbitrary radiation field is determined by discretizing incident rays from all directions into infinitesimal pencils of rays with solid angles $d\Omega = \sin\theta\, d\theta\, d\phi$

$$\dot{E} = \int_{surface} H\ dA = \int_{surface} \int_0^{2\pi} d\phi \int_0^{\pi} K \sin\theta \cos\theta\, d\theta \quad dA \tag{A.6}$$

and by replacing K we have

$$\dot{E} = \int_{surface} \int_0^{2\pi} d\phi \int_0^{\pi} \left\{ \int_0^{\infty} K_\nu d\nu \right\} \sin\theta \cos\theta\, d\theta \quad dA \tag{A.7}$$

If the outgoing and incoming radiation is isotropic and uniform with position on the surface then the net flow rate of energy across the surface is

$$\dot{E} = \pi \text{ (surface area)}(K_{Outgoing} - K_{Incoming}) \tag{A.8}$$

A.2.1 Numerical Approximation

The energy flow rate $\dot{E}$ through a surface in an arbitrary radiation field can be calculated numerically. This is done by approximating (1) the spectral radiance spectrums and the radiances as constant in each pencil of rays with a finite solid angle $\Delta\Omega$, and (2) the energy irradiances as constant over each finite element of surface area ΔA. The energy flow across the surface is numerically approximated as

$$\dot{E} = \sum_{Surface} (H)\Delta A = \sum_{surface} \left[\Delta A \sum_{all\ pencils} (K \cos\theta\ \Delta\Omega) \right] \tag{A.9}$$

where θ is the local angle between the radiation flux direction and the normal to surface area ΔA.

A.3 Polarization

Radiation is emitted when electric charges accelerate. The emission of "heat" radiation from a solid is due to the vibrations of atoms and molecules. In general, the atoms in a solid can vibrate in any direction. Consequently, the radiation emitted has a random plane of vibration and is referred to as unpolarized. In contrast, for plane polarized radiation the vibrations are in a single plane.

An unpolarized ray has a random distribution of plane polarized wavetrains, with different planes of vibration, but of equal magnitude. The unpolarized ray can be mathematically broken down into two equal, mutually perpendicular, plane polarized components, as shown below.

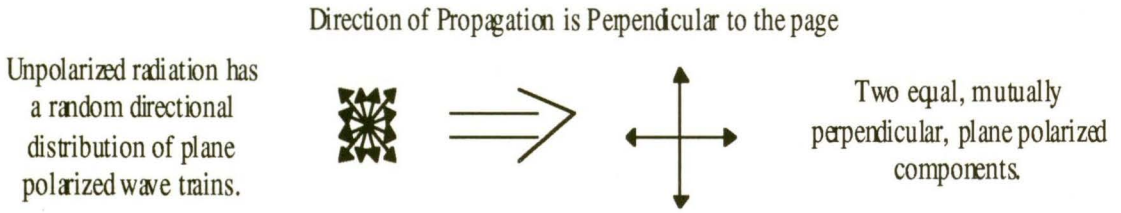


Figure A-4: Unpolarized radiation can be mathematically decomposed.

Planck's equation (2.2) was derived for plane polarized radiation. As a result, it must be multiplied by two for unpolarized radiation to agree with experimental results. Planck states* that "every (unpolarized) ray has just twice the intensity of one of its plane polarized components, which could, for example be obtained by passing the ray through a Nicole's prism".

A polarization factor p (or l) is included to generalize the equations (2.2) and (2.4) with respect to polarization. For unpolarized radiation $p = 2$ and for plane polarized radiation $p = 1$. In this thesis, unless otherwise indicated, the analysis is restricted to unpolarized TR for simplicity although there is no inherent limitation for application to polarized TR.

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* Page 6 of "The Theory of Heat Radiation" by Max Planck [1].

APPENDIX B: THE MATHEMATICAL FORM OF THE L_ν FUNCTION

As shown in section 4.3.1 Planck's spectral entropy radiance L_ν (2.4) is a monotonically increasing concave function of the spectral energy radiance K_ν. The implications that follow from this mathematical form raise the question of its validity. However, we will show here that from stability requirements the mathematical form of Planck's L_ν expression is expected. First we consider a material system alone and then a combined material-radiation system in equilibrium.

B.1 Material Systems

For material systems the internal entropy is a monotonically increasing concave function of the internal energy. This can be shown by considering the stability of a material system. The following approach is taken from Callen's text ([14], p. 203).

Consider two identical subsystems, each with the fundamental equation $S=S(U,V,N)$, separated by a totally restrictive wall. Consider the situation where the volume V and the mole number N of each subsystem are fixed, that is $S = S(U)$. Now suppose that the dependence of S on U is convex* rather than concave as qualitatively shown in figure B-1.

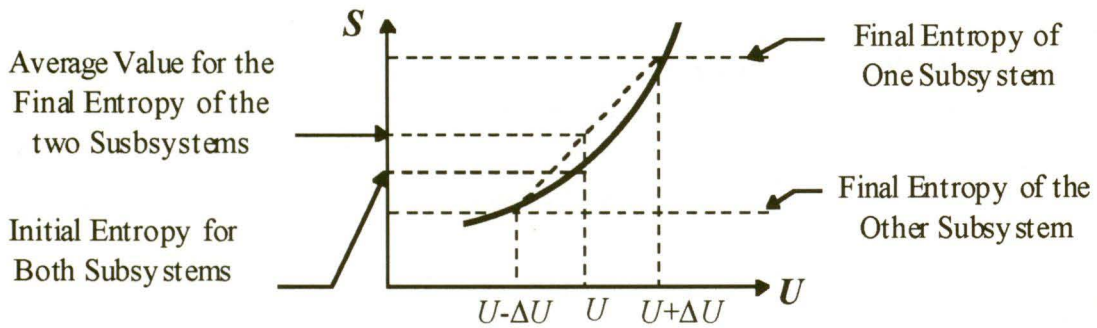

Figure B-1: Physically impossible convex $S = S(U)$ with a positive second derivative for a material system.

* The second derivative is always positive for a strictly convex function and always negative for a strictly concave function.

If we were to remove an amount of energy ΔU from one subsystem and transfer it to the other subsystem, then the average value of the entropy of the subsystems would increase from its initial value.

This means that if the adiabatic restraint were removed in such a system, energy would flow spontaneously across the wall; one subsystem would thereby increase its energy (and its temperature) at the expense of the other. Even within one subsystem, it would be advantageous to transfer energy from one region to another, developing internal inhomogenieties.

Thus, the condition of stability for material systems is the concavity of the entropy dependence on energy. This means that entropy is a maximum at the homogenous equilibrium condition, as demonstrated in the following figure.

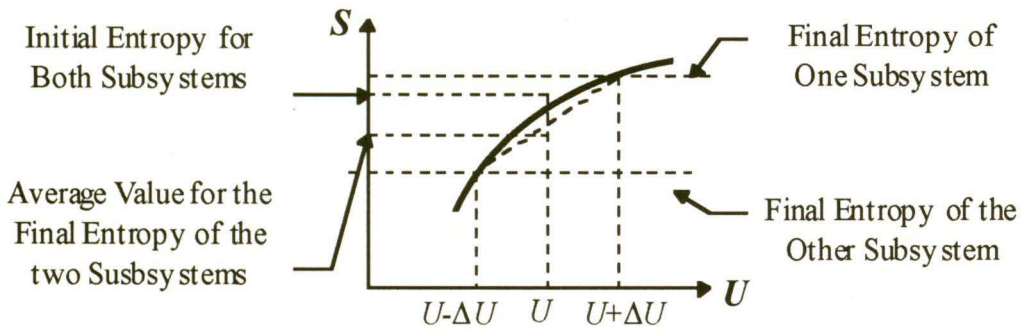

Figure B-2 Actual concave $S = S(U)$ with a negative second derivative for a material system.

The slope of the function $S(U)$ is the inverse of temperature T

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V,N} \tag{B.1}$$

and is always positive because $T > 0$. Or in other words, the greater the energy level the greater the entropy. This is equivalent to saying that $S(U)$ is a monotonically increasing function. In simpler terms this means that as U increases the entropy S and the temperature T increase, and the slope of $S(U)$, the inverse of the temperature, decreases.

B.2 A Radiation System in Equilibrium with a Material Enclosure

Consider an isotropic BR system enclosed in an evacuated cavity and in equilibrium with the material of the enclosure. For simplicity, the rigid material of the enclosure has uniform BB characteristics. The combined system is isolated from its surroundings. The internal energy and entropy of the radiation system are U and S, respectively. The equation of state for the radiation system is $S(U)$ because the volume is fixed.

The characteristics of the radiation system depend entirely on interaction with the material that surrounds it. This is because the radiation does not interact with itself and thus depends on reflection, absorption, and emission at the material surface to change the state of the TR in the cavity.

It is an observable fact that the equilibrium condition for an isolated material system containing an evacuated cavity, with uniform properties, and without heat generation sources, is the uniformity of temperature. Therefore, the state of the radiation system that it is in equilibrium with is uniformity as well.

From the "0^{th} law" of thermodynamics, at the equilibrium condition the slope of $S(U)$ for the radiation system must be the same as the slope of $S(U)$ for material system. This is equivalent to saying they must have the same temperature, where temperature is defined as:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{V,N} \qquad \textbf{(B. 2)}$$

For the material system $S(U)$ is a monotonically increasing function of the internal energy U. That is, the slope is always positive and decreases with increasing energy. Thus from the zeroth law of thermodynamics, $S(U)$ for the TR system must be a monotonically increasing concave function as well. This conclusion is in agreement with the functional form of Planck's spectral entropy radiance function (2.4).

B.3 Quantitative Dimensionless Plots of the L_v Function

The purpose of this section is to investigate quantitatively the dependence of the spectral entropy radiance L_v (2.4) on the spectral energy radiance (K_v) and frequency (v) independently. The dimensionless form of the entropy dependence on energy with frequency fixed was presented in section 4.3.1, equation (4.12). The dimensionaless form of the entropy dependence on frequency with energy fixed is given by

$$z_K = \left\{X_K^2\right\}\left\{\left(1+\frac{1}{X_K^3}\right)\ln\left(1+\frac{1}{X_K^3}\right)-\frac{1}{X_K^3}\ln\left(\frac{1}{X_K^3}\right)\right\} \qquad K_\upsilon = \textit{fixed} \tag{B.3}$$

where

$$z_K = \frac{1}{k}\left[\frac{hc}{K_\upsilon\sqrt{p}}\right]^{\frac{2}{3}} L_\upsilon \qquad \text{and} \qquad X_K = \left[\frac{ph}{c^2K_\upsilon}\right]^{\frac{1}{3}}\upsilon \tag{B.4}$$

are the K_v fixed dimensionless spectral entropy radiance and the dimensionless frequency, respectively. The quantitative plots of both z_v (4.12) and z_K (B.3) are shown in Figure B-3.

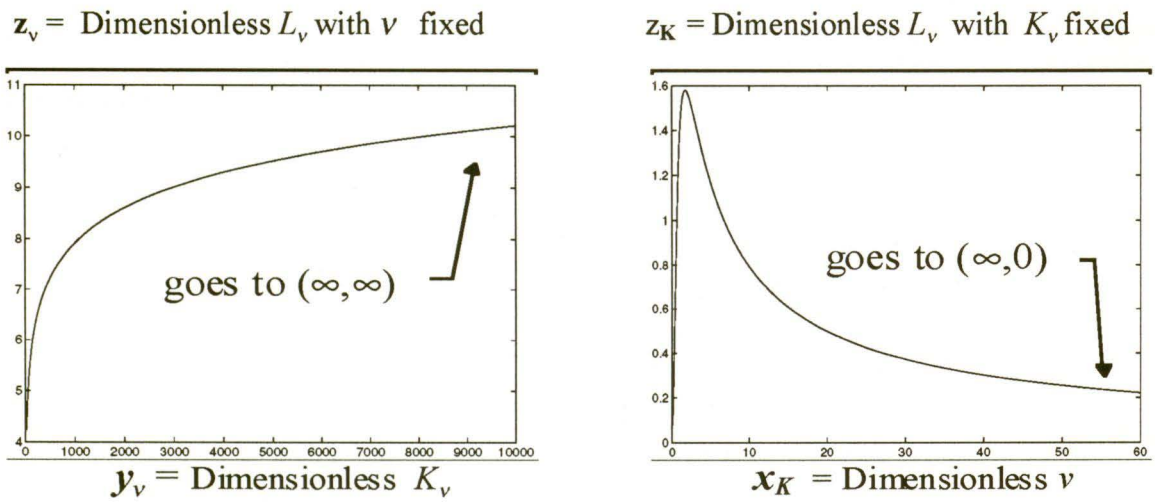

Figure B-2: Dimensionless spectral entropy radiance L_v plots; z_v represents entropy versus energy with frequency fixed, and z_K represents entropy versus frequency with K_v fixed.

The peak of the z_K plot ($x_K \approx 1.74$) corresponds to a boundary line on the K_ν versus frequency plane given by $K_\nu = (2.8)10^{-51}\ \nu^3$. To the right of the boundary line L_ν increases as ν decreases for K_ν fixed, and on the left vice versa. The locus of the peaks for the blackbody spectrums is given by $K_\nu = (9.3)10^{-52}\ \nu^3$. Thus, the boundary line is approximately three times the height of the locus of black body peaks. Thus, thermal radiation is confined to the region where L_ν increases as ν decreases for K_ν fixed.

In the literature this has been interpreted as follows. The energy of a single photon is $E = h\nu$. As the frequency decreases the number of photons required to have total energy K_ν increases. The greater number of photons means an increase in disorder, and thus an increase in entropy L_ν.

As an example of what areas in the z_ν and z_K plots are of interest consider a clear-sky emission spectrum from the Earth to space. The longwave radiation emitted from the Earth has a frequency range of about $(4)10^{12}$ to $(1.5)10^{15}$ hz (wavelengths of 0.2 to 75 μm), and a spectral energy radiance (K_ν) range of about zero to $(2)10^{-13}$ J/m^2·sr. This corresponds to $y_\nu < 0.4$ and $x_K > 20$.

APPENDIX C: BLACKBODY RADIATION (BR)

A blackbody absorbs all incident radiation and emits the maximum energy and entropy for a given material temperature. Consequently the family of blackbody curves encloses all other thermal emission spectrums and provides a reference point for comparing thermal spectrums. Furthermore, BR is referred to as equilibrium radiation. This is because a radiation system when in equilibrium with an isothermal material enclosure will have a BB spectrum regardless of the radiative characteristics of the material. A pore inside an isothermal solid is a good example. In this appendix various topics involving BR will be considered. The first is the derivation of the blackbody spectral energy radiance formula from the spectral entropy radiance expression.

C.1 Derivation of the K_ν Expression from the L_ν Expression

When Planck first introduced the K_ν expression (2.2) it was based on mathematical interpolation between experimentally observed low and high frequency forms. Later using equilibrium statistical thermodynamics he derived the L_ν expression (2.4). Then through the definition of temperature the K_ν expression could be derived analytically. This derivation is presented here to show consistency between equations (2.2) and (2.4).

Consider an isotropic BR enclosed, and in equilibrium with, an isothermal evacuated rigid cavity. The internal energy and entropy of the radiation in the cavity are U and S, respectively. The equation of state for the radiation system is $S=S(U)$ because the chemical potential is zero and the volume of the radiation is fixed.

The first *Tds* equation for the radiation system is

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS \qquad \textbf{(C.1)}$$

and by defining temperature in the usual manner

$$T \equiv \left(\frac{\partial U}{\partial S}\right)_V \tag{C.2}$$

the differential equation becomes $dU = TdS$. Note that at equilibrium the temperature T is the same for both the material and the radiation system (zeroth law).

Since the radiation is isotropic the energy (K) and the entropy (L) radiance are linearly related by the same constant $(c/4\pi\ V)$ to the energy (U) and entropy (S), respectively. Moreover, the volume is fixed so we have a total differential expression

$$\frac{dL}{dK} = \frac{1}{T} \tag{C.3}$$

From definition

$$\frac{1}{T_\upsilon} \equiv \frac{dL_\upsilon}{dK_\upsilon} \tag{C.4}$$

and for blackbody radiation $T_\upsilon = T$ thus

$$\frac{dL_\upsilon}{dK_\upsilon} = \frac{1}{T} \tag{C.5}$$

By differentiating the L_υ expression (2.4) with respect to K_υ we get

$$\frac{dL_\upsilon}{dK_\upsilon} = \frac{pk\upsilon^2}{c^2}\left\{\left(\frac{c^2}{ph\upsilon^3}\ln\left[1+\frac{c^2K_\upsilon}{ph\upsilon^3}\right]+1\right)-\left(\frac{c^2}{ph\upsilon^3}\ln\left[\frac{c^2K_\upsilon}{ph\upsilon^3}\right]+1\right)\right\} \tag{C.6}$$

and on substituting (C.6) into (C.5) we have

$$\frac{1}{T} = \frac{k}{h\upsilon}\ln\left[\frac{ph\upsilon^3}{c^2K_\upsilon}+1\right] \tag{C.7}$$

Re-arrangement of this expression produces Planck's spectral energy radiance expression (2.2) in its common form:

$$K_\upsilon = \frac{p\,h\upsilon^3}{c^2}\left(\frac{1}{e^{\frac{h\upsilon}{kT_\upsilon^*}}-1}\right) \tag{2.2}$$

C.2 The Internal Energy and Entropy of Isotropic BR from the First *Tds* Equation

The internal energy and entropy of BR can be calculated by integrating equations (2.2) and (2.4), respectively. Alternatively the energy and entropy can be calculated by integrating the first *Tds* equation for an isotropic and uniform radiation system [1], as also discussed by Bejan [7] p.474.

Consider a piston cylinder enclosure with perfectly reflecting walls with the exception of one blackbody wall maintained at a constant temperature T from an external thermal energy reservoir (TER).

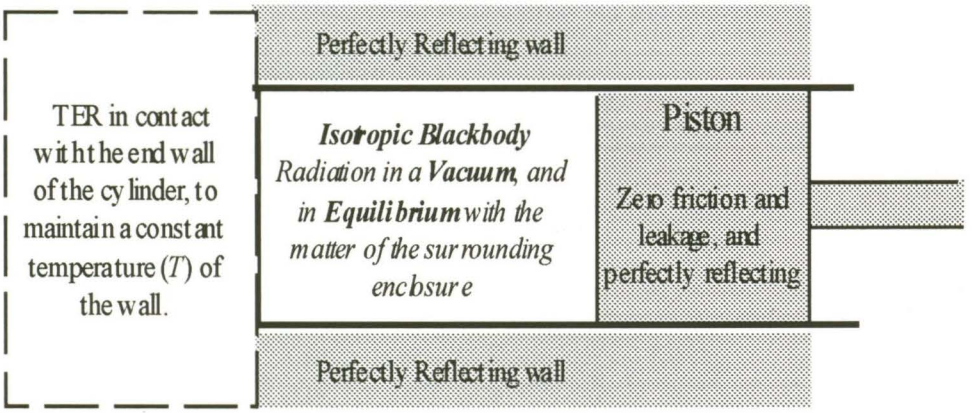

Figure C-1: Evacuated piston-cylinder assembly.

The equilibrium state relations for this radiation field can be derived by considering the change in state variables, between two equilibrium states, due to an internally reversible process. At equilibrium $T_{radiation}=T_{enclosure}= T$ of TER. When in an equilibrium state, just as any simple thermodynamic system, this system should satisfy the first *Tds* equation:

$$TdS = dU + PdV$$

The radiation pressure [1] is $P = u/3$, so the differential equation becomes

$$dS = \frac{dU}{T} + \frac{P}{T}dV = \frac{dU}{T} + \frac{u}{3T}dV \qquad \textbf{(C.8)}$$

and since $U = uV$ then $dU = Vdu + udV$ and we have

$$dS = \frac{V}{T}du + \frac{u}{T}dV + \frac{u}{3T}dV = \frac{V}{T}du + \frac{4u}{3T}dV \qquad \textbf{(C.9)}$$

therefore

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT} \qquad \text{and} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \frac{4u}{3T} \qquad \textbf{(C.10)}$$

Partial differentiation of both these expressions gives

$$\frac{\partial^2 S}{\partial T \partial V} = \frac{1}{T}\frac{du}{dT} = \frac{4}{3T}\frac{du}{dT} - \frac{4}{3}\frac{u}{T^2} \qquad \textbf{(C.11)}$$

By re-arranging this expression we find

$$\frac{1}{3T}\frac{du}{dT} = \frac{4}{3}\frac{u}{T^2} \qquad or \qquad \frac{du}{u} = 4\frac{dT}{T} \qquad \textbf{(C.12)}$$

Integration of this equation produces the expression for the specific (per volume) internal energy of isotropic black body radiation:

$$u = aT^4 = 4\pi K/c \qquad \textbf{(C.13)}$$

where $a = 48\pi\,\alpha\,k^4/(c^2h^3) = (7.59)10^{-16}$ J/m^3·K^4. To find the internal entropy we substitute (C.13) into equation (C.9)

$$dS = \frac{V}{T}\frac{du}{dT}dT + \frac{4u}{3T}dV = \frac{V}{T}\left(4aT^3\right)dT + \frac{4aT^4}{3T}dV \qquad \textbf{(C.14)}$$

and on re-arranging

$$dS = \frac{4a}{3}\left(3VT^2dT + T^3dV\right) = \frac{4a}{3}\,d\left(VT^3\right) \qquad \textbf{(C.15)}$$

Integration of equation (C.15) gives

$$S = \frac{4a}{3}VT^3 + \text{constant} \qquad \textbf{(C.16)}$$

and since $S = 0$ when $T_{radiation} = T_{enclosure} = 0$ (no radiation) the internal entropy is

$$S = 4aVT^3/3 \qquad \text{or} \qquad s = 4aT^3/3 = 4u/3T \qquad \textbf{(C.17)}$$

C.3 Equation of State for an Equilibrium BR System

Consider an evacuated pore inside an isothermal solid. The radiation system will be in equilibrium with the material of the enclosure in that (1) it is at steady state, (2) it has reached the maximum entropy given the present constraints, and (3) its state is independent of its past history.

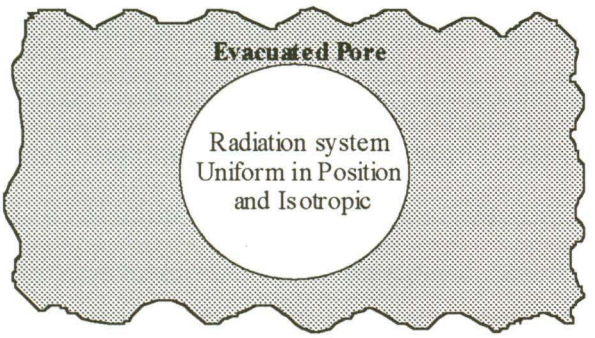

Figure C-2: Evacuated pore in an isothermal solid.

The radiation in the cavity will have a BB spectrum at temperature T regardless of the type of material of the enclosure. Because of this BR is sometimes referred to as equilibrium radiation. Furthermore, the radiation system will be isotropic and uniform because the solid is isothermal.

The fundamental equation of state is found by combining equations (C.17) and (C.13)

$$U_B = \left(\frac{3}{4}\right)^{4/3} a^{-1/3} V^{-1/3} S_B^{4/3} = D_B V^{-1/3} S_B^{4/3} \qquad \textbf{(C.18)}$$

where V is the volume of the cavity and $D_B = (7.46)10^4 \frac{mK^{4/3}}{J^{1/3}}$. The temperature of the radiation system is

$$T_{BR} \equiv \left(\frac{\partial U_B}{\partial S_B}\right)_V = \left(\frac{3}{4}\right)^{4/3} a^{-1/3} V^{-1/3} \left(\frac{4}{3} S_B^{1/3}\right) = T \qquad \textbf{(C.19)}$$

The state of equilibrium with the material system is completely determined by the material temperature.

The radiation system must have a black spectrum to be in equilibrium with the material of the enclosure. If mistakenly it is assumed that the equilibrium radiation in the enclosure has the same spectrum as the emission spectrum from the arbitrary material, then the calculated temperature of the radiation system, defined in the usual manner, is less than the material temperature; a violation of the 0^{th} law.

To further illustrate this point consider the following. At equilibrium there is a steady, equal and opposite, exchange of energy and entropy between the walls and the radiation system, similar to an equilibrium mixture of a liquid and it's vapor. An arbitrary material surface does not absorb all radiation incident on it. Therefore, the radiation incident from the radiation system must have higher irradiance than the emission from the surface. This is the case when the equilibrium radiation has a blackbody spectrum. Furthermore, the BR system represents the *maximum energy and entropy for a given material temperature*.

Although radiation does not interact with itself equilibrium is established because (1) emission of radiation by the enclosure is dependent on its temperature only while (2) absorption depends on the character of the incident radiation as well. Note that equilibrium is between the material of the cavity and the radiation system. The approach to equilibrium is not a maximization of the entropy of the radiation system for a fixed energy. It is the maximization of the energy and entropy of the radiation system for a given material temperature. However, the blackbody spectrum does not represent the maximum ratio of entropy-to-energy ratio for the radiation system itself.

At equilibrium, the magnitude of the equal and opposite energy and entropy exchange depends on the physical character of the walls. Black walls exchange the maximum energy and entropy with the radiation system because they emit the maximum amount of radiation for a given wall temperature, and absorb all incident radiation. A BB surface will ensure the fastest approach to the equilibrium state. In the next section we consider a special theoretical type of enclosure.

C.3.1 Perfectly reflecting theoretical enclosures and equilibrium

Now consider a situation where the radiation system is contained by an evacuated enclosure that completely isolates the radiation system. This type of enclosure has been termed "perfectly reflecting". Note that Kirchoff's law implies that a perfectly reflecting enclosure is a perfectly isolating enclosure.

This radiation is not in equilibrium because it is not in thermal contact, or in other words it does not exchange photons, with the material of the enclosure. Any radiation whatsoever could exist in such a theoretical enclosure. However, if a particle of real matter was inserted the radiation system would equilibriate to BR, thereby producing entropy. This would also be the case for real material enclosures that approach perfectly reflecting because there will always be some interaction (absorption/emission) between the radiation system and the enclosure. The radiation system, even if very slowly, will interact with the material of the enclosure and eventually become BR.

Now if the enclosure had real material properties with the exception of some finite area of its surface being a "special monochromatic material" then the equilibrium condition is still BR at the temperature of the enclosure.

If the evacuated enclosure was initially devoid of radiation and was made of a special "monochromatic material" then once the steady state condition is reached the cavity will be filled with monochromatic radiation given by Planck's formula (2.5). But, is this type of system in equilibrium? If we were to suddenly isolate the radiation system and add a minute piece of real material the system would move towards black body radiation, thereby producing entropy while the energy remains constant.

Note that when radiation is traveling through "empty space", then equilibrium doesn't have any meaning because the radiation does not interact with itself. Thus, the terms equilibrium (BR) and non-equilibrium (NBR) radiation are not applicable.

C.4 Some Useful Relationships for the Family of Blackbody Curves

It is useful to know the basic characteristics of the family of BR curves because they are used as a reference point for other TR. By differentiating the spectral energy radiance expression (2.2) with respect to frequency and setting the derivative to zero we find that the frequency (ν_{mK}) of the energy peak (maximum) is given by:

$$3\,e^{-\frac{h\upsilon_{mK}}{kT}} = 3 - \frac{h\upsilon_{mK}}{kT} \qquad \textbf{(C.20)}$$

Thus, this characteristic frequency is a linear function of temperature. By numerical calculation we find that

$$\nu_{mK} \approx 2.82144\ \frac{k}{h}\ T \qquad \textbf{(C.21)}$$

where T is in degrees Kelvin, and the subscript mK denotes maximum (m) and energy (K). Equation (C.21) is known as Wien's displacement law and was experimentally observed prior to the discovery of equation (2.2). On substituting equation (C.21) into (2.2) we find that the spectral energy radiance $K_\nu(\nu_{mK})$ in J/m^2·sr of the BB energy peak is a cubic function of the material emission temperature:

$$K_\nu(\nu_{mK}) = \frac{ph}{c^2}\frac{\left(2.821439\frac{k}{h}T\right)^3}{e^{2.82144}-1} \approx (1.8853)10^{-19}\ T^3 \quad \text{J/m}^2\cdot\text{sr}\cdot\text{K}^3 \qquad \textbf{(C.22)}$$

Consequently, the material emission temperature of BR or GR can be determined from the frequency of the peak.

Similarly, the frequency (ν_{mL}) of the BB entropy peak is a linear function of emission temperature

$$\nu_{mL} \approx 2.53823\ \frac{k}{h}\ T \qquad \textbf{(C.23)}$$

and the spectral entropy radiance $L_\nu(\nu_{mL})$ in J/m^2·sr·K is a quadratic function of emission temperature:

$$L_\nu(\nu_{mL}) \approx (2.5765)10^{-19}\ T^2 \quad \text{J/m}^2\cdot\text{sr}\cdot\text{K}^3 \qquad \textbf{(C.24)}$$

Thus, the frequency of the BB entropy peak is about 10% lower than the BB energy peak.

By substituting (C.21) into (C.22) we find that the locus of the peaks for the family of BB energy spectrums is given by

$$K_\nu = \frac{ph}{c^2}\frac{\nu^3}{e^{2.82144}-1} \approx (9.319)10^{-52}\ \nu^3 \quad \text{J·s}^3/\text{m}^2\text{·sr} \qquad \textbf{(C.25)}$$

Similarily, the locus of peaks for the BB entropy spectrums is:

$$L_\nu \approx (9.220)10^{-41}\ \nu^2 \quad \text{J·s}^2/\text{m}^2\text{·sr·K} \qquad \textbf{(C.26)}$$

The locus of BR energy (C.25) and entropy (C.26) peaks can be used to estimate the envelop for TR. This allows the validity of measured or calculated data to be verified; for each frequency the approximate maximum allowable values for K_ν and L_ν are given by (C.25) and (C.26).

The blackbody energy spectrum asymptotically approaches zero on both the low and high frequency sides. For determining spectrum overlap it is useful to describe cutoff points where the spectral radiance is a certain fraction n of the peak value:

$$K_\nu(\nu_{cutoff}) = n\ K_\nu(\nu_m) \qquad \textbf{(C.27)}$$

The low frequency cutoff of the spectrum is ν_L, and the high frequency cutoff is ν_H.

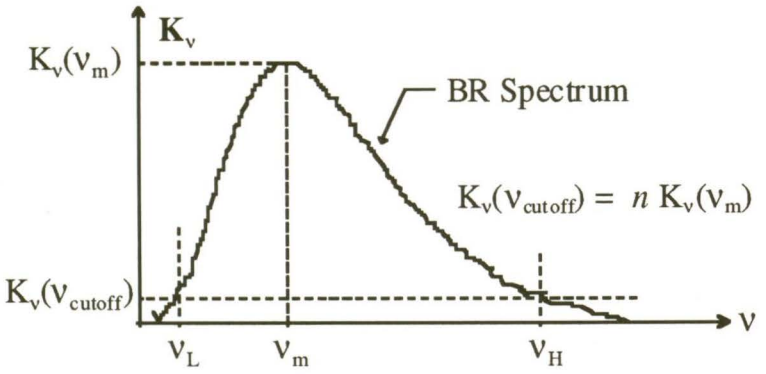

Figure C-3: Low and high frequency cutoff points for the BB spectrum.

Like any characteristic location in the energy spectrum, the frequencies ν_L and ν_H vary linearly with temperature, $\nu_L = g_L T$ and $\nu_H = g_H T$ where g_L and g_H are new constants that depend on the cutoff limit given by n. The following table shows the g constants for various n values.

Table C-1: Cutoff constants for BR.

n	g_L	g_H
0.01	$(2.5488)10^9$	$(2.4205)10^{11}$
0.05	$(5.9445)10^9$	$(1.9504)10^{11}$
0.10	$(8.7073)10^9$	$(1.7318)10^{11}$
0.25	$(14.942)10^9$	$(1.4148)10^{11}$
0.50	$(23.931)10^9$	$(1.1315)10^{11}$

* The units of g are $s^{-1}K^{-1}$

C.5 The "Shape" of TR Energy Spectrums

The dimensionless shape of the blackbody spectrum is found by defining the variable $\hat{\upsilon}$ that is the ratio of frequency ν to the frequency ν_{mK} of the peak of the BR energy spectrum:

$$\hat{\upsilon} \equiv \frac{\nu}{\nu_{mK}} \tag{C.28}$$

The shape of the BR energy spectrum is then given by the function $\varphi(\hat{\upsilon})$

$$\varphi(\hat{\upsilon}) \equiv \frac{K_\nu(\nu)}{K_\nu(\nu_{mK})} \tag{C.29}$$

Thus using equation (2.2) we have

$$\varphi(\hat{\upsilon}) = \frac{K_\upsilon(\upsilon)}{K_\upsilon(\upsilon_{mK})} = \frac{\upsilon^3}{\upsilon_{mK}^3}\frac{e^{\frac{h\upsilon_{mK}}{kT}}-1}{e^{\frac{h\upsilon}{kT}}-1} \approx (\hat{\upsilon})^3\frac{e^{2.821439}-1}{e^{2.821439(\hat{\upsilon})}-1} \approx \frac{(15.801)\,(\hat{\upsilon})^3}{e^{2.821439(\hat{\upsilon})}-1} \tag{C.30}$$

Note that GR has the same shape as the black body spectrum. To determine the dimensionless shape of a NBR spectrum consider the unique K_ν emission spectrum at some emission temperature T as shown in Figure C-4.

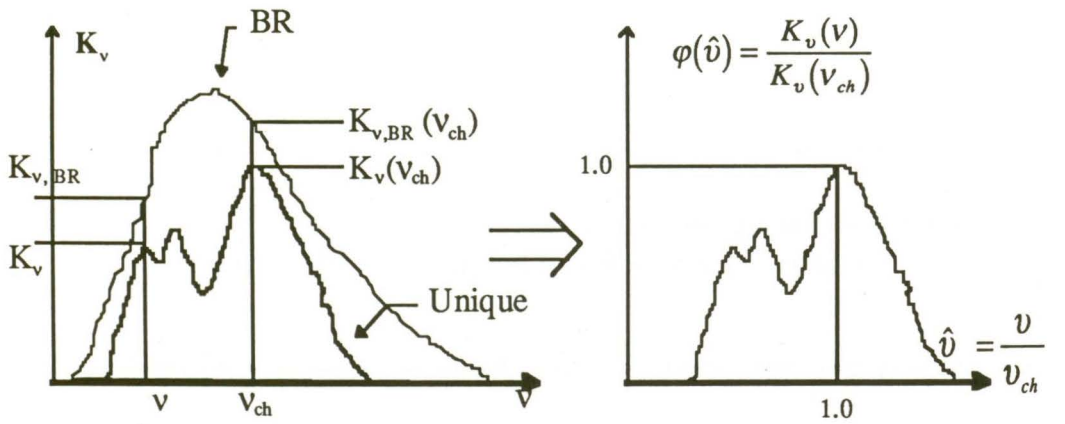

Figure C-4: Non-dimensionalizing the shape of a unique thermal spectrum

For this type of spectrum we define the variable $\hat{\upsilon}$ as the ratio of the frequency ν to the frequency ν_{ch} of some chosen characteristic location in the energy spectrum

$$\hat{\upsilon} \equiv \frac{\nu}{\nu_{ch}} \tag{C.31}$$

and the function $\varphi(\hat{\upsilon})$ as the ratio of $K_\nu(\nu)$ to $K_\nu(\nu_{ch})$:

$$\varphi(\hat{\upsilon}) \equiv \frac{K_\nu(\nu)}{K_\nu(\nu_{ch})} \tag{C.32}$$

Note that if the chosen characteristic location is the peak of the unique spectrum, as indicated in figure C-4, then we have $0 \leq \varphi(\hat{\upsilon}) \leq 1$.

If the shape $\varphi(\hat{\upsilon})$ of the unique spectrum is independent of temperature, that is if it retains geometric similarity and relative size with respect to BR with temperature as shown in Figure C-5, then the energy and entropy radiances are simple functions of temperature (section 4.2).

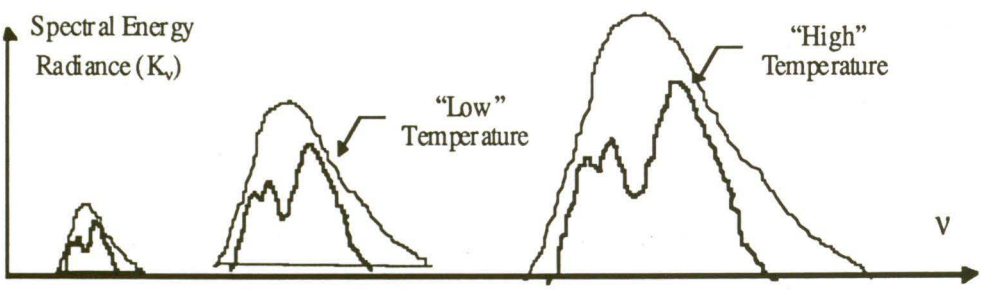

Figure C-5: A unique thermal spectrum that retains geometric similarity and relative size with respect to BR with temperature.

The relative size of a unique spectrum with respect to the BR spectrum is given by

$$b = \frac{K_\upsilon(\upsilon_{ch})}{K_{\upsilon,BR}(\upsilon_{ch})} \tag{C.33}$$

Note that for gray radiation b is equal to the emissivity (ε).

C.6 Dimensionless BR Energy and Entropy Spectrums

In section C.5 a dimensionless form of the BR energy spectrum was presented. However, the method used there is not easily applied to the entropy spectrum. In this section dimensionless forms of the BR energy and entropy spectrums are obtained in a manner similar to Beretta and Gyftopoulos [10].

By defining the dimensionless groups

$$X_{BB} = \frac{h}{kT}\upsilon \qquad y_{BB} = \frac{h^2c^2}{k^3T^3}K_\upsilon \qquad z_{BB} = \frac{h^2c^2}{k^3T^2}L_\upsilon \tag{C.34}$$

we obtain the dimensionless BR energy and entropy spectrums

$$y_{BB} = \frac{X_{BB}^3}{e^{X_{BB}} - 1} \qquad \text{and} \qquad z_{BB} = \frac{X_{BB}^2}{e^{X_{BB}} - 1} \ln\left[\frac{\left[e^{X_{BB}}\right]^{\left(e^{X_{BB}}\right)}}{\left[e^{X_{BB}} - 1\right]^{\left(e^{X_{BB}} - 1\right)}}\right] \tag{C.35}$$

where x_{BB} represents the *frequency*, y_{BB} the spectral *energy* radiance, and z_{BB} the spectral *entropy* radiance. The y_{BB} energy (lower spectrum) and the z_{BB} entropy (upper spectrum) are shown in Figure C-6.

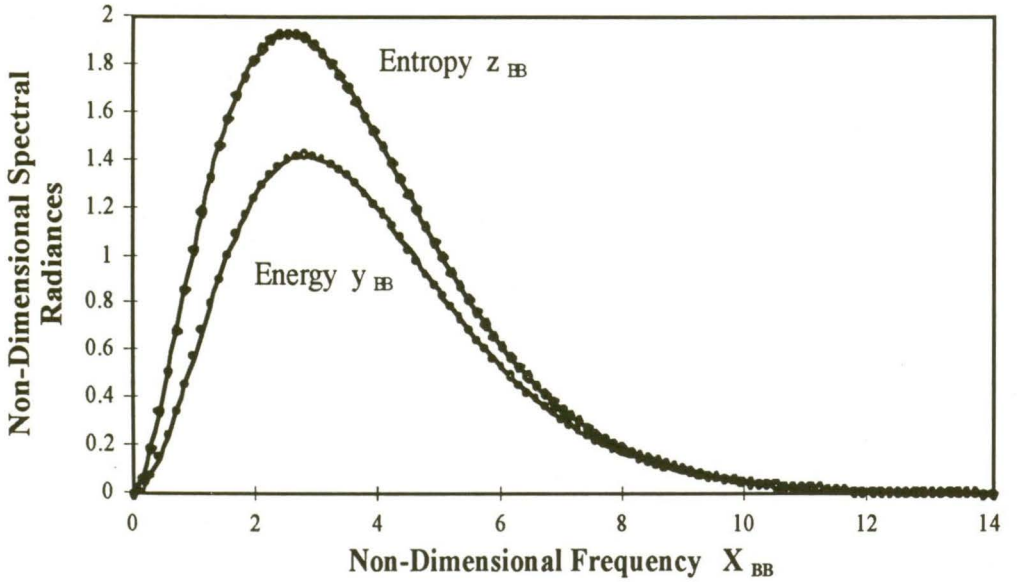

Figure C-6: The dimesionless BR energy (y_{BB}) and entropy (z_{BB}) spectrums.

The peak of the entropy plot is at slightly lower frequency than the peak of the energy spectrum (see section C.4). This is due to the fact that the spectral entropy-to-energy ratio is higher at lower frequencies.

Note that the dimensionless form for the BR energy spectrum presented here are related to the one presented in section C.5 by

$$\varphi(\hat{v}) = \frac{e^{\frac{h\upsilon_m}{kT}} - 1}{\left(\frac{h\upsilon_m}{kT}\right)^3} y_{BB} \approx (+0.70351)\ y_{BB} \qquad \textbf{(C.36)}$$

and

$$\hat{v} = \frac{kT}{h\upsilon_m} x_{BB} \approx (+0.35443)\ x_{BB} \qquad \textbf{(C.37)}$$

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