On the entropy of radiative heat transfer in engineering thermodynamics

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Abstract

The objective of this paper is to improve the understanding and also to simplify the calculation of the entropy transferred by thermal radiation (TR). Many thermodynamic texts incorrectly imply that the entropy flux of TR is the same as that for heat conduction, the heat flux divided by the local temperature (q/T). Also, fundamental equations, such as those derived from the Clausius inequality, express the entropy flux of TR in a q/T type form. However, for blackbody radiation (BR) emission a 4/3 factor is present and in this paper it is shown that the entropy flux of non-blackbody radiation (NBR) emission is even farther removed from q/T. The misuse of the heat conduction entropy flux equation for TR emission causes the irreversibility of a device to be underestimated whether the surface of the device is hot or cold relative to its surroundings. Further, it is shown that the reversible form of the Clausius expression applies when TR is involved yet the expression for irreversible processes does not apply. Finally, simple approximate expressions for the entropy of gray radiation (GR) are presented, as the exclusive use of numerical integration is laborious. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

All matter emits thermal radiation (TR) continuously as a result of its temperature. Thus, TR is an inherent part of our environment and it is an important factor in the thermodynamic analysis of many systems such as solar collectors, boilers and furnaces, spacecraft cooling systems, and

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Nomenclature

A	surface area (m^2)
c	speed of light $= 2.9979 \times 10^8$ m/s
ε	emissivity for gray radiation (GR)
k	Boltzmann's constant $= 1.38 \times 10^{-23}$ J/K
h	Planck's constant $= 6.626 \times 10^{-34}$ J s
$I(\varepsilon), m$	functions in (7) and (27)
$\dot{m}$	mass flow rate (kg/s)
$n(\varepsilon)$	coefficient in (11)
$\Theta(\varepsilon)$	function in (33)
$p(\varepsilon)$	function in (34)
p	state of polarization in (1) and (2)
q	heat flux (W/m^2)
$đQ$	infinitesimal heat transfer (J)
$\dot{Q}$	net heat transfer rate (W)
S	entropy of the system (J/K)
$\dot{S}$	net entropy transfer rate (W/K)
s	specific entropy per unit mass (J/kg K)
T	material emission temperature (K)
v	frequency (s^{-1})
x	non-dimensional group, hv/kT
σ	Stefan–Boltzmann constant $= (5.67)10^{-8}$ W/m^2 K^4
π	mathematical constant, 3.14159...
Π	entropy production (J/K)
$\dot{\Pi}$	entropy production rate (W/K)

cryogenic systems. However, thermodynamic texts are often misleading in stating that the entropy flux of 'heat' transfer is the ratio of the heat flux to the local temperature (q/T) with no restriction for TR (e.g. [1, p. 256 and 266; 2, p. 223; 3, p. 177]). It is well known in the fields of physics and solar engineering that the entropy flux for TR emission is not calculated in the same way as for heat conduction. For blackbody radiation (BR) emission the entropy flux is 4/3 times the energy flux divided by the emission temperature, while numerical integration is required to determine the entropy of non-blackbody radiation (NBR). In addition, some of the fundamental equations that are used in thermodynamics express the entropy flux of heat transfer in a q/T form.

In the present work our purpose is to:
1. determine the error that is introduced in second law analysis when the heat conduction relation is used for TR transfer;
2. obtain simple approximate expressions for calculating the entropy of gray radiation (GR) emission, as the exclusive use of numerical integration is laborious;
3. determine the q/T type relation for the NBR emission entropy flux, and
4. investigate whether the Clausius equality, and expressions extended from it for irreversible processes, are applicable when TR is involved.

Second-law analysis provides important understanding of thermal and chemical energy systems that cannot be obtained from energy analysis. The authors believe that the results of this research can help us to better model, analyze, design and optimize systems where TR is important.

2. Background

2.1. Planck's spectral energy and entropy formulas

The energy and entropy of unpolarized [1] TR is correctly calculated using the spectral energy and entropy expressions derived by Planck [4] using equilibrium statistical mechanics:

$$K_v = \frac{ph}{c^2} \frac{v^3}{e^{hv/kT} - 1},$$

(1)

and

$$L_v = \frac{pkv^2}{c^2} \left\{ \left(1 + \frac{c^2 K_v}{phv^3} \right) \ln \left[1 + \frac{c^2 K_v}{phv^3} \right] - \left(\frac{c^2 K_v}{phv^3} \right) \ln \left[\frac{c^2 K_v}{phv^3} \right] \right\},$$

(2)

where $p = 2$ for unpolarized TR and $p = 1$ for plane polarized TR. Eq. (1) expresses the spectral energy radiance of BR, i.e., the energy flow rate per unit frequency, area, and solid angle. A plot of K_v versus frequency v for various values of temperature T gives a family of BR energy spectra. Upon substituting (1) into (2) one obtains a family of BR entropy spectra. For arbitrary TR, the entropy spectrum is found by substituting K_v data, rather than (1) for BR, into (2). The energy K and entropy L radiance of any TR spectrum can be calculated by integrating K_v and L_v over frequency, respectively. That is, the energy radiance K and entropy radiance L are the area under the K_v and L_v spectrums, respectively (Table 1).

Recently, Landsberg and Tonge [5] used a non-equilibrium statistical mechanics approach to obtain the same result as Planck. They concluded [2] "This result, usually obtained from equilibrium statistical mechanics, is therefore of wider significance and represents a non-equilibrium entropy."

2.2. The entropy flux of thermal radiation

The energy spectrum of TR emitted from a solid depends on the nature of the emitting material and its temperature. Some materials can be adequately approximated as blackbody (BB) or graybody while others with a unique spectrum cannot.

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[1] For simplicity it is assumed in this paper that the TR is unpolarized ($p = 2$).
[2] Two assumptions were specified for this result to be exact: (1) the probability of finding N_j bosons in quantum state j is independent of the occupation numbers 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.

Table 1
TR energy and entropy nomenclature

	Energy		Entropy	
	Symbol	Units	Symbol	Units
Flow rate	$\dot{E}$	W	$\dot{S}$	W/K
Irradiance	H	(W/m^2)	J	W/K m^2
Radiance	K	W/m^2 sr	L	W/K m^2 sr
Spectral radiance	K_v	J/m^2 sr	L_v	J/K m^2 sr
Dimensionless spectral radiance	y_v	–	z_v	–

For BR equations (1) and (2) can be integrated over frequency and solid angle to obtain the energy and entropy irradiances (fluxes), respectively

$$H_{\mathrm{BR}} = \pi K_{\mathrm{BR}} = \sigma T^4, \qquad J_{\mathrm{BR}} = \pi L_{\mathrm{BR}} = \frac{4}{3}\sigma T^3, \tag{3}$$

where $\sigma = 2\pi^5 k^4/15c^2h^3$ is the Stefan–Boltzmann constant. Note that irradiances H and J are the integration of the radiances K and L over solid angle and have the units of energy or entropy flow rate per unit area, respectively.

To compare the entropy flux of BR emission to that of heat conduction we can express the entropy irradiance as

$$J_{\mathrm{BR}} = \frac{4}{3}\frac{H_{\mathrm{BR}}}{T}. \tag{4}$$

Note that TR transfer is generally a net transfer between incident, reflected, and emitted TR but in (4) we are considering TR emission alone.

By definition, the spectral energy irradiance for isotropic GR emission is

$$H_{\mathrm{GR}} = \pi K_{\mathrm{GR}} = \varepsilon\sigma T^4. \tag{5}$$

However, the entropy is not as easily calculated because the spectral entropy is not a linear function of the spectral energy. For GR the entropy irradiance is

$$J_{\mathrm{GR}} = \pi L_{\mathrm{GR}}$$
$$= \frac{2\pi k^4}{c^2 h^3} T^3 \int_0^\infty x^2 \left\{ \left(1 + \frac{\varepsilon}{e^x - 1}\right) \ln\left(1 + \frac{\varepsilon}{e^x - 1}\right) - \left(\frac{\varepsilon}{e^x - 1}\right) \ln\left(\frac{\varepsilon}{e^x - 1}\right) \right\} \mathrm{d}x, \tag{6}$$

where $x = hv/kT$. The entropy of GR (6) is a simple cubic function of the material emission temperature. This is also true of any TR emission that has an energy spectrum with a fixed shape independent of emission temperature [6]. The definite integral in (6) is a function of ε only and is called $I(\varepsilon)$ here, but was first recognized by Landsberg and Tonge [7] as $\varepsilon X(\varepsilon)4\pi^4/45$. Thus, we have

$$J_{\mathrm{GR}} = \frac{45}{4\pi^4} I(\varepsilon) J_{\mathrm{BR}} = \frac{45}{4\pi^4} I(\varepsilon) \frac{4\sigma}{3} T^3. \tag{7}$$

The integral $I(\varepsilon)$ has not been solved in closed form. Stephens and Obrien [8] presented an infinite series solution and Landsberg and Tonge [7] presented the approximate limiting solution for $\varepsilon < 0.10$

$$X(\varepsilon) \approx 0.9652 - 0.2777 \ln \varepsilon + 0.0511\varepsilon. \tag{8}$$

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

3. Analysis and results

3.1. Comparison of the entropy flux of TR emission and heat conduction

For heat conduction the entropy flux is the ratio of the heat flux and the local temperature (q/T). For TR 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, the entropy balance equation for a control volume (CV) is stated in textbooks as

$$\frac{\mathrm{d}S_{\mathrm{CV}}}{\mathrm{d}t} = \int_{\mathrm{CV\ boundary}} \frac{q}{T_{\mathrm{b}}} \, \mathrm{d}A + \sum_i \dot{m}_i s_i + \dot{\Pi}_{\mathrm{CV}}, \tag{9}$$

where S_{CV} is the entropy in the CV, T_{b} is the temperature at the boundary of the CV where heat flux q occurs, $\dot{m}_i$ is the mass flow rate into the system at port i ($\dot{m}_i < 0$ for mass flows out of the system), s_i is specific entropy per unit mass for flow i, and $\dot{\Pi}_{\mathrm{CV}}$ is entropy production rate in the CV. However, the entropy balance equation is correctly stated as

$$\frac{\mathrm{d}S_{CV}}{\mathrm{d}t} = \int_{\mathrm{CV\ boundary}} \left[\frac{q_{\mathrm{cc}}}{T_{\mathrm{b}}} + J_{\mathrm{Net}} \right] \mathrm{d}A + \sum_i \dot{m}_i s_i + \dot{\Pi}_{\mathrm{CV}}, \tag{10}$$

where J_{Net} is the net entropy flux (irradiance) of TR alone and q_{cc} is the heat flux by conduction or convection [3]; $q = q_{\mathrm{cc}} + H_{\mathrm{Net}}$, where H_{Net} is the net energy flux of TR.

To compare the entropy flux of isotropic [4] TR emission to that of heat conduction one may express the entropy flux as

$$J_{\mathrm{Emi}} = n\left(\frac{H_{\mathrm{Emi}}}{T} \right), \tag{11}$$

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[3] Note that the empirical surface coefficient of heat transfer is often a combination of convective and radiative transfer.

[4] Isotropy is specified so that we can consider fluxes (irradiances), rather than radiances, in a simple manner.
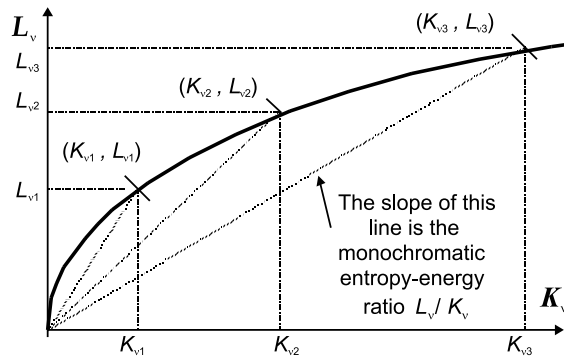
Fig. 1. Spectral entropy radiance L_v versus energy radiance K_v.

where n is dependent on the character [5] of the TR and the subscript Emi denotes emission. For the BR [6] expression (4) the coefficient n in (11) is equal to 4/3. However, the coefficient n for NBR is greater than 4/3. This means that the entropy flux of NBR emission is farther removed from q/T than that of BR emission. In other words, BR has a minimum ratio of entropy to energy for all TR with the same emission temperature. This conclusion may appear to violate the second-law of thermodynamics because BR is equilibrium TR and is thus associated with a state of maximum entropy.

The fact that BR has a minimum value of n can be proven by considering the functional dependence of Planck's spectral entropy radiance (2). The spectral entropy radiance expression can be non-dimensionalized as

$$z_v = (1 + y_v) \ln (1 + y_v) - y_v \ln (y_v), \tag{12}$$

where the non-dimensional spectral entropy and energy radiances, respectively, are

$$z_v = \frac{c^2}{pkv^2} L_v, \quad y_v = \frac{c^2}{phv^3} K_v. \tag{13}$$

Stability for a radiation system in equilibrium with a material enclosure requires that the L_v function is concave and monotonically increasing. This means that the slope of $L_v = L_v(K_v)$ is always positive, but decreasing in magnitude, as K_v increases (see Fig. 1). This expectation can be verified by examining the first and second derivatives of L_v with respect to K_v. The strictly positive slope (monotonically increasing) simply means that an increase in energy always results in an

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[5] The coefficient n is only a constant independent of emission temperature if the shape of the NBR energy spectrum is invariant within the temperature range of interest [6]. This condition is by definition satisfied for BR and GR.

[6] The occurrence of the 4/3 coefficient for BR entropy is evident from theoretical derivations but has not been explained physically. However, the 4/3 coefficient can be viewed as a direct consequence of the experimentally observable relation between BR energy and emission temperature, which is energy is proportional to T^4 [9]. This can be straightforwardly shown from equilibrium considerations without involving Planck's entropy formula (2) or Maxwell's radiation pressure.

increase in entropy. The decreasing slope with increasing energy (concave) means that the same increase in energy results in a higher increase in entropy at a lower temperature. This is simply the second law consequence of the fact that heat flows from a hot BR system to a cold one.

As can be seen in Fig. 1, the spectral entropy-to-energy ratio L_v/K_v increases as K_v decreases. For a given material emission temperature, a blackbody emits the maximum energy at each frequency. Thus, the blackbody curve encloses all other thermal emission spectrums emitted from materials with the same temperature. This means L_v/K_v is lower at each frequency and thus L/K is a minimum for BR. This result shows that, although BR represents the maximum possible energy and entropy, it has the minimum ratio of entropy to energy of all TR with the same emission temperature.

The entropy of GR can be chosen to illustrate that the coefficient n for NBR is greater than the value of 4/3 for BR. Using (7) the coefficient n in (11) for GR is

$$n = \frac{4}{3}\left(\frac{45}{4\pi^4}\right)\frac{I(\varepsilon)}{\varepsilon}. \tag{14}$$

Using (28) for $I(\varepsilon)$ this result becomes

$$n = \frac{4}{3}\left(1 - \frac{45}{4\pi^4}m\ln\varepsilon\right). \tag{15}$$

Fig. 2 illustrates the function $n(\varepsilon)$ using the approximation $m = 2.311 - 0.175\varepsilon$ listed in Table 2. For GR the coefficient n increases as emissivity decreases. For example, n reaches 1.5 for $\varepsilon = 0.60$ and $n = 2.0$ for $\varepsilon = 0.15$. Thus, the entropy flux of NBR emission can be much greater than that given by using the relation for heat conduction (q/T).

The fact that the value of n for NBR is greater than that for BR appears to violate the second law of thermodynamics because BR is associated with a state of maximum disorder or entropy. The equilibrium condition for an enclosed TR system is that of BR at the temperature of the enclosure independent of the radiative character of the enclosure material. This means that for a
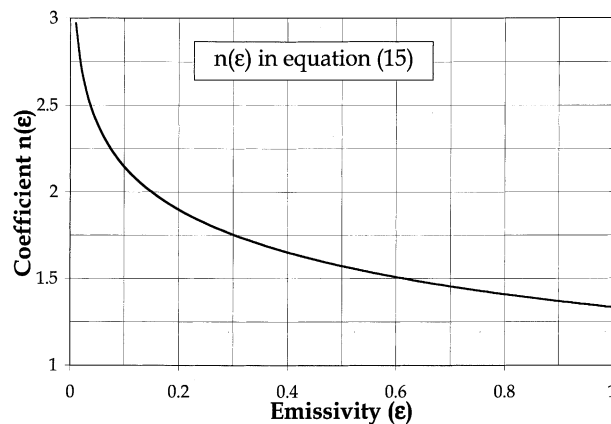

Fig. 2. The coefficient $n(\varepsilon)$ for GR.

Table 2
Accuracy of the approximation for the entropy of GR for two cases: $m = C_1$ and $m = C_2 - C_3\varepsilon$

Emissivity range	Case 1		Case 2		
	C_1	Max. error (%)	C_2	C_3	Max. error (%)
0.005–0.200	2.319	0.72	2.336	0.260	0.33
0.005–1.0	2.317	0.77	2.336	0.260	0.33
0.010–1.0	2.310	0.71	2.328	0.200	0.33
0.050–1.0	2.285	0.49	2.311	0.175	0.16
0.200–1.0	2.319	0.23	2.292	0.150	0.03

certain amount of energy the BR distribution has the maximum entropy. Planck [4, p. 88] states 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". However, Planck's statement refers to the spectral distribution of a certain amount of energy, rather than comparing BR and NBR emitted from materials with the same temperature and thus different energy.

Fig. 3 illustrates the BR and NBR spectrums at the same emission temperature, T_{High}, and the BR spectrum at temperature T_{Low} that has the same energy as the NBR spectrum at T_{High}. Note that the area under the K_ν spectrum gives the energy radiance K.

In conclusion, the ratios of entropy to energy for the three spectrums in Fig. 3 may be expressed as a continued inequality

$$\left(\frac{J}{H}\right)_{BR@\ T_{Low}} > \left(\frac{J}{H}\right)_{NBR@\ T_{High}} > \left(\frac{J}{H}\right)_{BR@\ T_{High}}. \tag{16}$$
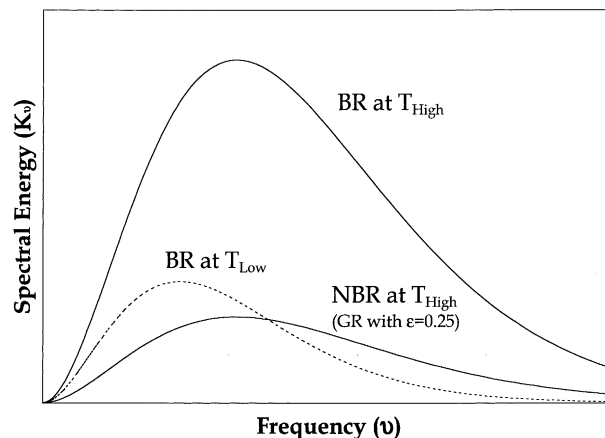
Fig. 3. Illustration of several TR spectrums.

Case A: Hot Device   Case B: Cold Device

$J_r > q_r/T$ q_r Gas $J_r < q_r/T$
Interaction
Region
$J_r = q_r/T$ (solid) $J_r = q_r/T$
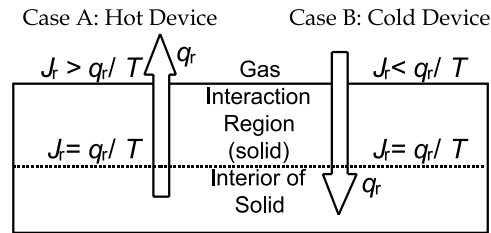Interior of q_r
Solid

Fig. 4. Net radiation entropy flux at a solid surface.

3.2. Implications for second law analysis with TR transfer

The results in Section 3.1 show that the error introduced can be severe when the entropy flux of TR emission is incorrectly understood to be q/T. However, in general the entropy transfer by TR from the surface of a device is a net transfer due to incident, reflected, and emitted TR fluxes. This complicates error analysis because of the large number of combinations between incident TR character, material character, and material temperature.

Error analysis is further complicated because the emitted and reflected entropy fluxes are generally not independent. TR entropy has a non-linear dependence on energy and the emitted and reflected fluxes are both outgoing fluxes, so if these energy spectrums overlap then the entropy is not independent. Consequently, for the sake of simplicity we will consider only qualitatively the error that occurs in the calculated entropy production rate for a device when the heat conduction relation q/T is used for TR transfer.

Consider TR transfer from the external surface of an energy conversion device at steady state. Fig. 4 shows cases where the device is both hot, and where it is cold, relative to its immediate surroundings. Note that J_r and q_r in Fig. 4 are the magnitudes of the *net* entropy and energy fluxes, respectively. The chosen thermodynamic boundary of the system encloses the device and is located immediately adjacent to its outer surface. Now consider an area on the surface of the device that is an opaque [7] solid and where the surroundings are in the gaseous state.

Both "convection" (q_c) and TR transfer (q_r) occur at the system boundary. Radiative transfer q_r is likely to be a significant portion of the total q when there are gases or a vacuum involved, such as when a solid–gas or a solid–vacuum interface exists at the system boundary. When q_r is nonzero there is entropy production due to radiation–matter interaction ($\dot{\Pi}_{RM}$) as can be determined by an entropy balance using Planck's spectral entropy radiance (2). This entropy production occurs in 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 TR. For

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[7] Opaque to the particular incident thermal radiation.

simplicity the thermal conductivity is large so that the temperature [8] in the interaction region is approximately uniform.

In both hot and cold cases the entropy flux q_r/T occurs at the lower boundary of the interaction region where heat transfer is simply heat conduction. So, when the entropy flux of the TR is taken as q_r/T, the entropy production within the interaction region of the system is neglected. Thus, we can conclude that the irreversibility (energy destruction rate) of the device is always underestimated whether the device is hot or cold relative to its surroundings.

3.3. The Clausius statement of the second law

Some of the fundamental equations that are used in thermodynamics express the entropy flux as the heat transfer divided by the local temperature. However, as we have seen in Section 3.1 this relation does not hold for TR emission. In this section we consider the implications of this observation for the Clausius equality and expressions derived from it for irreversible processes.

The Clausius inequality for a cycle,

$$\oint \frac{\mathrm{d}Q}{T} \leqslant 0, \tag{17}$$

is a consequence of the second law of thermodynamics. In (17) $\mathrm{d}Q$ represents an infinitesimal heat transfer to the system at the boundary where the temperature is T. The integration is carried out over the entire boundary and over a complete cycle. Physically, the Clausius inequality can be interpreted as the net transfer of entropy out of the system is positive over the cycle for real processes, and zero for reversible processes. If instead we look at a portion of the cycle, say between equilibrium states 1 and 2, then this inequality can be re-stated as

$$\Delta S_{12} \geqslant \int_1^2 \frac{\mathrm{d}Q}{T}. \tag{18}$$

The change in entropy of a closed system between two equilibrium states is greater than or equal to what can be accounted for due to entropy transfer by heat flow into the system during the process. This statement implies that entropy production during the process must be positive, or zero if the process is reversible

$$\Pi = \Delta S_{12} - \int_1^2 \frac{\mathrm{d}Q}{T} \geqslant 0. \tag{19}$$

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[8] Strictly speaking the temperature in the interaction region is not uniform. So it may be argued that the emission temperature and the temperature at the inner boundary of the interaction region are not strictly equal. However, the temperature variation is very small because (1) the interaction region is usually very thin, e.g. on the order of a few micrometers for metals, and (2) the temperature gradient decreases to zero at the surface of the solid because heat conduction decreases to zero at the surface. Furthermore, in a theoretical sense the temperature difference can be made arbitrarily small by specifying a sufficiently large thermal conductivity.
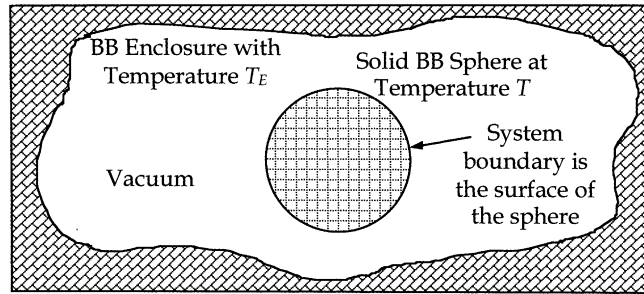
Fig. 5. Solid BB sphere system.

In all these statements the entropy transfer is expressed as the heat transfer divided by the local temperature. To determine the applicability of these equations when TR is involved, consider a system consisting of a solid isothermal BB sphere (see Fig. 5). The solid sphere is contained in a vacuum so the only form of heat transfer is by TR.

First, consider a quasi-static reversible energy transfer between the system and an enclosure with blackbody characteristics. Note that the shape of the enclosure does not influence the analysis because of its BB character (isotropic TR with no reflections). For reversible BR transfer, the temperature difference between the system and the enclosure must be infinitesimal. The *net* heat transfer rate is

$$\dot{Q}_{net} = 4\pi R^2 \sigma \left\{ (T + \Delta T)^4 - (T)^4 \right\}, \tag{20}$$

where R is the radius of the sphere and the temperature of the enclosure T_E is equal to $T + \Delta T$. For an infinitesimal temperature difference ΔT becomes a differential dd and terms of higher order can be neglected:

$$\dot{Q}_{net} = 4\pi R^2 \sigma \left\{ 4T^3 \, dT \right\}. \tag{21}$$

Similarly, using (3) the *net* entropy transfer rate at the system boundary is

$$\dot{S}_{net} = 4\pi R^2 \frac{4\sigma}{3} \left\{ (T + dT)^3 - (T)^3 \right\} = 4\pi R^2 \frac{4\sigma}{3} \left\{ 3T^2 \, dT \right\}. \tag{22}$$

The entropy transfer rate given by (22) is equal to the energy transfer expressed in (21) divided by the temperature T. Thus, the Clausius expression for reversible processes is valid when TR is involved. This occurs because for reversible energy transfer there is no entropy production so the entropy transfer by heat conduction (q/T) in the solid is equal to the net entropy transfer by the TR.

Now consider irreversible TR transfer between the system and its enclosure when the temperature difference is not infinitesimal. The net energy transfer rate to the system at the system boundary is

$$\dot{Q}_{net} = 4\pi R^2 \sigma \left\{ T_E^4 - T^4 \right\}, \tag{23}$$

where T_E is the temperature of the enclosure. Similarly, the net entropy transfer rate at the system boundary is

$$\dot{S}_{net} = 4\pi R^2 \frac{4\sigma}{3} \left\{ T_E^3 - T^3 \right\}.$$

(24)

The net energy transfer rate in (23) divided by the temperature T is

$$\frac{\dot{Q}_{net}}{T} = 4\pi R^2 \sigma \left\{ \frac{T_E^4}{T} - T^3 \right\}.$$

(25)

The entropy fluxes given by (24) and (25) are clearly not equal. Eq. (25) actually represents the entropy flux by heat conduction at the inner boundary of the interaction region, whereas (24) represents the entropy flux by TR transfer at the surface (system boundary). These two entropy fluxes are not equal because entropy production occurs in the interaction region.

Thus, in (18) đQ/T represents the entropy transfer at the interaction region boundary rather than the system boundary. Mathematically (18) is valid but from a thermodynamic perspective it is insufficient. In this context (18) states that the rate of entropy change must be greater than the entropy transfer rate into the system at the interaction region boundary. It would be more precise if (18) stated that the rate of entropy change must be greater than the entropy transfer rate into the system at the system boundary. To make this statement however, the entropy transfer cannot be specified as đQ/T.

However, careful examination of (19) reveals that this equation is incorrect in a thermodynamic sense. When this equation is applied to our illustration, the entropy production rate calculated is only due to heat conduction within the solid excluding the interaction region. The total entropy production includes the entropy production in the interaction region, which can be a large fraction of the total. For (19) to give the total entropy production rate as expected, the entropy transfer rate at the system boundary must be evaluated correctly. Thus, it must be either specified that the heat transfer does not include TR exchange, or the entropy transfer must not be given as đQ/T in (18) and (19).

3.4. Approximations for the entropy of NBR

The entropy of GR (6) is a cubic function of the emission temperature, where the value of the integral $I(\varepsilon)$,

$$I(\varepsilon) = \int_0^\infty x^2 \left\{ \left(1 + \frac{\varepsilon}{e^x - 1} \right) \ln \left(1 + \frac{\varepsilon}{e^x - 1} \right) - \left(\frac{\varepsilon}{e^x - 1} \right) \ln \left(\frac{\varepsilon}{e^x - 1} \right) \right\} dx,$$

(26)

can be determined using numerical integration once given the emissivity ε. However, attempts at finding a closed-form solution for $I(\varepsilon)$ suggest using the approximation

$$I(\varepsilon) \approx \varepsilon \{ a - m \ln \varepsilon \},$$

(27)

which reduces to the correct result at $\varepsilon = 1$ (BR) if the constant a is chosen as $4\pi^4/45$,

$$I(\varepsilon) \approx \varepsilon \left\{ \frac{4\pi^4}{45} - m \ln \varepsilon \right\}. \tag{28}$$

Any value for m in (28) satisfies the requirement that at an emissivity of zero (no TR) the entropy flux reduces to zero,

$$I(0) = \left[\lim_{\varepsilon=0} (-\varepsilon \ln \varepsilon) \right](m) = [0]m = 0. \tag{29}$$

The value for m can be chosen such that the approximation (28) reduces to zero at the same rate as (26) as ε decreases to zero,

$$m = \int_0^\infty \frac{x^2}{e^x - 1} \, dx = 2\zeta(3) = 2.4041\ldots, \tag{30}$$

where ζ is the Riemann–Zeta function. However, the approximate expression (28) is least accurate near $\varepsilon = 0$. So choosing m such that it is precise at $\varepsilon = 0$, that is $m = 2\zeta(3)$, results in a relatively inaccurate expression over the range of emissivity; within 1.9% over $0 \leqslant \varepsilon \leqslant 1$.

For improved accuracy, the optimum value for m can be determined for narrower emissivity ranges; for example, $m = 2.317$ for the emissivity range $0.005 \leqslant \varepsilon \leqslant 1$ which is within 0.77%, or $m = 2.319$ for $0.200 \leqslant \varepsilon \leqslant 1$ which is within 0.23%. The optimal value for m is chosen by using numerical integration data from (26). The percentage error caused by using (28) is calculated as a function of emissivity. "Best choice" of the parameter m refers to the solution that results in the lowest maximum percent error in $I(\varepsilon)$ over the specified emissivity range.

A more accurate expression (28) is obtained for any particular emissivity range if m is approximated as a linear function of emissivity; such as $m = -0.150\varepsilon + 2.292$ for $0.200 \leqslant \varepsilon \leqslant 1$ which is within 0.03%. Table 2 shows the maximum percent error in the entropy calculation for various emissivity ranges, for two cases $m = C_1$ and $m = C_2 - C_3\varepsilon$.

Alternatively, the entropy radiance of any NBR can be approximated as that of BR with the same energy radiance,

$$J_{\mathrm{NBR}} \approx \frac{4}{3} \sigma^{1/4} H_{\mathrm{NBR}}^{3/4}. \tag{31}$$

The justification for using this approximation can be seen by considering the entropy change during a spontaneous transition of an isolated NBR system to BR with the same energy. As a consequence of the second law of thermodynamics the entropy must increase during the transition. Thus, the entropy of BR with the same energy as given in (31) is always an overestimate of the NBR entropy. However, the percent increase in entropy during such a transition, and thus the percent that the NBR entropy is overestimated by (31), can be relatively small.

The accuracy of the approximation in (31) can be illustrated by considering GR as an example of NBR. While the entropy of GR is given by (6) and (7), the approximation in (31) for GR is

$$J_{\mathrm{GR}} \approx \frac{4}{3} \sigma \varepsilon^{3/4} T^3. \tag{32}$$

The error in using (32), i.e. the amount by which the GR entropy (7) is overestimated, is on a percentage basis

$$\Theta(\varepsilon) = \frac{(4\sigma/3)\varepsilon^{3/4}T^3 - J_{\mathrm{GR}}}{J_{\mathrm{GR}}}(100\%) = \frac{p(\varepsilon)}{(45/4\pi^4)I(\varepsilon)}(100\%), \tag{33}$$

where $p(\varepsilon)$ is proportional to the entropy production during a spontaneous transition to BR with the same energy, i.e.,

$$p(\varepsilon) = \varepsilon^{3/4} - \frac{45}{4\pi^4}I(\varepsilon). \tag{34}$$

The dependence on emissivity ε is illustrated in Fig. 6 for $p(\varepsilon)$ and in Fig. 7 for the percent increase in entropy $\Theta(\varepsilon)$. Fig. 6 shows that the entropy produced is always positive during the transition and thus the approximation (32) is always an overestimate of GR entropy.

Fig. 7 shows that for emissivity values greater than 0.50 the percent increase in entropy is very small, less than 1%. At $\varepsilon = 0.20$ the increase is about 5% and $\varepsilon = 0.10$ it is 10.5%. Thus, the error can be relatively low in approximating the entropy of GR as that of BR with the same energy (32). Likewise, the error introduced in using the approximation (31) for NBR is low as long as spectral emissivities are not too low.

4. Conclusions

When the entropy flux of TR is incorrectly understood to be q/T significant errors are introduced. For BR a 4/3 coefficient arises while for NBR emission the entropy flux is even farther removed from q/T. The correct evaluation of TR entropy is important when determining the second-law performance of energy conversion devices. The use of the q/T relation for TR transfer
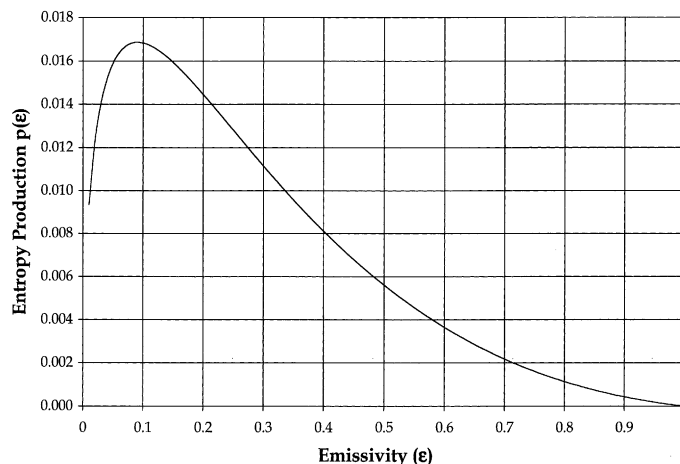

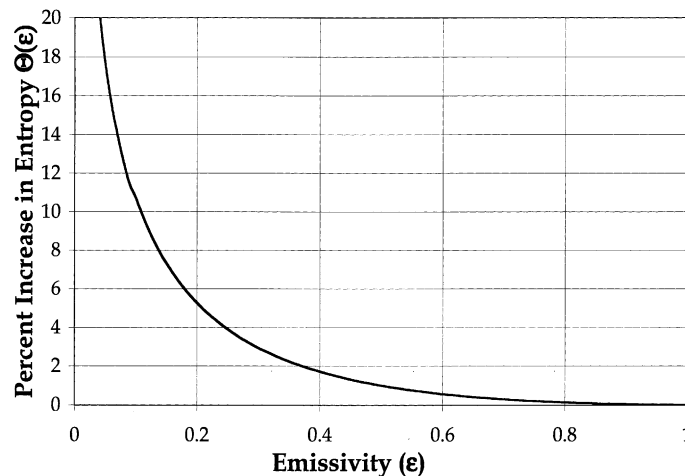Fig. 6. Dependence on emissivity of the function $p(\varepsilon)$ in (34).

Fig. 7. Percent increase in entropy $\Theta(\varepsilon)$ for an isolated transition of GR to BR (33), as a function of emissivity.

from an energy conversion device always causes the irreversibility of the device to be underestimated whether it is hot or cold relative to its surroundings.

The presence of q/T type expressions in fundamental equations of thermodynamics raises the question of their applicability when TR is involved. In this paper we show that the Clausius equality for reversible processes is applicable when TR is involved but expressions derived from it for irreversible processes are not applicable. These expressions should either be modified, or it should be stated that they do not apply when there is significant heat transfer by TR.

Also, approximate methods suitable for engineering applications have been developed for evaluating the entropy flux of TR. The approximations presented for GR allow the entropy fluxes to be evaluated simply and straightforwardly. Alternatively the entropy of any NBR can be estimated as that of BR with the same energy. The error is relatively low in using this approximation for GR over a large range of emissivities (e.g., within 1% for $\varepsilon > 0.5$). Likewise, this entropy approximation is relatively accurate for any NBR as long as the spectral emissivities are not too low.

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