

# RADIATION ENTROPY FLUX AND ENTROPY PRODUCTION OF THE EARTH SYSTEM

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[1] The study of the Earth's radiation entropy flux at the top of the atmosphere is reviewed with an emphasis on its estimation methods. Existing expressions for calculating radiation entropy flux scattered in different disciplines are surveyed, and their applicabilities are examined. It is found that the Earth's net radiation entropy flux estimated from these various expressions can differ substantially, more than the typical value of the entropy production rate associated with the atmospheric latent heat process. Comparison analysis shows that the commonly used expression of radiation entropy flux as the ratio of radiation energy flux to absolute temperature underestimates the Earth's radiation entropy flux by >30%.

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## 1. INTRODUCTION

[2] Earth's climate has changed over the industrial period, as manifested by increased global surface temperature and rising sea level [*Intergovernmental Panel on Climate Change (IPCC), 2007*]. The major cause is most likely anthropogenic greenhouse gas emissions. The impact of global climate change is expected to be huge, even disastrous, including threats to human health, increasing risks of extreme weather events (drought, flood, storm, fire, etc.), and changes in water resources and ecosystems. The ability to protect the unique habitable Earth system requires effective strategies for adapting to the changes in Earth's climate and for constraining future detrimental climate changes. Development of such strategies requires accurate quantification of past global climate change and capability for confident prediction of future climate change that would result from past and future changes in atmospheric composition.

[3] Current mainstream studies of the Earth's climate are primarily based on the principles of energy, momentum, and mass balances to develop climate models such as general circulation models (GCMs) to simulate various phenomena under investigation within the system. These models have made great contributions to the development of climate

Theoretical analysis reveals that the large difference in the Earth's reflected solar radiation entropy flux among the different expressions arises mainly from the difference of the Earth's reflection properties (i.e., Lambertian or specular) assumed in these expressions. For the Earth system with typical shortwave albedo of 0.30 and longwave emissivity between 0.50 and 1.00, the Earth's net radiation entropy flux derived from the most accurate Planck's spectral expression ranges from 1.272 to 1.284 W m<sup>-2</sup> K<sup>-1</sup>, amounting to the overall Earth's entropy production rate from 6.481 × 10<sup>14</sup> to 6.547 × 10<sup>14</sup> W K<sup>-1</sup>.

theories and to the projection of future climate change [e.g., *IPCC, 2007*]. However, because of the complexity of the Earth system, the state-of-the-science complex GCMs consider an increasing number of detailed processes. As a result, a large number of adjustable parameters are embedded in the sophisticated GCMs, and the model parameters are often tuned. But recent studies have indicated that the physics represented by model parameterizations are problematic, causing difficulty in accepting and/or in understanding model simulations [e.g., *Cess et al., 1989; Schwartz et al., 2007; Kerr, 2007; Kiehl, 2007; Knutti, 2008*]. Incorporation of additional uncertain climate forcing or feedbacks may even destroy the consistency between simulated and observed past global surface warming [e.g., *Knutti, 2008*]. Simple climate models with fewer tunable parameters such as energy balance models [e.g., *Frame et al., 2005; Hegerl et al., 2006; Wu and North, 2007*] (see *North et al. [1981]* for a review) and radiative-convective models [e.g., *Pauluis and Held, 2002a, 2002b; Held et al., 2007; Takahashi, 2009*] (see *Ramanathan and Coakley [1978]* for a review) have also been widely used in the investigation of global climate [e.g., *Manabe and Wetherald, 1967; Cess, 1974; North et al., 1983; Betts and Ridgway, 1989; Kim and North, 1991; Weaver and Ramanathan, 1995; Pujol and North, 2003*]. Although those simple models are capable of successfully simulating some basic climate phenomena with less need for tuning model

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parameters, they generally oversimplify many detailed physical processes. Furthermore, the uncertainties of climate forcing and climate sensitivity have remained significantly large [e.g., IPCC, 2007; Kiehl, 2007; Roe and Baker, 2007; Schwartz, 2008; Sanderson et al., 2008], becoming a barrier for accurately quantifying and predicting climate change [e.g., Knutti, 2008; Sokolov et al., 2010].

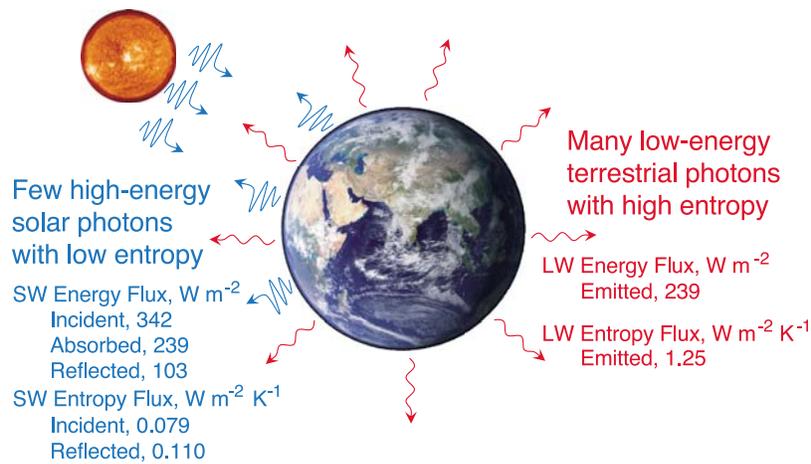
[4] To improve climate models and to reduce the large range of climate uncertainties, it appears necessary to seek additional constraint(s) of the Earth's climate system. Investigations along this line are generally related to the second law of thermodynamics wherein entropy and entropy production are fundamental components, and thermodynamic extremal entropy production principles are often used to explain some collective behaviors of the complex Earth's system without knowing the details of the dynamics within the system. Such thermodynamic investigations have provided crucial insight into various processes of climatic importance in the past several decades [e.g., Paltridge, 1975, 1978; Golitsyn and Mokhov, 1978; Nicolis and Nicolis, 1980; Grassl, 1981; Mobbs, 1982; Noda and Tokioka, 1983; Essex, 1984, 1987; Wyant et al., 1988; Lesins, 1990; Peixoto et al., 1991; Stephens and O'Brien, 1993; Goody and Abdou, 1996; Goody, 2000; Ozawa et al., 2003; Paltridge et al., 2007; Pauluis et al., 2008; Wang et al., 2008; Lucarini et al., 2010; Wu and Liu, 2010]. However, the entropic aspects of climate theory have not yet been developed as well as those based on energy, momentum, and mass balances.

[5] Furthermore, the Earth system as a whole is virtually driven and maintained by the radiation exchange between the Earth system and space. Solar (i.e., shortwave) radiation is the origin of almost all the processes on the Earth's surface and above, including oceanic and atmospheric circulations, weather, climate, and lifecycles. The Earth system absorbs incoming solar radiation, converts it into other energy forms through various irreversible processes, and reradiates terrestrial (i.e., longwave or infrared) radiation back to space. Under a steady state, the amount of energy emitted by the Earth system in the form of longwave radiation is balanced by the absorbed shortwave radiation energy. However, the emitted longwave radiation has much higher entropy than the absorbed shortwave counterpart because the temperature of the former is much lower than that of the latter. As will be derived in section 2, the resulting negative net entropy flux from the radiation exchange between the Earth system and space quantifies the rate of the Earth system's internal entropy production. As a measure of the overall strength of all the processes within the Earth system, the Earth system's internal entropy production is an important macroscopic constraint for the Earth system in addition to the principles on which the modern GCMs are built.

[6] However, the study of radiation entropy, although begun 1 century ago [Wien, 1894; Planck, 1913], has not yet been developed as well as that of radiation energy. Many fundamental issues such as the calculation methodology of nonblackbody radiation entropy have not been systematically

investigated. For example, a wide variety of expressions have been used in calculation of the Earth's radiation entropy flux. Some studies simply use radiation energy flux divided by the absolute temperature as the measure of radiation entropy flux. This approach assumes a direct analogy of radiation entropy to Clausius's definition of thermodynamic entropy (the definition is given in section 3) for a nonradiation material system [e.g., Noda and Tokioka, 1983; Peixoto et al., 1991; Ozawa et al., 2003]. Others estimate the radiation entropy flux by making a direct analogy to the expression of blackbody radiation entropy flux [e.g., Petela, 1961, 1964, 2003]. Still others employ and approximate the Planck "mechanical" expression of spectral radiation entropy flux [e.g., Aoki, 1983; Essex, 1984; Lesins, 1990; Stephens and O'Brien, 1993; Holden and Essex, 1997]. The values of the Earth's radiation entropy fluxes at the top of the atmosphere calculated from these different expressions can differ substantially [e.g., Noda and Tokioka, 1983; Stephens and O'Brien, 1993; Peixoto et al., 1991; Ozawa et al., 2003]. The inconsistency of the approaches for estimating the Earth's radiation entropy flux prohibits a sound understanding of the thermodynamics of the Earth system. Furthermore, the expressions for calculating radiation entropy flux have been scattered in different disciplines and developed for different purposes (e.g., engineering and Earth science). There is thus a need to survey and to examine these different expressions systematically in the context of improving the calculation of the Earth's radiation entropy flux.

[7] The primary objectives of this paper are to review the major expressions for evaluating radiation entropy flux developed in various disciplines, to systematically examine their applicabilities to the estimation of the Earth's radiation entropy flux at the top of the atmosphere and thus the Earth's internal entropy production rate, and to establish a firm theoretical foundation for future research. The rest of the paper is organized as follows. Section 2 discusses the entropy balance of the Earth system and the significance of the Earth's net radiation entropy flux in determining the Earth's climate. Section 3 briefly describes Planck's radiation theory along with some key concepts and principles that are essential and used throughout the paper. Section 4 summarizes various existing expressions for calculating nonblackbody radiation entropy flux and examines their underlying assumptions. Section 5 presents the new expressions for calculating the Earth's radiation entropy flux by combining the expressions discussed in section 4 and compares the Earth's radiation entropy flux calculated from those newly developed expressions. The errors relative to those directly calculated from the Planck "mechanical" expression (expression (8) below) are analyzed. Section 6 further examines the physics underlying the difference in the expressions for calculating the Earth's reflected solar radiation entropy flux. The major findings and future research are summarized in section 7. Supporting derivations are provided in Appendix A. A brief introduction to calculating radiation entropy flux of a gray body planet in radiative equilibrium is provided in Appendix B on the basis



**Figure 1.** The global average energy and entropy fluxes from the zero-dimensional model of the Earth system. Earth’s emitted LW and absorbed SW energy fluxes are balanced, but the entropy flux of the Earth’s emitted LW radiation is 1 order of magnitude greater than the entropy flux of the incident or reflected SW radiation. The values of radiation energy and entropy fluxes are calculated for Earth’s SW albedo of 0.30 and LW emissivity of 0.60 and for the solar constant  $1367 W m^{-2}$ . Adapted from *Stephens and O’Brien* [1993, Figure 1].

of Planck’s radiation theory. A summary of notation is listed in the notation section.

**2. WHY DO WE CARE ABOUT THE EARTH’S RADIATION ENTROPY FLUX?**

[8] The Earth system exchanges radiation with space, which drives and maintains almost all the processes within the Earth system. As shown in Figure 1, the essence of the Earth’s radiation exchange with space is that the high-energy photons with low entropy from the Sun enter the Earth system and the low-energy photons with high entropy are emitted from the Earth system to space [see also *Stephens and O’Brien*, 1993]. In general, the Earth system as a whole can be thought of as a multibody system that is closed to nonradiation material exchange and open to radiation exchange with space. For such a complex system, the net entropy flux resulting from the radiation exchange constrains the Earth system’s internal entropy production rate, a fundamental measure of the overall activities within the Earth system, including oceanic, atmospheric, and biological processes.

[9] The budget equation of entropy has been well established for any open system. Briefly, the entropy increase ( $dS$ ) of an open thermodynamic system is determined by the summation of the net entropy that flows into the system across the system’s boundary ( $dS_1$ ) and the total entropy production generated inside the system by irreversible processes ( $dS_2$ ) [e.g., *Prigogine*, 1980; *Stephens and O’Brien*, 1993], namely,

$$dS = dS_1 + dS_2. \tag{1}$$

[10] For the Earth system as a whole over a sufficiently long period of time, a steady state assumption is acceptable so that

the system’s entropy increase ( $dS$ ) is negligible. In other words, the Earth’s internal entropy production ( $dS_2$ ) can be quantified by the net entropy ( $-dS_1$ ) flowing out the system across the system’s boundary (the top of the atmosphere),

$$dS_2 = -dS_1. \tag{2}$$

[11] That is, the Earth’s entropy production rate can be quantified by the net entropy flux at the top of the atmosphere. Considering that the Earth system is closed to nonradiation material exchange with space, the Earth’s net entropy flux at the top of the atmosphere is determined by the net radiation entropy flux at the top of the atmosphere associated with the radiation exchange between the Earth system and space. In short, for the Earth system in a steady state, the global internal entropy production rate can be quantified by the Earth’s net radiation entropy flux at the top of the atmosphere.

**3. BASIC CONCEPTS AND PLANCK’S RADIATION THEORY**

[12] Early in 1865, Rudolf Clausius defined the quantity of the entropy change in a thermodynamic system as the total heat supplied to the system divided by the system’s absolute temperature [e.g., *Guggenheim*, 1959; *Ozawa et al.*, 2003]. That is, if a certain amount of heat  $dQ$  is supplied infinitely slowly (i.e., through a sequence of infinitesimal equilibrium states) to a system with an absolute temperature  $T$ , the system’s entropy  $S$  will change by  $dS = dQ/T$  (in units of  $J K^{-1}$ ). Clausius’s formulation of the thermodynamic entropy and the associated second law of thermodynamics (that is, the entropy of an isolated nonequilibrium system tends to increase over time, approaching the maximum value at equilibrium) constitutes a milestone in the classical thermodynamics. In 1877, seeking a theoretical explanation of the then-established laws

of thermodynamics at the molecular level, Ludwig Boltzmann proposed a statistical definition of entropy, which states that the entropy of a given macrostate is proportional to the natural logarithm of the number of microstates (or the thermodynamic probability) corresponding to this macrostate. Boltzmann's statistical definition of entropy establishes a clear connection between entropy at the macroscopic scale and the "random" motions at the microscopic scale and constitutes a seminal contribution to thermodynamics and statistical mechanics. However, both Clausius's thermodynamic and Boltzmann's statistical definitions of entropy were proposed for studying nonradiation material systems.

[13] Radiation exhibits unique properties that are distinct from the nonradiation material systems studied by Clausius or Boltzmann. In the form of electromagnetic waves, radiation can propagate through empty space with no need for a material medium. For example, solar radiation propagates through empty space from the Sun to the Earth or to other planets in the solar system. Photons of radiation, unlike molecules or atoms, have the property of wave-particle duality. *Wien* [1894] was probably the first to introduce the concept of radiation entropy by simply extending the concepts of temperature and entropy from a nonradiation material field to a radiation field (e.g., [http://nobelprize.org/nobel\\_prizes/physics/laureates/1911/wien-bio.html](http://nobelprize.org/nobel_prizes/physics/laureates/1911/wien-bio.html)). Wien also found that the wavelength of the maximum emission of blackbody radiation is inversely proportional to its absolute temperature [e.g., *Planck*, 1913; *Peixoto and Oort*, 1992]. A firm theoretical foundation on blackbody radiation was subsequently established by *Planck* [1913], among others. In his classical book, *Planck* [1913] formulated the theory of blackbody radiation from the angles of both thermodynamics and statistical mechanics. This section recaps the central elements of Planck's blackbody radiation theory that are essential to and used throughout this paper. Supporting derivations are given in Appendix A.

### 3.1. Thermodynamic Expression of Blackbody Radiation Entropy

[14] The thermodynamic expression of blackbody radiation entropy was obtained by applying the then-established thermodynamic principles together with Maxwell's theory on electromagnetic waves to a cavity system enclosing blackbody radiation at thermodynamic equilibrium [*Planck*, 1913, part II, chapter II] (a derivation is given in section A1):

$$S = \frac{4}{3} a T^3 V, \quad (3)$$

where  $T$  and  $V$  are the temperature and volume of the cavity system, respectively. The constant of proportionality equals four thirds of the radiation constant  $a$ . *Planck* [1913] named (3) as "thermodynamic expression" to differentiate it from his "spectral expression" for blackbody radiation entropy flux (expression (8) below). It should be emphasized that the factor "4/3" stems from the entropy contribution from radi-

ation pressure (see derivation in section A1). With (3), it is readily shown that the blackbody radiation entropy flux is given by (see section A2 for a detailed derivation)

$$J = \frac{4}{3} \sigma T^3, \quad (4a)$$

$$\sigma = \frac{ca}{4} = \frac{2\pi^5 \kappa^4}{15c^2 h^3}, \quad (4b)$$

where  $h$ ,  $c$ , and  $\kappa$  are the Planck constant, speed of light in vacuum, and the Boltzmann constant, respectively. It is worth noting that the Stefan-Boltzmann constant had been empirically determined before Planck provided the theoretical expression (4b) [*Planck*, 1913] (a derivation is given in section A5). Equation (4a) indicates that blackbody radiation entropy flux is proportional to the third power of the absolute temperature  $T$ , and the constant of proportionality equals four thirds of the Stefan-Boltzmann constant  $\sigma$ . Coupling (4a) with the well-known Stefan-Boltzmann law given by

$$E = \sigma T^4, \quad (5)$$

we obtain the following two equivalent identities for blackbody radiation entropy flux:

$$J = \frac{4}{3} \sigma^{1/4} E^{3/4} = \frac{4}{3} \frac{E}{T}. \quad (6)$$

[15] The first identity of (6) indicates that blackbody radiation entropy flux  $J$  exhibits a nonlinear relationship with blackbody radiation energy flux  $E$ ; the second identity shows that blackbody radiation entropy flux  $J$  is equal to a factor of 4/3 times the ratio of blackbody radiation energy flux  $E$  to blackbody equilibrium temperature  $T$ . The factor of 4/3 stems from the entropy contribution from radiation pressure, clearly suggesting that expressing blackbody radiation entropy flux as a ratio of blackbody radiation energy flux to temperature by direct analogy to Clausius's entropy for a nonradiation material system, as used in some studies, incorrectly ignores the important entropy contribution from radiation pressure.

### 3.2. Planck's Spectral Expression of Blackbody Radiation Entropy Flux

[16] Despite the great success of the thermodynamic theory on blackbody radiation, there were two fundamental questions left unanswered: (1) theoretical basis for the empirical constant  $\sigma$  and (2) the spectral behaviors of blackbody radiation energy and entropy. In search of answers to these questions, *Planck* [1913, part III, chapter I] extended the logarithmic dependence of entropy on the thermodynamic probability proposed by Boltzmann in 1877 for a nonradiation material system to more general physical systems including radiation. Furthermore, by applying the principle of maximum entropy of any equilibrium system and introducing the concept of radiation quantum to an ensemble of

oscillators of an emitting or absorbing system, *Planck* [1913] was able to derive the expressions of the spectral energy ( $I_\nu$ ) and entropy ( $L_\nu$ ) fluxes of a monochromatic (blackbody) radiation beam at a frequency of  $\nu$  in thermodynamic equilibrium (relevant derivations are given in section A3):

$$I_\nu = \frac{n_0 h \nu^3}{c^2} \left\{ \frac{1}{\exp\left(\frac{h\nu}{kT}\right) - 1} \right\}, \quad (7)$$

$$L_\nu = \frac{n_0 k \nu^2}{c^2} \cdot \left\{ \left(1 + \frac{c^2 I_\nu}{n_0 h \nu^3}\right) \ln\left(1 + \frac{c^2 I_\nu}{n_0 h \nu^3}\right) - \left(\frac{c^2 I_\nu}{n_0 h \nu^3}\right) \ln\left(\frac{c^2 I_\nu}{n_0 h \nu^3}\right) \right\}, \quad (8)$$

where  $I_\nu$  and  $L_\nu$  are blackbody spectral radiation energy and entropy fluxes per unit solid angle per unit frequency, respectively;  $T$  is the blackbody's absolute temperature; and  $n_0$  denotes the state of polarization, with  $n_0 = 1$  or  $2$  representing polarized or unpolarized rays, respectively. Equation (7) is the well-known Planck function or Planck's law, which is the basic expression for calculating  $I_\nu$  of blackbody radiation at a given temperature  $T$ . Equation (8) provides the method for calculating  $L_\nu$  from a given  $I_\nu$  and was called the "mechanical" expression of blackbody spectral radiation entropy flux by *Planck* [1913] to distinguish it from the thermodynamic expression of (3). For the sake of simplicity, (8) is hereinafter referred to as Planck's spectral expression.

[17] Equations (7) and (8) remarkably quantify the spectral behaviors of blackbody radiation energy and entropy fluxes. Many fundamental thermodynamic laws and expressions such as the Stefan-Boltzmann law and expression (4a) of blackbody radiation entropy flux as well as the radiation constant  $a$  and the Stefan-Boltzmann constant  $\sigma$  can be theoretically derived on the basis of equations (7) and (8) (see Appendix A for some derivations).

[18] It is worth emphasizing that although (8) was originally derived for a monochromatic radiation beam at thermodynamic equilibrium, it has been demonstrated to hold for nonblackbody radiation at a nonequilibrium condition as well [e.g., *Rosen*, 1954; *Ore*, 1955; *Landsberg and Tonge*, 1980] (we provide a solid derivation of this as well in section A3.2). Therefore, if one knows the spectral radiation energy flux  $I_\nu$  of any type of radiation over all the frequencies and directions,  $L_\nu$  can be calculated using (8), and thus the radiation entropy flux  $J$  through a surface with a known zenith angle  $\theta$  and solid angle  $\Omega$  can be calculated by

$$J = \int_0^\infty d\nu \int_\Omega L_\nu \cos \theta d\Omega. \quad (9)$$

[19] It follows from the preceding argument that unlike the thermodynamic expression (3) that only holds for blackbody radiation, Planck's spectral expression (8) has a much broader domain of application and has served as the basis for later

approximate expressions to calculate nonblackbody radiation entropy flux.

#### 4. EXISTING EXPRESSIONS FOR CALCULATING NONBLACKBODY RADIATION ENTROPY FLUX

[20] Planck's radiation theory indicates that blackbody radiation entropy flux, like blackbody radiation energy flux, is solely determined by the blackbody's temperature. Unfortunately, nonblackbody radiation processes abound in nature and technology. For example, the Earth system is not a blackbody from the perspectives of both incoming solar and outgoing terrestrial radiations. The incoming solar radiation is partially absorbed, reflected, and transmitted by various gases, aerosols, and clouds in the atmosphere. The Earth's surface reflects a small part of the incoming solar radiation, absorbs the rest, and reemits terrestrial radiation in the form of infrared radiation. The atmospheric layer absorbs some longwave radiation emitted by the Earth's surface and emits longwave radiation both upward toward outer space and downward toward the Earth's surface. The radiative properties of the atmosphere (scattering, absorption, emission, and transmission) depend on the composition/distribution of atmospheric gases and ambient particulates such as aerosols and cloud particles in such a complex way that the Earth system is anything but a blackbody [e.g., see *Peixoto and Oort*, 1992, Figure 6.2]. The nature of the Earth system being a nonblackbody renders the evaluation of the Earth's radiation entropy flux much more challenging than that of blackbody radiation entropy flux.

[21] As discussed in section 3, in principle, nonblackbody radiation entropy flux can be calculated by using (8) and (9) if the nonblackbody's spectral radiation energy flux is known over all frequencies at all solid angles. However, this numerical procedure is not trivial and is computationally demanding because of the nonlinearity in (8) between the nonblackbody spectral radiation energy and entropy fluxes and the integration involved in (9). As a result, analytical approximations are desirable. Over the last decades, many efforts have been devoted to seeking such analytical approximations for calculating nonblackbody radiation entropy flux in different fields, and several expressions have been developed [e.g., *Petela*, 1964; *Landsberg and Tonge*, 1979; *Stephens and O'Brien*, 1993; *Wright et al.*, 2001; *Wright*, 2007]. Below we summarize the major existing approximate expressions that have been scattered in various disciplines. Relevant derivations are given in section A6.

[22] The first approximate expression was introduced by *Petela* in the early 1960s. In search of an approach to calculating the maximum ability of thermal radiation to perform work in a given environment, which is essential for applications such as maximizing the efficiency of solar energy conversion, *Petela* considered a so-called "perfect" gray body whose spectral radiation energy flux is equal to the Planck function for blackbody radiation (7) times a frequency-independent constant defined as emissivity  $\varepsilon$  [*Petela*, 1961, 1964, 2003]. Under this condition, the radiation energy flux

of such an idealized gray body equals the corresponding blackbody radiation energy flux at the same emission temperature as the gray body times the emissivity, i.e.,

$$E = \varepsilon \sigma T^4. \quad (10)$$

By analogy to blackbody radiation theory (specifically, the Stefan-Boltzmann law (5) and the thermodynamic expression (3)), *Petela* [1961, 1964, 2003] proposed an expression for calculating the gray body radiation entropy flux,

$$J = \frac{4}{3} \varepsilon \sigma T^3. \quad (11)$$

[23] Equation (11) implicitly assumes that like the gray body radiation energy flux, the gray body radiation entropy flux is equal to the corresponding blackbody radiation entropy flux times the emissivity. This assumption seems reasonable at first glance, but careful inspection reveals that (11) is actually the result of substituting (10) into the third identity of (6):  $J = (4/3)(E/T)$ , an equation that describes the relationship between blackbody radiation energy and entropy fluxes. As will become clear, the expression of  $J = (4/3)(E/T)$  does not hold for gray body radiation, and thus expression (11) (hereinafter referred to as P61) holds only for blackbody radiation and represents an approximation for calculating gray body radiation entropy flux.

[24] *Landsberg and Tonge* [1979] (hereinafter referred to as LT79) recognized the deficiency of the Petela expression and sought to derive a more accurate approximation by a direct integration of Planck's spectral expression (8). They considered the so-called diluted blackbody radiation wherein the real photon number at each frequency equals a dilution factor ( $\delta < 1$ ) times the photon number at that frequency determined by the Planck function (7) at the same temperature as the diluted blackbody. The expressions for calculating the radiation energy ( $E$ ) and entropy ( $J$ ) fluxes for the diluted blackbody were derived by LT79 as follows:

$$E = \frac{B \delta \sigma T^4}{\pi}, \quad (12a)$$

$$B = \int \cos \theta d\Omega, \quad (12b)$$

$$J = \frac{4}{3} \frac{B \delta X(\delta) \sigma T^3}{\pi}, \quad (13a)$$

$$\delta X(\delta) = \frac{45}{4\pi^4} \int_0^\infty \left\{ \left(1 + \frac{\delta}{e^\beta - 1}\right) \ln \left(1 + \frac{\delta}{e^\beta - 1}\right) - \left(\frac{\delta}{e^\beta - 1}\right) \cdot \ln \left(\frac{\delta}{e^\beta - 1}\right) \right\} \beta^2 d\beta, \quad (13b)$$

where  $\beta = h\nu/\kappa T$  and  $T$  is the blackbody's radiation temperature. For  $\delta < 0.10$ , (13b) was simplified to

$$\delta X(\delta) \approx \delta(0.9652 - 0.2777 \ln \delta + 0.0511\delta). \quad (13c)$$

[25] Note that for the hemispheric flux of isotropic radiation, the geometric factor  $B$  becomes  $\pi$  ( $B = \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta d\theta = \pi$ ), and the only difference between the LT79 and P61 lies in  $X(\delta)$ . LT79 also derived a closed solution in terms of an infinite series that holds for any value of dilution factor, but the practical utility of this complete solution is generally limited as it is almost as complicated as the original integration form. Nevertheless, the complete solution allowed them to prove that  $X(\delta) = 1$  when  $\delta = 1$ , suggesting that like P61, LT79 recovers expression (4a) of blackbody radiation entropy flux. In other words, both LT79 and P61 are consistent with (4a) for the case of blackbody radiation. But the consistency ends with this idealized case. It was shown that for a diluted blackbody radiation with  $\delta < 1$ , LT79 yields a radiation entropy flux larger than that from P61, suggesting the difference between P61 and LT79 in estimating radiation entropy flux in general.

[26] It is worth noting that a diluted blackbody is mathematically equivalent to a gray body with the emissivity being equal to the dilution factor when the dilution factor is independent of radiation frequency. Physically, however, diluted blackbody is often applied to treating processes of "radiation dilution" such as scattering and absorption, and the dilution factor could embody reflectivity, absorptivity, or their combination. Furthermore, the diluted blackbody with a dilution factor  $\delta$  is different from the gray body with emissivity  $\delta$  in that the former has frequency-independent radiation temperature but the latter has frequency-dependent radiation temperature (as will be further discussed later in this section).

[27] The LT79 idea of developing an approximate expression for nonblackbody radiation entropy flux directly from Planck's spectral expression represents an important step forward in developing the methodology to estimate non-blackbody radiation entropy flux. Later studies have followed similar lines of research since then. *Stephens and O'Brien* [1993] (hereinafter referred to as SO93) applied a similar idea to develop an approximate expression for estimating the entropy flux carried by the solar radiation reflected by the Earth's system. Under the assumption that a distant blackbody Sun illuminates a Lambertian spherical surface of the Earth system (that is, the Earth's reflected solar radiation energy flux is the same in all directions and independent of the direction of incident solar radiation) with Earth's short-wave albedo  $\alpha_P$  independent of frequency, SO93 derived their expression for calculating the entropy flux of the Earth's reflected solar radiation (hereinafter marked as SR in relevant expressions) as follows:

$$J_{\text{SR}}^{\text{SO93}} = \frac{4}{3} \sigma T_{\text{Sun}}^3 \chi(\delta_0), \quad (14a)$$

$$\chi(\delta_0) = \frac{45}{4\pi^4} \int_0^\infty \left\{ \left(1 + \frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \ln \left(1 + \frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) - \left(\frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \ln \left(\frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \right\} \beta_{\text{Sun}}^2 d\beta_{\text{Sun}}, \quad (14b)$$

where  $\beta_{\text{Sun}} = h\nu/\kappa T_{\text{Sun}}$ ,  $\delta_0 = \alpha_P \cos\theta_0 (\Omega_0/\pi)$  plays the role of the dilution factor as defined in LT79,  $\cos\theta_0$  is cosine of solar

zenith angle to the Earth with a global averaged value of 0.25 (estimated as a ratio of the Earth's solar insolation at the top of the atmosphere to the solar constant  $1367 \text{ W m}^{-2}$  in analyzing the Earth's satellite measurements in SO93),  $\Omega_0 = 6.77 \times 10^{-5} \text{ sr}$  is the solar solid angle to the Earth, and  $T_{\text{Sun}} = 5779 \text{ K}$  is the Sun's effective emission temperature.

[28] Comparison of the LT79 and SO93 expressions ((13a), (13b), (14a), and (14b)) indicates that  $\delta_0$  in (14a) and (14b) can be viewed as the dilution factor  $\delta$  in (13a) and (13b), and  $\chi(\delta_0)$  in SO93 is likewise equivalent to  $\delta\chi(\delta)$  in LT79 for the Earth's reflected solar radiation when the Lambertian assumption is applied for the Earth system. Similar to LT79, SO93 deduced an analytical approximation of  $\chi(\delta_0)$  for  $\delta_0 \ll 1$ ,

$$\chi(\delta_0) \approx \delta_0[0.96515744 - 0.27765652 \ln(\delta_0)]. \quad (14c)$$

[29] Note that (14c) is virtually identical to (13c) except that the former keeps more decimals than the latter. SO93 also provided a complete expression for  $\chi(\delta_0)$  valid for  $0 \leq \delta_0 \leq 1$ . This complete expression is in a mathematical form slightly different from that given in LT79 and is equally complicated in practice. In some sense, the real contribution of SO93 is applying the LT79 idea developed in the engineering community to the study of the Earth's climate and relating the dilution factor to the shortwave albedo. SO93 also evaluated the Earth's radiation entropy flux as applied to a simple radiation transfer model and to the Earth Radiation Budget Experiment (ERBE) satellite measurements.

[30] The limitation of the LT79 and SO93 approximate expressions for calculating nonblackbody radiation entropy flux lies in that both were derived for small dilution factors ( $\delta < 0.10$ ) or  $\delta_0(\delta_0 \ll 1)$ . When the main concern is with solar radiation, the condition of the dilution factor  $\delta_0 \ll 1$  is often satisfied. For example, in the case of the Earth's reflection, the maximum  $\delta_0$  is  $\cos\theta_0(\Omega_0/\pi) = 5.39 \times 10^{-6} \ll 1$ . However, the approximation becomes problematic for gray body radiation wherein the emissivity falls between the extreme values of near zero and 1. For example, the typical emissivity of the current Earth's atmosphere likely falls between 0.5 and 1.0. In order to overcome this deficiency, *Wright et al.* [2001] (hereinafter referred to as WSHR01) developed an alternative approximation that not only is valid for any values of emissivity between 0 and 1 but also exhibits increased overall accuracy in calculation of gray body radiation entropy flux. Briefly, for an isotropic gray body emitter with a frequency-independent emissivity  $\varepsilon$ , the WSHR01 expression is written as

$$J^{\text{GR}} = \frac{2\pi\kappa^4}{c^2 h^3} T^3 F(\varepsilon), \quad (15a)$$

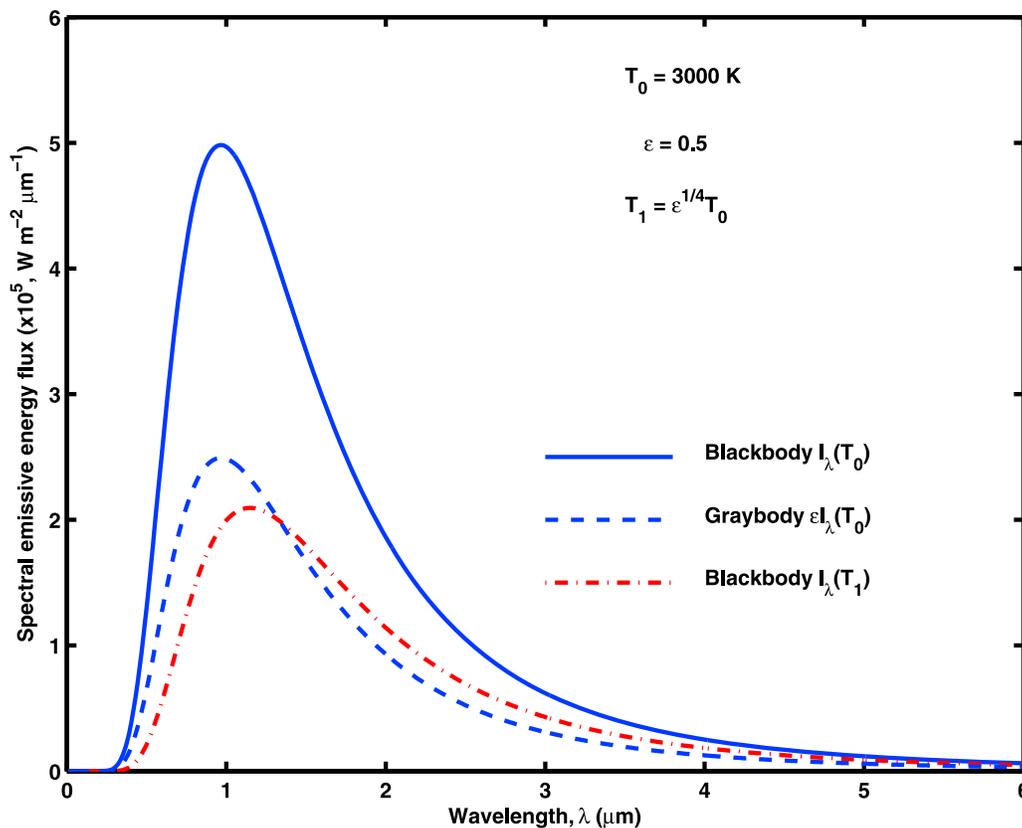
$$F(\varepsilon) = \int_0^\infty \left\{ \left(1 + \frac{\varepsilon}{e^\beta - 1}\right) \ln\left(1 + \frac{\varepsilon}{e^\beta - 1}\right) - \left(\frac{\varepsilon}{e^\beta - 1}\right) \cdot \ln\left(\frac{\varepsilon}{e^\beta - 1}\right) \right\} \beta^2 d\beta \approx \varepsilon \left\{ \frac{4\pi^4}{45} - m \ln \varepsilon \right\}, \quad (15b)$$

where  $\beta = h\nu/\kappa T$  and  $m = c_1$  or  $m = c_2 - c_3\varepsilon$  ( $c_1$ ,  $c_2$ , and  $c_3$  are constant coefficients). The percentage errors caused by (15a)

and (15b) were found to be  $\leq 1.9\%$  over  $0 \leq \varepsilon \leq 1$ , and the least accuracy occurs when  $\varepsilon$  is close to zero. The maximum percentage errors made by (15a) and (15b) in calculating radiation entropy flux for various emissivity ranges were shown in WSHR01's Table 2. In particular, for  $m = c_2 - c_3\varepsilon$  ( $c_2 = 2.336$  and  $c_3 = 0.260$ ), the maximum error of gray body radiation entropy flux calculated from the WSHR01 expressions (15a) and (15b) was argued to be only 0.33% within the emissivity range [0.005, 1.0] [*Wright et al.*, 2001]. WSHR01 showed that using an inappropriate expression of radiation entropy flux may cause an error in calculating irreversibility of a device (in an engineering field) no matter whether the surface of the device is hot or cold relative to its surroundings.

[31] *Zhang and Basu* [2007] investigated entropy flow and generation when incoherent multiple reflections are included. In their study, they reexamined the potential errors in Petela's expression for the case of gray body emission. They found that Petela's expression always underestimates the radiation entropy flux directly calculated from Planck's spectral expression (8) with the relative errors approaching zero as emissivity is close to 1 or 0. A similar finding was also reported by *Goody and Abdou* [1996] (see the "exact" curve shown by *Goody and Abdou* [1996, Figure A.1]). Apart from this, a gray body's spectral emissive energy flux peaks at a shorter wavelength (higher frequency) than its corresponding (with the same total emissive energy flux as the gray body) blackbody's spectral emissive energy flux (see Figure 2) [also see *Zhang and Basu*, 2007, Figure 3a]. The two spectral emissive energy fluxes cross only at some particular frequency. In other words, the gray body's radiation temperature is equal to the corresponding blackbody's radiation temperature only at that individual frequency. The result indicates that gray body's radiation temperature is indeed frequency-dependent [see *Zhang and Basu*, 2007, Figure 4]. This fact was noticed earlier by *Landsberg and Tonge* [1979]. It also suggests that it is inappropriate to approximate gray body radiation entropy flux to the radiation entropy flux of a corresponding (with the same total emissive energy flux as the gray body) blackbody like Petela's expression. *Zhang and Basu* [2007] also examined the accuracy of the expression of spectral radiation entropy flux ( $L_\nu = 4I_\nu/3T_\nu$ ) presented by *Bejan* [2006, expression (9.47)], indicating that for blackbody radiation (that is,  $T_\nu$  is a constant)  $L_\nu$  is linearly proportional to  $I_\nu$ , which obviously disobeys the nonlinearity dictated in Planck's nonlinear spectral expression (8). By plotting the spectral distributions based on (8) and  $L_\nu = 4I_\nu/3T_\nu$ , *Zhang and Basu* [2007] found that although  $L_\nu = 4I_\nu/3T_\nu$  theoretically leads to expression (4a) of blackbody radiation entropy flux, this expression can either underestimate or overestimate the spectral radiation entropy flux directly calculated from Planck's spectral expression (8) at different frequencies even for blackbody radiation [see *Zhang and Basu*, 2007, Figure 3b].

[32] Another commonly used expression for calculating radiation entropy flux is based on a direct analogy to Clausius's entropy definition proposed for a nonradiation material system, expressing radiation entropy flux as a ratio of radiation energy flux to absolute temperature [e.g., *Noda and*



**Figure 2.** Dependence of the spectral emissive energy flux on the radiation wavelength of blackbody radiation (blue solid line or red dash-dotted line) and gray body radiation (blue dashed line) calculated from Planck's function (7) with  $\nu = c/\lambda$ . It is evident that the spectral radiation energy fluxes of the gray body and the corresponding blackbody (with the same total emissive energy flux as the gray body) cross only at some specific wavelength (or frequency). In other words, the gray body's radiation temperature is frequency-dependent [see also *Zhang and Basu, 2007, Figure 3a*].

*Tokioka, 1983; Peixoto et al., 1991; Ozawa et al., 2003*]. The deficiency of this approach lies in its incomplete consideration of the entropic contributions from radiation-related processes [e.g., *Essex, 1984; Stephens and O'Brien, 1993; Wright et al., 2001; Wright, 2007*]. For example, as discussed in section 3, using this expression to calculate blackbody radiation entropy flux neglects the entropy contribution from blackbody radiation pressure. In a recent study, *Wright [2007]* further investigated this issue by examining the net radiation entropy flux of an absorbing system by using the so-called "entropy coefficient," which is the ratio of the net radiation entropy flux (the sum of incident, reflected, and emitted radiation entropy fluxes) to the radiation entropy flux calculated from the net radiation energy flux flowing into the system divided by the absolute temperature of the system ( $dQ/T$ ). He found that the expression  $dQ/T$  can either underestimate or overestimate the net radiation entropy flux, depending on the temperatures of incident and emitted radiations.

## 5. EXPRESSIONS FOR CALCULATING THE EARTH'S RADIATION ENTROPY FLUX

[33] As reviewed in section 4, most approximate expressions for calculating nonblackbody radiation entropy flux

were developed in disciplines other than Earth science. There has been no systematic study to compare the performances of these approximate expressions in evaluation of the Earth's radiation entropy fluxes. We will fill this gap in this section.

### 5.1. Zero-Dimensional Earth System Model and Various Expressions

[34] The Earth system can be viewed as a complex, open system that primarily exchanges radiation with its surrounding environment of space. Under a steady state, the first law of thermodynamics dictates that the emitted Earth's longwave radiation energy is balanced with its absorbed shortwave radiation energy. However, the radiation entropy does not obey the conservation law; instead, the emitted Earth's longwave radiation has much higher entropy than its absorbed shortwave radiation because of the conversion of the high-energy shortwave photons from a small solid angle into the low-energy longwave photons nearly isotropically. As will be presented in section 5.2 and Appendix B, the entropy of the Earth's reflected solar radiation is higher than that of the incident solar radiation as well because of the irreversible processes of the scattering by molecules, aerosols, and clouds. Another unique characteristic of the Earth system is that the solar radiation has its spectral radiation

energy flux mainly distributed within shortwave range whereas the terrestrial radiation has its spectral radiation energy flux mainly distributed within longwave (infrared) range, with little overlap [e.g., see *Peixoto and Oort*, 1992, Figure 6.2]. Accordingly, to the first-order approximation, we consider a simple zero-dimensional model for the Earth system that assumes the Earth system to be a spherical body as a whole with planetary shortwave albedo  $\alpha_p$  and longwave emissivity  $\varepsilon_p$ . The shortwave and longwave radiation processes are treated with the diluted blackbody and gray body approximations, respectively. Both the longwave emissivity  $\varepsilon_p$  and the shortwave albedo  $\alpha_p$  are assumed to be independent of radiation frequency. We also retain the same Lambertian assumption for the Earth's reflection of incident solar radiation as in SO93 as well. Figure 1 presents an illustration of the zero-dimensional model, along with some typical values of the global average energy and entropy fluxes that will be further discussed in the rest of this section and in Appendix B.

[35] For this zero-dimensional Earth system, we can obtain the exact expressions to calculate the radiation entropy fluxes as follows. First, the Earth's radiation entropy flux from the incident solar radiation can be calculated using  $(4/3)\sigma T_{\text{Sun}}^3 \cos\theta_0 \Omega_0/\pi$  according to expression (4a) of blackbody radiation entropy flux (the Sun is assumed as a blackbody). On the basis of Planck's spectral expression (8), the Earth's outgoing longwave (LW) radiation entropy flux and the Earth's reflected solar radiation entropy flux are given by

$$J_{\text{LW}}^{\text{Planck}} = \frac{2\pi\kappa^4}{c^2 h^3} T_P^3 \int_0^\infty \left\{ \left(1 + \frac{\varepsilon_P}{e^{\beta_P} - 1}\right) \ln\left(1 + \frac{\varepsilon_P}{e^{\beta_P} - 1}\right) - \left(\frac{\varepsilon_P}{e^{\beta_P} - 1}\right) \ln\left(\frac{\varepsilon_P}{e^{\beta_P} - 1}\right) \right\} \beta_P^2 d\beta_P, \quad (16)$$

$$J_{\text{SR}}^{\text{Planck}} = \frac{2\pi\kappa^4}{c^2 h^3} T_{\text{Sun}}^3 \int_0^\infty \left\{ \left(1 + \frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \ln\left(1 + \frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) - \left(\frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \ln\left(\frac{\delta_0}{e^{\beta_{\text{Sun}}} - 1}\right) \right\} \beta_{\text{Sun}}^2 d\beta_{\text{Sun}}, \quad (17)$$

where  $\beta_P = h\nu/\kappa T_P$  and  $\beta_{\text{Sun}} = h\nu/\kappa T_{\text{Sun}}$ . The Earth's effective emission temperature  $T_P$  can be determined on the basis of the Earth's energy balance equation, i.e.,  $Q_0(1 - \alpha_p) = 4\varepsilon_p\sigma T_P^4$ . It is worth mentioning that although both (16) and (17) are theoretically integrated over all the frequencies, in practice, the integration in (16) is mainly within LW range, and (17) is mainly within shortwave (SW) range because of the different properties of the LW and SW radiations. We will use the two expressions ((16) and (17)) as benchmarks in the following comparison study of various approximate expressions. A simple illustration for calculating a gray body planet's incident/reflected SW and emitted LW radiation entropy fluxes on the basis of Planck radiation theory is introduced in Appendix B.

[36] Likewise, applying the various approximate expressions discussed in section 4 to the Earth system, we can obtain the following sets of approximate expressions for expressions

(16) and (17). Briefly, for the Earth's emitted longwave radiation, we have

$$J_{\text{LW}}^{\text{P64}} = \frac{4}{3} \varepsilon_P \sigma T_P^3, \quad (18)$$

$$J_{\text{LW}}^{\text{LT79}} = [-0.2777 \ln(\varepsilon_P) + 0.9652 + 0.0511\varepsilon_P] \frac{4}{3} \varepsilon_P \sigma T_P^3, \quad (19)$$

$$J_{\text{LW}}^{\text{SO93}} = [-0.27765652 \ln(\varepsilon_P) + 0.96515744] \frac{4}{3} \varepsilon_P \sigma T_P^3, \quad (20)$$

$$J_{\text{LW}}^{\text{WSHR01}} = \left[ -\frac{45}{4\pi^4} (2.336 - 0.260\varepsilon_P) \ln \varepsilon_P + 1 \right] \frac{4}{3} \varepsilon_P \sigma T_P^3. \quad (21)$$

For the Earth's reflected solar radiation, we have

$$J_{\text{SR}}^{\text{P64}} = \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3, \quad (22)$$

$$J_{\text{SR}}^{\text{LT79}} = [-0.2777 \ln(\delta_0) + 0.9652 + 0.0511\delta_0] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3, \quad (23)$$

$$J_{\text{SR}}^{\text{SO93}} = [-0.27765652 \ln(\delta_0) + 0.96515744] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3, \quad (24)$$

$$J_{\text{SR}}^{\text{WSHR01}} = \left[ -\frac{45}{4\pi^4} (2.336 - 0.260\delta_0) \ln \delta_0 + 1 \right] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3. \quad (25)$$

[37] The Earth's net SW radiation entropy flux equals the Earth's reflected solar radiation entropy flux minus the entropy flux from the incident solar radiation, i.e.,  $J_{\text{SR}} - (4/3)\sigma T_{\text{Sun}}^3 \cos\theta_0 \Omega_0/\pi$ , a positive value indicative of outgoing flux. The Earth's net radiation entropy flux is the sum of the Earth's outgoing LW radiation entropy flux and the Earth's net SW radiation entropy flux, i.e.,  $J_{\text{LW}} + J_{\text{SR}} - (4/3)\sigma T_{\text{Sun}}^3 \cos\theta_0 \Omega_0/\pi$ .

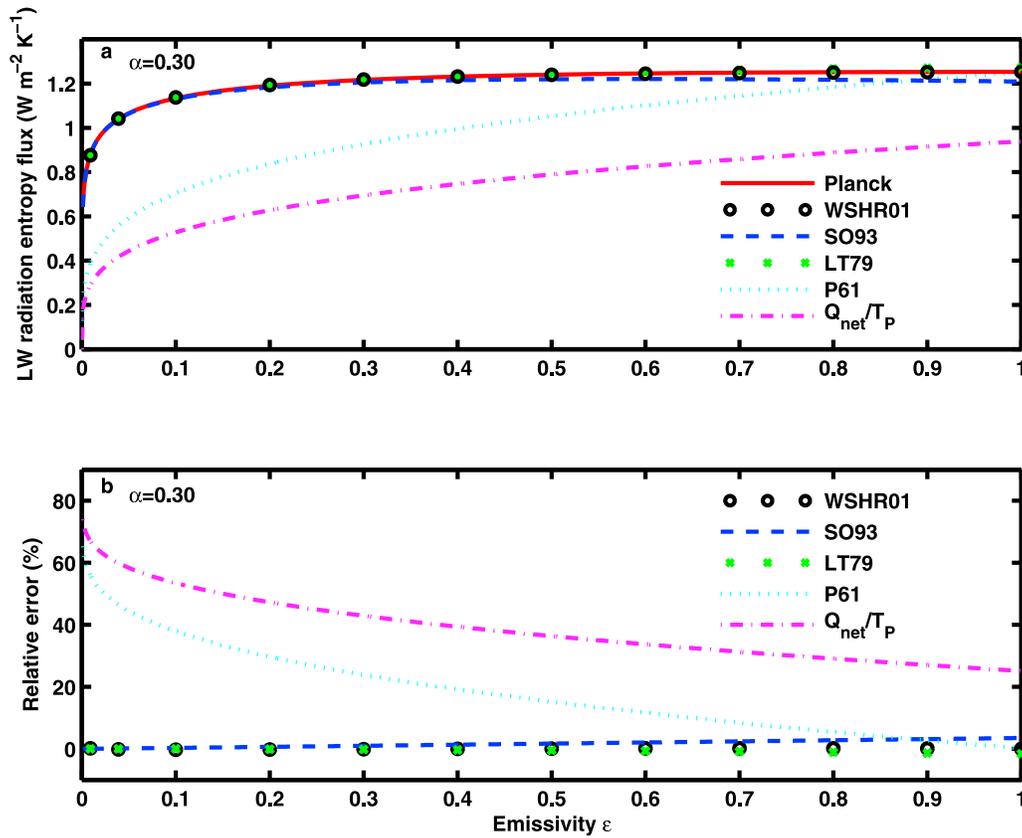
[38] In addition, if using the expression of radiation entropy flux as a ratio of radiation energy flux to absolute temperature, the Earth's outgoing LW radiation entropy flux and the Earth's reflected solar radiation entropy flux are expressed as

$$J_{\text{LW}}^M = \frac{(1 - \alpha_p)Q_0}{4T_P}, \quad (26)$$

$$J_{\text{SR}}^M = \frac{\alpha_p Q_0}{4T_{\text{Sun}}}, \quad (27)$$

where the superscript  $M$  signifies that these expressions come from an analogy to Clausius's entropy definition proposed for a nonradiation material system. For this case, the Earth's net SW radiation entropy flux equals  $J_{\text{SR}}^M - (4/3)\sigma T_{\text{Sun}}^3 \cos\theta_0 \Omega_0/\pi$ , and the Earth's net radiation entropy flux equals  $J_{\text{LW}}^M + J_{\text{SR}}^M - (4/3)\sigma T_{\text{Sun}}^3 \cos\theta_0 \Omega_0/\pi$ .

[39] If one uses the Earth's absorbed SW radiation energy flux at the top of the atmosphere over the Sun's effective



**Figure 3.** (a) The Earth's outgoing LW radiation entropy flux as a function of the Earth's LW emissivity. The solid curve, circles, dashed curve, crosses, dotted curve, and dash-dotted curve represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P61, and  $Q_{\text{net}}/T_P$  (i.e.,  $(1 - \alpha_P)Q_0/4T_P$ ), respectively. (b) The relative errors to the results from Planck's spectral expression (i.e., (Planck's spectral expression minus others) over Planck's spectral expression). Earth's SW albedo of 0.30 is used in these calculations.

emission temperature to calculate the Earth's net SW radiation entropy flux, the expression is

$$J_{\text{SW}}^M = \frac{(1 - \alpha_P)Q_0}{4T_{\text{Sun}}}. \quad (28)$$

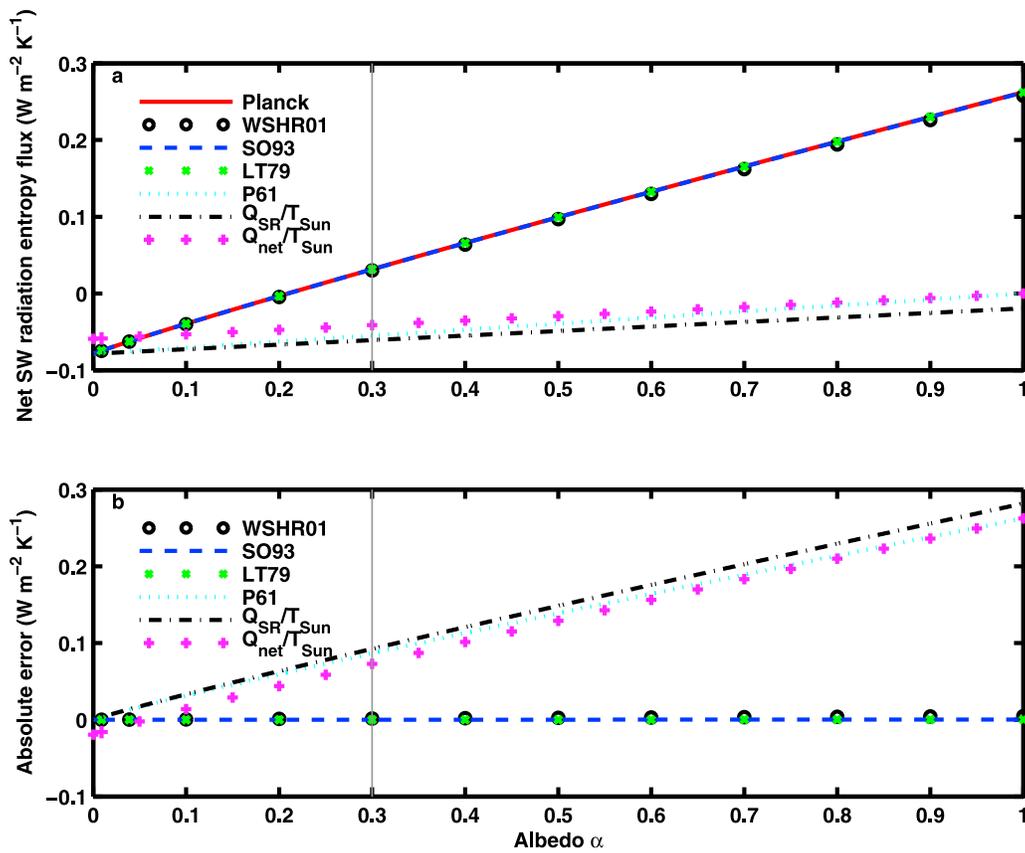
For this case, the Earth's net SW radiation entropy flux equals  $J_{\text{SW}}^M$ , and the Earth's net radiation entropy flux equals  $J_{\text{LW}}^M + J_{\text{SW}}^M$ .

## 5.2. Comparison Studies

[40] It is anticipated that the gray body Earth's outgoing LW radiation entropy flux ( $J_{\text{LW}}$ ) will depend on Earth's longwave emissivity and the Earth's reflected solar radiation entropy flux ( $J_{\text{SR}}$ ) will depend on Earth's shortwave albedo, and different approximate expressions will yield different results. This section compares the results calculated from these various expressions in the order of the Earth's LW radiation entropy flux, net SW radiation entropy flux, and net (total) radiation entropy flux. Analyses of the errors are performed relative to those directly calculated from a numerical integration of the most accurate Planck's spectral expression.

[41] Figures 3a and 3b show the Earth's LW radiation entropy fluxes as a function of Earth's longwave emissivity

calculated from the various approximate expressions and the corresponding relative errors compared to the results directly obtained from Planck's spectral expression, respectively. It is shown that among all the approximations, WSHR01 has the overall best performance in terms of the agreement with Planck's spectral expression. SO93 slightly underestimates and LT79 slightly overestimates the results from Planck's spectral expression as emissivity approaches 1.00, with SO93 having negligibly larger errors than LT79. Analytical examination of the SO93 and LT79 expressions reveals this fact more explicitly: When the emissivity approaches 1.00, SO93 and LT79 approach  $(4/3)\sigma T_P^3 \times 0.96515744$  and  $(4/3)\sigma T_P^3 \times 1.0163$ , respectively, instead of approaching the correct blackbody radiation entropy flux  $(4/3)\sigma T_P^3$ . The relatively poor performance for large values of emissivity is not surprising because both the SO93 and LT79 expressions were derived for small values of dilution factor or emissivity. P61 and  $Q_{\text{net}}/T$  (i.e.,  $(1 - \alpha_P)Q_0/4T_P$ ) clearly underestimate the results from Planck's spectral expression, especially for lower emissivity values. Their relative errors decrease when the emissivity increases (shown in Figure 3b). For emissivity  $> 0.50$ , the relative errors from P61 are within [0%, 15%], much smaller than those from  $Q_{\text{net}}/T_P$  (within [25%, 36%]). Notice that Figure 3a clearly shows that blackbody radiation



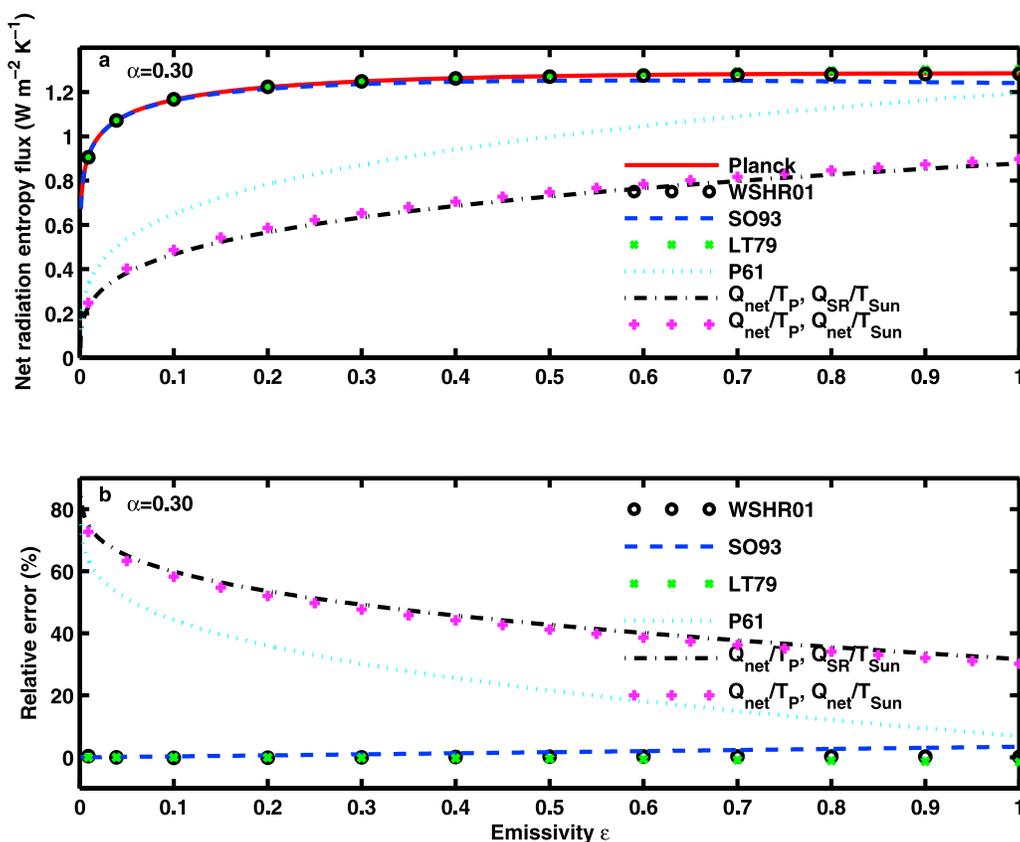
**Figure 4.** (a) The Earth's net SW radiation entropy flux as a function of the Earth's SW albedo (positive value indicates outgoing). The solid curve, circles, dashed curve, crosses, dotted curve, dash-dotted curve, and pluses represent the results from Planck's spectral expression, WSHR01, SO93, LT79, P61,  $Q_{SR}/T_{Sun}$  (i.e.,  $\alpha_P Q_0/4T_{Sun}$ ), and  $Q_{net}/T_{Sun}$  (i.e.,  $(1 - \alpha_P)Q_0/4T_{Sun}$ ), respectively. (b) The absolute errors to the results from Planck's spectral expression (i.e., Planck's spectral expression minus others). The thin gray lines in both Figures 4a and 4b mark the point of Earth's SW albedo of 0.30.

entropy flux (that is, emissivity equals 1.00) is equal to  $4/3$  multiplied by  $Q_{net}/T_P$ . Obviously, the P61 expression is able to correctly calculate this extreme case.

[42] For the likely range of the Earth's emissivity from 0.50 to 1.00, the magnitude of the Earth's outgoing LW radiation entropy flux calculated from Planck's spectral expression spans from 1.240 to 1.253 W m<sup>-2</sup> K<sup>-1</sup>. The magnitudes from WSHR01, SO93, LT79, P61, and  $Q_{net}/T_P$  are within [1.240, 1.253] W m<sup>-2</sup> K<sup>-1</sup>, [1.209, 1.220] W m<sup>-2</sup> K<sup>-1</sup>, [1.247, 1.273] W m<sup>-2</sup> K<sup>-1</sup>, [1.052, 1.252] W m<sup>-2</sup> K<sup>-1</sup>, and [0.789, 0.939] W m<sup>-2</sup> K<sup>-1</sup>, respectively. Thus, the WSHR01 expression ranks the best for calculating the gray body Earth's outgoing LW radiation entropy flux, followed by the SO93 and LT79 expressions; the worst is  $Q_{net}/T_P$ .

[43] Figures 4a and 4b show the Earth's net SW radiation entropy flux as a function of Earth's shortwave albedo and the absolute errors relative to those from Planck's spectral expression (i.e., Planck's spectral expression minus others), respectively. It is worth mentioning that the reason for analyzing absolute errors instead of relative errors is that the net SW radiation entropy flux from Planck's spectral expression has a zero point within the albedo range [0, 1]. The results are clearly separated into two groups. The first group consists of those derived by approximating Planck's spectral expression

(i.e., WSHR01, SO93, and LT79). A conspicuous feature of the results from this group is that they are all very close to the result directly obtained from Planck's spectral expression, with negligibly small positive absolute errors. Also noted is that in contrast to evaluating the Earth's outgoing LW radiation entropy flux, where WSHR01 performs the best among the three approximations, SO93 and LT79 outperform WSHR01 in estimation of the Earth's reflected solar radiation entropy flux. This stark contrast arises from the fact that the diluted factor  $\delta_0$  for calculating the Earth's reflected solar radiation entropy flux is always much less than 1, a condition on which the SO93 and LT79 expressions were based. On the contrary, the WSHR01 expression has the least accuracy under this condition. The second group consists of P61,  $Q_{SR}/T_{Sun}$  (i.e.,  $\alpha_P Q_0/4T_{Sun}$ ), and  $Q_{net}/T_{Sun}$  (i.e.,  $(1 - \alpha_P)Q_0/4T_{Sun}$ ). Unlike those in the first group, the expressions in this group tend to underestimate the entropy flux with large positive absolute errors, which are of the same magnitude as the Earth's net SW radiation entropy flux directly obtained from Planck's spectral expression. The values of the net SW radiation entropy flux from the second group are close to each other and present small negative values within [0, -0.1] W m<sup>-2</sup> K<sup>-1</sup>. Clearly, the errors from this group are much larger than those from the first group. Another noticeable feature is that the performance



**Figure 5.** (a) The Earth’s net radiation entropy flux as a function of the Earth’s LW emissivity. The solid curve, circles, dashed curve, crosses, dotted curve, dash-dotted curve, and pluses represent the results from Planck’s spectral expression, WSHR01, SO93, LT79, P61, a combination of  $Q_{\text{net}}/T_P$  (i.e.,  $(1 - \alpha_P)Q_0/4T_P$ ) and  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e.,  $\alpha_P Q_0/4T_{\text{Sun}}$ ), and a combination of  $Q_{\text{net}}/T_P$  and  $Q_{\text{net}}/T_{\text{Sun}}$  (i.e.,  $(1 - \alpha_P)Q_0/4T_{\text{Sun}}$ ), respectively. (b) The relative errors to the results from Planck’s spectral expression (i.e., (Planck’s spectral expression minus others) over Planck’s spectral expression).

of the second group degrades as Earth’s shortwave albedo increases.

[44] The differences among the various approximate expressions are more evident from a quantitative comparison of the Earth’s net SW radiation entropy flux for the typical shortwave albedo of 0.30. The magnitudes are 0.0316, 0.0299, 0.0315, 0.0315,  $-0.0550$ ,  $-0.0609$ , and  $-0.0414 \text{ W m}^{-2} \text{K}^{-1}$  for Planck’s spectral expression, WSHR01, SO93, LT79, P61,  $Q_{\text{SR}}/T_{\text{Sun}}$ , and  $Q_{\text{net}}/T_{\text{Sun}}$ , respectively. Obviously, the Earth’s net SW radiation entropy flux (Figure 4a) is much smaller in magnitude than the Earth’s outgoing LW radiation entropy flux (Figure 3a). Note that the result from  $Q_{\text{net}}/T_{\text{Sun}}$  ( $-0.0414 \text{ W m}^{-2} \text{K}^{-1}$ ) is almost identical to the value  $-0.0413 \text{ W m}^{-2} \text{K}^{-1}$  obtained by Peixoto *et al.* [1991], where  $Q_{\text{net}} = 238 \text{ W m}^{-2}$  and  $T_{\text{Sun}} = 5760 \text{ K}$  were used for calculating  $Q_{\text{net}}/T_{\text{Sun}}$ . Clearly, the SO93 and LT79 expressions perform the best for calculating the Earth’s net SW radiation entropy flux, while  $Q_{\text{SR}}/T_{\text{Sun}}$  ranks the worst. More discussions on the cause of the difference in the calculated Earth’s net SW radiation entropy flux are deferred to section 6.

[45] Figure 5a shows the Earth’s net radiation entropy flux (i.e., the Earth’s outgoing LW radiation entropy flux plus the Earth’s net SW radiation entropy flux), and Figure 5b shows

the relative errors to those from Planck’s spectral expression. As expected, the characteristics of the Earth’s net radiation entropy flux are similar to those of the Earth’s outgoing LW radiation entropy flux shown in Figure 3a.

[46] Over the range [0.50, 1.00] of Earth’s longwave emissivity, the magnitude of the Earth’s net radiation entropy flux from Planck’s spectral expression spans from 1.272 to 1.285  $\text{W m}^{-2} \text{K}^{-1}$ . This range of radiation entropy flux corresponds to the Earth’s internal entropy production rate from  $6.481 \times 10^{14}$  to  $6.547 \times 10^{14} \text{ W K}^{-1}$  when the Earth’s radius is  $6.367 \times 10^6 \text{ m}$ , an average of the Earth’s equatorial radius  $6.378 \times 10^6 \text{ m}$  and polar radius  $6.356 \times 10^6 \text{ m}$  ([http://oceanworld.tamu.edu/resources/ocng\\_textbook/contents.html](http://oceanworld.tamu.edu/resources/ocng_textbook/contents.html)). The values of the Earth’s net radiation entropy flux from WSHR01, SO93, and LT79 range within [1.270, 1.283]  $\text{W m}^{-2} \text{K}^{-1}$ , [1.241, 1.251]  $\text{W m}^{-2} \text{K}^{-1}$ , and [1.278, 1.305]  $\text{W m}^{-2} \text{K}^{-1}$ , respectively. As shown in Figure 5b, the relative errors from WSHR01, SO93, and LT79 to those from Planck’s spectral expression are negligible, within [0.13%, 0.19%], within [1.64%, 3.41%], and within [0.48%, 1.58%], respectively. In other words, WSHR01, SO93, and LT79 are good approximate expressions for calculating the gray body Earth’s net radiation entropy flux. However, the expression of

$Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$  (i.e.,  $(1 - \alpha_P)Q_0/4T_P - (1 - \alpha_P)Q_0/4T_{\text{Sun}}$ ) deviates significantly from Planck's spectral expression. The Earth's net radiation entropy flux from this expression is between 0.748 and 0.897  $\text{W m}^{-2} \text{K}^{-1}$ , which corresponds to the relative error from 30% to 41%. It is interesting to note that our estimate from the expression  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$  is very close to 0.884  $\text{W m}^{-2} \text{K}^{-1}$  estimated by *Peixoto et al.* [1991] for the Earth's net radiation entropy flux at the top of the atmosphere on the basis of the expression  $dQ/T$  and the evaluation of the Earth's incoming solar radiation energy flux and three parts of the Earth's outgoing LW radiation energy fluxes (emissions by atmosphere, clouds, and the Earth's surface) at the top of the atmosphere. The Earth's net radiation entropy flux at the top of the atmosphere from  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$  is also close to the value of 0.90  $\text{W m}^{-2} \text{K}^{-1}$  given by *Ozawa et al.* [2003], which was calculated from the expression  $Q_{\text{net}}/T_a - Q_{\text{net}}/T_{\text{Sun}}$  ( $T_a$  is a brightness temperature of the Earth's atmosphere) and using an observed global mean radiation energy flux 240  $\text{W m}^{-2}$  at the top of the atmosphere as the Earth's net radiation energy flux  $Q_{\text{net}}$ , under the assumptions of the brightness temperatures of solar radiation  $T_{\text{Sun}} = 5800 \text{ K}$  and of the Earth's atmosphere  $T_a = 255 \text{ K}$ . The Earth's net radiation entropy flux from  $Q_{\text{net}}/T_P$  and  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e., separately calculate the reflected solar radiation entropy flux) is close to that from  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$ . The latter shows a slightly smaller error in comparison to that from Planck's spectral expression than the former.

[47] The accuracy of the P61 expression increases as Earth's longwave emissivity increases (Figure 5a). The magnitude of the Earth's net radiation entropy flux from the P61 expression is within [0.997, 1.197]  $\text{W m}^{-2} \text{K}^{-1}$  for Earth's longwave emissivity range [0.50, 1.00]. The corresponding relative errors are within [7%, 22%]. The Earth's net radiation entropy flux from the P61 expression is close to the value of 1.187  $\text{W m}^{-2} \text{K}^{-1}$  given by *Aoki* [1983], where expression (4a) of blackbody radiation entropy flux was used to calculate the Earth's absorbed SW radiation entropy flux and the Earth's emitted LW radiation entropy flux without separately calculating the Earth's reflected solar radiation entropy flux (after calculating the net amount of the Earth's radiation entropy from the absorbed SW radiation and emitted LW radiation and globally averaging the net Earth's radiation entropy to obtain the Earth's net radiation entropy flux of 1.187  $\text{W m}^{-2} \text{K}^{-1}$ ). The Earth's net radiation entropy flux using the P61 expression is also close to the value of 1.204  $\text{W m}^{-2} \text{K}^{-1}$  given by *Weiss* [1996], where expression (4a) of blackbody radiation entropy flux was used to calculate the Earth's absorbed SW and emitted LW radiation entropy fluxes (the Earth's net radiation energy flux  $Q_{\text{net}}$  used for calculating the Earth's net radiation entropy flux equals one quarter of the solar constant multiplied by the Earth's coalbedo of 0.72). A similar value of 600  $\text{TW K}^{-1}$ , equivalent to 1.178  $\text{W m}^{-2} \text{K}^{-1}$  when the Earth's radius is  $6.367 \times 10^6 \text{ m}$ , was obtained by *Fortak* [1979] as well, where expression (4a) of blackbody radiation entropy flux was used to calculate the Earth's absorbed SW and emitted LW radiation entropy fluxes (using the solar radiant energy of 17,344  $\text{TW}$ , the Sun's

radiation emission temperature of 5770 K, the radiation emission temperature of 257 K of the Earth-atmosphere system, and Earth's shortwave albedo of 0.30).

[48] It should be emphasized that the magnitude of the Earth's net SW radiation entropy flux is almost 40 times smaller than that of the Earth's outgoing LW radiation entropy flux based on the most accurate Planck's spectral expression. It indicates that the Earth's outgoing LW radiation entropy flux dominates the Earth's net radiation entropy flux.

[49] It is noteworthy that the Earth's radiation entropy fluxes for other values of Earth's shortwave albedo from 0.00 to 1.00 are also examined in this study. The results exhibit similar patterns to the ones shown here and thus are omitted.

## 6. LAMBERTIAN OR SPECULAR REFLECTION: HIDDEN PHYSICS

[50] As shown in Figure 4a, the Earth's net SW radiation entropy flux from different expressions exhibits opposite signs for most values of Earth's shortwave albedo. Because the entropy flux from the incident solar radiation is the same for all the cases, the opposite signs of the Earth's net SW radiation entropy flux can be attributed to the difference in the expressions used for calculating the Earth's reflected solar radiation entropy flux. Moreover, the difference between the Earth's reflected solar radiation entropy flux from Planck's spectral expression and that from the P61 expression for the extreme case of  $\alpha_P = 1$  is difficult to understand because the P61 expression is expected to agree with Planck's spectral expression when  $\alpha_P = 1$  or 0, as discussed in section 4 and by *Zhang and Basu* [2007]. Therefore, there must be some fundamental physical difference in those expressions for calculating the Earth's reflected solar radiation entropy flux. This section seeks to uncover the physics hidden in the various expressions.

[51] Radiation reflection is generally divided into two different types: Lambertian or specular reflection. The former represents an idealized diffuse reflection whereby the reflected radiation is the same in all directions and independent of the direction of incident radiation; this case often involves radiation penetration into the medium and multiple scattering by its molecules or particles. The latter is a simple mirror-like reflection in which radiation from a single incoming direction is reflected to a single outgoing direction conforming to Fresnel's reflection law. The calculation of the Earth's reflected solar radiation entropy flux ((17) in section 5) assumes that the Earth's reflection of incident solar radiation is Lambertian, which indicates that the spectral energy flux of the Earth's reflected solar radiation ( $\alpha_P I_\nu^{\text{Sun}}$ ) is the same in all directions and independent of the direction of incident solar radiation (i.e., the same within solar zenith angle from 0 to  $\pi/2$  in the illuminating hemisphere). Under this assumption, the spectral energy flux  $I_\nu$  of the Earth's reflected solar radiation equals

$$I_\nu = \frac{\alpha_P \cos \theta_0 \Omega_0}{\pi} I_\nu^{\text{Sun}}. \quad (29)$$

[52] By integrating (29) over all the frequencies for the spherical Earth system, one can obtain the Earth's reflected solar radiation energy flux, namely,

$$\int d\nu \int_0^{2\pi} d\phi \int_0^{\pi/2} I_\nu \sin\theta \cos\theta d\theta = \alpha_P \cos\theta_0 \Omega_0 \int I_\nu^{\text{Sun}} d\nu. \quad (30)$$

Now supposing that the Earth's reflection of incident solar radiation is specular instead of Lambertian, the spectral energy flux  $I_\nu$  of the Earth's reflected solar radiation should be equal to Earth's shortwave albedo  $\alpha_P$  times that of incident solar radiation, i.e.,

$$I_\nu = \alpha_P I_\nu^{\text{Sun}}. \quad (31)$$

[53] Integration of (31) over the effective solid angle  $\Omega_0$  of the Earth's reflected solar radiation beams and over all frequencies leads to the Earth's reflected solar radiation energy flux (i.e.,  $\int d\nu \int_{\Omega_0} I_\nu \cos\theta d\Omega = \alpha_P \int d\nu \int_{\Omega_0} I_\nu^{\text{Sun}} \cos\theta d\Omega = \alpha_P \cos\theta_0 \Omega_0 \int I_\nu^{\text{Sun}} d\nu$ ), which is identical to the Lambertian case (30). However, the physical meanings underlying (29) or (31) are totally different. The spectral energy flux ( $I_\nu$ ) per unit solid angle per unit frequency of the former is averaged over the Lambertian Earth's surface while that of the latter is only effective within the solid angle  $\Omega_0$ .

[54] If we use expression (31) of the spectral radiation energy flux corresponding to specular reflection instead of (29) corresponding to Lambertian reflection, the expression for calculating the Earth's reflected solar radiation entropy flux can be derived by using Planck's spectral expression (8) and then conducting the integration over the effective solid angle  $\Omega_0$  and over all frequencies on the basis of (9), namely,

$$J_{\text{SR}}^{\text{Planck\_new}} = \frac{2\pi k^4}{c^2 h^3} T_{\text{Sun}}^3 \delta_1 \int_0^\infty \left\{ \left( 1 + \frac{\alpha_P}{e^{\beta_{\text{Sun}}}} - 1 \right) \ln \left( 1 + \frac{\alpha_P}{e^{\beta_{\text{Sun}}}} - 1 \right) - \left( \frac{\alpha_P}{e^{\beta_{\text{Sun}}}} - 1 \right) \ln \left( \frac{\alpha_P}{e^{\beta_{\text{Sun}}}} - 1 \right) \right\} \beta_{\text{Sun}}^2 d\beta_{\text{Sun}}, \quad (32)$$

where  $\delta_1 = \cos\theta_0 \Omega_0 / \pi$ . By employing the approximate expressions developed by LT79, SO93, and WSHR01, (32) can be further simplified to

$$J_{\text{SR}}^{\text{LT79\_new}} = [-0.2777 \ln(\alpha_P) + 0.9652 + 0.0511 \alpha_P] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3, \quad (33)$$

$$J_{\text{SR}}^{\text{SO93\_new}} = [-0.27765652 \ln(\alpha_P) + 0.96515744] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3, \quad (34)$$

$$J_{\text{SR}}^{\text{WSHR01\_new}} = \left[ -\frac{45}{4\pi^4} (2.336 - 0.260 \alpha_P) \ln \alpha_P + 1 \right] \frac{4}{3} \delta_0 \sigma T_{\text{Sun}}^3. \quad (35)$$

[55] Figure 6 shows the Earth's reflected solar radiation entropy flux in the case in which the Earth's reflection to

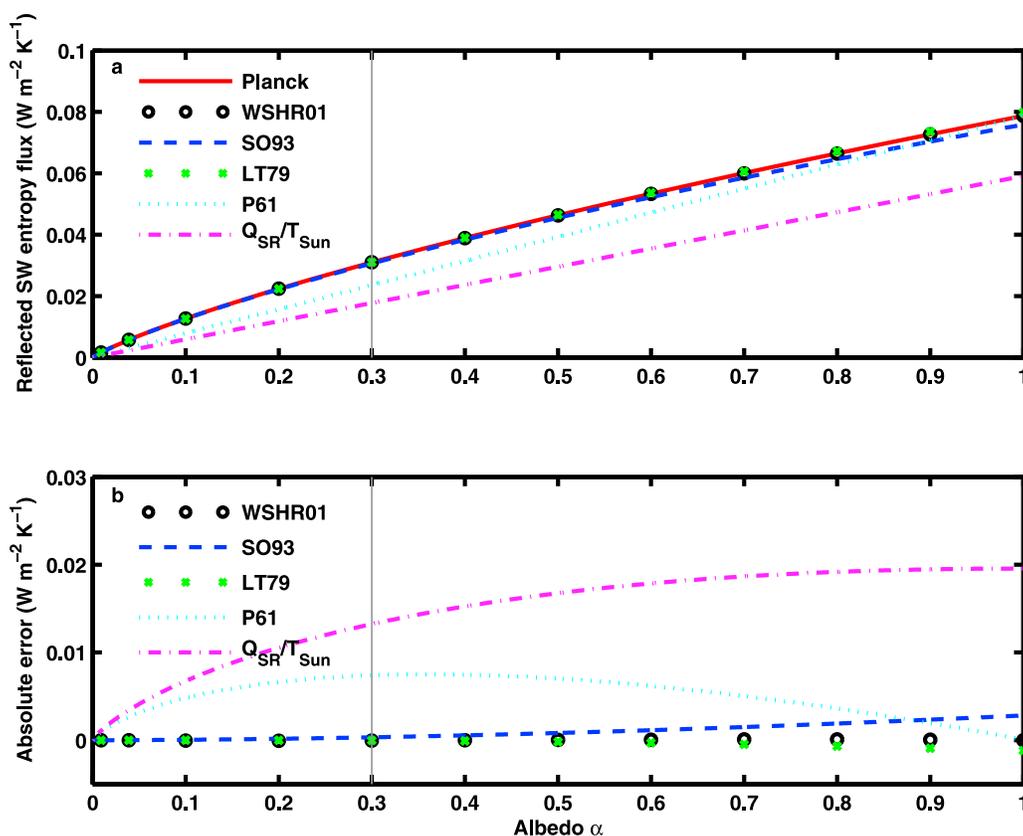
incident solar radiation is specular. As can be seen, the results from WSHR01, SO93, and LT79 are very close to those from Planck's spectral expression. The result from P61 agrees well with that from Planck's spectral expression as Earth's shortwave albedo tends to 1. The one-third difference between the results from  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e.,  $\alpha_P Q_0/4T_{\text{Sun}}$ ) and from Planck's spectral expression for the extreme case ( $\alpha_P = 1$ ) is also clearly shown in Figure 6.

[56] The results shown in Figure 6 suggest that the calculation of the Earth's reflected solar radiation entropy flux from the P61 expression or  $Q_{\text{SR}}/T_{\text{Sun}}$  requires the assumption that the Earth's reflection is specular. This assumption is not realistic for the Earth system because the Earth's reflection of incident solar radiation is known to be diffusive, involving multiple scattering and absorption by atmospheric gases, aerosols, and clouds. Therefore, both the P61 expression and  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e., the Earth's reflected solar radiation energy flux over the Sun's effective emission temperature) are fundamentally flawed and thus not appropriate for calculating the Earth's reflected solar radiation entropy flux.

[57] In addition, SO93 provided a test on the accuracy of Lambertian assumption in calculating the Earth's reflected solar radiation entropy flux by employing a radiative transfer model. SO93 showed that Lambertian assumption leads to an overestimate of the Earth's reflected solar radiation entropy flux by 20%; that is, multiplying an ad hoc factor of 0.80 with the obtained reflected solar radiation entropy flux under Lambertian assumption can provide a good estimate. Although the Earth's specular reflection leads to an unrealistic Earth's reflected solar radiation entropy flux of  $0.0310 \text{ W m}^{-2} \text{ K}^{-1}$ , which is much smaller than  $0.1102 \text{ W m}^{-2} \text{ K}^{-1}$  under Lambertian assumption, these results imply that the real Earth's reflection may operate somewhere between Lambertian and specular reflections, relatively closer to Lambertian reflection than to specular reflection.

## 7. CONCLUDING REMARKS

[58] This study reviews major existing expressions for calculating radiation entropy flux developed in different disciplines, analyzes their physical underpinnings, and examines their applicabilities to evaluating the Earth's radiation entropy flux. It is argued that the existing approximate expressions can be generally classified into three groups. The first group is based on the analogy to the familiar concept of thermodynamic entropy that expresses radiation entropy flux as the ratio of radiation energy flux to absolute temperature. Despite being straightforward, the expressions of this group ignore some important entropic contributions such as radiation pressure and generally underestimate the radiation entropy flux even for the simplest case of blackbody radiation. The second group, the P61 expression, is based on the analogy between gray body (or diluted blackbody) radiation and blackbody radiation. This expression recovers expression (4a) of blackbody radiation entropy flux, but the incorrect linear analogy of a gray body's radiation energy over entropy to a blackbody's radiation energy over entropy [Petela, 2003] causes this expression to have a great deficiency in calculating



**Figure 6.** (a) The Earth’s reflected solar radiation entropy flux as a function of the Earth’s SW albedo for the case that the Earth’s reflection to incident solar radiation is specular. The solid curve, circles, dashed curve, crosses, dotted curve, and dash-dotted curve represent the results from Planck’s spectral expression, WSHR01, SO93, LT79, P61, and  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e.,  $\alpha_P Q_0/4T_{\text{Sun}}$ ), respectively. (b) The absolute errors to the results from Planck’s spectral expression (i.e., Planck’s spectral expression minus others). The thin gray lines in both Figures 6a and 6b refer to Earth’s SW albedo of 0.30.

a gray body’s radiation entropy flux. The third group, consisting of LT79, SO93, and WSHR01, is obtained by approximating the integration of Planck’s spectral expression and represents the best physics among the three groups of approximation. Note that there are differences among the expressions even within the same group.

[59] Comparison analyses of the different approximate expressions show that the difference of the Earth’s net radiation entropy flux arising from the different expressions can be substantial. The worst approximation is from the expression of a combination of  $Q_{\text{net}}/T_P$  and  $Q_{\text{SR}}/T_{\text{Sun}}$ , which belongs to the first group and separately calculates the reflected solar radiation entropy flux. The second worst performer is from the expression  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$ , which suffers from errors as large as  $0.387\text{--}0.524 \text{ W m}^{-2} \text{K}^{-1}$  (relative errors of  $>30\%$ ) compared to those from Planck’s spectral expression. To put it into perspective, such errors are comparable to the largest entropy production term of the Earth system associated with atmospheric latent heat release, which is  $0.298 \text{ W m}^{-2} \text{K}^{-1}$  according to Peixoto *et al.* [1991].

[60] As reviewed in section 3, Planck [1913] explicitly introduced two kinds of entropy expressions: the “thermodynamic” expression (3) of radiation entropy and the “mechanical” expression (8) of spectral radiation entropy flux. In

Planck’s cavity experiment for blackbody radiation [Planck, 1913], the “heat-supplied” term  $d\dot{Q}$  in the “thermodynamic” expression was found to include two parts: emissive radiant energy (photon energy,  $u dV$ ) and work done ( $p dV$ ) by the cavity system against the external force of pressure (which equals blackbody radiation pressure  $p$  for the equilibrium cavity system). Because blackbody radiation pressure ( $p = u/3$ ) has been explicitly derived by Planck [1913], it is not difficult to derive expression (4a) of blackbody radiation entropy flux on the basis of the thermodynamic expression (3) of radiation entropy (a derivation is given in section A1). However, the situation is much more complicated for nonblackbody radiation, and it is difficult to use the “thermodynamic” expression for calculating nonblackbody radiation entropy flux. The reasons are obvious: First, a general expression for calculating nonblackbody radiation entropy flux for a system includes more than the above two contributing terms (i.e., variation in the internal energy of the system and work done by the system) (e.g., <http://home.att.net/~numericana/answer/heat.htm>). Second, even for the case in which nonblackbody radiation entropy can be estimated by the above two terms (which means all other contributions are negligible), we must calculate nonblackbody radiation pressure beforehand, which is associated with the calculation

of electromagnetic momentum [e.g., *Crenshaw*, 2007] and thus is not trivial, in general. The significant underestimation from  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$  or  $Q_{\text{net}}/T_P$  and  $Q_{\text{SR}}/T_{\text{Sun}}$  is indeed due to the inappropriate use of the expression of radiation energy flux over absolute temperature for calculating radiation entropy flux. Actually, expression (4a) of blackbody radiation entropy flux indicates that the expression of radiation energy flux over absolute temperature cannot account for radiation entropy flux even for the simplest case of blackbody radiation (details are discussed in section 3).

[61] The relative errors of the Earth's net radiation entropy flux from the P61 expression compared to those from Planck's spectral expression rank as the third largest among all the expressions, being from 22% to 7% as Earth's longwave emissivity goes from 0.50 to 1.00. The error decreases quickly as the emissivity increases. As mentioned before, the P61 expression in fact comes from an analogy to the properties of blackbody radiation and thus cannot account for a gray body's radiation entropy flux. This expression can also be thought to be equivalent to the expression  $L_\nu = 4I_\nu/3T_\nu$  (presented by *Bejan* [2006]) under the assumption of isotropic radiation emission (or absorption) with emissivity (or absorptivity) independent of frequency for an equilibrium system. As discussed in section 4, Bejan's expression may cause errors in estimating spectral radiation entropy flux even for blackbody radiation, shown by *Zhang and Basu* [2007, Figure 3b]. In any case, the errors from the P61 expression essentially arise from the expression's incorrect analogy to blackbody radiation. Nevertheless, its errors are shown to be much less than those from  $Q_{\text{net}}/T_P - Q_{\text{net}}/T_{\text{Sun}}$  or  $Q_{\text{net}}/T_P$  and  $Q_{\text{SR}}/T_{\text{Sun}}$  on the basis of the results from this study.

[62] Moreover, from the perspective of the Earth's reflection, the calculations of the Earth's reflected solar radiation entropy flux from Planck's spectral expression and from the P61 expression or  $Q_{\text{SR}}/T_{\text{Sun}}$  (i.e.,  $\alpha_P Q_0/4T_{\text{Sun}}$ ) are demonstrated to have different physical bases. The former is based on Lambertian assumption for the Earth's reflection of incident solar radiation, while the latter is shown to require the assumption of a specular Earth's reflection. Because the real Earth's reflection tends to be more like a Lambertian (idealized diffusive) reflection than a specular (mirror-like) reflection, we recommend that the calculation of the Earth's reflected solar radiation entropy flux should avoid using the P61 expression or  $Q_{\text{SR}}/T_{\text{Sun}}$ .

[63] The approximate expressions developed from Planck's spectral expression perform reasonably well, in general. The relative errors of the Earth's net radiation entropy flux from WSHR01, SO93, and LT79 compared to those from Planck's spectral expression are negligible, within [0.13%, 0.19%], [1.64%, 3.41%], and [0.48%, 1.58%], respectively, when Earth's shortwave albedo is 0.30 and longwave emissivity ranges from 0.50 to 1.00. In other words, they are useful approximate expressions for calculating the gray body Earth's net radiation entropy flux.

[64] In summary, this study highlights the need for caution in choosing the expression for calculating the Earth's radiation entropy flux. The expressions derived from approximating Planck's spectral expression, such as WSHR01,

SO93, or LT79, are reasonably accurate for most applications. The WSHR01 expression exhibits the best performance in calculating the Earth's LW radiation entropy flux, while the SO93 and LT79 expressions are the best when the dilution factor or emissivity is small, for example, for calculating the Earth's reflected solar and thus net SW radiation entropy flux. For Earth's shortwave albedo 0.30 and longwave emissivity from 0.50 to 1.00, the Earth's net radiation entropy flux calculated from Planck's spectral expression ranges from 1.272 to 1.285  $\text{W m}^{-2} \text{K}^{-1}$ , suggesting the Earth's internal entropy production rate ranges from  $6.481 \times 10^{14}$  to  $6.547 \times 10^{14} \text{W K}^{-1}$  at a steady state. Of the Earth's net radiation entropy flux from 1.272 to 1.285  $\text{W m}^{-2} \text{K}^{-1}$ , the corresponding Earth's outgoing LW radiation entropy flux ranges from 1.240 to 1.253  $\text{W m}^{-2} \text{K}^{-1}$ , while the Earth's net SW radiation entropy flux is only 0.032  $\text{W m}^{-2} \text{K}^{-1}$ . This extremely uneven partition between the Earth's shortwave and longwave radiation entropy fluxes implies the critical importance of those processes that affect the Earth's longwave radiation in determining the overall internal entropy production of the Earth system.

[65] A few points are noteworthy. First, the quantities of the Earth's radiation entropy fluxes from this study depend upon some assumptions such as a gray body Earth for calculating the Earth's outgoing LW radiation entropy flux and a diluted blackbody Earth with Lambertian reflection of incident solar radiation for calculating the Earth's reflected SW radiation entropy flux. Although the expressions developed in this study represent a useful extension from a blackbody Earth assumption, the Earth system is clearly neither a gray body nor a diluted blackbody because the radiation property of the Earth's system as a whole is not isotropic and frequency-independent. A more accurate calculation can be conducted by directly integrating Planck's spectral expression (8) if all the necessary parameters can be obtained, e.g., from satellite measurements such as Earth Radiation Budget Experiment (ERBE) or Clouds and the Earth's Radiant Energy System (CERES). Second, this study treats the Earth system as a whole, without considering the spatial distribution of the entropy flux within the Earth system. A few studies have investigated such problems by using more advanced models such as radiative equilibrium models or radiative-convective models [e.g., *Li et al.*, 1994; *Li and Chylek*, 1994; *Ozawa and Ohmura*, 1997; *Pujol and Fort*, 2002; *Wang et al.*, 2008]. However, the expressions used for calculating the Earth's radiation entropy flux in these studies suffer from the same deficiencies as those addressed here for the zero-dimensional Earth system. Therefore, it would be useful to systematically examine the influences of the different expressions of radiation entropy flux on the results from more advanced models than the simple zero-dimensional model discussed in this paper.

[66] Finally, the majority of the approximate expressions were originally developed by the engineering community in search of an engineering solution for optimal conversion of solar energy into useful work. Such engineering studies have stimulated and demonstrated the need to seriously investigate

issues related to radiation entropy in design of the technology of maximizing energy conversion efficiency. This paper has clearly demonstrated the critical role of the radiation entropy flux in quantifying the overall entropy production rate of the Earth system and thus in determining the Earth's climate. To some extent, the Earth system can be regarded as a huge "heat engine," and the ultimate climate is closely related to its efficiency in converting solar radiation energy into work. Close interactions between the two communities are obviously mutually beneficial. The necessity for such interdisciplinary interactions in the context of studying radiation entropy is further reinforced by the concurrent twofold challenges in battling climate change: to understand/predict global climate (change) and to develop clean renewable energy to reduce emissions of greenhouse gases. In conclusion, we would like to call for such much needed interactions.

## APPENDIX A: DERIVATION OF KEY EQUATIONS

[67] Derivations of key thermodynamic equations are crucial for a sound understanding of thermodynamic theories. Considering that the previous derivations of relevant key equations are scattered in different fields and are not readily available, we summarize and expand the details of the derivations of the key equations in this appendix. Notice that some derivations (sections A3 and A4) are new to the best of the authors' knowledge.

### A1. Derivation of the Thermodynamic Expression (3) of Blackbody Radiation Entropy

[68] The thermodynamic expression (3) of blackbody radiation entropy  $S$  can be derived straightforwardly by using the first law of thermodynamics, Clausius's thermodynamic entropy definition, Maxwell's radiation pressure, and the Stefan-Boltzmann law. According to the first law of thermodynamics, the change of a system's internal energy ( $dU$ ) is equal to the amount of heat received by the system ( $d\tilde{Q}$ ) minus the amount of work done by the system on its surroundings ( $pdV$ ), namely,

$$dU = d\tilde{Q} - pdV, \quad (\text{A1})$$

where  $dV$  is the volume change of the system and  $p$  is the system's external force of pressure.

[69] For a blackbody radiation system, on the basis of Clausius's thermodynamic entropy definition (at the beginning of section 3), the system's entropy change  $dS$  is equal to

$$dS = \frac{d\tilde{Q}}{T}, \quad (\text{A2})$$

where  $T$  is the system's absolute temperature. Integration of (A2) with (A1) gives the system's total entropy change,

$$S = \int dS = \int \frac{d\tilde{Q}}{T} = \int \frac{dU + pdV}{T} = \int \frac{udV + pdV}{T}, \quad (\text{A3})$$

where  $u$  is the blackbody's spatial radiation energy density.

[70] For blackbody radiation, as will be derived in section A1.1, its radiation pressure  $p$  is determined by its spatial radiation energy density  $u$ ,

$$p = \frac{u}{3}, \quad (\text{A4})$$

with

$$u = aT^4, \quad (\text{A5})$$

where  $a$  is a radiation constant which was empirically determined before the birth of Planck's radiation theory and can be explicitly derived by using Planck's radiation theory (see a derivation in section A5). The radiation pressure  $p$  has the same units as pressure,  $\text{J m}^{-3}$ , measuring the mechanical force exerted by blackbody radiation on a unit area. Expression (A4) is "Maxwell radiation pressure," which was explicitly derived by *Planck* [1913] (see a derivation in section A1.1). Expression (A5) is the well-known  $T^4$  radiation law (or the Stefan-Boltzmann law), which was first empirically discovered by Josef Stefan in 1879 and was then theoretically derived by Boltzmann in 1884 using Maxwell radiation pressure and fundamental thermodynamic principles [e.g., *Planck*, 1913, p. 63; *Crepeau*, 2007] (see a derivation in section A1.2). Substitution of (A4) and (A5) into (A3) leads to the thermodynamic expression (3) of blackbody radiation entropy:

$$S = \frac{4}{3} aT^3 V.$$

#### A1.1. Derivation of Expression (A4) of Maxwell's Radiation Pressure

[71] Expression (A4) of Maxwell's radiation pressure can be derived on the basis of Maxwell's theory on the electric or magnetic field strength of an electromagnetic process in vacuum and Poynting's theorem about the energy conservation for an electromagnetic field [*Planck*, 1913, see part II, chapter I]. According to Maxwell's theory and Poynting's theorem, the mechanical force  $\tilde{F}$  exerted by blackbody radiation at a unit solid angle on a surface element  $d\lambda$  is proportional to blackbody radiant power  $I d\lambda$  per unit solid angle,

$$\tilde{F} = \frac{2 \cos \theta}{c} I d\lambda, \quad (\text{A6})$$

where  $\theta$  is the zenith angle of radiation beams.

[72] Integration of (A6) over all solid angles leads to the following version of expression (A4) of Maxwell's radiation pressure:

$$\begin{aligned} p &= \frac{\int_{\Omega} \tilde{F} \cos \theta d\Omega}{d\lambda} = \frac{2}{c} \int_{\Omega} I \cos^2 \theta d\Omega \\ &= \frac{2I}{c} \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin \theta \cos^2 \theta d\theta = \frac{4\pi I}{3c} = \frac{u}{3}, \end{aligned}$$

where  $\Omega$  is the solid angle of radiation beams and  $\phi$  is the azimuth angle. Note that the relationship of the third identity in (A43) between the energy flux ( $J$ ) per unit solid angle and the spatial energy density ( $u$ ) of blackbody radiation is used in the derivation of the last identity above. Note also that for blackbody radiation  $I$  is a constant (uniform) in all directions.

### A1.2. Derivation of Expression (A5) of the Stefan-Boltzmann Law

[73] On the basis of expression (A4) of Maxwell's radiation pressure, the total internal energy  $U$  for a system  $V$  containing blackbody radiation can be written as

$$U = uV = 3pV. \quad (\text{A7})$$

Thus, according to the first law of thermodynamics, the heat  $d\tilde{Q}$  received by the system can be written as

$$d\tilde{Q} = dU + pdV = 4pdV + 3Vdp. \quad (\text{A8})$$

Substitution of (A8) into (A2) leads to

$$dS = \frac{d\tilde{Q}}{T} = 4\frac{p}{T}dV + 3\frac{V}{T}dp. \quad (\text{A9a})$$

In other words,

$$\frac{\partial S}{\partial V} = 4\frac{p}{T}, \quad (\text{A9b})$$

$$\frac{\partial S}{\partial p} = 3\frac{V}{T}. \quad (\text{A9c})$$

Thus, with (A9b) we have

$$\frac{\partial^2 S}{\partial V \partial p} = 4\frac{1}{T} - 4\frac{p}{T^2} \frac{dT}{dp}, \quad (\text{A10a})$$

and with (A9c) we have

$$\frac{\partial^2 S}{\partial V \partial p} = 3\frac{1}{T}. \quad (\text{A10b})$$

Note that when we conduct a partial derivative for expression (A9c) to derive expression (A10b), radiation pressure is kept as a constant so that radiation temperature is kept as a constant as well on the basis of expressions (A4) and (A5). Equality of (A10a) and (A10b) leads to

$$\frac{dp}{p} = 4\frac{dT}{T}. \quad (\text{A11})$$

Integration of (A11) leads to

$$p = C_0 T^4, \quad (\text{A12})$$

where  $C_0$  is an integration constant. Substitution of (A12) into (A4) leads to the following version of (A5) of the Stefan-Boltzmann law:

$$u = 3p = 3C_0 T^4 = aT^4,$$

where  $a$  is a constant.

### A2. Derivation of Expression (4a) of Blackbody Radiation Entropy Flux Based on the Thermodynamic Expression (3) of Blackbody Radiation Entropy

[74] Supposing that  $L$  and  $s$  are the entropy flux per unit solid angle and the spatial entropy density of blackbody radiation uniform in all directions, respectively, we have

$$s = \frac{1}{c} \int L d\Omega = \frac{4\pi L}{c}, \quad (\text{A13})$$

where  $c$  is radiation velocity (i.e., the speed of light in vacuum) on which the radiation is propagated and  $\Omega$  is the solid angle of the radiation. Integration of  $L$  over all solid angles leads to the expression of blackbody radiation entropy flux  $J$ ,

$$J = \int L \cos \theta d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi/2} L \sin \theta \cos \theta d\theta = \pi L, \quad (\text{A14})$$

where  $\theta$  and  $\Omega$  are the zenith angle and solid angle of radiation beams and  $\varphi$  is the azimuth angle. Substitution of (A13) into (A14) together with (3) leads to the following version of expression (4a) of blackbody radiation entropy flux:

$$J = \pi L = \frac{c}{4} s = \frac{c}{4} \frac{S}{V} = \frac{c}{4} \times \frac{4}{3} \frac{aT^3 V}{V} = \frac{4}{3} \frac{ac}{4} T^3 = \frac{4}{3} \sigma T^3,$$

where  $\sigma (=ac/4)$  is the Stefan-Boltzmann constant, which can be explicitly derived by using Planck's radiation theory (see a derivation in section A5).

### A3. Derivation of Planck's Spectral Expressions of Blackbody Radiation Energy (7) and Entropy (8) Fluxes

[75] As we mentioned in section 3, Planck's spectral expressions of blackbody radiation energy (7) and entropy (8) fluxes provide a sound theoretical explanation about the spectral behaviors of blackbody radiation. Many fundamental laws and expressions of thermodynamics such as the Stefan-Boltzmann law and expression (4a) of blackbody radiation entropy flux as well as the radiation constants  $a$  and  $\sigma$  can be theoretically derived on the basis of the two expressions. The

following are the relevant derivations we generate on the basis of *Planck* [1913].

### A3.1. Derivation of Planck's Spectral Expression (7) of Blackbody Radiation Energy Flux

[76] In the study of the electrodynamic stationary state of blackbody radiation in vacuum (i.e., a system of  $N$  oscillators), *Planck* [1913, see part II, chapter V] discovered the linear relationship between the spectral energy flux ( $\tilde{I}_\nu$ ) of a plane polarized monochromatic (blackbody) radiation beam at a frequency of  $\nu$  and the spectral energy flux ( $\tilde{K}_\nu$ ) of its vibration component exciting the oscillators, namely,

$$\tilde{I}_\nu = \frac{3c}{32\pi^2} \tilde{K}_\nu, \quad (\text{A15})$$

where  $c$  is the speed of light in vacuum. In addition, *Planck* [1913, see part IV, chapter IV] also found the relationship between the spectral energy flux ( $\tilde{K}_\nu$ ) of its vibration component and the total energy ( $\tilde{E}$ ) of the  $N$  oscillators,

$$\gamma \tilde{K}_\nu = \frac{\tilde{E}}{Nh\nu} - \frac{1}{2}, \quad (\text{A16})$$

with the factor of proportionality  $\gamma$  being

$$\gamma = \frac{3c^3}{32\pi^2 h\nu^3}, \quad (\text{A17})$$

where  $h$  is the Planck constant, a proportionality constant between a photon's energy and the frequency of its associated electromagnetic wave, in units of J s (see notation section for the constant's value).

[77] Furthermore, the relationship between the entropy  $\tilde{S}$  of the system of the  $N$  oscillators in thermodynamic equilibrium and the total energy ( $\tilde{E}$ ) of the system was also discovered by *Planck* [1913, see part III, chapter III] on the basis of the principle of maximum entropy of the equilibrium system,

$$\tilde{S} = \kappa N \left\{ \left( \frac{\tilde{E}}{Nh\nu} + \frac{1}{2} \right) \ln \left( \frac{\tilde{E}}{Nh\nu} + \frac{1}{2} \right) - \left( \frac{\tilde{E}}{Nh\nu} - \frac{1}{2} \right) \cdot \ln \left( \frac{\tilde{E}}{Nh\nu} - \frac{1}{2} \right) \right\}, \quad (\text{A18})$$

where  $\kappa$  is the Boltzmann constant. According to the second law of thermodynamics ( $d\tilde{S} = d\tilde{E}/T$ ) with (A18), the relationship between the total energy ( $\tilde{E}$ ) of the  $N$  oscillators and the temperature  $T$  of the  $N$  oscillators [see also *Planck*, 1913, part III, chapter III] can be expressed as

$$\tilde{E} = Nh\nu \left( \frac{1}{2} + \frac{1}{e^{\frac{h\nu}{T}} - 1} \right). \quad (\text{A19})$$

Application of the equality of the temperature  $T$  (A19) to the temperature of blackbody radiation into (A16) with (A17) leads to the expression of the spectral energy flux ( $\tilde{K}_\nu$ ),

$$\tilde{K}_\nu = \frac{32\pi^2 h\nu^3}{3c^3} \frac{1}{e^{\frac{h\nu}{T}} - 1}. \quad (\text{A20})$$

[78] Substitution of (A20) into (A15) leads to an expression of the spectral energy flux ( $\tilde{I}_\nu$ ) of a plane polarized monochromatic (blackbody) radiation beam at a frequency of  $\nu$ ,

$$\tilde{I}_\nu = \frac{3c}{32\pi^2} \tilde{K}_\nu = \frac{3c}{32\pi^2} \times \frac{32\pi^2 h\nu^3}{3c^3} \frac{1}{e^{\frac{h\nu}{T}} - 1} = \frac{h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{T}} - 1}. \quad (\text{A21})$$

Obviously, the spectral energy flux ( $\tilde{I}_\nu^{\text{unpolarized}}$ ) of a plane unpolarized monochromatic (blackbody) radiation beam at a frequency of  $\nu$  is equal to 2 times the spectral energy flux ( $\tilde{I}_\nu$ ) of a plane polarized monochromatic (blackbody) radiation beam at a frequency of  $\nu$ ,

$$\tilde{I}_\nu^{\text{unpolarized}} = 2 \times \tilde{I}_\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{T}} - 1}. \quad (\text{A22})$$

Expressions (A21) and (A22) consist of Planck's spectral expression (7) of blackbody radiation energy flux.

### A3.2. Derivation of Planck's Spectral Expression (8) of Blackbody Radiation Entropy Flux

[79] Our following derivation of Planck's spectral expression (8) of blackbody radiation entropy flux is different from those given by previous investigators such as *Rosen* [1954], *Ore* [1955], and *Landsberg and Tonge* [1980]. We derive (8) directly from the functional relation (expression (A23)) between blackbody's spectral energy ( $I_\nu$ ) and entropy ( $L_\nu$ ) fluxes discovered by *Planck* [1913, part II, chapter IV, equation (134)] and thus demonstrate the generality of (8) for any radiation field (including nonequilibrium radiation fields).

[80] In the study of the entropy and temperature of monochromatic radiation, *Planck* [1913] discovered the relationship between the spectral energy ( $I_\nu$ ) and entropy ( $L_\nu$ ) fluxes of a monochromatic (blackbody) radiation beam at a frequency of  $\nu$ , namely,

$$L_\nu = \frac{\nu^2}{c^2} f \left( \frac{c^2 I_\nu}{\nu^2} \right). \quad (\text{A23})$$

For the purpose of deriving the unknown function  $f$  in (A23), we introduce the following two new variables:

$$x = \frac{c^2 I_\nu}{\nu^2}, \quad (\text{A24})$$

$$y = \frac{c^2 L_\nu}{\nu^2}. \quad (\text{A25})$$

Substitution of (A24) and (A25) into (A23) leads to

$$y = f(x). \quad (\text{A26})$$

According to the property of monochromatic radiation temperature discovered by *Planck* [1913, part II, chapter IV], the following equation holds:

$$dL_\nu = \frac{dI_\nu}{T}, \quad (\text{A27})$$

where  $T$  is the temperature of the radiation beams.

[81] With (A24) and (A25), (A27) can be rewritten as

$$dy = \frac{dx}{T}. \quad (\text{A28})$$

Substituting expression (7) of the spectral energy flux ( $I_\nu$ ) into (A24), we get

$$x = \frac{c^2 I_\nu}{\nu^2} = \frac{n_0 h \nu}{\exp\left(\frac{h \nu}{\kappa T}\right) - 1}. \quad (\text{A29})$$

Expression (A29) can be rewritten as

$$\frac{1}{T} = \frac{\kappa}{h \nu} [\ln(n_0 h \nu + x) - \ln x]. \quad (\text{A30})$$

Substitution of (A30) into (A28) and then conducting integration leads to

$$\begin{aligned} y &= \frac{\kappa}{h \nu} \int [\ln(n_0 h \nu + x) - \ln x] dx \\ &= \frac{\kappa}{h \nu} \left[ x \ln(n_0 h \nu + x) - \int \frac{x dx}{n_0 h \nu + x} - x(\ln x - 1) \right] + \text{const} \\ &= \frac{\kappa}{h \nu} [(n_0 h \nu + x) \ln(n_0 h \nu + x) - x \ln x] + \text{const}. \end{aligned} \quad (\text{A31})$$

[82] Note that formulas 2.728 (1) and 2.723 (1) in the work by *Gradshteyn and Ryzhik* [1980] are used in the derivation of the second equality above. Equation (A31) clearly shows the dependence of the function  $f(x)$  on  $x$ .

[83] Substitution of (A24) and (A25) into (A31) gives

$$\begin{aligned} L_\nu &= \frac{\nu^2 \kappa}{c^2 h \nu} \left[ \left( n_0 h \nu + \frac{c^2 I_\nu}{\nu^2} \right) \ln \left( n_0 h \nu + \frac{c^2 I_\nu}{\nu^2} \right) - \frac{c^2 I_\nu}{\nu^2} \ln \frac{c^2 I_\nu}{\nu^2} \right] + \text{const} \\ &= \frac{n_0 \kappa \nu^2}{c^2} \left[ \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \ln \left( n_0 h \nu + \frac{c^2 I_\nu}{\nu^2} \right) - \frac{c^2 I_\nu}{n_0 h \nu^3} \ln \frac{c^2 I_\nu}{\nu^2} \right] + \text{const} \\ &= \frac{n_0 \kappa \nu^2}{c^2} \left[ \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \ln \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) - \frac{c^2 I_\nu}{n_0 h \nu^3} \ln \frac{c^2 I_\nu}{n_0 h \nu^3} \right] + \tilde{C}_0, \end{aligned} \quad (\text{A32})$$

which leads to the Planck's spectral expression (8) of blackbody radiation entropy flux,

$$L_\nu = \frac{n_0 \kappa \nu^2}{c^2} \left[ \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \ln \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) - \frac{c^2 I_\nu}{n_0 h \nu^3} \ln \frac{c^2 I_\nu}{n_0 h \nu^3} \right],$$

where the derivation of the last equality above employs the fact that the constant  $\tilde{C}_0$  in (A32) must be equal to zero. This fact comes from the striking demonstrations of expression (4a) of blackbody radiation entropy flux separately by using the thermodynamic expression (3) of blackbody radiation entropy (see section A1) and by using the Planck's spectral expression (8) of blackbody radiation entropy flux (see section A4).

#### A4. Derivation of Expression (4a) of Blackbody Radiation Entropy Flux Based on Planck's Spectral Expression (8) of Blackbody Radiation Entropy Flux

[84] We generate the following derivation of expression (4a) of blackbody radiation entropy flux directly from Planck's spectral expression (8) of blackbody radiation entropy flux. To the best of the authors' knowledge, such a derivation has not yet been presented.

[85] On the basis of Planck's spectral expression (8) of blackbody radiation entropy flux, the expression of blackbody radiation entropy flux  $J$  through a surface with a known zenith angle  $\theta$  and solid angle  $\Omega$  can be written as

$$\begin{aligned} J &= \int_0^\infty d\nu \int_\Omega L_\nu \cos \theta d\Omega \\ &= \int_0^\infty d\nu \int_\Omega \frac{n_0 \kappa \nu^2}{c^2} \left\{ \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \ln \left( 1 + \frac{c^2 I_\nu}{n_0 h \nu^3} \right) - \left( \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \ln \left( \frac{c^2 I_\nu}{n_0 h \nu^3} \right) \right\} \cos \theta d\Omega \\ &= \int_0^\infty \frac{2\pi \kappa \nu^2}{c^2} \left\{ \left( 1 + \frac{c^2 I_\nu}{2h\nu^3} \right) \ln \left( 1 + \frac{c^2 I_\nu}{2h\nu^3} \right) - \left( \frac{c^2 I_\nu}{2h\nu^3} \right) \ln \left( \frac{c^2 I_\nu}{2h\nu^3} \right) \right\} d\nu \\ &= \frac{2\pi \kappa^4}{c^2 h^3} T^3 \int_0^\infty \left\{ \left( 1 + \frac{1}{e^\beta - 1} \right) \ln \left( 1 + \frac{1}{e^\beta - 1} \right) - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right\} \beta^2 d\beta, \end{aligned} \quad (\text{A33})$$

where  $\beta = h\nu/\kappa T$ ,  $T$  is the blackbody's equilibrium temperature, and  $I_\nu$  is the blackbody's spectral radiation energy flux per unit solid angle per unit frequency.

[86] Expression (A33) can be further simplified according to the following derivation:

$$\begin{aligned} &\int_0^\infty \left\{ \beta^2 \left[ \left( 1 + \frac{1}{e^\beta - 1} \right) \ln \left( 1 + \frac{1}{e^\beta - 1} \right) - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right] \right\} d\beta \\ &= \int_0^\infty \left\{ \beta^2 \left[ \left( \frac{e^\beta}{e^\beta - 1} \right) \ln \left( \frac{e^\beta}{e^\beta - 1} \right) - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right] \right\} d\beta \\ &= \int_0^\infty \left\{ \beta^2 \left[ \left( \frac{e^\beta}{e^\beta - 1} \right) \ln(e^\beta) + \left( \frac{e^\beta}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right] \right\} d\beta \\ &= \int_0^\infty \left\{ \beta^2 \left[ \left( \frac{e^\beta}{e^\beta - 1} \right) \beta + \ln \left( \frac{1}{e^\beta - 1} \right) \right] \right\} d\beta \\ &= \int_0^\infty \left\{ \beta^2 \left[ \left( 1 + \frac{1}{e^\beta - 1} \right) \beta - \ln(e^\beta - 1) \right] \right\} d\beta \\ &= \int_0^\infty \left( \frac{\beta^3}{e^\beta - 1} \right) d\beta + \int_0^\infty [\beta^3 - \beta^2 \ln(e^\beta - 1)] d\beta \end{aligned} \quad (\text{A34})$$

and

$$\begin{aligned}
 \int_0^\infty [\beta^3 - \beta^2 \ln(e^\beta - 1)] d\beta &= \int_0^\infty \beta^3 d\beta - \frac{1}{3} \int_0^\infty \ln(e^\beta - 1) d\beta^3 \\
 &= \int_0^\infty \beta^3 d\beta - \frac{1}{3} [\beta^3 \ln(e^\beta - 1)]|_0^\infty + \frac{1}{3} \int_0^\infty \beta^3 d[\ln(e^\beta - 1)] \\
 &= \int_0^\infty \beta^3 d\beta - \frac{1}{3} [\beta^3 \ln(e^\beta - 1)]|_0^\infty + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{e^\beta}{e^\beta - 1} \right) d\beta \\
 &= \frac{4}{3} \int_0^\infty \beta^3 d\beta - \frac{1}{3} [\beta^3 \ln(e^\beta - 1)]|_0^\infty + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{\beta^3}{3} [\beta - \ln(e^\beta - 1)]|_0^\infty + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \lim_{\beta \rightarrow \infty} \left\{ \frac{\beta^3}{3} [\beta - \ln(e^\beta - 1)] \right\} - \lim_{\beta \rightarrow 0} \left\{ \frac{\beta^3}{3} [\beta - \ln(e^\beta - 1)] \right\} \\
 &\quad + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{1}{3} \lim_{\beta \rightarrow \infty} \{ \beta^3 [\beta - \ln(e^\beta - 1)] \} - \frac{1}{3} \lim_{\beta \rightarrow 0} \{ \beta^3 \ln(e^\beta - 1) \} \\
 &\quad + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{1}{3} \lim_{\beta \rightarrow \infty} \{ \beta^3 [\beta - \ln(e^\beta)] \} - \frac{1}{3} \lim_{\beta \rightarrow 0} \left\{ \beta^3 \ln \left( \sum_{n=1}^\infty \beta^n \right) \right\} \\
 &\quad + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{1}{3} \lim_{\beta \rightarrow \infty} \{ \beta^3 [\beta - \beta] \} + \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{1}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta. \tag{A35}
 \end{aligned}$$

Substitution of (A35) into (A34) with the properties of the Riemann zeta function  $\zeta(n)$  and the gamma function  $\Gamma(n)$  leads to

$$\begin{aligned}
 \int_0^\infty \left\{ \beta^2 \left[ \left( 1 + \frac{1}{e^\beta - 1} \right) \ln \left( 1 + \frac{1}{e^\beta - 1} \right) \right. \right. \\
 \left. \left. - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right] \right\} d\beta \\
 &= \frac{4}{3} \int_0^\infty \beta^3 \left( \frac{1}{e^\beta - 1} \right) d\beta \\
 &= \frac{4}{3} \times \Gamma(4) \times \zeta(4) \\
 &= \frac{4}{3} \times 3! \times \frac{\pi^4}{90} \\
 &= \frac{4\pi^4}{45}. \tag{A36}
 \end{aligned}$$

Substitution of (A36) into (A33) leads to the following version of expression (4a) of blackbody radiation entropy flux:

$$\begin{aligned}
 J &= \int_0^\infty d\nu \int_\Omega L_\nu \cos \theta d\Omega \\
 &= \frac{2\pi\kappa^4}{c^2 h^3} T^3 \int_0^\infty \left\{ \left( 1 + \frac{1}{e^\beta - 1} \right) \ln \left( 1 + \frac{1}{e^\beta - 1} \right) \right. \\
 &\quad \left. - \left( \frac{1}{e^\beta - 1} \right) \ln \left( \frac{1}{e^\beta - 1} \right) \right\} \beta^2 d\beta \\
 &= \frac{2\pi\kappa^4}{c^2 h^3} T^3 \times \frac{4\pi^4}{45} \\
 &= \frac{4}{3} \left( \frac{2\pi^5 \kappa^4}{15c^2 h^3} \right) T^3 \\
 &= \frac{4}{3} \sigma T^3.
 \end{aligned}$$

Note that expression (4b) of the Stefan-Boltzmann constant  $\sigma$  can be explicitly derived by using Planck's function (7) (see a derivation in section A5).

### A5. Derivation of the Radiation Constant $a$ and the Stefan-Boltzmann Constant $\sigma$

[87] The radiation constant  $a$  and thus the Stefan-Boltzmann constant  $\sigma$  can be explicitly derived on the basis of Planck's function (7) [Planck, 1913], as shown in the following. On the basis of Planck's spectral expression of blackbody radiation energy (7) and entropy (8) fluxes, the spectral spatial energy ( $u_\nu$ ) and entropy ( $s_\nu$ ) densities for uniform monochromatic unpolarized radiation beams at a frequency of  $\nu$  can be written as

$$u_\nu = \frac{1}{c} \int I_\nu d\Omega = \frac{4\pi I_\nu}{c} = \frac{8\pi h\nu^3}{c^3} \left\{ \frac{1}{\exp\left(\frac{h\nu}{\kappa T}\right) - 1} \right\}, \tag{A37}$$

$$\begin{aligned}
 s_\nu &= \frac{1}{c} \int L_\nu d\Omega = \frac{4\pi L_\nu}{c} = \frac{8\pi\kappa\nu^2}{c^3} \left\{ \left( 1 + \frac{c^3 u_\nu}{8\pi h\nu^3} \right) \ln \left( 1 + \frac{c^3 u_\nu}{8\pi h\nu^3} \right) \right. \\
 &\quad \left. - \left( \frac{c^3 u_\nu}{8\pi h\nu^3} \right) \ln \left( \frac{c^3 u_\nu}{8\pi h\nu^3} \right) \right\}. \tag{A38}
 \end{aligned}$$

[88] Integration of (A37) over all frequencies leads to the spatial energy density ( $u$ ) of blackbody radiation,

$$\begin{aligned}
 u &= 8\pi h c^{-3} \int_0^\infty \left\{ \exp\left(-\frac{h\nu}{\kappa T}\right) + \exp\left(-2\frac{h\nu}{\kappa T}\right) \right. \\
 &\quad \left. + \exp\left(-3\frac{h\nu}{\kappa T}\right) + \dots \right\} \nu^3 d\nu. \tag{A39}
 \end{aligned}$$

Expression (A39) can be further simplified according to the following derivation:

$$\begin{aligned}
& \int_0^\infty \exp\left(-n \frac{h\nu}{\kappa T}\right) \nu^3 d\nu \\
&= \left(-\frac{\kappa T}{nh}\right) \int_0^\infty \nu^3 d\left\{\exp\left(-n \frac{h\nu}{\kappa T}\right)\right\} \\
&= \left\{\left(-\frac{\kappa T}{nh}\right) \nu^3 \exp\left(-n \frac{h\nu}{\kappa T}\right)\right\}\Bigg|_0^\infty \\
&\quad - \left(-\frac{3\kappa T}{nh}\right) \int_0^\infty \exp\left(-n \frac{h\nu}{\kappa T}\right) \nu^2 d\nu \\
&= \left(\frac{3\kappa T}{nh}\right) \int_0^\infty \exp\left(-n \frac{h\nu}{\kappa T}\right) \nu^2 d\nu \\
&= \left(\frac{3\kappa T}{nh}\right) \left(\frac{2\kappa T}{nh}\right) \int_0^\infty \exp\left(-n \frac{h\nu}{\kappa T}\right) \nu d\nu \\
&= \left(\frac{3\kappa T}{nh}\right) \left(\frac{2\kappa T}{nh}\right) \left(\frac{\kappa T}{nh}\right) \int_0^\infty \exp\left(-n \frac{h\nu}{\kappa T}\right) d\nu \\
&= \left(\frac{3\kappa T}{nh}\right) \left(\frac{2\kappa T}{nh}\right) \left(\frac{\kappa T}{nh}\right) \left(-\frac{\kappa T}{nh}\right) \exp\left(-n \frac{h\nu}{\kappa T}\right)\Bigg|_0^\infty \\
&= \left(\frac{6\kappa^4}{n^4 h^4}\right) T^4. \tag{A40}
\end{aligned}$$

On the basis of (A40) with the properties of the Riemann zeta function  $\zeta(n)$ , (A39) can be rewritten as

$$\begin{aligned}
u &= 8\pi h c^{-3} \int_0^\infty \left\{ \exp\left(-\frac{h\nu}{\kappa T}\right) + \exp\left(-2\frac{h\nu}{\kappa T}\right) \right. \\
&\quad \left. + \exp\left(-3\frac{h\nu}{\kappa T}\right) + \dots \right\} \nu^3 d\nu \\
&= 8\pi h c^{-3} \sum_{n=1}^\infty \left(\frac{6\kappa^4}{n^4 h^4}\right) T^4 \\
&= \frac{48\pi\kappa^4}{c^3 h^3} \left(\sum_{n=1}^\infty \frac{1}{n^4}\right) T^4 \\
&= \frac{48\pi\kappa^4}{c^3 h^3} \zeta(4) T^4 \\
&= \frac{48\pi\kappa^4}{c^3 h^3} \times \frac{\pi^4}{90} \times T^4 \\
&= \left(\frac{8\pi^5 \kappa^4}{15c^3 h^3}\right) T^4, \tag{A41}
\end{aligned}$$

which leads to expression (A5),

$$u = aT^4.$$

[89] As shown above, the radiation constant  $a$  in the well-known  $T^4$  radiation law (or the Stefan-Boltzmann law) is theoretically determined according to (A41),

$$a = \frac{8\pi^5 \kappa^4}{15c^3 h^3}. \tag{A42}$$

Moreover, the spatial energy ( $u$ ) and entropy ( $s$ ) densities of the blackbody radiation can be written as the integrations of

its spectral spatial energy ( $u_\nu$ ) and entropy ( $s_\nu$ ) densities over all frequencies,

$$u = \int_0^\infty u_\nu d\nu = \frac{4\pi}{c} \int_0^\infty I_\nu d\nu = \frac{4\pi I}{c}, \tag{A43}$$

$$s = \int_0^\infty s_\nu d\nu = \frac{4\pi}{c} \int_0^\infty L_\nu d\nu = \frac{4\pi L}{c}, \tag{A44}$$

where  $I$  and  $L$  are the blackbody radiation energy and entropy fluxes per unit solid angle.  $I$  and  $L$  generally depend on the solid angle of a radiation beam but are constants for uniform radiation beams such as blackbody radiation [Planck, 1913].

[90] Equality of (A5) and (A43) leads to

$$\pi I = \frac{ac}{4} T^4. \tag{A45}$$

On the basis of expressions (A44) and (A45), the blackbody radiation energy ( $E$ ) and entropy ( $J$ ) fluxes can be written as

$$E = \int I \cos \theta d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi/2} I \sin \theta \cos \theta d\theta = \pi I = \frac{ac}{4} T^4, \tag{A46}$$

$$J = \int L \cos \theta d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi/2} L \sin \theta \cos \theta d\theta = \pi L = \frac{c}{4} s, \tag{A47}$$

where  $\theta$  and  $\Omega$  are the zenith angle and solid angle of radiation beams and  $\varphi$  is the azimuth angle. The Stefan-Boltzmann constant  $\sigma$  is thus theoretically determined according to (A46) with (A42),

$$\sigma = \frac{ac}{4} = \frac{8\pi^5 \kappa^4}{15c^3 h^3} \times \frac{c}{4} = \frac{2\pi^5 \kappa^4}{15c^2 h^3}. \tag{A48}$$

## A6. Derivation of the LT79, SO93, and WSHR01 Expressions for Nonblackbody Radiation Entropy Flux

[91] The LT79, SO93, and WSHR01 expressions ((13a), (14a), and (15a), respectively) of nonblackbody radiation entropy flux were all derived by directly approximating Planck's spectral expression (8) after plugging the corresponding nonblackbody spectral radiation energy flux into (8). LT79 considered a diluted blackbody radiation, which has its spectral radiation energy flux being a constant dilution factor times Planck's function (7) at the same temperature as the diluted blackbody. SO93 focused on the Earth's reflected solar radiation, which has its spectral radiation energy flux being a constant small parameter (i.e., a constant Earth's shortwave albedo after conducting a hemispheric average of the solar solid angle to the Earth) times Planck's function (7) of the solar radiation. WSHR01 is concerned with gray body radiation emission, which has its spectral radiation energy flux being a constant emissivity times Planck's function (7) at the gray body emission temperature. For the sake of simplicity, we present only the derivation of the LT79 expression (13a) of nonblackbody

radiation entropy flux as follows [see *Landsberg and Tonge*, 1979].

[92] According to Planck's radiation theory, the spectral energy ( $I_\nu$ ) and entropy ( $L_\nu$ ) fluxes for the LT79 diluted blackbody radiation are written as

$$I_\nu(\delta) = \frac{2\delta h\nu^3}{c^2} \left\{ \frac{1}{\exp\left(\frac{h\nu}{\kappa T}\right) - 1} \right\}, \quad (\text{A49})$$

$$L_\nu(\delta) = \frac{2\kappa\nu^2}{c^2} \left\{ \left[ 1 + \frac{c^2 I_\nu(\delta)}{2h\nu^3} \right] \ln \left[ 1 + \frac{c^2 I_\nu(\delta)}{2h\nu^3} \right] - \left[ \frac{c^2 I_\nu(\delta)}{2h\nu^3} \right] \ln \left[ \frac{c^2 I_\nu(\delta)}{2h\nu^3} \right] \right\}. \quad (\text{A50})$$

Integrations of (A49) and (A50) over all frequencies ( $\nu$ ) and over all solid angles ( $\Omega$ ) yield the energy ( $E$ ) and entropy ( $J$ ) fluxes for the diluted blackbody radiation,

$$E = \iint I_\nu(\delta) \cos\theta d\nu d\Omega = \frac{B\delta\sigma T^4}{\pi}, \quad (\text{A51})$$

$$J = \iint L_\nu(\delta) \cos\theta d\nu d\Omega = \frac{\frac{4}{3}B\delta X(\delta)\sigma T^3}{\pi},$$

with

$$\delta X(\delta) = \frac{45}{4}\pi^{-4} \int_0^\infty \left\{ \left( 1 + \frac{\delta}{e^\beta - 1} \right) \ln \left( 1 + \frac{\delta}{e^\beta - 1} \right) - \left( \frac{\delta}{e^\beta - 1} \right) \ln \left( \frac{\delta}{e^\beta - 1} \right) \right\} \beta^2 d\beta$$

(see equations (13a) and (13b)), where  $\beta = h\nu/\kappa T$ ,  $T$  is the absolute temperature of the diluted blackbody radiation, and  $B = \int \cos\theta d\Omega$  is a geometric factor; for the isotropic diluted blackbody radiation over a hemisphere,  $B = \int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta d\theta = \pi$ .

## APPENDIX B: RADIATION ENTROPY FLUXES OF A GRAY BODY PLANET IN RADIATIVE EQUILIBRIUM

[93] This appendix introduces the basic calculations of the radiation entropy fluxes for a spherical gray body planet in radiative equilibrium. The gray body planet discussed in this appendix is thought to be an idealized Earth-like spherical planet with the planet's albedo  $\alpha_P = 0.30$ . The name "gray body" comes from the planet's radiation properties, i.e., incomplete radiation absorption and emission with frequency-independent albedo and emissivity.

[94] Solar radiation from the blackbody Sun impinges on the gray body planet, of which 30% is reflected back to space and the rest is absorbed by the planet. The planet reradiates the same amount of radiation energy (as absorbed solar radiation) back to space to maintain its radiative equilibrium state. This simple process involves irreversible radiative energy transfer and thus leads to the increase of the planet's entropy. The entropy exchange involved in this radiative

energy transfer consists of the following three parts, which can be calculated on the basis of Planck's radiation theory.

### B1. Entropy Flux $J_{\text{solar}}^{(\text{in})}$ From Incident Solar Radiation

[95] The entropy flux  $J_{\text{solar}}^{(\text{in})}$  from incident solar radiation can be calculated according to expression (4a) of blackbody radiation entropy flux, that is,

$$J_{\text{solar}}^{(\text{in})} = \frac{4}{3}\sigma T_{\text{Sun}}^3 \frac{\int_{\Omega_0} \cos\theta d\Omega}{\int_0^{2\pi} d\phi \int_0^{\pi/2} \sin\theta \cos\theta d\theta} = \frac{4}{3}\sigma T_{\text{Sun}}^3 \cos\theta_0 \frac{\Omega_0}{\pi} = 0.0786 \text{ W m}^{-2} \text{ K}^{-1}, \quad (\text{B1})$$

where the Sun's effective emission temperature  $T_{\text{Sun}} (=5779 \text{ K})$  and the global averaged cosine of solar zenith angle  $\cos\theta_0 (=0.25)$  and solar solid angle  $\Omega_0 (=6.77 \times 10^{-5} \text{ sr})$  to the planet are used.

### B2. Planet's Reflected Solar Radiation Entropy Flux $J_{\text{solar}}^{(\text{out})}$

[96] Supposing that the planet's reflection of incident solar radiation is Lambertian (that is, the reflected solar radiation is the same in all directions and independent of the direction of incident solar radiation), we get the spectral energy flux  $I_\nu$  of the planet's reflected solar radiation equal to  $\alpha_P \cos\theta_0 \Omega_0 I_\nu^{\text{Sun}}/\pi$  (the reflected solar spectral radiation energy flux  $\alpha_P I_\nu^{\text{Sun}}$  is averaged over the Lambertian planet surface). Thus, the planet's reflected solar radiation entropy flux  $J_{\text{solar}}^{(\text{out})}$  can be calculated using Planck's spectral expression (8) with (9) as

$$J_{\text{solar}}^{(\text{out})} = \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left( 1 + \frac{c^2 \delta_0 I_\nu^{\text{Sun}}}{2h\nu^3} \right) \ln \left( 1 + \frac{c^2 \delta_0 I_\nu^{\text{Sun}}}{2h\nu^3} \right) - \left( \frac{c^2 \delta_0 I_\nu^{\text{Sun}}}{2h\nu^3} \right) \ln \left( \frac{c^2 \delta_0 I_\nu^{\text{Sun}}}{2h\nu^3} \right) \right\} d\nu = 0.1102 \text{ W m}^{-2} \text{ K}^{-1}, \quad (\text{B2})$$

where  $\delta_0 = \alpha_P \cos\theta_0 \Omega_0/\pi$ ; the spectral energy flux of incident solar radiation per unit solid angle per unit frequency is  $I_\nu^{\text{Sun}} = 2h\nu^3/c^2 \{ 1/[\exp(h\nu/\kappa T_{\text{Sun}}) - 1] \}$ ;  $h$ ,  $c$ , and  $\kappa$  are the Planck constant, speed of light in vacuum, and the Boltzmann constant, respectively; and  $\nu$  is frequency.

[97] However, if we suppose the planet's reflection of incident solar radiation to be specular (mirror-like), the spectral energy flux  $I_\nu$  of the planet's reflected solar radiation equals  $\alpha_P I_\nu^{\text{Sun}}$  (existing only within an effective solar solid angle  $\Omega_0$  with solar zenith angle  $\theta_0$  to the planet). For such a case, the planet's reflected solar radiation entropy flux  $J_{\text{solar}}^{(\text{out})}$  can be calculated using Planck's spectral expression (8) with (9) as

$$J_{\text{solar}}^{(\text{out})} = \int_0^\infty \frac{2\pi\kappa\nu^2 \delta_1}{c^2} \left\{ \left( 1 + \frac{c^2 \alpha_P I_\nu^{\text{Sun}}}{2h\nu^3} \right) \ln \left( 1 + \frac{c^2 \alpha_P I_\nu^{\text{Sun}}}{2h\nu^3} \right) - \left( \frac{c^2 \alpha_P I_\nu^{\text{Sun}}}{2h\nu^3} \right) \ln \left( \frac{c^2 \alpha_P I_\nu^{\text{Sun}}}{2h\nu^3} \right) \right\} d\nu = 0.0310 \text{ W m}^{-2} \text{ K}^{-1}, \quad (\text{B3})$$

where  $\delta_1 = \cos\theta_0 \Omega_0/\pi$ .

**TABLE B1. A Gray Body Planet's Radiation Entropy Flux Corresponding to Different Reflection Properties<sup>a</sup>**

Reflection	Lambertian	Specular
$\varepsilon_P$	[0.001, 0.50], [0.50, 1.00]	[0.001, 0.50], [0.50, 1.00]
$T_P$	>303.08, <303.08	>303.08, <303.08
$J_{\text{planet}}^{(\text{out})}$	[0.642, 1.240], [1.240, 1.253]	[0.642, 1.240], [1.240, 1.253]
$J_{\text{solar}}^{(\text{out})}$	0.110, 0.110	0.031, 0.031
$J_{\text{solar}}^{(\text{in})}$	0.079, 0.079	0.079, 0.079
$J_{\text{planet}}^{(\text{out})} + J_{\text{solar}}^{(\text{out})} - J_{\text{solar}}^{(\text{in})}$	[0.673, 1.271], [1.271, 1.284]	[0.594, 1.192], [1.192, 1.205]

<sup>a</sup>The temperature ( $T$ ) is expressed in units of K, and the entropy fluxes ( $J$ ) are in  $\text{W m}^{-2} \text{K}^{-1}$ .

[98] The calculation above is under the assumption that the planet's albedo  $\alpha_P$  is equal to 0.30. A generalization to other values of albedo is straightforward. Notice that SO93 presented the net radiation entropy flux as a function of albedo for various hypothetical Earth-like planets in radiative equilibrium [see *Stephens and O'Brien*, 1993, Figure 12].

### B3. Entropy Flux $J_{\text{planet}}^{(\text{out})}$ From the Planet's Radiation Emission

[99] The entropy flux  $J_{\text{planet}}^{(\text{out})}$  from the planet's radiation emission (with emissivity  $\varepsilon_P$ ) can be calculated on the basis of Planck's spectral expression (8) with (9) as

$$J_{\text{planet}}^{(\text{out})} = \int_0^\infty \frac{2\pi\kappa\nu^2}{c^2} \left\{ \left( 1 + \frac{c^2\varepsilon_P I_\nu^P}{2h\nu^3} \right) \ln \left( 1 + \frac{c^2\varepsilon_P I_\nu^P}{2h\nu^3} \right) - \left( \frac{c^2\varepsilon_P I_\nu^P}{2h\nu^3} \right) \ln \left( \frac{c^2\varepsilon_P I_\nu^P}{2h\nu^3} \right) \right\} d\nu \quad (\text{B4})$$

where  $I_\nu^P$  is the corresponding (at the same emission temperature  $T_P$  as the planet) blackbody spectral radiation energy flux, i.e.,  $I_\nu^P = 2h\nu^3/c^2 \{1/[\exp(h\nu/\kappa T_P) - 1]\}$ . For a given emissivity  $\varepsilon_P$ ,  $T_P$  can be determined according to the planet's radiative equilibrium hypothesis; that is, the planet's absorbed solar radiation energy flux equals the planet's emitted radiation energy flux ( $\pi R^2 Q_0 (1 - \alpha_P) = 4\pi R^2 \varepsilon_P \sigma T_P^4$ , where  $Q_0$  is the solar constant  $1367 \text{ W m}^{-2}$  and  $R$  is the planet's radius). If the planet's emissivity  $\varepsilon_P$  ranges within [0.50, 1.00] (the corresponding planet's effective emission temperature  $T_P < 303.08 \text{ K}$ , like the Earth system), the entropy flux from the planet's radiation emission is within [1.2403, 1.2529]  $\text{W m}^{-2} \text{K}^{-1}$ . If the planet's emissivity  $\varepsilon_P$  is within [0.001, 0.50] (the corresponding planet's effective emission temperature  $T_P > 303.08 \text{ K}$ ), the entropy flux from the planet's radiation emission is within [0.6423, 1.2403]  $\text{W m}^{-2} \text{K}^{-1}$ .

[100] Summation of the three parts [ $J_{\text{planet}}^{(\text{out})} + J_{\text{solar}}^{(\text{out})} - J_{\text{solar}}^{(\text{in})}$ ] leads to the planet's net radiation entropy flux. A summary of the radiation entropy flux for the gray body planet under different conditions is shown in Table B1.

### NOTATION

Roman symbols

- $a$  radiation constant,  $7.5737 \times 10^{-16} \text{ J m}^{-3} \text{K}^{-4}$ .
- $B$  a geometrical factor in (12a), (12b), and (13a);  $B = \int \cos\theta d\Omega$ , and  $B = \pi$  over a hemisphere.
- $c$  speed of light in vacuum,  $2.9979 \times 10^8 \text{ m s}^{-1}$ .
- $c_1, c_2,$  and  $c_3$  constant coefficients for  $m$  in (15b).
- $E$  radiation energy flux (the rate of radiation energy flowing through a unit area),  $\text{W m}^{-2}$ ; in optics this is called "irradiance" (radiant power per unit area, incident on a surface) or "radiant emittance" (radiant power per unit area, emitted from a surface), and in physics this is called "intensity" (power per unit area).
- $F(\varepsilon)$  a function of emissivity  $\varepsilon$  in (15a) and (15b).
- $h$  the Planck constant,  $6.626 \times 10^{-34} \text{ J s}$ .
- $I$  radiation energy flux per unit solid angle,  $\text{W m}^{-2} \text{sr}^{-1}$ ; in astronomy it is called "radiance" (radiant power per unit solid angle per unit area).
- $I_\nu$  spectral radiation energy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s}$ .
- $I_\nu^P$  corresponding (at the same emission temperature  $T_P$  as the Earth or planet) blackbody spectral radiation energy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s}$ .
- $I_\nu^{\text{Sun}}$  the blackbody Sun's spectral radiation energy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s}$ .
- $J$  radiation entropy flux (the rate of radiation entropy flowing through a unit area),  $\text{W m}^{-2} \text{K}^{-1}$ .
- $J^{\text{GR}}$  gray body radiation entropy flux,  $\text{W m}^{-2} \text{K}^{-1}$ .
- $J_{\text{LW}}$  LW radiation entropy flux,  $\text{W m}^{-2} \text{K}^{-1}$ .
- $J_{\text{SR}}$  reflected solar radiation entropy flux,  $\text{W m}^{-2} \text{K}^{-1}$ .
- $J_{\text{SW}}$  SW radiation entropy flux,  $\text{W m}^{-2} \text{K}^{-1}$ .
- $L$  radiation entropy flux per unit solid angle,  $\text{W m}^{-2} \text{sr}^{-1} \text{K}^{-1}$ .
- $L_\nu$  spectral radiation entropy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$ .
- $L_\nu^{\text{GR}}$  gray body spectral radiation entropy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$ .
- $L_\nu^{\text{SR}}$  reflected solar spectral radiation entropy flux per unit solid angle per unit frequency,  $\text{W m}^{-2} \text{sr}^{-1} \text{s K}^{-1}$ .

$m$	a coefficient in (15b).
$n_0$	state of polarization in (7) and (8), $n_0 = 1$ or 2 for a polarized or unpolarized ray.
$p$	radiation pressure, $\text{J m}^{-3}$ .
$\tilde{Q}$	heat, J.
$Q_0$	solar constant, $1367 \text{ W m}^{-2}$ .
$Q_{\text{net}}$	the Earth's net LW (or SW) radiation energy flux $((1 - \alpha_P)Q_0/4)$ flowing through the top of the atmosphere, $\text{W m}^{-2}$ .
$Q_{\text{SR}}$	reflected solar radiation energy flux $(\alpha_P Q_0/4)$ , $\text{W m}^{-2}$ .
$dQ$	exchange of radiation energy flux, $\text{W m}^{-2}$ .
$s$	spatial radiation entropy density (i.e., volume density of radiation entropy), $\text{J m}^{-3} \text{ K}^{-1}$ .
$S$	entropy, $\text{J K}^{-1}$ .
$s_\nu$	spectral spatial radiation entropy density per unit frequency, $\text{J m}^{-3} \text{ K}^{-1} \text{ s}$ .
$T$	temperature, K.
$T_a$	a brightness temperature of the Earth's atmosphere given by <i>Ozawa et al.</i> [2003], K.
$T_P$	the Earth's (or a planet's) effective emission temperature, K.
$T_{\text{Sun}}$	the Sun's effective emission temperature, 5779 K.
$T_\nu$	temperature of monochromatic radiation beams at frequency $\nu$ , K.
$u$	spatial radiation energy density (i.e., volume density of radiation energy), $\text{J m}^{-3}$ .
$U$	blackbody radiation energy, J.
$u_\nu$	spectral spatial radiation energy density per unit frequency, $\text{J m}^{-3} \text{ s}$ .
$V$	volume, $\text{m}^3$ .
$X(\delta)$	a function of the dilution factor $\delta$ in (13a) and (13b).

## Greek symbols

$\alpha_P$	the Earth's (or a planet's) albedo.
$\beta$	nondimensional group, $h\nu/\kappa T$ .
$\beta_P$	nondimensional group, $h\nu/\kappa T_P$ .
$\beta_{\text{Sun}}$	nondimensional group, $h\nu/\kappa T_{\text{Sun}}$ .
$\delta$	a diluted factor, i.e., the photon number of a diluted unpolarized blackbody radiation divided by that of the corresponding (at the same emission temperature as the diluted blackbody) unpolarized blackbody radiation.
$\delta_0$	nondimensional group, $\alpha_P \cos\theta_0 \Omega_0/\pi$ .
$\delta_1$	nondimensional group, $\cos\theta_0 \Omega_0/\pi$ .
$\varepsilon$	emissivity.
$\varepsilon_P$	the Earth's (or a planet's) emissivity.
$\theta$	zenith angle, deg.
$\cos\theta_0$	cosine of solar zenith angle to the Earth.
$\kappa$	the Boltzmann constant, $1.381 \times 10^{-23} \text{ J K}^{-1}$ .
$\nu$	frequency, $\text{s}^{-1}$ .
$\sigma$	the Stefan-Boltzmann constant, $5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ .

$\varphi$	azimuth angle, deg.
$\chi(\delta_0)$	an asymptotic expression in (14a)–(14c).
$\Omega$	solid angle, sr.
$\Omega_0$	solar solid angle to the Earth, $6.77 \times 10^{-5} \text{ sr}$ .

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