ELSEVIER
Physica A 243 (1997) 275–303
PHYSICA A

Information-theoretical approach to radiative transfer

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Received 6 December 1996; revised 26 February 1997

Abstract

The maximum entropy formalism is used to obtain the radiation and matter distribution functions for radiative systems in steady nonequilibrium states, under the gray approximation. The radiation distribution function is expanded in a smallness parameter, which vanishes at equilibrium. In the first near-equilibrium approximation, we derive the results of near-equilibrium diffusion theory. This may be regarded as an analogue to the kinetic-theoretical result, according to which in the first Enskog approximation, the Fourier heat conduction equation is obtained. The theory is also developed up to the second order, leading to results which apply to situations further away from equilibrium than those corresponding to near-equilibrium diffusion theory. A simple application is analyzed.

1. Introduction

The thermodynamics of nonequilibrium radiation contains several subtle and controversial points. Even the concept of temperature is controversial when dealing with nonequilibrium radiative systems. The classical approach [1–3] makes use of a matter local temperature and a radiation temperature $T_\nu(\boldsymbol{x}, \hat{\Omega}, t)$ that depends not only on position and time but also on frequency and direction. This radiation temperature T_ν is defined through the following equation [1–3]:

$$f_r(\boldsymbol{x}, \hat{\Omega}, \nu, t) = \frac{1}{e^{h\nu/k_B T_\nu} - 1},$$

with f_r the radiation distribution function, $\boldsymbol{x}$ the position, $\hat{\Omega}$ the direction of propagation and ν the frequency of radiation, t the time, h the Planck constant and k_B the Boltzmann constant (in equilibrium states, f_r is the Planck distribution function and therefore, $T_\nu = T$ does not depend on direction and frequency; it does not depend

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PII S0378-4371(97)00277-X

either, of course, on $\boldsymbol{x}$ nor t). We may note however, that it would be possible in principle to follow a similar approach to matter systems, by defining a matter temperature $T_{cm}(\boldsymbol{x}, \hat{\Omega}_m, t)$ which would depend on the direction of motion $\hat{\Omega}_m$ and the velocity c_m of the molecules ($\hat{\Omega}_m = \boldsymbol{c}_m/c_m$) making use of a definition that could be, for a classical ideal monatomic nonrelativistic gas with number density of molecules n, (barycentric) velocity $\boldsymbol{v}$ and molecular mass m [4],

$$f_m(\boldsymbol{x}, \hat{\Omega}_m, c_m, t) = (2\pi\hbar)^3 \frac{n}{(2\pi m k_B T_{cm})^{3/2}} \exp\left[-\frac{m(\boldsymbol{c}_m - \boldsymbol{v})^2}{2k_B T_{cm}} \right],$$

with f_m the matter distribution function and $\hbar = h/2\pi$. Since in equilibrium states f_m is the Maxwell–Boltzmann distribution function, one would have that in equilibrium $T_{cm} = T$ [4] and therefore T_{cm} would not depend on either the direction of motion nor the velocity c_m. Since the energy of a photon is completely determined by its frequency, and the energy of a particle in the case considered is determined completely by its velocity, we see that T_{cm} plays in the case of matter a similar role to the one played by T_ν for radiation. Therefore, if it were strictly necessary to make use of T_ν in order to deal with nonequilibrium radiative systems, it could seem reasonable to expect that it would be necessary to make use of T_{cm} in order to deal with nonequilibrium matter systems. However, we known that this is not necessary. Either phenomenological thermodynamics [5,6], kinetic theory [7–9] or statistical mechanics [10–12] provide adequate descriptions of nonequilibrium matter systems without need to complicate their respective theoretical frameworks making use of T_{cm}. From this point of view, it seems worthwhile to try to deal with nonequilibrium radiative systems without the introduction of a radiation temperature that depends on frequency and direction, and such an approach will be followed in the present paper.

It may seem surprising that the statistical–mechanical derivation of the complete description of radiative systems in equilibrium (the Planck function) has not been so far extended on nonequilibrium states (recently, a statistical–mechanical generalization of the Planck function has been proposed [13] in the framework of nonextensive statistical mechanics and thermodynamics [14], although this is a different problem than the one we have just mentioned, in the sense that in [13] one does not assume that the considered system is not in thermal equilibrium but analyzes the very interesting possibility of an influence of gravitation on light that might cause a non-Planckian spectrum in the cosmic microwave background radiation). In fact, a somehow similar situation has taken place for matter systems: microscopic derivations of theories of nonequilibrium thermodynamics [5,6,9,15] have often been based on kinetic theory approaches, although it has been recently argued that information theory may provide a statistical–mechanical approach that allows to handle more general situations [16–18].

One further motivation for studying radiative transfer situations is that, in contrast with matter [19], the distribution function for photons is extremely easy to observe directly: the intensity spectrum emitted by a black body in thermodynamic equilibrium is related to Planck's distribution function in a very simple way. Is it possible to extend this result (the Planckian intensity) to steady nonequilibrium states? This is the central question we would like to tackle in the present paper. Minerbo [20] applied the information theory approach to a radiation gas under the constraint of a non-vanishing radiative flux. Whereas in [20] a monochromatic ensemble of photons is assumed, in the present paper this assumption will be dropped. On the other hand, it should be remembered that a thermodynamic theory of radiation should include a matter content as well. For systems subject to dynamical evolution, this follows from the fact that the interaction between photons is entirely negligible [2]. We will argue in the present paper that also for nonequilibrium steady states, the interaction of radiation and matter is of thermodynamic importance.

The plan of the paper is as follows: In Section 2, we first give a short summary of information theory. We feel this to be necessary, although a little repetitive, because the author is convinced that the fact that the motivation for the use of information theory is obviated in many papers has caused some resistance to accept it as a reasonable candidate for the statistical–mechanical description of nonequilibrium systems. We then apply information theory to find out the distribution functions of radiation and matter. In Section 3, the radiation distribution function is written in terms of thermodynamical quantities, and we compare our results with those obtained by previous approaches. In Section 4 we illustrate the results for a specific system and Section 5 is devoted to concluding remarks.

2. Information theory

As it is well-known [21], a property of the Maxwell–Boltzmann distribution function is that it is the most probable distribution function for a system of matter particles among all possible distribution functions such that they are consistent with the prescribed values of the total number and internal energy of the particles. This means that, if we choose a microscopic state of the gas at random from among all its possible microscopic states that are mathematically consistent with given values of the total particle number and internal energy, then the probability that the chosen microscopic state has a Maxwell–Boltzmann distribution which is greater than for any other distribution. It must not be forgotten, however, that in the case of equilibrium the former argument leaves place for other possible, less probable, distribution functions, and we can make use of the Boltzmann equation (which rests on the assumption of molecular chaos) in order to see that only the Maxwell–Boltzmann distribution function is consistent with equilibrium states [21]. In spite of this, since many years ago many authors have tried to extend the most-probable approach to nonequilibrium states by requiring the satisfaction of additional constraints, such as the constraint of a given heat flux, etc. [22–24,11]. This idea was independently given and developed by Jaynes [10], who noted that Shannon's mathematical theory of communication allows us to interpret the Boltzmann entropy density of a system as a measure of the information about the system that is not contained in the distribution function. Then the most probable distribution function for a given macroscopic state of the system will be the one that, even in nonequilibrium states, maximizes the entropy density of the system under a set of constraints, corresponding to the physical parameters which specify the macroscopic state of the system. To assert that the actual distribution function of the particles of a physical system, in *nonequilibrium* states, has the property of being the most probable distribution function, is only an assumption, and is called the principle of maximum entropy. It has been noted many times [10,25–27] that there is an inherent vagueness in this principle, at least in its present form, since it does not specify what constraints should be used for a given physical system. It may therefore be said that in practice one chooses parameters that seem relevant for the physical situation considered (e.g., the conductive heat flux for the study of heat conduction), makes use of them as additional constraints, and waits for the usefulness or inadequacy of the principle to become clear after its predictions are compared with experimental results. In this respect it is worthwhile to mention that impressive agreement between the predictions of information theory and experiments in the field of nuclear physics has been reported by Fröhner [28]. On the other hand, it is adequate to stress that the argument that the entropy cannot be a maximum in nonequilibrium systems cannot be used against information theory, because when applying the principle of maximum entropy to nonequilibrium systems what one is ultimately doing is to choose one among all the possible distribution functions for a *single* macroscopic nonequilibrium state (e.g., a state with a given particle number density, a given internal energy density and a given nonvanishing heat flux), and not among all the possible distribution functions for *any* nonequilibrium or equilibrium state. Another relevant question is how one may, after use has been made of the principle of maximum entropy, find out constitutive or evolution equations for the thermodynamical variables of the system. We will deal with this problem at the point where it becomes necessary to do so (specifically, in the text between Eqs. (22) and (23)).

In the present paper, we will make use of the principle of maximum entropy in radiative transfer situations and will assume for simplicity that the matter part of the system is a classical ideal gas. The total entropy density of the system is [2,4]

$$s = s_m + s_r = -k_B \int_{R^3} \frac{d^3 p_m}{(2\pi\hbar)^3} f_m \ln f_m + 2k_B \int_{R^3} \frac{d^2 p_r}{(2\pi\hbar)^3} [(1+f_r)\ln(1+f_r) - f_r \ln f_r], \tag{1}$$

where the subindexes m and r stand for matter and radiation (photons), and f and p are the corresponding distribution functions and momenta, respectively.

We assume for simplicity that the heat flux in the system is only due to radiation. According to the statistical–mechanical definition of the distribution functions, we have for the total energy density u, matter number density n and radiative energy flux $\boldsymbol{F}$,

$$u = u_m + u_r = \int_{R^3} \frac{d^3 p_m}{(2\pi\hbar)^3} \frac{p_m^2}{2m} f_m + 2 \int_{R^3} \frac{d^3 p_r}{(2\pi\hbar)^3} p_r c f_r \,, \tag{2}$$

$$n = \int_{R^3} \frac{d^3 p_m}{(2\pi\hbar)^3} f_m \,, \tag{3}$$

$$\boldsymbol{F} = 2 \int_{R^3} \frac{d^3 p_r}{(2\pi\hbar)^3} p_r c \boldsymbol{c} f_r \,, \tag{4}$$

where the matter has been assumed to be composed of nonrelativistic monatomic molecules for simplicity, and $\boldsymbol{c}$ is the photon velocity, i.e., a vector of length the velocity of light in vacuum c and direction corresponding to that of the photon motion. Although a matter (or conductive) heat flux and the matter velocity can be treated as additional constraints [6,16], they are not included here for the sake of simplicity, i.e., we neglect heat conduction and also heat convection (the matter gas is assumed to be at rest). We make use of the principle of maximum entropy, by maximizing Eq. (1) under the constraints (2)–(4). In this way, one finally obtains for the distribution functions

$$f_m = \exp\left[-1 - \lambda - \beta \frac{p_m^2}{2m} \right], \tag{5}$$

$$f_r = 1/(\exp[\beta p_r c - \boldsymbol{\gamma} \cdot p_r c \boldsymbol{c}] - 1)\,, \tag{6}$$

with λ, β and $\boldsymbol{\gamma}$ Lagrange multipliers (the minus sign in front of $\boldsymbol{\gamma}$ is chosen for later convenience).

Substitution of Eq. (5) into Eq. (3) and integration over all possible values of $\boldsymbol{p}_m$ yields

$$n = \frac{\exp[-1-\lambda]}{(2\pi\hbar)^3} \left(\frac{2\pi m}{\beta} \right)^{3/2}, \tag{7}$$

where the integral has been solved with the use of formula 3.461-2 of Ref. [29]. From Eq. (7) we can write the matter distribution function (5) as

$$f_m = (2\pi\hbar)^3 n \left(\frac{\beta}{2\pi m} \right)^{3/2} \exp\left[-\beta \frac{p_m^2}{2m} \right], \tag{8}$$

which, when inserted into u_m given by Eq. (2) yields, after integration,

$$u_m = \frac{3}{2} \frac{n}{\beta}\,. \tag{9}$$

Eq. (8) corresponds, as we shall explicitly see when we introduce the concept of temperature for our system, to the Maxwell–Boltzmann distribution function. Eq. (6)

is a nonequilibrium result from information theory that has appeared from time to time in the literature [20,30–33,16]. However, its use leads to more complicated integrals than the use of Eq. (5), and for this reason it is better to follow the approach in [16]: we assume that the z-axis can be chosen parallel to γ, so that $\boldsymbol{\gamma} = (0, 0, \gamma)$. Then, insertion of Eq. (6) into u_r, given by Eq. (2), and into Eq. (4) and integration over all possible values of $\boldsymbol{p}_r$ yields, respectively,

$$u_r = \frac{\pi^2}{45c^3\hbar^3\beta^4} \frac{3+\varepsilon^2}{(1-\varepsilon^2)^3}, \tag{10}$$

$$\boldsymbol{F} = \left(0, 0, \frac{4\pi^2}{45c^2\hbar^3\beta^4} \frac{\varepsilon}{(1-\varepsilon^2)^3}\right) \equiv (0, 0, F), \tag{11}$$

where the integrals have been solved with the use of formula 3.411-1 of Ref. [29] and we have defined ε through

$$\boldsymbol{\varepsilon} \equiv (0, 0, \varepsilon) \equiv \left(0, 0, \frac{c\gamma}{\beta}\right). \tag{12}$$

We note from Eq. (11) that the simplifying assumption that the z-axis can be chosen parallel to γ implies that we are dealing with situations in which the radiative heat flux $\boldsymbol{F}$ has the direction of the z-axis.

Since the radiative energy density must according to Eq. (2) to positive, Eq. (10) implies that $-1 < \varepsilon < 1$. From now on we will for simplicity fix our attention into situations such that $F \geqslant 0$, thus according to Eq. (11) we have $0 \leqslant \varepsilon \leqslant 1$.

Eqs. (10) and (11) allow to find out ε in terms of F and u_r

$$\varepsilon = \frac{2 - \sqrt{4 - 3(F/cu_r)^2}}{F/cu_r}. \tag{13}$$

From Eq. (13) it is easy to see that ε is a strictly increasing function of F/cu_r. Thus, we may interpret the parameter ε as follows: in equilibrium, the photon velocities are distributed in an absolutely random way (in direction) so that the radiation is isotropic and according to Eq. (4) $\boldsymbol{F} = 0$, which in view of Eq. (11) or (13) implies that $\varepsilon = 0$. For $\boldsymbol{F} \neq 0$, the system is not in equilibrium and, the higher the value of F/cu_r is, the more ordered (or anisotropic) the radiation is and the higher the value of ε is. As the well-known maximum value $F \to cu_r$ (which follows from Eq. (4) and u_r, given by Eq. (2)) is approached, almost all of the photons move in the same direction and ε approaches its limiting value ($\varepsilon \to 1$). Thus, ε may be regarded as a smallness parameter that measures how much far away from thermodynamic equilibrium the system is.

The radiative entropy density is, according to Eqs. (1),(6) and (12),

$$s_r = \frac{2k_B}{(2\pi\hbar)^3} \int_{R^3} d^3p_r \left[\ln(1+f_r) + f_r \ln\left(1 + \frac{1}{f_r}\right)\right] = \frac{4\pi^2 k_B}{45c^3\hbar^3\beta^3} \frac{1}{(1-\varepsilon^2)^2}, \tag{14}$$

where the necessary integrals have been solved applying the procedure in p. 186 of Ref. [2] and formula 3.411-1 of Ref. [29]. Making use of Eq. (10), the radiative entropy (14) may be written as

$$s_r = \frac{4\pi^{1/2}k_B}{(45c^3\hbar^3)^{1/4}} u_r^{3/4} \frac{(1-\varepsilon^2)^{1/4}}{(3+\varepsilon^2)^{3/4}}, \tag{15}$$

which implies that for a given value of u_r, the radiative entropy decreases with increasing ε, i.e., with increasing order of the system. It is possible to show that Eq. (15) is equivalent to the corresponding equation for a purely radiative system that has been obtained both on macroscopic grounds [34] and through rather cumbersome information-theoretical calculations [31,16]. Since we clearly have $s_r \geqslant 0$, Eq. (14) implies that $\beta > 0$ and Eq. (12) implies that $\gamma \geqslant 0$.

Eqs. (10) and (11) also allow for $\boldsymbol{F}$ to be written as

$$\boldsymbol{F} = (0, 0, F) = 4cu_r\varepsilon/(3+\varepsilon^2). \tag{16}$$

On the other hand, the radiative pressure tensor is [35]

$$\boldsymbol{P}_r = \frac{2}{c}\int_{R^3} \frac{d^3p_r}{(2\pi\hbar)^3} p_r \boldsymbol{cc} f_r, \tag{17}$$

with $(\boldsymbol{cc})_{ij} \equiv c_i c_j$. Eq. (17) may be written, after insertion of (6), integration with the use of formula 3.411-1 of Ref. [29], and use of Eqs. (12) and (10), as

$$\boldsymbol{P}_r = u_r \frac{1}{3+\varepsilon^2}\begin{pmatrix} 1-\varepsilon^2 & 0 & 0 \\ 0 & 1-\varepsilon^2 & 0 \\ 0 & 0 & 1+3\varepsilon^2 \end{pmatrix}, \tag{18}$$

which in equilibrium ($\varepsilon = 0$) reduces, as it should, to $\boldsymbol{P}_r = \frac{1}{3}u_r\boldsymbol{U}$, with $\boldsymbol{U}$ the identity matrix, and in the extreme nonequilibrium limit $\varepsilon \to 1$ becomes

$$\boldsymbol{P}_r \to u_r \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

also a well-known result both from classical electrodynamics [40,1] and the quantum theory [36].

3. Identification of the Lagrange multipliers

The information-theoretical photon distribution function (6) depends on the parameters β and γ (or β and ε), which must be related to measurable quantities if we want to compare the predictions of the theory with experiment. In order to do this, let us consider for a moment a matter system composed of a nonrelativistic monatomic classical ideal gas. The temperature T of the system is usually defined through the following equation [5,7] (recall that in the present paper u_m stands for the internal energy per unit volume, not per unit mass)

$$u_m = \tfrac{3}{2} n k_B T \,, \tag{19}$$

both in equilibrium and in nonequilibrium states. We will here make use of this expression, so that we find from Eqs. (19) and (9) that

$$\beta = \frac{1}{k_B T}\,, \tag{20}$$

and Eq. (8) becomes the Maxwell–Boltzmann distribution function for a gas at rest (see note [4]). It may be argued that there is no reason to accept the validity of Eq. (19) as a definition of temperature, since the system considered is composed not only of matter (monatomic ideal gas) but also of radiation. It is true that Eq. (19) gives a purely statistical definition of T, but it is shown in Appendix A that the definition (19) of T is equivalent, for the system considered in this paper, to the thermodynamical definition of temperature (i.e., the inverse of the partial derivative of the specific entropy with respect to the specific energy of the system, which in our case is composed of matter and radiation). Now since in our system there is radiation in addition to matter, one might be tempted to require, in analogy with Eq. (19), that $u_r = aT^4$ (with $a = \pi^2 k_B^4 / 15 c^3 \hbar^3$ the blackbody constant), a well-known *equilibrium* relationship [2]. However, we have already defined T by means of Eq. (19) and shown that this definition corresponds to the thermodynamical concept of temperature. We cannot introduce a new definition for T. Then there is no reason to think that $u_r = aT^4$ is valid outside equilibrium. Even if the relationship $u_r = aT^4$ does hold in some nonequilibrium states [36,38] (this will indeed be shown to be so in the present paper), it should not be taken as an ad hoc postulate in any statistical–mechanical theory. In other words, since this result, namely $u_r = aT^4$, is *derived* by equilibrium statistical mechanics, any nonequilibrium statistical mechanical approach should *derive*, not *assume*: (i) its validity in the special case of thermodynamic equilibrium, and (ii) its validity, or the validity of a more general law, in nonequilibrium states. In fact, all of these considerations say nothing really new, but it is in this spirit that we may follow Mihalas and Mihalas [38] and introduce a *parameter* T_r through

$$u_r = aT_r^4 \,, \tag{21}$$

and keep in mind that T_r is just a parameter related to the radiation part of the system, but in general has no thermodynamical meaning (see Appendix A), so that the use of T_r in nonequilibrium is justified only as a way to characterize arbitrary radiation fields, a conclusion that has been stressed previously [38].

It follows from Eqs. (10), (20) and (21) that the radiation parameter T_r is related to the temperature of the radiation-matter system as follows:

$$T_r = T \, \frac{(1 + (\varepsilon^2/3))^{1/4}}{(1 - \varepsilon^2)^{3/4}} \,. \tag{22}$$

In the first line of this section it has been pointed out that both β and ε must be related to measurable quantities. In other words, we need two equations in which only β, ε and measurable quantities (such as T) appear. We have so far only one such equation, namely Eq. (20). In order to find out another one, we may recall that we have seen in Section 2 that ε is related to the anisotropy of the radiation field; on the other hand, the radiation anisotropy is expected intuitively to be related to the temperature distribution (for example, we may think about a star: there are more photons moving in the outwards radial direction than inwards, and the temperature decreases with increasing distance to the stellar center). Therefore, we expect ε to be related to the temperature distribution in the system. However, we shall find that the radiation anisotropy (and, therefore, both the parameter ε and the radiation distribution function) is related not only to the temperature distribution but also to the interaction processes between the matter and radiation (in fact, this can also be expected intuitively by thinking about the case of a star: if almost none of the photons created by the nuclear reactions in the interior of the star interact with matter before leaving the stellar surface, we expect the radiation to be extremely anisotropic, whereas in the case the most photons are absorbed by matter before reaching the surface, their energy will be reemitted in all directions and the radiation field inside the star will be less anisotropic than in the previous case). Before going ahead, however, a short comment about a rather more general information-theoretical problem will be useful.

Any general statistical–mechanical method for nonequilibrium systems must certainly be able to find out constitutive and evolution equations for the system variables. For example, it should be able to derive, as a special case, Fourier's law of heat conduction for matter systems. However, the principle of maximum entropy on its own is unable to attain such a goal, simply because all it yields is an expression for the distribution function. Many authors have overcome this difficulty by combining maximum-entropy distribution functions with other methods, such as the Boltzmann equation [11], the Liouville equation [41] or the nonequilibrium statistical operator method [42,43,17]. With this perspective, we have looked for an evolution equation for the radiation distribution function in order to combine it with the former information-theoretical results. We have decided to make use of the radiative transfer equation, because in spite of its mathematical simplicity (as compared, e.g., with the Boltzmann equation for matter systems) it is extremely successful, up to the point that it is almost always used in radiative transfer problems (see, e.g., [36–39]). In the present paper we will for simplicity consider only steady-state situations, a rather usual attitude in information theory (see, e.g., [6,16,25]). Moreover, in order to construct a simple model that allows for the fundamental features of our approach to be stressed without much mathematical complexity, we make the following simplifying assumptions: the absorption coefficient κ does not change appreciably with the frequency of the photons (the gray or one-group approximation [36]), and scattering and induced processes can be neglected. Under these assumptions the radiative transfer equation reads [36,37]

$$\hat{\Omega}\cdot\nabla I_\nu = -\kappa I_\nu + j_\nu\,, \tag{23}$$

where $\hat{\Omega} \equiv \boldsymbol{c}/c$ is the unit vector in the photon direction of motion, I_ν is the intensity of radiation, j_ν is the emission coefficient and we have made use of the fact that we are considering steady states. We are therefore assuming the same equation as in almost all of the existing studies on radiative transfer, and it is to be noted that it includes two interaction coefficients κ and j_ν. These coefficients, which play a role similar to that of the elastic (and reactive) cross-sections in the Boltzmann equation for matter systems, depend on a multitude of microscopic processes and can for this reason be found out only by means of lengthy quantum–mechanical calculations [36].

As it is well-known [44,45], multiplication of Eq. (23) by $\hat{\Omega}$, integration over all frequencies and solid angles and use of the expressions for $\boldsymbol{P}_r$ and $\boldsymbol{F}$ already mentioned in note [35] yields

$$c\nabla\cdot\boldsymbol{P}_r = -\kappa\boldsymbol{F}\,, \tag{24}$$

with

$$(\nabla\cdot\boldsymbol{P}_r)_i \equiv \sum_{j=1}^{3}\frac{\partial P_{r_{ji}}}{\partial x_i}\,.$$

From Eqs. (18) and (11), we have respectively, $P_{r_{ji}} = 0$ for $j \neq i$ and $\boldsymbol{F} = (0,0,F)$. This allows us to write Eq. (24) more explicitly,

$$c\,\frac{\partial P_{rii}}{\partial x_i} = -\kappa F_i = 0 \quad (i = x, y)\,,$$

$$c\,\frac{\partial P_{rzz}}{\partial z} = -\kappa F\,. \tag{25}$$

Eq. (25) will be used to relate the nonequilibrium parameter $\boldsymbol{\varepsilon} = (0,0,\varepsilon)$ (see Eq. (12)) to measurable quantities. In order to find out the radiation intensity in nonequilibrium steady states, we shall also need the following equation, which follows from the general relationship between I_ν and f_r, already mentioned in note [35], and from Eqs. (6), (12) and (20),

$$I_\nu = \frac{2h\nu^3}{c^2}\,\frac{1}{\exp\left[\dfrac{h\nu}{k_B T}(1-\boldsymbol{\varepsilon}\cdot\hat{\Omega})\right]-1}\,. \tag{26}$$

Because of mathematical complexities, we have not succeeded in developing the model presented here in exact analytical form for systems arbitrarily far away from equilibrium states. We will therefore consider three cases, increasingly further away from equilibrium.

3.1. $\varepsilon = 0$

According to Section 2, this corresponds to thermodynamic equilibrium. For $\varepsilon = 0$, Eq. (26) reduces, as it should, to the Planck function, i.e., $I_\nu = I_{\nu\,\mathrm{Planck}}$, with

$$I_{\nu\,\mathrm{Planck}} = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/k_BT} - 1}, \tag{27}$$

Eq. (22) yields $T_r = T$, and Eqs. (21), (16) and (15) reduce to $u_r = aT^4$, $\boldsymbol{F} = 0$ and $s_r = \frac{4}{3}aT^3$, also as they should [2]. Finally, Eq. (18) yields $\boldsymbol{P}_r = (aT^4/3)\boldsymbol{U}$ and substitution of the former results for $\boldsymbol{P}_r$ and $\boldsymbol{F}$ into Eq. (25) yields $\nabla T = 0$, so that the temperature of the equilibrium system is uniform, as it should.

3.2. First-order approximation

Up to the first order in the nonequilibrium parameter ε, Eq. (22) gives $T_r = T$ and Eqs. (21), (16) and (18) yield, respectively,

$$u_r = aT^4 + O(\varepsilon^2), \tag{28}$$

$$\boldsymbol{F} = \frac{4acT^4}{3} \boldsymbol{\varepsilon} + O(\varepsilon^2), \tag{29}$$

$$\boldsymbol{P}_r = \frac{aT^4}{3} \boldsymbol{U} + O(\varepsilon^2), \tag{30}$$

where we have recalled that $\boldsymbol{\varepsilon} = (0, 0, \varepsilon)$ (see Eq. (12)). From Eqs. (25), (29) and (30) it follows that, in the first-order approximation, $\boldsymbol{\varepsilon}$ may be written in terms of measurable quantities as

$$\boldsymbol{\varepsilon} = (0, 0, \varepsilon) = -\frac{1}{\kappa T} \nabla T, \tag{31}$$

so that Eq. (29) becomes

$$\boldsymbol{F} = -\frac{4acT^3}{3\kappa} \nabla T + O(\varepsilon^2). \tag{32}$$

At the same order of approximation, the radiation intensity can be obtained by expanding Eq. (26) up to first order in the smallness parameter ε. This yields, making use also of Eq. (31),

$$I_\nu = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/k_BT} - 1} - \frac{2h^2\nu^4}{k_B c^2 \kappa T^2} \frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT} - 1)^2} \nabla T \cdot \hat{\Omega} + O(\varepsilon^2). \tag{33}$$

Eq. (33) is the main result of near-equilibrium diffusion theory [46], an approximate description of radiative transfer which has been previously obtained [36,38]. It is very encouraging that this result also follows from the method used here, although the spirit of the present approach and those in [36,38] are very different. In [36], one assumes that I_ν consists of an isotropic term and a first-order anisotropic correction (the Eddington approximation), which when introduced into Eq. (23) leads, after neglecting second derivatives and making use of the additional assumption of radiative local thermodynamic equilibrium (i.e., the assumption that $j_\nu = \kappa I_{\nu\,\mathrm{Planck}}$, which has been discussed at length in [39]), to the same result (Eq. (33)). A somehow similar derivation can be found in [38]. The author of [36] explicitly notes that it seems rather surprising that a reasonably accurate description is obtained on the basis of so many assumptions, namely: the Eddington approximation, the neglect of second derivatives of the isotropic term and radiative local thermodynamic equilibrium. In contrast, in the present statistical–mechanical derivation the accuracy of near-equilibrium diffusion theory is not surprising, since we have only assumed the principle of maximum entropy (which is not used in [36 and 38]) and a single additional assumption, namely that the state of the system is near equilibrium. As we have seen, this last point is expressed mathematically as the assumption that the photon distribution function can be expanded up to first order in the nonequilibrium that the photon distribution function can be expanded up to first order in the nonequilibrium parameter ε. Moreover, the present approach allows, as we will see in Section 3.3, to consider systems which are further away from thermodynamic equilibrium than those described by near-equilibrium diffusion theory.

It has been previously noted [38], on the basis of Eqs. (32) and (28), that the near-equilibrium result (33), which applies to radiative systems, is closely analogous to the first Enskog approximation [7] to conductive matter systems: in both cases, a near-equilibrium state is assumed and it is found that the energy density is fixed by the local temperature, and that the heat flux is proportional to the temperature gradient (Eq. (32) is a radiative analogue to the Fourier heat conduction equation). We have apparently provided a much simpler derivation of all these radiative results. One may then conclude that information theory is a very useful complement of the radiative transfer equation, in the sense that it makes it possible to drop many assumptions that are necessary in other approaches. Whereas a somehow analogous informational-theoretical analysis for matter systems is well-known [11,6], and shows that information theory is a very useful complement to the Boltzmann equation, the corresponding analysis of radiative systems had not been carried out before.

It is also worthwhile to note that the near-equilibrium expression (33) is valid for small values of ε, $\varepsilon \ll 1$. From Eq. (31) we see that this condition may be written as

$$\frac{|\nabla T|}{T} \ll \kappa\,. \tag{34}$$

It is interesting to compare the condition (34), which ensures the validity of the first-order maximum-entropy approximation to radiative systems, with the condition that ensures the validity of the first Enskog kinetic-theory approximation to conductive, purely matter systems. This last condition reads [47] $|\nabla T|/T \ll \frac{1}{l}$, with l the mean-free path. However, the mean-free path of a photon is precisely κ^{-1} [36], so that condition (34) is equivalent to the one just recalled. This once more reinforces the analogy between the first-order maximum-entropy theory for radiative systems and the first Enskog theory for matter systems.

3.3. Second-order approximation

One of the differences between previous approaches [36,38] and the one presented in this paper is that the latter provides a general formalism that is not restricted to near-equilibrium states. However, we will now see that mathematical complexities arise when considering far-from-equilibrium situations.

Up to second order in the nonequilibrium parameter ε, Eqs. (16) and (18) yield, respectively, making use of (21),

$$\boldsymbol{F} = \frac{4acT_r^4}{3}\boldsymbol{\varepsilon} + O(\varepsilon^3)\,, \tag{35}$$

$$\boldsymbol{P}_r = \frac{aT_r^4}{3}\boldsymbol{U} + \frac{4aT_r^4}{9}\varepsilon^2\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} + O(\varepsilon^3)\,, \tag{36}$$

where it is to be noted that the radiation parameter T_r appears. Its relation with the temperature of the radiation-matter system is obtained by expanding Eq. (22) up to second order in the smallness parameter ε,

$$T_r = T\left(1 + \frac{5}{6}\varepsilon^2\right) + O(\varepsilon^3)\,. \tag{37}$$

In order to find out the radiation intensity we need, as in Section 3.2, an expression for $\boldsymbol{\varepsilon}$ in terms of measurable quantities (we stress that T is a measurable quantity, whereas T_r is not). This mathematical problem is not straightforward in general. However, in Appendix B it is shown that, for the simple case in which T depends only on the z coordinate and the temperature gradient is uniform, we have

$$\boldsymbol{\varepsilon} = (0, 0, \varepsilon) = -\frac{1}{\kappa T}\nabla T\,, \tag{38}$$

so that the first-order result (31) remains valid up to second order also.

The intensity is given by the second-order expansion in the smallness parameter ε, obtained from Eq. (26). This yields, making use of Eq. (38),

$$I_\nu = I_{\nu\,\mathrm{Planck}}[1 + \phi_1 + \phi_2] + O(\varepsilon^3)\,, \tag{39}$$

with

$$\phi_1 = -\frac{h\nu}{k_B\kappa T^2}\frac{e^{h\nu/k_BT}}{e^{h\nu/k_BT} - 1}\nabla T \cdot \hat{\Omega}\,, \tag{40}$$

$$\phi_2 = \frac{h^2\nu^2}{2k_B^2\kappa^2T^4}\frac{e^{h\nu/k_BT} + 1}{(e^{h\nu/k_BT} - 1)^2}e^{h\nu/k_BT}(\nabla T \cdot \hat{\Omega})^2\,. \tag{41}$$

We can note that, insofar as they yield an expression for the intensity of nonequilibrium radiation that generalizes a first-order expression (Eq. (33)) that is closely analogous to the first Enskog approximation for matter systems, Eqs. (39)–(41) may be regarded as a radiative analog of the Burnett (or second Enskog) approximation for matter systems [7].

4. Application

In order to illustrate the results of the model, let us consider a simple radiative system, namely a cavity with highly absorbing internal walls and containing an ideal gas (see Fig. 1). It is very important, in order to grasp the physical state of the system, that in view of the direction dependence in Eq. (26), there is an anisotropic emission of radiation by the internal walls of the cavity in nonequilibrium situations. Such a conclusion could also have been advanced intuitively in a simple way by considering the case of a star instead of a cavity. Any small part of the gas and radiation in a star can be regarded as a cavity with highly absorbing internal walls and a nonuniform temperature (and thus a nonvanishing net radiative energy flux F), such as that shown in Fig. 1 (in this case the z-axis would correspond to the outwards radial direction of the star). This picture is at the very basis of the theory of stellar structure [37] and in this case, instead of the solid walls of the cavity depicted in Fig. 1, we only have particles of gas. But the radiation intensity is anisotropic at any point of the star, and

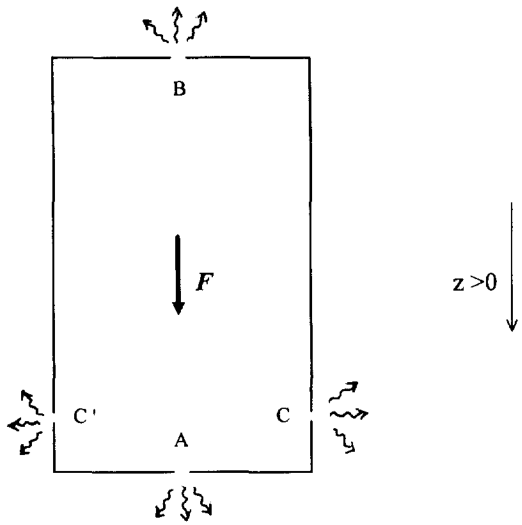


Fig. 1. Cavity containing an ideal gas. Radiation may leave the cavity through one or several small apertures, which in the figure are located at points A, B, C and C′. If the temperature at the walls varies with the z coordinate and decreases downwards, the system is in a nonequilibrium state and there is a nonvanishing net radiative energy flux F inside the enclosure.

specifically at the points that would correspond to the solid walls of the cavity in Fig. 1.

In order for our results to be applicable, let us assume that the walls of the enclosure are heated in a way such that the system reaches and maintains a stationary one-dimensional temperature distribution $T(z)$ (see Fig. 1). In order to prevent convective effects, we assume that T decreases downwards (i.e., with increasing $z, dT/dz \leqslant 0$). In fact, as far as the author knows, such an experiment has not been proposed or carried out before, except in the well-known equilibrium case ($dT/dz = 0$), for which the blackbody intensity is observed to be Planckian, in agreement with the results of equilibrium statistical mechanics.

4.1. First-order approximation

Let us consider the predictions of the first-order maximum-entropy theory, i.e., of near-equilibrium diffusion theory (the second-order theory will be used later on in order to find out under which conditions the first-order results can be treated). According to Eq. (32), there will be a radiative energy flux $F > 0$ in the direction shown in Fig. 1. We want to study the intensity of the radiation that leaves the enclosure through a small aperture, which may be located at different places (e.g., at points A, B, C and C′ in Fig. 1). This is directly measurable experimentally. We first note that, according to Eq. (33),

$$I_\nu = \frac{2h\nu^3}{c^2}\frac{1}{e^{h\nu/k_BT}-1} - \frac{2h^2\nu^4}{k_Bc^2\kappa T^2}\frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}\frac{dT}{dz}\cos\theta + O(\varepsilon^2)\,, \tag{42}$$

where θ is the angle between the direction $\hat{\Omega}$ corresponding to I_ν and the z-axis, and both T and dT/dz may depend on the z-coordinate in general.

It might seem inconsistent that Eq. (42) depends only on the thermodynamical quantities T and ∇T: one would expect intuitively the distribution function of radiation at, say, point B in Fig. 1, to depend on the values of T in all the points of the walls of the enclosure. This apparent inconsistency is solved as follows: the condition (34) for the near-equilibrium expression (42) to be a good approximation reads in the considered case

$$\frac{|dT/dz|}{T} \ll \kappa\,, \tag{43}$$

which means that Eq. (42) may be applied if the absorption coefficient is large enough to compensate for the variations of T along the cavity, in the sense that the absorption of the radiation emitted at, say, points A, C and C′ in Fig. 1 as it travels towards point B is responsible for the fact that the radiation at point B does not depend on the values of T at, say, points A, C and C′, but only on the values of T at points very close to point B, i.e., on the values of T and dT/dz at point B.

Since I_ν is an intensity per unit solid angle [36,37], the intensity emitted by the cavity i_ν due to the photons that, coming from all possible directions, leave the enclosure through the aperture A in Fig. 1, is

$$i_{\nu A} = \int_0^{2\pi} d\varphi \int_0^{\pi/2} d\theta \sin\theta \cos\theta \, I_{\nu A} \, . \tag{44}$$

Similarly, i_ν at the other apertures in Fig. 1 is given by

$$i_{\nu B} = - \int_0^{2\pi} d\varphi \int_{\pi/2}^{\pi} d\theta \sin\theta \cos\theta I_{\nu B} \, . \tag{45}$$

$$i_{\nu C} = \int_0^{2\pi} d\psi \int_0^{\pi/2} d\chi \sin\chi \cos\chi \, I_{\nu C} \, , \tag{46}$$

$$i_{\nu C'} = - \int_0^{2\pi} d\psi \int_{\pi/2}^{\pi} d\chi \sin\chi \cos\chi \, I_{\nu C'} \, , \tag{47}$$

where the new angles introduced in Eqs. (46) and (47) take into account the fact that the apertures located in points C and C′ are not normal but parallel to the z-axis; it may be seen (either directly or by means of formula 10.92 of Ref. [48]) that $\cos\theta = \sin\chi \sin\psi$. Taking this into account, substitution of Eq. (42) into Eqs. (44)–(47) and integration yields

$$i_{\nu A} = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T_A} - 1} - \frac{4\pi h^2 \nu^4}{3k_B c^2 \kappa T_A^2} \left. \frac{dT}{dz} \right|_A \frac{e^{h\nu/k_B T_A}}{(e^{h\nu/k_B T_A} - 1)^2} + O(\varepsilon_A^2) \, , \tag{48}$$

$$i_{\nu B} = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T_B} - 1} + \frac{4\pi h^2 \nu^4}{3k_B c^2 \kappa T_B^2} \left. \frac{dT}{dz} \right|_B \frac{e^{h\nu/k_B T_B}}{(e^{h\nu/k_B T_B} - 1)^2} + O(\varepsilon_B^2) \, , \tag{49}$$

$$i_{\nu C} = i_{\nu C'} = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{h\nu/k_B T_C} - 1} + O(\varepsilon_C^2) \, , \tag{50}$$

where we have taken into account that $T_C = T_{C'}$, since points C and C′ in Fig. 1 have the same value of z. We note that, up to first order in ε, the intensities emitted through the apertures C and C′ are Planckian.

We can also find out the total energy fluxes $q = \int_0^\infty i_\nu d\nu$ leaving the cavity by integration of (48)–(50). This gives

$$q_A = \frac{ac}{4} T_A^4 - \frac{2ac}{3\kappa} T_A^3 \left.\frac{dT}{dz}\right|_A + O(\varepsilon_A^2), \tag{51}$$

$$q_B = \frac{ac}{4} T_B^4 + \frac{2ac}{3\kappa} T_B^3 \left.\frac{dT}{dz}\right|_B + O(\varepsilon_B^2), \tag{52}$$

$$q_C = q_{C'} = \frac{ac}{4} T_C^4 + O(\varepsilon_C^2), \tag{53}$$

where the necessary integrals have been solved with the use of formulae 3.411-1 and 3.423-2 of Ref. [29]. In equilibrium ($\varepsilon = 0$ and $dT/dz = 0$), Eqs. (51)–(53) become the Stefan–Boltzmann law $q = (ac/4)T^4$, as they should.

We will now give some rough numerical estimations of the nonequilibrium spectral distributions with the intention that the possibility of comparing them with experiment becomes made as clear as possible.

For the spectral intensity distribution i_λ emitted per unit wavelength by the blackbody ($\lambda = c/\nu$ stands for the wavelength), in equilibrium one would have the usual Planckian expression,

$$I_{\lambda\,\text{Planck}} = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/k_B T\lambda} - 1}, \tag{54}$$

whereas in the near-equilibrium diffusion theory, it is easy to see from Eqs. (48) and (49) that

$$i_{\lambda A} = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/k_B T_A \lambda} - 1} + \frac{4\pi c^3 h^2}{3 k_B \kappa T_A^2 \lambda^6} \left|\frac{dT}{dz}\right| \frac{e^{hc/k_B T_A \lambda}}{(e^{hc/k_B T_A \lambda} - 1)^2} + O(\varepsilon_A^2), \tag{55}$$

$$i_{\lambda B} = \frac{2\pi c^2 h}{\lambda^5} \frac{1}{e^{hc/k_B T_B \lambda} - 1} - \frac{4\pi c^3 h^2}{3 k_B \kappa T_B^2 \lambda^6} \left|\frac{dT}{dz}\right| \frac{e^{hc/k_B T_B \lambda}}{(e^{hc/k_B T_B \lambda} - 1)^2} + O(\varepsilon_B^2), \tag{56}$$

where for simplicity we have considered states such that the temperature gradient is uniform and we have recalled that we are considering situations such that $dT/dz < 0$.

Assuming that $T_A = 2000$ K, $T_B = 2001$ K and $\kappa = 10\ \text{m}^{-1}$ [49], we plot in Fig. 2 the intensity spectrum according to Eqs. (55) and (56) for uniform temperature gradients of -5 K/m (so that the distance between the points A and B in the cavity depicted in Fig. 1 would have to be 20 cm, and Eq. (31) yields $\varepsilon_A = 2.5 \times 10^{-4}$, $\varepsilon_B = 2.499 \times 10^{-4}$) and -10 K/m (so that the distance between points A and B in Fig. 1 would have to be 10 cm, and (31) yields $\varepsilon_A = 5 \times 10^{-4}$, $\varepsilon_B = 4.998 \times 10^{-4}$). The dashed lines in Fig. 2 correspond to the equilibrium spectra, i.e., those that would be emitted by the blackbody cavity shown in Fig. 1 if the temperature gradient vanished,

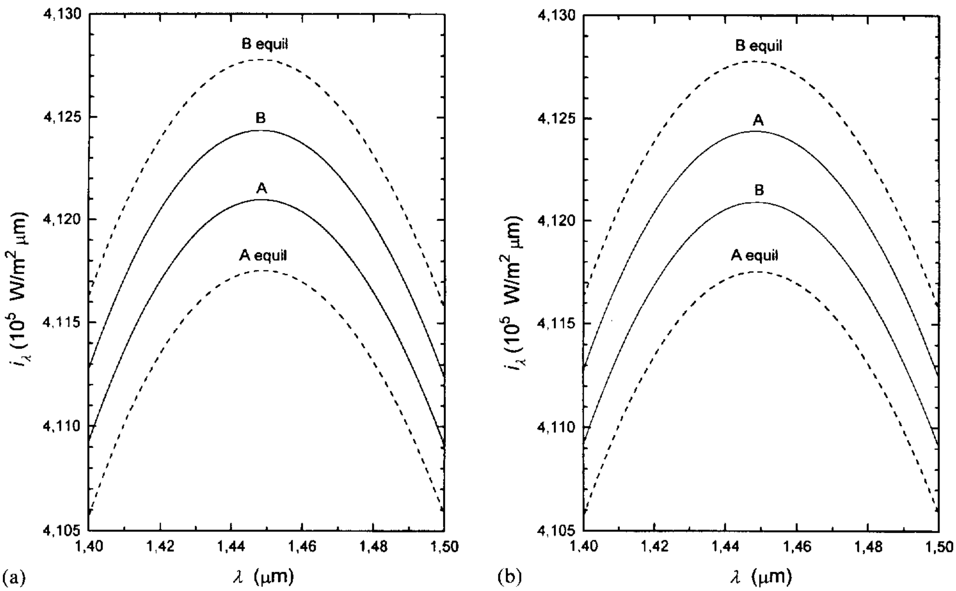


Fig. 2. Spectra of the radiation emitted by the cavity shown in Fig. 1 through the apertures A and B in near-equilibrium steady states (full curves), for $T_A = 2000$ K, $T_B = 2001$ K, $\kappa = 10\ \mathrm{m}^{-1}$ and a uniform temperature gradient of -5 K/m (a) and -10 K/m (b). Equilibrium spectra (dashed curves) with $T_A = 2000$ K and $T_B = 2001$ K are included for comparison.

and have been obtained from Eq. (54) with $T_A = 2000$ K and $T_B = 2001$ K. Since we are considering near-equilibrium situations, a plot over a wide spectral region would make all curves to appear superimposed, so that Fig. 2 only shows a narrow wavelength range near the maximum of intensity. The corrections with respect to the equilibrium results are of about 0.1% in Fig. 2a and of about 0.2% in Fig. 2b, which should be measurable.

4.2. Second-order approximation

We have seen that in the previous estimations the nonequilibrium smallness parameter ε is only of the order of 10^{-4}. This is much less than unity, so that the system should be near equilibrium and we expect the former first-order results to hold. However, we may carry out a more elaborate approach making use of the second-order maximum-entropy theory.

We consider again the physical situation depicted in Fig. 1. According to Eqs. (39)–(41), the second-order expression that replaces the first-order result (42) for the intensity may be written as

$$I_\nu = I_{\nu\,\mathrm{Planck}}(T)[1 + \tilde{\Phi}_1(T,\nabla T)\cos\theta + \tilde{\Phi}_2(T,\nabla T)\cos^2\theta] + O(\varepsilon^3)\,, \tag{57}$$

with

$$\tilde{\phi}_1(T,\nabla T) = -\frac{h\nu}{k_B\kappa T^2}\frac{e^{h\nu/k_BT}}{e^{h\nu/k_BT}-1}\frac{dT}{dz}, \tag{58}$$

$$\tilde{\phi}_2(T,\nabla T) = \frac{1}{2}\frac{h^2\nu^2}{k_B^2\kappa^2T^4}\frac{e^{h\nu/k_BT}+1}{(e^{h\nu/k_BT}-1)^2}e^{h\nu/k_BT}\left(\frac{dT}{dz}\right)^2. \tag{59}$$

Making use of Eq. (57) into Eqs. (44)–(47), we find

$$i_{\nu A} = \pi I_{\nu\,\text{Planck}}(T_A)[1+\tfrac{2}{3}\tilde{\phi}_1(T_A,\nabla T)+\tfrac{1}{2}\tilde{\phi}_2(T_A,\nabla T)] + O(\varepsilon_A^3), \tag{60}$$

$$i_{\nu B} = \pi I_{\nu\,\text{Planck}}(T_B)[1-\tfrac{2}{3}\tilde{\phi}_1(T_B,\nabla T)+\tfrac{1}{2}\tilde{\phi}_2(T_B,\nabla T)] + O(\varepsilon_B^3), \tag{61}$$

$$i_{\nu C} = i_{\nu C'} = \pi I_{\nu\,\text{Planck}}(T_C)[1+\tfrac{1}{4}\tilde{\phi}_2(T_C,\nabla T)] + O(\varepsilon_C^3). \tag{62}$$

We note that, in contrast with the first-order (or near-equilibrium diffusion) result (50), the intensity (62) emitted by the cavity through the apertures C and C′ in Fig. 1 is no longer Planckian when second-order terms are taken into account, and we find that Eqs. (55) and (56) are replaced, also in the second-order approximation, by

$$i_{\lambda A} = i_{\lambda\,\text{Planck}}(T_A)[1+\phi_{\lambda 1}(T_A,\nabla T)+\phi_{\lambda 2}(T_A,\nabla T)] + O(\varepsilon_A^3), \tag{63}$$

$$i_{\lambda B} = i_{\lambda\,\text{Planck}}(T_B)[1-\phi_{\lambda 1}(T_B,\nabla T)+\phi_{\lambda 2}(T_B,\nabla T)] + O(\varepsilon_B^3), \tag{64}$$

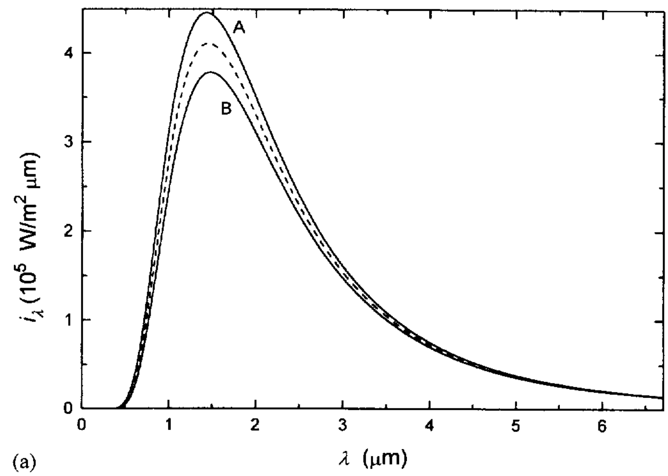
with

$$\phi_{\lambda 1}(T,\nabla T) = -\frac{2}{3}\frac{hc}{k_B\kappa T^2\lambda}\frac{e^{hc/k_BT\lambda}}{e^{hc/k_BT\lambda}-1}\frac{dT}{dz}, \tag{65}$$

$$\phi_{\lambda 2}(T,\nabla T) = \frac{1}{4}\frac{h^2c^2}{k_B^2\kappa^2T^4\lambda^2}\frac{e^{hc/k_BT\lambda}+1}{(e^{hc/k_BT\lambda}-1)^2}e^{hc/k_BT\lambda}\left(\frac{dT}{dz}\right)^2. \tag{66}$$

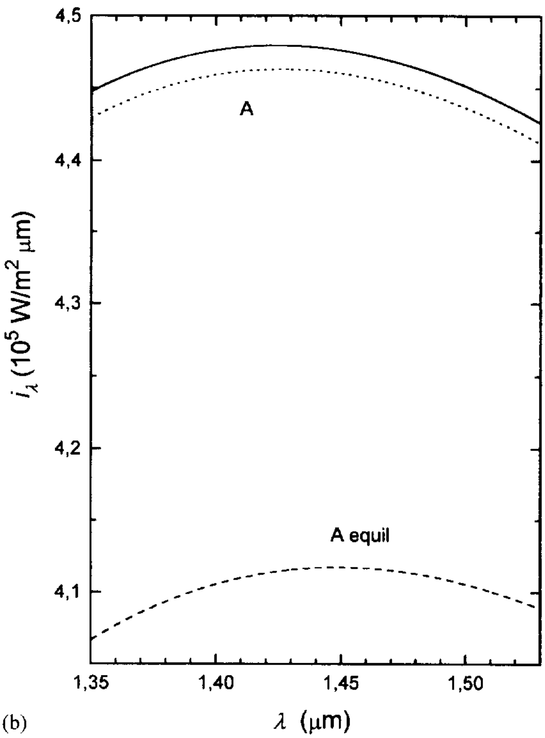
In the former subsection we have obtained first-order corrections with respect to the equilibrium spectra. These corrections were found to be about 0.1% or 0.2%. When the same values for T_A, T_B, κ and dT/dz as those used in the previous subsection are used into Eqs. (63)–(66), it is seen that the second-order corrections with respect to the equilibrium spectra are only of about10^{-4}%. This confirms the reliability of the first-order results in the situation considered, as it was expected intuitively on the basis of the small values of the parameter ε (which are of the order of 10^{-4}).

The fact that the second-order corrections are so small in the former cases make us expect that the first-order theory should be reliable in situations further away from equilibrium than those considered up to now. This is interesting from two points of view: it will yield higher corrections, thus it will make it easier to compare the theory with experiments; and it will give us some quantitative feeling of the range under which near-equilibrium diffusion theory is valid. We note from Eq. (38) or (31) that, for a fixed value of the temperature, the nonequilibrium parameter ε can be increased either by considering higher values of the norm of the temperature gradient or lower values of the absorption coefficient. If we consider as before $T_A = 2000$ K and $T_B = 2001$ K, it is possible that higher values of the temperature gradient than those assumed up to now could be interesting in the context of astrophysics or plasma physics applications, but not in order to carry out the experiment proposed in Fig. 1 in the laboratory since in that case the distance between the points A and B would have to be extremely small. On the other hand, lower values of the absorption coefficient can be obtained simply by decreasing the density of the gas in the cavity [51,49]. Let us therefore consider the case $\kappa = 0.1\ \mathrm{m}^{-1}$. We also assume $dT/dz = -5$ K/m. In this case Eq. (38) yields $\varepsilon_A = 0.025$ and $\varepsilon_B = 0.02499$, and from Eqs. (55) and (56) we find out the first-order spectral distributions, which we plot in Fig. 3(a). The dashed line in Fig. 3(a) corresponds to the equilibrium (or Planckian) spectra (Eq. (54)) at the temperatures $T_A = 2000$ K and $T_B = 2001$ K, which are not distinguishable from each other in Fig. 3(a). Somehow similarly, Fig. 3(a) in fact also includes second-order spectra (obtained from Eqs. (63)–(66)), but they are not distinguishable from the first-order ones. Therefore, in Fig. 3(b) we show the same spectra for the aperture A as those in Fig. 3(a), but only for a narrow wavelength range near the maxima of intensity (We note from Fig. 3(b) that in nonequilibrium, the maximum of intensity is not the same as in equilibrium. This indicates that the nonequilibrium steady-state extension of the Planck function dealt with in the present paper leads to an extension



(a)

Fig. 3. Spectra of the radiation emitted through the apertures A and B by the cavity shown in Fig. 1 in nonequilibrium steady states (with $T_A = 2000$ K, $T_B = 2001$ K, $\kappa = 0.1\ \mathrm{m}^{-1}$ and a uniform temperature gradient of -5 K/m), compared with equilibrium spectra (dashed curves). The dashed curve in (a) corresponds to equilibrium (or Planckian) spectra with $T_A = 2000$ K and $T_B = 2001$ K (these two spectra are not distinguishable from each other in this figure), whereas the full lines A and B correspond to the nonequilibrium spectra (the first- and second-order spectra are not distinguishable from each other in (a) either). (b) shows the same spectra as (a) for the aperture A, but only in a narrow wavelength range near the maxima. In this way, we can distinguish the spectrum, emitted through the aperture A and obtained according to the first-order theory (dotted line), from the second-order one (full line). The equilibrium spectrum, for a temperature of 2000 K is shown as a dashed line.



(b)

Fig. 3. (Continued).

of Wien's displacement law. We plan to deal with this topic in future work). From Figs. 3(a) and 3(b), we find that the first-order corrections with respect to the equilibrium spectra are as large as 8.5%, whereas the second-order approximation yields an additional correction of about 0.4%. It may be noted that even in this case (in which ε is of the order of 10^{-2}), the first-order theory gives reasonably accurate spectra. On the other hand, Figs. 2 and 3(a) are easy to understand keeping in mind that the emission of radiation by the internal walls of the cavity in Fig. 1 is anisotropic (see the text at the beginning of this section): the emission is stronger in the downwards directions in Fig. 1 than in the upwards ones.

We conclude that, at least in the simple situation considered here, the model yields measurable predictions for the radiative properties of steady nonequilibrium systems, and that such predictions go beyond those corresponding to near-equilibrium diffusion theory.

5. Concluding remarks

A model for the description of matter-radiation systems in steady non-equilibrium situations has been presented. Since conductive and convective effects have been neglected, we have considered situations in which heat transfer is purely radiative.

The theory presented here is based on the principle of maximum entropy and on the steady-state radiative transfer equation (23). This model includes a smallness parameter ε that is a measure of how much far away from thermodynamic equilibrium the system is. The first-order approximation yields the same results as the so-called near-equilibrium diffusion theory of radiative transfer, without need of the additional assumptions that are necessary in previous approaches. This maximum-entropy first-order theory may be regarded as a radiative analogue of the first Enskog theory of matter systems. It has been shown that information theory provides a general framework in order to deal with further away from equilibrium situations, and the second-order approximation has been solved analytically in a simple case. This leads to an expression for the intensity of radiation (Eqs. (39)–(41)) that may be tested experimentally.

Some of the directions along which it would be interesting to extend the present model are the following.

(i) To try to consider situations arbitrarily far away from equilibrium in order to try to predict deviations from Planck's spectrum due to arbitrarily high-temperature gradients. This will probably turn out to be a mathematically complicated, but physically interesting problem. A typical situation is found in the outer layers of stars. For example, making use of the standard solar model results for κ and T into Eq. (31), we find that at the center of the Sun ε is only of the order of 10^{-14} [52], so that $\varepsilon \ll 1$ and the intensity spectrum is thus extremely close to Planckian in spite of the nonvanishing temperature gradient. On the other hand, at the solar surface (31) yields $\varepsilon \approx 0.5$ [52], so that the first-order theory should be expected to become invalid. The theory developed in the present paper should be extended to situations arbitrarily far away from equilibrium in order to be able to cope with so strongly anisotropic radiation fields.

(ii) To drop the assumption that the absorption coefficient is independent of frequency, in order to try to obtain more realistic predictions to be compared with experimental results. Similarly, it would also be of interest to include scattering and induced processes. In fact, it is straightforward to see that the present model allows for the inclusion of out-scattering simply by replacing the absorption coefficient κ in all equations by the total interaction coefficient (i.e., the sum of the absorption coefficient and the scattering coefficient [36]).

(iii) To try to find out specific applications that allowed to compare the present model with different statistical–mechanical [13] and kinetic–theoretical [53] approaches that also yield nonequilibrium corrections to the Planck distribution function.

(iv) To try to extend the present model into a much wider conceptual framework, by replacing the entropy density (1) and constraints (2)–(4) by those given by the generalized axioms of the recently introduced nonextensive statistical mechanics [14]. The ultimate goal would be, of course, to obtain results that improved agreement with experimental results in radiative transfer situations, in a similar way to what has already been done for a large variety of physical systems (see the last paper in [14] and the references therein).

(v) The present approach may be useful in order to discuss in detail the concept of temperature in nonequilibrium systems (see Appendix A). However, this is a subtle, difficult and controversial topic [6,45,54–60] and it would therefore seem proper to consider several kinds of nonequilibrium systems (not just radiative ones) in order to address it adequately.

Acknowledgements

It is with great pleasure that the author would like to thank D. Jou for suggesting this problem and for his guidance, and J.A. González for checking part of the calculations. Both of them made valuable suggestions on a preliminary version of the manuscript. Discussions with J.E. Llebot, J. Martí and J. Miró are also acknowledged. Computing equipment used in this work has been partially funded by the Comisión Interministerial de Ciencia y Tecnologia of the spanish government under grant No. CLI95-1867.

Appendix A. Proof of consistency between Eq. (19) and the thermodynamical definition of temperature

Let $\tilde{s}_m$ and $\tilde{u}_m$ stand for the matter entropy per unit mass and internal energy per unit mass, respectively. They are related to the matter entropy and internal energy densities, used in Section 2, through

$$\tilde{s}_m = \frac{s_m}{\rho}, \tag{A.1}$$

$$\tilde{u}_m = \frac{u_m}{\rho}, \tag{A.2}$$

where $\rho = mn$ is the matter density. The radiation entropy and energy per unit mass of matter are, respectively,

$$\tilde{s}_r = \frac{s_r}{\rho}, \tag{A.3}$$

$$\tilde{u}_r = \frac{u_r}{\rho}. \tag{A.4}$$

We will first obtain an equation for $d\tilde{s}_m$ from information theory.

From Eq. (1) we have

$$ds_m = -k_B \int_{R^3} \frac{d^2 p_m}{(2\pi\hbar)^3} \frac{d}{df_m} [f_m \ln f_m] \, df_m$$

$$= k_B \lambda \int_{R^3} \frac{d^3 p_m}{(2\pi\hbar)^3} df_m + k_B \beta \int_{R^3} \frac{d^3 p_m}{(2\pi\hbar)^3} \frac{p_m^2}{2m} df_m , \tag{A.5}$$

where we have made use of Eq. (5). According to Eqs. (3) and (2), Eq. (A.5) may be written as

$$ds_m = k_B \lambda \, dn + k_B \beta \, du_m . \tag{A.6}$$

On the other hand, insertion of Eq. (5) into s_m, given by Eq. (1), and use of Eqs. (3) and (2) yields

$$s_m = k_B(1 + \lambda) n + k_B \beta u_m . \tag{A.7}$$

From Eqs. (A.1), (A.6) and (A.7) we find

$$d\tilde{s}_m = \frac{k_B \beta}{\rho} du_m + k_B(\beta u_m + n) \, d\left(\frac{1}{\rho}\right), \tag{A.8}$$

where we have recalled that $\rho = mn$. Making use of Eq. (A2), Eq. (A.8) may be written as

$$d\tilde{s}_m = k_B \beta \, d\tilde{u}_m + k_B n \, d\left(\frac{1}{\rho}\right). \tag{A.9}$$

The former equation refers to the matter content of the system. We now look for a similar expression for $d\tilde{s}_r$. From Eqs. (1) and (6) we find that

$$ds_r = 2k_B \int_{R^3} \frac{d^3 p_r}{(2\pi\hbar)^3} \frac{d}{df_r} [(1 + f_r) \ln (1 + f_r) - f_r \ln f_r] \, df_r$$

$$= 2k_B \beta \int_{R^3} \frac{d^3 p_r}{(2\pi\hbar)^3} p_r c \, df_r - 2k_B \gamma \int_{R^3} \frac{d^3 p_r}{(2\pi\hbar)^3} p_r c c \, df_r , \tag{A.10}$$

which may be written, making use of Eqs. (2) and (4), as

$$ds_r = k_B \beta \, du_r - k_B \gamma \cdot d\boldsymbol{F} . \tag{A.11}$$

On the other hand, Eq. (14) may be written, making use of the blackbody constant definition $a = \pi^2 k_B^4 / 15 c^3 \hbar^3$, as

$$s_r = \frac{4a}{3k_B^3 \beta^3} \frac{1}{(1 - \varepsilon^2)^2} . \tag{A.12}$$

From Eqs. (A.3),(A.11),(A.12) and (A.4) it is found that

$$d\tilde{s}_r = k_B\beta\, d\tilde{u}_r + \left(-k_B\beta u_r + \frac{4a}{3k_B^3\beta^3}\frac{1}{(1-\varepsilon^2)^2}\right) d\left(\frac{1}{\rho}\right) - \frac{k_B}{\rho}\gamma\cdot d\boldsymbol{F}\,. \tag{A.13}$$

This information-theoretical result applies to the radiation part of the system, in the same way as Eq. (A.9) applies to the matter part.

The two components, namely matter and radiation, are mixed together in the physical system under consideration, and interact with each other through absorption and emission processes (any photon in the system has been emitted by matter and will sooner or later be absorbed by matter). Therefore, a thermodynamic (i.e., macroscopic) description must refer to the composed system and not to matter and radiation separately. Let us denote the total entropy and energy densities per unit mass by $\tilde{s} = s/\rho$ and $\tilde{u} = u/\rho$, respectively. We have, in accordance with the first equalities in (1) and (2), and to Eqs. (A.1)–(A.4), that $\tilde{s} = \tilde{s}_m + \tilde{s}_r$ and $\tilde{u} = \tilde{u}_m + \tilde{u}_r$. Making use of Eqs. (A.9) and (A.13) we find that

$$d\tilde{s} = k_B\beta\, d\tilde{u} + \left(k_B n - k_B\beta u_r + \frac{4a}{3k_B^3\beta^3}\frac{1}{(1-\varepsilon^2)^2}\right) d\left(\frac{1}{\rho}\right) - \frac{k_B}{\rho}\gamma\cdot d\boldsymbol{F}\,. \tag{A.14}$$

We note that $\tilde{s}$ does not depend only on $\tilde{u}$ and ρ, but also on $\boldsymbol{F}$. Heat-flux dependencies of the specific entropy have been studied many times in purely matter systems (see, e.g., [33] and references therein). The dependence that we have noted from (A.14) is analogous to those just recalled, with the difference that in our case it is the radiative flux $\boldsymbol{F}$ instead of the conductive flux $\boldsymbol{q}$ that appears.

If we require that the temperature should be defined thermodynamically through $1/T \equiv \partial\tilde{s}/\partial\tilde{u}$, we see from Eq. (A.14) that $\beta = 1/k_B T$. This is precisely Eq. (20), which has been obtained from the statistical definition of temperature (19). We therefore see that, in the case considered, it is equivalent to make use of Eq. (19) or of $1/T = \partial\tilde{s}/\partial\tilde{u}$ in order to define T. We conclude that the quantity T, defined through (19), is the thermodynamical temperature of the system. We also conclude that the quantity T_r, defined through Eq. (21), has no thermodynamical meaning at all, and should be only regarded as one way to parametrize the radiation field.

Here we have only paid attention to the first term of those on the right-hand side of Eq. (A.14). A detailed analysis of the remaining terms is useful for the discussion of the generalized temperature of extended irreversible thermodynamics [6,54–58]. This concept has still not been dealt with from a statistical–mechanical perspective in radiative transfer situations [45], and it would be interesting to do so. However, we stress that this is not a straightforward but a very subtle and controversial [54–60] problem and we defer it to future work. On the other hand, a relevant point here is to note that use of (20) into Eq. (A.14) yields, in thermodynamic equilibrium ($\boldsymbol{F} = 0$ and therefore $\varepsilon = 0$ and $\gamma = 0$, see Eqs. (13) and (12)),

$$d\tilde{s} = \frac{1}{T}\, d\tilde{u} + \left(k_B n + \frac{u_r}{3T}\right) d\left(\frac{1}{\rho}\right), \tag{A.15}$$

where we have made use of the fact that $u_r = aT^4$, which is obtained from Eq. (10) in equilibrium and Eq. (20). The differentials in (A.15) should be regarded as small differences of the corresponding quantities between closely equilibrium states of the system. At this point, and in order to avoid confusion, it is better to denote such differentials by means of the symbol δ instead of d. Then Eq. (A.15) reads

$$\delta\tilde{s} = \frac{1}{T}\,\delta\tilde{u} + \left(k_B n + \frac{u_r}{3T}\right)\delta\left(\frac{1}{\rho}\right).$$

Since we are now dealing with equilibrium situations, all quantities are uniform and by integration of this result over the whole mass of the system one immediately finds, as it should be, consistency with well-known equilibrium results: the phenomenological equilibrium Gibbs equation for the system, namely

$$\delta S = \frac{1}{T}\,\delta U + \frac{p_m + p_r}{T}\,\delta V\,,$$

(with $S = \int \tilde{s}\,dm$, $U = \int \tilde{u}\,dm$ and $V = \int \frac{1}{\rho}\,dm$ the total entropy, total energy and volume of the radiation-matter system, respectively) and equations $p_m = nk_B T$ and $p_r = u_r/3$.

Appendix B. Derivation of Eq. (38)

For the purpose of this appendix, we will need to find out P_{rzz} and u_r in terms of T and $\boldsymbol{\varepsilon}$, up to second order in ε. One way to do this is to substitute Eq. (37) into (36) and (21). This yields

$$P_{rzz} = \frac{aT^4}{3}(1 + 6\varepsilon^2) + O(\varepsilon^3)\,, \tag{B.1}$$

$$u_r = aT^4(1 + \tfrac{10}{3}\varepsilon^2) + O(\varepsilon^3)\,, \tag{B.2}$$

and Eq. (B.2) generalizes the well-known *equilibrium* relationship $u_r = aT^4$. We will also need to write down $\boldsymbol{F}$ in terms of T and $\boldsymbol{\varepsilon}$, but up to third order in ε. This can be easily done from Eqs. (16) and (B.2),

$$\boldsymbol{F} = \frac{4acT^4}{3}(1 + 3\varepsilon^2)\boldsymbol{\varepsilon} + O(\varepsilon^4)\,. \tag{B.3}$$

As we shall now see, it is not easy to find out an expression for $\boldsymbol{\varepsilon}$ in terms of measurable quantities at the present level of approximation. We shall therefore not deal with the general solution for $\boldsymbol{\varepsilon}$, but with a special, the simplest possible case, by considering situations such that both T and $\boldsymbol{\varepsilon}$ depend only on the z coordinate (the compatibility of both conditions is an ansatz to be checked a posteriori). In this case we may write down the second Eq. in (25), making use of (B.1) and (B.3), as

$$\frac{1}{T}\left(\frac{1}{3} + 2\varepsilon^2\right)\frac{dT}{dz} + \varepsilon\,\frac{d\varepsilon}{dz} = -\frac{\kappa}{3}\,\varepsilon(1 + 3\varepsilon^2)\,. \tag{B.4}$$

From this equation and keeping in mind that we are interested in second-order results we obtain

$$\varepsilon = -(1 + 3\varepsilon^2)\frac{1}{T\kappa}\frac{dT}{dz} - \frac{3}{\kappa}\varepsilon\frac{d\varepsilon}{dz}. \tag{B.5}$$

It is easy to see that in case we had not included the third-order term in (B.3), Eq. (B.5) would have missed a term that is relevant at the present level of approximation. One may also easily check that the first Eq. in (25) is satisfied in the considered case. Nevertheless, in contrast with the first-order result (31), Eq. (B.5) is not still an explicit expression for ε in terms of measurable quantities. We may however make use of the method of successive approximations [61]. We assume that the result (31) can be considered as a first subapproximation,

$$\boldsymbol{\varepsilon}^{(1)} = (0, 0, \varepsilon^{(1)}) = -\frac{1}{\kappa T}\nabla T. \tag{B.6}$$

Let us, again for simplicity, consider states such that $\nabla T = (0, 0, dT/dz)$ is uniform. Inserting the value given by Eq. (B.6) for ε on the right-hand side of Eq. (B.5), and calling $\varepsilon^{(2)}$ the left-hand side we obtain

$$\boldsymbol{\varepsilon}^{(2)} = (0, 0, \varepsilon^{(2)}) = -\frac{\nabla T}{\kappa T}. \tag{B.7}$$

This is a very simple result, because it is the same as (B.6), which corresponds to the first subapproximation. Indeed, it is easy to check that (B.7) is, in fact, the exact solution of Eq. (B.5) or (B.4) in situations such that the temperature gradient is uniform. Therefore, we can assert that in such situations

$$\boldsymbol{\varepsilon} = -(1/\kappa T)\nabla T \tag{B.8}$$

is the analytical solution for the nonequilibrium parameter $\boldsymbol{\varepsilon} = (0, 0, \varepsilon)$ working not only up to the first, but also up to the second-order of approximation. This completes the derivation of Eq. (38).

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