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A Comparison Between Information-Theoretic and Phenomenological Descriptions of Nonequilibrium Radiation

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We present two approaches to the description of nonequilibrium radiation. The first approach is based on information statistical theory, whereas the second one is based on the hypothesis of radiative local thermodynamic equilibrium (RLTE). Both methods are applied to describe the radiation inside an infinite medium where a uniform temperature gradient has been established. The absorption coefficient is allowed to be frequency dependent. It is found that both approaches cannot be consistent beyond the first-order approximation. We argue that this shows the limitations of existing models of radiative transfer based on information theory.

KEY WORDS: Radiative transfer; information theory; local thermodynamic equilibrium.

I. INTRODUCTION

Equilibrium thermodynamics(1) is consistent with the results of equilibrium statistical physics(2) and also with those from kinetic theories(3) in the special case of equilibrium. Similarly, the analysis of near-equilibrium *matter* systems is well-established at present because consistent results follow from the near-equilibrium extensions of the three methods we have mentioned (namely, local-equilibrium irreversible thermodynamics,(4, 5) nonequilibrium information statistical theory(6, 7) and Chapman–Enskog kinetic-theoretical approaches(3)). Such results have been checked to be in agreement with experimental measurements for a variety of situations, including conductive and convective heat transfer, diffusion, viscous flow, electrical conduction,

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etc.(3, 8) However, for the case of radiative transfer the situation is very different. A well-established nonequilibrium radiation distribution function that has been tested in the laboratory does not seem to be available at present. It is therefore important to analyze this topic by means of different approaches in order to evaluate the validity of the hypothesis and simplifications used in each case. Furthermore, the distribution must be valid in conditions attainable in real material systems so that the experimental verification could be envisaged.

The main purpose of the present paper is to present two different ways to determine the distribution function of nonequilibrium radiation and to compare their results. Both methods will be applied to solve the simplest non-equilibrium situation one can imagine, namely an infinite medium with a uniform temperature gradient and at a steady state. In Section II, we make uses of information statistical theory. In Section III, we apply a phenomenological approach based on the hypothesis of radiative local thermodynamical equilibrium (RLTE). No specific hypothesis will be made upon the nature of the material subsystem. Its interaction with the radiation subsystem will be characterized by its absorption coefficient. An arbitrary dependence of the absorption coefficient on the photon energy will be allowed. The intensity of radiation will be calculated up to second order in a perturbative expansion on powers of the temperature gradient. The results given by both approaches are compared in Section IV. Finally, Section V is devoted to some concluding remarks.

II. INFORMATION STATISTICAL THEORY

Information statistical theory was derived by Jaynes,(9) who was motivated by the desire to free statistical physics from its often apparent, misleading dependence on specific mechanical models. A compelling check of the applicability of information theory to nonequilibrium states is that it provides a derivation for the near-equilibrium, first-order distribution function of matter under heat conduction and/or convection,(6, 7) and the result thus derived is the same as that obtained from the Grad kinetic theory,(10, 11) which in turn coincides (for sufficiently slow phenomena) with that derived by means of the Chapman–Enskog approach.(3)

In order to apply information theory, we begin by considering the entropy density of photons with momentum in a differential dp_r (centered at p_r), divided by $(p_r^2\, dp_r)$. This can be written as(2)

$$\tilde{S}_{p_r} = \frac{2k}{h^3} \int_{4\pi} d\Omega [(1+f_r) \ln(1+f_r) - f_r \ln f_r] \tag{1}$$

where $d\Omega$ is a differential of solid angle (i.e., $d^3p_r = p_r^2\,dp_r\,d\Omega = p_r^2\,dp_r \times \sin\theta\,d\theta\,d\varphi$), $f_r(\vec{p}_r)$ is the momentum distribution function of radiation, k is the Boltzmann constant and h is the Planck constant. Equation (1) is valid both in equilibrium and in nonequilibrium states.$^{(2)}$ The energy density and energy flux, both of them divided by ($p_r^2\,dp_r$), of the same photons as those considered above, are

$$\tilde{U}_{p_r} = \frac{2}{h^3}\int_{4\pi} d\Omega\, p_r c f_r \tag{2}$$

$$\vec{F}_{p_r} = \frac{2}{h^3}\int_{4\pi} d\Omega\, p_r c \vec{c} f_r \tag{3}$$

respectively. Here $\vec{c}$ is the photon velocity and $c = |\vec{c}|$ is the speed of light in *vacuo*. We apply information statistical theory$^{(9)}$ by maximizing the entropy density (1) under the constraints of fixed values of $\tilde{U}_{p_r}$ and $\vec{F}_{p_r}$. As it is always done in information theory, we follow the standard procedure from the textbooks on Calculus$^{(12)}$ by defining the function

$$\begin{aligned}\Phi(f_r, \beta_{p_r}, \gamma_{p_r}) = \tilde{S}_{p_r} - \beta_{p_r}\left(\frac{2k}{h^3}\int_{4\pi} d\Omega\, p_r c f_r - k\tilde{U}_{p_r}\right)\\ - \vec{\gamma}_{p_r}\cdot\left(-\frac{2k}{h^3}\int_{4\pi} d\Omega\, p_r c\vec{c} f_r + k\vec{F}_{p_r}\right)\end{aligned}$$

with β_{p_r} and $\vec{\gamma}_{p_r}$ Lagrange multipliers, and requiring that $\partial\Phi/\partial f_r = 0$. This yields the radiation distribution

$$f_{r\,\mathrm{IST}} = \frac{1}{\exp[\beta_{p_r} p_r c - \vec{\gamma}_{p_r}\cdot p_r c\vec{c}\,] - 1} \tag{4}$$

where the subindex IST denotes that this result has been obtained by means of information statistical theory (note that we have obtained a negative sign in front of $\vec{\gamma}_{p_r}$ by writting the constraint (3) in $\Phi(f_r, \beta_{p_r}, \gamma_{p_r})$ appropriately-this will make comparison to previous work simpler). A distribution function of the form (4) was first derived by Minerbo.$^{(13)}$ Other authors$^{(14)}$ did not consider the spectral quantities (1)–(3) but the corresponding ones integrated over p_r, which allowed them to introduce p_r—independent multipliers β and $\vec{\gamma}$. In ref. 15 it was shown that this also allows to identify β and $\vec{\gamma}$ in terms of measurable quantities, but assuming a very specific system, namely one such that: (i) the absorption of radiation by matter is frequency-independent (grey approximation); and (ii) the matter part is a classical ideal gas. In this section, we shall extend the statistical derivation in ref. 15 to an arbitrary matter content of the system: (i) the grey approximation will be dropped; and (ii) a classical ideal gas for the matter part will be no longer assumed. A general approach, such as the one presented below, is appealing not only conceptually but also because it is realistic in the sense that for most materials the dependence of the optical absorption on the radiation frequency is important. Moreover, very few materials behave as an ideal gas.

In order to identify the Lagrange multipliers β_{p_r} and $\vec{\gamma}_{p_r}$, we begin by finding out the differential of the radiation entropy density. Equations (1)–(4) yield

$$\begin{aligned} d\tilde{S}_{p_r} &= \frac{2k}{h^3} \int_{4\pi} d\Omega \, \frac{d}{df_r} \left((1+f_r) \ln(1+f_r) - f_r \ln f_r \right) df_r \\ &= k\beta_{p_r} \, d\tilde{U}_{p_r} - k\vec{\gamma}_{p_r} \cdot d\vec{F}_{p_r} \end{aligned} \tag{5}$$

We can write the spectral entropy and energy densities as

$$\begin{aligned} \tilde{S}_{p_r} &= \rho S_{p_r} \\ \tilde{U}_{p_r} &= \rho U_{p_r} \end{aligned} \tag{6}$$

where ρ is the matter density. S_{p_r} and U_{p_r} are the spectral entropy and energy of radiation, respectively, both of them per unit mass of matter in the system. The differential of the spectral specific entropy is

$$dS_{p_r} = k\beta_{p_r} \, dU_{p_r} - \frac{k}{\rho} \vec{\gamma}_{p_r} \cdot d\vec{F}_{p_r} + (\rho S_{p_r} - k\rho \beta_{p_r} U_{p_r}) \, dv \tag{7}$$

where $v = 1/\rho$ is the specific volume. We denote the spectral temperature of radiation by T_{p_r}. From its thermodynamical definition, namely(7)

$$\frac{1}{T_{p_r}} \equiv \frac{\partial S_{p_r}}{\partial U_{p_r}} \tag{8}$$

and the extended Gibbs equation (7) we identify the Lagrange multiplier β_{p_r} as

$$\beta_{p_r} = \frac{1}{kT_{p_r}} \tag{9}$$

According to these results, the temperature of radiation is a spectral function, i.e., it depends on the photon momentum. This was pointed out by Planck(16) and Landau and Lifshitz.(2)

We still have to relate the other multiplier that appears in the radiation distribution (4), namely $\vec{\gamma}_{p_r}$, to thermodynamical quantities. In order to do so, we consider the radiative transfer equation(17, 18)

$$\frac{1}{c}\frac{\partial I_\nu}{\partial t}+\hat{\Omega}\cdot\vec{\nabla}I_\nu=-\sigma_\nu I_\nu+\varepsilon_\nu \tag{10}$$

where $\hat{\Omega}\equiv\vec{c}/c$. Here σ_ν and ε_ν are, respectively, the absorption coefficient and the emissivity and will in general depend on the radiation frequency ν. The emissivity is taken independent on the intensity, i.e., we discard any kind of stimulated emission. This is valid unless the intensity is very high. The transfer equation (10) is used in all treatises on radiative transfer,(17, 18) and it simply states that the change in the intensity I_ν in the $\hat{\Omega}$ direction (between two space-time points separated by a time interval dt and by a position vector $\hat{\Omega}c\,dt$) is due to the absorption and emission processes. The meaning of this equation can also be understood as follows. The intensity (per unit solid angle) of radiation is related to the photon distribution function through[19]

$$I_\nu=\frac{2h\nu^3}{c^2}f_r \tag{11}$$

so that multiplication of the transfer equation (10) by $c/(hp_r^2)$ and use of Eqs. (2) and (3) yields

$$\frac{\partial\tilde{U}_{p_r}}{\partial t}+\vec{\nabla}\cdot\vec{F}_{p_r}=-\sigma_\nu c\tilde{U}_{p_r}+\varepsilon_{p_r} \tag{12}$$

where $\varepsilon_{p_r}\equiv c\varepsilon_\nu/hp_r^2$. We see that the radiative transfer Eq. (10) yields Eq. (12), which after integration over an arbitrary volume states that the rate of change of the energy of radiation is due to the flux of photons entering (and leaving) the volume considered as well as to the absorption and emission of radiation within it.

Since our main aim in the present paper is to compare the results of information theory with those following from a near-equilibrium phenomenological approach (Section III), we restrict our attention to near-equilibrium states. Because the equilibrium (or Planckian) distribution corresponds to Eq. (4) with $\vec{\gamma}_{p_r}=0$, we assume (analogously to the wellknown procedure in the information-theoretical approach to heat conduction in ideal matter gases)(7) that near-equilibrium states correspond to small values of $\vec{\gamma}_{p_r}$, an ansatz to be checked *a posteriori*. By performing a

MacLaurin expansion of the distribution (4) up to second order in $\vec{\gamma}_{p_r}$ we obtain

$$f_{r\,\mathrm{IST}} = \frac{1}{\exp[\eta_{p_r}]-1}\left(1+\frac{\exp[\eta_{p_r}]}{\exp[\eta_{p_r}]-1}\,p_r c\vec{c}\cdot\vec{\gamma}_{p_r}\right.$$
$$\left.+\frac{\exp[\eta_{p_r}](\exp[\eta_{p_r}]+1)}{2(\exp[\eta_{p_r}]-1)^2}\,p_r^2c^2(\vec{c}\cdot\vec{\gamma}_{p_r})^2\right) \tag{13}$$

where $\eta_{p_r}\equiv p_r c/kT_{p_r}$ and use has been made of Eq. (9). From Eq. (11), we can rewrite Eq. (13) as

$$I_{\nu\,\mathrm{IST}} = \frac{2h\nu^3}{c^2}\frac{1}{\exp[\eta_{p_r}]-1}\left(1+h\nu\frac{\exp[\eta_{p_r}]}{\exp[\eta_{p_r}]-1}\,(\vec{c}\cdot\vec{\gamma}_{p_r})\right.$$
$$\left.+\frac{h^2\nu^2}{2}\frac{\exp[\eta_{p_r}](\exp[\eta_{p_r}]+1)}{(\exp[\eta_{p_r}]-1)^2}(\vec{c}\cdot\vec{\gamma}_{p_r})^2\right) \tag{14}$$

and we may write $\eta_{p_r}=h\nu/kT_{p_r}$ since the energy of a photon is $p_r c=h\nu$.

If the system is in a steady state, multiplication of the radiative transfer equation (10) by $\vec{c}/c$ and integration over all solid angles yields

$$\int_{4\pi} d\Omega\left(\frac{\vec{c}}{c}\cdot\vec{\nabla}I_\nu\right)\frac{\vec{c}}{c} = -\sigma_\nu\int_{4\pi} d\Omega\, I_\nu\,\frac{\vec{c}}{c} \tag{15}$$

where $d\Omega$ is a differential of solid angle (in polar coordinates, $d\Omega=\sin\theta\, d\theta\, d\varphi$). In order to obtain simple expressions, let us assume that the temperature gradient is uniform. There are several ways of finding out $\vec{\gamma}_{p_r}$. The simplest one is the following. In previous work it was found that this multiplier can be written as $\vec{\gamma}=-\vec{\nabla}T/\sigma ckT^2$ for grey materials with absorption coefficient σ (see Eqs. (12), (20) and (38) in ref. 15). This was derived under the *ad hoc* assumption that a common temperature T could be shared by matter and radiation. Since we are looking for the generalization of this result to nongrey materials (i.e., to materials with a frequency-dependent absorption coefficient σ_ν) interacting with radiation with spectral temperature T_{p_r}, it seems reasonable to expect that its simplest generalization to the case here considered, namely

$$\vec{\gamma}_{p_r} = -\frac{\vec{\nabla}T_{p_r}}{\sigma_\nu ckT_{p_r}^2} \tag{16}$$

is the proper result. Indeed, in the Appendix we show that this expression is the solution to Eq. (15) implied by the information-theoretical intensity (14), up to second-order in the temperature gradient.

We make use of Eq. (16) into the intensity (14),

$$I_{\nu\,\mathrm{IST}} = I_{\nu\,\mathrm{Planck}}(1 + \phi^{(1)} + \phi^{(2)}) \tag{17}$$

where

$$I_{\nu\,\mathrm{Planck}} = \frac{2h\nu^3}{c^2} \frac{1}{\exp[\eta_{p_r}] - 1} \tag{18}$$

is the Planck intensity with temperature T_{p_r}, and the first- and second-order nonequilibrium corrections are, according to information statistical theory,

$$\phi^{(1)}_{\mathrm{IST}} = -\frac{\eta_{p_r}}{\sigma_\nu T_{p_r}} \frac{\exp[\eta_{p_r}]}{\exp[\eta_{p_r}] - 1} (\hat{\Omega} \cdot \vec{\nabla} T_{p_r}) \tag{19}$$

$$\phi^{(2)}_{\mathrm{IST}} = \frac{\eta^2_{p_r}}{2\sigma^2_\nu T^2_{p_r}} \frac{\exp[\eta_{p_r}](\exp[\eta_{p_r}] + 1)}{(\exp[\eta_{p_r}] - 1)^2} (\hat{\Omega} \cdot \vec{\nabla} T_{p_r})^2 \tag{20}$$

The nonequilibrium intensity (17) corresponds—according to the approach followed in this section—to thermal radiation emitted by near-equilibrium matter systems. This means that radiation due to other emission processes (e.g., fluorescence) is not considered. We would like to stress that, in contrast to what was done in refs. 15 and 25, we have not applied the grey approximation, which is rather restrictive since the absorption coefficient is strongly dependent on frequency for most materials.(18, 19)

III. RADIATIVE LOCAL-THERMODYNAMIC EQUILIBRIUM

The radiative local thermodynamic equilibrium (RLTE) approach yields a natural extension of the Planckian distribution. It is based on the phenomenological assumption that the state of the material subsystem can be described at any point by a local temperature and that, as far as the stimulated emission can be neglected, the emissivity of the material is the same as it would be at equilibrium. This is the usual approach that can be found in the classic text by Chandrasekhar.(20) The equation of radiative transfer (10) gives at equilibrium

$$\varepsilon_\nu = \sigma_\nu I_{\nu\,\mathrm{Planck}}(T_m) \tag{21}$$

where T_m is the local matter temperature.

This value of the emissivity can be now substituted in Eq. (10). As in the previous section, we consider steady states. Integration along an arbitrary direction $\hat{\Omega}$ gives the intensity of photons moving per unit solid angle centered at this direction,

$$I_\nu(0, \hat{\Omega}) = I_\nu(-s, \hat{\Omega}) \exp[-\sigma_\nu s] + \int_{-s}^{0} \sigma_\nu I_{\nu\ \text{Planck}}(T_m(s')) \exp[-\sigma_\nu |s'|]\, ds' \tag{22}$$

This solution is readily interpreted as follows (see Fig. 1). The intensity at point $s = 0$ results from the intensity at an arbitrary distance s, reduced by the factor $\exp(-\sigma_\nu s)$ that accounts for the absorption, plus the radiation due to the emission of all the subvolumes contained along the $\hat{\Omega}$ direction (the corresponding intensities appear inside the integral, and are also affected by absorption). So, within the RLTE approach the intensity can be calculated easily if the temperature distribution is known. Now, in order to compare to the results of the previous section, a uniform gradient will be assumed

$$T_m(z) = T_m + \frac{dT_m}{dz} z$$

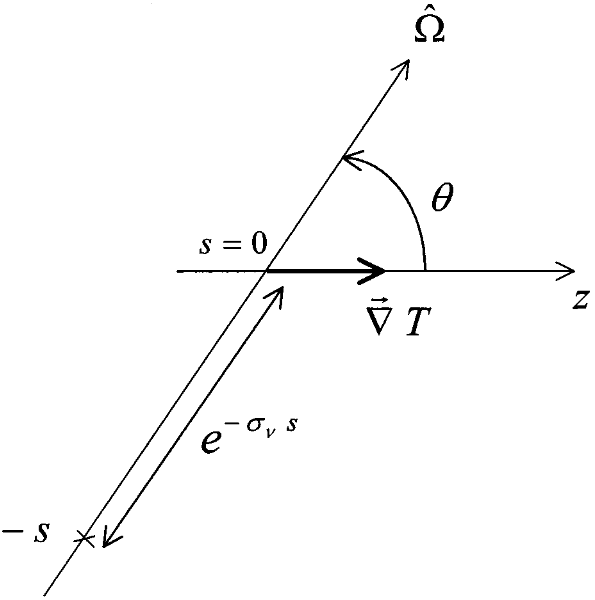

Fig. 1. The radiation emited by any subvolume located along the $\hat{\Omega}$ direction will reach the reference point $s = 0$ (observer) after being attenuated due to absorption. The effect is accounted for by the factor $\exp[-\sigma_\nu s]$ appearing in Eq. (22).

For an infinite medium, the intensity will be

$$I_{\nu\,\mathbf{RLTE}} \equiv I_\nu(0, \hat{\Omega}) = \sigma_\nu \int_{-\infty}^{0} I_{\nu\,\mathbf{Planck}}(T_m(z)) \exp[\sigma_\nu z/\cos\theta]\, \frac{dz}{\cos\theta} \tag{23}$$

where θ is the angle between the z and $\hat{\Omega}$ directions (see Fig. 1). Expansion of the exponential up to second order in z and integration gives the intensity

$$I_{\nu\,\mathbf{RLTE}} = I_{\nu\,\mathbf{Planck}}(1 + \phi^{(1)}_{\mathbf{RLTE}} + \phi^{(2)}_{\mathbf{RLTE}}) \tag{24}$$

where

$$I_{\nu\,\mathbf{Planck}} = \frac{2h\nu^3}{c^2} \frac{1}{\exp[\eta_m] - 1} \tag{25}$$

is the Planckian intensity at temperature T_m, $\eta_m \equiv h\nu/kT_m$ and the non-equilibrium corrections are

$$\phi^{(1)}_{\mathbf{RLTE}} = -\frac{\eta_m}{\sigma_\nu T_m} \frac{\exp[\eta_m]}{\exp[\eta_m] - 1} (\hat{\Omega} \cdot \vec{\nabla} T_m) \tag{26}$$

$$\phi^{(2)}_{\mathbf{RLTE}} = \frac{\eta_m^2}{\sigma_\nu^2 T_m^2} \frac{\left[\begin{array}{l} \exp[\eta_m] \\ \quad \times \{(\exp[\eta_m] + 1) + (2/\eta_m)(-\exp[\eta_m] + 1)\} \end{array}\right]}{(\exp[\eta_m] - 1)^2} (\hat{\Omega} \cdot \vec{\nabla} T_m)^2 \tag{27}$$

where we have applied that $\hat{\Omega} \cdot \vec{\nabla} T_m = (dT_m/dz) \cos\theta$ (see Fig. 1). The first order RLTE correction can be found in treatises specialized in radiation hydrodynamics (Pomraning$^{(17)}$ and Mihalas and Mihalas$^{(21)}$), where the derivation is much more complex than ours. Furthermore, the derivation given by Pomraning makes use of additional assumptions that apparently restrict the validity of the solution. However, our derivation makes clear that the solution is exact and, additionally, although we have not gone beyond the second order, higher order terms can be easily calculated from Eq. (23).

IV. COMPARISON BETWEEN THE STATISTICAL AND PHENOMENOLOGICAL DESCRIPTIONS

In Section II, we have presented a derivation of the thermal radiation emitted in a system under a temperature gradient. That derivation is based on Information Statistical Theory (IST). The result is given by

Eqs. (17)–(20), and it depends on the radiation spectral temperature T_{p_r}. In Section III, we have followed a different approach, which is not statistical but based on the phenomenological assumption of RLTE. The corresponding result is given by Eqs. (24)–(27), and it depends on the matter temperature T_m. In none of both derivations have we assumed a specific matter content for the system. We can now compare the results of both approaches. In order to do so, we should find a relationship between the radiation and matter temperatures. Due to the fact that a departure from equilibrium will imply, in general, an exchange of heat between the radiation and matter subsystems, it is reasonable to consider that $T_{p_r} - T_m$ should increase with the temperature gradient. A higher temperature gradient corresponds to a state further away from equilibrium. So, we try the relationship

$$T_{p_r} = T_m + a_{p_r}(T_m)(\hat{\Omega} \cdot \vec{\nabla} T_m) + b_{p_r}(T_m)(\hat{\Omega} \cdot \vec{\nabla} T_m)^2 \tag{28}$$

where $a_{p_r}(T_m)$ and $b_{p_r}(T_m)$ are unknown functions of p_r and T_m. If the intensities $I_{\nu\,\mathrm{RLTE}}$ and $I_{\nu\,\mathrm{IST}}$ constituted equivalent descriptions of the radiation field, then substituting Eq. (28) into $I_{\nu\,\mathrm{IST}}$ (Eqs. (17)–(20)) and equating the second-order result to $I_{\nu\,\mathrm{RLTE}}$ (Eqs. (24)–(27)) would allow to determine $a_{p_r}(T_m)$ and $b_{p_r}(T_m)$ and, consequently, the relationship between T_{p_r} and T_m. The IST and RLTE intensities coincide up to first order only if $a_{p_r}(T_m) = 0$. This means that first-order agreement between IST and RLTE implies that the radiation temperature equals the mater temperature and is independent of the photon momentum up to the first order in $\vec{\nabla} T_m$,

$$T_{p_r} = T_m + b_{p_r}(T_m)(\hat{\Omega} \cdot \vec{\nabla} T_m)^2 \tag{29}$$

Concerning the second order, both approaches give the same functional dependence if $b_{p_r}(T_m) = -1/T_m \sigma_\nu^2$. However, in this case, $\phi^{(2)}_{\mathrm{IST}}$ and $\phi^{(2)}_{\mathrm{RLTE}}$ differ by a factor of 2. In fact, it is not possible to find out $b_{p_r}(T_m)$ such that it gives accordance between IST and RLTE at the second order. So, the question arises about the correctness of the result given by the IST approach. A simple argument will be given below to demonstrate that this second-order result is contradictory with the optical behaviour of ionic impurities in solids.

Imagine a transparent solid matrix where a ionic impurity has been dissolved up to a concentration low enough so that the impurities do not interact. This means that their wavefunction is independent of concentration N. In this case, the optical absorption coefficient can be written as[22]

$$\sigma_\nu = N S_\nu \tag{30}$$

where S_ν is the optical cross-section of one single impurity ion. S_ν accounts for the interaction between the radiation and a single ion and, consequently, governs the absorption and emission processes at the atomic scale. Now, the intensity at any point results from the radiation emitted and absorbed by all the impurities and must obey the radiative transfer equation (Eq. (10)). Once the intensity is known, this equation can serve to calculate the emissivity. So, introducing $I_{\nu\,\mathrm{IST}}$ into Eq. (10) in the steady state and making use of Eqs. (29) and (30) one obtains

$$\frac{\varepsilon_{\nu\,\mathrm{IST}}}{N} = S_\nu I_{\nu\,\mathrm{Planck}} + S_\nu I_{\nu\,\mathrm{Planck}} (\phi^{(2)}_{\mathrm{IST}} - \phi^{(2)}_{\mathrm{RLTE}}) \tag{31}$$

which corresponds to the emissivity per impurity ion in the IST approach. As expected, up to first order, the emissivity coincides with that of RLTE (Eq. (21)). However, since both $\phi^{(2)}_{\mathrm{IST}}$ and $\phi^{(2)}_{\mathrm{RLTE}}$ contain the factor $1/\sigma_\nu^2$ (see Eqs. (20) and (27)), from Eqs. (29) and (30) it follows that the second term in Eq. (31) is proportional to

$$\left(\frac{\hat{\Omega} \cdot \vec{\nabla} T_m}{N S_\nu} \right)^2 S_\nu \tag{32}$$

thus the second-order result derived from the IST approach implies that the emissivity per ion would depend on the ion concentration N. The interaction between each ion and the radiation would no longer be independent of the neighbouring ions. This conclusion is in contradiction with the usual behaviour of ion impurities that leads to Eq. (30). So, it seems unavoidable to conclude that the second-order intensity obtained by means of the IST approach is incorrect.

We have shown a limitation of the information-statistical model presented in Section II. This limitation may be due to the well-known problem that information theory is a probabilistic method and does not specify what constraints should be used for a given physical system. In fact, the approach in Section II makes use of the spectral energy (2) and flux (3) of radiation as constraints, but no constraint on how matter radiates in nonequilibrium is imposed. From this perspective the information-theoretical approach presented is very different from the local-equilibrium one (Section III), which relies on an specific assumption on how matter radiates in nonequilibrium (see Eq. (21)). Since information theory finds the most probable description under a state of partial knowledge, in the case of radiative transfer it seems plausible that this partial knowledge should include some statement on how matter radiates in nonequilibrium. This could also provide a specific relationship between the radiation (spectral) and matter temperatures. We thus see that information theory of radiative transfer is certainly more complicated than that of purely matter systems. Any further work on information theory of heat radiation should, in our opinion, be able to cope with the fundamental limitation presented in the previous paragraph.

The main point of the present paper has been to show the limitations of simple models based on information theory when applied to heat radiation. Comparison to the results from radiative local equilibrium has allowed us to identify such limitations. Before closing this paper, we would like to compare our results to other work. Some authors have analyzed the inclusion of a constraint on the photon number flux in the maximization of the entropy density,(23, 24) but it is simple to see that the corresponding results(25) again lead to the conclusion that the emissivity per ion would depend on the concentration N, which as explained above is not acceptable. On the other hand, Struchtrup has presented a very complete theory including many additional moments in the entropy maximization,(26, 27) which he uses together with the RLTE hypothesis (21). Although his method yields interesting results for a variety of situations,(26, 27) it may be pointed out that the RLTE assumption on its own yields an expression for the nonequilibrium intensity (Section III), thus it is not clear that this assumption should be used together with the principle of maximum entropy. Another approach to nonequilibrium radiation is based on the proposal that the equilibrium expression $\rho u_r = aT^4$ be assumed to hold for arbitrarily far-from-equilibrium systems.(28) This is a possible way to introduce the temperature in nonequilibrium radiative systems, but we would like to stress that Boltzmann's derivation of the Stefan law is based on a different definition, namely $T^{-1} \equiv \partial s/\partial u$, which: (i) leads to the result $\rho u_r = aT^4$ (and to Stefan's law) only in the case of equilibrium;(29, 30) and (ii) is the same definition of temperature as the one we have applied in our statistical approach (see the text above Eq. (9)).

Finally we stress that the assumption that matter radiates locally in thermal equilibrium (RLTE assumption) is acceptable near equilibrium but, since it is based on the local extension of an equilibrium result (Planckian emission), we cannot *a priori* assure that it will hold for systems arbitrarily far away from equilibrium. Indeed, in the case of matter systems there are many phenomena (e.g., ultrasound propagation, shock waves, light scattering...) showing that the local state of strongly nonequilibrium systems is determined not only by the local temperature but also by higher spatial derivatives of the temperature (this is indeed the basis of extended irreversible thermodynamics).(7, 31) In contrast, RLTE assumes that the local state of the system is determined only by the local value of the matter temperature (see Section III).

If statistical physics of nonequilibrium radiation could be developed in order to avoid the shortcoming pointed out in the present paper, one would eventually be able to show whether RLTE can be trusted or not in arbitrary nonequilibrium systems. This could be of importance in systems where nonequilibrium radiation plays an important role, such as astrophysics,(18) sonoluminescence,(32) industrial furnaces,(33) shock waves(34) and plasma physics.(35)

V. CONCLUDING REMARKS

In this paper we have presented two approaches to the description of nonequilibrium radiation. The first model is based on Information Statistical Theory, IST (Section II). It relies on constraints concerning the local conditions. The contribution of the rest of the system to the local radiation is accounted for by means of local quantities (namely, the spectral energy density and flux). The second approach relies on the assumption of Radiative Local Thermodynamic Equilibrium, RLTE (Section III). It corresponds to an integral analysis that takes into account the whole system in the calculation of the intensity at a given point. Although both approaches are completely independent, they are consistent up to the first order. We have shown that the second-order term given by the IST model is inconsistent with the well-established radiative behavior of impurities in solids (Section IV).

APPENDIX A: IDENTIFICATION OF THE LAGRANGE MULTIPLIER $\vec{\gamma}_{p_r}$

In this appendix we show that Eq. (16) is the solution to Eq. (15) up to secondorder in the temperature gradient. As mentioned in the text, we assume for simplicity a uniform temperature gradient. For the sake of mathematical simplicity, let us also consider a situation in which all quantities depend only on the z-coordinate. Then, use of Eq. (16) into (14) yields, after neglecting third- and higher-order terms in the temperature gradient,

$$\frac{dI_\nu}{dz}=\frac{2h^2\nu^4}{kc^2T_{p_r}^2}\left[\frac{dT_{p_r}}{dz}\frac{\exp[\eta_{p_r}]}{(\exp[\eta_{p_r}]-1)^2}+\frac{h\nu c_z}{\sigma_\nu ckT_{p_r}^2}\left(\frac{dT_{p_r}}{dz}\right)^2\frac{d}{d\eta_{p_r}}\left(\frac{\exp[\eta_{p_r}]}{\exp[\eta_{p_r}]-1}\right)\right.$$
$$\left.+\frac{2c_z}{\sigma_\nu cT_{p_r}}\left(\frac{dT_{p_r}}{dz}\right)^2\frac{\exp[\eta_{p_r}]}{(\exp[\eta_{p_r}]-1)^2}\right] \tag{A1}$$

We use this expression to compute the left-hand side of Eq. (15). After noting that the integrals containing the two last terms in (A1) vanish, and computing the single remaining integral, we find

$$\int_{4\pi} d\Omega \left(\frac{c_z}{c} \frac{dI_\nu}{dz} \right) \frac{\vec{c}}{c} = \left(0, 0, \frac{8\pi h^2 \nu^4}{3kc^2 T_{p_r}^2} \frac{dT_{p_r}}{dz} \frac{\exp[\eta_{p_r}]}{(\exp[\eta_{p_r}]-1)^2} \right) \tag{A2}$$

On the other hand, use of the information-theoretical intensity (14) and of Eq. (16) into the right-hand side of Eq. (15) shows at once that the integrals arising from the first and third terms in Eq. (14) vanish and

$$-\sigma_\nu \int_{4\pi} d\Omega\, I_\nu \frac{\vec{c}}{c} = \frac{2h^2 \nu^4}{kc^2 T_{p_r}^2} \frac{dT_{p_r}}{dz} \frac{\exp[\eta_{p_r}]}{(\exp[\eta_{p_r}]-1)^2} \int_{4\pi} d\Omega \frac{c_z}{c} \frac{\vec{c}}{c}$$

which is easily seen to be the same as the left-hand side of Eq. (15), as given by (A2). This shows that Eq. (16) is the solution to Eq. (15), which was to be expected from the arguments given above Eq. (16). The reason why the formalism in previous papers (e.g., ref. 15) could be applied only to grey materials is that there the entropy maximization was performed for the spectrally-integrated entropy and under spectrally-integrated constraints of the energy and flux, so that the Lagrange multipliers β_{p_r} and $\vec{\gamma}_{p_r}$ (denoted as β and $\vec{\gamma}$ in those papers) did not depend on the photon momentum (or frequency), which is inconsistent with, e.g., Eq. (16), except in the rather restrictive case of grey matter (i.e., $\sigma_\nu \equiv \sigma$ independent of frequency).

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