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Thermodynamics of nonequilibrium radiation. (I) General theory

A.R. Vasconcellos[a], J. Fort[b,*], D. Jou[c,d], R. Luzzi[a]

[a] *Instituto de Física "Gleb Wataghin", Universidade Estadual de, Campinas, Unicamp, 13083-970 Campinas, Sao Paulo, Brazil*

[b] *Departament de Física, Escola Politècnica Superior, Universitat de Girona, Avda. Lluis Santalo s/n, 17071 Girona, Catalonia, Spain*

[c] *Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Catalonia, Spain*

[d] *Also at the Institut d'Estudis Catalans, Carme 47, 08001 Barcelona, Catalonia, Spain*

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Abstract

An in-depth study of the thermodynamics of nonequilibrium radiation is presented. The characterization of its nonequilibrium macroscopic state is performed in the framework of Informational Statistical Thermodynamics. This is done in terms of a nonequilibrium Dirac–Landau–Wigner single particle density matrix, or, alternatively, in terms of the conjugated intensive nonequilibrium thermodynamic variables. When a local description is not required, the global one can be done by giving the nonequilibrium populations in the different modes. Also, alternatively, we can introduce a nonequilibrium temperature (quasi-temperature) per mode. This is compared to a couple of contracted descriptions. The evolution of the resulting nonequilibrium thermodynamic state and the eventual experimental determination are given in the follow-up article.

Keywords: Nonequilibrium radiation; Informational Statistical Thermodynamics; Radiation Nonequilibrium Temperature

1. Introduction

The thermodynamics of radiation in equilibrium has been well established with the classical works developed in the late nineteenth century and the beginning of the twentieth. The distribution of photons of the black body radiation in equilibrium with matter at a given temperature is given by the well-known Planck distribution function. The

* Corresponding author. Fax: +34-972-41-80-98.
E-mail address: joaquim.fort@udg.es (J. Fort).

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situation is not so clear-cut in the case of radiation out of equilibrium, mainly in conditions far away from equilibrium. Some attempts to deal with this situation have been proposed. For example in a classical-like (or Onsagerian) irreversible thermodynamics (for example [1,2]), implying a local equilibrium hypothesis, one defines a local Planck distribution characterized by a space- and time-dependent nonequilibrium temperature [3]. Attempts to go beyond this limitation by entering the domain of irreversible thermodynamics [4] are due to several authors [5–21]. Nonequilibrium concepts in solar energy radiation and maximal nonequilibrium thermodynamic efficiencies for the conversion of black-body radiation have been derived by Landsberg [22,23]. More recently, the possibility has been investigated that the present black-body cosmic radiation might (even under the assumption of thermal equilibrium) follow slightly modified thermodynamic properties due to long-range gravitational influence. In this case, the influence under consideration could be related to a small long-range memory of times when matter and light were still strongly coupled, or it could be due to more complex phenomena. Tsallis et al. [24] have dealt with this question in terms of what can be considered as a statistics appropriate for describing the macrostate of systems governed by some kind of fractal dynamics [25,26]. Maybe something similar could be applied to black-body radiation in small "containers" with rugged surfaces (e.g., quantum wells in semiconductors). Here we address another particular, but relevant, situation which is black-body radiation (in a "normal container" and no fractal dynamics present) arbitrarily away from equilibrium conditions.

All of these treatments and others have addressed the delicate fact that nonequilibrium thermodynamics is a controversial matter, with several schools of thought presently attempting to derive acceptable basic foundations and proper operational methods for it [27–34]. Lazlo Tisza has classified the several levels of description of thermodynamics [35], and together with Lebowitz [36] have praised the approach based on statistical mechanics as the most promising one. To this level belongs the so-called Informational Statistical Thermodynamics (IST for short), which was initiated by Hobson [37] after the seminal articles by Jaynes on the foundations of statistical mechanics on information theory [38,39]. IST has been lately systematized and further developed on the basis of the nonequilibrium statistical operator method (NESOM) [40–45]. The latter is founded on Jaynes' principle of maximization of informational entropy and then is referred to as MaxEnt-NESOM [46–48] and can be considered as being encompassed in Jaynes' Predictive Statistical Mechanics [49].

MaxEnt-NESOM provides the basis for the construction of a response function theory for the description and analysis of experiments on systems arbitrarily away from equilibrium, and of a nonlinear quantum kinetic theory which describes the irreversible evolution in time of the nonequilibrium macroscopic state of the system. We resort here to MaxEnt-NESOM-based IST and kinetic theory for the development of an in-depth study of the thermodynamics of nonequilibrium radiation. In this paper we present and discuss the general theory, and in the follow-up article we deal with the evolution of the nonequilibrium thermodynamic state of radiation in matter, and a particular experiment devised for establishing the validation of the theory is presented.

2. Thermodynamic state of nonequilibrium radiation

Let us consider a general experiment in which a material sample is in contact with a thermal reservoir at temperature T_0. Initially the different charged particles in the sample are in equilibrium with the black-body radiation they produce, but they are driven out of equilibrium by the action of an external source (a specific case shall be described in the follow-up article). The Hamiltonian $\hat{H}$ of the system is composed of the Hamiltonians of the free subsystems of the sample and of the radiation, plus the energy operators corresponding to the interactions between themselves and with the pumping source and the reservoir. Next, according to MaxEnt-NESOM we need to choose the basic dynamical operators deemed necessary for the characterization of the state of interest.

In arbitrary nonequilibrium conditions the system of photons can be completely characterized by the set of all possible observables of the system. This is equivalent to providing the single-particle and two-particle dynamical operators [50,51]. However, since pairs of photons do not interact, we need to consider only the Dirac–Landau–Wigner one-particle dynamical operator. In second quantization and in the space of quantum states characterized by the wavevector $\vec{k}$ (we omit the polarization index for simplicity) we have the quantities

$$\left\{ a^\dagger_{\vec{k}} a_{\vec{k}} \equiv \hat{N}_{\vec{k}};\; a^\dagger_{\vec{k}+\frac{1}{2}\vec{Q}} a_{\vec{k}-\frac{1}{2}\vec{Q}} \equiv \hat{N}_{\vec{k}\vec{Q}} \right\} , \tag{1}$$

where $a_{\vec{k}}$ $\left(a^\dagger_{\vec{k}}\right)$ are the usual annihilation (creation) operators in plane-wave states of momentum $\vec{k}$. In Eq. (1) the first set of operators are the so-called population operators and the other set, where $\vec{Q} \neq 0$, are nondiagonal contributions which describe the change in space (with wavevector $\vec{Q}$) of the dynamical observables. Moreover, since the photons are bosons, coherent states are possible and we would need to include also the amplitudes $a_{\vec{k}}$ and $a^\dagger_{\vec{k}}$ in the basic set. But, since we are not going to consider coherent states here, as would be the case of laser action, the amplitudes are disregarded. Furthermore, we shall consider experiments where the detection apparatus does not have space resolution, but collects global information. Hence, we can also disregard the quantities $\hat{N}_{\vec{k}\vec{Q}}$; they can be relevant in a study of a thermo-hydrodynamics of the radiation field, which shall be the subject of a future article. The MaxEnt-NESOM statistical operator is, in Zubarev's approach [52], given by

$$\rho_\varepsilon(t) = \exp\left\{ -\hat{S}(t,0) + \int_{-\infty}^{t} \mathrm{d}t' \mathrm{e}^{\varepsilon(t'-t)} \frac{\mathrm{d}}{\mathrm{d}t'} \hat{S}(t', t'-t) \right\} , \tag{2}$$

where

$$\hat{S}(t,0) = \phi(t)\hat{1} + \sum_{\vec{k}} F_{\vec{k}}(t) \hat{N}_{\vec{k}} + \hat{\zeta}(t,0) \tag{3}$$

is the so-called informational statistical entropy operator [53], and

$$\hat{S}(t', t'-t) = \exp\left\{ -\frac{1}{i\hbar}(t'-t)\hat{H} \right\} \hat{S}(t',0) \exp\left\{ \frac{1}{i\hbar}(t'-t)\hat{H} \right\} . \tag{4}$$

In Eq. (3) we have introduced the Lagrange multipliers (intensive nonequilibrium variables) $F_{\vec{k}}(t)$, and $\phi(t)$, a kind of logarithm of a nonequilibrium partition function, ensures the normalization of the statistical operator. This refers to the radiation, and in $\hat{\zeta}$ we have collected the contribution from all of the other subsystems in the sample, whose detail is not necessary to be given here. We recall that ε is a positive infinitesimal that goes to zero after the trace operation in the calculation of averages has been performed.

The space of states in IST is the one defined by the average values over the nonequilibrium ensemble of the dynamical operators, that is, for the system of photons it is given by the populations

$$N_{\vec{k}}(t) = Tr\{\hat{N}_{\vec{k}}\rho_\varepsilon(t)\} = Tr\{\hat{N}_{\vec{k}}\bar{\rho}(t,0)\} , \tag{5}$$

where

$$\bar{\rho}(t,0) = \exp\{-\hat{S}(t,0)\} \tag{6}$$

and, we recall, the average value with the statistical operator coincides with the one calculated with the auxiliary operator of Eq. (6) only for the case of the basic variables but not for any other observable [46–48,52].

A direct calculation for this case of a system of bosons results in

$$N_{\vec{k}}(t) = [\exp\{F_{\vec{k}}(t)\} - 1]^{-1} \tag{7}$$

and therefore

$$F_{\vec{k}}(t) = \ln\left[1 + \frac{1}{N_{\vec{k}}(t)}\right] \tag{8}$$

what shows us the equivalence of a thermodynamical description in terms of either the basic macrovariables (the populations of Eq. (7) here) or the Lagrange multipliers in MaxEnt-NESOM (the intensive nonequilibrium thermodynamic variables of Eq. (8) here).

Thus, the thermodynamic state of the nonequilibrium radiation is fully characterized by either one of the sets

$$\{N_{\vec{k}}(t)\} \text{ or } \{F_{\vec{k}}(t)\} . \tag{9}$$

One consists evidently in giving the populations in all of the normal quantum states $\vec{k}$ (including of course the polarization). The other is to provide the set of Lagrange multipliers, which have of course to be determined if we are going to use Eq. (7). In the follow-up article we tackle the question of how to determine such a state, together with its evolution.

We are now in conditions to provide alternative definitions of the intensive nonequilibrium thermodynamic variables that characterize the macrostate of the radiation. One is due to Landsberg [13–21] who introduces the concept of quasi-chemical potential per mode $\mu_{\vec{k}}(t)$, what follows after writing

$$F_{\vec{k}}(t) = \frac{\hbar\Omega_{\vec{k}} - \mu_{\vec{k}}(t)}{k_B T_0} , \tag{10}$$

where $\Omega_{\vec{k}}$ is the frequency dispersion relation of the photons in the radiation field and k_B is the Boltzmann constant.

Another alternative is to introduce a kind of nonequilibrium temperature, which is referred to as *quasitemperature per mode* $T^*_{\vec{k}}(t)$, through the expression

$$F_{\vec{k}}(t) = \frac{\hbar\Omega_{\vec{k}}}{k_B T^*_{\vec{k}}(t)} . \tag{11}$$

This is what is also done in semiconductor physics in the case of a similar system of boson-like quasiparticles, namely the optical phonons [54], and then these quasitemperatures per mode can be "measured" in experiments of Raman scattering [55]. Their evolution in time can be followed in ultrafast (pico- and femto-second scales) time-resolved optical experiments. We notice that once the pumping source is switched off and the system attains the final equilibrium with the reservoir, the quasi-chemical potential in Eq. (10) goes to zero, or the quasitemperature in Eq. (11) goes to T_0, and in both cases the population of Eq. (7) tends to the Planck distribution in equilibrium, as it should. The main thermodynamic properties of nonequilibrium radiation are then given by

$$E(t) = \sum_{\vec{k}} \hbar\Omega_{\vec{k}} N_{\vec{k}}(t) \tag{12}$$

for the energy, and

$$\bar{S}_{ph}(t) = Tr\{\hat{S}_{ph}(t,0)\rho_\varepsilon(t)\} = \phi(t) + \sum_{\vec{k}} F_{\vec{k}}(t) N_{\vec{k}}(t) \tag{13}$$

for the informational statistical entropy (the index ph stands for photons in the radiation field, that is the average of the operator of Eq. (3) except for $\hat{\zeta}$, which is the operator of the rest of the sample and the reservoirs). Using Eq. (8) and that

$$\phi(t) = Tr\left\{\exp\left[-\sum_{\vec{k}} F_{\vec{k}}(t)\hat{N}_{\vec{k}}\right]\right\} = \sum_{\vec{k}} \ln[1 + N_{\vec{k}}(t)] , \tag{14}$$

we arrive to the expression

$$\bar{S}_{ph}(t) = \sum_{\vec{k}} \{[1 + N_{\vec{k}}(t)]\ln[1 + N_{\vec{k}}(t)] - N_{\vec{k}}(t)\ln N_{\vec{k}}(t)\} . \tag{15}$$

This expression has the same form as the one in equilibrium, but the nonequilibrium populations enter in the place of the equilibrium ones. A Gibbs-like relation follows from Eq. (13), namely

$$d\bar{S}_{ph}(t) = \sum_{\vec{k}} F_{\vec{k}}(t)\, dN_{\vec{k}}(t) , \tag{16}$$

where we have taken into account that

$$\mathrm{d}\ln\bar{Z}(t) \equiv \mathrm{d}\phi(t) = -\sum_{\vec{k}} N_{\vec{k}}(t)\,\mathrm{d}F_{\vec{k}}(t) , \tag{17}$$

where $\bar{Z}(t)$ is a nonequilibrium partition function and $\phi(t)$ plays the role of a kind of nonequilibrium thermodynamic potential. The differential coefficients of these quantities are then

$$\frac{\partial \phi(t)}{\partial F_{\vec{k}}(t)} = -N_{\vec{k}}(t)\,, \tag{18}$$

$$\frac{\partial \bar{S}_{ph}(t)}{\partial N_{\vec{k}}(t)} = F_{\vec{k}}(t) \equiv \frac{\hbar\Omega_{\vec{k}}}{k_B T^*_{\vec{k}}(t)}\,. \tag{19}$$

Evidently, Eq. (19) can be rewritten as

$$k_B \frac{\partial \bar{S}_{ph}(t)}{\partial E_{\vec{k}}(t)} = \frac{1}{T^*_{\vec{k}}(t)}\,, \tag{20}$$

where $E_{\vec{k}}(t) = \hbar\Omega_{\vec{k}} N_{\vec{k}}(t)$ is the energy in mode $\vec{k}$, and this Eq. (20) reinforces the fact that $T^*_{\vec{k}}(t)$ can be considered as a temperature-like variable of mode $\vec{k}$. Moreover, Eq. (19) plays the role of an equation of state (in fact a set of them corresponding to the different values of $\vec{k}$), giving the relation between the intensive thermodynamic variables (the Lagrange multipliers in MaxEnt-NESOM) and the basic macrovariables; this relation is in the present case explicitly given in Eq. (8).

Similar to the case of lattice vibrations [56], we can introduce a specific heat per mode

$$C_{\vec{k}}(t) = \frac{\partial E(t)}{\partial T^*_{\vec{k}}(t)} = T^*_{\vec{k}}(t) \frac{\partial \bar{S}_{ph}(t)}{\partial T^*_{\vec{k}}(t)} = k_B \left[\frac{\hbar\Omega_{\vec{k}}}{k_B T^*_{\vec{k}}(t)}\right]^2 N_{\vec{k}}(t)[1 + N_{\vec{k}}(t)]\,, \tag{21}$$

which in the limit of $\hbar\Omega_{\vec{k}}/k_B T^*_{\vec{k}}(t) \ll 1$ goes over the classical expression

$$C_{\vec{k}}(t) \simeq k_B \tag{22}$$

that is, the same value k_B for each mode, while at high frequencies has the exponential form

$$C_{\vec{k}}(t) \simeq k_B [F_{\vec{k}}(t)]^2 \exp\{-F_{\vec{k}}(t)\}\,. \tag{23}$$

Finally, without entering into details, we mention that the thermodynamics of nonequilibrium radiation satisfies the general properties that [40–45]:

(1) In the thermodynamic limit the informational-statistical entropy acquires a Boltzmann-like expression, namely

$$\bar{S}_{ph}(t) \to \ln W(\{N_{\vec{k}}(t)\})\,, \tag{24}$$

where W is the number of quantum states compatible at any time t with the imposed constraints in the variational process in MaxEnt-NESOM, in the present case the set of populations in Eq. (5).

(2) Given the informational-statistical entropy production,

$$\bar{\sigma}(t) = \frac{d}{dt}\bar{S}(t) = Tr\left\{\frac{1}{i\hbar}[\hat{S}(t,0), H]\right\} = \sum_{\vec{k}} F_{\vec{k}}(t) \frac{d}{dt} N_{\vec{k}}(t) + \frac{d}{dt}\bar{\zeta}(t)\,, \tag{25}$$

it can be separated into two parts, $\bar{\sigma}(t)=\bar{\sigma}_i(t)+\bar{\sigma}_e(t)$, consisting of the internal entropy production (due to internal interactions in the system, i.e., the sample) and an external one (interactions of the system with sources and reservoirs). For steady states in the linear regime (Onsagerian domain) around equilibrium, a principle of minimum entropy production is satisfied. This ensures the stability of such steady states, which is a consequence of the fact that Onsager symmetry relations are satisfied. Outside the linear regime (nonlinear domain of thermodynamics), this is not so in general and the steady state can be unstable against the formation of synergetic ordering in the form of Prigogine's dissipative structures.

(3) Another quantity of relevance in nonlinear nonequilibrium thermodynamics is the change in time of the informational-statistical entropy,

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{\sigma}(t)=\frac{d_F}{\mathrm{d}t}\bar{\sigma}(t)+\frac{d_Q}{\mathrm{d}t}\bar{\sigma}(t)\,, \tag{26}$$

which can be separated in a part, d_F, due to the change in time of the intensive nonequilibrium thermodynamic variables (the $F_{\vec{k}}(t)$ in the present case), and another, d_Q, due to the change in time of the macrovariables (the $N_{\vec{k}}(t)$ here). A thermodynamic criterion of evolution holds, namely that along the trajectories followed by the macrovariables in the thermodynamic space of states (which are governed by the equations of evolution described in the follow-up article) it is verified that

$$\frac{d_F}{\mathrm{d}t}\bar{\sigma}(t)\leqslant 0\,. \tag{27}$$

(4) Furthermore, a thermodynamic (in)stability criterion applies, namely that steady states become unstable (against the formation of synergetic ordering) if the quantity

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\delta^2\bar{S}(t)=\bar{\sigma}(t)-\bar{\sigma}(t)^{ss}\,, \tag{28}$$

called excess-entropy production, becomes negative. This quantity consists of the difference between the entropy production in a state slightly departed from the steady state and that in the latter one.

Concerning the nonequilibrium radiation, if we take it as the system of interest and then the other subsystems in the sample together with the sources and reservoirs as external ones, there is no internal production of entropy (the photons do not interact between themselves). The criterion of evolution, Eq. (27), is satisfied (cf. follow-up article), and with the interactions corresponding to the degrees of freedom of the sample being linear in the photon field amplitude, their steady states are always stable.

(5) The quantity $\phi(t)$, which plays the role of the logarithm of a nonequilibrium partition function, i.e., $\phi(t)=\ln\bar{Z}(t)$, is given by [cf. Eq. (14)]

$$\mathrm{e}^{\phi(t)}=Tr\left\{\exp\left[-\sum_{\vec{k}}F_{\vec{k}}(t)\hat{N}_{\vec{k}}\right]\right\}=\prod_{\vec{k}}[1-\exp\{-F_{\vec{k}}(t)\}]^{-1}=\bar{Z}(t) \tag{29}$$

and then

$$\phi(t)=\ln\bar{Z}(t)=-\sum_{\vec{k}}\ln[1-\exp\{-F_{\vec{k}}(t)\}] \tag{30}$$

having the property that

$$\frac{\delta\phi(t)}{\delta F_{\vec{k}}(t)} = \frac{\delta \ln \bar{Z}(t)}{\delta F_{\vec{k}}(t)} = -\,N_{\vec{k}}(t)\,. \tag{31}$$

Moreover, the time-dependent radiation pressure (second rank) tensor is given by the flux of the momentum of the photons, that is

$$P^{[2]}(t) = \frac{1}{V}\sum_{\vec{k}} \left[\hbar\vec{k}c\frac{\vec{k}}{k}\right] N_{\vec{k}}(t)\,, \tag{32}$$

where $[\cdots]$ indicates tensorial product of vectors and V the volume. It can be rewritten as

$$\begin{aligned} P^{[2]}(t) &= \frac{1}{V}\sum_{\vec{k}} \hbar\Omega_{\vec{k}} \left[\frac{\vec{k}}{k}\frac{\vec{k}}{k}\right] N_{\vec{k}}(t) \\ &= \frac{1}{3}\frac{E(t)}{V} 1^{[2]} + P^{[2](v)}(t) \end{aligned} \tag{33}$$

being separated into a diagonal part ($1^{[2]}$ is the unit rank-two tensor) and a nondiagonal one (the viscous shear pressure). The scalar pressure is

$$p(t) = \frac{1}{3} Tr\{P^{[2]}(t)\} = \frac{1}{3}\frac{E(t)}{V} \tag{34}$$

recovering in any conditions and at any time the usual relation between pressure and energy density.

We proceed now to present another possible description of the thermodynamic state of the nonequilibrium radiation, and to discuss contracted forms of it (i.e., approximate descriptions).

3. Nonequilibrium grand-canonical-like description

In Section 2 we noticed that a complete description of the nonequilibrium radiation can be done in terms of single-particle dynamical operators [cf. Eq. (1)]. An alternative one can be constructed in terms of independent linear combinations of them, namely the generalized nonequilibrium grand-canonical ensemble [57–59]. For that purpose, the densities of energy and of particles are introduced, as well as their fluxes of all order. As in Eq. (1), we can separate the global parts and the local inhomogeneities, we disregard the latter (as done in Section 2), and then we introduce

$$\hat{H}_{ph} = \sum_{\vec{k}} \hbar\Omega_{\vec{k}}\hat{N}_{\vec{k}}\,, \tag{35}$$

$$\hat{\vec{I}}_h = \sum_{\vec{k}} \hbar\Omega_{\vec{k}}\vec{u}(\vec{k})\hat{N}_{\vec{k}}\,, \tag{36}$$

$$\hat{\vec{I}}_n = \sum_{\vec{k}} \vec{u}(\vec{k})\hat{N}_{\vec{k}}\,, \tag{37}$$

$$\widehat{I^{[r]}}_h = \sum_{\vec{k}} \hbar\Omega_{\vec{k}} u^{[r]}(\vec{k})\hat{N}_{\vec{k}} \,, \tag{38}$$

$$\widehat{I^{[r]}}_n = \sum_{\vec{k}} u^{[r]}(\vec{k})\hat{N}_{\vec{k}} \,, \tag{39}$$

where

$$\vec{u}(\vec{k}) = \nabla_{\vec{k}}\Omega_{\vec{k}} = c\vec{k}/k \,, \tag{40}$$

is a generating velocity (and the velocity of the photons in state $\vec{k}$),

$$u^{[r]}(\vec{k}) = [\vec{u}(\vec{k})\ldots(r\text{-times})\ldots\vec{u}(\vec{k})] \,, \tag{41}$$

with the square brackets indicating tensorial product of vectors, and $r = 2, 3, \ldots$ indicates the order of the flux and also its tensorial rank. Index h refers to fluxes of energy and n to fluxes of particles; the number operator is not included since we are dealing with photons.

Eqs. (35)–(39) define the now basic set of dynamical operators in MaxEnt-NESOM, whose average values over the nonequilibrium ensemble define the basic macrovariables which are

$$\{E(t), \vec{I}_h(t), \vec{I}_n(t), \{I_h^{[r]}(t)\}, \{I_n^{[r]}(t)\}\} \,, \tag{42}$$

and the corresponding Lagrange multipliers are indicated as

$$\{\beta(t), \vec{F}_h(t), \vec{F}_n(t), \{F_h^{[r]}(t)\}, \{F_n^{[r]}(t)\}\} \,. \tag{43}$$

We notice that now the nonequilibrium statistical operator [cf. Eq. (2)] can be expressed in terms of an informational-statistical entropy operator which is the one of Eq. (3) once we rewrite the Lagrange multipliers as

$$\begin{aligned} F_{\vec{k}}(t) &= \beta(t)\hbar\Omega_{\vec{k}} + \vec{F}_h(t)\cdot\hbar\Omega_{\vec{k}}\vec{u}(\vec{k}) + \vec{F}_n(t)\cdot\vec{u}(\vec{k}) \\ &\quad + \sum_{n\geqslant 2}[F_h^{[r]}(t)\otimes\hbar\Omega_{\vec{k}}u^{[r]}(\vec{k}) + F_n^{[r]}(t)\otimes u^{[r]}(\vec{k})] \,, \end{aligned} \tag{44}$$

where dots stand as usual for scalar products, and $\otimes$ stands for fully-contracted tensorial product. We can then see the complete equivalence of both descriptions.

We recall that

$$E(t) = Tr\{\hat{H}_{ph}\rho_\varepsilon(t)\} = Tr\{\hat{H}_{ph}\bar{\rho}(t,0)\} = \sum_{\vec{k}} \hbar\Omega_{\vec{k}}\bar{N}_{\vec{k}}(t) \tag{45}$$

and similarly for all the other macrovariables (the fluxes), in all of them the quantity $\bar{N}_{\vec{k}}(t)$ appearing, given by Eq. (7) but with $F_{\vec{k}}(t)$ given by Eq. (44).

We proceed now to introduce contracted descriptions.

3.1. First contracted description

We begin by considering the most contracted description possible, consisting into retaining in the basic set only the energy of the nonequilibrium radiation. This implies to disregard all of the fluxes or, better to say, to put all of the Lagrange parameters associated to the fluxes equal to zero. Of course this should be determined by the experimental conditions, as for example in the case considered in the follow-up article. The sets of basic variables are then simply composed of the dynamical one, the macrovariable and the Lagrange multiplier, that is

$$\{\hat{H}_{ph}\};\ \{E(t)\};\ \{\beta_I(t)\} \tag{46}$$

with

$$E(t) = \sum_{\vec{k}} \hbar\Omega_{\vec{k}} \bar{N}^I_{\vec{k}}(t)\,, \tag{47}$$

where

$$\bar{N}^I_{\vec{k}}(t) = (\exp[\beta_I(t)\hbar\Omega_{\vec{k}}] - 1)^{-1}\,. \tag{48}$$

Writing $\Omega_{\vec{k}} = c|\vec{k}|$, with c the speed of photons, going over to the continuum in the usual way, namely $\sum_{\vec{k}} \to 2V/(2\pi)^3 \int \mathrm{d}^3k$, where the factor 2 accounts for the fact that photons have two independent polarizations, after integration we have for the energy density that

$$\frac{E(t)}{V} = \frac{\pi^2}{15\hbar^3 c^3 \beta_I^4(t)} = a[T_I^*(t)]^4\,, \tag{49}$$

where we have defined the quasitemperature through $k_B T_I^*(t) = \beta_I^{-1}(t)$,

$$a = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} \tag{50}$$

is the blackbody constant and V is the volume of the system. In the absence of perturbations, when the system attains final equilibrium T_I^* goes over the temperature in equilibrium with the reservoirs, and the usual T^4-law of equilibrium thermodynamics is recovered.

The logarithm of the partition function, i.e., $\phi(t)$, is given by

$$\phi_I(t) = \ln \bar{Z}_I(t) = \sum_{\vec{k}} \ln[1 - \mathrm{e}^{-\beta_I\hbar\Omega_{\vec{k}}}]^{-1} = \frac{\pi^2 V}{45\hbar^3 c^3 \beta_I^3(t)}\,. \tag{51}$$

We can define a nonequilibrium grand-canonical thermodynamic potential as

$$\Psi_I(t) = -\,\beta_I^{-1}(t) \ln \bar{Z}(t)\,, \tag{52}$$

and from it we can get the radiation pressure in this representation, namely

$$p(t) = -\,\frac{\partial \Psi_I(t)}{\partial V} = \frac{\pi^2}{45\hbar^3 c^3 \beta_I^4(t)} = \frac{1}{3}\frac{E(t)}{V}\,, \tag{53}$$

given in terms of the Lagrange parameter in this description, but equal to one-third of the energy density which is a basic variable.

Furthermore, it can be noticed that the number of nonequilibrated photons at time t is

$$\bar{N}(t) = \sum_{\vec{k}} \bar{N}_{\vec{k}}(t) = \int \mathrm{d}\omega N(\omega) = \frac{\zeta(3)}{\pi^2[\hbar c \beta_I(t)]^3} V\,, \tag{54}$$

where ζ is the Riemann zeta function and we have defined

$$N(\omega)=\frac{V}{\pi^2}\frac{\omega^2}{c^3}[\exp\{\beta_I(t)\omega\}-1]^{-1}\,. \tag{55}$$

Hence, the energy per photon is

$$e(t)=\frac{E(t)}{\bar{N}(t)}=\frac{\pi^4}{30\zeta(3)}k_BT_I^*(t)\simeq 2.7k_BT_I^*(t)\,. \tag{56}$$

3.2. Second contracted description

Let us consider an experiment where the flux of energy can be relevant (see, e.g., Refs. [5–12]), and the flux of particles need also be considered (as a result of Onsager cross-linking of fluxes: the equivalent of the effect of thermo-striction in matter or of thermo-electricity for charged particles). The basic sets of variables are

$$\{\hat{H}_{ph},\hat{\vec{I}}_h,\hat{\vec{I}}_n\}\,, \tag{57}$$

i.e., the dynamical ones;

$$\{E(t),\vec{I}_h(t),\vec{I}_n(t)\}\,, \tag{58}$$

i.e., the macrovariables; and

$$\{\beta_{II}(t),\vec{F}_{hII}(t),\vec{F}_{nII}(t)\}\,, \tag{59}$$

which are the Lagrange multipliers, with

$$E(t)=\sum_{\vec{k}}\hbar\Omega_{\vec{k}}\bar{N}^{II}_{\vec{k}}(t)\,, \tag{60}$$

$$\vec{I}_h(t)=\sum_{\vec{k}}\hbar\Omega_{\vec{k}}\nabla_{\vec{k}}\Omega_{\vec{k}}\bar{N}^{II}_{\vec{k}}(t)\,, \tag{61}$$

$$\vec{I}_n(t)=\sum_{\vec{k}}\nabla_{\vec{k}}\Omega_{\vec{k}}\bar{N}^{II}_{\vec{k}}(t)\,, \tag{62}$$

which is the particle number flux, and

$$\bar{N}^{II}_{\vec{k}}(t)=(\exp[\beta_{II}(t)\hbar\Omega_{\vec{k}}+\vec{F}_{hII}(t)\cdot\hbar\Omega_{\vec{k}}\nabla_{\vec{k}}\Omega_{\vec{k}}+\vec{F}_{nII}(t)\cdot\nabla_{\vec{k}}\Omega_{\vec{k}}]-1)^{-1}\,, \tag{63}$$

with $\Omega_{\vec{k}}=c|\vec{k}|$ and $\nabla_{\vec{k}}\Omega_{\vec{k}}=c\vec{k}/|\vec{k}|$. Considering that in the exponent in this equation the terms containing $\vec{F}_{hII}$ and $\vec{F}_{nII}$ are much smaller than the first one (near-equilibrium state), a second-order Taylor expansion in them yields, after some algebra, that

$$E(t)=\varepsilon_{II}(t)+a_1(t)|\vec{F}_{hII}(t)|^2+a_2(t)|\vec{F}_{nII}(t)|^2+a_3(t)\vec{F}_{hII}(t)\cdot\vec{F}_{nII}(t)\,, \tag{64}$$

$$\vec{I}_h(t)=b_1(t)\vec{F}_{hII}(t)+b_2(t)\vec{F}_{nII}(t)\,, \tag{65}$$

$$\vec{I}_n(t)=c_1(t)\vec{F}_{hII}(t)+c_2(t)\vec{F}_{nII}(t) \tag{66}$$

with coefficients a's, b's and c's given in Appendix A, the dependence on time of these coefficients being due to the presence in them of $\beta_{II}(t)$, that is, the reciprocal of the quasitemperature in this description, namely $\beta_{II}^{-1}(t) = k_B T_{II}^*(t)$. Moreover, the first term on the right-hand side of Eq. (64) is given by

$$\varepsilon_{II}(t) = \sum_{\vec{k}} \hbar\Omega_{\vec{k}} \bar{N}_{\vec{k}}^0(t) = a[T_{II}^*(t)]^4 , \tag{67}$$

where

$$\bar{N}_{\vec{k}}^0(t) = (\exp[\beta_{II}(t)\hbar\Omega_{\vec{k}}] - 1)^{-1} , \tag{68}$$

and a given by Eq. (50).

We can see that Eq. (64) is composed of a term, ε_{II}, with a $[T_{II}^*]^4$-form law, however, in terms of the quasitemperature that this description defines (it is worth stressing that in any description the basic variables (here E, $\vec{I}_h$, $\vec{I}_n$) are the same since they are physical properties of the system, but the intensive nonequilibrium thermodynamic variables are dependent on the description). But E contains other terms which are dependent on the other Lagrange multipliers: it can be noticed that if we redefine them in the form

$$\vec{F}_{hII}(t) = \beta_{II}(t)\vec{v}_h(t)/c^2 , \tag{69}$$

$$\vec{F}_{nII}(t) = \vec{v}_n(t)/c^2 \tag{70}$$

i.e., introducing the drift velocities for energy, $\vec{v}_h(t)$, and for particle motion, $\vec{v}_n(t)$, we have

$$E(t) = a[T_{II}^*(t)]^4 + \tilde{a}_1(t)v_h^2(t) + \tilde{a}_2(t)v_n^2(t) + \tilde{a}_3(t)\vec{v}_h(t)\cdot\vec{v}_n(t) \tag{71}$$

with $\tilde{a}_1 = a_1\beta_{II}^2(t)/c^4$, $\tilde{a}_2 = a_2/c^4$ and $\tilde{a}_3 = a_3\beta_{II}(t)/c^4$, and we can interpret the energy of the nonequilibrium radiation as composed of a purely thermal-motion contribution plus what we can call a kinetic-motion contribution.

Furthermore, using Eqs. (65) and (66) we find that

$$\vec{I}_h(t) = \tilde{b}_1(t)\vec{v}_h(t) + \tilde{b}_2(t)\vec{v}_n(t) , \tag{72}$$

$$\vec{I}_n(t) = \tilde{c}_1(t)\vec{v}_h(t) + \tilde{c}_2(t)\vec{v}_n(t) \tag{73}$$

i.e., the flux of energy and of particle number expressed in terms of the drift velocities, and $\tilde{b}_1 = b_1\beta_{II}(t)/c^2$, $\tilde{b}_2 = b_2/c^2$, $\tilde{c}_1 = c_1\beta_{II}(t)/c^2$, $\tilde{c}_2 = c_2/c^2$.

Finally, we notice that the flux of informational-statistical entropy is in this case

$$\vec{I}_s(t) \equiv \frac{\vec{I}_q^{II}(t)}{T_{II}^*(t)} = \beta_{II}(t)\vec{I}_h(t) = \beta_{II}(t)[\tilde{b}_1(t)\vec{v}_h(t) + \tilde{b}_2(t)\vec{v}_n(t)] , \tag{74}$$

which defines a flux of heat $\vec{I}_q^{II}(t)$, due only to the flux of energy; that of particles (the photon number flux) does not contribute in this case of radiation because no particle number is present in the basic set (differently to the case of matter, where it would be present in Eq. (74) accompanied by a quasi-chemical potential).

As final words in this section we stress that a complete description is that in Section 2, which defines a quasitemperature for each mode, and then $T_{\vec{k}}^*(t)$ for all $\vec{k}$ in reciprocal space fully characterizes the nonequilibrium macroscopic state of the radiation. As shown at the beginning of Section 3 an alternative complete description is provided by introducing the generalized nonequilibrium grand-canonical ensemble. On the basis of the latter, contracted (approximate) descriptions can be used, with the most contracted one (Section 3.1) consisting in retaining only the energy as basic variable and then we have an approximate description in terms of a single quasitemperature $T_I^*(t)$. The contracted description which includes the energy and the fluxes of energy and particles (Section 3.2) leads to an approximate description in terms of a quasitemperature $T_{II}^*(t)$ [different from that of the previous description, i.e., $T_I^*(t) \neq T_{II}^*(t)$] and two drift velocities $\vec{v}_h(t)$ and $\vec{v}_n(t)$. When fluxes are included, the energy presents besides a term with a fourth-power law in the quasitemperature in the given description, additional terms which can be considered as kinetic-like contributions due to the motion characterized by the fluxes.

Moreover, another important point is that whereas the quantities $N_{\vec{k}}$ of Eq. (7) and in Eq. (45) are the correct populations, the quantities $N_{\vec{k}}^I$ of Eq. (48) and $N_{\vec{k}}^{II}$ of Eq. (63) are not, they are only approximate expressions depending on the truncated description we are using.

4. Concluding remarks

We have performed a study of the thermodynamics of nonequilibrium radiation, done in the framework of informational-statistical thermodynamics. This, as noticed, implies describing irreversible thermodynamics on the basis of statistical mechanics for nonequilibrium systems. In particular we have resorted for the latter to the approach founded on Jaynes' Predictive Statistical Mechanics.

In the most general approach (in Section 2) a mesoscopic statistical nonequilibrium thermodynamics has been introduced in the sense that the space of states is characterized by the populations of photons in all of their possible quantum-mechanical states. As noticed, an alternative—and also complete—description can be made in terms of the Lagrange multipliers (that the variational method introduces) associated to the populations—they are said to be thermodynamically conjugated. They can be interpreted as the reciprocal of a nonequilibrium-temperature-like variable (dubbed quasitemperature) for each mode. This quasitemperature per mode evolves in time (until a steady state is achieved under the action of a constant pumping source, or returns to equilibrium after switching off the external source), and, as shown in the follow-up article, can be determined via experimental measurements (and its evolution followed in experiments of ultrafast optical spectroscopy).

Different nonequilibrium thermodynamic properties have been discussed at the end of Section 2 and so we do not go over them in these concluding remarks.

In Section 3 we have first reformulated the mesoscopic nonequilibrium thermodynamics of radiation of Section 2, along an interesting line in informational-statistical thermodynamics based on the construction of a generalized nonequilibrium grand-canonical ensemble. In that way a kind of thermo-hydrodynamics is introduced, describing the system in terms of energy, particle number (not the case for the present system of photons), and their fluxes of all order (the vectorial ones or currents of energy and particles and the tensorial ones as the flux of the flux or second-order flux, and so on). Using this approach one can introduce truncations in the description of the system (that is, reducing the number of fluxes that are considered) [60].

In Section 3.1, we have considered the most contracted description possible, namely introducing only the energy of radiation. The conjugated Lagrange multiplier can be interpreted as the reciprocal of a time-dependent quasitemperature, and a time-dependent fourth-power law of the Stefan–Boltzmann type applies to such a quasitemperature. The radiation pressure can be evaluated and it follows the rule of being one third of the time-evolving energy density.

In a slightly extended description, in Section 3.2, we have introduced besides the energy of radiation, the vectorial fluxes (currents) of energy and particles. The corresponding Lagrange multipliers can be, in this case, associated with, respectively, a quasitemperature and drift velocities of energy and particles. We have seen that then, when the currents are relevant and cannot be excluded of the set of basic variables, the energy has two types of contributions [cf. Eq. (71)], namely a part with the form of a fourth-power of the quasitemperature, plus another part which is a bilinear form in the drift velocities: we have called them purely thermal contribution and kinetic-motion contribution, respectively.

We notice that in this description it would be possible to define a pseudotemperature of the nonequilibrated radiation by imposing on the energy, as given in this truncated description by Eq. (71), a fourth-power law in terms of this pseudotemperature, say $T_{rad}(t)$, meaning then that the latter is given in terms of the Lagrange multipliers by the expression

$$a[T_{rad}(t)]^4 = a[T_{II}^*(t)]^4 \left[1 + \frac{1}{a} k_B^4 \beta_{II}^4(t)(\tilde{a}_1(t) v_h^2(t) + \tilde{a}_2(t) v_n^2(t) + \tilde{a}_3(t) \vec{v}_h(t) \cdot \vec{v}_n(t))\right] . \quad (75)$$

We can see that in the case of the truncation of Section 3.1, this pseudotemperature of the radiation coincides with the quasitemperature $T_I^*(t)$.

Moreover, the fluxes [currents of Eqs. (72) and (73)] are linear combinations of the drift velocities, as expected, and so is the flux (current) of informational-statistical entropy [cf. Eq. (74)]. Finally, in this truncated description, the radiation pressure, which is derived from the second-order flux of energy, satisfies the law of being one third of the density of energy. Hence, such radiation pressure has two contributions, namely, one arising from the thermal motion and another one which depends on the kinetic motion and is a bilinear expression in the drift velocities.

In summary, the nonequilibrium thermodynamic state of radiation in bulk is completely described by the determination of the populations in each mode or, alternatively, by the quasitemperature in each mode. However, depending on the characteristics of the situation (usually determined by the experimental protocol) it is possible to use truncated thermo-hydrodynamic descriptions in terms of the densities of energy and particles and, eventually, a reduced set of their fluxes (first fluxes or currents, second-order fluxes, etc.)

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Appendix A. The coefficients in Eqs. (64) – (66)

As said in the main text, after some algebra we find the expressions up to second order in the variables F's- of Eqs. (64)–(66), where the coefficients are

$$a_1(t) = V\frac{2\pi^2}{9\hbar^3 c}[k_B T^*_{II}(t)]^6 , \tag{A.1}$$

$$a_2(t) = V\frac{1}{6\hbar^3 c}[k_B T^*_{II}(t)]^4 , \tag{A.2}$$

$$a_3(t) = V\frac{8\zeta(3)}{\pi^2\hbar^3 c}[k_B T^*_{II}(t)]^5 , \tag{A.3}$$

$$b_1(t) = -V\frac{4\pi^2}{45\hbar^3 c}[k_B T^*_{II}(t)]^5 , \tag{A.4}$$

$$b_2(t) = -V\frac{2\zeta(3)}{\pi^2\hbar^3 c}[k_B T^*_{II}(t)]^4 , \tag{A.5}$$

$$c_1(t) = b_2(t) , \tag{A.6}$$

$$c_2(t) = -V\frac{1}{9\hbar^3 c}[k_B T^*_{II}(t)]^3 , \tag{A.7}$$

where ζ is the Riemann zeta function.

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