Lagrange Multipliers in Extended Irreversible Thermodynamics and in Informational Statistical Thermodynamics^{*}

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We discuss the physical interpretation of the Lagrange multipliers appearing in the information-theoretical description of nonequilibrium steady states characterized by a heat flux or a viscous pressure. Some of the multipliers have a classical counterpart (temperature, pressure, chemical potential,...) but their equations of state are modified by the fluxes, whereas some others, those which are related to nonequilibrium constraints, do not have an analogous in the equilibrium theory. We give definite results for the Lagrange multipliers, the partition function and the nonequilibrium entropy in some simple situations which provide explicit illustrations of their dependence on the fluxes. We end with some comments about the experimental verification of this dependence for the Lagrange multipliers conjugated to the internal energy.

Introduction

Information Statistical Thermodynamics [1-5] is a very powerful and elegant method for the analysis of systems in nonequilibrium situations. Amongst its wealth of interesting aspects, it provides a framework for the discussion of the thermodynamics of nonequilibrium systems beyond the local-equilibrium hypothesis, mainly the so-called extended irreversible thermodynamics (EIT for short) [6-8]. Such a thermodynamic theory describes the systems in an extended phase space which uses as variables not only the conserved ones but also the usual dissipative fluxes and, in some occasions, additional higher-order fluxes.

Information theory has been used to provide a basis for the generalized entropy and entropy flux used in extended irreversible thermodynamics and for the evolution equations of the fluxes, and to generalize them to the nonlinear domain [10-21]. Here, we will specialize our discussion on how EIT allows one to identify in physical terms the nonclassical Lagrange multipliers related to nonequilibrium constraints, and on some problems related with the identification of the Lagrange multiplier conjugated to the energy, which plays the role of the inverse of a temperature or quasitemperature. Indeed, at equilibrium, the nature of the Lagrange multipliers is elucidated by comparing the microscopic expression for the differential of the entropy with the macroscopic Gibbs equation. Out of equilibrium, the problem is to find the corresponding macroscopic Gibbs equation with an unambiguous identification of the parameters. EIT provides, at least up to second order in the fluxes, such a Gibbs equation.

Furthermore, in Section III we will show explicitly the partition function and the nonequilibrium entropy for a few simple illustrative situations: the ideal gas under viscous pressure and heat flux, the ideal relativistic gas and the electromagnetic radiation under energy flux, and finally the harmonic chain under heat flux. These explicit examples illustrate in a clear way the usefulness of information theoretical arguments for EIT, both for providing a general microscopic basis of the Gibbs equation, as for allowing to go beyond the

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second-order approximation in the dependence of the entropy on the fluxes, and they may be helpful even as a pedagogical introduction to the use of information theory in nonequilibrium situations.

II. Information theoretical description of systems in nonequilibrium steady states

Consider a system of N particles characterized by their positions and momenta, $\mu' = \{\mathbf{r}_1, \mathbf{p}_1, ..., \mathbf{r}_N, \mathbf{p}_N\}$ and assume that we know the local mean values $\langle \mathbf{A}_i \rangle$ of a set of extensive observables $\mathbf{A}_i(\mu')$. The problem is to obtain the probability density $f_N(\mu')$ which maximizes the information in the system compatible with the measured quantities. In other words, the objective is to calculate the probability density which maximizes the global entropy S defined by

$$S = -k_B (h^{3N} N!)^{-1} \int f_N(\mu') \ln f_N(\mu') d\Gamma_N \qquad (1)$$

subject to the constraints

$$(h^{3N}N!)^{-1}\int f_N(\mu')\mathbf{A}_i(\mu')d\Gamma_N = <\mathbf{A}_i> \quad (2)$$

for any observable \mathbf{A}_i at any point \mathbf{r} . Here $d\Gamma_N = d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N$ is the volume element in the phase space, h is the Planck constant, and k_B the Boltzmann constant. For simplicity, we shall focus our attention on steady states where the mean values of the quantities do not depend on time, since we are more interested in the way of generalizing the concept of Gibbs ensembles to nonequilibrium steady states, thus providing a further basis for the understanding of the nonequilibrium entropy and the equations of state of EIT.

To achieve the maximization of S subject to constraints (2), one has to maximize the quantity

$$-k_B \int [f_N \ln f_N + f_N \lambda_0 + f_N \sum_I \boldsymbol{\lambda}_i(\mathbf{r}) \cdot \mathbf{A}_i(\mu')] d\Gamma_n, \quad (3)$$

where the $\lambda_i(\mathbf{r})$ are the Lagrange multipliers corresponding to the quantities $\mathbf{A}_i(\mathbf{r})$). The dot between

 λ_i and \mathbf{A}_i indicates a scalar product. Explicit examples will be considered in Section III. Finally, λ_0 is the Lagrange multiplier accounting for normalization. In what follows, subscript *i* starts with i = 1, and λ_0 is written as $\lambda_0 = \ln Z$, with Z the partition function. Expression (3) is an extremum under the condition that f_N satisfies

$$\frac{\partial}{\partial f_N} [f_N \ln f_N + f_N \lambda_0 + f_N \sum_i \boldsymbol{\lambda}_i(\mathbf{r}) \cdot \mathbf{A}_i(\boldsymbol{\mu}')] = 0.$$
(4)

This yields

$$f_N = Z^{-1} \exp[-\sum_i \lambda_i \cdot \mathbf{A}_i(\mu')], \qquad (5)$$

where the partition function Z is defined as

$$Z = (h^{3N}N!)^{-1} \int \exp\left[-\sum_{i} \lambda_{i} \cdot \mathbf{A}_{i}(\mu')\right] d\Gamma_{N}$$
 (6)

thus ensuring the normalisation condition for f_N .

The Lagrange multipliers are derived from constraints (2). The latter may be written in the compact form

$$-\frac{\partial \ln Z}{\partial \lambda_i} = <\mathbf{A}_i>,\tag{7}$$

as follows from definition (6) of Z and relations (2). Introduction of the distribution density (5) in the definition (1) for the entropy yields

$$S(\mathbf{r}) = k_B \ln Z + \sum_i \lambda_i \cdot \langle \mathbf{A}_i \rangle], \qquad (8)$$

On the other hand, the second moments of the macroscopic values of the observables $\mathbf{A}_i(\mu')$ around their average values are also obtained by differentiation of (6):

$$\langle (\mathbf{A}_{i}(\mu') - \langle \mathbf{A}_{i} \rangle) (\mathbf{A}_{j}(\mu') - \langle \mathbf{A}_{j} \rangle) \rangle = \frac{\partial^{2} \ln Z}{\partial \boldsymbol{\lambda}_{1} \partial \boldsymbol{\lambda}_{j}}.$$
(9)

Expression (9) may be written in terms of the second derivatives of the generalized entropy as

$$\langle (\mathbf{A}_{i}(\mu') - \langle \mathbf{A}_{i} \rangle) (\mathbf{A}_{j}(\mu') - \langle \mathbf{A}_{j} \rangle) \rangle = -\frac{1}{k_{B}} \left[\left(\frac{\partial^{2} S}{\partial \langle \mathbf{A}_{i} \rangle \partial \langle \mathbf{A}_{j} \rangle} \right)^{-1} \right].$$
(10)

In equilibrium, when one system is in contact with a thermal bath in such a way that its average energy is known, one takes as observable quantity the Hamiltonian of the system, $A(\mu') = \mathcal{H}(\mu')$. The corresponding distribution function (5) is that of the canonical ensemble

$$f_N = Z^{-1} \exp[-\beta \mathcal{H}(\mu')]. \tag{11}$$

If in addition to the energy the number of particles is chosen as an observable quantity with a specified mean value, the distribution function takes the form

$$f = Z^{-1} \exp[-\beta \mathcal{H}(\mu') - \alpha N'], \qquad (12)$$

with N' the microscopic particle-number operator.

Up to now, the Lagrange multipliers α and β of (11) or (12) are not assigned a physical meaning. To obtain their physical interpretation, let us take the differential expression of (8), namely

$$dS = k_B \sum_{i} \lambda_i \cdot d < \mathbf{A}_i > +k_B \sum_{i} < \mathbf{A}_i > \cdot d\lambda_i + k_B d \ln Z = k_B \sum_{i} \lambda_i \cdot d < \mathbf{A}_i > .$$
(13)

The second equality follows from differentiating the expression (7) for Z with respect to the Lagrange multipliers, which results in $d \ln Z = -\sum_i \langle \mathbf{A}_i \rangle \cdot d \boldsymbol{\lambda}_i$. By identification of (13) with the Gibbs equation of classical thermodynamics,

$$dS = T^{-1}dU - \mu T^{-1}dN, \tag{14}$$

one is led to the usual identifications $\beta = (k_B T)^{-1}$, and $\alpha = -\mu (k_B T)^{-1}$, with T the absolute temperature and μ the chemical potential.

In a nonequilibrium state characterized by \mathbf{P}^{ν} and \mathbf{q} , the viscous pressure tensor and energy flux respectively, in addition of the classical variables, one should take into account the constraints on the fluxes. This would lead to a distribution function of the form

$$f = Z^{-1} \exp[-\beta \mathcal{H} - \alpha N - \lambda_{\mathbf{P}} : \mathbf{P}^{\nu} - \lambda_{\mathbf{q}} \cdot \mathbf{q}] \quad (15)$$

Note that the Lagrange multipliers $\lambda_{\mathbf{P}\nu}$ and $\lambda_{\mathbf{q}}$ do not have any analogue in classical thermodynamics and therefore cannot be identified in an equilibrium theory. The Gibbs equation corresponding to (15) is

$$dS = k_B \beta dU + k_B \alpha dN + k_B \lambda_{\mathbf{P}\nu} : d\mathbf{P}^\nu + k_B \lambda_{\mathbf{q}} \cdot d\mathbf{q}.$$
(16)

EIT is, nowadays, the only thermodynamic theory which provides a Gibbs equation depending on the viscous pressure and a heat flux. Such an equation has the form [6,7]

$$dS = \theta^{-1}dU + \pi\theta^{-1}dV - \mu dN - \left(\frac{\tau_1 V}{\lambda T^2}\right)\mathbf{q} \cdot d\mathbf{q} - \left(\frac{\tau_2 V}{2\eta T}\right)\mathbf{P}^{\nu} : d\mathbf{P}^{\nu}$$
(17)

where τ_1 and τ_2 are the relaxation times of the heat flux and of the viscous pressure, respectively, V is the volume, λ and η are the thermal conductivity and the shear viscosity, and θ and η are the temperature and the pressure in the nonequilibrium state. We have used the symbols θ and π rather than T and p to emphasize that these quantities do not coincide with the lo-

cal equilibrium expressions for the temperature and the pressure, i.e. with the expressions of T and p obtained from the caloric and the thermal equations of state for the corresponding values of U, V and N. We neglect for simplicity the bulk viscous effects (i.e. $p^{\nu} = 0$), so that in what follows \mathbf{P}^{ν} must be understood as the shear

pressure tensor.

The relaxation times are defined through the evolution equations for the fluxes

$$\tau_1 \dot{\mathbf{q}} + \mathbf{q} = -\lambda \nabla \theta \tag{18}$$

$$\tau_2 \dot{\mathbf{P}}^{\nu} + \mathbf{P}^{\nu} = -2\eta \mathbf{V}^s \tag{19}$$

where the dot over quantities stands for material derivative and \mathbf{V}^s is the symmetric part of the velocity gradient $\nabla \mathbf{V}$. These equations are usually known as Maxwell-Cattaneo equations and they are useful to describe, for instance, thermal waves and viscoelastic effects. They reduce to the classical Fourier and Newton-Stokes equations in the limit of vanishing relaxation times, and they may be generalized by including different kinds of couplings between the heat flux and the viscous pressure, or higher-order fluxes, or nonlinear terms. Such generalizations and their corresponding physical applications may be found in [6-9].

Comparison of (16) with (17) allows us to identify the Lagrange multipliers as

$$\beta = \frac{1}{k_B \theta}, \mathbf{\lambda}_{\mathbf{P}^{\nu}} = -\frac{\tau_2 V}{2k_B \eta T} \mathbf{P}^{\nu}, \mathbf{\lambda}_{\mathbf{q}} = -\frac{\tau_1 V}{k_B \lambda T^2} \mathbf{q}.$$
 (20)

In this section we have limited our considerations to nonequilibrium steady states. Dynamical equations could also be obtained by following several methods, such as those of Robertson [22], Zubarev [3] or the nonequilibrium statistical operator method [5].

It is important to emphasize that the distribution function (5) is not the exact one describing the system, but an approximate distribution function which gives exact results for the variables taken as constraints, but not for other variables. In fact, in order that the description may be self-consistent, one should introduce as constraints all the *slow* variables (i.e. all the variables whose time scale is of the order of the time scale of observation) in accordance to the Zubarev-Peletminskii symmetry condition [5] for internal consistency. Furthermore, expression (5) lacks information about the dissipation and the microscopic dynamics of the system, i.e. about the dynamics of the *fast* variables not included as constraints in the maximum-entropy description. According to the MaxEnt-NESOM approach, the statistical operator (density matrix) describing the system in Zubarev's approach has the form [5]

$$\rho_{\kappa}(t) = \bar{\rho}(t,0) + \rho_{\kappa}'(t) \tag{21}$$

Here, $\bar{\rho}(t, 0)$ is a "coarse-grained" nondissipative term which has the Gibbsian-like form given by (5), whereas ρ'_{κ} is given by

$$\rho_{\kappa}'(t) = \exp\left[\kappa \int_{-\infty}^{t} dt' e^{\kappa(t-t')} \ln \bar{\rho}(t',t'-t)\right], \quad (22)$$

where $\kappa(\kappa^{-1}$ can be considered as a lifetime) is a positive infinitesimal that goes to zero after the calculation of the averages is performed. The distribution function $\bar{\rho}(t,0)$ gives the thermodynamics of the system in the "coarse-grained" space defined by the macroscopic variables, whereas the function ρ'_{κ} which does not influence the thermodynamics because it does not contribute to the partition function neither to the value of the macroscopic variables, describes the microscopic dynamics of the fast variables which have not been included in the thermodynamic description, and consequently the dissipation and the transport coefficients. The statistical operator $\rho'_{\kappa}(t)$ satisfies a modified form of the Liouville equation with infinitesimal sources related to κ which break its time-reversal symmetry and introduce dissipativity, whereas the coarse-grained part ρ does not satisfy by itself the Liouville equation. It is interesting to notice that the exact distribution function $\rho'_{\kappa}(t)$ is not needed to formulate a thermodynamic framework in the space of the selected macrovariables, but that for this purpose it is sufficient the part of ρ_{κ} describing such variables.

One must note that the information-theoretical methods do not specify which variables should be used for the description of the system. The above-mentioned Zubarev-Peletminskii condition [5] implies that in principle one should have all the variables decaying with a relaxation time comparable to the experimental time. This suggests to be careful in using a truncation procedure. Indeed, some systems exhibit a hierarchy of variables whose relaxation times differ widely and tend to zero in a very fast way for higher-order variables. In other systems, instead, all the nonconserved variables decay with almost the same relaxation time, and that would indicate, in principle, that all the relaxation variables should be taken into account, and not only a finite number of them.

III. Entropy in nonequilibrium steady states: simple explicit examples

In this section we shall provide the explicit expression for the nonequilibrium partition function and the nonequilibrium entropy for several simple situations which supply clear illustrations of the influence of the fluxes on the thermodynamic functions. We begin in Subsection III.1 by dealing with the classical ideal gas under heat flux and viscous pressure in a linear approximation. In Subsections III.2 and III.3 we go beyond the linear approximation for nonvanishing viscous pressure and zero heat flux, and for vanishing viscous pressure and nonzero heat flux, respectively; Subsections III.4 and III.5 are dedicated to the study of a harmonic chain with a nonvanishing heat flux and a relativistic ideal gas with a nonvanishing energy flux.

III.1. Ideal gas under heat flux and viscous pressure: linear approximation

As a first application we consider an ideal

monatomic gas out of equilibrium subjected to a heat flux and a viscous pressure. At each position, the mean values of the particle number density n, the energy density per unit volume ρu , the momentum density ρv , the heat flux \mathbf{q} , and the components of the pressure tensor \mathbf{P} are supposed to be known. Since the equilibrium pressure p is fixed by u and n, the independent knowledge of \mathbf{P} is a constraint on the viscous part \mathbf{P}^{ν} of the pressure tensor.

The constraints on the distribution function f are thus

$$n(\mathbf{r}) = \int f(\mathbf{r}, \mathbf{c}) d\mathbf{c}, \qquad (23)$$

$$\rho v(\mathbf{r}) = \int m \mathbf{c} f(\mathbf{r}, \mathbf{c}) d\mathbf{c}, \qquad (24)$$

$$\rho u(\mathbf{r}) = \frac{3}{2} n k_B T(\mathbf{r}) = \int \frac{1}{2} m C^2 f(\mathbf{r}, \mathbf{c}) d\mathbf{c}, \qquad (25)$$

$$\mathbf{P}^{\nu}(\mathbf{r}) = \int m \mathbf{C} \mathbf{C} f(\mathbf{r}, \mathbf{c}) d\mathbf{c} - p \mathbf{1}, \qquad (26)$$

and

$$\mathbf{q}(\mathbf{r}) = \int \frac{1}{2} m C^2 \mathbf{C} f(\mathbf{r}, \mathbf{c}) d\mathbf{c}, \qquad (27)$$

with C the peculiar molecular velocity, and 1 the unit tensor.

The distribution function (15) maximizing the entropy has the form

$$f = \exp\left[-\alpha - \beta \frac{1}{2}mC^2 - \boldsymbol{\lambda}_{\nu} \cdot \mathbf{C} - \boldsymbol{\lambda}_{\mathbf{P}}^{\nu} : (m\mathbf{C}\mathbf{C} - p\mathbf{1} - \boldsymbol{\lambda}_{\mathbf{q}} \cdot \frac{1}{2}mC^2\mathbf{C}\right] .$$
(28)

Here we have included a Lagrange multiplier λ_{ν} in order to ensure the constraint (24) on the value of the velocity. Expanding the exponential in (28) up to first order in the nonequilibrium terms results in

$$f(\mathbf{r},\mathbf{c}) = \exp\left[-\alpha - \beta \frac{1}{2}mC^2\right] \left[1 - \boldsymbol{\lambda}_{\nu} \cdot \mathbf{C} - \boldsymbol{\lambda}_{\mathbf{P}}^{\nu} : (m\mathbf{C}\mathbf{C} - p\mathbf{1}) - \boldsymbol{\lambda}_q \cdot \frac{1}{2}mC^2\mathbf{C}\right] .$$
(29)

After substitution of (29) in (23)-(27), one is led to

$$\exp(-\alpha) = n \left(\frac{m}{2\pi k_B T}\right)^{3/2} , \beta = \frac{1}{k_B T} , \qquad (30)$$

$$\boldsymbol{\lambda}_{\nu} = \frac{m}{pk_BT} \mathbf{q}, \quad \boldsymbol{\lambda}_{\mathbf{P}^{\nu}} = -\frac{1}{2pk_BT} \mathbf{P}^{\nu}, \quad \boldsymbol{\lambda}_q = -\frac{2m}{5pk_B^2T^2} \mathbf{q}. \tag{31}$$

Bearing these results in mind, we can see that (29) becomes

$$f(\mathbf{r}, \mathbf{c}) = n \left(\frac{m}{2k_B T}\right)^{3/2} \exp\left[-\frac{mC^2}{2k_B T}\right] \left\{1 + \frac{1}{2pk_B T} m\mathbf{C}\mathbf{C} : \mathbf{P}^{\nu} + \frac{2m}{5pk_B^2 T^2} \left[\frac{1}{2}mC^2 - \frac{5}{2}k_B T\right]\mathbf{C} \cdot \mathbf{q}\right\}.$$
 (32)

This is nothing but the expression of the distribution function derived within the Grad's thirteen-moment approximation in kinetic theory [6-7].

III.2 Classical ideal gas under shear flow

The simplest example allowing for a nonlinear analysis is the classical ideal gas under shear (thermal effects are not present) [23] with the constraints (23)-(26). The technique of Lagrange multipliers gives for the distribution function which maximizes the entropy

$$f = z^{-1} \exp\left\{-\frac{1}{2}\left[\sum_{i} (\beta + 2\lambda_{ij})mC_i^2 + \sum_{i} \sum_{j \ (>i)} 2\lambda_{ij} mC_i C_j\right]\right\}$$
(33)

where β and $\lambda_{ij} (\equiv \lambda_{P_{ij}^{\nu}})$ are the Lagrange multipliers corresponding to the constraints on the energy and on the viscous pressure tensor and z is the one-particle partition function. Explicit integration of the partition function z gives

$$z = \frac{(2\pi)^{3/2} V}{m^{3/2} |\mathbf{M}|^{1/2}} \tag{34}$$

with $|\mathbf{M}|$ the determinant of the matrix

$$\mathbf{M} = \begin{pmatrix} \beta + 2\lambda_{11} & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \beta + 2\lambda_{22} & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \beta + 2\lambda_{33} \end{pmatrix}$$
(35)

The condition $Tr\mathbf{P}^{\nu} = 0$ implies $\lambda_{11} + \lambda_{22} + \lambda_{33} = 0$. The Lagrange multipliers are obtained from the constraints, which may be written in the compact form

$$u = -\frac{1}{V} \frac{\partial \ln z}{\partial \beta}; \quad P_{ij}^{\nu} = -\frac{N}{V} \frac{\partial \ln z}{\partial \lambda_{ij}}$$
(36)

We shall restrict our attention to the case where the system is submitted to a fixed shear viscous pressure P_{12}^{ν} , corresponding to a plane Couette flow. In this case the only nonvanishing Lagrange multipliers are β and λ_{12} , and one has

$$z = \frac{(2\pi)^{3/2}V}{m^{3/2}(\beta^3 - \beta\lambda_{12}^2)^{1/2}}.$$
 (37)

The Lagrange multipliers may be obtained in terms of u and P_{12}^{ν} as

$$\beta = \frac{1-y}{2Vu[R^2 + (1-y)]}; \quad \lambda_{12} = \frac{3R^2 + 2(1-y)}{2VuR[R^2 + (1-y)]}$$
(38)

with $R = P_{12}^{\nu}/Nu$ and $y = (1+3R^2)^{1/2}$. Note that near equilibrium, i.e. when $\lambda_{12} \rightarrow 0$, expressions in (38) tend to $\beta = 3/(2Vu)$ and $\lambda_{12} = -\beta^2(V/N)P_{12}^{\nu}$ respectively. Thus, when $P_{12}^{\nu} = 0$ one recovers from (33) the standard Maxwell-Boltzmann distribution function and β becomes $\beta = (k_B T)^{-1}$, with T the local-equilibrium temperature.

The entropy has the form

$$S = S_{eq} + \frac{Nk_B}{2} \ln \frac{27R^2[R^2 - (y-1)]^2}{2(y-1)^3}$$
(39)

with S_{eq} the equilibrium entropy. The Lagrange multipliers may be identified as

$$\beta = \frac{1}{k_B \theta}; \quad \lambda_{12} = -\frac{\tau P_{12}^{\nu}}{\eta k_B T} = \frac{\tau \dot{\gamma}}{k_B T} \tag{40}$$

Notice that we do not have information on τ neither on η , but only on their ratio. This lack of information on τ would be obtained from the part ρ'_{κ} in (21). Anyway this identification of the Lagrange multiplier allows one to introduce the shear rate $\dot{\gamma}$ in the description of the system in terms of τ . Consequently, we are now able to identify the viscosity as

$$\eta = -\frac{P_{12}^{\nu}}{\dot{\gamma}} = -\frac{3}{2}\eta_0 \frac{R^2[R^2 + (1-y)]}{R^2 + (2/3)(1-y)}$$
(41)

which describes shear-thinning, i.e. the reduction of the viscosity with increasing shear rate. For low values of R, (41) tends to η_0 which is the shear viscosity in the linear regime, whereas it tends to $\eta(\dot{\gamma}) = 0$ when $R \to 1$. The physical meaning of the Lagrange multipliers beyond the linear approximation in the fluxes is a topic of current research [31-32].

III.3 Classical gas with nonvanishing heat flux

Consider a classical non-relativistic gas under fixed values of the energy and the heat flux, at zero speed. The distribution function, according to the maximumentropy formalism, should be [24,25]

$$f = Z^{-1} \exp\left[-\beta \frac{1}{2}mC^2 - \boldsymbol{\gamma} \cdot \left(\frac{1}{2}mC^2 - \frac{5}{2}\beta^{-1}\right)\mathbf{C}\right]$$
(42)

where the factor $5/(2\beta)$ guarantees that the mean speed is zero. This distribution diverges for high values of the molecular speed, because the operator for the heat flux is odd in the velocity; to avoid this divergence, it is usual to expand (42) in powers of **q** as it has been said above. Grad's approach is found if one truncates the expansion in the first-order in **q**. However, if one keeps second-order terms in **q**, one finds for β and γ the following expressions

$$\beta = (k_B T)^{-1} \left[1 + \left(\frac{2}{5} m p^2 k_B T \right) \mathbf{q} \cdot \mathbf{q} \right], \qquad (43)$$

$$\boldsymbol{\gamma} = -\frac{2}{5} \frac{m}{pk_B^2 T} \mathbf{q}.$$
 (44)

The expression for γ coincides with that obtained from the Grad expansion: this is not surprising, because both formulations must agree up to the first order in the fluxes. It is especially worth of stress that the Lagrange multiplier β is in general different from $(k_BT)^{-1}$ and that it depends on the heat flux. In Grad's approach, where the second terms in **q** are omitted, one has $\beta = (k_B T)^{-1}$. This is the reason why the question of the difference between absolute temperature and localequilibrium absolute temperature [36] does not appear in kinetic theory, where the latter one is always used by definition [37].

III.4 Ideal relativistic gas with nonvanishing heat flux

As a further illustration, consider a relativistic gas in a nonequilibrium steady state, with prescribed internal energy U and integrated energy flux $\mathbf{J} = V\mathbf{q}$, where V is the volume and \mathbf{q} the energy flux, i.e. the energy transported per unit area and time [25]. The distribution function maximizing the entropy reads

$$f = Z^{-1} \exp[-\beta \sum_{i} p_i c - \boldsymbol{\gamma} \cdot \sum_{i} p_i c \mathbf{c}], \qquad (45)$$

where $p_i c$ is the microscopic expression for the energy of the *i*th particle and $p_i cc$ is the particle contribution to the energy flow (all particles are supposed to move at speed c). In contrast with the classical gas studied in Section III.3, the distibution function (45) does not diverge because the dependence of the energy flux in terms of the momentum is of the first order, instead of the third order as in the classical gas. This allows one to obtain explicit expressions for the partition function without need of any truncation of the exponential. The partition function is defined as

$$Z = \frac{V^N}{N!h^{3N}} \int d\mathbf{p}_1 \dots \int d\mathbf{p}_N \exp\left[-\sum_i p_i c - \boldsymbol{\gamma} \cdot \sum_i p_i c\mathbf{c}\right].$$
(46)

The factor V^N comes from integration over positions of the particles. The explicit value of (46) is

$$Z = \frac{1}{N!} \left(\frac{8\pi V}{\beta^3 c^3 h^3}\right)^N \left[1 - \frac{c^2 \gamma^2}{\beta^2}\right]^{-2N} .$$
(47)

We determine the Lagrange multipliers β and γ from the conditions on the mean energy and the mean energy flux, which can be obtained, according to (7), in terms of the derivatives of $\ln Z$ with respect to β and γ . Solving for β and γ we are led respectively to

$$\beta = \frac{3N}{U} \frac{1}{y-1} \tag{48}$$

and

$$\boldsymbol{\gamma} = \frac{3N}{J^2} \frac{y-2}{y-1} \mathbf{J},\tag{49}$$

where y stands for

$$y = \left[4 - 3\left(\frac{J}{cU}\right)^2\right]^{1/2}.$$
 (50)

It follows from (48) and (49) that for J = 0 one has $\gamma = 0$ and $\beta = (k_B T)^{-1}$; in addition, we recover from (47) the usual equilibrium expression for the partition function. In general, $\beta \neq (k_B T)^{-1}$, and one is led for the non-equilibrium temperature to the expression $\theta = T(y - 1)$. Furthermore, it is seen that β and γ diverge for y = 1, i.e. when J tends to Uc. This domain of validity of J is easy to interpret, because cU is the maximum energy flow which may be expected: it corresponds to the energy U carried at the maximum possible speed, which is precisely c.

The entropy is given by $S = k_B [\ln Z + \beta U + \gamma \cdot \mathbf{J}]$ and it may be cast in the form

$$S = S_{eq} + Nk_B \ln\left[\frac{1}{16}(y-1)(y+2)^2\right].$$
 (51)

which shows how the entropy depends on the energy flux \mathbf{J} in a non-quadratic way.

It is easy to obtain from (45) the pressure tensor for the relativistic gas under a heat flux \mathbf{q} which has the form

$$\mathbf{P} = \frac{U}{V} \left[\frac{1}{3} (y-1) \mathbf{1} - \frac{1}{q^2} (y-2) \mathbf{q} \mathbf{q} \right] \quad . \tag{52}$$

Observe that for y = 2, the pressure tensor reduces to $\mathbf{P} = (1/3)(U/V)\mathbf{1} = p\mathbf{1}$ which corresponds to the equilibrium pressure tensor. The term in $\mathbf{q}\mathbf{q}$ becomes very important when the energy flux approaches cU(i.e. $y \to 1$) and it plays an important role in radiation hydrodynamics, where one writes the pressure tensor as [26, 27]

$$\mathbf{P} = \frac{U}{V} \left(\frac{1-\chi}{2} \mathbf{1} + \frac{3\chi - 1}{2} \frac{\mathbf{q}\mathbf{q}}{q^2} \right) , \qquad (53)$$

 χ being the so-called Eddington factor.

Let us finally comment on the behaviour of the entropy when the energy flux approaches its maximum value. We have seen that (51) is diverging instead of vanishing. This is the result of using classical rather than quantum statistics. If one wishes to study electromagnetic radiation, the relevant statistics is that of Bose-Einstein and one should maximize the corresponding expression for the entropy, namely

$$S = -k_B (h^{3N} N!)^{-1} \int [f \ln f - (1+f) \ln(1+f)] d\Gamma.$$
(54)

This yields for the distribution function

$$f = [\exp(\beta pc + \boldsymbol{\gamma} \cdot pc\mathbf{c}) - 1]^{-1} .$$
 (55)

Here, we do not consider a fixed number of particles because we are dealing with photons whose particle number is not fixed. The calculations of β and γ are rather cumbersome [30] and the final results are

$$\beta = \frac{1}{2k_B} \left(\frac{aV}{U}\right)^{1/4} \frac{(y+2)^{1/2}}{(y-1)^{3/4}} , \qquad (56)$$

 and

$$\gamma = -\frac{3}{4} \left(\frac{a}{V}\right) \frac{\mathbf{J}}{c^2 U^2} \frac{1}{(y+2)^{1/2} (y-1)^{3/4}} .$$
 (57)

Here, a is the radiation constant in the well-known expression $U = aT^4V$ for the internal energy of radiation at equilibrium. The entropy becomes

$$\frac{S}{V} = \frac{2}{3}a^{1/4} \left(\frac{U}{V}\right)^{1/4} (y-1)^{3/4} (y+2)^{1/2}, \qquad (58)$$

which tends to the expected value $S/V = (4/3)aT^3$ at equilibrium (J = 0, i.e. y = 2) and which vanishes for $J^2 \rightarrow c^2 U^2$.

III.5 Harmonic chain with nonvanishing heat flux

In a harmonic chain, the phonon mean free path is infinite, so that the energy flux along it is not proportional to the temperature gradient but to the temperature difference between the reservoirs located at its ends. To avoid complications associated with the boundary conditions, Miller and Larson [28] considered a closed chain forming a ring. In this case, the system turns out to be a "superconductor" of thermal energy, because of its infinite heat conductivity: a heat flux lasts indefinitely. Such a chain ring is characterized by the constraints

$$\langle \mathcal{H} \rangle = U$$
 , $\langle \mathcal{J} \rangle = Q$, (59)

with \mathcal{H} the Hamiltonian of the system, \mathcal{J} the heat flux operator, U the mean (internal) energy of the chain, and Q the mean heat flux along the ring.

The system consists of a linear chain of N particles of mass m connected to its nearest neighbours by Hookean springs with stiffness κ . One may choose a system of dimensionless quantities where the mass is expressed in terms of m, time in units of $(m/\kappa)^{1/2}$, and energy in units of $(h/2\pi)(\kappa/m)^{1/2}$. Let q_{α} be the displacement from equilibrium for each particle α ($\alpha = 1, ..., N$) and p_{α} its conjugate momentum.

The Hamiltonian of the system $\mathcal{H}(q_1, p_1, ..., q_N, p_N)$ is given by

$$\mathcal{H} = \frac{1}{2} \sum_{\alpha} p_{\alpha}^{2} + \frac{1}{2} \sum_{\alpha} (q_{\alpha+1} - q_{\alpha})^{2}.$$
 (60)

The microscopic operator $\mathcal{J}(q_1, p_1, ..., q_N, p_N)$ for the heat flux is

$$\mathcal{J} = -\frac{1}{2}N\sum_{\alpha}(q_{\alpha+1}p_{\alpha} - q_{\alpha}p_{\alpha+1}).$$
(61)

It can also be checked by using Hamilton's equations that \mathcal{H} is a constant of the motion.

Now we transform \mathcal{H} and \mathcal{J} in terms of normal coordinates η_{α} and canonical momenta $\xi_{\alpha} = d\eta_{\alpha}/dt$, which reduce the potential energy to a canonical quadratic form. The transformation matrix **A** relating **q** and η , defined by $\eta = \mathbf{A} \cdot \mathbf{q}$, is given by

$$A_{\alpha\gamma} = (1/N)^{1/2} [\sin(2\pi\alpha\gamma/N) + \cos(2\pi\alpha\gamma/N)].$$
 (62)

In terms of the normal coordinates, the Hamiltonian of the system becomes

$$\mathcal{H}(\eta,\xi) = \frac{1}{2} \sum_{\alpha} (\xi_{\alpha}^2 + \omega_{\alpha}^2 \eta_{\alpha}^2), \tag{63}$$

where ω_{α} , the angular frequency of the α th mode, is given by $\omega_{\alpha} = 2\sin(\pi\alpha/N)$. Taking into account that matrix **A** is orthogonal and symmetric (**A** = **A**⁻¹), the heat flux operator (61) reads as

$$\mathcal{J} = -\frac{1}{N} \sum_{\mu} \sin(2\pi\mu/N) [\eta_{\mu}\xi_{N-\mu} - \eta_{N-\mu}\xi_{\mu}], \quad (64)$$

with M = N/2 if N is even and M = (1/2)(N-1) if N is odd.

The dimension of the phase space of the system under study is 2N, but by assuming that the centre of mass of the system remains fixed, the dimension is effectively reduced to 2(N-1). The probability distribution function maximizing the entropy is

$$f = Z^{-1} \exp[-\beta \mathcal{H} - \gamma \mathcal{J}], \qquad (65)$$

where β and γ are the respective Lagrange multipliers and Z is the partition function

$$Z = (h^{N-1})^{-1} \int \exp[-\beta \mathcal{H} - \gamma \mathcal{J}] d\Gamma_{N-1}.$$
 (66)

Integration of (66) yields, after tedious calculations,

$$Z = \left\{ \frac{1}{2} \beta [1 + (1 - y^2)^{1/2}] \right\}^{-N}.$$
 (67)

The Lagrange multipliers β and γ may be found in terms of U and Q through the constraints. One obtains for β and y

$$\beta = \frac{1+x^2}{\epsilon(1-x^2)}, \quad y = \frac{2x}{(1-x^2)} \tag{68}$$

with $\epsilon = U/N$ and $x = Q/\epsilon$. In terms of these quantities, (67) becomes

$$Z = [\epsilon (1 - x^2)]^N.$$
(69)

For x = 0 one recovers the usual equilibrium results, whereas for $x^2 \to 1$ both β and y diverge.

The entropy and the generalized Lagrange multiplier β deserve special comments. The entropy may be written as

$$S = k_B(\beta U + \gamma Q + \ln Z). \tag{70}$$

In the thermodynamic limit when N tends to infinity, the entropy per particle turns out to be, in view of the explicit form of Z,

$$s = \lim_{N \to \infty} \frac{S}{N} = k_B [1 + \ln \epsilon + \ln(1 - x^2)] = S_{eq} + k_B \ln(1 - x^2).$$
(71)

The dependence of this expression on the heat flux Q provides a further corroboration of the basic assertions of extended irreversible thermodynamics, stating that the entropy is a function of the heat flux out of equilibrium, and allows one to explore higher-order terms in the heat flux.

The Lagrange multiplier β can be interpreted in terms of a generalized absolute temperature θ defined as $\theta = (k_B \beta)^{-1}$; from (68) one has

$$\theta^{-1} = T^{-1} \left(\frac{1+x^2}{1-x^2} \right) = T^{-1} \left(1 + \frac{2x^2}{1-x^2} \right), \quad (72)$$

indicating that the generalized temperature θ differs from the usual local equilibrium temperature $T(\equiv \epsilon/k_B)$ by terms at least of order x^2 or Q^2 . The same result can be obtained from (71) and the definition $\theta^{-1} = (\partial s/\partial \epsilon)_Q$.

The entropy (71) diverges when $x \to 1$, i.e. when the absolute temperature $\theta = 1/k_B\beta$ tends to zero (in this limit the heat flux tends to the maximum value). This is so because of the use of classical statistics rather than quantum statistics. Indeed, when the non-equilibrium temperature θ becomes lower than the Einstein temperature of the lattice, it is necessary to resort to Bose-Einstein's rather than classical statistics [26]; therefore the results obtained by Miller and Larson are no longer valid for a heat flux larger than a given value. Consider a harmonic chain with a linearized dispersion relation $\omega_{\mathbf{k}} = c|\mathbf{k}|$, c being the phonon speed and $|\mathbf{k}|$ the magnitude of the wavevector. A quantum analysis of the system under the constraint of a fixed energy density ϵ and fixed energy flux q yields for the distribution function maximizing the entropy

$$f(k;\beta,\gamma) = \left[\exp(\beta\hbar c |\mathbf{k}| + \gamma\hbar c^2 |\mathbf{k}|) - 1\right]^{-1}, \quad (73)$$

where β and γ are the Lagrange multipliers.

The entropy behaviour in the quantum limit when $\epsilon_D(\beta \pm \gamma c) \gg 1$ (with ϵ_D the Debye energy $\epsilon_D = \hbar c \pi / l$) is

$$s = \frac{k_B}{2} \left(\frac{\pi}{6\hbar}\right) \left[(\epsilon c + q)^{1/2} + (\epsilon c - q)^{1/2} \right].$$
(74)

The Lagrange multipliers β and γ are given by

$$\beta = \frac{1}{2} \left(\frac{\pi}{6\hbar}\right)^{1/2} \left[\frac{1}{(\epsilon c + q)^{1/2}} + \frac{1}{(\epsilon c - q)^{1/2}}\right]$$
$$= \frac{1}{2k_B T} \left[\frac{1}{(1 + x)^{1/2}} + \frac{1}{(1 - x)^{1/2}}\right]$$
(75)

$$y = \frac{1}{2c} \left(\frac{\pi}{6\hbar}\right)^{1/2} \left[\frac{1}{(\epsilon c + q)^{1/2}} - \frac{1}{(\epsilon c - q)^{1/2}}\right]$$
$$= \frac{1}{2ck_BT} \left[\frac{1}{(1+x)^{1/2}} - \frac{1}{(1-x)^{1/2}}\right]$$
(76)

where $T(\epsilon) \equiv (6\hbar c \epsilon / k_B^2 \pi)^{1/2}$ is the local-equilibrium temperature and $x = q/\epsilon c$. At equilibrium, q = 0 and consequently y = 0, $\beta = (k_B T)^{-1}$ and (73) becomes the equilibrium Bose-Einstein distribution function. Also the quantum equation of state at low T

$$\epsilon = \frac{k_B^2 \pi^2}{3hc} T^2 \tag{77}$$

derives by comparing the two forms of expression (75). Note that (68) are not recovered in the classical limit because, in the present problem, the linearized dispersion $\omega_{\mathbf{k}} = c|\mathbf{k}|$ instead of the exact dispersion relation has been used.

It is interesting to note that the expression for the specific heat at constant heat flux defined as $c_q = (\partial \epsilon / \partial \theta)_q$ is

$$c_q = \frac{4\epsilon^{3/2}}{k_B\theta^2} \left(\frac{6\hbar c}{\pi}\right)^{1/2} \frac{(1-x^2)^{3/2}}{(1+x)^{3/2} + (1-x)^{3/2}}.$$
 (78)

The reason for using this definition instead of the conventional $\partial \epsilon / \partial T$ is that according to EIT in a nonequilibrium steady state a thermometer measures θ rather than T [36]. Note that c_q vanishes in the limit when $x \to 1$, i.e. when the heat flux tends to its maximum value, and this corresponds to a third-law-like behaviour [29].

It is remarkable to acknowledge that the description of systems at high values of the energy flux density requires to be performed in the frame of quantum statistics. The specific value of the heat capacity of the lattice tends to zero when the nonequilibrium absolute temperature θ tends to zero. This provides a generalization of the third law to nonequilibrium steady states: indeed, in equilibrium, θ coincides with the equilibrium temperature so that the vanishing of θ means the vanishing of T; however, in nonequilibrium, even at a nonzero value of T, θ may become zero at sufficiently high values of the heat flux.

IV. Summary

The relations between information theory and EIT have been very fruitful. Here, we have outlined only a specific aspect, namely, the connection between the general Gibbs equation obtained from information theory and the phenomenological Gibbs equation of extended thermodynamics, and we have mentioned how this comparison allows for an interpretation of the nonclassical Lagrange multipliers, at least in a linear approximation.

Furthermore, in the examples given in Section III, we have emphasized in an explicit way how information theory allows us to obtain for the nonequilibrium entropy an expression beyond the second-order approximation in the fluxes, to which the former versions of EIT were limited. This raises interesting problems about the interpretation of the Lagrange multipliers beyond the linear order in the fluxes [31, 32]. In contrast, it is very difficult to obtain higher-order contributions of the fluxes to the entropy starting from kinetic theory, because the solution methods of the Boltzmann equation are usually of a perturbative nature.

For simplicity, we have not dealt with dynamical aspects. In fact, information theory provides the basis

not only for the Gibbs equation, but also for a more detailed form of transport equations providing, for instance, a dynamical description of second sound and thermal waves [33, 34], which were the physical phenomena that first arouse the interest in extended irreversible thermodynamics, as well as many other phenomena. However, dynamical arguments are necessary to clarify the variables which should be used in the description, according to their relaxation time. For ideal gases, all the moments of the relaxation function decay with a comparable relaxation time, and therefore all them should be included in principle in the description. Nevertheless, in practice only a small number of them are measurable and controllable. In order to have only a finite number of variables one must devise some asymptotic methods, rather than truncations [38].

Finally, we would like to emphasize that the differences between the nonequilibrium temperature (or quasitemperature) and the local-equilibrium temperature which has been explicitly seen in the illustrations presented in Section III, has been experimentally observed in high-resolution spectroscopy of highly photoexcited plasma in semiconductors [35], which provides a very adequate experimental background for the testing and corroboration of these theoretical concepts. In fact, for very short times (femtoseconds) after the excitation of the plasma each single quasi-particle quantum mechanical state of the system has its own quasitemperature. However, after roughly 500 femtoseconds, statistical mechanics becomes applicable with a single quasitemperature for the carriers, due to their strong internal interaction (the phonons still keep different quasitemperatures for each normal mode). The quasitemperature of the carriers can be determined from luminescence spectra. When one compares the spectra when the system is not submitted to any flux and when the system has a current flowing through it, the dependence of the temperature on the fluxes is indeed observed. The analysis is rather cumbersome, because it implies not only heat and electric current but also their crossed (thermoelectric) effects, but the final theoretical result is in good agreement with the observations.

Nonclassical nonequilibrium corrections are not exclusive of the Lagrange multiplier conjugated to the energy, i.e. to nonequilibrium temperature, but also of the Lagrange multipliers conjugated to the volume and to the number of particles (i.e. to pressure and chemical potential). In fact, the influence of a nonvanishing viscous pressure may have important consequences in the chemical potential of polymer solutions, thus leading to a shift of several degrees of the spinodal line and the critical point corresponding to phase separation [39]. In summary, the Lagrange multipliers appearing in information statistical thermodynamics open very interesting questions, either from the theoretical point of view as from a practical perspective.

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