



Computation of energy exchanges by combining information theory and a key thermodynamic relation: Physical applications

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ARTICLE INFO

Article history:

Received 24 June 2009

Received in revised form 29 October 2009

Available online 12 November 2009

PACS:

05.70.-a

05.30.-d

02.50.-r

03.67.-a

Keywords:

Thermodynamics

Equilibrium microscopic probability distribution

Information theory

ABSTRACT

By considering a simple thermodynamic system, in thermal equilibrium at a temperature T and in the presence of an external parameter A , we focus our attention on the particular thermodynamic (macroscopic) relation $dU = TdS + \delta W$. Using standard axioms from information theory and the fact that the microscopic energy levels depend upon the external parameter A , we show that all usual results of statistical mechanics for reversible processes follow straightforwardly, without invoking the Maximum Entropy principle. For the simple system considered herein, two distinct forms of heat contributions appear naturally in the Clausius definition of entropy, $TdS = \delta Q^{(T)} + \delta Q^{(A)} = C_A^{(T)}dT + C_T^{(A)}dA$. We give a special attention to the amount of heat $\delta Q^{(A)} = C_T^{(A)}dA$, associated with an infinitesimal variation dA at fixed temperature, for which a “generalized heat capacity”, $C_T^{(A)} = T(\partial S/\partial A)_T$, may be defined. The usefulness of these results is illustrated by considering some simple thermodynamic cycles.

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1. Introduction

The first and second laws of thermodynamics are two most important statements of physics [1]. They constitute strong pillars of our present understanding of nature. Of course, statistical mechanics (SM) adds an underlying microscopic substratum that is able to explain not only these two laws but the whole of thermodynamics itself [2–11]. One of the basic ingredients of SM is a microscopic probability distribution (PD) that controls the population of microstates of the system under consideration [5–8,11]. Restricting our considerations to equilibrium situations, here we will be mainly concerned with designing – from a perspective to be explained immediately below – a detailed SM-picture. This picture exemplifies a way in which many important equilibrium results from SM can be obtained from a few simple assumptions, *without the need of invoking* the Maximum Entropy principle (MaxEnt) of Jaynes [12]. This approach illustrates that MaxEnt or the alternative hypothesis for the equiprobability of microstates of an isolated system is not a necessary condition to derive the essential results of SM (see examples of this in Refs. [13–15]).

Just four ingredients are needed for this development:

- (i) the macroscopic and phenomenological relation,

$$dU = TdS + \delta W; \quad (1.1)$$

- (ii) Kinchin's first axiom of information theory: *the information measure depends only on the pertinent probability distribution* [16];

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- (iii) the concavity of the entropy with respect to its associated probabilities;
- (iv) the fact that the analytical form $\epsilon_i(\{A\})$ of the system of interest's energy eigenvalues ϵ_i is a function of a set of external parameters $\{A\}$.

Herein we will show that such ingredients are sufficient for recovering the equilibrium results of SM. In other words, Eq. (1.1), supplemented by a minimum of microscopic information [items (ii)–(iv)], is all one needs in order to build the mighty edifice of equilibrium SM. Most of our analysis is restricted to a simple thermodynamic system, in thermal equilibrium at a temperature T and in the presence of a single external parameter A . We show that two distinct forms of heat contributions appear naturally in the macroscopic entropy, $T dS = \delta Q^{(T)} + \delta Q^{(A)} = C_A^{(T)} dT + C_T^{(A)} dA$. Through this approach, we derive an important relation for the “generalized heat capacity” $C_T^{(A)}$, associated with an infinitesimal variation dA in the thermodynamically independent parameter A of the system. Such a relation involves correlations between the energy eigenvalues and their derivatives with respect to the parameter A – is original to our knowledge – providing a direct way to calculate heat exchanges in given thermodynamic transformations. A preliminary illustration of the usefulness of this relation was presented in Ref. [15], where the heat exchanges in the isothermal transformations of a simple ideal-gas Carnot cycle were calculated directly. This should be contrasted with the standard procedure employed to calculate such a quantity (cf., e.g., Refs. [2,4,6,7]): (a) One uses the fact that $dU = 0$ in an ideal-gas isothermal transformation; (b) Then, one applies the ideal-gas equation of state in order to calculate the work done by the gas in the corresponding transformation; (c) The amount of absorbed heat equals the work done by the gas. Such a procedure may become tedious in some cases, mainly for those thermodynamic transformations where $dU \neq 0$; herein we discuss in detail a direct – and much simpler – way of calculating heat exchanges.

In Section 2 we revise the main results of the above formalism [14,15], deriving general expressions for the different forms of heat. We present three different procedures of calculating $C_T^{(A)}$ for a given physical system (where the two last ones represent original contributions of the present work): (i) From the microscopic point of view, if the energy eigenvalues of the corresponding Hamiltonian are known, the heat capacity $C_T^{(A)}$ is directly related to the correlations involving the energy eigenvalues, as well as their derivatives with respect to A ; (ii) Also microscopically, using standard statistical mechanics procedures, from the knowledge of the canonical-ensemble partition function; (iii) Macroscopically, from the parameter thermodynamically conjugate to A . The relations deduced herein provide direct ways of to calculate heat exchanges in thermodynamic transformations, particularly in isothermal processes. Additionally, we analyze adiabatic transformations in view of the new form of heat $\delta Q^{(A)}$ and conclude that for such a transformation to occur, it is necessary that at least two parameters of the system should vary, leading to more than one form of heat that cancel each other. For the simple system considered herein, characterized by the parameters T and A , both forms of heat exchanges occur, but restricted to $\delta Q^{(T)} = -\delta Q^{(A)}$ at each stage of the adiabatic transformation. In Section 3 we apply these results to study some magnetic thermodynamic cycles; in such cases, the external parameter consists in an applied magnetic field H , for which the heat capacity $C_T^{(H)}$ may be calculated within the present formalism and then, the amount of heat $\delta Q^{(H)} = C_T^{(H)} dH$ is computed for isothermal transformations in several thermodynamic cycles. Finally, in Section 4 we present our main conclusions.

2. Forms of heat exchanges

For completeness, in this section we will revise some of the results obtained in a previous publication [15]. Let us start by considering a *simple*, one-component system [3], that is, composed by a single chemical species, macroscopically homogeneous, and isotropic. The system is composed by a number of particles N , and it is found in thermal equilibrium at a temperature T . Although the following discussion may be easily generalized for an arbitrary set of external parameters, $\{A\}$, herein, for simplicity's sake, we will consider just one (generic) external parameter, denoted from now on by A . The macroscopic equilibrium thermal state of such a one-component system is described in self-explanatory notation by the set of thermodynamically independent parameters, T, A, N [3]. We shall here consider a quite general information measure S that, according to Kinchin's first axiom for information theory [16], depends exclusively on the PD $\{p_i\}$, i.e., $S \equiv S(\{p_i\})$; in addition to that we also assume that $S(\{p_i\})$ may be written in the simple form [17–20],

$$S(\{p_i\}) = \sum_{i=1}^W r(p_i); \quad [r(0) = r(1) = 0], \tag{2.1}$$

where W represents the total number of microstates and $r(p_i)$ is a concave function of each p_i , implying the concavity of $S(\{p_i\})$ (see, e.g., [19]). The energy eigenvalues of the Hamiltonian ϵ_i are functions of A and N , namely, $\{\epsilon_i\} = \{\epsilon_i(A, N)\}$. In the present analysis, we take N as fixed, in such a way that the dependence of the energy eigenvalues on N disappears, i.e., $\{\epsilon_i\} = \{\epsilon_i(A)\}$. The associated PD that describes the system depends, then, on the external parameters in the way

$$p_i = p_i(T, \epsilon_i(A)). \tag{2.2}$$

The mean energy U is given by [21–23,20,24]

$$U = \sum_{i=1}^W p_i \epsilon_i, \tag{2.3}$$

where the sum runs over a set of quantum numbers, that serves to enumerate the microstates (W represents the total number of microstates) and characterize the corresponding levels of energy ϵ_i . Now, in view of Eqs. (2.2) and (2.1), we can write

$$dp_i = \frac{\partial p_i}{\partial T} dT + \sum_{j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA, \tag{2.4}$$

$$T dS = T \sum_{i=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT + T \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA \equiv \delta Q^{(T)} + \delta Q^{(A)}, \tag{2.5}$$

where from the heat forms above, one readily identifies the standard heat capacity, $C_A^{(T)}$,

$$\delta Q^{(T)} = C_A^{(T)} dT; \quad C_A^{(T)} = T \left(\frac{\partial S}{\partial T} \right)_A = T \sum_{i=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T}, \tag{2.6}$$

as well as a “generalized heat capacity”, $C_T^{(A)}$,

$$\delta Q^{(A)} = C_T^{(A)} dA; \quad C_T^{(A)} = T \left(\frac{\partial S}{\partial A} \right)_T = T \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A}. \tag{2.7}$$

It should be mentioned that the above concept of generalized heat capacity is hardly explored within thermodynamics textbooks (for an exception, see Ref. [4]); herein, we will analyze further this quantity from the microscopic point of view of Refs. [14,15] and calculate it for some simple physical systems.

In a similar way, using Eqs. (2.2) and (2.3), one gets for the internal energy,

$$dU = \sum_{i=1}^W \frac{\partial p_i}{\partial T} \epsilon_i dT + \sum_{i,j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} \epsilon_i dA + \sum_{i=1}^W p_i \frac{\partial \epsilon_i}{\partial A} dA. \tag{2.8}$$

If one considers the key thermodynamic relation,

$$dU = T dS + \delta W = \delta Q^{(T)} + \delta Q^{(A)} + \delta W, \tag{2.9}$$

within the present scenario, by making use of Eq. (2.5), we can recast Eq. (2.9) in the *microscopic* fashion (involving the microstates’ PD),

$$dU = T \left(\sum_{i=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT + \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA \right) + \delta W, \tag{2.10}$$

which is to be compared with Eq. (2.8). It should be stressed that although $\delta Q^{(A)}$ and δW are both associated with variations in the external parameter A , they are related to different forms of energy; as will be shown in the next section, these quantities correspond to the last two terms on the r.h.s. of Eq. (2.8), respectively. Only in exceptional cases, these two quantities may be related in a simple way, e.g., in an isothermal transformation of an ideal gas, where $dU = \delta Q^{(T)} = 0$ and then, from Eq. (2.9), one gets that $\delta Q^{(A)} = -\delta W$. In what follows, we will explore the fact that Eqs. (2.8) and (2.10) must be equal for arbitrary changes in T and A .

2.1. Changes in the temperature

Let us now consider changes in the temperature only, i.e., A fixed. Enforcing equality in the coefficients of dT appearing in Eqs. (2.8) and (2.10), we obtain

$$\sum_{i=1}^W \frac{\partial p_i}{\partial T} \epsilon_i dT = T \sum_{i=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT, \tag{2.11}$$

where we are assuming, as it is obvious, that the mechanical work δW appearing in Eq. (2.10) does not depend explicitly on the temperature. The equation above must be satisfied together with the normalization condition [cf. Eq. (2.4)],

$$\sum_{i=1}^W dp_i = \sum_{i=1}^W \frac{\partial p_i}{\partial T} dT = 0, \tag{2.12}$$

leading to the result [15],

$$\epsilon_i - T \frac{\partial S}{\partial p_i} \equiv K = \text{constant}; \quad (i = 1, 2, \dots, W). \tag{2.13}$$

Eq. (2.13) yields an expression for any of the W probabilities p_i ’s, as shown in an earlier publication, recovering exactly the PD that is obtained using the MaxEnt principle [14].

As an illustration, if we consider the Shannon entropy,

$$S = -k_B \sum_i p_i \ln p_i, \tag{2.14}$$

Eq. (2.13) leads to the Boltzmann–Gibbs factor

$$p_i = \frac{1}{Z} e^{-\beta \epsilon_i}, \quad [\beta = 1/(k_B T)], \tag{2.15}$$

where the partition function Z reads

$$Z = \sum_{i=1}^W e^{-\beta \epsilon_i} = e^{1-\beta K}, \tag{2.16}$$

yielding a relation between K and Z . These results entail

$$\frac{\partial p_i}{\partial \epsilon_j} = -\beta p_i (\delta_{ij} - p_j), \tag{2.17}$$

$$-\frac{\partial \ln Z}{\partial \beta} = \sum_{i=1}^W p_i \epsilon_i = U, \tag{2.18}$$

$$\frac{\partial \ln Z}{\partial A} = -\beta \sum_{i=1}^W p_i \frac{\partial \epsilon_i}{\partial A} = -\beta \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle, \tag{2.19}$$

$$\frac{\partial^2 \ln Z}{\partial \beta \partial A} = -\left\langle \frac{\partial \epsilon}{\partial A} \right\rangle + \beta \left\langle \epsilon \frac{\partial \epsilon}{\partial A} \right\rangle - \beta \langle \epsilon \rangle \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle, \tag{2.20}$$

$$\frac{\partial^2 \ln Z}{\partial \beta \partial A} - \frac{1}{\beta} \frac{\partial \ln Z}{\partial A} = \beta \left[\left\langle \epsilon \frac{\partial \epsilon}{\partial A} \right\rangle - \langle \epsilon \rangle \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle \right] = \beta \Gamma_{\epsilon, \delta \epsilon}, \tag{2.21}$$

where we have used $\langle a \rangle \equiv \sum_i p_i a_i$ and $\langle ab \rangle \equiv \sum_i p_i a_i b_i$, as usual. From now on, we shall call the factor of beta on the r.h.s of Eq. (2.21), i.e., $\Gamma_{\epsilon, \delta \epsilon}$, the *energy–energy displacement correlation*. It is important to notice that *no information about the p_i has thus far been invoked*. Next, we analyze changes in both temperature and external parameter.

2.2. Changes in both temperature and external parameter

Let us now analyze the second term on the r.h.s. of Eq. (2.8); using Eq. (2.13), one gets that

$$\begin{aligned} \sum_{i,j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} \epsilon_i dA &= \sum_{i,j=1}^W \left[T \frac{\partial S}{\partial p_i} + K \right] \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA \\ &= T \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA + K \sum_{i,j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA. \end{aligned} \tag{2.22}$$

Now using that

$$\frac{\partial}{\partial A} \sum_i p_i = 0 \Rightarrow \sum_{i,j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} dA = 0, \tag{2.23}$$

one gets,

$$\sum_{i,j=1}^W \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} \epsilon_i dA = \left(T \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial A} \right) dA = \delta Q^{(A)} = C_T^{(A)} dA, \tag{2.24}$$

where we have used the definition of generalized heat capacity [cf. Eq. (2.7)]. By comparing Eqs. (2.8) and (2.10) in view of the above result, one concludes that the mechanical work associated with an infinitesimal variation dA is given by

$$\delta W = \sum_{i=1}^W p_i \frac{\partial \epsilon_i}{\partial A} dA = \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle dA. \tag{2.25}$$

Now, if one uses Eq. (2.19), one may introduce the “generalized force”, $\mathcal{F}^{(A)}$, conjugated to the parameter A , in such a way that

$$\delta W = \mathcal{F}^{(A)} dA; \quad \mathcal{F}^{(A)} = \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial A}, \tag{2.26}$$

as defined in some textbooks (see, e.g., Refs. [7,8]).

Making use of Eqs. (2.13) and (2.17) the generalized heat capacity of Eq. (2.7) may be also written, for the case of Shannon's entropy,

$$\begin{aligned} C_T^{(A)} &= -\beta \sum_{i,j=1}^W (\epsilon_i - K) p_i (\delta_{i,j} - p_j) \frac{\partial \epsilon_j}{\partial A} \\ &= -\beta \left[\sum_{i=1}^W p_i \epsilon_i \frac{\partial \epsilon_i}{\partial A} - \left(\sum_{i=1}^W p_i \epsilon_i \right) \left(\sum_{j=1}^W p_j \frac{\partial \epsilon_j}{\partial A} \right) \right] \\ &= -\beta \left[\left\langle \epsilon \frac{\partial \epsilon}{\partial A} \right\rangle - \langle \epsilon \rangle \left\langle \frac{\partial \epsilon}{\partial A} \right\rangle \right] = -\beta \Gamma_{\epsilon, \delta \epsilon}. \end{aligned} \quad (2.27)$$

Therefore, the generalized heat capacity is directly related to the energy–energy displacement correlation; combining the above result with the one of Eq. (2.21), one has that

$$C_T^{(A)} = -\beta \Gamma_{\epsilon, \delta \epsilon} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial A} - \frac{\partial^2 \ln Z}{\partial \beta \partial A}. \quad (2.28)$$

It is important to point out that whereas the standard heat capacity $C_A^{(T)}$ should be always positive within the canonical ensemble, from the equations above one sees that there is not such a restriction for the heat capacity $C_T^{(A)}$. Moreover, using the above relation together with the definition of generalized force in Eq. (2.26), one obtains,

$$C_T^{(A)} = \beta \frac{\partial \mathcal{F}^{(A)}}{\partial \beta} = -T \frac{\partial \mathcal{F}^{(A)}}{\partial T}. \quad (2.29)$$

As a simple illustration of this result, we consider the ideal gas, for which $\delta W = -PdV$ ($\mathcal{F}^{(V)} = -P$), and so,

$$C_T^{(V)} = T \frac{\partial P}{\partial T} = T \frac{\partial [(Nk_B T)/V]}{\partial T} = P, \quad (2.30)$$

which agrees with the result of Ref. [15] [cf. Eq. (41)], where such a quantity was calculated through the correlation function $\Gamma_{\epsilon, \delta \epsilon}$.

Therefore, whenever an external parameter A changes quasi-statically, heat is generated or absorbed, in such a way that one may define an associated generalized heat capacity $C_T^{(A)}$. We have shown above three equivalent ways of calculating this quantity for a given physical system, two of them being original contributions of this paper: (i) Microscopically, through the correlation between the energy eigenvalues and their corresponding shift originated by the A -variation [cf. Eq. (2.27)] [14,15]; (ii) Also microscopically, using standard SM procedures, from the knowledge of the canonical-ensemble partition function [cf. Eq. (2.28)]; (iii) Macroscopically, by considering the derivative of its associated generalized force with respect to the temperature [cf. Eq. (2.29)]. It should be emphasized, at this point, that Eqs. (2.28) and (2.29) represent two important new equations (as far as we know) that allow us to calculate heat exchanges explicitly; in particular, Eq. (2.28) will be used in the next section for some physical illustrations of the present results. Obviously, the relation of Eq. (2.29) is the one relevant for physical measurements. It should be mentioned at this point that although the concept of a generalized force, $\mathcal{F}^{(A)}$, may be found in some textbooks (see, e.g., Refs. [7,8]), the above-presented relation with the heat capacity $C_T^{(A)}$ is original. The quantity $C_T^{(A)}$ contributes to a rather unfamiliar term in the Clausius relation,

$$T dS = \delta Q = \delta Q^{(T)} + \delta Q^{(A)} = C_A^{(T)} dT + C_T^{(A)} dA, \quad (2.31)$$

which is usually formulated in terms of the first contribution only, i.e., the contribution associated with the variation in temperature.

In fact, in adiabatic transformations, one sees that this new form of heat, $\delta Q^{(A)}$, is essential for such a transformation to take place, since it is necessary that at least two parameters of the system should vary, leading to more than one form of heat that cancel each other. Therefore, for the system considered above, both forms of heat exchanges occur, but restricted to $\delta Q^{(T)} = -\delta Q^{(A)}$ at each stage of the adiabatic transformation.

In what follows we analyze some simple magnetic models, for which we choose the external magnetic field H as the thermodynamically independent parameter. Considering an adiabatic transformation in such systems, one sets $dS = 0$ in Eq. (2.5) to yield,

$$\sum_i \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT = - \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial H} dH, \quad (2.32)$$

and using Eqs. (2.6) and (2.7), one may write,

$$\frac{dT}{dH} = - \left(\sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial H} \right) / \left(\sum_i \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} \right), \quad \Rightarrow \quad \frac{dT}{dH} = - \frac{C_T^{(H)}}{C_H^{(T)}}. \quad (2.33)$$

The equation above will be used in the adiabatic transformations of the thermodynamic cycles to be considered below.

The models to be considered are the ideal Ising paramagnet (IP) and the one-dimensional Ising model (1DIM) in the presence of an external magnetic field. The heat capacity $C_T^{(H)}$ may be calculated within the present formalism, as well as the corresponding amount of heat associated with given thermodynamic transformations. The IP and 1DIM will represent the working substances of the thermodynamic cycles to be considered below. From now on, we assume that S corresponds to the Shannon information measure [cf. Eq. (2.14)], associated with the Boltzmann–Gibbs factor [Eq. (2.15)], for which some of the results of the previous section [essentially those following Eq. (2.14)] apply.

3. Thermodynamic cycles of the Ising paramagnet

In this section we consider the IP as the working substance; the concomitant Hamiltonian associated with N localized Ising spins reads

$$\mathcal{H} = -\mu H \sum_{i=1}^N \sigma_i; \quad (\sigma_i = \pm 1), \quad (3.1)$$

where μ represents the Bohr magneton ($\mu = 9.27 \times 10^{-24}$ J/T). The corresponding partition function is given by [5,7,8],

$$Z(T, H) = [2 \cosh(\beta\mu H)]^N; \quad \Rightarrow \quad \frac{1}{N} \log Z(T, H) = \log[2 \cosh(\beta\mu H)], \quad (3.2)$$

leading to the internal energy,

$$U = \langle \mathcal{H} \rangle = -\frac{\partial \log Z}{\partial \beta} = -N\mu H \tanh(\beta\mu H), \quad (3.3)$$

and its associated fluctuations,

$$\langle (\Delta U)^2 \rangle \equiv \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = N[\mu H \operatorname{sech}(\beta\mu H)]^2. \quad (3.4)$$

The total magnetization and the internal energy are related in a simple way,

$$M = \frac{1}{\beta\mu} \frac{\partial \log Z}{\partial H} = N\mu \tanh(\beta\mu H); \quad \Rightarrow \quad U = -MH. \quad (3.5)$$

It is clear that for the IP,

$$\frac{\partial \epsilon_i}{\partial H} = \frac{\epsilon_i}{H}, \quad (3.6)$$

from which one may calculate the mechanical work of Eq. (2.25),

$$\delta W = \sum_{i=1}^W p_i \frac{\partial \epsilon_i}{\partial H} dH = \sum_{i=1}^W p_i \frac{\epsilon_i}{H} dH = \frac{U}{H} dH = -M dH, \quad (3.7)$$

as well as the heat capacities of Eqs. (2.6) and (2.7),

$$C_H^{(T)} = k_B \beta^2 \langle (\Delta U)^2 \rangle, \quad (3.8)$$

$$C_T^{(H)} = -\frac{\beta}{H} \langle (\Delta U)^2 \rangle. \quad (3.9)$$

From the equations above one sees that the standard heat capacity $C_H^{(T)}$ (usually denoted by C_H in the literature), related to changes in temperature at fixed H , is always a positive quantity; in contrast, the heat capacity $C_T^{(H)}$, associated with field changes at fixed temperature, presents a sign opposite to the one of the applied field.

One may now compute the heat exchanges in the following reversible thermodynamic transformations:

(a) Isofield transformation, from an initial state with a given temperature T_i [$\beta_i = (k_B T_i)^{-1}$] to a final state with a temperature T_f [$\beta_f = (k_B T_f)^{-1}$], at fixed field H :

$$Q^{(T)} = \int_{T_i}^{T_f} C_H^{(T)} dT = N\mu H [\tanh(\beta_i \mu H) - \tanh(\beta_f \mu H)], \quad (3.10)$$

which corresponds to the standard way of calculating the heat exchange on such a transformation.

(b) Isothermal transformation, from an initial state characterized by a field H_i to a final state with a field H_f , at a fixed temperature T :

$$Q^{(H)} = \int_{H_i}^{H_f} C_T^{(H)} dH = \frac{N}{\beta} \left\{ -\log [\cosh(\beta\mu H_i)] + \log [\cosh(\beta\mu H_f)] \right\} \\ + N\mu H_i \tanh(\beta\mu H_i) - N\mu H_f \tanh(\beta\mu H_f), \quad (3.11)$$

corresponding to an original (as far as we know) way of calculating directly the heat exchange on such a transformation.

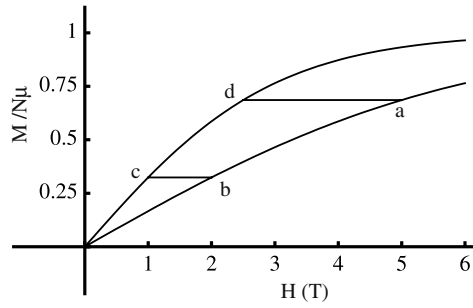


Fig. 1. The Carnot cycle for an ideal paramagnet as a working substance, represented in the plane magnetization versus magnetic field. The cycle operates between the temperatures $T_1 = 2$ K (upper curve) and $T_2 = 4$ K (lower curve). The transformations $a \rightarrow b$ and $c \rightarrow d$ are isothermal, whereas $b \rightarrow c$ and $d \rightarrow a$ are adiabatic. In the abscissa, the magnetic field H is given in Tesla, and in the ordinate one has a dimensionless quantity, i.e., the magnetization per spin scaled in units of the Bohr magneton.

(c) For an adiabatic transformation, substituting Eqs. (3.8) and (3.9) in Eq. (2.33) one gets that

$$\frac{dT}{dH} = -\frac{C_T^{(H)}}{C_H^{(T)}} = -\frac{T}{H}. \tag{3.12}$$

Integrating the equation above from an initial state (T_1, H_1) to a final state (T_2, H_2) we obtain the well-known relation

$$\frac{T_1}{H_1} = \frac{T_2}{H_2} = \text{constant}, \tag{3.13}$$

used to lower the temperature of a paramagnetic system in an adiabatic transformation, simply by lowering the intensity of the magnetic field (cf., e.g., Ref. [7]). Conversely, if one assumes Eq. (3.12), i.e., $dT/dH = T/H$, then, using Eqs. (3.8) and (3.9) one gets that

$$\frac{\delta Q^{(T)}}{\delta Q^{(H)}} = \frac{C_H^{(T)} dT}{C_T^{(H)} dH} = -k_B \beta H \frac{dT}{dH} = -\frac{H}{T} \frac{dT}{dH} = -1, \tag{3.14}$$

showing that in the adiabatic transformation both forms of heat are nonzero, but they are restricted to $\delta Q^{(T)} = -\delta Q^{(H)}$ in each stage of the transformation.

Considering the thermodynamic transformations above, one can construct several thermodynamic cycles, as discussed below.

(i) The Carnot cycle (cf. Fig. 1): This cycle is defined in terms of two isothermal, intercalated by adiabatic transformations. Herein, we start the cycle from state a, and follow the thermodynamic path $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$, according to Fig. 1. It is important to mention that, due to the peculiar property $(T/H) = \text{constant}$ of Eq. (3.13), the magnetization [cf. Eq. (3.5)] remains constant in the adiabatic transformations $b \rightarrow c$ and $d \rightarrow a$. Moreover, once the two temperatures T_1 and T_2 are defined (herein we have chosen $T_1 = 2$ K and $T_2 = 4$ K), as well as one value for the field at each of the adiabatic transformations (herein we have chosen $H_a = 5$ T and $H_c = 1$ T), the remaining values for the fields are obtained from Eq. (3.13): $H_b = 2$ T and $H_d = 2.5$ T. The efficiency of the Carnot cycle depends only on temperatures T_1 and T_2 ,

$$\eta = 1 - \frac{T_1}{T_2}, \tag{3.15}$$

which, for the temperatures chosen, yields $\eta = 0.5$. As an illustration of the present formalism, we calculated directly the heat exchanges in the isothermal transformations of this cycle using Eq. (3.11), and have obtained, $Q_{cd}^{(H)} \approx -5.65262 \times 10^{-24}$ Joules (temperature T_1) and $Q_{ab}^{(H)} \approx 1.13052 \times 10^{-23}$ Joules (temperature T_2), which may be substituted in the general definition of efficiency of a given thermodynamic cycle,

$$\eta = 1 - \frac{|\text{total heat lost}|}{|\text{total heat absorbed}|} = 1 - \frac{|Q_{cd}^{(H)}|}{|Q_{ab}^{(H)}|}, \tag{3.16}$$

leading to $\eta \approx 0.50000177$, where the discrepancy from the exact value is due to computer numerical roundings. One should remind that the calculation of the amounts of heat $Q_{ab}^{(H)}$ and $Q_{cd}^{(H)}$ through standard methods is done indirectly, i.e., computing the work and variation of internal energy for each of the transformations $a \rightarrow b$ and $c \rightarrow d$.

(ii) The Brayton cycle (cf. Fig. 2): This cycle is useful from the technological point of view (see, e.g., Ref. [25]) and is defined in terms of two isofield (which were chosen herein to occur at fields $H_a = 5$ T and $H_b = 1$ T, respectively), intercalated by adiabatic transformations. The cycle starts from state a and follows the thermodynamic path $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$ of

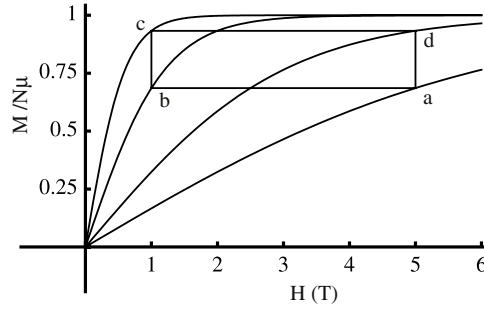


Fig. 2. The Brayton cycle for an ideal paramagnet as a working substance, represented in the plane magnetization versus magnetic field. Four isothermal curves are shown, namely, $T_1 = 0.4$ K, $T_2 = 0.8$ K, $T_3 = 2$ K, and $T_4 = 4$ K, from top to bottom. The transformations $a \rightarrow b$ and $c \rightarrow d$ are adiabatic, whereas $b \rightarrow c$ and $d \rightarrow a$ are isofield, at $H_b = 1$ T and $H_a = 5$ T, respectively. In the abscissa, the magnetic field H is given in Tesla, and in the ordinate one has a dimensionless quantity, i.e., the magnetization per spin scaled in units of the Bohr magneton.

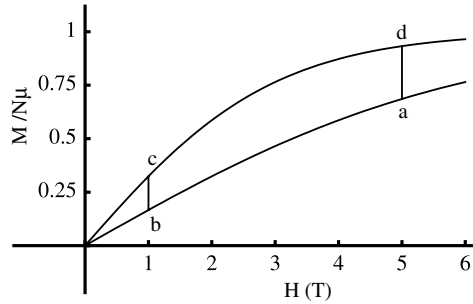


Fig. 3. The cycle-3 for an ideal paramagnet as a working substance, represented in the plane magnetization versus magnetic field. The cycle operates between the temperatures $T_1 = 2$ K (upper curve) and $T_2 = 4$ K (lower curve). The transformations $a \rightarrow b$ and $c \rightarrow d$ are isothermal, whereas $b \rightarrow c$ and $d \rightarrow a$ are isofield, at $H_b = 1$ T and $H_a = 5$ T, respectively. In the abscissa, the magnetic field H is given in Tesla, and in the ordinate one has a dimensionless quantity, i.e., the magnetization per spin scaled in units of the Bohr magneton.

Fig. 2. The adiabatic transformations obey Eq. (3.13), leading to paths of constant magnetization. Now, one has the standard heat exchanges for the isofield transformations, given by Eq. (3.10). One gets, $Q_{bc}^{(T)} \approx -2.29099 \times 10^{-24}$ Joules (field H_b) and $Q_{da}^{(T)} \approx 1.14550 \times 10^{-23}$ Joules (field H_a), leading to $\eta \approx 0.8$.

(iii) For completeness, we introduce now a thermodynamic cycle defined by two isothermal, intercalated by isofield transformations, as shown in Fig. 3, to be called herein, cycle-3. Like the previous cycles, cycle-3 starts from state a , following the transformations $a \rightarrow b \rightarrow c \rightarrow d \rightarrow a$. Since there is no adiabatic transformation, one should have heat exchanges in all four thermodynamic transformations of cycle-3, i.e., the standard heat exchanges given by Eq. (3.10) in the isofield transformations, as well as the heat exchanges at constant temperature, given by Eq. (3.11), in the isothermal transformations. For the isofield transformations one gets that $Q_{bc}^{(T)} \approx -1.45920 \times 10^{-24}$ Joules (field H_b) and $Q_{da}^{(T)} \approx 1.14550 \times 10^{-23}$ Joules (field H_a), whereas for the isothermal ones, $Q_{cd}^{(H)} \approx -1.35983 \times 10^{-23}$ Joules (temperature T_1) and $Q_{ab}^{(H)} \approx 1.34840 \times 10^{-23}$ Joules (temperature T_2). In this case, the efficiency of Eq. (3.16) becomes

$$\eta = 1 - \frac{|Q_{cd}^{(H)}| + |Q_{bc}^{(T)}|}{|Q_{ab}^{(H)}| + |Q_{da}^{(T)}|}, \quad (3.17)$$

leading to $\eta \approx 0.396226$. Comparing this result with the one of Carnot's engine ($\eta = 0.5$), one gets a confirmation of Carnot's theorem [6], which states that no thermodynamic cycle operating between two given temperatures is more efficient than a Carnot engine.

4. Thermodynamic cycles of the one-dimensional Ising model

Let us now analyze the 1DIM as the working substance, for which the Hamiltonian consists of N interacting spins in a chain, under the presence of a uniform external magnetic field H ,

$$\mathcal{H} = -J \sum_{i=1}^N \sigma_i \sigma_{i+1} - \mu H \sum_{i=1}^N \sigma_i; \quad (\sigma_i = \pm 1), \quad (4.1)$$

where J denotes a uniform positive coupling constant and we are assuming periodic boundary conditions, $\sigma_{N+1} \equiv \sigma_1$. Notice that taking $J = 0$, one recovers the IP discussed in the previous section.

It should be mentioned that most of the analytic results that appear below were obtained through a standard program for algebraic calculations. Let us then, define the quantities,

$$c_1(T, H) = \exp(\beta J) \cosh(\beta \mu H), \quad (4.2)$$

$$c_2(T, H) = \exp(\beta J) \sinh(\beta \mu H), \quad (4.3)$$

$$c_3(T, H) = \exp(4\beta J) - 1, \quad (4.4)$$

$$\xi(T, H) = \exp(-\beta J) [1 + \exp(4\beta J) \sinh^2(\beta \mu H)]^{1/2}. \quad (4.5)$$

The partition function of this model is well known (see, e.g., Ref. [6]),

$$\frac{1}{N} \log Z(T, H) = \log\{c_1(T, H) + \xi(T, H)\}. \quad (4.6)$$

The corresponding internal energy and magnetization are given by

$$U = -\frac{N}{c_1(T, H) + \xi(T, H)} \left\{ Jc_1(T, H) + \mu Hc_2(T, H) + \frac{1}{2\xi(T, H)} [\exp(-2\beta J) \times (-2J + \exp(4\beta J)(2J \sinh^2(\beta \mu H) + \mu H \sinh(2\beta \mu H))] \right\}, \quad (4.7)$$

$$M = N\mu \frac{c_2(T, H)}{\xi(T, H)}. \quad (4.8)$$

For the heat capacities, one has

$$C_H^{(T)} = Nk_B\beta^2 \frac{b_1(T, H)}{b_2(T, H)}, \quad (4.9)$$

$$b_1(T, H) = \exp(-\beta J) \left\{ -[4J^2(-2 + \exp(4\beta J)) - (2 + \exp(4\beta J))\mu^2 H^2] \cosh(\beta \mu H) + \exp(4\beta J)(4J^2 + \mu^2 H^2) \cosh(3\beta \mu H) - 4J\mu H(-2 + \exp(4\beta J)) \sinh(\beta \mu H) + 2 \exp(3\beta J) [(-4J^2 + \mu^2 H^2) \xi(T, H) + (4J^2 + \mu^2 H^2) \cosh(2\beta \mu H) \xi(T, H) + 2J\mu H(2\xi(T, H) \sinh(2\beta \mu H) + \exp(\beta J) \sinh(3\beta \mu H))] \right\}, \quad (4.10)$$

$$b_2(T, H) = 2\xi(T, H) [1 + \exp(4\beta J) \sinh^2(\beta \mu H)] [c_1(T, H) + \xi(T, H)]^2, \quad (4.11)$$

$$C_T^{(H)} = -\frac{N\beta\mu \exp(3\beta J) [\mu H \cosh(\beta \mu H) + 2J \sinh(\beta \mu H)] \xi(T, H)}{[1 + \exp(4\beta J) \sinh^2(\beta \mu H)]^2}. \quad (4.12)$$

Using the heat capacities above, one can (in principle) calculate the heat exchanges $Q^{(T)}$ and $Q^{(H)}$, associated with the isofield and isothermal transformations, respectively. However, we did not succeed in obtaining an analytic expression for the integral $Q^{(T)} = \int_{T_i}^{T_f} C_H^{(T)} dT$; therefore, for the thermodynamic cycles that follow, such a quantity was computed numerically, for given values of T_i and T_f . In what concerns $Q^{(H)}$ one has

$$Q^{(H)} = \int_{H_i}^{H_f} C_T^{(H)} dH = \frac{N}{\beta} \frac{a_1(T, H_i)}{a_2(T, H_i)} - \frac{N}{\beta} \frac{a_1(T, H_f)}{a_2(T, H_f)} \quad (4.13)$$

$$a_1(T, H) = \exp(2\beta J) \{-2\beta J \cosh(\beta \mu H) + \beta \mu Hc_3(T, H) \sinh(\beta \mu H) - \exp(\beta J) \xi(T, H) \times c_3(T, H) \log[\sqrt{2} (\exp(2\beta J) \cosh(\beta \mu H) + \exp(\beta J) \xi(T, H))]\}, \quad (4.14)$$

$$a_2(T, H) = \exp(\beta J) \xi(T, H) c_3(T, H). \quad (4.15)$$

Let us now use the quantities defined above by considering the same thermodynamic cycles of the previous section for the 1DIM as a working substance. If not specified explicitly, in the following applications we have chosen the coupling constant $J = 4 \times 10^{-24}$ Joules, which is typically of the same order of magnitude of μH . Additionally, for the adiabatic transformations, given an initial state one can follow its thermodynamic path by making use of Eq. (2.33), with $C_H^{(T)}$ and $C_T^{(H)}$ given by Eqs. (4.9) and (4.12), respectively. From Eq. (2.33) one may compute a new thermodynamic state, infinitesimally close to the initial one, and repeat this procedure to calculate further states, up to the final state of the transformation.

(i) The Carnot cycle: For the 1DIM this cycle is qualitatively analogous to the one exhibited in Fig. 1, except for the adiabatic transformations that show slight deviations from perfect straight lines. Considering $T_1 = 2$ K and $T_2 = 4$ K, as well as $H_a = 5$ T and $H_c = 1$ T, the remaining values for the fields were obtained from the procedure described above, using Eq. (2.33): $H_b \approx 2.379805$ T and $H_d \approx 2.202979$ T. The heat exchanges, using Eq. (4.13)–(4.4), are $Q_{cd}^{(H)} \approx -5.72096 \times 10^{-24}$ Joules (temperature T_1) and $Q_{ab}^{(H)} \approx 1.14460 \times 10^{-23}$ Joules (temperature T_2), which may be substituted in Eq. (3.16) to yield $\eta \approx 0.500178$, reproducing up to three decimal digits, the exact value given by Eq. (3.15).

(ii) The Brayton cycle: As before, the adiabatic transformations exhibit slight deviations from perfect straight lines, in such a way that the four isothermal curves in Fig. 2 become now $T_1 = 0.614282$ K, $T_2 = 1.127570$ K, $T_3 = 2$ K, and $T_4 = 4$ K, from top to bottom. Considering the isofield transformations at the same values for the fields, namely, $H_a = 5$ T and $H_b = 1$ T, the heat exchanges were calculated by integrating numerically Eq. (4.9) in the corresponding temperature intervals. In this case, one gets, $Q_{bc}^{(T)} \approx -3.47678 \times 10^{-24}$ Joules (field H_b) and $Q_{da}^{(T)} \approx 1.18497 \times 10^{-23}$ Joules (field H_a), leading to $\eta \approx 0.706593$. Comparing this result with the one obtained for the IP, one notices that the Brayton cycle becomes less efficient in the case of interacting spins. In order to confirm this, we have calculated the efficiency of the Brayton cycle for a 1DIM characterized by a coupling constant $J = 8 \times 10^{-24}$ Joules, i.e., twice the one considered above, leading to $\eta \approx 0.637072$.

(iii) Let us now analyze cycle-3 for the 1DIM, considering the same values of temperature and magnetic fields of Fig. 3. For the isofield transformations one gets that $Q_{bc}^{(T)} \approx -2.76770 \times 10^{-24}$ Joules (field H_b) and $Q_{da}^{(T)} \approx 1.18497 \times 10^{-23}$ Joules (field H_a), whereas for the isothermal ones, $Q_{cd}^{(H)} \approx -1.37929 \times 10^{-23}$ Joules (temperature T_1) and $Q_{ab}^{(H)} \approx 1.56307 \times 10^{-23}$ Joules (temperature T_2). Substituting these results in Eq. (3.17), one gets an efficiency that is typically the same of the IP case. In order to investigate further the dependence of the efficiency of cycle-3 with respect to the interaction between spins, we have repeated the calculations above for a 1DIM characterized by the coupling constants $J = 8 \times 10^{-24}$ Joules and $J = 4 \times 10^{-23}$ Joules, leading to $\eta \approx 0.392479$ and $\eta \approx 0.226880$, respectively. These results suggest that the efficiency of cycle-3 is less sensitive to the presence of interactions between spins than Brayton's cycle; only for a sufficiently large coupling constant (typically when $J \sim \mu H$) one gets a significant decrease in the efficiency of cycle-3.

5. Conclusions

We have considered a simple thermodynamic system, in thermal equilibrium at a temperature T and in the presence of an external parameter A . Using the thermodynamic relation $dU = TdS + \delta W$, as well as the first axiom from information theory, *the information measure depends only on the pertinent probability distribution*, assuming the concavity of the entropy with respect to its associated probabilities and using the fact that the microscopic energy levels depend upon the external parameter A , we have shown that all usual results of statistical mechanics for reversible processes follow straightforwardly, without invoking the Maximum Entropy principle. In particular, we have discussed the two distinct forms of heat contributions that appear naturally in the Clausius definition of entropy, $TdS = \delta Q^{(T)} + \delta Q^{(A)} = C_A^{(T)} dT + C_T^{(A)} dA$.

A special attention has been given to the amount of heat $\delta Q^{(A)} = C_T^{(A)} dA$, associated with an infinitesimal variation dA at fixed temperature, for which a “generalized heat capacity”, $C_T^{(A)} = T(\partial S/\partial A)_T$, was defined. We have found three different ways of calculating this quantity for a given physical system: (i) From the microscopic point of view, if the energy eigenvalues of the corresponding Hamiltonian are known, the heat capacity $C_T^{(A)}$ is directly related to the correlations involving the energy eigenvalues, as well as their derivatives with respect to A [14,15]; (ii) Also microscopically, using standard SM procedures, from the knowledge of the canonical-ensemble partition function; (iii) Macroscopically, from the parameter thermodynamically conjugate to A (denominated herein as generalized force). The results described in (ii) and (iii) are expressed in terms of two important new equations (as far as we know) that allow us to calculate heat exchanges explicitly. In particular, procedure (ii) was used herein in simple physical illustrations, whereas the one of (iii) is relevant for physical measurements. These relations provide direct ways to calculate heat exchanges in thermodynamic transformations, e.g., in isothermal processes. We have analyzed adiabatic transformations in view of the new form of heat $\delta Q^{(A)}$ and concluded that for such a transformation to occur, it is necessary that at least two parameters of the system should vary, leading to more than one form of heat that cancel each other.

As illustrations of our formalism, simple thermodynamic cycles were considered, with the following working substances: (a) The Ising paramagnet, i.e., Ising spins in the presence of an external magnetic field H ; (b) The one-dimensional Ising model (i.e., a chain of interacting spins with a coupling constant $J > 0$) in the presence of an external magnetic field H . For these simple systems, defined in terms of the thermodynamically independent parameters T and H , both forms of heat exchanges, $\delta Q^{(T)}$ and $\delta Q^{(H)}$, were considered in several thermodynamic transformations. In particular, for the isothermal transformations, the amount of exchanged heat $Q^{(H)}$ has been calculated directly by integrating $C_T^{(H)} dH$. This procedure should be contrasted with the indirect – standard method – for calculating this quantity, i.e., by computing both the work and the variation of internal energy for the transformation. In what concerns the adiabatic transformations, we have verified that $\delta Q^{(T)} = -\delta Q^{(H)}$ at each stage of these transformations. In what concerns the efficiencies of the thermodynamic cycles considered, the Carnot engine presented an efficiency that is independent of the working substance, in agreement with thermodynamics. The other cycles presented higher efficiencies in the case of non-interacting (or weakly-interacting) spins, suggesting that better magnetic cycles should be constructed from weakly-interacting magnetic substances.

The results presented within the approach described above corroborate and enhance the powerful formalisms of thermodynamics and statistical mechanics for an appropriate description of natural phenomena.

Acknowledgements

EMFC and FDN thank the partial financial supports from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES), Brazilian scientific agencies.

References

- [1] R.B. Lindsay, H. Margenau, *Foundations of Physics*, Dover, NY, 1957.
- [2] H.B. Callen, *Thermodynamics*, J. Wiley, NY, 1960.
- [3] E.A. Desloge, *Thermal Physics*, Holt, Rhinehart and Winston, NY, 1968.
- [4] C.J. Adkins, *Equilibrium Thermodynamics*, 2nd ed., McGraw-Hill Book Company, London, 1975.
- [5] R.K. Pathria, *Statistical Mechanics*, Pergamon Press, Exeter, 1993.
- [6] K. Huang, *Statistical Mechanics*, 2nd ed., J. Wiley, New York, 1987.
- [7] F. Reif, *Statistical and Thermal Physics*, McGraw-Hill, NY, 1965.
- [8] R. Balian, *From Microphysics to Macrophysics*, Volume I, Springer-Verlag, Berlin, 1991.
- [9] E.T. Jaynes, *Phys. Rev.* 106 (1957) 620; 108, 171 (1957);
R.D. Rosenkrantz (Ed.), *Papers on Probability, Statistics and Statistical Physics*, Reidel, Dordrecht, Boston, 1987;
A. Katz, *Principles of Statistical Mechanics, The Information Theory Approach*, Freeman and Co., San Francisco, 1967.
- [10] B.H. Lavenda, *Statistical Physics*, J. Wiley, New York, 1991;
B.H. Lavenda, *Thermodynamics of Extremes*, Albion, West Sussex, 1995.
- [11] J.W. Gibbs, *Elementary Principles in Statistical Mechanics*, in: *Collected Works*, Yale University Press, New Haven, 1948.
- [12] E.T. Jaynes, *Phys. Rev.* 106 (1957) 620, 108, 171 (1957).
- [13] J. Naudts, E.V. der Straeten, *J. Stat. Mech.* (2004) P12002.
- [14] A. Plastino, E.M.F. Curado, *Phys. Rev. E* 72 (2005) 047103.
- [15] E.M.F. Curado, A. Plastino, *Physica A* 386 (2007) 155.
- [16] A.Y. Kinchin, *Mathematical Foundations of Information Theory*, Dover, NY, 1957.
- [17] A.R. Plastino, A. Plastino, *Phys. Lett. A* 226 (1997) 257.
- [18] R.S. Mendes, *Physica A* 242 (1997) 299.
- [19] E.M.F. Curado, *Braz. J. Phys.* 29 (1999) 36.
- [20] E.M.F. Curado, F.D. Nobre, *Physica A* 335 (2004) 94.
- [21] M. Gell-Mann, C. Tsallis (Eds.), *Nonextensive Entropy: Interdisciplinary Applications*, Oxford University Press, Oxford, 2004;
V. Latora, A. Rapisarda, C. Tsallis, *Physica A* 305 (2002) 129 (and references therein);
S. Abe, Y. Okamoto (Eds.), *Nonextensive Statistical Mechanics and its Applications*, Springer Verlag, Berlin, 2001;
A.R. Plastino, A. Plastino, *Phys. Lett. A* 193 (1994) 140.
- [22] E.M.F. Curado, C. Tsallis, *J. Phys. A* 24 (1991) L69.
- [23] C. Tsallis, R.S. Mendes, A.R. Plastino, *Physica A* 261 (1998) 534.
- [24] R. Rossignoli, N. Canosa, *Phys. Rev. Lett.* 88 (2002) 170401.
- [25] L. Chen, Z. Yan, *J. Appl. Phys.* 75 (1994) 1249.