Information theory based relations between thermodynamic’s 1st. and 2nd. laws

E. M. F. Curado\textsuperscript{a} and A. Plastino\textsuperscript{b}

\textsuperscript{a}Centro Brasileiro de Pesquisas Físicas (CBPF)
Rua Xavier Sigaud 150 - Urca - Rio de Janeiro - Brasil

\textsuperscript{b}Instituto de Física (IFLP), Facultad de Ciencias Exactas,
Universidad Nacional de La Plata and
Argentina’s National Council (CONICET)
C.C. 727, 1900 La Plata, Argentina

Abstract

We focus attention on some particular thermodynamic relations (PTR). Using information theory concepts we show that, for a reversible process, microscopic considerations related to these PTR make the concomitant informational contents of the first and second laws equivalent. The pertinent demonstration is obtained when trying to ascertain the corresponding equilibrium microscopic probability distribution. We also describe other instances in which the above mentioned informational equivalence does not hold.

Pacs: 05.70.-a, 05.30.-d, 3.67.-a, 2.50.-r

Keywords: Thermodynamics, Microscopic probability distribution, First law, Second law.

* Corresponding author. Phone / Fax: +55-21-2141-7369
Email addresses: evaldo@cbpf.br (E. M. F. Curado), plastino@fisica.unlp.edu.ar (A. Plastino).
1 Introduction

The first and second laws of thermodynamics are two of physics’ most important statements. They constitute strong pillars of our present understanding of Nature. Of course, statistical mechanics adds an underlying microscopic substratum that is able to explain not only these two laws but the whole of thermodynamics itself [1,2,3,4,5,6,7,8,9]. One of its basic ingredients is an equilibrium microscopic probability distribution (PD) that controls the population of microstates of the system under consideration [2]. We will be mainly concerned here with changes in the independent external parameters and in how these changes will affect the microstate-population.

We regard as independent external parameters both extensive and intensive parameters defining the macroscopic thermodynamic state of the system. The extensive parameters, known with (experimental) certainty, help to define the Hilbert space (HS) in which the system can be represented. The intensive parameters are associated with some physical quantities of which only the average value is known. They are related to the mean values of the corresponding operators acting on the HS previously defined. The eigenvalues of these operators are, therefore, functions of the extensive parameters defining the HS. The microscopic equilibrium PD is an explicit function of the intensive parameters and an implicit function - by means of the eigenvalues of the above referred to operators (known in average) - of the extensive parameters defining the HS.

In a previous effort [10] we have shown that

- enforcing the relation $dU = TdS$ in an infinitesimal microscopic change $p_i \rightarrow p_i + dp_i$ of the probability distribution (PD) that describes the equilibrium properties of an arbitrary system
- univocally determines this PD, and furthermore,
- the ensuing $\{p_i\}$ coincides with that obtained following the maximum entropy principle (MaxEnt) tenet of extremizing the entropy $S$ subject to an assumedly known mean value $U$ of the system’s energy.

Such a result undoubtedly exhibits a first law-second law relation “flavor”. Here we wish to further pursue travelling the road paved in [10] by now considering only given infinitesimal macroscopic changes (as opposite to the microscopic ones dealt with in [10]) in both the (i) intensive and (ii) extensive parameters of the system, in order to ascertain if such a flavor becomes more intense and transforms itself into concrete thermal relations.
2 Homogenous, isotropic, one-component systems

Let us start our endeavor by considering simple, one-component systems [1], that is, composed by a single chemical species, macroscopically homogenous, and isotropic [1]. The macroscopic equilibrium thermal state of such a simple, one-component system is described, in self-explanatory notation, by $T, V, N$ [1]. We shall here consider a quite general information measure $S$ that, according to Kinchin’s axioms for information theory [5], depends exclusively on the probability distribution $\{p_i\}$

$$S = S(\{p_i\}). \quad (1)$$

Contrary-wise, in [10], that uses a different perspective from the present one, a specific form for $S$ is used, namely ($f$ is an arbitrary smooth function of the $p_i$ such that $pf(p)$ is concave)

$$S = k \sum_{i=1}^{W} p_i f(p_i). \quad (2)$$

We will adopt in this communication the following notation: $W$ is the number of microscopic states, Boltzmann’s constant is denoted by $k$, and the sum runs over a set of quantum numbers, collectively denoted by $i$ (characterizing levels of energy $\epsilon_i$), that specify an appropriate basis in Hilbert’s space. In [10] attention is exclusively focused upon infinitesimal changes in the $\{p_i\}$ for an $S$ given by (1), which is NOT our perspective here. Let us repeat again that we do not use here (2) but rather the more general form (1).

Consider further the quantity $U$ that represents the mean value of the Hamiltonian, and, as befits an homogenous, isotropic, one-component system in the Helmholtz free energy representation [1],

1. as external parameters the volume ($V$) and the number of particles ($N$) (“exactly” known and used to define the Hilbert space),
2. as intensive variable the temperature $T$, associated with the mean value of the internal energy $U$.

The energy eigenvalues of the Hamiltonian $\epsilon_i$ are, obviously, functions of the volume and of the number of particles, namely, $\{\epsilon_i\} = \{\epsilon_i(V,N)\}$. From now on, for simplicity, we take $N$ as fixed, and drop thereby the dependence of the energy eigenvalues on $N$, i.e., $\{\epsilon_i\} = \{\epsilon_i(V)\}$. The probability distribution (PD) depends, then, on the external parameters in the fashion

$$p_i = p_i(T, \epsilon_i(V)). \quad (3)$$
Also, let us suppose that $g$ is an arbitrary smooth, monotonic function of the $p_i$ such that $g(0) = 0$ and $g(1) = 1$. We do not need to require the condition $\sum_i g(p_i) = 1$. The mean energy $U$ could be written as $[11,12,13,14,15,16,17]$,

$$U = \sum_{i=1}^{W} g(p_i) \epsilon_i . \quad (4)$$

The critical difference between this work and that of [10] is to be found in the following assumption, on which we entirely base our considerations:

\begin{center}
the temperature $T$ and the volume $V$ reversibly change in the fashion

$$T \rightarrow T + dT \text{ and } V \rightarrow V + dV.$$ \hfill (5)
\end{center}

As a consequence of (5), corresponding changes $dp_i$, $dS$, $d\epsilon_i$, and $dU$ are generated in, respectively, $p_i$, $S$, $\epsilon_i$, and $U$. Variations in, respectively, $p_i$, $S$, and $U$ write

$$dp_i = \frac{\partial p_i}{\partial T} dT + \sum_{j=1}^{W} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} dV, \quad (6)$$

$$dS = \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT + \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} dV, \quad (7)$$

and

$$dU = \sum_{i=1}^{W} \frac{\partial g}{\partial p_i} \frac{\partial p_i}{\partial T} \epsilon_i dT + \sum_{i,j=1}^{W} \frac{\partial g}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} \epsilon_i dV + \sum_{i=1}^{W} g(p_i) \frac{\partial \epsilon_i}{\partial V} dV, \quad (8)$$

where, for simplicity, we have considered non-degenerate levels. Clearly, on account of normalization, the changes in $p_i$ must satisfy the relation

$$\sum_i dp_i = 0. \quad (9)$$

### 3 First law considerations

The first law of thermodynamics for a reversible process reads

$$dU = \delta Q + \delta W = TdS + \delta W, \quad (10)$$
where we have used the Clausius relation $\delta Q = T \delta S$. Multiplying Eq. (7) by $T$ we can recast Eq. (10) in the fashion

$$dU = T \left( \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT + \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial \epsilon_j} dV \right) + \delta W.$$ (11)

3.1 Changes in the temperature

Eqs. (8) and (11) must be equal for arbitrary changes in $T$ and $V$. As these quantities can be changed in an independent way, let us first consider changes just in $T$. Enforcing equality in the coefficients of $dT$ appearing in Eqs. (8) and (11) we obtain

$$\sum_{i=1}^{W} \frac{\partial g}{\partial p_i} \epsilon_i dT = T \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} dT,$$ (12)

that must be satisfied together with [Cf. (6)]

$$\sum_i d p_i = \sum_i \frac{\partial p_i}{\partial T} dT = 0.$$ (13)

We recast now (12) in the fashion

$$\sum_{i=1}^{W} \left( \frac{\partial g}{\partial p_i} \epsilon_i - T \frac{\partial S}{\partial p_i} \right) \frac{\partial p_i}{\partial T} dT \equiv \sum_i K_i \frac{\partial p_i}{\partial T} dT = 0.$$ (14)

Since the $W p_i$'s are not independent ($\sum_{i=1}^{W} p_i = 1$), we can separate the sum in (14) into two parts, i.e.,

$$\sum_{i=1}^{W-1} \left( \frac{\partial g}{\partial p_i} \epsilon_i - T \frac{\partial S}{\partial p_i} \right) \frac{\partial p_i}{\partial T} dT + \left( \frac{\partial g}{\partial p_W} \epsilon_W - T \frac{\partial S}{\partial p_W} \right) \frac{\partial p_W}{\partial T} dT = 0.$$ (15)

Picking out level $W$ for special attention is arbitrary. Any other $i$–level could have been chosen as well, as the example given below will illustrate. Taking into account now that, from Eq. (13),

$$\frac{\partial p_W}{\partial T} = - \sum_{i=1}^{W-1} \frac{\partial p_i}{\partial T},$$ (16)
we see that Eq. (15) can be rewritten as

\[
\sum_{i=1}^{W-1} \left[ \left( \frac{\partial g}{\partial p_i} \epsilon_i - T \frac{\partial S}{\partial p_i} \right) - \left( \frac{\partial g}{\partial p_W} \epsilon_W - T \frac{\partial S}{\partial p_W} \right) \right] \frac{\partial p_i}{\partial T} dT = 0. 
\] (17)

As the \( W - 1 \) \( p_i \)'s are now independent, the term into brackets should vanish, which entails

\[
\frac{\partial g}{\partial p_i} \epsilon_i - T \frac{\partial S}{\partial p_i} - \left( \frac{\partial g}{\partial p_W} \epsilon_W - T \frac{\partial S}{\partial p_W} \right) = 0,
\] (18)

for all \( i = 1, \cdots, W - 1 \). Let us call the term into parentheses as

\[
K_W = \frac{\partial g}{\partial p_W} \epsilon_W - T \frac{\partial S}{\partial p_W} \equiv K. 
\] (19)

We can now cast Eq. (18) as

\[
\frac{\partial g}{\partial p_i} \epsilon_i - T \frac{\partial S}{\partial p_i} - K = 0; \quad (i = 1, \cdots, W - 1),
\] (20)

an equation that, hopefully, should yield a definite expression for \( W - 1 \) of the \( p_i \)'s, the remaining one being fixed by normalization.

**Example**

Consider the Shannon orthodox instance

\[
S = -k \sum_i p_i \ln p_i \\
g(p_i) = p_i \\
\frac{\partial S}{\partial p_i} = -k[\ln p_i + 1].
\] (21)

Here equation (20) yields

\[
\ln p_i = -\left[ \frac{\epsilon_i}{kT} + \left( 1 - \frac{K}{kT} \right) \right]; \text{ i.e.,} \\
p_i = Z^{-1} e^{-\epsilon_i/kT} \\
\ln Z = 1 - K/kT, 
\] (22)

showing, as anticipated, that we could have selected any \( i \)-level other than \( i = W \) above without affecting the final result.
In order to better understand the meaning of equation (20), let us assume now that you wish to extremize $S$ subject to the constraint of a fixed $U$, a process usually referred to as the MaxEnt one [5]. This is achieved via a Lagrange multiplier $\beta$. We need also a normalization Lagrange multiplier $\xi$,

$$\delta_{\{ p_i \}}[S/k - \beta U - \xi \sum_i p_i] = 0,$$

leading to

$$0 = \delta_{p_i} \left( S/k - \beta \sum_j g(p_j)\epsilon_j - \xi \sum_j p_j \right),$$

implying

$$\frac{1}{k} \frac{\partial S}{\partial p_i} - \beta \frac{\partial g}{\partial p_i} \epsilon_i - \xi = 0,$$

that, after setting $\xi = -\beta K$, and calling $\beta = 1/kT$, becomes

$$T \frac{\partial S}{\partial p_i} - \frac{\partial g}{\partial p_i} \epsilon_i + K = 0.$$

Clearly, (20) and (26), are one and the same equation! Eq. (26) is, in fact, valid for all $W$ states due the definition of the $i$-independent term $K$ given by Eq. (19). Therefore, we have demonstrated that

• starting from Eq. (10) and
• considering just changes in the intensive parameter $T$,
• yields the equilibrium PD obtained using MaxEnt (with the energy constraint).

It has thus been shown that, for a simple system, an alternative way to obtain the equilibrium PD without using MaxEnt exists that only considers changes in the intensive parameter $T$ of the first law [Eq. (10)].

### 3.2 Changes in the extensive parameter

Let us now deal with the effect of changes in the extensive parameters that define the Hilbert space in which our system “lives” and notice that Eq. (11) can be written in the fashion
\[ dU = \delta Q + \delta W = TdS + \delta W = \]
\[
T \left( dT \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} + dV \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} \right) + \delta W, \tag{27}
\]
i.e.,
\[
TdS = Q_T dT + Q_V dV; \quad Q_T = T \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T},
\]
\[ Q_V = T \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V}. \tag{28} \]

Let us now substitute the expression for \( \frac{\partial g}{\partial p_i} \epsilon_i \) given by Eqs. (19) and (20),
\[
\frac{\partial g}{\partial p_i} \epsilon_i = T \frac{\partial S}{\partial p_i} + K; \quad (i = 1, \ldots, W), \tag{29}
\]
into the second term of the R.H.S. of Eq. (8),
\[
\sum_{i,j=1}^{W} \frac{\partial g}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} \epsilon_i dV =
\]
\[
= \sum_{i,j=1}^{W} \left[ T \frac{\partial S}{\partial p_i} + K \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} \right] \epsilon_i dV =
\]
\[
= T \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} + K \sum_{i,j=1}^{W} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} =
\]
\[
= \left( T \sum_{i,j=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} \right) dV = Q_V dV, \tag{30}
\]
on account of the fact that
\[
K \sum_{i,j=1}^{W} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} dV = 0; \quad \text{since} \quad (\partial / \partial V) \sum_{i} p_i = 0. \tag{31}
\]

We recognize in the term \( Q_V dV \) of the last line of (30) a "volume contribution" to Clausius' relation \( \delta Q = TdS \), an original contribution of the present work.
We see that *changes in the equilibrium PD caused by modifications in the extensive parameters defining the Hilbert space of the system* give also a contribution to the “heat part” of the first law.

Finally, for Eq. (8) to become equal to Eq. (27) we have to demand, in view of the above developments,

\[ \delta W = dV \left[ \sum_i g(p_i) \frac{\partial \epsilon_i}{\partial V} \right], \quad (32) \]

the quantity within the brackets being the mean value,

\[ \left\langle \frac{\partial \epsilon}{\partial V} \right\rangle = \sum_i g(p_i) \frac{\partial \epsilon_i}{\partial V}, \quad (33) \]

usually associated in the textbooks with the work done by the system.

Summing up, our analysis of simple systems has shown that

- if we consider the first law written on the form (10)
- changes in the intensive parameter lead to the obtention of the equilibrium PD (an alternative way to the MaxEnt principle) and
- changes in the extensive-Hilbert-space-determining parameter lead to two contributions
  (1) one related to heat and
  (2) the other related to work.

4 More general systems

More general systems can be considered by: (i) considering multi-component ones, and/or (ii) by adding additional extensive variables [1]. As the numbers of components \(N_1, \ldots, N_S\) of a multi-component system are themselves extensive variables, we can considerably amplify the preceding considerations by considering, instead of just one extensive quantity (volume) as we did before, \(M\) of them \(X_1, \ldots, X_M\) [1]. The conclusions reached in the previous Section can then be straightforwardly generalized. One would deal with one intensive parameter \((T)\) and \(M\) extensive-Hilbert-space-determining ones, where one of them would be the volume. Eq. (28) generalizes to

\[ TdS = Q_T \, dT + \sum_{\nu=1}^{M} Q_\nu \, dX_\nu; \quad Q_T = T \sum_{i=1}^{W} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} \]
\[ Q_\nu = T \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial X_\nu}, \]  

(34)

while \( dU \) is now

\[
dU = \sum_{i=1}^W \frac{\partial g}{\partial p_i} \frac{\partial p_i}{\partial T} \epsilon_i dT + \sum_{\nu=1}^M \left[ \sum_{i,j=1}^W \frac{\partial g}{\partial p_i} \frac{\partial \epsilon_j}{\partial X_\nu} \epsilon_i dX_\nu + \sum_{i=1}^W g(p_i) \frac{\partial \epsilon_i}{\partial X_\nu} dX_\nu \right].
\]

(35)

where, again for simplicity we have considered non-degenerate levels. The changes in \( p_i \) must of course still satisfy the relation

\[ \sum_i dp_i = 0. \]

(36)

Eq. (35) gets simplified, following the lines developed above, to

\[
dU = \delta Q + \delta W = T dS + \delta W =
\]

\[ T \left( dT \sum_{i=1}^W \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} + \sum_{\nu=1}^M dX_\nu \left[ \sum_{i,j=1}^W \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial X_\nu} \right] \right) + \delta W, \]

(37)

with

\[ \delta W = \sum_{\nu=1}^M \delta W_\nu, \]

(38)

where

\[ \delta W_\nu = dX_\nu \left[ \sum_{i=1}^W g(p_i) \frac{\partial \epsilon_i}{\partial X_\nu} \right], \]

(39)

involving the mean value

\[ \left\langle \frac{\partial \epsilon}{\partial X_\nu} \right\rangle = \sum_i g(p_i) \frac{\partial \epsilon_i}{\partial X_\nu}, \]

(40)

usually associated in the textbooks with the work done by the system in changing the external parameter \( X_\nu \).
5 Carnot cycle revisited

Let us now consider an ideal gas performing a Carnot cycle, constituted by two isothermal and two adiabatic “trajectories”. The external parameters that are changing in this reversible transformation are: (i) an intensive parameter, the temperature ($T$), and (ii) an extensive parameter, the volume ($V$).

5.1 Isothermal reversible transformation

In an isothermal transformation $dT = 0$, implying $dU = 0$. Eqs. (7) and (8) write now

$$dS = \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} dV,$$

and

$$dU = \sum_{i,j} \frac{\partial g}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} \epsilon_i dV + \sum_{i=1}^{W} g(p_i) \frac{\partial \epsilon_i}{\partial V} dV .$$

Clearly, from Eq. (41), the heat term in this transformation can be identified with

$$\delta Q = TdS = T \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} dV,$$

and has its origin in the way changes in the energy levels, due to the volume transformation, affect the population of the microscopic states. The ensuing PD-changes have an impact on the entropy, since heat is exchanged in this transformation. As we have shown in Eq. (30)

$$\delta Q = T \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} dV = \sum_{i,j} \frac{\partial g}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} \epsilon_i dV,$$

and, as $dU = 0$ from Eq. (42), we see that the heat term should be equal to minus the work term, implying

$$T \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} dV = \sum_{i,j} \frac{\partial g}{\partial p_i} \frac{\partial \epsilon_j}{\partial V} \epsilon_i dV = -\sum_{i=1}^{W} g(p_i) \frac{\partial \epsilon_i}{\partial V} dV ,$$

11
where the work done is given by the term
\[ W = \sum_{i=1}^{W} g(p_i) \frac{\partial \epsilon_i}{\partial V} dV = \left\langle \frac{\partial \epsilon}{\partial V} \right\rangle = \delta W, \tag{46} \]

as it is usually understood. Eq. (44) is a microscopic recipe for evaluating the heat term in an isothermal reversible transformation without computing first the work term.

5.2 Adiabatic transformation

Since here \( dS = 0 \), Eq. (7) yields
\[ \sum_{i} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T} dT = - \sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V} dV, \tag{47} \]

and the equation for the associated trajectory in the \((T, V)\)-plane of the adiabatic reversible transformation can be given as
\[ \frac{dT}{dV} = - \left( \frac{\sum_{i,j} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial \epsilon_j} \frac{\partial \epsilon_j}{\partial V}}{\sum_{i} \frac{\partial S}{\partial p_i} \frac{\partial p_i}{\partial T}} \right). \tag{48} \]

Using Eqs. (12), (30) and (47) we can see that Eq. (8) can be written, for this transformation, as
\[ dU = \sum_{i} g(p_i) \frac{\partial \epsilon_i}{\partial V} dV, \tag{49} \]

and it contains only the work term, as it is well-known.

5.3 Process without work

In this kind of process we should have
\[ dU = \delta Q = T dS, \tag{50} \]

that are due, according to the present viewpoint, to changes affecting only the intensive parameter \( T \). If there is no change in any of the extensive parameters defining the Hilbert space, there cannot be a work term, as the eigenvalues
of the operators in this Hilbert space will not change. Thus, changes in the intensive parameters induce only heat-changes, i.e., $dS$–variations, and not $W$–ones.

6 Conclusions

This paper advanced a new microscopic picture of the “first law-second law” marriage for any arbitrary entropic functional of the underlying probability distribution. We have

• exhibited the microscopic details of the way in which
  (1) changes in the macroscopic intensive variables affect only the heat part of the first law, while
  (2) displaying the same informational content that we can be obtained using MaxEnt.
• Changes in the macroscopic extensive variables used to define the Hilbert space of system affect both the heat and the work part of the first law. Recourse to first-law considerations allows one to visualize the way in which changes in the extensive variables affect the PD and, in turn, do give a contribution to heat terms, a new result.

Acknowledgments: The authors thank Renio S. Mendes for valuable discussions. E.M.F.C. also thanks PRONEX and CNPq (Brazil) for partial support.

References

[1] H. B. Callen, *Thermodynamics* (J. Wiley, NY, 1960); E. A. Desloge, *Thermal physics* (Holt, Rhinehart and Winston, NY, 1968).

[2] R.K. Pathria, *Statistical Mechanics* (Pergamon Press, Exeter, 1993).

[3] F. Reif, *Statistical and thermal physics* (McGraw-Hill, NY, 1965).

[4] J. J.Sakurai, *Modern quantum mechanics* (Benjamin, Menlo Park, Ca., 1985).

[5] E. T. Jaynes, Phys. Rev. 106, 620 (1957); 108, 171 (1957); *Papers on probability, statistics and statistical physics*, edited by R. D. Rosenkrantz (Reidel, Dordrecht, Boston, 1987); A. Katz, *Principles of Statistical Mechanics, The Information Theory Approach* (Freeman and Co., San Francisco, 1967).

[6] B. H. Lavenda, *Statistical Physics* (Wiley, New York, 1991); B. H. Lavenda, *Thermodynamics of Extremes* (Albion, West Sussex, 1995).

[7] A. R. Plastino and A. Plastino, Phys. Lett. A 177 (1993) 177.
[8] A. R. Plastino and A. Plastino, Phys. Lett. A 226 (1997) 257.

[9] R. S. Mendes, Physica A 242 (1997) 299.

[10] A. Plastino and E. Curado, Phys. Rev. E 72 (2005) 047103.

[11] E. M. F. Curado, Braz. J. Phys. 29 (1999) 36.

[12] M. Gell-Mann and C. Tsallis, Eds. *Nonextensive Entropy: Interdisciplinary applications* (Oxford University Press, Oxford, 2004); V. Latora, A. Rapisarda, and C. Tsallis, Physica A 305 (2002) 129 (and references therein); S. Abe and Y. Okamoto, Eds. *Nonextensive statistical mechanics and its applications* (Springer Verlag, Berlin, 2001); A. R. Plastino and A. Plastino, Phys. Lett. A 193 (1994) 140.

[13] C. Tsallis, Braz. J. Phys. 29 (1999) 1; A. Plastino and A. R. Plastino, Braz. J. Phys. 29 (1999) 50.

[14] E. M. F. Curado and C. Tsallis, J. Phys. A 24 (1991) L69.

[15] C. Tsallis, R. S. Mendes, and A. R. Plastino, Physica A 261 (1998) 534.

[16] E. M. F. Curado and F. D. Nobre, Physica A 335 (2004) 94.

[17] R. Rossignoli and N. Canosa, Phys. Rev. Lett. 88 (2002) 170401.