On a heuristic point of view related to quantum nonequilibrium statistical mechanics

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In this paper I propose a new way for counting the microstates of a system out of equilibrium. As, according to quantum mechanics, things happen as if a given particle can be found in more than one state at once, I extend this concept to propose the coherent access by a particle to the available states of a system. By coherent access I mean the possibility for the particle to act as if it is populating more than one microstate at once. This hypothesis has experimental implications, since the thermodynamical probability and, as a consequence, the Bose-Einstein distribution as well as the argument of the Boltzmann factor is modified.

Keywords: Tsallis entropy; nonextensivity; nonequilibrium statistical mechanics

I. INTRODUCTION

Nowadays, the development of new entropic forms has been followed by an increasing interest, as can be seen, for example, in Refs. [1, 2]. Although it is possible to formulate new entropies from a strictly mathematical point of view [1], without connection with the physics implicated in such formulations, recently some works have appeared trying to understand the link between the physical situation and the mathematical formulation [3, 4]. In this meantime, some works have appeared raising the question of a possible pseudononextensivity stemming from the generalized entropic forms [5, 6].

In general, nonextensive formulations are related to nonequilibrium situations, where the Boltzmann factor \( \exp(-\beta E) \), presumably, plays not a preponderant role, being difficult, if not impossible, to associate a definite temperature to the system. In some cases, however, by considering situations only slightly out of the equilibrium, it is possible to ascribe a temperature to the system, which results in a distribution function different from that of Boltzmann [7].

In this paper, inspired by some ideas from quantum optics, I propose a new way for counting accessible states to a given particle, in such a way that its thermodynamical probability \( \Omega \) is modified, with direct consequences in the entropic form \( S \propto \Omega \) of the system. As is well known in the quantum optics domain, which deals fundamentally with nonequilibrium systems, an initially pure state can be described, in its most general form, as a superposition of each state physically accessible to the particle. The role of the reservoir, even at the idealized zero temperature, is to lead the system to a complete mixture at the end of the so-called decoherence time \( \tau_D \).

Thus, even before the thermalization occurs the loss of coherence of the system, or, in other words, the system capacity to access, coherently, every possible state. This state of affairs suggests an entirely new way to count the accessible states. It is this connection, until now not explored, between the new way to count the accessible states and its consequences to the entropic form of the system that we will explore in the next sections.

II. REDEFINING THE MICROSTATES

In statistical mechanics, to define a microstate it is necessary to take into account the (un)distinguishability of the particles, which gives rise to different configurations (see Tab.1). For calculating all the possible configurations we now take into account, beside this characteristic, this another one: the possibility to the particle simultaneously access more than one state, or, to avoid eventual difficulties related to interpretations matter inherent to the quantum formalism, the possibility to the particle to coherently access the available states. This situation is shown in Tab. 2 for the case of two identical particles having two accessible states. Note that if the particles are distinguishable, the corresponding configuration is different.

Comparing Tab.I and Tab.II, we see that, clearly, the nonequilibrium situation requires a new way for counting microstates. This new way to count, shown in Tab.2, can be rep-

TABLE I: The configuration of two accessible states for a) two indistinguishable particles and b) two distinguishable particles. (1) denotes the first available state and (2) denotes the second available state.

|        | (1) | (2) |
|--------|-----|-----|
| a      | a   | a   |
| a.a    | a.a | a.a |

(a)

|        | (1) | (2) |
|--------|-----|-----|
| a      | a   | b   |
| b      | a   | a   |

(b)

TABLE II: A system out of equilibrium composed by two particles having two accessible states. (1) denotes the first available state, (2) denotes the second available state, and (12) denotes the coherent access to both states.

|        | (1) | (2) | (12) |
|--------|-----|-----|------|
| o      | o   | o   | o    |
| o      | o   | o   | o    |
| o      | o   | o   | o    |

Comparing Tab.I and Tab.II, we see that, clearly, the nonequilibrium situation requires a new way for counting microstates. This new way to count, shown in Tab.2, can be rep-
presented by the following sequences, where the number between parentheses indicates the state occupied and the letter following the parenthesis indicates the corresponding occupation by the particle \(a\), which is identical to all the others:

\[
(1) a(2)a(12); (1) a(2)(12)a; (1)(2)a(12); (1)(2)a(12)a;
\]

As for example, the last sequence, \((1)(2)(12)a\), corresponds to two particles accessing coherently the two states (1) and (2), while the second sequence, \((1) a(2)(12)a\) corresponds to one particle accessing the state (1) and the other accessing coherently the states (1) and (2). Note that, as the sequence must initiate by a number, and existing three possible number of states, 1, 2, and 12, will remain 3 – 1 numbers plus two letters \(a\) (particles) to be set in whatever order (permutation).

Therefore, the number of unrepeated sequences is

\[
\omega^* = \frac{3 \times (3 - 1 + 2)!}{2!3!} = 6,
\]

where we have put a superscript (*) to remind us that we are treating with nonequilibrium situation. Proceeding in a general manner, for \(g_j\) sublevels with \(N_j^*\) particles, the number \(w_j^*\) of unrepeated sequences is

\[
w_j^* = \frac{G_j(\sum G_j - N_j^* - 1)!}{G_j!N_j^*!} = \frac{(G_j - N_j^* - 1)!}{(G_j - 1)!N_j^*!},
\]

where \(G_j = \sum_{k=1}^{g_j} C_{g_j,k} = \frac{n!n!}{n!(n-m)!m!}\) is the number of possible sequences formed from \(g_j\), and \(C_{n,m} = n!(n-m)!m!\). Taking as example the configuration given by Tab.2, where \(g_j = 1\), \(N_j = 2\), \(G_j = \sum_{k=1}^{2} C_{2,k}\), thus \(G_j = C_{2,1} + C_{2,2} = 3\); then

\[
w_j^* = \frac{(3 + 2 - 1)!}{(3 - 1)!2!} = 6,
\]

which is the number of sequences given in Eq.1 corresponding to Tab.2. Therefore, the nonequilibrium thermodynamical probability \(w_k^*\) for a given macrostate \(k\) is

\[
w_k^* = \frac{(G_j + N_j^* - 1)!}{(G_j - 1)!N_j^*!}.
\]

As \(G_j = \sum_{k=1}^{g_j} C_{g_j,k} = C_{g_j,1} + \sum_{k=2}^{g_j} C_{g_j,k}\), and \(C_{g_j,1} = g_j\), letting \(L_{gj} = \sum_{k=2}^{g_j} C_{g_j,k}\), then Eq.5 can be written as

\[
w_k^* = \prod_j \frac{(g_j + L_{gj} + N_j^* - 1)!}{(g_j + L_{gj} - 1)!N_j^*!}.
\]

From Eq.5 we can see that the only changing in the thermodynamical probability is the appearance of the factor \(L_{gj}\) modifying the degeneracy \(g_j\), and, as a consequence, modifying also the number of macrostates, \(\Omega = \sum_k w_k^*\), and the entropy of the system. Before ending this section, we call attention to the plausibility in presume that, given a system out of the equilibrium with \(N^*\) particles and \(n\) levels, each of this having \(g_j\) sublevels, as the equilibrium is established \((L_{gj} \to 0)\), the \(N^*\) particles of the system accommodate by the \(n_j\) levels, with each level receiving \(N_j^*\) particles, which are distributed by the sublevels. Also, as it is easily verified, Eq.6 gives rise to a Bose-Einstein-like statistics, with \(g_j\) replaced by \(G_j\). That is so can be checked in the following manner, proceeding by analogy with the equilibrium situation: First, we take the ln from both sides of Eq.6. Second, we use the Stirling formula. Third, we differentiate with respect to \(N_j^*\) and use \(\partial \ln w_j^*/\partial N_j^* = \epsilon_j^*\), where \(\epsilon_j^*\) generalizes \(\epsilon_j = \beta E_j\), \(\beta = 1/kT\), to find

\[
\frac{N_j^*}{G_j} = \frac{1}{\exp(\epsilon_j^*) - 1} - 1.
\]

This is an interesting point, having experimental implication: the Bose-Einstein statistics is corrected, since the equality \(G_j = g_j\) and \(\epsilon_j^* = \epsilon_j\) will be valid only when the complete equilibrium is reestablished. Thus, for systems only slightly out of the equilibrium, the energy emitted should be slightly different from that corresponding to the system in equilibrium. Note that, as \(\epsilon_j^* = \epsilon_j = \beta E_j\) when the equilibrium is restated, it is convenient to expand \(\epsilon_j^*\) in power series of \(\epsilon\)

\[
\epsilon_j^* = \epsilon_0 + \frac{\partial \epsilon_j^*}{\partial \epsilon} \epsilon_j + \frac{1}{2!} \frac{\partial^2 \epsilon_j^*}{\partial \epsilon^2} \epsilon_j^2 + \frac{1}{3!} \frac{\partial^3 \epsilon_j^*}{\partial \epsilon^3} \epsilon_j^3 + \cdots,
\]

which, requiring that \(\epsilon_j^* \to \epsilon_j = \beta E_j\) when the equilibrium is restated, gives \(\epsilon_0 = 0\) and \(\frac{\partial \epsilon_j^*}{\partial \epsilon} = 1\), such that the first order correction to the Bose-Einstein distribution can be explicitly written as

\[
\frac{N_j^*}{G_j} = \frac{1}{\exp\left[\beta E + \alpha_1 (\beta E)^2\right] - 1},
\]

where we have kept only a few terms and put \(\frac{1}{\beta} \frac{\partial \epsilon_j^*}{\partial \epsilon} = \alpha_1\).

Note that from this approach the net effect stemming from the nonequilibrium on a given system is the increasing in the degeneracy, which in turn increases the available states given by \(\Omega\). The Boltzmann factor, to be recovered when \(\exp(\beta^* \epsilon_j^*) \gg 1\), is modified, and we will explore more about this in the next Section. The choice of the more convenient entropic form associated to this new thermodynamical probability is discussed in the last Section.

### III. THE NONEQUILIBRIUM PARTITION FUNCTION

Let us focus our attention to the bosonic particles, since the other cases are similar. By definition, the partition function is defined as a sum in all microstates (ms):

\[
Z = \sum_{ms} \exp(-\beta E),
\]

where \(E\) is the energy of the system and \(\beta\) is related to the temperature \(T\) of the system by the Boltzmann constant \(\beta\).
where we have dropped out the superscript and the index the best entropic form related to it. Of course, in this case the total number of particles is simply $N = \sum_i n_i$.

For an out of equilibrium system, we introduce the coherent access hypothesis to several states, which consists in maintaining the same form as that of Eq. (9), but replacing $\sum_i n_i \epsilon(i)$ by $\sum_{ij, n_{ij}} \epsilon(i, j,...)$, where $n_{ij}$ must be interpreted as being the number of particles coherently accessing the energy levels $\epsilon(i)$ and $\epsilon(j)$. For example, as discussed in Section I and represented in Tab. 2, $\epsilon(i, j)$ represents the coherent access related to the energy levels $i$ and $j$, and $\epsilon(1, 2)$ represents, for example, the states (1) and (2) being coherently populated.

For demonstrating that the partition function preserves its form given by Eq. (9) even at the nonequilibrium situation, it is enough to maintain this following postulate, which is valid for equilibrium situation: that two systems, in contact with a third one, as for example a reservoir at temperature $T$, act independently of each other while both the systems exchange energy with the reservoir. Although this demonstration is straightforward, for completeness we address the reader to the appendix. Continuing to denote the nonequilibrium quantities with a superscript ($\ast$), thus according to Eq. (26) of the appendix, if $P(\epsilon_j^* = \beta^* E_j^*)$ is the probability for a given system out of the equilibrium in a particular microstate whose configuration is described by $\epsilon_j^* = \beta^* E_j^*$, then

$$P(\epsilon_j^*) = \frac{\exp(-\epsilon_j^*)}{Z^*}.$$  \hspace{1cm} (10)

Now, using Eq. (8) and requiring that $\epsilon_j^* \rightarrow \beta E_j$ when the equilibrium is restated, the Eq. (10) can now be written as

$$P(\epsilon_j^*) = \frac{1}{Z^*} \exp \left[ -\beta E_j - \alpha_1 (\beta E_j)^2 - \alpha_2 (\beta E_j)^3 + \alpha_3 (\beta E_j) \right] \ldots,$$  \hspace{1cm} (11)

where the other constants were renamed for convenience as $\frac{\alpha_0}{\alpha_1} = \alpha_{n-1}$. Such a state of affairs giving origin to an infinite number of free parameters was studied in Refs. [5, 9] in a different context. Note that for systems only slightly out of the equilibrium this last equation can be written as

$$P(E) = \frac{1}{Z} \exp \left[ -\beta E - \alpha_1 (\beta E)^2 \right],$$  \hspace{1cm} (12)

where we have dropped out the superscript and the index $i$. Some experiments seem to point for the importance of this last term, which modifies the Boltzmann factor [7].

### IV. CONNECTION WITH ENTRISTIC FORMS

As discussed in Section I, since the thermodynamical probability was modified, a natural question emerging is what is the best entropic form related to it. Of course, depending on our choice we will face with different implications. Once there is a plenty of entropic forms at our disposal, we will focus our attention only in two of them: the Boltzmann-Gibbs ($S_{BG}$) and the Tsallis ($S_q$) entropies. As is well known, while the first is extensive, i.e., $S_{BG}(A + B) = S_{BG}(A) + S_{BG}(B)$, the second in general is not, i.e., $S_q(A + B) \neq S_q(A) + S_q(B)$ if $q \neq 1$.

Let us begin adopting the Boltzmann-Gibbs entropy, assuming for now that the single effect of the nonequilibrium is to increase the degeneracy of the system, as seen in Section I. It will be possible to reconcile Eq. (11) to an extensive entropic form such as that of Boltzmann and Gibbs? Indeed, that this is possible was shown in Ref. [5], in the following way. Given the density operator $\rho$ of the system and the Boltzmann constant $k$, for maximizing the Boltzmann-Gibbs entropy $S_{BG} = -kT \rho \ln \rho$ subjected to the constraints given by the moments

$$\langle (\Delta E)^n \rangle = Tr \rho H^n,$$  \hspace{1cm} (13)

$n$ integer, we vary $\rho$ in $S_{BG}$ and in those for the constraints, Eq. (13), multiplying each constraint by the undetermined Lagrange multiplier $\beta_n$, and adding the result, obtaining

$$Tr \left( 1 + \sum_{n=0}^{\infty} \beta_n H^n \right) \delta \rho = 0.$$  \hspace{1cm} (14)

Since all the variations are independent and $\delta \rho$ is arbitrary, it follows the extended (non-Maxwellian) distribution $\ln \rho = -1 - \sum_{n=0}^{\infty} \beta_n H^n$, or, equivalently

$$\rho = Z^{-1} \exp(- \sum_{n=1}^{\infty} \beta_n H^n).$$  \hspace{1cm} (15)

where the partition function is $Z = Tr \exp(- \sum_{n=1}^{\infty} \beta_n H^n)$. In the energy representation where $H |E\rangle = E |E\rangle$, Eq. (15) now reads,

$$P(E) = Z^{-1} \exp(- \sum_{n=1}^{\infty} \beta_n E^n) = Z^{-1} \times \exp \left( -\beta_1 E + \beta_2 E^2 + \beta_3 E^3 + \beta_4 E^4 \ldots \right)$$  \hspace{1cm} (16)

with $Z = \sum_{E} \exp(- \sum_{n=1}^{\infty} \beta_n E^n)$. The Lagrange multipliers $\beta_k$ are formally obtained from $\beta_k = -\frac{\partial \ln Z}{\partial E_k}$, considering $E_k = Y_k$ as independent variables. The equality between Eq. (16) and Eq. (11) is guaranteed, provided that $\beta_n = \alpha_n - 1 \beta_n$ and $\beta_1 = \alpha_0 = \beta$. Therefore, according to this view nonequilibrium systems remains extensive, although requiring a posteriori knowledge of the variance (second central moment), the coefficient of skewness (third central moment), the kurtosis (fourth central moment), and so on, thus giving rise virtually to an infinite number of free parameters.

Of course, instead of using infinite parameters, we could just use a single one by redefining a new ensemble fully determined by this single parameter. An aesthetically appealing
way to do so is to expand Eq. (11) in terms of the Tsallis entropic index \([8]\), as we will see in a moment. Consider the following expanded form of Eq. (11):
\[
P(E_j) = \frac{1}{Z} \exp \left\{ \frac{1}{1-q} \left[ (1-q) \beta E_j - \frac{(1-q)^2}{2} (\beta E_j)^2 - \frac{(1-q)^3}{3} (\beta E_j)^3 + \frac{(1-q)^4}{4} (\beta E_j)^4 \right] \right\},
\]
(17)
where in general \(\alpha_n = \frac{(q-1)^{n-1}}{n}\). This is equivalent to the statement that the old ensemble which depended of \(\beta, \{\alpha_n\}\) and \(E_j\) becomes now a function of only \(\beta, q\) and \(E_j\). Eq. (17) can be rewritten as
\[
P(E_j) = \frac{1}{Z} \exp \left\{ \frac{1}{1-q} \left[ (1-q) \beta E_j - \frac{(1-q)^2}{2} (\beta E_j)^2 - \frac{(1-q)^3}{3} (\beta E_j)^3 + \frac{(1-q)^4}{4} (\beta E_j)^4 \right] \right\},
\]
(18)
where it is easily recognized the expanded form of the logarithm function \(\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \ldots\), \(x = (1-q)\beta E_j\), such that Eq. (18) becomes
\[
P(E) = \frac{1}{Z} \left[ 1 - (1-q) \beta E \right]^{1/(1-q)},
\]
(19)
which is the \(q\)-distribution stemming from the extremization of Tsallis entropy
\[
S_q = k \frac{1 - \sum_j p_j^q}{q-1}
\]
(20)
when considering a family of constraints determined by the \(q\)-expectation value of the energy
\[
\langle E \rangle_q = \frac{\sum_j p_j^q E_j}{\sum_j p_j^q}
\]
(21)
besides the norm constraint \(\sum_j p_j^q = 1\). Therefore, a formal agreement between Tsallis and Boltzmann-Gibbs entropies is afforded. As pointed out in Ref. [5], this formal equivalence between the Boltzmann-Gibbs and Tsallis entropy gives rise to an important issue related to a possible pseudononextensivity.

V. CONCLUSION

In this paper I explored an analogy between the nonequilibrium thermodynamics and some well-established situations from quantum optics, concerning the problem of coherent access to the multiple states available to a given particle. As a consequence of the coherent access hypotheses, the process of counting the possible states of a physical system is modified. I have found a modification on both Bose-Einstein and Boltzmann-Gibbs distribution, which is in principle experimentally detectable. Actually, it is possible that the correction to the Boltzmann factor obtained by the method developed here is the one suggested by some experiments [7]. Although I have exemplified for the specific case of bosons, the extension to fermions is straightforward. Finally, I expect that the coherent access hypothesis introduced here eventually makes possible the exploration of new ways of treating problems related to nonequilibrium situations, or differing from the equilibrium in a slightly manner.

Appendix I

To demonstrate that the partition function and the Boltzmann factor retain the same form as Eq. (9) in the nonequilibrium situation, it is enough to follow the usual derivation, as for example, that given in Ref. [10]. Thus, consider a system composed by two subsystems \(A\) and \(B\). The probability for this composed system to be in the energy state \(E_{A+B}^*\) is \(P_{A+B}(E_{A+B}^*)\), where the superscript (*) reminds us that the system is out of equilibrium. If, as usual, the interaction energy can be neglected, thus the energy of the composed system is \(E_{A+B}^* = E_A^* + E_B^*\), and
\[
P_{A+B}(E_{A+B}^*) = P_A(E_A^*) + P_B(E_B^*)
\]
(22)
is the probability for the composed system to be in a particular state such that the subsystem \(A\) has an energy \(E_A^*\), and, at the same time, the subsystem \(B\) has an energy \(E_B^*\). Now, suppose that these two subsystems is put in contact with a third system, for example, a reservoir at temperature \(T\). While persisting the nonequilibrium situation (and even after that), the two subsystems \(A\) and \(B\) act independently of each other, with both subsystems eventually exchanging energy with the reservoir. Beside that, the energy exchanged with the reservoir by a given subsystem does not influence the energy that the other subsystem can exchange with this same reservoir. This assumption, valid for two systems in equilibrium with a reservoir, is here assumed to be valid also when the equilibrium was not reached. Therefore, as these events are independent, we can write
\[
P(E_{A+B}^*) = P(E_A^*)P(E_B^*).
\]
(23)
Differentiating Eq. (23) with respect to \(E_A^*\) and \(E_B^*\) and equating this result we obtain \((dP/dE_A^*) = P_A''\)
\[
P_A'(E_A^*)P_B(E_B^*) = P_A(E_A^*)P_B''(E_B^*)
\]
(24)
Next, separating the variables and equating the result to a constant, we have
\[
\frac{P_A'(E_A^*)}{P_A(E_A^*)} = \frac{P_B'(E_B^*)}{P_B(E_B^*)} = -\beta^*
\]
(25)
where $\beta^*$ is a constant independent from either $E_A^*$ or $E_B^*$. Of course, in the equilibrium situation we must have $\beta^* \to \beta = 1/kT$. From Eq. (25) follows, therefore, our desired result

$$P(E^*) = \frac{\exp(-\beta^*E^*)}{Z^*}, \quad (26)$$

where the partition function for the nonequilibrium situation is $Z^*$ and the index were dropped given the validity of Eq. (26) for the two subsystems.

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