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Sensitivity of the Population of States to the Value of *q* and Legitimate Range of *q* in Tsallis Statistics

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In the framework of the Tsallis statistical mechanics, we study the change of the population of states when the parameter q is varied, for some model systems; the results show that the difference between predictions of the Boltzmann-Gibbs and Tsallis statistics can be much smaller than the precision of any existing experiment. Also, the relation between privilege of rare and frequent events and the value of q is restudied. It is shown that positive q privilege frequent and negative q privilege rare events. Finally, the convergence criteria of the partition function of some simple model systems, in the framework of Tsallis statistical mechanics, is studied. Based on this study, we conjecture that $q \leq 1$, in the thermodynamic limit.

Keywords: Non-extensive statistical mechanics, Tsallis statistics, Legitimate range of q, Privilege of rare events, Sensitivity to q

INTRODUCTION

The Boltzmann-Gibbs (BG) entropy is defined as

$$S = -\mathrm{k}\sum_i p_i \ln p_i \tag{1}$$

where p_i is the probability of finding the system in the state i and k_B is the Boltzmann constant. According to the information theory-based formulation of statistical mechanics, we can consider the appropriate constraints for each ensemble and derive the probability of having the system in each of its states by finding the extremum of the entropy, (1) [1]. A generalized form for the entropy is [2]

$$S_q = \mathrm{k}\frac{1-\sum_i p_i^{\,q}}{q-1} \tag{2}$$

where q is the nonextensivity index, and k is a constant. Statistical Mechanics is generalized, by finding the extremum of (2) instead of (1). The result is called *Nonextensive Statistical Mechanics* or *Tsallis Statistics*. Equation (2) goes to Eq. (1) in the limit of $q \to 1$; also, every relation in this new statistics goes to its corresponding relation in the BG statistics, in the limit of $q \to 1$ [3]. The distribution functions arising in this statistics have found wide applications through sciences which were commonly considered to be out of the realm of statistical mechanics [4]. The q-expectation value of an operator A is defined through $\langle A\rangle_q = \sum_{i=1}^{W} p_i^{\,q} A_i$, where A_i represent the value of the observable A when the system is in the state i; this definition is replaced for the usual expectation value relation $\langle A\rangle = \sum_i p_i A_i$ in the BG statistics. It is claimed that, systems containing long-range interactions and/or long-range microscopic memory (*i.e.*, non-Markovian processes) have to be described by Tsallis Statistics.

The normalization condition and the energy constraint of the canonical ensemble in the BG statistics are, respectively,

$$\sum_{i=1}^{W} p_i = 1 \quad \text{and} \quad \sum_{i=1}^{W} p_i \varepsilon_i = U, \tag{3}$$

where ε_i represents the energy of the system in its i'th microstate and W is the number of microstates. While, the

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normalization condition is generally accepted, the energy constraint is somehow ambiguous in this generalization. First, it has been considered to be the same as (3) [2], this assumption yields

$$p_i = [(1-q)(\alpha + \beta\varepsilon_i)]^{\frac{1}{1-q}}, \tag{4}$$

where α and β are undetermined Lagrange multipliers. The position of the Lagrange multiplier α makes it difficult to find its value by using the normalization condition in (3). Thus, Curado and Tsallis suggest [5]

$$\sum_{i=1}^{W} p_i{}^q \varepsilon_i = U_q \tag{5}$$

as the energy constraint, which results, respectively in the following probability and partition function,

$$P_i = (Z_q)^{-1}\ [1-(1-q)\beta\varepsilon_i]^{\frac{1}{1-q}} \quad \text{and}$$
$$Z_q = \sum_i [1-(1-q)\beta\varepsilon_i]^{\frac{1}{1-q}} \tag{6}$$

There are more complex proposals for the normalization choice [6]; but, it is shown that these versions of P_i and Z_q are all equivalent to each other. They can be transformed to each other by the appropriate change of variable, *i.e.*, $\beta \rightarrow \beta'$ [7]. It should be mentioned that wherever the expression in square brackets is negative $P_i = 0$ by postulate.

We can ask whether it is possible for a system to have the same probability for each state both with a value of q not equal to one and with the BG statistics. Thus, in section (2), we study the sensitivity of the population of states to the value of q. The effect of the parameter q on the weight of rare and frequent events is addressed in section (3). The beauty of the statistical-mechanics is in evaluating macroscopic properties from microscopic properties. But in the non-extensive formalism, we need to know the value of q in addition to the microscopic properties. Although, there is no general way for evaluating q a priori; but, confining the range of possible values of q will be addressed in section (4).

SENSITIVITY OF THE POPULATION OF STATES TO THE VALUE OF *q*

The population of states in a two state system with energies 0 and ε are, respectively,

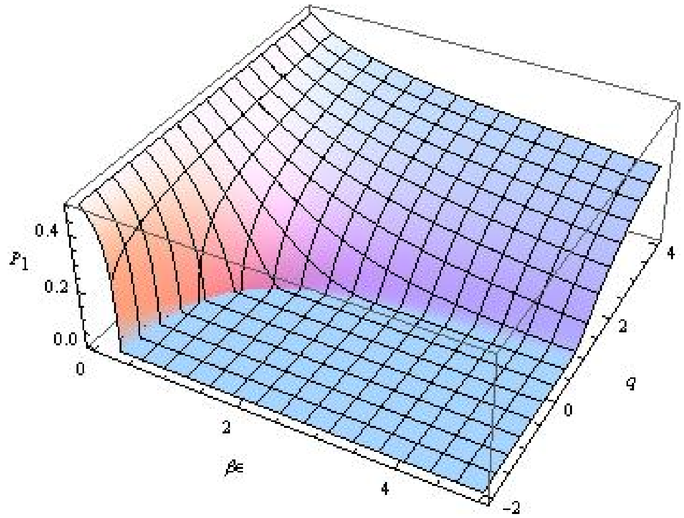

Fig. 1. The probability of a two-state system being in the higher energy state, *vs*. q and $\beta\varepsilon$.

$$P_0 = \frac{1}{1+[1-(1-q)\beta\varepsilon]^{\frac{1}{1-q}}} \quad \text{and} \quad P_1 = \frac{[1-(1-q)\beta\varepsilon]^{\frac{1}{1-q}}}{1+[1-(1-q)\beta\varepsilon]^{\frac{1}{1-q}}} \tag{7}$$

Because of the form of these equations, it is difficult to study their behavior analytically. P_1 *vs*. q and $\beta\varepsilon$ have been sketched in Fig. 1. At constant values of q, we can see the increase of P_1 toward 0.5 by decreasing the value of $\beta\varepsilon$, as expected by the inverse temperature interpretation of β. At constant $\beta\varepsilon$, it is seen that q is playing a role similar to the temperature.

It can be shown that the energy gap for a spin 1/2 system, in a magnetic field of the order of one Tesla, is of the order of 10^{-23} J for electrons and 10^{-27}J for nuclei. Thus, for a two state system we assume $\varepsilon = 10^{-25}$ J, yielding $\beta\varepsilon = 10^{-2}/\text{T}$.

Therefore, for a temperature range of 1 to 0.01 K, $\beta\varepsilon$ ranges from 0.01 to 1. P_1 as a function of q has been sketched in Fig. 2, for the values of $\beta\varepsilon$ equal to 0.01 and 4. In the first case, for a unit change in q the population of the higher energy state undergoes a change of the order of 10^{-5}, while in the second case that change is of the order of 10^{-1}. Thus, for a two state system the sensitivity to the value of q increases by decreasing the temperature. For a typical value of energy

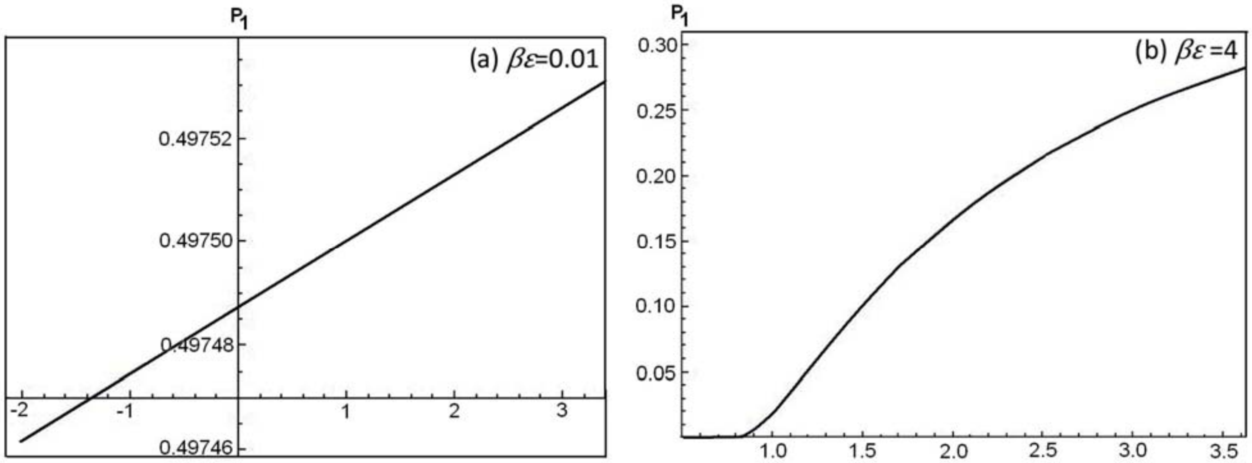

Fig. 2. The probability of a two-state system being in the excited state as a function of q.

separation between states, it seems impossible to observe the effect of a change in q, unless considering very low temperatures.

Studying S_q *vs*. q and $\beta\varepsilon$ shows that higher values of q reduce the sensitivity of S_q to $\beta\varepsilon$, and q is again playing a role similar to temperature. This is a peculiar graph, since it contains a number of peaks; its study is reserved for the future. For a harmonic oscillator, $h\upsilon/k_B$ ranges from 6215 for H_2 to 133 for K_2 [8]. Thus, $\Delta E = h\upsilon$ for the vibration of a diatomic molecule is of the order of 10^{-20} J, resulting in $\beta\varepsilon = 10^3/T$. Studying the populations of the ground and first excited state versus q at different values of $\beta\varepsilon$ shows that the sensitivity of the population of the ground and first excited states to the value of q increases with decreasing the temperature.

RARE EVENT WEIGHT

Since the expectation value of an observable is evaluated through $\langle A\rangle = \sum_i p_i A_i$, $q < 1$ ($q > 1$) is considered to privilege the rare (frequent) event [3] as an evident result of $P_i \leq 1$. But there is a complication arising from the fact that P_i itself is q-dependent. In Fig. 1 P_1 is the rare event and P_0 is the frequent event, this figure shows the greater the value of q the higher the probability of the rare event. Thus, in order to make a valid judgment regarding the effect of q on rare or frequent events, we must study

$$p_i^{\,q} \propto [1-(1-q)\beta\varepsilon_i]^{q/(1-q)} \tag{8}$$

To study (8), the definition of rare (frequent) as the state with smaller (larger) probability lose its meaning. But, we can define the state with a larger (smaller) ε as the rare (frequent) event. For large values of q, $P_i \propto [1-(1-q)\beta\varepsilon_i]^{-1}$, which is preferring the frequent event. A numerical study of (8) for small values of q shows the privilege of rare events for negative values of q (when they are allowed) and privilege of frequent events for positive values of q. The case of $q = 0$ resembles the case of $T = 0$ in Fermi-Dirac statistics, all states have the same weight, until the maximum value of $\beta\varepsilon = 1$ is reached.

THE LEGITIMATE RANGE OF q

In order to obtain physical properties of a system from its partition function, the partition function must be a definite function of the system's externally determined parameters. Therefore, a partition function which is divergent does not represent a physical system. For an N-dimensional (D) harmonic oscillator with a single frequency, υ, the partition function is

$$Z_q = \sum_{n=0}^{\infty} \frac{(N+n-1)!}{(N-1)!\,n!}\,[1+(q-1)\beta h\upsilon(n+N/2)]^{1/(1-q)} \tag{7}$$

where $n = \sum_i n_i$ is the sum of excitations. Note that, even in the absence of any interaction, the overall partition function of the system is not equal to multiplication of the single mode partition functions. In the limit of large n, the multiplicity (apart from the constant e^N/N^{N-1}) behaves like n^{N-1}. Therefore, the series converge for $q < 1+ 1/N$. For the 1-D case, it is easy to use the integral test and consider the truncation of the series to get $q < 2$.

For a d-D particle in a box, by approximating the sum in the partition function as an integral, we have $Z_q \propto \int_0^\infty \varepsilon^{(d/2-1)}[1+(q-1)\beta\varepsilon]^{1/(1-q)}d\varepsilon$. The convergence condition for this integral is $1+2/d > q$. In the case of 1-D, it is easy to show that the partition function is convergent for $q < 3$.

In the 2-D rigid rotor, $Z_q=\sum_{j=1}^{\infty} 2\,[1-(1-q)\beta(\hbar^2/2I)j^2]^{1/(1-q)}+1$. In the limit of large j, the terms of this series will behave like $j^{2/(1-q)}$. Considering the range of q where the series is truncated, and using the integral test, we have $q < 3$ as the acceptable range of q. In the 3-D rigid rotor, $Z_q = \sum_{j=0}^{\infty}(2j+1)\,[1-(1-q)\beta(\hbar^2/2I)j(j+1)]^{1/(1-q)}$. In the limit of large j, the terms behave like $j^{(3-q)/(1-q)}$; Therefore, $q < 2$ yields a convergent partition function.

CONCLUSIONS

In non-extensive statistical mechanics there is a limitation imposed on the values of q, due to the convergence of the partition function series. By considering the results of section (4), we can see that in an ideal gas, where $d \to \infty$ or in a bath of harmonic oscillators where $N \to \infty$, we have $q \leq 1$. Based on this observation, we conjecture that in the thermodynamic limit, regardless of the specific system under consideration, we must have $q \leq 1$. At the same time a large negative value of q doesn't seem physical because it freezes the system in a few number of its lower energy levels. For nano-systems the number of particles in the system is not so large; thus, q may be slightly larger than 1. This may be a starting point for the study of nonextensivity in nano-systems.

Revisiting the common believe regarding the effect of q on rare and frequent events show that contrary to what is considered in the literature positive values of q privilege the frequent event, while negative values of q privilege rare events.

Physical properties of a system depend on the value of q through the population of states. The sensitivity of the population of states to the value of q decreases with increasing the temperature, for some model systems. Therefore, it is possible for a system believed to obey the BG statistics, to obey the Tsallis statistics with a value of $q \neq 1$ but close to 1. This can be verifiable only in infinitely low temperature experiments.

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REFERENCES

[1] A. Katz, Principles of Statistical Mechanics, The Information Theory Approach W.H. Freeman, 1967.
[2] C. Tsallis J. Stat. Phys. 52 (1988) 479.
[3] C. Tsallis, in: S. Abe, Y. Okamoto (Eds.), Nonextensive Statistical Mechanics and its Applications, 560, Lecture Notes in Physics, Springer, New York, 2001.
[4] M. Gell-mann, C. Tsallis (Eds.), Nonextensive Entropy-Interdisciplinary Applications. SFI Studies in the Sciences of Complexity, Oxford University Press, Toronto, 2004.
[5] E. Curado, C. Tsallis. J. Phys. A 24 (1991) L69.
[6] C. Tsallis, R. Mendes, A. Plastino. Physica A 261 (1998) 543.
[7] G. Ferri, S. Martínez, A. Plastino, Physica A 347 (2005) 205.
[8] D. McQuarrie, Statistical Mechanics, University Science Books, Sausalito, 2000.