

THE NONEXTENSIVE GENERALIZATION OF BOLTZMANN-GIBBS STATISTICS
AND
ITS APPLICATIONS

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G. B. BAĞCI

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Sinan Bilikmen
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Ramazan Sever
Supervisor

Examining Committee Members

Prof. Dr. Namık Kemal Pak (METU, PHYS) _____

Prof. Dr. Ramazan Sever (METU, PHYS) _____

Prof. Dr. Metin Durgut (METU, PHYS) _____

Prof. Dr. Cevdet Tezcan (BAŞKENT Univ., EE) _____

Prof. Dr. Mehmet Tomak (METU, PHYS) _____

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Name- surname: G. B. Bađcı

Signature :

ABSTRACT

THE NONEXTENSIVE GENERALIZATION OF BOLTZMANN-GIBBS STATISTICS AND ITS APPLICATIONS

Bağcı, G. B.

Ph. D., Department of Physics

Supervisor: Prof. Dr. Ramazan Sever

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This thesis analyzes the nonextensive generalization of Boltzmann-Gibbs statistics and study its applications to some physical models such as isotropic rigid and non-rigid rotators. The thesis will also try to show what kind of internal energy constraint must be chosen for entropy optimization in a mathematically consistent manner.

Keywords: Nonextensive Statistics, Isotropic Rigid Rotator, Non-rigid Rotator, Constraints

ÖZ

BOLTZMANN-GİBBS İSTATİSTİĞİNİN NONEKSTENSİF GENELLEŞTİRİLMESİ VE UYGULAMALARI

Bağcı, G. B.

Doktora, Fizik Bölümü

Tez Yöneticisi: Prof. Dr. Ramazan Sever

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Bu tez Boltzmann-Gibbs istatistiğinin nonekstensif bir şekilde genelleştirilmesini çözümler ve bu genelleştirmenin, katı ve katı olmayan dönücü gibi bazı fiziksel modellere uygulanmasını çalışır. Tez, entropi optimizasyonu için matematiksel yapıyı bozmadan, hangi tür enerji konstraintlerinin de seçilmesi gerektiğini göstermeye çalışacaktır.

Anahtar Kelimeler: Nonekstensif istatistik , İotropik Katı Dönücü, Katı Olmayan Dönücü, Konstraintler

For

Oben Sezer

Ünal

and

Fikriye Teyzem

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CHAPTER 1

INTRODUCTION

If we would be asked about the *universality* of Newtonian mechanics, we would answer no justifiably. If the same question would be directed to a nineteenth century physicist, he would say yes to this question convinced that Newtonian mechanics is to be the ultimate theory. Today we know that Newtonian mechanics has to be replaced by quantum mechanics when the involved masses are very small, by special relativity if the involved speeds are very high compared to speed of light, or by general relativity if the masses are very large. As Tsallis writes: “... It is our present understanding that only in the $(m, 1/c, G) \rightarrow (0, 0, 0)$ limit, Newtonian mechanics appears to be strictly correct” [1].

The same kind of question may be asked about Boltzmann-Gibbs (BG) statistical mechanics and standard thermodynamics: Are they *universal*? In the first page of the second part of his Vorlesungen ueber Gastheorie [2], Ludwig Boltzmann qualifies the concept of ideal gas by writing: “When the distance at which two gas molecules interact with each other noticeably is vanishingly small relative to the average distance between a molecule and its nearest neighbor-or, as one can also say, when the space occupied by the molecules is negligible compared to the space filled by the gas-...”. If he would be our contemporary, he would perhaps tell us that he was addressing systems with *short range* interactions. Tisza, in his book on thermodynamics [3], writes: “The situation is different for the additivity postulate..., the validity of which cannot be inferred from general principles. We have to require that the interaction energy between thermodynamic systems be negligible. This assumption is closely related to the homogeneity postulate... From the molecular point of the view, additivity and homogeneity can be expected to be reasonable approximations for systems containing many particles, provided that the intermolecular forces have a short range character,...” when referring to the usual thermodynamic functions such as internal energy, entropy etc. Also, Peter Landsberg, in his Statistical Mechanics and Thermodynamics [4],

writes: "The presence of long-range forces causes important amendments to thermodynamics, some of which are not fully investigated as yet".

We now can cite some other examples from different areas of physics which shows clearly the need for a generalization of BG statistics. For example, A. M. Salzberg [5], in 1965, writes: "The exact equilibrium statistical mechanics of one and two dimensional gases, in which the particles interact through gravitational forces, is obtained. It is found that these systems are characterized by nonextensive thermodynamics leading to behaviour somewhat reminiscent of the formation of a star from interstellar dust... One interesting complication which arises in these gases is the nonextensive nature of the thermodynamic functions". W. C. Saslaw writes [6]: "This equation of state also illustrates another important general aspects of gravitational thermodynamics. When interactions are important, the thermodynamic parameters may lose their simple intensive and extensive properties for subregions of a given system". Also, R. Balian [7] writes along these lines, asserting: "Important development have taken place in mathematical physics. The conditions for the validity of the thermodynamic limit have been established, showing under what circumstances the entropy is an extensive quantity. This enables us to understand the limitations that exist, for instance in astrophysics...".

Some other objections opposed to universality of BG statistical mechanics are directed from black hole thermodynamics and superstrings. Landsberg writes [8]: "If two identical black holes are merged, the presence of long-range forces in the form of gravity leads to a more complicated situation, and the entropy is not extensive". Likewise, D. Pavon [9], in his book called Thermodynamics of Superstrings published in 1987, writes: "Superstring entropy is neither homogeneous i.e., $S(kE) \neq k S(E)$ nor concave but it is superadditive. Superadditivity means that the entropy of a composite system must be greater than the combined entropies of the subsystems making up the total system".

Another example might be cited from economics although it is not a physical science. The interaction between physics and economics is not new, indeed a good example can be cited to be the work by von Neumann and Morgenstern [10]. In 1992, economists Dow and Werlang states [11]: "With a nonadditive probability measure, the

“probability” that either of two mutually exclusive events will occur is not necessarily equal to the sum of their two “probabilities”. If it is less than the sum, the expected-utility calculations using this probability measure will reflect uncertainty aversion as well as (possibly) risk aversion. The reader may be disturbed by the “probabilities” that do not sum to one”.

Having cited these general examples related to a need of generalization of BG statistical mechanics, we will outline such an idea in the next chapter. In Chapter 3, we will apply this form of generalization to isotropic rigid and non-rigid rotators. In Chapter 4, we will discuss some issues related to constraints and relative entropy. Conclusion will form Chapter 5.

CHAPTER 2

THEORY OF NONEXTENSIVE STATISTICS

2.1 Outline of the Theory

In 1988, C. Tsallis [12] postulated the following form of generalized entropy:

$$S_q \equiv k \frac{1 - \sum_i p_i^q}{q-1} \quad (q \in R; \sum_i p_i = 1), \quad (2.1)$$

or, in general,

$$S_q \equiv k \frac{1 - \text{Tr} \rho^q}{q-1}, \quad (2.2)$$

where k is a positive constant, $\{p_i\}$ are the probabilities of microscopic states, and ρ the corresponding density operator. The parameter q is called nonextensivity parameter or entropic index. This new entropy formula recovers the usual Boltzmann-Gibbs entropy in the $q \rightarrow 1$ limit which has the form:

$$S_{BG} = -k \sum_{i=1} p_i \ln p_i. \quad (2.3)$$

The reason that q is called the nonextensivity parameter is due to following pseudo-additivity rule:

$$S_q(A+B) = S_q(A) + S_q(B) + (1-q) \frac{S_q(A)S_q(B)}{k}, \quad (2.4)$$

where A and B are two independent systems in the sense that the probabilities $A+B$ factorize into those of A and B . Since $S_q \geq 0$ for all values of q , we can say that $q < 1$, $q = 1$ and $q > 1$ correspond to superextensivity, extensivity and subextensivity respectively.

Another important property is the following. Suppose that the set of W possibilities is arbitrarily separated into two subsets having respectively W_L and W_M possibilities ($W_L + W_M = W$). We define

$$p_L = \sum_{i=1}^{W_L} p_i . \quad (2.5)$$

and

$$p_M = \sum_{i=W_L+1}^W p_i . \quad (2.6)$$

so that

$$S_q(\{p_i\}) = S_q(p_L, p_M) + p_L^q S_q(\{p_i / p_L\}) + p_M^q S_q(\{p_i / p_M\}), \quad (2.7)$$

where the sets $\{p_i / p_L\}$ and $\{p_i / p_M\}$ are the conditional probabilities. This would be the famous Shannon's property if there would occur p_L and p_M instead of p_L^q and p_M^q respectively. The equation (2.7) is a new property of Tsallis statistics. Since the probabilities $\{p_i\}$ are numbers between zero and unity, we will have

$$p_i^q > p_i \quad \text{for } q < 1 \quad (2.8)$$

and

$$p_i^q < p_i \quad \text{for } q > 1 \quad (2.9)$$

Therefore, $q < 1$ and $q > 1$ will respectively privilege the *rare* and the *frequent* events. This simple property lies at the heart of nonextensive statistics proposed by Tsallis.

Another interesting property is the following: The Boltzmann-Gibbs entropy S_{BG} satisfies the following relation

$$-k \left[\frac{d}{d\alpha} \sum_{i=1}^W p_i^\alpha \right]_{\alpha=1} = -k \sum_{i=1}^W p_i \ln p_i \equiv S_{BG}. \quad (2.10)$$

F. Jackson [13] had introduced in 1909 the following generalized differential operator (applied to an arbitrary function $f(x)$):

$$D_q f(x) \equiv \frac{f(qx) - f(x)}{qx - x}, \quad (2.11)$$

which recovers the usual derivative in the limit $q \rightarrow 1$. Sumiyoshi Abe [14] showed that

$$-k \left[D_q \sum_{i=1}^W p_i^\alpha \right]_{\alpha=1} = k \frac{1 - \sum_i p_i^q}{q - 1} \equiv S_q. \quad (2.12)$$

S_q has, with regard to $\{p_i\}$, a definite concavity for all values of q : It is concave for $q > 0$, and convex for $q < 0$. In this sense, it differs from Renyi entropy.

Having introduced this new form of nonextensive entropy, we must now proceed in derivation of nonextensive partition function, internal energy and heat capacity

expressions. But, in order to be able to derive equations related to thermodynamic observables such as heat capacity, we must define the form of constraint which we will use in nonextensive entropy extremization (maximize for $q>0$ and minimize for $q<0$). For the microcanonical ensemble (isolated system) there will be only one constraint, namely

$$\sum_{i=1}^W p_i = 1. \quad (2.13)$$

In this case, the optimization of S_q yields to equiprobability, i.e., $p_i = 1/W$ for $\forall i$, hence

$$S_q = k \ln_q W, \quad (2.14)$$

with

$$\ln_q x \equiv \frac{x^{1-q} - 1}{1-q}, \quad (2.15)$$

thus generalizing the celebrated Boltzmann's formula. Note that

$$\ln_q x = \ln x \quad \text{as } q \rightarrow 1. \quad (2.16)$$

The inverse function of $\ln_q x$ is e_q^x which is defined as

$$e_q^x \equiv [1+(1-q)x]^{1/(1-q)}. \quad (2.17)$$

As is being expected, $e_q^x = e^x$ as $q \rightarrow 1$. The problem arises in the canonical (i.e. the case in which the system is in thermal contact with a reservoir) and grand canonical cases (we will not address grand canonical case due to its resemblance to the canonical case). Historically, there did exist three choices for the internal energy constraint, which might be named as the first, second and third choices. The first choice [15] has been made right at the beginning of nonextensive formalism (NEXT hereafter) which happens to be

$$\sum_{i=1}^W p_i \varepsilon_i = U^{(1)}, \quad (2.18)$$

where the superindex (1) stands for first choice and the $\{\varepsilon_i\}$ are the eigenvalues of the (quantum) Hamiltonian of the system. In other words, the standard definition of internal energy has been maintained within generalization. It quickly became evident that this choice of internal energy constraint was inadequate for handling the serious

mathematical difficulties present in a variety of anomalous systems such as the Levy superdiffusion. Then, the second choice became the natural way out of the difficulties [16]. This choice is

$$\sum_{i=1}^W p_i^q \varepsilon_i = U_q^{(2)}, \quad (2.19)$$

where the superindex (2) stands for the second choice. The extremization of S_q now yields

$$p_i^{(2)} = \frac{[1 - (1 - q)\beta\varepsilon_i]^{1/(1-q)}}{Z_q^{(2)}}, \quad (2.20)$$

with the generalized partition function given by

$$Z_q^{(2)}(\beta) \equiv \sum_{j=1}^W [1 - (1 - q)\beta\varepsilon_j]^{1/(1-q)}, \quad (2.21)$$

which coincides with the result produced by the first choice excepting for the fact that now $(1-q)$ plays the role that was before played by $(q-1)$. The parameter β is the Lagrange parameter associated with the internal energy.

Inspection of Equations (2.20) and (2.21) shows us two main notions about NEXT formalism: First, these two equations recover the usual Boltzmann-Gibbs counterpart in the limit $q \rightarrow 1$. Second, as can be seen immediately by Equation (2.20), p_i depends on the microscopic energy as a *power law* instead of the familiar exponential. This distribution presents a cut-off (i.e., vanishing probabilities for energy levels high enough to produce a negative value for the argument of the e_q function) for all values of $q < 1$, whereas this phenomenon occurred, in the first choice, for $q > 1$. The present equilibrium distribution can be conveniently written as

$$p_i^{(2)} = \frac{e_q^{-\beta\varepsilon_i}}{\sum_{j=1}^W e_q^{-\beta\varepsilon_j}}, \quad (2.22)$$

which formally resembles the Boltzmann-Gibbs result. In fact, this resemblance to Boltzmann-Gibbs formalism will be present along the entire formalism. By introducing

$$T \equiv \frac{1}{k\beta}, \quad (2.23)$$

We write, for the temperature as an observable,

$$\frac{1}{T} = \frac{\partial S_q}{\partial U_q^{(2)}}, \quad (2.24)$$

Similarly, we have

$$F_q^{(2)} \equiv U_q^{(2)} - TS_q = -\frac{1}{\beta} \ln_q Z_q^{(2)}, \quad (2.25)$$

$$U_q^{(2)} = -\frac{\partial \ln_q Z_q^{(2)}}{\partial \beta}, \quad (2.26)$$

and

$$C_q^{(2)} \equiv T \frac{\partial S_q}{\partial T} = \frac{\partial U_q^{(2)}}{\partial T} = -T \frac{\partial^2 F_q^{(2)}}{\partial T^2}, \quad (2.27)$$

for free energy, internal energy and heat capacity respectively. As can be seen, Legendre structure remains valid for all values of q . In spite of its successes, this choice implies three strange consequences: The first consequence is that the distribution given by Eqs. (2.20) and (2.21) is not invariant through uniform translation of the energy spectrum $\{\varepsilon_i\}$, i.e., the thermodynamical results depend on the choice of the origin of energies. In practice, this point can be avoided by choosing the ground energy as the zero point for the energies. But, theoretically, this point is disturbing. The second consequence is related to q -expectation values i.e.,

$$O_q^{(2)} \equiv \langle O_i \rangle_q \equiv \sum_{i=1}^W p_i^q O_i, \quad (2.28)$$

where $\{O_i\}$ are the eigenvalues associated with an arbitrary observable O (we assume that the observable commutes with the density operator for simplicity). According to the definition above, we get

$$\langle 1 \rangle_q = \sum_{i=1}^W p_i^q. \quad (2.29)$$

This simple observation shows that the expectatin value of 1 is not equal to 1 if we go on using the choice expressed in Eq. (2.19). This point is not easy to interpret indeed.

Finally, the third unfamiliar consequence is that, if two systems A and B satisfy

$$p_{ij}^{A+B} = p_i^A p_j^B ; \varepsilon_{ij}^{A+B} = \varepsilon_i^A \varepsilon_j^B , \quad (2.30)$$

then we have

$$U_q^{(2)}(A+B) = U_q^{(2)}(A) + U_q^{(2)}(B) + (1-q) \left[U_q^{(2)}(A) \frac{S_q(B)}{k} + U_q^{(2)}(B) \frac{S_q(A)}{k} \right], \quad (31)$$

which generally differs from $U_q^{(2)}(A) + U_q^{(2)}(B)$. In other words, the first principle of thermodynamics (conservation of energy) does not preserve macroscopically the same form it has microscopically. One can argue that, if we are willing to consider nonadditivity of entropy, why is it so strange to accept the same for the energy? The point is that entropy is an informational quantity whereas energy is a mechanical one. Since NEXT formalism does not at all alter things at the level of the dynamics, it is kind of against intuition to have a break-down of energy conservation in this case.

We now discuss the third choice of constraint [17]. To be able to remedy all previous difficulties, we introduce the last internal energy constraint as follows:

$$\frac{\sum_{i=1}^W p_i^q \varepsilon_i}{\sum_{i=1}^W p_i^q} = U_q^{(3)}, \quad (2.32)$$

i.e., we weigh the Hamiltonian eigenvalues with the set of probabilities on the left hand side of the Equation above. These probabilities are referred to as *escort probabilities* [18] in the literature. The superscript (3) stands for third choice. The optimization of S_q now yields

$$p_i^{(3)} = \frac{\exp_q[-\beta(\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^W (p_j^{(3)})^q]^{1/(1-q)}}{\sum_{i=1}^W \exp_q[-\beta(\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^W (p_j^{(3)})^q]^{1/(1-q)}}, \quad (2.33)$$

where the denominator is nothing but the corresponding partition function denoted by

$\bar{Z}_q^{(3)}(\beta)$. It can be shown that

$$\frac{1}{T} = \frac{\partial S_q}{\partial U_q^{(3)}}, \quad (2.34)$$

and

$$F_q^{(3)} \equiv U_q^{(3)} - TS_q = U_q^{(3)} - \frac{1}{\beta} \ln_q \bar{Z}_q^{(3)}, \quad (2.35)$$

hence

$$S_q = k \ln_q \bar{Z}_q^{(3)}. \quad (2.36)$$

We notice that $\bar{Z}_q^{(3)}$ refers to the energy levels $\{\varepsilon_i\}$ with regard to $U_q^{(3)}$. In order to use, instead, zero as the reference energy, we can define $Z_q^{(3)}$ through

$$\ln_q Z_q^{(3)} = \ln_q \bar{Z}_q^{(3)} - \beta U_q^{(3)}. \quad (2.37)$$

Finally, we have

$$F_q^{(3)} = - \frac{1}{\beta} \ln_q Z_q^{(3)} \quad (2.38)$$

and

$$U_q^{(3)} = - \frac{\partial \ln_q Z_q^{(3)}}{\partial \beta}. \quad (2.39)$$

For specific heat expression, we have

$$C_q^{(3)} \equiv T \frac{\partial S_q}{\partial T} = \frac{\partial U_q^{(3)}}{\partial T} = -T \frac{\partial^2 F_q^{(3)}}{\partial T^2}. \quad (2.40)$$

Obviously, this last choice too preserves the Legendre structure. It is also the remedy for all our previous difficulties.

First, if we add a constant ε_0 to all $\{\varepsilon_i\}$ we have that $U_q^{(3)}$ becomes $U_q^{(3)} + \varepsilon_0$ which leaves invariant the differences $\{\varepsilon_i - U_q^{(3)}\}$, which, in turn leaves *invariant* the set of probabilities $\{p_i^{(3)}\}$, hence all thermostatical quantities.

Second, the definition of $U_q^{(3)}$ suggests the following *normalized q-expectation values*:

$$O_q^{(3)} \equiv \langle\langle O_i \rangle\rangle_q \equiv \frac{\sum_{i=1}^W p_i^q O_i}{\sum_{i=1}^W p_i^q} = \frac{\langle O_i \rangle_q}{\langle 1 \rangle_q}, \quad (2.41)$$

where O is any observable. It is trivial now to show that $\langle\langle 1 \rangle\rangle_q = 1$ for $\forall q$.

Third, it is also trivial to show that, for systems A and B mentioned previously [19],

$$U_q^{(3)}(A+B) = U_q^{(3)}(A) + U_q^{(3)}(B), \quad (2.42)$$

thus recovering the standard thermodynamics.

One important remark to be made is that if we take out as factors, in both numerator and denominator of Eq. (2.33), the quantity $\exp_q[-\beta(\varepsilon_i - U_q^{(3)}) / \sum_{j=1}^W (p_j^{(3)})^q]$, and then cancel them, we obtain

$$p_i^{(3)}(\beta) = \frac{e_q^{-\beta' \varepsilon_i}}{Z_q^{(3)'}} \quad (2.43)$$

with

$$\beta' = \frac{\beta}{\sum_{j=1}^W (p_j^{(3)})^q + (1-q)\beta U_q^{(3)}}. \quad (2.44)$$

Therefore, by defining $T' \equiv 1/(k\beta')$ and using the following relation

$$\sum_{i=1}^W (p_i^{(3)})^q = (\bar{Z}_q^{(3)})^{1-q}, \quad (2.45)$$

We get

$$T'(T) = T[Z_q^{(3)}(\beta(T))]^{1-q} + (1-q)U_q^{(3)}(\beta(T))/k. \quad (2.46)$$

We can immediately check that

$$p_i^{(3)}(\beta) = p_i^{(2)}(\beta') \quad (2.47)$$

and

$$Z_q^{(3)' }(\beta) = Z_q^{(2)}(\beta'). \quad (2.48)$$

In other words, the equilibrium probabilities associated with the third choice *coincide* with those associated with the second choice *but with a renormalized temperature* given by Eq. (2.48). This is the reason for which *all the theorems* which do not explicitly use the specific temperature dependence of the involved thermostistical quantities (but rather only use that the system is at some fixed arbitrary fine temperature) remain valid. Moreover, all the systems for which the second-choice formalism was successful in providing satisfactory theoretical and/or experimental results such as anomalous diffusions and turbulence are also successful in the third-choice formalism because they do not involve specific thermal dependences.

The main change about this last internal energy constraint is that we made use of what is called *escort probabilities*. Let us make some important observations about the escort probabilities $\{P_i^{(q)}\}$ defined through

$$P_i^{(q)} \equiv \frac{P_i^q}{\sum_{j=1}^W P_j^q} \quad (2.49)$$

with

$$\sum_{i=1}^W P_i^{(q)} = 1 \quad (2.50)$$

from which follows the dual relation

$$p_i = \frac{[P_i^{(q)}]^{1/q}}{\sum_{j=1}^W [P_j^{(q)}]^{1/q}} \quad (2.51)$$

as well as

$$\sum_{i=1}^W p_i^q = \frac{1}{\left\{ \sum_{i=1}^W [P_i^{(q)}]^{1/q} \right\}^q} . \quad (2.52)$$

The Eqs. (2.49) and (2.51) have, within the present formalism, a role analogous to the direct and inverse Lorentz transformations in Special Relativity.

Second, we notice that $O_q^{(3)}$ becomes an usual mean value when expressed in terms of probabilities $\{P_i^{(q)}\}$, i.e.,

$$O_q^{(3)} = \sum_{i=1}^W P_i^{(q)} O_i . \quad (2.53)$$

Third, the entropy can be written as

$$S_q = k \frac{1 - \left\{ \sum_{i=1}^W [P_i^{(q)}]^{1/q} \right\}^{-q}}{q-1} . \quad (2.54)$$

Consequently, the equilibrium escort probabilities can be alternatively found by optimizing S_q as given by Eq. (2.54) with the constraints (2.50) and

$$\sum_{i=1}^W P_i^{(q)} \varepsilon_i = U_q^{(3)} = U_q . \quad (2.55)$$

Although the third choice appears to be conceptually simpler than the second one, calculations of concrete thermal dependences look like being much harder, since the equations for the $\{p_i\}$ are implicit. If we are not interested in thermal dependences, we better work within the second choice. But, even if we want to compute thermal dependences, there is an easy way to avoid the implicit equations for the probabilities. Indeed, inspecting Eq. (2.44) and after some algebra, we get

$$\beta = \beta' \frac{\sum_{j=1}^W [p_j^{(2)}(\beta')]^q}{1 - (1-q)\beta' U_q^{(2)}(\beta') / \sum_{j=1}^W [p_j^{(2)}(\beta')]^q}. \quad (2.56)$$

Armed with this equation, we can implement a practical prescription to compute thermodynamical properties within the third choice, without the need to solve implicit equations on the microstates probabilities $p_j^{(3)}$. First of all, one has to compute, for each value of β' belonging to an appropriate range, and using the expressions (2.43), the microstate probabilities $p_j^{(3)}(\beta) = p_j^{(2)}(\beta')$. Then it is possible to evaluate the quantities

$$\sum_{j=1}^W (p_j^{(3)})^q \text{ and } U_q^{(3)}.$$

Finally, by recourse to Eq. (2.56) one obtains the corresponding values of the true inverse temperature β . Then, for each value of the parameter β' , one has now the concomitant values, respectively, of β and $U_q^{(3)}$. Of course, these last ones are the physically meaningful ones. Within this scheme, β' is only an *intermediate* parameter introduced for the sake of computation. Specific heat will be

$$C_q^{(3)}(\beta) = -k\beta^2 \frac{dU_q^{(3)}(\beta)}{d\beta}. \quad (2.57)$$

We can also address the issues of heat and work within the third choice[20]. If we use Eq. (2.36) we obtain

$$dS_q = k \frac{d\bar{Z}_q^{(3)}}{(\bar{Z}_q^{(3)})^q}, \quad (2.58)$$

which, performing the differential operation on partition function explicitly yields

$$dU_q^{(3)} = TdS_q + \sum_{j=1}^W \frac{(p_j^{(3)})^q}{\sum_{i=1}^W (p_i^{(3)})^q} d\varepsilon_j = \sum_{j=1}^W P_j^{(q)} d\varepsilon_j. \quad (2.59)$$

We can consequently identify (for a quasi-static process) the heat transfer as

$$\delta Q_q^{(3)} = TdS_q, \quad (2.60)$$

and the work performed as

$$\delta W_q^{(3)} = \sum_r F_r^{(3)} d\lambda_r, \quad (2.61)$$

where the generalized force $F_r^{(3)}$ is given by

$$F_r^{(3)} \equiv - \frac{\sum_{j=1}^W (p_j^{(3)})^q \partial \varepsilon_j / \partial \lambda_r}{\sum_{j=1}^W (p_j^{(3)})^q} = - \sum_{j=1}^W P_j^{(q)} \frac{\partial \varepsilon_j}{\partial \lambda_r}, \quad (2.62)$$

the set $\{\lambda_r\}$ being the external parameters on which the energy spectrum depends. In other words, we have that

$$dU_q^{(3)} = \delta Q_q^{(3)} - \delta W_q^{(3)}, \quad (2.63)$$

i.e., as we already saw previously, *the first principle of thermodynamics holds as usual for all q values* [21].

2.2 Nonextensive Ehrenfest Theorem

In this Section, we will try to see what kind of form we will have for the Ehrenfest theorem in nonextensive context [22]. Since we will not make use of explicit dependence on specific heat, we can use second choice. Using Eqs. (2.2), (2.13) and (2.19), through variational procedure we have

$$\delta [S_q - \lambda_0 \text{Tr}(\rho) - \sum_i \lambda_i \text{Tr}(\rho^q O_i)] = 0, \quad (2.64)$$

where the λ 's are Lagrange multipliers related to normalization and second constraint respectively and O_i is any operator.

The Eq. (2.64) yields the density matrix which extremalizes Tsallis entropy which is

$$\rho = Z^{-1} (1 - (-q) \sum_i \lambda_i O_i)^{1/(1-q)}, \quad (2.65)$$

where Z stands for

$$Z = [q^{-1} (1 - (q-1)\lambda_0)]^{1/(1-q)}. \quad (2.66)$$

Having seen how to handle density matrix in nonextensive statistics, we observe that if D stands for the statistical operator, the von Neumann-Liouville equation governs the temporal evolution of any analytic function of D . In particular, if H stands for Hamiltonian operator, one has

$$d(D^q)/dt = (-i/\hbar) [H, D^q], \quad (2.67)$$

from which follows

$$d(\langle O_i \rangle_q)/dt = (-i/\hbar) \langle [O_i, H] \rangle_q, \quad (2.68)$$

i.e., the generalized Tsallis expectation values obey Ehrenfest theorem.

2.3 Nonextensive Langevin and Fokker-Planck Equations

As is well known, the Langevin and Fokker-Planck equations lie at the heart of ordinary non-equilibrium statistical mechanics [23]. For a Brownian particle i moving under a potential V and subject to an additional random force $F_i(t)$, we have

$$\frac{dX_i}{dt} = -\frac{1}{\eta} \frac{\partial V}{\partial X_i} + F_i(t), \quad (2.69)$$

where η is the viscosity and $F_i(t)$ is a Gaussian distributed random variable with zero mean and variance

$$\langle F_i(t_1) F_j(t_2) \rangle = 2A \delta_{ij} \delta(t_2 - t_1). \quad (2.70)$$

The associated Fokker-Planck equation that describes the temporal evolution of the probability distribution of X_i , $P(X_i, t)$ has the form

$$\frac{\partial P}{\partial t} = \sum_i \left[\frac{\partial}{\partial X_i} \frac{1}{\eta} \left(\frac{\partial V}{\partial X_i} P \right) + A \frac{\partial^2 P}{\partial X_i^2} \right]. \quad (2.71)$$

Under very general conditions on the potential V , the Fokker-Planck equation has a stationary solution that corresponds to the canonical Boltzmann-Gibbs distribution $P \propto e^{-\beta V}$ [24].

To be able to generalize the Eqs. (2.69) and (2.71), we introduce a *generalized potential*

$$\bar{V} = \frac{1}{\beta(q-1)} \ln[1 + \beta(q-1)V]. \quad (2.72)$$

Then, we can write the Langevin and Fokker-Planck equations in terms of \bar{V} *preserving the form of the equations* but only substituting \bar{V} instead of V into the Eqs. (2.69) and (2.71).

If we have

$$P \propto [1 - \beta(1-q)V]^{1/(1-q)}, \quad (2.73)$$

Then

$$\frac{\partial P}{\partial t} = 0. \quad (2.74)$$

Moreover

$$\begin{aligned} \frac{\partial P}{\partial X_i} &= -\frac{\beta P}{1 - \beta(1-q)V} \frac{\partial V}{\partial X_i} \\ &= \frac{P}{(1-q)} \frac{\partial}{\partial X_i} \ln[1 - \beta(1-q)V] \\ &= -\beta P \frac{\partial \bar{V}}{\partial X_i}. \end{aligned} \quad (2.75)$$

Substitution of these terms back into Eq. (2.71), we get

$$0 = \sum_i \frac{\partial}{\partial X_i} ((1/\eta - A\beta) \frac{\partial \bar{V}}{\partial X_i} P). \quad (2.76)$$

This last equality is satisfied if

$$\eta A \beta = 1 \quad (2.77)$$

This is one of the celebrated Einstein relations for the Brownian motion that is preserved invariant in the NEXT formalism [25].

It is interesting to note that the generalized canonical distribution can be written as a standard canonical distribution in terms of \bar{V} ,

$$P \propto [1 - \beta(1-q)V]^{1/(1-q)} \quad (2.78)$$

$$= \exp\left(-\beta \frac{1}{\beta(q-1)} \ln[1 - \beta(1-q)V]\right) \quad (2.79)$$

$$= e^{-\beta\bar{V}} \quad (2.80)$$

2.4 Nonextensive Liouville Equation

Let us consider a general classical deterministic dynamical system whose evolution is governed by the equations of motion

$$\frac{dz}{dt} = w(z), \quad (2.81)$$

where z denotes a point in the concomitant N -dimensional phase space and both z and $w \in R^N$. A statistical ensemble of systems evolving according to Eq. (2.81) is described by a probability distribution $F(z,t)$. The evolution of this distribution is given by the well-known Liouville equation [26]

$$\frac{\partial F}{\partial t} + \nabla \cdot (wF) = 0, \quad (2.82)$$

where ∇ denotes the N -dimensional differential operator

$$\nabla = \left(\frac{\partial}{\partial z_1}, \frac{\partial}{\partial z_2}, \dots, \frac{\partial}{\partial z_N} \right). \quad (2.83)$$

In the particular case of a Hamiltonian system with n degrees of freedom, we have $N=2n$, $z = (q_1, q_2, \dots, q_n, p_1, \dots, p_n)$, and

$$w_i = \frac{\partial H}{\partial p_i} \quad (i = 1, \dots, n) \quad (2.84)$$

$$w_i = -\frac{\partial H}{\partial q_i} \quad (i = n+1, \dots, 2n) \quad (2.85)$$

where the q_i , p_i represent generalized coordinates and momenta, respectively. Hamiltonian dynamics has the important feature of having zero divergence [27]

$$\nabla \cdot w = \sum_{i=1}^n \left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) = 0. \quad (2.86)$$

The rate of change of a dynamical quantity $A(z,t)$ is given by

$$\frac{dA}{dt} = w \cdot \nabla A + \frac{\partial A}{\partial t}. \quad (2.87)$$

Given a probability distribution F , its associated escort distribution \tilde{F} is defined as

$$\tilde{F} = \frac{F^q}{\int F^q d^N z} \quad (2.88)$$

and the escort-mean value reads

$$\langle A \rangle_q = \int \tilde{F} A d^N z. \quad (2.89)$$

We also define the quantity I_q as

$$I_q = \int F^q d^N z. \quad (2.90)$$

If we look for its derivative we see

$$\frac{dI_q}{dt} = \int \frac{\partial F^q}{\partial t} d^N z = q \int \frac{\partial F}{\partial t} F^{q-1} d^N z, \quad (2.91)$$

that, due to Eq. (2.82) becomes

$$\frac{dI_q}{dt} = -q \int [\nabla \cdot (wF)] F^{q-1} d^N z, \quad (2.92)$$

which, after integration by parts twice becomes

$$\frac{dI_q}{dt} = (1-q) \int F^q [\nabla \cdot w] d^N z = (1-q) I_q \langle [\nabla \cdot w] \rangle_q. \quad (2.93)$$

Before proceeding further along these lines, let us inspect the rate of change of nonextensive entropy: This entropy can be written in terms of probability distribution F to give

$$S_q[F] = \frac{1}{q-1} [1 - \int F^q d^N z] = \frac{1}{q-1} [1 - I_q], \quad (2.94)$$

which entails that

$$I_q = [1 + (1-q)S_q]. \quad (2.95)$$

Using Eqs. (2.93) and (2.95), we obtain

$$\frac{dS_q}{dt} = [1 + (1-q)S_q] \langle \nabla \cdot w \rangle_q. \quad (2.96)$$

We see that the rate of change of S_q is determined by the escort-mean value of the divergence of the flow in the phase space,

$$\langle \nabla \cdot w \rangle_q = \frac{\int F^q \nabla \cdot w d^N z}{\int F^q d^N z}. \quad (2.97)$$

Eq. (2.96) is a generalization of an important relation connecting the time derivative of Boltzmann-Gibbs entropy and the average divergence of the phase space flow [28, 29], which is recovered when $q=1$,

$$\frac{dS_1}{dt} = \langle \nabla \cdot w \rangle. \quad (2.98)$$

The particular case of interest is the one where the divergence of flow in phase space is constant,

$$\nabla \cdot w = D = \text{const.}, \quad (2.99)$$

that is, when $\nabla \cdot w$ assumes a constant value D throughout phase space. In this case, we have

$$\frac{dS_q}{dt} = D[1 + (1-q)S_q], \quad (2.100)$$

which leads to

$$S_q(t) = \frac{1}{1-q} \{ [1 + (1-q)S_q(t=0)] \exp[(1-q)Dt] - 1 \}. \quad (2.101)$$

For $\forall q \neq 1$, S_q depends on time in an exponential way, but it exhibits a linear time dependence for $q=1$. Let us write Eq. (2.89) in the following form

$$\langle A \rangle_q = \frac{1}{[1 + (1-q)S_q]} \int F^q A d^N z, \quad (2.102)$$

in terms of $S_q[F]$. Taking the time derivative of Equation above, using Eqs. (2.87), (2.93), (2.96) and following Equation

$$\frac{d}{dt} \int F^q A d^N z = \int F^q (w \cdot \nabla A) d^N z + (1-q) \int F^q A (\nabla \cdot w) d^N z + \int F^q \frac{\partial A}{\partial t} d^N z. \quad (2.103)$$

We finally get

$$\frac{d}{dt} \langle A \rangle_q = \langle w \cdot \nabla A \rangle_q + (1-q) \{ \langle A \nabla \cdot w \rangle_q - \langle A \rangle_q \langle \nabla \cdot w \rangle_q \} + \langle \frac{\partial A}{\partial t} \rangle_q. \quad (2.104)$$

In the limit case $q \rightarrow 1$, one recovers the standard equation of motion for the mean value of A

$$\frac{d}{dt} \langle A \rangle_1 = \langle w \cdot \nabla A \rangle_1 + \langle \frac{\partial A}{\partial t} \rangle_1. \quad (2.105)$$

Finally, we address the evolution equation for the escort distributions \tilde{F} :

$$\frac{\partial \tilde{F}}{\partial t} = \frac{1}{[1 + (1-q)S_q]^2} [[1 + (1-q)S_q] q F^{q-1} \frac{\partial F}{\partial t} - (1-q) \frac{dS}{dt} F^q], \quad (2.106)$$

which, after some algebra, leads to the evolution equation

$$\frac{\partial \tilde{F}}{\partial t} + \nabla \cdot (\tilde{F} w) = (1-q) \tilde{F} [\nabla \cdot w - \langle \nabla \cdot w \rangle_q]. \quad (2.107)$$

The right hand side of Eq. (2.107) has the same form as the corresponding part of Liouville equation. But, when $q \neq 1$, the left hand side of Eq. (2.107) (which vanishes in Liouville equation) is not in general equal to zero. However, this term vanishes for all q values if the flow in phase space has a constant divergence (Eq. (2.99)) [30].

CHAPTER 3

RIGID AND NON-RIGID ROTATOR MODELS IN NONEXTENSIVE THERMOSTATISTICS

3.1 General Outline of the Rigid And Non-Rigid Rotators

Rotating molecules can also absorb and emit infra-red and micro-wave radiation. The frequencies of absorption can be used to determine the rotational energy levels of the molecule accurately. The expression for the energy levels of the rigid rotator is given by the expression [31]

$$E_l = \frac{h^2}{8\pi^2 I} l(l+1) . \quad (3.1)$$

In this expression l is the rotational quantum number and I is the moment of inertia of the molecule which is defined as

$$I = \sum_i^N m_i r_i^2 = \mu r^2 , \quad (3.2)$$

where m_i is the mass of the i th atom which is at a distance r_i from the centre of mass of the molecule around which rotations take place and μ is the reduced mass. From moments of inertia, the geometry of the molecule can be accurately evaluated. Microwave and infra-red spectroscopy of gases are some of the most powerful tools to determine the structure of molecules [32].

The vibrational spectra of gases do not show the simple band systems as predicted by the harmonic/anharmonic oscillator models, but are generally very complex. The fine structure can be adequately explained by the coupling of rotation and vibration i.e., the rotational quantum number changes also during a vibrational transition. The combined harmonic oscillator plus rigid rotator approach predicts the energy levels for a rotating oscillator to be

$$E = h\nu\left(n + \frac{1}{2}\right) + \frac{h^2}{8\pi^2 I} l(l+1). \quad (3.3)$$

Real molecules are neither harmonic nor rigid rotators; the vibrations are anharmonic and bond length changes during vibrational transitions and during rotation (centrifugal stretching). Suitable corrections must be made to take these effects into account.

Instead of studying the quantum nature of the rigid rotator separately, the Schrodinger equation of non-rigid rotator plus harmonic oscillator will be directly solved in this Section. For this purpose, we consider a diatomic molecule consisting of atoms having masses m_1 and m_2 which are at a distance r apart. The atoms are r_1 and r_2 cm away from the centre of mass M of the molecule respectively. The Cartesian coordinates of the first atom are (x_1, y_1, z_1) and those of the second atom (x_2, y_2, z_2) . The classical Hamiltonian function $H = T + V$, where T is the kinetic energy and V the potential energy function, in Cartesian coordinates given by

$$H = \frac{1}{2} m_1 \left[\left(\frac{dx_1}{dt} \right)^2 + \left(\frac{dy_1}{dt} \right)^2 + \left(\frac{dz_1}{dt} \right)^2 \right] + \frac{1}{2} m_2 \left[\left(\frac{dx_2}{dt} \right)^2 + \left(\frac{dy_2}{dt} \right)^2 + \left(\frac{dz_2}{dt} \right)^2 \right] + V(x, y, z). \quad (3.4)$$

To simplify the expression for V , a transformation to spherical coordinates r, θ and ϕ is made. The origin of the spherical coordinate system is chosen in such a way that the origin is at one of the two atoms. In this system

$$V = \frac{1}{2} kr^2. \quad (3.5)$$

The coordinate of the centre of mass on the Y-axis are given by

$$m_1 y_1 + m_2 y_2 = (m_1 + m_2) y, \quad (3.6)$$

and similarly for the X- and Z-axis. Writing

$$x_2 - x_1 = r \sin \theta \cos \phi, \quad (3.7)$$

$$y_2 - y_1 = r \sin \theta \sin \phi, \quad (3.8)$$

$$z_2 - z_1 = r \cos \theta. \quad (3.9)$$

If (x_2, y_2, z_2) are eliminated, we finally get

$$x_1 = x - \left(\frac{m_2}{m_1 + m_2}\right)r \sin \theta \cos \phi, \quad (3.10)$$

$$y_1 = y - \left(\frac{m_2}{m_1 + m_2}\right)r \sin \theta \sin \phi, \quad (3.11)$$

$$z_1 = z - \left(\frac{m_2}{m_1 + m_2}\right)r \cos \theta. \quad (3.12)$$

Substitution (including the time derivatives) yields

$$H = \frac{1}{2}(m_1 + m_2)\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2\right] + \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) + \frac{1}{2}kr^2 \quad (3.13)$$

This expression must be changed to contain the momenta conjugate to x , y , z , r , θ and ϕ to be of the use. The momentum of a particle in one dimension is defined as

$$p_x = mv. \quad (3.14)$$

The momenta conjugate to r , θ and ϕ respectively are

$$p_r = \mu\dot{r}; \quad p_\theta = \mu r^2\dot{\theta}; \quad p_\phi = \mu r^2 \sin^2 \theta \dot{\phi}. \quad (3.15)$$

Substitution of Eqs. above into the Eq. (3.13), we obtain

$$H = \frac{1}{2(m_1 + m_2)}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2\mu}\left(p_r^2 + \frac{p_\theta^2}{r^2} + \frac{p_\phi^2}{r^2 \sin^2 \theta}\right) + V(r). \quad (3.16)$$

In quantum mechanics, we have

$$p_q \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial q}. \quad (3.17)$$

We obtain the quantum mechanical Hamiltonian by inserting Eq. (3.17) into Eq. (3.16)

$$H = \frac{\hbar^2}{2(m_1 + m_2)}\nabla^2 + \frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] + V(r) \quad (3.18)$$

This operator consists of two separate parts-one containing only r , θ and ϕ and the other only x , y , z . the Schroedinger equation reads [33]

$$H\Psi = E\Psi. \quad (3.19)$$

To separate Schroedinger equation for the Hamiltonian above, we write

$$\Psi(x, y, z, r, \theta, \phi) = \psi(x, y, z)\Phi(r, \theta, \phi), \quad (3.20)$$

each being equal to a separation constant E. It yields

$$\nabla^2 \psi + \frac{2}{\hbar^2}(E' - E)\psi = 0, \quad (3.21)$$

and

$$\begin{aligned} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Phi}{\partial \theta} \right) + \\ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 \Phi}{\partial \phi^2} + \frac{2\mu}{\hbar^2} (E - V(r))\Phi = 0 \end{aligned} \quad (3.22)$$

Equation (3.21) describes the translational motion of the molecule. The rotating-vibrating molecule can, therefore, be treated as if were stationary with one atom at the spherical coordinate origin. It is in general possible to separate the translational motion of atomic and molecular systems from the internal motion by the same procedure adopted here.

The equation describing the internal degrees of freedom may be further separated by substituting

$$\Phi(r, \theta, \phi) = R(r) \cdot \chi(\theta, \phi), \quad (3.23)$$

which gives the following two equations after arrangement

$$\frac{1}{R} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{2\mu}{\hbar^2} (E - V(r))r^2 = \lambda, \quad (3.24)$$

and

$$-\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \chi}{\partial \theta} \right) - \frac{1}{\sin^2 \theta} \frac{\partial^2 \chi}{\partial \phi^2} = \lambda \chi, \quad (3.25)$$

where λ is a constant. The Eq. (3.24) is called *radial equation*. The second equation can be further split into two separate equations by the substitution

$$\chi(\theta, \phi) = \Theta(\theta) \cdot \Phi(\phi), \quad (3.26)$$

yielding,

$$\frac{d^2 \Phi}{d\phi^2} + m^2 \Phi = 0, \quad (3.27)$$

and

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \Theta}{\partial \theta} \right) - \frac{m^2 \Theta}{\sin^2 \theta} + \lambda \Theta = 0. \quad (3.28)$$

Eqs. (3.27), (3.28) and (3.24) must be solved (in that order) to determine the energy values. The general solution for Eq. (3.27) is

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi}. \quad (3.29)$$

This function is required to be single valued at the point $\phi = 0$ and also at the point $\phi = 2\pi$; This can only be when m is zero or a positive or negative integer, i.e., $m = 0, \pm 1, \pm 2, \dots$. Because m occurs as the square in the differential equation, both $\Phi(m)$ and $\Phi(-m)$ satisfy the equation for a given value of $|m|$. There are thus two equivalent solutions for $|m \neq 0|$

$$\begin{aligned} \Phi_m &= \frac{1}{\sqrt{\pi}} \sin|m|\phi \\ \Phi_m &= \frac{1}{\sqrt{\pi}} \cos|m|\phi \end{aligned} \quad (3.30)$$

and

for $m = 0$,

$$\Phi_0 = \frac{1}{\sqrt{2\pi}}. \quad (3.31)$$

The Eq. (3.28) can be solved by changing to a new variable,

$$z = \cos \theta, \quad (3.32)$$

and writing

$$\Theta(\theta) = P(z), \quad (3.33)$$

also noting that

$$\frac{d\Theta}{d\theta} = \frac{dP}{dz} \frac{dz}{d\theta} = -\left(\frac{dP}{dz}\right) \sin \theta. \quad (3.34)$$

The result of the substitutions yields

$$\frac{d}{dz} \left[(1-z^2) \frac{dP(z)}{dz} \right] + \left[\lambda - \frac{m^2}{1-z^2} \right] P(z) = 0. \quad (3.35)$$

This equation is identical with the associated Legendre differential equation [34], λ having the characteristic values

$$\lambda = l(l+1), \quad (3.36)$$

where l is an integer, i.e., $l = |m|, |m|+1, \dots$. The solutions for the associated Legendre equations are the associated Legendre polynomials of degree l and order $|m|$, which are defined as

$$P_l^{|m|}(z) = (1-z^2)^{|m|/2} \frac{d^{|m|}}{dz^{|m|}} P_l(z), \quad (3.37)$$

where $P_l(z)$ is the Legendre polynomial in z having degree l i.e.,

$$P_l^m(z) = \frac{(1-z^2)^{m/2} (2l)!}{2^l l! (l-m)!} \left[z^{l-m} - \frac{(l-m)(l-m-1)}{2(2l-1)} z^{l-m-2} + \dots \right]. \quad (3.38)$$

The solution of the Θ equation is thus

$$\Theta_{lm} = \sqrt{\frac{(2l+1)(l-|m|)!}{2(l+|m|)!}} P_l^{|m|}(\cos \theta). \quad (3.39)$$

For example, we will have

$$\Theta_{0,0}(\theta) = \frac{\sqrt{2}}{2}, \quad (3.40)$$

or

$$\Theta_{1,-1}(\theta) = \Theta_{1,+1}(\theta) = \frac{\sqrt{3}}{2} \sin \theta. \quad (3.41)$$

To solve radial equation, the substitution

$$R(r) = \frac{S(r)}{r}, \quad (3.42)$$

is made in the Eq. (3.24). It then becomes

$$\frac{d^2 S}{dr^2} + \left[-\frac{l(l+1)}{r^2} + \frac{2\mu}{\hbar^2} (E - V(r)) \right] S = 0. \quad (3.43)$$

The form of $V(r)$ is important. As a first approximation, $V(r)$ is chosen to be harmonic in the change in the internuclear distance, i.e.

$$V(r) = \frac{k}{2} (r - r_e)^2. \quad (3.44)$$

If variables are changed, putting $r-r_e = x$, this equation becomes

$$\frac{d^2 S}{dx^2} + \left[-\frac{l(l+1)}{(x+r_e)^2} + \frac{2\mu}{\hbar^2} \left(E - \frac{k}{2} x^2 \right) \right] S = 0. \quad (3.45)$$

If the second term is assumed as perturbation, we get

$$\frac{d^2 S}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{k}{2} x^2 \right] S = 0. \quad (3.46)$$

Eq. (3.32) is of the same form as the harmonic oscillator wave equation. The boundary conditions are not exactly identical with those of the harmonic oscillator problem, but are sufficiently close, so that we can accept the following solution

$$S_n(x) = C_n e^{-\frac{1}{2}\beta x^2} H_n(\sqrt{\beta}x), \quad (3.47)$$

where H_n is the n th Hermite polynomial. The energy levels are, as usual, given by

$$E_n = (n+1/2)h\nu_e. \quad (3.48)$$

The first order perturbation can be found as

$$E'_n = \frac{\hbar^2}{\mu} l(l+1) \int_{-\infty}^{+\infty} S_n(x) \left[\frac{1}{(x+r_e)^2} \right] S_n(x) dx. \quad (3.49)$$

The integral can be easily evaluated by expanding the term within the parantheses in terms of (x/r_e) . Keeping only the first three terms in the expansion, we get

$$E'_n = B'_n l(l+1). \quad (3.50)$$

The second order correction is

$$E''_n = -D'[l(l+1)]^2. \quad (3.51)$$

The complete expression for the energy is thus

$$E = (n+1/2)h\nu_e + B'_n J(J+1) - D'[J(J+1)]^2, \quad (3.52)$$

where J has been used instead of l for the rotational quantum number. The first term in the energy expression is due to the vibration of the molecule, the second to the rotation of the molecule and the third to centrifugal stretching of the molecule.

3.2 Rigid And Non-Rigid Rotator In Ordinary Thermostatistics

In this Section, we will study the second and third terms in the Eq. (3.52) in a statistical context. The first term is harmonic oscillator term and even though it is important in the applications, we focus now only to those terms, which might be called as rigid and nonrigid rotator terms. The rigid rotator term reads

$$E_{\text{rot}} = B'_n J(J+1). \quad (3.53)$$

Taking the degeneracy of the system i.e., $(2J+1)$ into consideration, we can write down the partition function for this model as

$$Z_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) \exp\left\{-\frac{B'_n J(J+1)}{kT}\right\}, \quad (3.54)$$

Writing

$$\frac{B'_n}{k} \equiv \Theta_r, \quad (3.55)$$

The values of Θ_r , for all gases except the ones involving the isotopes H and D, are much smaller than the room temperature. For example, the value of Θ_r for HCl is about 15 K, for N_2 , O_2 and NO it lies between 2 and 3 K, while for Cl_2 it is about one-third of a degree. On the other hand, the values of Θ_r for H_2 and HD are respectively 85 K, 64 K [35, 36]. These numbers give us an idea of respective temperature ranges in which the effects arising from the *discreteness* of the rotational states are expected to be important.

We get

$$Z_{\text{rot}}(T) = \sum_{J=0}^{\infty} (2J+1) \exp\left\{-\frac{\Theta_r J(J+1)}{T}\right\}. \quad (3.56)$$

For $T \gg \Theta_r$ (high temperature limit), the spectrum of the rotational states may be approximated by a continuum. The summation can then be replaced by an integration:

$$Z_{\text{rot}}(T) \approx \int_0^{\infty} dJ (2J+1) \exp\left\{-\frac{\Theta_r J(J+1)}{T}\right\}. \quad (3.57)$$

Identifying $J(J+1) = x$, we evaluate the integral as

$$Z_{\text{rot}} = \frac{T}{\Theta_r}. \quad (3.58)$$

The internal energy can be calculated using the formula

$$U = -kT^2 \frac{\partial}{\partial T} \ln Z_{\text{rot}}, \quad (3.59)$$

and it gives

$$U_{\text{rot}} = kT. \quad (3.60)$$

The rotational specific heat is obtained from

$$(C_v)_{\text{rot}} = \frac{\partial U}{\partial T}. \quad (3.61)$$

Using Eqs. (3.60) and (3.61), we have

$$(C_v)_{\text{rot}} = k, \quad (3.62)$$

consistent with the equipartition theorem.

A better evaluation of the sum in Eq. (3.56) can be made with the help of the Euler-Maclaurin formula, viz.

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} f(x) dx + \frac{1}{2} f(0) - \frac{1}{12} f'(0) + \frac{1}{720} f'''(0) - \dots \quad (3.63)$$

Writing

$$f(x) = (2x+1) \exp\{-x(x+1)\Theta_r/T\}, \quad (3.64)$$

one obtains

$$Z_{\text{rot}}(T) = T/\Theta_r + 1/3 + (1/15) \Theta_r/T + (4/315)(\Theta_r/T)^2 + \dots, \quad (3.65)$$

which is the so-called *Mullholland formula*; as expected, the main term of this formula is identical with the classical partition function (3.58). The corresponding result for the specific heat is

$$(C_v)_{\text{rot}} = k \{1 + (1/45)(\Theta_r/T)^2 + \dots\}, \quad (3.66)$$

which shows that at high temperatures the rotational specific heat *decreases* with the temperature and ultimately tends to the classical value k . Thus, at high (but finite) temperatures the rotational specific heat of a diatomic gas is greater than the classical value. On the other hand, it must go to zero as $T \rightarrow 0$.

In the other limiting case, when $T \ll \Theta_r$ (low temperature limit), one may retain only the first few terms of the sum in Eq. (3.56); then the partition function becomes

$$Z_{rot}(T) = 1 + 3e^{-2\Theta_r/T} + 5e^{-6\Theta_r/T} + \dots, \quad (3.67)$$

whence one obtains, *in the lowest approximation*

$$(C_V)_{rot} \cong 12k\left(\frac{\Theta_r}{T}\right)^2 e^{-2\Theta_r/T}. \quad (3.68)$$

Thus, as $T \rightarrow 0$, the specific heat drops exponentially to zero. We conclude that at low enough temperatures the rotational degrees of freedom of the molecules are also *frozen*.

Next, we study the non-rigid rotator in high and low temperature limits. The energy eigenvalues of non-rigid rotator (considering only the non-rigidity term) is given by

$$E_{nrot} = D[J(J+1)]^2. \quad (3.69)$$

Treating the problem in the same manner as rigid rotator case, we write for the high temperature limit,

$$Z_{nrot}(T) \approx \int_0^{\infty} dJ(2J+1) \exp\left\{-\frac{DJ^2(J+1)^2}{T}\right\}, \quad (3.70)$$

where $D = D'/k$. Making the substitution $J(J+1) = x$, we obtain

$$\int_0^{\infty} dx \exp\left\{-\frac{Dx^2}{T}\right\} = \frac{\sqrt{\pi}}{2} \sqrt{\frac{T}{D}}, \quad (3.71)$$

i.e., we obtain the partition function as

$$Z_{nrot}(T) = \frac{\sqrt{\pi}}{2} \sqrt{\frac{T}{D}}. \quad (3.72)$$

Using Eq. (3.59) with the partition function above,

$$U_{nrot} = kT \frac{\sqrt{\pi}}{4} \sqrt{\frac{T}{D}}. \quad (3.73)$$

The specific heat becomes

$$(C_V)_{nrot} = \frac{3}{8} k \left(\frac{\pi T}{D}\right)^{1/2}. \quad (3.74)$$

In the low temperature limit, we have, as partition function,

$$Z_{nrot}(T) = 1 + 3e^{-4D/T} + 5e^{-36D/T} + \dots, \quad (3.75)$$

The internal energy contribution due to non-rigidity term becomes

$$U_{nrot} = -k \frac{12De^{-4D/T} + 180De^{-36D/T}}{1 + 3e^{-4D/T} + 5e^{-36D/T}}. \quad (3.76)$$

The specific heat term becomes

$$(C_V)_{nrot} = -\frac{48D^2 e^{32D/T} k (320 + 135e^{4D/T} + e^{36D/T})}{T^2 (5 + 3e^{32D/T} + e^{36/T})^2}. \quad (3.77)$$

Of course, taking the minus sign in Eq. (3.52) into consideration, we realize that there will be a positive correction to specific heat value of the rigid rotator by a value given by Eq. (3.77) in the low temperature limit.

3.3 Rigid And Non-Rigid Rotator Models In Tsallis Thermostatistics

In this Section, we will study these two models, i.e., rigid and non-rigid rotators in the framework of Tsallis statistics [37]. Using the energy levels of rigid rotator, we write the nonextensive partition function as

$$Z_q = \sum_{J=0}^{\infty} (2J+1) \left[1 - (1-q) \frac{J(J+1)\theta_r}{T} \right]^{1/(1-q)}. \quad (3.78)$$

Now, let us take a look at its analytic solutions in the high temperature limit. At high temperatures, $\theta/T \ll 1$ and the term in the parentheses in Eq. (3.78) changes slowly as J changes. So, we take it as a continuous function of J . Letting $J(J+1) = x$, we obtain

$$Z_q = \int_0^{\infty} dx \left[1 - (1-q)x \frac{\theta_r}{T} \right]^{1/(1-q)}. \quad (3.79)$$

For the interval $1 < q < 2$, solution to the above integral is

$$Z_q = \frac{1}{(2-q)} \frac{T}{\theta_r}. \quad (3.80)$$

As q goes to 1, we get

$$Z_{q \rightarrow 1} = \frac{T}{\theta_r}. \quad (3.81)$$

The expression above is exactly the Maxwell-Boltzmann (MB) partition function for the isotropic rigid rotator in the high temperature limit. Thus, we calculate the generalized internal energy function from

$$U_q = -\frac{\partial}{\partial \beta} \frac{Z_q^{1-q} - 1}{1-q}, \quad (3.82)$$

in the nonextensive case. It becomes

$$U_q = \frac{\alpha^{1-q} \beta^{q-2}}{(2-q)^{1-q}}, \quad 1 < q < 2 \quad (3.83)$$

where $\alpha \equiv \frac{1}{k\theta_r}$. It is important to see that again, in the limit as q approaches to 1, we

obtain the result already known in MB statistics, i.e.,

$$U_{q \rightarrow 1} = k_B T. \quad (3.84)$$

It is also possible to calculate the specific heat in this context by using

$$C_q = \frac{\partial U_q}{\partial T}, \quad (3.85)$$

where U_q is the internal energy function. We immediately get

$$C_q = \left(\frac{\alpha}{2-q}\right)^{1-q} \frac{(2-q)T^{1-q}}{k^{q-2}}. \quad (3.86)$$

As can be easily verified

$$C_{q \rightarrow 1} = k_B. \quad (3.87)$$

All these calculations are carried out by using the second constraint of internal energy. But, we know that this choice of internal energy had some intrinsic problems within itself so that we have to consider redoing all those previous calculations in accordance with the third internal energy constraint. As is pointed in Chapter 2, there are two ways to do this: Firstly, we can recalculate all thermodynamical quantities with this new internal energy constraint by forming the new partition function. Another method is to find the relation between the temperature parameters of the old and new calculations. If one has all thermodynamical functions calculated with the old constraint and the relation between temperature parameters is known, it is possible to modify all previous calculations carried out with the second constraint. This is the method we will follow, because we already have the solutions with respect to old constraint.

We begin by writing all previous calculations in terms of intermediate variable t' where $t' \equiv 1/(\beta'\varepsilon)$. From now on, the superscript (2) will refer to calculations done with the second constraint.

The partition function of the rigid rotator in the high temperature limit becomes

$$Z_q^{(2)}(\beta') = \frac{1}{(2-q)} \frac{T'}{\theta_r} = \frac{t'}{(2-q)}. \quad (3.88)$$

Thus, we first evaluate

$$\sum_j [p_j^{(2)}(\beta')]^q = \sum_j \frac{[1 - (1-q)\beta'\varepsilon_j]^{q/(1-q)}}{Z_q^{q(2)}}. \quad (3.99)$$

By defining

$$\sum_j [1 - (1-q)\beta'\varepsilon_j]^{q/(1-q)} = t', \quad (3.100)$$

we write the Eq. (3.99) as

$$\sum_j [p_j^{(2)}(\beta')]^q = (2-q)^q (t')^{1-q}. \quad (3.101)$$

We then use Eq. (2.56), i.e.,

$$\beta = \beta' \frac{\sum_{j=1}^W [p_j^{(2)}(\beta')]^q}{1 - (1-q)\beta' U_q^{(2)}(\beta') / \sum_{j=1}^W [p_j^{(2)}(\beta')]^q}, \quad (3.102)$$

and substituting Eq. (3.101) into Eq. (3.102), we obtain

$$t' = (2-q)^{(q+1)/q} t'^{1/q}. \quad (3.103)$$

Then, using Eq. (2.48), we have

$$Z_q^{(3)}(\beta) = (2-q)^{1/q} t'^{-1/q}. \quad (3.104)$$

Next, using

$$p_j^{(3)}(\beta) = p_j^{(2)}(\beta'), \quad (3.105)$$

we can form $p_j^{(3)}(\beta)$. Next, we use the relation (2.45) to be able to obtain the following partition function

$$(\bar{Z}_q^{(3)})^{1-q} = (2-q)^{1/q} t'^{(1-q)/q}. \quad (3.106)$$

Using this partition function, one can calculate all thermodynamic observables such as internal energy or heat capacity. Using Eq. (2.38) and Eq. (2.40) respectively, we obtain

$$U_q^{(3)} = (2-q)^{1/q} t^{1/q}, \quad (3.107)$$

and

$$C_q^{(3)} = \frac{k}{q} (2-q)^{1/q} t^{(1-q)/q}. \quad (3.108)$$

Again, as $q \rightarrow 1$, $C_q^{(3)} \rightarrow k_B$ is obtained. This is the ordinary rotational specific heat of the isotropic rigid rotator for high temperature limit in accordance with the equipartition theorem. A plot has been made under the title Fig. 1 to be able to understand the behaviour of $C_q^{(3)}$ with changing reduced temperature, which is defined as $t = T/\theta_r$.

Now, we are interested in solutions for the low temperature limit. At low temperatures, we look at the first few terms in the summation in Eq. (3.78) to write

$$Z_q \cong 1 + 3 \left[1 - 2(1-q) \frac{\theta_r}{T} \right]^{1/(1-q)}. \quad (3.109)$$

This is nothing but the well-known partition function of the rigid rotator in low temperature limit in MB statistics if $(1-q)$ is small enough. This is the case if we make q closer to 1. For such a choice, the partition function takes the form

$$Z_{q \rightarrow 1} \cong 1 + 3 \exp(-2\theta_r / T). \quad (3.110)$$

If we identify

$$\tau = \left[1 + 3 \left[1 - 2(1-q) \frac{\beta}{\alpha} \right] \right]^{1/(1-q)}, \quad (3.111)$$

and

$$\sigma = \left[1 - 2(1-q) \frac{\beta}{\alpha} \right], \quad (3.112)$$

we can write the nonextensive internal energy function as

$$U_q = \frac{6}{\alpha} \tau^{-q} \sigma^{q/(1-q)}. \quad (3.113)$$

This is a relatively long expression but when we look for its value as q approaches 1, we see that it is of the form

$$U_{q \rightarrow 1} = \frac{6k_B\theta_r}{Z_{q \rightarrow 1}} \exp(-2\theta_r / T), \quad (3.114)$$

with $1/\alpha = k_B\theta$ in the $q \rightarrow 1$ limit. Calculation of specific heat gives

$$C_q = \frac{12q}{\alpha^2 k T^2} \tau^{-q} \sigma^{\frac{2q-1}{1-q}} - \frac{36q}{\alpha^2 k T^2} \tau^{-q-1} \sigma^{\frac{2q}{1-q}}. \quad (3.115)$$

As $q \rightarrow 1$, the above expression takes the form

$$C_{q \rightarrow 1} = \frac{12}{\alpha^2 k_B T^2} \exp(-2\theta_r / T). \quad (3.116)$$

This limiting value of heat capacity is obtained by observing that $\frac{1}{Z_{q \rightarrow 1}}$ is almost equal

to unity for low temperature partition function values. At first sight, Eq. (3.116) looks different from Eq. (3.68): In fact, they are not. Since

$$\frac{1}{\alpha^2} = k_B^2 \theta_r^2, \quad (3.117)$$

we get, from Eq. (3.116)

$$C_{q \rightarrow 1} = 12k_B \left(\frac{\theta_r}{T}\right)^2 \exp(-2\theta_r / T), \quad (3.118)$$

which is identical to Eq. (3.68).

To modify Eq. (3.115) for example in accordance with the third constraint, we can substitute Eq. (3.103) into Eq. (3.78) and take the first two terms to get the low temperature limit partition function. This is redundant due to two main reasons though: Firstly, when the ground state energy eigenvalue is zero, there occurs no difference between the second and third constraint calculations as long as thermodynamic observables are concerned. Secondly, if we inspect Eq. (3.103), we see that in the limit as q approaches 1, $t' = t$ i.e., both second and third constraint calculations have the same limiting value for thermodynamic observables.

The behaviour of rigid rotator model in the low temperature limit is plotted in Fig. 2. The interesting feature in these plots is that specific heat function of the rigid rotator in the low temperature regime attains the same shape as the classical one but with a narrower width and a shift in the peak to the left. By increasing the values of q , specific heat function attains the same shape as the classical one but with a narrower width and

a shift in peak to the left. This behaviour suggests that the nonextensivity parameter q behaves as a scale parameter in this regime.

Now, we can solve the non-rigid rotator term in Tsallis statistics. We consider Eq. (3.52) neglecting only the first term which happens to be the harmonic term. Therefore, the nonextensive partition function reads

$$Z_q = \sum_{J=0}^{\infty} (2J+1) [1 - \beta(1-q)B'J(J+1) + \beta(1-q)DJ^2(J+1)^2]^{1/(1-q)}. \quad (3.119)$$

As before, for high temperature limit, we replace summation by integral and get

$$Z_q^{nonrigid} = \int_0^{\infty} dx [ax^2 + bx + 1]^{1/(1-q)}, \quad (3.120)$$

where

$$a = \beta(1-q)D, \quad (3.121)$$

and

$$b = -\beta(1-q)B'. \quad (3.122)$$

The integral in Eq. (3.120) can be rewritten in factorial form

$$Z_q^{nonrigid} = (mn)^{\frac{1}{1-q}} \int_0^{\infty} dx \left(x + \frac{1}{m}\right)^{1/(1-q)} \left(x + \frac{1}{n}\right)^{1/(1-q)}, \quad (3.123)$$

where $m = b-n$ and $n = \frac{b}{2} [1 \pm (1 - 4\frac{a}{b^2})^{1/2}]$. The following general form can be used to

solve the integral

$$\int_0^{\infty} dx x^{\nu-1} (x + \mathcal{G})^{-\mu} (x + \gamma)^{-\xi} = \mathcal{G}^{-\mu} \gamma^{\nu-\xi} \text{Beta}(\nu, \mu - \nu + \xi) {}_2F_1(\mu, \nu; \mu + \xi; 1 - \frac{\gamma}{\mathcal{G}}), \quad (3.124)$$

where

$$\mu = \frac{1}{q-1}; \nu = 1; \gamma = \frac{1}{n}; \mathcal{G} = \frac{1}{m}. \quad (3.125)$$

The function ${}_2F_1(\rho, \mu; \gamma; x)$ is the hypergeometric function defined by

$${}_2F_1(\rho, \mu; \gamma; x) = \frac{\Gamma(\gamma)}{\Gamma(\mu)\Gamma(\gamma - \mu)} \int_0^1 dt t^{\mu-1} (1-t)^{\gamma-\mu-1} (1-xt)^{-\rho}, \quad (3.126)$$

where the parameters satisfy $\nu > 0$ and $\mu > \nu - \xi$. Here we see that $\nu = 1$ and $q > 1$.

Thus, we simply get

$$\mu = \xi = \frac{1}{q-1}. \quad (3.127)$$

By using the condition $\mu > \nu - \xi$, we obtain an upper limit for q as $q < 3$. Therefore, we have solution range for q as $1 < q < 3$. Thus, we get the partition function as

$$Z_q^{nonrigid} = \frac{(q-1)}{(3-q)n} {}_2F_1\left(1, \frac{1}{q-1}; \frac{2}{q-1}; 1 - \frac{m}{n}\right). \quad (3.128)$$

In order to get the compact expression for the partition function above, we made use of the following identity:

$$\text{Beta}\left(1, \frac{2}{q-1} - 1\right) = \frac{q-1}{3-q}. \quad (3.129)$$

The resulting internal energy and heat capacity expressions may be found exactly in the same manner. Behaviour of heat capacity in the high temperature limit is plotted in Fig. 3. In all plots related to non-rigid rotator, the values 10.397 and 4.1×10^{-5} have been used for the B' and D parameters respectively for HCl molecule [38].

Finally, we need to investigate non-rigid rotator model in the low temperature limit [39]. Taking the first few terms in the Eq. (3.119), we obtain

$$Z_q^{nonrigid} \cong 1 + 3[1 - 2B'(1-q)\beta + 4D(1-q)\beta]^{1-q}. \quad (3.130)$$

Internal energy term resulting from this partition function is

$$U_q^{nonrigid} = 6(B' - 2D)[1 + 2(B' - 2D)(q-1)\beta]^{1-q} [1 + 3(1 + 2(B' - 2D)(q-1)\beta)^{1-q}]^{-q} \quad (3.131)$$

The specific heat function of non-rigid rotator for this case is illustrated in Fig. 4, with the same B' and D values as before [40]. We present Fig. 1 through Fig. 4 in the next 4 pages.

CHAPTER 4

RELATIVE ENTROPY, SECOND LAW OF THERMODYNAMICS AND CONSTRAINTS IN NONEXTENSIVE STATISTICS

4.1 The Physical Meaning of Ordinary Definition of Relative Entropy

The definition of relative entropy [41-43] used throughout the NEXT literature reads

$$K_q[p \parallel r] = \frac{1}{1-q} [1 - \sum_i (p_i)^q (r_i)^{1-q}], \quad (4.1)$$

where r_i is a reference distribution. To be able to understand its physical meaning in NEXT formalism, we optimize Tsallis entropy by using escort distributions (i.e., third choice):

$$\delta \left[\frac{1}{1-q} (\sum_i p_i^q - 1) - \alpha \sum_i p_i - \beta \frac{\sum_i p_i^q \varepsilon_i}{\sum_i p_i^q} \right] = 0, \quad (4.2)$$

which gives

$$\frac{q}{1-q} \tilde{p}_i^{q-1} - \alpha - \frac{q\beta}{\sum_i \tilde{p}_i^q} \tilde{p}_i^{q-1} \left[\varepsilon_i - \frac{\sum_i \tilde{p}_i^q \varepsilon_i}{\sum_i \tilde{p}_i^q} \right] = 0. \quad (4.3)$$

The Equation above can be written in the following form

$$\frac{q}{1-q} \tilde{p}_i^{q-1} - \alpha - q\beta^* \tilde{p}_i^{q-1} [\varepsilon_i - \tilde{U}_q] = 0, \quad (4.4)$$

where

$$\beta^* = \frac{\beta}{\sum_i \tilde{p}_i^q} \quad (4.5)$$

and

$$\alpha = \frac{q}{1-q} [1 + (1-q)\tilde{S}_q]. \quad (4.6)$$

\tilde{S}_q and \tilde{U}_q are the values of S_q and U_q calculated in terms of the maximum entropy distribution \tilde{p}_i [44, 45, 46]. Eqs. (4.4) and (4.6) lead to

$$\tilde{p}_i = \frac{1}{\tilde{Z}_q} [1 - (1-q)\beta^*(\varepsilon_i - \tilde{U}_q)]^{1/(1-q)}, \quad (4.7)$$

$$\tilde{Z}_q = [1 + (1-q)\tilde{S}_q]^{1/(1-q)}, \quad (4.8)$$

$$= \sum_i [1 - (1-q)\beta^*(\varepsilon_i - \tilde{U}_q)]^{1/(1-q)}. \quad (4.9)$$

Substituting $r_i = \tilde{p}_i$ into Eq. (4.1) and using Eqs. (4.7), (4.9), we obtain

$$K_q[\mathbf{p} \parallel \tilde{\mathbf{p}}] = \frac{\hat{\beta}}{\sum_i (\tilde{p}_i)^q} (U_q - \tilde{U}_q - \frac{1}{\hat{\beta}} S_q + \frac{1}{\hat{\beta}} \tilde{S}_q), \quad (4.10)$$

where

$$\hat{\beta} = \beta^* \sum_i (p_i)^q. \quad (4.11)$$

The Eq. (4.10) can be cast into a more explicit form if we identify the terms within the parantheses explicitly as

$$F_q = U_q - \frac{1}{\hat{\beta}} S_q \quad (4.12)$$

and

$$\tilde{F}_q = \tilde{U}_q - \frac{1}{\hat{\beta}} \tilde{S}_q. \quad (4.13)$$

The Eq. (4.10) can be rewritten in the following form now

$$K_q[\mathbf{p} \parallel \tilde{\mathbf{p}}] = \frac{\hat{\beta}}{\sum_i (\tilde{p}_i)^q} (F_q - \tilde{F}_q). \quad (4.14)$$

Inspection of the Equation above clearly shows that physical meaning relative entropy is nothing but the free energy differences [47].

4.2 Relative Entropy and The Second Law of Thermodynamics

Under the previously explained constraints of normalization and internal energy (see Section 2.1), the Tsallis entropy is found to be optimized by the following state:

$$\tilde{\rho} = \frac{1}{Z_q} e_q(-\beta^*(H - \tilde{U}_q)), \quad (4.15)$$

where

$$Z_q = \text{Tr}_q(-\beta^*(H - \tilde{U}_q)). \quad (4.16)$$

Here, $e_q(x)$ denotes the q-exponential function. \tilde{U}_q and β^* are given by

$$\tilde{U}_q = \frac{\text{Tr}(\tilde{\rho}^q H)}{\text{Tr}(\tilde{\rho}^q)}, \quad (4.17)$$

$$\beta^* = \frac{\beta}{\text{Tr}(\tilde{\rho}^q)}, \quad (4.18)$$

where β is a Lagrange multiplier associated with the internal energy constraint.

Before proceeding to the second law, it seems appropriate to formulate the first law of thermodynamics to identify the quantity of heat. For this purpose, let us consider the generalized internal energy

$$U_q = \frac{\text{Tr}(\rho^q H)}{\text{Tr}(\rho^q)}. \quad (4.19)$$

We are concerned with small change of this quantity from \tilde{U}^q and therefore ρ and $\tilde{\rho}$ are close to each other. Taking the variation of U_q , we obtain the first law

$$\delta'Q_q = \delta U_q + \delta'W_q, \quad (4.20)$$

where $\delta'Q_q$ and $\delta'W_q$ are the small changes of the quantity of heat and work [48,49] given by

$$\delta'Q_q = \frac{\text{Tr}[\delta\rho^q (H - U_q)]}{\text{Tr}(\rho^q)}, \quad (4.21)$$

$$\delta'W_q = -\langle \delta H \rangle_q = -\frac{\text{Tr}(\rho^q \delta H)}{\text{Tr}(\rho^q)}, \quad (4.22)$$

respectively. We write Eq. (4.1) as

$$K_q[\rho \parallel \sigma] = \frac{1}{1-q} [1 - \text{Tr}(\rho^q \sigma^{1-q})]. \quad (4.23)$$

Since we want to compare ρ with $\tilde{\rho}$ in Eq. (4.15) [50], we need to evaluate $K_q[\rho \parallel \tilde{\rho}]$. Therefore, by substitution of $\tilde{\rho}$ instead of σ , and using

$$(Z_q)^{1-q} = \text{Tr} \tilde{\rho}^q, \quad (4.24)$$

We obtain

$$K_q[\rho \parallel \tilde{\rho}] = \frac{1}{\text{Tr} \tilde{\rho}^q} \{S_q[\tilde{\rho}] - S_q[\rho] + \beta^* \text{Tr}[\rho^q (H - \tilde{U}_q)]\}. \quad (4.25)$$

Taking the variation of $K_q[\rho \parallel \tilde{\rho}]$ with respect to ρ , i.e., $\rho \rightarrow \rho + \delta\rho$ and

$$\text{Tr} \delta\rho = 0, \quad (4.26)$$

with fixed $\tilde{\rho}$, we get

$$(\text{Tr} \tilde{\rho}^q) \delta K_q[\rho \parallel \tilde{\rho}] = -\delta S_q[\rho] + \beta^* \text{Tr}[\delta\rho^q (H - U_q)], \quad (4.27)$$

where $\delta\rho^q \tilde{U}_q$ has been replaced by $\delta\rho^q U_q$, since ρ is close to $\tilde{\rho}$ and therefore the difference between these two quantities are of higher order infinitesimal. Using Eq. (4.21), we have

$$(\text{Tr} \tilde{\rho}^q) \delta K_q[\rho \parallel \tilde{\rho}] = -\delta S_q[\rho] + \beta \delta'Q_q, \quad (4.28)$$

A similar case has been studied for Renyi entropy in Ref. [51-53].

In order to establish Clausius' inequality

$$\beta \delta'Q_q \leq \delta S_q[\rho], \quad (4.29)$$

it is necessary to show that $\delta K_q[\rho \parallel \tilde{\rho}]$ is negative. To calculate this term, we represent the variation by a trace-preserving completely positive unital map, $\rho \rightarrow \rho + \delta\rho \equiv \Lambda(\rho)$:

$$\Lambda(\rho) = \sum_k V_k \rho V_k^\dagger. \quad (4.30)$$

V_k 's are certain operators satisfying the trace-preserving condition

$$\sum_k V_k^\dagger V_k = I, \quad (4.31)$$

with the identity operator I . The unital condition reads

$$\Lambda(I) = I, \quad (4.32)$$

which in turn gives

$$\sum_k V_k V_k^\dagger = I. \quad (4.33)$$

These two conditions are compatible if V_k 's are normal, that is,

$$[V_k, V_k^\dagger] = 0 \text{ for } \forall k. \quad (4.34)$$

Since $\tilde{\rho}$ is fixed, we have

$$\Lambda(\tilde{\rho}) = \tilde{\rho}, \quad (4.35)$$

which is fulfilled if

$$[V_k, \tilde{\rho}] = 0. \quad (4.36)$$

Thus, the variation must be understood as

$$\delta K_q[\rho \parallel \tilde{\rho}] = K_q[\Lambda(\rho) \parallel \tilde{\rho}] - K_q[\rho \parallel \tilde{\rho}]. \quad (4.37)$$

Now, let A be a positive operator. Then, the function

$$f(A) = A^q \quad (q > 0), \quad (4.38)$$

is operator monotone, that is, for another positive operator B , such that $B \geq A$, holds

$$B^q \geq A^q. \quad (4.39)$$

A very important point is that if $q > 2$, then this operator function does not possess

definite convexity. The function $f(A)$ is operator concave (convex), i.e.,

$$f(\lambda A + (1-\lambda)B) \geq (\leq) \lambda f(A) + (1-\lambda)f(B) \text{ if } q \in (0,1] \text{ (} q \in (1,2]), \quad (4.40)$$

where $\lambda \in (0,1)$. In other words,

$$\begin{aligned} F(A) &= A^q \quad \text{for } q \in (0,1] \\ &= -A^q \quad \text{for } q \in (1,2]. \end{aligned} \quad (4.41)$$

is operator concave. Then, Ando's Theorem [54] states that

$$F\left(\sum_k V_k A V_k^\dagger\right) \geq \sum_k V_k F(A) V_k^\dagger. \quad (4.42)$$

Using this theorem, we have

$$\tilde{\rho}^{(1-q)/2} [\Lambda(\rho)]^q \tilde{\rho}^{(1-q)/2} \geq \Lambda(\tilde{\rho}^{(1-q)/2} \rho^q \tilde{\rho}^{(1-q)/2}) \quad (q \in (0,1]), \quad (4.43)$$

$$\tilde{\rho}^{(1-q)/2} [\Lambda(\rho)]^q \tilde{\rho}^{(1-q)/2} \leq \Lambda(\tilde{\rho}^{(1-q)/2} \rho^q \tilde{\rho}^{(1-q)/2}) \quad (q \in (1,2]). \quad (4.44)$$

Therefore, using Eq. (5.23), we finally get

$$K_q[\Lambda(\rho) \parallel \tilde{\rho}] \leq K_q[\rho \parallel \tilde{\rho}] \quad (q \in (0,2]), \quad (4.45)$$

which establishes Clausius' inequality in Eq. (4.29) [55].

Thus, it has been shown that the second law of thermodynamics holds in NEXT with $q \in (0,2]$ [56,57]. This Section also proves how important the concept of relative theory is in studies of nonequilibrium statistical physics.

5.3 Deformed Exponentials and A New Definition of Relative Entropy In Nonextensive Formalism

As it is explained earlier, Tsallis statistics indeed can be achieved by replacing the usual exponential by q exponential i.e., $\exp_q(x)$. This kind of particular forms of exponential function which has been invented to suit the needs of generalization of Boltzmann-Gibbs formalism is called *deformed exponentials* [58], and corresponding logarithms are called *deformed logarithms*. This Section will be devoted to a general study of these functions and a new relative entropy definition which will emerge from this discussion.

As usual, our generalized exponentials and logarithms must satisfy the requirements met by their corresponding usual counterparts. We call these forms as κ -deformed exponentials (or logarithms) in general. We denote the κ -deformed exponential function as $\exp_\kappa(x)$. The deformation number κ is a number we will not specify further. It has to satisfy following assumptions

- I. $\exp_\kappa(x) \geq 0$ for all real x . $\exp_\kappa(x) = \infty$ is allowed.
- II. $\exp_\kappa(0) = 1$.
- III. $\exp_\kappa(x)$ is a convex function which is strictly increasing in all points where its value is not zero or infinite.
- IV. $\exp_\kappa(x)$ goes fast enough to zero when x goes to $-\infty$, so that $\int_0^\infty dx \exp_\kappa(-x) < \infty$.

- V. $\ln_\kappa(x)$ is a strictly increasing concave function, defined for all $x > 0$.
- VI. $\ln_\kappa(1) = 0$.
- VII. $\int_0^1 dx \ln_\kappa(x)$ is finite.

The inverse of a κ -deformed exponential function is a κ -deformed logarithm. The integral of the κ -deformed logarithm is given by

$$F_\kappa(x) = \int_1^x dy \ln_\kappa(y), \quad x > 0. \quad (4.46)$$

This function satisfies $F_\kappa(x) \geq 0$, $F_\kappa(1) = 0$, and $F_\kappa(0) < \infty$. It is convex because the derivative of $\ln_\kappa(x)$ is increasing.

Let us introduce a new function, denoted by $\omega_\kappa(x)$,

$$\omega_\kappa(x) = (x-1)F_\kappa(0) - xF_\kappa(1/x). \quad (4.47)$$

This function is again a κ -deformed logarithm, provided that

$$\int_0^1 dx \ln_\kappa(1/x) < +\infty. \quad (4.48)$$

To be able to see why $\omega_\kappa(x)$ might be called a κ -deformed logarithm, we list

- I. $\omega_\kappa(x)$ is a strictly increasing concave function. To see this, we write

$$F_\kappa(x) = x \ln_\kappa(x) - \int_1^x y d \ln_\kappa(y). \quad (4.49)$$

This expression is used to write the derivative of $\omega_\kappa(x)$ as

$$\frac{d}{dx} \omega_\kappa(x) = F_\kappa(0) - F_\kappa(1/x) + (1/x) \ln_\kappa(1/x) \quad (4.50)$$

$$= \int_0^{1/x} y d \ln_\kappa(y). \quad (4.51)$$

Because $\ln_\kappa(y)$ is a strictly increasing function, the latter expression is strictly positive for all $x > 0$. Hence, $\omega_\kappa(x)$ is strictly increasing. It is also clear from Eq. (4.51) that the derivative of $\omega_\kappa(x)$ is a decreasing function. Hence $\omega_\kappa(x)$ is concave.

- II. $\omega_\kappa(1) = 0$ since $F_\kappa(1) = 0$.

- III. We finally need to show $\int_0^1 dx \omega_\kappa(x)$ is finite. For this purpose, we write, using integration by parts,

$$\int_0^1 dx \omega_\kappa(x) = -F_\kappa(0) - \int_0^1 dx x \int_0^{1/x} dy \ln_\kappa(y), \quad (4.52)$$

$$= -F_\kappa(0) - \frac{1}{2} \int_0^1 dx \left[\frac{d}{dx} (x^2 \int_0^{1/x} dy \ln_\kappa(y)) + \ln_\kappa(1/x) \right], \quad (4.53)$$

$$= -\frac{1}{2} F_\kappa(0) - \frac{1}{2} \int_0^1 dx \ln_\kappa(1/x), \quad (4.54)$$

which is finite by assumption (4.48).

$\omega_\kappa(x)$ is called *deduced logarithmic function*. It satisfies the equation

$$\frac{d}{dx} (x \omega_\kappa(1/x)) = -F_\kappa(0) - \ln_\kappa(x). \quad (4.55)$$

At this point, let us give two deformed logarithms existing in the literature as examples to make all previous points clearer: First, Tsallis' deformed logarithm will be explained briefly. It is given by

$$\ln_\kappa(x) = \left(1 + \frac{1}{\kappa}\right)(x^\kappa - 1), \quad (4.56)$$

where $-1 < \kappa < +1$. The inverse function is

$$\exp_\kappa(x) = \left[1 + \frac{\kappa}{1 + \kappa} x\right]_+^{1/\kappa}, \quad (4.57)$$

where $[x]_+ = \max\{x, 0\}$. For $\kappa = 0$, these functions coincide with the usual definitions of logarithmic and exponential functions.

$\ln_\kappa(x)$ is a strictly increasing concave function. Indeed, we have

$$\frac{d}{dx} \ln_\kappa(x) = (1 + \kappa)x^{\kappa-1}, \quad (4.58)$$

$$\frac{d^2}{dx^2} \ln_\kappa(x) = -(1 - \kappa^2)x^{\kappa-2}. \quad (4.59)$$

It is obvious that the first derivative is always strictly positive, and that the second derivative is negative.

$\ln_\kappa(1) = 0$ and $\int_0^1 dx \ln_\kappa(x)$ is finite and indeed equal to -1 . These facts show that the κ -deformed logarithm in Eq. (4.56) satisfies the assumptions. In the context of Tsallis' thermostatics, one simply uses the notations $\exp_q(x)$ and $\ln_q(x)$ with q related to κ by $q = 1 + \kappa$ [59]. Moreover, we have

$$F_{\kappa}(x) = \left(1 + \frac{1}{\kappa}\right) \int_1^x dy (y^{\kappa} - 1) \quad (4.60)$$

$$= \frac{1}{\kappa} (x^{1+\kappa} - 1) - \left(1 + \frac{1}{\kappa}\right) (x - 1). \quad (4.61)$$

In particular, one has

$$F_{\kappa}(0) = 1. \quad (4.62)$$

We can write, for deduced logarithm

$$\omega_{\kappa}(x) = x - 1 - x \frac{F_{-\kappa}(1/x)}{F_{-\kappa}(0)} \quad (4.63)$$

$$= \frac{1}{\kappa} (1 - x^{-\kappa}). \quad (4.64)$$

Second, Kaniadakis' deformed exponential function [60, 61] is

$$\exp_{\kappa}(x) = (\kappa x + \sqrt{1 + \kappa^2 x^2})^{1/\kappa}, \quad (4.65)$$

where $-1 < \kappa < +1$ and $\kappa \neq 0$. The inverse function is

$$\ln_{\kappa}(x) = \frac{1}{2\kappa} (x^{\kappa} - x^{-\kappa}). \quad (4.66)$$

In the limit $\kappa = 0$, these functions coincide with the usual definitions of logarithmic and exponential functions. We have

$$\int_0^1 dx \ln_{\kappa}(x) = \frac{-1}{1 - \kappa^2}, \quad (4.67)$$

Also, we calculate

$$F_{\kappa}(x) = \int_1^x \frac{1}{2\kappa} (y^{\kappa} - y^{-\kappa}), \quad (4.68)$$

$$= \frac{1}{1 - \kappa^2} + \frac{1}{2\kappa} \left[\frac{1}{1 + \kappa} x^{1+\kappa} - \frac{1}{1 - \kappa} x^{1-\kappa} \right]. \quad (4.69)$$

In particular, note that

$$F_{\kappa}(0) = \frac{1}{1 - \kappa^2}. \quad (4.70)$$

The deduced logarithm is then given by

$$\omega_{\kappa}(x) = (x - 1)F_{\kappa}(0) - xF_{\kappa}(1/x), \quad (4.71)$$

$$= -\frac{1}{1-\kappa^2} + \frac{1}{\sqrt{1-\kappa^2}} \ln_{\kappa} \left(\left(\frac{1+\kappa}{1-\kappa} \right)^{1/2\kappa} x \right). \quad (4.72)$$

It is possible to use the ideas developed above to be able to calculate information content: The amount of information, contained in the knowledge that event k has possibility p_k , equals $\omega(1/p_k)$, where $\omega(x)$ is an increasing function. Hence, less probable events have a higher information content. Hartley's measure of information [62] corresponds with the choice $\omega(x) = \ln(x)$.

The obvious generalization is then to take $\omega(x)$ equal to the κ -deformed logarithm. Rather, we let $\omega(x) = \omega_{\kappa}(x)$ with right hand side being nothing but the deduced logarithm. The average information content $I_{\kappa}(p)$ is then given by

$$I_{\kappa}(p) = \sum_k p_k I_k \leq \infty \quad \text{with} \quad I_k = \omega_{\kappa}(1/p_k). \quad (4.73)$$

Using the definition of $\omega_{\kappa}(x)$, we immediately get

$$I_{\kappa}(p) = \sum_k ((1-p_k)F_{\kappa}(0) - F_{\kappa}(p_k)). \quad (4.74)$$

Because $F_{\kappa}(x)$ is convex, one has

$$F_{\kappa}(p_k) \leq p_k F_{\kappa}(1) + (1-p_k)F_{\kappa}(0) \quad (4.75)$$

$$= (1-p_k)F_{\kappa}(0). \quad (4.76)$$

Therefore, one has always

$$I_{\kappa}(p) \geq 0. \quad (4.77)$$

$I_{\kappa}(p) = 0$ if and only if $p_k = 1$ for a single value of k . This follows because $F_{\kappa}(x)$ is strictly decreasing on the interval $0 \leq x \leq 1$. $I_{\kappa}(p)$ is a concave function. This means that, if p and q are two probability distributions, then

$$I_{\kappa}(\lambda p + (1-\lambda)q) \geq \lambda I_{\kappa}(p) + (1-\lambda)I_{\kappa}(q) \quad (4.78)$$

holds for any λ , $0 \leq \lambda \leq 1$. This follows immediately from Eq. (4.74) since $F_{\kappa}(x)$ is a convex function.

If $\omega_{\kappa}(x)$ coincides with the usual logarithmic function then one finds

$$I_{\kappa}(p) = -\sum_k p_k \ln p_k. \quad (4.79)$$

This is Shannon's expression for information content [63]. Now, if $\omega_\kappa(x)$ equals Tsallis' deformed logarithm, as given in Eq. (4.64), then average information content equals

$$I_\kappa^{Tsallis}(p) = \frac{1}{\kappa} \left(1 - \sum_k p_k^{1+\kappa} \right). \quad (4.80)$$

This is the entropy functional used in Tsallis thermostatics.

The optimization of information content $I_\kappa(p)$ under a linear constraint such as the internal energy constraint used in Tsallis formalism can be achieved with ease. The substitution of Eq. (4.80) will be enough to reach this purpose. Of course, due to generality of this Section, only by changing the form of information content, we can obtain similar results for Kaniadakis' deduced logarithm.

Apart from being a general frame, deformed logarithms and exponentials enable us to write some new generalizations of Boltzmann-Gibbs statistics in a unified manner. In relevant examples of thermostatics, the density of states $\rho(E)$ increases as a power law $\rho(E) \sim E^{\alpha N}$ with N being the number of particles and $\alpha > 0$. The increase of density of states compensates the exponential decrease of probability density $p(E)$. The maximum of the product $\rho(E)p(E)$ is reached at some macroscopic energy far above the ground state energy [64]. Indeed, one can write

$$\rho(E)p(E) = \frac{1}{Z(T)} \exp(\log \rho(E) - E/T). \quad (4.81)$$

The argument of the exponential function is maximal if E satisfies

$$\frac{\rho'(E)}{\rho(E)} = \frac{1}{T}, \quad (4.82)$$

where $\rho'(E)$ is the derivative of $\rho(E)$ with respect to E . If $\rho(E) \sim E^{\alpha N}$ holds, then $E \cong \alpha NT$ follows, which is the equipartition theorem.

As a consequence of equipartition theorem, it is not easy to verify the Boltzmann-Gibbs distribution experimentally. The energy of the system under study is always equal to the value predicted by Eq. (4.82), with negligible fluctuations. This indicates that the actual form of probability distribution $p(E)$ is not very essential. Alternative expressions for $p(E)$ are acceptable if they satisfy the equipartition theorem and reproduce thermodynamics. An indication of the need for a generalization of

Boltzmann-Gibbs is the general use of temperature-dependent Hamiltonians in applied statistical physics. The following well-known expression

$$p(E) = \frac{e^{-E/T}}{\int dE \rho(E) e^{-E/T}}, \quad (4.83)$$

predicts the probability density $p(E)$ at all temperatures. In many cases, this prediction is not very accurate, probably because of an incomplete knowledge of the density of states $\rho(E)$. However, instead of making $\rho(E)$ temperature-dependent, which is not supported by theory, one can as well try to replace the Boltzmann-Gibbs distribution by another expression more appropriate for the problem at hand.

We then start with a generalization of equipartition theorem Eq. (4.82)

$$\frac{1}{T} = \frac{-p'(E)}{\phi(p(E))}, \quad (4.84)$$

where ϕ is an increasing positive function, defined for $x \geq 0$. The Eq. (4.84) holds for all energies E and temperatures T . Then the equation for the maximum of $\rho(E)p(E)$ becomes

$$0 = \frac{d}{dE}(\rho(E)p(E)), \quad (4.85)$$

$$= \rho'(E)p(E) - \frac{1}{T}\rho(E)\phi(p(E)). \quad (4.86)$$

The expression above can be written as

$$\frac{\rho'(E)}{\rho(E)} = \frac{1}{T} \frac{\phi(p(E))}{p(E)}. \quad (4.87)$$

This last equation generalizes the equipartition theorem. The Boltzmann-Gibbs case is recovered when $\phi(x) = x$.

The postulate in Eq. (4.84) fixes the form of the probability distribution $p(E)$. To be able to see this, let us introduce the deformed logarithm

$$\ln_{\phi}(x) = \int_1^x dy \frac{1}{\phi(y)}. \quad (4.88)$$

As can be seen very easily, when $\phi(x) = x$, we recover $\log(x)$. The inverse of this function can be denoted as $\exp_{\phi}(x)$. Using the identity

$$\phi(x) = \exp'_\phi(\ln_\phi(x)), \quad (4.89)$$

we write Eq. (5.84) as

$$p'(E) = -\frac{1}{T} \exp'_\phi[\ln_\phi(p(E))]. \quad (4.90)$$

Integrating the Equation above, we get

$$p(E) = \exp_\phi(G_\phi(T) - E/T). \quad (4.91)$$

The function $G_\phi(T)$ is the integration constant and must be chosen in accordance with

$$1 = \int dE \rho(E) p(E). \quad (4.92)$$

Eq. (4.91) resembles Boltzmann-Gibbs distribution in Eq. (4.83). An important difference is that the normalization constant appears inside the function $\exp_\phi(x)$.

When $\phi(x) = x$, one has $G_\phi(T) = -\log(Z(T))$. Starting from Eq. (4.91), one can develop a generalized thermostatics.

In general, it is difficult to calculate integration constant $G_\phi(T)$ but one can obtain its temperature derivative in terms of previously discussed *escort probabilities*. The generalized definition is

$$P(E) = \frac{1}{Z(T)} \phi(p(E)), \quad (4.93)$$

With normalization factor

$$Z(T) = \int dE \rho(E) \phi(p(E)). \quad (4.94)$$

Expectation values with respect to P(E) are denoted as

$$\langle f \rangle_* = \int dE \rho(E) P(E) f(E). \quad (4.95)$$

P(E) coincides with p(E) in the Boltzmann-Gibbs case i.e., $\phi(x) = x$ for all x. Next, we calculate, using Eqs. (4.89) and (4.93)

$$\frac{d}{dT} p(E) = \exp'_\phi(G_\phi(T) - E/T) \left(\frac{d}{dT} G_\phi(T) + \frac{E}{T^2} \right), \quad (4.96)$$

$$= Z(T) P(E) \left(\frac{d}{dT} G_\phi(T) + \frac{E}{T^2} \right). \quad (4.97)$$

From Eqs. (4.92) and (4.97), we get

$$0 = \int dE \rho(E) \frac{dp(E)}{dT}, \quad (4.98)$$

$$= Z(T) \frac{d}{dT} G_\phi(T) + \frac{Z(T)}{T^2} \langle E \rangle_*, \quad (4.99)$$

which, at last gives,

$$\frac{d}{dT} G_\phi(T) = -\frac{1}{T^2} \langle E \rangle_*. \quad (4.100)$$

Combining Eq. (4.97) with Eq. (4.100), we also have

$$\frac{dp(E)}{dT} = \frac{Z(T)P(E)}{T^2} (E - \langle E \rangle_*). \quad (4.101)$$

Having derived these general equations, there remains the question whether the generalized thermostatics is compatible with thermodynamics.

Our starting point will be establishing thermal stability. Internal energy $U(T)$ is defined by $\langle E \rangle$. Using Eq. (4.101), we obtain

$$\frac{dU(T)}{dT} = \int dE \rho(E) E \frac{dp(E)}{dT}, \quad (4.102)$$

$$= \int dE \rho(E) E \frac{Z(T)P(E)}{T^2} (E - \langle E \rangle_*), \quad (4.103)$$

$$= \frac{Z(T)}{T^2} (\langle E^2 \rangle_* - \langle E \rangle_*^2), \quad (4.104)$$

$$\geq 0. \quad (4.105)$$

Hence, average energy is an increasing function of temperature. However, we also need to prove another relation between entropy and temperature in order to show thermal stability. For this purpose, we define

$$S_\phi(p) = \int dE \rho(E) [(1 - p(E)) F_\phi(0) - F_\phi(p(E))], \quad (4.106)$$

with

$$F_\phi(x) = \int_1^x dy \ln_\phi(y). \quad (4.107)$$

Let us postulate that thermodynamic entropy $S(T)$ equals the value of the above entropy functional in Eq. (4.106) with p given by Eq. (4.91). Then one gets

$$\frac{dS(T)}{dT} = \int dE \rho(E) (-\ln_\phi(p(E)) - F_\phi(0)) \frac{dp(E)}{dT}, \quad (4.108)$$

$$= \int dE \rho(E) \left(-G_\phi(T) + \frac{E}{T} - F_\phi(0) \right) \frac{dp(E)}{dT}, \quad (4.109)$$

$$= \frac{1}{T} \frac{dU(T)}{dT}. \quad (4.110)$$

We needed to make use of the fact that $p(E)$ is normalized to 1. This shows that

$$\frac{1}{T} = \frac{dS}{dU}. \quad (4.111)$$

Because energy is an increasing function of temperature, one concludes that entropy S is a concave function of energy U . This property is known as thermal stability.

One can introduce the Helmholtz free energy $F(T)$ by the relation

$$F(T) = U(T) - TS(T). \quad (4.112)$$

From Eq. (5.110), it follows that

$$\frac{d}{d\beta} \beta F(T) = U(T) \quad \text{with} \quad \beta = \frac{1}{T}. \quad (4.113)$$

Comparison of Eq. (4.100) with Eq. (4.112), we see that $F(T)$ is replaced by $T G_\phi(T)$, $U(T) = \langle E \rangle$ replaced by $\langle E \rangle_*$. Finally, this shows that $T G_\phi(T)$ equals the free energy associated with the escort probability distribution $P(E)$, up to a constant independent of temperature T .

The most obvious generalization of Boltzmann-Gibbs thermostatics is obtained by the choice

$$\phi(x) = x^q \quad \text{with} \quad q > 0. \quad (4.114)$$

It reproduces Tsallis thermostatics with some minor changes. The corresponding deformed logarithmic and exponential functions [65] are

$$\ln_q(x) = \frac{1}{1-q} (x^{1-q} - 1) \quad (4.115)$$

and

$$\exp_q(x) = [1 + (1-q)x]_+^{1/(1-q)}. \quad (4.116)$$

The probability distribution $p(E)$ becomes

$$p(E) = [1 + (1-q)(G_q(T) - E/T)]_+^{1/(1-q)}, \quad (4.117)$$

$$= \frac{1}{z_q(T)} [1 - (1-q)\beta_q^*(T)E]_+^{1/(1-q)}, \quad (4.118)$$

with

$$z_q(T) = (1 + (1-q)G_q(T))^{1/(q-1)} \quad (4.119)$$

and

$$\beta_q^*(T) = z_q(T)^{1-q} / T. \quad (4.120)$$

A nice feature of Tsallis thermostatics is that the correspondence between $p(E)$ and the escort $P(E)$ leads to a dual structure, called “ $q \leftrightarrow 1/q$ ” duality, i.e.,

$$P(E) = \frac{p(E)^q}{Z_q(T)} \quad (4.121)$$

and

$$p(E) = \frac{P(E)^{1/q}}{Z_{1/q}(T)}. \quad (4.122)$$

However, there also exists a “ $q \leftrightarrow 2-q$ ” duality. Given $\ln_\phi(x)$, a new deformed logarithmic function $\ln_\psi(x)$ is obtained by

$$\ln_\psi(x) = (x-1)F_\phi(0) - xF_\phi(1/x), \quad (4.123)$$

with $\psi(x)$ is given by

$$\frac{1}{\psi(x)} = F_\phi(0) - F_\phi(1/x) + \frac{1}{x} \ln_\phi(1/x). \quad (4.124)$$

When $\phi(x) = x^q$, we get

$$\psi(x) = (2-q)x^{2-q}. \quad (4.125)$$

Hence, deformed logarithms $\ln_q(x)$ and $\ln_{2-q}(x)$ can be deduced from each other, up to a constant factor, by the relation (4.123). The definition of entropy can be rewritten as

$$S_\phi(p) = \int dE \rho(E) p(E) \ln_\psi(1/p(E)). \quad (4.126)$$

With $\psi(x) = x^q$, Eq. (5.126) gives us Tsallis entropy, i.e.,

$$S_q(p) = \int dE \rho(E) \frac{(p(E)^q - p(E))}{1-q}. \quad (4.127)$$

In the literature, it has been preferred to use always the above expression for entropy functional. Instead, the definition of average energy has been changed from $\langle E \rangle$ to $\langle E \rangle_*$. In fact, a change from $p(E)$ to $P(E)$ would do the work without the need for changing the definition of average energy.

Now, we are ready to discuss the central issue of this Section, which is the relative entropy concept. A possible generalization of relative entropy (also called divergence) can be defined by

$$I[p \parallel q] = \sum_k q_k f(p_k / q_k), \quad (4.128)$$

with $f(x)$ being a convex function, defined for $x > 0$, strictly convex at $x = 1$ [66,67, 68]. Alternative expressions of the form

$$D[p \parallel q] = \sum_k [f(p_k) - f(q_k) - (p_k - q_k)f'(q_k)], \quad (4.129)$$

with $f'(x)$ being the derivative of $f(x)$, are called relative entropies of Bergmann type [69, 70]. The Eqs. (4.128) and (4.129) are identical in the case when

$$f(x) = x \log(x). \quad (4.130)$$

Hence, there is no need to make a difference between the two forms in the standard theory.

Now, note that we can write Eq. (4.74), using also Eq. (4.46)

$$I_\kappa(p) = -F_\kappa(0) - \sum_k \int_0^{p_k} dx \ln_\kappa(x). \quad (4.131)$$

From Eq. (4.128), we write, for the relative entropy

$$I_\kappa[p \parallel q] = - \sum_k p_k \omega_\kappa(q_k / p_k). \quad (4.132)$$

Using the definition of ω_κ , one obtains

$$I_\kappa[p \parallel q] = \sum_k \int_{q_k}^{p_k} dx \ln_\kappa(x / q_k). \quad (4.133)$$

$I_\kappa[p \parallel q] \geq 0$ and $I_\kappa[p \parallel q]$ is jointly convex in p and q . $I_\kappa[p \parallel q] = 0$ implies $p = q$. For example, using Eq. (4.64), we obtain the Tsallis form of relative entropy which reads

$$I_\kappa(p \parallel q) = \frac{1}{\kappa} \sum_k p_k \left(\left(\frac{p_k}{q_k} \right)^\kappa - 1 \right). \quad (4.134)$$

But, as pointed out before, there is also relative entropy definition of Bergmann type in the mathematical literature. There is no nonextensive relative entropy of Bergmann type. For this purpose, we proceed with Eq. (4.133)

$$D_{\kappa}[p \parallel q] = \sum_k \int_{q_k}^{p_k} dx (\ln_{\kappa}(x) - \ln_{\kappa}(q_k)), \quad (4.135)$$

$$= \sum_k [F_{\kappa}(p_k) - F_{\kappa}(q_k) - (p_k - q_k) \ln_{\kappa}(q_k)], \quad (4.136)$$

$$= I_{\kappa}(q) - I_{\kappa}(p) - \sum_k (p_k - q_k) \ln_{\kappa}(q_k). \quad (5.137)$$

This last expression is of Bergmann type. Positivity of $D_{\kappa}[p \parallel q]$ follows immediately since $\ln_{\kappa}(x)$ is an increasing function x . As usual, $D_{\kappa}[p \parallel q] = 0$ implies $p = q$. Convexity in the first argument is explicit. For nonextensive statistics a la Tsallis, we get

$$D_{\kappa}[p \parallel q] = \frac{1}{\kappa} \sum_k p_k (p_k^{\kappa} - q_k^{\kappa}) - \sum_k (p_k - q_k) q_k^{\kappa}. \quad (4.138)$$

This expression is of the form (4.129) and certainly different than Eq. (4.134) [71].

The equation above forms a new relative entropy definition of Bergmann type in the framework of Tsallis statistics complementing the one provided by Eq. (4.134). The physical meaning of Eq. (4.1) which is exactly the same as Eq. (4.134), had already been given in Section I. Now, let us address the same issue for the new relative entropy expression above. Using first choice of internal energy constraint, we write

$$\delta \left[\frac{1}{1-q} (\sum_i p_i^q - 1) - \alpha \sum_i p_i - \beta \sum_i p_i \varepsilon_i \right] = 0, \quad (4.139)$$

which yields

$$\frac{q}{1-q} \tilde{p}_i^{q-1} - \alpha - \beta \varepsilon_i = 0. \quad (4.140)$$

Multiplying both sides by \tilde{p}_i , summing up and assuming that \tilde{p}_i is normalized, one gets

$$\frac{q}{1-q} [1 + (1-q) \tilde{S}_q] - \alpha - \beta \tilde{U} = 0, \quad (4.141)$$

where \tilde{S}_q is the value of the Tsallis entropy for the stationary distribution \tilde{p}_i and $\tilde{U}_q = \sum_i \varepsilon_i \tilde{p}_i$. Note that all these calculations are being carried out with respect to first

internal energy constraint. Substitution of α into Eq. (4.141), we have

$$\tilde{p}_i = [1 + (1 - q)\tilde{S}_q - \frac{q-1}{q}\beta(\varepsilon_i - \tilde{U}_q)]^{1/(q-1)}. \quad (4.142)$$

Substitution of Eq. (4.142) into Eq. (4.138) yields

$$D_q[p \parallel q] = -S_q + \tilde{S}_q + \beta U - \beta \tilde{U}, \quad (4.143)$$

$$= F_q - \tilde{F}_q, \quad (4.144)$$

which is nothing but the difference between the free energies. This proves that the two different expressions of relative entropy i.e., $K_q[p \parallel r]$ and $D_q[p \parallel q]$ are on equal footing as long as only their physical meanings are being considered. One main difference between these two expressions is that first is related to third choice of internal energy constraint whereas the latter is related to first internal energy constraint.

One might still argue that $D_q[p \parallel q]$ can be written in such a way as to conform to the third choice of internal energy constraint: Modifying equation (4.139) in terms of escort probabilities, we can write

$$\delta \left[\frac{1}{1 - (1/q)} \left(\sum_i P_i^{1/q} - 1 \right) - \alpha \sum_i P_i - \beta \sum_i P_i \varepsilon_i \right] = 0, \quad (4.145)$$

since we can always make use of the fact that escort probabilities are normalized and it might be used together with the rule $q \rightarrow 1/q$. As can be immediately understood, the last term in the equation above is nothing but the third choice of internal energy constraint. This yields

$$\frac{1/q}{1 - (1/q)} [1 + (1 - (1/q))\tilde{S}_q] - \alpha - \beta \tilde{U} = 0. \quad (4.146)$$

Finally, we get

$$\tilde{P}_i = [1 + (1 - (1/q))\tilde{S}_q - \frac{1/q - 1}{1/q}\beta(\varepsilon_i - \tilde{U}_q)]^{1/(1/q-1)}. \quad (4.147)$$

We must note, however, that entropy and internal energy definitions in the equation above is all written with third choice in contrast to Eq. (4.142). Now, when we

substitute the expression above into the definition of $D_q[p \parallel q]$ which is being modified as

$$D_\kappa[P \parallel Q] = \frac{1}{\kappa} \sum_k P_k (P_k^\kappa - Q_k^\kappa) - \sum_k (P_k - Q_k) Q_k^\kappa, \quad (4.148)$$

where P and Q represents escort probabilities and κ becomes equal to $(1/q)-1$ instead of $(q-1)$. Using the expression above likewise, we are led to

$$D_q[p \parallel q] = F_q - \tilde{F}_q, \quad (4.149)$$

where F_q 's represent the free energies with respect to third choice of constraint. This seemingly shows that $D_q[p \parallel q]$ too can be written in way which will conform to third constraint. Is it really so? The answer is a solid no due to two severe flaws: Firstly, in the optimization in Eq. (4.145), we made use of the escort probabilities being normalized to unity. However, this condition cannot be put as a constraint since escort probabilities are already defined very explicitly in Chapter 2. The second term in Eq. (4.145) is nothing but an identity. This, in turn means that if normalization is used as a constraint, then escort probabilities as a definition must be discarded, and accordingly what has been known as escort probabilities until now has to be regarded as a basic independent variable. Then, the first term in Eq. (4.145) i.e., the entropy formula written in terms of P_i 's has to be interpreted as a new quantity, which is different than the original Tsallis entropy [72].

Secondly, due to the relation

$$\sum_{i=1}^W (p_i)^q = \left[\sum_{i=1}^W (P_i)^{1/q} \right]^{-q}, \quad (4.150)$$

the entropy functional which will be used in the optimization can be written as

$$S_q[P] = \frac{1}{1-q} \left\{ \left[\sum_i P_i^{1/q} \right]^{-q} - 1 \right\}. \quad (4.151)$$

$S_q[P]$ has a severe mathematical problem which becomes explicit when it has been written this way: It is not concave for $0 < q < 1$ since $f(r;q) \equiv \partial^2 S_q[P] / \partial r^2$, with respect to (r,q) in the case of $P_1 = r$, $P_2 = 1-r$ where $0 < r < 1$. Then, it is easily seen (through a three dimensional Mathematica plot) that $f(r;q)$ changes its sign when $0 < q < 1$. This regime is a very important regime (recall that $q=1$ means ordinary statistics!), therefore

we see that the theory exhibits instability in this regime and the new relative entropy expression is destined to be related to be considered in the frame of second choice of internal energy constraint.

4.4 Two Definitions of Relative Entropies And Constraints In Nonextensive Formalism

In this Section, we will compare the previously discussed forms of two relative entropies i.e., $K_q[p \parallel r]$ and $D_q[p \parallel q]$. Up to now, main difference between them has been related to internal energy constraint.

First of all, we notice that, in the limit $q \rightarrow 1$, both $K_q[p \parallel r]$ and $D_q[p \parallel q]$ becomes the Kullback-Leibler relative entropy

$$H[p \parallel r] = \sum_i p_i \ln(p_i / r_i). \quad (4.152)$$

The following expression is often used for the formula above

$$H[p \parallel r] = \frac{d}{dx} \sum_i (p_i)^x (r_i)^{1-x} \Big|_{x \rightarrow 1}. \quad (4.153)$$

$K_q[p \parallel r]$ is obtained by replacing the differential operator by the Jackson q -differential operator, i.e.,

$$H[p \parallel r] = D_q \sum_i (p_i)^x (r_i)^{1-x} \Big|_{x \rightarrow 1}, \quad (4.154)$$

where D_q is defined as

$$D_q f(x) = [f(qx) - f(x)] / [x(q - 1)], \quad (4.155)$$

which converges to the ordinary differential in the limit $q \rightarrow 1$. No such simple correspondence is known to exist between $H[p \parallel r]$ and $D_q[p \parallel q]$.

Convexity is one of the most important properties fulfilled by relative entropy. Taking the second order derivatives of $D_q[p \parallel q]$ with respect to the arguments, one finds that it is convex in p_i but not in r_i .

On the other hand, like the Kullback-Leibler relative entropy, $K_q[p \parallel r]$ is found to be jointly convex, i.e.,

$$K_q[\sum_a \lambda_a p_{(a)} \parallel \sum_a \lambda_a r_{(a)}] \leq \sum_a \lambda_a K_q[p_{(a)} \parallel r_{(a)}], \quad (4.156)$$

where $\lambda_a > 0$ and $\sum_a \lambda_a = 1$. This property is stronger than individual convexity in p_i and r_i .

Finally, we compare them in terms of *composability*: Like the Kullback-Leibler relative entropy, $K_q[p \parallel r]$ is “composable”, but $D_q[p \parallel q]$ is not. In fact, for factorized joint distributions of a composite system (A,B) i.e.,

$$p_{ij}(A,B) = p_{(1)i}(A) p_{(2)j}(B), \quad (4.157)$$

$$r_{ij}(A,B) = r_{(1)i}(A) r_{(2)j}(B). \quad (4.158)$$

In this case, $K_q[p_{(1)}p_{(2)} \parallel r_{(1)}r_{(2)}]$ yields

$$\begin{aligned} K_q[p_{(1)}p_{(2)} \parallel r_{(1)}r_{(2)}] &= K_q[p_{(1)} \parallel r_{(1)}] + K_q[p_{(2)} \parallel r_{(2)}] \\ &\quad + (q-1) K_q[p_{(1)} \parallel r_{(1)}] K_q[p_{(2)} \parallel r_{(2)}], \end{aligned} \quad (5.159)$$

whereas no such closed relation exists for $D_q[p_{(1)}p_{(2)} \parallel r_{(1)}r_{(2)}]$.

All considerations above point out to same fact that $K_q[p \parallel r]$ has indeed more favorable properties than those of $D_q[p \parallel q]$.

The choice of $K_q[p \parallel r]$ is in fact supported by a set of axioms. About a quarter century ago, Shore and Johnson have proposed the axioms for minimum cross entropy (i.e., relative entropy) principle [73-75]. They are composed of the following five axioms (which will be presented in a nonabstract manner):

Axiom I (Uniqueness): If the same problem is solved twice, then the same answer is expected to result both times.

Axiom II (Invariance): The same answer is expected when the same problem is solved in two different coordinate systems, in which the posteriors (i.e., p_i) in the two systems should be related by the coordinate transformation.

Axiom III (System Independence): It should not matter whether one accounts for independent information about independent systems separately in terms of their marginal distributions or in terms of the joint distribution.

Axiom IV (Subset Independence): It should not matter whether one treats independent subsets of the states of the systems in terms of their separate conditional distributions or in terms of the joint distribution.

Axiom V (Expansability): In the absence of new information, the prior (i.e., r_i or so-called reference distribution) should not be changed.

These axioms are extremely general and natural, and thus it is likely that they cannot be denied by any physical situation we are interested in. According to studies carried out by Shore and Johnson, any relative entropy $J[p \parallel r]$ with the prior r_i and a posterior p_i satisfying the axioms I-V has to have the following form:

$$J[p \parallel r] = \sum_i p_i h(p_i / r_i), \quad (4.160)$$

where $h(x)$ is some function.

It is important to realize that such a function $h(x)$ exists for $K_q[p \parallel r]$:

$$h(x) = \frac{1}{1-q} (1 - x^{q-1}), \quad (4.161)$$

whereas $D_q[p \parallel r]$ cannot be put into the form of Eq. (4.160). Therefore, we see that the relative entropy expression related to third constraint i.e., $K_q[p \parallel r]$ satisfies all of the Shore-Johnson axioms.

Since right from the beginning, we identified the relative entropy $K_q[p \parallel r]$ with third internal energy constraint and $D_q[p \parallel r]$ with the second choice, all the arguments up to now also give us the clue why third choice of constraint is superior and therefore preferable to the second choice of internal energy constraint [47].

CHAPTER 5

CONCLUSION

We studied nonextensive generalization of Boltzmann-Gibbs statistical mechanics offered by Constantino Tsallis in 1988 [76-95]. In Chapter 2, the outline of the theory has been provided. As is easily seen, a lot of nonextensive generalizations of previous ideas have been succeeded by writing them down in such a way as to include nonextensivity parameter q in an appropriate manner [96-110]. In all these cases, in the limit $q \rightarrow 1$, usual Boltzmann-Gibbs results have been obtained whether it be nonxtensive Langevin equation or else.

In Chapter 3, we have seen the solutions of isotropic rigid and non-rigid rotator models in nonextensive framework. One important aspect of these solutions was the emphasis put on changing from the second constraint to the third one as long as thermodynamic observables are being concerned. A possible scaling too has been discovered along the way.

In nonextensive statistics, one vital issue was the problematics of constraints. Both second and third constraints were able to provide nonextensive solutions. In Chapter 4, it has been discovered that the solution to this problem was intrinsically related to a concept called relative entropy. Having been able to write two distinct forms of relative entropy expressions, the first being related to second and later being related to third constraints, we have shown that a rigorous mathematical analysis of these two expressions led on favor of third choice of internal energy constraint.

In this thesis, no mention has been made of the success of experimental evidence in nonextensive statistics. Huang and Driscoll [111] had in 1994 some quite interesting nonneutral electronic plasma experiments done in a metallic cylinder in the presence of an axial magnetic field. They observed a turbulent state, the electronic density radial distribution of which was measured. Boghosian showed in 1996 that their case precisely corresponds to the optimization of Tsallis entropy with $q=1/2$ [112].

Another experimental success came from a distinct field of physics, namely, solar neutrino physics. The famous problem regarding the solar neutrino problem is that the calculations within the so-called standard solar model (SSM) provide a neutrino flux which is double of what has really been observed on Earth's surface. At least, two possibilities are to be scrutinized: First of all, neutrinos can oscillate in such a way that only part of them can be detected by current experimental devices. Secondly, the neutrino flux is related to the total area of the so-called Gamow peak, which is in turn due to the product of the thermal equilibrium BG distribution (which decreases with energy) and penetration factor (which increases with energy). The position of the peak is at energies 10 times larger than kT , therefore only the far tail of the distribution is concerned. Quarati et al. argue that very slight departures from $q = 1$ (of the order of 0.01) are enough to modify the area of the Gamow peak. This slight nonextensivity thus solves the famous solar neutrino problem [113-115].

Since early ideas of Fermi, and later Feynman, a thermodynamical equilibrium scenario has been developed for the distribution of transverse momenta in the hadronic jets emerging from electron-positron annihilation after central collisions at energies ranging 14 to 161 GeV. Hagedorn developed a full theory based on BG statistics. The central idea that higher collision energies do not increase the transverse momenta temperature T but instead increase the number of involved bosons that are produced could not be realized by Hagedorn's calculations. Adopting two parameters, T and q , Bediaga et al. [116, 117] obtained fits on amazingly large sets of experimental data. Wilk in Warsaw [118-120] have provided further evidences for the applicability of nonextensive statistics into high energy physics.

Distribution of peculiar velocities of spiral galaxies (whose data obtained by COBE satellite) has been shown to fit with $q = 0.24$ [121]. This has been carried out by Tsallis and Quarati. Glazier, in Notre Dame University, measured for horizontal velocities of Hydra viridissima in physiological solution. The data well fitted to $q = 1.5$ [122].

Nonextensive statistics had been applied to some ideas ranging from Zipf Law [123, 124], teen birth phenomena [125], internet traffic [126, 127], random matrix theory [128-130], long-range Hamiltonians [131, 132], aging [133, 134] to chaotic maps [135-139].

Recently, inspired by nonextensive statistics, a new investigation has been started under the name of superstatistics [140-142]. Superstatistics provide a more general framework in which nonextensive case is only one of the cases, which can occur as far as statistics is concerned. There happens to be appearing many developments in these fields in the close future.

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VITA

Gokhan Baris Bagci was born in Iskenderun, Hatay on July 11, 1975. He received his B. S degree in Physics from the Middle East Technical University in 1996. He later received his M. Sc. in Physics in 1998. He worked in Middle East Technical University as a graduate assistant from 1998 to 2001.