

THE NONADDITIVE GENERALIZATION OF KLIMONTOVICH'S S-THEOREM
FOR OPEN SYSTEMS AND BOLTZMANN'S ORTHODES

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We show that the nonadditive open systems can be studied in a consistent manner by using a generalized version of S-theorem. This new generalized S-theorem can further be considered as an indication of self-organization in nonadditive open systems as prescribed by Haken. The nonadditive S-theorem is then illustrated by using the modified Van der Pol oscillator. Finally, Tsallis entropy as an equilibrium entropy is studied by using Boltzmann's method of orthodes. This part of dissertation shows that Tsallis ensemble is on equal footing with the microcanonical, canonical and grand canonical ensembles. However, the associated entropy turns out to be Renyi entropy.

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CHAPTER 1

INTRODUCTION

Although an admirer of Boltzmann, Einstein never accepted Boltzmann principle $S = k \log W$ and argued that the statistics of the system (W) must follow from its dynamics. Therefore, a thermostatistical framework cannot be postulated *a priori* [1, 2]. The recent progress in nonequilibrium statistical physics justifies Einstein's view, since we now have many different statistics occurring in nature depending on the underlying fluctuations, the structure of the phase space and different non-equilibrium conditions. For example, we now know that Dirac delta type of fluctuations in the intensive variable $\beta = \frac{1}{T}$ where T is temperature, give rise to Boltzmann statistics. However, a different type of fluctuation provides us with an even richer variety of statistics completely different than the Boltzmann-Gibbs (BG) statistics [3]. Therefore, it is imperative to understand under what conditions BG statistics holds and must be replaced by a new statistics.

The subject of this dissertation is the emergence of a new formalism when we cannot rely on the Boltzmann formulation (or Gibbs for that matter). These cases are not fictitious and have been reported for some time [4-10]. In fact, Boltzmann himself had mentioned the limitations of his own theory, stating that it would not be valid for long-range forces. The examples for which Boltzmann entropy fails are many but some of them includes turbulence [4, 5], electron-positron annihilation [6], kinetic theory [7], quantum chaos [8], quantum entanglement [9], anomalous diffusion [10]. Almost all these examples have one thing in common. They have meta-stable equilibrium distributions of the inverse power law form, not exponential as Boltzmann suggested. In this sense, we need a new entropy expression, which will lead to inverse power law distributions as the stationary equilibrium distribution.

In this dissertation, I will mainly consider two such related entropy expressions: Tsallis entropy [11] and incomplete statistics (IS) entropy [12], although there are many other

candidates [13, 14]. Both Tsallis and IS entropy break the additivity postulate which is satisfied by Boltzmann entropy. On the other hand, since these entropies are expected to work even for long-range interactions, this is not surprising. In fact, L. Tisza [15] remarks that the additivity postulate cannot be inferred from general principles and must be taken as an approximation for cases with intramolecular forces of short-range character. The main difference between the two is the degree of our knowledge of the system, since the Tsallis entropy is based on the assumption that we can know all the microstates whereas the IS entropy is not.

Much is known about these entropies and many developments have been made. However, a formalism based on these two entropies for open systems is missing so far. My primary contribution is to give such a formalism within the context of Tsallis and IS entropies. These results are reported in Chapters 5 and 6. We see that a new concept called “renormalized entropy” is necessary in order to generalize these two entropies to open systems. Moreover, this formalism will also allow us to have a criterion for self-organization in nonadditive open systems.

Another relevant issue is raised in Chapter 7 and is further elaborated in Chapter 8. We introduce Boltzmann’s method of orthodes in Chapter 7. Boltzmann’s method allows one to base equilibrium thermostatics without the need to use probabilistic arguments. Moreover, the results obtained from this method can be applied to physical systems of any size. In other words, one does not need to invoke the thermodynamic limit. This aspect is important since recently we can deal with small systems possessing few degrees of freedom. We would still like to investigate them in terms of their temperature and other thermodynamic functions. Is this possible? The answer is positive and its roots can be traced back to Boltzmann.

Chapter 8 is on the application of the method of orthodes to the Tsallis ensemble. I show that as far as heat theorem is concerned, the Tsallis ensemble is on equal footing with the microcanonical, canonical and grand canonical ensembles. Surprisingly, the associated entropy turns out to be the Rényi entropy [13].

The conclusions are given in Chapter 9.

CHAPTER 2

NONADDITIVE TSALLIS ENTROPY

2.1. General Formalism

In order to generalize Boltzmann-Gibbs entropy (BG), C. Tsallis [11, 16, 17] proposed a one-parameter generalization of BG entropy i.e., the Tsallis entropy in 1988. The Tsallis entropy can be written as

$$(2.1) \quad S_q(p) = k \frac{\sum_i^W p_i^q - \sum_i^W p_i}{1 - q}$$

where p_i is the probability of the system in the i th microstate, and W is the *total* number of configurations of the system. For the cases with $q < 0$, one must be cautious not to include the probability assignments, which will result in divergences in the entropy expression above. The constant k is the Boltzmann constant that will be taken as unity in most of this dissertation. The parameter q is a real number called the entropic index or nonadditivity parameter.

The parameter q is called the nonadditivity parameter because the entropy of two independent systems A and B where $p_{ij}(A+B) = p_i(A)p_j(B)$ is

$$(2.2) \quad S_q(A+B)/k = [S_q(A)] + [S_q(B)] + (1-q)[S_q(A)][S_q(B)].$$

This equation shows a drastic departure from the BG entropy since the BG entropy is completely additive in the sense described above. The possibilities $q < 1$, $q = 1$ and $q > 1$ are called superadditive, additive and subadditive, respectively. The naming of these cases can be easily understood if we note that $p_i^q > p_i$ for $q < 1$ (i.e., the superadditive case), because the probability values are between zero and one. In this sense, Tsallis entropy presents us with a means of emphasizing the rare and frequent events. It is a general

feature of Tsallis entropy that it (and all associated thermodynamic functions) becomes BG entropy in the $q \rightarrow 1$ limit.

Another general structure underlying the definition of the Tsallis entropy is given in terms of deformed exponentials. In this framework, one defines a q -deformed logarithm

$$(2.3) \quad \ln_q(x) = \frac{x^{1-q} - 1}{1 - q}.$$

The q -exponential is defined as

$$(2.4) \quad \exp_q(x) = (1 + (1 - q)x)^{\frac{1}{1-q}}.$$

These definitions become the ordinary logarithm and exponential in the $q \rightarrow 1$ limit.

One can now rewrite the Tsallis entropy in terms of q -deformed logarithm as

$$(2.5) \quad S_q = - \sum_i p_i \ln_q(1/p_i).$$

The Tsallis entropy was originally maximized by

$$(2.6) \quad \delta(S_q - \alpha \sum_{i=1}^w p_i - \beta \sum_{i=1}^w p_i \epsilon_i) = 0$$

where the Lagrange multipliers are denoted by α and β . The energy of the i th microstate is denoted by ϵ_i . This maximization resulted in the stationary equilibrium distribution

$$(2.7) \quad p_i^{(1)} = \frac{[1 - (q - 1)\beta\epsilon_i]^{1/(q-1)}}{Z_q^{(1)}}$$

where $Z_q^{(1)} = \sum_j [1 - (q - 1)\beta\epsilon_j]^{1/(q-1)}$ is the partition function. The superscript (1) indicates that the above maximization has been carried out with respect to the internal energy constraint

$$(2.8) \quad \sum_i^W p_i \varepsilon_i = U_q^{(1)}.$$

However, this choice of constraints did not solve the problems regarding the Lévy distribution since second moment would still diverge under the maximization [18]. Since one expected to obtain a more general framework from Tsallis entropy that includes Lévy distribution as a subset, a new expression for the internal energy constraint was proposed,

$$(2.9) \quad \sum_i^W p_i^q \varepsilon_i = U_q^{(2)}.$$

The maximization of the Tsallis entropy subject to this internal energy constraint now results in the following stationary equilibrium distribution

$$(2.10) \quad p_i^{(2)} = \frac{[1 - (1 - q)\beta \varepsilon_i]^{1/(1-q)}}{Z_q^{(2)}}$$

where the denominator is the associated partition function $Z_q^{(2)} = \sum_j [1 - (1 - q)\beta \varepsilon_j]^{1/(1-q)}$. This equilibrium distribution preserves the Legendre structure regardless of q . The inverse temperature can be obtained as

$$(2.11) \quad \beta = \frac{\partial S_q}{\partial U_q^{(2)}}.$$

The internal energy function and the partition function with this *second* constraint becomes

$$(2.12) \quad U_q^{(2)} = -\frac{\partial \ln_q Z_q^{(2)}}{\partial \beta}.$$

The free energy is defined as

$$(2.13) \quad F_q^{(2)} = U_q^{(2)} - \frac{1}{\beta} S_q = -\frac{1}{\beta} \ln_q Z_q^{(2)}$$

and the heat capacity is given by the following equation

$$(2.14) \quad C_q^{(2)} = \frac{\partial U_q^{(2)}}{\partial T}.$$

This choice of constraint, i.e. the second constraint in the nonadditive formalism enabled one to obtain the Lévy distribution as a result of the maximization of Tsallis entropy. However, it soon faced three severe objections. First, the equilibrium distribution obtained from the maximization of the Tsallis entropy subject to the second constraint is not invariant under uniform translation of ε_i . In this sense, the thermodynamical results depend on the choice of the origin of the energies. Second is the need to use expectation value of the form $\sum_i^W p_i^q O_i = \langle O_q \rangle^{(2)}$ for any observable O . However, this expectation value is not normalized and moreover yields

$$(2.15) \quad \langle 1 \rangle^{(2)} \neq 1.$$

Third, the use of the second constraint is related to the violation of macroscopic energy conservation. In order to see this, we assume two systems A and B satisfy $p_{ij}^{AB} = p_i^A p_j^B$ such that $\varepsilon_{ij}^{AB} = \varepsilon_i^A + \varepsilon_j^B$. Now, it can be shown that

$$(2.16) \quad U_q^{(2)}(A+B) = U_q^{(2)}(A) + U_q^{(2)}(B) + (1-q)[U_q^{(2)}(A)S_q(B) + U_q^{(2)}(B)S_q(A)],$$

which is different than $U_q^{(2)}(A) + U_q^{(2)}(B)$. The above equation shows that the energy is not conserved macroscopically for $q \neq 1$. This violates the first principle of thermodynamics. A question might be asked at this point: why can we not accept the violation of the first law since we have embraced the nonadditivity of the entropy? However, the entropy is inherently an informational definition whereas the first law is a mechanical law. In other words, we do not accept any change at the level of dynamics although we adopt a different nonadditive entropy definition.

In order to overcome all these difficulties, a third choice of constraints has been adopted in the nonadditive formalism [19]. This third choice is called escort distribution and written as

$$(2.17) \quad U_q^{(3)} = \frac{\sum_{i=1}^w p_i^q \epsilon_i}{\sum_{i=1}^w p_i^q}.$$

This constraint is similar to the second constraint but it is normalized. The maximization of the Tsallis entropy with the above constraint yields the following stationary equilibrium distribution

$$(2.18) \quad p_i^{(3)} = \frac{[1 - (1 - q)\beta(\epsilon_i - U_q^{(3)}) / \sum_{j=1}^w (p_j^{(3)})^q]^{1/(1-q)}}{Z_q^{(3)}}$$

where the partition function $Z_q^{(3)}$ is given by

$$(2.19) \quad Z_q^{(3)} = \sum_{i=1}^w [1 - (1 - q)\beta(\epsilon_i - U_q^{(3)}) / \sum_{j=1}^w (p_j^{(3)})^q]^{1/(1-q)}.$$

This choice too respects the Legendre structure and the inverse temperature is

$$(2.20) \quad \beta = \frac{\partial S_q}{\partial U_q^{(3)}}.$$

The internal energy function and the partition function with the *third* constraint becomes

$$(2.21) \quad U_q^{(3)} = -\frac{\partial \ln_q Z_q^{(3)}}{\partial \beta}.$$

The free energy is defined as

$$(2.22) \quad F_q^{(3)} = U_q^{(3)} - \frac{1}{\beta} S_q = -\frac{1}{\beta} \ln_q Z_q^{(3)}$$

and the heat capacity is given by the following equation

$$(2.23) \quad C_q^{(3)} = \frac{\partial U_q^{(3)}}{\partial T}.$$

In addition to the preservation of the Legendre structure, the third constraint also solves the previous difficulties. First, if we add a constant ε_0 to all micro-energies ε_i , $U_q^{(3)}$ becomes $U_q^{(3)} + \varepsilon_0$. This in turn leaves invariant all the differences $\varepsilon_i - U_q^{(3)}$. Therefore, the probability distribution $p_i^{(3)}$ is invariant under uniform translation of the energy ε_i . Second, we see that the expectation value of an observable is now defined as

$$(2.24) \quad \langle O_q \rangle^{(3)} = \frac{\sum_{i=1}^w p_i^q O_i}{\sum_{j=1}^w p_j^q}.$$

This preserves the norm of 1 for every q ,

$$(2.25) \quad \langle 1 \rangle^{(3)} = \frac{\sum_{i=1}^w p_i^q}{\sum_{j=1}^w p_j^q} = 1.$$

Third, we also preserve the first law of thermodynamics since

$$(2.26) \quad U_q^{(3)}(A + B) = U_q^{(3)}(A) + U_q^{(3)}(B)$$

where A and B are two independent systems.

2.2. Meaning of the Nonadditivity Parameter

The parameter q is associated with the nonadditivity of the entropy values of the independent systems A and B . This is why it is called the nonadditivity index. However, since the Tsallis entropy is a one-parameter generalization of BG entropy, it is very important to understand the physical meaning of this parameter i.e., q . The nonadditivity parameter can indeed be given a physical meaning in terms of fluctuations. This idea has first been put forth by Wilk and Włodarczyk [20]. Wilk et al. considered a general function $G_q(x)$, which is written in terms of q -exponential defined in Eq. (2.4)

$$(2.27) \quad G_q(x) = C_q [1 - (1 - q) \frac{x}{\lambda}]^{1/(1-q)}.$$

As expected,

$$(2.28) \quad G_{q=1} = c \exp(-\frac{x}{\lambda}).$$

Adopting the abbreviation $\alpha = 1/(q - 1)$, Wilk et al. looks for a function $f(1/\lambda)$, which leads from the exponential to the inverse power law of q-exponential type in Eq. (2.27) with a fluctuation around the mean value $1/\lambda_0$. This can be written as

$$(2.29) \quad G_q(x; \lambda_0) = C_q \int_0^\infty \exp(-\frac{x}{\lambda}) f(1/\lambda) d(1/\lambda).$$

The solution for such a function $f(1/\lambda)$ is given in terms of Euler gamma function

$$(2.30) \quad f(\frac{1}{\lambda}) = \frac{1}{\Gamma(\alpha)} (\alpha \lambda_0) (\frac{\alpha \lambda_0}{\lambda})^{\alpha-1} \exp(-\frac{\alpha \lambda_0}{\lambda}).$$

The mean of this distribution is

$$(2.31) \quad \left\langle \frac{1}{\lambda} \right\rangle = \frac{1}{\lambda}$$

with the variance

$$(2.32) \quad \left\langle \left(\frac{1}{\lambda} \right)^2 \right\rangle - \left\langle \frac{1}{\lambda} \right\rangle^2 = \frac{1}{\alpha \lambda_0^2}.$$

This first observation between the fluctuation and the nonadditivity parameter q has been generalized by the so-called *superstatistics* [4]. After its first formulation, the superstatistics found many fields of application for itself. Some of these applications can be cited as hydrodynamic turbulence [21], cosmic rays [22], solar flares [23], random matrix theory [24] and hydro-climatic fluctuations [25]. Beck and Cohen [4] considered a driven nonequilibrium system composed of regions that exhibit spatio-temporal fluctuations of

an intensive quantity. This intensive quantity can be pressure or chemical potential. However, Beck and Cohen considered this fluctuating quantity to be β . This case cannot be treated by the fluctuation theory of Onsager and Machlup since their theory is restricted to the extensive variables only. The superstatistics on the other hand deals with a nonequilibrium steady state of a macroscopic system and focuses on the fluctuations of the intensive quantities. The nonequilibrium steady state is made up of many smaller cells that are temporarily in local equilibrium. The intensive quantity (i.e., inverse temperature) β is constant in each cell. Each cell is large enough to obey statistical mechanics and the distribution of the intensive variable β is determined by $f(\beta)$. If E is the energy of the microstate associated with each cell, an effective Boltzmann factor is written as

$$(2.33) \quad B(E) = \int_0^\infty d\beta f(\beta) q_\beta(x)$$

where $q_\beta(x) = \frac{e^{-\beta H(x)}}{Z'}$. If the distribution $f(\beta)$ is peaked about β_0 i.e.,

$$(2.34) \quad f(\beta) = \delta(\beta - \beta_0),$$

one recovers the ordinary Boltzmann factor. The distribution $f(\beta)$ can be chosen in many ways. However, there are some limitations such as the normalization. Moreover, the new statistics too must be normalizable i.e., the integral $\int_0^\infty dE B(E)$ must exist. The new statistics obtained from the superstatistics must reduce to BG statistics whenever there are no fluctuations of the intensive quantity. Now, following Wilk et al., we consider a Gamma distribution defined as

$$(2.35) \quad f(\beta) = \frac{1}{b\Gamma(c)} \left(\frac{\beta}{b}\right)^{c-1} e^{-\beta/b}$$

where $c > 0$ and $b > 0$. The mean and the variance of the intensive variable β is

$$(2.36) \quad \langle \beta \rangle = bc; \quad \sigma^2 = b^2 c.$$

The generalized Boltzmann factor for the above case can be found by integration and reads

$$(2.37) \quad B(E) = (1 + bE)^{-c}.$$

Identifying $c = 1/(q - 1)$, we can write the above generalized Boltzmann factor as

$$(2.38) \quad B(E) = (1 + (q - 1) \langle \beta \rangle E)^{1/(1-q)},$$

which is the Tsallis distribution. Note that it is normalizable for $c > 1$. According to the superstatistical framework, different probability distributions associated with the fluctuations of the intensive variables give rise to different statistics. The Tsallis distribution is only one of them!

2.3. Hyperensembles, Superstatistics and Tsallis Entropy

The superstatistics provides a very general framework to relate the underlying fluctuations of the intensive variables to the newly emerging out-of-equilibrium statistics different than BG statistics. However, one missing link is the *ad hoc* probability distribution of the fluctuation i.e., $f(\beta)$. If we can fix this distribution of the fluctuation through some method, then the superstatistics will have a stronger foundation. One way to solve this is provided by Gavin Crooks [26]. Crooks considered the concept of *hyperensembles* and the maximization of the hyperensemble in order to determine the so-far *ad hoc* distribution of the fluctuation. The "hyperensemble" is an ensemble of ensembles, whose each member has the same instantaneous Hamiltonian, but described by a different probability distribution. Instead of finding the probability distribution of the system, one looks for the metaprobability $P(\theta)$ that maximizes the entropy H of the hyperensemble i.e.,

$$(2.39) \quad H = - \int P(\theta) \log\left(\frac{P(\theta)}{m(\theta)}\right).$$

In the above equation, $m(\theta)$ acts as a prior and is a measure on the space of the probability distributions. It ensures the invariance of the entropy under different parametrizations. Having chosen the form of the hyperentropy, we need to fix the constraints in order to maximize the hyperentropy. The constraints can be chosen as the normalization and mean energy i.e.,

$$(2.40) \quad \int P(\theta) d\theta = 1$$

and

$$(2.41) \quad \langle\langle E \rangle\rangle = \int P(\theta) \left(\sum_i \theta_i E_i \right) d\theta = 1.$$

Lastly, we need a measure of how far the hyperstate is to the state of equilibrium. For this purpose, we consider the following entropy as a constraint

$$(2.42) \quad \langle S \rangle = \int P(\theta) \left(- \sum_i \theta_i \log \theta_i \right) d\theta = 1.$$

The maximization of the hyperentropy subject to these constraints yields

$$(2.43) \quad P(\theta) = m(\theta) e^{-\lambda_0 - \lambda_1 \langle E \rangle - \lambda_2 S(\theta)}$$

where $S(\theta) = - \sum_i \theta_i \log \theta_i$. The constraints can be reselected without loss of generality so that $\lambda_0 = Z(\beta, \lambda)$, $\lambda_1 = \beta$ and $\lambda_2 = -\lambda$. The above equation then reads

$$(2.44) \quad P(\theta) = \frac{m(\theta)}{Z(\beta, \lambda)} e^{-\beta \langle E \rangle + \lambda S(\theta)}.$$

The hyperprobability distribution in Eq. (2.44) is the probability of the fluctuations of the intensive variables i.e., $f(\beta)$ given by Eq. (2.33). Therefore, as superstatistics is the underlying framework in terms of the fluctuations, the maximization in terms of hyperensembles is what lies underneath the fluctuations. Combining these two, we are

armed with a unified view of the strange statistics emerging in different systems such as q-exponential distribution. It is important to see how the ideas of superstatistics and hyperensembles work together in a unique manner. For this purpose, we first consider the microcanonical ensemble. The probability distribution of the microcanonical ensemble is given by

$$(2.45) \quad q_\beta(x) = \frac{\delta(E - H(x))}{\rho(E)}$$

where the density of states ρ equals $\int dE \delta(E - H(x))$. The microcanonical entropy is equal to $S = \ln \rho(E)$, where we set the Boltzmann constant equal to unity. Having set also λ to unity, the substitution of Eq. (2.45) into Eq. (2.44) results

$$(2.46) \quad P(\theta) = \frac{m(\theta)}{Z(\beta)} \rho(E) e^{-\beta \langle E \rangle}.$$

The hyperprobability distribution $P(\theta)$ found above is nothing but $f(\beta)$ in Eq. (2.33). Therefore, the substitution of $P(\theta)$ in Eq. (2.33) gives

$$(2.47) \quad B(E) = \frac{m}{Z(\beta)} e^{-\beta E}.$$

This is an important results since what appears to be microcanonical at the hyperensemble level becomes canonical BG statistics after the fluctuations of the intensive variable β is taken into account through the superstatistical framework [27]. It is worth remark that no ad hoc move has been made in the above calculation. All that was necessary is to use the fluctuation of the intensive variable and hyperensemble entropy maximization. One point needs to be clarified though. Crooks originally proposed the hyperensemble maximization as a means to study out-of-equilibrium systems. However, both microcanonical and canonical cases are relevant to equilibrium. In fact, this is why we could set λ to unity since this is the Lagrange multiplier, which is associated with the distance off equilibrium.

Although we have seen how the probability of the fluctuations can be found by the maximization of the hyperensembles, we have not studied the q-exponential distribution

stemming from the Tsallis entropy. The reason for this is that there is yet no way to find inverse Gamma distributions, which are responsible for q -exponential distribution through the hyperensemble method. We know that the fluctuations of the inverse Gamma form result in the q -exponential distribution. However, this is an ad hoc move as long as it cannot be derived through hyperensemble maximization. This is an open problem waiting to be solved.

CHAPTER 3

NONADDITIVE REACTION RATE

One example for the use of the nonadditive Tsallis entropy can be given by studying the reaction rates. The classical formulation given by Kramers [28] and developed ever since always results in survival probability distributions in the form of exponentials. Kramers was able to calculate the dependence of escape probability on viscosity and temperature through his model. Kramers' model has been extended by scientists like Hänggi et al. [29], Montroll and Schuler [30] for example to consider non-Markovian effects [31]. It is worth to notice that all these attempts ended up in having a survival probability which decays exponentially in time. However, there are some reactions, which provides survival probabilities of the inverse power law form. In other words, one needs a nonexponential treatment of this subject. The need of generalizing Kramers' rate in such a way as to have a nonexponential decay in time is due to the off-equilibrium condition since this condition creates genuine power laws [32, 33, 34]. In this chapter, I will first outline the ordinary Kramers' reaction rate formulation due to Risken [35] and then provide a new theory, which functions in terms of inverse power law survival probabilities. By generalizing survival probability using nonadditive Tsallis formalism, I obtain a survival probability which is of the form of an inverse power law in the asymptotic regime. I also compare this to some recent experimental findings in protein rebinding [36, 37, 38]. Indeed, it has been shown by T. D. Frank and Daffertshofer [39] that nonlinear Fokker-Planck equations can result in survival probabilities of the q -exponential form. Moreover, Plastino et al. [40] considered nonlinear reaction-diffusion equations with nonlinear diffusion and reaction term and showed that they possess exact time-dependent particular solutions of Tsallis' maximum entropy form. Recently, Niven [41] approached the reaction rate problem in nonadditive formalism from a different point of view by considering q as the reaction order.

It is worth remark that there has been only one attempt to generalize Kramers' reaction rate problem so as to include inverse power law survival probability distributions. However, this attempt has been made to generalize the reaction rate of Kramers through the use of Mittag-Leffler function where survival probabilities have been in the form of inverse power law asymptotically [42]. Although q -exponentials provided by the Tsallis formalism result in inverse power laws asymptotically like Mittag-Leffler function, one main difference between the two is concerned with the interpolation. Mittag-Leffler function interpolates between the stretched exponential and inverse power law, whereas the q -exponential distribution is a genuine inverse power law without interpolation. Therefore, it is important to see whether one can have a generalization of Kramers' reaction rate in terms of q -exponentials such that a fitting with the experimental data can be based on this theory. The same experimental data has been used by Tsallis et al. [43] in order to explain fractal behavior of the experiment through Lyapunov exponents. Our approach is completely different since it is based on Kramers' model and off-equilibrium conditions which generate genuine inverse power laws. Within this approach, not only experimental findings in protein rebinding [36, 37, 38] will be explained but also the inverse power law behavior found in Ref. [34] in which a stretched exponential and inverse power law distribution with different powers are interpolated. The Mittag-Leffler function requires the same power for stretched exponential and inverse power law behavior, therefore cannot explain the situation in Ref. [34] whereas the survival probability of the form of q -exponential can.

3.1. Kramers' Reaction Rate: the Classical Theory and the Ubiquity of the Exponentials

Kramers [28] considered a point particle in phase space which is initially trapped in an asymmetric well under a potential V . In addition to this, the particle is also assumed to be subject to the random Brownian forces of the surrounding medium in thermal equilibrium. The particle can escape over the potential barrier which means a transition from the well of reactants to the well of products. Kramers also assumed that the height of the potential barrier is very large compared with the temperature of the environment ensuring a slow diffusion process from the well of reactants to the well of products. It is also assumed that the potential associated with the well of reactants is given by

$$(3.1) \quad V(x_{\min}) = \frac{1}{2}m(2\pi\omega)^2x^2,$$

whereas the potential around the barrier is given by

$$(3.2) \quad V(x_{\max}) = \Delta V - \frac{1}{2}m(2\pi\omega\iota)^2(x - x_{\max})^2.$$

The parameters x_{\min} and x_{\max} are the coordinates whereas ω and $\omega\iota$ are the corresponding angular frequencies for the well of reactants and products respectively. $\Delta V = V(x_{\max}) - V(x_{\min})$ is the height of the potential barrier and m denotes the mass of the particle. Kramers has taken the mass term equal to unity in his derivation and started by writing the Fokker-Planck equation concerning the diffusion from the well of the reactants to the well of the products as follows

$$(3.3) \quad \frac{\partial p}{\partial t} = \frac{\partial V}{\partial x} \frac{\partial p}{\partial v} - v \frac{\partial p}{\partial x} + \eta \frac{\partial}{\partial v} (vp + \beta^{-1} \frac{\partial p}{\partial v})$$

where η is the viscosity and β is the inverse temperature. He then considered the large viscosity limit, where the effect of the Brownian forces on the velocity of the particle is much larger than that of the external force $-\frac{\partial V}{\partial x}$. Then, for any arbitrary initial distribution, we expect the Maxwell distribution in velocity i.e., $p(x, v, t) = \sigma(x, t)e^{-\beta v^2/2}$ to be reached after some time of the order of $1/\eta$. From then on, a slow distribution of the density function σ in the position coordinate will take place. This diffusion can further be described by the Smoluchowski diffusion equation given as

$$(3.4) \quad \frac{\partial \sigma}{\partial t} = -\frac{\partial}{\partial x} \left(-\frac{1}{\eta} \frac{\partial V}{\partial x} \sigma - \frac{\beta^{-1}}{\eta} \frac{\partial \sigma}{\partial x} \right)$$

where $\frac{\beta^{-1}}{\eta}$ is the diffusion constant. The stationary diffusion current obeys the law

$$(3.5) \quad w = -\frac{1}{\eta} \frac{\partial V}{\partial x} \sigma - \frac{\beta^{-1}}{\eta} \frac{\partial \sigma}{\partial x} = \text{constant}.$$

The above equation can also be written as

$$(3.6) \quad w = -\frac{\beta^{-1}}{\eta} e^{-\beta V} \frac{\partial}{\partial x} (\sigma e^{\beta V}).$$

Integrating the above equation along the well of reactants to the well of the products, Kramers obtains an explicit expression for the diffusion current

$$(3.7) \quad w = \frac{\beta^{-1} |\sigma e^{\beta V}|_A^B}{\int_A^B dx \eta e^{\beta V}}.$$

The letter A denotes the position of the well of reactants while the letter B denotes the position of the products.

Kramers then considers the large viscosity limit i.e., overdamped limit. In this limit, he assumes that no particle has yet arrived at point B, whereas thermal equilibrium is reached at A. Therefore, the application of Eq. (3.7) in the high viscosity limit reads

$$(3.8) \quad w = \frac{\beta^{-1} \sigma_A}{\eta} \left(\int_A^B dx \eta e^{\beta V} \right)^{-1}$$

where

$$(3.9) \quad \sigma_A = (\sigma e^{\beta V})_{near A}.$$

The number n_A of particles near A can be calculated with the help of Eq. (3.1) (setting mass term equal to unity) by

$$(3.10) \quad n_A = \int_{-\infty}^{+\infty} dx \sigma_A e^{-\beta \frac{1}{2} (2\pi\omega)^2 x^2} = \frac{\sigma_A}{\omega} \sqrt{\frac{\beta^{-1}}{2\pi}}.$$

The reaction rate r is defined as the probability in unit time that a particle originally caught at A escapes to B i.e.,

$$(3.11) \quad r = \frac{w}{n_A}.$$

In order to have an explicit reaction rate expression, I consider that the dominant potential will be given by Eq. (3.2) and therefore substitute this expression into Eq. (3.8) to obtain

$$(3.12) \quad r \cong \frac{2\pi\omega\omega'}{\eta} e^{-\beta\Delta V}.$$

Note that the reaction rate for the overdamped case can also be written as

$$(3.13) \quad r \cong \frac{1}{2\pi m} \eta^{-1} \sqrt{V''(x_{\min}) |V''(x_{\max})|} e^{-\beta\Delta V}$$

by the substitution of Eqs. (3.1) and (3.2).

Next, Kramers considers the low viscosity limit. However, before proceeding, he restricts his analysis to the case, where the oscillatory motion would be observed in the absence of Brownian forces. In this sense, the Brownian forces in the low viscosity limit will only gradually change the ensemble of distributions over the different energy values. He then denotes the area inside a curve of constant energy as I , which is equal to $\oint p dx$. The diffusion equation corresponding to this case is written as

$$(3.14) \quad \frac{\partial p}{\partial t} = \eta \frac{\partial}{\partial I} (Ip + I\beta^{-1} \frac{\partial p}{\partial E}).$$

A stationary state of diffusion with the current density w corresponds to

$$(3.15) \quad w = -\eta(Ip + I\beta^{-1} \frac{\partial p}{\partial E}) = -\eta I \beta^{-1} e^{-\beta E} \frac{\partial}{\partial E} (p e^{\beta E}).$$

Integrating the above equation from the point A to point B, I obtain

$$(3.16) \quad w = \frac{\eta \beta^{-1} |p e^{\beta E}|_A^B}{\int_A^B dE \frac{e^{\beta E}}{I}}.$$

Proceeding in a similar manner as in the case of high viscosity, I calculate w as

$$(3.17) \quad w \simeq \eta p_A \frac{\Delta V}{\omega} e^{-\beta\Delta V}.$$

The number of particles is now calculated as

$$(3.18) \quad n_A = \frac{p_A}{\beta\omega}.$$

Finally, the reaction rate can be found as dividing the two terms above so that I obtain the reaction rate in the low viscosity (underdamped) limit

$$(3.19) \quad r \simeq \frac{w}{n_A} = \eta\Delta V\beta e^{-\beta\Delta V}.$$

The inspection of Eqs. (3.13) and (3.19) shows that the reaction rate for both overdamped and underdamped cases are of exponential form. This is indeed a result of the fact that the underlying dynamics has been described by linear Fokker-Planck equations whose solutions are exponential. In this sense, one can consider a general picture by writing for the survival probability as

$$(3.20) \quad p_{survival}(t) = \exp(-rt)$$

where r denotes the rate of the process and t is time parameter. In the overdamped case, the rate is given by Eq. (3.13) whereas the underdamped rate is provided by Eq. (3.19). However, it is worth remark that the main structure is exponential in both cases as can be seen from Eq. (3.20).

3.2. Kramers' Nonadditive Reaction Rate: the Ubiquity of the Inverse Power Laws

As we have seen in the previous section, Kramers' reaction rate is based linear Fokker-Planck equations, which resulted in the reaction rates of the exponential form. However, the recent progress in the Fokker-Planck equations resulted in fractional Fokker-Planck equations [42] and non-linear Fokker-Planck equations (NLFPE) [39]. Both of them result in inverse power law distributions asymptotically as the stationary distribution. In this sense, a generalization of Kramers' reaction rate is necessary. The NLFPE derived by Frank and Daffertshofer in the case of a generalized Kramers' rate problem is given as

$$(3.21) \quad \frac{\partial p(x, v, t)}{\partial t} = \left\{ -v \frac{\partial}{\partial x} + \frac{\partial}{\partial v} \left(\frac{\partial V(x)}{\partial x} + \gamma v \right) \right\} p(x, v, t) + \lambda \gamma \frac{\partial}{\partial v} M(p) \frac{\partial}{\partial v} \hat{L} S.$$

In the equation above, γ denotes the friction constant, λ denotes the Lagrange multiplier associated with the energy. The S denotes the entropy functional written in terms of probability density. The above equation reduces to Kramers type Fokker-Planck equation when the entropy functional S becomes Boltzmann-Gibbs entropy. The operator \hat{L} has the explicit form

$$(3.22) \quad \hat{L} S \equiv S(p) - p \frac{dS(p)}{dp}.$$

Inserting the Tsallis entropy given by Eq. (2.1) into Eq. (3.21) and setting $M(p)$ equal to 1, we obtain the Kramers equation for the nonadditive Tsallis formalism

$$(3.23) \quad \frac{\partial p(x, v, t)}{\partial t} = \left\{ -v \frac{\partial}{\partial x} + \frac{\partial}{\partial v} \left(\frac{\partial V(x)}{\partial x} + \gamma v \right) \right\} p(x, v, t) + \lambda \gamma \frac{\partial^2}{\partial v^2} p^Q$$

where Q is the particular nonadditivity parameter of Tsallis entropy. The stationary solution to the above equation, after some rearrangement, is given by

$$(3.24) \quad p_q(t) = \exp_q(-rt) = [1 + (q-1)rt]^{1/(1-q)}$$

where I have assumed $Q = 2 - q$. The probability density $p_q(t)$ is normalized as a survival probability in the sense that it is equal to 1 at $t=0$, mimicking the exponential case given by Eq. (3.20). The q -exponential is defined as

$$(3.25) \quad \exp_q x \equiv [1 + (1-q)x]^{1/(1-q)}.$$

As expected, this function becomes the usual exponential function as $q \rightarrow 1$. By reference to Eq. (3.24), I now have a survival probability of the inverse power law form.

In order to generalize Kramers' reaction rate to the nonadditive case, I note that the ordinary reaction rate can be calculated as following:

$$(3.26) \quad r \equiv \frac{p(t=0)}{\widehat{p}(u=0)}$$

where $\widehat{p}(u)$ is the Laplace transform of the function $p(t)$ given by Eq. (3.20). Laplace transform $\widehat{p}(u)$ of $p(t)$ is defined by $\widehat{p}(u) = \int_0^{\infty} p(t)e^{-ut}dt$. Note that when the Laplace variable u is equal to zero, we have the normalization of the function $p(t)$. Similarly then, I write

$$(3.27) \quad r_q \equiv \frac{p_q(t=0)}{\widehat{p}_q(u=0)}$$

where the Laplace transform is defined in the same way above. The Laplace transform $\widehat{p}_q(u)$ at $u = 0$ is the integral of the function $p_q(t)$ from zero to infinity i.e., its normalization. This is obtained as

$$(3.28) \quad \widehat{p}_q(u=0) = \frac{1}{r} \frac{1}{2-q}, q < 2$$

where r is the ordinary rate of the process i.e., $r = r_{q \rightarrow 1}$. The constraint $q < 2$ has been put since the Laplace integral otherwise diverges. Since $p_q(t=0) = 1$, I obtain the generalized reaction rate as

$$(3.29) \quad r_q = (2-q)r_{q \rightarrow 1}, q < 2.$$

The Eq. (3.29) is valid for both overdamped and underdamped cases as long as $r_{q \rightarrow 1}$ is taken to be of the form in Eqs. (3.12) (or the equivalent form given by Eq. (3.13)) and (3.19) i.e., the ordinary (additive) reaction rates for the overdamped and underdamped cases. For the former case, I get

$$(3.30) \quad r_q = \eta_q^{-1} \frac{\sqrt{V''(x_{\min})/V''(x_{\max})}}{2\pi m} e^{-\beta\Delta V}$$

where

$$(3.31) \quad \eta_q = \frac{\eta}{(2 - q)}.$$

For the latter, I have

$$(3.32) \quad r_q = \eta'_q \beta \Delta V e^{-\beta \Delta V}$$

where

$$(3.33) \quad \eta'_q = (2 - q)\eta.$$

From Eqs. (3.31) and (3.33), we see that $\eta/\eta_q = (2 - q)$ and $\eta'_q/\eta = (2 - q)$, respectively: The nonextensive friction constants (i.e., η_q and η'_q in the overdamped and underdamped cases respectively) is rescaled by the same factor $(2 - q)$. We also note that nonadditive formalism gives rise to turnover in the dependence of friction since $r_q \propto \eta_q^{-1}$ and $r_q \propto \eta'_q$ in the overdamped and underdamped cases respectively as can be seen from Eqs. (3.30) and (3.32). This turnover is already inherent in the Eqs. (3.12) and (3.19), which is the additive theory and I successfully preserved this form in nonadditive formalism.

The Kramers' theory is also being used for investigating the chemical reactions in the proteins. However, the related survival probability in this case is non-exponential. In fact, the experiment of ligand CO rebinding to myoglobin after photodissociation as investigated by Iben et al. [36] shows an inverse power law behaviour in the time asymptotic limit until one reaches a certain higher critical temperature T_c . Glöckle and Nonnenmacher [37] assumed this power to be temperature dependent and equal to $\alpha(T) = 0.41T/120$ to take the change in the protein-solvent system into account. In Fig. 1, I provide some plots for survival probability $p_q(t)$ for $q = 2.8, 3.1$ and 3.4 , which correspond to these experimental findings [38] for temperature values $T = 160$ K, 140 K and 120 K, respectively. This plot shows that as temperature increases, the nonadditivity of the system becomes less and less dominant.

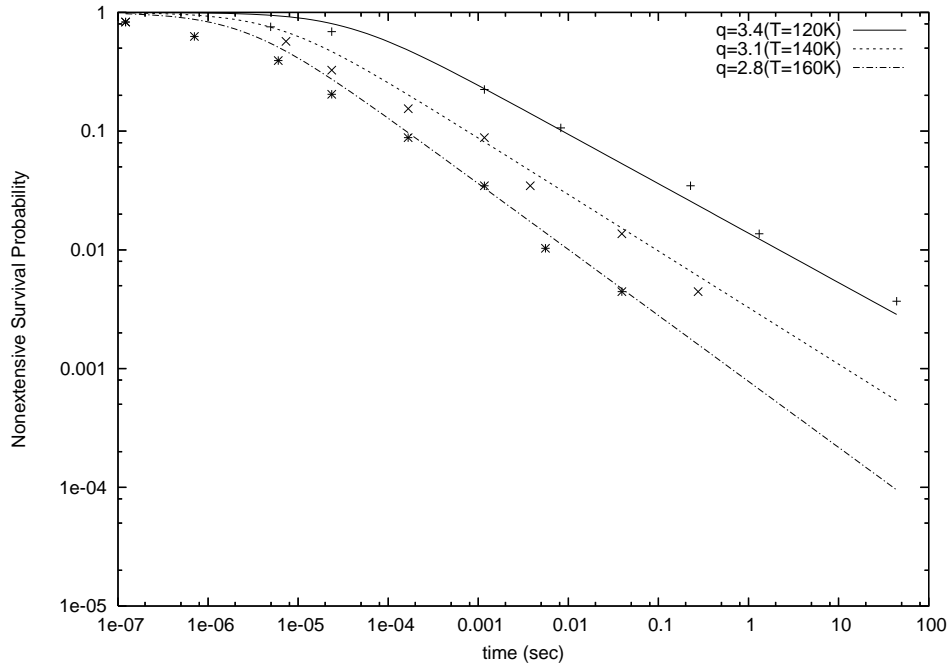


Figure 3.1. The nonadditive survival probability $p_q(t)$ given by Eq. (3.8) versus time for the temperatures 120 K, 140 K and 160 K corresponding to the values of q equal to 3.4, 3.1 and 2.8 respectively.

In summary, I have studied nonadditive generalization of Kramers' reaction rate by writing the survival probability as a q -exponential. I showed that the dependence of non-additive Kramers' rate to the nonadditive friction term in the high viscosity limit changes to inverse proportionality in the low viscosity limit. In fact, this is a property of the ordinary Kramers' theory and nonadditive formalism preserves this important turnover. I calculated nonadditive reaction rate by making use of Laplace transform and observed that the relation between the additive and nonadditive cases is found out to be linear. Therefore, the Arrhenius nature of the Kramers' rate is preserved. I then referred to some experimental data concerning the ligand CO rebinding to myoglobin after photodissociation. In this experiment, survival probability is of the form of inverse power law with a power depending on temperature due to change in the protein-solvent system in the time

asymptotic limit. It has been shown in Fig.1 by plotting nonadditive survival probability for various temperature values that some q values which are different than 1 correspond to these distinct cases. I propose this to be a signature of nonadditivity in the photodissociation of the process of CO rebinding to myoglobin. Moreover, Fig.1 shows that as temperature increases, the nonadditivity of the system becomes less and less dominant. Therefore, this phenomenological picture is in accordance with the experimental findings which indicate that the survival probability becomes exponential at a higher temperature. This transition from power law to exponential can be seen by the inspection of Fig.1, since as temperature continues to increase, we expect the nonadditivity parameter q to drop to 1 at some higher critical temperature, which means the transition to exponential case. In Ref [42], this behavior has been tried to be explained by the use of Mittag-Leffler function, but I believe that nonadditive scenario gives a more adequate picture since Mittag-Leffler forces one to interpolate between the stretched exponential and inverse power law behavior with same exponent only. In fact, if one inspects Ref. [34], one immediately sees that it is a stretched exponential and inverse power law distribution with different powers to be interpolated. This cannot be done using Mittag-Leffler function, which requires the same power for stretched exponential and inverse power law behavior. My final remark is about Ref. [43], which uses the same experimental findings as I did in Fig.1, but the novelty here compared to Ref. [43] lies in the use of different approaches. I tried to generalize Kramers' rate in a way which will provide survival probabilities of inverse power law [44], whereas Ref. [43] treats the same subject from the point of view that the same set of data can be used in order to explain fractal behavior of the experiment through Lyapunov exponents.

CHAPTER 4

GENERALIZATION OF THE GIBBS' AND S-THEOREM TO OPEN SYSTEMS

In this chapter, I will first review Gibbs' theorem [3] and then S-theorem due to Klimontovich [45-51]. The Gibbs' theorem rests on the comparison of states with equal energies. It can be generalized to open systems with matter or energy influx. This has been provided by Klimontovich and has been named as S-theorem [45-51]. I show that the fact that S-theorem can be seen as a criterion for the self-organization as defined by Haken [52].

4.1. Gibbs' Theorem

In this Section, I will present the Gibbs' theorem. Gibbs considers two distributions p and r , both normalized to unity i.e., $\int p(E)d\Omega = \int r(E)d\Omega = 1$, where Ω denotes phase-space and $d\Omega = dq_1 \dots dp_n$. The probability distribution p is the canonical distribution

$$(4.1) \quad p(E) = e^\eta$$

where $\eta = -\beta E$. The distribution r is any other distribution having the same mean energy as $p(E)$ and can be written as

$$(4.2) \quad r(E) = e^{\eta + \Delta\eta}.$$

Since the mean energies of these distributions are assumed to be equal to one another, we can write

$$(4.3) \quad \int \eta e^\eta d\Omega = \int \eta e^{\eta + \Delta\eta} d\Omega.$$

We need to prove, under these assumptions, that

$$(4.4) \quad \int \eta e^\eta d\Omega < \int (\eta + \Delta\eta) e^{\eta+\Delta\eta} d\Omega,$$

since the multiplications of both sides by minus one will change the sign of equality. By Eq. (4.3), the inequality (4.4) takes the form

$$(4.5) \quad \int \Delta\eta e^{\eta+\Delta\eta} d\Omega > 0.$$

Due to the normalization, Eq. (4.5) can be rewritten as

$$(4.6) \quad \int (\Delta\eta e^{\Delta\eta} + 1 - e^{\Delta\eta}) e^\eta d\Omega > 0.$$

The term $(\Delta\eta e^{\Delta\eta} + 1 - e^{\Delta\eta})$ is a decreasing function for negative values of $\Delta\eta$, and an increasing function for positive values of $\Delta\eta$. It becomes zero when $\Delta\eta$ is equal to zero. Therefore, the inequality (4.6) is proved. Hence, we can say that the Gibbs' theorem orders the entropy values in such a way that the canonical entropy associated with the equilibrium distribution is maximum.

4.2. Open Systems and Klimontovich's S-theorem

Although Gibbs' theorem is central to the canonical ensembles, one of the main assumptions of Gibbs was to consider equal mean energy ensembles as we have seen in the previous Section. It is in this sense that it needs to be generalized in order to be applied to the open systems. The open systems are those systems in which an energy or matter influx can be observed so that the mean energy is not constant.

The generalization of the Gibbs' theorem for open systems has been first offered by Yu. L. Klimontovich [45-51]. Klimontovich's formalism consists in equating the average energies of the stationary distributions so that the entropy lowering i.e., $\Delta S = S_{eq} - S_{neq} \geq 0$, where the subscripts denote the equilibrium and nonequilibrium states respectively. This result is called S-theorem by Klimontovich. Instead of entropy lowering based on ordinary

stationary distributions, I will use renormalized entropy R , which is defined as $(-\Delta S)$, where the mean energies are set equal to one another. Then, S theorem states that

$$(4.7) \quad R = S_{neq} - \tilde{S}_{eq} \leq 0.$$

The superscript \sim indicates that the new equilibrium entropy is obtained by renormalization of the old equilibrium distribution. The equality occurs only when the system stays at equilibrium for all times.

In order to understand the S-theorem, it is instructive to see how it works in practical cases. For this purpose, the sustained pendulum serves as a good example, using the modified Van der Pol oscillator suggested by Engel-Herbert and Ebeling [45-51]. This model is called the modified Van der Pol oscillator due to the additional term proportional to the cube of the velocity.

The Langevin equation for the modified Van der Pol oscillator is

$$(4.8) \quad \frac{dx}{dt} = v, \quad \frac{dv}{dt} + (a + bE)v + \omega_0^2 x = y(t)$$

where ω_0 is the eigenfrequency, and b is the nonlinear friction coefficient. The term a can be written in terms of two other parameters i.e.,

$$(4.9) \quad a = \gamma - a_f$$

where γ is the coefficient of linear friction and a_f is the feedback coefficient (or called control parameter) for this particular physical system. The energy E of oscillation is

$$(4.10) \quad E = \frac{1}{2}(v^2 + \omega_0^2 x^2).$$

Note that the mass term is set equal to unity in the equation above. The random Langevin source $y(t)$ has the following properties

$$(4.11) \quad \langle y(t) \rangle = 0, \langle y(t)y(t') \rangle = 2D\delta(t - t')$$

where the intensity of the random source D is a positive constant. It is not connected with the temperature via Einstein's formula in general, since the system can be in one of the nonequilibrium stationary states. If we assume that the dissipation is small and random forces exerted on the oscillator are weak i.e., $\gamma, |a|, b\langle E \rangle \ll \omega_0$, then the stationary distribution can be found from Fokker-Planck equation [46]

$$(4.12) \quad f_0(E) = C \exp\left(-\frac{aE + \frac{1}{2}bE^2}{D}\right)$$

where C is a normalization constant. The state of equilibrium corresponds to the case when the feedback parameter a_f is equal to zero. Then the corresponding distribution function becomes

$$(4.13) \quad r(E) = C \exp\left(-\frac{\gamma E + \frac{1}{2}bE^2}{D}\right).$$

Assuming [46]

$$(4.14) \quad b\langle E \rangle / \gamma \sim Db/\gamma^2 \ll 1,$$

the stationary equilibrium distribution becomes

$$(4.15) \quad r(E) = \frac{\gamma}{D} \exp\left(-\frac{\gamma E}{D}\right).$$

Now, I increase the control parameter to a value different from zero and create a nonequilibrium state in the system. In the modified Van der Pol oscillator, the threshold of generation is defined as the state when the feedback parameter a_f is equal to γ . Then, according to Eq. (4.9), $a=0$. Therefore, the distribution function for this case becomes

$$(4.16) \quad p(E) = \sqrt{\frac{2b}{\pi D}} \exp\left(-\frac{bE^2}{2D}\right).$$

Once I have the distribution functions, I use

$$(4.17) \quad \langle E \rangle = \int dE p(E) E; \quad S_{BG} = - \int dE p(E) \ln p(E)$$

to calculate the corresponding entropy and mean energy expressions for the equilibrium as

$$(4.18) \quad S_{BG}(r)^{(eq)} = \ln\left(\frac{D}{\gamma}\right) + 1; \quad \langle E \rangle^{(eq)} = \frac{D}{\gamma}$$

and for the off-equilibrium case

$$(4.19) \quad S_{BG}(p)^{(neq)} = \ln\left(\sqrt{\frac{\pi D}{2b}}\right) + \frac{1}{2}; \quad \langle E \rangle^{(neq)} = \sqrt{\frac{2D}{\pi b}}.$$

The subscript denotes that the calculations have been carried out by using Boltzmann-Gibbs entropy (BG), where the superscripts (eq) and (neq) denote equilibrium and nonequilibrium states, respectively. Note that the units are chosen such that the Boltzmann constant k is equal to one. I have now two distinct entropy expressions corresponding to equilibrium and off-equilibrium cases. If I calculate the entropy lowering directly from Gibbs' theorem, also considering Eq. (4.14), I see that Gibbs' theorem is violated, i.e.,

$$(4.20) \quad \Delta S = S_{neq} - S_{eq} > 0.$$

It is at this stage that S-theorem can be put to use. This is done by “renormalizing” the mean energies of both states so that they are be equal to one another. If I choose the nonequilibrium state as the reference state, the renormalization is

$$(4.21) \quad \langle \tilde{E} \rangle^{(eq)} = \langle \tilde{E} \rangle^{(neq)} = \sqrt{\frac{2D}{\pi b}}$$

where \sim denotes the renormalized quantities. This renormalization procedure will provide a new intensity of the random force associated with the equilibrium state, which is given by

$$(4.22) \quad \tilde{D}^{(eq)} = \gamma \sqrt{\frac{2D}{\pi b}}.$$

Note that the random force intensity relevant to the nonequilibrium distribution will not change at all since I have chosen it as the reference state. Substituting this new intensity expression into Eqs. (4.15) and (4.18), we obtain the renormalized equilibrium distribution function

$$(4.23) \quad \tilde{r}(E) = \sqrt{\frac{\pi b}{2D}} \exp\left(-\sqrt{\frac{\pi b}{2D}} E\right)$$

and the associated entropy expression is

$$(4.24) \quad S(\tilde{r}) = \ln\left(\sqrt{\frac{2D}{\pi b}}\right) + 1.$$

The renormalized entropy is now

$$(4.25) \quad R = S_{neq} - \tilde{S}_{eq} = -0.05 < 0.$$

This result is independent of the parameters. Thus, the equilibrium entropy is maximum even for additive open systems if one renormalizes the mean energies of the states, confirming that Klimontovich's S theorem is a generalization of Gibbs' theorem for open systems. However, the scope of the S-theorem is not limited to the equilibrium distributions since one can compare two nonequilibrium distributions to see which one is closer to equilibrium just by calculating the corresponding renormalized entropies.

4.3. An Alternative Derivation of the S-theorem: Renormalized Entropy and Kullback-Leibler Relative Entropy

In this section, I give an abstract derivation of S-theorem. In order to do this, I suppose that I have two distinct probability distributions i.e. $p=\{p_i\}$ and $r=\{r_i\}$, which are normalized to unity, i.e. $\sum_i p_i = \sum_i r_i = 1$. These distributions refer to the state of a physical system with different control parameters. In this sense, they can be chosen to be equilibrium or nonequilibrium distributions corresponding to different values of the control parameter. The stationary equilibrium distribution is obtained when the relevant control parameter is set to zero. As the value of control parameter increases, the system moves away from the equilibrium state. The determination of control parameter itself might not be easy for some systems, but I will not address this issue here. Assuming that we have a well-defined control parameter for the system, such as the feedback coefficient in the Van der Pol model, I obtain an alternative derivation of Klimontovich's S-theorem due to Quiroga et al. [56, 57]. The discrete picture is adopted, but the results can easily be generalized to the continuous domain.

I begin by noting that I can calculate the corresponding BG entropy, once I have the relevant distribution functions by using

$$(4.26) \quad S_{BG}(p) = - \sum_i p_i \ln p_i,$$

as I have done in the previous section. Next, I set the mean energies equal to one another. In other words, I renormalize the states in such a way that they possess the same mean energy. For this purpose, Klimontovich [45-51] defines effective mean energy U_{eff} for the system as

$$(4.27) \quad U_{eff} \equiv - \ln f_0(E)$$

where $f_0(E)$ is given by Eq. (4.12). It is called effective mean energy since this quantity will depend on the control parameter and change as the control parameter varies. The

mean energy associated with the stationary distributions will not be same even though the total energy is kept constant. From the stationary distribution given by Eq. (4.12) in the previous section and using Eq. (4.27), we see that the effective mean energy is equal to $(aE + \frac{1}{2}bE^2)$. The effective mean energy is referred to as the microscopic entropy analogue in Ref. [58], since its average results in BG entropy. The renormalization of energies corresponding to the probability distributions p and r can then be written as

$$(4.28) \quad \langle U_{eff} \rangle^{(1)} = \langle U_{eff} \rangle^{(2)}$$

where superscripts denote the different states. The equation above can be written in a more explicit form as

$$(4.29) \quad \sum_i \tilde{r}_i \ln r_i = \sum_i p_i \ln r_i$$

where \tilde{r} is the renormalized distribution obtained after equating the mean energies. Note that the form of effective mean energy has been taken as $(-\ln r(E))$ in Eq. (4.29), since the probability distribution r represents the state to be renormalized, whereas the probability distribution represented by p is the reference state. The renormalized distribution function corresponding to $r=\{r_i\}$ can be written in the form of escort probability distribution [59] i.e.,

$$(4.30) \quad \tilde{r}_i = \frac{r_i^\beta}{C}$$

where the constant C is found from the normalization condition and the exponent β can be found from the renormalization of energies i.e., through Eq. (4.29). In this sense, S-theorem can be thought as a procedure of converting ordinary probability distribution r to its escort counterpart \tilde{r} . The exponent is determined by the renormalization of energies as given by Eq. (4.28) in general. Klimontovich combined ordinary, additive BG entropy together with the escort distribution, whose exponent is given by the renormalization condition, in order to generalize Gibbs' theorem for open, nonequilibrium systems. It is

important to understand the equivalence of this approach with the one presented in the previous section.

Let us reconsider the modified Van der Pol oscillator to find the renormalized distribution function by using the constraints of normalization and renormalization. Substitution of Eq. (4.15) into Eq. (4.30) above, and making use of normalization condition, we obtain

$$(4.31) \quad C = \frac{1}{\beta} \left(\frac{\gamma}{D} \right)^{\beta-1}.$$

Substituting the normalization constant C back into Eq. (4.15), we obtain for the continuous case

$$(4.32) \quad \tilde{r}(E) = \frac{\beta\gamma}{D} \exp\left(-\frac{\beta\gamma}{D}E\right).$$

In order to obtain the explicit form of the renormalized equilibrium distribution function, I need to obtain β and this can be done by using Eq. (4.28). The right hand side of Eq. (4.28) is calculated as

$$(4.33) \quad \int_0^\infty dE p(E) \ln r(E) = \ln\left(\frac{\gamma}{D}\right) - \gamma \sqrt{\frac{2}{\pi b D}},$$

whereas the left hand side of Eq. (4.28) is calculated to be

$$(4.34) \quad \int_0^\infty dE \tilde{r}(E) \ln r(E) = \ln\left(\frac{\gamma}{D}\right) - \frac{1}{\beta}.$$

Since Klimontovich's S-theorem requires mean energies to be equal to one another, I set two equations above equal to one another to obtain β as

$$(4.35) \quad \beta = \frac{1}{\gamma} \sqrt{\frac{\pi b D}{2}}.$$

If I insert the above expression into Eq. (4.32), I obtain the renormalized equilibrium distribution

$$(4.36) \quad \tilde{r}(E) = \sqrt{\frac{\pi b}{2D}} \exp\left(-\sqrt{\frac{\pi b}{2D}} E\right),$$

which is the same as Eq.(4.23). This shows the equivalence of two distinct treatments presented in the previous and present section.

I am now ready to introduce the alternative formulation of additive S-theorem of Klimontovich, based on the renormalization of the escort distribution. The renormalized entropy of Klimontovich is defined as

$$(4.37) \quad R(p||\tilde{r}) \equiv S(p) - S(\tilde{r})$$

where $R(p||\tilde{r})$ is written instead of R for the renormalized entropy. Thus, the explicit dependence of renormalized entropy on two distinct probability distributions and the requirement of equating their mean energies are apparent. Using the definition of BG entropy given by Eq. (4.17), I obtain

$$(4.38) \quad R(p||\tilde{r}) = -\sum_i p_i \ln p_i + \sum_i \tilde{r}_i \ln \tilde{r}_i.$$

Using Eqs. (4.29) and (4.30) in the equation above for the second term on the right hand side of the equation, we get

$$(4.39) \quad R(p||\tilde{r}) = -\sum_i p_i \ln(p_i/\tilde{r}_i).$$

Comparing Eq. (4.39) with Kullback-Leibler (K-L) relative entropy [60]

$$(4.40) \quad K[p||r] \equiv \sum_i p_i \ln(p_i/r_i),$$

we find the relation obtained by Quiroga et al. [56, 57]

$$(4.41) \quad R(p||\tilde{r}) = - \sum_i p_i \ln(p_i/\tilde{r}_i) = -K[p||\tilde{r}].$$

This final result shows us that renormalized entropy and negative of the K-L entropy are equal to one another. However, this equality does not suffice to conclude that Eq. (4.41) is an alternative derivation of Klimontovich's S-theorem, since this theorem requires renormalized entropy to be negative for all values of the control parameter. In order to see that this is indeed the case, it suffices to recall that K-L entropy is positive definite [60]. Due to the minus sign in the equation above, we conclude

$$(4.42) \quad R(p||\tilde{r}) = S_{neq} - \tilde{S}_{eq} = -K[p||\tilde{r}] < 0,$$

which implies $\tilde{S}_{eq} > S_{neq}$. In other words, one can use renormalized entropy or K-L entropies in order to study self-organization once one employs the escort distribution and renormalization of mean energy values.

CHAPTER 5

NONADDITIVE GENERALIZATION OF KLIMONTOVICH'S S-THEOREM IN OPEN SYSTEMS AND CONSTRAINTS

Gibbs' theorem ensures that the canonical Gibbs distribution is the one with maximum entropy among all possible normalized distributions, that have the same mean energy. However, Gibbs' theorem rests on two main assumptions. First of all, it is based on the canonical distribution of exponential form. Second, it assumes that the mean energies of the compared distributions are equal. As we have seen in Chapter 4, this is the reason why Klimontovich generalized it in the case of open systems, since the equality of the mean energies fails in this case due to the energy and/or matter influx. Defining a new quantity called "renormalized entropy", Klimontovich's S-theorem provides the correct ordering of entropies with respect to their distance from the equilibrium state. Nonequilibrium states are created by energy and/or matter influx and can be modeled by changing the control parameter. When the control parameter is set equal to zero, we have the equilibrium distribution. In other words, the S-theorem ensures that the equilibrium distribution corresponding to the zero value of the control parameter has the maximum entropy even in open systems. It is therefore a generalization of Gibbs' theorem, which ensures that the canonical equilibrium distribution has the maximum entropy. The S-theorem is valid even when we compare two nonequilibrium distributions, providing a relative measure of order also in this case. On the other hand, Klimontovich's generalization is still based on the distribution functions of the exponential form. Due to the increasing evidence of inverse power law type of stationary distributions encountered in nature, another generalization of Gibbs' theorem and consequently the S-theorem is required.

The aim of this chapter is to attain this goal by using Tsallis entropy, since the stationary distributions of this entropy are of inverse power law form. I will generalize Klimontovich's S-theorem to nonadditive systems with stationary distributions of inverse

power law form, so that it can then be used for nonadditive open systems and it has a wider scope.

5.1. Nonadditive Generalization of S-theorem

As we have seen in Chapter 2, the Tsallis entropy has the stationary distributions of the inverse power law form. The Tsallis entropy is given by

$$(5.1) \quad S_q(p) = \frac{\sum_{i=1}^W p_i^q - 1}{1 - q}$$

where p_i is the probability of the system in the i th microstate, and W is the total number of the configurations of the system. The entropic index q is a real number, which characterizes the degree of nonadditivity. The Tsallis entropy obeys the following pseudo-additivity rule:

$$(5.2) \quad S_q(A + B) = [S_q(A)] + [S_q(B)] + (1 - q)[S_q(A)][S_q(B)]$$

where A and B are two independent systems i.e., $p_{ij}(A+B) = p_i(A)p_j(B)$. As $q \rightarrow 1$, the nonadditive Tsallis entropy given by Eq. (5.1) becomes the usual BG entropy

$$(5.3) \quad S_{q \rightarrow 1} = - \sum_{i=1}^W p_i \ln p_i.$$

In order to generalize the S-theorem using the nonadditive Tsallis entropy, I use the alternative derivation explained in Chapter 4. To do so, I need to define a new "effective mean energy", which is also the microscopic analogue of the associated entropy definition i.e., Tsallis entropy. This can be done by noting that Tsallis entropy is an entropy based on deformed logarithms. Therefore, I have the corresponding definition of logarithmic function in Tsallis framework, namely, q -logarithm,

$$(5.4) \quad \ln_q(x) = \frac{x^{1-q} - 1}{1 - q}.$$

It becomes a natural logarithm when the nonadditivity index q approaches 1.

The q -logarithm function enables one to generalize the previous definition of the effective mean energy i.e., Eq. (4.27) as

$$(5.5) \quad U_{eff}^q = \ln_q(1/f_0(E)).$$

Note that it becomes the ordinary effective energy expression given by Eq. (4.27) when the parameter q approaches 1 as expected. Since the state to be renormalized is represented by the probability distribution r in our formalism, effective mean energy will be considered as $\ln_q(1/r(E))$. Using the equality of mean energies of two different states and also the normalization condition, I obtain

$$(5.6) \quad \sum_k r_k^{q-1} \tilde{r}_k = \sum_k r_k^{q-1} p_k.$$

I now use the same definition of renormalized entropy given by Eq. (4.37), but substitute Tsallis entropy instead of BG entropy to obtain

$$(5.7) \quad R_q(p||\tilde{r}) = -\left[\frac{1}{(q-1)}\left(\sum_k p_k^q - \sum_k \tilde{r}_k^q\right)\right].$$

By adding and subtracting a term, I can rewrite the above equation as

$$(5.8) \quad R_q(p||\tilde{r}) = -\left[\frac{1}{(q-1)}\left(\sum_k p_k^q - \sum_k \tilde{r}_k^q + (q-1) \sum_k \tilde{r}_k^q - (q-1) \sum_k \tilde{r}_k^q\right)\right].$$

I proceed by using ordinary probability definition for r now, given by $\tilde{r}_k = \frac{r_k}{C}$, where C is a normalization constant. This is not the same as the case when I derived additive S-theorem, since I used escort distribution in its derivation.

I now need to calculate $\sum_k \tilde{r}_k^q$ explicitly, since I can then obtain the nonadditive renormalized entropy. This term is

$$(5.9) \quad \sum_k \tilde{r}_k^q = \sum_k p_k \tilde{r}_k^{q-1}$$

where I have also used the equality of the mean energies in Eq. (5.6). Substituting this expression for the last two terms in Eq. (5.8), I finally obtain

$$(5.10) \quad R_q(p||\tilde{r}) = -\left(\frac{\sum_k p_k^q}{q-1} + \sum_k \tilde{r}_k^q - \frac{1}{q-1} \sum_k p_k \tilde{r}_k^{q-1} - \sum_k p_k \tilde{r}_k^{q-1}\right),$$

which is the nonadditive renormalized entropy expression.

I cannot yet conclude that S-theorem is generalized for nonadditive systems, since I am not sure if Eq. (5.10) is negative for all values of the parameter q . Only if it is negative for all q values, I can safely conclude that it gives the relative ordering of states. This will be done in next section.

5.2. Nonadditive Renormalized Entropy and Relative Entropy Definitions of the Tsallis Type

The relative entropy expression associated with the BG entropy is called Kullback-Leibler (K-L) entropy [60] as pointed out in previous chapter and written as

$$(5.11) \quad K[p||r] \equiv \sum_i p_i \ln(p_i/r_i)$$

where r is called the prior probability distribution and p is called the posterior probability distribution. The K-L entropy is positive definite and becomes zero only if the prior and posterior distributions are equal to one another.

In generalized thermostatics, we also have relative entropy expressions. However, for any entropy written in terms of deformed exponential and/or logarithmic functions, we have two distinct expressions of relative entropy [61], namely, Bregman type [62] and Csiszár type [63]. We will denote the former as B-type and the latter as C-type from now on. In the case of BG entropy, these two expressions become same and equal to K-L entropy. In all other generalized thermostatical frameworks, they yield to two distinct expressions.

In the case of generalized thermostatics based on Tsallis entropy, the B-type relative entropy is given by

$$(5.12) \quad K_q[p||r] = \frac{\sum_k p_k^q}{q-1} + \sum_k r_k^q - \frac{1}{q-1} \sum_k p_k r_k^{q-1} - \sum_k p_k r_k^{q-1},$$

whereas C-type reads

$$(5.13) \quad I_q[p||r] = \frac{1}{1-q} [1 - \sum_k p_k^q r_k^{1-q}].$$

Noting the following relationship between the ordinary derivative and K-L entropy

$$(5.14) \quad K[p||r] = \frac{d}{dx} \sum_i (p_i)^x (r_i)^{1-x} \Big|_{x \rightarrow 1},$$

One can look for a similar relationship for the B and C-type Tsallis relative entropies. Although there is no such relationship for B-type, there is a similar mathematical relationship for C-type Tsallis relative entropy, which can be written as,

$$(5.15) \quad I_q[p||r] = D_q \sum_i (p_i)^x (r_i)^{1-x} \Big|_{x \rightarrow 1}$$

where Jackson q -differential operator D_q [64] is defined as

$$(5.16) \quad D_q f(x) = [f(qx) - f(x)]/[x(q-1)].$$

Both of these nonadditive relative entropies become K-L entropy as the parameter q approaches 1 as expected and they are both positive for $q > 0$ and negative for $q < 0$.

The comparison of the nonadditive renormalized entropy given by Eq. (5.10) with these two relative entropy expressions i.e., Eqs. (5.12) and (5.13) shows that the nonadditive renormalized entropy can be written in terms of B-type Tsallis relative entropy in Eq. (5.13)

$$(5.17) \quad R_q(p||\tilde{r}) = -K_q[p||\tilde{r}].$$

Since B-type relative entropy is positive for $q > 0$, I prove that the nonadditive renormalized entropy $R_q(p||\tilde{r})$ is negative for positive values of the nonadditivity index q . Therefore, I have proved in general that the renormalized equilibrium distribution has the maximum entropy compared to all other distributions created by nonzero values of the control parameter i.e.,

$$(5.18) \quad R_q(p||\tilde{r}) = S_q(p) - \tilde{S}_q(r) = -K_q[p||\tilde{r}] < 0,$$

which implies

$$(5.19) \quad \tilde{S}_q(r) > S_q(p).$$

The notation \sim is used in the above equation in order to remind the reader that I still need to renormalize mean energy values.

One issue needs clarification at this point: I have assumed $q > 0$ although it can have negative values. Once it is negative though, it is easy to see that $\tilde{S}_q(r) < S_q(p)$, which violates the S-theorem. The point is that the Tsallis entropy is thermodynamically stable only for positive values of the nonadditivity parameter q [65]. Therefore, the region corresponding to $q < 0$ is omitted above, since one expects that the Tsallis entropy to be stable if one would use it in a generalized thermostistical framework.

5.3. Nonadditive S-theorem and Constraints

The B and C-type relative entropies both share all the mathematical properties with K-L entropy. On the other hand, the investigation in the previous section led to B-type Tsallis relative entropy and not the C-type. Then, it is natural to ask whether this has a deeper meaning, since S-theorem seemingly cannot be generalized by using C-type relative entropy.

The question posed above has in fact a profound answer. Although these two relative entropies share some mathematical properties such as being positive definite, they do not share the same physical meaning. In order to explain what I mean by the word "physical

meaning”, it is enough to focus on K-L entropy in ordinary BG thermostatics. The K-L (relative) entropy reads [60]

$$(5.20) \quad K[p||r] \equiv \sum_i p_i \ln(p_i/r_i).$$

The K-L entropy can be thought as a generalization of BG entropy in the sense that both are equal to one another, apart from a multiplicative constant, when the prior distribution in relative entropy definition is known with certainty i.e., a probability of one is assigned to it. Therefore, it is always possible to obtain BG entropy as a particular case of corresponding relative entropy expression, so called K-L entropy. The converse is not true since K-L relative entropy is a two-probability distribution generalization of BG entropy. This situation can be compared to the case of Tsallis and BG entropies: the Tsallis entropy is considered to be a generalization of BG entropy simply due to the fact that its parameter can be adjusted in such a way that it results in BG entropy as a particular case. Whenever the nonadditivity index q becomes 1, one obtains BG entropy as a particular case. In this sense, any relative entropy definition associated with a particular entropy is a generalization of that particular entropy in terms of probabilities whereas generalized entropies such as the Tsallis entropy are seen to be generalization in terms of some parameter q .

A second issue regarding the importance of the concept of relative entropy is that ordinary BG entropy cannot be generalized to a continuum rigorously just by changing summation to integration since it fails to be invariant under different parametrizations. On the other hand, the relative entropy definition does not face any of these problems. Therefore, relative entropy is more general in its domain of applicability since it can be used in the continuum case unlike ordinary BG entropy. All of the remarks above can be summarized by the statement that the concept of relative entropy is a generalization of the corresponding entropy definition both in terms of probability distributions and continuum case.

In order to study the physical meaning of any relative entropy in a thermostatistical framework, one has first to obtain the equilibrium distribution associated with the entropy of that particular thermostatics. In this section, I maximize BG entropy subject to some constraints following the well known recipe of entropy maximization. Let us assume that the internal energy function is given by $U = \sum_i \epsilon_i p_i$, where ϵ_i denotes the energy of the i th microstate. In order to obtain the equilibrium distribution associated with BG entropy, I maximize the following functional

$$(5.21) \quad \Phi(p) = - \sum_i^W p_i \ln p_i - \alpha \sum_i^W p_i - \beta \sum_i^W \epsilon_i p_i$$

where α and β are Lagrange multipliers related to normalization and internal energy constraints respectively. Equating the derivative of the functional to zero, we obtain

$$(5.22) \quad \frac{\delta \Phi(p)}{\delta p_i} = -\ln \tilde{p}_i - 1 - \alpha - \beta \epsilon_i = 0.$$

The tilde denotes the equilibrium distribution obtained by the maximization of BG entropy. By multiplying Eq. (5.22) by \tilde{p}_i and summing over i , using the normalization and internal energy constraints, I have

$$(5.23) \quad \alpha + 1 = \tilde{S}_{BG} - \beta \tilde{U}.$$

Substitution of Eq. (5.23) into Eq. (5.22) results in the following equilibrium distribution

$$(5.24) \quad \tilde{p}_i = e^{-\tilde{S}_{BG}} e^{\beta \tilde{U}} e^{-\beta \epsilon_i}.$$

If I now use the equilibrium distribution \tilde{p} as the reference distribution in K-L entropy, I can write

$$(5.25) \quad K[p||\tilde{p}] = \sum_i p_i \ln(p_i/\tilde{p}_i).$$

The equation above can be rewritten as

$$(5.26) \quad K[p||\tilde{p}] = -S_{BG} - \sum_i p_i \ln \tilde{p}_i.$$

I then insert the equilibrium distribution given by Eq. (5.24) in the equation above to find

$$(5.27) \quad K[p||\tilde{p}] = -S_{BG} - \sum_i p_i (-\tilde{S}_{BG} + \beta \tilde{U} - \beta \epsilon_i).$$

Carrying out the summation, we have

$$(5.28) \quad K[p||\tilde{p}] = -S_{BG} + \tilde{S}_{BG} - \beta \tilde{U} + \beta U,$$

which can be cast into the form

$$(5.29) \quad K[p||\tilde{p}] = \beta (F_{BG} - \tilde{F}_{BG}).$$

The free energy term is given as usual by $F = U - S_{BG}/\beta$. The result above shows that the physical meaning of the K-L entropy is nothing but the difference of the off-equilibrium and equilibrium free energies when the reference distribution is taken to be the equilibrium distribution given by Eq. (5.24) above. This result is very important and can be used, for example, to study equilibrium fluctuations or non-equilibrium relaxation of polymer chains [66].

Since the K-L entropy plays the role of a generalized free energy expression when the underlying thermostatistics is given by BG entropy, then our previous question concerning the Tsallis relative entropies can be restated: can they (one or both) play the role of a generalized free energy expression in nonadditive thermostatistics? If they can, what are the conditions for this to be realized?

In order to answer questions posed above, I need to obtain the stationary distribution obtained from the maximization of Tsallis entropy similar to the treatment of the physical meaning of K-L entropy. The functional to be maximized is written as

$$(5.30) \quad \delta(S_q - \alpha \sum_{i=1}^w p_i - \beta \sum_{i=1}^w p_i \varepsilon_i) = 0,$$

which gives

$$(5.31) \quad \frac{q}{1-q} (\tilde{p}^{ord})^{q-1} - \alpha - \beta \varepsilon_i = 0.$$

The superscript (ord) indicated that I have used the ordinary constraint i.e., the first choice mentioned in chapter 2. I then multiply Eq. (5.31) by \tilde{p}^{ord} and sum over the index i so that I get

$$(5.32) \quad \alpha = \frac{q}{1-q} [1 + (1-q) \tilde{S}_q^{(ord)}] - \beta \tilde{U}^{(ord)}.$$

The tilde denotes the values calculated in terms of the maximum entropy distribution \tilde{p}^{ord} . I obtain the explicit form of the maximum probability distribution by substituting α into Eq. (5.31), which gives

$$(5.33) \quad \tilde{p}_i^{(ord)} = [1 - \frac{q-1}{q} \frac{\beta}{\sum_i (\tilde{p}_i^{ord})^q} (\varepsilon_i - \tilde{U}^{(ord)})]_+^{1/(q-1)} [1 + (1-q) \tilde{S}_q^{(ord)}]^{1/(q-1)}$$

where $[a]_+ \equiv \max\{0, a\}$.

As I did in order to find the physical meaning of the K-L entropy, if I substitute the equilibrium distribution in Eq. (5.33) as the prior r into the B-type relative entropy expression given by Eq. (5.12), one sees after some algebra

$$(5.34) \quad K_q[p||\tilde{p}^{(ord)}] = \beta(F_q^{(ord)} - \tilde{F}_q^{(ord)})$$

where the corresponding free energies are given as

$$(5.35) \quad F_q^{(ord)} = U^{(ord)} - \frac{1}{\beta} S_q; \quad \tilde{F}_q^{(ord)} = \tilde{U}^{(ord)} - \frac{1}{\beta} \tilde{S}_q^{(ord)}.$$

This is an important result, since it shows that the B-type relative entropy can be given a physical meaning in terms of free energy differences. In other words, the B-type Tsallis relative entropy plays the role of a generalized free energy distribution.

What is even more interesting is that the B-type relative entropy acquires this physical interpretation when the equilibrium distribution is obtained by the maximization of the Tsallis entropy with the first choice of the constraints i.e., ordinary probability. Therefore, B-type relative entropy is the one associated with the first constraint i.e., ordinary probability.

The question remains as to whether C-type Tsallis relative entropy can be given a similar kind of physical meaning. The answer turns out to be positive. In order to see this, I use

$$(5.36) \quad \delta(S_q - \alpha \sum_i p_i - \beta \frac{\sum_i p_i^q \epsilon_i}{\sum_j p_j^q}) = 0,$$

instead of the maximization of the functional in Eq. (5.30). The above functional explicitly shows that we are now using escort distribution and escort averaging. This means for example that the internal energy constraint is written as $U^{(esc)} = \frac{\sum_i p_i^q \epsilon_i}{\sum_j p_j^q}$. The superscript (esc) denotes that the calculations are made in terms of escort distribution. Proceeding in a similar manner to Eqs. (5.31)-(5.33), I obtain, for the stationary equilibrium distribution

$$(5.37) \quad \tilde{p}_i^{(esc)} = [1 - (1 - q) \frac{\beta}{\sum_i (\tilde{p}_i^{(esc)})^q} (\epsilon_i - \tilde{U}^{(esc)})]_+^{1/(1-q)} [1 + (1 - q) \tilde{S}_q^{(esc)}]^{-1/(1-q)}.$$

I then substitute the equilibrium distribution in Eq. (5.37) as the prior r into the C-type relative entropy expression given by Eq. (5.13) and see that it can be written as

$$(5.38) \quad I_q[p \parallel \tilde{p}^{(esc)}] = \frac{\hat{\beta}}{\sum_i (\tilde{p}_i^{(esc)})^q} (F_q^{(esc)} - \tilde{F}_q^{(esc)})$$

where the corresponding free energies are given as

$$(5.39) \quad F_q^{(esc)} = U^{(esc)} - \frac{1}{\hat{\beta}} S_q; \quad \tilde{F}_q^{(esc)} = \tilde{U}^{(esc)} - \frac{1}{\hat{\beta}} \tilde{S}_q^{(esc)}.$$

The term $\hat{\beta}$ is equal to

$$(5.40) \quad \hat{\beta} = \beta \frac{\sum_i (p_i^{(esc)})^q}{\sum_j (\tilde{p}_j^{(esc)})^q}.$$

Therefore, I can state that the C-type relative entropy plays the role of a generalized free energy distribution only if the Tsallis entropy is maximized with third constraint i.e., escort distribution.

In summary, the B-type relative entropy is the relative entropy compatible with the ordinary probability definition, whereas the C-type relative entropy is compatible with the escort distribution [67].

The aforementioned connection between the Tsallis relative entropies and the constraints sheds new light on the generalization of the nonadditive S-theorem, i.e., the generalization of the Tsallis entropy to the open systems. The nonadditive S-theorem in Eq. (5.17), which is the main ingredient for the nonadditive generalization of the S-theorem *requires* the B-type Tsallis entropy. This relative entropy is the one compatible with the ordinary distribution. In other words, the generalization of the Tsallis entropy to open systems in the framework of the S-theorem is achieved not by using escort distribution but ordinary probability distribution. This is against the common belief in the literature that one needs escort distribution for all practical purposes when one uses the Tsallis entropy [19].

It is even more interesting to note that the ordinary S-theorem is based on turning the ordinary reference distribution into the corresponding escort distribution, where the exponent of the escort distribution is obtained through an energy renormalization procedure. Therefore, the ordinary S-theorem due to Klimontovich is based on the use of ordinary BG entropy, escort distribution and energy renormalization. When one adopts nonadditive Tsallis entropy, one is forced to use ordinary probability instead of the escort

distribution, since nonadditive Tsallis entropy is already a one parameter generalization of BG entropy that leaves no room for the use of the escort distribution. On the other hand, BG entropy is not general enough to handle open systems by itself, so it needs the escort distribution. In both additive and nonadditive S-theorem however, the renormalization of mean energies is needed.

One might ask whether it is not possible to obtain a nonadditive generalization of the S-theorem by using the C-type relative entropy, reviving the possibility of basing the Tsallis formalism on the use of the escort distribution again. This has been tried by Rinat G. Zaripov [58]. In order to assess the value of his work, I will briefly review it here.

Zaripov [58] begins by the maximization of the following functional

$$(5.41) \quad \delta(S_q - \alpha \sum_i p_i - \beta \sum_i p_i^q \epsilon_i) = 0.$$

By this variation, he obtains the equilibrium distribution. Then, he considers the equality of the mean energies in a manner similar to Eq. (4.18), but the averaging is done by using the unnormalized escort distribution

$$(5.42) \quad \langle U_{eff}^q \rangle = \sum_i p_i^q \epsilon_i.$$

Zaripov is finally able to derive a new nonadditive renormalized entropy expression in terms of C-type Tsallis relative entropy i.e.,

$$(5.43) \quad R_q(p||\tilde{r}) = -I_q[p||\tilde{r}].$$

Naturally, this nonadditive renormalized entropy is also positive for q values greater than zero as the nonadditive renormalized entropy derived previously and given by Eq. (5.17).

A close inspection of Eqs. (5.41)-(5.43) shows that the work of Zaripov is flawed in some serious aspects. First of all, the inspection of Eq. (5.41) shows that Zaripov uses the second constraint for the internal energy when he maximizes the Tsallis entropy. On the other hand, in the same equation, he keeps the ordinary normalization condition. This

procedure is tantamount to saying that his mean value expressions are not normalized at all, as explained in Chapter 2. Indeed, this point surfaces again in Eq. (5.42). Then, he ends up with Eq. (5.43), which is a nonadditive renormalized entropy expression written in terms of the C-type relative entropy. This is not consistent, since he obtained the maximization of the Tsallis entropy in Eq. (5.41) and average energy in Eq. (5.42) with the second constraint. On the other hand, he ended up in C-type relative entropy, which is the Tsallis relative entropy associated with the escort distribution. In other words, Zaripov was able to obtain an expression for the nonadditive renormalized entropy in terms of the escort distribution without using the escort distribution itself. Therefore, since the work carried out by Zaripov suffers from aforementioned inconsistencies, it has no sound basis.

Moreover, the thermodynamic stability criterion [65] is not invoked so that Zaripov considers that the S-theorem cannot be generalized to the region $q < 0$ in the case of the Tsallis nonadditive entropy. In addition, the one of the most important result of this generalization scheme misses his attention, since the connection with the problem of constraints has not been addressed in his work. This is easy to understand, since the relation between the nonadditive relative entropies and the constraints has been established in Ref. [67] four years after the publication of Ref. [58].

Finally, it is worth remarking that the letter S in the S-theorem stands for “self-organization”, not entropy. The renormalized entropy (additive or nonadditive) expression orders the entropies in such a way that one has a more ordered state (i.e., decrease in entropy) as the control parameter increases while the system is receding from equilibrium. This decrease of entropy on ordering is called self-organization by Haken [52] and the renormalized entropy can be considered as a measure of self-organization for open systems. Due to this feature, the (additive) S-theorem has been used in many numerical models depending on a control parameter, such as the logistic map [68], heart rate variability [69, 70] and the analysis of electroencephalograms of epilepsy patients [71]. I hope that in the future the nonadditive S-theorem as a complexity measure can be applied to numerical cases such as logistic map or EEG signal analysis as its additive counterpart has been used.

5.4. Application to the Modified Van der Pol Oscillator

As an illustration of the nonadditive S-theorem, I revisit the modified Van der Pol oscillator studied in Chapter 4, but this time with the nonadditive S-theorem. In order to do this, I need to calculate the nonadditive renormalized entropy, which is equal to $-K_q[p||\tilde{r}]$. Therefore, I calculate the nonadditive relative entropy $K_q[p||\tilde{r}]$, taking also the renormalization of energy into account to obtain the nonadditive renormalized entropy. I first assume that the underlying mechanics (i.e., Fokker-Planck equation) does not change, so that I can use the same distribution functions obtained in Chapter 4.

Using the explicit form of the nonadditive relative entropy $K_q[p||\tilde{r}]$, which can be obtained by the combination of Eqs. (5.13) and (5.17), I calculate, after some algebra,

$$(5.44) \quad R_q(p||\tilde{r}) = \frac{1}{1-q} \int_0^\infty dE p^q - \int_0^\infty dE \tilde{r}^q + \frac{1}{q-1} \int_0^\infty dE p \tilde{r}^{q-1} + \int_0^\infty dE p \tilde{r}^{q-1}$$

where I have written the equations in the continuous domain, with integrals instead of summations. The first integral on the right-hand side is calculated as

$$(5.45) \quad \int_0^\infty dE p^q = \int_0^\infty dE \left(\frac{2b}{\pi D}\right)^{q/2} e^{-bqE^2/2D} = \left(\frac{2b}{\pi D}\right)^{q/2} \left(\frac{D\pi}{2bq}\right)^{1/2}$$

and the second integral is

$$(5.46) \quad \int_0^\infty dE \tilde{r}^q = \int_0^\infty dE \left(\frac{\pi b}{2D}\right)^{q/2} e^{-\sqrt{\frac{\pi b}{2D}} q E} = \frac{1}{q} \left(\frac{\pi b}{2D}\right)^{(q-1)/2}.$$

The third and fourth integrals are the same form and can be calculated by completing the squares. The last integral is

$$(5.47) \quad \begin{aligned} \int_0^\infty dE p \tilde{r}^{q-1} &= \int_0^\infty dE \left(\frac{2b}{\pi D}\right)^{1/2} \left(\frac{\pi b}{2D}\right)^{(q-1)/2} e^{-(q-1)(\frac{\pi b}{2D})^{1/2} E} e^{-\frac{bE^2}{2D}} \\ &= \frac{2}{\pi} \left(\frac{\pi b}{2D}\right)^{q/2} e^{(q-1)^2 \frac{\pi}{4}} \sqrt{\frac{\pi D}{2b}} \operatorname{erfc}\left(\frac{\sqrt{\pi}}{2}(q-1)\right) \end{aligned}$$

where the complementary error function $\operatorname{erfc}(x)$ is

$$(5.48) \quad \text{erfc}(x) = 1 - \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt.$$

Substituting Eqs. (5.45)-(5.47) into Eq. (5.44), I finally obtain the nonadditive renormalized entropy expression

$$(5.49) \quad R_q(p||\tilde{r}) = S_q(p) - S_q(\tilde{r}) = \frac{1}{(1-q)} \left(\left(\frac{2b}{\pi D} \right)^{q/2} \sqrt{\frac{\pi D}{2bq}} - \frac{1}{q} \left(\frac{\pi b}{2D} \right)^{(q-1)/2} + \right. \\ \left. \left(\frac{q}{q-1} \right) \frac{2}{\pi} \left(\frac{\pi b}{2D} \right)^{q/2} e^{(q-1)^2 \frac{\pi}{4}} \sqrt{\frac{\pi D}{2b}} \text{erfc} \left(\frac{\sqrt{\pi}}{2} (q-1) \right) \right).$$

The nonadditive renormalized entropy expression above is always negative for positive values of nonadditivity parameter q , i.e.,

$$(5.50) \quad R_q(p||\tilde{r}) < 0.$$

In Figs. 5.1 and 5.2, I plot the nonadditive renormalized entropy for some particular values of the intensity of the random source D and nonlinear friction coefficient b as a function of the nonadditivity parameter q . It is always negative as expected [72]. Moreover, it attains the value -0.05 as q becomes 1 independent of the intensity of random force D and nonlinear friction coefficient b . Note that this is exactly the value we obtained by using ordinary additive renormalized entropy given by Eq.(4.25) in Chapter 4.

Although the above treatment of the modified Van der Pol oscillator is correct as far as nonadditive open systems are considered, another possibility is to change underlying dynamics using the Fokker-Planck equation. The modified Van der Pol oscillator in Chapter 4 was based on the following Fokker-Planck equation

$$(5.51) \quad \frac{\partial f(E, t)}{\partial t} = \frac{\partial}{\partial E} \left(DE \frac{\partial f(E, t)}{\partial t} \right) + \frac{\partial}{\partial E} [(a + bE) E f(E, t)].$$

This results in the stationary solutions of the exponential form given by Eq. (4.12). However, a full nonadditive treatment must naturally based on the stationary distributions

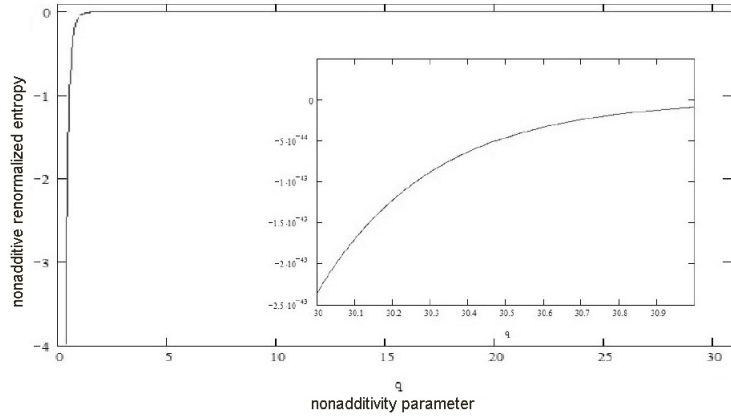


Figure 5.1. The nonadditive renormalized entropy versus the nonadditivity parameter q , where the intensity of the random source is $D=50$ and nonlinear friction coefficient is $b=0.05$.

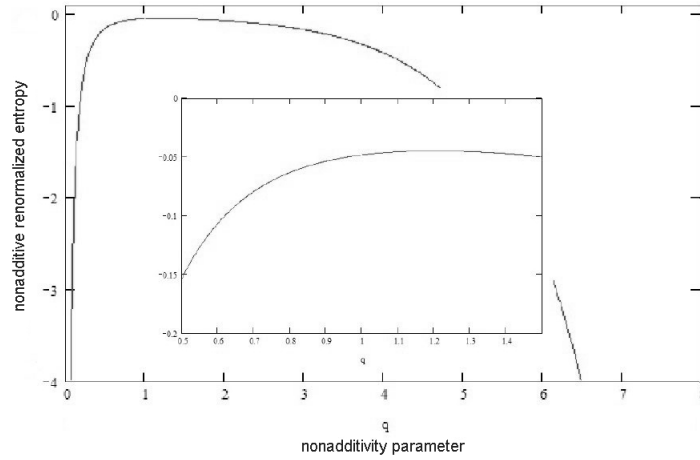


Figure 5.2. The nonadditive renormalized entropy versus the nonadditivity parameter q , where the intensity of the random source is $D=5$ and nonlinear friction coefficient is $b=20$.

of q -exponential form. This is usually succeeded by changing the dynamics so as to be described by the nonlinear Fokker-Planck equation as we have seen in Chapter 3 [73, 74, 39]. However, there is a more elegant way to obtain stationary distributions of q -exponential form. One first notes that the modified Van der Pol oscillator used previously corresponds to the following equation

$$(5.52) \quad \dot{v} = -x + f(E, u_1, u_2)v + \sigma\xi$$

where the function $f(E, u_1, u_2)$ is given by

$$(5.53) \quad f(E, u_1, u_2) = -u_1 - 2u_2E.$$

The term E is the energy of the harmonic oscillator and the u 's are the control parameters. The noise term and σ are equal to $\sigma\xi(t) = y(t)$ and $\sigma = \sqrt{2D}$, respectively. If I also choose the control parameters as $u_1 = a$ and $u_2 = b/2$, I exactly obtain the modified Van der Pol oscillator equation used by Klimontovich. However, this modified oscillator has a more general solution i.e.,

$$(5.54) \quad f_0(E) = C \exp\left(\frac{2}{\sigma^2} \int dE f(E, u_1, u_2)\right).$$

The function $f(E, u_1, u_2)$ is quite arbitrary and can be changed to another expression as long as the new expression can be written in terms of the energy E and the control parameters. This point is crucial in understanding the modified Van der Pol oscillator since one can instead choose

$$(5.55) \quad f(E, u_1, u_2) = \frac{-u_1 - 2u_2E}{1 + \frac{(1-q)}{D}(u_1E + u_2E^2)}.$$

This new choice of the function $f(E, u_1, u_2)$, through Eq. (5.54), results in the following stationary distribution

$$(5.56) \quad f_{0,q}(E) = C \exp_{2-q}\left(-\frac{aE + \frac{1}{2}bE^2}{D}\right)$$

where C is the normalization constant and the control parameters are again written as $u_1 = a$ and $u_2 = b/2$. The q -exponential is defined by

$$(5.57) \quad \exp_q(x) = [1 + (1 - q)x]^{\frac{1}{1-q}}.$$

In order to assess the importance of the expression in Eq. (5.56), it suffices to remember that $p^{(1)} \propto \exp_{(2-q)}(-x)$. Therefore, the corresponding equilibrium distribution associated with zero value of the control parameter is

$$(5.58) \quad r_q(E) = A \exp_{2-q}\left(-\frac{\gamma E}{D}\right).$$

The normalization constant A can be found easily by integration and is equal to $A = \frac{\gamma q}{D}$ for q values between 0 and 1. Therefore, the equilibrium distribution function is given by

$$(5.59) \quad r_q(E) = \frac{\gamma q}{D} \exp_{2-q}\left(-\frac{\gamma E}{D}\right)$$

for $0 \leq q < 1$. Now, I increase the control parameter to a value different from zero and create nonequilibrium state in the system. In Van der Pol oscillator, the threshold of generation is defined as the state when feedback parameter a_f is equal to γ . Then, according to Eq. (4.9), $a=0$. Therefore, the distribution function for this case can be written as

$$(5.60) \quad p_q(E) = B \exp_{2-q}\left(-\frac{bE^2}{2D}\right).$$

The normalization constant B can be calculated by using the transformation $\sqrt{\frac{(1-q)b}{2D}}E = x$. Having done this, the normalization constant is found as

$$(5.61) \quad B = \sqrt{\frac{(1-q)b}{2D}} \left(\int_0^\infty dx (1 + x^2)^{\frac{1}{q-1}} \right)^{-1}.$$

The integral above can be evaluated by changing the variable x^2 to u , so that

$$(5.62) \quad B = \sqrt{\frac{2(1-q)b}{D}} \left(\int_0^\infty du u^{-1/2} (1 + u)^{\frac{1}{q-1}} \right)^{-1}.$$

This last integral can be calculated by using the following integral

$$(5.63) \quad \int_0^\infty du u^{\mu-1} (1 + \beta u)^{-\nu} = \beta^{-\mu} B(\mu, \nu - \mu)$$

where $B(a, b)$ denotes the incomplete Beta function for $|\arg \beta| < \pi$ and $\text{Re} \nu > \text{Re} \mu > 0$.

Finally, the distribution function p_q is given by

$$(5.64) \quad p_q(E) = \sqrt{\frac{2(1-q)b}{D}} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-1} [1 + (1-q)\frac{b}{2D}E^2]^{\frac{1}{q-1}}.$$

Moreover, I observe that the renormalization of energies i.e., Eq. (5.6) becomes

$$(5.65) \quad \int_0^\infty dE E \tilde{r}_q(E) = \int_0^\infty dE E p_q(E).$$

In order to solve the integral on the right hand side above, I make the transformation

$\sqrt{\frac{(1-q)b}{2D}} E = x$ and obtain

$$(5.66) \quad \int_0^\infty dE E p_q(E) = \sqrt{\frac{2(1-q)b}{D}} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-1} (\frac{2D}{(1-q)b}) \int_0^\infty dx x (1 + x^2)^{\frac{1}{q-1}}.$$

Next, I make the transformation $x^2 = u$ so that

$$(5.67) \quad \int_0^\infty dE E p_q(E) = \sqrt{\frac{2(1-q)b}{D}} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-1} (\frac{D}{(1-q)b}) \int_0^\infty du (1+u)^{\frac{1}{q-1}}.$$

Changing the variable $1 + u$ to v , I finally obtain

$$(5.68) \quad \int_0^\infty dE E p_q(E) = \sqrt{(1-q)} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-1} \sqrt{\frac{2D}{bq^2}}$$

for $0 < q \leq 1$. For the integral on the left of Eq. (5.65), I make the transformation

$1 + (1-q)\frac{\gamma}{D}E = x$ in order to get

$$(5.69) \quad \int_0^\infty dE E \tilde{r}_q(E) = \frac{\tilde{D}}{(2q-1)\gamma}$$

for $\frac{1}{2} \leq q < 1$. Therefore, Eq. (5.65) becomes

$$(5.70) \quad \tilde{D} = (2q-1)\gamma \sqrt{(1-q)} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-1} \sqrt{\frac{2D}{bq^2}}$$

for $\frac{1}{2} \leq q < 1$. Therefore, the nonadditive renormalized entropy is calculated as

$$(5.71) \quad R_q[p||\tilde{r}] = (1-q)^{-1} \left(\frac{2(1-q)b}{D} \right)^{(q-1)/2} [B(\frac{1}{2}, \frac{1}{1-q} - \frac{1}{2})]^{-q} B(\frac{1}{2}, \frac{q}{1-q} - \frac{1}{2}) - (1-q)^{-1} q^q \gamma^{q-1} \frac{\tilde{D}^{1-q}}{(2q-1)}$$

for $\frac{1}{2} \leq q < 1$, where \tilde{D} is given by Eq. (5.70). The nonadditive renormalized entropy expression above is always negative for positive values of nonadditivity parameter q i.e., $R_q(p||\tilde{r}) < 0$ as before since it is again the negative of the B-type Tsallis relative entropy together with renormalization of the corresponding mean energies. I plot the nonadditive renormalized entropy in Eq. (5.71) for some particular values of the intensity of the random source D and nonlinear friction coefficient b in Figs. 5.3 and 5.4. This nonadditive renormalized entropy too attains the value -0.05 as q becomes 1, independent of the intensity of random force D and nonlinear friction coefficient b .

The most important difference in changing the underlying dynamics so that the stationary distribution is of the q -exponential form is the confinement of the q values to a range between 0.5 and 1. If one uses a linear Fokker-Planck equation with Tsallis entropy, the nonadditivity index q can take any value without limitations. However, the change in the dynamics so as to make it nonlinear, results in some privileged q values. This seems to be a general feature whenever one studies physical systems depending on a control parameter [76, 77, 78]. However, whether these q values can form an equivalence class or not is important. There is no answer to this question yet. I hope that in the future these multitude of q values can be generalized under one main idea.

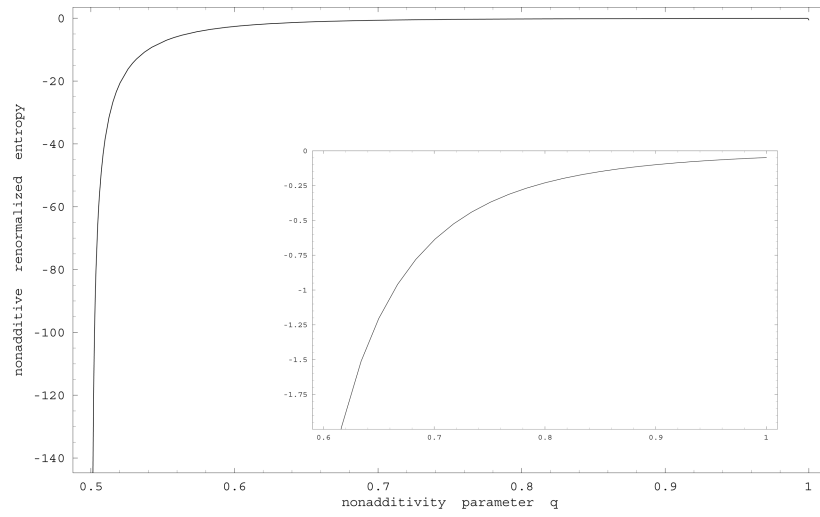


Figure 5.3. The nonadditive renormalized entropy with q -exponential versus the nonadditivity parameter q , where the intensity of the random source is $D=50$ and nonlinear friction coefficient is $b=0.05$.

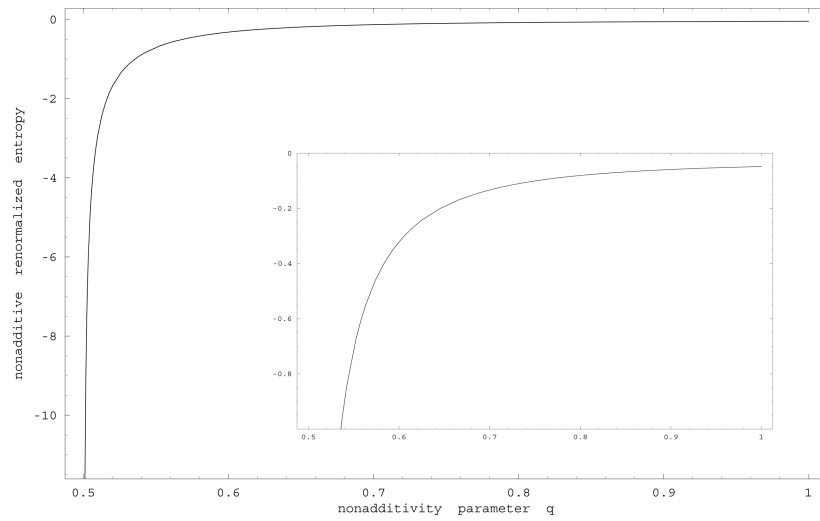


Figure 5.4. The nonadditive renormalized entropy with q -exponential versus the nonadditivity parameter q , where the intensity of the random source $D=2$ and nonlinear friction coefficient $b=70$.

CHAPTER 6

NONADDITIVE GENERALIZATION OF KLIMONTOVICH'S S-THEOREM IN OPEN SYSTEMS WITH INCOMPLETE STATISTICS

Many different entropy measures such as Rényi [13], Sharma-Mittal [14] and Tsallis measures [11] have been proposed in order to generalize BG entropy. All these entropy measures are different from one another in fundamental ways. For example, Tsallis entropy measure is nonadditive, whereas Rényi measure is additive. Although both Tsallis and Sharma-Mittal measures are nonadditive, the Tsallis entropy is one-parameter generalization of the BG entropy whereas Sharma-Mittal entropy is a two-parameter generalization of the BG entropy. Despite their differences though, all these entropy measures share a common feature in that they are all based on the assumption of complete statistics, which is even shared by the entropy measure they claim to generalize i.e., BG entropy. The assumption of complete statistics implies that all states regarding the system are countable and known completely by us. We have full knowledge of the interactions taking place in the system of interest, thereby implying the ordinary normalization condition $\sum_i p_i = 1$. However, this scenario is challenged in some cases of interest since one cannot obtain all the information regarding the system under investigation in these particular situations. One such possibility can be mentioned when confronted with fractal phase spaces [4, 5]. One can then have singularities and inaccessible points, that renders the assumption of complete statistics useless. Moreover, even when one knows all the states, one might not be able to calculate the probability distribution exactly corresponding to these states. This case too requires a new approach based on the incompleteness of description.

Recently, Wang [12] proposed a new nonadditive entropy based on Tsallis entropy by replacing the complete normalization condition with an incomplete one depending on a free positive parameter q . This new framework is called the formalism of incomplete

statistics (IS). The parameter q plays the role of Hausdorff dimension divided by the topological dimension of the phase space when IS formalism is considered for nonequilibrium systems evolving in hierarchically heterogeneous phase space, connecting the concept of information and the topological dimension of some fractal sets [79]. However, another interpretation of this parameter is related to the neglected interaction. When no interaction is neglected, the parameter q becomes equal to unity, thereby reducing the results of IS formalism to those of complete statistics described by BG entropy. This idea can be traced back to A. Rényi, who used it for the information loss in the case of incomplete statistics although he did not pursue it in the framework of a generalized thermostatics [80].

In the next section, I will outline the IS formalism in general and list some of its properties. The generalization of IS entropy to open systems through S-theorem will be realized in section 6.2.

6.1. Incomplete Statistics

The point of departure of the IS formalism is the nonadditive Tsallis entropy [11]

$$(6.1) \quad S_q^{Tsallis}(p) = \frac{\sum_i^W p_i^q - \sum_i^W p_i}{1 - q}$$

where p_i is the probability of the system in the i th microstate, W is the total number of the configurations of the system. Note that Boltzmann constant k is set to unity throughout the paper. The entropic index q is a real number, which characterizes the degree of nonadditivity since Tsallis entropy obeys the following pseudo-additivity rule:

$$(6.2) \quad S_q(A + B)/k = [S_q(A)] + [S_q(B)] + (1 - q)[S_q(A)][S_q(B)]$$

where A and B are two independent systems i.e., $p_{ij}(A+B)=p_i(A)p_j(B)$. Obviously, this formalism assumes that we have complete access to all random variables since the summation in Eq. (6.1) is over the total number of configurations W . This assumption also lies at the center of the normalization of probability distribution, since it considers

that all the information relevant to the physical system under consideration is accessible to us. On the other hand, IS formalism challenges this issue since a complete description of a physical system requires the determination of exact Hamiltonian and exact solution of the equations of motion associated with the Hamiltonian. However, it is possible in practice that we may not know analytically all the interactions, which must appear in the relevant Hamiltonian. This failure in our knowledge of exact Hamiltonian results in the incompleteness of the countable states. If this is the case, the ordinary normalization of the probability distribution will not hold and must be avoided. This observation lies at the heart of IS formalism since Wang proposes to replace the ordinary i.e., complete normalization $\sum_i^w p_i = 1$ with the incomplete normalization given by

$$(6.3) \quad \sum_i^w p_i^q = 1$$

where w denotes the states accessible to us. Since these states do not now form a complete set, w can be greater or smaller than the real number of all possible states. The incompleteness parameter q is positive and can be considered as a measure of neglected interactions. When all the interaction is taken into account, it is equal to 1, recovering the ordinary normalization. As a result of incomplete normalization, the expectation value of an observable \hat{O} is consistently given by

$$(6.4) \quad \langle \hat{O} \rangle = \sum_{i=1}^w p_i^q O_i.$$

The incomplete normalization given by Eq. (6.3) enables one to write a new entropy based on incomplete statistics whose point of departure is Tsallis entropy in Eq. (6.1). This new entropy expression reads

$$(6.5) \quad S_q(p) = \frac{1 - \sum_i^w p_i}{1 - q}.$$

The stationary equilibrium distribution for IS entropy in the canonical case can be found by applying the Lagrange method

$$(6.6) \quad \delta(S_q + \frac{\alpha}{1-q} \sum_{i=1}^w p_i^q - \alpha\beta \sum_{i=1}^w p_i^q \epsilon_i) = 0.$$

The resulting canonical equilibrium distribution [12] in IS formalism is then given by

$$(6.7) \quad p_i^{eq} = [1 - (1-q)\beta\epsilon_i]^{1/(1-q)}$$

apart from normalization. The energy of the i th microstate is denoted by ϵ_i where the Lagrange multipliers are denoted by α and β . However, it is easy to verify that the canonical equilibrium distribution given by Eq. (6.7) is not invariant under the uniform translation of the energy parameter ϵ_i . Moreover, the Lagrange multiplier β is not identical with the inverse temperature [81, 82]. These difficulties are easily overcome by the maximization of the IS entropy in Eq. (6.5) as follows

$$(6.8) \quad \delta(S_q - \alpha \sum_{i=1}^w p_i^q - \beta \sum_{i=1}^w p_i^q \epsilon_i) = 0,$$

which results

$$(6.9) \quad p_i^{eq} = [1 - (1-q)q\beta(\epsilon_i - U_q) / \sum_{j=1}^w p_j]^{1/(1-q)}$$

where $U_q = \sum_{i=1}^w p_i^q \epsilon_i$ is the internal energy and the normalization constant is not explicitly written. This canonical equilibrium distribution is invariant under uniform translation of energy parameter and the Lagrange multiplier β is identical with inverse temperature [82].

One important connection between IS formalism and the incompleteness parameter q emerges when one considers the self-similar fractal phase-space. For illustration, I consider the Sierpinski carpet shown in Fig. 6.1. The Sierpinski carpet can be obtained by imagining a full square of length l and then continue to divide it into three at equal lengths i.e., $l/3$ and remove the central square. Therefore, in the first iteration $C(1)$ for example, I will have 8 squares, each with a surface area of $l^2/3^2$. At k th iteration, the

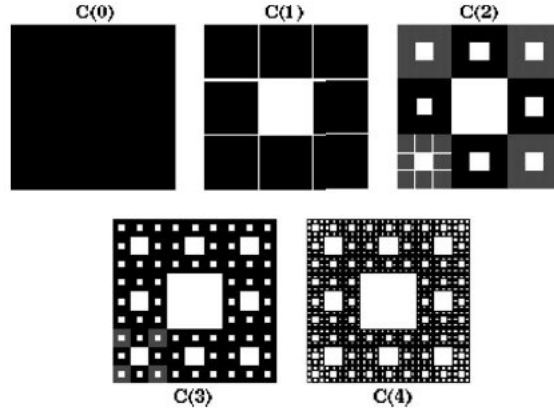


Figure 6.1. The Sierpinski carpet.

side of the squares will be $1/3^k$ and the total number of squares will be equal to 8^k . The total surface after k-iteration will be given by

$$(6.10) \quad S_k = W_k s_k = l^2 \left(\frac{8}{9}\right)^k$$

where W_k denotes the total number of squares after k-iteration and s_k denotes the surface of each square after k-iteration. If the segments do not have the same size, I can generalize the Eq. (6.10) as

$$(6.11) \quad S_k = \sum_{i=1}^{W_k} s_k(i).$$

I then suppose that the density of state is identical everywhere on the segments and the dynamics in phase-space is quasi-ergodic i.e., every point on the segments is equally visited.

The classical probability definition is defined in terms of relative frequency of visits of each point so that it reads

$$(6.12) \quad p_i = \frac{s_k(i)}{S_k},$$

i.e., the surface of each square after the k th iteration divided by the total surface after k th iteration. This definition is even normalized as can be seen using Eq. (6.12) together with Eq. (6.11). However, as the number of iterations increases, this probability definition will go to zero. This means that all probabilities will be null. In short, this probability definition makes no sense. Therefore, I define a new probability definition as

$$(6.13) \quad p_i = \frac{s_k(i)}{l^2}$$

where the two comes from the carpet being two dimensional in Euclidian space i.e., its topological dimension $d = 2$. Then, I write

$$(6.14) \quad \sum_{i=1}^{W_k} \left(\frac{s_k(i)}{l^2} \right)^{d_f/2} = 1$$

where the fractal dimension d_f is equal to $\ln 8 / \ln 3$ for the Sierpinski carpet. The s_k again denotes the surface of each square after k -iteration and is equal to $l^2/9^k$. Therefore, this new probability definition too is normalized

$$(6.15) \quad \sum_{i=1}^{W_k} \left(\frac{s_k(i)}{l^2} \right)^{d_f/2} = 8^k \left(\frac{1}{3^k} \right)^{d_f} = \left(\frac{8}{3^{d_f}} \right)^k = 1$$

by using the definition of fractal dimension $8 = 3^{d_f}$. A comparison with Eq. (6.3) shows that

$$(6.16) \quad q = d_f/d.$$

This relation is very important and is worth remark. First of all, it should be noted that the sum is over all the W_k segments at the k th iteration and this does not mean the sum over all possible states (the black portion removed after each iteration). Moreover, if the fractal dimension d_f is larger than the topological dimension d , it means that the system has more states than W_k . When it is the case that the fractal dimension d_f is less than the topological dimension d , this means that the system has less states than W_k . Whenever

the fractal and topological dimensions coincide, we have the complete information about the system, thereby having the incompleteness parameter q equal to 1.

The comment above begs some explanation. In order to elucidate the remark made above, let us define Ω , which is equal to

$$(6.17) \quad \Omega = \sum_{i=1}^{W_k} p_i.$$

This definition of Ω denotes the incompleteness since it would be equal to 1 for a statistics based on complete information. Therefore, any deviation from 1 in the value of Ω is an indication of the incompleteness of the underlying statistics. Then, I can write

$$(6.18) \quad \sum_{i=1}^{W_k-1} p_i^q + (\Omega - \sum_{i=1}^{W_k-1} p_i)^q = 1$$

for any $0 < p_i < 1$. In order to illustrate the relation between the incompleteness parameter q and the incompleteness measure Ω , I consider an incomplete probability distribution given by

$$(6.19) \quad \{p_{i=1\dots 5}\} = \{0.10, 0.15, 0.20, 0.25, \Omega - 0.70\}.$$

The Fig. 6.2 shows that $\Omega > 1$ when $q > 1$ and $\Omega < 1$ when $q < 1$. It is indeed in this sense that the parameter q is called incompleteness parameter.

The connection between the incompleteness parameter and the fractal dimension d_f was first found in Ref. [79] for monofractals (i.e., the segments are of the same size) and later has been generalized to multifractals with segments of variable size [83].

6.2. Open Systems with Incomplete Statistics

Gibbs' theorem established the fact that the entropy corresponding to the canonical distribution is maximum and it can be taken as an indication for the importance of the canonical ensemble. However, Gibbs' theorem relies on two major assumptions. Firstly, the system under consideration is governed by complete statistics, which is described by

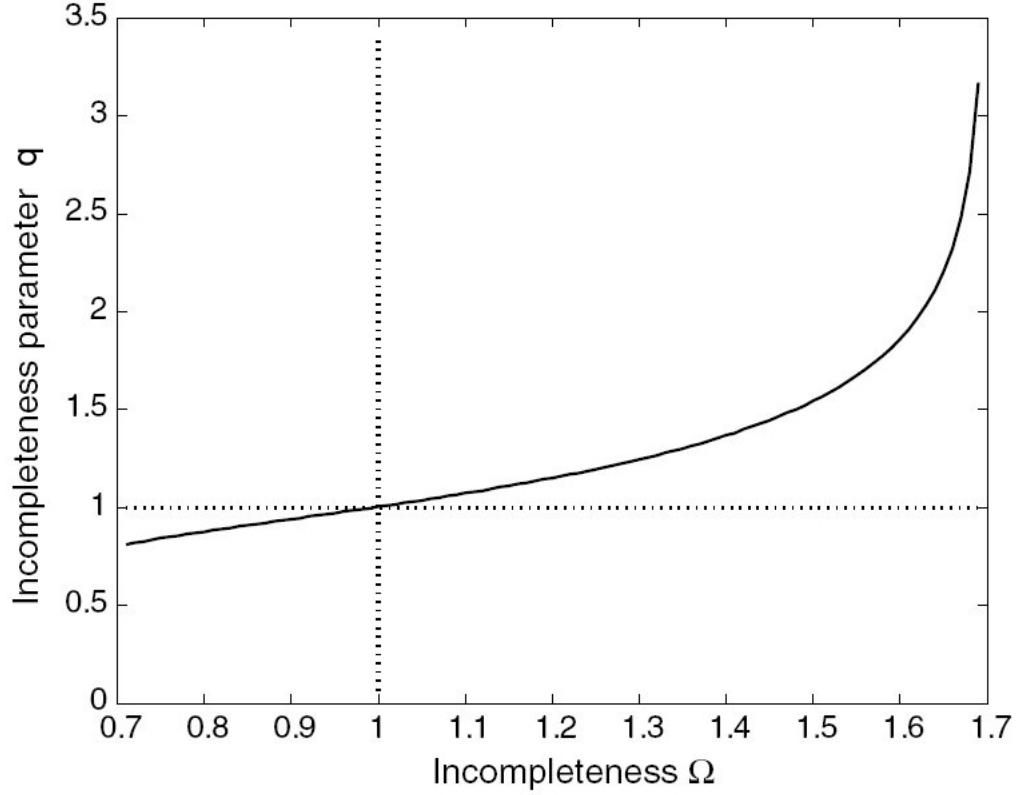


Figure 6.2. The dependence of Ω on q for the incomplete distribution given by Eq. (6.19).

BG measure. Due to this assumption, Gibbs' theorem is limited to the cases, where the stationary equilibrium distribution is exponential. Second, Gibbs' theorem is limited to the cases, where the average internal energy is kept constant. Our aim in this paper is to generalize Gibbs' theorem for open systems with incomplete statistics. It is highly probable indeed that one cannot write all the interactions governing such a system since open systems are subject to many interactions whose equations of motion are not fully solvable. This in turn will result in only some states being accessible to us, so the use of incomplete statistics is required. Moreover, an open system might have a metastable stationary state described by an inverse power law as IS suggests, instead of an exponential as Klimontovich assumed [45, 46, 47, 48].

All these considerations requires us to generalize Gibbs' theorem for open systems with incomplete statistics. In order to do this, I first define a new quantity named renormalized entropy R_q^{IS} as

$$(6.20) \quad R_q^{IS} \equiv S_q^{neq}(r) - \tilde{S}_q^{eq}(\tilde{p}_{eq}).$$

The generalization of Gibbs' theorem is now equivalent to showing that renormalized entropy expression above is negative i.e., $R_q^{IS} < 0$, since this implies that $\tilde{S}_q^{eq} > S_q^{neq}$. However, I know that this cannot be proved on the basis of ordinary Gibbs' theorem, since it compares distributions with the same mean energy which is not the case for open systems. Therefore, Klimontovich proposed a generalization of Gibbs' theorem for open systems with complete statistics by equating the mean energies of the equilibrium and nonequilibrium states [45, 46, 47, 48]. Due to this effective mean energy equalization, I denote the equilibrium entropy by a tilde since this is not the original equilibrium entropy but the one obtained after using the effective mean energy equalization. Two distinct incomplete probability distributions i.e. \tilde{p}_{eq} and r in Eq. (6.10) denotes the renormalized equilibrium and nonequilibrium probability distributions respectively. The corresponding IS entropy expressions are denoted by $\tilde{S}_q^{eq}(\tilde{p}_{eq})$ and $S_q^{neq}(r)$. From now on, I will drop the subscript from the equilibrium probability distribution so that it should be understood that the probability distributions p and \tilde{p} denote the ordinary and renormalized equilibrium distributions, respectively. The renormalized equilibrium probability distribution \tilde{p} and nonequilibrium probability distribution r obey the incomplete normalization summarized by Eq. (6.3) i.e., $\sum_i^w \tilde{p}_i^q = \sum_i^w r_i^q = 1$, which is implicitly taken into account in the definition of IS entropy given by Eq. (6.5).

In order to proceed, I need to define effective mean energy in terms of the equilibrium state associated with the incomplete statistics. This can be achieved by defining

$$(6.21) \quad U_{eff} \equiv -\ln_q p_i$$

where the q-logarithm is simply defined as

$$(6.22) \quad \ln_q(x) = \frac{x^{1-q} - 1}{1 - q}.$$

This definition of effective mean energy is central to our generalization and therefore requires some explanation. The effective mean energy is defined in terms of the unnormalized equilibrium distribution. In this sense, if one applies this definition to the unnormalized equilibrium distribution given by Eq. (6.7) above, one sees that $U_{eff} = \beta \epsilon_i$. The application of the effective mean energy to the canonical equilibrium distribution in Eq. (6.9) however results in $U_{eff} = q\beta(\epsilon_i - U_q)$. This observation explains why it is called effective mean energy since it is always proportional to the multiplication of the Lagrange multiplier β associated with the internal energy constraint and the energy of the i th microstate. The calculations in this paper are general in the sense that both equilibrium distributions can be used. However, a consistent treatment would be through the adoption of the canonical equilibrium distribution in Eq. (6.9) due to its explicit dependence on temperature through β . The open systems are usually treated by using a control parameter, which controls the matter or energy influx into the system due to its interaction with the environment. In this sense, the state with the zero value of the control parameter is the equilibrium distribution and all the other stationary states with control parameter values different from zero correspond to nonequilibrium distributions. Having clarified this important issue, I can rewrite the equalization of effective mean energies of the two states as

$$(6.23) \quad \langle U_{eff} \rangle^{(eq)} = \langle U_{eff} \rangle^{(neq)}$$

where superscripts 1 and 2 denote the renormalized equilibrium and ordinary nonequilibrium states respectively so that the averages must be taken in terms of \tilde{p}_i^q and r_i^q . The Eq. (6.13) can be explicitly written as

$$(6.24) \quad \sum_{i=1}^w \tilde{p}_i^q U_{eff} = \sum_{i=1}^w r_i^q U_{eff}.$$

The substitution of the effective mean energy defined in Eq. (6.21) into Eq. (6.24) yields

$$(6.25) \quad \sum_{i=1}^w \tilde{p}_i^q \left(\frac{p_i^{1-q} - 1}{q - 1} \right) = \sum_{i=1}^w r_i^q \left(\frac{p_i^{1-q} - 1}{q - 1} \right).$$

Due to the normalization i.e., $\sum_i^w \tilde{p}_i^q = \sum_i^w r_i^q = 1$, the above equation can be rewritten as

$$(6.26) \quad \sum_{i=1}^w \tilde{p}_i^q p_i^{1-q} = \sum_{i=1}^w r_i^q p_i^{1-q}.$$

The probability distribution \tilde{p} can be considered as the normalized and renormalized (i.e., effective mean energy equalization) counterpart of the ordinary equilibrium distribution p . Therefore, I can substitute $\tilde{p}_i^q = \frac{p_i^q}{\sum_i p_i^q}$ into Eq. (6.26) and obtain

$$(6.27) \quad \sum_{i=1}^w \tilde{p}_i = \sum_{i=1}^w r_i^q \tilde{p}_i^{1-q}.$$

On the other hand, I can also obtain an explicit form of renormalized entropy defined by Eq. (6.20) by substituting the IS entropy in Eq. (6.5) explicitly, which gives

$$(6.28) \quad R_q^{IS} = \frac{1}{(q-1)} \left(\sum_{i=1}^w r_i - \sum_{i=1}^w \tilde{p}_i \right).$$

Making use of the equalization of the effective mean energies of equilibrium and nonequilibrium states given by Eq. (6.27), we obtain

$$(6.29) \quad R_q^{IS} = \frac{1}{(q-1)} \left(\sum_{i=1}^w r_i - \sum_{i=1}^w r_i^q \tilde{p}_i^{1-q} \right).$$

The final step in our treatment is to show that the renormalized entropy R_q^{IS} is negative for all positive values of the incompleteness parameter q . This can be achieved by rewriting the above renormalized entropy expression as

$$(6.30) \quad R_q^{IS} = - \sum_{i=1}^w r_i \left[\frac{(r_i/\tilde{p}_i)^{q-1} - 1}{q-1} \right].$$

A mathematical inequality [84], with the plausible assumption $r_i/p_i \geq 0$, states

$$(6.31) \quad \frac{(r_i/\tilde{p}_i)^{q-1} - 1}{q-1} \geq 1 - \tilde{p}_i/r_i, \quad q > 0.$$

Multiplying both sides of the above inequality with r_i and summing over i , I obtain

$$(6.32) \quad \sum_{i=1}^w r_i \frac{(r_i/\tilde{p}_i)^{q-1} - 1}{q-1} \geq \sum_{i=1}^w (r_i - \tilde{p}_i), \quad q > 0.$$

Comparing the inequality above with the expressions given by Eqs. (6.28) and (6.30), I see that the above inequality takes the form

$$(6.33) \quad -R_q^{IS} \geq (q-1)R_q^{IS}, \quad q > 0.$$

Since the above inequality is valid only for q values greater than zero, it implies

$$(6.34) \quad R_q^{IS} \leq 0.$$

The equality holds only if the two distributions are the same. Since I assume that the states under question are two different states, one being renormalized equilibrium state and the other being nonequilibrium state, I can drop the equality sign above. Moreover, remembering the original definition of renormalized entropy in Eq. (6.20), I see that

$$(6.35) \quad R_q^{IS} = S_q^{neq} - \tilde{S}_q^{eq} < 0 \Rightarrow \tilde{S}_q^{eq} > S_q^{neq},$$

i.e., the (renormalized) equilibrium entropy is greater than the nonequilibrium entropy for open systems with incomplete statistics. Naturally, one recovers the result based on complete statistics of BG entropy i.e., $S^{eq} > S^{neq}$ by taking the $q \rightarrow 1$ limit in Eq. (6.35). In summary, one will have a more ordered state as the control parameter increases while

the system is receding off equilibrium. This decrease of entropy on ordering is called self-organization by Haken [52] and the renormalized entropy R_q^{IS} can also be taken as a measure of self-organization for open systems described by IS.

By generalizing Gibbs' theorem for open systems described by IS formalism, I have shown that the stationary equilibrium state obtained from IS is the state of maximum entropy even in the presence of energy or matter influx. The treatment here can be considered as a generalization of ordinary S-theorem (and of Gibbs' theorem for that matter) developed by Klimontovich since the latter is a particular case of the former in the $q \rightarrow 1$ limit. In this sense, the incompleteness is a more general framework since the results assuming complete statistics can be obtained from IS even in the case of open systems. This generalization of Gibbs' theorem is essential if one would like to understand better the IS formalism. It is less likely that we will have complete knowledge of the system as the interaction terms governing the system increase which would generally be the case with open systems. Finally, we have shown that one obtains a more ordered state i.e., a state of lesser entropy as the control parameter increases. In this sense, the renormalized entropy expression obtained in this dissertation serves as a criterion of self-organization [52] in open systems described by IS [85].

CHAPTER 7

BOLTZMANN'S METHOD OF ORTHODES AND THE MICROCANONICAL ENTROPY

In this chapter, I will outline the Boltzmann's method of orthodes and its importance for the microcanonical ensembles. The main difference between this chapter and the previous ones is that the Boltzmann's method of orthodes is applicable only to equilibrium systems. In fact, Boltzmann's method of orthodes [86] is founded on the work of Helmholtz [87]. He attempted to prove thermodynamics relations for systems at equilibrium based solely on mechanistic arguments, without invoking probabilistic arguments. A good review of Boltzmann's method of orthodes can be found in Ref. [88].

7.1. Boltzmann's Method of Orthodes

One of the main disputes about the foundation of statistical mechanics is whether it can be founded on purely dynamical laws or purely mechanistic arguments. Many scientists and philosophers alike hold the view that a statistical treatment is necessarily based on the law of large numbers and the thermodynamic limit even though each particle forming the system conforms to Newtonian dynamics. Others advocate the view that mechanical concepts such as ergodicity and mixing suffice for a sound foundation for all statistical physics. Historically, the origin for the latter can be traced back to Helmholtz [87] and Boltzmann [86]. The core of their research programme consisted of proving the validity of the heat theorem or combined first and second laws of thermodynamics,

$$(7.1) \quad dS = \frac{dE + PdV}{T}$$

for the equilibrium on purely mechanical grounds. Helmholtz succeeded in realizing this goal for the one-dimensional case. It was finally Boltzmann who generalized Helmholtz's result for all dimensions by relying on the concept of ergodicity. The ergodicity is one of

the central concepts in the foundations of statistical physics. However, its relevance to statistical physics and its provability is still at debate. Helmholtz showed that the heat theorem is satisfied if the generating function for the exact differential is given by

$$(7.2) \quad S(E, V) = \log 2 \int_{x_-}^{x_+} \frac{dx}{h} \sqrt{2m(E - \varphi(x, V))}.$$

Here, the notation x_{\pm} stands for the turning points, The potential energy must be U-shaped since Helmholtz theorem applies only to *monocyclic* systems. These systems are assumed to be such that there is one periodic trajectory per energy level. φ denotes the potential energy. In this sense, harmonic oscillator is monocyclic whereas a particle inside a double well is not. The temperature is defined in accordance with the equipartition theorem and the pressure in accordance with the usual expression,

$$(7.3) \quad T \doteq 2 \langle K \rangle_t$$

$$(7.4) \quad P \doteq - \left\langle \frac{\partial H}{\partial V} \right\rangle_t.$$

The $\langle \cdot \rangle_t$ denotes time average over one period of the orbit. Thus, I obtain a completely mechanical description of equilibrium thermodynamics due to the Helmholtz theorem in Eq. (7.2). This theorem has been recently generalized to any number of degrees of freedom [89]. The importance of this result can be summarized as follows. First, it provides the link connecting Hertz to Helmholtz-Boltzmann. Hertz initially employed the idea that equilibrium thermodynamics is independent of the size of the system and purely on mechanical arguments so that the main ingredient for both happened to be the equipartition theorem *and* adiabatic invariance [90, 91].

The method of orthodes is simple and powerful. It gives us the equilibrium thermodynamics through mechanical arguments only. Moreover, It does so without invoking the thermodynamic limit so that it chooses the entropy expressions, that are compatible with the systems of any size.

This method of orthodes is not limited to microcanonical, canonical or grand canonical entropies even though these entropies formed the major line of investigation for Boltzmann. This method is general and can be applied even to systems with inverse power law equilibrium distribution as we will see in the next chapter. I consider Tsallis entropy in the framework of the method of orthodes.

However, before proceeding to apply this method to Tsallis entropy, I use the method of orthodes to present some results concerning the microcanonical entropy definition in ordinary Boltzmannian context.

7.2. Method of Orthodes and the Microcanonical Entropy

Since the seminal work of Gibbs [3], there are two definitions of microcanonical entropy. They are volume and surface entropies. In order to illustrate the definition of these two distinct microcanonical definitions of entropy and the difference between the two, the ideal gas serves as a good example. The ideal gas model is considered idealized in regards to its two essential features. First, it only takes into account the kinetic energies of the particles composing it, thereby neglecting all the interactions between the particles. Second, the atomic structure of the environment (e.g., container) is ignored, so that the role of the environment is only to make particles of the ideal gas collide elastically with the idealized surfaces.

As a result of these two idealizations, the Hamiltonian for the ideal gas is

$$(7.5) \quad H = \frac{1}{2m} \sum_{i=1}^N p_i^2$$

assuming that our ideal gas is composed of N particles and the notations m and p_i denote the mass and the momentum of each particle. The general expression of volume entropy [92] is

$$(7.6) \quad S_{\Phi}(E, V) = \log \Phi(E, V),$$

where

$$(7.7) \quad \Phi(E, V) = \frac{1}{h^{3N}} \int_{H \leq E} d^3 p_1 \dots d^3 p_N d^3 q_1 \dots d^3 q_N.$$

In accordance with the definition above, we see that the volume entropy is the logarithm of the $6N$ -dimensional phase-space volume of the region enclosed by the constant energy hyper-surface. The role of the constant h , with dimensions of action, in Eq. (7.7) is to make the volume entropy dimensionless. The volume of the phase space associated with the ideal gas described by the Hamiltonian in Eq. (7.5) is then calculated as [92]

$$(7.8) \quad \Phi(E, V) = C_{3N} \left[\frac{V}{h^3} (2mE)^{3/2} \right]^N$$

where C_{3N} is given as

$$(7.9) \quad C_{3N} = \frac{\pi^{3N/2}}{\Gamma(\frac{3N}{2} + 1)}.$$

The $\Gamma(x)$ in the denominator is the gamma function with the argument x . In order to obtain the volume entropy, it suffices to take the logarithm of the phase space volume given by Eq.(7.8), which gives

$$(7.10) \quad S_\Phi(V, E) = \log A + N \log V + \frac{3N}{2} \log E$$

where A is a constant depending on h , m and N . The thermodynamics of the system can be calculated by taking partial derivative of the volume entropy with respect to extensive variables i.e., energy E and volume V . The first partial derivative evidently provides the expression for the temperature i.e.,

$$(7.11) \quad \frac{1}{T_\Phi} \doteq \frac{\partial \log S_\Phi(V, E)}{\partial E} = \frac{3N}{2E},$$

whereas the partial derivative of the volume entropy with respect to extensive variable V provides the equation of state for the ideal gas,

$$(7.12) \quad \left(\frac{P}{T}\right)_\Phi = \frac{\partial \log S_\Phi(V, E)}{\partial V} = \frac{N}{V}.$$

The subscript Φ indicates that these quantities are calculated by using the volume entropy.

The ideal gas model can also be studied by using surface entropy, however [92]. The general definition of the surface entropy is given as

$$(7.13) \quad S_\Omega(E, V) = \log \Omega(E, V)$$

where the function Ω is defined as

$$(7.14) \quad \Omega(E, V) = \frac{1}{h^{3N}} \int d^3 p_1 \dots d^3 p_N d^3 q_1 \dots d^3 q_N \delta(E - H).$$

The symbol $\delta(x)$ represents the Dirac delta function. In this sense, Ω represents the phase-space volume of the infinitesimally thin shell of constant energy E . In fact, this definition of the quantity Ω is nothing but the density of states of the system at the energy E . Assuming the smoothness of the hyper-surfaces of constant energy, one has

$$(7.15) \quad \Omega(E, V) = \frac{\partial}{\partial E} \Phi(E, V).$$

This is the explanation for the term “surface entropy”, since Ω is equal to the derivative of the volume entropy, that suggests it can be called “surface entropy”. It is now easy to see that, *for ideal gases*, the surface entropy and the volume entropy are related through

$$(7.16) \quad S_\Omega(E, V) = S_\Phi(E, V) + \log \left(\frac{3N}{2E} \right).$$

The expressions for the temperature and equation of state for the ideal gas can be calculated by making use of Eqs. (7.11) and (7.12), but this time through surface entropy to get

$$(7.17) \quad \frac{1}{T_{\Omega}} \doteq \frac{\partial \log S_{\Omega}(V, E)}{\partial E} = \left(\frac{3N}{2} - 1 \right) \frac{1}{E}$$

and

$$(7.18) \quad \left(\frac{P}{T} \right)_{\Omega} \doteq \frac{\partial \log S_{\Omega}(V, E)}{\partial V} = \frac{N}{V}.$$

Some remarks are in order: the surface entropy given by Eq. (7.16) is not equal to the volume entropy obtained before i.e., Eq.(7.10) since the former includes some non-trivial additional term depending on the energy and number of molecules of the ideal gas under study. Comparison of Eqs. (7.12) and (7.18) shows that they result in the same equation of state. The crucial point is to understand the equality of the volume and surface entropies in the thermodynamic limit. In the thermodynamic limit, the extensive properties of the systems such as energy become directly proportional to the size of the system i.e., number of particles composing the ideal gas or volume of the container. Then, the additional term in the surface entropy expression in Eq.(7.16) becomes a constant. This shows that, *for ideal gases*, the volume and surface entropies are equivalent to one another *only* in the thermodynamic limit.

Having noted the equivalence of surface and volume entropies occurring only in the thermodynamic limit, it is important to understand the difference between the two regarding the equipartition theorem. The equipartition theorem states that each harmonic term in the Hamiltonian contributes $T/2$ to the energy of the system. In ideal gas model, the number of harmonic terms is $3N$ since we have N particles in three dimensional space. Therefore, the total energy of the ideal gas must be equal to $3NT/2$. Inspection of Eqs. (7.11) and (7.17) shows explicitly that the volume entropy S_{Φ} is consistent with the equipartition theorem whereas the surface entropy S_{Ω} is not. The usual textbook explanation of this point is again by invoking the concept of thermodynamic limit [92]. Since this limit presupposes the existence of many degrees of freedom i.e., large N values, one is led to conclude that the difference between the Eqs. (7.11) and (7.17) is negligible.

However, it should be noted that the volume entropy S_Φ is consistent with the equipartition theorem independent of the number of degrees of freedom. In order to assess the importance of the equipartition theorem, I refer to the treatment of this subject due to Khinchin [93]. According to him, I can rewrite the equipartition theorem as

$$(7.19) \quad \left(\frac{2K}{3N}\right)^{-1} = \frac{\partial S_\Phi(E, V)}{\partial E}.$$

If one agrees to name the quantity $(\frac{2K}{3N})^{-1}$ as the temperature of the system under investigation, one immediately obtains the fundamental thermodynamic relation

$$(7.20) \quad \frac{1}{T} = \frac{\partial S_\Phi(E, V)}{\partial E} = \frac{1}{T_\Phi}.$$

Note that this result is independent of number of degrees of freedom and does not need the thermodynamic limit to be invoked at all. Further, it is not restricted to ideal gases. Therefore it is very general and fundamental [93]. In fact this is one of the two main reasons that led [90, 91] to choose the volume entropy as the entropic function and not the surface entropy. The other reason is the *adiabatic invariance* of the volume entropy.

I finally remark on the difference between these two forms of entropies as to whether or not they are adiabatic invariant. Before proceeding, let us elucidate the meaning of adiabatic invariance and its importance. A quantity is (mechanically) an adiabatic invariant if it is constant under the slow variation of the external parameter (e.g., in the ideal gas example, the external parameter is the volume V). The concept of adiabatic invariance is very useful in addressing thermodynamic behavior from a mechanical point of view because quasi-static transformations, which are at the very heart of thermodynamic theory, can be conveniently modelled as adiabatic transformations [89]. According to thermodynamic theory, the entropy remains constant along quasi-static transformations of thermally isolated systems. Therefore, our candidate expression of microcanonical entropy should be an adiabatic invariant. It is a well established fact that, under the assumption of ergodicity, the volume entropy is adiabatic invariant, whereas the surface

entropy is not [94, 95]. However, in the thermodynamic limit for the ideal gas model, the surface entropy is an adiabatic invariant even though it so in general.

7.3. Dynamical Derivation of the Boltzmann's Principle and the Volume Entropy

In this section, my main concern will be an alternative and recent dynamical derivation of definition of entropy due to Bianucci et al. (their results will be refereed as BMWG from now on since the full list of authors includes also Mannella, West and Grigolini) [96]. Their work may help us understand and appreciate the importance of volume entropy in the context of equilibrium. The scope of the work carried out by BMWG in fact extends to the nonequilibrium situations as well, since these authors first obtain a Fokker-Planck equation, that can be used to study systems under both equilibrium and nonequilibrium conditions. They derive the canonical distribution as the equilibrium state of their particular Fokker-Planck equation through dynamical arguments only. In spite of this broader scope of their work, I will refer to their results only in aspects relevant to the equilibrium state of the physical system under consideration. BMGW presents their main objective very clearly at the beginning of their paper: they want to generalize the Boltzmann principle only through dynamical arguments so as to include low dimensional systems into its scope. What they consider as the Boltzmann principle is Eq. (7.13). In their work the Boltzmann principle is derived dynamically rather than being assumed. This programme was initiated by Khinchin, who thought it was possible to derive the Boltzmann principle purely on mechanical grounds to obtain the thermodynamic property of the physical system under scrutiny. In order to establish a dynamical picture, which enables them to derive the Boltzmann principle, BMWG adopts the following picture: they assume a division of variables concerning the description of the physical system. The first group of variables enables them to study the macroscopic properties of the system. These variables are associated with the system of interest, since they are the ones that are of main importance as far as thermodynamic description of the system is considered. The second group, in contrast to the former group, are called the irrelevant variables, since they are associated with the microscopic description of the system. This division is essentially tantamount to divide the system into two i.e., the system of interest and the booster.

The word booster requires for some explanation since it is not a common term used in the literature. The common practice in this area is to use the term “thermostat” for dynamical studies of statistical systems. However, concerning the aim of BMWG, the work “thermostat” is misleading in two regards. First, the standard approach in the literature assumes that the thermostat consists of infinite number of degrees of freedom. In other words, the word “thermostat” implies that the thermodynamic limit is already invoked. However, the aim of BMWG is to obtain a generalized derivation of Boltzmann principle independent of degrees of freedom. Second, the thermostats in standard treatment in the literature are almost always placed initially in canonical equilibrium, which contradicts with the objective of BMWG since they do not invoke canonical equilibrium but derive it from dynamical arguments only. Because of these two important differences in approach, these authors adopt the word “booster” instead of the ordinary term “thermostat”. In order to proceed, BMWG make the following assumptions. Although the results of these authors are general in scope, when they study the equilibrium case and relevant expression of temperature, they assume in particular that the system of interest is a linear oscillator. They then assume that the booster can be studied through linear response theory of [97], together with the assumption that the coupling parameter Δ between the booster and the system of interest is sufficiently small. These two assumptions make a perturbative treatment possible, which enables in turn the modulation of the system of interest by the action of the booster. I will not enter here into a detailed discussion of these assumptions. For the purposes of the present dissertation it will suffice to mention that after employing these assumptions together with projection method introduced by [98], BMWG finally derives the general form of Boltzmann principle which is given by

$$(7.21) \quad \frac{1}{T} = \frac{\partial S_{\Omega}(E, V)}{\partial E} + DCT$$

where T is calculated from the average kinetic energy and DCT denotes a correction term, called by BMWG the *dynamical correction term*. This correction term is called dynamical since it depends on the correlation function of the booster. This equation led them to

conclude that they derived a general expression of the Boltzmann principle independent of degrees of freedom. This dynamical correction term vanishes in the thermodynamic limit. In other words, this general form recovers the ordinary Boltzmann principle in the thermodynamic limit. This modern and complicated dynamical approach to the foundations of the Boltzmann principle, based on projection method, linear response theory and separation between booster and system of interest, seems however contrived once the Equipartition Theorem is considered. By looking at Eq. (7.17) it appears evident that the dynamical correction term stems because the surface entropy has been used instead of the volume entropy by BMWG. In fact it is easily seen that:

$$(7.22) \quad DCT = \frac{\partial}{\partial E}(S_{\Phi} - S_{\Omega}).$$

This also explains why DCT goes to zero in the Thermodynamic Limit. Artur Adib [99] has the merit of having pointed this out in his paper entitled “Does the Boltzmann principle need a dynamical correction?”. Adib first notes that the Boltzmann principle introduced by BMWG is written in terms of surface entropy. Then, he identifies the correction term of BMWG to be the result of the employment of surface entropy and is not needed when one uses the volume entropy (to make a connection with the case of ideal gas treated in Section 2, the correction term would be the additional term $(-1/E)$ that appears in Eq. (7.17)). Moreover, Adib numerically verifies this result by using a model of quartic oscillators. One might be curious as to whether the numerical models of Adib and BMWG work under same assumptions i.e., they are equivalent and therefore can justify a thorough comparison. It should be remarked that both models have finite correlation times and are ergodic. The main difference between the two is that the model adopted by BMWG assumes a booster Hamiltonian depending on harmonic terms whereas the model by Adib does not include any harmonic term. This absence allows Adib to tackle the problem analytically and does not have any bearing as far as the justification of the comparison is considered. Based on his analytical calculations and numerical simulations, Adib concludes that Boltzmann principle does not need a correction term if one employs

volume entropy instead of surface entropy. The work of BMWG is important, because it quantifies the difference of surface and volume inverse temperatures (i.e., the dynamical correction term) in terms of the system's correlation function.

In summary, these two forms of microcanonical entropy expressions i.e., volume and surface entropies are not equivalent to one another in microscopic systems. Even though they yield the same equation of state for the ideal gas treated in this section, the volume entropy conforms the equipartition theorem and is adiabatic invariant independent of the number of degrees of freedom, without restriction to ideal cases. On the other hand, the surface entropy possesses these properties only in the thermodynamic limit i.e., when $N \rightarrow \infty$, and for ideal systems with quadratic Hamiltonian only (ideal gases and crystals).

Although I have limited our discussion to systems at equilibrium, it should be remarked that the correct entropy is recently found to be the volume entropy even for the non-equilibrium cases where the second law is proved through the volume entropy [100]. However, it is possible to prove that the second law is violated if one uses the surface entropy [101].

CHAPTER 8

BOLTZMANN'S METHOD OF ORTHODES AND THE TSALLIS ENTROPY

As I have explained in the previous chapter, Boltzmann's method of orthodes consists of proving the validity of the heat theorem i.e.,

$$(8.1) \quad dS = \frac{dE + PdV}{T}$$

for the systems at equilibrium on purely mechanical grounds. Helmholtz showed that the heat theorem is satisfied if the generating function for the exact differential is given by

$$(8.2) \quad S(E, V) = \log 2 \int_{x_-}^{x_+} \frac{dx}{h} \sqrt{2m(E - \varphi(x, V))}$$

and the temperature T , the pressure P are defined by the equipartition theorem and the time average of the relevant mechanical quantities, respectively as

$$(8.3) \quad T \doteq 2 \langle K \rangle_t$$

$$(8.4) \quad P \doteq - \left\langle \frac{\partial H}{\partial V} \right\rangle_t.$$

Here, the notation x_{\pm} stands for the turning points, φ denotes the potential energy. The potential energy must be U-shaped since Helmholtz theorem applies only to *monocyclic* systems.

I now write the Tsallis distribution

$$(8.5) \quad \rho(z; E, V) = \frac{[1 - \frac{\beta}{\alpha}(H(z; V) - E)]^{\alpha-1}}{N}$$

where $N(E, V)$ is the partition function, i.e., normalization. It is naturally equal to

$$(8.6) \quad N(E, V) = \int dz [1 - \frac{\beta}{\alpha} (H(z; V) - E)]^{\alpha-1}.$$

The parameter β satisfies $\langle H \rangle = E$. Therefore, β is a function of E and V . The integration is over the phase-space coordinate $z = (q_1, q_2, \dots, q_f, p_1, p_2, \dots, p_f)$. The parameter α is related to the nonadditivity parameter q through the following relation

$$(8.7) \quad \alpha = \frac{1}{1 - q}.$$

V is an external parameter and can be taken as the volume for example.

It has been proved that the Tsallis distribution $\rho(z; E, V)$ conforms to the equipartition theorem [102, 103] i.e.,

$$(8.8) \quad 2 \left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{\beta} = T.$$

I also define \hat{N}

$$(8.9) \quad \hat{N}(E, V) = \int dz [1 - \frac{\beta}{\alpha} (H(z; V) - E)]^{\alpha}.$$

It can be proved that [102]

$$(8.10) \quad \hat{N}(E, V) = N(E, V).$$

Now, I can continue to prove the orthodicity of the Tsallis ensemble described by Eq. (8.5). In order to do this, I first take the partial derivative of \hat{N} with respect to E so that

$$(8.11) \quad \frac{\partial \hat{N}}{\partial E} = \int dz [1 - \frac{\beta}{\alpha} (H - E)]^{\alpha-1} [-\frac{\partial \beta}{\partial E} (H - E) + \beta].$$

The Eq. (8.11) can be rewritten as

$$(8.12) \quad \frac{\partial \hat{N}}{\partial E} = -N \frac{\partial \beta}{\partial E} \langle H - E \rangle + N\beta.$$

Since $\langle H \rangle = E$ and $\hat{N}(E, V) = N(E, V)$, I obtain

$$(8.13) \quad \frac{\partial \hat{N}}{\partial E} = \hat{N}\beta = \frac{\hat{N}}{T}.$$

I then take the partial derivative of \hat{N} with respect to V

$$(8.14) \quad \frac{\partial \hat{N}}{\partial V} = \int dz [1 - \frac{\beta}{\alpha}(H - E)]^{\alpha-1} [\frac{\partial \beta}{\partial V}(E - H) - \beta \frac{\partial H}{\partial V}].$$

The above equation can be rewritten as

$$(8.15) \quad \frac{\partial \hat{N}}{\partial V} = N \frac{\partial \beta}{\partial V} \langle E - H \rangle - N\beta \left\langle \frac{\partial H}{\partial V} \right\rangle.$$

Since $P = \left\langle -\frac{\partial H}{\partial V} \right\rangle$, we finally obtain

$$(8.16) \quad \frac{\partial \hat{N}}{\partial V} = \hat{N} \frac{P}{T}.$$

The term $d\hat{N}$ can be calculated as

$$(8.17) \quad d\hat{N} = \frac{\partial \hat{N}}{\partial E} dE + \frac{\partial \hat{N}}{\partial V} dV.$$

The substitution of the Eqs. (8.13) and (8.16) on Eq. (8.17) yields

$$(8.18) \quad dS = \frac{d\hat{N}}{\hat{N}} = \frac{dE + PdV}{T}.$$

This final result is of central importance, since it shows that the Tsallis ensemble is on equal footing as the microcanonical, canonical and grandcanonical ensembles as far as Boltzmann's method of orthodes i.e., heat theorem is considered.

On the other hand, this result is surprising since it shows that the entropy associated with the Tsallis ensemble is not q -logarithm of the distribution $\rho(z; E, V)$ as held generally, but with ordinary logarithm. Therefore, the Tsallis entropy for systems at equilibrium reads

$$(8.19) \quad S(E, V) = \log N(E, V).$$

Moreover, the Tsallis entropy satisfying heat theorem can easily be seen to be equal to the Rényi entropy S^R

$$(8.20) \quad S^R = \frac{1}{1 - \alpha} \log \int dz \rho^\alpha$$

of order $\alpha = \frac{1}{q}$, due to the important relation $\hat{N} = N$ given by Eq. (8.10) [102, 103].

In summary, the Tsallis ensemble satisfies heat theorem as prescribed by the Boltzmann's method of orthodes and is on equal footing with other orthodes such as canonical or grandcanonical ensembles in this regard. On the other hand, the associated entropy to be used becomes the Rényi entropy of the order $\frac{1}{q}$ [104]. It is worth remark that all these considerations apply to the use of the Tsallis entropy at equilibrium.

CHAPTER 9

CONCLUSION

The recent theoretical and experimental progress in statistical physics has provided many examples where the ordinary Boltzmann-Gibbs thermostatistics fails. Among such examples, the systems with long-range interaction [105], self-gravitation [106] and fractal behavior [107] can be cited. The failure of the Boltzmann-Gibbs thermostatistics can be realized in many different ways. For example, for the dynamical systems in fractal phase space, the ordinary probability definition diverges. Therefore, they require a change in the fundamental probability definition and normalization condition [79]. The failure can also be shown by the limitations of the Boltzmann-Gibbs entropy definition itself. This entropy is additive, and thus cannot be used for nonadditive systems.

One such failure of ordinary thermostatistics has been its lack of different stationary distributions. When one maximizes the Boltzmann-Gibbs entropy subject to the normalization and internal energy constraint, one can only obtain an exponential stationary distribution. However, we now know the existence of systems with many different metastable states, exhibiting stretched exponentials, inverse power laws or inverse gamma distributions as their associated stationary distributions [4, 22]. Obviously, the Boltzmann-Gibbs entropy cannot satisfy these cases by itself. Due to these reasons, the last two decades have been extensively devoted to the generalization of Boltzmann-Gibbs entropy.

Many new entropy definitions have been proposed in order to produce this generalization. Some of them, but not all, are the Tsallis entropy [11], Sharma-Mittal entropy [14], Kaniadakis entropy [108], the incomplete statistics entropy [12] and Rényi entropy [13]. Although all these entropies yield stationary distributions of the inverse power law form, they are in fact very different from one another. For example, the Sharma-Mittal entropy [14] is a two-parameter generalization of the Boltzmann-Gibbs entropy, whereas Tsallis and Rényi entropies are single parameter generalizations. On the other hand, the

Tsallis entropy is nonadditive while Rényi entropy is completely additive. In other words, it is still an open problem to choose between these alternatives or to use each of them for different purposes. This picture is surprising after all since the goal was the unification of different stationary distributions under one generalized entropy expression.

In this dissertation, I mainly investigate two entropy definitions and some associated issues. These entropies are Tsallis and incomplete statistics (IS). Both yield the same type of stationary distributions, i.e., inverse power law distributions. They both generalize the Boltzmann-Gibbs entropy through the use of a single free parameter. On the other hand, the nature and physical meaning of this single parameter is very different for these entropies.

As I have outlined in Chapter 2, the nonadditivity parameter q associated with the Tsallis entropy is a measure of the fluctuation of the intensive variables, such as temperature. The incompleteness parameter q in the IS entropy is, however, a measure of the neglected interactions and the incompleteness of our knowledge about the physical system. Therefore, one must be very careful when one studies these generalized entropies.

Despite the failure of Boltzmann-Gibbs entropy according to our current understanding, it had enjoyed a great success in its applications to many diverse fields. One such example is provided by the well-known Kramers' reaction rate problem [28]. According to the model constructed by Kramers, the reaction rates, in both low and high viscosity limits, are of exponential form. This is not surprising after all when one realizes that Kramers' model is based on linear Fokker-Planck equation whose stationary solutions are exponential. The difficulty is that we now have some experimental and numerical results, which do not conform to this exponential behavior. In fact, the survival probabilities related to the reaction rates obtained from these experimental and numerical findings are of the inverse power law form in the time domain [36].

There are two main paths to follow in order to generalize Kramers' rate. First, one may adopt a *fractional* Fokker-Planck equation so that one obtains an inverse power law asymptotically [42]. Second, one may use the *nonlinear* Fokker-Planck equation, Tsallis entropy [73, 74] and q -exponential functions on which this entropy is based. One again

obtains survival probabilities of inverse power law form [44]. Both of these approaches give a good fit to the existing experimental data. The major difference between the two approaches is that there is as yet no entropy definition for the fractional approach [109].

The major use of the Tsallis entropy is believed to be for systems which are driven out of equilibrium. Although open systems are such cases, there is no proper framework in which the Tsallis entropy could be used for such systems. Such a general treatment has been achieved in Chapter 5. By defining a new quantity called “nonadditive renormalized entropy”, I have shown that the nonadditive open systems described by the Tsallis entropy can be studied in a consistent manner. By consistency, I mean that the stationary equilibrium distribution has the maximum entropy even for open systems. The renormalized entropy can also be used as a measure of self-organization in open systems, since it is a measure of order for entropy values. Open systems are systems which can be modeled by a control parameter in order to simulate energy and/or matter influx. According to (additive or nonadditive) renormalized entropy, the entropy of the system decreases as the control parameter increases. Since the zero value of the control parameter denotes the stationary equilibrium distribution, this means a continuous decrease in entropy values of the system as it is more and more driven out of equilibrium. Since entropy is a measure of disorder, the smaller the entropy, the more ordered the system is. Thus, the use of the term “control parameter” is justified in the sense that Haken's definition of self-organization [52] is realized even for nonadditive open systems.

The additive S-theorem has also been used as a measure of (numerical) complexity for the logistic map [68], heart rate variability [69, 70] and the analysis of electroencephalograms of epilepsy patients [71]. I hope that the same applications and others may be made in the near future with the nonadditive S-theorem developed in this dissertation.

The discussion of nonadditive open systems illuminated a very interesting topic, namely the constraints, i.e., how the average will be taken. Since the beginning of the nonadditive formalism in the first paper of Constantino Tsallis in 1988 [11], the question as to which constraint is more suitable for this new entropy has been an issue [110]. The original choice of constraints was the ordinary probability definition. However, any attempt to

obtain Lévy distributions from the Tsallis entropy failed with this constraint since the second moment of the Lévy distribution diverged. Therefore, the physicists working in this field switched to second constraint as defined in Chapter 2. Unfortunately, this new definition also had its flaws. For example, this constraint was unnormalized and violated energy conservation. The final choice was the so-called escort distributions. Everything seems to work fine with this constraint but, unfortunately, the transition from the ordinary probability definition (first choice of constraints) to the escort distribution (the third and last choice of constraints) was *ad hoc*. The problem with the constraints is to find some criterion to choose between these two.

The nonadditive S-theorem proved to be one such criterion, since it shows that the nonadditive thermostatics described by the Tsallis entropy can be generalized to open systems only through the use of ordinary constraints. So far, I could neither formulate nor find in the literature a nonadditive generalization of S-theorem with the escort distribution. The S-theorem stands as a unique theorem in its relation to the constraints in the nonadditive formalism. Its additive counterpart is formed by a combination of the ordinary Boltzmann-Gibbs entropy together with the escort distribution. To the best of my knowledge, this latter is the only case in which the Boltzmann-Gibbs entropy is used together with the escort distribution. The general view of generalized thermostatics involves the entropy maximization procedure of Jaynes [111] and the use of Boltzmann-Gibbs entropy is allowed only with the ordinary probability distribution as shown by Jaynes. However, the S-theorem is not based on entropy maximization and therefore deserves a different treatment.

Despite the multitude of the different entropy expressions, almost all of these entropies have one feature in common. They assume that our knowledge of the system is complete i.e., we know all about the system. According to this assumption, we have access to all microstates and the corresponding probability distributions. This fact means that the ordinary normalization is used. It assumes that we know the probability of every microstate of our physical system. This picture is, of course, inadequate, since one can encounter some situations for which one does not have all the information or chooses to

neglect some interaction. For these situations, Alexander Wang proposed the incomplete statistics formalism (IS) [12, 79]. This formalism is a nonadditive, single parameter (it too is called q) generalization of Boltzmann-Gibbs entropy. The only difference between it and BG entropy is the normalization so that the associated entropy again yields inverse power law distribution as a stationary solution. The generalization of this formalism to open systems is essential, since it is less likely that we will have complete knowledge of the system since the interaction terms governing the system increase for open systems. This generalization has been achieved in Chapter 6.

In Chapter 7, I have introduced a method dating back to Boltzmann, called the method of orthodes. The method of orthodes is to show if the heat theorem is satisfied by the distribution associated with the particular entropy. It happens that the microcanonical, canonical and grand canonical distributions all are orthodes, since they satisfy the heat theorem [89].

There are three points to emphasize on the importance of the method of orthodes. The first one is that it provides a criterion for the equilibrium description of the thermostatics associated with one particular entropy. Therefore, it cannot state anything relevant on the systems off equilibrium. Second, it does so purely on mechanical arguments. In other words, the method of orthodes shows whether that entropy can be used as a valid entropy at equilibrium without invoking probabilistic arguments. The third point is central, since the method of orthodes works for all system sizes. It can be used as a criterion for equilibrium thermostatics for small systems as well as large systems. In other words, one does not need to invoke the thermodynamic limit. If an entropy expression passes the test of orthode by Boltzmann, that particular entropy expression can be used for systems of any size as long as the system is at equilibrium.

I have then shown that the Tsallis distribution is such an orthode so that it can be used as a suitable entropy expression for systems of any size at equilibrium. However, a surprising result was found in my application of the method of orthodes to the Tsallis ensemble. The corresponding entropy expression was found to be the Rényi entropy of the

order $\frac{1}{q}$. Therefore, I proved that the Tsallis distribution is an orthode whose associated entropy is given by the Rényi entropy [104].

The generalized thermostatics have come a long way in almost 20 years. Much progress has been made, but one central theorem is still missing. It is a generalized central limit theorem whose basin of attraction is q -exponential obtained from the maximization of the Tsallis entropy. In the case of Gaussian distribution, we have central limit theorem so that we now know why the exponentials are so ubiquitous [112]. In the case of Lévy distributions, we also have a generalized central limit theorem [113]. On the other hand, as yet we have none in the case of q -exponentials. This topic, in my opinion, will prove to be important in the future progress of this field of research [114].

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