# THERMODYNAMICS AND STATISTICAL MECHANICS FOR COMPLEX SYSTEMS — FOUNDATIONS AND APPLICATIONS

Constantino Tsallis

Centro Brasileiro de Pesquisas Físicas
and
National Institute of Science and Technology for Complex Systems
Rua Xavier Sigaud 150, 22290-180 Rio de Janeiro, Brazil
and
Santa Fe Institute, 1399 Hyde Park Road, Santa Fe, New Mexico 87501, USA

The complexity (or simplicity) of a system can be characterized through very many paths. A quite interesting and operational one, which we follow here, consists in making use of entropic concepts. The thermodynamical and statistical-mechanical foundations of this approach, as well as its (analytical, computational, observational, and experimental) applications for natural, artificial and social systems will be briefly reviewed.

## 1. Introduction

In the 1860s, Clausius introduced [1] the concept of entropy (noted $S$) within thermodynamics. This most relevant step basically concluded the foundations of this science, and enabled its expression in terms of the so-called principles of thermodynamics (nowadays referred to as zeroth, first, second, third principles). One decade later, Boltzmann postulated [2, 3] an entropic functional (noted $S_{\mathrm{BG}}$ where BG stands for Boltzmann–Gibbs, in order to also incorporate the refinements introduced by Gibbs [4]), which connects the macroscopic entropy introduced by Clausius with the microscopic world. The entropy $S_{\mathrm{BG}}$ is essentially consistent with the entire structure of classical thermodynamics, and constitutes the basis of the theory (very important in contemporary physics) referred to as statistical mechanics. During nearly 140 years, BG statistical mechanics keeps providing uncountable excellent predictions for many kinds of thermal and similar phenomena. This has somehow — wrongly! — sedimented in the mind of many

physicists that no other statistical-mechanical theory is possible, and that $S_{BG}$ is not only sufficient but also necessary for thermodynamics to be satisfied. The scenario has gradually and substantially evolved during the last 25 years, especially through the proposal of nonadditive entropies as a basis for possibly generalizing BG statistical mechanics [5].

The whole process exhibits a strong analogy with the history of mechanics. At the end of the XIX century, mechanics was a synonym of the Newtonian or classical mechanics. But soon after, quantum and relativistic mechanics were formulated, and there are now several theories within mechanics, which contain the Newtonian mechanics as a particular case. In the present review, we argue that more than one theory exists within statistical mechanics, which nevertheless remain related to thermodynamics, the BG statistical mechanics playing, of course, the basic reference role.

## 2. Nonadditive entropies and nonextensive statistical mechanics

### 2.1. Nonadditive entropies

For a system constituted by $N$ elements that globally admits $W$ microscopic configurations (*complexions* in the language of Boltzmann's time), we have the BG entropy given by

$$S_{BG}(N) \equiv -k \sum_{i=1}^{W(N)} p_i \ln p_i \,, \qquad \sum_{i=1}^{W(N)} p_i = 1 \,, \tag{1}$$

where $k$ is a conventional constant (typically Boltzmann constant $k_B$), and $\{p_i\}$ are the probabilities. When all probabilities are equal, *i.e.*, $p_i = 1/W(N)$, we recover the celebrated Boltzmann formula

$$S_{BG}(N) = k \ln W(N) \,. \tag{2}$$

If the system is such that, in the $N \to \infty$ limit,

$$W(N) \propto \mu^N \,, \tag{3}$$

where $\mu > 1$ is a constant, then Eq. (2) implies $S_{BG}(N) \propto N$, which provides an *extensive* entropy (*i.e.*, $0 < \lim_{N\to\infty} S(N)/N < \infty$), in conformity with thermodynamics. For example, if we have $N$ independent two-faced fair coins, we have that $W(N) = 2^N$, hence $S_{BG} = kN \ln 2$.

But if the elements of the system are strongly correlated, it frequently happens that the number of admissible microscopic configurations decreases drastically, and it might essentially become, in the $N \to \infty$ limit, a zero-Lebesgue measure set. For example, a wide class of systems yield

$$W(N) \propto N^\rho \,, \qquad \rho > 0 \,, \tag{4}$$

hence $S_{\mathrm{BG}}(N) \propto \ln N$, thus violating the thermodynamic extensivity of the entropy. A natural way out appears to be to define *nonadditive* entropies such as [5]

$$S_q(N) \equiv k\frac{1 - \sum_{i=1}^{W(N)} p_i^q}{q-1} = k\sum_{i=1}^{W(N)} p_i \ln_q \frac{1}{p_i} = -k\sum_{i=1}^{W(N)} p_i^q \ln_q p_i$$

$$= -k\sum_{i=1}^{W(N)} p_i \ln_{2-q} p_i \,,$$

$$\sum_{i=1}^{W(N)} p_i = 1\,, \qquad q \in \mathcal{R}\,, \qquad S_1 = S_{\mathrm{BG}}\,, \tag{5}$$

where the $q$-logarithmic function is defined as $\ln_q z \equiv \frac{z^{1-q}-1}{1-q}$ ($z > 0\,; \ln_1 z = \ln z$). If all admissible events are equally probable, *i.e.*, $p_1 = 1/W(N)$, we have

$$S_q(N) = k\ln_q W(N)\,. \tag{6}$$

If $W(N)$ is given by Eq. (4), we straightforwardly verify that $S_{q=1-1/\rho}(N) \propto N$, thus satisfying the thermodynamic extensivity of the entropy as desirable.

It is easy to verify that, if $A$ and $B$ are two probabilistically independent systems, the entropy of the total system $A + B$ satisfies

$$\frac{S_q(A+B)}{k} = \frac{S_q(A)}{k} + \frac{S_q(B)}{k} + (1-q)\frac{S_q(A)}{k}\frac{S_q(B)}{k}\,. \tag{7}$$

In other words, by using Penrose's definition of entropic additivity [6], we have that the entropic functional $S_q$ is *nonadditive* for all values of $q$ except for $q = 1$, value for which it recovers the *additive* BG functional $S_{\mathrm{BG}}$.

We can summarize these facts by saying that, if the system is such that $W(N)$ is given by Eq. (3) (which basically means independence or weak correlations), the additive entropy $S_{\mathrm{BG}}$ is extensive and the nonadditive entropy $S_q$ is nonextensive for all $q \neq 1$, whereas, if $W(N)$ is given by Eq. (4) (which is a frequent class of strong correlations), $S_q$ is extensive for $q = 1 - \frac{1}{\rho}$ and nonextensive for all other values of $q$, including $q = 1$. As we see, additivity depends only on the entropic functional and is easy to determine. Extensivity, in contrast, depends on both the entropic functional and the system, and can generically be quite hard to analytically determine.

Another interesting case occurs if

$$W(N) \propto \nu^{N^\gamma}\,, \qquad \nu > 1\,, \qquad 0 < \gamma < 1\,, \tag{8}$$

which also essentially corresponds to zero-Lebesgue measure for the occupancy of phase space (or of the analogous spaces for quantum systems). To tackle this case, we may use the following entropy [7, 8]:

$$S_\delta(N) \equiv k \sum_{i=1}^{W(N)} p_i \left( \ln \frac{1}{p_i} \right)^\delta, \qquad \sum_{i=1}^{W(N)} p_i = 1, \qquad S_1 = S_{\mathrm{BG}}. \qquad (9)$$

This entropy becomes, for equal probabilities, *i.e.*, $p_i = 1/W(N)$,

$$S_\delta(N) = k(\ln W)^\delta. \qquad (10)$$

We can verify that $S_{\delta=1/\gamma}(N) \propto N$, in conformity with thermodynamics. Also, if $A$ and $B$ are probabilistically independent, we have that, for $\delta \neq 1$,

$$S_\delta(A + B) \neq S_q(A) + S_q(B), \qquad (11)$$

hence $S_\delta$ is nonadditive.

It is worth emphasizing that $\mu^N \gg \nu^{N^\delta} \gg N^\rho$, which exhibits that both nonexponential cases (4) (power law) and (8) (stretched exponential) correspond essentially to zero-Lebesgue measure problems in what concerns the occupancy of phase space. Let us finally mention that all three entropies that have been discussed here can be unified through

$$S_{q,\delta}(N) \equiv k \sum_{i=1}^{W(N)} p_i \left( \ln_q \frac{1}{p_i} \right)^\delta,$$

$$\sum_{i=1}^{W(N)} p_i = 1, \qquad S_{q,1} = S_q, \qquad S_{1,\delta} = S_\delta, \qquad S_{1,1} = S_{\mathrm{BG}}. \qquad (12)$$

A summary of the present subsection is presented in Table I.

### 2.2. Extensive entropies

Let us answer here an interesting question: *Since we admit entropic functionals that might be nonadditive, why do we not admit nonextensive entropies as well?* (This question was first pointed to me in these terms by A. Coniglio.)

To discuss thermodynamics and its Legendre-transform structure on general grounds, let us remind a typical form of the thermodynamical energy $G$ (Gibbs energy) of a generic $d$-dimensional system [9]

$$\begin{aligned}
G(V, T, p, \mu, H, \dots) &= U(V, T, p, \mu, H, \dots) - TS(V, T, p, \mu, H, \dots) \\
&\quad + pV - \mu N(V, T, p, \mu, H, \dots) \\
&\quad - HM(V, T, p, \mu, H, \dots) - \dots, \qquad (13)
\end{aligned}$$

TABLE I

Entropic functionals and classes of systems (*exponential*, *power-law* and *stretched-exponential*, see the text) for which the entropy is extensive, *i.e.*, proportional to the number $N$ of elements. $W(N)$ is the number of admissible microscopic configurations of a system with $N$ elements (only configurations with nonvanishing occurrence probability are considered admissible). We also see the specific values of $q$ and $\delta$ for which respectively $S_q$ and $S_\delta$ are extensive. From [10].

| | Entropy | | |
|---|---|---|---|
| $W(N)$ $N \to \infty$ | $S_{\mathrm{BG}}$ (Additive) | $S_q$ $(q \neq 1)$ (Nonadditive) | $S_\delta$ $(\delta \neq 1)$ (Nonadditive) |
| $\sim \mu^N$ $(\mu > 1)$ | Extensive | Nonextensive | Nonextensive |
| $\sim N^\rho$ $(\rho > 0)$ | Nonextensive | Extensive $(q = 1 - 1/\rho)$ | Nonextensive |
| $\sim \nu^{N^\gamma}$ $(\nu > 1; 0 < \gamma < 1)$ | Nonextensive | Nonextensive | Extensive $(\delta = 1/\gamma)$ |

where $T, p, \mu, H$ are the temperature, pressure, chemical potential, external magnetic field respectively, and $U, S, V, N, M$ are the internal energy, entropy, volume, number of particles (in turn proportional to the number of degrees of freedom), magnetization, respectively. From the Legendre structure, we identify three classes of variables, namely *(i)* those that are expected to *always be extensive* like $N$ itself $(S, V, N, M, \ldots)$, *i.e.*, scaling with the ($d$-dimensional) volume $V = L^d \propto N$, where $L$ is a characteristic linear dimension of the system (clearly, $V \propto A^{d/(d-1)}$, where $A$ is the $d$-dimensional area)[1], *(ii)* those that characterize the external conditions under which the system is placed $(T, p, \mu, H, \ldots)$, scaling with $L^\theta$, and *(iii)* those that represent energies $(G, U)$, scaling with $L^\epsilon$.

It trivially follows

$$\epsilon = \theta + d. \tag{14}$$

If we divide Eq. (13) by $L^{\theta+d}$ and consider the large $L$ limit (*i.e.*, the thermodynamical limit), we obtain

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[1] Within the thermodynamical Legendre-transform structure, it is, of course, natural that $S, V, N, M$ belong to the same class. The variable $N$ is *extensive* by definition. Therefore, so must clearly also be the entropy $S$, as well as $V, M$.

$$g\left(\frac{T}{L^\theta}, \frac{p}{L^\theta}, \frac{\mu}{L^\theta}, \frac{H}{L^\theta}, \cdots\right) = u\left(\frac{T}{L^\theta}, \frac{p}{L^\theta}, \frac{\mu}{L^\theta}, \frac{H}{L^\theta}, \cdots\right)$$
$$-\frac{T}{L^\theta}\, s\left(\frac{T}{L^\theta}, \frac{p}{L^\theta}, \frac{\mu}{L^\theta}, \frac{H}{L^\theta}, \cdots\right)$$
$$+\frac{p}{L^\theta} - \frac{\mu}{L^\theta}\, n\left(\frac{T}{L^\theta}, \frac{p}{L^\theta}, \frac{\mu}{L^\theta}, \frac{H}{L^\theta}, \cdots\right)$$
$$-\frac{H}{L^\theta}\, m\left(\frac{T}{L^\theta}, \frac{p}{L^\theta}, \frac{\mu}{L^\theta}, \frac{H}{L^\theta}, \cdots\right) - \cdots, \quad (15)$$

where $g \equiv \lim_{L\to\infty} G/L^{\theta+d}$, $u \equiv \lim_{L\to\infty} U/L^{\theta+d}$, $s \equiv \lim_{L\to\infty} S/L^d$, $n \equiv \lim_{L\to\infty} N/L^d$, $m \equiv \lim_{L\to\infty} M/L^d$. The three types of thermodynamical scalings that have emerged are represented in Fig. 1. Physical illustrations of these various behaviours, including black holes, can be found in [11].
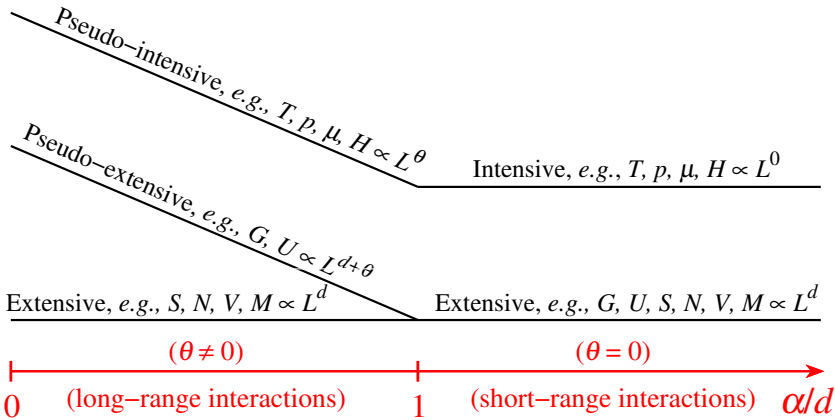


Fig. 1. Representation of the different scaling regimes of Eq. (15) for classical $d$-dimensional systems. For attractive long-range interactions (*i.e.*, $0 \leq \alpha/d \leq 1$, $\alpha$ characterizes the interaction range in a potential with the form $1/r^\alpha$), we may distinguish three classes of thermodynamic variables, namely, those scaling with $L^\theta$, named *pseudo-intensive* ($L$ is a characteristic linear length, $\theta$ is a system-dependent parameter), those scaling with $L^{d+\theta}$, the *pseudo-extensive* ones (the energies), and those scaling with $L^d$ (which are always extensive). For short-range interactions (*i.e.*, $\alpha > d$), we have $\theta = 0$ and the energies recover their standard $L^d$ extensive scaling, falling in the same class of $S$, $N$, $V$, *etc.*, whereas the previous pseudo-intensive variables become truly intensive ones (independent of $L$); this is the region, with two classes of variables, that is covered by the traditional textbooks of thermodynamics. From [10].

The correctness of these scalings has been repeatedly checked in the literature for many types of fluid, magnetic, percolating, polymerized systems [12–23]: details can be found in those papers.

Besides the above general Legendre structure which mandates the thermodynamical entropy to be extensive in all cases, there exist other consistent arguments as well, which come from large deviation theory considerations (see [24] and references therein). However, the presentation of those arguments here remains out of the present scope.

### 2.3. Nonextensive statistical mechanics

The optimization of nonextensive entropies such as $S_q$ with appropriate constraints [25, 26] yields what is referred in the literature as *nonextensive statistical mechanics*. The word *nonextensive* comes here from the (internal) energy $U(N)$, which is typically indeed nonextensive (typically $\lim_{N\to\infty} U(N)/N$ diverges), *not* from the entropy, which is not necessarily taken to be additive in order to be precisely always extensive.

In other words, in BG statistical mechanics, both the energy and the entropy are extensive; in nonextensive statistical mechanics, the energy is nonextensive (superextensive for long-range-interacting many-body Hamiltonian systems), but the entropy remains extensive. The entropic extensivity within BG thermostatistics is guaranteed by the additive BG entropic functional; the entropic extensivity within nonextensive thermostatistics is guaranteed by nonadditive entropic functionals such as $S_q$ and $S_\delta$. Let us mention at this point a regrettable misname that has been a source of not few confusions in the literature: the title of the book [27] should have been *Nonadditive Entropy*, and not *Nonextensive Entropy*.

If the linear mean value of a random variable $x$ is finite, the optimization of $S_q[p(x)]$ yields the $q$-exponential function $p(x) \propto e_q^{-\beta x}$, where $\beta$ is related to the Lagrange parameter, and the function $e_q^z$ is defined as follows

$$e_q^z \equiv [1 + (1-q)z]^{\frac{1}{1-q}} , \tag{16}$$

if $1 + (1-q)z > 0$, and zero otherwise. This function is the inverse of $\ln_q z$ previously defined; also, $e_1^z = e^z$.

If the linear mean value vanishes and the quadratic mean value is nonvanishing, the optimization of $S_q[(p(x)]$ yields $p(x) \propto e_q^{-\beta x^2}$, currently referred to in the literature as $q$-Gaussian.

In what concerns the thermostatistics corresponding to $S_\delta$ and $S_{q,\delta}$, the basic results are already available in [28] and [29], respectively.

To end this section, let us remind that the indices $q$ and $\delta$ are to be determined from first principles, *i.e.*, essentially from mechanics. One illustrative such calculation can be found in [30, 31]: see Fig. 2.
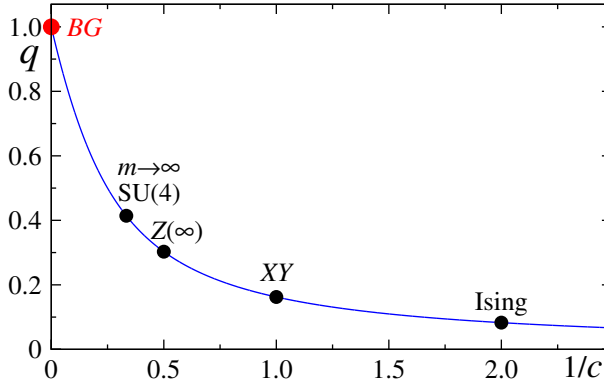
Fig. 2. The index $q$ has been determined [30] from first principles, namely from the universality class of the Hamiltonian, characterized by the central charge $c$. The values $c = 1/2$ and $c = 1$, respectively, correspond to the Ising and $XY$ ferromagnetic chains in the presence of transverse field at $T = 0$ criticality. For other models, see [32, 33]. In the $c \to \infty$ limit, we recover the Boltzmann–Gibbs (BG) value, *i.e.*, $q = 1$. For arbitrary value of $c$, the subsystem *nonadditive* entropy $S_q$ is thermodynamically *extensive* for, and only for, $q = \frac{\sqrt{9+c^2}-3}{c}$.

## 3. Applications

Nonadditive entropies and nonextensive statistical mechanics have been relevant to a wide number of predictions, verifications and applications in natural, artificial and social systems [34]. We briefly mention here some of them.

There have been various applications to long-range-interacting many-body classical Hamiltonians such as the $XY$ ferromagnet and the Fermi–Pasta–Ulam models ([35, 36] and references therein), self-organized criticality [37], turbulence [38, 39], low-dimensional dissipative maps [40–45], low-dimensional conservative maps [46, 47], anomalous diffusion [48, 49], the Heisenberg model with long-range interactions [50, 51] (by the way, the quantum analog with long-range interactions remains an open problem; for the short-range model see, for instance, [52] and references therein), spin glass relaxation [53], cold atoms in optical lattices [54, 55], ion trapping [56], over-damped motion of vortices in type-II superconductors [57–61], dusty plasma [62], the so-called $q$-triplet in solar wind and similar phenomena [63–71], asymptotically scale-free networks [72], black-hole physics [11, 73–75], non-linear relativistic and quantum equations [76]. The $q$-generalization of central limit theorems and related properties [77–80] is worth special mentioning.

Let us specifically add here recent applications in high-energy physics at the LHC/CERN and elsewhere [81–98]. A typical illustration is presented in [31, 99, 100]: see, for instance, Fig. 3 (some tiny log-periodic oscillations are observed on top of the $q$-exponentials, which might be related to some microscopic fractality [101]).
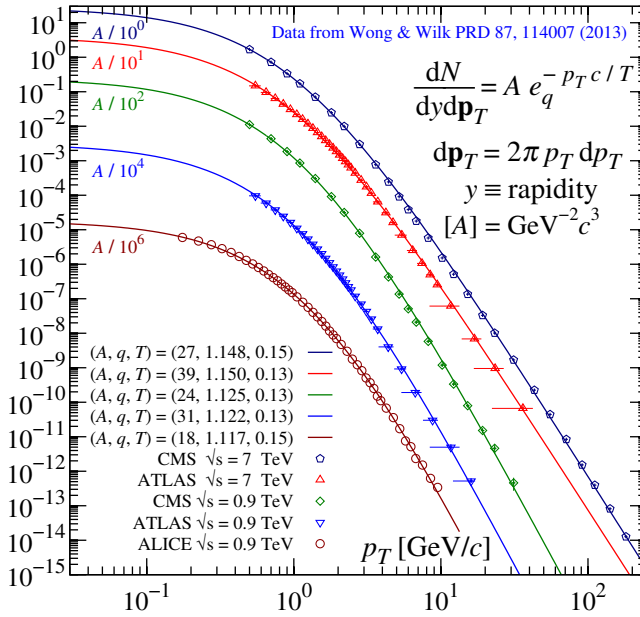


Fig. 3. Experimental distributions of the transverse moments in hadronic jets at the CMS, ALICE and ATLAS detectors at the LHC. The data are from [99]. They can be remarkably well fitted (along fourteen decades) with the $q$-exponential function $e_q^x \equiv [1 + (1-q)x]^{1/(1-q)}$, which, under appropriate constraints, extremizes the entropy $S_q$. See details in [100].

Many other applications (in economics, linguistics, geophysics, neurosciences) can be found in [27, 102].

## 4. Final remarks

The logical path we have followed here is to satisfy in all cases the extensivity of the entropy, since this property is mandated by classical thermodynamics. For standard systems (essentially ergodic, which implies an occupation of phase space with a nonzero-Lebesgue measure), this requirement is satisfied by the Boltzmann–Gibbs entropic functional, which is additive. For nonstandard systems (essentially nonergodic, which typically emerges through a zero-Lebesgue-measure occupation of phase space), this require-

ment is, for wide classes of systems, satisfied for nonadditive entropic functionals such as $S_q$ and $S_\delta$. The indices $q$ and $\delta$ are to be determined from first principles, namely from mechanics (classical, quantum, relativistic). When this is analytically intractable, they may be determined from mesoscopic arguments (*e.g.*, from Langevin-like and Fokker–Planck-like equations), or simply through fitting. The extremization of these nonadditive entropies under appropriate constraints yields a generalization of Boltzmann–Gibbs statistical mechanics, currently referred to as nonextensive statistical mechanics. The amazing number of phenomena in natural, artificial and social systems which do follow (not rarely through many experimental or numerical decades) $q$-exponential and $q$-Gaussian behaviours together with their analytical connections provide, as far as we can see, a neat validation of these concepts. Various interesting questions remain open, such as — to name just one — the analytical connection between the indices $q$ and the exponent characterizing the range of long-range-interacting many-body Hamiltonians.

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