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Third law of thermodynamics as a key test of generalized entropies

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The laws of thermodynamics constrain the formulation of statistical mechanics at the microscopic level. The third law of thermodynamics states that the entropy must vanish at absolute zero temperature for systems with nondegenerate ground states in equilibrium. Conversely, the entropy can vanish only at absolute zero temperature. Here we ask whether or not generalized entropies satisfy this fundamental property. We propose a direct analytical procedure to test if a generalized entropy satisfies the third law, assuming only very general assumptions for the entropy S and energy U of an arbitrary N-level classical system. Mathematically, the method relies on exact calculation of $\beta = dS/dU$ in terms of the microstate probabilities p_i. To illustrate this approach, we present exact results for the two best known generalizations of statistical mechanics. Specifically, we study the Kaniadakis entropy S_κ, which is additive, and the Tsallis entropy S_q, which is nonadditive. We show that the Kaniadakis entropy correctly satisfies the third law only for $-1 < \kappa < +1$, thereby shedding light on why κ is conventionally restricted to this interval. Surprisingly, however, the Tsallis entropy violates the third law for $q < 1$. Finally, we give a concrete example of the power of our proposed method by applying it to a paradigmatic system: the one-dimensional ferromagnetic Ising model with nearest-neighbor interactions.

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I. INTRODUCTION

Thermodynamics is a *phenomenological* theory believed to hold for all physical systems that meet proper minimum general necessary conditions [1]. These systems range spectacularly in diversity, from regions around black holes at the centers of galaxies to biochemical reactions in living organisms. The backbone of thermodynamics is formed by very few but extremely general laws, governing a huge spectrum of distinct behavior in nature. Statistical mechanics aims to bridge the fundamental *microscopic description* of classical and quantum mechanics with the *macroscopic behavior* described by thermodynamics.

Toward that end, the Boltzmann-Gibbs entropy is a fundamental quantity in statistical physics. Indeed, for the vast majority of systems, it adequately captures all the important aspects of thermodynamic entropy [2,3]. Nevertheless, several generalizations of the Boltzmann-Gibbs entropy have been proposed (e.g., see Refs. [4–12]). Some, such as the Rényi entropy, are not particularly well suited to statistical mechanics. Others have found wide application in studies of diverse phenomena [7,8]. Two of the most commonly used generalized entropies are the Tsallis entropy [9,10], which is nonadditive, and the Kaniadakis entropy [11,12], which is additive. To gain a better understanding about the distinct formulations for statistical mechanical entropy, we ask whether or not generalized entropies satisfy one of the basic laws mentioned above: the third law of thermodynamics. Our focus here is the development of an analytical method to answer this question. As an important application, we then use this method to check whether or not the Kaniadakis and Tsallis entropies are compatible with it.

One may wonder why generalized entropies should be considered (in fact, this is a relatively old concern [13]). First, some formal results indicate that there are classes of systems that might demand extensions of the concept of entropy [14]. Another oft-mentioned justification is to be able to deal with Hamiltonians with long-range interactions [9,10]. However, there is no known reason to believe *a priori* that a particular choice will be "the" correct entropy for systems with long-range correlations. The existence of a number of competing proposals is a sign that there may be no unique solution to this problem. Recently, it has been proved that nonadditive entropies violate the Shore and Johnson axioms [2]. Moreover, systems with long-range interactions have been successfully studied using conventional (Boltzmann-Gibbs) statistical mechanics [15]. Further, it has been shown that nonexponential distributions can arise via maximization of the Boltzmann-Gibbs-Shannon entropy together with a nonextensive energy [3]. On the other hand, it has been claimed that nonadditive entropies emerge from strong correlations between random variables of the system, and the Shore and Johnson hypothesis do not adequately address this issue [16]. Also, generalized entropies are compatible with the maximum entropy principle in the context of nonextensive, nonergodic, and complex statistical systems [4]. Despite the controversy, or perhaps because of it, research goes on in this field. For example, the framework of generalized entropies has been successfully used as a tool for studying complex systems and nonlinear dynamics [10]. Generalized entropies furthermore inspired other approaches, e.g., superstatistics and Kaniadakis statistics [8,11,12]. For instance, the entropy of the black hole has been discussed in the context of the Tsallis formulation [17,18].

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Kaniadakis statistics has been applied in astrophysics, e.g., relativistic plasmas [19] and stellar rotational velocities [20].

Given the growing interest in generalized entropies, an unavoidable issue is to know whether or not they are compatible with the laws of thermodynamics. An inconsistency with the zeroth law has been pointed out in [21], and a solution based on nonadditive composition rules has been proposed in [22]. The second law has also been studied in this context [23] (see the discussion and references below).

Our goal is to discover precisely when generalized entropies are compatible with the third law of thermodynamics, which states that the entropy of a condensed-matter system in thermodynamic equilibrium approaches zero as the absolute temperature approaches zero [24,25] [we ignore the (trivial) case of degenerate ground states and assume, without loss of generality, a nondegenerate ground state]. Since the entropy is non-negative and the negative of the entropy is a convex function of the internal energy, it is easy to show that the entropy cannot become zero at positive absolute temperatures. The third law and its converse thus guarantee that the entropy can vanish if and only if the absolute temperature vanishes. We emphasize a fundamental point, often overlooked in previous works (and one of the reasons this specific compatibility test should be chosen). The third law must be verified by *all* Hamiltonian systems, irrespective of whether or not long-range interactions are present. Therefore, its satisfiability is a powerful constraint and hence a crucial check. The third law should be satisfied by any credible and reliable microscopic description of matter, regardless of the type and details of the interaction (or "forces") between the constituents.

With this stated purpose, we start with simple but general considerations about the expressions for the entropy S and energy U of a system having an arbitrary number N of microstate configurations. Then, taking $\beta = 1/(k_B T)$ in the traditional Boltzmann-Gibbs scenario (for simplicity, setting the Boltzmann constant $k_B = 1$), we write the thermodynamic macroscopic relation $\beta = dS/dU$ in terms of the state's microscopic probabilities p's. Finally, we determine the relation between the low entropy limit $S \to 0$ (or more generally $S \to S_{\min}$; see the next section) and the low-temperature limit $\beta \to +\infty$. The main result reported here is therefore an analytical method to test whether claimed generalizations of statistical mechanics are compatible with the third law of thermodynamics.

We apply the procedure to the Boltzmann-Gibbs entropy (as a comparison standard) and also to the Kaniadakis and Tsallis entropies (abbreviated as BG, K, and T, respectively). For the latter two, we illustrate the power of the method by unveiling the ranges of their parameters for which the third law is satisfied. We focus on the K and T formulations because of their previously mentioned importance. But we emphasize that the present approach can in fact be used for any generalized statistical mechanical entropy. The K entropy obeys the third law provided its free parameter is restricted to the values usually assumed in the literature. But we find that the Tsallis entropy can vanish at nonzero temperatures in certain ranges of q. Our results raise questions about whether it can properly generalize statistical mechanics.

Finally, as a concrete example, we consider the paradigmatic one-dimensional (1D) Ising model, which is one of the most important models in all of physics. The Ising model plays the role of the "simple harmonic oscillator" of statistical mechanics, and we know *a priori* that it must satisfy the third law. The reason we have chosen the 1D Ising model is that we can calculate the exact solutions in any statistical mechanical framework. Almost a century ago, Ising [26] solved the problem in the canonical ensemble, which is equivalent to using the Boltzmann-Gibbs entropy. But the Ising model can also be solved exactly in nonstandard ensembles using generalized statistical mechanical entropies.

II. THE METHOD

Consider a general system, whose energies E_λ for the possible microscopic configurations are ordered as $E_0 < E_1 \leqslant E_2 \leqslant \cdots \leqslant E_N$, N arbitrary. The state $\lambda = 0$ then characterizes the lowest-energy state, also called the ground state. Any degeneracies for the ground state can easily be treated separately, without changing the relevant physical discussion, so we do not consider degeneracy here. Let the probability for the system to be in the microscopic state $\lambda = 0,1,\ldots,N$ be $0 \leqslant p_\lambda \leqslant 1$, where $\sum_\lambda p_\lambda = 1$. Let $n = 1,2,\ldots,N$, so that n spans the same integers as λ except for $\lambda = 0$. Then, from a mathematical point of view, we can consider all p_n as independent variables and express p_0 as a function of the p_n, as follows: $p_0 = p_0(p_1,p_2,\ldots,p_N) = 1 - \sum_n p_n$. In this way, letting f be any function of the probabilities, we get $\partial f(p_0)/\partial p_n = -\partial f(p_0)/\partial p_0$.

Let us write the system entropy S and energy U as

$$S = -p_0\, s(p_0) - \sum_n p_n\, s(p_n), \tag{1}$$

$$U = \frac{1}{P}\left[p_0\, u(p_0)\, E_0 + \sum_n p_n\, u(p_n)\, E_n\right]. \tag{2}$$

Here, P is a normalization, usually (but not always, see below) taken as 1. Boltzmann-Gibbs statistical mechanics and many generalizations of it can be recast in the above form if one also assumes the following general properties:

(i) $s(p) \leqslant 0$: This is to guarantee non-negative entropy.

(ii) $\lim_{p\to 0} p\, s(p) = s(1) = 0$: Full knowledge that a state is not (is the only one) available should decrease to zero the loss of information associated with that state (the whole system).

(iii) $u(p)$ is well behaved for any $0 \leqslant p \leqslant 1$: uE might be seen as an effective energy of each microscopic state (of "bare" energy E), conceivably due to the interactions with the others. So, it should not diverge or present discontinuous changes as p varies.

(iv) $u(1) = 1$: If just a single state is occupied, its own bare energy should not be changed given that eventual interactions between the microstates would be absent (unless in the case of self-interaction, not assumed in this work).

(v) P is a well-behaved function of the $\{p_\lambda\}$'s: P is just a normalization for the energy expression; moreover, if $p_\lambda = 1$ for a given λ (with all the other p's being zero), then $P = 1$.

In addition to the above, the expressions for S and U must also bear a fundamental relation. In any proper statistical mechanical formalism, a relevant parameter to characterize equilibrium in a thermal process is given by $\beta = dS/dU$

(see, e.g., the clear discussion in [27]). The connection with thermodynamics is thereby established through the association $\beta = 1/T$, with T the thermodynamic temperature. In one-parameter generalizations of the BG entropy, the thermodynamic temperature $\beta = dS/dU$ no longer necessarily equals the generalized statistical mechanical temperature β_α, where α is the tunable generalization parameter. So β may differ from β_α in $p_\lambda = \mathcal{F}(\beta_\alpha E_\lambda)$, with $\mathcal{F}$ depending on the specific formulation and generalizing the usual exponential function of BG. In general, $\beta_\alpha = \zeta\,\beta$ [for $0 < \zeta = \zeta(\alpha) \neq \zeta(T)$]. But note that $\zeta \neq 1$ does not change the fact that β should diverge with T going to zero. Obviously, for the BG entropy, we have the equality $\zeta = 1$. For K and T entropies one finds, respectively, $\zeta = 1/\sqrt{1-\alpha^2}$ $(-1 < \alpha < +1)$ [12] and $\zeta = 1$ [28,29].

We have previously discussed that the third law guarantees that $S = 0$ if and only if $T = 0$ $(\beta \to +\infty)$. However, since we are considering generalized statistics, we may relax the $S = 0$ condition, assuming instead

$$S \to S_{\min} \quad \text{if and only if} \quad \beta \to +\infty, \tag{3}$$

where $S_{\min}$ is the lowest possible entropy in a given context (e.g., for a specific value of the formulation parameter α). The issue is hence to determine when the "extended" third law, (3), holds true. For the sake of argument, consider a generic set of parameters Λ controlling the variation of both S and U, where the low entropy state is given by $S(\Lambda_0) = S_{\min}$. In what follows, we will focus on the "only if" direction in condition (3), since the "if" direction is easy. In the low entropy limit, we have

$$\beta = \frac{dS}{dU} = \lim_{\Lambda\to\Lambda_0} \frac{S(\Lambda) - S_{\min}}{U(\Lambda) - U(\Lambda_0)}.$$

Therefore, $\beta \to +\infty$ requires (a) $U(\Lambda_0)$ to be (at least a local) minimum, otherwise we cannot get the correct positive signal in the limit; and (b) for $\Lambda \to \Lambda_0$, $|\Delta U|$ must decay sufficiently faster than $|\Delta S|$, thus yielding the proper divergent behavior.

From the functional forms of Eqs. (1) and (2), it is natural to use the probabilities $\{p_\lambda\}$ to check for (3). Indeed, by writing $\beta = \sum_n \beta_n = \sum_n \partial S/\partial p_n\,(\partial U/\partial p_n)^{-1}$, we get

$$\begin{aligned}\frac{\partial S}{\partial p_n} &= -p_n \frac{\partial s(p_n)}{\partial p_n} - s(p_n) + p_0 \frac{\partial s(p_0)}{\partial p_0} + s(p_0),\\ \frac{\partial U}{\partial p_n} &= \frac{1}{P}\left[E_n\left(p_n \frac{\partial u(p_n)}{\partial p_n} + u(p_n)\right)\right.\\ &\quad \left. - E_0\left(p_0\frac{\partial u(p_0)}{\partial p_0} + u(p_0)\right)\right] - \frac{U}{P}\frac{\partial P}{\partial p_n}.\end{aligned} \tag{4}$$

Here the β_n is the contribution to β from energy level n. In summary, one first determines which set $\{p_\lambda\}$ leads to a minimum for S, next one analyzes how U and β_n behave in this limit, and finally one compares the results with the third law, (3).

A. Boltzmann-Gibbs statistics

It is instructive to apply the above framework to the standard BG statistics, for which

$$s(p) = \ln[p], \quad u(p) = 1, \quad P = 1. \tag{5}$$

Then $\partial U/\partial p_n = E_n - E_0$ and $\partial S/\partial p_n = -\ln[p_n/p_0]$. Since in this case $p_0 \to 1$ (consequently with all the other p_n's vanishing) implies that $S \to 0$ and U goes to its minimum possible value of E_0, we need to calculate $\lim_{p_0\to 1,\{p_n\}\to 0} \beta_n$, or

$$\lim_{\substack{p_n\to 0\\ p_0 = 1}} \beta_n = -\lim_{p_n \to 0} \frac{\ln[p_n]}{(E_n - E_0)} = +\infty \quad \forall\, n. \tag{6}$$

Thus, we verify that the third law and its converse are satisfied (furthermore with the usual $S_{\min} = 0$ for a nondegenerate ground state). Indeed, it could not be otherwise because BG statistics is compatible with thermodynamics.

III. EXACT RESULTS FOR TWO GENERALIZED STATISTICS

We now consider the two well-studied Kaniadakis and Tsallis statistics. Let $\alpha = \kappa$ for the Kaniadakis case and $\alpha = q - 1$ for the Tsallis case. Then we have

$$\begin{aligned} s(p) &= \frac{p^\alpha - p^{-\alpha}}{2\alpha},\ u(p) = 1,\quad P = 1, \qquad \text{for } K,\\ s(p) &= \frac{p^\alpha - 1}{\alpha}, \quad u(p) = p^\alpha,\ P = \sum_\lambda p_\lambda^{1+\alpha} \text{ for } T.\end{aligned} \tag{7}$$

For the K formulation, $-1 < \alpha < +1$, whereas for the T, α is real. For convenience we use the same label, α, as the parameter in the two statistics. In both, $\alpha \to 0$ corresponds to the BG. Hence, in our derivations we do not need to be mathematically concerned with the $\alpha = 0$ case. Lastly for Tsallis, depending on α the previous properties (ii), (iii), and (v) may not hold true for $p = 0$.

For convenience, let us denote by $\mathcal{L}_0$ and $\mathcal{L}_\infty$, respectively, the limits $p_0 \to 1$ and $\{p_n\} \to 0$ and $p_\lambda \to 1/(N+1)$ $\forall\,\lambda$. We recall that in the BG canonical ensemble, $\mathcal{L}_0$ $(\mathcal{L}_\infty)$ corresponds to $T \to 0$ $(T \to +\infty)$. Finally, in all of the subsequent calculations, the procedural order will be the following: (a) consider completely arbitrary $\{p_\lambda\}'$s, (b) assume specific values for α, and finally (c) take the proper limits, e.g., for $\mathcal{L}_0$: $p_0 \to 1$ and $\{p_n\} \to 0$ (with the rates in which the p_n's vanish specified whenever necessary).

A. The Kaniadakis formulation

In this case, we have that

$$U \xrightarrow{\mathcal{L}_0} E_0,\quad U \xrightarrow{\mathcal{L}_\infty} (N+1)^{-1}\sum_\lambda E_\lambda \quad (\text{any } \alpha), \tag{8}$$

$$\begin{aligned} S &\xrightarrow{\mathcal{L}_0} S_{\min},\quad S \xrightarrow{\mathcal{L}_\infty} S_{\max} \quad (|\alpha| \leqslant 1),\\ S &\xrightarrow{\mathcal{L}_0} S_{\max},\quad S \xrightarrow{\mathcal{L}_\infty} S_{\min} \quad (|\alpha| > 1).\end{aligned} \tag{9}$$

$$\begin{aligned} &S_{\min} = 0, \qquad S_{\max} = S_{N+1} \quad (|\alpha| < 1),\\ &S_{\min} = N/2, \quad S_{\max} = S_{N+1} \quad (|\alpha| = 1),\\ &S_{\min} = S_{N+1}, \quad S_{\max} = +\infty \quad (|\alpha| > 1),\\ &S_{N+1} = [(N+1)^{|\alpha|} - (N+1)^{-|\alpha|}]/(2|\alpha|),\end{aligned} \tag{10}$$

$$\begin{aligned}\frac{\partial S}{\partial p_n} &= -\frac{(\alpha+1)}{2\alpha}\left(p_n^\alpha - p_0^\alpha\right) - \frac{(\alpha-1)}{2\alpha}\left(p_n^{-\alpha} - p_0^{-\alpha}\right),\\ \frac{\partial U}{\partial p_n} &= E_n - E_0.\end{aligned} \tag{11}$$

Note the limit $\mathcal{L}_0$ always leads to a minimum for U regardless the value of α, but it yields $S_{\min}$ if $|\alpha| \leqslant 1$ and $S_{\max}$ if $|\alpha| > 1$ (in this latter case with $S \to S_{\min}$ for $\mathcal{L}_\infty$). So, we have

$$\lim_{\substack{p_n \to 0 \\ p_0 = 1}} \beta_n = \lim_{p_n \to 0} \frac{(\alpha+1)\left(1-p_n^{\alpha}\right)+(\alpha-1)\left(1-p_n^{-\alpha}\right)}{2\alpha\,(E_n-E_0)} = \begin{cases} +\infty & \text{if } |\alpha| < 1, \\ (E_n-E_0)^{-1} & \text{if } |\alpha| = 1. \end{cases} \quad (12)$$

For K, the third law (in the common case of $S_{\min} = 0$) is true for $|\alpha| < 1$, which is the range usually assumed for α [12]. If $|\alpha| = 1$ (note $S_{\max} = S_{N+1} > S_{\min} = N/2$), the extended third law is violated if we demand it to be independent of the system's particular features [see the following discussion regarding the character of $\beta = \sum_n \beta_n = \sum_n (E_n - E_0)^{-1}$]. Finally, we have already observed that if the same specific limit $\mathcal{L}$ yielding $S_{\min}$ does not also result in a (local) minimum for U, (3) automatically is not satisfied. The K statistics clearly illustrates this fact for $|\alpha| > 1$, when $\mathcal{L}_\infty$ gives a minimum for S, but not a local minimum for U. Thus, calculating the limit $\mathcal{L}_\infty$ for β_n [using Eq. (11) with $|\alpha| > 1$], one obtains $\beta_n \to 0$, contradicting the third law. For completeness, we also observe that the limit $\mathcal{L}_0$ for β_n when $|\alpha| > 1$ is $-\infty$.

In Ref. [12], the interval $-1 < \alpha < +1$ has been established through intricate and subtle considerations, e.g., imposing concavity, additivity, and extensively to the statistics. From the above, one sees that the third law can be a much simpler way to determine the acceptable values for the formulation parameter α.

B. The Tsallis formulation

For the T entropy, we have

$$\begin{aligned} &U \xrightarrow{\mathcal{L}_0} E_0, && U \xrightarrow{\mathcal{L}_\infty} U_{N+1} \quad (\alpha+1>0),\\ &U \xrightarrow{\mathcal{L}_0} U_{N+1}, && U \xrightarrow{\mathcal{L}_\infty} U_{N+1} \quad (\alpha+1=0),\\ &U \xrightarrow{\mathcal{L}_0} (N_*)^{-1}\sum_{n_*} E_{n_*}, && U \xrightarrow{\mathcal{L}_\infty} U_{N+1} \quad (\alpha+1<0),\\ &U_{N+1} = (N+1)^{-1}\sum_{\lambda} E_\lambda. \end{aligned} \quad (13)$$

In the above, $\{n_*\}$ denotes the labels of all the N_* probabilities p'_{n_*}s, which go to zero at the same rate[1] and vanish faster than any other $p_n \notin \{p_{n_*}\}$ (for comparison, in the BG canonical ensemble with nondegenerate states, $N_* = 1$ since if $T \to 0$, $p_N = \exp[-\beta E_N]/\sum_\lambda \exp[-\beta E_\lambda]$ is the fastest decaying p),

$$\begin{aligned} &S \xrightarrow{\mathcal{L}_0} S_{\min}, \quad S \xrightarrow{\mathcal{L}_\infty} S_{\max} \quad (\alpha+1 \geqslant 0),\\ &S \xrightarrow{\mathcal{L}_0} S_{\max}, \quad S \xrightarrow{\mathcal{L}_\infty} S_{\min} \quad (\alpha+1 < 0), \end{aligned} \quad (14)$$

$$\begin{aligned} &S_{\min} = 0, \quad S_{\max} = S_{N+1} \quad (\alpha+1>0),\\ &S_{\min} = S_{N+1}, \quad S_{\max} = S_{N+1} \quad (\alpha+1=0),\\ &S_{\min} = S_{N+1}, \quad S_{\max} = +\infty \quad (\alpha+1<0),\\ &S_{N+1} = [1-(N+1)^{-\alpha}]/\alpha, \end{aligned} \quad (15)$$

$$\begin{aligned} \frac{\partial S}{\partial p_n} &= -\frac{(\alpha+1)}{\alpha}\left(p_n^{\alpha} - p_0^{\alpha}\right),\\ \frac{\partial U}{\partial p_n} &= \frac{(\alpha+1)}{P}\left[(E_n - U)p_n^{\alpha} - (E_0 - U)p_0^{\alpha}\right]. \end{aligned} \quad (16)$$

Then, for $\alpha + 1 > 0$ we have the normal trend, with $\mathcal{L}_0$ resulting in a minimum for U and S (moreover, with $S_{\min} = 0$). The value $\alpha + 1 = 0$ leads to constant U and S regardless of the p'_λs [30] [in agreement with Eq. (16), since identically $\partial S/\partial p_n = \partial U/\partial p_n = 0$ because the multiplicative term $\alpha + 1$, which is null in this case]. Hence $dS/dU = 0$ and $\beta = 0$ for $\alpha = -1$. Finally, if $\alpha + 1 < 0$, $S_{\min}$ is obtained from the limit $\mathcal{L}_\infty$. On the other hand, exactly which limit yields a (local) minimum for U will depend on the behavior of the p'_ns and on the properties of the system energy spectrum. Notice for the T statistics there are no general closed analytical expressions for the p'_λs, only implicit relations [5]. But as is clarified below, this latter information is not essential to check for condition (3).

For each β_n, we calculate the proper limits $\mathcal{L}_0$: setting $p_0 = 1$ and taking $p_n \to 0$, when $\alpha + 1 > 0$; and $\mathcal{L}_\infty$: setting $p_\lambda = (N+1)^{-1}\,\forall\,\lambda$, when $\alpha + 1 < 0$. For $\alpha = -1$, we already have seen that (3) cannot hold. We get thus

$$\begin{aligned} \lim_{\substack{p_n \to 0 \\ p_0 = 1}} \beta_n &= \frac{1}{\alpha}\lim_{p_n \to 0}\frac{\left(p_n^{-\alpha}-1\right)}{(E_n-E_0)} \quad \text{if } \alpha > -1,\\ &= \begin{cases} +\infty & \text{if } \alpha \geqslant 0,\\ \frac{-\alpha^{-1}}{E_n - E_0} & \text{if } -1 < \alpha < 0, \end{cases}\\ \lim_{p_\lambda \to \frac{1}{N+1}} \beta_n &= \frac{-1}{\alpha(N+1)^{\alpha}}\lim_{p_n \to p_0}\frac{(p_n/p_0)^{\alpha}-1}{(E_n-E_0)} \quad \text{if } \alpha < -1,\\ &= 0. \end{aligned} \quad (17)$$

To summarize, when $\alpha \geqslant 0$ (or $q \geqslant 1$), T vanishes as S vanishes, in agreement with the third law. For $\alpha \leqslant -1$ ($q \leqslant 0$), condition (3) is not observed. Moreover, for this parameter range, the T entropy is also known not to be convex (see Sec. V). Finally, as for the K with $|\alpha| = 1$, for T with $-1 < \alpha < 0$, we find $\beta = |\alpha|^{-1}\sum_n (E_n - E_0)^{-1}$. Obviously, for N finite (a relevant example being the Ising model below), the third law is not obeyed. Even with N infinite, (3) will not stand, e.g., if $1/(E_n - E_0) \sim 1/n^{\gamma}$ for all $n \geqslant N_\gamma$ and $\gamma > 1$. Therefore, to have a general physical law, i.e., spectrum-independent (which is the case for the Boltzmann-Gibbs entropy and for the Kaniadakis entropy only if $-1 < \alpha < +1$), this range for the statistics parameter should be excluded. As far as we know, a restriction to the range $0 < q < 1$ for the T formulation has not been previously reported in the literature.

IV. AN IMPORTANT EXAMPLE: THE ISING MODEL

The 1D Ising model, with zero field and periodic boundary conditions, is defined by the Hamiltonian ($\sigma_{N+1} = \sigma_1$)

$$H = -J\sum_{i=1}^{N}\sigma_i\sigma_{i+1}. \quad (18)$$

[1] The corresponding energy reads $(N_*)^{-1}\sum_{n_*}\gamma_{n_*}E_{n_*}$ for $p_{n_*} = \Gamma_{n_*}p_*$ and $\Gamma_{n_*} \to \gamma_{n_*}$ (γ_{n_*} a finite constant) when $p_* \to 0$. For simplicity, in our analysis we assume $\gamma_{n_*} = 1$.

The N spins take values $\sigma_i = \pm 1$. The thermodynamic limit follows from $N \to \infty$. We denote by p_- and p_+ the probabilities that a randomly chosen pair of neighboring spins has the bond in the low-energy $-J$ (i.e., parallel spins) and high-energy $+J$ (antiparallel spins) states, respectively. In the microcanonical ensemble, the internal energy per spin is simply $U = J(p_+ - p_-)$, where $p_+ + p_- = 1$.

The essential and very useful property of the 1D Ising model—not shared by its 2D and 3D counterparts—is that although on the one hand there are spin-spin correlations at finite temperatures, on the other hand the bonds are uncorrelated at nonzero temperatures. Indeed, the bond energies become independent and identically distributed random variables, and the system reduces to a collection of uncoupled two-level systems. This feature allows us to calculate the entropy per spin of the 1D Ising model for any choice of entropy formula.

Thus, the Boltzmann-Gibbs entropy per bond (or spin) is given by our previous general expression with $N = 1$, $\lambda = 0$ ($\lambda = 1$) corresponding to the state $-$ ($+$), $E_0 = E_- = -J$, $E_1 = E_+ = +J$, and $\beta = \beta_1$. Here we briefly digress and note from the relations in Eq. (5) and $p_- + p_+ = 1$ that $p_\pm = \exp[\mp\beta J]/Z$, with $Z = 2\cosh[\beta J]$ the partition function. So, $U = -J\tanh[\beta J]$ recovering Ising's expression for the internal energy at zero field. Moreover, $S = \beta U + \ln[Z]$ (which also can be cast as the well-known relation $TS = U - F$ since the free energy is given by $F = -\ln[Z]/\beta$). Our exact results show then that $\beta = \beta_1 = +\infty$ only when S is zero (which is also true for the case of negative temperatures when $p_- \to 0$). Of course, this is not a surprise; in fact, it was already implied by Ising's original exact solution based on the transfer matrix method. Another relevant fact here is the exact behavior of U and S at small temperatures (β large). It is a simple exercise to verify that U goes to its minimum of $-J$ much faster than S goes to zero.

Now, we consider our previous calculations for the Kaniadakis and Tsallis entropies, again in the case of $N = 1$. We are of course assuming a departure from the canonical ensemble, but still we can obtain exact solutions for the Ising model for generalized entropies. So, for the Kaniadakis entropy (in the commonly assumed range $-1 < \alpha < +1$), the third law is always observed (and as for the Boltzmann-Gibbs entropy, this also being the case for negative temperatures: $p_- \to 0$). On the other hand, for the Tsallis entropy with $\alpha \leqslant -1$, (3) is not satisfied (perhaps not a surprise given the behavior of S in this interval; see the next section). However, we unexpectedly find that the third law is also violated by the T formulation when $-1 < \alpha < 0$ since $S = 0$ at $T_0 = 2J/|\alpha|$.

Figure 1 shows for the Ising model in the Kaniadakis formulation some examples of the behavior of S and β versus p_+ in the conventional $|\alpha| < 1$ case, as well as for $|\alpha| \geqslant 1$ (with $2J = 1$). In agreement with the third law, when $|\alpha| < 1$, β (which is the inverse of thermodynamic temperature) goes to $+\infty$ as the system settles down completely into the ground state, i.e., as $p_- \to 1$ and $p_+ \to 0$.

Figures 2 and 3 illustrate the Ising model in the Tsallis formulation (in both graphs we have again used $2J = 1$ for convenience). Figure 2 displays how S, U, and β behave for selected values of $\alpha = q - 1$ as the probability p_+ of being in

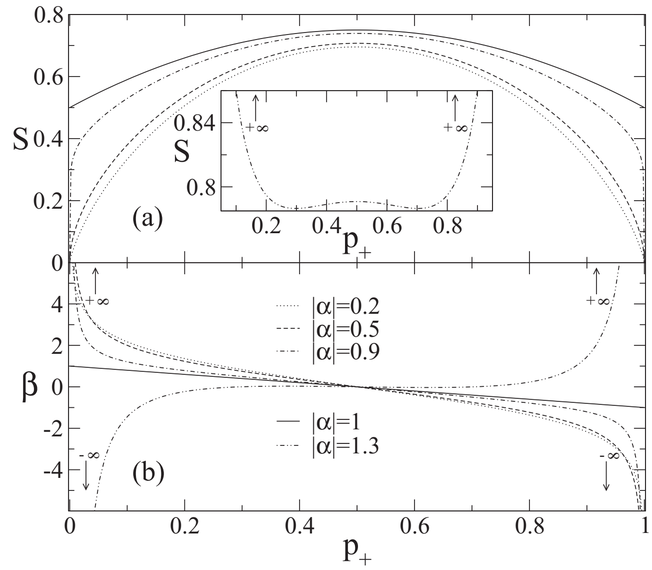

FIG. 1. The Kaniadakis entropy for the 1D Ising model is well-behaved. Here, $\alpha = \kappa$ and $2J = 1$. The (a) entropy S and (b) $\beta = 1/T$ as a function of the probability p_+ of a bond being in the excited state. For the valid parameter range $|\alpha| < 1$, β correctly diverges in the vanishing entropy limit $p_+ \to 0$, in agreement with the third law of thermodynamics.

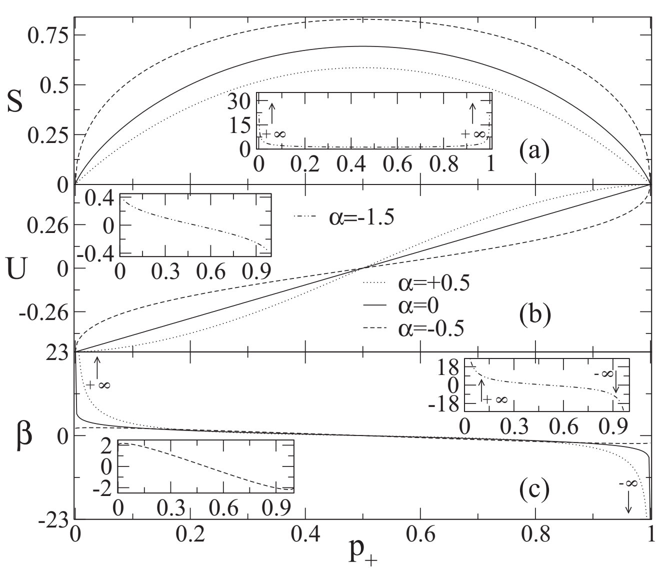

FIG. 2. The Tsallis entropy of the Ising model behaves anomalously in the limit of zero entropy, because not only does it directly violate the third law for $q < 0$, but it also violates the converse of the third law for $q < 1$. The Ising model (a) entropy S, (b) energy U, and (c) $\beta = 1/T$ as a function of the probability p_+ of a randomly chosen bond being in the excited state and for distinct values of α. Here $E_+ - E_- = 2J = 1$. For $\alpha \geqslant 0$ ($q \geqslant 1$), we see the normal behavior of vanishing entropy and divergent β in the limit of $p_+ \to 0$, thus observing the third law. On the other hand, the entropy does not vanish [inset in (a)] and the energy does not go to a minimum [inset in (b)] for $\alpha < -1$ (or $q < 0$), violating the third law [top inset in (c)]. Moreover, for $-1 < \alpha < 0$ ($0 < q < 1$) surprisingly the third law is also violated because entropy can vanish at finite β, i.e., nonzero temperature $T = 1/\beta$ [bottom inset in (c)].

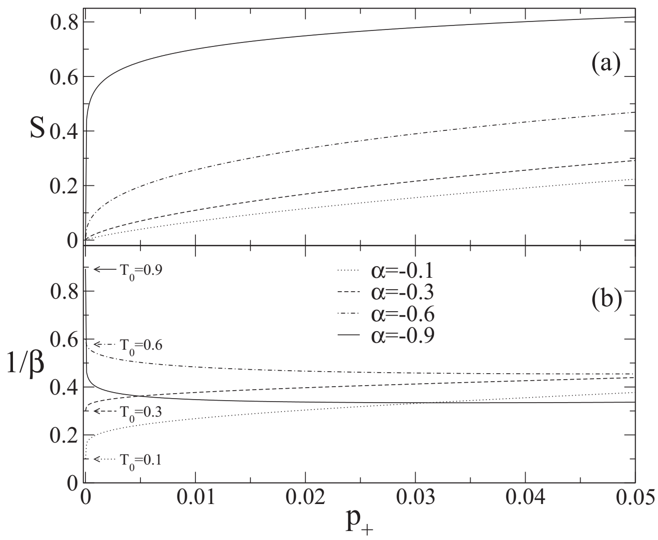

FIG. 3. The Tsallis entropy can vanish at nonzero temperatures, in violation of (the converse of) the third law. Here $-1 < \alpha < 0$, where $q = \alpha + 1$. The Ising model (a) entropy S and (b) the temperature $1/\beta$ as a function of p_+ (around 0) for some α values. For $p_+ \to 0$, $1/\beta$ tends to T_0, the temperature at which the entropy vanishes. The positive temperatures seen violate the third law of thermodynamics.

the higher-energy state is varied. Whereas for $\alpha \geqslant 0$ ($q \geqslant 1$), β diverges (T falls to zero) as $p_+ \to 0$, in contrast for $\alpha < 0$ ($q < 1$) the temperature does not vanish as it should. Figure 3 shows the S and the absolute temperature ($1/\beta$) in the even more intriguing interval of $-1 < \alpha < 0$ ($0 < q < 1$), when the entropy does vanish for $p_+ \to 0$ and $p_- \to 1$, but the third law is violated.

V. DISCUSSION AND CONCLUSION

Recall that in statistical mechanics, a vanishing entropy $S = 0$ means that we have complete knowledge or information of the system description at any level, i.e., there is no uncertainty about the microstate. In both classical and quantum mechanics, a positive absolute temperature $T > 0$ guarantees thermal fluctuations of energy, so that it is impossible to know with complete certainty whether or nor the system is in the ground state. So, for systems in thermal equilibrium, it should be impossible for the entropy to vanish if $T \neq 0$ [31]. Yet one of the analyzed entropies, the Tsallis, does precisely this (at least for $\alpha < 0$ or equivalently $q < 1$). In contrast, the Kaniadakis entropy (in its proper parameter range $-1 < \alpha < +1$) behaves in a manner consistent with the third law. We conjecture that the additive property of the Kaniadakis entropy is the reason for this compatibility with the third law.

Previous works have shown that for some q values, the Tsallis entropy is incompatible with the second law of thermodynamics. By investigating the second law of thermodynamics in the context of kinetic theory, the Tsallis statistics has been studied in the classical [6], the relativistic [32], and also in the quantum-mechanical regimes [33]. Another study considered the convexity property of the generalized relative entropy in the quantum regime [34], leading to the constraint $q \in (0,2]$ for the Tsallis entropy (see, e.g., [6,32,33]). Putting together these previous results with those reported here, we conclude that the Tsallis entropy is compatible with *all* the laws of thermodynamics only for q in the range $1 \leqslant q \leqslant 2$ ($0 \leqslant \alpha \leqslant 1$).

Concerning our concrete particular example, it could be argued (although not very convincingly in our opinion) that because the 1D Ising model with nearest-neighbor interactions does not possess long-range interactions, then our conclusions above are not justified. In the near future, we hope to explicitly study Hamiltonians with long-range interactions, but for now we can foresee a direct rebuttal to this objection. The third law of thermodynamics does not distinguish between short- versus long-range interactions, but rather is sensitive only to the features of the lowest energy levels. So, although two-level Hamiltonian systems cannot be considered to have any interactions at all (whether short- or long-range), they must still obey the third law of thermodynamics. More generally, our analysis of N-level systems has proven conclusively that in fact the Boltzmann-Gibbs and Kaniadakis entropies both satisfy the third law of thermodynamics. But for $q < 1$, the Tsallis entropy does not. Our results have nothing to do with the range of interactions (if any). Rather, they pertain to the way S goes to minimum in relation to the behavior of U at low temperatures.

Finally, recent experimental results in the Tsallis formulation confirm deviations from a Gaussian neighbor for velocity distributions. Some examples are as follows: the velocities of cold atoms in dissipative optical lattices ($q = 1.396 \pm 0.005$) [35]; the velocities of particles in quasi-two-dimensional dusty plasma ($q = 1.08 \pm 0.01$) [36]; single ions in radiofrequency traps interacting with a classical buffer gas ($q = 1.03-1.87$) [37]; transverse momenta distributions at LHC experiments [38]; etc. Remarkably, all these experimental values for q are within our predicted interval $1 \leqslant q \leqslant 2$ for thermodynamic validity.

We conclude by recalling a well-known statement attributed to Albert Einstein: "Classical thermodynamics . . . is the only physical theory of universal content which I am convinced . . . will never be overthrown." Therefore, in proposing generalized entropies, it is necessary to determine whether they are in fact properly defined in terms of necessary conditions. But which principles should be used to construct them? It follows that no attempt to extend the thermodynamic or Boltzmann-Gibbs entropy can lead to a general physical theory without passing through the key test of compatibility with the laws of thermodynamics. The third law, very important in a "down to earth" way in science, is valid irrespective of the microscopic details and deals with a very objective aspect: how matter behaves at very low temperatures. Here, we have explicitly shown how to perform the test of compatibility with the third law.

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[1] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985).

[2] S. Presse, K. Ghosh, J. Lee, and K. A. Dill, Nonadditive entropies yield probability distributions with biases not warranted by the data, Phys. Rev. Lett. **111**, 180604 (2013).

[3] J. Peterson, P. F. Dixit, and K. A. Dill, A maximum entropy framework for nonexponential distributions, Proc. Natl. Acad. Sci. USA **110**, 20380 (2013).

[4] R. Hanel, S. Thurner, and M. Gell-Mann, How multiplicity determines entropy and the derivation of the maximum entropy principle for complex systems, Proc. Natl. Acad. Sci. USA **111**, 6905 (2014).

[5] R. Salazar and R. Toral, Scaling laws for a system with long-range interactions within Tsallis statistics, Phys. Rev. Lett. **83**, 4233 (1999).

[6] J. A. S. Lima, R. Silva, and A. R. Plastino, Nonextensive thermostatistics and the H-theorem, Phys. Rev. Lett. **86**, 2938 (2001).

[7] C. Beck, Generalized information and entropy in physics, Contemp. Phys. **50**, 495 (2009).

[8] C. Beck and E. G. D. Cohen, Superstatistics, Physica A **322**, 267 (2003).

[9] C. Tsallis, Possible generalization of Boltzmann-Gibbs statistics, J. Stat. Phys. **52**, 479 (1988).

[10] M. Gell-Mann and C. Tsallis, *Nonextensive Entropy: Interdisciplinary Applications* (Oxford University Press, New York, 2004).

[11] G. Kaniadakis, Non-linear kinetics underlying generalized statistics, Physica A **296**, 405 (2001).

[12] G. Kaniadakis, Statistical mechanics in the context of special relativity, Phys. Rev. E **66**, 056125 (2002).

[13] P. W. Bridgman, The thermodynamics of plastic deformation and generalized entropy, Rev. Mod. Phys. **22**, 56 (1950).

[14] R. Hanel and S. Thurner, When do generalized entropies apply? How phase space volume determines entropy, Europhys. Lett. **95**, 50003 (2011).

[15] Y. Levin, R. Pakter, F. B. Rizzato, T. N. Teles, and F. P. C. Benetti, Nonequilibrium statistical mechanics of systems with long-range interactions, Phys. Rep. **535**, 1 (2013).

[16] C. Tsallis, Comment on "Nonadditive entropies yield probability distributions with biases not warranted by the data" by Presse *et al.*, arXiv:1404.1257.

[17] T. S. Biro and V. G. Czinner, A q-parameter bound for particle spectra based on black hole thermodynamics with Renyi entropy, Phys. Lett. B **726**, 861 (2013).

[18] C. Tsallis and L. J. L. Cirto, Black hole thermodynamical entropy, Eur. Phys. J. C **73**, 2487 (2013).

[19] G. Lapenta, S. Markidis, A. Marocchino, and G. Kaniadakis, Relaxation of relativistic plasmas under the effect of wave-particle interaction, Astrophys. J. **666**, 949 (2008).

[20] J. C. Carvalho, J. D. do Nascimento Jr., R. Silva, and J. R. De Medeiros, Non-Gaussian statistics and stellar rotational velocities of main sequence field stars, Astrophys. J. Lett. **696**, L48 (2009).

[21] M. Nauenberg, Critique of q-entropy for thermal statistics, Phys. Rev. E **67**, 036114 (2003).

[22] T. S. Biro and P. Van, Zeroth law compatibility of nonadditive thermodynamics, Phys. Rev. E **83**, 061147 (2011).

[23] A. N. Gorban, General H-theorem and entropies that violate the second law, Entropy **16**, 2408 (2014).

[24] W. Nernst, Über die berechnung chemischer gleichgewichte aus thermischen messungen, Nachr. K. Ges. Wiss. Gött. **1**, 1 (1906).

[25] W. Nernst, Überber die beziehung zwischen warmeentwicklung und maximaler arbeit bei kondensierten systemen, Er. K. Pr. Akad. Wiss. **52**, 933 (1906).

[26] E. Ising, Beitrag zur theorie des ferromagnetismus, Z. Phys. **31**, 253 (1925).

[27] R. K. Pathria and P. D. Beale, *Statistical Mechanics* (Academic, Boston, 2011).

[28] S. Abe, Temperature of nonextensive system: Tsallis entropy as Clausius entropy, Physica A **368**, 430 (2006).

[29] Z. Huang, B. Lin, and J. Chen, A new expression of the probability distribution in incomplete statistics and fundamental thermodynamic relations, Chaos Sol. Fract. **40**, 1277 (2009).

[30] F. C. Blondeau, A. Delahaies, and D. Rousseau, Tsallis entropy measure of noise-aided information transmission in a binary channel, Phys. Lett. A **375**, 2211 (2011).

[31] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939).

[32] A. Lavagno, Relativistic nonextensive thermodynamics, Phys. Lett. A **301**, 13 (2002).

[33] R. Silva, D. H. L. Anselmo, and J. S. Alcaniz, Nonextensive quantum H-theorem, Europhys. Lett. **89**, 10004 (2010).

[34] S. Abe and A. K. Rajagopal, Validity of the second law in nonextensive quantum thermodynamics, Phys. Rev. Lett. **91**, 120601 (2003).

[35] P. Douglas, S. Bergamini, and F. Renzoni, Tunable Tsallis distributions in dissipative optical lattices, Phys. Rev. Lett. **96**, 110601 (2006).

[36] B. Liu and J. Goree, Superdiffusion and non-Gaussian statistics in a driven-dissipative 2D dusty plasma, Phys. Rev. Lett. **100**, 055003 (2008).

[37] R. M. Pickup, R. Cywinski, C. Pappas, B. Farago, and P. Fouquet, Generalized spinglass relaxation, Phys. Rev. Lett. **102**, 097202 (2009).

[38] V. Khachatryan *et al.* (CMS Collaboration), Transverse-momentum and pseudorapidity distributions of charged hadrons in pp collisions at $\sqrt{s} = 7$ TeV, Phys. Rev. Lett. **105**, 022002 (2010).