

Thermodynamic framework for the ground state of a simple quantum system

Andre M. C. Souza^{1,2,*} and Fernando D. Nobre^{2,3,†}

¹*Departamento de Física, Universidade Federal de Sergipe, 49100-000 São Cristóvão - SE, Brazil*

²*National Institute of Science and Technology for Complex Systems, Rua Xavier Sigaud 150, 22290-180 Rio de Janeiro - RJ, Brazil*

³*Centro Brasileiro de Pesquisas Físicas, Rua Xavier Sigaud 150, 22290-180 Rio de Janeiro - RJ, Brazil*

(Received 17 October 2016; published 9 January 2017)

The ground state of a two-level system (associated with probabilities p and $1 - p$, respectively) defined by a general Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{V}$ is studied. The simple case characterized by $\lambda = 0$, whose Hamiltonian \hat{H}_0 is represented by a diagonal matrix, is well established and solvable within Boltzmann-Gibbs statistical mechanics; in particular, it follows the third law of thermodynamics, presenting zero entropy ($S_{\text{BG}} = 0$) at zero temperature ($T = 0$). Herein it is shown that the introduction of a perturbation $\lambda \hat{V}$ ($\lambda > 0$) in the Hamiltonian may lead to a nontrivial ground state, characterized by an entropy $S[p]$ (with $S[p] \neq S_{\text{BG}}[p]$), if the Hermitian operator \hat{V} is represented by a 2×2 matrix, defined by nonzero off-diagonal elements $V_{12} = V_{21} = -z$, where z is a real positive number. Hence, this new term in the Hamiltonian, presenting $V_{12} \neq 0$, may produce physically significant changes in the ground state, and especially, it allows for the introduction of an effective temperature θ ($\theta \propto \lambda z$), which is shown to be a parameter conjugated to the entropy S . Based on this, one introduces an infinitesimal heatlike quantity, $\delta Q = \theta dS$, leading to a consistent thermodynamic framework, and by proposing an infinitesimal form for the first law, a Carnot cycle and thermodynamic potentials are obtained. All results found are very similar to those of usual thermodynamics, through the identification $T \leftrightarrow \theta$, and particularly the form for the efficiency of the proposed Carnot Cycle. Moreover, S also follows a behavior typical of a third law, i.e., $S \rightarrow 0$, when $\theta \rightarrow 0$.

DOI: [10.1103/PhysRevE.95.012111](https://doi.org/10.1103/PhysRevE.95.012111)

I. INTRODUCTION

The emergence of quantum mechanics represented one of the most important scientific revolutions of the 20th century [1]. Even nowadays, some of its consequences and predictions appear intriguing, and should take place mostly at very low temperatures, so that thermal effects become negligible, such as quantum phase transitions [2] and quantum entanglement [3]. As a well-known example, one has an ideal gas of fermions, for which the Fermi temperature T_F is defined at $T = 0$ [4], being directly related to the concentration of electrons, in such a way that it may present large variations depending on the physical system, e.g., $T_F \approx 10^4$ K for electrons in metals [5,6], or $T_F \approx 10^9$ K for electrons in white dwarf stars [6]. Hence, in the case of simple metals (e.g., Cu, for which $T_F \approx 8.0 \times 10^4$ K [5]) at low temperatures ($T \ll T_F$), one may still have electrons with significantly high energies, as if they were under temperatures of the order 10^4 K, as a direct consequence of the Pauli exclusion principle. Such nontrivial phenomena occur for a well-defined ground state, which, according to Boltzmann-Gibbs (BG) statistical mechanics, should obey the third law of thermodynamics, implying that the entropy per particle $\lim_{N \rightarrow 0} (S_{\text{BG}}/N) \rightarrow 0$ as $T \rightarrow 0$.

The theory of quantum phase transitions applies to singularities in the ground state, so strictly speaking it holds for $T = 0$ [2]. Since real experiments are carried at some nonzero temperature, the central task in this area is to understand how the $T = 0$ singularities affect physical properties at finite

temperatures, where thermal fluctuations also take place. Contrary to the phase transitions at finite temperatures, which are driven by thermal fluctuations, the quantum phase transitions at $T = 0$ are driven by the Heisenberg uncertainty principle. Hence, the low-temperature effects, close to a quantum critical point, present a competition between quantum and thermal fluctuations. However, one of the most intriguing aspects concerns the fact that such a rich critical behavior, taking place for $T \approx 0$, occurs typically for a negligible entropy, $S_{\text{BG}} \approx 0$. This means that quantum phase transitions, although presenting many properties similar to the thermal ones, cannot be described by some type of “thermodynamic” approach.

The study of nonadditive entropic forms (i.e., out of the scope of BG entropy S_{BG}) has emerged recently as an appropriate framework for dealing with a wide variety of complex systems (see, e.g., Refs. [7,8] for a thorough classification of entropic forms). The association of nonadditive entropic forms with nonlinear Fokker-Planck equations has been much investigated lately [9–23], relating many nonlinear phenomena occurring in complex systems with generalized entropies. These connections appeared mostly by means of generalized forms of the H theorem, proven by making use of nonlinear Fokker-Planck equations. A particular interest has been dedicated to the nonlinear Fokker-Planck equation leading to anomalous diffusion [24,25], which is associated with Tsallis entropy [26], being able to cope with a large range of natural phenomena [27,28]. Following this procedure, recent analyses [29–33] have shown that a system of interacting vortices, currently considered as an appropriate model for describing type-II superconductors [34], is deeply related with nonextensive statistical mechanics [26–28]. Curiously, a consistent thermodynamic framework has been presented for this system by neglecting thermal effects [35–40]. The whole thermodynamic procedure was based on the introduction of

*amcsouza@ufs.br

†Author to whom all correspondence should be addressed: fdnobre@cbpf.br

an appropriate effective-temperature definition (denoted by θ) [35], exhibiting properties very similar to those of the usual thermodynamic temperature T , which are as follows: (a) q is a positive quantity by definition; (b) it is thermodynamically conjugated to Tsallis generalized entropy per particle, S_q , with $q = 2$, characteristic of nonextensive statistical mechanics (in this way, a heat contribution was defined, $\delta Q = \theta dS_2$); (c) it is proportional to the density of vortices n . This property yields the desirable possibility for varying θ , since recent experimental research in type-II superconductors led to considerable advances in the ability to control many properties of these vortices, including their density; (d) it is characterized by values that are much higher than typical room temperatures ($\theta \gg T$), so that the thermal noise can be neglected as a good approximation ($T/\theta \simeq 0$); (e) it is consistent with the definition of a Carnot cycle, whose efficiency was shown to be $\eta = 1 - (\theta_2/\theta_1)$, where θ_1 and θ_2 represent the effective temperatures associated with the isothermal transformations of the cycle, with $\theta_1 > \theta_2$ [36]; (f) since the whole approach emerged from a nonlinear Fokker-Planck equation, defined for a continuous probability distribution, the analog to the third law of thermodynamics was not fulfilled, as expected [35].

In the present work, we explore another physical system, for which we reinforce the adequacy of introducing a thermodynamic framework by neglecting thermal effects. Although the thermodynamic procedure is closely related to the one developed in Refs. [35–40], the identification of the entropic form and effective-temperature parameter are pursued following a different approach; in particular, the system considered is defined by discrete probabilities. Herein we study the ground state of two-level systems [associated with probabilities p and $(1 - p)$, respectively] defined by a general Hamiltonian $\hat{H} = \hat{H}_0 + \lambda \hat{V}$, and in order to deal properly with the quantum effects of such a ground state, one needs to neglect the thermal effects by setting $T = 0$. The simple case characterized by $\lambda = 0$, whose Hamiltonian \hat{H}_0 is represented by a diagonal matrix, is well established within both quantum mechanics [1] and BG statistical mechanics [4–6], following the third law of thermodynamics, i.e., $S_{BG} = 0$. Herein, it is shown that the introduction of the perturbation $\lambda \hat{V}$ ($\lambda > 0$) in the Hamiltonian may affect qualitatively the ground state, leading to a nontrivial entropy $S[p]$ (with $S[p] \neq S_{BG}[p]$), if the Hermitian operator \hat{V} is represented by a 2×2 matrix, characterized by nonzero off-diagonal elements $V_{12} = V_{21} = -z$, where z is a real positive number. The present approach is based on Ref. [41], where a thermodynamic procedure for studying the ground state of quantum systems was introduced and applied to the Hubbard model; the main idea consisted in taking the interaction term $\lambda \hat{V}$ into account only through the corresponding wave functions.

In the next section, we define the physical system and identify its associated entropic form $S[p]$, expressed only in terms of the probabilities p and $1 - p$; we verify that $S[p]$ follows essential requirements for an appropriate thermodynamic framework. In Sec. III we extremize $S[p]$ under standard constraints, obtaining the equilibrium distribution p_{eq} , which is shown to depend on the ratio $\lambda z/\Delta$. Using p_{eq} , one may calculate the equilibrium entropy and internal energy U , so that the fundamental relation ($\partial S/\partial U = 1/\theta$) leads to the effective-temperature definition $\theta = 2z\lambda/k$, as

well as to an infinitesimal heatlike quantity, $\delta Q = \theta dS$. Hence, fundamental thermodynamic quantities are expressed in terms of the ratio $k\theta/\Delta$, and important limits are analyzed. In Sec. IV, we introduce an infinitesimal work contribution so as to obtain an analogous to the first law of thermodynamics; Legendre transformations for distinct pairs of independent variables are considered in order to derive different potentials and Maxwell relations. In Sec. V, we define physical transformations and construct a Carnot cycle, characterized by an efficiency $\eta = 1 - (\theta_2/\theta_1)$, where θ_1 and θ_2 correspond to the effective temperatures associated with the two isothermal transformations of the cycle, with $\theta_1 > \theta_2$. Finally, in Sec. VI we present our conclusions.

II. THE SYSTEM AND ITS ASSOCIATED ENTROPY

Herein we will study the general case of two energy levels, based on the following Hamiltonian:

$$\hat{H} = \hat{H}_0 + \lambda \hat{V}, \quad (2.1)$$

where

$$\hat{H}_0 = \begin{pmatrix} 0 & 0 \\ 0 & \Delta \end{pmatrix}, \quad \hat{V} = \begin{pmatrix} x & -z \\ -z & y \end{pmatrix}, \quad (2.2)$$

with $\lambda \geq 0$ representing a dimensionless real parameter, so that x , y , z , and Δ are real numbers with dimensions of energy. The particular case $\lambda = 0$ recovers the well-known pedagogical example, with energy levels $\varepsilon_0(0) = 0$ and $\varepsilon_1(0) = \Delta > 0$, fully described within BG statistical mechanics [4–6].

In what concerns the present analysis, the most important elements in the matrix \hat{V} will turn out to be the off-diagonal ones, as will be shown later on; moreover, these elements should take on negative real values, i.e., $z > 0$. The energies of the two levels of the Hamiltonian \hat{H} are given by

$$\varepsilon_i(\lambda) = \frac{\lambda(x + y) + \Delta \pm \sqrt{[\lambda(y - x) + \Delta]^2 + (2z\lambda)^2}}{2}, \quad (2.3)$$

$i = 0, 1,$

where the minus (plus) sign corresponds to the ground-state (higher-state) energy with $i = 0$ ($i = 1$), recovering $\varepsilon_0(0) = 0$ [$\varepsilon_1(0) = \Delta$] for $\lambda = 0$. Moreover, the ground state $|\psi_0(\lambda)\rangle$ of \hat{H} , defined as $\hat{H}(\lambda)|\psi_0(\lambda)\rangle = \varepsilon_0(\lambda)|\psi_0(\lambda)\rangle$, can be expressed in terms the two noninteracting states $|\phi_+\rangle$ and $|\phi_-\rangle$,

$$|\psi_0(\lambda)\rangle = a_-|\phi_-\rangle + a_+|\phi_+\rangle, \quad |\phi_+\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad (2.4)$$

$$|\phi_-\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix},$$

with the coefficients $a_+ = \sqrt{p}e^{i\alpha}$ and $a_- = \sqrt{1-p}e^{i\beta}$. It should be mentioned that $|\psi_0(\lambda)\rangle$ recovers $|\psi_0(0)\rangle = |\phi_+\rangle$ in the case $\lambda = 0$; indeed, it will be shown later on that $p = 1$ in this limit. Hence, the system is in a pure state in the case $\lambda = 0$ (for which its entropy should be zero), whereas for $\lambda > 0$ it is found in a mixed state, with the corresponding probabilities $|a_+|^2 = p$ and $|a_-|^2 = 1 - p$, respectively. The introduction of the term $\lambda \hat{V}$ in the Hamiltonian resembles the effects of a temperature, leading to probabilities ($0 < p < 1$) associated with the two energy levels; as a consequence, its entropy should be nonzero, being a functional only of p .

In what follows, we extend tools developed in standard statistical mechanics to study the ground state of quantum systems. Essentially, the present approach is based on Ref. [41], where a thermodynamic procedure for studying the ground state of quantum systems was introduced and applied to the Hubbard model. The essential idea consists in the fact that, for certain classes of quantum systems, changing the intensities of the interaction between particles of the system (in the present case, changing λ) corresponds to considering different occupation probabilities for noninteracting microstate energy levels. Let us then consider the internal energy given by

$$\tilde{U}(\lambda) = \langle \psi_0(\lambda) | \hat{H} | \psi_0(\lambda) \rangle = p\varepsilon_0(\lambda) + (1-p)\varepsilon_1(\lambda), \quad (2.5)$$

which satisfies

$$\begin{aligned} \tilde{U}(\lambda) &= \langle \psi_0(\lambda) | \hat{H} | \psi_0(\lambda) \rangle = \langle \psi_0(\lambda) | \hat{H}_0 + \lambda \hat{V} | \psi_0(\lambda) \rangle \\ &= (a_-^* \langle \phi_- | + a_+^* \langle \phi_+ |) \hat{H}_0 (a_- | \phi_- \rangle + a_+ | \phi_+ \rangle) \\ &\quad + \lambda \langle \psi_0(\lambda) | \hat{V} | \psi_0(\lambda) \rangle \\ &= p\varepsilon_0(0) + (1-p)\varepsilon_1(0) + \lambda \langle \psi_0(\lambda) | \hat{V} | \psi_0(\lambda) \rangle \\ &\geq (1-p)\Delta + \lambda V_0, \end{aligned} \quad (2.6)$$

where we have used the noninteracting states of Eq. (2.4), and we introduced $0 \leq V_0 \leq \langle \psi_0(\lambda) | \hat{V} | \psi_0(\lambda) \rangle$ as a lower bound for the eigenvalues of \hat{V} . The idea developed in Ref. [41] consists in using

$$\begin{aligned} U(\lambda) &= \langle \psi_0(\lambda) | \hat{H}_0 | \psi_0(\lambda) \rangle \\ &= p\varepsilon_0(0) + (1-p)\varepsilon_1(0) = (1-p)\Delta, \end{aligned} \quad (2.7)$$

instead of the internal energy of Eq. (2.5). The energy above presents a lower value, i.e., $U(\lambda) \leq \tilde{U}(\lambda)$, and it will be considered hereafter as the internal energy of the system. Therefore, the effects of $\lambda \hat{V}$ will be taken into account only through the wave function [appearing in $U(\lambda)$ above in the probabilities], whereas the energy levels are left unchanged. Later on, we will show that, for the present system, this approximation for the internal energy will not affect the results qualitatively.

Let us now analyze the quantity

$$\mathcal{I}(\lambda) = \langle \psi_0(0) | \hat{V} | \psi_0(0) \rangle - \langle \psi_0(\lambda) | \hat{V} | \psi_0(\lambda) \rangle, \quad (2.8)$$

which corresponds to the difference of the expectation values of \hat{V} , calculated with the ground states for $\lambda = 0$ and $\lambda > 0$; one obtains

$$\mathcal{I}(\lambda) = (x-y)(1-p) + z(a_+ a_-^* + a_-^* a_+). \quad (2.9)$$

From now on, we will restrict ourselves to the particular case

$$\alpha = \beta, \quad x = y = 0, \quad (2.10)$$

where the first choice [equal phases for the coefficients of Eq. (2.4)] is very common in standard quantum mechanics [1], whereas the second (concerning the parameters x and y) comes from the fact that the ground-state energy can be defined apart from an additive constant. Taking into account the above conditions, one gets that $\mathcal{I}(\lambda)$ may be directly related to the following entropic form:

$$S[p] = \frac{k}{2z} \mathcal{I}(\lambda) = k\sqrt{p(1-p)}, \quad (2.11)$$

where k corresponds to a positive constant with dimensions of entropy. It should be mentioned that the functional $S[p]$ satisfies the first three Khinchin axioms [42]: (i) It varies continuously on p ; (ii) it is maximum at equiprobability ($p = 1/2$), being guaranteed by the concavity of $\sqrt{p(1-p)}$ on p ; and (iii) the addition of an event with zero probability does not change the entropy, which is ensured by $S[0] = 0$; furthermore, we also have that $S[1] = 0$. However, the fourth Khinchin axiom (the one concerning additivity) is violated, as happens to all nonadditive entropic forms [7,8]. In the next section, we extremize the entropy of Eq. (2.11) in order to obtain its associated equilibrium distribution.

III. EQUILIBRIUM DISTRIBUTION AND EFFECTIVE TEMPERATURE

Now, extremizing $S[p]$ with the usual constraints of normalization of probabilities and internal energy defined according to Eq. (2.7), one obtains the equilibrium distribution

$$p_{\text{eq}} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{1 + (2z\lambda/\Delta)^2}} \right). \quad (3.1)$$

Using the equilibrium distribution above in Eq. (2.11) and expressing S in terms of U , one can calculate

$$\left(\frac{\partial S}{\partial U} \right)_\Delta = \frac{k}{2z\lambda}, \quad (3.2)$$

from which one readily identifies an effective temperature θ , defined as

$$k\theta = 2z\lambda, \quad (3.3)$$

where the particular dependence $S \equiv S(U, \Delta)$ [considered in Eq. (3.2)] will become clear in the next section.

At this point, one should recall that in the previous section we carried out an approximation for the internal energy by considering Eq. (2.7) instead of Eq. (2.5); in fact, the results of Eqs. (3.1)–(3.3) also hold for the internal energy $\tilde{U}(\lambda)$ by replacing $\Delta \rightarrow [\varepsilon_1(\lambda) - \varepsilon_0(\lambda)]$. Therefore, the whole thermodynamic procedure to be developed hereafter will remain valid by a simple redefinition of the gap between the two energy levels. Consequently, for systems described by energy spectra characterized by more than two levels, one expects that the approximation of replacing the internal energy of Eq. (2.5) by that in Eq. (2.7) should not yield significant qualitative changes in its thermodynamic quantities.

Let us now introduce a dimensionless variable, defined as the ratio between two relevant energies of the problem,

$$\tau = \frac{k\theta}{\Delta} = \frac{2z\lambda}{\Delta}, \quad (3.4)$$

from which one can define the “low-temperature” ($\tau \ll 1$) and “high-temperature” ($\tau \gg 1$) regimes. In terms of this variable, one has for the Hamiltonian and equilibrium distribution,

$$\hat{H} = \Delta \begin{pmatrix} 0 & -\tau/2 \\ -\tau/2 & 1 \end{pmatrix}, \quad (3.5)$$

$$p_{\text{eq}} = \frac{1}{2} \left(1 + \frac{1}{\sqrt{1 + \tau^2}} \right). \quad (3.6)$$

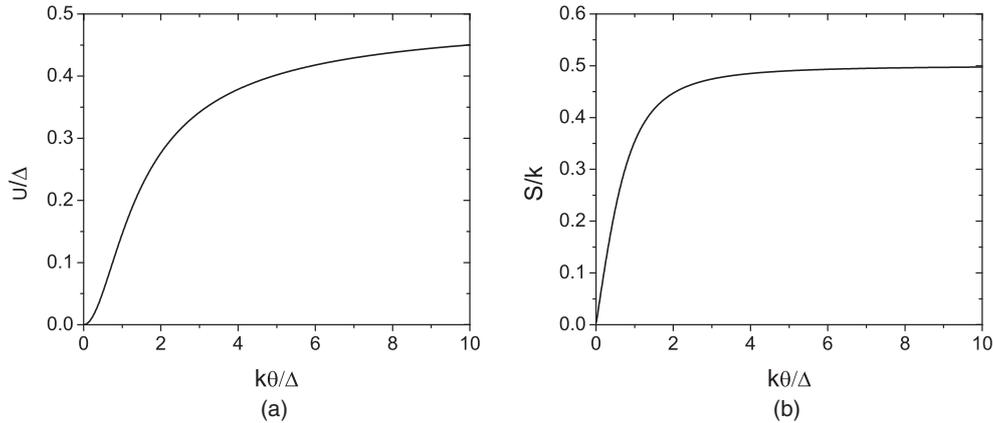


FIG. 1. (a) The internal energy of Eq. (3.7) (in units of Δ) is exhibited vs the dimensionless variable $\tau = (k\theta/\Delta)$; (b) the same representation is used for the dimensionless entropy of Eq. (3.8).

Moreover, the internal energy and entropy become

$$U = \frac{\Delta}{2} \left(1 - \frac{1}{\sqrt{1 + \tau^2}} \right), \quad (3.7)$$

$$S = \frac{k\tau}{2\sqrt{1 + \tau^2}}, \quad (3.8)$$

from which one can define the free energy

$$F = U - \theta S = \frac{\Delta}{2} (1 - \sqrt{1 + \tau^2}). \quad (3.9)$$

The consistency of the definitions above is indicated by the following equalities:

$$\frac{\partial U}{\partial \theta} = \theta \frac{\partial S}{\partial \theta} = -\theta \frac{\partial^2 F}{\partial \theta^2} = \frac{k\tau}{2(1 + \tau^2)^{3/2}} \geq 0, \quad (3.10)$$

to be identified later on as specific heat. Moreover, in the limit $\theta \rightarrow 0$ one obtains the expected results for a quantum system at low temperatures, namely $p_{\text{eq}} \rightarrow 1$, $U \sim \theta^2/4$, $S \sim \theta/2$, $F \sim -\theta^2/4$, and $(\partial U/\partial \theta) \sim \theta/2$. The result $p_{\text{eq}} \rightarrow 1$ (i.e., the system approaching a pure state), leading to $S \rightarrow 0$, may be understood as an analog to the third law of thermodynamics.

In Fig. 1 we represent the dimensionless internal energy U/Δ [Fig. 1(a)] and entropy S/k [Fig. 1(b)] versus τ . Both quantities approach zero, as $\tau \rightarrow 0$, growing for increasing values of τ . However, for sufficiently large temperatures, i.e., $\tau \gg 1$, one reaches equiprobability ($p_{\text{eq}} \rightarrow 1/2$), so that the quantities of Fig. 1 approach well-defined upper bounds, i.e., $(U/\Delta) \rightarrow 1/2$ and $(S/k) \rightarrow 1/2$, typical of a two-level system.

In what follows, we will propose a form for the first law of thermodynamics, consider Legendre transformations in order to derive other thermodynamic potentials, define response functions, and show that the present system follows a cycle that is analogous to a Carnot cycle.

IV. FIRST LAW AND THERMODYNAMIC POTENTIALS

From Eq. (2.7), $U = \Delta(1 - p)$, and so

$$dU = -\Delta dp + (1 - p)d\Delta, \quad (4.1)$$

showing two distinct forms of energy exchange associated with variations in the occupation probabilities and energy levels, respectively. Usually, the former contribution is identified with heat, whereas changes in the energy levels are associated with work (see, e.g., Ref. [43]); hence, it appears intuitive to consider

$$\delta Q = -\Delta dp = \theta dS, \quad \delta W = (1 - p)d\Delta = \sigma d\Delta, \quad (4.2)$$

where $\sigma = 1 - p$ is dimensionless, appearing as the parameter thermodynamically conjugated to Δ , to be determined later on. Therefore, herein we propose the following form for the first law:

$$dU = \delta Q + \delta W = \theta dS + \sigma d\Delta, \quad (4.3)$$

where δW corresponds to the work done *on* the system; the consistency of this proposal for the first law will be shown throughout the rest of this paper. Now, using the equilibrium distribution in Eq. (3.6),

$$\sigma = 1 - p_{\text{eq}} = \frac{1}{2} \left(1 - \frac{1}{\sqrt{1 + (k\theta/\Delta)^2}} \right), \quad (4.4)$$

which represents the equation of state, expressing the parameter σ in terms of θ and Δ . Hence, σ is positive and restricted to $0 \leq \sigma \leq 1/2$, behaving as $\sigma \approx \tau^2/4$ ($\tau \rightarrow 0$) and $\sigma \approx (1 - \tau^{-1})/2$ ($\tau \rightarrow \infty$).

In what follows, we will perform Legendre transformations, and considering the first-law form of Eq. (4.3), we will derive other thermodynamic potentials. Usual thermodynamic properties such as Maxwell relations and response functions will be analyzed.

A. Internal energy

From the first law in Eq. (4.3) one has that $S = S(U, \Delta)$, or equivalently, $U = U(S, \Delta)$; then, manipulating Eqs. (3.7) and (3.8), one obtains

$$U(S, \Delta) = \frac{\Delta}{2} \left[1 - \sqrt{1 - \left(\frac{2S}{k} \right)^2} \right]. \quad (4.5)$$

From Eq. (4.3) one gets the equivalent to Eqs. (3.2) and (3.3), as well as the equation of state [Eq. (4.4)],

$$\left(\frac{\partial U}{\partial S}\right)_\Delta = \theta, \quad \left(\frac{\partial U}{\partial \Delta}\right)_S = \sigma. \quad (4.6)$$

Considering that $U(S, \Delta)$ is a state function, its second derivatives must be independent of the order of differentiation; this yields the following Maxwell relation:

$$\frac{\partial^2 U}{\partial \Delta \partial S} = \frac{\partial^2 U}{\partial S \partial \Delta} \Rightarrow \left(\frac{\partial \sigma}{\partial S}\right)_\Delta = \left(\frac{\partial \theta}{\partial \Delta}\right)_S. \quad (4.7)$$

B. Helmholtz free energy

The Helmholtz free energy was already introduced in Eq. (3.9); indeed,

$$F(\theta, \Delta) = U - \theta S; \quad \Rightarrow \quad dF = -S d\theta + \sigma d\Delta, \quad (4.8)$$

so that

$$\left(\frac{\partial F}{\partial \theta}\right)_\Delta = -S, \quad \left(\frac{\partial F}{\partial \Delta}\right)_\theta = \sigma. \quad (4.9)$$

The associated Maxwell relation follows from its second derivatives,

$$\frac{\partial^2 F}{\partial \Delta \partial \theta} = \frac{\partial^2 F}{\partial \theta \partial \Delta} \Rightarrow \left(\frac{\partial S}{\partial \Delta}\right)_\theta = -\left(\frac{\partial \sigma}{\partial \theta}\right)_\Delta. \quad (4.10)$$

C. Gibbs free energy

The Gibbs free energy is obtained by means of the following Legendre transformation:

$$G(\theta, \sigma) = F - \sigma \Delta \quad \Rightarrow \quad dG = -S d\theta - \Delta d\sigma, \quad (4.11)$$

leading to

$$\left(\frac{\partial G}{\partial \theta}\right)_\sigma = -S, \quad \left(\frac{\partial G}{\partial \sigma}\right)_\theta = -\Delta. \quad (4.12)$$

One can express $G(\theta, \sigma)$ as

$$G(\theta, \sigma) = -k\theta\sqrt{\sigma(1-\sigma)}, \quad (4.13)$$

whereas the associated Maxwell relation is given by

$$\left(\frac{\partial S}{\partial \sigma}\right)_\theta = \left(\frac{\partial \Delta}{\partial \theta}\right)_\sigma. \quad (4.14)$$

D. Enthalpy

The enthalpy is defined as

$$H(S, \sigma) = U - \sigma \Delta = 0, \quad (4.15)$$

which is identically zero, following from the internal energy of Eq. (3.7) and the equation of state in Eq. (4.4). Considering an infinitesimal transformation and Eq. (4.3), one obtains

$$dH = \theta dS - \Delta d\sigma = 0 \quad \Rightarrow \quad \theta dS = \Delta d\sigma, \quad (4.16)$$

showing that an adiabatic transformation corresponds to $\sigma = \text{const}$.

The curious situation of an identically zero enthalpy was found also for a system of interacting vortices submitted to an external harmonic potential [38], as well as under a general powerlike confining potential [40]. The consequences

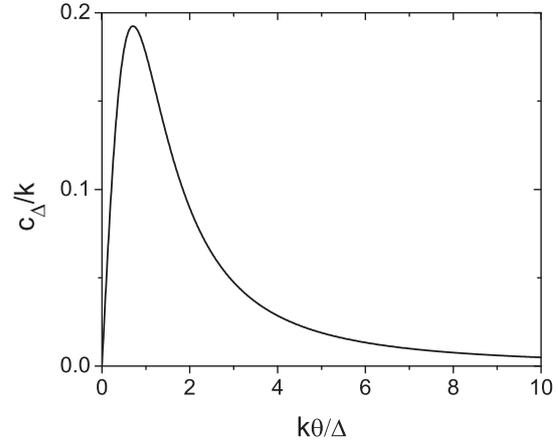


FIG. 2. The rescaled dimensionless specific heat c_Δ [defined in Eq. (4.17)] is represented vs the dimensionless variable $\tau = k\theta/\Delta$.

of this result will appear in some response functions, to be investigated next.

E. Response functions

The specific heat for Δ fixed follows from Eq. (3.10),

$$c_\Delta = \left(\frac{\partial U}{\partial \theta}\right)_\Delta = \frac{k\tau}{2(1+\tau^2)^{3/2}}, \quad (4.17)$$

being exhibited in Fig. 2. From the expression above, one gets the low-temperature behavior $(c_\Delta/k) \sim \tau/2$ as $\theta \rightarrow 0$, compatible with a quantum system. Moreover, in Fig. 2 one notices a maximum, analogous to the Schottky anomaly that appears frequently in the specific heat versus temperature T , in standard two-level systems [4–6]. Such a maximum occurs for $\tau \approx 1$, separating the “low-temperature” ($\tau \ll 1$) and “high-temperature” ($\tau \gg 1$) regimes. In the latter regime, the specific heat of Eq. (4.17) vanishes as $(c_\Delta/k) \sim 1/(2\tau^2)$, showing a behavior similar to those of many systems in contact with a thermal bath, as $T \rightarrow \infty$.

As a direct consequence of Eq. (4.15) one gets a trivial c_σ ,

$$c_\sigma = \left(\frac{\partial H}{\partial \theta}\right)_\sigma = 0. \quad (4.18)$$

This result implies that the present system cannot exchange “heat” (i.e., it cannot vary its entropy) for σ fixed, as a consequence of Eq. (4.16), which defines adiabatic transformations as those occurring for $\sigma = \text{const}$. Therefore, a complete thermodynamic description is given in terms of three potentials, namely internal energy, $U(S, \Delta)$, and free energies, $F(\theta, \Delta)$ and $G(\theta, \sigma)$; the enthalpy $H(S, \sigma)$ does not contain any new information.

One can also investigate quantities analogous to the coefficient of expansion and isothermal compressibility, defined, respectively, as

$$\gamma = \frac{1}{\Delta} \left(\frac{\partial \Delta}{\partial \theta}\right)_\sigma = \frac{1}{\theta} \quad (4.19)$$

and

$$\kappa = -\frac{1}{\Delta} \left(\frac{\partial \Delta}{\partial \sigma} \right)_\theta = \frac{2}{\tau^2} (1 + \tau^2)^{3/2}, \quad (4.20)$$

which are both positive. Manipulating Eqs. (4.17), (4.19), and (4.20), one verifies that these quantities satisfy

$$c_\Delta = \Delta \theta \frac{\gamma^2}{\kappa}, \quad (4.21)$$

similar to the relation obtained for a system of interacting vortices [38,40]. Indeed, the relation of Eq. (4.21) may be derived directly from standard calculations, similarly to what was done in Refs. [38,40], and it should be compared with $c_p - c_v = vT\gamma^2/\kappa$ of usual thermodynamics [5,6].

V. THE CARNOT CYCLE

The consistency of the proposal of Eq. (4.3) for the first law was indicated in the previous sections; herein, we will reinforce this aspect by introducing a cycle analogous to the Carnot cycle of standard thermodynamics. To achieve this, we will consider physical transformations similar to the usual adiabatic ($S = \text{const}$) and isothermal ($\theta = \text{const}$) ones. The adiabatic transformations were already defined by means of Eq. (4.16), which are those occurring for

$$\sigma = \frac{U}{\Delta} = \text{const} \quad \Rightarrow \quad \frac{k\theta}{\Delta} = \text{const}, \quad (5.1)$$

where we have used the equation of state in Eq. (4.4) for the latter condition. Hence, the total work done *on* the system in an adiabatic transformation, from an initial state characterized by (θ_i, Δ_i) to a final one specified by (θ_f, Δ_f) , is given by

$$u_f - u_i = W = \int_{\Delta_i}^{\Delta_f} \sigma d\Delta = \sigma(\Delta_f - \Delta_i), \quad (5.2)$$

so that work is positive (negative) for $\Delta_f > \Delta_i$ ($\Delta_f < \Delta_i$). Along this transformation, the parameter σ is left unchanged, being given by [cf. Eq. (4.4)]

$$\begin{aligned} \sigma &= \frac{1}{2} \left(1 - \frac{1}{\sqrt{1 + (k\theta_i/\Delta_i)^2}} \right) \\ &= \frac{1}{2} \left(1 - \frac{1}{\sqrt{1 + (k\theta_f/\Delta_f)^2}} \right). \end{aligned} \quad (5.3)$$

For an isothermal transformation at a temperature θ , one has both heat and work contributions; hence, from an initial state given by (θ, Δ_i) to a final one with (θ, Δ_f) , these energy exchanges are given by

$$\begin{aligned} Q &= \int_{S_i}^{S_f} \theta dS = \theta(S_f - S_i) \\ &= \frac{(k\theta)^2}{2} \left\{ \frac{1}{\Delta_f} \frac{1}{\sqrt{1 + (k\theta/\Delta_f)^2}} - \frac{1}{\Delta_i} \frac{1}{\sqrt{1 + (k\theta/\Delta_i)^2}} \right\} \end{aligned} \quad (5.4)$$

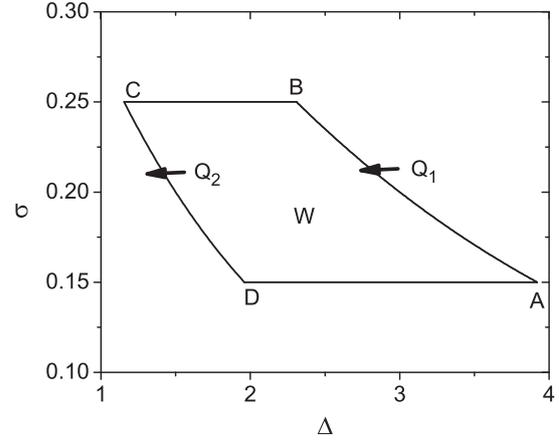


FIG. 3. The Carnot cycle ($A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$) is represented in the plane σ (dimensionless) vs Δ (dimensions of energy, e.g., Joules), with two isothermal and two adiabatic transformations intercalated. The transformations for σ constant are adiabatic, and herein they were chosen to occur for $\sigma = 0.25$ ($B \rightarrow C$) and $\sigma = 0.15$ ($D \rightarrow A$). The isothermal transformations are obtained from the equation of state [cf. Eq. (4.4)] at conveniently chosen values of θ_1 ($A \rightarrow B$) and θ_2 ($C \rightarrow D$), with $\theta_1 > \theta_2$. An amount of heat Q_1 is absorbed at θ_1 , and Q_2 is released at θ_2 ; the work quantities W_{AB} and W_{BC} are negative, whereas W_{CD} and W_{DA} are positive, so that the area inside the cycle represents the total work W done *on* the system, being negative, as expected from Eq. (4.3). The cycle above holds for any system of units, e.g., by considering all quantities with dimensions of energy in Joules.

and

$$\begin{aligned} W &= \int_{\Delta_i}^{\Delta_f} \sigma d\Delta \\ &= \frac{1}{2}(\Delta_f - \Delta_i) - \frac{1}{2} \left\{ \Delta_f \sqrt{1 + (k\theta/\Delta_f)^2} \right. \\ &\quad \left. - \Delta_i \sqrt{1 + (k\theta/\Delta_i)^2} \right\}. \end{aligned} \quad (5.5)$$

It should be mentioned that the sign of W does not come immediately from the above equation; however, we have proven in Appendix A that $W > 0$ ($W < 0$) if $\Delta_f > \Delta_i$ ($\Delta_f < \Delta_i$). Consistently, the sum of these two forms of energy coincides with the internal energy difference calculated from Eq. (3.7),

$$\begin{aligned} u_f - u_i &= Q + W = \frac{1}{2}(\Delta_f - \Delta_i) \\ &\quad - \frac{1}{2} \left\{ \frac{\Delta_f}{\sqrt{1 + (k\theta/\Delta_f)^2}} - \frac{\Delta_i}{\sqrt{1 + (k\theta/\Delta_i)^2}} \right\}. \end{aligned} \quad (5.6)$$

In Fig. 3 we represent the analog to the Carnot cycle of standard thermodynamics by considering two isothermal and two adiabatic processes, intercalated. Next, we describe the main properties of this cycle. (i) An amount of heat Q_1 is absorbed in the isothermal process at the higher temperature θ_1 , whereas the system releases heat Q_2 in the isothermal process at the lower temperature θ_2 . (ii) In a plot σ versus

Δ (like the one in Fig. 3), the work associated with a given process corresponds to the area below such transformation. The total work done *on* the system, calculated as $W = W_{AB} + W_{BC} + W_{CD} + W_{DA}$, is given by the area enclosed in the cycle of Fig. 3, being negative, as expected from Eq. (4.3). If one defines $\mathcal{W} = -W$ as the work done *by* the system, the variation of internal energy is zero for the complete cycle, and one has $Q_1 = \mathcal{W} + Q_2$ (conventionalizing all three of these quantities as positive). (iii) Manipulating Eqs. (4.4) and (5.4), one obtains the well-known result relating the two isothermal processes, $(Q_1/Q_2) = (\theta_1/\theta_2)$, leading to the celebrated efficiency of the Carnot cycle,

$$\eta = \frac{\mathcal{W}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1} \quad (0 \leq \eta \leq 1). \quad (5.7)$$

This result provides a strong support for the fundamental relation considered herein, as an analog to the first law of thermodynamics [cf. Eq. (4.3)], as appropriate for this system.

In Appendix B, we have shown that the entropic form of Eq. (2.11) satisfies an H theorem in the case of an isolated system, guaranteeing that $(dS/dt) \geq 0$. This result, derived from a microscopic approach by means of a master equation, will now be considered to hold macroscopically, corresponding then to the second law of thermodynamics, which states that $\Delta S \geq 0$ for an isolated system. Furthermore, using the Carnot cycle of Fig. 3, one obtains the two famous historical formulations [5], as discussed below.

(a) Kelvin formulation: “It is impossible to construct a perfect heat machine.” Such a desirable perfect type of engine corresponds to $Q_2 = 0$ in the Carnot cycle of Fig. 3, i.e., $Q_1 = \mathcal{W}$, so that the heat extracted from the reservoir at higher effective temperature is totally transformed into work. Considering one complete cycle, the change of entropy of the isolated system (defined as the reservoir at temperature θ_1 together with the device) equals that of the reservoir, $\Delta S = -Q_1/\theta_1 \leq 0$, leading to a decrease in the total entropy, which is prohibited.

(b) Clausius statement: “It is impossible to construct a perfect refrigerator.” A refrigerator is defined as a cycle operating in the reverse way, with respect to that of Fig. 3, and the perfect refrigerator operates with no work, i.e., $Q_1 = Q_2$. In this case, the refrigerator extracts heat Q_2 from the reservoir at lower temperature and transfers it totally to the reservoir at higher temperature. Hence, considering the two reservoirs and the device as an isolated system, the total change in the entropy in a complete cycle is given by

$$\Delta S = \frac{Q_1}{\theta_1} - \frac{Q_2}{\theta_2} = Q_1 \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right) \leq 0 \quad (5.8)$$

since $Q_1 > 0$ and $\theta_1 > \theta_2$; consequently, a decrease in the total entropy makes this process also prohibited.

VI. CONCLUSIONS

We have studied the ground state of a quantum system characterized by two energy levels, associated with probabilities p and $1 - p$, respectively, and defined by a general Hamiltonian, $\hat{H} = \hat{H}_0 + \lambda \hat{V}$. The contribution \hat{H}_0 is expressed by a diagonal matrix, with energy values 0 and Δ , so that for $\lambda = 0$ one recovers the well-known example, solvable

within Boltzmann-Gibbs statistical mechanics, presenting a zero entropy ($S_{BG} = 0$) at zero temperature ($T = 0$).

The aim of the present study was to show that by considering the contribution $\lambda \hat{V}$ ($\lambda > 0$), with \hat{V} being represented by a nondiagonal matrix, the ground state becomes nontrivial in the sense that one may define an effective-temperature parameter, as well as an associated entropy. The matrix elements of the resulting Hamiltonian become $H_{11} = 0$, $H_{22} = \Delta$, $H_{12} = H_{21} = -\lambda z$, where z is a positive real number. The approach was based on the idea of keeping the energy levels as unperturbed (i.e., energies 0 and Δ), whereas the contribution $\lambda \hat{V}$ is taken into account through the wave function [41].

We have shown that some expectation values, calculated from the ground state for $\lambda = 0$, $|\psi_0(0)\rangle$ (a pure state), and the one for $\lambda > 0$, $|\psi_0(\lambda)\rangle$ (a mixed state with probabilities p and $1 - p$), may become particularly interesting. For instance, the difference of the expectation values of \hat{V} , $\mathcal{I}(\lambda) = \langle \psi_0(0) | \hat{V} | \psi_0(0) \rangle - \langle \psi_0(\lambda) | \hat{V} | \psi_0(\lambda) \rangle$, turned up to be directly related to the entropic form $S[p] = k\sqrt{p(1-p)}$, which presents a nontrivial behavior for $T = 0$. Moreover, we have also identified an effective-temperature parameter, θ , given by $k\theta = 2\lambda z$, so that $\theta \geq 0$. In this way, by extremizing the entropy $S[p]$ we have obtained an equilibrium distribution p_{eq} , depending only on the ratio of two typical energies of the system, $(k\theta)/\Delta$.

From the equilibrium distribution p_{eq} , we have defined equilibrium quantities for $\theta > 0$, in a form analogous to those of standard thermodynamics for $T > 0$; we have shown that a consistent thermodynamic framework holds for $\theta > 0$, and the main results of our analysis are described next. (i) By proposing an infinitesimal form for the first law, we defined Legendre transformations in order to derive thermodynamic potentials that were shown to follow Maxwell relations. (ii) Response functions were introduced, and particularly a quantity analogous to a specific heat (defined for $\Delta = \text{const}$) showed a behavior for increasing values of θ very similar to that of a two-level system for $T > 0$, exhibiting a Schottky anomaly for $k\theta \approx \Delta$. (iii) Introducing transformations characterized by $\theta = \text{const}$ (denominated as isothermal) and $S = \text{const}$ (denominated as adiabatic), we have constructed a cycle analogous to the Carnot cycle, which presented an efficiency $\eta = 1 - (\theta_2/\theta_1)$, where θ_1 and θ_2 correspond to the effective temperatures associated with the two isothermal transformations of the cycle, with $\theta_1 > \theta_2$. (iv) Based on the Carnot cycle, as well as on an H theorem stating that the present entropy satisfies $(dS/dt) \geq 0$ for an isolated system, we discussed the second law of thermodynamics, particularly the historical formulations of Kelvin and Clausius. (v) Finally, a result similar to the third law of thermodynamics was verified in the sense that one approaches a pure state in the limit $\theta \rightarrow 0$, i.e., $p_{eq} \rightarrow 1$, so that $S \rightarrow 0$.

The effective temperature, $k\theta = 2\lambda z$, is essentially associated with the off-diagonal terms of the Hamiltonian, $H_{12} = H_{21} = -\lambda z$, which appear due to the perturbation $\lambda \hat{V}$, being responsible, therefore, for the nontrivial ground-state properties. From an experimental point of view, the perturbation $\lambda \hat{V}$ should come from an external agent; this external parameter, together with the temperature T , must be appropriately tuned, yielding $\theta \gg T$, so that usual thermal effects become irrelevant. In this sense, the results shown

herein are associated with a nonadditive entropic form; it should be mentioned that these properties cannot be captured by the additive Boltzmann-Gibbs entropy, which is negligible ($S_{BG} \approx 0$) for sufficiently low temperatures T . As the simplest physical example, one may consider a single particle of spin $1/2$ submitted to two perpendicular external fields, e.g., along directions z and x (h_z and h_x , respectively), restricted to $h_z, h_x \gg kT$. Starting with the spin aligned along the field h_z , one obtains the gap Δ between the two levels; a possible change of direction due to the perpendicular field h_x will change the gap, and consequently this contribution can be associated with work. Moreover, in this simple example, the effective temperature appears to be $k\theta \propto h_x$.

These results corroborate investigations pursued for a system of interacting vortices, usually considered for modeling type-II superconductors, for which typical values of an effective temperature introduced were evaluated as much higher than usual temperatures of standard superconducting phases; in this case, the entropic form conjugated to the effective temperature was shown to be S_2 [35–40], i.e., the particular case $q = 2$ of the entropy S_q that appears in nonextensive statistical mechanics. In these previous studies, the entropy $S_2 \equiv S_2[p(x,t)]$ emerged from an identification with a nonlinear Fokker-Planck equation, describing the time evolution of a continuous probability distribution $p(x,t)$, so that an analog to the third law of thermodynamics was not fulfilled. The present approach, showing that perturbations in the ground state may lead to nontrivial behavior in a simple two-level system, characterized by a consistent thermodynamic framework (including a result similar to the third law of thermodynamics), may help us to understand better certain curious properties presented by some physical systems in which thermal effects are neglected, particularly those described by discrete probabilities.

ACKNOWLEDGMENTS

The authors are thankful to C. Tsallis, E. M. F. Curado, and R. F. S. Andrade for fruitful conversations. The partial financial support from CNPq, CAPES, and FAPERJ (Brazilian funding agencies) is acknowledged.

APPENDIX A

In this appendix, we will show that the work done *on* the system, in the isothermal transformations of the Carnot cycle of Fig. 3, presents a well-defined sign, e.g., $W \geq 0$ if $\Delta_f \geq \Delta_i$ (cf. transformation $C \rightarrow D$ of Fig. 3). We prove this in two steps: (i) Assuming $W \geq 0$, we show that $\Delta_f \geq \Delta_i$; (ii) considering $\Delta_f \geq \Delta_i$, we show that $W \geq 0$. Let us then consider the work contribution of Eq. (5.5),

$$W = \int_{\Delta_i}^{\Delta_f} \sigma d\Delta = \frac{1}{2}(\Delta_f - \Delta_i) - \frac{1}{2}\{\Delta_f \sqrt{1 + (k\theta/\Delta_f)^2} - \Delta_i \sqrt{1 + (k\theta/\Delta_i)^2}\}, \quad (\text{A1})$$

and introduce two dimensionless real variables,

$$a \equiv \frac{\Delta_f}{\Delta_i}, \quad b \equiv \frac{k\theta}{\Delta_i}, \quad (\text{A2})$$

which are both positive by definition, since $\Delta_f \geq 0$ and $\Delta_i \geq 0$. In terms of these variables, the work expression of Eq. (A1) leads to

$$\begin{aligned} \frac{2W}{\Delta_i} &= (a - 1) - (\sqrt{a^2 + b^2} - \sqrt{1 + b^2}) \\ &= (a + \sqrt{1 + b^2}) - (1 + \sqrt{a^2 + b^2}). \end{aligned} \quad (\text{A3})$$

(i) Proof that $W \geq 0$ implies $\Delta_f \geq \Delta_i$. In this part of the proof, we use the fact that $a + \sqrt{1 + b^2} \geq 0$ and $1 + \sqrt{a^2 + b^2} \geq 0$ in Eq. (A3); consequently, assuming $W \geq 0$, one has that

$$\frac{(a + \sqrt{1 + b^2})}{(1 + \sqrt{a^2 + b^2})} \geq 1. \quad (\text{A4})$$

By squaring both sides of the inequality above, one obtains

$$\frac{(a + \sqrt{1 + b^2})^2}{(1 + \sqrt{a^2 + b^2})^2} = \frac{(1 + a^2 + b^2 + 2a\sqrt{1 + b^2})}{(1 + a^2 + b^2 + 2\sqrt{a^2 + b^2})} \geq 1, \quad (\text{A5})$$

leading to

$$\frac{a\sqrt{1 + b^2}}{\sqrt{a^2 + b^2}} = \frac{\sqrt{a^2 + a^2b^2}}{\sqrt{a^2 + b^2}} \geq 1, \quad (\text{A6})$$

and so

$$a^2 = \left(\frac{\Delta_f}{\Delta_i}\right)^2 \geq 1 \quad \Rightarrow \quad \Delta_f \geq \Delta_i. \quad (\text{A7})$$

(ii) Proof that $\Delta_f \geq \Delta_i$ implies $W \geq 0$. This part of the proof follows closely the steps of part (i) in the reverse way. Since $\Delta_f \geq \Delta_i$, one has

$$\left(\frac{\Delta_f}{\Delta_i}\right)^2 = a^2 = \frac{a^2b^2}{b^2} \geq 1 \quad (\text{A8})$$

so that

$$\frac{2\sqrt{a^2 + a^2b^2}}{2\sqrt{a^2 + b^2}} = \frac{2a\sqrt{1 + b^2}}{2\sqrt{a^2 + b^2}} \geq 1 \quad (\text{A9})$$

leading to

$$\frac{(1 + a^2 + b^2 + 2a\sqrt{1 + b^2})}{(1 + a^2 + b^2 + 2\sqrt{a^2 + b^2})} = \frac{(a + \sqrt{1 + b^2})^2}{(1 + \sqrt{a^2 + b^2})^2} \geq 1. \quad (\text{A10})$$

Hence,

$$\begin{aligned} a + \sqrt{1 + b^2} &\geq 1 + \sqrt{a^2 + b^2} \\ &\Rightarrow (a + \sqrt{1 + b^2}) - (1 + \sqrt{a^2 + b^2}) \geq 0, \end{aligned} \quad (\text{A11})$$

and comparing this inequality with Eq. (A3), one concludes that $W \geq 0$.

The proof that $W \leq 0$ if $\Delta_f \leq \Delta_i$ (as happens in the isothermal transformation $A \rightarrow B$ of Fig. 3) may be worked

out also in two steps, in a similar way to the above proof. In this case, one uses $a \equiv (\Delta_f/\Delta_i) \leq 1$, so that all previous inequalities will appear reversed.

APPENDIX B

In this appendix, we will show that the entropic form of Eq. (2.11),

$$\begin{aligned} S[p_1(t), p_2(t)] &= k\sqrt{p_1(t)p_2(t)}, \\ p_1(t) + p_2(t) &= 1, \end{aligned} \quad (\text{B1})$$

satisfies an H theorem in the case of an isolated system, guaranteeing that $(dS/dt) \geq 0$. For this, let us consider the time derivative of the entropic form above,

$$\begin{aligned} \frac{dS}{dt} &= \frac{k}{2} [p_1(t)p_2(t)]^{-1/2} \left[p_2(t) \frac{dp_1(t)}{dt} + p_1(t) \frac{dp_2(t)}{dt} \right] \\ &= \frac{k}{2} [p_1(t)p_2(t)]^{-1/2} [p_2(t) - p_1(t)] \frac{dp_1(t)}{dt}, \end{aligned} \quad (\text{B2})$$

where the last equality came from the normalization condition in Eq. (B1), leading to $(dp_2/dt) = -(dp_1/dt)$. Following

Refs. [44,45], we now make use of a master equation in order to prove the H theorem; for the present two-level system, the master equation gives that

$$\frac{dp_1(t)}{dt} = p_2(t)w_{21}(t) - p_1(t)w_{12}(t), \quad (\text{B3})$$

where $w_{12}(t)$ denotes the probability transition rate associated with a transition from state 1 to state 2 [i.e., $w_{12}(t)\Delta t$ represents the probability for a transition from state 1 to 2 to occur during the time interval $t \rightarrow t + \Delta t$].

Now, considering an isolated system, one assumes the symmetry for the transition rates [44], i.e., $w_{12}(t) = w_{21}(t)$; hence, substituting Eq. (B3) into Eq. (B4) one gets

$$\frac{dS}{dt} = \frac{k}{2} [p_1(t)p_2(t)]^{-1/2} [p_2(t) - p_1(t)]^2 w_{12}(t) \geq 0, \quad (\text{B4})$$

showing that the entropy of Eq. (B1) should increase (or remain unchanged) in time.

-
- [1] R. L. Liboff, *Introductory Quantum Mechanics*, 4th ed. (Addison Wesley, San Francisco, 2003).
- [2] S. Sachdev, *Quantum Phase Transitions*, 2nd ed. (Cambridge University Press, Cambridge, 2011).
- [3] B. Schumacher and M. Westmoreland, *Quantum Processes, Systems, and Information* (Cambridge University Press, Cambridge, 2010).
- [4] L. E. Reichl, *A Modern Course in Statistical Physics*, 2nd ed. (Wiley, New York, 1998).
- [5] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965).
- [6] H. B. Callen, *Thermodynamics*, 2nd ed. (Wiley, New York, 1985).
- [7] R. Hanel and S. Thurner, A comprehensive classification of complex statistical systems and an axiomatic derivation of their entropy and distribution functions, *Europhys. Lett.* **93**, 20006 (2011).
- [8] R. Hanel and S. Thurner, Generalized (c, d)-entropy and aging random walks, *Entropy* **15**, 5324 (2013).
- [9] T. D. Frank, *Nonlinear Fokker-Planck Equations: Fundamentals and Applications* (Springer, Berlin, 2005).
- [10] M. Shiino, Free energies based on generalized entropies and H-theorems for nonlinear Fokker-Planck equations, *J. Math. Phys.* **42**, 2540 (2001).
- [11] G. Kaniadakis, Non-linear kinetics underlying generalized statistics, *Physica A* **296**, 405 (2001).
- [12] G. Kaniadakis, H-theorem and generalized entropies within the framework of nonlinear kinetics, *Phys. Lett. A* **288**, 283 (2001).
- [13] T. D. Frank and A. Daffertshofer, H-theorem for nonlinear Fokker-Planck equations related to generalized thermostats, *Physica A* **295**, 455 (2001).
- [14] T. D. Frank, Generalized Fokker-Planck equations derived from generalized linear nonequilibrium thermodynamics, *Physica A* **310**, 397 (2002).
- [15] M. Shiino, Stability analysis of mean-field-type nonlinear Fokker-Planck equations associated with a generalized entropy and its application to the self-gravitating system, *Phys. Rev. E* **67**, 056118 (2003).
- [16] P. H. Chavanis, Generalized thermodynamics and Fokker-Planck equations: Applications to stellar dynamics and two-dimensional turbulence, *Phys. Rev. E* **68**, 036108 (2003).
- [17] P. H. Chavanis, Generalized Fokker-Planck equations and effective thermodynamics, *Physica A* **340**, 57 (2004).
- [18] V. Schwämmle, F. D. Nobre, and E. M. F. Curado, Consequences of the H theorem from nonlinear Fokker-Planck equations, *Phys. Rev. E* **76**, 041123 (2007).
- [19] V. Schwämmle, E. M. F. Curado, and F. D. Nobre, A general nonlinear Fokker-Planck equation and its associated entropy, *Eur. Phys. J. B* **58**, 159 (2007).
- [20] P. H. Chavanis, Nonlinear mean field Fokker-Planck equations. Application to the chemotaxis of biological populations, *Eur. Phys. J. B* **62**, 179 (2008).
- [21] V. Schwämmle, E. M. F. Curado, and F. D. Nobre, Dynamics of normal and anomalous diffusion in nonlinear Fokker-Planck equations, *Eur. Phys. J. B* **70**, 107 (2009).
- [22] M. Shiino, Nonlinear Fokker-Planck equations associated with generalized entropies: Dynamical characterization and stability analyses, *J. Phys.: Conf. Ser.* **201**, 012004 (2010).
- [23] M. S. Ribeiro, F. D. Nobre, and E. M. F. Curado, Classes of N-dimensional nonlinear Fokker-Planck equations associated to Tsallis entropy, *Entropy* **13**, 1928 (2011).
- [24] A. R. Plastino and A. Plastino, Non-extensive statistical mechanics and generalized Fokker-Planck equation, *Physica A* **222**, 347 (1995).
- [25] C. Tsallis and D. J. Bukman, Anomalous diffusion in the presence of external forces: Exact time-dependent solutions and their thermostats, *Phys. Rev. E* **54**, R2197 (1996).

- [26] C. Tsallis, Possible generalization of Boltzmann-Gibbs statistics, *J. Stat. Phys.* **52**, 479 (1988).
- [27] C. Tsallis, *Introduction to Nonextensive Statistical Mechanics* (Springer, New York, 2009).
- [28] C. Tsallis, An introduction to nonadditive entropies and a thermostistical approach to inanimate and living matter, *Contemp. Phys.* **55**, 179 (2014).
- [29] S. Zapperi, A. A. Moreira, and J. S. Andrade, Flux Front Penetration in Disordered Superconductors, *Phys. Rev. Lett.* **86**, 3622 (2001).
- [30] J. S. Andrade, Jr., G. F. T. da Silva, A. A. Moreira, F. D. Nobre, and E. M. F. Curado, Thermostatistics of Overdamped Motion of Interacting Particles, *Phys. Rev. Lett.* **105**, 260601 (2010).
- [31] M. S. Ribeiro, F. D. Nobre, and E. M. F. Curado, Time evolution of interacting vortices under overdamped motion, *Phys. Rev. E* **85**, 021146 (2012).
- [32] M. S. Ribeiro, F. D. Nobre, and E. M. F. Curado, Overdamped motion of interacting particles in general confining potentials: Time-dependent and stationary-state analyses, *Eur. Phys. J. B* **85**, 309 (2012).
- [33] M. S. Ribeiro, F. D. Nobre, and E. M. F. Curado, Comment on “Vortex distribution in a confining potential”, *Phys. Rev. E* **90**, 026101 (2014).
- [34] C. P. Poole, Jr., H. A. Farach, and R. J. Creswick, *Superconductivity* (Academic, London, 1995).
- [35] F. D. Nobre, A. M. C. Souza, and E. M. F. Curado, Effective-temperature concept: A physical application for nonextensive statistical mechanics, *Phys. Rev. E* **86**, 061113 (2012).
- [36] E. M. F. Curado, A. M. C. Souza, F. D. Nobre, and R. F. S. Andrade, Carnot cycle for interacting particles in the absence of thermal noise, *Phys. Rev. E* **89**, 022117 (2014).
- [37] R. F. S. Andrade, A. M. C. Souza, E. M. F. Curado, and F. D. Nobre, A thermodynamical formalism describing mechanical interactions, *Europhys. Lett.* **108**, 20001 (2014).
- [38] F. D. Nobre, E. M. F. Curado, A. M. C. Souza, and R. F. S. Andrade, Consistent thermodynamic framework for interacting particles by neglecting thermal noise, *Phys. Rev. E* **91**, 022135 (2015).
- [39] M. S. Ribeiro, G. A. Casas, and F. D. Nobre, Second law and entropy production in a nonextensive system, *Phys. Rev. E* **91**, 012140 (2015).
- [40] M. S. Ribeiro and F. D. Nobre, Repulsive particles under a general external potential: Thermodynamics by neglecting thermal noise, *Phys. Rev. E* **94**, 022120 (2016).
- [41] A. M. C. Souza, Describing the ground state of quantum systems through statistical mechanics, *Physica A* **390**, 2686 (2011).
- [42] A. I. Khinchin, *Mathematical Foundations of Information Theory* (Dover, New York, 1957).
- [43] R. Balian, *From Microphysics to Macrophysics* (Springer, Berlin, 1991), Vols. I and II.
- [44] B. Diu, C. Guthmann, D. Lederer, and B. Roulet, *Éléments de Physique Statistique* (Hermann, Paris, 1989).
- [45] G. A. Casas, F. D. Nobre, and E. M. F. Curado, H theorem for generalized entropic forms within a master-equation framework, *Phys. Rev. E* **93**, 032145 (2016).