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Microcanonical entropy for classical systems

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The entropy definition in the microcanonical ensemble is revisited. We propose a novel definition for the microcanonical entropy that resolve the debate on the correct definition of the microcanonical entropy. In particular we show that this entropy definition fixes the problem inherent the exact extensivity of the caloric equation. Furthermore, this entropy reproduces results which are in agreement with the ones predicted with standard Boltzmann entropy when applied to macroscopic systems. On the contrary, the predictions obtained with the standard Boltzmann entropy and with the entropy we propose, are different for small system sizes. Thus, we conclude that the Boltzmann entropy provides a correct description for macroscopic systems whereas extremely small systems should be better described with the entropy that we propose here.

Keywords: microcanonical ensemble

In many of statistical physics applications the entropy notion enters as a basic concept suitable for characterize the behaviour of macroscopic systems [1–6]. In the present manuscript, we address the problem of the correct definition of the microcanonical entropy for classical systems. In fact, the latter concern has recently become a matter of a debate where it has been discussed which one between the Boltzmann and the Gibbs definition provides the correct entropy.

A mechanically and adiabatically isolated system, at the equilibrium and composed of a macroscopic number of interacting particles is statistically described with the microcanonical ensemble. In this statistic description the relevant thermodynamical quantities are derived from the entropy S through suitable thermodynamic relations. Now, there are -at least- two accepted definitions for the microcanonical entropy, the ones commonly referred to as Boltzmann entropy and Gibbs entropy. The former is proportional to the logarithm of the density of microstates at a given “energy shell”, whereas the latter is proportional to the logarithm of the number of microstates up to a given energy. The debate as to which of these definitions of entropy is the correct one dates back to many years ago [7–16].

Very recently [17–19], it has been argued that the Gibbs entropy yields a consistent thermodynamics, and they have been discussed some consistency issues that, the microcanonical statistical mechanics founded on the Boltzmann entropy, would unveil [17, 18, 20–24]. These and other related arguments [25–27] have been contended [28–35], in what has become a lively debate. Although this may seem a marginal issue, it has crucial consequences about the foundations of statistical mechanics. For instance the negative temperatures notion wouldn’t make sense, since they are a well founded concept in the Boltzmann description, whereas, they are forbidden in the case of the Gibbs entropy since the number of microstates with energy below a given value E is a non-decreasing function of E . Even if we do not share the point of view of authors of Refs. [17–19, 23, 24], as we

have clarified in Refs. [36, 37] where we have shown that the Boltzmann entropy provides a consistent description of the microcanonical ensemble, in our opinion these authors must be given credit for having raised this key question.

A further issue raised by the authors of Refs. [17–19, 23, 24] pertains to the fact that the caloric equation of state, for instance in the simple case of an isolated ideal gas system, derived with the Boltzmann entropy is not strictly extensive. About this point, in Ref. [36, 38], we have shown that the correction to the extensive behaviour, is of the order of $1/(nd)$, and therefore it vanishes in the limit of infinite degrees of freedom. Although in the case of a macroscopic system (as the ones more often considered in statistical mechanics) this is not an issue and it represents just an aesthetical mathematical problem, it pose a relevant matter when microcanonical thermodynamics is applied to systems that for their nature do not admit the thermodynamic limit. Examples of the latter class include proteins, DNA helix, nanosystems.

In the present manuscript we propose a modified version of the Boltzmann entropy that overcomes all of these issues. In fact, this entropy reproduces the same results as the Boltzmann entropy for systems with a macroscopic number of particles and predicts the correct extensivity for the caloric equation in the case of small systems. Let $H(x)$ be a classical Hamiltonian describing an autonomous many-body system of n interacting particles in d spatial dimensions, whose coordinates and canonical momenta $(q_1 \dots, p_1, \dots)$ are represented as N -component vectors $x \in \mathbb{R}^N$, with $N = 2nd$. Moreover, we assume that no other conserved quantities do exist in addition to the total energy H [39, 40]. Let $M_E = \{x \in \mathbb{R}^N | H(x) \leq E\}$ be the set of phase-space states with total energy less than or equal to E . The Gibbs entropy for this system is

$$S_G(E) = \kappa_B \ln \Omega(E), \quad (1)$$

where κ_B is the Boltzmann constant and

$$\Omega(E) = \frac{1}{h^{nd}} \int d^N x \Theta(E - H(x)), \quad (2)$$

is the number of states with energy below E . h is the Planck constant and Θ is the Heaviside function.

The Boltzmann entropy concerns the energy level sets $\Sigma_E = \{x \in \mathbb{R}^N | H(x) = E\}$, and is given in terms of $\omega(E) = \partial\Omega/\partial E$, according to

$$S_B(E) = \kappa_B \ln(\omega(E)\Delta), \quad (3)$$

where the constant Δ with the dimension of energy makes the argument of the logarithm dimensionless, and

$$\omega(E) = \frac{1}{h^{nd}} \int d^N x \delta(E - H(x)), \quad (4)$$

is expressed in terms of the Dirac δ function. Remarkably, in the case of smooth level sets Σ_E , $\omega(E)$ can be cast in the following form [39–41]

$$\omega(E) = \frac{1}{h^{nd}} \int_{\Sigma_E} \frac{m^{N-1}(\Sigma_E)}{\|\nabla H(x)\|}, \quad (5)$$

where $m^{N-1}(\Sigma_E)$ is the metric induced from \mathbb{R}^N on the hypersurface Σ_E and $\|\nabla H(x)\|$ is the norm of the gradient of H at x .

The entropy that we propose here is

$$S(E) = \kappa_B \ln(\sigma(E)\Delta^{1/2}), \quad (6)$$

where

$$\sigma(E) = \frac{1}{h^{nd}} \int_{\Sigma_E} m^{N-1}(\Sigma_E). \quad (7)$$

In the case of a system of identical particles, to avoid the Gibbs paradox it is in order to introduce a factor $1/n!$ in the definitions of Ω , ω and σ , Eqs. (2), (4), (5) and (7), as we will do in the following.

The entropy is the fundamental thermodynamic potential of the microcanonical ensemble from which secondary thermodynamic quantities are obtained by derivatives with respect to the control parameter: the total energy E , the occupied volume V and, possibly, further Hamiltonian parameters A_μ (in the following we omit to indicate explicitly the dependence by A_μ in order to simplify the notation). The inverse temperatures $\beta = (\kappa_B T)^{-1}$ is derived from the the entropy according to $\beta = (\partial S/\partial E)/\kappa_B$, thus in the three cases under consideration we have

$$\beta_G = \frac{\Omega'}{\Omega}, \quad (8)$$

$$\beta_B = \frac{\omega'}{\omega}, \quad (9)$$

$$\beta = \frac{\sigma'}{\sigma}, \quad (10)$$

where the symbol $'$ denotes the partial derivative of the corresponding term with respect to energy E .

A basic requisite for S is to allow the measure of temperature and the other secondary thermodynamic quantities via microcanonical averages. In terms of the microscopic dynamics, from the Liouville theorem it follows that the invariant measure $d\mu$ for the dynamics on each energy level-set Σ_E is $d\mu = m^{N-1}(\Sigma_E)/\|\nabla H\|$. In the case of the Boltzmann entropy, the temperature definition meets the mentioned requisite since

$$\beta_B = \left\langle \nabla \left(\frac{\nabla H}{\|\nabla H\|^2} \right) \right\rangle, \quad (11)$$

where $\langle \rangle$ indicates the microcanonical average

$$\langle \phi \rangle = \frac{1}{\omega} \int_{\Sigma_E} \phi d\mu. \quad (12)$$

Eq. (11) is derived in Ref. [41] for the case of many-particle systems for which the energy is the only conserved quantity, and in Refs. [39, 40] for the general case of two or more conserved quantities. On the contrary, the Gibbs definition of temperature does not meet such important requisite as diffusely discussed in Ref. [36]. By using by the Federer-Laurence derivation formula [39, 40, 42, 43], in the case of the proposed entropy we get

$$\beta = \frac{\sigma'}{\sigma} = \frac{\sigma'/\omega}{\sigma/\omega} = \frac{\langle \nabla \left(\frac{\nabla H}{\|\nabla H\|} \right) \rangle}{\langle \|\nabla H\| \rangle}. \quad (13)$$

This shows that also S , besides S_B , satisfies the requirement to provide secondary thermodynamic quantities measurable as microcanonical averages. In passing, we note that under the hypothesis of ergodicity, the averages of each dynamical observable of the system can be equivalently measured along the dynamics.

As a simple test let us consider a classical ideal gas in d -spatial dimensions composed of n identical particles of mass m for which it is easy matter to verify that

$$\Omega(E, V) = \frac{V^n (2\pi m)^{nd/2}}{\Gamma(\frac{nd}{2} + 1) n! h^{nd}} E^{nd/2}, \quad (14)$$

$$\omega(E, V) = \frac{V^n (2\pi m)^{nd/2}}{\Gamma(\frac{nd}{2}) n! h^{nd}} E^{nd/2-1}, \quad (15)$$

$$\sigma(E, V) = \frac{2V^n (2\pi m)^{nd/2}}{\Gamma(\frac{nd}{2}) n! h^{nd}} E^{(nd-1)/2}, \quad (16)$$

where the factor $1/n!$ is introduced in order to avoid the Gibbs paradox. From these formulas one finds the following expression of the caloric equation

$$\beta_G^{-1} = \frac{E}{nd/2}, \quad (17)$$

$$\beta_B^{-1} = \frac{E}{(nd/2 - 1)}, \quad (18)$$

$$\beta^{-1} = \frac{E}{(nd - 1)/2}. \quad (19)$$

In the count for the degrees of freedom for a system of free particles, just the kinetic term contributes. Thus, in d spatial dimensions a system of n particles have nd degrees of freedom and, by setting the energy E to a given value we are left with $nd - 1$ degrees of freedom. Therefore, among these only the latter expression is exactly extensive and, hence, rigorously satisfies the equipartition theorem for any n . With an analogous calculation, it is easy matter to show that for a system of n independent identical harmonic oscillators, of mass m and frequency ν in d spatial dimensions the caloric equations derived from the three entropies are

$$\beta_G^{-1} = \frac{E}{nd}, \quad (20)$$

$$\beta_B^{-1} = \frac{E}{(nd - 1)}, \quad (21)$$

$$\beta^{-1} = \frac{E}{(2nd - 1)/2}. \quad (22)$$

In this case, either the coordinates and the motional degrees of freedom contribute to the count of the degrees of freedom of the system. Thus, when the energy has a fixed value E , the number of degrees of freedom are $2nd - 1$ and only S brings to the correct equipartition formula.

In addition to lead up the correct relation between total energy and true number of degrees of freedom, the entropy we propose rigorously satisfies the postulate of equal a-priori probability which is a very foundations of the equilibrium microcanonic statistical mechanics. As a matter of fact, for a generic isolated physical-system at the equilibrium, a given thermodynamic state is completely determined when we know the values of the macroscopic parameters as energy, volume, and possibly further external parameters, that characterize such system. In this way, from a thermodynamic point of view we do not distinguish between the states of the system represented by different points on the same energy level and consistent with the further constraints. This is just what Eq. (5) does, it “counts the number of microstates satisfying the macroscopic constraint $H = E$, consistently to the above mentioned postulate. On the contrary, the standard Boltzmann entropy adopts a place-dependent weight $1/\|\nabla H\|$.

In order to better clarify the connection between the Boltzmann entropy and that one we propose, let us perform the following rough calculation. For a system with N degrees of freedom, if $\Delta E \ll E$, approximatively we have

$$\Omega(E + \Delta E) - \Omega(E) \approx \omega(E)\Delta E + O(\Delta E^2), \quad (23)$$

on the other hand, for the Cavalieri's principle, we have

$$\Omega(E + \Delta E) - \Omega(E) \approx \left(\sigma(E)\Delta^{1/2} \right) \frac{\Delta E}{\Delta} + O(\Delta E^2). \quad (24)$$

Hence it results $\sigma(E)\Delta^{1/2} = \omega(E)\Delta + O(N^2)$ and, consequently

$$\lim_{N \rightarrow \infty} \frac{1}{N} \left(\ln(\sigma\Delta^{1/2}) - \ln(\omega\Delta) \right) = 0. \quad (25)$$

This makes evident that in the limit of large number of degrees of freedom, the proposed entropy predicts the same results as the Boltzmann entropy, whereas, in the case of systems with small N the two entropies differ from each other.

In order to verify our assumption, we have tested the proposed entropy on two systems: the two dimensional Φ^4 model and a one dimensional model of rotors.

The ϕ^4 model [44–47] is defined by the Hamiltonian

$$H = \sum_{\mathbf{j}} \frac{1}{2} \pi_{\mathbf{j}}^2 + V(\phi) \quad (26)$$

where

$$V(\phi) = \sum_{\mathbf{j}} \left[\frac{\lambda}{4!} \phi_{\mathbf{j}}^4 - \frac{\mu^2}{2} \phi_{\mathbf{j}}^2 + \frac{J}{4} \sum_{\mathbf{k} \in I(\mathbf{j})} (\phi_{\mathbf{j}} - \phi_{\mathbf{k}})^2 \right], \quad (27)$$

$\pi_{\mathbf{j}}$ is the conjugate momentum of the variable $\phi_{\mathbf{j}}$ that defines the field at \mathbf{j}^{th} site. Indeed, $\mathbf{j} = (j_1, j_2)$ denotes a site of a two dimensional lattice and $I(\mathbf{j})$ are the nearest neighbour lattice sites of the \mathbf{j}^{th} site. The coordinates of the sites are integer numbers $j_k = 1, \dots, N_k$, $k = 1, 2$, so that the total number of sites in the lattice is $N = N_1 N_2$. Furthermore periodic boundary conditions are assumed. The local potential displays a double-well shape whose minima are located at $\pm \sqrt{3! \mu^2 / \lambda}$ and to which it corresponds the ground-state energy per particle $e_0 = -3! \mu^4 / (2\lambda)$. At low-energies the system is dominated by an ordered phase where the time averages of the local field are not vanishing. By increasing the system energy the system undergoes a second order phase-transition and the local \mathbb{Z}_2 symmetry is restored. In fact, at high energies the time averages of the local field go to zero.

The second model [32] is composed by N rotators with canonical coordinates $\phi_1, \dots, \phi_N, \pi_1, \dots, \pi_N$ and Hamiltonian

$$H = \sum_{j=1}^N [1 - \cos(\pi_j)] + \epsilon \sum_{j=1}^N [1 - \cos(\phi_j - \phi_{j-1})], \quad (28)$$

where is assumed $\phi_0 = 0$. The form of kinetic and potential terms in (28) makes the energy bounded either from above and from below and such Hamiltonian implies the existence of negative Boltzmann temperatures [32].

We have numerically integrated the equation of motion associated to the Hamiltonian of both the models, by using a third order symplectic algorithm and starting from initial conditions corresponding to different values of the system total energy E . We have measured along

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