

On the dispute between Boltzmann and Gibbs entropy

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Very recently, the validity of the concept of negative temperature has been challenged by several authors since they consider Boltzmann's entropy (that allows negative temperatures) inconsistent from a mathematical and statistical point of view, whereas they consider Gibbs' entropy (that does not admit negative temperatures) the correct definition for microcanonical entropy.

In the present paper we prove that for systems with equivalence of the statistical ensembles Boltzmann entropy is the correct microcanonical entropy. Analytical results on two systems supporting negative temperatures, confirm the scenario we propose. In addition, we corroborate our proof by numeric simulations on an explicit lattice system showing that negative temperature equilibrium states are accessible and obey standard statistical mechanics prevision.

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INTRODUCTION

The concept of negative absolute temperature was¹ invoked to explain the results of experiments with nuclear-spin systems carried out by [2], [3] and [4]. Shortly after these experiments, [5] discussed the thermodynamic implications of negative absolute temperature and their meaning in statistical mechanics, thereby granting this concept a well-grounded place in physics [6, 7].

The microcanonical ensemble, which provides the statistical description of an isolated system at equilibrium, is the most appropriate venue to discuss negative temperatures. In this ensemble, the thermodynamic quantities, like temperature and specific heat, are derived from the entropy through suitable thermodynamic relations. For instance, the inverse temperature is proportional to the derivative of the entropy with respect to the energy. In equilibrium statistical mechanics, there are at least two commonly accepted definitions of entropy: the Boltzmann entropy is proportional to the logarithm of the number of microstates in a given "energy shell", whereas the Gibbs entropy 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 has been going on for a long time, [8–17] although the general consensus is that they are basically interchangeable. In fact, for standard systems² with a large number of degrees of freedom they are practically equivalent. Full equivalence is obtained in the thermodynamic limit. The existence of negative-temperature states provides a major bone of contention in the debate. In fact,

negative temperatures emerge in the Boltzmann description whenever the number of microstates in a given energy shell is a decreasing function of the relevant energy. On the contrary, the Gibbs temperature can never be negative, since the number of microstates with energy below a given value is always a non-decreasing function of such value. Thus, systems admitting negative (Boltzmann) temperatures provide an ideal context to address the question of the correct definition of entropy.

Recently, in several recent papers [18–20] it was argued that for a broad class of physical systems, including standard classical Hamiltonian systems, only the Gibbs entropy yields a consistent thermodynamics, and that, consequently, negative temperatures are not achievable within a standard thermodynamical framework. In this respect, what is usually referred to Boltzmann *temperature* would not possess the required properties for a temperature [18, 19, 21–24]. These and other related arguments [25–27] have been contended by several authors [28–32], in what has become a lively debate.

In the present paper we focus on the class of systems (standard or not) whose canonical (or, possibly, grand canonical) ensemble is equivalent to the microcanonical ensemble. We show that such equivalence can be rigorously satisfied only if the thermodynamics of the latter ensemble is derived by the Boltzmann entropy. For such systems we show that the Boltzmann temperature provides a consistent description with those ones of the canonical and grand canonical ensembles. On the contrary, the temperature predicted by Gibbs is irreconcilable with that one of the latter ensembles.

The outline of the paper is the following. In Sec. we summarize the essential features of systems in which negative Boltzmann temperatures are expected. In Sec. we consider an isolated Hamiltonian system and, under the hypothesis of ergodicity, we show that only in the case of the Boltzmann entropy all the thermodynamic quantities are derived as time averages (along the dynamics) of suitable functions. In Sec. we prove that, for systems whose canonical and microcanonical ensembles are equiv-

¹ This was not the first place where negative temperatures have been considered, in fact [1] two years before proposed the existence of negative temperatures in order to explain the formation of large scale vortices by clustering of small ones in hydrodynamic systems.

² With "standard system" we mean a system with unbounded energy from above for which the energy goes to infinity when one of the canonical coordinates goes to infinity.

alent, the correct correspondence between β and ϵ is the one derived with the Boltzmann entropy. Furthermore we show that, in the thermodynamic limit, the Gibbs and Boltzmann temperatures do coincide when the latter is positive whereas the inverse Gibbs temperature is identically null in the region where Boltzmann provides negative values for the temperature. In Sec. we show that the mathematical relations that come from thermodynamic consistence constraint are well satisfied by the Boltzmann entropy and that, in the case of statistical ensemble equivalence, s_B is the only correct microcanonical entropy. In section , we give two examples of systems supporting negative Boltzmann temperatures for which the grand-canonical (or canonical) ensemble and the microcanonical description given by the Boltzmann entropy do agree on the whole parameter space and on the complete range of values of the energy-density. We show that the equipartition theorem fails for system with negative Boltzmann temperatures in Sec. . In Sec. we show through numerical simulations on a specific system, that negative temperatures are accessible. We show that irrespective of the sign of the temperature, a large microcanonical lattice acts as a thermostat for a small grand canonical sublattice, and this confirms the ensemble equivalence. Furthermore, we have shown that, irrespective of the sign of the temperature, two isolated systems at equilibrium at different inverse temperatures, reach an equilibrium state at an intermediate inverse temperature, after that they are brought in contact.

NEGATIVE TEMPERATURES

The microcanonical ensemble describes the equilibrium properties of an isolated system, that is to say in which energy, and possibly further quantities, are conserved. Within the microcanonical description, all the thermodynamic quantities are derived from the entropy, for instance the inverse temperature of the system is defined as

$$\beta = \frac{1}{k_B} \frac{\partial s}{\partial \epsilon}, \quad (1)$$

where k_B is the Boltzmann constant and $s(\epsilon)$ is the entropy density corresponding to a given energy density ϵ . The two alternative definitions for the entropy used in equilibrium statistical mechanics are ascribed to Boltzmann and Gibbs³. According to Boltzmann's definition

$$s_B(\epsilon) = L^{-1} k_B \ln(\omega(\epsilon)\Delta), \quad (2)$$

where $\omega(\epsilon)$ is the density of microstates at a fixed value energy density ϵ and, possibly, at a fixed value of the

additional conserved quantities, Δ is a constant with the same dimension as ϵ , and L is the number of degrees of freedom in the system. The Gibbs entropy is

$$s_G(\epsilon) = L^{-1} k_B \ln \Omega(\epsilon), \quad (3)$$

where $\Omega(\epsilon)$ is the number of microstates with energy density less than or equal to ϵ and, possibly, at a fixed value of the additional conserved quantities. It is known that in the thermodynamic limit these two definitions of entropy lead to equivalent thermodynamic results in “standard” systems [34]. So far, these two entropy definitions are often used in an alternative (interchangeable) way in statistical mechanics, by resorting to the most suitable form depending on the specific problem considered. These two entropy definitions are connected by the relation between ω and Ω

$$\omega(\epsilon) = \frac{\partial \Omega}{\partial \epsilon}(\epsilon), \quad (4)$$

Since $\partial \Omega / \partial \epsilon \geq 0$, Gibbs' temperatures are not negative and consequently the two entropies have incompatible outcomes if applied to systems that admit negative Boltzmann temperatures.

A necessary (although not sufficient) condition for a system for having negative temperatures is the boundedness of the energy (as in the case of nuclear-spin systems discussed by Pound *et al*), in this case a local maximum inside the system's density energy interval of the Boltzmann entropy $s_B(\epsilon)$ is not forbidden and, both positive and negative Boltzmann temperatures are possible.

Hamiltonians with bounded energies can also be characterized by the existence of more than one first integral of motion and, for this reason, in addition to the statistical mechanics of systems with one first integral, we will consider also the case of systems with more than one first integrals. Within the latter class for instance there are models usually employed for describing ultracold atoms. The possibility of observing negative temperature states in ultracold systems, has been theoretically predicted by some authors with different approaches [35–37] and, the experimental evidence of the existence of states for motional degrees of freedom of a bosonic gas at negative (Boltzmann) temperatures, have been achieved a few years ago by [38]. The validity of this remarkable experiment has been contested in the former paper by Dunkel and Hilbert [18]. Successively, these same authors and Hanggi have co-signed some papers [19, 20] in which is affirmed that for a broad class of systems that includes all “standard classical Hamiltonian systems, only the Gibbs entropy (which implies a non-negative temperature) satisfies all three thermodynamic laws exactly. The criticisms raised by [18] have engendered a glowing debate between supporters of the Gibbs entropy [19–24, 26, 27, 31] and the ones that consider the Boltzmann entropy correct [28–30, 39–41].

³ We refer to [33] for historical details.

**DYNAMICS AND STATISTICAL MECHANICS
FOR CLASSICAL SYSTEMS**

Let us consider first a generic classical many-particle system described by an autonomous Hamiltonian $H(x_1, \dots, x_L)$, in which the energy is the sole first integral of motion. The Boltzmann entropy density $s_B(\epsilon)$ in this case is given by

$$s_B(\epsilon) = L^{-1} k_B \ln \int d^L \mathbf{x} \delta(L\epsilon - H(\mathbf{x})), \quad (5)$$

whereas the one of Gibbs is

$$s_G(\epsilon) = L^{-1} k_B \ln \int d^L \mathbf{x} \Theta(L\epsilon - H(\mathbf{x})), \quad (6)$$

where δ is the Dirac function and Θ is the Heaviside function.

As a consequence of the conservation of energy, the system dynamics takes place on energy-level sets. From Liouville theorem it descends that the measure of the Euclidean volume is preserved by the dynamics and this induces a measure μ conserved on each energy level set Σ_ϵ of energy density ϵ which is given by [42, 43]

$$d\mu = \frac{d\Sigma}{\|\nabla H\|}, \quad (7)$$

where $d\Sigma$ is the Euclidean measure induced on Σ_ϵ and $\|\cdot\|$ is the Euclidean norm.

This means that, under the hypothesis of ergodicity, the averages of each dynamical observable Φ of the system can be equivalently measured along the dynamics as

$$\langle \Phi \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau dt \Phi(t), \quad (8)$$

or as average on the hypersurface Σ_ϵ according to

$$\langle \Phi \rangle = \frac{\int_{\Sigma_\epsilon} d\mu \Phi}{\int_{\Sigma_\epsilon} d\mu}. \quad (9)$$

Now, it is reasonable to expect that the temperature, the specific heat, and the other thermodynamic observables could be measured as time averages of suitable observables Φ along the dynamics, in a way analogous to Eq. (8). Consequently, when ergodicity holds, the measures of these quantities have to be derived from averages upon the energy level sets Σ_ϵ , according to Eq. (9). Furthermore, temperature, specific heat and other thermodynamic quantities depend on derivatives of the microcanonical entropy with respect to energy. Therefore, they are computed by means of a functional of the form (9) *if and only if* the microcanonical entropy is defined à la Boltzmann. This fact is proven by [44] in the case of many-particle systems for which the Hamiltonian is the only conserved quantity, and in Ref. [45] and Ref. [46]

for the case of two and $k \in \mathbb{N}$ conserved quantities, respectively. In the simpler case studied in Ref. [44] e.g., it results

$$s_B = L^{-1} k_B \ln \int_{\Sigma_\epsilon} d\mu,$$

and from the definition (1) in the case of Boltzmann we obtain ⁴

$$\beta_B = \frac{\int_{\Sigma_\epsilon} d\mu \nabla \cdot (\nabla H / \|\nabla H\|^2)}{\int_{\Sigma_\epsilon} d\mu}, \quad (10)$$

where $\beta_B = 1/(k_B T_B)$. In the case of s_G the expression for the inverse temperature is

$$\beta_G = \frac{\int_{\Sigma_\epsilon} d\mu}{\int_{M_\epsilon} d^L \mathbf{x}}, \quad (11)$$

where $M_\epsilon = \{\mathbf{x} \in \mathbb{R}^L | H(\mathbf{x}) \leq L\epsilon\}$, that cannot be expressed in the form (9). In other words, by adopting the Gibbs entropy definition when ergodicity holds true, one has to trust in the very singular fact that time averages of thermodynamic quantities taken along the dynamics (and then on the energy level set Σ_ϵ) coincide with the averages of quantities taken on a set that includes all the energy levels below to the one on which the dynamics takes place, analogously to Eq. (11) of the inverse temperature⁵. About this point, one could comment that the Gibbs temperature could be measured as a microcanonical average by resorting to the equipartition theorem. Nevertheless, as we will show in Sec. , for instance in the case of systems with negative Boltzmann temperatures, the “standard” equipartition theorem fails. Thus, we conclude interpreting this as a first signal of inconsistency for the Gibbs entropy.

It is worth emphasizing that in the case of $k > 1$ conserved quantities, a geometric structure similar to the one of Eq. (10) keeps on to be valid. In fact, in Ref. [45] it has been considered the case $k = 2$ by studying a general classical autonomous many-body Hamiltonian system, whose coordinates and canonical momenta are indicated with $\mathbf{x} \in \mathbb{R}^L$, and for which $V(\mathbf{x})$ is a further conserved quantity in involution with H . For such a system, the motion takes place on the manifolds $\mathcal{M} = \Sigma_\epsilon \cap V_u$, where $V_u = \{(\mathbf{x}) \in \mathbb{R}^L | V(\mathbf{x}) = Lu\}$ are subsets of \mathbb{R}^L where V is constant. In Ref. [45] it is shown that

$$s_B = L^{-1} k_B \ln \int d^L \mathbf{x} \delta(H(\mathbf{x}) - L\epsilon) \delta(V(\mathbf{x}) - Lu) = L^{-1} k_B \ln \int_{\mathcal{M}} \frac{d\tau}{W}, \quad (12)$$

⁴ The Federer-Laurence derivation formula [47, 48] is $\partial^k (\int_{\Sigma_\epsilon} \psi d\Sigma) / \partial \epsilon^k = L^k \int_{\Sigma_\epsilon} A^k(\psi) d\Sigma$, where $A(\bullet) = 1 / \|\nabla H\| \nabla \cdot (\nabla H / \|\nabla H\| \nabla H \|\bullet\|)$.

⁵ In addition to the case of the inverse temperature, the same scenario hold for the chemical potential.

where $d\tau$ is the volume form of \mathcal{M} , and

$$W = \left[\sum_{\mu < \nu = 1}^L \left(\frac{\partial H}{\partial x^\mu} \frac{\partial V}{\partial x^\nu} - \frac{\partial H}{\partial x^\nu} \frac{\partial V}{\partial x^\mu} \right)^2 \right]^{1/2}. \quad (13)$$

Furthermore, in [45] it is derived the generalization of (10) that gives the microcanonical inverse temperature for these systems, it results

$$\beta_B = \frac{\int_{\mathcal{M}} d\tau \Phi_2}{\int_{\mathcal{M}} d\tau}, \quad (14)$$

where the complicated functional is now

$$\Phi_2(x) = \frac{W}{\nabla H \cdot n^\xi} \left[\nabla \left(\frac{n^\xi}{W} \right) - \frac{(n^\nu \cdot \nabla)(n^\xi)}{W} \cdot n^\nu \right], \quad (15)$$

that is given in terms of the unitary vectors $n^H = \nabla H / \|\nabla H\|$ and $n^V = \nabla V / \|\nabla V\|$ through the vector $\xi = n^H - (n^H \cdot n^V)n^V$, from which is defined the unitary vector $n^\xi = \xi / \|\xi\|$ that appears in Eq. (15). *Remarkably, by exchanging H and V in expression (15) the functional so obtained allows to measure the chemical potential of the system. This fact shows a further “esthetic advantage” of the Boltzmann entropy: it leads to expressions formally identical independently from the number of conserved quantities.*

COMPARISON BETWEEN STATISTICAL ENSEMBLES

In a statistical description of a many-body system, temperature has a different meaning depending on the statistical ensemble. In the canonical ensemble and in the grand-canonical one, (inverse) temperature is just a Lagrangian parameter that is introduced in order to fix the mean energy. On the contrary, in the microcanonical ensemble the temperature is a quantity derived from the entropy density s , according to the relation $T = (\partial s / \partial \epsilon)^{-1}$. Therefore it is clear that $T(\epsilon)$ will depend on the entropy definition assumed within the microcanonical statistical description. The main point here is that the meaning of temperature cannot be reduced to the issue of the coherent definition inside to microcanonical ensemble, at least if there is equivalence of ensembles. In the latter case, one expects that temperature, or more in general thermodynamics, defined for a system by two microscopic models, for instance canonical and microcanonical, coincide in the thermodynamic limit and they coincide with the experimentally known thermodynamics of such system [49]. This amounts to requiring that the thermodynamics of a large isolated (microcanonical) system and the thermodynamics of a “small” (even if big enough) subsystem of it coincide. In fact, in the thermodynamic limit, the complement of the subsystem, acts on it as a

thermostat and the subsystem is well described in the canonical ensemble. The problem of equivalence of ensembles is only incompletely solved [50], for instance it is known that systems with long-range interaction can violate this equivalence. In fact, for this class of systems the energy is not additive: a system cannot be divided into independent macroscopic parts at variance of the case of the short-range interaction. In the following we show that if there is equivalence between statistical ensembles, Helmholtz free energy density is the Legendre transform of Boltzmann entropy density and vice versa. Consequently, thermodynamics derived for a systems by Boltzmann entropy and by canonical partition function rigorously coincide in the thermodynamic limit. We consider this as a strong evidence supporting the legitimacy of the Boltzmann entropy. Let us now discuss about a case where there is not equivalence between canonical and microcanonical ensembles. This is the case of a system with long-range interaction that undergoes a first-order phase transition. We refer to [51] for details. In summary the Boltzmann entropy for a system with these features is not a concave function, consequently it cannot be the Legendre transformation of the Helmholtz free-energy density, and $\beta_B(\epsilon)$ is a not-invertible function. In cases like this, the canonical ensemble has not foundation since it cannot be derived from the microcanonical ensemble, unlike the case of the additive systems [52], where it can. Therefore, the case of the long-range interactions are outside the class of systems to which our proof applies. Nevertheless we consider Boltzmann’s entropy the correct definition also for this class of systems.

In the following we will consider two explicit systems, one of which has two conserved quantities, accordingly in this section we give our proof for a system with this feature. The restriction of our derivation to the case of a system where energy is the sole conserved quantity is straightforward. Let us consider an arbitrary classical many-body Hamiltonian system with $k = 2$ first integrals of motion, H and a further conserved quantity V which is in involution with H . In order to compare the canonical and the microcanonical description for such class of systems, we decompose the canonical partition function as follows [49]

$$\begin{aligned} Z(\beta, L) &= \int d^L \mathbf{x} e^{-\beta H(\mathbf{x})} \delta(Lu - V(\mathbf{x})) = \\ &= L \int_{\epsilon_m}^{\epsilon_M} d\epsilon e^{-\beta L \left(\epsilon - \frac{s_B(\epsilon)}{k_B \beta} \right)} \end{aligned} \quad (16)$$

where ϵ_m and ϵ_M are the minimum and the maximum of the admitted energy density $\epsilon := E/L$, respectively and $s_B(\epsilon)$ is exactly Boltzmann’s microcanonical entropy density. Furthermore, note that we have made use of the generalization [45] of the co-area formula [47] which is of very general validity and holds also for Hausdorff measurable sets. It is worth emphasizing that in Eq. (16) β represents just a (Lagrangian) parameter and it

is only thanks to the comparison between canonical and microcanonical ensemble that one can ascribe to β the meaning of inverse temperature [49]. In order to connect the canonical description to the microcanonical description one has to observe that, roughly speaking, the partition function Z_L depends on the competition between the two terms $e^{-\beta\epsilon L}$ and e^{Ls_B/k_B} which are exponentially decreasing and increasing with L , respectively. Thus, by the saddle point/Laplace method, the following asymptotic approximation ($L \gg 1$) for the partition function holds

$$Z_L(\beta) \approx L \sqrt{\frac{2\pi k_B}{-L s_B''}} e^{-\beta L \left(\epsilon^* - \frac{s_B(\epsilon^*)}{k_B \beta} \right)} \quad (17)$$

where $s_B'' = \frac{\partial^2 s_B}{\partial \epsilon^2}(\epsilon^*)$, and $\epsilon^* := \epsilon(\beta)$ is the solution of

$$\beta = \frac{1}{k_B} \frac{\partial s_B}{\partial \epsilon}(\epsilon). \quad (18)$$

Therefore the canonical free energy f is

$$f(\beta) := \lim_{L \rightarrow \infty} -\frac{1}{\beta L} \ln Z_L(\beta) = \left(\epsilon^* - \frac{s_B^\infty(\epsilon^*)}{k_B \beta} \right), \quad (19)$$

where β and ϵ^* are related by Eq. (18), *the Boltzmann definition of microcanonical temperature*. In other words, the thermodynamic limit of the dimensionless Boltzmann's entropy $s_B^\infty(\epsilon)/k_B$, as a function of the density energy ϵ , and the dimensionless Helmholtz free energy $\beta f(\beta)$, as a function of the inverse Boltzmann absolute temperature β , are connected by a Legendre transformation

$$\beta f(\beta) = \inf_{\epsilon} \left(\beta \epsilon - s_B^\infty(\epsilon)/k_B \right), \quad (20)$$

and this relation is valid only in the case of Boltzmann's definitions. This fact shows that whenever there is equivalence between the canonical and the microcanonical ensemble, *the only possible definition for the microcanonical temperature is the Boltzmann's*.

It is worth remarking a general behaviour of system admitting negative Boltzmann temperatures. From Eqs. (4) and (5) it follows

$$\Omega(\epsilon) = \int_{\epsilon_{min}}^{\epsilon} d\epsilon' e^{L s_B(\epsilon')/k_B}, \quad (21)$$

thus when $s_B(\epsilon)$ has a local maximum at $\tilde{\epsilon}$ by using the Laplace method we deduce the following asymptotic approximate ($L \gg 1$) expressions

$$\Omega(\epsilon) \approx \frac{k_B}{L s_B'(\tilde{\epsilon})} e^{L s_B(\tilde{\epsilon})/k_B}, \quad \epsilon < \tilde{\epsilon} \quad (22)$$

$$\Omega(\epsilon) \approx \sqrt{-\frac{2\pi k_B}{L s_B''(\tilde{\epsilon})}} e^{L s_B(\tilde{\epsilon})/k_B}, \quad \epsilon > \tilde{\epsilon}, \quad (23)$$

which, in the thermodynamic limit, yields

$$\beta_G(\epsilon) := \beta_B(\epsilon), \quad \epsilon < \tilde{\epsilon} \quad (24)$$

$$\beta_G(\epsilon) := 0, \quad \epsilon > \tilde{\epsilon}. \quad (25)$$

The peculiar behaviour just here summarized shows in which way the Gibbs entropy and the Boltzmann entropy are inequivalent in the thermodynamic limit in the case of systems that allow negative Boltzmann temperatures.

CRITIQUE OF CONSISTENCY OF BOLTZMANN ENTROPY

The criticisms to the thermodynamic consistency of the Boltzmann's entropy raised by [18] and [20] are based on the fact that, Gibbs entropy ($s = s_G$) satisfies the identities

$$\left(\frac{\partial s}{\partial \epsilon} \right)_{\mathbf{a}}^{-1} \left(\frac{\partial s}{\partial a_\mu} \right)_{\epsilon, a_\nu \neq a_\mu} = - \left(\frac{\partial \epsilon}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} \quad (26)$$

$$\left(\frac{\partial s}{\partial \epsilon} \right)_{\mathbf{a}}^{-1} \left(\frac{\partial s}{\partial a_\mu} \right)_{\epsilon, a_\nu \neq a_\mu} = - \left\langle \frac{\partial h}{\partial a_\mu} \right\rangle, \quad (27)$$

whereas Boltzmann entropy ($s = s_B$) does not. Here a_μ are intensive parameters of the Hamiltonian density $h = H/L$ and $\langle \cdot \rangle$ denotes the microcanonical average calculated with the density operator

$$\rho = \frac{\delta(H - E)}{\int d^N \mathbf{x} \delta(H(\mathbf{x}) - E)}.$$

Actually, it is easy to prove that Eq. (26) holds also in the case $s = s_B$. In fact, identity (26) is a trivial consequence of the chain relation (see pag. 20 of [53]) which is valid independently from the chosen entropy definition, and it is a mere consequence of the fact that there exists an equation of state for the entropy density s , energy density ϵ and some further density parameters a (e.g. the system volume density). Let us prove this point. Let F be a differentiable function which defines a surface by means of the equation $F(s, \epsilon, a) = const$, it is easy matter to verify that

$$\left(\frac{\partial s}{\partial \epsilon} \right)_a \left(\frac{\partial \epsilon}{\partial a} \right)_s \left(\frac{\partial a}{\partial s} \right)_\epsilon = -1, \quad (28)$$

in fact it is $\partial_s F ds + \partial_\epsilon F d\epsilon + \partial_a F da = 0$, and hence, in the case of a variation with $da = 0$, we get

$$\left(\frac{\partial s}{\partial \epsilon} \right)_a = - \left(\frac{\partial_\epsilon F}{\partial_s F} \right).$$

By a cyclic permutation of the symbols s, ϵ, a , we get the identities

$$\left(\frac{\partial \epsilon}{\partial a} \right)_s = - \left(\frac{\partial_a F}{\partial_\epsilon F} \right), \quad \left(\frac{\partial a}{\partial s} \right)_\epsilon = - \left(\frac{\partial_s F}{\partial_a F} \right),$$

and hence Eq. (28). Now, for both the entropies we can write the following equation

$$F(s, \epsilon, a) := s - k \ln \mathcal{O}(\epsilon, \mathbf{a}) = 0, \quad (29)$$

where in the case of Gibbs' entropy density, s_G , $\mathcal{O} := \Omega$, whereas for case of Boltzmann's entropy density, s_B , $\mathcal{O} := \omega$. In both the cases, from Eq. (28) we get

$$\left(\frac{\partial \epsilon}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} \left(\frac{\partial a_\mu}{\partial s} \right)_{\epsilon, a_\nu \neq a_\mu} \left(\frac{\partial s}{\partial \epsilon} \right)_{\mathbf{a}} = -1,$$

and hence

$$T \left(\frac{\partial s}{\partial a_\mu} \right)_{\epsilon, a_\nu \neq a_\mu} = - \left(\frac{\partial \epsilon}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu}, \quad (30)$$

where $T = (\partial s / \partial \epsilon)_{\mathbf{a}}^{-1}$. This proves that the equality of Eq. (26) is valid both in the case of the Gibbs' entropy and in the Boltzmann case.

Let us now consider Eq. (27). By resorting to the Gauss theorem, one can prove that this identity is rigorously verified only in the case of the Gibbs entropy $s = s_G$. Thus, [18] have concluded that the identity between the second members of Eqs. (26) and (27) is the proof of the thermodynamic and mathematical consistency of Gibbs entropy and a proof of inconsistency for the Boltzmann entropy, since the latter does not satisfies such identities.

Nevertheless, identity

$$\left(\frac{\partial \epsilon}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} := \left(\frac{\partial \langle h \rangle}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} = \left\langle \frac{\partial h}{\partial a_\mu} \right\rangle \quad (31)$$

is rigorously valid only when $\langle \cdot \rangle$ is the canonical averages whereas it does not hold for the case of the microcanonical density operator ρ . See appendix for further considerations about this point.

On the contrary, one can derive a robust consistency condition for systems for which there is statistical ensemble equivalence. In fact, the first member of equation (27) is minus the generalized pressure p_μ and, *from the thermodynamic Maxwell relations that are valid independently from any given statistical ensemble*, it results [53]

$$p_\mu = - \left(\frac{\partial f}{\partial a_\mu} \right)_{T, a_\nu \neq a_\mu}.$$

Now, we have proved Eq. (19) that holds when entropy is a concave function, e.g. for standard systems with short range interaction. Thus for this class of systems Eq. (19) yields⁶

$$p_\mu = - \left(\frac{\partial \epsilon^*}{\partial a_\mu} - \frac{\frac{\partial s_B^\infty(\epsilon^*)}{\partial a_\mu}}{k_B \beta} - \frac{\frac{\partial s_B^\infty(\epsilon^*)}{\partial \epsilon^*}}{k_B \beta} \frac{\partial \epsilon^*}{\partial a_\mu} \right) = \frac{1}{k_B \beta} \frac{\partial s_B^\infty(\epsilon^*)}{\partial a_\mu} \quad (32)$$

⁶ note $\epsilon^* = \epsilon^*(a_\mu)$, $s_B^\infty(\epsilon^*) = s_B^\infty(\epsilon^*(a_\mu), a_\mu)$

that compared with the first member of Eq. (27) states that $s = s_B$ is the only one consistent choice for the entropy.

A further point that deserves a discussion concerns the question of the integrating factor raised by [24]. In his work, he deduces that microcanonical entropy is an exact differential form if and only if it is a function of Ω . The proof of the above assertion, is affected by the same mistake as the proof of inconsistency given by [18]. Indeed a key point in the proof given by Campisi is the identification

$$p_\mu \equiv \left(\frac{\partial \epsilon}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} = \left\langle \frac{\partial h}{\partial a_\mu} \right\rangle$$

that, as we have recalled above, is true only for the canonical ensemble, i.e. when $\langle \cdot \rangle$ is the canonical average. The second law of thermodynamics for the heat density q reads

$$\delta q = d\epsilon + \sum_\mu p_\mu da_\mu,$$

thus, in systems where all the statistical ensembles are equivalent, from Eq. (32) we get

$$\delta q = d\epsilon + \sum_\mu \frac{1}{k_B \beta} \left(\frac{\partial s_B^\infty}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} da_\mu$$

which yields

$$ds \equiv \frac{\delta q}{T} = \frac{d\epsilon}{T} + \sum_\mu \left(\frac{\partial s_B^\infty}{\partial a_\mu} \right)_{s, a_\nu \neq a_\mu} da_\mu.$$

Thus, the choice $s = s_B^\infty$ and $T = (\partial s_B^\infty / \partial \epsilon)^{-1}$ makes s_B^∞ an exact differential form, and this ensures the perfect thermodynamic consistency of Boltzmann's entropy.

While we were finalizing the present paper we have came to knowledge of paper [39] that contains results in agreement with that of the present section.

PARADIGMATIC EVIDENCES

In this section we consider two different systems supporting negative-temperature states. The first one is a collection of N undistinguishable uncoupled 1/2 spins in a magnetic field B , like the one considered in [18] and [24]. This is a particular case of the class of systems discussed in the seminal work by [5]. Next, we address a tight-binding model describing N classical, or quantum, particles hopping across the sites of a lattice of length L , which bears relevance to a recent experiment where negative-temperature states have been created for motional degrees of freedom of ultracold atoms loaded in an optical lattice [38]. In our calculation we assume the systems as at the thermodynamic equilibrium without considering the dynamical process necessary to realize such

equilibrium. For both models we show that the Boltzmann microcanonical ensemble produces results that are equivalent to those obtained in the canonical (and, possibly, grand canonical) ensemble, where the inverse temperature is just an external parameter.

The Hamiltonian for the first system is

$$H = -mB \sum_{j=1}^N \sigma_j \quad (33)$$

where m is the magnetic moment of the individual spin and $\sigma_j = \pm 1$. The canonical partition function for this system is easily evaluated as

$$Z = 2^N \cosh^N(\beta mB) = e^{-\beta A}, \quad (34)$$

where A is the Helmholtz free energy. The internal energy and the entropy are then

$$E = -\frac{\partial}{\partial \beta} \log Z = -NmB \tanh(\beta mB), \quad (35)$$

$$S = k_B \beta^2 \frac{\partial}{\partial \beta} A = k_B N \left[\log 2 + \log(\cosh(\beta mB)) - \beta mB \tanh(\beta mB) \right]. \quad (36)$$

Inverting Eq. (35) for $h = E/(NmB)$, where $h \in [-1, 1]$, and plugging the result into Eq. (36) yields

$$\beta = -\operatorname{arctanh}(h) \quad (37)$$

$$S = \frac{k_B N}{2} [2 \log 2 - (1+h) \log(1+h) - (1-h) \log(1-h)]. \quad (38)$$

Thus, the temperature is positive for $h < 0$ and negative for $h > 0$. Note that the entropy in Eq. (38) is a concave function featuring a maximum at $h = 0$ and, more importantly, its derivative with respect to h coincides with the function giving the temperature at a fixed energy density, Eq. (37). In other words, the inverse temperature and entropy obtained in the canonical ensemble are linked by the relation that is expected to hold true in the microcanonical ensemble. In fact, this is a specific instance of the general relation discussed in Sec. .

It is not hard to show that Eq. (38) coincides with the microcanonical Boltzmann entropy $S_B = k_B \log(\omega)$, where $\omega(h)$ is the number of microstates corresponding to energy density h . It is sufficient to observe that a state at energy density h is such that $(1-h)N/2$ spins are aligned along the magnetic field, and $N - n = (1+h)N/2$ spins are aligned against it. Therefore

$$\omega(h) = \binom{N}{n} = \frac{N!}{\left(\frac{1+h}{2}N\right)! \left(\frac{1-h}{2}N\right)!} \quad (39)$$

and our claim is easily proven by making use of Stirling's approximation, in view of the large number of spins.

As to the Gibbs entropy,

$$\Omega(h) = \sum_{k=0}^{(1-h)N/2} \binom{N}{k} = \int_{-1}^h \tilde{\omega}(h') dh' \quad (40)$$

with $\tilde{\omega}(h) = \frac{N}{2} \omega(h) = e^{\frac{N}{2} f(h)}$, with $f(h) = \frac{2}{N} \log\left(\frac{N}{2}\right) + 2 \log 2 - (1+h) \log(1+h) - (1-h) \log(1-h)$, a concave function having a maximum at $h = 0$. Thus, repeating the general argument illustrated in Sec. , $\beta_G(h) = \beta_B(h)$ for $h < 0$, and $\beta_G(h) = 0$ for $h \geq 0$.

In passing, we observe that the severe shortcomings attributed to the Boltzmann entropy in Ref. [24] are an artifact of the erroneous definition of the Boltzmann entropy adopted there. Indeed, the argument of the logarithm in the formula for S_B should be a pure number, namely the number of microstates corresponding to a given energy.

In Ref. [24], the Boltzmann entropy is defined as the logarithm of the *density of states*, $\bar{\omega}(E) = \omega(E/mBN)/2mB$, that one has to introduce in the calculation of Ω when switching from a sum to an integral over *energies*:

$$\Omega(E) = \int_{-mBN}^E \bar{\omega}(E') dE' \quad (41)$$

Equation (41) is surely equivalent to Eq. (40) — where the integral is over adimensional *energy densities* —, except for the fact that $\bar{\omega}(E)$ cannot be the argument of a logarithm, in that it has the dimension of an inverse energy. In order to use it in the definition of the Boltzmann entropy, it must be multiplied by $\varepsilon = mB$, as correctly stated in Eq. (1) of Ref. [24]. Expectedly, this produces the original number of microstates $\omega(E/mBN)$ and, in turn, the correct Boltzmann entropy. When this is plugged into Eq. (31) of Ref. [24], the expected magnetization is obtained, $M = -E/B$, and no spurious phase transition appears at $h = 0$. In fact, it is S_G that appears to signal such a spurious phase transition, through the nonanalyticity of $\beta_G(h)$ at $h = 0$.

As second case, we consider a quantum and a classical model, of an ideal gas of noninteracting bosons hopping on a one-dimensional lattice. In the former case the dynamics is defined by Hamiltonian

$$\hat{H} = -\sum_{j=1}^L \hat{a}_j \hat{a}_{j+1}^\dagger + \text{h.c.}, \quad (42)$$

where \hat{a}_j (\hat{a}_j^\dagger) is the boson annihilation (creation) operator at site j and where periodic boundary conditions have been assumed. In addition to the energy, the present system has a further conserved quantity, the total number of bosons

$$\hat{N} = \sum_{j=1}^L \hat{a}_j^\dagger \hat{a}_j. \quad (43)$$

By plugging $\hat{a}_j = 1/\sqrt{L} \sum_{k=0}^{L-1} \exp(-i2\pi kj/L) \hat{b}_k$ into Eqs. (42) and (43) we get

$$\hat{H} = - \sum_{k=0}^{L-1} \epsilon_k \hat{b}_k \hat{b}_k^\dagger + \text{h.c.}, \quad \text{and} \quad \hat{N} = \sum_{k=0}^{L-1} \hat{b}_k^\dagger \hat{b}_k \quad (44)$$

respectively, where the indices k run over the dual lattice sites and \hat{b}_k^\dagger and \hat{b}_k are creation and annihilation boson operators, respectively. The energy density levels $\epsilon_{\{n_k\}}$ of system are

$$\epsilon_{\{n_k\}} = L^{-1} \sum_{k=0}^{L-1} \epsilon_k n_k, \quad (45)$$

where n_k are integer numbers of the spectrum of $\hat{b}_k^\dagger \hat{b}_k$. The single particle energies ϵ_k for a uniform lattice result

$$\epsilon_k = -2 \cos(2\pi k/L), \quad k = 0, \dots, L-1. \quad (46)$$

Furthermore, each energy level has also a given total number of atoms $N = \sum_{k=0}^{L-1} n_k$. The classical model for this system is obtained when $b_k \rightarrow z_k$ and consistently $b_k^\dagger \rightarrow z_k^*$, where $z_k = (x_k + iy_k) \in \mathbb{C}$ ($k = 0, \dots, L-1$). Also in this case, the Hamiltonian and the total number of particles

$$\mathcal{H} = \sum_{k=0}^{L-1} \epsilon_k |z_k|^2, \quad \mathcal{N} = \sum_{k=0}^{L-1} |z_k|^2 \quad (47)$$

are conserved quantities. In the following of the present section, we compare $\beta(\epsilon)$ derived in the canonical or grand-canonical ensembles, $\beta_B(\epsilon)$ derived in the micro-canonical ensemble with the Boltzmann entropy, and $\beta_G(\epsilon)$ derived with the Gibbs entropy. Our analysis shows clearly a great agreement between $\beta(\epsilon)$ and $\beta_B(\epsilon)$, whereas $\beta(\epsilon)$ and $\beta_G(\epsilon)$ are absolutely irreconcilable on half of the domain of ϵ .

Ideal quantum gas: grand-canonical description. By the canonical partition function for the quantum model

$$Z_N(\beta) = \sum_{\{n_k\}} \exp[-\beta L \epsilon_{\{n_k\}}], \quad (48)$$

where $\sum_{k=0}^{L-1} n_k = N$, we get grand-partition function

$$\mathcal{Q} = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N(\beta) = \prod_{k=0}^{L-1} \frac{e^{-\beta(\mu - \epsilon_k)}}{e^{-\beta(\mu - \epsilon_k)} - 1}, \quad (49)$$

where the chemical potential μ has been introduced in order to fix the mean number of particles. From the mean number of bosons in the level ϵ_k

$$\langle n_k \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \quad (50)$$

we calculate the average number of bosons

$$N = \sum_{k=0}^{L-1} \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}, \quad (51)$$

and the energy density of the system

$$\epsilon = L^{-1} \sum_{k=0}^{L-1} \frac{\epsilon_k}{e^{\beta(\epsilon_k - \mu)} - 1}. \quad (52)$$

After Eq. (50), the condition $\langle n_k \rangle \geq 0$ imposes the constrain $\beta(\epsilon_k - \mu) > 0$ that can be satisfied in two cases: First, when $\mu < \epsilon_k$ ($k = 0, \dots, L-1$), $\beta > 0$; Second, for $\mu > \epsilon_k$ ($k = 0, \dots, L-1$) necessarily it results $\beta < 0$. Hence, in the latter case, we observe an inversion of population, namely $\langle n_k \rangle < \langle n'_k \rangle$ with $\epsilon'_k > \epsilon_k$. For a given value of N/L , the inverse temperature β is a function of the energy density ϵ , in fact, by using Eq. (51) and (52) it is possible to getting rid of the chemical potential and β is thus expressed as a function of ϵ . Figure 1 shows (gray) numerical results for β vs ϵ for the case $a = 1$ with $L = 20$ sites where it is evident that positive and negative values of β are allowed.

Ideal quantum gas: canonical description. From the partition function (48) it is possible to compute the average of the energy density as a function of β . We have done this numerically by generating all the microscopic configurations with $N = L = 20$, and by averaging the density energy (45) with respect to the canonical weight

$$\frac{e^{-\beta L \epsilon_{\{n_k\}}}}{Z_N(\beta)},$$

as a function of β . The resulting curve is shown in Fig. 1 (red).

Ideal quantum gas: microcanonical description. In this case we have to calculate the density of states $\omega_N(\epsilon)$ at energy density ϵ for a system with N particles. We have obtained an approximation to $\omega_N(\epsilon)$ by binning the energies of all the configurations with $N = L = 20$, which we generated as described above. In Fig. 1 we compare the inverse temperature β_B vs the energy density ϵ (blue), obtained from the Boltzmann entropy and $\beta(\epsilon)$ derived in the grand-canonical (gray) and in the canonical ensemble (red) for the case of $N = L = 20$. Already for this small system size it is evident the great agreement of $\beta(\epsilon)$ between the case of Boltzmann definition and the corresponding relations derived in the grand-canonical and canonical ensembles. As we have recalled earlier, the Gibbs entropy yields a non-negative inverse temperature, irrespective of the energy density, $\beta_G(\epsilon) > 0$. Now we show that the condition $\beta > 0$ and $\epsilon > 0$ cannot be satisfied in the grand canonical ensemble. Since $\langle n_k \rangle \geq 0$ for all k , from Eq. (50) we deduce $\beta(\epsilon_k - \mu) > 0$ and, given that $\beta > 0$ necessarily $(\epsilon_k - \mu) > 0$, and, in this manner $\epsilon_k > \epsilon'_k$ implies $\langle n'_k \rangle > \langle n_k \rangle$. Furthermore, the single particle density levels ϵ_k have zero average ($\sum_k \epsilon_k = 0$), therefore for this weighted average we get

$$\sum_{k=0}^{L-1} \epsilon_k \langle n_k \rangle < 0,$$

which proves our assertion. As it is clearly shown in Fig. 1, $\beta(\epsilon)$ (gray) derived with the grand canonical ensemble and $\beta_G(\epsilon)$ (black) derived with the Gibbs' entropy are absolutely irreconcilable in the region of $\epsilon > 0$.

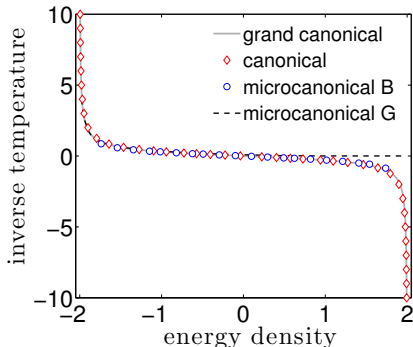


FIG. 1. Quantum system. Relation between β and ϵ for the three ensembles. All the curves refer to a lattice comprising $L = 20$ sites with a density of one particle per site.

Classical limit of the ideal quantum gas: grand canonical description. For the classical model the grand canonical partition

$$\mathcal{Q}_c = \prod_{k=0}^{L-1} \frac{\pi}{\beta(\epsilon_k - \mu)}, \quad (53)$$

yields

$$\langle n_k \rangle = \langle |z_k|^2 \rangle = \frac{1}{\beta} \frac{1}{\epsilon_k - \mu}. \quad (54)$$

Hence the average energy density is

$$\epsilon = \frac{1}{\beta L} \sum_{k=0}^{L-1} \frac{\epsilon_k}{\epsilon_k - \mu} \quad (55)$$

where the chemical potential μ is determined by the condition

$$N = \frac{1}{\beta} \sum_{k=0}^{L-1} \frac{1}{\epsilon_k - \mu}, \quad (56)$$

and it is $\mu < \epsilon_k$ ($k = 0, \dots, L-1$) in the region of positive temperatures, whereas for negative-temperature it results $\mu > \epsilon_k$ ⁷. Thus, one can derive the energy density

$$\epsilon = \frac{1}{\beta L} [L + \mu N \beta]. \quad (57)$$

In the thermodynamic limit $N, L \gg 1$, we can consider the continuous limit for our system

$$N = \frac{1}{\beta} \sum_{k=0}^{L-1} \frac{1}{\epsilon_k - \mu} \approx \frac{L}{|\beta| \sqrt{\mu^2 - 4}}. \quad (58)$$

Solving for the chemical potential we get

$$\mu = -2 \operatorname{sign}(\beta) \sqrt{1 + \frac{1}{4\beta^2 a^2}}, \quad (59)$$

where $a = \frac{N}{L}$ is the particle density. Plugging Eq. (59) in the continuous limit of Eq. (55) we get

$$\epsilon = \frac{1}{\beta} - 2a \operatorname{sign}(\beta) \sqrt{1 + \frac{1}{4\beta^2 a^2}}. \quad (60)$$

By Eqs. (57) and (60) we get

$$\mu = \frac{\epsilon^2 + 4a^2}{2a\epsilon}$$

that plugged in (57) yields

$$\beta = -\frac{2\epsilon}{(4a^2 - \epsilon^2)}, \quad (61)$$

in which is evident that $\beta(\epsilon)$ and $\epsilon(\beta)$ are smooth functions. Therefore, as expected, the energy density can be used to determine the inverse temperature and chemical potential of the system at equilibrium.

A few comments are worthwhile. The expression for the grand canonical partition function, Eq. (53), could suggest that the point $\beta = 0$ corresponds to a singular point where some kind of phase transition takes place. This is not the case. Indeed it is easy to show from Eq. (59) that for $\beta \rightarrow 0$, $\beta\epsilon_k \rightarrow 0$ but $\beta\mu \rightarrow -(a)^{-1}$ and, hence, \mathcal{Q}_c does not diverge at $\beta = 0$. In figure 2 it is

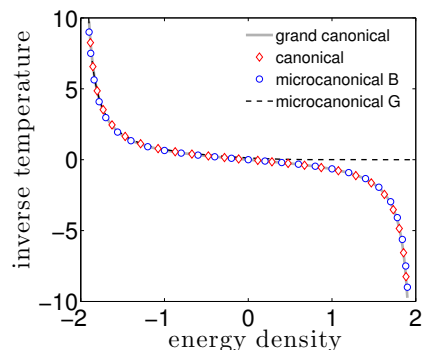


FIG. 2. Classical system. Relation between β and ϵ for the three ensembles. All the curves refer to a lattice comprising $L = 20$ sites with a density of one particle per site.

plotted the curve (61) (gray).

⁷ Notably, Eq. (54) is the classical limit ($a \gg 1$) of the quantum result in Eq. (50).

Classical limit of the ideal quantum gas: canonical description. The basic object in this ensemble is the canonical partition function

$$Z_N(\beta) = \int dx dy e^{-\beta \sum_{k=0}^{L-1} \epsilon_k (x_k^2 + y_k^2)} \delta \left[N - \sum_{k=0}^{L-1} (x_k^2 + y_k^2) \right], \quad (62)$$

which, in the case of an even number of sites L , can be recast as

$$Z_N(\beta) = \frac{\pi^L}{\beta^{(L-1)L^2}} B_N(\beta) \quad (63)$$

where

$$B_N(\beta) = -\frac{1}{2} \sum_{k=0}^{L-1} [\beta(4 - \epsilon_k^2)N + \epsilon_k] e^{-\beta \epsilon_k N}. \quad (64)$$

The energy density in this case is

$$\epsilon = \frac{L-1}{L\beta} - \frac{1}{L} \frac{\partial}{\partial \beta} \ln B_N(\beta) \quad (65)$$

In Fig. 2 (red) we show the curve $\beta(\epsilon)$ derived by numerically solving Eq. (65) for β .

Classical limit of the ideal quantum gas: microcanonical description. We want to calculate the Boltzmann entropy for the classical system introduced above. According to Boltzmann, the entropy depends on the density of states

$$\omega(\epsilon, N) = \int dx dy \delta \left[\epsilon N - \sum_{k=0}^{L-1} \epsilon_k (x_k^2 + y_k^2) \right] \delta \left[N - \sum_{k=0}^{L-1} (x_k^2 + y_k^2) \right] \quad (66)$$

through Eq. (5). By a direct calculation, in the case of a lattice of $L = 2\ell$ sites, one gets

$$\omega(\epsilon, N) = \frac{\pi^L N^{L-2}}{(L-2)! L^2} \chi(\epsilon, N) \quad (67)$$

where $\epsilon_0 < \epsilon < \epsilon_\ell$, the single particle energies $\epsilon_0, \epsilon_\ell$ are defined in (46), and

$$\chi(\epsilon, N) = (\epsilon - \epsilon_0)^{L-2} - \sum_{k=1, \epsilon_k < \epsilon}^{\ell-1} [(L-2)(\epsilon_\ell - \epsilon_k)(\epsilon_k - \epsilon_0)(\epsilon - \epsilon_k)^{L-3} + \epsilon_k(\epsilon - \epsilon_k)^{L-2}] \quad (68)$$

from which it is possible to derive $\beta_B(\epsilon)$ by means the standard definition $\beta_B = \partial_\epsilon \omega / \omega$. Fig. 2 compares the inverse microcanonical temperature β_B vs ϵ (blue) for a lattice of $L = 20$ sites and one particle per site, Eq. (61) obtained in the grand canonical ensemble (gray) and the analogue relation derived in the canonical ensemble (red).

Fig. 2 shows beyond a shadow of a doubt the agreement between the functions $\beta(\epsilon)$ derived from the Boltzmann's definition, and the one in the grand canonical ensemble. In particular they both predict negative temperatures in the domain of positive-energy densities. Furthermore from (68) we have derived $\Omega(\epsilon, N)$ from which it is possible to derive the inverse Gibbs temperature by means the standard definition $\beta_G = \omega / \Omega$. In Fig. 2 we show the curve $\beta_G(\epsilon)$ (black) derived in such way. Also for the classical model, $\beta_G(\epsilon)$ does not agree with the curves $\beta(\epsilon)$ obtained in the grand canonical and canonical ensembles.

For the first system considered in this section, we have shown that $\beta(\epsilon)$ derived within the canonical description agrees with $\beta_B(\epsilon)$ derived within the Boltzmann microcanonical description. Furthermore, we have considered a second system, an ideal gas both in the classical and in the quantum case, and we have shown that $\beta(\epsilon)$ derived within the grand canonical and canonical descriptions agree with the same quantity derived within a microcanonical description à la Boltzmann, whereas are irreconcilable with the analogues quantity derived using the Gibbs entropy. We have shown that, for these systems the ensemble equivalence holds true provided that the Boltzmann entropy is used within microcanonical ensemble. Furthermore, we have seen that for the classical case of the second system, the grand canonical approach gives an explicit form for $\beta(\epsilon)$, i.e. Eq. (61). In view of the clear agreement between the grand canonical and the microcanonical result, we can conclude

$$\omega(\epsilon) \approx \omega^0 (4a^2 - \epsilon^2)^L, \quad (69)$$

where $\omega^0 = \exp(Ls_B^0/k_B)$ does not depend on ϵ . Plugging $s_B = s_B^0 + k_B \ln(4a^2 - \epsilon^2)$ and $\tilde{\epsilon} = 0$ in the Eqs. (22) - (25), we deduce: First, $T_B(\epsilon)$ is well defined within the whole range of value of $\epsilon \neq 0$, Second, for $L \rightarrow \infty$ $T_G(\epsilon) \rightarrow T_B(\epsilon)$ in $\epsilon < 0$, Third, in the thermodynamic limit T_G is well defined only in the domain of ϵ corresponding to positive temperatures T_B and it is infinity for $\epsilon \geq 0$. This fact has dramatic consequences about the thermodynamic consistency of Gibbs' entropy, as we will show in Sec. .

In the light of these facts, it is evident that thermodynamics derived from Boltzmann's entropy is perfectly consistent, both mathematically and thermodynamically, with the thermodynamics derived in the grand-canonical and canonical ensembles, whereas the thermodynamics derived from Gibbs' entropy is inconsistent with that of these latter ensembles.

EQUIPARTITION THEOREM

While the Hamiltonian dynamics takes place on the phase-space hypersurface corresponding to a given value of the energy density (and possibly of the other conserved

quantities), the Gibbs entropy requires measures involving all the energy level sets with density energy below such value. It is therefore not immediately clear how β_G can be measured as an ensemble or time average. The usual answer to this question given by the supporters of the Gibbs entropy is to use the equipartition theorem. This can be cast into the form

$$\beta_G^{-1} = \langle x_k \frac{\partial H}{\partial x_k} \rangle, \quad (70)$$

where x_k denotes any component of the set of dynamical coordinates and the angle brackets denote the standard microcanonical average. Nevertheless Eq. (70) fails exactly in the case of systems that admit negative temperature. For instance, in the case of system (47) reported in Sec. , in the region $\epsilon > 0$ (corresponding to negative Boltzmann temperatures) the r.h.s. of Eq. (70) with $x_k = z_k$ is $\epsilon_k \langle |z_k|^2 \rangle$ which is a well defined quantity for any system size L . On the contrary, as we have proved above, l.h.s. goes to infinity as L increases, therefore Eq. (70) cannot be satisfied. The reason of this failure of the equipartition theorem, in the case of systems that admit negative temperatures, stems from ignoring boundary terms in the derivation of Eq. (70). For instance, in the case of systems with bounded energy spectrum, like the systems admitting negative Boltzmann temperatures, the identity of Eq. (70) is no more valid and must be corrected with

$$\langle x_j \frac{\partial H}{\partial x_k} \rangle = \frac{\delta_{jk}}{\beta_G} - \frac{1}{\omega} \int dx \partial_j [x_k \Theta(E - H)], \quad (71)$$

that includes boundary terms. In fact, such terms in the case of systems with bounded energy spectrum (and/or bounded coordinates), can be not null, at variance with standard systems where $x \rightarrow \infty$ yields $H \rightarrow \infty$.

In the case of standard systems, i.e. with unbounded energy spectrum, Eq. (70) holds, but in this case the thermodynamic quantities derived from the Gibbs entropy differ from those obtained with the Boltzmann's definition of entropy for quantities which are irrelevant from the statistical point of view, since they vanish in the thermodynamic limit.

In the case of the classical model of lattice ideal gas (47), by a direct calculation one can show that even in the canonical ensemble the equipartition theorem does not have the celebrated form of Eq. (70), with the microcanonical average replaced by the canonical one, but the following

$$\langle x_k \partial_j H \rangle_c = -\delta_{j,k} \frac{\epsilon_k}{\beta} \frac{\partial \ln B_N(\beta)}{\partial \epsilon_k}. \quad (72)$$

where, with a glance at (64), the dependence on the mode index k is evident. For the same system (71) is

$$\langle x_k \partial_j H \rangle = -\frac{1}{2} \delta_{j,k} \frac{N}{L-1} \frac{\partial_{\epsilon_k} \chi(\epsilon, L)}{\chi(\epsilon, L+1)}. \quad (73)$$

Therefore, for systems with bounded energy spectrum, the equipartition theorem assumes an unexpected mathematical form which is perfectly defined within the Boltzmann description. On the contrary, identity (70) becomes meaningless for this class of systems proving in such a way the flimsiness of Gibbs microcanonical thermodynamics.

We conclude that the identity (70) cannot be advocated as proof in favour of Gibbs entropy, since it fails in the case of systems where Gibbs and Boltzmann disagree. The correct identity (71), shows that there is not equipartition. Furthermore, since Eq. (70) is incorrect, it cannot be used to measure the Gibbs temperature as a microcanonical average at variance with what affirmed in several papers [18, 19, 24].

MEASURING TEMPERATURE

Making a temperature measurement on a system brings about, inevitably, a contact between the system and a second ‘‘small system’’. Especially in the present context a particular care has to be employed when we choose a second calibrated system (thermometer) to attach to the first one (sample) in order to determine the temperature of the latter. The thermometer has to detect the sample temperature without destroying its equilibrium. This means that a thermometer capable of sustaining negative temperatures must be employed with a sample admitting negative temperatures. Indeed, the whole system, obtained by glueing together a ‘‘small’’ system with unbounded energies, like an harmonic oscillator, to the sample would be a system with unbounded energies, that is without negative temperatures. This aspect that appears as a good reasoning, has been diffusely discussed by Ramsey in its paper [5] even if several authors [18, 19, 25] seem to have missed this point.

Furthermore, it makes sense to ask oneself if (and how) two systems admitting negative temperatures reach equilibrium when joined together at an initial different temperature.

In particular, a relevant question is whether the two joined systems reach eventually the same inverse temperature and if, or not, this latter is intermediate respect to the initial inverse temperatures of the two systems as we expect from statistical mechanics of positive temperatures [53]. In order to directly verify if the Boltzmann temperature complies with this requisite, we have simulated an experiment in which two different systems that admit negative temperatures, at different initial temperatures, are brought to contact with each other. Thus we have considered two systems described by the following Hamiltonians

$$H_j = - \sum_{\mathbf{r}\mathbf{r}'} z_{\mathbf{r}}^* A_{\mathbf{r}\mathbf{r}'} z_{\mathbf{r}'} - U_j \sum_{\mathbf{r}} \log(1 + |z_{\mathbf{r}}|^2), \quad j = 1, 2, \quad (74)$$

where, for each system, the indices \mathbf{r} and \mathbf{r}' run over a two-dimensional lattice and $A_{\mathbf{r}\mathbf{r}'}$ is the adjacency matrix that describes the nearest-neighbour interaction in two spatial dimensions. In (74) we have added to a kinetic term similar that of Hamiltonian (47), an onsite nonlinear potential, in order to make the systems not integrable. Note, that also with the addition of this latter term, the system admits negative temperatures. We started with the two systems isolated with each other. In our simulations we have prepared the initial configuration of equilibrium for the two systems at different temperatures (β_j^0 , $j = 1, 2$), by means of a long time integration of the equations of motion of the two separated systems. The inverse temperatures β_j^0 ($j = 1, 2$), have been measured with Eq. (14), that descends from the Boltzmann entropy. The two systems of 64×64 sites have been joined to form a single lattice. In the simulation reported in Fig. 3 we set $U_1 = 0.1$ and $\beta_1^0 \approx -1.38$, $U_2 = 0.75$ and $\beta_2^0 \approx 29.89$. We integrated the equations of motion of the whole system. In Fig. 3 we report the inverse temperature for the whole system (black), subsystem 1 (blue) and subsystem 2 (red). As it was expected, we observe that the inverse temperature of the whole system, after a short transient, reaches an asymptotic value $\beta^f \approx 0.09$ intermediate between the initial values of the inverse temperatures of the two original systems. Also, the inverse temperatures of the two subsystems approach the value of $\beta(t)$ along the time. Furthermore, this value remains stable on long time scales. For detail about these numerical results we refer to [41], where we have presented analytical and numerical evidence that Boltzmann microcanonical entropy allows the description of phase transitions occurring at (negative Boltzmann temperatures) high energy densities, at variance with Gibbs temperature.

It is worth remarking that, whereas this process of thermalization is well explained with the Boltzmann temperature, we cannot say the same for the inverse temperature of Gibbs for which it is $\beta_1^0 = \infty$ with $\beta_2^0 \approx 29.89$ and $\beta^f < \infty$.

Finally we have verified that, irrespective of the sign of the temperature, a large lattice (that realizes a microcanonical ensemble) acts as a thermostat for a small sublattice (that realizes a grand canonical ensemble) and that the temperatures measures for the two systems agree, thus confirming the equivalence between the microcanonical and the grand canonical ensemble.

FINAL REMARKS

We have addressed the question of the right definition of microcanonical entropy, for systems for which the equivalence of the statistical ensembles is verified. We have shown that the correct map between the canonical average of the energy for systems with one or more conserved quantities and the Lagrangian parameter β is that

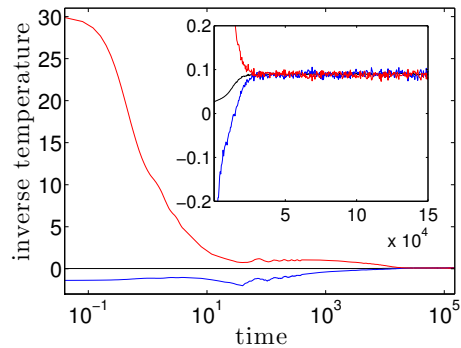


FIG. 3. The figure shows the thermalization of the subsystems 1 and 2 after that they are attached at initially different inverse temperatures. The black line is the evolution of the inverse temperature of the whole system, the blue line is the inverse temperature of system 1 and the red line is the inverse temperature of the subsystem 2. The inset shows a zoom of the last part of evolution.

descending from the Boltzmann entropy. Moreover, we have shown that the only consistent definition for the microcanonical entropy is that of Boltzmann. In fact, while for standard systems both these entropies lead to equivalent thermodynamic results in the thermodynamic limit [34], in the case of systems with bounded energy spectrum, negative Boltzmann temperatures are admitted, and the two microcanonical entropies lead to irreconcilable results. In particular, when the latter circumstance is verified, the inverse temperature derived by the Gibbs' entropy coincides with the one of Boltzmann within the region of energy density where the latter is positive, and is identically null where the Boltzmann temperature is negative. In this way, it could happen that in correspondence of the energies where β_B changes sign, β_G is not a differentiable function of ϵ . But this conflicts with the fact that the canonical and grand canonical partition functions are smooth functions of ϵ in correspondence of such points. On the contrary, $\beta_B(\epsilon)$ is a smooth function of ϵ , and no consistence issue of this kind arises for Boltzmann entropy. For all these reasons we conclude that the correct definition for the microcanonical entropy is the one of Boltzmann.

Microscopic dynamics and Eq. (31)

In Supplementary Information of Ref. [18], the authors try to pave the link between the second member of Eq. (31) and the microcanonical dynamics in order to prove the second of identity in (31). They consider an isolated system whose dynamics is governed by a Hamiltonian $H(\mathbf{A}(t))$ that doesn't depend explicitly on time and, through the Hamilton-Heisenberg equation, [18] derive the following expression for the time derivative of

H

$$\frac{dH}{dt} = \sum_{\mu} \frac{\partial H}{\partial A_{\mu}} \frac{dA_{\mu}}{dt}. \quad (\text{A.75})$$

Then, the authors operate an average over some suitable defined ensemble of the latter equation. The only meaningful measure that one can consider for the microcanonical dynamics is the measure ergodic invariant for the dynamics, that is that one of Eq. (7). Therefore we obtain

$$\left\langle \frac{dH}{dt} \right\rangle = \sum_{\mu} \left\langle \frac{\partial H}{\partial A_{\mu}} \right\rangle \frac{dA_{\mu}}{dt}, \quad (\text{A.76})$$

where average $\langle \cdot \rangle$ is defined in Eq. (9). At this point in Ref. [18] the authors write

$$\left\langle \frac{dH}{dt} \right\rangle = \frac{d\langle H \rangle}{dt} = \frac{dE}{dt}, \quad (\text{A.77})$$

but this identity is incorrect. In fact, both the hypersurface Σ_E on which the microcanonical averages are computed, according to Eq. (9), and the term $1/\|\nabla H\|$, appearing in the measure (7), depend on \mathbf{A} , and then on time t . One can verify that Eq. (A.77) has to be corrected according to

$$\begin{aligned} \frac{d\langle H \rangle}{dt} &= \left\langle \frac{dH}{dt} \right\rangle - \left\langle H \frac{1}{\|\nabla H\|} \frac{d\|\nabla H\|}{dt} \right\rangle + \\ &\langle H \rangle \left\langle \frac{1}{\|\nabla H\|} \frac{d\|\nabla H\|}{dt} \right\rangle, \end{aligned} \quad (\text{A.78})$$

from which we get

$$\begin{aligned} \frac{dE}{dt} &= \sum_{\mu} \left[\left\langle \frac{\partial H}{\partial A_{\mu}} \right\rangle - \left\langle H \frac{1}{\|\nabla H\|} \frac{\partial \|\nabla H\|}{\partial A_{\mu}} \right\rangle + \right. \\ &\left. \langle H \rangle \left\langle \frac{1}{\|\nabla H\|} \frac{\partial \|\nabla H\|}{\partial A_{\mu}} \right\rangle \right] \frac{dA_{\mu}}{dt}, \end{aligned} \quad (\text{A.79})$$

from the latter by using the identities $h = H/L$ and $a_{\mu} = A_{\mu}/L$ we obtain an expression that differs dramatically from Eq. (31).

A further, and even more basic issue in this proof is that it presumes to be able to design a microscopic dynamics, in which a the thermodynamic transformation driven by the functions $A_{\mu}(t)$, realizes a transformation in which the entropy is constant. But this is possible only after having adopted a specific definition for entropy: this is a tautology.

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