Boltzmann vs Gibbs: a finite-size match

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January 28, 2015

Abstract

The long standing contrast between Boltzmann’s and Gibbs’ approach to statistical thermodynamics has been recently rekindled by Dunkel and Hilbert [1], who criticize the notion of negative absolute temperature (NAT), as a misleading consequence of Boltzmann’s definition of entropy. A different definition, due to Gibbs, has been proposed, which forbids NAT and makes the energy equipartition rigorous in arbitrary sized systems. The two approaches, however, are shown to converge to the same results in the thermodynamical limit. A vigorous debate followed ref. [1], with arguments against [2, 3] and in favor [4, 5, 6, 7] of Gibbs’ entropy. In an attempt to leave the speculative level and give the discussion some deal of concreteness, we analyze the practical consequences of Gibbs’ definition in two finite-size systems: a non interacting gas of $N$ atoms with two-level internal spectrum, and an Ising model of $N$ interacting spins. It is shown that for certain measurable quantities, the difference resulting from Boltzmann’s and Gibbs’ approach vanishes as $N^{-1/2}$, much less rapidly than the $1/N$ slope expected. As shown by numerical estimates, this makes the experimental solution of the controversy a feasible task.

Key words: Entropy; Statistical thermodynamics;

1 Introduction

The notion of negative absolute temperature (NAT) [8, 9] has been recently re-freshed by Braun et al [10]. The main factor of novelty was the claim that the NAT regime was attained in a system with a continuous upperly bounded spectrum, in contrast to the preceding experiments based on two-level systems [8, 9]. Soon after, however, the notion of NAT was criticized by Dunkel and Hilbert [1], as a misleading consequence of Boltzmann’s definition of entropy

$$S_B(E) = \ln \left[ \sum_{\eta} \delta_{H(\eta), E} \right],$$

(1)
in an isolated (micro-canonical) system of Hamiltonian $H(\eta)$, $\eta$ being any state variable and $\delta$ a generalized Kronecker symbol (Boltzmann constant $k_B = 1$). Actually, from the definition of absolute temperature

$$T = \left( \frac{\partial S}{\partial E} \right)^{-1}, \quad (2)$$

it is seen that NAT occurs whenever $S(E)$ is a decreasing function of the energy, which is possible for the entropy, $S(E)$, if the energy is upperly bounded (i.e. $H(\eta) < E_{Max}$) and the higher energy levels can be overpopulated by suitable external processes. As stressed in Ref. [1], instead, Gibbs’ entropy

$$S_G(E) = \ln \left[ \sum_{\eta} \Theta (E - H(\eta)) \right], \quad (3)$$

($\Theta(\cdot)$ being the Heaviside function) is an increasing function of $E$ and thereby excludes any NAT regime by definition. In Ref. [1] the authors stress that Gibbs’ definition of entropy refers to a micro-canonical system (a claim that will be reconsidered in what follows) and satisfies the equipartition theorem in any case, while Boltzmann’s entropy fails in very small systems, with a number of particles of order unity.

What we playfully call the "Boltzmann vs Gibbs match" is right the debate about Boltzmann’s (eqn. (1)) and Gibbs’ (eqn. (3)) definition of entropy [2, 3, 4, 5, 6, 7]. As it is a rule for most polemics involving the entropy, the discussion may look a little bit academic, especially in view of equation (14) of ref. [1], which shows that the two entropies (1) and (3) give the same temperature expression, in the thermodynamic limit, with a difference that vanishes as the inverse heat capacity. Given that Boltzmann and Gibbs’s picture lead to the same results in large systems, the alternative looks as follows: either there exists a measurable size effect displaying some difference between eqn.s (1) and (3), or any discussion remains confined to a merely speculative level. The second possibility looks, at a first sight, much more likely, once one efforts the question how small the size should be, for this effect to be detectable. Actually, one might be tempted to assume that the smallness criterion is determined by $1/N$ ($N$ being the number of particles), since from eqn. (14) of ref. [1] the temperatures resulting from eqn. (3) and (1) differ by terms proportional to the inverse of an extensive quantity (the heat capacity). If this were always the case, any experimental test, like one based on the "minimal quantum thermometer" suggested in ref. [1], would become extremely difficult, if not impossible. Fairly surprisingly, we shall show that, in certain two-level systems, the difference between certain measurable quantities, derived from eq.n (3) and (1), vanishes as $1/\sqrt{N}$. This result makes the experimental comparison

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1 This title should not be confused with Jaynes’ one [11]: Gibbs vs Boltzmann entropies, that deals with the (supposed) inadequacy of Boltzmann combinatorial method in describing interacting systems.
between the two approaches much more accessible, since detecting effects small to order \(1/\sqrt{N}\) is certainly easier than to order \(1/N\), especially in view of the recent technical progresses of small particle physics. This is the "finite-size match" that we are going to outline in the next sections.

Though we shall refer to two-level systems, that represent the preferred framework for NAT experiments, we are not specifically interested in the NAT problem. We address to a more fundamental point, that intrigues people since the foundations of statistical thermodynamics, i.e. the definition of entropy in terms of the microscopic dynamical states of the system. Very recently, Hilbert, Hänggi and Dunkel performed an exhaustive survey of several possible definitions of entropy in continuous spectrum systems [12], with special attention to their consistency with the three principles of thermodynamics. It turns out that the only definition of entropy that satisfies the three principles in arbitrary small systems, is eq.n [3]. The flaws expected from other definitions are, in turn, finite-size effects whose measured presence would support a widespread opinion (contrasted by Hilbert, Hänggi and Dunkel) that thermodynamics applies only to large systems.

Another point that we address in the present work is the role of the constraints in the construction of the thermodynamical functions. Actually, different constraints (micro-canonical, canonical, grand-canonical) yield different fluctuations about the equilibrium values of the thermodynamical quantities. Another widespread opinion is that the equilibrium values are, themselves, independent from the constraints. This justifies the experimental evidence that the constraints are irrelevant in the thermodynamical limit (and far from the phase transitions), since the relative weights of the fluctuations vanish as \(1/\sqrt{N}\). However, the difference between eq.n [3] and [1] is not due to the fluctuations, but to the genuine notion of thermal equilibrium. Indeed, Gibbs’s entropy [3] postulates what, in Boltzmann’s language, sounds like a sort of new ergodic hypothesis, that (in contrast to what claimed in ref. [1]) looks hardly appliable to micro-canonical systems. Why should states with energy less than \(E\) be involved, if \(E\) is strictly conserved? In this concern, it is only Boltzmann’s entropy [1] that is consistent with the dynamics of an isolated system. A reasonable possibility is that Gibbs’ and Boltzmann’s entropies refer to canonical and micro-canonical constraints, respectively. If so, a first relevant consequence would be that the size effects of the constraints do reflect on the equilibrium values too.

What precedes motivates our program of giving the size effects of interest an analytical form, then studying the feasibility of ad hoc experiments revealing which of the two entropy definitions does fit better with physical reality, both in canonical and in micro-canonical systems.

\[2\] Which is hated and rejected by many Gibbs supporters [13].
2 A gas of non interacting two-level particles

The simplest system for testing the differences between the two entropies (1) and (3) is a non interacting gas of \( N \) two-level particles, with populations \( n_{\pm} \) in each level \( \pm \epsilon \). While Boltzmann predicts \( n_+ = n_- = N/2 \), for \( T \to \infty \) Gibbs predicts \( n_+ (T) \) increasing continuously up to an inverted population regime \( n_+ \to N, \ n_- \to 0 \) at \( T = \infty \). At this stage one might wonder why laser devices need a resonant external field, in order to get an overpopulated level, if this could be obtained simply by thermal activation. The point is that in the Gibbs framework, the size of the gas (represented by the particle number \( N \)) plays a crucial role in determining how high the temperature should be, to achieve a significant overpopulation of the upper level. This is what we are going to show in the present section.

On setting \( n_{\pm} = (N \pm m)/2 \), the energy of the gas (as far as the two-level part is concerned) reads:

\[
E(m) = \epsilon m.
\]

Since the condition \( E(m) < E \) implies \( m < E/\epsilon \), Gibbs’ entropy reads:

\[
S_G(E) = \ln \left[ \sum_{m \leq E/\epsilon} \frac{N!}{(N+m/2)! (N-m/2)!} \right].
\]

If \( N \gg 1 \), the entropy can be expressed in an integral form, making use of Stirling formula for the factorials:

\[
S_G(E) = \ln \left[ 2^N \int_{-1}^{z(E)} dx e^{-\phi(x)} \right],
\]

with

\[
z(E) = \frac{E}{N\epsilon} \in [-1, 1]
\]

and

\[
\phi(x) = [(1 + x)\ln(1 + x) + (1 - x)\ln(1 - x)] = \\
\phi(z) + \ln \left( \frac{1 + z}{1 - z} \right) (x - z) + \frac{1}{1 - z^2} (x - z)^2 + \ldots
\]

The series expansion in eq.n (5c) will be used in Appendix. The temperature follows from eq.n (2), on account of eq.ns (5):

\[
T(E) = N\epsilon e^{\frac{2}{\epsilon} \phi(z(E))} \int_{-1}^{z(E)} dx e^{-\frac{2}{\epsilon} \phi(x)}.
\]
For $N \gg 1$, the following expressions are derived in Appendix:

$$T(E) = \left[ \ln \left( \frac{1 - z(E)}{1 + z(E)} \right) \right]^{-1}$$

for $E < 0$, $|E| \gg \epsilon \sqrt{N/2}$ \hspace{1cm} (7a)

$$= \frac{1}{2} \sqrt{\frac{\pi N}{2}}$$

for $E = 0$ \hspace{1cm} (7b)

$$= \frac{1}{2} \sqrt{\frac{\pi N}{2}} \exp \left[ \frac{N}{2} \phi(z(E)) \right] \times$$

$$\times \left[ 1 + \text{erf} \left( z(E) \sqrt{\frac{N}{2}} \right) \right]$$

for $0 < E \ll \epsilon N$ \hspace{1cm} (7c)

The condition $E < 0$ corresponds to the thermal regime in which the Boltzmann temperature $T_B$ is positive and the lower level is always more populated than the higher one. Actually, equation (7a) recovers exactly the standard result:

$$z(T) = e^{-\epsilon/T} - e^{\epsilon/T}$$

as can be easily shown by solving (7a) with respect to $z(E)$, then using eqs. (5b) and (4). It is well known that $E = 0$ is a singularity point for Boltzmann temperature $T_B(E)$, since $\lim_{E \to 0} \pm T_B(E) = \mp \infty$ (see, for instance, Fig. 1 in ref. [1]). The condition $E > 0$, in fact, corresponds to what would be the NAT regime, that should be attained by "super heating" the system above $E = 0$, according to Boltzmann’s picture\(^4\).

From a formal viewpoint, the results eqs. (7), obtained in the Gibbs framework, cures the singularity of the Boltzmann temperature at $E = 0$ and brings the gas continuously to any positive value of the energy, i.e., to any thermally activated overpopulation of the upper level. However, it is easily shown from eq. (7c) that the temperature diverges exponentially with $N$, for $E > 0$ (Fig. 1), while the crossing temperature

$$T_G = \epsilon \sqrt{\frac{\pi N}{2}}$$

at $E = 0$ (eq. (7b)), diverges with the square root of the system size. Hence, the regime $E > 0$ would be unaccessible to any thermal process, for $N \to \infty$, even in the Gibbs framework. In this (non trivial) sense Gibbs and Boltzmann do converge to the same results in the thermodynamic limit. However, in a finite-size system, the regime $E > 0$ (or, equivalently, $z > 0$) is not forbidden in principle, and could

\(^4\)This is what Sokolov criticizes as “hotter than hot" [7].
Figure 1: Gibbs temperature of a two-level gas in the Boltzmann NAT regime $E > 0$.
The logarithmic plot shows the exponential increase of $T$ in the particle number $N$, for different positive values of $z$, corresponding to a thermally activated overpopulation of the upper level.
be accessed by an appropriate experimental set up. This is what we are going to exploit in what follows.

Let us derive an expression for $z$ as a function of $T$ and $N$, recalling that $z$ (eq.n (5b)) is the fractional difference between the higher and lower level populations. Assuming $0 < z \ll 1$, which means $\phi(z) = z^2 + \cdots$, and defining $\theta = z\sqrt{N/2}$, equation (7c) yields:

$$\theta = \left[\ln\left(\frac{T}{T_G (1 + \text{erf}(\theta))}\right)\right]^{1/2} \Rightarrow z \approx \sqrt{\frac{2}{N}\ln\left(\frac{T}{T_G}\right)} \quad (T > 2T_G) , \quad (10)$$

since erf($\theta$) ranges between 0 and 1 and does not affect the result significantly. At fixed temperature $T$ ($> 2T_G$), the overpopulation factor $z$ decreases with the square root of the system size. Due to the logarithmic dependence, the value of $z$ is almost insensitive to $T$. Hence, the feasibility of an experiment possibly measuring $z > 0$ at a positive temperature rests on two main difficulties: first, a crossing temperature $T_G \propto \sqrt{N}$ not so large as to prevent high precision measurements; second, an overpopulation factor $z \propto \sqrt{1/N}$ not so small as to escape the instrumental sensitivity.

Consider a gas of $N$ atoms of $^3$He, in a volume $V$, each carrying a spin magnetic moment $\mu_{\text{Bohr}} \approx 10^{-20} \text{emu}$. Let $B$ be an external uniform magnetic field. From eq.n (10), the total induced moment $\mu_{\text{tot}} = \pm \mu_{\text{Bohr}} (n_+ - n_-)$ reads, according to Gibbs:

$$\mu_{\text{tot}}^G \approx -\text{sign}(B) \mu_{\text{Bohr}} \sqrt{2N\ln\left(\frac{T}{T_G}\right)} , \quad (11a)$$

while Boltzmann (eq.n (8) with $\epsilon \ll T$) yields:

$$\mu_{\text{tot}}^B \approx \text{sign}(B) \mu_{\text{Bohr}} N \frac{\epsilon}{T} , \quad (11b)$$

with $\epsilon = |B| \mu_{\text{Bohr}}$. Note that $\mu_{\text{tot}}^G$ is antiparallel and $\mu_{\text{tot}}^B$ parallel to $B$, since the former comes from the overpopulation of the upper level, while the latter comes from the overpopulation of the lower one. SQUID magnetometers, that are the highest sensitivity instruments currently available, can measure magnetic moment intensities down to $\mu_m \approx 10^{-8} \text{emu}$. For $T$ larger than, but comparable to $T_G$, the condition $|\mu_{\text{tot}}^G| \approx \mu_m$ (eq.n (11a)) yields the order of magnitude $N \approx 10^{24}$ for the minimum number of atoms required to produce a detectable value of $\mu_{\text{tot}}^G$. Efficient SQUID devices usually operate at temperatures of 10 K at most, which determines an upper limit for $T_G$. From eq.n (9), however, this turns into an upper limit for $|B|$

$$|B| = \sqrt{\frac{2}{N\pi} \frac{T_G}{\mu_{\text{Bohr}}} \approx 10^{-7} \text{G} \quad (12)}$$

5The condition $T > 2T_G$ ensures that the quantity in square root is positive, for any value of $\theta$, but the solution of the equation exists for any $T > T_G$. Note that $z \ll 1$ does not imply $\theta \ll 1$. 

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With those values of \( N, B \) and \( T \), one sees that \( |\mu_{\text{tot}}^B| \approx 10^{-8} \text{emu} \) (eq.n (11b)) is comparable in magnitude to \( |\mu_{\text{tot}}^G| \), so that the measurable difference between Boltzmann’s and Gibbs’ predictions results mainly in the opposite orientation of a small induced magnetic moment.

As for the volume \( V \) of the gas, one should recall that the size of the sample does also play a role, in the feasibility of the experiment. It can be easily seen that \( V \approx 10 \text{ cm}^3 \), corresponding to a density of \( 10^{23} \text{ cm}^{-3} \) of \(^3\text{He} \) atoms, at \( T \approx 10 \text{ K} \), yields degeneration effects less than 10%. This looks a still tolerable error factor for the implicit approximation assumed so far, that the two-level energy is statistically independent from the translational energy (which is false, for degenerate gases).

In conclusion, some cube centimeters of \(^3\text{He} \), with density about \( 10^{23} \text{ cm}^{-3} \), at a temperature about 10 K, under the action of a magnetic field of \( 10^{-7} \text{ G} \), could be a good candidate as a referee of the Boltzmann vs Gibbs match. If the measured magnetic moment (spin polarization) of the gas, induced by the field, were anti-parallel to the field itself, the resulting thermally activated overpopulation of the upper level would provide a strong experimental support to Gibbs’ definition of entropy. If this occurs only under canonic constraints, but not in isolation, the hypothesis that Gibbs’ and Boltzmann’s entropies do refer to different constraints would be supported in turn.

3 Interacting two-level systems: Weiss ferromagnetism revisited

Another system for testing the consequences of Gibb’s definition of entropy is a ferromagnetic material, modeled by an Ising lattice of \( N = n_+ + n_- \) interacting magnetic moments with only "up" (+) and "down" (−) orientations. In the mean field approximation, the energy reads:

\[
\mathcal{E}(z, \rho) = -JN \left(z^2 + 2\rho z \right), \quad z = \frac{n_+ - n_-}{N},
\]

where \( J > 0 \) is half the coupling constant of the moment-moment interaction, \( z \) is the magnetization and \( \rho \equiv \mu_0 B/(2J) \) is the energy contribute from an external uniform magnetic field, in units of \( 2J \). In a first-order approximation in \( \rho \) (\( |\rho| \ll 1 \)), the condition \( \mathcal{E}(x, \rho) \leq E \) implies:

\[
x \geq |z(E)| - \rho \quad \text{or} \quad x \leq -|z(E)| - \rho,
\]

with

\[
|z(E)| = \left| \frac{E}{JN} \right|^{1/2} \quad \text{and} \quad -(1 + \rho) \leq \frac{E}{JN} \leq 0.
\]
In the same limit $N \gg 1$ and with the same method used for eq.n (3), the preceding formulas yield, for Gibbs’ entropy:
\[
S_G(z) = \ln \left[ 2^N \left( \int_{|z|}^{1} dx \, e^{-\frac{N}{2}\phi(x)} + \int_{-1}^{-|z|} dx \, e^{-\frac{N}{2}\phi(x)} \right) \right] = \\
= \ln \left[ 2^{N+1} \int_{|z|}^{1} dx \, e^{-\frac{N}{2}\phi(x)} + o(\rho^2) \right].
\] (15)

Instead of using eq.n (2) as a definition of $T$, as we did in Section 2, here we rewrite (2) as $d \left( E - T S \right) / dE = 0$, i.e. as an equilibrium condition, determining the value of $E(T)$, by minimizing the Helmholtz free energy (per particle) $\Psi = (E - TS)/N$. According to eqns (13) and (15), the free energy of interest reads, to first order in $\rho$:
\[
\Psi_G(z, \rho) = -J \left( z^2 + 2\rho z \right) - \frac{T}{N} \ln \left[ 2^{N+1} \int_{|z|}^{1} dx \, e^{-\frac{N}{2}\phi(x)} \right].
\] (16)

The minima in $z$ of $\Psi_G$ correspond to the equilibrium values of the magnetization. First, let us study the perfectly symmetric system at $\rho = 0$. The extremants of $\Psi_G(z, 0)$ follow from the equation
\[
\frac{\partial \Psi_G(z, 0)}{\partial z} = -2Jz + \text{sign}(z) \frac{T}{N} e^{-\frac{N}{2}\phi(z)} \left[ \int_{|z|}^{1} dx \, e^{-\frac{N}{2}\phi(x)} \right]^{-1} = 0,
\]
which yields (see Appendix):
\[
|z| = \frac{T}{2J} \ln \left( \frac{1 + |z|}{1 - |z|} \right) \quad \text{for} \quad |z| \gg \sqrt{\frac{1}{2N}}, \quad (17a)
\]
\[
= \frac{T}{J\sqrt{2N\pi}} \equiv z_G \quad \text{for} \quad |z| \leq \sqrt{\frac{1}{2N}}. \quad (17b)
\]

In agreement with the rule that Gibbs and Boltzmann converge to the same results in large systems, Boltzmann’s picture of Weiss ferromagnetism is recovered from eq.ns (17), in the limit $N \to \infty$. Indeed, one easily sees that in this limit $z = 0$ is always a solution, while other two solutions $\pm z_{\text{weiss}}$ exist, from eq.n (17a), provided $T < T_c = 2J$. The solutions $\pm z_{\text{weiss}}$ correspond to two minima of the Helmholtz free energy and yield the *spontaneous magnetization*, below the Curie temperature $T_c$, where, according to Boltzmann, $z = 0$ is a maximum (i.e., an unstable equilibrium state). Above $T_c$, the solution $z = 0$ is the only minimum of Boltzmann’s free energy, which marks the transition from the ferromagnetic to the paramagnetic phase. All this is displayed by the dashed line plots in Fig. 2.

In a finite system, Gibbs and Boltzmann pictures of Weiss ferromagnetism differ for small values of $|z|$. Indeed, for $T < T_c$, the solutions $\pm T/(J\sqrt{2N\pi})$ of
Figure 2: Gibbs (full lines) and Boltzmann (dashed lines) Helmholtz free energies as a function of $z$ (arbitrary units, $N = 200$).

(a) Paramagnetic regime ($T = 1.25 \times T_c$): $z = 0$ is the only stable equilibrium state, both for Boltzmann and for Gibbs.

(b) Ferromagnetic regime ($T = 0.75 \times T_c$): In addition to the two ferromagnetic states $\pm z_{\text{weiss}}$, Gibbs predicts the permanence of a stable paramagnetic state at $z = 0$. 

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eqn (17b) correspond to two maxima of $\Psi_G(z, 0)$, while $z = 0$ is always a minimum, as can be seen by the full line plots in Fig. 2a and by noticing that (eqn (17b)):
\[
\lim_{z \to 0^\pm} \frac{\partial \Psi_G(z, 0)}{\partial z} = \pm T \sqrt{\frac{2}{N\pi}},
\]
which shows that the minimum at $z = 0$ corresponds to the terminal point of a downward cusp, as sketched in Fig. 3.

Figure 3: Details of the paramagnetic minimum of the free energy (arbitrary units) predicted by Gibbs in the ferromagnetic regime ($T = 0.5 \times T_c$).
The minimum corresponds to the terminal point of a downward cusp. The horizontal lines help to visualize the decrease ($\propto N^{-1/2}$), with increasing system’s size, of the free energy barrier that stabilizes the equilibrium.

In conclusion, the difference between Boltzmann and Gibbs in a finite-size ferromagnet, at zero external field, is that the former predicts an unstable paramagnetic state $z = 0$ in the ferromagnetic phase ($T < T_c$), while the latter predicts the persistence of a stable paramagnetic phase, coexisting with the two ferromagnetic states $\pm z_{\text{weiss}}$. In other words, Boltzmann predicts what is called a "spontaneous symmetry breaking" at $T = T_c$, in which an arbitrary small external field makes the
system fall in one of the two ferromagnetic states ± \( z \)\(_{\text{weiss}} \). at \( T < T_c \). Gibbs, in contrast, predicts a lower limit \( B_m \) of the external field, below which the paramagnetic state persists, even in the ferromagnetic phase. The calculation of \( B_m = 2J\rho_m/\mu_0 \) follows from eq.n (16), by looking for the small extremants in the presence of a small field:

\[
\frac{\partial \Psi_G(z, \rho)}{\partial z} = 0 \Rightarrow 2(z + \rho) = \text{sign}(z) z_G \quad \text{for } |z| \leq \sqrt{\frac{1}{2N}}.
\]

For this equation to have two solutions, for both signs of \( z \) (which preserves the minimum in between), it is necessary that

\[
|\rho| < \rho_m = \frac{z_G}{2} = \frac{T}{T_c\sqrt{2N\pi}}.
\]

This shows that in a finite-size magnet, realized by elementary units of magnetic moment \( \mu_0 \), the symmetry breaking predicted by Gibbs is not "spontaneous", but involves a lower limiting value of the external magnetic field:

\[
|B| > B_m = \frac{T}{\mu_0\sqrt{2N\pi}} \quad (T < T_c).
\]

vanishing with the inverse square root of \( N \). The decrease of \( B_m(N) \) with increasing \( N \) corresponds to the "smoothing out" of the cuspid minimum, as shown by Fig. 3.

The advantage of using a ferromagnetic material for testing the validity of Gibbs’ entropy is that the recent developments of micro and nano-physics make it possible to prepare magnetic particles, containing controllable (and small) numbers of magnetic moments. Actually, size-effect measurements on such micro-magnets have become current in recent years [14]. In the present case, one could measure \( B_m \) with high sensitivity magnetometers, for different particles’ size. If SQUID magnetometers were to be used, at the largest operative temperature of about 10 K, with \( \mu_0 \approx \mu_{\text{Bohr}} \), equation (18) yields \( B_{\text{min}} \approx 10^{-6} \text{G} \) for a cube millimeter of magnetic sample, with a density \( N/V \approx 10^{23} \text{cm}^{-3} \) typical of metals.

4 Conclusions

The contrast between Boltzmann’s and Gibbs’ approach to statistical thermodynamics is a long standing question, that comes to the light, time to time, since about one century, in different contexts, but with the same underlying leitmotiv: which states are available to the system, and the way they must be counted. All this obviously reflects on the entropy. Dunkel and Hilbert, in ref. [1] (see also ref. [12]), add a new element of discussion, by refreshing an almost forgotten definition of entropy, due to Gibbs (eq.n (3)), that forbids negative absolute temperature (NAT), in contrast to the current expression [1], usually attributed to Boltzmann.
The arguments in ref. [1] have raised a discussion on the validity of eq. (3), as an alternative to eq. (1) [2, 3, 4, 5, 6, 7]. The two expressions differ in the phase space regions uniformly occupied by the system: a surface of constant energy $E$, for Boltzmann; a volume containing all states with energy less than $E$, for Gibbs. While Boltzmann’s definition cannot apply but to an isolated, micro-canonical system, Gibbs entropy seems more appropriate for canonical systems, whose energy can fluctuate, due to the heat exchanges with a thermal bath. This, however, contrasts with what is claimed in refs. [1, 6]. Hence, in addition to the question about which of the two expressions is correct, one should also explore the possibility that both expressions are correct, but refer to canonical and micro-canonical constraints, respectively.

Since Gibbs and Boltzmann entropies yield the same results in the thermodynamical limit $N \to \infty$, any possible measurable consequence of what precedes results in a size effect and is thereby far from easy to exploit. A superficial reading of eq. (14) in ref. [1] might lead to the conclusion that the smallness of the differences between eq. (1) and (3) vanish as $1/N$ (the inverse of an extensive quantity like the heat capacity). If so, any experimental test, such as the “minimal quantum thermometer” suggested in ref. [1], would become extremely difficult, if not impossible.

The aim of the present work was to explore the possibility of concrete experimental procedures, deciding the winner (if any) of what we playfully called the Boltzmann vs Gibbs match, or claiming that the two opponents actually play on different playgrounds, if Boltzmann and Gibbs entropies would result to refer to different constraints.

The study of two-level systems, both in the form of gases (Section 2), and of interacting Ising spins (Section 3), shows that the smallness factor to be accounted for is not $1/N$, but $1/\sqrt{N}$, which makes any experimental procedure much more feasible. In particular, it has been seen that some cube centimeters of $^3$He, with density about $10^{23} \text{cm}^{-3}$, at a temperature of tens Kelvins, under the action of a magnetic field of $10^{-7} \text{G}$, could be an appropriate system for an experimental test, possibly revealing the most striking effect of Gibbs entropy, i.e. a thermally activated overpopulation of the upper level. As a possible alternative in the same thermal conditions, we suggest the study of the ferromagnetic transition of submillimetric metallic particles, as a function of the number of interacting magnetic moments, under the action of weak external magnetic fields ($\approx 10^{-6} \text{G}$). The effect supporting Gibbs entropy would be an anomalous persistence of the paramagnetic regime, below the Curie temperature $T_c$, that should be destabilized by an external magnetic field proportional to $1/\sqrt{N}$. The orders of magnitude involved in the measurements sketched above look fairly accessible to concrete experiments, which opens the possibility of an important advance in the thermodynamics of small systems, and in the genuine foundations of statistical thermodynamics.
A Appendix

For $N \gg 1$, the contributes to the integral

$$
I \equiv \int_{-1}^{z} e^{-\frac{N}{2}[\phi(z)+a(x-z)+b(x-z)^2+\cdots]} \, dx
$$

in eq.n (6) come from the minimum of $\phi(x)$ (positive and symmetric) in the integration interval $[-1, z(E)]$. So, $\phi(x)$ can be approximated by the first three terms in eq.n (5c), which yields:

$$
e^{\frac{N}{2}\phi(z)} I \approx \int_{-(1+z)}^{0} e^{-\frac{N}{2}(ay+b)^2} \, dy = \frac{1}{L_N} \int_{-(1+z)L_N}^{0} e^{-(Q^2+\Lambda_N Q)} \, dQ , \quad (A.1a)
$$

with

$$
L_N \equiv \sqrt{\frac{Nb}{2}}, \quad \Lambda_N \equiv a\sqrt{\frac{N}{2b}} . \quad (A.1b)
$$

If $E < 0$, one has $z(E) < 0$ in turn (eq.n (5b)), and $\Lambda_N < 0$. If $|\Lambda_N|$ is large, $Q^2$ can be neglected in the exponent of the integrand in eq.n (A.1a), which yields:

$$
e^{\frac{N}{2}\phi(z)} I \approx \frac{1}{L_N} \int_{-\infty}^{0} e^{-\Lambda_N Q} \, dQ = \frac{2}{|a(z)|N} \quad \text{for} \quad |\Lambda_N| \gg 1 . \quad (A.2)
$$

On replacing expression (A.2) in eq.n (6), one gets eq.n (7a), with the same validity condition (recall eq.n.s (5c) and (A.1b)).

If $E > 0$ ($z, \Lambda_N > 0$), the integral in eq.n (A.1a) can be calculated by completing the square in the exponent:

$$
\int_{|z|}^{1} e^{-\frac{N}{2}[\phi(z)+a(x-z)+b(x-z)^2+\cdots]} \, dx , \quad (A.4)
$$

in eq.n (3) can be calculated with the same method, for $|\Lambda_N| \gg 1$ (eq.n (17a)) and $|\Lambda_N| \leq 1$ (eq.n (17b)).

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**Acknowledgments**
The author is grateful to Dr. R. Costa for his bibliographical contribution and for useful discussions, and to Prof. L. Del Bianco for her explanations about SQUIDs' and magnetic moment measurements in general.