Microcanonical analysis of Boltzmann and Gibbs entropies in trapped cold atomic gases

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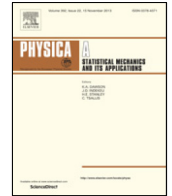Daniel E. Sheehy
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ABSTRACT

We analyze a gas of noninteracting fermions confined to a one-dimensional harmonic oscillator potential, with the aim of distinguishing between two proposed definitions of the thermodynamic entropy in the microcanonical ensemble, namely the standard Boltzmann entropy and the Gibbs (or volume) entropy. The distinction between these two definitions is crucial for systems with an upper bound on allowed energy levels, where the Boltzmann definition can lead to the notion of negative absolute temperature. Although negative temperatures do not exist for the system of fermions studied here, we still find a significant difference between the Boltzmann and Gibbs entropies, and between the corresponding temperatures with the Gibbs temperature being closer (for small particle number) to the temperature based on a grand canonical picture.

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1. Introduction

Recent work by Dunkel and Hilbert [1] (DH), motivated by classic early experiments on spin systems [2,3] and recent experiments on cold atomic gases [4] confined to optical lattices, has proposed that the notion of negative absolute temperatures arises from a definition of entropy that is thermodynamically inconsistent.

The idea of negative temperatures has existed at least since the 1950's, when it was applied to understand experiments on spin systems [2,3], and since then it has become standard textbook material in thermodynamics and statistical physics. More recently, evidence of negative temperature has been found in experiments on cold atomic gases [4]. In each case, negative temperatures arise because the system in question possesses an upper bound in the total energy E. For energies close to the upper bound, the number of available microstates (which is directly related to the Boltzmann entropy) decreases with increasing energy, implying a negative absolute temperature using the Boltzmann entropy definition.

For a quantum system defined by Hamiltonian H, the Boltzmann entropy can be written as

$$S_B(E) = k_B \ln\left[\varepsilon \Omega(E)\right], \tag{1}$$

where k_B is Boltzmann's constant and $\Omega(E) = \text{Tr}\left[\delta(E - H)\right]$ counts the number of microstates at energy E. Here, ε is a parameter with units of energy chosen so that the argument of the logarithm is dimensionless. In Ref. [1], DH argue for an alternate "volume" definition of entropy (due to Gibbs) that instead counts all microstates up to energy E. We can define the Gibbs entropy as:

$$S_G(E) = k_B \ln\left[\text{Tr}\Theta(E - H)\right], \tag{2}$$

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with Θ the Heaviside step function. Although less well-known, the Gibbs entropy has appeared in some thermodynamics textbooks (e.g., Ref. [5]). For either case, the temperature is defined by the usual relation

$$\frac{1}{T} = \frac{\partial S}{\partial E}, \tag{3}$$

and we thus define the Boltzmann (T_B) and Gibbs (T_G) temperatures by combining Eq. (1) or Eq. (2) with Eq. (3). For spin systems in magnetic fields, as well as the system of cold atomic gases in optical lattices studied in Ref. [4], the difference in these entropy definitions leads to a situation in which T_B can be negative, while T_G is positive. The proposal by DH that the Gibbs definition is the correct one has led to a spirited debate in the literature [6–14]. Here our goal is to investigate how these different entropy definitions could be measured in a specific experimental system, namely trapped ultracold fermionic atomic gases.

2. Main results

In this paper we study the distinction between Gibbs and Boltzmann entropies and temperatures in the context of ultracold trapped atomic gases, which are perhaps the simplest system that can truly be taken to be in the microcanonical ensemble. We study N identical fermionic atoms confined in a quasi-one dimensional trapping potential (realized by a trap that exhibits tight confinement in two directions and weak confinement in the third). Of course, this system does not have an upper energy bound, and therefore is not expected to exhibit negative temperature. Nonetheless, there is still a difference between the Gibbs and Boltzmann entropy definitions, implying a difference between T_B and T_G that could be experimentally significant at small N. Since experiments on cold atomic gases have already accessed the small-N regime [15] and have realized the quasi-1D regime using an optical lattice potential [16,17], we propose that our results may be relevant for future experiments that can distinguish between the Boltzmann and Gibbs temperature definitions, shedding further light on this controversy.

In asking the question of which temperature definition, Boltzmann or Gibbs, is correct, we need a third temperature scale to compare to. A common way to measure the temperature in cold atomic gas experiments is by measuring the atom density vs. position and comparing to a theoretical formula based on the Fermi distribution [18]. Inspired by this, we shall define a third temperature scale, T_{GC}, based on the grand-canonical picture in which single-particle levels are occupied according to the Fermi distribution. One question that we shall address is whether the expected value of T_{GC} is closer to T_B or T_G (if either) for a 1D trapped fermionic atomic gas assumed to be in the microcanonical ensemble at total particle number N and energy E. A natural objection to this line of reasoning is that T_{GC} only holds rigorously for large N, in the thermodynamic limit (where number and energy fluctuations can be neglected), whereas we consider the regime of small N (where the difference between T_B and T_G is largest). However, in practice we find that the microcanonical density profile is very accurately fit by the grand canonical picture even in the small N regime. This implies that an experiment attempting to extract the temperature by observing the local density as a function of position would "measure" a temperature close to T_{GC}.

Our main result can be seen in Fig. 1 that compares these entropy and temperature definitions for the case of $N = 5$ fermions. This figure shows that, at least in the small N regime, the inequalities $S_G > S_B$ and $T_{GC} \simeq T_G < T_B$ hold. Indeed, the difference between T_G and T_B increases with increasing energy, while T_{GC} remains close to T_G suggesting that, at least at small N, the Gibbs definition is the appropriate one (i.e., closer to the definition consistent with a grand-canonical picture based on the Fermi distribution). As discussed below, the difference between T_G and T_B decreases with increasing N (as seen in Fig. 2), consistent with the expectation that they should be equal in the thermodynamic limit. We argue below, however, that for any fixed N, for sufficiently large energy, the qualitative behavior shown in Fig. 1 holds.

3. System Hamiltonian and entropy calculations

We study a single-species gas of atomic fermions confined to a harmonic trapping potential that is anisotropic, satisfying $\omega_y = \omega_z \gg \omega_x$. At sufficiently low numbers of particles, such that the system chemical potential is also much less than $\hbar\omega_z$, such a gas can be accurately modeled by the one-dimensional second quantized Hamiltonian

$$H = \int dx\, \Psi^\dagger(x)\left[\frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2\right]\Psi(x), \tag{4}$$

where $\hat{p} = -i\hbar\frac{d}{dx}$ is the momentum operator, m the particle mass, and the fermionic field operators $\Psi(x)$ satisfy the anticommutation relation $\{\Psi(x), \Psi^\dagger(x')\} = \delta(x - x')$. It is convenient to express H in terms of mode operators c_n, which are related to the field operators by

$$\Psi(x) = \sum_{n=0}^{\infty} \psi_n(x) c_n, \tag{5}$$

where $\psi_n(x)$ is the well-known solution to the one-dimensional quantum harmonic oscillator,

$$\psi_n(x) = \frac{1}{\sqrt{2^n n!} a^{1/4}} \frac{1}{\pi^{1/4}} e^{-\frac{x^2}{2a^2}} H_n(x/a), \tag{6}$$
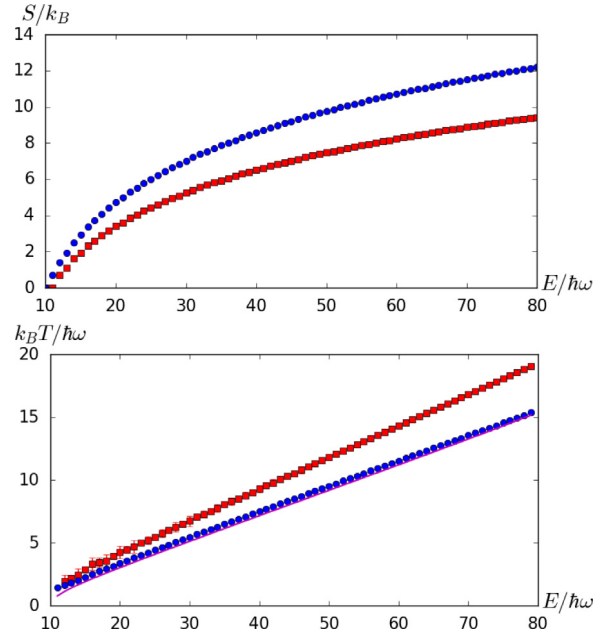
Fig. 1. The top panel compares the Gibbs (S_G, blue circles) and Boltzmann (S_B, red squares) entropy definitions for a trapped 1D fermionic atomic gas with $N = 5$ fermions as a function of energy E normalized to the oscillator energy. The bottom panel compares the Gibbs (T_G, blue circles) and Boltzmann temperatures (T_B, red squares), showing a clear difference that increases with increasing E. The purple line in the bottom panel is the grand-canonical temperature T_{GC} that is obtained assuming the grand-canonical number and energy equations [Eqs. (14) and (15)] hold. The small error bars on the T_G and T_B results indicate the uncertainty in evaluating the derivative Eq. (3) given that we only have entropy values at discrete values of E.
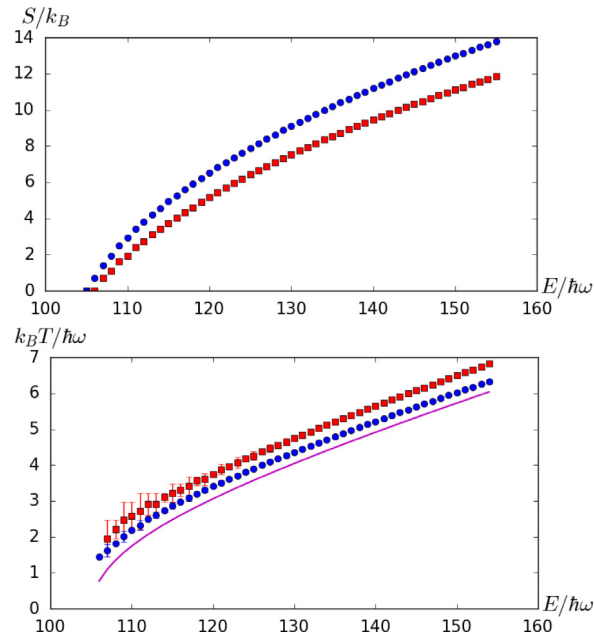

Fig. 2. As in Fig. 1, the top panel compares the Gibbs (S_G, blue circles) and Boltzmann (S_B, red squares) entropy definitions for a 1D fermionic atomic gas with $N = 15$ fermions as a function of energy E normalized to the oscillator energy $\hbar\omega$. The bottom panel compares the Gibbs (S_G, blue circles) and Boltzmann temperatures (T_B, red squares), showing a modest difference that increases with increasing E (as in the $N = 5$ case, Fig. 1). The purple line in the bottom panel is the grand-canonical temperature T_{GC} that is obtained assuming the grand-canonical number and energy equations [Eqs. (14) and (15)] hold.

where $H_n(x)$ is the nth Hermite polynomial and $a = \sqrt{\frac{\hbar}{m\omega}}$ is the oscillator length. The corresponding eigenvalue is $\epsilon_n = \hbar\omega(n + \frac{1}{2})$, giving for the system Hamiltonian, after plugging Eq. (5) into Eq. (4),

$$H = \sum_{n=0}^{\infty} \epsilon_n c_n^\dagger c_n. \tag{7}$$

Henceforth, we shall measure lengths in units of the oscillator length and measure energies relative to $\hbar\omega$. It is also convenient to drop the zero point energy, so that $\epsilon_n = n$. Our next task is to analyze the behavior of a gas of N fermions, described by H, in the microcanonical ensemble. Then, a member of this ensemble is described by a wavefunction with certain levels occupied:

$$|\Psi\rangle = c_{n_1}^\dagger c_{n_2}^\dagger \cdots c_{n_N}^\dagger |0\rangle, \tag{8}$$

with $|0\rangle$ the vacuum state. Due to the Pauli principle, no two n_i may coincide.

Since the energy eigenvalues are discrete, our definition of $\Omega(E, N)$ will differ from that given below Eq. (1) but instead simply count the total number of allowed microstates with total energy E. Indeed, since the single-particle energies are integers, the energy eigenvalue of $|\Psi\rangle$, $E[\{n_i\}] = \sum_{i=1}^{N} n_i$, is also an integer, so that the problem of determining $\Omega(E, N)$ is related to the well-known integer partitioning problem. Following standard notation, we define $P(n)$ to be the total number of partitions of the integer n and $P(n, m)$ to be the number of partitions of the integer n into exactly m parts so that, for example, $P(3) = 3$ (with the partitions being $\{\{3\}, \{2, 1\}, \{1, 1, 1\}\}$) and $P(5, 3) = 2$ (with the partitions being $\{\{3, 1, 1\}, \{2, 2, 1\}\}$). Both functions allow repetitions of integers appearing in the partitions, which we must exclude due to the Pauli principle. However, it turns out that the number of partitions of the integer n into exactly m parts excluding repetitions, $Q(n, m)$, is related to $P(n, m)$ by:

$$Q(n, m) = P(n - \frac{1}{2}m(m - 1), m). \tag{9}$$

To verify this well-known identity, we establish a one-to-one correspondence between partitions associated with the left and right sides of this formula. Thus, consider one of the partitions on the right side, which is of the form $\{n_1, n_2 \cdots, n_{m-1}, n_m\}$. By definition, this partition has energy $E[\{n_i\}] = n - \frac{1}{2}m(m - 1)$ and may contain some number of repeated integers but satisfies $n_i \geq n_{i+1}$ (with larger integers to the left as in the above examples). However, a new partition with no repeated integers can be obtained by incrementing the integers in this partition thusly: $\{n_1 + m - 1, n_2 + m - 2, \ldots, n_{m-1} + 1, n_m\}$. This partition clearly satisfies $n_i > n_{i+1}$, and has energy n since the increments of each integer add to $\frac{1}{2}m(m - 1)$. Since it is clear that any restricted partition (corresponding to $Q(n, m)$) can be connected to an unrestricted partition (corresponding to $P(n - \frac{1}{2}m(m - 1), m)$), the relation Eq. (9) holds. To obtain our final expression for $\Omega(E, N)$ in terms of $Q(n, m)$, we recall that a fermion in the lowest level $n = 0$ has zero energy (not contributing to E). This finally implies that the total number of microstates has two contributions:

$$\Omega(E, N) = Q(E, N) + Q(E, N - 1), \tag{10}$$

with the first (second) term on the right side corresponding to microstates in which the $n = 0$ level is unoccupied (occupied).

In terms of Eq. (10), the Boltzmann entropy is

$$S_B(E) = k_B \ln \Omega(E, N), \tag{11}$$

while the Gibbs entropy sums over all allowed total energies less than E:

$$S_G(E) = k_B \ln \sum_{E' < E} \Omega(E', N). \tag{12}$$

In Figs. 1 and 2, we show our numerical results for S_B and S_G (top panel) along with the Boltzmann and Gibbs temperatures (bottom panel) as a function of the total system energy E. Due to the Pauli principle, the minimum system energy is

$$E_{\min} = \frac{1}{2}N(N - 1), \tag{13}$$

We see that the Gibbs entropy is larger than the Boltzmann entropy, $S_G > S_B$, with a difference that increases with increasing system energy. Similarly, the Gibbs temperature (obtained by numerically differentiating the entropy results and using Eq. (3)) is lower than the Boltzmann temperature. The solid line in the bottom panel of Figs. 1 and 2 shows the "grand-canonical" temperature T_{GC}, extracted by assuming that the equations for the grand-canonical ensemble hold:

$$N = \sum_{n=0}^{\infty} n_F(\epsilon_n - \mu), \tag{14}$$

$$E = \sum_{n=0}^{\infty} \epsilon_n n_F(\epsilon_n - \mu), \tag{15}$$
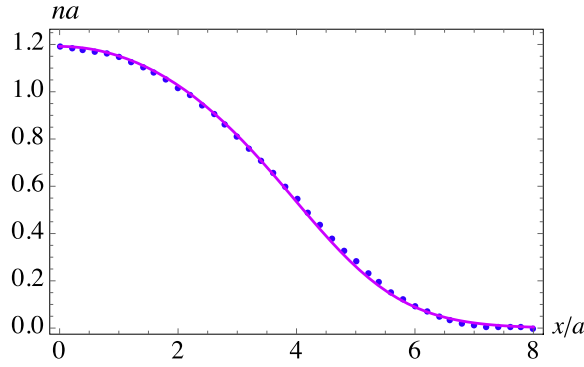
Fig. 3. Plot of local density n (normalized to a^{-1} with a the oscillator length) vs. position x (normalized to a) for a system with $N = 9$ particles and energy $E = 60\hbar\omega$, comparing the microcanonical density according to Eq. (16) (solid points) to the grand-canonical density (solid purple line) Eq. (17).

with $n_F(x) = \frac{1}{e^{\beta x}+1}$ (and $\beta = \frac{1}{k_B T}$) the Fermi distribution. Although these only determine the mean particle number and energy (with fluctuations that vanish in the thermodynamic limit), they provide a unique prediction that can be compared to T_B and T_G.

We now argue that the local density profile of a 1D trapped fermionic gas in the microcanonical ensemble is approximately consistent with the grand canonical ensemble picture even at small N. To establish this, in Fig. 3, we compare the microcanonical density,

$$n(x) = \frac{1}{\Omega(E,N)} \sum_{\{n_i\}} \sum_{i=1}^{N} |\psi_{n_i}(x)|^2, \tag{16}$$

for the case of $E = 60$ and $N = 9$, to the grand canonical density

$$n_{GC}(x) = \sum_{n=0}^{\infty} n_F(E_n - \mu) |\psi_n(x)|^2, \tag{17}$$

using the temperature ($T_{GC} = 4.4$) and chemical potential ($\mu_{GC} = 7.8$) obtained by solving Eqs. (14) and (15) for the same system parameters. For these parameters, $T_G \simeq 4.8$ while $T_B \simeq 5.5$. In cold atomic gas experiments, the temperature is often extracted by measuring the density profile (and assuming the grand-canonical picture holds). Thus, the close agreement in Fig. 3 suggests that a cloud at this energy and particle number would be "measured" to have a temperature given by T_{GC}, closer to T_G.

4. Universal entropy at low energies

Our results suggest that the Gibbs and Boltzmann entropy and temperature definitions agree at small E but differ at large E, with the Gibbs temperature definition being closer to the grand-canonical temperature. In this section we show that the Gibbs and Boltzmann entropy formulas have a universal form at low energies that greatly simplifies their calculation. We will propose that the approximate agreement between T_B and T_G is related to the fact that the universal formulas hold at low energies, and that the deviation of T_B from T_G occurs when the system is outside of the universal regime.

To establish the existence of the universal entropy formulas, we define the relative $\epsilon = E - E_{min}$ with E_{min} the minimum energy Eq. (13). Then, as illustrated in Fig. 4, the Gibbs entropies, plotted as a function of ϵ, are universal (independent of N) for sufficiently small ϵ. A similar universality holds for S_B.

This universality at small ϵ follows from the following mathematical identity for the integer partition function [19]:

$$P(n,m) = P(n-m) \qquad \text{for } m \geq \frac{n}{2}, \tag{18}$$

relating $P(n,m)$ to the unrestricted partition function at small n. When this result is combined with Eq. (9) and plugged into Eq. (10), we find

$$\Omega(E,N) = P(\epsilon) \qquad \text{for } \epsilon \leq N - 1, \tag{19}$$

where we note that only the second term of Eq. (10) contributes in this small-ϵ regime. In this context, the identity Eq. (19) can be related, physically, to the Pauli principle: for $\epsilon = 0$, the only allowed microstate of the N fermion gas is the ground state which has all levels filled up to the Fermi level $n_F = N - 1$. If we increase the energy of our system to
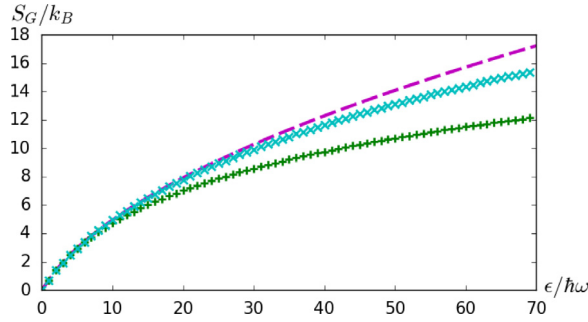
Fig. 4. Gibbs entropy, normalized to k_B, as a function of the energy relative to the minimum energy ($\epsilon = E - E_{\min}(N)$), for the cases of $N = 5$ (green plusses) and $N = 10$ (blue crosses). They agree with each other and with the universal entropy (following from plugging Eq. (19) into Eq. (12)) (dashed purple) at low ϵ and diverge at large ϵ.

small ϵ, the allowed microstates simply correspond to particle–hole excitations of this ground state in which fermions are promoted from levels slightly below n_F to slightly above n_F. In these microstates, all levels up to level $m = N - \epsilon - 1$ (at least) are occupied. This follows because exciting a fermion from a lower level would cost too much energy, and implies that the number of microstates is given by the number of ways to construct such excitations i.e., by the number of *unrestricted* partitions of ϵ. This implies Eq. (19). This picture holds for the microstates only for $m \geq 0$, implying the restriction $\epsilon \leq N - 1$.

Eq. (19) implies the following expressions for the Boltzmann and Gibbs entropies in the universal regime:

$$S_B(\epsilon) = k_B \ln P(\epsilon), \quad \text{for } 0 < \epsilon \leq N - 1, \tag{20}$$

$$S_G(\epsilon) = k_B \ln \sum_{\epsilon'=0}^{\epsilon} P(\epsilon'), \quad \text{for } 0 < \epsilon \leq N - 1. \tag{21}$$

The calculation of S_B and S_G via Eqs. (20) and (21) is much easier than via the direct formula Eq. (10) since they depend only on the unrestricted integer partition function. In fact, a convenient asymptotic large-ϵ formula for $P(\epsilon)$ has been derived by Hardy and Ramanujan [20]

$$P(\epsilon) \simeq \frac{1}{4\epsilon\sqrt{3}} e^{\pi\sqrt{\frac{2\epsilon}{3}}}, \tag{22}$$

which allows a straightforward approximate numerical evaluation of S_G and S_B in the large ϵ regime. In the top panel Fig. 5, we compare S_G and S_B computed using Eqs. (20) and (21) along with Eq. (22), with the comparison between T_G and T_B appearing in the bottom panel. The close agreement between these curves is natural, given that we expect the difference between the Gibbs and Boltzmann entropies to vanish in the large system "thermodynamic" limit. We propose that, since the universal formulas Eqs. (20) and (21) only hold for $\epsilon < N - 1$, the large difference between S_B and S_G that we find for small N occurs when these systems are outside of the universal regime and that, for any fixed N, the approximate agreement between S_B and S_G holds only for $\epsilon < N - 1$, with differences between S_B and S_G (and between T_G and T_B) occurring for large ϵ.

5. Concluding remarks

The question of the correct theoretical description of finite quantum systems (e.g., microcanonical or canonical) has been an ongoing question for theoretical investigation. Recent work has argued that the canonical ensemble naturally emerges for finite quantum systems coupled to a bath [21–23]. Swendsen and collaborators have argued that although finite systems seemingly possess discrete energy levels, interaction effects (such as with a heat bath) generally lead to a continuous energy distribution, also implying the appropriateness of the canonical ensemble [24–26]. However, work by Hänggi et al. [27] refutes this, showing that the Gibbs entropy in the microcanonical ensemble satisfies all thermodynamic laws. These authors further claim that entropy formulations in the canonical and grand canonical ensemble are only approximations and are inexact compared to the microcanonical definitions. In our analysis, we proceeded in using the microcanonical ensemble to compare the Boltzmann and Gibbs definitions of entropy in order to determine an experimentally identifiable difference between the temperatures predicted by the two definitions.

We have investigated the Gibbs (S_G) and Boltzmann (S_B) entropies for a system of N fermions in a one-dimensional harmonic oscillator potential with total energy E, finding that the Gibbs and Boltzmann entropy and temperature definitions approximately agree at small E while diverging from each other at large E. In the large energy regime, we find that the corresponding Boltzmann temperature is much higher than the Gibbs temperature, with the latter being close to T_{GC}, the temperature expected based on the grand-canonical ensemble. Thus, we find a striking (and potentially
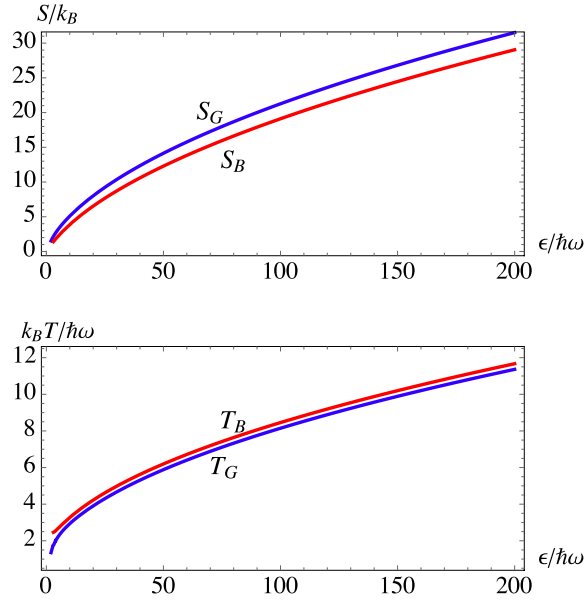
Fig. 5. The top panel shows the Gibbs and Boltzmann entropies, normalized to the Boltzmann constant, as a function of system energy using the formulas Eqs. (20) and (21) (valid for sufficiently low $\epsilon = E - E_{\min}$) along with the Hardy–Ramanujan asymptotic approximation for the integer partition function (Eq. (22)). The bottom panel shows the corresponding Gibbs and Boltzmann temperatures, obtained by numerical differentiation of the results in the top panel along with Eq. (3).

experimentally observable) difference between the Gibbs and Boltzmann pictures for the entropy and temperature in the microcanonical ensemble.

For sufficiently large N, standard thermodynamics arguments imply that the difference between S_G and S_B should vanish. We found that the agreement between S_G and S_B at low energies is connected to the existence of universal formulas for these entropies that apply for sufficiently small $\epsilon = E - E_{\min}$, allowing us to numerically establish agreement among these entropy and temperature definitions for larger N.

We proposed that, for any fixed N, this agreement will break down for larger system energies (beyond the universal regime). This would imply that any system at fixed N would exhibit the qualitative behavior shown in Figs. 1 and 2 for sufficiently large E, with the difference between S_B and S_G (and between T_B and T_G) increasing with increasing E. Since establishing this is quite numerically intensive (except for the small N cases presented here), we leave further investigation of this issue for future work.

Acknowledgments

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