Gibbs, Boltzmann, and negative temperatures

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In a recent paper, Dunkel and Hilbert [Nature Physics 10, 67–72 (2014)] use an entropy definition due to Gibbs to provide a ‘consistent thermostatistics’ which forbids negative absolute temperatures. Here we argue that the Gibbs entropy fails to satisfy a basic requirement of thermodynamics, namely that when two bodies are in thermal equilibrium, they should be at the same temperature. The entropy definition due to Boltzmann does meet this test, and moreover in the thermodynamic limit can be shown to satisfy Dunkel and Hilbert’s consistency criterion. Thus, far from being forbidden, negative temperatures are inevitable, in systems with bounded energy spectra.

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The concept of negative temperature is one which has been discussed extensively in the past [1–9], and continues to attract attention to the present day [10–15]. For classical systems with many degrees of freedom, our discussion will focus only on systems with very few degrees of freedom. In what follows, we leave out the additive constant, again, that is immaterial for the remainder of our argument.

In a recent article [15] Dunkel and Hilbert argued that the use of Boltzmann’s definition of entropy in the above expression for the temperature leads to unphysical predictions [16]. They propose instead to define entropy using Gibbs’ notion of ‘extension in phase space’ (see below) [17]. They argue that this approach, which they attribute to Gibbs [18], cannot give rise to negative temperatures nor can it predict the existence of Carnot cycles with an efficiency larger than one. Moreover, they show that the Boltzmann approach gives rise to unphysical predictions for systems with very few degrees of freedom. In what follows, we will ignore the latter point. As Gibbs himself stated on several occasions, it is unreasonable to expect a meaningful correspondence between statistical mechanics and thermodynamics for systems with only a few degrees of freedom. Our discussion will focus only on systems with very many degrees of freedom, i.e. those which are in the proverbial ‘thermodynamic limit’ [19].

The point about negative temperatures and Carnot cycles is more interesting. We shall argue below that Dunkel and Hilbert are mistaken in their attempt to consign the Boltzmann entropy to the ‘trash can of history’, and that instead it is the Gibbs entropy which fails to meet a basic criterion of thermodynamics. In contrast, the Boltzmann entropy does meet this basic test, and we also prove that it satisfies Dunkel and Hilbert’s consistency criterion in the thermodynamic limit. With the Boltzmann entropy, negative temperatures are inevitable in systems with bounded energy spectra, but this is not a problem if one pays attention to the details as explained by Ramsey over half a century ago [2]. To round off we present a pedagogical example in which we construct a concrete example of a Carnot cycle connecting reservoirs of opposite temperatures, thereby exhibiting a Carnot efficiency bigger than one.

I. CRITIQUE OF THE GIBBS ENTROPY

Let us briefly define the key quantities in modern notation. In particular, we will replace Gibb’s ‘extension in phase space’ by \( \Omega(E) \), the total number of quantum states of a system with an energy less than or equal to \( E \). For classical systems with many degrees of freedom, \( \Omega(E) \) is dominated by the number of states very close to \( E \). To compute the number of states in a narrow interval \( \Delta \epsilon \) around \( E \), we simply differentiate \( \Omega(E) \) with respect to \( E \), to obtain

\[
\frac{\partial \Omega(E)}{\partial E} \Delta \epsilon \equiv \omega(E) \Delta \epsilon.
\]  

(1)

Boltzmann’s definition of entropy is

\[
S_B(E) = k_B \ln \omega(E) + \text{constant}.
\]  

(2)

In contrast, Gibbs also considered other definitions of entropy, including

\[
S_G(E) = \ln \Omega(E) + \text{constant}.
\]  

(3)

Of course, Gibbs did not include \( k_B \) in his definition but, again, that is immaterial for the remainder of our argument. In what follows, we leave out the additive constant,
as it is irrelevant for a discussion of thermal equilibrium and heat engines.

The definition of temperature in thermodynamics is

\[ T = \left( \frac{\partial S(E)}{\partial E} \right)^{-1} \]  \hspace{1cm} (4)

For classical systems with many degrees of freedom, the difference in the value of the temperature based on \( S_1 \) and \( S_G \) is negligible; the reason being that for such systems \( \omega(E) \) increases very steeply with \( E \), hence a constraint \( \epsilon \leq E \) is almost equivalent with \( \epsilon = E \). However, for systems with an energy that is bounded from above, \( \omega(E) \) may decrease for large energies, whereas \( \Omega(E) \) is monotonically increasing. An example is a system of \( N \) non-interacting spins, which we shall discuss in more detail below. In the regime where \( \omega(E) \) is not a monotonically increasing function of \( E \), the two definitions of entropy lead to very different results for the temperature of a macroscopic system (one negative, the other positive). Only one can be right. It turns out that, in contrast to a macroscopic system (one negative, the other positive).

\[ \frac{\partial \ln \omega(T_1, T_2)}{\partial E_1} = 0. \]  \hspace{1cm} (6)

Using the fact that \( dE_1 = -dE_2 \) we obtain

\[ \frac{\partial \ln \omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \omega_2(E_2)}{\partial E_2} \]  \hspace{1cm} (7)

and hence

\[ \frac{1}{T_1} = \frac{1}{T_2}. \]  \hspace{1cm} (8)

Note that we obtain this result only if we use the Boltzmann entropy \( S = k_B \ln \omega \).

\[ \text{But, should the Gibbs entropy be so lightly dismissed? After all, as Dunkel and Hilbert point out, there is a mathematically rigorous equipartition theorem (Eq. (8) of Ref. [15]) which features } S_G \text{ and would appear to single out the associated temperature } T_G = (\partial S/G/\partial E)^{-1} \text{ as a privileged quantity. However, it is dangerous to extrapolate from this that equality of } T_G \text{ can be used to gauge whether systems are in thermal equilibrium; this can easily lead to absurd results. For example, consider the finite-size spin system in Fig. 1 of Ref. [15]. In the population-inverted state (see below for the definition) the Boltzmann temperature is negative but } T_G \text{ is positive and finite. One can easily construct a classical system (for example a perfect gas) with the same value of } ]
$T_G$. Should one therefore conclude that the spin system with an inverted population can be in thermal equilibrium with a perfect gas? Of course not! The spin system would lose energy to the gas raising the (Boltzmann) entropy of both. In the conventional picture of course, a population inverted state has a negative Boltzmann temperature and is always ‘hotter’ than a normal system with a positive Boltzmann temperature, so one would always expect heat transfer to take place.

The only remaining point to discuss is Dunkel and Hilbert’s consistency criterion. In Ref. [13] it is proved that $S_B$ satisfies this requirement, independent of system size. Dunkel and Hilbert further argue that $S_B$ must therefore fail this requirement because typically $S_B \neq S_G$ for small systems. However it can be proved that in the thermodynamic limit $S_B$ does satisfy the consistency criterion. In Appendix VI A we present such a proof. Our conclusion therefore is that $S_B$ meets all the requirements one would expect of a thermodynamic entropy, whereas $S_G$ does not.

II. NEGATIVE TEMPERATURES AND CARNOT CYCLES

Now that we have convinced ourselves we should use Boltzmann’s definition of entropy, the implication is that if $\omega(E)$ is not a monotonically increasing function of $E$, negative temperatures are inevitable. Are negative temperatures a problem? Not really. First of all, heat still only flows from ‘hot’ (low $1/T$) to ‘cold’ (high $1/T$). But indeed, Carnot efficiencies can be larger than one [23]. This may seem strange, but it violates no known law of nature.

Let us consider a Carnot cycle operating between two heat reservoirs (see Fig. 1). The ‘hot’ reservoir 1 operates at a negative temperature $T_1 < 0$. The ‘cold’ reservoir 2 operates at a positive temperature $T_2 > 0$. We now operate an engine between the two reservoirs. The first law of thermodynamics states that the work $w$ done by the engine must be equal to the heat $q_1 - q_2$ absorbed by the engine (energy conservation). It is important to look at the sign definitions: a positive sign of $q_1$ means that heat flows out of reservoir 1. A positive sign of $q_2$ means that heat flows into reservoir 2. Each stage in the cycle is reversible so that the entropy changes of the engine are respectively $\Delta S_1 = q_1/T_1$ and $\Delta S_2 = -q_2/T_2$. Perhaps confusingly, $\Delta S_1 < 0$, but this must be so because when heat flows out of a negative temperature reservoir, its entropy increases. Now, since $S$ is a state function, the total entropy of the engine does not change, and $\Delta S_1 + \Delta S_2 = 0$. This implies

$$\frac{q_1}{T_1} = \frac{-q_2}{T_2}. \quad (9)$$

If $T_1$ is negative and $T_2$ is positive, then the signs of $q_1$ and $q_2$ must be opposite. Hence, if heat flows out of reservoir 1 ($q_1 > 0$), then reversibility of the engine requires that heat also flows out of reservoir 2 ($q_2 < 0$). In such a situation, the work done is

$$w = q_1 - q_2 = q_1 - |q_2|. \quad (10)$$

The efficiency of the Carnot cycle is defined as the ratio

$$\eta = \frac{w}{q_1} = 1 + \frac{|q_2|}{q_1} > 1. \quad (11)$$

![Figure 1](image-url)
Hence, indeed, the Carnot efficiency is larger than one. However, no physical law forbids that. There is one potential point of concern: it would seem that it is possible to run an engine in contact with a single, negative-temperature heat bath. Whilst this is true, negative temperature heat baths do not occur naturally; they have to be prepared (in the case of lasers, we call this ‘pumping’). If the total heat and work budget includes the preparation of the negative-temperature heat bath from a system at positive temperatures, then it turns out that it is still not possible to run an engine sustainably by extracting heat from a single reservoir. Negative temperatures do not imply perpetual motion.

III. SPIN SYSTEMS

Spin systems form an excellent arena to explore the issues raised here [2]. For example, such a system can also provide the ‘working material’ for a heat engine which can withstand both positive and negative temperatures in a Carnot cycle. For a mechanical analog, see Ref. [11].

A. Two level system

The simplest case to consider is a system of $N_0$ spins in a ground state with zero energy and $N_1$ spins are in an excited state at energy $\epsilon$, such that the total number of spins $N = N_0 + N_1$ is fixed. Often one can visualise the $N_0$ spins as ‘down’ and the $N_1$ spins as ‘up’, but care is needed with this mental picture as we shall consider cases where $\epsilon < 0$ and $N_1 > N_0$ (population inversion). We shall suppose that the spins are distinguishable so that the number of states which can accommodate this arrangement of spins is $\omega = N!/(N_0! N_1!)$. For this system, the energy and (Boltzmann) entropy are therefore, respectively,

$$E = \epsilon N_1,$$

$$S = \ln \omega = N \ln N - N_0 \ln N_0 - N_1 \ln N_1. \quad (12)$$

We have supposed $N \gg 1$ in the entropy expression. For notational simplicity we set $k_B = 1$ and drop the subscript ‘B’ from $S_B$ since we shall be exclusively considering the Boltzmann entropy.

Since $N_0 = N - N_1$, and $N$ is fixed, the (Boltzmann) temperature of the spin system is

$$T = \frac{\partial S}{\partial E} = \frac{(\ln N_0 + 1) - (\ln N_1 + 1)}{\epsilon} = -\frac{N_0}{N_1}. \quad (13)$$

Therefore one obtains the familiar Boltzmann result

$$N_1 = N_0 e^{-\epsilon/T}. \quad (14)$$

It follows that

$$\frac{N_1}{N} = \frac{e^{-\epsilon/T}}{1 + e^{-\epsilon/T}}, \quad \frac{N_0}{N} = \frac{1}{1 + e^{-\epsilon/T}}. \quad (15)$$

The free energy $F = E - TS$ has to be expressed in terms of its ‘natural’ variables, $T$ and $N$. We first have

$$S = N \ln N - N_0 \ln N_0 - N_1 \ln N_1$$

$$= (N_0 + N_1) \ln N - N_0 \ln N_0 - N_1 \ln N_1 \quad (16)$$

$$= -N_0 \ln(N_0/N) - N_1 \ln(N_1/N).$$

Consequently,

$$F = \epsilon N_1 + TN_0 \ln N_0/N + TN_1 \ln N_1/N. \quad (17)$$

We substitute Eqs. (15) into this to find

$$F = -TN \ln(1 + e^{-\epsilon/T}). \quad (18)$$

This rather neat result follows after a few lines of algebra which is left as an exercise for the reader. It can also be derived from the partition function sum, which is left as a further exercise.

From Eq. (18), the quantity conjugate to $\epsilon$ is

$$\frac{\partial F}{\partial \epsilon} = -\frac{N e^{-\epsilon/T}}{1 + e^{-\epsilon/T}} = -N_1. \quad (19)$$

In this sense, to within a minus sign, $N_1$ is the natural order parameter to describe the arrangement of the spins. For this system, the $\epsilon$-$N_1$ plane is the analog of the $p$-$V$ diagram encountered in textbooks. The first expression in Eqs. (15) serves as an ‘equation of state’, providing isotherms in the $\epsilon$-$N_1$ plane.

For completeness, the entropy as a function of $T$ and $N$ follows most simply by solving $F = E - TS$. Substituting the relevant expressions, one finds (another exercise!)

$$\frac{S}{N} = \frac{\epsilon}{T} \frac{e^{-\epsilon/T}}{1 + e^{-\epsilon/T}} + \ln(1 + e^{-\epsilon/T}). \quad (20)$$

This function only depends on the ratio $\epsilon/T$, and is in fact symmetric about $\epsilon/T = 0$, although this is not immediately obvious. It is shown in Fig. 2.

If we examine the derivations, we see that all of the above holds for positive and negative $\epsilon$, and more crucially for positive and negative $T$ too. If $\epsilon > 0$ and $T > 0$
the entropy can be written as

$$S = \frac{N}{N_1} \ln \left(1 - \frac{E}{E_M}\right) \ln \left(1 - \frac{E}{E_M}\right) - \frac{E}{E_M} \ln \frac{E}{E_M}.$$  \hfill (21)

This function has the non-monotonic shape shown in Fig. 3 with a maximum at $E^* = E_M/2$. Therefore the spin system has a negative temperature for $E > E_M/2$. The maximum in $S(E)$ corresponds to $1/T = 0$, which suggests that it should be impossible to pass adiabatically (i.e. at constant $S$) from positive to negative temperature through $1/T = 0$. This is in fact a general result [4].

Isotherms for the spin system in the $\epsilon$-$N_1$ plane are illustrated in Fig. 3, for both positive and negative temperatures. The spin system can be moved along an isotherm by connecting it to a thermal reservoir and changing $\epsilon$. The thermal reservoir could be, for example, a much larger spin system, which can be at a positive or negative temperature.

Adiabatic changes in the spin system correspond to changing $\epsilon$ without changing the distribution of spins. One can see from Eq. (12) that keeping $N_0$ and $N_1$ fixed leaves the entropy $S$ unchanged. Adiabats in the $\epsilon$-$N_1$ plane in Fig. 3 are therefore horizontal lines. One further point can be made. Since $N_0$ and $N_1$ depend on the ratio $\epsilon/T$, it follows that $T$ remains strictly proportional to $\epsilon$ in an adiabatic change (cf. Eq. (20)). This observation implies that we can invert the temperature of the spin system adiabatically, by changing the sign of $\epsilon$.

\section{B. Three level system}

The three level system is worth considering because it has some novel features not encountered in the two level system, and it sheds further light on the problems associated with the Gibbs entropy. The main new feature is that a three level spin system has an internal (macroscopic) degree of freedom, since specifying the energy and total number of spins is insufficient to fix all the population levels. We start by noting the analog of Eq. (12):

$$N = N_0 + N_1 + N_2,$$

$$E = \epsilon_1 N_1 + \epsilon_2 N_2,$$

$$S = N \ln N - N_0 \ln N_0 - N_1 \ln N_1 - N_2 \ln N_2.$$  \hfill (22)

We have now explicitly included the constraint on the total number of spins. The entropy in this is Boltzmann’s $S = \ln \omega$. There is absolutely no disagreement that the most likely macroscopic arrangement of spins is the one which maximises $\omega$, and hence $S$. To solve this, the usual (textbook) method is to introduce Lagrange multipliers for the constraints (i.e. $\mu$ for $N$, and $\beta$ for $E$). However the problem is sufficiently simple that one can also proceed, for example, by eliminating $N_1$ and $N_2$ from the above, to find $S$ as a function of $N_0$ alone, which is then maximised. This is certainly something which everyone should try, at least once! A slightly more elegant method is to differentiate all of the above to get

$$dN = dN_0 + dN_1 + dN_2 = 0,$$

$$dE = \epsilon_1 dN_1 + \epsilon_2 dN_2 = 0,$$

$$dS = - (\ln N_0 + 1) dN_0 - (\ln N_1 + 1) dN_1$$

$$- (\ln N_2 + 1) dN_2.$$  \hfill (23)

We eliminate $dN_1$ and $dN_2$ between these as though they are algebraic quantities to find

$$dS = - \left( \ln N_0 + \frac{\epsilon_2}{\epsilon_1 - \epsilon_2} \ln N_1 + \frac{\epsilon_1}{\epsilon_2 - \epsilon_1} \ln N_2 \right) dN_0.$$  \hfill (24)

The coefficient in here is precisely $\partial S/\partial N_0$ which would be obtained from the more cumbersome approach. The condition that $S$ is a maximum corresponds to requiring $\partial S/\partial N_0 = 0$. After a small rearrangement, this leads to

$$\frac{1}{\epsilon_1} \ln \frac{N_1}{N_0} = \frac{1}{\epsilon_2} \ln \frac{N_2}{N_0}.$$  \hfill (25)
Let us pause for a moment to see what this is telling us. An experimentalist, for instance, would note that measurement of the relative population of one level (e. g. \(N_1/N_0\)) can be used to make a prediction of the relative population of the other level. Also, if there is a population inversion for one level (e. g. \(N_1/N_0 > 1\) when \(\epsilon_1 > 0\)), there must be population inversion for the other level too. Most likely though, the experimentalist will complain that we have dressed a standard result up in rather unfamiliar language. In Eq. (23), let us call the quantity on either side of the equality \(\sim 1/T\) (or \(\sim 1/k_B T\) if we wish to retain the Boltzmann constant). Then, Eq. (23) can be written

\[
N_1 = N_0 e^{-\epsilon_1/T}, \quad N_2 = N_0 e^{-\epsilon_2/T}.
\]

In other words, the populations satisfy the Boltzmann distribution. The actual value of \(T\) is determined by the constraints on \(N\) and \(E\). The case where \(T < 0\) corresponds to population inversion and will inevitably arise if \(E\) is made big enough at fixed \(N\). Measuring the relative population of one level is the same as measuring \(T\). When \(T\) is known, the relative population of the other level can be predicted. It is easy to see that this generalises to multilevel systems (this is where the Lagrange multiplier method comes into its own), and it matters not one jot or tittle whether \(T\) is positive or negative.

But, what happens to the Gibbs entropy and \(T_G\) in this problem? Recall that we are concerned with large systems where in the normally populated state there is no difference between \(T_G\) and \(T\). In the population inverted state however, \(T_G\) diverges exponentially with system size and has a complicated dependence on the Boltzmann temperature as a function of energy (see Appendix [VIB]). From an experimental point of view this makes \(T_G\) pretty much useless.

Note that in the discussion thus far, the three level spin system has been kept isolated (i. e. in the microcanonical ensemble) and no reservoirs have been involved. We therefore cannot be accused of introducing an assumption of ensemble equivalence by sleight-of-hand. But we feel obliged to point to one more piece of evidence to support the ascendancy of the Boltzmann entropy. Specifically, once \(T\) is measured, the spin system is assured of being in thermal equilibrium with a heat reservoir at that same temperature, irrespective of the sign of \(T\).

C. Carnot cycle with efficiency greater than one

We now return to the two level system and use our knowledge of the thermodynamics outlined above to construct a Carnot cycle which operates between positive and negative temperature reservoirs, along the lines of the general discussion in the previous section. The cycle is shown the thick solid line in the \(\epsilon-N_1\) plane in Fig. 5. The corresponding changes in the spin population are illustrated above the main plot. Our construction can be viewed as a generalisation of the adiabatic demagnetisation procedure widely used as a refrigeration method in experimental low temperature physics [24].

Beginning with the upper left corner, and moving counterclockwise, the cycle starts with a spin system in an inverted state with \(\epsilon < 0\) in contact with a ‘hot’ reservoir at some temperature \(T_1 < 0\). The first step consists in isothermally increasing \(|\epsilon|\). The entropy of the spin system decreases in this step by some finite amount \(\Delta S\) (cf. Fig. 2 noting that \(\epsilon/T > 0\) increases). Since we are proceeding reversibly, the entropy decrease of the spin system is balanced by an entropy increase in the reservoir. Because of the peculiar properties of the negative temperature ‘hot’ reservoir, this means that the spin system withdraws an amount of heat \(q_1 = |\Delta S/T_1|\) from this reservoir. Next, contact with the reservoir is removed and the spin population is inverted adiabatically by reversing the sign of \(\epsilon\) to arrive at the lower right corner. In the third step, the now normally populated spin system is brought into contact with the ‘cold’ reservoir at \(T_2 > 0\), and \(\epsilon\) is decreased isothermally (thus decreasing \(\epsilon/T\)). This is continued until the entropy has increased by the exact same amount \(\Delta S\) lost in the first step. Correspondingly the system also withdraws an amount of heat \(q_2 = \Delta S/T_2\) from this reservoir. Finally the cold reservoir is removed and the population inverted adiabatically once again to return to the upper left corner. Since the system withdraws heat from both reservoirs, the conventionally defined Carnot efficiency \(\eta = 1 - T_2/T_1\) is larger than one, as claimed in the general discussion.

One point needs addressing since \(T \propto \epsilon\) and population inversion is achieved by reversing the sign of \(\epsilon\). Clearly, this avoids the aforementioned technical problem of adiabatically connecting regions of opposite temperature through \(1/T = 0\) but it means that the system passes through a state where \(T = 0\), in apparent contravention of the third law of thermodynamics. However, by keeping \(\epsilon/T\) finite, we are not putting all the spins in the same state, which would be a violation of the third law. Our thought experiment violates no fundamental principle. Nevertheless it is clear that any attempt at a practical realisation would be frustrated by the third law, in the form which states that the entropy \(S \to 0\) as \(T \to 0\). According to this, it is impossible to connect states with entropies \(S > 0\) by an adiabatic process that passes through absolute zero.

The discrepancy arises, of course, because an idealised system of non-interacting spins does not exist in reality. Remnant interactions between spins, or with the environment, provide the necessary means to enforce the third law in the real world [24]. We can escape this by allowing a little irreversibility to creep in, and ‘jump around’ the problem at \(T = 0\). This point has been discussed recently in Ref. [14]. If we do so, the efficiency will fall below that of the ideal, reversible cycle. But of course that will happen anyway in any practical realisation. The point is that the ideal efficiency of the engine can be arranged to be considerably greater than one, so it seems
to us there is no fundamental reason why the efficiency of a practical engine could not also be bigger than one, even if it falls short of the Carnot ideal.

IV. DISCUSSION

Let us summarise. Our claim is that the Gibbs entropy fails to meet a very basic expectation—the second law of thermodynamics. The Boltzmann entropy does meet this requirement. Moreover, in the thermodynamic limit the Boltzmann entropy also satisfies the consistency criterion demanded by Dunkel and Hilbert. Therefore we see no reason why the Boltzmann entropy should be displaced from its position as the lynchpin connecting statistical mechanics with thermodynamics.

Proponents of the Gibbs entropy may claim that we have taken it out of context, and that it should only be discussed in relation to isolated systems (i.e. in the microcanonical ensemble). This would seem to be a singularly narrow definition of temperature since it means we are not allowed to use it in the context of thermal equilibrium [24]. But, as we have seen for the three level spin system, even with such an extreme position, the Gibbs entropy provides little in the way of added value.

What are we to make of the fact that the Gibbs entropy satisfies certain exact mathematical theorems, as adduced by Dunkel and Hilbert. Of course we do not dispute these. Rather, we say that for small systems they are evidence of the well-known inequivalence of ensembles, and the difficulty in finding a suitable entropy definition [25]. For large systems, the theorems can be used to prove that the Boltzmann entropy acquires certain desired features. But if the exact theorems lead towards nonsensical conclusions (for example that the temperature diverges exponentially with system size), then what they are telling us is that the interpretation is wrong. The original position is seen to become untenable.

With our viewpoint, negative temperatures are inevitable in systems with bounded energy spectra. The necessary extension of the formalism of thermodynamics to treat this was described by Ramsey in 1956 [2]. For sure, one must abandon the postulate that the entropy be an increasing function of energy. But as so many times in the history of science, an abandoned postulate opens the door to an enriched formalism, capable of describing phenomena which were simply not envisaged in the foundational era of the subject.

V. ACKNOWLEDGMENTS

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VI. APPENDICES

The derivations here use rather more advanced mathematics than we have employed in the main text, it seems appropriate to confine them to Appendices. We do not claim much originality and indeed the material can be found in many textbooks [27, 28].

A. Thermodynamic consistency of $S_B$

We prove that in the thermodynamic limit $S_B$ satisfies the consistency criterion specified by Dunkel and Hilbert in Ref. [15].

We first prove that in the canonical ensemble [28]

$$\frac{- \partial F}{\partial A_\mu} |_T = - \left< \frac{\partial H}{\partial A_\mu} \right>_T.$$  \hfill (27)

In this, $A_\mu$ is some parameter in the Hamiltonian $H$, for example the position of a wall. The left hand side (LHS) is the generalised thermal force, corresponding to this parameter. The right hand side (RHS) is the canonical ensemble average of the generalised mechanical force, corresponding to the same parameter. These forces are said to be conjugate to $A_\mu$. For example, in standard thermodynamics $(p, V)$ form a well-known conjugate pair, and in our spin system $(-N_1, \epsilon)$ form another conjugate pair [29]. Eq. (27) is well known and forms the basis of a wide variety of Monte-Carlo free energy sampling methods.

The ensemble average in Eq. (27) is given by

$$\left< \cdots \right>_T = \frac{\text{Tr}[\cdots e^{-\beta H}]}{\text{Tr}[e^{-\beta H}]}.$$  \hfill (28)

where ‘Tr’ can be read as ‘sum over states’ and $\beta = 1/k_BT$. Provided there is a bounded energy spectrum, the sums remain well defined for $\beta < 0$.

The proof of Eq. (27) is quite easy and starts from the expression which defines the free energy,

$$e^{-\beta F} = \text{Tr}[e^{-\beta H}].$$  \hfill (29)

Differentiating both sides with respect to $A_\mu$ gives

$$- \beta \frac{\partial F}{\partial A_\mu} |_T e^{-\beta F} = - \beta \left[ \text{Tr} \left[ \frac{\partial H}{\partial A_\mu} e^{-\beta H} \right] \right].$$  \hfill (30)

Eq. (27) is obtained by dividing Eq. (30) by Eq. (29), and cancelling $\beta$.

In order to recover the consistency criterion of Dunkel and Hilbert, what we need to do is transfer these results to the microcanonical ensemble. To do this we first define the microcanonical ensemble average

$$\left< \cdots \right>_E = \frac{\text{Tr}[\cdots \delta(E - H)]}{\text{Tr}[\delta(E - H)]}.$$  \hfill (31)
and the microcanonical Boltzmann entropy via
\[ \text{Tr}[\delta(E - H)] = e^{S_n/k_B}. \] (32)
In these the Dirac δ-function selects only those states with energy E.

With these in hand we can write
\[ \text{Tr}[(\cdots) e^{-\beta H}] = \int_0^\infty dE e^{-\beta E} \text{Tr}[(\cdots) \delta(E - H)]. \] (33)
and therefore
\[ e^{-\beta F} (\cdots)_T = \int_0^\infty dE e^{-\beta E} e^{S_n/k_B} (\cdots)_E. \] (34)
A special case obtains when (\cdots) = 1, namely
\[ e^{-\beta F} = \int_0^\infty dE e^{-\beta E + S_n/k_B}. \] (35)
Eqs. (34) and (35) have the structure of Laplace transforms, with (E, β) being the transform variables. They are valid irrespective of system size [30]. As the system size increases though, the integrand in both cases becomes dominated by the peak in the exponential. Therefore we can evaluate the integrals by the saddle-point method [27]. Taking Eq. (35) first, one has
\[ -\beta F = -\beta E + \frac{S_n}{k_B} \quad \text{where} \quad -\beta + \frac{\partial}{\partial E} \left( \frac{S_n}{k_B} \right) = 0. \] (36)
The second expression is the condition that the integrand is a maximum, as a function of E. We now recall that \( \beta = 1/k_B T \) and so the above can be rearranged to
\[ F = E - T S_B \quad \text{where} \quad \frac{1}{T} = \frac{\partial S_B}{\partial E}. \] (37)
Thus the saddle-point method has converted the Laplace transform into a Legendre transform. Eq. (37) looks very familiar but we should emphasis that T is the temperature in the canonical ensemble. So we have also proved that, in the thermodynamic limit,
\[ T = T_B. \] (38)
This can be viewed as an expression of the zeroth law of thermodynamics.

Turning now to Eq. (34) and proceeding in the same way, the thermodynamic functions cancel, leaving
\[ (\cdots)_T = (\cdots)_E. \] (39)
This confirms that ensemble averages are equivalent in the thermodynamic limit.

The next step in the proof consists in differentiating the first of Eqs. (37) with respect to \( A_\mu \), paying careful attention to the dependent variables. One finds
\[ \frac{\partial F}{\partial A_\mu} \bigg|_T = \left( 1 - T \frac{\partial S_B}{\partial E} \right) \frac{\partial E}{\partial A_\mu} - T \frac{\partial S_B}{\partial A_\mu} \bigg|_E. \] (40)
The first term on the RHS vanishes, by virtue of the second of Eqs. (37). Therefore
\[ \frac{\partial F}{\partial A_\mu} \bigg|_T = -T \frac{\partial S_B}{\partial A_\mu} \bigg|_E. \] (41)
Recalling Eqs. (27), (38) and (33), we have now proved
\[ T_B \frac{\partial S_B}{\partial A_\mu} |_E = -\left( \frac{\partial H}{\partial A_\mu} / E \right). \] (42)
This is exactly Dunkel and Hilbert’s consisteny criterion (cf. Eq. (7) in Ref. [15]). It holds in the thermodynamic limit and is our desired result [31].

**B. Some properties of \( T_G \)**

We wish to know the behaviour of \( T_G \) in the limit of large system size. Starting from the definitions, \( k_B T_G = (\partial \ln \Omega / \partial E)^{-1} \) and \( \partial \Omega / \partial E = \omega \), we find \( k_B T_G = \Omega / \omega \), as in Ref. [15]. From this we obtain
\[ T_G = k_B^{-1} \int_0^E dE' e^{(S_n(E') - S_n(E))/k_B}. \] (43)
This compact expression essentially contains everything we need to know about the behaviour of \( T_G \). The argument of the exponential is proportional to the system size (i.e., extensive). Therefore, for large systems, the value of \( T_G \) is determined by the location of the maximum.

There are two cases. If \( S_B \) is monotonically increasing up to \( E \), the integral is determined by the behaviour at the upper limit of integration. Setting \( \Delta E = E - E' \) we first have
\[ S_B(E') - S_B(E) = -\Delta E/T_B + O(\Delta E^2) \] (44)
since \( 1/T_B = \partial S_B / \partial E \). Changing integration variable to \( \Delta E \) we then have
\[ T_G = k_B^{-1} \int_0^E d(\Delta E) e^{-\Delta E/k_B T_B} \] (45)
The upper integration limit can be replaced by \( \infty \) since the correction becomes vanishingly small in the limit of a large system size. The integral can then be done,
\[ T_G = k_B^{-1} \int_0^\infty d(\Delta E) e^{-\Delta E/k_B T_B} = T_B. \] (46)
Therefore we conclude that as long as \( S_B \) is monotonically increasing, \( T_G = T_B \) in the thermodynamic limit.

In the second case the maximum of the argument of the exponential in Eq. (43) occurs at \( E^* \), somewhere in between the integration limits (note that \( S_B(E) \) is just an offset). Approximating the integral by the maximum value of the integrand we find
\[ T_G = k_B^{-1} e^{(S_n(E^*) - S_n(E))/k_B}. \] (47)
This demonstrates that to leading order \( T_G \) grows exponentially with system size. Again recalling that \( 1/T_B = \partial S_B / \partial E \), we have finally
\[ T_G = k_B^{-1} \exp(-\int_{E^*}^E dE'/k_B T_B). \] (48)
Hence to leading order \( T_G \) acquires a complicated dependence on the Boltzmann temperature between \( E^* \) and \( E \). Note that \( T_B < 0 \) in Eq. (48), so \( T_G \) is still an increasing function of \( E \).
A topical example may clarify this point. Suppose that

This statement makes more sense if we introduce the Elementary Principles of Statistical

J. Willard Gibbs, 28

A. L. Kuzemsky, Int. J. Mod. Phys. B 28

This claim is not fully substantiated by Chapter XIV of

Strictly speaking the definition is due to Planck rather

J. Dunkel and S. Hilbert, Nature Physics 77, 040403 (2010).

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we note that the essential arguments in this paper were already given more than twenty years ago [9].

Strictly speaking the definition is due to Planck rather than Boltzmann, see M. Planck, “Über das Gesetz der Energieverteilung im Normalspectrum,” Annalen der Physik (Leipzig) 309, 553–563 (1901).

J. Willard Gibbs, Elementary Principles of Statistical Mechanics (Charles Scribner’s sons, New York, Edward Arnold, London, 1902).

This claim is not fully substantiated by Chapter XIV of Ref. [17]; see pp. 171–172 and Eq. (488) on p. 174.

A. L. Kuzemsky, Int. J. Mod. Phys. B 28, 1430004 (2014).

Of course, this is something of a tautology because we define ‘hot’ and ‘cold’ in this way. The crucial word is therefore ‘never’.

This statement makes more sense if we introduce the width of the energy shell $\Delta \epsilon$. However, the ergodic hypothesis only requires that $\Delta \epsilon$ is so small that $\omega(E)$ is constant between $E$ and $E + \Delta \epsilon$. We note that the ergodic hypothesis is not disputed by Dunkel and Hilbert in Ref. [19].

A topical example may clarify this point. Suppose that there is social unrest in the banking sector because bank employees working in branch offices (the ‘proletariat’) find that their wages are too low, and that those of the executives (the ‘bourgeoisie’) are too high. This problem could be solved by raising the average salary per employee, while decreasing the average salary (including bonuses) for executives, such that the total sum spent on salaries remains the same. That would be the ‘Boltzmann’ solution. The ‘Gibbs’ solution according to Ref. [19] would be to increase the maximum salary of bank employees, for example to $1M/yr$, a measure from which very few, if any, employees would benefit, whilst decreasing the maximum salary for executives accordingly (say from $10bn/yr$ to $1bn/yr$), such that the maximum amount that could be spent on salaries remains the same. Most likely, very few executives would protest. But more importantly, this measure would not result in any substantial transfer of money (our equivalent of ‘heat’) from one reservoir to the other. In Marxist terminology, there is no redistribution of wealth from the bourgeoisie to the proletariat. Hence, it is not a strategy that is likely to satisfy the bank employees.

We use throughout the standard definition of Carnot efficiency as the ratio between the work done and the heat extracted from the hot reservoir, in one cycle of the engine. As we explain in the text, with reservoirs of opposite temperatures, heat is also extracted from the cold reservoir. If one defines the efficiency to be the ratio of the work done to the heat extracted from both reservoirs, the efficiency can never be greater than one [7, 11].

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With this standpoint, it is then surely illogical to discuss the Gibbs entropy in the context of heat engines which necessarily involve thermal contacts.

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E. Schrödinger, E, Statistical Thermodynamics, (CUP, Cambridge, 1952).

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In the spin system, the Hamiltonian $H = \epsilon \sum_{i=1}^{M} s_i$, where $s_i = 0$ or 1 according to whether the $i$-th spin is in the ground state or excited state. Eq. (27) is then satisfied almost trivially since $\partial H/\partial \epsilon = (\sum_{i=1}^{M} s_i) = N_1$.

This demonstrates the well known ensemble invariance for small systems since in that case $-\partial F/\partial T \neq S_T$.

Another proof that $S_B$ satisfies the consistency criterion starts by considering, in addition to the Gibbs entropy $S_G = k_B \ln \text{Tr}[\Theta(E - H)]$, the complementary entropy function $S_C = k_B \ln \text{Tr}[\Theta(H - E)]$. By adapting Eq. (7) in Ref. [17] one can easily show that $S_C$ also meets the consistency criterion. Then from $S_G$ and $S_C$ a piecewise continuous approximation to $S_B$ can be constructed which becomes exact in the thermodynamic limit.