

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 [1–8], and continues to attract attention to the present day [9–11]. Formally, a negative temperature corresponds to a system under conditions in which the number of states $\omega(E)$ in the vicinity of energy E is a decreasing function, to wit $1/T \equiv \partial S/\partial E < 0$ where $S = k_B \ln \omega$ is the Boltzmann entropy. This situation usually arises in a system with a bounded energy spectrum. It has been realised experimentally in famous early work on nuclear spin systems by Purcell and Pound [1], and in very recent experiments on ultracold quantum gases by Braun *et al.*[9]. The existence of negative temperatures leads naturally to many questions about whether Carnot cycles can be constructed using negative temperature reservoirs, and whether the consequent Carnot efficiency can be greater than one [7, 8].

In a recent article [11] Dunkel and Hilbert argued that the use of Boltzmann’s definition of entropy [12] in the above expression for the temperature leads to unphysical predictions. They propose instead to define entropy using Gibbs’ notion of ‘extension in phase space’ [13] (see below). They argue that this approach, which they attribute to Gibbs [14], 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’ [15]. The point about negative temperatures and Carnot cycles is more interesting. We shall argue below that Dunkel and Hilbert are mistaken on both counts because the Gibbs entropy 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. We thereby recover complete agreement with classical thermodynamics.

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 one can 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

$$\frac{\partial\Omega(E)}{\partial E} \Delta\epsilon \equiv \omega(E) \Delta\epsilon. \quad (1)$$

Boltzmann’s definition of entropy is

$$S_B(E) = k_B \ln \omega(E) + \text{constant}. \quad (2)$$

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

$$S_G(E) = k_B \ln \Omega(E) + \text{constant}. \quad (3)$$

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

$$T = \left(\frac{\partial S(E)}{\partial E} \right)^{-1} \quad (4)$$

For classical systems with many degrees of freedom, the difference in the value of the temperature based on S_B 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 what is argued in Ref. [11], to meet a basic requirement of thermodynamics we must use the definition based on Boltzmann's entropy $S_B(E)$.

The nub of our argument turns on the behaviour of systems, considered jointly, which are able to exchange energy. We shall argue that the condition for these to be in thermal equilibrium is that they all have the same temperature *à la* Boltzmann. This is essentially what is often termed 'the zeroth law of thermodynamics'. It implies that the Boltzmann entropy, *and only that*, can be used to construct a universal thermodynamic temperature scale. Without this basis, the whole edifice of classical thermodynamics is built on sand.

To see this, let us briefly restate the key properties that the statistical mechanical entropy and temperature should reproduce in order to correspond with the thermodynamic quantities defined by Clausius:

1. if a closed system is in equilibrium, its entropy must be at a maximum;
2. heat never spontaneously flows from cold to hot [16];
3. at the end of one cycle of an reversible heat engine the entropy of the system (*i. e.* engine plus temperature reservoirs) has not changed.

It should be stressed that Clausius' thermodynamics is based on experimental observations, not on axioms. To construct statistical mechanics, we need to make an *ergodic hypothesis*: 'A system at a given energy E is equally likely to be found in any of its $\omega(E)$ quantum states' [17].

Let us consider a closed system with total energy E , comprised of two subsystems with energies E_1 and E_2 . We assume that the absolute value of the interaction energy between the two subsystems is much smaller than E . In that case, $E = E_1 + E_2$. The total number of states of this system is given by

$$\omega_T(E_1, E_2) = \omega_1(E_1) \times \omega_2(E_2). \quad (5)$$

Of course, we can write the same expression for $\Omega(E_1, E_2)$ but, importantly, if we consider all the states for which $E_1 + E_2 \leq E$, we are *not* describing a system at fixed energy E , but rather a system with a fixed maximum energy E [18]. For classical systems, this distinction is irrelevant in the thermodynamic limit, but for a system with an energy that is bounded from above (say $E \leq E_M$), the difference is crucial. To illustrate this, let us consider an extreme (but perfectly legitimate) example: suppose that we have chosen E_2 such that it is less than E_M , then increasing E_2 by an amount ΔE does not correspond to an energy transfer from system 1 to system 2: there is no relation between ΔE and heat transfer and all relation with thermodynamics is lost. To establish a link with thermodynamics it is essential that the total energy E is equal to the sum $E_1 + E_2$. This condition can only be enforced if we work with subsystems that have well-defined energies, not just systems with an energy below a particular value.

Let us next consider what happens if we allow energy exchange between systems 1 and 2. In equilibrium, the entropy should be at a maximum with respect to a small energy transfer from system 1 to system 2. Hence

$$\frac{\partial \ln \omega_T(E)}{\partial E_1} = 0. \quad (6)$$

Using the fact that $dE_1 = -dE_2$ we obtain

$$\frac{\partial \ln \omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \omega_2(E_2)}{\partial E_2} \quad (7)$$

and hence

$$\frac{1}{T_1} = \frac{1}{T_2}. \quad (8)$$

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

The only remaining point to discuss is Dunkel and Hilbert's consistency criterion. In Ref. [11] it is proved that S_G satisfies this requirement, independent of system size. Dunkel and Hilbert further argue that S_B must therefore fail this requirement whenever $S_B \neq S_G$. This is certainly true for small systems, but it can be proved that in the thermodynamic limit S_B *does* satisfy the consistency criterion, whether or not $S_G \neq S_B$. In the Appendix we present such a proof.

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. This may seem strange, but it violates no known law of nature.

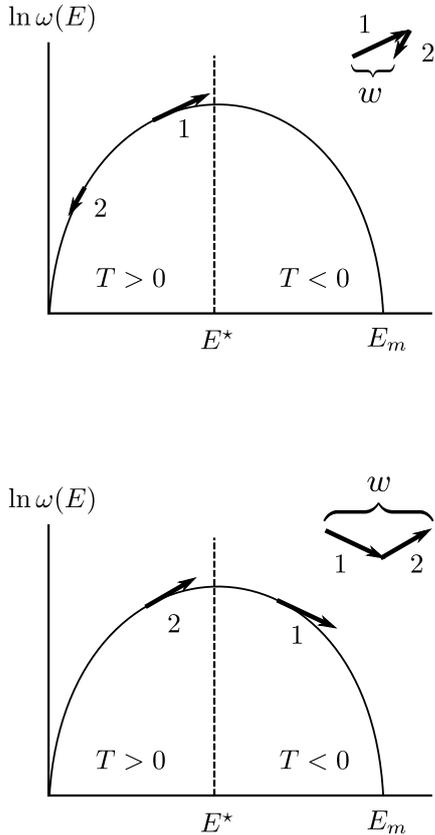


Figure 1. If a reversible heat engine operates between reservoirs 1 and 2 that both have positive temperatures (top panel; $T_1 > T_2$), then the condition that S is constant implies that as heat flows out of reservoir 1, heat must flow into reservoir 2. However, if a reversible heat engine operates between reservoir (1) at a negative temperature and another (2) at positive temperature (bottom panel), then the condition that S is constant implies that as heat flows out of reservoir 1, heat must also flow out of reservoir 2. The curves in these figures represent the entropy of the engine. Since $\Delta S = q/T$ and $1/T = \partial S/\partial E$, it follows that $\partial S/\partial E = \Delta S/q$ and the arrows have a specific geometric interpretation: the horizontal displacement is the heat gain q and the vertical displacement is the entropy change ΔS . The Carnot cycle itself can then be represented by combining the arrows vectorially since in the adiabatic steps $q = \Delta S = 0$. The resultant vector should have no net vertical displacement since the net entropy change should vanish, but the net horizontal displacement represents w , the amount of energy available to do useful work. This graphical construction is shown in the insets in the main panels. It demonstrates why the Carnot efficiency $\eta \equiv w/q_1 < 1$ in the top panel, and $\eta > 1$ in the bottom panel.

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

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

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 [19] (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.

III. TWO-LEVEL SPIN SYSTEM

A two-level spin system is an excellent arena to explore the issues raised here, a point also noted by Dunkel and Hilbert [20]. Such a system provides a working material which can withstand both positive and negative temperatures in a Carnot cycle. The system contains N_0 spins in a ground state with zero energy and N_1 spins are in an excited state at energy ϵ , 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,

$$\begin{aligned} E &= \epsilon N_1, \\ S &= \ln \omega = N \ln N - N_0 \ln N_0 - N_1 \ln N_1. \end{aligned} \quad (12)$$

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 temperature of the spin system is

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

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

$$\begin{aligned} S &= N \ln N - N_0 \ln N_0 - N_1 \ln N_1 \\ &= (N_0 + N_1) \ln N - N_0 \ln N_0 - N_1 \ln N_1 \\ &= -N_0 \ln(N_0/N) - N_1 \ln(N_1/N). \end{aligned} \quad (16)$$

Consequently,

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

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, which is left as a further exercise.

From Eq. (18), the quantity conjugate to ϵ 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 ϵ - N_1 plane is the analogue of the p - V diagram encountered in textbooks. The first expression in Eqs. (15) serves as an ‘equation of state’, providing isotherms in the ϵ - 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!)

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

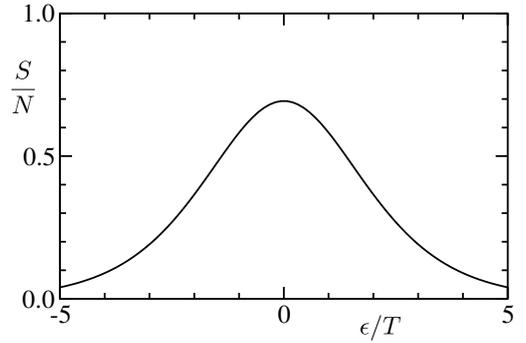


Figure 2. The entropy function of Eq. (20).

This function only depends on the ratio ϵ/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 ϵ , and more crucially for positive and negative T too. If $\epsilon > 0$ and $T > 0$ the spin population is ‘normal’ in the sense that the majority of spins are in the ground state, whereas if $\epsilon > 0$ and $T < 0$ the spin population is ‘inverted’ in the sense that the majority of spins are in the excited state. An analogous situation holds, *mutatis mutandis*, if $\epsilon < 0$.

These inverted states are well defined and correspond to a total energy which is closer to the absolute maximum or minimum energy, $E_M = \epsilon N$, than to $E = 0$, as we now demonstrate. Since $E = \epsilon N_1$, $E_M = \epsilon N$, and $N_0 = N - N_1$, the entropy can be written as

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

This function has the non-monotonic shape shown in Fig. 1, 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 [6].

Isotherms for the spin system in the ϵ - 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 ϵ . 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 ϵ 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 ϵ - 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 ϵ/T , it follows that T remains strictly proportional to ϵ 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 ϵ .

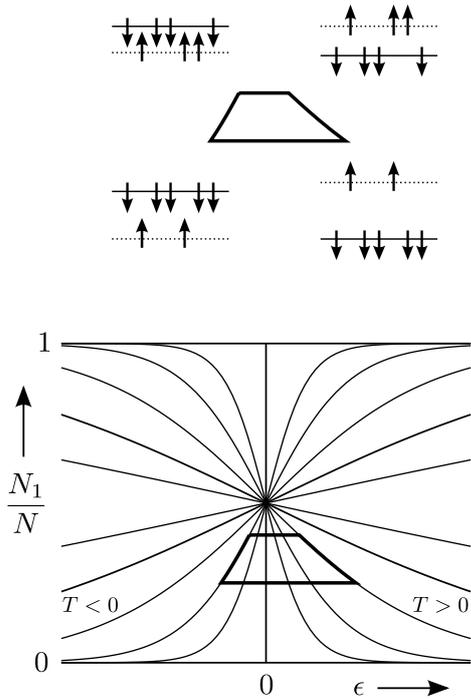


Figure 3. A Carnot cycle connecting isotherms of opposite temperatures. The thin lines in the ϵ - N_1 plane (lower plot) are isotherms, from the first expression in Eqs. (15).

We now use this spin system and 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 ϵ - N_1 plane in Fig. 3. 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 [21].

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 ΔS (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 ϵ 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 ϵ is decreased isothermally (thus decreasing

ϵ/T). This is continued until the entropy has increased by the exact same amount ΔS 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 ϵ . 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 ϵ/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 $S \rightarrow 0$ as $T \rightarrow 0$. 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 [21]. 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. [10]. 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. ACKNOWLEDGMENTS

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V. APPENDIX

We prove that in the thermodynamic limit S_B satisfies the consistency criterion specified by Dunkel and Hilbert in Ref. [11]. Since the proof uses rather more advanced mathematics than we have employed in the main text, it seems appropriate to confine it to an Appendix.

We first prove that in the *canonical* ensemble,

$$-\left. \frac{\partial F}{\partial A_\mu} \right|_T = -\left\langle \frac{\partial H}{\partial A_\mu} \right\rangle_T. \quad (22)$$

In this, A_μ is some parameter in the Hamiltonian H , for example the position of a wall. The left hand side (LHS) is the generalised *thermodynamic* 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_μ . 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 [22].

The ensemble average in Eq. (22) is given by

$$\langle \dots \rangle_T = \frac{\text{Tr}[(\dots) e^{-\beta H}]}{\text{Tr}[e^{-\beta H}]}, \quad (23)$$

where ‘Tr’ can be read as ‘sum over states’ and $\beta = 1/k_B T$. This just expresses the fact that in the canonical ensemble average the states are weighted by the Boltzmann factor. Provided there is a bounded energy spectrum the sums remain well defined for $\beta < 0$.

The proof of Eq. (22) is quite easy and starts from the expression which defines the free energy,

$$e^{-\beta F} = \text{Tr}[e^{-\beta H}]. \quad (24)$$

Differentiating both sides with respect to A_μ gives

$$-\beta \left. \frac{\partial F}{\partial A_\mu} \right|_T e^{-\beta F} = -\beta \text{Tr} \left[\frac{\partial H}{\partial A_\mu} e^{-\beta H} \right]. \quad (25)$$

Eq. (22) is obtained by dividing Eq. (25) by Eq. (24), and cancelling β .

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

$$\langle \dots \rangle_E = \frac{\text{Tr}[(\dots) \delta(E - H)]}{\text{Tr}[\delta(E - H)]}, \quad (26)$$

and the microcanonical Boltzmann entropy *via*

$$\text{Tr}[\delta(E - H)] = e^{S_B/k_B}. \quad (27)$$

In these the Dirac δ -function selects only those states with energy E .

With these in hand we can write

$$\text{Tr}[(\dots) e^{-\beta H}] = \int_0^\infty dE e^{-\beta E} \text{Tr}[(\dots) \delta(E - H)]. \quad (28)$$

and therefore

$$e^{-\beta F} \langle \dots \rangle_T = \int_0^\infty dE e^{-\beta E + S_B/k_B} \langle \dots \rangle_E. \quad (29)$$

A special case obtains when $(\dots) = 1$, namely

$$e^{-\beta F} = \int_0^\infty dE e^{-\beta E + S_B/k_B}. \quad (30)$$

Eqs. (29) and (30) have the structure of *Laplace transforms*, with (E, β) being the transform variables. They are valid irrespective of system size [23]. 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 steepest descents. Taking Eq. (30) first, one has

$$-\beta F = -\beta E + \frac{S_B}{k_B} \quad \text{where} \quad -\beta + \frac{\partial}{\partial E} \left(\frac{S_B}{k_B} \right) = 0. \quad (31)$$

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

$$F = E - T S_B \quad \text{where} \quad \frac{1}{T} = \frac{\partial S_B}{\partial E}. \quad (32)$$

Thus steepest descents converts the Laplace transform into a *Legendre transform*. Eq. (32) looks very familiar but we should emphasise that T is the temperature in the canonical ensemble. So we have also proved that, in the thermodynamic limit,

$$T = T_B. \quad (33)$$

This can be viewed as an expression of the zeroth law of thermodynamics.

Turning now to Eq. (29) and proceeding in the same way, we find that the thermodynamic functions cancel, leaving

$$\langle \dots \rangle_T = \langle \dots \rangle_E. \quad (34)$$

This confirms the folklore that ensemble averages are equivalent in the thermodynamic limit [15].

The next step in the proof consists in differentiating the first of Eqs. (32) with respect to A_μ , paying careful attention to the dependent variables. One finds

$$\left. \frac{\partial F}{\partial A_\mu} \right|_T = \left(1 - T \frac{\partial S_B}{\partial E} \right) \frac{\partial E}{\partial A_\mu} - T \left. \frac{\partial S_B}{\partial A_\mu} \right|_E. \quad (35)$$

The first term on the RHS vanishes, by virtue of the second of Eqs. (32). Therefore

$$\left. \frac{\partial F}{\partial A_\mu} \right|_T = -T \left. \frac{\partial S_B}{\partial A_\mu} \right|_E. \quad (36)$$

Recalling Eqs. (22), (33) and (34), we have now proved

$$T_B \left. \frac{\partial S_B}{\partial A_\mu} \right|_E = - \left\langle \frac{\partial H}{\partial A_\mu} \right\rangle_E. \quad (37)$$

This is exactly Dunkel and Hilbert’s consistency criterion (*cf.* Eq. (7) in Ref. [11]). It holds in the thermodynamic limit and is our desired result [24].

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- [14] This claim is not fully substantiated by Chapter XIV of Ref. [13]; see pp. 171–172 and Eq. 488 on p. 174.
- [15] A. L. Kuzemsky, Int. J. Mod. Phys. B **28**, 1430004 (2014).
- [16] Of course, this is something of a tautology because we *define* ‘hot’ and ‘cold’ in this way. The crucial word is therefore ‘never’.
- [17] 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 fact they use it themselves in defining thermal averages—see the second line of Eq. (7) in Ref. [11].
- [18] 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. [11] 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.
- [19] At least, in the kind of universe that we are familiar with.
- [20] In the Supplementary Material for Ref. [11].
- [21] J. R. Waldram, *The theory of thermodynamics* (Cambridge University Press, Cambridge, 1985) see pp. 186–190.
- [22] In the spin system, the Hamiltonian $H = \epsilon \sum_{i=1}^M s_i$, where s_i is 0 or 1 according to whether the i -th spin is in the ground state or excited state. Eq. (22) is then satisfied almost trivially since $-\langle \partial H / \partial \epsilon \rangle = -\langle \sum_{i=1}^M s_i \rangle = -N_1$.
- [23] In general, for small systems $-\partial F / \partial T \neq S_B \neq S_G$; and these do not exhaust the possibilities, see for example J. Naudts, Europhys. Lett. **69**, 719 (2005).
- [24] 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 $\bar{S}_G = k_B \ln \text{Tr}[\Theta(H - E)]$. By adapting Eq. (7) in Ref. [11] one can easily show that \bar{S}_G *also* meets the consistency criterion. Then from S_G and \bar{S}_G a piecewise continuous approximation to the Boltzmann entropy can be assembled which becomes equal to S_B in the thermodynamic limit.