

Consistent thermostatics forbids negative absolute temperatures

Jörn Dunkel^{1,*} and Stefan Hilbert²

¹*Department of Mathematics, Massachusetts Institute of Technology,
77 Massachusetts Avenue E17-412, Cambridge, MA 02139-4307, USA*

²*Max Planck Institute for Astrophysics, Karl-Schwarzschild-Str. 1, 85748 Garching, Germany*

Justification of the thermostatical self-consistency condition

We briefly summarize known facts that suffice to derive the thermostatical self-consistency condition [Eq. (6) in the Main Text]

$$T \left(\frac{\partial S}{\partial A_\mu} \right)_{E, A_\nu \neq A_\mu} = - \left(\frac{\partial E}{\partial A_\mu} \right)_{S, A_\nu \neq A_\mu} = - \left\langle \frac{\partial H}{\partial A_\mu} \right\rangle. \quad (1)$$

As explained below, the first equality follow directly from of the rules of differential calculus, and the second equality from the Hamiltonian or Heisenberg equations of motion.

To justify the first equality, recall that thermodynamics [1] builds on the assumption that the entropy S of a system in thermal equilibrium is a state function which, for isolated systems, can be written as a function $S(E, A)$ of the system's internal energy E and possibly other external parameters $A = (A_1, \dots)$, such as volume, particle number, magnetic field strength, etc. Formal differential calculus, combined with the usual definitions of secondary thermodynamic observables (temperature, pressure, etc.), yields the fundamental differential relation of thermodynamics

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right)_{A_\mu} dE + \sum_{\mu} \left(\frac{\partial S}{\partial A_\mu} \right)_{E, A_\nu \neq \mu} dA_\mu \\ &\equiv \frac{1}{T} dE + \sum_{\mu} \frac{a_\mu}{T} dA_\mu, \end{aligned} \quad (2)$$

where subscripts $\{E, A_\mu\}$ indicate quantities kept constant during partial differentiation. Assuming $S(E, A)$ is locally invertible, so that the energy can be expressed in the form $E(S, A)$, Eq. (2) can be recast with respect to energy E as

$$\begin{aligned} dE &= \left(\frac{\partial E}{\partial S} \right)_{A_\mu} dS - \sum_{\mu} \left(\frac{\partial E}{\partial A_\mu} \right)_{S, A_\nu \neq \mu} dA_\mu \\ &= T dS - \sum_{\mu} \left(\frac{\partial E}{\partial A_\mu} \right)_{S, A_\nu \neq \mu} dA_\mu. \end{aligned} \quad (3)$$

Multiplying Eq. (2) by T and comparing with Eq. (3) gives, by virtue of linear independence of the differentials dA_μ ,

$$T \left(\frac{\partial S}{\partial A_\mu} \right)_{E, A_\nu \neq \mu} = - \left(\frac{\partial E}{\partial A_\mu} \right)_{S, A_\nu \neq \mu}, \quad (4)$$

which is the first equality in Eq. (1).

To justify the second equality in Eq. (1), we relate the expression on the rhs. of Eq. (4) to the microscopic dynamics. To this end, we consider isolated systems, merely assuming that the dynamics of any observable $O(t)$ is governed by a Hamiltonian $H(A(t))$ with time-dependent external control parameters $A(t)$ through the Hamilton-Heisenberg equations

$$\frac{d}{dt} O(t) = \mathcal{L}[H, O(t)] + \frac{\partial O}{\partial t}, \quad (5)$$

*Electronic address: dunkel@math.mit.edu

which holds for sufficiently slow parameter variations,¹ i.e. processes that are adiabatic in the (quantum)mechanical sense. For classical systems, the Lie-bracket $\mathcal{L}[H, O]$ is given by the Poisson-bracket, whereas for quantum systems we have $\mathcal{L}[O, H] = (i/\hbar)[O, H]$ with the usual commutator $[\cdot, \cdot]$.

To make the connection with thermodynamics, we specifically consider $O(t) = H(A(t))$. In this case, because of $\mathcal{L}[H, H] = 0$, Eq. (5) reduces to

$$\frac{dH}{dt} = \sum_{\mu} \frac{\partial H}{\partial A_{\mu}} \frac{dA_{\mu}}{dt}. \tag{6}$$

Averaging over some suitably defined ensemble, and identifying $E = \langle H \rangle$, we find

$$\frac{dE}{dt} = \sum_{\mu} \left\langle \frac{\partial H}{\partial A_{\mu}} \right\rangle \frac{dA_{\mu}}{dt}. \tag{7}$$

This equation states that the change dE in internal energy of an isolated system, whose dynamics is governed by Eq. (5), is equal to the sum of various forms of work $\langle \partial H / \partial A_{\mu} \rangle dA_{\mu}$ (mechanical, electric, magnetic, etc.) performed on the system.² Identifying ‘heat’ δQ with a change of internal energy that cannot be attributed to some form of work, Eq. (7) shows that processes governed by the Hamilton-Heisenberg equation (5) do not involve any energy change by heat.³ Therefore, within a consistent thermostistical framework, such processes should also be adiabatic in the conventional thermodynamic sense.

To compare the microscopically derived relation (7) with the standard thermodynamical relations, let us consider some thermodynamic process $t \mapsto (E(t), S(t), A(t))$. For such a process, Eq. (3) states that

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial S} \right)_A \frac{dS}{dt} + \sum_{\mu} \left(\frac{\partial E}{\partial A_{\mu}} \right)_{S, A_{\nu \neq \mu}} \frac{dA_{\mu}}{dt}. \tag{8}$$

In particular, for adiabatic processes characterized by $dS/dt = (1/T)(\delta Q/dt) = 0$, this reduces to

$$\frac{dE}{dt} = \sum_{\mu} \left(\frac{\partial E}{\partial A_{\mu}} \right)_{S, A_{\nu \neq \mu}} \frac{dA_{\mu}}{dt}. \tag{9}$$

Comparing Eqs. (7) and (9) justifies the second equality in the consistency relation (1).

More generally, the above considerations show that an adiabatic process in the mechanical sense is also an adiabatic process in the thermodynamic sense, if and only if the entropy $S(E, A)$ is an adiabatic invariant in the mechanical sense, as already noted by Hertz [2] in 1910. Entropy definitions that are not adiabatically invariant violate the consistency relation (1) and break the correspondence between mechanical and thermodynamic adiabatic processes. Moreover, and most disturbingly from a practical point of view, such inconsistent entropy definitions also destroy the equivalence between the mechanical stresses $F_{\mu} = -\langle \partial H / \partial A_{\mu} \rangle$ and their thermodynamic counterparts $a_{\mu} = -(\partial E / \partial A_{\mu})_{S, A_{\nu \neq \mu}}$. This is the reason for why the Boltzmann entropy S_B , which is not an adiabatic invariant, can give nonsensical results for the pressure $p_B = -(\partial E / \partial V)_{S_B, A_i} \neq -\langle \partial H / \partial V \rangle = p$ and similarly for other observables, such as magnetization, etc. By contrast, the Gibbs entropy S_G , which is an adiabatic invariant [2], does not suffer from such inconsistencies.

Uniqueness of solutions of Eq. (1)

Mathematically, the consistency relations (1) define a system of linear homogeneous first-order differential equations for the entropy $S(E, A)$, which may be rewritten in the form

$$0 = \frac{\partial S(E, A)}{\partial A_{\mu}} + \left\langle \frac{\partial H}{\partial A_{\mu}} \right\rangle \frac{\partial S(E, A)}{\partial E}, \quad \forall \mu \forall (E, A) : \omega(E, A) > 0. \tag{10}$$

¹ ‘Slow’ means that the time scales of the energy change induced by the parameter variation are large compared to the dynamical time scales of the system.

² This is the work actually required to change the system parameters A_{μ} (e.g. the volume) by a small amount dA_{μ} against the system’s ‘resistance’ $\langle \partial H / \partial A_{\mu} \rangle$ (e.g. the mechanical pressure), which can be measured at least in principle and very often also in practice.

³ Since the systems under consideration are isolated, it is obvious that there can be no heat exchange with the environment, but Eq. (7) shows that there is also no heat generated internally.

Under moderate assumptions about the analytic behaviour of $H(A)$, there exists a solution to the equations for $S(E, A)$ in the physically accessible parameter region $\{(E, A) | \omega(E, A) > 0\}$, namely the phase volume $\Omega(E, A)$ [2–4]. This solution is, however, not unique. In particular, for any solution S and any sufficiently smooth function f , $S_f(E, A) \equiv f(S(E, A))$ is also a solution. Thus, additional criteria are needed to uniquely define the entropy. These may include conventions for the normalization or the zero point of the entropy, or requiring extensivity of the entropy for particular model systems. Most importantly, the entropy should be compatible with conventional measurement-based definitions of ‘temperature’, e.g. via classical ideal gas thermometer or the classical Carnot cycle with a classical ideal gas as medium. Compatibility with the ideal gas law, combined with sensible normalization conditions that account for ground-state and ‘mixing’ entropy, suffices to single out the Gibbs entropy.

Proof of Eq. (14) in the Main Text

To prove the temperature formula

$$T_B = \frac{T_G}{1 - k_B/C}, \quad (11)$$

we recall that by definition

$$k_B T_G = \frac{\Omega}{\Omega'} = \frac{\Omega}{\omega}, \quad k_B T_B = \frac{\omega}{\omega'} = \frac{\Omega'}{\Omega''}, \quad (12)$$

where primes denote partial derivatives with respect to energy E . Then, from the definition of the (inverse) heat capacity, one finds

$$\frac{1}{C} \equiv \left(\frac{\partial T_G}{\partial E} \right) = \frac{1}{k_B} \left(\frac{\Omega}{\Omega'} \right)' = \frac{1}{k_B} \frac{\Omega' \Omega'' - \Omega \Omega'''}{(\Omega')^2} = \frac{1}{k_B} \left[1 - \frac{\Omega \Omega'''}{(\Omega')^2} \right] = \frac{1}{k_B} \left(1 - \frac{T_G}{T_B} \right), \quad (13)$$

which can be solved for T_B to yield Eq. (11). Note that Eqs. (11) and (13) are valid regardless of particle number N , provided the derivatives of Ω up to second order exist. In particular, as directly evident from Eq. (13), when the energy of a finite system with $N < \infty$ and $T_G < \infty$ approaches a critical value E_* where the density of states $\omega = \Omega'$ has a non-singular maximum, such that $\omega' = \Omega'' = 0$ or equivalently $|T_B| \rightarrow \infty$, then $C \rightarrow k_B$ regardless of system size⁴ N . The non-extensivity of C for $E \geq E_*$ simply reflects the physical reality that it is not possible to create population inversion by conventional heating. We further illustrate this general result by means of analytically tractable spin models in the next section.

Extensivity and heat capacity of spin systems

To illustrate the non-trivial scaling of entropy and heat capacity with system size for spin systems with bounded energy spectrum, it is useful to discuss indistinguishable and distinguishable particles separately. Below, we first demonstrate that, for indistinguishable particles, symmetry requirements on the wavefunction can lead to non-extensive scaling behavior for both Boltzmann and Gibbs entropy. To clarify this fact, we consider as exactly solvable examples the generic spin (oscillator) model from the Main Text for the analytically tractable cases $L = 1$ (two single particle levels) and $L = 2$ (three single particle levels). Subsequently, we refer to a classical Ising chain to show that, even when both S_B and S_G scale extensively with particle number N , they can still differ substantially in the thermodynamic limit.

Two-level systems (indistinguishable particles). For the generic spin model from the Main Text with $L = 1$, each of the $n = 1, \dots, N$ particles can occupy one of the two single-particle levels $\ell_n = 0$ or $\ell_n = 1$. Considering indistinguishable bosons, the total N -particle energy $E = \epsilon \sum_{n=1}^N \ell_n$ can take values $0 \leq E \leq \epsilon N$ and, due to symmetry requirements on the wavefunction, there is exactly one N -particle state per N -particle energy value E , i.e.,

⁴ This statement remains true for infinite systems, but their mathematical treatment requires some extra care because it is possible that in the thermodynamic limit both T_B and T_G diverge at E_* whilst the heat capacity remains finite or approaches zero; see the Ising chain example below.

the degeneracy per N -particle level is constant, $g_N(E) = 1$, thus yielding a constant⁵ DoS $\omega_N(E) = 1/\epsilon$ and a linearly increasing integrated DoS $\Omega_N(E) = 1 + E/\epsilon$. Hence, regardless of systems size N

$$S_B(E, N) = k_B \ln g_N(E) \equiv 0, \tag{14}$$

$$S_G(E, N) = k_B \ln \Omega_N(E) = k_B \ln(1 + E/\epsilon). \tag{15}$$

Whilst, at least formally, S_B is trivially extensive, it does not give the correct heat capacity $C = (\partial T/\partial E)^{-1}$, which is only obtained from the non-extensive Gibbs entropy S_G as $C = k_B$ (intuitively, a minimal heat transfer process would correspond to causing a single spin to flip through the absorption or emission of a photon). Note that C is independent of N , which already signals that the entropy cannot scale extensively with particle number in this example. To see this explicitly, let us define the energy per particle $\bar{E} = E/N$ and compute the entropy per particle

$$\bar{S}_G(\bar{E}, N) := \frac{1}{N} S_G(E, N) = \frac{k_B}{N} \ln(1 + N\bar{E}/\epsilon). \tag{16}$$

Then, for large N , one finds that

$$\bar{S}_G(\bar{E}, N) \simeq \frac{1}{N} \ln(\bar{E}/\epsilon) + \frac{1}{N} \ln N. \tag{17}$$

The fact that $\bar{S}_G(\bar{E}, N) \rightarrow 0$ as $N \rightarrow \infty$ clarifies that the usual thermodynamic limit is not well-defined for this system of indistinguishable particles, but one can, of course, compute relevant thermodynamic quantities, such as the heat capacity, for arbitrary N from the Gibbs entropy S_G .

Three level systems (indistinguishable particles). We next consider the slightly more complex case $L = 2$, where each of the $n = 1, \dots, N$ particles can occupy one of the three single-particle level $\ell_n = 0, 1, 2$. Considering indistinguishable bosons as before, the total N -particle energy $E = \epsilon \sum_{n=1}^N \ell_n$ can take values $0 \leq E \leq 2\epsilon N =: E_+$. Symmetry of the wavefunction under particle exchange implies that the total number of N -particle states is $\Omega_N(E_+) = (N + 2)!/(N!2!) = (N + 2)(N + 1)/2$, and that an N -particle state with energy E has degeneracy

$$g_N(E) = \Theta(E_+/2 - E - 1) [1 + E/(2\epsilon)] + \Theta(E - E_+/2) [1 + (E_+ - E)/(2\epsilon)], \tag{18}$$

where $\lfloor x \rfloor$ denotes the largest integer $k \leq x$, and $\Theta(x) \equiv 0, x < 0$ and $\Theta(x) \equiv 1, x \geq 0$. The DoS can be formally defined by $\omega_N(E) = g_N(E)/\epsilon$, and becomes maximal at $E_* = E_+/2 = \epsilon N$, where it takes the value $\omega(E_*) = \lfloor 1 + N/2 \rfloor/\epsilon$. From Eq. (18), it is straightforward to compute exactly the integrated DoS $\Omega_N(E)$, but the resulting expression is rather lengthy and does not offer much direct insight. The physical essence can be more readily captured by noting that $\omega_N = g_N/\epsilon$ is approximately a piecewise linear function of E ,

$$\omega_N(E) \simeq \frac{1}{4\epsilon} + \frac{\omega(E_*)}{E_* + 2\epsilon} \begin{cases} E + \epsilon, & 0 < E < E_*, \\ E_+ + \epsilon - E, & E_* < E < E_+. \end{cases} \tag{19}$$

Integrating Eq. (19) over E with boundary condition $\Omega_N(0) = 1$, we find for the integrated DoS

$$\Omega_N(E) \simeq 1 + \frac{E}{4\epsilon} + \frac{\omega(E_*)}{2(E_* + 2\epsilon)} \begin{cases} E(E + 2\epsilon), & 0 < E < E_*, \\ 2(E\epsilon + E_*^2) - (E - E_+)^2, & E_* < E < E_+. \end{cases} \tag{20}$$

One can easily verify, by numerical summation of Eq. (18) or otherwise, that this is indeed a very good approximation to the exact integrated DoS.

Now focussing on large systems with $N \gg 1$ and energy values sufficiently far from the boundaries, $\epsilon \ll E \ll E_+ - \epsilon$, the above expression for ω_N and Ω_N reduce asymptotically to

$$\omega_N(E) \simeq \frac{1}{2\epsilon^2} \begin{cases} E, & \epsilon \ll E < \epsilon N, \\ E_+ - E, & \epsilon N < E \ll 2\epsilon N = E_+, \end{cases} \tag{21}$$

⁵ This example is equivalent to a single-particle quantum oscillator with energy cut-off at $E = \epsilon N$.

and

$$\Omega_N(E) \simeq \frac{1}{4\epsilon^2} \begin{cases} E^2, & \epsilon \ll E < \epsilon N, \\ 2EE_+ - E^2 - E_+^2/2, & \epsilon N < E \ll 2\epsilon N. \end{cases} \quad (22)$$

It is evident from Eqs. (21) and (22) that, similar to the preceding example, neither the associated Boltzmann entropy $S_B = k_B \ln \epsilon \omega$ nor the Gibbs entropy $S_G = k_B \ln \Omega$ scale extensively with particle number N . This is a consequence of the fact that, for quantum systems with bounded spectrum, the number of states at fixed energy per particle does not always grow exponentially with N due to the limited availability of single-particle energy levels and the symmetry constraints on the wavefunction. Furthermore, Eq. (21) implies that the Boltzmann temperature

$$k_B T_B = \frac{\omega}{\omega'} = \begin{cases} +E, & \epsilon \ll E < \epsilon N, \\ -E, & \epsilon N < E \ll 2\epsilon N, \end{cases} \quad (23)$$

exhibits a finite jump whilst changing sign at $E_* = \epsilon N$. By contrast, the Gibbs temperature

$$k_B T_G = \frac{\Omega}{\omega} = \frac{1}{2} \begin{cases} E, & \epsilon \ll E < \epsilon N, \\ \frac{2EE_+ - E^2 - E_+^2/2}{E_+ - E}, & \epsilon N < E \ll 2\epsilon N. \end{cases} \quad (24)$$

remains positive over the full energy range, exhibiting a strong increase in the region $E > E_*$ that reflects the practically vanishing heat capacity in the population inverted regime. More precisely, one finds from the above formula for T_G that

$$\frac{C}{k_B} = \begin{cases} 2, & \epsilon \ll E < \epsilon N, \\ 2 - \frac{2E_+^2}{3E_+^2 - 4E_+E + 2E^2}, & \epsilon N < E \ll 2\epsilon N. \end{cases} \quad (25)$$

Note that, because Ω'' is discontinuous at $E_* = E_+/2$ in this example, the total heat capacity C also drops discontinuously from $2k_B$ to $2k_B/3$ at E_* before approaching zero as $E \rightarrow E_+$.

To summarize briefly: The sub-exponential N -scaling of ω and Ω in the two above examples arises from (i) the restrictions on the number of available one-particle levels and (ii) the permutation symmetry of the wavefunction. To isolate the effects of (i), it is useful to study a classical Ising chain that consists of N distinguishable particles. This helps to clarify that, even when both S_B and S_G grow extensively with particle number N , they do not necessarily have identical thermodynamic limits.

Ising chain (distinguishable particles). We consider $n = 1, \dots, N$ weakly interacting distinguishable particles that can occupy two single-particle energy levels, labeled by $\ell_n = 0, 1$ and spaced by an energy gap ϵ . The total energy E of the N -particle system can take values in $0 \leq E \leq \epsilon N =: E_+$, and we denote the number of particles occupying the upper single-particle state by $Z = E/\epsilon$. The degeneracy of an N -particle energy level $E = Z\epsilon$ is

$$g_N(E) = \frac{N!}{(E/\epsilon)!(N - E/\epsilon)!} = \frac{N!}{Z!(N - Z)!}, \quad (26)$$

and the DoS is given by $\omega_N(E) = g_N(E)/\epsilon$. As before, we define the mean energy per particle by $\bar{E} := E/N = \epsilon Z/N$, where Z/N is the fraction of particles occupying the upper levels. For large $N \gg 1$ and constant \bar{E} , we have

$$g_N(\bar{E}N) \simeq e^{-N[(1-\bar{E}/\epsilon)\ln(1-\bar{E}/\epsilon) + (\bar{E}/\epsilon)\ln(\bar{E}/\epsilon)]}. \quad (27)$$

This implies immediately that the associated Boltzmann entropy $S_B = k_B \ln \epsilon \omega = k_B \ln g$ is extensive (i.e., scales linearly with N). Thus, in the thermodynamic limit, the Boltzmann entropy per particle, $\bar{S}_B = S_B/N$, becomes

$$\bar{S}_B \simeq -k_B[(1 - \bar{E}/\epsilon)\ln(1 - \bar{E}/\epsilon) + (\bar{E}/\epsilon)\ln(\bar{E}/\epsilon)], \quad (28)$$

and the associated Boltzmann ‘temperature’

$$k_B T_B = \frac{\epsilon}{2 \operatorname{arctanh}(1 - 2\bar{E}/\epsilon)} \quad (29)$$

diverges at $\bar{E} = \epsilon/2$. In particular, we see that T_B is positive for $\bar{E} < \epsilon/2$ but becomes negative when $\bar{E} > \epsilon/2$.

In order to compare with the corresponding Gibbs entropy, it is useful to note that Eq. (28) can be (quite accurately) approximated by the parabola⁶

$$\bar{S}_B \approx k_B(\ln 2)[(1 - 2\bar{E}'/\epsilon)^2 - 1]. \quad (30)$$

Adopting this simplification, one finds for the associated Boltzmann temperature

$$k_B T_B \approx \frac{\epsilon}{(\ln 16)(1 - 2\bar{E}/\epsilon)}, \quad (31)$$

which is both qualitatively and quantitatively very similar to Eq. (29).

To compute the Gibbs entropy, we must determine the integrated DoS Ω_N , which according to Eqs. (27) and (28), is given by

$$\Omega_N(E) - \Omega_N(0) \simeq \frac{1}{\epsilon} \int_0^E dE' g_N(E') \simeq \int_0^E dE' e^{-N\bar{S}_B}. \quad (32)$$

Changing the integration variable from the total energy E' to the energy per particle $\bar{E}' = E'/N$, inserting the harmonic approximation (30) for \bar{S}_B , and noting that the groundstate is non-degenerate, $\Omega_N(0) = 1$, we obtain

$$\begin{aligned} \Omega_N(E) &\approx 1 + \frac{N}{\epsilon} \int_0^{\bar{E}} d\bar{E}' \exp\{-N(\ln 2)[(1 - 2\bar{E}'/\epsilon)^2 - 1]\} \\ &= 1 + 2^{N-2} \left(\frac{\pi N}{\ln 2}\right)^{1/2} \left\{ \operatorname{erf}(\sqrt{N \ln 2}) - \operatorname{erf}[(1 - 2\bar{E}/\epsilon)\sqrt{N \ln 2}] \right\}. \end{aligned} \quad (33)$$

This result implies that also the Gibbs entropy $S_G = k_B \ln \Omega$ becomes extensive for sufficiently large N and, hence, the thermodynamic limit is well-defined. More precisely, letting $N \rightarrow \infty$ at constant energy per particle \bar{E} , one obtains the Gibbs entropy per particle, $\bar{S}_G = S_G/N$, as

$$\bar{S}_G \approx k_B(\ln 2) \begin{cases} 4(1 - \bar{E}/\epsilon)(\bar{E}/\epsilon), & \bar{E} < \epsilon/2, \\ 1, & \bar{E} \geq \epsilon/2, \end{cases} \quad (34)$$

and from this the absolute thermodynamic temperature

$$k_B T_G \approx \begin{cases} \frac{\epsilon}{(\ln 16)(1 - 2\bar{E}/\epsilon)}, & \bar{E} < \epsilon/2, \\ +\infty, & \bar{E} \geq \epsilon/2. \end{cases} \quad (35)$$

By comparing with Eq. (31), we see that, in the thermodynamic limit:

1. T_B and T_G become equal for subcritical energy values $\bar{E} < \epsilon/2$, corresponding the non-population inverted phase, but
2. T_B and T_G differ in the population inverted regime $\bar{E} > \epsilon/2$.

Strictly speaking, Eq. (33) implies that, for finite Ising chains, T_G remains finite over the full energy range $(0, E_+)$ but grows extremely rapidly when the specific energy \bar{E} is increased beyond $\epsilon/2$. In the thermodynamic limit, however, T_G diverges to $+\infty$ at $\bar{E} = \epsilon/2$ and remains at this value when the energy is increased further. An explicit calculation of the heat capacity C for the Ising model confirms that $C(E_+/2) = k_B$ for all N , in agreement with the statements after Eq. (13) and signaling that the total heat capacity is not extensive in the population-inverted regime $\bar{E} \geq \epsilon/2$. More precisely, one finds for the heat capacity per particle $\bar{C} = C/N$ that

$$\bar{C} \approx k_B \begin{cases} (\ln 4)(1 - 2\bar{E}/\epsilon)^2, & \bar{E} < \epsilon/2, \\ 0, & \bar{E} \geq \epsilon/2. \end{cases} \quad (36)$$

⁶ This corresponds to an effective Stirling-type approximation for the degeneracies g_N , tailored to match the boundary conditions at $E = 0$ and $E = E_+$.

Moreover, the total heat capacity C , although scaling extensively with N for $\bar{E} < \epsilon/2$, also vanishes⁷ for $\bar{E} > \epsilon/2$. Thus, the Gibbs entropy predicts correctly that the heat capacity C of the infinite Ising chain becomes zero for $\bar{E} > \epsilon/2$, reflecting the fact that population inversion in an infinite system cannot be achieved by conventional heating.

In conclusion, the above calculations for the Ising model illustrate that, even when both S_B and S_G are extensive at subcritical energies, they do not necessarily have identical thermodynamical limits in the population-inverted regime. That the Gibbs entropy S_G produces reasonable results for the Ising chain in the thermodynamic limit may be regarded as a valuable cross-check, but is in fact not very surprising given that S_G fulfills the thermostatistical self-consistency criteria.

Invalid arguments against the Gibbs entropy

Both the general arguments and the specific examples in the Main Text show that the Boltzmann entropy is not a consistent thermostatistical entropy, whereas the Gibbs entropy respects the thermodynamic relations (2) and also gives reasonable results for all analytically tractable models. Despite its conceptual advantages, the Gibbs formalism is sometimes met with skepticism that appears to be rooted in habitual preference of the Boltzmann entropy rather than unbiased evaluation of facts. In various discussions over the last decade, we have met a number of recurrent arguments opposing the Gibbs entropy as being conceptually inferior to the Boltzmann entropy. None of those objections, however, seems capable of withstanding careful inspection. It might therefore be helpful to list, and address explicitly, the most frequently encountered ‘spurious’ arguments against the Gibbs entropy that may seem plausible at first but turn out to be unsubstantiated.

1. *The Gibbs entropy violates the second law $dS \geq 0$ for closed systems, whereas the Boltzmann entropy does not.* This statement is incorrect, simply because for closed systems with fixed control parameters (i.e., constant energy, volume, etc.) both Gibbs and Boltzmann entropy are constant. This general fact, which follows trivially from the definitions of S_G and S_B , is directly illustrated by the classical ideal gas example discussed in the Main Text.

2. *Thermodynamic entropy must be equal to Shannon’s information entropy, and this is true only for the Boltzmann entropy.* This argument can be discarded for several reasons. Clearly, entropic information measures themselves are a matter of convention [5], and there exists a large number of different entropies (Shannon, Renyi, Kuhlback entropies, etc.), each having their own virtues and drawbacks as measures of information [6]. However, only few of those entropies, when combined with an appropriate probability distribution, define ensembles [7] that obey the fundamental thermodynamic relations (2). It so happens that the entropy of the canonical ensemble coincides with Shannon’s popular information measure. But the canonical ensemble (infinite bath) and the more fundamental MC ensemble (no bath) correspond to completely different physical situations [8] and, accordingly, the MC entropy is, in general, not equivalent to Shannon’s information entropy (except in those limit cases where MC and canonical ensembles become equivalent). Just by considering classical Hamiltonian systems, one can easily verify that neither S_B nor S_G belong to the class of Shannon entropies. This does not mean that these two different entropies cannot be viewed as measures of information. Both Gibbs and Boltzmann entropy encode valuable physical information about the underlying energy spectra, but only one of them, S_G , agrees with thermodynamics. Although it may seem desirable to unify information theory and thermodynamic concepts for formal or aesthetic reasons, some reservation is in order [4] when such attempts cause mathematical inconsistencies and fail to produce reasonable results in the simplest analytically tractable cases.

From a more general perspective, it could in fact be fruitful to consider the possibility of using thermodynamic criteria as a means for discriminating between different types of information entropy [5]. That is, instead of postulating that thermodynamic entropy must be equal to Shannon entropy, it might be advisable to demand thermostatistical self-consistency in order to single out the particular form of information entropy that it is most suitable for describing a given physical situation.

3. *Non-degenerate states must have zero thermodynamic entropy, and this is true only for the Boltzmann entropy.* This argument again traces back to confusing thermodynamic and Shannon-type information entropies [4]. Physical systems that possess non-degenerate spectra can be used to store energy, and one can perform work on them by changing their parameters. It seems reasonable to demand that a well-defined thermodynamic formalism is able to account for these facts. Hence, entropy definitions that are insensitive to the full energetic structure of the spectrum by only counting degeneracies of individual levels are not particularly promising candidates for capturing thermodynamic properties. Moreover, it is not true that the Boltzmann entropy, when defined with respect to a

⁷ The emergence of a singularity in C at $\bar{E} = \epsilon/2$ in the thermodynamic limit can be interpreted as a phase transition.

coarse-grained DoS, as commonly assumed in applications, assigns zero entropy to non-degenerate spectra, as the DoS merely measures the total number of states in predefined energy intervals but does not explicitly reflect the degeneracies of the individual states. If, however, one were to postulate that the thermodynamic entropy of an energy level E_n with degeneracy g_n is exactly equal to $k_B \ln g_n$, then this would lead to other undesirable consequences: Degeneracies usually reflect symmetries that can be broken by infinitesimal parameter variations or small defects in a sample. That is, if one were to adopt $k_B \ln g_n$, then the entropy of the system could be set to zero, for many or even all energy levels, by a very small perturbation that lifts the exact degeneracy, even though actual physical properties (e.g., heat capacity, conductivity) are not likely to be that dramatically affected by minor deviations from the exact symmetry. By contrast, an integral measure such as the Gibbs entropy responds much more continuously (although not necessarily smoothly) to such infinitesimal changes. By adopting the proper normalization for the ground-state entropy, $S_G(E_0) = k_B \ln \Omega(E_0) = k_B \ln g_0$, the Gibbs entropy also agrees with the experimentally confirmed residual entropy [9–11].

4. *If the spectrum is invariant under $E \rightarrow -E$, then so should be the entropy.* At first sight, this statement may look like a neat symmetry argument in support of the Boltzmann entropy, which indeed exhibits this property (see example in Fig. 1 of the Main Text). However, such an additional axiom would be in conflict with the postulates of traditional thermodynamics, which require S to be a monotonic function of the energy [1]. On rare occasions, it can be beneficial or even necessary to remove, replace and adapt certain axioms even in a well-tested theory, but such radical steps need to be justified by substantial experimental evidence. The motivation for the ‘new’ entropy invariance postulate is the rather vague idea that, for systems with a DoS as shown in Fig. 1 of the Main Text, the maximum energy state (‘all spins up’) is equivalent to the lowest energy state (‘all spins down’). Whilst this may be correct if one is only interested in comparing degeneracies, an experimentalist who performs thermodynamic manipulations will certainly be able to distinguish the groundstate from the highest-energy state through their capability to absorb or release energy quanta. Since thermostatics should be able to connect experiment with theory, it seems reasonable to maintain that the thermodynamic entropy should reflect absolute differences between energy-states.

5. *Thermodynamic relations can only be expected to hold for large systems, so it is not a problem that the Boltzmann entropy does not work for small quantum systems.* Apart from the fact that the Boltzmann entropy does not obey the fundamental thermodynamic relation (1), it seems unwise to build a theoretical framework on postulates that fail in the simplest test cases, especially, when Gibbs’ original proposal [3] appears to work perfectly fine for systems of arbitrary size⁸. A logically correct statement would be: The Boltzmann entropy produces reasonable results for a number of large systems because it happens to approach the thermodynamically consistent Gibbs entropy in those (limit) cases. To use two slightly provocative analogies: It does not seem advisable to replace the Schrödinger equation by a theory that fails to reproduce the hydrogen spectrum but claims to predict more accurately the spectral properties of larger quantum systems. Nor would it seem a good idea to trust a numerical algorithm that produces exciting results for large systems but fails to produce sensible results for one- or two-particle test scenarios. If one applies similar standards to the axiomatic foundations of thermostatics, then the Boltzmann entropy should be replaced by the Gibbs entropy S_G , implying that negative absolute temperatures cannot be achieved.

6. *The Gibbs entropy is probably correct for small quantum systems and classical systems, but one should use the Boltzmann entropy for intermediate quantum systems.* To assume that a theoretical framework that is known to be inconsistent in the low-energy limit of small quantum systems as well as in the high-energy limit of classical systems, may be preferable in some intermediate regime seems adventurous at best.

We hope that the discussion in this part, although presented in an unusual form, is helpful for the objective evaluation of Gibbs and Boltzmann entropy⁹. It should be emphasized, however, that no false or correct argument against the Gibbs entropy can cure the thermodynamic incompatibility of the Boltzmann entropy.

[1] H. B. Callen. *Thermodynamics and an Introduction to Thermostatistics*. Wiley, New York, 1985.

[2] P. Hertz. Über die mechanischen Grundlagen der Thermodynamik. *Annalen der Physik (Leipzig)*, 33:225–274, 537–552, 1910.

⁸ A practical ‘advantage’ of large systems is that thermodynamic quantities typically become ‘sharp’ [8] when considering a suitably defined thermodynamic limit, whereas for small systems fluctuations around the mean values are relevant. However, this does not mean that thermostatics itself must become invalid for small systems. In fact, the Gibbs formalism [3] works perfectly even for small MC systems [7, 12].

⁹ One could add another ‘argument’ to the above list: ‘The Boltzmann entropy is prevalent in modern textbooks and has been more frequently used for more than 50 years and, therefore, is most likely correct’— we do not think such reasoning is constructive.

- [3] J. W. Gibbs. *Elementary Principles in Statistical Mechanics*. Dover, New York, reprint of the 1902 edition, 1960.
- [4] A. I. Khinchin. *Mathematical Foundations of Statistical Mechanics*. Dover, New York, 1949.
- [5] A. Rényi. On measures of entropy and information. In *Proc. Fourth Berkeley Symp. on Math. Statist. and Prob.*, volume 1, pages 547–561. UC Press, 1961.
- [6] A. Wehrl. General properties of entropy. *Rev. Mod. Phys.*, 50(2):221–260, 1978.
- [7] M. Campisi. Thermodynamics with generalized ensembles: The class of dual orthodes. *Physica A*, 385:501–517, 2007.
- [8] R. Becker. *Theory of Heat*. Springer, New York, 1967.
- [9] W. F. Giaque and H. L. Johnston. Symmetrical and antisymmetrical hydrogen and the third law of thermodynamics. Thermal equilibrium and the triple point pressure. *J. Am. Chem. Soc.*, 50(12):3221–3228, 1928.
- [10] L. Pauling. The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement. *J. Am. Chem. Soc.*, 57(12):2680–2684, 1935.
- [11] M. Campisi, P. Talkner, and P. Hänggi. Thermodynamics and fluctuation theorems for a strongly coupled open quantum system: an exactly solvable case. *J. Phys. A: Math. Theor.*, 42:392002, 2009.
- [12] J. Dunkel and S. Hilbert. Phase transitions in small systems: Microcanonical vs. canonical ensembles. *Physica A*, 370(2):390–406, 2006.