

Consistent thermostatics forbids negative absolute temperatures

Jörn Dunkel^{1*} and Stefan Hilbert²

Over the past 60 years, a considerable number of theories and experiments have claimed the existence of negative absolute temperature in spin systems and ultracold quantum gases. This has led to speculation that ultracold gases may be dark-energy analogues and also suggests the feasibility of heat engines with efficiencies larger than one. Here, we prove that all previous negative temperature claims and their implications are invalid as they arise from the use of an entropy definition that is inconsistent both mathematically and thermodynamically. We show that the underlying conceptual deficiencies can be overcome if one adopts a microcanonical entropy functional originally derived by Gibbs. The resulting thermodynamic framework is self-consistent and implies that absolute temperature remains positive even for systems with a bounded spectrum. In addition, we propose a minimal quantum thermometer that can be implemented with available experimental techniques.

Positivity of absolute temperature T , a key postulate of thermodynamics¹, has repeatedly been challenged both theoretically^{2–4} and experimentally^{5–7}. If indeed realizable, negative temperature systems promise profound practical and conceptual consequences. They might not only facilitate the creation of hyper-efficient heat engines^{2–4} but could also help⁷ to resolve the cosmological dark-energy puzzle^{8,9}. Measurements of negative absolute temperature were first reported in 1951 by Purcell and Pound⁵ in seminal work on the population inversion in nuclear spin systems. Five years later, Ramsay's comprehensive theoretical study² clarified hypothetical ramifications of negative temperature states, most notably the possibility to achieve Carnot efficiencies $\eta > 1$ (refs 3,4). Recently, the first experimental realization of an ultracold bosonic quantum gas⁷ with a bounded spectrum has attracted considerable attention¹⁰ as another apparent example system with $T < 0$, encouraging speculation that cold-atom gases could serve as laboratory dark-energy analogues.

Here, we show that claims of negative absolute temperature in spin systems and quantum gases are generally invalid, as they arise from the use of a popular yet inconsistent microcanonical entropy definition attributed to Boltzmann¹¹. By means of rigorous derivations¹² and exactly solvable examples, we will demonstrate that the Boltzmann entropy, despite being advocated in most modern textbooks¹³, is incompatible with the differential structure of thermostatics, fails to give sensible predictions for analytically tractable quantum and classical systems, and violates equipartition in the classical limit. The general mathematical incompatibility implies that it is logically inconsistent to insert negative Boltzmann 'temperatures' into standard thermodynamic relations, thus explaining paradoxical (wrong) results for Carnot efficiencies and other observables. The deficiencies of the Boltzmann entropy can be overcome by adopting a self-consistent entropy concept that was derived by Gibbs more than 100 years ago¹⁴, but has been mostly forgotten ever since. Unlike the Boltzmann entropy, Gibbs' entropy fulfils the fundamental thermostatical relations and produces sensible predictions for heat capacities and other thermodynamic observables in all exactly computable test cases. The

Gibbs formalism yields strictly non-negative absolute temperatures even for quantum systems with a bounded spectrum, thereby invalidating all previous negative temperature claims.

Negative absolute temperatures?

The seemingly plausible standard argument in favour of negative absolute temperatures goes as follows¹⁰: assume a suitably designed many-particle quantum system with a bounded spectrum^{5,7} can be driven to a stable state of population inversion, so that most particles occupy high-energy one-particle levels. In this case, the one-particle energy distribution will be an increasing function of the one-particle energy ϵ . To fit^{7,10} such a distribution with a Boltzmann factor $\propto \exp(-\beta\epsilon)$, β must be negative, implying a negative Boltzmann 'temperature' $T_B = (k_B\beta)^{-1} < 0$. Although this reasoning may indeed seem straightforward, the arguments below clarify that T_B is, in general, not the absolute thermodynamic temperature T , unless one is willing to abandon the mathematical consistency of thermostatics. We shall prove that the parameter $T_B = (k_B\beta)^{-1}$, as determined by Purcell and Pound⁵ and more recently also in ref. 7 is, in fact, a function of both temperature T and heat capacity C . This function $T_B(T, C)$ can indeed become negative, whereas the actual thermodynamic temperature T always remains positive.

Entropies of closed systems

When interpreting thermodynamic data of new many-body states⁷, one of the first questions to be addressed is the choice of the appropriate thermostatical ensemble^{15,16}. Equivalence of the microcanonical and other statistical ensembles cannot—in fact, must not—be taken for granted for systems that are characterized by a non-monotonic^{2,4,7} density of states (DOS) or that can undergo phase-transitions due to attractive interactions¹⁷—gravity being a prominent example¹⁸. Population-inverted systems are generally thermodynamically unstable when coupled to a (non-population-inverted) heat bath and, hence, must be prepared in isolation^{5–7}. In ultracold quantum gases⁷ that have been isolated from the environment to suppress decoherence, both particle number and energy are in good approximation conserved. Therefore,

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

²Max Planck Institute for Astrophysics, Karl-Schwarzschild-Straße 1, Garching 85748, Germany. *e-mail: dunkel@math.mit.edu

barring other physical or topological constraints, any *ab initio* thermostistical treatment should start from the microcanonical ensemble. We will first prove that only the Gibbs entropy provides a consistent thermostistical model for the microcanonical density operator. Instructive examples will be discussed subsequently.

We consider a (quantum or classical) system with microscopic variables ξ governed by the Hamiltonian $H = H(\xi; V, A)$, where V denotes volume and $A = (A_1, \dots)$ summarizes other external parameters. If the dynamics conserves the energy E , all thermostistical information about the system is contained in the microcanonical density operator

$$\rho(\xi; E, V, A) = \frac{\delta(E - H)}{\omega} \quad (1)$$

which is normalized by the DOS

$$\omega(E, V, A) = \text{Tr}[\delta(E - H)]$$

When considering quantum systems, we assume, as usual, that equation (1) has a well-defined operator interpretation, for example, as a limit of an operator series. For classical systems, the trace simply becomes a phase-space integral over ξ . The average of some quantity F with respect to ρ is denoted by $\langle F \rangle \equiv \text{Tr}[F\rho]$, and we define the integrated DOS

$$\Omega(E, V, A) = \text{Tr}[\Theta(E - H)]$$

which is related to the DOS ω by differentiation,

$$\omega = \frac{\partial \Omega}{\partial E} \equiv \Omega'$$

Intuitively, for a quantum system with spectrum $\{E_n\}$, the quantity $\Omega(E_n, V, A)$ counts the number of eigenstates with energy less than or equal to E_n .

Given the microcanonical density operator from equation (1), one can find two competing definitions for the microcanonical entropy in the literature^{12–14,17,19,20}:

$$S_B(E, V, A) = k_B \ln(\epsilon \omega),$$

$$S_G(E, V, A) = k_B \ln(\Omega)$$

where ϵ is a constant with dimensions of energy, required to make the argument of the logarithm dimensionless. The Boltzmann entropy S_B is advocated by most modern textbooks¹³ and used by most authors nowadays^{2,4,5,7}. The second candidate S_G is often attributed to Hertz²¹ but was in fact already derived by Gibbs in 1902 (ref. 14, Chapter XIV). For this reason, we shall refer to S_G as Gibbs entropy. Hertz proved in 1910 that S_G is an adiabatic invariant²¹. His work was highly commended by Planck²² and Einstein, who closes his comment²³ by stating that he would not have written some of his papers had he been aware of Gibbs' comprehensive treatise¹⁴.

Thermostistical consistency conditions

The entropy S constitutes the fundamental thermodynamic potential of the microcanonical ensemble. Given S , secondary thermodynamic observables, such as temperature T or pressure p , are obtained by differentiation with respect to the natural control variables $\{E, V, A\}$. Denoting partial derivatives with respect to E by a prime, the two formal temperatures associated with S_B and S_G are given by

$$T_B(E, V, A) = \left(\frac{\partial S_B}{\partial E} \right)^{-1} = \frac{1}{k_B} \frac{\omega}{\omega'} = \frac{1}{k_B} \frac{\Omega'}{\Omega''} \quad (2)$$

$$T_G(E, V, A) = \left(\frac{\partial S_G}{\partial E} \right)^{-1} = \frac{1}{k_B} \frac{\Omega}{\Omega'} = \frac{1}{k_B} \frac{\Omega}{\omega} \quad (3)$$

Note that T_B becomes negative if $\omega' < 0$, that is, if the DOS is non-monotonic, whereas T_G is always non-negative, because Ω is a monotonic function of E . The question as to whether T_B or T_G defines the thermodynamic absolute temperature T can be decided unambiguously by considering the differential structure of thermodynamics, which is encoded in the fundamental relation

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial E} \right) dE + \left(\frac{\partial S}{\partial V} \right) dV + \sum_i \left(\frac{\partial S}{\partial A_i} \right) dA_i \\ &\equiv \frac{1}{T} dE + \frac{p}{T} dV + \sum_i \frac{a_i}{T} dA_i \end{aligned} \quad (4)$$

All consistent thermostistical models, corresponding to pairs (ρ, S) where ρ is a density operator and S an entropy potential, must satisfy equation (4). If one abandons this requirement, any relation to thermodynamics is lost.

Equation (4) imposes stringent constraints on possible entropy candidates. For example, for an adiabatic (that is, isentropic) volume change with $dS = 0$ and other parameters fixed ($dA_i = 0$), one finds the consistency condition

$$p = T \left(\frac{\partial S}{\partial V} \right) = - \left(\frac{\partial E}{\partial V} \right) = - \left\langle \frac{\partial H}{\partial V} \right\rangle \quad (5)$$

More generally, for any adiabatic variation of some parameter $A_\mu \in \{V, A_i\}$ of the Hamiltonian H , one must have (Supplementary Information)

$$T \left(\frac{\partial S}{\partial A_\mu} \right)_E = - \left(\frac{\partial E}{\partial A_\mu} \right)_S = - \left\langle \frac{\partial H}{\partial A_\mu} \right\rangle \quad (6)$$

where $T \equiv (\partial S / \partial E)^{-1}$ and subscripts S and E indicate quantities kept constant, respectively. The first equality in equation (6) follows directly from equation (4). The second equality demands correct identification of thermodynamic quantities with statistical expectation values, guaranteeing for example that mechanically measured gas pressure agrees with abstract thermodynamic pressure. The conditions in equation (6) not only ensure that the thermodynamic potential S fulfils the fundamental differential relation (equation (4)). For a given density operator ρ , they can be used to separate consistent entropy definitions from inconsistent ones.

Using only the properties of the microcanonical density operator as defined in equation (1), one finds²⁴

$$\begin{aligned} T_G \left(\frac{\partial S_G}{\partial A_\mu} \right) &= \frac{1}{\omega} \frac{\partial}{\partial A_\mu} \text{Tr} \left[\Theta(E - H) \right] = - \frac{1}{\omega} \text{Tr} \left[- \frac{\partial}{\partial A_\mu} \Theta(E - H) \right] \\ &= - \text{Tr} \left[\left(\frac{\partial H}{\partial A_\mu} \right) \frac{\delta(E - H)}{\omega} \right] = - \left\langle \frac{\partial H}{\partial A_\mu} \right\rangle \end{aligned} \quad (7)$$

This proves that the pair (ρ, S_G) fulfils equation (6) and, hence, constitutes a consistent thermostistical model for the microcanonical density operator ρ . Moreover, because generally $T_B(\partial S_B / \partial A_\mu) \neq T_G(\partial S_G / \partial A_\mu)$, it is a trivial corollary that the Boltzmann entropy S_B violates equation (6) and hence cannot be a thermodynamic entropy, implying that it is inconsistent to insert the Boltzmann 'temperature' T_B into equations of state or efficiency formulae that assume validity of the fundamental thermodynamic relations (equation (4)).

Similarly to equation (7), it is straightforward to show that, for standard classical Hamiltonian systems with confined trajectories and a finite ground-state energy, only the Gibbs temperature T_G satisfies the mathematically rigorous equipartition theorem¹²

$$\left\langle \xi_i \frac{\partial H}{\partial \xi_j} \right\rangle \equiv \text{Tr} \left[\left(\xi_i \frac{\partial H}{\partial \xi_j} \right) \rho \right] = k_B T_G \delta_{ij} \quad (8)$$

for all canonical coordinates $\xi = (\xi_1, \dots)$. The key steps of the proof are identical to those in equation (7); that is, one merely exploits the chain rule relation $\partial \Theta(E-H)/\partial \lambda = -(\partial H/\partial \lambda)\delta(E-H)$, which holds for any variable λ in the Hamiltonian H . Equation (8) is essentially a phase-space version of Stokes' theorem¹², relating a surface (flux) integral on the energy shell to the enclosed phase-space volume.

Small systems

Differences between S_B and S_G are negligible for most macroscopic systems with monotonic DOS ω , but can be significant for small systems¹². This can already be seen for a classical ideal gas in d -space dimensions, where¹⁷

$$\Omega(E, V) = \alpha E^{dN/2} V^N, \quad \alpha = \frac{(2\pi m)^{dN/2}}{N! h^d \Gamma(dN/2 + 1)}$$

for N identical particles of mass m and Planck constant h . From this, one finds that only the Gibbs temperature yields exact equipartition

$$E = \left(\frac{dN}{2} - 1\right) k_B T_B, \tag{9}$$

$$E = \frac{dN}{2} k_B T_G \tag{10}$$

Clearly, equation (9) yields paradoxical results for $dN = 1$, where it predicts negative temperature $T_B < 0$ and heat capacity $C_B < 0$, and also for $dN = 2$, where the temperature T_B must be infinite. This is a manifestation of the fact that S_B is not an exact thermodynamic entropy. In contrast, the Gibbs entropy S_G produces the reasonable equation (10), which is a special case of the more general equipartition theorem (equation (8)).

That S_G also is the more appropriate choice for isolated quantum systems, as relevant to the interpretation of the experiments by Purcell and Pound⁵ and Braun *et al.*⁷, can be readily illustrated by two other basic examples: for a simple harmonic oscillator with spectrum

$$E_n = \hbar \nu \left(n + \frac{1}{2}\right), \quad n = 0, 1, \dots, \infty$$

we find by inversion and analytic interpolation $\Omega = 1 + n = 1/2 + E/(\hbar \nu)$ and, hence, from the Gibbs entropy $S_G = k_B \ln \Omega$ the caloric equation of state

$$k_B T_G = \frac{\hbar \nu}{2} + E$$

which, when combined with the quantum virial theorem, yields an equipartition-type statement for this particular example (equipartition is not a generic feature of quantum systems). Furthermore, $T = T_G$ gives a sensible prediction for the heat capacity,

$$C = \left(\frac{\partial T}{\partial E}\right)^{-1} = k_B$$

accounting for the fact that even a single oscillator can serve as minimal quantum heat reservoir. More precisely, the energy of a quantum oscillator can be changed by performing work through a variation of its frequency ν , or by injecting or removing energy quanta, corresponding to heat transfer in the thermodynamic picture. The Gibbs entropy S_G quantifies these processes in a sensible manner. In contrast, the Boltzmann entropy $S_B = k_B \ln(\epsilon \omega)$ with $\omega = (\hbar \nu)^{-1}$ assigns the same constant entropy to all energy states, yielding the nonsensical result $T_B = \infty$ for all energy eigenvalues E_n and making it impossible to compute the heat

capacity of the oscillator. The failure of the Boltzmann entropy S_B for this basic example should raise doubts about its applicability to more complex quantum systems⁷.

That S_B violates fundamental thermodynamic relations not only for classical but also for quantum systems can be further illustrated by considering a quantum particle in a one-dimensional infinite square-well of length L , for which the spectral formula

$$E_n = a n^2 / L^2, \quad a = \hbar^2 \pi^2 / (2m), \quad n = 1, 2, \dots, \infty \tag{11}$$

implies $\Omega = n = L\sqrt{E/a}$. In this case, the Gibbs entropy $S_G = k_B \ln \Omega$ gives

$$k_B T_G = 2E, \quad p_G \equiv T_G \left(\frac{\partial S_G}{\partial L}\right) = \frac{2E}{L}$$

as well as the heat capacity $C = k_B/2$, in agreement with physical intuition. In particular, the pressure equation is consistent with condition (equation (5)), as can be seen by differentiating equation (11) with respect to the volume L ,

$$p \equiv -\frac{\partial E}{\partial L} = \frac{2E}{L} = p_G$$

That is, p_G coincides with the mechanical pressure as obtained from kinetic theory¹⁹.

In contrast, we find from $S_B = k_B \ln(\epsilon \omega)$ with $\omega = L/(2\sqrt{Ea})$ for the Boltzmann temperature

$$k_B T_B = -2E < 0$$

Although this result in itself seems questionable, unless one believes that a quantum particle in a one-dimensional box is a dark-energy candidate, it also implies a violation of equation (5), because

$$p_B \equiv T_B \left(\frac{\partial S_B}{\partial L}\right) = -\frac{2E}{L} \neq p$$

This contradiction corroborates that S_B cannot be the correct entropy for quantum systems.

We still mention that one sometimes encounters the *ad hoc* convention that, because the spectrum in equation (11) is non-degenerate, the 'thermodynamic' entropy should be zero for all states. However, such a postulate entails several other inconsistencies (Supplementary Information). Focusing on the example at hand, the convention $S = 0$ would again imply the nonsensical result $T = \infty$, misrepresenting the physical fact that also a single degree of freedom in a box-like confinement can store heat in finite amounts.

Measuring T_B instead of T

For classical systems, the equipartition theorem (equation (8)) implies that an isolated classical gas thermometer shows, strictly speaking, the Gibbs temperature $T = T_G$, not T_B . When brought into (weak) thermal contact with an otherwise isolated system, a gas thermometer indicates the absolute temperature T of the compound system. In the quantum case, the Gibbs temperature T can be determined with the help of a bosonic oscillator that is prepared in the ground state and then weakly coupled to the quantum system of interest, because $(k_B T)^{-1}$ is proportional to the probability that the oscillator has remained in the ground state after some equilibration period (Methods). Thus, the Gibbs entropy provides not only the consistent thermostatical description of isolated systems but also a sound practical basis for classical and quantum thermometers.

It remains to clarify why previous experiments^{5,7} measured T_B and not the absolute temperature T . The authors of ref. 7,

for example, estimate ‘temperature’ by fitting a quasi-exponential Bose–Einstein function to their experimentally obtained one-particle energy distributions¹⁰. Their system contains $N \gg 1$ particles with Hamiltonian H_N and DOS ω_N . The formally exact microcanonical one-particle density operator reads

$$\rho_1 = \text{Tr}_{N-1}[\rho_N] = \frac{\text{Tr}_{N-1}[\delta(E - H_N)]}{\omega_N} \quad (12)$$

To obtain an exponential (canonical) fitting formula, as used in the experiments, one first has to rewrite ρ_1 in the equivalent form $\rho_1 = \exp[\ln \rho_1]$. Applying a standard steepest descent approximation^{13,19} to the logarithm and assuming discrete one-particle levels E_ℓ , one finds for the relative occupancy p_ℓ of one-particle level E_ℓ the canonical form

$$p_\ell \simeq \frac{e^{-E_\ell/(k_B T_B)}}{Z}, \quad Z = \sum_\ell e^{-E_\ell/(k_B T_B)} \quad (13)$$

The key observation here is that the exponential approximation (equation (13)) features T_B and not the absolute thermodynamic Gibbs temperature $T = T_G$. This becomes obvious by writing equation (12) for a given one-particle energy E_ℓ as $p_\ell = \omega_{N-1}(E - E_\ell)/\omega_N(E) = \exp[\ln \omega_{N-1}(E - E_\ell)]/\omega_N(E)$ and expanding $\ln \omega_{N-1}(E - E_\ell)$ for small E_ℓ , which gives $p_\ell \propto \exp[-E_\ell/(k_B T_{B,N-1})]$, where $k_B T_{B,N-1} \equiv \omega_{N-1}(E)/\omega'_{N-1}(E)$, in agreement with equation (2). That is, T_B in equation (13) is actually the Boltzmann temperature of the $(N-1)$ -particle system.

Hence, by fitting the one-particle distribution, one determines the Boltzmann temperature T_B , which can be negative, whereas the thermodynamic Gibbs temperature $T = T_G$ is always non-negative. The formal definitions of T_G and T_B imply the exact general relation (Supplementary Information)

$$T_B = \frac{T_G}{1 - k_B/C} \quad (14)$$

where $C = (\partial T_G/\partial E)^{-1}$ is the total thermodynamic heat capacity associated with $T = T_G$. As evident from equation (14), differences between T_G and T_B become relevant only if $|C|$ is close to or smaller than k_B ; in particular, T_B is negative if $0 < C < k_B$ as realized in the population-inverted regime (Supplementary Information).

Quantum systems with a bounded spectrum

That the difference between T_G and T_B is negligible for conventional macroscopic systems^{13,19} may explain why they are rarely distinguished in most modern textbooks apart from a few exceptions^{12,19}. However, for quantum systems with a bounded energy spectrum, S_G and S_B are generally very different (Fig. 1), and a careful distinction between T_G and T_B becomes necessary. To demonstrate this, we consider a generic quantum model relevant for the correct interpretation of the experiments by Purcell and Pound⁵ and Braun *et al.*⁷ (see Supplementary Information for additional examples). The model consists of N weakly interacting bosonic oscillators or spins with Hamiltonian

$$H_N \simeq \sum_{n=1}^N h_n$$

Each oscillator can occupy non-degenerate single-particle energy levels $E_{\ell_n} = \epsilon \ell_n$ with spacing ϵ and $\ell_n = 0, 1, \dots, L$. Assuming indistinguishable bosons, permissible N -particle states can be labelled by $\Lambda = (\ell_1, \dots, \ell_N)$, where $0 \leq \ell_1 \leq \ell_2 \leq \dots \leq \ell_N \leq L$. The associated energy eigenvalues $E_\Lambda = \epsilon(\ell_1 + \dots + \ell_N)$ are bounded by $0 \leq E_\Lambda \leq E_+ = \epsilon LN$. The DOS $\omega_N(E) = \text{Tr}_N[\delta(E - H_N)]$ counts the degeneracy of the eigenvalues E and equals

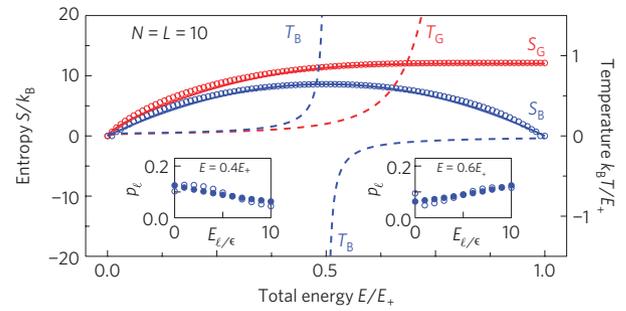


Figure 1 | Non-negativity of the absolute temperature in quantum systems with a bounded spectrum. Thermodynamic functions for N weakly coupled bosonic oscillators with $(L+1)$ single-particle levels $E_\ell = \ell\epsilon$, $\ell = 0, \dots, L$, are shown for $N = L = 10$, corresponding to 184,756 states in the energy band $[E_-, E_+] = [0, LN\epsilon]$. Open circles show exact numerical data; lines represent analytical results based on the Gaussian approximation of the DOS ω . The thermodynamic Gibbs entropy $S = S_G = k_B \ln \Omega$ grows monotonically with the total energy E , whereas the Boltzmann (or surface) entropy $S_B = k_B \ln(\epsilon\omega)$ does not. Accordingly, the absolute temperature $T = T_G$ remains positive, whereas the Boltzmann temperature T_B , as measured in ref. 7, exhibits a singularity at $E_* = \epsilon NL/2$. Note that, although T_G increases rapidly for $E > E_*/2$, it remains finite because $\omega(E) > 0$. For $N \rightarrow \infty$, T_G approaches the positive branch of T_B (Supplementary Information). Insets: exact relative occupancies p_ℓ (open circles) of one-particle energy levels are shown for two different values of the total energy. They agree qualitatively with those in Figs 1A and 3 of ref. 7, and can be approximately reproduced by an exponential distribution (filled circles) with parameter T_B , see equation (13). Quantitative deviations are due to limited sample size (N, L) in the simulations and use of the Gaussian approximation for T_B in the analytical calculations.

the number of integer partitions²⁵ of $z = E/\epsilon$ into N addends $\ell_n \leq L$. For $N, L \gg 1$, the DOS can be approximated by a continuous Gaussian,

$$\omega(E) = \omega_* \exp[-(E - E_*)^2/\sigma^2]$$

The degeneracy attains its maximum ω_* at the centre $E_* = E_+/2$ of the energy band (Fig. 1). The integrated DOS reads

$$\begin{aligned} \Omega(E) &= \text{Tr}_N[\Theta(E - H_N)] \\ &\simeq 1 + \int_0^E \omega(E') dE' \\ &= 1 + \frac{\omega_* \sqrt{\pi} \sigma}{2} \left[\text{erf}\left(\frac{E - E_*}{\sigma}\right) + \text{erf}\left(\frac{E_*}{\sigma}\right) \right] \end{aligned}$$

where the parameters σ and ω_* are determined by the boundary condition $\omega(0) = 1/\epsilon$ and the total number²⁵ of possible N -particle states $\Omega(E_+) = (N+L)/(N!L!)$. From this, we find that

$$k_B T_B = \frac{\sigma^2}{E_+ - 2E}$$

diverges and changes sign as E crosses $E_* = E_+/2$, whereas the absolute temperature $T = T_G(E) = k_B^{-1} \Omega/\omega$ grows monotonically but remains finite for finite particle number (Fig. 1). In a quantum system with a bounded spectrum as illustrated in Fig. 1, the heat capacity C decreases rapidly towards k_B as the energy approaches $E_* = E_+/2$, and C does not scale homogeneously with system size anymore as $E \rightarrow E_+$ owing to combinatorial constraints on the number of available states (Supplemen-

tary Information). Such constraints lead to a strong effective coupling between the spin degrees of freedom, thereby invalidating basic assumptions in the derivation of canonical distributions, such as equation (13).

In summary, for systems with a bounded spectrum, the effective Boltzmann temperature T_B differs not only quantitatively but also qualitatively from the actual thermodynamic temperature $T = T_G > 0$. Unfortunately, the measurement conventions adopted by Braun *et al.*⁷, and similarly those by Purcell and Pound⁵, are designed to measure T_B instead of T_G .

Carnot efficiencies > 1?

The above arguments show that the Boltzmann entropy S_B is not a consistent thermodynamic entropy, neither for classical nor for quantum systems, whereas the Gibbs entropy S_G provides a consistent thermodynamic formalism in the low-energy limit (small quantum systems), in the high-energy limit (classical systems) and in between. Regrettably, S_B has become so widely accepted nowadays that, even when its application to exotic states of matter⁷ leads to dubious claims, these are rarely questioned. One example are speculations^{2,4,7} that population-inverted systems can drive Carnot machines with efficiency > 1 . To evaluate such statements, recall that a Carnot cycle, by definition, consists of four successive steps: isothermal expansion; isentropic expansion; isothermal compression; isentropic compression. The two isothermal steps require a hot and cold bath with temperatures T^H and T^C , respectively, and the two isentropic steps can be thought of as place-holders for other work-like parameter variations (changes of external magnetic fields, and so on). The associated Carnot efficiency

$$\eta = 1 - \frac{T^C}{T^H} \quad (15)$$

owes its popularity to the fact that it presents an upper bound for other heat engines¹⁹. To realize values $\eta > 1$, one requires either T^C or T^H to be negative. At least formally, this seems to be achievable by considering systems as in Fig. 1 and naively inserting positive and negative Boltzmann temperature values $T_B \geq 0$ into equation (15).

Speculations^{2,4,7} of this type are unsubstantiated for several reasons. First, T_B is not a consistent thermodynamic temperature, and, if at all, one should use the absolute temperature $T = T_G > 0$ in equation (15), which immediately forbids $\eta > 1$. Second, to change back and forth between population-inverted states with $T_B < 0$ and non-inverted states with $T_B > 0$, work must be performed non-adiabatically²⁶, for example, by rapidly switching a magnetic field. As the thermodynamic entropy is not conserved during such switching processes, the resulting cycle is not of the Carnot type anymore and requires careful energy balance calculations³. In particular, such an analysis has to account for the peculiar fact that, when the heat engine is capable of undergoing population inversion, both a hot and cold bath may inject heat into the system. Properly defined efficiencies of thermodynamic cycles that involve systems with lower and upper energy bounds are, in general, not just simple functions of T_G or T_B . Naive application of equation (15) can be severely misleading in those cases.

On a final note, groundbreaking experiments such as those by Purcell and Pound⁵ and Braun *et al.*⁷ are essential for verifying the conceptual foundations of thermodynamics and thermostatistics. Such studies disclose previously unexplored regimes, thereby enabling us to test and, where necessary, expand theoretical concepts that will allow us to make predictions and are essential for the development of new technologies. However, the correct interpretation of data and the consistent formulation of heat and work exchange¹⁵ under extreme physical conditions (for example, at ultracold or ultrahot²⁷ temperatures, or on atomic or astronomical scales) require special care when it comes to applying

the definitions and conventions that constitute a specific theoretical framework. When interpreted within a consistent thermostatical theory, as developed by Gibbs¹⁴ more than a century ago, neither the work of Purcell and Pound⁵ nor recent experiments⁷ provide evidence for negative absolute temperatures. Unfortunately, this also means that cold atom gases are less likely to mimic dark energy.

Methods

Minimal quantum thermometer. A simple quantum thermometer for measuring the thermodynamic Gibbs temperature $T = T_G$ can be realized with a heavy atom in a one-dimensional harmonic trap. The measurement protocol is as follows: before coupling thermometer and system, one must prepare the isolated system in a state with well-defined energy $E = E_S$ and the thermometer oscillator with small angular frequency ν in the ground state $E_T = \hbar\nu/2$. After coupling the thermometer to the system, the total energy remains conserved, but redistribution of energy may take place. A measurement of the thermometer energy after a sufficiently long equilibration period will produce an oscillator eigenvalue $E'_T = \hbar\nu(n' + 1/2)$, where $n' \in \{0, \dots, \lfloor (E - E_0)/(\hbar\nu) \rfloor\}$, with E_0 denoting the system's ground state and $\lfloor x \rfloor$ the integer part. If the total energy remains conserved and the thermometer oscillator is non-degenerate, the probability $P[E'_T|E]$ of measuring a specific oscillator energy E'_T is equal to the microcanonical probability of finding the system in a state $E'_S = E - (E'_T - E_T) \leq E$:

$$P[E'_T|E] = \frac{g(E + E_T - E'_T)}{\Omega(E)}$$

where $g(E'_S)$ is the degeneracy of the level E'_S of the system, and

$$\Omega(E) = \sum_{E'_S \leq E} g(E'_S)$$

Assuming that the energy levels lie sufficiently dense ($\nu \rightarrow 0$) we can approximate the discrete probabilities $P[E'_T|E] \simeq p(E'_T|E)dE'_T$ by the probability density

$$p(E'_T|E) = \frac{\omega(E + E_T - E'_T)}{\Omega(E)}$$

This distribution can be obtained by repeating the experiment many times, and a simple estimator for the (inverse) absolute temperature $T > 0$ is (equation (3))

$$\frac{1}{k_B T} = \frac{\omega(E)}{\Omega(E)} = p(E_T|E) \quad (16)$$

In practice, one would measure $p(E'_T|E)$ for $E'_T > E_T = \hbar\nu/2$ and extrapolate to $E'_T = E_T$. The thermometer equation (16) is applicable to systems with and without population inversion. The precision of this minimal thermometer is set by the oscillator frequency ν and the number of measurements.

Received 10 July 2013; accepted 18 October 2013; published online 8 December 2013

References

- Callen, H. B. *Thermodynamics and an Introduction to Thermostatistics* (Wiley, 1985).
- Ramsay, N. F. Thermodynamics and statistical mechanics at negative absolute temperatures. *Phys. Rev.* **103**, 20–28 (1956).
- Landsberg, P. T. Heat engines and heat pumps at positive and negative absolute temperature. *J. Phys. A* **10**, 1773–1780 (1977).
- Rapp, A., Mandt, S. & Rosch, A. Equilibration rates and negative absolute temperatures for ultracold atoms in optical lattices. *Phys. Rev. Lett.* **105**, 220405 (2010).
- Purcell, E. M. & Pound, R. V. A nuclear spin system at negative temperature. *Phys. Rev.* **81**, 279–280 (1951).
- Hakonen, P. & Lounasmaa, O. V. Negative absolute temperature—hot spins in spontaneous magnetic order. *Science* **265**, 1821–1825 (1994).
- Braun, S. *et al.* Negative absolute temperature for motional degrees of freedom. *Science* **339**, 52–55 (2013).
- Peebles, P. J. & Ratra, B. The cosmological constant and dark energy. *Rev. Mod. Phys.* **75**, 559–606 (2003).
- Loeb, A. Thinking outside the simulation box. *Nature Phys.* **9**, 384–386 (2013).
- Carr, L. D. Negative temperatures? *Science* **339**, 42–43 (2013).
- Sommerfeld, A. *Vorlesungen über Theoretische Physik (Band 5): Thermodynamik und Statistik* 181–183 (Verlag Harri Deutsch, 2011).
- Khinchin, A. I. *Mathematical Foundations of Statistical Mechanics* (Dover, 1949).
- Huang, K. *Statistical Mechanics* 2nd edn (Wiley, 1987).
- Gibbs, J. W. *Elementary Principles in Statistical Mechanics* (Dover, 1960) (Reprint of the 1902 edition).

15. Campisi, M., Talkner, P. & Hänggi, P. Fluctuation theorem for arbitrary open quantum systems. *Phys. Rev. Lett.* **102**, 210401 (2009).
16. Campisi, M. & Kobe, D. Derivation of the Boltzmann principle. *Am. J. Phys.* **78**, 608–615 (2010).
17. Dunkel, J. & Hilbert, S. Phase transitions in small systems: Microcanonical vs. canonical ensembles. *Physica A* **370**, 390–406 (2006).
18. Votyakov, E. V., Hidmi, H. I., De Martino, A. & Gross, D. H. E. Microcanonical mean-field thermodynamics of self-gravitating and rotating systems. *Phys. Rev. Lett.* **89**, 031101 (2002).
19. Becker, R. *Theory of Heat* (Springer, 1967).
20. Campisi, M. Thermodynamics with generalized ensembles: The class of dual orthodoxes. *Physica A* **385**, 501–517 (2007).
21. Hertz, P. Über die mechanischen Grundlagen der Thermodynamik. *Ann. Phys. (Leipz.)* **33** 225–274; 537–552 (1910).
22. Hoffmann, D. ‘... you can’t say anyone to their face: your paper is rubbish.’ Max Planck as Editor of *Annalen der Physik*. *Ann. Phys. (Berlin)* **17**, 273–301 (2008).
23. Einstein, A. Bemerkungen zu den P. Hertzschen Arbeiten: ‘Über die mechanischen Grundlagen der Thermodynamik’. *Ann. Phys. (Leipz.)* **34**, 175–176 (1911).
24. Campisi, M. On the mechanical foundations of thermodynamics: The generalized Helmholtz theorem. *Stud. Hist. Philos. Mod. Phys.* **36**, 275–290 (2005).
25. Stanley, R. P. *Enumerative Combinatorics* 2nd edn, Vol. 1 (Cambridge Studies in Advanced Mathematics, Cambridge Univ. Press, 2000).
26. Tremblay, A.-M. Comment on ‘Negative Kelvin temperatures: Some anomalies and a speculation’. *Am. J. Phys.* **44**, 994–995 (1975).
27. Dunkel, J., Hänggi, P. & Hilbert, S. Nonlocal observables and lightcone averaging in relativistic thermodynamics. *Nature Phys.* **5**, 741–747 (2009).

Acknowledgements

We thank I. Bloch, W. Hofstetter and U. Schneider for constructive discussions. We are grateful to M. Campisi for pointing out equation (14), and to P. Kopietz, P. Talkner, R. E. Goldstein and, in particular, P. Hänggi for helpful comments.

Author contributions

All authors contributed to all aspects of this work.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to J.D.

Competing financial interests

The authors declare no competing financial interests.

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 thermostistical 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 thermostistical 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 thermostistical 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.

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 thermostistical 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 thermostistical 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 thermostistical 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. Giauque 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.