

Consistent thermostatics forbids negative absolute temperatures

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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,

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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

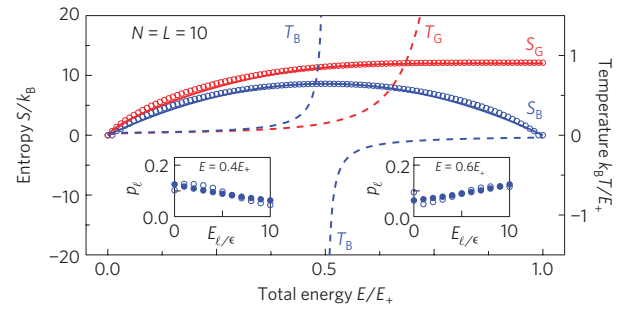


Figure 1 | Non-negativity of the absolute temperature in quantum systems with a bounded spectrum. Thermodynamic functions for N weakly coupled bosonic oscillators with $(L+1)$ single-particle levels $E_\ell = \ell\epsilon$, $\ell = 0, \dots, L$, are shown for $N = L = 10$, corresponding to 184,756 states 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

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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

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Competing financial interests

The authors declare no competing financial interests.