Consistent thermostatistics 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 thermodynamics$^1$, 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$^{8,9}$ but could also help$^7$ to resolve the cosmological dark-energy puzzle$^{8,9}$. Measurements of negative absolute temperature were first reported in 1951 by Purcell and Pound$^8$ in seminal work on the population inversion in nuclear spin systems. Five years later, Ramsey’s comprehensive theoretical study$^9$ clarified hypothetical ramifications of negative temperatures states, most notably the possibility to achieve Carnot efficiencies $\eta > 1$ (refs 3,4). Recently, the first experimental realization of an ultracold bosonic quantum gas$^7$ with a bounded spectrum has attracted considerable attention$^{10}$ 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 Boltzmann$^1$. By means of rigorous derivations$^{11}$ and exactly solvable examples, we will demonstrate that the Boltzmann entropy, despite being advocated in most modern textbooks$^{13}$, is incompatible with the differential structure of thermostatistics, 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 ago$^{14}$, but has been mostly forgotten ever since. Unlike the Boltzmann entropy, Gibbs’ entropy fulfills the fundamental thermostatistical 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 follows$^{10}$: assume a suitably designed many-particle quantum system with a bounded spectrum$^7$ 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 $E$. To fit$^{11,10}$ such a distribution with a Boltzmann factor $\exp(\beta E)$, $\beta$ 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 thermostatistics. We shall prove that the parameter $T_B = (k_B \beta)^{-1}$, as determined by Purcell and Pound$^8$ 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 states$^7$, one of the first questions to be addressed is the choice of the appropriate statistical 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 interactions$^{12}$—gravity being a prominent example$^{18}$. Population-inverted systems are generally thermodynamically unstable when coupled to a (non-population-inverted) heat bath and, hence, must be prepared in isolation$^{7,17}$. In ultracold quantum gases$^7$ 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 \textit{ab initio} thermostatistical treatment should start from the microcanonical ensemble. We will first prove that only the Gibbs entropy provides a consistent thermostatistical model for the microcanonical density operator. Instructive examples will be discussed subsequently.

We consider a (quantum or classical) system with microscopic variables \(\xi\) governed by the Hamiltonian \(H = H(\xi; V, A)\), where \(V\) denotes volume and \(A = (A_1, \ldots)\) summarizes other external parameters. If the dynamics conserves the energy \(E\), all thermostatistical information about the system is contained in the microcanonical density operator
\[
\rho(\xi; E, V, A) = \frac{\delta(E - H)}{\omega}
\]
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 \(\xi\). The average of some quantity \(F\) with respect to \(\rho\) 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 \(\omega\) by differentiation,
\[
\omega = \frac{\partial \Omega}{\partial E} = \Omega'
\]
Intuitively, for a quantum system with spectrum \(E_n\), the quantity \(\Omega(E, V, A)\) counts the number of eigenstates with energy less than or equal to \(E\).

Given the microcanonical density operator from equation (1), one can find two competing definitions for the microcanonical entropy in the literature\cite{12,13,14,15,16,17,18,19,20}:
\[
S_B(E, V, A) = k_B \ln(\omega/E),
\]
\[
S_G(E, V, A) = k_B \ln(\Omega)
\]
where \(\epsilon\) 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 textbooks\textsuperscript{13} and used by most authors nowadays\textsuperscript{14,15,16,17,18,19,20}. The second candidate \(S_G\) is often attributed to Hertz\textsuperscript{21} 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 invariant\textsuperscript{21}. His work was highly commended by Planck\textsuperscript{22} and Einstein, who closes his comment\textsuperscript{23} by stating that he would not have written some of his papers had he been aware of Gibbs’ comprehensive treatise\textsuperscript{24}.

### Thermostatistical 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
\[
T_B(E, V, A) = \left(\frac{\partial S_B}{\partial E}\right)^{-1} = \frac{1}{k_B} \frac{\omega'}{\omega} = \frac{1}{k_B} \frac{\Omega'}{\Omega}
\]
\[
T_G(E, V, A) = \left(\frac{\partial S_G}{\partial E}\right)^{-1} = \frac{1}{k_B} \frac{\Omega'}{\Omega} = \frac{1}{k_B} \frac{\omega'}{\omega}
\]

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 \(\Omega\) 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
\[
dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \sum_i \frac{\partial S}{\partial A_i} dA_i
\]
\[
= \frac{1}{T} dE + \frac{p}{T} dV + \sum_i \frac{\partial f_i}{\partial A_i} dA_i
\]
All consistent thermostatistical models, corresponding to pairs \((\rho, S)\) where \(\rho\) 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 \(\delta S = 0\) and other parameters fixed \((dA_i = 0)\), one finds the consistency condition
\[
p = T \left(\frac{\partial S}{\partial V}\right) = - \left(\frac{\partial E}{\partial V}\right) = - \left(\frac{\partial H}{\partial V}\right)
\]
More generally, for any adiabatic variation of some parameter \(A_\mu \in [V, A_i]\) of the Hamiltonian \(H\), one must have (Supplementary Information)
\[
T \left(\frac{\partial S}{\partial A_\mu}\right) = - \left(\frac{\partial E}{\partial A_\mu}\right)_S = - \left(\frac{\partial H}{\partial A_\mu}\right)_S
\]
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 \(\rho\), 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 finds\textsuperscript{24}
\[
T_G \left(\frac{\partial S_G}{\partial A_\mu}\right) = \frac{1}{k_B} \frac{\partial}{\partial A_\mu} \text{Tr} \left[\Theta(E - H)\right] = - \frac{1}{k_B} \text{Tr} \left[- \frac{\partial}{\partial A_\mu} \Theta(E - H)\right]
\]
\[
= - \text{Tr} \left[\delta H \left(\frac{\partial E}{\partial A_\mu}\right)_\omega\right] = \delta H \left(\frac{\partial S_G}{\partial A_\mu}\right)_\omega
\]
This proves that the pair \((\rho, S_G)\) fulfils equation (6) and, hence, constitutes a consistent thermostatistical model for the microcanonical density operator \(\rho\). 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 theorem\textsuperscript{12}
\[
\left\langle \xi_i \frac{\partial H}{\partial \xi_i} \right\rangle = \text{Tr} \left[\xi_i \frac{\partial H}{\partial \xi_i}\right] \rho = k_B T_G \delta_{ij}
\]
for all canonical coordinates $\xi = (\xi_1, \ldots)$. The key steps of the proof are identical to those in equation (7); that is, one merely exploits the chain rule relation $\delta \Theta(E-H)/\delta \lambda = -(\partial H/\partial \lambda) \delta (E-H)$, which holds for any variable $\lambda$ in the Hamiltonian $H$. Equation (8) is essentially a phase-space version of Stokes’ theorem, 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 $\omega_n$, but can be significant for small systems. This can already be seen for a classical ideal gas in $d$-space dimensions, where

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

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

$$
E = \frac{dN}{2} k_B T_G, \quad (9)
$$

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 Pound and Braun et al, can be readily illustrated by two other basic examples: for a simple harmonic oscillator with spectrum

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

we find by inversion and analytic interpolation

$$
\Omega = 1 + n = 1/2 + E/(\hbar \nu) \quad \text{and, hence, from the Gibbs entropy}
$$

$$
S_G = k_B \ln \Omega \quad \text{the caloric equation of state}
$$

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

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 $\nu$, 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 $S_B = k_B \ln(\omega)$ 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 systems.

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

$$
E_n = an^2/L^2, \quad a = \hbar^2 \pi^2/(2m), \quad n = 1, 2, \ldots, \infty
$$

(11)

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

$$
k_B T_G = 2E, \quad p_G = \frac{\partial S_G}{\partial L} = \frac{2E}{L}
$$

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 $L$,

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

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

In contrast, we find from $S_B = k_B \ln(\omega)$ 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

$$
p_B = \frac{\partial S_B}{\partial L} = -\frac{2E}{L} \neq p
$$

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 $T_B$ 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 statististical description of isolated systems but also a sound practical basis for classical and quantum thermometers.

It remains to clarify why previous experiments 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 distributions.10. Their system contains \( N \gg 1 \) particles with Hamiltonian \( H_N \) and DOS \( \omega_N \). The formally exact microcanonical one-particle density operator reads

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

(12)

To obtain an exponential (canonical) fitting formula, as used in the experiments, one first has to rewrite \( \rho_t \) in the equivalent form \( \rho_t = \exp[\ln(\rho_t)] \). Applying a standard steepest descent approximation1,19 to the logarithm and assuming discrete one-particle levels \( E_i \), one finds for the relative occupancy \( \rho_t \) of one-particle level \( E_i \) the canonical form

\[
\rho_t \simeq \frac{e^{-E_i/(k_BT)}}{Z}, \quad Z = \sum_i e^{-E_i/(k_BT)}
\]

(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 \( E_i \) as

\[
\rho_t = \omega_{N-1}(E - E_i)/\omega_N(E) = \exp[\ln(\omega_{N-1}(E - E_i))/\omega_N(E)]
\]

and expanding \( \ln(\omega_{N-1}(E - E_i)) \) for small \( E_i \), which gives \( \rho_t \propto \exp[-E_i/(k_BT_{B,N-1})] \), where \( k_BT_{B,N-1} = \omega_{N-1}(E)\omega_N(E) \), 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)

\[
T_B = \frac{T_G}{1 - k_B/C}
\]

(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 systems1,19 may explain why they are rarely distinguished in most modern textbooks apart from a few exceptions12,19. 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 energy spectrum relevant for the correct interpretation of the experiments by Purcell and Pound3 and Braun et al.7 (see Supplementary Information for additional examples). The model consists of \( N \) weakly interacting bosonic oscillators or spins with Hamiltonian

\[
H_N \simeq \sum_{n=1}^{N} \hbar \omega_n
\]

Each oscillator can occupy non-degenerate single-particle energy levels \( E_n = \epsilon_n \) with spacing \( \epsilon \) and \( \epsilon_0 = 0, 1, \ldots \). Assuming indistinguishable bosons, permissible \( N \)-particle states can be labelled by \( \Lambda = (\ell_1, \ldots, \ell_N) \), where \( 0 \leq \ell_1 \leq \ell_2 \leq \cdots \leq \ell_N \leq L \). The associated energy eigenvalues \( E_N = \epsilon(\ell_1 + \cdots + \ell_N) \) are bounded by \( 0 \leq E_N \leq E_{\epsilon} = \epsilon LN \). The DOS \( \omega_N(E) = \text{Tr}_N[\delta(E - H_N)] \) counts the degeneracy of the eigenvalues \( E \) and equals

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,

\[
\omega(E) = \omega_\epsilon \exp[-(E - E_{\epsilon})^2/\sigma^2]
\]

The degeneracy attains its maximum \( \omega_\epsilon \) at the centre \( E_\epsilon = E_{\epsilon}/2 \) of the energy band (Fig. 1). The integrated DOS reads

\[
\Omega(E) = \frac{1}{2\pi\sigma} \left[ \text{erf} \left( \frac{E - E_{\epsilon}}{\sigma} \right) + \text{erf} \left( \frac{E_{\epsilon}}{\sigma} \right) \right]
\]

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

\[
k_B T_B = \frac{\sigma^2}{E_{\epsilon} - 2E_{\epsilon}}
\]

diverges and changes sign as \( E \) crosses \( E_\epsilon = E_{\epsilon}/2 \), whereas the absolute temperature \( T = T_N(E) = k_B^{-1} \Omega/\omega_\epsilon \) 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 \( E_{\epsilon} = E_{\epsilon}/2 \), and \( C \) does not scale homogeneously with system size anymore as \( E \to E_{\epsilon} \) owing to combinatorial constraints on the number of available states (Supplemen-
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 matter\(^{11}\) 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 engines.\(^{19}\) To realize values \( \eta > 1 \), one requires either \( T_C < T_H \) or \( T_C > T_H \) 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-adiabatically\(^ {26}\), 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 calculations.\(^3\) 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 \( T_C \) 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 Pound\(^5\) and Braun et al.\(^7\) are essential for verifying the conceptual foundations of thermodynamics and thermostatics. 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 exchange\(^{15}\) under extreme physical conditions (for example, at ultracold or ultrahot\(^ {27}\) 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 Gibbs\(^ {14}\) more than a century ago, neither the work of Purcell and Pound\(^7\) nor recent experiments\(^8\) 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 \( E = E_i \) and the thermometer oscillator with small angular frequency \( \nu \) in the ground state \( E_i = h\nu/2 \). 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 \( E_j = h\nu(n + 1/2) \), where \( n = 0, 1, \ldots, [(E_j - E_i)/(h\nu)] \), with \( E_i \) denoting the system’s ground state and \( \nu \) the integer part. If the total energy remains conserved and the thermometer oscillator is non-degenerate, the probability \( p(E_j) \) of measuring a specific oscillator energy \( E_j \) is equal to the microcanonical probability of finding the system in a state

\[
P(E_j) = \frac{g(E_j - E_i)}{\Omega(E)}
\]

where \( g(E_j) \) is the degeneracy of the level \( E_j \) of the system, and

\[
\Omega(E) = \sum_{E_i} g(E_i)
\]

Assuming that the energy levels lie sufficiently dense (\( \nu \to 0 \)) we can approximate the discrete probabilities \( p(E_j) \approx p(E_i)\Omega(E_i)/\Omega(E) \) by the probability density

\[
p(E_j) = \frac{\alpha(E_i + E_j - E_i)}{\Omega(E)}
\]

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))

\[
\eta = \frac{1}{T} \frac{\alpha(E_i)\Omega(E)}{\Omega(E_i)}
\]

In practice, one would measure \( p(E_i) \) for \( E_i > E_i = h\nu/2 \) and extrapolate to \( E_i = E_i \). The thermometer equation (16) is applicable to systems with and without population inversion. The precision of this minimal thermometer is set by the oscillator angular frequency \( \nu \) 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.

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