Relative energy constraint in Boltzmann's surface entropy eliminates thermodynamic inconsistencies and allows negative absolute temperatures

Ananth Govind Rajan[a)]
Department of Chemical Engineering, Indian Institute of Science, Bengaluru, Karnataka 560012, India

(Dated: 4 January 2024)

Over the past century, an intense debate in statistical mechanics has been about the correctness of Boltzmann's surface entropy versus Gibbs' volume entropy, for isolated systems. Both entropies make significantly different predictions for systems with few degrees of freedom. Even in the thermodynamic limit, they can disagree—while Boltzmann entropy allows negative absolute temperatures to exist, Gibbs entropy precludes such a possibility. Here, we show that modifying Boltzmann's entropy via a relative energy tolerance eliminates thermodynamic inconsistencies in several model systems with unbounded energy spectra by ensuring positive, finite temperatures. Concomitantly, the proposed entropy allows for negative temperatures in systems with bounded spectra and closely matches canonical ensemble predictions. This work conclusively remedies the prevalent deficiencies of the Gibbs and Boltzmann entropy formulations and paves the way for the use of the modified Boltzmann entropy in the microcanonical ensemble, allowing negative temperatures to exist.

The microcanonical ensemble in statistical mechanics, originally proposed by Gibbs over a century ago[1], continues to receive a significant extent of attention[2–6]. In the physics literature, there exist two competing entropy definitions in the microcanonical ensemble: Gibbs' volume entropy (also referred to as the Hertz entropy)[1,7–10], based on the phase space volume and Boltzmann's surface entropy[11,12] (also referred to as the Boltzmann-Planck entropy), based on the phase space density. Even though Boltzmann's surface entropy dominated textbook discourses[13–17], many studies favored the use of the Gibbs entropy[5,8–10,18,19]. About a decade ago, Dunkel and Hilbert indicated that Boltzmann's surface entropy leads to violations of equipartition and unphysical results, i.e., negative/infinite temperatures, for some model systems with unbounded spectra[5]. Subsequently, several articles appeared that pointed out that Gibbs entropy suffers from serious objections such as the consideration of all states with energy lower than energy E, rather than only the states at the desired energy, and the inability to allow for negative temperatures in systems with non-monotonically increasing density of states[6,12,20–24].

Although the Boltzmann and Gibbs entropies *usually* agree for very large systems, they differ significantly and lead to widely varying temperatures for isolated systems with few degrees of freedom[25]. (In some cases, even in the thermodynamic limit, e.g., the case of a two-state system (see below), they can disagree.) Note that the principles of statistical mechanics can be applied to systems with few degrees of freedom, as the statistical averaging is carried out over the classical phase space or the available quantum states, rather than over the degrees of freedom[6,26–28]. Thus, even quantities like the temperature of an isolated quantum state[29–31] or the entropy of a few-body system are well defined[32,33].

a)Electronic mail: ananthgr@iisc.ac.in

In light of this fact, that both entropy definitions have shortcomings for small systems[22] is particularly unnerving. Indeed, the lack of a universal microcanonical entropy formulation not only adversely impacts the fundamental physical understanding of the thermodynamics of small systems[34], but also could impede technological progress in the future, wherein systems of few atoms, molecules, or electrons are increasingly becoming physically realizable[35]. In this work, we show that the consideration of a relative energy tolerance in the microcanonical ensemble eliminates all thermodynamic inconsistencies put forth in previous work pertaining to systems with unbounded spectra, while at the same time allowing negative temperatures in systems with bounded spectra.

Formulation of the relative-energy constrained Boltzmann entropy. Considering the microcanonical (NVE) ensemble with fixed number of particles N, volume V, and energy E, the Gibbs entropy (S_G) is defined as $S_G = k_B \ln \Omega$, where Ω denotes the volume of the classical phase space or the number of quantum states in the region $E' < E$ (Figure 1a). For a classical system, this can be written as

$$\Omega = \frac{1}{h^{dN} N!} \int d\mathrm{r}^N d\mathrm{p}^N \Theta(E - H)$$

where Θ is the Heaviside step function, $\Theta(x) = \begin{cases} 1; & x > 0 \\ 0; & x \leq 0 \end{cases}$, h is Planck's constant, d is the dimensionality of the system, $\mathbf{r}^N$ denotes the positions of the particles, and $\mathbf{p}^N$ denotes their momenta. Alternatively, for a quantum-mechanical system, we can write

$$\Omega = \mathrm{Tr}[\Theta(E - H)] \tag{1}$$

where Tr denotes the trace, i.e., the sum over quantum states in a Hilbert space. In contrast, the Boltzmann entropy (S_B) is conventionally defined as $S_B = k_B \ln \omega$,

where

$$\omega = \frac{1}{h^{dN} N!} \int d\mathrm{r}^N d\mathrm{p}^N \delta\left(\frac{H-E}{\epsilon}\right)$$

or

$$\omega = \mathrm{Tr}\left[\delta\left(\frac{H-E}{\epsilon}\right)\right] \tag{2}$$

and ϵ is an absolute energy tolerance, as visualized in Figure 1a. Physically, the tolerance appears because no system is perfectly isolated, and some amount of perturbation or broadening in the energy occurs due to the system's interactions with its surroundings (Figure 1b).

From Eq. (1) and (2), one can infer that

$$\omega = \epsilon \frac{\partial \Omega}{\partial E} \tag{3}$$

Even for a discrete spectrum, although direct enumeration is often used as a simplification[36], Eq. (3) is preferred[14,37], as it allows the correct definition of entropy for nondegenerate quantum systems[38,39]. Typically, ϵ has been interpreted to be a fixed constant in Eq. (3), and this has led to inconsistent results for simple systems with unbounded energy levels, e.g., negative temperatures for an ideal gas with one degree of freedom or infinite temperature for a quantum harmonic oscillator and an ideal gas with two degrees of freedom. We suggest here that instead of using an absolute energy tolerance, the energy tolerance in the microcanonical ensemble should be defined relative to the system's energy (Figure 1c). Indeed, a system with 1 J of energy and with 1 eV $= 1.602 \times 10^{-19}$ J of energy should not use the same tolerance in the microcanonical ensemble. This is because the higher the energy of a system, the greater its interaction with its surroundings, causing more broadening or perturbation in its energy. Thus, we propose that the constraint inside the delta function should be expressed in terms of the relative error of $H_r = \frac{H}{E}$ from 1. In terms of the phase space integrals or Hilbert space summations, doing so amounts to applying a constraint on H without using up a degree of freedom. Thus, classically, one should write

$$\omega_r = \frac{1}{h^{dN} N!} \int d\mathbf{r}^N d\mathbf{p}^N \delta\left(\frac{H_r - 1}{\epsilon_r}\right) \tag{4}$$

whereas for a quantum-mechanical system, we should write

$$\omega_r = \mathrm{Tr}\left[\delta\left(\frac{H_r - 1}{\epsilon_r}\right)\right] \tag{5}$$

where ϵ_r is a relative error tolerance. In Eqs. (4) and (5), we have used the subscript r to denote the use of the relative deviation from the desired energy. It can be shown that $\omega_r = \epsilon_r E \frac{\partial \Omega}{\partial E}$, as indicated in Figure 1c. Note that there is some precedent in the literature for adopting an energy-dependent tolerance[38,39].

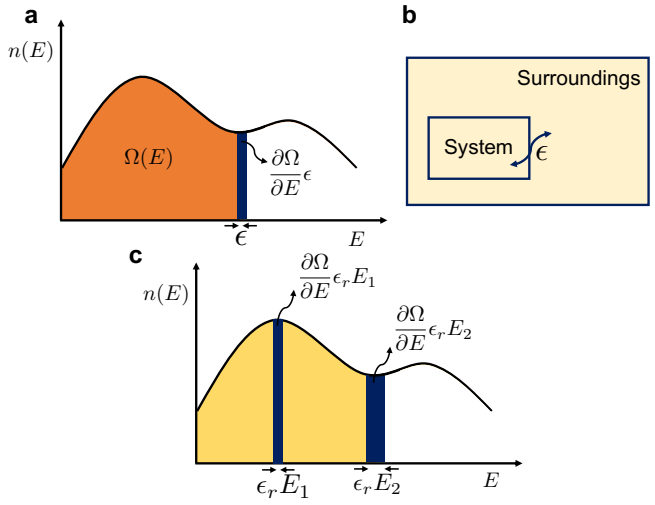

FIG. 1. Motivation and explanation of the relative-energy-constrained Boltzmann entropy. (a) For a density of states $n(E)$, the Gibbs entropy is defined by the logarithm of the area under the curve, i.e., Ω, while the Boltzmann entropy is defined by the logarithm of the change in area due to a fixed energy perturbation ϵ, i.e., $\frac{\partial \Omega}{\partial E}\epsilon$. (b) Interaction of a system with its surroundings leads to smearing of the system's energy E by a perturbation ϵ. (c) The proposed entropy considers an energy-dependent energy perturbation, given as $\epsilon_r E$.

We now apply the new approach for calculating the microcanonical relative-energy-constrained Boltzmann entropy, $S_{B_r} = k_B \ln \omega_r$, and the corresponding temperature

$$\frac{1}{T_{B_r}} = \frac{\partial S_{B_r}}{\partial E} \tag{6}$$

to several example systems. One may think that converting an absolute energy constraint to a relative energy constraint would not affect the calculation of entropy significantly. However, as seen in Table I, we conclusively show that using a relative constraint preserves the degrees of freedom of a system and thus leads to thermodynamically consistent behavior for various isolated systems with few degrees of freedom.

Application of the modified entropy to example systems: d-dimensional monoatomic ideal gas. Consider a d-dimensional monoatomic ideal gas consisting of N atoms of mass m each, occupying a total volume V. This system has unbounded energy levels and thus should not have negative temperature, as correctly argued by Dunkel and Hilbert[5]. The volume of the phase space for this system is[19]

$$\Omega = \frac{V^N}{h^{dN} N!} \frac{(2\pi m)^{\frac{dN}{2}}}{\Gamma\left(\frac{dN}{2}+1\right)} E^{\frac{dN}{2}}.$$

TABLE I. Comparison of the predictions of the Gibbs, conventional Boltzmann, and proposed modified Boltzmann entropies in the microcanonical ensemble with the corresponding predictions in the canonical ensemble. Only the relative-energy-constrained Boltzmann entropy leads to predictions consistent with the canonical ensemble in every case considered.

System	**Gibbs**	**Conventional Boltzmann**	**Modified Boltzmann**	**Canonical**
3D ideal gas	$E=\frac{3N}{2}k_BT$	$E=\left(\frac{3N}{2}-1\right)k_BT$	$E=\frac{3N}{2}k_BT$	$E=\frac{3N}{2}k_BT$
Harmonic oscillator (high T)	$E=k_BT-\frac{h\nu}{2}$	$T=\infty$	$E=k_BT$	$E=k_BT$
Harmonic oscillator (any T)[a]	$\frac{E-E_0}{h\nu}=\frac{3-\exp\left(\frac{\theta}{T}\right)}{2\exp\left(\frac{\theta}{T}\right)-2}$	$T=\infty$	$\frac{E-E_0}{h\nu}=\frac{1}{\exp\left(\frac{\theta}{T}\right)-1}$	$\frac{E-E_0}{h\nu}=\frac{1}{\exp\left(\frac{\theta}{T}\right)-1}$
Particle in 1D box	$E=\frac{k_BT}{2}$	$E=-\frac{k_BT}{2}$	$E=\frac{k_BT}{2}$	$E=\frac{k_BT}{2}$
Negative temperatures?	No	Yes	Yes	Yes

[a] Note that $E_0=\frac{1}{2}h\nu$ and $\theta=\frac{h\nu}{k_B}$ for the harmonic oscillator.

Further, the number of states can be written as

$$\omega=\frac{V^N}{h^{dN}N!}\frac{(2\pi m)^{\frac{dN}{2}}}{\Gamma\left(\frac{dN}{2}\right)}E^{\frac{dN}{2}-1}\epsilon.$$

The Gibbs temperature (T_G) can be calculated using the equation $\frac{1}{T_G}=\frac{\partial S_G}{\partial E}$ to obtain $E=\frac{dN}{2}k_BT_G$. However, using the analogous equation for Boltzmann temperature, assuming a *fixed energy tolerance* ϵ, leads to $E=\left(\frac{dN}{2}-1\right)k_BT_B$. Note that if $dN=1$, i.e., the system has one degree of freedom, one obtains negative temperatures whereas if $dN=2$, i.e., the system has two degrees of freedom, one gets infinite temperature[5]. This is a serious shortcoming of the Boltzmann entropy, as pointed out by Dunkel and Hilbert[5], as one is led to predict negative/infinite temperature for a system whose energy is unbounded. Considering a *fractional energy tolerance*, one however obtains $\omega_r=\frac{V^N}{h^{dN}N!}\frac{(2\pi m)^{\frac{dN}{2}}}{\Gamma\left(\frac{dN}{2}\right)}E^{\frac{dN}{2}}\epsilon_r$, which combined with Eq. (6) leads to

$$E=\frac{dN}{2}k_BT_{B_r}.$$

The above equation not only disallows negative/infinite temperatures for an ideal gas but fixes the disagreement between the energy of a three-dimensional ideal gas as traditionally calculated in the canonical $\left(E=\frac{3N}{2}k_BT\right)$ and microcanonical $\left(E=\left(\frac{3N}{2}-1\right)k_BT\right)$ ensembles (see Table I)!

Quantum harmonic oscillator. For a quantum harmonic oscillator, the energy of the system is given as[40] $E_n=h\nu\left(n+\frac{1}{2}\right)$, where $n=0,1,2,...$ and ν represents the frequency of vibration of the oscillator. It follows that $\Omega=1+n=\frac{E}{h\nu}+\frac{1}{2}$. At the high-temperature limit, the states can be treated as a continuum, so that $k_BT_G=\frac{h\nu}{2}+E$. Although applying the original definition of Boltzmann entropy leads to infinite temperature, the newly proposed definition (Eq. (5)) results in $\omega_r=\frac{\epsilon_rE}{h\nu}$, leading to $E=k_BT_{B_r}$, which predicts finite, positive temperatures. Again, only the relative-energy-constrained Boltzmann entropy leads to predictions consistent with the canonical ensemble (Table I)! One can also derive expressions valid for the temperature under all cases, using discretized definitions of the partition function and temperature (see, e.g., ref.[41]), as shown in the Supplementary Information[42] and in Table I. The ensuing E vs. T relationships for various entropy choices are plotted in Figure 2. Therein, one sees that only the *modified* Boltzmann entropy predicts thermodynamically consistent results at *all* temperatures, including the existence of the zero-point energy $\left(\frac{1}{2}h\nu\right)$ and agreeing with the high-temperature prediction of $E=k_BT$. On the contrary, while the Gibbs entropy fails to predict the existence of a zero-point energy (i.e., leads to a Planck oscillator rather than a Schrodinger oscillator[14]!), the Boltzmann entropy predicts infinite temperatures for all energies. Note that, to the best of the author's knowledge, this is the first derivation of the temperature of a *single, isolated* quantum harmonic oscillator, i.e., in the microcanonical ensemble; previous expressions relied on the consideration of multiple oscillators, in the limit of a large number of oscillators (see, e.g.,[43] and[44]).

Quantum particle in a 1D box. The energy of a quantum particle in a one-dimensional (1D) box is given as[40] $E_n=\frac{an^2}{L^2}$, where $a=\frac{\hbar^2\pi^2}{2m}$ and $n=1,2,3,...$, so that $\Omega=L\sqrt{\frac{E}{a}}$. At high temperatures, the states form a continuum, and we find that $E=\frac{k_BT_G}{2}$ and $P_G=T_G\frac{\partial S_G}{\partial L}=\frac{2E}{L}$. This statistical-mechanical pressure equals the thermodynamic pressure calculated as $P_T=-\frac{\partial E}{\partial L}$. Now, although the conventional Boltzmann entropy leads to a negative temperature $\left(E=-\frac{k_BT_B}{2}\right)$ and negative pressure $\left(P_B=-\frac{2E}{L}\right)$, the newly proposed definition of Boltzmann entropy fixes these predictions, as seen in Table I, to yield $E=\frac{k_BT_{B_r}}{2}$ and $P_{B_r}=\frac{2E}{L}$.

Two-level system and the possibility of negative temperatures. We now demonstrate that the newly proposed definition of Boltzmann entropy still allows for negative temperatures for systems having non-monotonic density of states[12,21,22], i.e., a bounded phase space. Considering the well-known case of a two-state system, with energy levels 0 and E_1 and N_0 particles occupying the ground state and N_1 particles occupying the excited state, the energy of the system is $E=N_1E_1$ and the number of particles is $N=N_0+N_1$. It follows that the number of

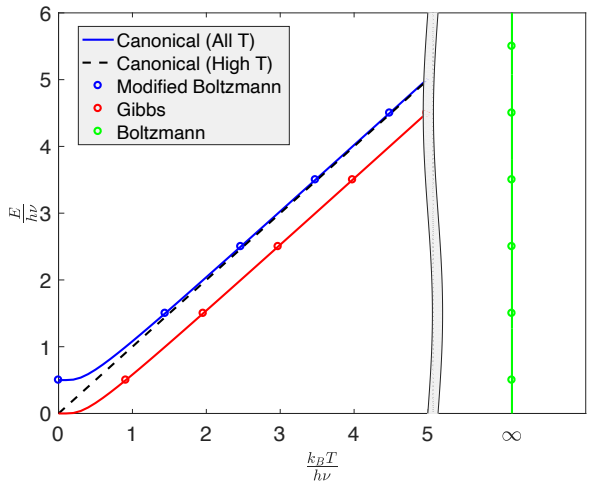

FIG. 2. Comparison of various microcanonical entropies in terms of their ability to predict the thermodynamic behavior of a quantum harmonic oscillator. The canonical prediction is shown using a blue line and the high-temperature canonical/modified Boltzmann predictions are shown using a dashed black line. Blue, red, and green circles represent predictions of the modified Boltzmann, Gibbs, and conventional Boltzmann entropies in the microcanonical ensemble. In these cases, lines are simply a guide. Only the modified Boltzmann entropy predicts the existence of the correct zero-point energy at 0 K and degenerates to the limit of $k_B T$ at high temperatures.

states with energy less than or equal to E is

$$\Omega = \sum_{N_0'=1}^{N_1} \frac{N!}{N_0'! N_1'!}$$

where $N_1 = E/E_1$ and $N_1' = N - N_0'$. The original Boltzmann partition function is given as

$$\omega = \frac{\Delta\Omega}{\Delta E}\epsilon = \frac{N!}{(N_0-1)!(N_1+1)!}\frac{\epsilon}{E_1}.$$

where $\Delta\Omega$ is obtained as the difference in the summation expressions of Ω with N_0' going up to (N_1+1) and N_1. Considering a large number of particles and applying Stirling's approximation results in

$$S_B = k_B N \ln N - k_B(N_0-1)\ln(N_0-1) - k_B(N_1+1)\ln(N_1+1) + k_B \ln\frac{\epsilon}{E_1}.$$

For fixed N, the absolute-energy-constrained Boltzmann temperature can be determined to be

$$T_B = \frac{\Delta E}{\Delta S_B} = \frac{E_1}{k_B \ln\left(\frac{(N_0-1)^{N_0-1}(N_1+1)^{N_1+1}}{(N_0-2)^{N_0-2}(N_1+2)^{N_1+2}}\right)}.$$

Since we are considering a large number of particles, the temperature reduces to $T_B = \frac{E_1}{k_B \ln\left(\frac{N_0}{N_1}\right)}$. Now, if $E_1 > 0$ and $N_0 < N_1$, i.e., we consider a system exhibiting "population inversion", we find that $T_B < 0$. Analogously, the modified Boltzmann partition function is given as

$$\omega_r = \frac{\Delta\Omega}{\Delta E}\epsilon_r E = \frac{N!}{(N_0-1)!(N_1+1)!}\frac{\epsilon_r E}{E_1}.$$

This leads to, via the Stirling's approximation, the following expression for the temperature:

$$T_{B_r} = \frac{\Delta E}{\Delta S_{B_r}} = \frac{E_1}{k_B \ln\left(\frac{(N_0-1)^{N_0-1}(N_1+1)^{N_1+2}}{(N_0-2)^{N_0-2}(N_1+2)^{N_1+2}N_1}\right)},$$

which also simplifies, for a large number of particles, to $T_{B_r} = \frac{E_1}{k_B \ln\left(\frac{N_0}{N_1}\right)}$, also allowing negative temperatures. (This is the same expression that one obtains by direct enumeration as well[12].) On the other hand, Gibbs entropy would not admit negative temperatures at all due to a monotonically increasing total number of states. Thus, Gibbs entropy cannot account for systems with bounded spectra in a thermodynamically consistent manner[12,45,46]. Note that this also indicates that Gibbs and Boltzmann entropies can disagree, even in the thermodynamic limit. Now, according to the above discussion, the newly proposed relative-energy-constrained Boltzmann entropy (S_{B_r}) allows for both negative and positive temperatures, and in the appropriate contexts in which they should be seen, i.e., systems with bounded and unbounded phase space, respectively (see Table I). Therefore, this work indicates that previous negative temperature measurements for various systems are indeed correct[47–53], unlike what is stated in ref.[5]. In fact, another argument against negative temperature, viz., the incorrect interpretation of Carnot efficiencies being more than one has also been addressed by Abraham and Penrose[54].

Conclusions. In this work, we introduced a relative energy constraint in the calculation of the microcanonical partition function, which eliminates negative/infinite temperatures for systems with unbounded spectra, such as ideal gases with a few degrees of freedom, a quantum harmonic oscillator, and a quantum particle confined in an infinite well. At the same time, the proposed entropy definition allows for negative temperatures for systems with non-monotonic density of states, i.e., a bounded spectrum, such as a two-state system with population inversion. This makes the proposed entropy definition the one that is the closest to predictions from the canonical ensemble in each case considered (see Table I). The physical insight underlying the proposed approach is that systems with higher energy will interact more with their surroundings, thus causing a larger perturbation in their energy. Mathematically, while an absolute energy constraint uses up one degree of freedom from the system (by fixing the value of E), the use of a relative energy constraint fixes only the ratio H/E, thus retaining the original number of degrees of freedom of the system and resulting in the correct scaling of energy with tempera-

ture for various systems. Thereby, we proposed a resolution to the ongoing debate in microcanonical statistical mechanics on the use of the Gibbs volume entropy and Boltzmann surface entropy. Overall, this work sets the foundation for using the relative-energy-constrained Boltzmann surface entropy in the microcanonical ensemble of statistical mechanics. Thereby, the work puts on firm theoretical footing the existence of negative temperatures for systems with bounded energy spectra. Finally, this work lays a solid foundation for accurate theoretical descriptions of isolated systems with few degrees of freedom using statistical mechanics.

ACKNOWLEDGMENTS

A.G.R. acknowledges the Infosys Foundation, Bengaluru for an Infosys Young Investigator grant. A.G.R. thanks Profs. B. J. Cherayil, K. G. Ayappa, N. M. Dixit, P. K. Maiti, P. R. Nott, and S. N. Punnathanam for insightful discussions, and Profs. A. Gupta and S. K. Gupta for valuable suggestions regarding the manuscript.

[1] J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Charles Scribner's Sons, 1902).
[2] E. M. Pearson, T. Halicioglu, and W. A. Tiller, "Laplace-Transform Technique for Deriving Thermodynamic Equations from the Classical Microcanonical Ensemble," Phys. Rev. A **32**, 3030 (1985).
[3] M. J. Uline, D. W. Siderius, and D. S. Corti, "On the generalized equipartition theorem in molecular dynamics ensembles and the microcanonical thermodynamics of small systems," J. Chem. Phys. **128**, 124301 (2008).
[4] S. Davis, "Calculation of microcanonical entropy differences from configurational averages," Phys. Rev. E **84**, 050101 (2011).
[5] J. Dunkel and S. Hilbert, "Consistent thermostatistics forbids negative absolute temperatures," Nat. Phys. **10**, 67–72 (2014).
[6] D. S. Corti, D. Ohadi, R. Fariello, and M. J. Uline, "Microcanonical thermodynamics of small ideal gas systems," J. Phys. Chem. B **127**, 3431–3442 (2023).
[7] P. Hertz, "Über die mechanischen Grundlagen der Thermodynamik," Ann. Phys. (Leipzig) **338**, 225–274 (1910).
[8] H. H. Rugh, "Microthermodynamic formalism," Phys. Rev. E **64**, 055101 (2001), arXiv:0201062 [nlin].
[9] M. Campisi and D. H. Kobe, "Derivation of the Boltzmann principle," Am. J. Phys. **78**, 608–615 (2010).
[10] M. Campisi, "Construction of microcanonical entropy on thermodynamic pillars," Phys. Rev. E **91**, 052147 (2015), arXiv:1411.2425.
[11] D. H. Gross and J. F. Kenney, "The microcanonical thermodynamics of finite systems: The microscopic origin of condensation and phase separations, and the conditions for heat flow from lower to higher temperatures," J. Chem. Phys. **122** (2005), 10.1063/1.1901658.
[12] D. Frenkel and P. B. Warren, "Gibbs, Boltzmann, and Negative Temperatures," Am. J. Phys. **83**, 163–170 (2015), arXiv:1403.4299.
[13] K. Huang, *Statistical Mechanics*, 2nd ed. (John Wiley & Sons, Inc., 1987).
[14] R. K. Pathria and P. D. Beale, *Statistical Mechanics*, 3rd ed. (Elsevier, 2011).
[15] M. Tuckerman, *Statistical Mechanics: Theory and Molecular Simulation* (Oxford university press, 2010).
[16] R. H. Swendsen, *An Introduction to Statistical Mechanics and Thermodynamics* (Oxford University Press, 2012).
[17] M. S. Shell, *Thermodynamics and Statistical Mechanics: An Integrated Approach* (Cambridge University Press, 2015).
[18] V. Berdichevsky, I. Kunin, and F. Hussain, "Negative temperature of vortex motion," Physical Review A **43**, 2050–2051 (1991).
[19] J. Dunkel and S. Hilbert, "Phase transitions in small systems: Microcanonical vs. canonical ensembles," Phys. A: Stat. Mech. **370**, 390–406 (2006).
[20] U. Schneider, S. Mandt, A. Rapp, S. Braun, H. Weimer, I. Bloch, and A. Rosch, "Comment on "Consistent thermostatistics forbids negative absolute temperatures"," (2014), arXiv:1407.4127.
[21] R. H. Swendsen and J.-S. Wang, "Gibbs Volume Entropy is Incorrect," Phys. Rev. E **92**, 020103 (2015).
[22] R. Swendsen, "Thermodynamics, Statistical Mechanics and Entropy," Entropy **19**, 603 (2017).
[23] D. A. Lavis, "The question of negative temperatures in thermodynamics and statistical mechanics," Stud. Hist. Philos. Sci. **67**, 26–63 (2019).
[24] R. Lustig, "Microcanonical thermodynamics of three and four atoms," Journal of Chemical Physics **150**, 074303 (2019).
[25] M. Barbatti, "Defining the temperature of an isolated molecule," The Journal of Chemical Physics **156** (2022), 10.1063/5.0090205.
[26] R. V. Jensen and R. Shankar, "Statistical behavior in deterministic quantum systems with few degrees of freedom," Physical Review Letters **54**, 1879–1882 (1985).
[27] B. Chirikov, F. Izrailev, and V. Tayursky, "Numerical experiments on the statistical behaviour of dynamical systems with a few degrees of freedom," Computer Physics Communications **5**, 11–16 (1973).
[28] L. Cerino, G. Gradenigo, A. Sarracino, D. Villamaina, and A. Vulpiani, "Fluctuations in partitioning systems with few degrees of freedom," Physical Review E **89**, 042105 (2014), arXiv:1403.2896.
[29] P. Lipka-Bartosik, M. Perarnau-Llobet, and N. Brunner, "Operational definition of the temperature of a quantum state," Physical Review Letters **130**, 040401 (2023).
[30] M. T. Mitchison, A. Purkayastha, M. Brenes, A. Silva, and J. Goold, "Taking the temperature of a pure quantum state," Physical Review A **105**, L030201 (2022), arXiv:2103.16601.
[31] P. C. Burke, G. Nakerst, and M. Haque, "Assigning temperatures to eigenstates," Physical Review E **107**, 024102 (2023), arXiv:2111.05083.
[32] G. D. Phillies, "The one-atom ideal gas," in *Elementary Lectures in Statistical Mechanics* (Springer, New York, NY, 2000) pp. 39–54.
[33] L. F. Santos, A. Polkovnikov, and M. Rigol, "Entropy of isolated quantum systems after a quench," Physical Review Letters **107**, 040601 (2011), arXiv:1103.0557.
[34] J. U. Andersen, E. Bonderup, and K. Hansen, "On the concept of temperature for a small isolated system," The Journal of Chemical Physics **114**, 6518–6525 (2001).
[35] N. Hartman, C. Olsen, S. Lüscher, M. Samani, S. Fallahi, G. C. Gardner, M. Manfra, and J. Folk, "Direct entropy measurement in a mesoscopic quantum system," Nature Physics **14**, 1083–1086 (2018), arXiv:1905.12388.
[36] H. Park, Y. W. Kim, and J. Yi, "Entropies of the microcanonical ensemble," AIP Advances **12** (2022), 10.1063/5.0087157.
[37] L. D. Landau and E. M. Lifshitz, *Statistical Physics: Volume 5*, Vol. 5 (Elsevier, 2013).
[38] P. C. Burke and M. Haque, "Entropy and temperature in finite isolated quantum systems," Phys. Rev. E **107**, 034125 (2023), arXiv:2210.02380.
[39] V. Gurarie, "The equivalence between the canonical and microcanonical ensembles when applied to large systems," Am. J. Phys. **75**, 747–751 (2007).
[40] D. J. Griffiths and D. F. Schroeter, *Introduction to quantum mechanics* (Cambridge University Press, 2018).
[41] E. N. Miranda and D. S. Bertoldi, "Thermostatistics of small systems: exact results in the microcanonical formalism," European Journal of Physics **34**, 1075–1087 (2013), arXiv:1509.09300.
[42] "See the supplementary information for a derivation of the energy

expression for a quantum harmonic oscillator in the microcanonical ensemble valid at all temperatures and high-temperature limits for the energy of a quantum harmonic oscillator," .
[43]R. B. Shirts, "A comparison of boltzmann and gibbs definitions of microcanonical entropy for small systems," AIP Advances **11** (2021), 10.1063/5.0073086.
[44]M. Kardar, *Statistical Physics of Particles* (Cambridge University Press, 2007).
[45]N. F. Ramsey, "Thermodynamics and Statistical Mechanics at Negative Absolute Temperatures," Phys. Rev. **103**, 20–28 (1956).
[46]J. M. G. Vilar and J. M. Rubi, "Communication: System-size scaling of Boltzmann and alternate Gibbs entropies," J. Chem. Phys. **140**, 201101 (2014).
[47]E. M. Purcell and R. V. Pound, "A Nuclear Spin System at Negative Temperature," Phys. Rev. **81**, 279–280 (1951).
[48]A. Javan, "Possibility of production of negative temperature in gas discharges," Phys. Rev. Lett. **3**, 87–89 (1959).
[49]P. Hakonen and O. V. Lounasmaa, "Negative Absolute Temperatures: "Hot" Spins in Spontaneous Magnetic Order," Science **265**, 1821–1825 (1994).
[50]A. P. Mosk, "Atomic gases at negative kinetic temperature," Phys. Rev. Lett. **95**, 040403 (2005).
[51]A. Rapp, S. Mandt, and A. Rosch, "Equilibration Rates and Negative Absolute Temperatures for Ultracold Atoms in Optical Lattices," Phys. Rev. Lett. **105**, 220405 (2010), arXiv:1008.0468.
[52]S. Braun, J. P. Ronzheimer, M. Schreiber, S. S. Hodgman, T. Rom, I. Bloch, and U. Schneider, "Negative Absolute Temperature for Motional Degrees of Freedom," Science **339**, 52–55 (2013), arXiv:1211.0545.
[53]K. Baudin, J. Garnier, A. Fusaro, N. Berti, C. Michel, K. Krupa, G. Millot, and A. Picozzi, "Observation of Light Thermalization to Negative-Temperature Rayleigh-Jeans Equilibrium States in Multimode Optical Fibers," Phys. Rev. Lett. **130**, 063801 (2023), arXiv:2301.02796.
[54]E. Abraham and O. Penrose, "Physics of negative absolute temperatures," Phys. Rev. E **95**, 012125 (2017).