

# Meaning of temperature in different thermostistical ensembles

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Depending on the exact experimental conditions, the thermodynamic properties of physical systems can be related to one or more thermostistical ensembles. Here, we survey the notion of thermodynamic temperature in different statistical ensembles, focusing in particular on subtleties that arise when ensembles become non-equivalent. The 'mother' of all ensembles, the microcanonical ensemble, uses entropy and internal energy (the most fundamental, dynamically conserved quantity) to derive temperature as a secondary thermodynamic variable. Over the past century, some confusion has been caused by the fact that several competing microcanonical entropy definitions are used in the literature, most commonly the volume and surface entropies introduced by Gibbs. It can be proved, however, that only the volume entropy satisfies exactly the traditional form of the laws of thermodynamics for a broad class of physical systems, including all standard classical Hamiltonian systems, regardless of their size. This mathematically rigorous fact implies that negative 'absolute' temperatures and Carnot efficiencies more than 1 are not achievable within a standard thermodynamical framework. As an important offspring of microcanonical thermostistics, we shall briefly consider the

canonical ensemble and comment on the validity of the Boltzmann weight factor. We conclude by addressing open mathematical problems that arise for systems with discrete energy spectra.

## 1. Introduction

The fundamental differential relation [1]

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_Z \quad (1.1)$$

connects the thermodynamic state functions temperature  $T$ , internal energy  $E$  and entropy  $S$ . Given  $S$  as a function of  $E$ , and possibly other constant control parameters  $Z = (Z_1, \dots)$  in the Hamiltonian such as volume or an external magnetic field, equation (1.1) in fact *defines* the thermodynamic temperature. The concept of entropy was introduced by Rudolf Clausius [2] in 1865. Clausius chose the symbol  $S$  in honour of (Nicolas Léonard) Sadi Carnot, who laid the groundwork for the second law of thermodynamics. The celebrated Clausius relation  $dS = \delta Q/T$  identifies the inverse of the thermodynamic temperature  $T$  as the integrating factor for the second law, with  $\delta Q \stackrel{\geq}{\leq} 0$  denoting quasi-static and reversible infinitesimal heat exchange. After Clausius' seminal paper [2], it took about 30 more years until Gibbs [3], Einstein, Planck [4,5]<sup>1</sup> and others [6,7] were able to connect firmly thermodynamics and statistical mechanics—and yet certain aspects of this connection have remained a subject of debate up to this day.

The standard approach in statistical mechanics is to identify thermodynamic state functions with specific average values of a suitably chosen statistical ensemble that correctly reflects the physical conditions under which measurements are performed (perfect isolation, coupling to an energy or matter reservoir, etc.). The most fundamental statistical ensemble is the microcanonical ensemble (MCE), describing the thermodynamics of isolated systems that are governed by energy conservation and which, at equilibrium,<sup>2</sup> cannot exchange heat or matter with their surroundings. The MCE is the foundation of other thermostistical ensembles, including the canonical ensemble (which permits permanent energy and/or heat exchange with the environment) and the grand-canonical ensemble (which allows both energy and matter exchange). These two subordinate ensembles can be derived from the MCE by considering a subsystem of interest that is *weakly* coupled to the rest of the globally isolated microcanonical system, which is then interpreted as an environment (heat bath or particle reservoir) for the particular subsystem.

Recent experimental advances make it possible to investigate thermodynamic properties of very small systems (single molecules, Brownian colloids or even individual atoms) that may be, in good approximation, decoupled from the environment or that can be in weak or strong contact with a much larger system. Such finite-system studies provide a valuable testbed for the notion and meaning of thermodynamic temperature in the context of various statistical ensembles. Particularly interesting from a theoretical and practical perspective are situations in which different ensemble descriptions are not guaranteed to be equivalent. Ensemble inequivalence is more norm than exception in finite-size systems but can also occur in macroscopic systems with long-range interactions or when the density of states (DoS) is a non-monotonic function of energy. Equilibrium systems of the latter type are often classified as anomalous [1] and, if entropy is chosen naively, they can give rise to the paradoxical notion of a negative 'absolute' temperature.

<sup>1</sup>In [5] see in particular §117, p. 226 and also equation (372) on p. 252, where the Gibbs volume  $\Omega(E, Z)$  is selected to define the entropy.

<sup>2</sup>To change the energy of a microcanonical system, an external operator can vary the control parameters  $Z$ , or inject or extract heat by coupling the system temporarily to an external heat source or sink. However, such couplings have to be switched off during the equilibration phase.

In the remainder of this contribution, we will survey the meaning of temperature in thermodynamics by summarizing and commenting on results from recent more detailed studies [8,9].

## 2. Microcanonical thermodynamics and absolute temperature

The MCE describes the thermostatics of a strictly isolated system through the density operator  $\rho = \delta(E - H)/\omega$ , where the normalization constant  $\omega$  is the DoS. The MCE is the most fundamental ensemble as it only relies on the conservation of energy  $E$ , arising from the time-translation invariance of the underlying Hamiltonian  $H$ . External thermodynamic control parameters  $Z$ , such as available system volume, particle numbers, electric or magnetic fields, enter as parameters through the Hamiltonian  $H(Z)$  and the DoS  $\omega(E, Z)$ . To connect the MCE to thermodynamics, Gibbs [3] studied two different candidates for the thermodynamic entropy of an isolated system. The first is the *volume entropy*, which in modern notation takes the form

$$S_G = k_B \ln \Omega(E, Z). \quad (2.1)$$

Here,  $k_B$  denotes the Boltzmann constant and the dimensionless *volume* quantity  $\Omega(E, Z)$  is the integrated DoS, classically obtained by integrating the non-negative DoS  $\omega \geq 0$  up to energy  $E$ ,

$$\Omega(E, Z) = \int_0^E dE' \omega(E', Z), \quad (2.2)$$

assuming zero ground-state energy for a physically stable system. Since  $\Omega$  is a non-decreasing function of  $E$ , the temperature  $T_G$  obtained from  $S_G$  and equation (1.1) is strictly non-negative.

For classical Hamiltonian systems  $H(\xi, Z)$  with phase-space variables  $\xi$ , the integrated DoS  $\Omega(E, Z)$  equals the properly normalized (via division by the symmetries of the degrees of freedom) and dimensionless (via division by the appropriate power of Planck's constant) integrated phase-space volume up to the energy  $E$ . We may write this formally as

$$\Omega(E, Z) = Tr_{\xi} \Theta[E - H(\xi, Z)], \quad (2.3)$$

where  $\Theta$  denotes the unit step function and  $Tr$  the phase-space integral over distinguishable microstates  $\xi$ . For isolated quantum systems with discrete energy spectra,  $\xi$  comprises the complete set of quantum numbers, and we may interpret  $\Omega$  in equation (2.3) as a discrete level counting function, defined on the spectrum  $\{E_n\}$  of the Hamiltonian. Intuitively, the discrete function  $\Omega(E_n, Z)$  sums the eigenspace dimensions of the eigenvalues  $E_j \leq E_n$ . In the quantum case, one needs to postulate additional smoothing procedures before one can apply differential thermodynamic relations such as equation (1.1) (see discussion in §4).

Following Gibbs' seminal work, Hertz [6,7] demonstrated the mechanical adiabatic invariance of the volume entropy  $S_G$  for classical systems. The exact connection between  $S_G$ , its corresponding temperature  $T_G$  and equipartition for classical finite-size systems was emphasized in early works by Schlüter [10] and Khinchin [11]. More recent discussions and applications of Gibbs' volume entropy can be found in [8,9,12–21].

The second microcanonical entropy candidate studied by Gibbs [3] is the *surface entropy*,

$$S_B = k_B \ln[\omega(E, Z)\epsilon]. \quad (2.4)$$

The quantity  $\epsilon$  denotes an arbitrary energy constant, needed to make the argument of the logarithm dimensionless. That the definition of  $S_B$  requires such an additional *ad hoc* parameter is conceptually unappealing, but bears no relevance for thermodynamic quantities that are related to derivatives of  $S_B(E, Z)$ —provided  $\epsilon$  is assumed to be independent of  $(E, Z)$ . One can show however that the presence of  $\epsilon$  can cause  $S_B$  to violate Planck's formulation of the second law [8]. For discrete quantum systems with singular DoS  $\omega$ , equation (2.4) also requires additional interpolation and/or smoothing procedures (see §4). The subscript 'B' in equation (2.4) signals that this definition is also commonly referred to as Boltzmann entropy nowadays, which unfortunately does not seem to reflect properly the actual history. Although

Boltzmann's tombstone famously carries the entropy formula  $S = k_B \log W$ , it was, according to Arnold Sommerfeld [22], Max Planck [4,5] who first established this relation. As described in many textbooks, the entropy expression  $S_B$  in equation (2.4) can be heuristically obtained by identifying  $\log = \ln$  and interpreting  $W = \epsilon \omega(E, Z)$  as the number of microstates accessible to a physical system at energy  $E$ . This may explain the popularity of the term 'Boltzmann entropy'.

It is well known that for macroscopic *normal* systems [1] with a large number of microscopic degrees of freedom, most of the phase-space volume is contained in a narrow shell just below the energy  $E$ . In such cases, the two entropy definitions become essentially indistinguishable and predict practically identical thermodynamic equations of state. There exists, however, a wide range of systems for which  $S_B$  and  $S_G$  are non-equivalent.

### (a) Self-consistency checks

The question as to whether  $S_G$  or  $S_B$  are viable candidates for the thermodynamic entropy of isolated systems can be answered directly by testing either candidate against the laws of thermodynamics. The approximation-free analysis in [8] shows that for a broad class of physical systems, which includes all standard classical Hamiltonian systems<sup>3</sup> of *arbitrary* size, the Gibbs volume entropy  $S_G$  satisfies the traditional formulations of the zeroth, first and second laws exactly. By contrast, the surface entropy  $S_B$  is found to violate these laws in many situations [3,8,9]. While referring the reader to [8] for technical details, we briefly summarize the most essential results.

(i) That  $S_G$ , but not  $S_B$ , satisfies the zeroth law is a reflection of the fact [8,10,11,15–17,21] that only  $S_G$  satisfies the microcanonical equipartition theorem exactly. More precisely, denoting the microcanonical averages by  $\langle \cdot \rangle_E$ , the Stokes theorem implies [11] that, for all standard classical Hamiltonian systems with topologically simple phase space  $\mathbb{R}^d$ , the equipartition identity<sup>4</sup>

$$k_B T_G = k_B \left( \frac{\partial S_G}{\partial E} \right)_Z^{-1} = \left\langle \xi_k \frac{\partial H}{\partial \xi_k} \right\rangle_E \quad (2.5)$$

holds for *any* of the canonical coordinates  $(\xi_1, \dots, \xi_d)$ . By contrast, this relation is *in general* violated for the surface entropy, ruling out  $S_B$  as a consistent thermodynamic entropy.

(ii) Compliance of  $S = S_G$  and  $T = T_G$  with the first law

$$dS = \frac{1}{T} dE + \sum_i \frac{F_i}{T} dZ_i, \quad F_i := T \left( \frac{\partial S}{\partial Z_i} \right)_E \stackrel{!}{=} - \left\langle \frac{\partial H}{\partial Z_i} \right\rangle_E, \quad (2.6)$$

follows directly from a simple integration by parts [8,20]. Note that the last equality in equation (2.6) ensures that statistical averages agree with thermodynamic observables. One can easily verify that this consistency criterion is, in general, violated for the Boltzmann entropy  $S_B$ .

(iii) Planck's second law of thermodynamics for isolated systems can be, in essence, stated as follows: consider two isolated microcanonical systems that are initially separated and have entropies  $S_1(E_1)$  and  $S_2(E_2)$ , respectively. Now couple the two systems weakly and let them equilibrate. Assuming energy conservation throughout the process, the joint equilibrated system is again microcanonical and has entropy  $S_{1+2}(E_{1+2}) = S_{1+2}(E_1 + E_2)$ . Then, Planck's second law demands that the entropy of the final state is larger than the sum of the initial entropies

$$S_{1+2}(E_{1+2}) \geq S_1(E_1) + S_2(E_2). \quad (2.7)$$

Basic integral convolution properties imply that equation (2.7) is always satisfied for  $S_G$  (in most cases, even with strictly ' $>$ ') but not necessarily by  $S_B$  [8].

<sup>3</sup>These are confined systems with quadratic kinetic energy and finite ground-state energy.

<sup>4</sup>For systems with complex phase-space topology, equation (2.5) can be violated, see example in §2b, where the phase-space regions corresponding to clockwise and anticlockwise motion become disconnected for supercritical energy values. Such topologically peculiar systems do not thermalize in the traditional sense. However, for the most commonly considered standard classical Hamiltonian systems, equation (2.5) is strictly satisfied.

In this context, it is worthwhile to note that any subsequent attempt to decouple the two systems results in non-microcanonical distributions for the separated systems, since the exact individual energies are not known any more due to the permanent energy exchange during the equilibration phase (i.e. thermal coupling is irreversible). This means that, without further manipulation or measurements (or the introduction of a Maxwell demon), the total entropy remains  $S_{1+2}(E_1 + E_2)$  after separation, a fact that has been missed by authors [23], who recently criticised the Gibbs entropy. Unsurprisingly, this basic error led to paradoxical conclusions [23], such as an apparent violation of mathematically exact inequalities.

For completeness, we mention that previous studies rarely focused on the third law, mainly because it is well known that many classical systems (including the ideal gas) do not obey the third law. Typically, verification of the third law requires a consistent quantum-mechanical treatment.<sup>5</sup> Evidently, the Gibbs entropy satisfies  $S_G(E_0) = k_B \ln g_0$  with  $g_0$  denoting the degeneracy of the ground-state energy  $E_0$  and hence fulfills the most basic version of the third law.

## (b) Positive and negative temperatures: an example

The primary thermodynamic state variables of an isolated system with Hamiltonian  $H(Z) = E$  are energy  $E$  and control parameters  $Z$ . By contrast, the temperature  $T$  is a secondary derived quantity determined by equation (1.1). For the Gibbs volume entropy, one finds explicitly

$$k_B T_G = \frac{\Omega(E, Z)}{\omega(E, Z)}, \quad \omega(E, Z) = \frac{\partial \Omega}{\partial E}. \quad (2.8)$$

As both the integrated DoS  $\Omega \geq 0$  and the DoS  $\omega \geq 0$  are non-negative, the Gibbs temperature is strictly non-negative. For comparison, the Boltzmann temperature is given by

$$k_B T_B = \frac{\omega(E, Z)}{\nu(E, Z)}, \quad \nu(E, Z) = \frac{\partial \omega}{\partial E}. \quad (2.9)$$

The Boltzmann temperature  $T_B$  is negative whenever the DoS  $\omega$  is locally decreasing with  $E$  (see example in figure 2). This happens for Ising-type spin or laser systems in the population-inverted regime, as well as in Hamiltonian systems exhibiting singular points in their DoS that separate regions of  $\nu(E, Z) > 0$  with regions with negative-valued  $\nu(E, Z)$ .

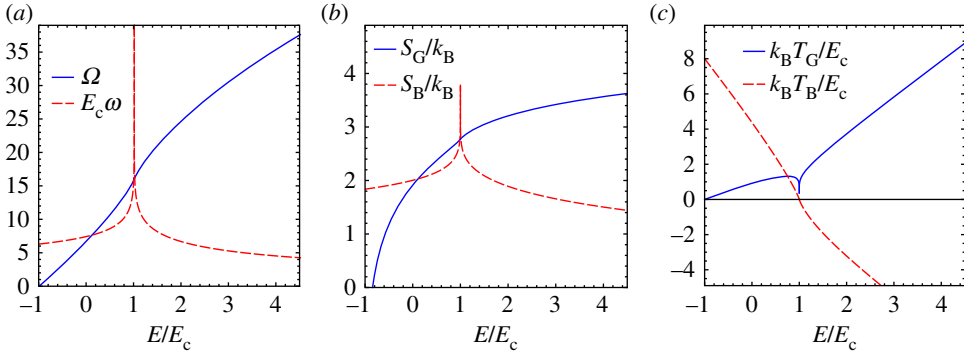
An instructive one-dimensional example [21] is the classical pendulum (mass  $m$ , length  $L$ , gravitational acceleration  $g$ ) with Hamiltonian

$$H(\phi, p_\phi) = \frac{p_\phi^2}{2m} - mgL \cos \phi. \quad (2.10)$$

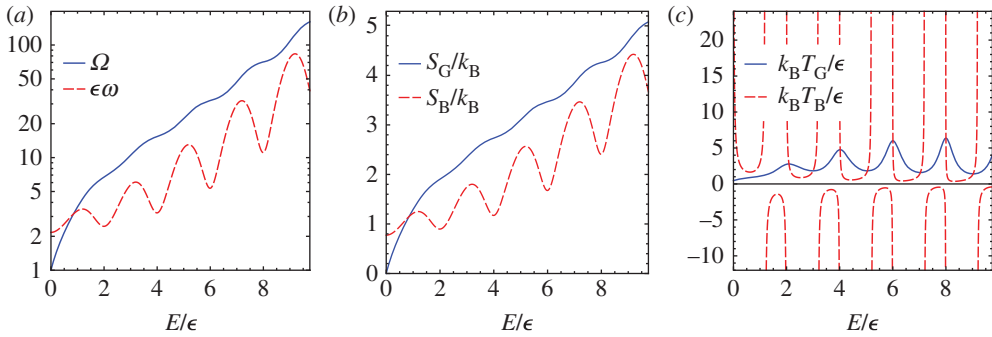
The energy range is bounded from below but unbounded from above,  $-mgL < E < \infty$ . The DoS  $\omega$  can be given analytically in terms of complete elliptic integrals of the first kind [21]. The DoS increases in the oscillatory regime  $-mgL < E < mgL$ , exhibits a singularity at  $E_c = mgL$ , where the orbit period diverges, and decreases in the continuous-rotation regime,  $mgL < E < \infty$  (figure 1a). Accordingly, the Boltzmann entropy decays monotonically as  $E \rightarrow \infty$  (figure 1b), implying a negative Boltzmann temperature for  $E > mgL$ . By contrast, the Gibbs temperature is positive for all  $E > -mgL$  (figure 1c). In particular, for  $E \gg mgL$ , any further increase of energy is, in essence, purely kinetic and the system approaches an ideal one-particle gas on a circle, which should asymptotically satisfy  $E = +\frac{1}{2}k_B T$ , unless one is willing to give up this standard caloric equation of state. It is easy to check that this relation holds only for  $T = T_G$  (figure 1c).

## (c) Additional remarks

<sup>5</sup>As a note of caution: one can find many partially conflicting versions of the third law in the literature, and some naive formulations are not applicable to isolated systems, or only apply to systems with non-degenerate ground state or finite energy gap between ground-state and lowest excited energy levels.



**Figure 1.** Microcanonical thermostatics of the pendulum with Hamiltonian (2.10). (a) The integrated DoS  $\Omega$  (blue) grows monotonically while the DoS  $\omega$  (red dashed) exhibits a singular peak at the critical energy  $E_c = mgl$ , indicating a change in the phase-space topology. (b) The Gibbs entropy  $S_G$  (blue) increases monotonically, whereas the Boltzmann entropy  $S_B$  (red dashed) becomes singular at  $E_c$  and decays for  $E > E_c$ . (c) The Gibbs temperature  $T_G$  (blue) approaches asymptotically the caloric equation of state of the ideal one-particle gas, whereas the Boltzmann temperature  $T_B$  (red dashed) becomes negative for  $E > E_c$ .



**Figure 2.** Non-uniqueness of microcanonical temperatures for a system with non-monotonic DoS; figure adapted from [8]. (a) DoS  $\omega$  (red dashed) and integrated DoS  $\Omega$  (blue) for the example in eqn (23) of [8]. (b) Gibbs volume entropy  $S_G$  (blue) and Boltzmann surface entropy  $S_B$  (red dashed). (c) Gibbs temperature  $T_G$  (blue) and Boltzmann temperature  $T_B$  (red dashed). The example illustrates that, in general, neither the Gibbs nor the Boltzmann temperature uniquely characterize the thermal state of an isolated system because the same temperature value can correspond to different energy values.

### (i) Heat does not always flow from hot to cold

The thermodynamic state of an isolated system is completely determined by the primary state variables  $(E, Z)$ . As temperature is not a primary state variable, it cannot, in general, uniquely characterize the thermodynamic state of a microcanonical system (figure 2). This means there exist situations where neither the Gibbs temperature  $T_G$  nor the Boltzmann temperature  $T_B$  can predict the energy flow between weakly coupled systems that had different temperatures before contact [8]. For instance, for a system with oscillatory DoS, two or more significantly different energy values can have the same temperature, regardless of which entropy definition one adopts (figure 2c). Therefore, the naive formulation of the second law ‘heat always flows from hot to cold’ does not hold in general. Likewise invalid are versions of the zeroth law that claim that isolated systems with equal temperatures should not produce a net heat flow between them when brought into thermal contact. This can again be readily seen by considering, for example, the coupling of an ideal gas to a system with oscillatory DoS as in figure 2.



## (ii) Thermodynamics applies to equilibrium systems of any size.

It takes little effort to verify that equations (2.5)–(2.7) hold exactly for standard classical ergodic Hamiltonian systems with an arbitrary number of degrees of freedom  $N$ . Similarly, the canonical ensemble discussed below can be applied to (sub)systems of any size. These mathematical facts are widely appreciated by many colleagues [9,12–15,18,19,21]—in particular those interested in understanding DNA folding [24], microscopic information storage and erasure [25] and fluctuation phenomena [26]—and yet remain ignored by a few others [23,27]. When judged objectively, there is no doubt that the application of thermodynamic concepts to finite systems has considerably advanced our understanding of biophysical, colloidal and quantum processes.<sup>6</sup> Compared with infinite-systems thermodynamics, a practical difference is given by the fact that fluctuations generally play a (much) more important role in small systems. The presence of fluctuations, of course, does not mean that it is forbidden to characterize single DNA molecules thermodynamically; on the contrary, such fluctuations typically contain important additional thermodynamic and energetic information that is usually lost in the infinite-system limit. Therefore, it would seem wiser to focus on understanding better the fluctuations of thermostistical variables in finite systems, such as those of virial quantities on the r.h.s. of equation (2.6), instead of discarding finite-system thermodynamics on purely habitual grounds [27]. Dogmatic insistence on the thermodynamic limit  $N \rightarrow \infty$  is about as useful as insisting on the Newtonian limit, corresponding to speed of light  $c \rightarrow \infty$ , in relativity. In both cases, things may become simpler, but one is missing out on relevant physics.

## (iii) Clausius relation and Carnot efficiency

Campisi [9] showed recently that the inverse Gibbs temperature  $T_G^{-1}$  appears naturally as the integrating factor in the Clausius relation for virtually all practically relevant physical systems. This corroborates the fact that the Gibbs temperature  $T_G$  should be identified with the *absolute* thermodynamic temperature  $T$ , unless one is willing to abandon the Clausius relation. Moreover, the non-negativity of the Gibbs temperature directly implies that Carnot efficiencies cannot exceed 1.

## (iv) Thermodynamic potentials can be ‘non-local’

It is sometimes argued that the Gibbs entropy cannot be the ‘correct’ thermodynamic entropy as it is based on the integrated phase-space volume  $\Omega$ , which is a ‘non-local’ quantity that arises from a summation over states in an extended energy range. This argument might appear superficially appealing but it is ill-founded for (at least) two reasons. First, the microcanonical averages appearing in equations (2.5) and (2.6) are computed purely locally on the energy surface in phase space. Yet, the Stokes theorem implies that they can be related to the enclosed phase-space volume [11] and, hence, entropy should be a non-local volume-related quantity. Second, if we insisted on purely local potentials everywhere in physics then we would have to stop using force potentials in mechanics, which are in essence ‘non-local’ integrals over local forces experienced by particles. At this point, however, it is helpful to recall why such non-local potentials are introduced in mechanics in the first place: they allow us to define an important conserved quantity, *energy*. Just as the energy is invariant under infinitesimal time translations, the integrated phase-space volume  $\Omega$  is invariant under infinitesimal adiabatic parameter translations [6,7,15]. Hence, it should not be surprising but rather be expected that thermodynamic potentials may be non-local in energy space.

<sup>6</sup>Most of the experimental applications involve the canonical ensemble, as DNA molecules [24] or colloids [25,26] are typically held in a liquid bath that acts as a canonical thermostat. However, if one accepts the applicability of canonical thermostatics to finite systems, then there exist no mathematical or logical or physical reasons that forbid the application of microcanonical statistics to finite systems, because equations (2.5)–(2.7) hold for systems of any size. Of course, the thermostatical characterization of small systems should not just be limited to the mean values appearing in equations (2.5) and (2.6) but should also include a careful fluctuation analysis of the underlying stochastic observables.

### (v) Ising models are bad benchmarks

When using specific theoretical models to illustrate alleged pros and cons of certain entropy definitions, then it is advisable to verify first that these models respect superordinate experimentally established knowledge. Specifically, while the observed stability of matter implies the existence of lower energy bounds on Hamiltonians, there exists no evidence to date for strict upper energy bounds. This means that  $E \rightarrow -E$  is not a fundamental symmetry of physics and, hence, one should not impose such energy-reflection symmetry on thermodynamic quantities. For the same reason, it is not advisable to base arguments exclusively on Ising-type models, which are *ad hoc* truncations of more fundamental Hamiltonians that are *not* bounded from above, if one wants to evaluate the conceptual validity of a certain thermostistical framework.

### (vi) Ensemble (in)equivalence

Although  $S_G$ ,  $S_B$  and other entropy candidates [8] often yield practically indistinguishable predictions for the thermodynamic properties of large *normal* systems [1], such as quasi-ideal gases with macroscopic particle numbers, they can produce substantially different predictions for finite mesoscopic systems, for *ad hoc* truncated Hamiltonians with upper energy bounds or even for macroscopic gravitational systems [28]. This implies (see discussion in §3) that, in general, microcanonical and canonical descriptions are not equivalent, which is not surprising as they refer to different physical conditions (complete isolation versus coupling to an infinite bath).

## 3. Temperature in the canonical ensemble

The canonical Boltzmann factor  $e^{-\beta H}$ , where  $T = (k_B \beta)^{-1}$  is commonly identified with the bath temperature, has become one of the most frequently employed statistical tools in physics. It is therefore conceptually important and practically useful to understand potential validity limits, which arise from assumptions and approximations made during the derivation from the underlying MCE.

### (a) Boltzmann factor and temperature

We briefly summarize the key assumptions underlying the derivation of the Boltzmann factor by considering a system of interest  $S$  which is coupled to another system  $B$  that acts as a heat bath. The starting point of the derivation is the microcanonical density operator  $\rho^T(\xi|E^T, Z) = \delta[E^T - H^T(\xi, Z)]/\omega^T(E^T, Z)$  of the total system  $T = S + B$ . The first key assumption en route to the Boltzmann factor is *weak coupling*, which means that one neglects system–bath interaction contributions to the total energy and Hamiltonian, by writing  $E^T = E^S + E^B$  and  $H^T = H^S + H^B$ . Because the total energy  $E^T$  is fixed, the probability weight  $P(E^S|E^T, Z)$  to find the fluctuating energy value  $E^S$  of the subsystem  $S$  is given by [1,8,29]

$$P(E^S|E^T, Z) = \frac{\omega^S(E^S)\omega^B(E^T - E^S)}{\omega^T(E^T)}. \quad (3.1)$$

Here,  $\omega^S(E^S)$  denotes the DoS of the subsystem energy value  $E^S$ , while  $\omega^B(E^B)$  is the DoS of the bath at energy  $E^B = E^T - E^S$ , and  $\omega^T(E^T)$  the total DoS at the total energy  $E^T$ . Equation (3.1) can be equivalently rewritten as

$$P(E^S|E^T, Z) = \frac{\omega^S(E^S)}{\epsilon \omega^T(E^T)} \exp \left[ \frac{S_B^B(E^T - E^S)}{k_B} \right], \quad (3.2)$$

where  $S_B^B(E^B) = S_B^B(E^T - E^S)$  denotes the Boltzmann entropy of the *bath*. As the next step in the standard derivation [1,29], one expands the Boltzmann entropy in the exponent around some



conveniently chosen value  $\bar{E}^{\mathcal{B}}$ , typically taken to be the expectation value  $E^{\mathcal{B}}$  of the bath energy,<sup>7</sup> keeping terms up to linear order:

$$S_{\mathcal{B}}^{\mathcal{B}}(E^{\mathcal{T}} - E^{\mathcal{S}}) = S_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}}) + \frac{1}{T_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}})}(E^{\mathcal{T}} - E^{\mathcal{S}} - \bar{E}^{\mathcal{B}}) + \dots, \quad (3.3)$$

where  $T_{\mathcal{B}}^{\mathcal{B}} = (\partial S_{\mathcal{B}}^{\mathcal{B}} / \partial E^{\mathcal{B}})^{-1}$  is the Boltzmann temperature of the bath. Note that equation (3.3) is essentially an expansion in the energy fluctuations of the bath  $\delta E^{\mathcal{B}} = E^{\mathcal{B}} - \bar{E}^{\mathcal{B}} = (E^{\mathcal{T}} - E^{\mathcal{S}}) - \bar{E}^{\mathcal{B}}$ . Inserting expansion (3.3) into equation (3.2) gives

$$P(E^{\mathcal{S}} | E^{\mathcal{T}}, Z) = \frac{\omega^{\mathcal{S}}(E^{\mathcal{S}})}{\epsilon \omega^{\mathcal{T}}(E^{\mathcal{T}})} \exp \left[ \frac{S_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}})}{k_{\mathcal{B}}} + \frac{(E^{\mathcal{T}} - \bar{E}^{\mathcal{B}}) - E^{\mathcal{S}}}{k_{\mathcal{B}} T_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}})} + \dots \right]. \quad (3.4)$$

Assuming *all* higher-order terms can be neglected,<sup>8</sup> one obtains the standard result

$$P(E^{\mathcal{S}} | E^{\mathcal{T}}, Z) = \frac{\omega^{\mathcal{S}}(E^{\mathcal{S}})}{Z_{\mathcal{C}}} \exp \left[ -\frac{E^{\mathcal{S}}}{k_{\mathcal{B}} T_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}})} \right], \quad (3.5)$$

where all remaining  $E^{\mathcal{S}}$ -independent terms have been absorbed into the normalizing constant  $Z_{\mathcal{C}}$ , which is the canonical partition function.

Thus, the temperature entering the celebrated Boltzmann factor  $\exp(-\beta E^{\mathcal{S}})$  is the *Boltzmann temperature*  $T_{\mathcal{B}}^{\mathcal{B}}$  of the *bath*. One may therefore be tempted to assume that  $T_{\mathcal{B}}^{\mathcal{B}}$  can be identified with the thermodynamic temperature of the total system. However, this is logically incorrect because  $T_{\mathcal{B}}^{\mathcal{B}}(\bar{E}^{\mathcal{B}})$  is in general not equal [8] to the total system Boltzmann temperature  $T_{\mathcal{B}}^{\mathcal{T}}(E^{\mathcal{T}})$  or Gibbs temperature  $T_{\mathcal{G}}^{\mathcal{T}}(E^{\mathcal{T}})$ , with the latter being the actual thermodynamic temperature. Of course, when the bath is macroscopically large and normal (e.g. ideal gas-like) from a thermostistical viewpoint, then the effective temperature  $T_{\mathcal{B}}^{\mathcal{B}}$  practically coincides with the Gibbs temperature of the total system  $\mathcal{T}$ , as well as with the *average*<sup>9</sup> Gibbs temperatures [8] of the bath  $\mathcal{B}$  and the system  $\mathcal{S}$ . By contrast, when considering finite thermostats (i.e. a bath with a finite number of microstates), then the exponential Boltzmann has to be replaced by a generalized Boltzmann factor, which may assume the form of a Tsallis–Rényi escort distribution [30].

## (b) Beyond weak coupling

Having surveyed the notion of temperature in the canonical ensemble, we still address another subtlety that concerns the heat capacities of nano-systems. When studying the thermodynamic properties of nano-scale devices, one naturally encounters the question whether the weak coupling approximation remains justified. Indeed, for a typical nano-system in contact with a heat bath, the coupling energy is usually of the order of the average system energy. Therefore, coupling terms in the Hamiltonian can no longer be neglected. This issue was investigated in detail in [31–33], which focused on the question how the canonical heat capacity is affected when nano-subsystems are *strongly* coupled to a large normal bath. These studies showed that the reduced canonical weight (or reduced density operator in quantum mechanics) of a strongly coupled small system is no longer of the Boltzmann form, when expressed in terms of the bare subsystem energy  $E^{\mathcal{S}}$  or corresponding Hamilton operator  $H^{\mathcal{S}}$ . Instead, the canonical weight now features a renormalized subsystem Hamiltonian that depends explicitly on both effective bath

<sup>7</sup>Replacing the expansion point  $\bar{E}^{\mathcal{B}}$  by the mode is not recommendable, as this procedure becomes ambiguous or even ill-defined when the DoS  $\omega^{\mathcal{B}}(E^{\mathcal{B}})$  of the bath is oscillating or monotonically increasing.

<sup>8</sup>The approximate formulae (3.4) and (3.5) neglect all higher-order contributions in the Taylor expansion of  $S_{\mathcal{B}}^{\mathcal{B}}$ . For example, the coefficient in front of the quadratic term is proportional to  $\partial^2 S_{\mathcal{B}}^{\mathcal{B}} / \partial^2 E^{\mathcal{B}} = -1 / (T_{\mathcal{B}}^{\mathcal{B}})^2 C_{\mathcal{B}}^{\mathcal{B}}$ , where  $C_{\mathcal{B}}^{\mathcal{B}} = \partial E^{\mathcal{B}} / \partial T_{\mathcal{B}}^{\mathcal{B}}$  is the canonical specific heat of the bath. For this term to vanish individually,  $C_{\mathcal{B}}^{\mathcal{B}}$  has to be sufficiently large. Roughly speaking, one can expect that the second-order as well as higher-order expansion terms become negligible if the Boltzmann temperature  $T_{\mathcal{B}}^{\mathcal{B}}$  changes only slowly when the bath energy is varied. This typically requires a large bath.

<sup>9</sup>Since system  $\mathcal{S}$  and bath  $\mathcal{B}$  can permanently exchange energy, subject to the constraint  $E^{\mathcal{T}} = E^{\mathcal{S}} + E^{\mathcal{B}} = \text{const.}$ , their temperatures have to be defined as statistical averages with respect to the microcanonical density operator of the total system  $\mathcal{T}$  (see Sec. III.D in [8]).

temperature  $T_B$  and coupling strength. Moreover, as a main consequence, the canonical specific heat of the subsystem is not guaranteed to be positive and can, in fact, attain *negative* values even for  $T_B > 0$  [31–33]. The thermodynamic entropy<sup>10</sup> of such a strongly coupled quantum system, obtained from its canonical partition function via the free energy, assumes a form that is close (but not exactly equal) to the quantum conditional entropy, and can become negative for  $T_B > 0$  [33]. This does not affect, however, the validity of the third law as stated above, which holds true for  $T_B \rightarrow 0$  even when a small quantum subsystem is strongly coupled to a heat bath; see fig. 3 in [33] for an example.

### (c) Thermodynamic versus information entropy

We conclude our discussion of the canonical ensemble with brief remarks on thermodynamic and information-theoretic entropies. The exponential Boltzmann distribution (3.5) is directly linked to the entropy  $S_C = -k_B \text{Tr}(\rho \ln \rho)$ , as already noted by Gibbs [3], who discussed  $S_C$  exclusively in the context of the canonical ensemble. Nowadays,  $S_C$  is commonly referred to as the *canonical* Gibbs–Shannon entropy in classical statistical mechanics and as the von Neumann entropy in quantum statistics. It is well known that the canonical distribution (3.5) can be obtained by maximizing  $S_C$  under the assumption that the mean energy  $\bar{E}^S$  is given. However, such a purely formal ‘derivation’ conceals the underlying physical assumptions that determine the range of validity of the Boltzmann distribution (3.5). Also, entropy maximization arguments often leave the impression that there is a direct one-to-one correspondence between thermodynamics and information theory, which is somewhat misleading for a number of reasons. First, there exist many different information measures [34] and the Shannon entropy is just one of them—although an admittedly very nice one. Second, the Shannon entropy can be used to quantify the information content of arbitrary probability measures that, in most cases, have no relation to the thermodynamic equilibrium distributions. Third, the most fundamental equilibrium ensemble, the MCE, has a thermodynamic entropy that does not belong to the class of Shannon entropies. Therefore, some reservation seems in order when attempts are made to identify information-theoretic measures generically with thermodynamic entropies and vice versa. A similar note of caution applies when one tries to relate information-theoretic inequalities to thermodynamic inequalities that arise in the context of the second law or from thermodynamic stability considerations [29]. Potential analogies between thermodynamics and information theory are interesting and deserve to be explored in great detail, but they should not necessarily be raised to the level of postulates, when they have been shown to be incomplete and may obscure physical insight.

## 4. Open questions

The above discussion implicitly assumed that all derivatives exist and are well behaved. This is typically the case for classical Hamiltonian systems with the exception of critical points [17], as also encountered in the pendulum example above [21]. For quantum systems, the problem is generally more subtle since quantum-mechanical energy spectra can be partially or completely discrete, and are typically very sensitive to small perturbations that can break symmetry-related degeneracies. Similar effects occur in classical approximations to quantum systems, as for example the classical Ising model. Whenever one faces a completely or partially discrete spectrum  $\{E_i\}$ , the corresponding DoS  $\omega(E, Z)$  becomes formally singular and essentially reduces to a collection of  $\delta$ -functions at those discrete energy values,  $\omega(E) = \sum_i g_i \delta(E - E_i)$ , where  $g_i$  is the degeneracy of the energy value  $E_i$ . In this case, the construction of a differentiable DoS requires some sort of smoothing procedure. This issue is closely related to the so-called ‘Weyl problem’ of finding asymptotic approximations for the eigenvalue distributions of Hermitian operators in

<sup>10</sup>For non-weakly coupled systems, correlations between bath and system cannot be neglected and, therefore, the thermodynamic entropy of such subsystems is no longer given by the classical Gibbs–Shannon entropy or the quantum-mechanical von Neumann entropy.

finite domains, by applying some suitable averaging procedure to obtain a continuous DoS [35]. For canonical systems, one typically uses such a smoothed DoS of the underlying energy spectrum at high ambient temperatures.

When the spectrum exhibits a discrete range, then one can define the integrated DoS  $\Omega(E, Z)$ , which enters the microcanonical Gibbs entropy  $S_G$ , in at least two different ways. The most commonly used method simply integrates the discrete DoS  $\omega(E, Z)$  over  $E$ , which results in a step function  $\tilde{\Omega}$  that gives rise to singular thermodynamic derivatives. This approach seems unsatisfactory mathematically, for one simply integrates over the ‘forbidden’ part<sup>11</sup> of the spectrum while completely ignoring structural information encoded in the amplitude values  $g_i$  of  $\omega$  in the interpolation regions  $(E_i, E_{i+1})$ . A potentially better method [8] is based on analytic interpolation of the discrete level counting function  $\Omega(E_n) = \sum_{E_j \leq E_n} \dim \mathcal{H}_j$ , where  $\mathcal{H}_j$  is the eigenspace of  $E_j$ . Although the most natural interpolations appear obvious when  $\Omega(E_n)$  can be written as  $\Omega(E_n) = f(n)$  for some known function  $f$  (see examples in [8]), there remain open questions as to how to treat rigorously cases where no such closed-form representation is known.<sup>12</sup>

## 5. Conclusion

Gibbsian thermodynamics [3,6,7] works consistently for finite and infinite systems, because the underlying mathematical and statistical foundations, most importantly Liouville’s theorem, merely rely on generic conservation laws that arise from the Hamiltonian structure of the microscopic dynamics. Working with infinite systems is generally easier as this limit often (but not always) forgives a certain laxness in defining entropy and thermostistical observables, because various different definitions may show the same asymptotic behaviour when the particle number  $N$  is allowed to go to  $\infty$ . As mentioned before, this is quite analogous to the fact that the Newtonian limit  $c \rightarrow \infty$  is generally easier to handle than a full relativistic treatment at finite speed of light  $c$ , which of course does not mean that Newtonian dynamics is more correct than relativity. Just as relativity compels us to think more carefully about how to formulate fundamental physical laws, the thermostistical analysis of finite systems forces us to pay more rigorous attention to mathematical and physical consistency criteria [8] in thermodynamics. This profound insight can be attributed to Gibbs, who wrote on page 179 of his fundamental treatise [3]: ‘It would seem that in general averages are the most important, and that they lend themselves better to analytical transformations. This consideration would give preference to the system of variables in which  $\log V$  [=  $S_G$  in our notation] is the analogue of entropy. Moreover, if we make  $\phi$  [=  $S_B$  in our notation] the analogue of entropy, we are embarrassed by the necessity of making numerous exceptions for systems of one or two degrees of freedoms.’ Gibbs was, of course, well aware that statistical fluctuations become important in finite systems and that, therefore, the exact thermodynamic mean value relations (2.5) and (2.6) have to be complemented by detailed fluctuation analysis, as nowadays the norm in DNA and colloid experiments [24–26].

In this contribution, we have surveyed the notion of thermodynamic temperature in the microcanonical and the canonical ensemble. For isolated microcanonical systems, the Gibbs volume entropy fulfils exactly the standard laws of thermodynamics as well as equipartition for a wide range of systems, including all classical standard Hamiltonian systems regardless of their size. For finite systems, fluctuation analysis provides important physical information beyond the mean values that define standard thermodynamic state variables. The microcanonical Gibbs formalism agrees with the Clausius relation [9], implies strictly non-negative temperatures and, hence, ensures Carnot efficiencies  $\leq 1$ . By contrast, the Boltzmann entropy, which can yield ‘negative absolute temperatures’, is not a consistent thermodynamic entropy if one adopts the standard laws of thermodynamics, as summarized in equations (2.5)–(2.7). It is therefore not

<sup>11</sup>The union of intervals  $(E_i, E_{i+1})$ .

<sup>12</sup>Another practical, but not quite as elegant, approach is to replace derivatives with finite differences, which in essence corresponds to linear and higher-order polynomial interpolations.

obvious to us why one should favour an entropy that can violate Planck's law (2.7) over one that fulfils it rigorously.

Notwithstanding, the Boltzmann temperature plays an important role as an effective bath temperature in the canonical ensemble, describing a subsystem that is in weak contact with a quasi-infinite environment. If the bath behaves normally (e.g. ideal gas-like), then the Boltzmann temperature practically coincides with the Gibbs temperature. Subtle differences arise, however, for systems that are non-weakly coupled to an environment, as typically the case for nano-scale devices. In the presence of strong coupling, the specific heat of the device can become negative [31,32] even though the total system consisting of device and bath is thermodynamically stable. This feature is in stark contrast to the weak coupling case, where the canonical specific heat of the subsystem is strictly positive.

Last and not least, some authors [23,27,36] have recently criticised the microcanonical Gibbs formalism [3,5] by limiting their discussion to infinite systems and advocating modified versions of the thermodynamic laws, tailored to favour their own preferred entropy definitions. If one accepts such reasoning, then one must also be willing to replace the exact equations (2.5)–(2.7) with inexact approximations—which seems a steep price to pay. The exactness of equations (2.5)–(2.7) is not a consequence of specific postulates but follows from basic differential and integral calculus (the ‘proofs’ are trivial and take only a few lines [8]). Hence, even if one dislikes the Gibbs formalism as developed in [3,5–7], one should at least acknowledge the correctness of the mathematically rigorous results (2.5)–(2.7). Moreover, instead of focusing on the discussion of abstract postulates [27], it may also be useful to remind ourselves that the purpose of any thermodynamic theory should be the prediction of physically measurable quantities, such as pressure, magnetization, etc., which correspond to operationally well-defined statistical averages. The last equality in equation (2.6) demands that thermodynamic and statistical (kinetic) definitions of pressure and other observables are compatible for systems of arbitrary size. This essential compatibility criterion is exactly satisfied for the Gibbs entropy but not for Boltzmann-type entropies.

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## References

1. Kubo R. 1965 *Statistical mechanics: an advanced course with problems and solutions*, section 1.6. Amsterdam, The Netherlands: Elsevier.
2. Clausius R. 1865 Über verschiedene für die Anwendung bequeme Formen der Hauptgleichungen der mechanischen Wärmetheorie. *Ann. Phys.* **125**, 353–400.
3. Gibbs JW. 1902 *Elementary principles in statistical mechanics*. New York, NY: Charles Scribner's Sons.
4. Planck M. 1906 Entropie und Wahrscheinlichkeit, *Vorlesungen über die Theorie der Wärmestrahlung*, ch. 4, §136, p. 139. Leipzig, Germany: J. A. Barth.
5. Planck M. 1957 *Introduction to theoretical physics*, vol. V, *Theory of heat* (Transl. by HL Brose, 2nd printing). New York, NY: Macmillan.
6. Hertz P. 1910 Über die mechanischen Grundlagen der thermodynamik. Part I. *Ann. Phys.* **33**, 225–274. (doi:10.1002/andp.19103381202)

7. Hertz P. 1910 Über die mechanischen Grundlagen der thermodynamik. Part II. *Ann. Phys.* **33**, 537–552. (doi:10.1002/andp.19103381305)
8. Hilbert S, Hänggi P, Dunkel J. 2014 Thermodynamic laws in isolated systems. *Phys. Rev. E* **90**, 062116. (doi:10.1103/PhysRevE.90.062116)
9. Campisi M. 2015 Construction of microcanonical entropy on thermodynamic pillars. *Phys. Rev. E* **91**, 052147. (doi:10.1103/PhysRevE.91.052147)
10. Schlüter A. 1948 Zur Statistik klassischer Gesamtheiten. *Z. Naturforsch.* **3A**, 350–360. (doi:10.1515/zna-1948-0605)
11. Khinchin AI. 1949 *Mathematical foundations of statistical mechanics*. New York, NY: Dover.
12. Berdichevsky V, Kunin I, Hussain F. 1991 Negative temperature of vortex motion. *Phys. Rev. A* **43**, 2050–2051. (doi:10.1103/PhysRevA.43.2050)
13. Berdichevsky V, Kunin I, Hussain F. 1991 Reply to “Comment on ‘Negative temperature of vortex motion’”. *Phys. Rev. A* **44**, 8439–8440. (doi:10.1103/PhysRevA.44.8439)
14. Berdichevsky V, Kunin I, Hussain F. 1993 Reply to “Comment on ‘Negative temperature of vortex motion’”. *Phys. Rev. E* **47**, 2968–2969. (doi:10.1103/PhysRevE.47.2968)
15. Berdichevsky VL. 1988 The connection between thermodynamic entropy and probability. *J. Appl. Math. Mech.* **52**, 738–746. (doi:10.1016/0021-8928(88)90009-3)
16. Campisi M. 2005 On the mechanical foundations of thermodynamics: the generalized Helmholtz theorem. *Stud. Hist. Phil. Mod. Phys.* **36**, 275–290. (doi:10.1016/j.shpsb.2005.01.001)
17. Dunkel J, Hilbert S. 2006 Phase transitions in small systems: microcanonical vs. canonical ensembles. *Physica A* **370**, 390–406. (doi:10.1016/j.physa.2006.05.018)
18. Casetti L, Kastner M, Nerattini R. 2009 Kinetic energy and microcanonical nonanalyticities in finite and infinite systems. *J. Stat. Mech.: Theory Exp.* **2009**, P07036. (doi:10.1088/1742-5468/2009/07/P07036)
19. Junghans C, Bachmann M, Janke W. 2008 Thermodynamics of peptide aggregation processes: an analysis from perspectives of three statistical ensembles. *J. Chem. Phys.* **128**, 085103. (doi:10.1063/1.2830233)
20. Dunkel J, Hilbert S. 2014 Consistent thermostatics forbids negative absolute temperatures. *Nat. Phys.* **10**, 67–72 (note supplementary information). (doi:10.1038/nphys2815)
21. Baeten M, Naudts J. 2011 On the thermodynamics of classical microcanonical systems. *Entropy* **13**, 1186–1199. (doi:10.3390/e13061186)
22. Sommerfeld A. 1951 *Vorlesungen über Theoretische Physik*, vol. V, *Thermodynamik und Statistik* (reprinted 2011, see pp. 181–183). Frankfurt am Main, Germany: Harri Deutsch.
23. Swendsen RH, Wang JS. 2014 Negative temperatures and the definition of entropy. (<http://arxiv.org/abs/1410.4619>)
24. Alemany A, Ribezzi M, Ritort F. 2011 Recent progress in fluctuation theorems and free energy recovery. In *Nonequilibrium statistical physics today: Proc. 11th Granada Seminar on Computational and Statistical Physics, La Herradura, Spain, 13–17 September 2010* (eds PL Garrido, J Marro, F de los Santos). AIP Conf. Proc., vol. 1332, pp. 96–110. Melville, NY: AIP Publishing. (doi:10.1063/1.3569489)
25. Bérut A, Arakelyan A, Petrosyan A, Ciliberto S, Dillenschneider R, Lutz E. 2012 Experimental verification of Landauer’s principle linking information and thermodynamics. *Nature* **483**, 187–190. (doi:10.1038/nature10872)
26. Roldan E, Martinez IA, Parrondo JMR, Petrov D. 2014 Universal features in the energetics of symmetry breaking. *Nat. Phys.* **10**, 457–461. (doi:10.1038/nphys2940)
27. Swendsen RH, Wang JS. 2015 Gibbs volume entropy is incorrect. *Phys. Rev. E* **92**, 020103. (doi:10.1103/PhysRevE.92.020103)
28. Votyakov EV, Hidmi HI, De Martino A, Gross DHE. 2002 Microcanonical mean-field thermodynamics of self-gravitating and rotating systems. *Phys. Rev. Lett.* **89**, 031101. (doi:10.1103/PhysRevLett.89.031101)
29. Callen HB. 1985 *Thermodynamics and an introduction to thermostatistics*, rev. edn, section 8. New York, NY: John Wiley and Sons.
30. Campisi M, Talkner P, Hänggi P. 2009 Finite bath fluctuation theorem. *Phys. Rev. E* **80**, 031145. (doi:10.1103/PhysRevE.80.031145)
31. Hänggi P, Ingold GL, Talkner P. 2008 Finite quantum dissipation: the challenge of obtaining specific heat. *New J. Phys.* **10**, 115008. (doi:10.1088/1367-2630/10/11/115008)

32. Hänggi P, Ingold GL, Talkner P. 2009 Specific heat anomalies of open quantum systems. *Phys. Rev. E* **79**, 061105. (doi:10.1103/PhysRevE.79.061105)
33. Campisi M, Talkner P, Hänggi P. 2009 Thermodynamics and fluctuation theorems for a strongly coupled open quantum system: an exactly solvable case. *J. Phys. A: Math. Theor.* **42**, 392002. (doi:10.1088/1751-8113/42/39/392002)
34. Rényi A. 1961 On measures of entropy and information. In *Proc. Fourth Berkeley Symp. on Mathematical Statistics and Probability*, vol. 1, *Contributions to the Theory of Statistics*, pp. 547–561. Berkeley, CA: University of California Press. (See <http://projecteuclid.org/euclid.bsmmsp/1200512181>)
35. Balthes HP. 1976 *Spectra of finite systems: a review of Weyl's problem*. Zürich, Switzerland: Bibliographisches Institut Mannheim/Wien/Zürich. (See <http://smallsystems.isn-oldenburg.de/Docs/THEO3/publications/spectra.finite.systems.pdf>)
36. Wang JS. 2015 Critique of the Gibbs volume entropy and its implication. (<http://arxiv.org/abs/1507.02022>)