

# The role of temperature in different thermodynamic ensembles

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## I. INTRODUCTION

Let us elaborate on the notion of thermodynamic entropy  $S$  (Clausius 1865) and its consequences within its statistical mechanical description<sup>1</sup>. The celebrated Clausius relation identifies the inverse thermodynamic temperature  $T$  as the integrating factor for the second Law in the form that  $dS = \delta Q/T$ , with  $\delta Q$  being the quasistatic and reversible infinitesimal heat exchange. We first address the most fundamental statistical equilibrium ensemble, namely the microcanonical ensemble (MCE). Please bear in mind that the canonical and the grand canonical ensemble follow from this MCE. – It was J.W. Gibbs who first put forward two notions of thermodynamic entropy for an isolated MCE-system that I commonly will refer to as (i) *volume entropy*, i.e.

$$S_{\text{volume}} := S_G = k_B \ln \Omega(E, Z), \quad (1)$$

where  $k_B$  is the Boltzmann constant and the dimensionless quantity  $\Omega(E, Z)$  is the integrated, non-negative valued density of states (DoS)  $\omega(E, Z)$  over energies not exceeding  $E$ .  $Z$  denotes the set of external control parameters such as the available volume, particle numbers, magnetic field, etc.. Note that within classical statistical mechanics  $\Omega(E, Z)$  equals the properly normalized, dimensionless total available phase space volume up to the energy  $E$ . In this context, Gibbs also considered a second expression, namely the (ii) *surface entropy*, reading

$$S_{\text{surface}} := S_B = k_B \ln[\epsilon \omega(E, \lambda)]. \quad (2)$$

This entropy expression is also known (incorrectly) as the Boltzmann entropy. Here  $\epsilon$  denotes a small energy constant required to make the argument of the logarithm dimensionless. The fact that the definition of  $S_B$  requires an additional energy constant  $\epsilon$  is conceptually displeasing, but bears no relevance for physical quantities that are related to derivatives of  $S_B$ .

Historically<sup>1</sup>, Boltzmann's tombstone famously carries the formula  $S = k_B \log W$ , although, following the discussion by Sommerfeld in his book [reprinted, Vorlesungen über Theoretische Physik (volume V): Thermodynamik und Statistik (Verlag Harri Deutsch, Frankfurt am Main, 2011), pp. 181 - 183] it was Planck, and not Boltzmann, who established this equation. As described in many textbooks, the entropy expression  $S_B$  defined in Eq. (2) is 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  $E$ . Perhaps it is for this reason that the entropy  $S_{\text{surface}}$  is commonly termed 'Boltzmann entropy' nowadays.

The problem thus arises: **Which entropy should we use?** The consistency with the thermodynamics of isolated systems yields a unique answer: The validity for the celebrated 0-th, 1-st and 2-nd thermodynamic Law then uniquely singles out the microcanonical Gibbs entropy  $S_G$ <sup>1</sup>. A different reasoning<sup>2</sup> yielding this very same finding uses the two thermodynamic pillars that for the validity of the (i) Clausius relation as an exact differential the inverse temperature of the (ii) ideal gas law must fix the integrating factor. A profound recent finding is that any microcanonical entropy expression other than the Gibbs volume entropy, – such as for example the Boltzmann entropy –, can lead to thermodynamical inconsistencies<sup>1,2</sup>.

The thermodynamic temperature is a *derived* quantity: Given an entropy expression it is given by

$$T^{-1} = \partial S / \partial E. \quad (3)$$

J.W. Gibbs considered yet another entropy expression  $S_N = -k_B \text{Tr}[\rho \ln \rho]$ , where  $\rho$  is the corresponding thermal equilibrium density function for a  $N$ -particle system. One should stress here that Gibbs used this definition mainly when describing systems weakly coupled to a heat bath within the framework of the canonical ensemble. Nowadays,  $S_N$  is commonly referred to as the *canonical* Gibbs entropy in classical statistical mechanics, as von Neumann entropy in quantum statistics, or as Shannon entropy in information theory.

The most salient results in Ref. [1] and in Ref. [2] are:

- Demanding additivity of  $S$  under *factorization* of  $\Omega(E, Z)$  (which in turn implies energetically decoupled systems that prevent an energy exchange) uniquely selects the logarithm  $\ln$  to yield the microcanonical Gibbs temperature  $T_G$ , reading

$$k_B T_G(E, Z) = k_B [\partial S_G / \partial E]^{-1} = \Omega(E, Z) / \omega(E, Z). \quad (4)$$

Because the DoS  $\omega(E, Z)$  is non-negative, the 'volume'  $\Omega(E, Z)$  is a monotonically increasing function of  $E$ . Thus, the Gibbs temperature necessarily has a definite sign, being always non-negative!

- Only for the Gibbs entropy  $S_G$  does the thermodynamic temperature obey classical equipartition; i.e.,  $k_B T = [\partial S_G / \partial E]^{-1} = \langle \xi_k \partial H / \partial \xi_k \rangle$  with  $\xi_k$  a phase space degree and  $H$  the microscopic Hamiltonian. This feature rules out already the Boltzmann expression  $S_B$  as a consistent thermodynamic entropy. The same remark applies to the thermodynamic generalized forces  $p_i$ . These must obey the consistency relation

$$p_i := T_G \left( \partial S_G / \partial Z_i \right)_E \stackrel{!}{=} - \left\langle \partial H / \partial Z_i \right\rangle_E, \quad (5)$$

for any system of arbitrary size. This consistency relation is violated for the Boltzmann entropy. For a elucidative demonstration of this breakdown of consistency for  $S_B$  see the results for the magnetization of a system of  $N \gg 1$  distinguishable and non-interacting spin 1/2 systems in Ref.<sup>2</sup>

- Although  $S_G$  and  $S_B$  and other entropy candidates often yield practically indistinguishable predictions for the thermodynamic properties of *normal* systems (see in: R. Kubo, *Statistical Mechanics: An Advanced Course with Problems and Solutions* (Elsevier B. V., Amsterdam, 1965), Sec. 1.6 therein), such as quasi-ideal gases with macroscopic particle numbers, they can produce substantially different predictions for mesoscopic, finite systems and ad hoc truncated Hamiltonians with upper energy bounds. This being so, the microcanonical description is thus generally not equivalent with a canonical description.
- Neither the Gibbs temperature nor the Boltzmann temperature do predict the energy flow between weakly coupled systems which were prepared before coupling at initially different temperatures. The naive formulation of the second law that heat always flows from ‘hot’ to ‘cold’ is thus in general not valid; i.e., it does not always (for example, with the DoS exhibiting local maxima) present a strict formulation of the second Law of thermodynamics.

## II. FINITE SYSTEMS: INEQUIVALENCE OF ENSEMBLES AND OPEN PROBLEMS

**Shortcomings** that relate to the thermodynamics of isolated *small* systems are illustrated when sticking to the (Boltzmann)-surface entropy<sup>3,4</sup>. Most of all, the uncritical use of Boltzmann entropy for microcanonical systems may formally yield negative values for the absolute temperatures. This is not only physically incorrect for the concept of an absolute temperature, but also would violate thermodynamic stability if the system is brought into (weak) contact with an omnipresent sort of environment of radiation source or otherwise with no upper bound in energy.

We further address canonical ensemble entropy for

quantum systems that interact *strongly* with an environment. Then, the *canonical* (!) specific heat can assume *negative* values away from absolute zero temperature<sup>5</sup>. Likewise, the thermodynamic entropy for a strongly coupled system, assuming a form close to the quantum conditional entropy, but *not* quite, can be negative away from absolute  $T = 0$ <sup>6</sup>.

**One unsolved problem** is the case for quantum systems with discrete spectra. Here too the volume  $\Omega(E, Z)$  is well defined as the sum over the number of energy eigenvalues, accounting also for the degeneracy of corresponding eigenstates  $E_n$ , so that the quantum Gibbs entropy has a well defined meaning. A small grain of salt occurs nevertheless: All the considerations thus far relied on the technical assumption that the integrated density of states  $\Omega(E, Z)$  is continuous and piecewise differentiable, the latter assumed particularly so with respect to energy  $E$ . As a working principle one may use analytic continuations of the discrete level counting functions  $\Omega(E_n, Z)$  and  $\omega(E_n, Z)$  that are, however, defined strictly speaking only on the discrete set  $E_n$  of isolated points of the spectrum<sup>1</sup>. This procedure yields in parts astonishingly reasonable results. As temperature approaches zero, however, difficulties occur, such as the failure of microcanonical specific heat not approaching zero as  $T \rightarrow 0$ , this despite the fact that  $S_G$  does obey the 3-rd Law at its lowest energy  $E = E_{groundstate}$ . In distinct contrast, coupling the system weakly to a heat bath yields the canonical description of these quantum systems for which the canonical partition function  $Y(\beta, Z)$ , i.e. the Laplace transform of the DoS at the canonical parameter  $\beta := (k_B T_{can})^{-1}$  (being the corresponding integrating factor<sup>2</sup>) becomes well defined at all temperatures. The corresponding canonical specific heat values now vanish for  $T \rightarrow 0$ . This again reflects the non-equivalence between the two ensemble descriptions for finite size quantum systems.

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<sup>1</sup> S. Hilbert, P. Hänggi, and J. Dunkel, *Thermodynamic Laws in Isolated Systems*, Phys. Rev. E **90**, 062116 (2014).

<sup>2</sup> M. Campisi, *Construction of microcanonical entropy on thermodynamic pillars*, arXiv:1411.2425v3.

<sup>3</sup> J. Dunkel and S. Hilbert, *Phase transitions in small systems: microcanonical vs. canonical ensembles*, Physica A **370**, 390 (2006).

<sup>4</sup> M. Campisi, *On the mechanical foundations of thermodynamics: The generalized Helmholtz theorem* *Studies in History and Philosophy of Modern Physics* **36**, 275 (2005).

<sup>5</sup> P. Hänggi, G.L. Ingold, and P. Talkner, *Finite quantum dissipation: the challenge of obtaining specific heat*, New J. Phys. **10**, 115008 (2008); *ibid*, *Specific heat anomalies of open quantum systems*, Phys. Rev. E **79**, 061105 (2009).

<sup>6</sup> M. Campisi, P. Talkner, and P. Hänggi, *Thermodynamics and fluctuation theorems for a strongly coupled open quantum system: an exactly solvable case*, J. Phys. A: Math. Theor. (Fast Track) **42**, 392002 (2009).