

KEY ISSUES REVIEW

Thermodynamics of finite systems: a key issues review

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Key Issues Review

Thermodynamics of finite systems: a key issues review

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Abstract

A little over ten years ago, Campisi, and Dunkel and Hilbert, published papers claiming that the Gibbs (volume) entropy of a classical system was correct, and that the Boltzmann (surface) entropy was not. They claimed further that the quantum version of the Gibbs entropy was also correct, and that the phenomenon of negative temperatures was thermodynamically inconsistent. Their work began a vigorous debate of exactly how the entropy, both classical and quantum, should be defined. The debate has called into question the basis of thermodynamics, along with fundamental ideas such as whether heat always flows from hot to cold. The purpose of this paper is to sum up the present status—admittedly from my point of view.

I will show that standard thermodynamics, with some minor generalizations, is correct, and the alternative thermodynamics suggested by Hilbert, Hänggi, and Dunkel is not. Heat does not flow from cold to hot. Negative temperatures are thermodynamically consistent. The small ‘errors’ in the Boltzmann entropy that started the whole debate are shown to be a consequence of the micro-canonical assumption of an energy distribution of zero width. Improved expressions for the entropy are found when this assumption is abandoned.

Keywords: thermodynamics, statistical mechanics, entropy

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1. Introduction

In recent years, a controversy has arisen about how we are to understand and express some fundamental concepts in statistical mechanics and thermodynamics. The debate has centered on the concept of negative temperatures [1, 2], but it goes much deeper. It has been proposed by some authors [3–15] that:

1. The definition of the thermodynamic entropy should be based on the integral over all points in phase space below the energy of the system, which is referred to as the Gibbs entropy [16]¹.
2. The Gibbs entropy is the only expression consistent with thermodynamics [5].
3. A definition of the entropy in terms of an integral over a constant energy surface in phase space, known as the Boltzmann entropy [17, 18], is rejected.
4. Negative temperatures are excluded due to the structure of the Gibbs entropy [5].
5. The entropy is not additive, i.e. the entropy of a composite system is not given by the sum of the entropies of the individual systems [12]².
6. When two systems are at the same temperature, they will not necessarily be in equilibrium if they are put in thermal contact [12].
7. Heat can flow from cold to hot [12, 15].

¹ I am using the term ‘Gibbs entropy’ to refer to the definition of the entropy in terms of the logarithm of the volume of phase space with energy less than a given energy. It is not to be confused with another definition of entropy due to Gibbs in terms of an integral of $\int \rho \ln \rho$, where ρ is the probability of a microscopic state.

² I am distinguishing additivity from extensivity. The entropies of two systems are additive when $S_{A,B} = S_A + S_B$. The entropy of a system is extensive when $\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$. If a system is homogeneous, additivity implies extensivity.

8. Thermodynamics applies to systems of any size—even a single particle [12, 15].

Other authors, myself included, have disputed these points [19–34]. The most fundamentally important issue in the debate is whether entropy is additive in thermodynamics, but the one that has aroused the most interest is whether negative temperatures provide a consistent description of systems with a decreasing density of states in some energy region.

Since the domain of thermodynamics is part of the debate, I will discuss it in section 2. I am skeptical that thermodynamics can be usefully extended to small systems, but since thermodynamics must at least apply to macroscopic systems, this extension is not important for my arguments.

Some authors view the controversy as solely concerning the choice between the Gibbs expression for the entropy and the Boltzmann expression [12, 13]. I regard this as too limited, since there are better options than either. I will, however, have something to say about this limited controversy in section 5.5.

The situation is complicated by the very different views of thermodynamics taken by the two sides, which makes it difficult to achieve consensus. For this reason, I consider the two opposing descriptions of thermodynamics: the standard version [35–43], as described by Tisza and Callen [44–46], and the alternative proposed by Hilbert, Hänggi, and Dunkel (HHD) [12, 15]. These two may not cover all opinions, but they will provide a starting point for discussion.

The two views of thermodynamics are presented in sections 3 and 4. The most important difference is that standard thermodynamics gives the entropy of a composite system as the sum of the entropies of the individual systems, whether or not there is a constraint restricting the exchange of energy, particles, etc. between the two systems. When a constraint is released, the total entropy is maximized, so that the derivative of the total entropy with respect to the released variable vanishes. This leads to the prediction that two systems at the same temperature can be brought into thermal contact with each other without changing their state. In contrast, HHD reject the additivity of entropy for interacting systems, and regard the prediction that heat flows from hot to cold as ‘naive’ [12].

Another disagreement lies in the precision of thermodynamic predictions. I maintain that thermodynamic fluctuations prevent any measurement of the properties of macroscopic systems from being predicted with arbitrary precision. As a general rule, relative fluctuations are of the order of $1/\sqrt{N}$, where N is the typical number of particles in the system of interest. Repeated measurements of the same property will differ by a corresponding amount.

However, $1/\sqrt{N}$ is usually very small for macroscopic systems. If a system contains 10^{20} particles (less than a thousandth of a mole) the relative uncertainty due to fluctuations will be of the order of 10^{-10} . If only eight or nine digits are required, a unique prediction can be made. Thermodynamics applies to experiments for which there is a sufficient number of particles so that the thermal fluctuations are smaller than the precision of measurement. This means that a single measurement is sufficient to determine the outcome of a thermodynamic experiment. Thermodynamics can be regarded as a

deterministic theory, subject to the limits on the precision of predictions.

This view is not undisputed. The opposing view of HHD is that thermodynamics should predict the exact average value of a quantity of interest [3–15]. Even a discrepancy of the order of $1/N$ is not permitted. However, the form of the entropy that they advocate does not fulfill this strict criterion for all measurable variables.

I will discuss the two microcanonical theories of entropy in statistical mechanics in section 5, including the special case of a first-order transition. Then I will turn to quantum statistical mechanics, which is where negative temperatures most naturally arise. In sections 6 and 7, I will give two expressions for the entropy that do predict the exact averages. I will deal with the problem of continuity [28], which HHD regard as an open problem [15], and show that the thermodynamic entropy should be formulated differently than either the Boltzmann or the Gibbs version [28, 29, 47].

2. The scope of thermodynamics

Among the subjects of disagreement is the question of the domain of applicability of thermodynamics. Traditionally, thermodynamics has been applied to many-body systems, but some of those who oppose the concept of negative temperatures also think that thermodynamics should be extended to very small systems—even down to a system consisting of a single particle. Others, who are mostly not in this group, believe that thermodynamics is only valid in the limit of infinite systems, which has been called the ‘thermodynamic limit’ [48–51]. These three domains are essentially different, implying that a single theory might not be appropriate to describe them all.

2.1. Finite macroscopic systems

What I mean by a ‘finite macroscopic system’ is that the magnitude of the fluctuations for any quantity of interest is substantially smaller than the resolution of the experiments that thermodynamics is intended to describe. If this condition is satisfied, the predictions of statistical mechanics and thermodynamics are deterministic. This is the regime in which thermodynamics is most useful, since it makes unambiguous predictions of the outcomes of experiments.

Gibbs expressed it clearly in the Preface to his book on ‘Elementary Principles in Statistical Mechanics’:

The laws of thermodynamics, as empirically determined, express the approximate and probable behavior of systems of a great number of particles, or, more precisely, they express the laws of mechanics of such systems as they appear to beings who have not the fineness of perception to enable them to appreciate quantities of the order of magnitude of those which relate to single particles, and who cannot repeat their experiments often enough to obtain any but the most probable results [16].

The experimentally observed value of a quantity of interest is predicted to be given by the location of a narrow peak

in the probability distribution for that quantity. The location can be specified in a variety of ways. The mean, the mode, the median, or any quantity that can be shown to be within the range of the peak gives the same value within the resolution of the experiment. Claims to be able to distinguish between the mean and the mode are not experimentally practical. The difference is of order $1/N$, while the width of the peak is of order $1/\sqrt{N}$. To resolve the difference between the mean and the mode of the energy for a system containing as few as 10^{12} particles would require one measurement of better than N -digit accuracy every second for over 30 000 years [27].

A particularly useful feature of the application of thermodynamics to finite macroscopic systems is that only a single measurement is necessary to check a thermodynamic prediction. There are, of course, reasons to make multiple measurements—any experiment must be replicable—but repeated measurements are not required for statistical averaging.

2.2. Small systems

I take a ‘small system’ to mean one for which the fluctuations of a quantity of interest are not smaller than the experimental resolution. There are many such systems that are of great theoretical and experimental importance. Biological molecules, just to name one class of interesting materials, are the subject of major research efforts.

The goal of any theory of the properties of small systems is fundamentally different than that of thermodynamics. Deterministic predictions are essentially impossible due to the inherent fluctuations, which are part of the essential physics.

A difference in applying thermodynamic equations to small systems lies in the necessity of making many measurements to determine the average value of a single quantity. For example, since the probability distribution for quantities of interest are broader than the experimental resolution, repeated measurements are needed to determine the average value of the total energy. For small systems, the details of the fluctuations are almost always of interest, while for macroscopic systems, the fluctuations are too small to measure.

The second law of thermodynamics is not applicable to a small system in its usual form. The fluctuations that make many measurements necessary also mean that a human experimenter can play the role of a kind of Maxwell’s demon. For example, if a small number of particles are moving in a container with a removable partition, simply wait until a large fluctuation is observed, and then insert the partition. A less probable state will be produced, and the entropy will be lowered without doing work on the system.

The problem is further complicated by interactions with other systems that can usually be neglected for finite macroscopic systems. If a system consists of only a few molecules, the exchange of energy with the outside world must involve at least one other atom, the effects of which cannot be neglected at the level of accuracy claimed.

Another aspect of applying thermodynamic equations to small systems is that the desired information is usually very different. For the simplest thermodynamic systems, there

are only three independent variables: energy, volume, and number of particles. Several more variables are needed if the system contains different types of particles or electric or magnetic fields, but that's about all. For small systems, many more variables are of interest. For example, when a biological molecule has two or more long-lived configurations, histograms of the energy and the separation of specific atoms might be important to consider. Statistical mechanics calculations are much more appropriate in this case than thermodynamics.

For these reasons, I do not believe that applying thermodynamic equations to small systems is particularly useful. The subject is too important to be limited by an inappropriate application of thermodynamics.

2.3. Infinite systems

The term 'thermodynamic limit' usually refers to the entropy (or other thermodynamic function) divided by the number of particles (S/N) in the limit of an infinite system ($N \rightarrow \infty$) [48–51]. The name comes from the belief that it is only in this limit that thermodynamics is strictly valid, which is not correct in my opinion. My view is that thermodynamics is valid for finite macroscopic systems, as defined in section 2.1. Furthermore, the limit of $N \rightarrow \infty$ has several disadvantages.

The most obvious disadvantage is that thermodynamics predictions come from using the full entropy and not the entropy per particle. If two systems at different temperatures are put in thermal contact with each other and allowed to come to equilibrium, the final temperature will depend on the relative sizes.

If the behavior of the entropy per particle in the limit $N \rightarrow \infty$ differs qualitatively from that of a corresponding finite macroscopic system, the finite system takes precedence. This is the case for first-order phase transitions, for which some proposed forms of entropy display a region with positive curvature in a plot of S versus U . Such a positive curvature is forbidden by an exact thermodynamic inequality. The magnitude of the positive curvature *diverges* for short-range interactions as $N^{1-1/d}$, where d is the dimension of the system, although the curvature becomes zero for S/N versus U/N in the limit $N \rightarrow \infty$. For long-range interactions, the magnitude of the positive curvature *diverges* as N , and the curvature remains positive for S/N versus U/N in the limit $N \rightarrow \infty$ [47, 49].

If the system is essentially non-extensive, such as a gas that has a container with adsorbing walls, all physics affected by that non-extensive nature will be lost in the limit $N \rightarrow \infty$. For such systems, the thermodynamic limit distorts the true physics.

3. Standard thermodynamics

In this section and the one following it, I compare standard thermodynamics and the version of thermodynamics suggested by HHD, to see how well each satisfies the goal of thermodynamics. This goal has been described by Callen as follows:

The single, all-encompassing problem of thermodynamics is the determination of the equilibrium state that eventually results after the removal of internal constraints in a closed, composite system [45, 46].

It should be noted that determining the state after the imposition of constraints, such as separating two systems in thermal equilibrium, is also part of the fundamental problem. Callen did not mention it because it is trivial in standard thermodynamics. I mention it here because it is not trivial in HHD thermodynamics (see section 4).

Callen's postulates for thermodynamics [45, 46] represented a great advance in understanding the underlying structure of the theory, and codifying the standard views [35–43]. They play an essential role in establishing the mathematical requirements of the entropy, clarifying the reasons for the essential features, and confirming that any suggested form satisfies all necessary conditions.

I have previously proposed modifications of the Callen postulates: Once was for didactic reasons in my book [43], and again to take recent developments into account [34, 52]. I will not repeat the modified postulates from my book, but I will give the original Callen postulates in section 3.1 for comparison with the reduced list of essential postulates in section 3.2. A minimal set of four essential postulates is proposed, together with three optional postulates, for special situations. A more complete description of why each postulate is necessary is in [34].

3.1. Callen's postulates

Before giving his postulates, Callen restricts them to 'simple systems', defined as

systems that are macroscopically homogeneous, isotropic, uncharged, and chemically inert, that are sufficiently large that surface effects can be neglected, and that are not acted on by electric, magnetic, or gravitational fields [45, 46].

The postulates themselves follow.

Callen's Postulate 1:

There exist particular states (called equilibrium states) of simple systems that, macroscopically, are characterized completely by the internal energy U , the volume V , and the mole numbers N_1, N_2, \dots, N_r of the chemical components [45, 46].

I only write the equations for one type of particle (the generalization is trivial), and use N to denote the number of particles, instead of the number of moles.

Callen's Postulate 2:

There exists a function (called the entropy S) of the extensive variables of any composite system, defined for all equilibrium states and having the following property: The values assumed by the extensive parameters in the absence of an internal constraint are those which maximize the entropy over the manifold of constrained equilibrium states [45, 46].

Callen's Postulate 3:

The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy [45, 46].

Callen's Postulate 4:

The entropy of any system vanishes in the state for which $(\partial U/\partial S)_{V,N} = 0$ (that is, at the zero of temperature) [45, 46].

3.2. The essential thermodynamic postulates

Simpler postulates with fewer conditions are sufficient for consistent thermodynamics. A list of the essential postulates, which I have explained in more detail in [34], are given below.

Postulate 1: Equilibrium States

There exist equilibrium states of a macroscopic system that are characterized uniquely by a small number of extensive variables [34].

The term 'state function' is used for a function of the small number of variables necessary to specify an equilibrium state. The primary variables are the extensive ones, which specify quantities.

Postulate 2: Entropy Maximization

The values assumed by the extensive parameters of an isolated composite system in the absence of an internal constraint are those that maximize the entropy over the set of all constrained macroscopic states [34].

This postulate requires that the total entropy cannot decrease when a constraint is released. It also indicates how the new values of the extensive variables can be calculated.

Postulate 3: Additivity

The entropy of a composite system is additive over the constituent subsystems [34].

Additivity means that

$$S_{j,k}(E_j, V_j, N_j; E_k, V_k, N_k) = S_j(E_j, V_j, N_j) + S_k(E_k, V_k, N_k), \quad (1)$$

where S_j and S_k are the entropies of systems j and k . There are no other conditions that the joint entropy must satisfy.

Postulate 4: Continuity and differentiability

The entropy is a continuous and differentiable function of the extensive parameters [34].

The entropy, S , can be shown to be a continuous function of the energy, U , even for finite quantum systems [28].

3.3. Optional thermodynamic postulates

The remaining postulates are important for more limited cases.

Postulate 5: Extensivity

The entropy is an extensive function of the extensive variables [34].

Extensivity means that

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N). \quad (2)$$

This postulate requires the system to be homogeneous. It is not always true, but it is useful for studying bulk material properties.

Postulate 6: Monotonicity

The entropy is a monotonically increasing function of the energy for equilibrium values of the energy [34].

This postulate enables the inversion of $S = S(E, V, N)$ to obtain $U = U(S, V, N)$. Several thermodynamic potentials can then be derived in a familiar form, although this is not necessary. Massieu functions, which are Legendre transforms of the entropy with respect to the energy or the particle number [53, 54], can be used for a general treatment [28, 29, 47].

Postulate 7: Nernst Postulate

The entropy of any system is non-negative [34].

The Nernst postulate, or third law of thermodynamics, has not been phrased here in terms of the limit $(\partial U/\partial S)_{V,N} \rightarrow 0$, as is usual. It is true for all quantum systems.

That completes the set of thermodynamic postulates. Section 3.4 discusses some important consequences of these postulates, which are commonly used, but in conflict with HHD [12, 13, 15]. Section 3.5 will show how the laws of thermodynamics follow from these postulates, and the specific form they take. The results will be compared and contrasted with the HHD formulation of the laws of thermodynamics, which differ in several essential ways.

3.4. Consequences of the postulates

Standard thermodynamics begins with the existence of state functions, which depend on the extensive variables, but do not depend on the history of the system in any way.

The entropy is a particularly important state function, which is assumed to have a variety of properties. The most important property of the entropy is that it goes to a maximum if any internal constraints are released. If, for example, two systems (labelled j and k) are put into thermal contact with each other (the constraint on the exchange of energy between the systems is released), the equilibrium values of the individual energies U_j^* and U_k^* satisfy

$$S_{j,k}(U_j^*, N_j; U_k^*, N_k) \geq S_{j,k}(U_j, N_j; U_k, N_k) \quad (3)$$

for any distribution of the energies U_j and U_k , with fixed total energy $U_{j,k} = U_j + U_k = U_j^* + U_k^*$ and fixed particle numbers N_j and N_k . U_j^* and U_k^* are the equilibrium values of the thermodynamic energy, and are predicted by maximizing the entropy. The same procedure can be applied to any other extensive variable (V , N , etc.) to predict the equilibrium values for any thermodynamic experiment.

From the third postulate (additivity), the entropy of a composite system is the sum of the entropies of the individual systems

$$S_{j,k}(U_j, N_j; U_k, N_k) = S_j(U_j, N_j) + S_k(U_k, N_k). \quad (4)$$

If the entropy is continuous and differentiable (fourth postulate), equation (4) then implies that at equilibrium,

$$\begin{aligned} \frac{\partial}{\partial U_j} S_{j,k}(U_j, N_j; U_{j,k} - U_j, N_k) &= \frac{\partial}{\partial U_j} S_j(U_j, N_j) \\ &+ \frac{\partial U_k}{\partial U_j} \frac{\partial}{\partial U_k} S_k(U_k, N_k) \\ &= 0 \end{aligned} \quad (5)$$

or, since $\partial U_k / \partial U_j = \partial(U_{j,k} - U_j) / \partial U_j = -1$,

$$\frac{\partial}{\partial U_j} S_j(U_j, N_j) = \frac{\partial}{\partial U_k} S_k(U_k, N_k). \quad (6)$$

This last equation requires that if two systems are in equilibrium with respect to energy transfer, $\partial S_j / \partial U_k$ must have the same value as the corresponding property of system k . That property must be some function of the temperature, and comparison with the entropy of the classical ideal gas [43–46] shows it to be the inverse temperature.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V,N}. \quad (7)$$

If this procedure is extended to the other extensive variables, other intensive variables may be derived to describe equilibrium with respect to volume (P/T), particle number ($-\mu/T$), etc.

In summary, standard thermodynamics assumes that the entropies of individual systems (S_j) are known. It then predicts the entropy of an arbitrary composite system, as well as the values of the extensive parameters after release and/or imposition of any constraints.

3.5. The laws of thermodynamics

The laws of thermodynamics were essential to the historical development of the theory. They arise naturally as consequences of the postulates.

The first law of thermodynamics is just the conservation of energy. It is so well established that it is no longer surprising, although the identification of the phenomenon of heat as a form of energy transfer was one of the great achievements of the nineteenth century. It is to be found in (or underlying) all equations of thermodynamics, most explicitly in the form,

$$dU = \bar{d}Q + \bar{d}W, \quad (8)$$

where dU is the differential change in the internal energy of a system, $\bar{d}Q$ is the heat added to the system, and $\bar{d}W$ is the work done on the system (the symbol \bar{d} indicates an inexact differential).

The second law of thermodynamics is a direct consequence of the second essential postulate. It can be written as

$$\Delta S \geq 0, \quad (9)$$

where ΔS indicates a change of the total entropy upon release of any constraint.

The third law of thermodynamics is also known as the Nernst postulate. It has been discussed in section 3.3.

The zeroth law of thermodynamics was the last to be named. It was recognized to be of great importance, but the laws numbered 1–3 were already well established. It is given by Fowler and Guggenheim [36] in the form

If two assemblies are each in thermal equilibrium with a third assembly, they are in thermal equilibrium with each other.

It is a direct consequence of equation (6), which follows from essential postulates 2 and 3.

Next, I consider the alternative version of thermodynamics presented by Hilbert *et al* in [12], and elaborated by Hänggi *et al* in [15].

4. HHD thermodynamics

The HHD version of thermodynamics differs radically from the standard version, with far-reaching implications [12, 15]. For clarity, throughout this section the HHD entropy and other thermodynamic functions will be denoted by the subscript ‘HHD’.

Although HHD always use the subscript ‘G’ (Gibbs) for their entropy, I have not found any evidence that Gibbs himself advocated the HHD thermodynamic principles that are discussed in this section. The Gibbs entropy is defined in section 5.2. It may be used with either HHD or standard thermodynamics.

An essential assumption of HHD thermodynamics is that each system that it applies to has a single, well-defined energy. This does not mean that the width of the energy distribution is approximated by a delta function because it is very narrow; it means that the energy is specified exactly for a classical system, and is given by an exact energy eigenvalue for quantum systems. Since thermal contact between two systems leaves them with broadened energy distributions when they are separated, HHD thermodynamics does not apply to such individual systems [15]. This is also discussed in section 8.5.3.

4.1. HHD temperature

The temperature in the HHD version of thermodynamics is defined by an equation which looks superficially like equation (7) for standard thermodynamics

$$\frac{1}{T_{\text{HHD}}} = \left(\frac{\partial S_{\text{HHD}}}{\partial U} \right)_{V,N}. \quad (10)$$

However, since HHD reject equation (6) (which equates the corresponding partial derivatives with respect to energy in two systems in thermal contact) as being ‘naive’ [12], the HHD temperature cannot be justified by the same arguments that led to equation (7). In [12] this equation for the temperature is ‘obtained according to the basic rules of thermodynamics by partial differentiation’, and in [15] they state that equation (10) ‘defines the thermodynamic temperature’. Since HHD offer no other reason for regarding T_{HHD} as the temperature, it must

be regarded as an unproved assumption of their theory. This is an important point because the HHD definition of temperature is essential to their assertion that heat can flow from a cold object to a hot object.

T_{HHD} can also take on the same value for different states of a given system [12, 15].

4.2. HHD entropy for a composite system

HHD thermodynamics is really a combination of thermodynamics and statistical mechanics. The HHD entropy of a composite system is not the sum of the entropies of the individual systems, *unless* the individual systems are *not* in thermal equilibrium with each other. If the individual systems are in thermal equilibrium with each other, a separate calculation in statistical mechanics is necessary to find the total HHD entropy. The entropy of the composite system cannot be obtained from the entropies of the individual systems by any obvious operation.

Every time a constraint is released, a new calculation in statistical mechanics is required. As a consequence, HHD thermodynamics is not fully determined by specifying the M entropy functions of the M individual systems. It also requires $M(M-1)/2$ entropy functions for interactions involving two systems, $M(M-1)(M-2)/6$ entropy functions for interactions involving three systems, and so on. For a complete evaluation of the conditions of thermal equilibrium, a total of $2^M - 1$ calculations of entropy would be necessary, in contrast to M calculations of the individual entropy functions for standard thermodynamics.

4.3. HHD reject additivity

In his book, ‘Elementary Principles in Statistical Mechanics’, Gibbs wrote that,

The most simple test of the equality of temperature of two bodies is that they remain in equilibrium when brought into thermal contact [16].

The additivity of entropy requires the Gibbs test to be valid (see section 3.4), but HHD reject it, calling this position ‘naive’ [12, 15].

The Gibbs test for the equality of temperatures is *not* satisfied by the Gibbs entropy with standard thermodynamics *when applied to a decreasing density of states*. Consequently, to maintain the viability of the Gibbs entropy, HHD thermodynamics rejects additivity.

However, additivity is a necessary consequence of the second law. Consider two isolated systems, A and B , with entropies S_A and S_B . Assume that if they are brought together, ‘there would be no net energy transfer between the systems’ [12]. Denote their joint entropy after they are brought into thermal equilibrium as $S_{A,B}$. Then $S_{A,B} \geq S_A + S_B$, to avoid an immediate violation of the second law. Next, separate A and B . Now $S_A + S_B \geq S_{A,B}$, again to avoid a violation of the second law. The only way to satisfy both inequalities is for $S_A + S_B = S_{A,B}$, which is the condition of additivity.

In rejecting additivity, HHD have conceded that their thermodynamics can make no prediction of anything measurable for a system whose energy is not known exactly. Normal $1/\sqrt{N}$ fluctuations due to previous contact with another system are sufficient to exclude a prediction [15].

The cause of these limitations is the doctrine that HHD thermodynamics only applies to systems with a precisely specified energy. Although the usual interpretation of the Boltzmann entropy is that it makes an approximation to the very narrow real energy distribution, this is not the case for HHD thermodynamics [12, 15]. Since all systems that have been in thermal contact with another system exhibit fluctuations of order $1/\sqrt{N}$, it is hard to avoid concluding that HHD thermodynamics has no application in the real world.

4.4. HHD entropy is not a function of the extensive observables

Unlike standard thermodynamics (see Postulate 1 in section 3.2) the entropy in HHD thermodynamics is not a function of the extensive variables alone [12, 15]. For magnetic systems, they define entropy to be a function of magnetic field, instead of magnetization. From one point of view, there is nothing wrong with this; the entropy as a function of the magnetization is a valid equation of state. However, it is not a fundamental equation, from which all thermodynamic information can be obtained [43, 45, 46].

The use of magnetic field as the independent variable is the origin of the incorrect results obtained by Campisi for the magnetization as a function of energy [13]. The error was ascribed to the Boltzmann entropy, but a calculation starting from the entropy as a function of magnetization gives the correct answer. Abraham and Penrose have also commented that a calculation starting from the entropy as a function of magnetic field is ambiguous [33].

HHD thermodynamics is also primarily a theory of the energy dependence of the entropy. There is no procedure, such as that described in the previous section for thermal equilibrium, for calculating the entropy when two systems exchange particles. Presumably, another calculation in statistical mechanics is necessary. Such calculation would inevitably involve $N!$ and show a relative error of order $\ln(N)/N$, which is even larger than the relative error of $1/N$ that they objected to in the first place.

4.5. The HHD versions of the laws of thermodynamics

Instead of basing their version of thermodynamics on postulates, HHD give their own version of the laws of thermodynamics. They are worth examining in detail since they differ from the usual expressions in crucial ways.

4.5.1. HHD’s zeroth law. For the zeroth law, HHD mention the formulation:

If two systems A and B are in thermal equilibrium with each other, and B is in thermal equilibrium with a third system C , then A and C are also in thermal equilibrium with each other [12].

This phrasing seems quite reasonable. However, they limit their interpretation of ‘thermal equilibrium’ to systems actually in thermal contact.

Two systems are in thermal equilibrium, if and only if they are in contact so they can exchange energy, and they have relaxed to a state in which there is no average net transfer of energy between them anymore [12].

HHD also define ‘potential’ thermal equilibrium as:

Two systems are in potential thermal equilibrium if they are not in thermal contact, but there would be no net energy transfer between the systems if they were brought into (hypothetical) thermal contact [12].

They do not regard potential thermal equilibrium as being equivalent to thermal equilibrium, except in the special case that the two separated systems were in thermal equilibrium and have not subsequently been in contact with any other systems (see [15] and section 8.5).

The total HHD entropy of two systems is different depending on whether they are in thermal equilibrium or potential thermal equilibrium, even if no macroscopic measurement can distinguish between the two cases [15].

HHD reject the usual interpretation of using either thermal equilibrium or potential thermal equilibrium in the expression of the zeroth law, claiming that,

none of the considered temperature definitions satisfies this requirement [12].

Actually, T_B only has an error of order $1/N$, which is much less than the $1/\sqrt{N}$ -fluctuations and experimentally unmeasurable for macroscopic systems [27]. T_C and T_{GC} satisfy the condition for potential equilibrium exactly. It is only T_G that seriously fails to satisfy the requirements of the usual zeroth law.

HHD’s final version of the zeroth law is that

One can assign to every thermal equilibrium system a real-valued ‘temperature’ T , such that the temperature of any of its subsystems is equal to T [12].

Since the HHD version of the zeroth law restricts attention to systems that are in thermal contact with each other, it does not confront the difficulty of having seven distinct values of T_G to choose from when the systems are separated, as had been pointed out earlier [27]. This ambiguity prevents the construction of a thermometer to measure T_G .

4.5.2. HHD’s first law. The first law of thermodynamics is the conservation of energy, which is not controversial.

4.5.3. HHD’s second law. The second law is quite different in HHD from its form in standard thermodynamics. As mentioned in section 4.2, in HHD thermodynamics the total entropy of two or more systems in equilibrium with each other is not obtained from the entropies of its constituent systems, but from a separate calculation in statistical mechanics. Furthermore, the calculation only produces the total entropy as a function of the total energy, $S_{\text{HHD},j,k}(E_j + E_k, N_j, N_k)$. As a

consequence, the HHD entropy of a composite system is independent of the distribution of energy between the individual systems. The equilibrium values of the energies of the individual systems, E_j^* and E_k^* , cannot be determined by the location of the maximum of the entropy [15]. As far as I have been able to tell, the equilibrium values cannot be predicted in any other way by HHD thermodynamics. The equilibrium values E_j^* and E_k^* remain unknown until they are measured [15].

Imposing a constraint by separating two systems that were in equilibrium with each other creates a special problem, because each system now has a width to the energy probability distribution. Since the entropy is only defined for a system with a unique energy, it is not defined for the individual systems after they are separated [15]. The view of HHD is that the two systems are still in equilibrium with each other after they have been separated, and still have a total entropy of $S_{\text{HHD},j,k}(E_j + E_k, N_j, N_k)$ until they interact with a third system.

In 2015, Wang and I published an argument challenging the claim that HHD thermodynamics always satisfied the second law [27]. Our argument showed that the joint entropy was strictly greater than the sum of the individual entropies,

$$S_{\text{HHD};1,2}(E_1 + E_2) > S_{\text{HHD};1}(E_1^{\text{eq}}) + S_{\text{HHD};2}(E_2^{\text{eq}}), \quad (11)$$

where E_1^{eq} and E_2^{eq} were the equilibrium values of the energies of the individual systems after they were separated. Therefore, we concluded that the total entropy decreased when the systems were separated.

HHD objected as follows:

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 [27], who recently criticised the Gibbs entropy [15].

We had assumed that the entropies of systems 1 and 2 would be state functions in HHD thermodynamics, as they are in standard thermodynamics. Apparently, this is not the case. It is true that the individual energies would be not be known *exactly*, but they should be calculable with sufficient accuracy to demonstrate the violation of the second law. The point that we missed was that HHD thermodynamics is saved from making the incorrect prediction that $\Delta S < 0$, by making no prediction at all.

It is quite true that even if the individual systems were in an exact energy state before the experiment, they would not be afterwards [28]. Apparently, in the absence of a measurement of the *exact* energy, HHD thermodynamics makes no prediction.

In this connection, the quote from HHD’s [15] in this subsection includes the remarkable statement that, ‘thermal

coupling is irreversible', which would make the analysis of the Carnot cycle impossible if it were true.

4.5.4. *HHD's third law.* HHD did not discuss the third law (Nernst postulate), but no disagreement is expected.

4.6. Difficulties with three systems

HHD thermodynamics difficulties increase if three systems are considered.

Imagine three systems that somehow start in exact energy states, E_A , E_B , and E_C . Systems A and B are brought to equilibrium with each other and then decoupled. Systems A and B are now in equilibrium with each other and their total entropy, $S_{\text{HHD},A,B}(E_A + E_B)$, is found from a calculation in statistical mechanics. The individual energies E_A^* and E_B^* are unknown, because HHD thermodynamics makes no prediction. Now bring system B into thermal equilibrium with system C , and later separate them. The new energies E_B^{**} and E_C^{**} are unknown, and their sum is unknown. The situation is now that: (1) A is still in equilibrium with B , but its energy E_A^* is unknown, and its share of the entropy $S_{\text{HHD},A,B}(E_A + E_B)$, is also unknown, (2) B is not in equilibrium with A . B is in equilibrium with C , but the energy E_B^{**} is unknown, (3) C is in equilibrium with B , but its energy E_C^{**} is unknown, (4) the joint entropy of B and C is unknown because the total energy of B and C , $E_B^* + E_C = E_B^{**} + E_C^{**}$ is also unknown.

It is easily demonstrated that standard thermodynamics correctly calculates the final energies E_A^* , E_B^{**} , and E_C^{**} , along with the final entropies $S_A(E_A^*)$, $S_B(E_B^{**})$, and $S_C(E_C^{**})$.

4.7. A basic question about HHD thermodynamics

Given the restriction of the applicability of HHD thermodynamics to systems with precisely specified energy, the question arises as to whether any such systems exist. I agree with HHD that after a system has been in thermal equilibrium with another system it does not have a precisely specified energy [28]. However, every system has been in contact with another system at some point in its history, which would seem to contradict the basic HHD assumption about the initial conditions for their thermodynamics.

The point is an important one. If HHD decide to abandon the restriction to systems with exactly known energies and say that the HHD entropy also applies to systems with a narrow energy distribution, they are subject to Wang and my demonstration that their entropy violates the second law [52].

5. The Boltzmann entropy and the Gibbs entropy

5.1. The classical model

Since the Callen postulates determine equilibrium by maximizing the entropy after the release of constraints in a composite system, it is appropriate to construct such a composite system from $M \geq 2$ systems that we are interested in (M can be very large, since all systems that might exchange energy,

volume, or particles should be included). Assume that interactions between systems may be neglected. Then, the total Hamiltonian is the sum of contributions from each system

$$H_T = \sum_{j=1}^M H_j(E_j, V_j, N_j). \quad (12)$$

The energy, volume, and particle number of system j are given by E_j , V_j , and N_j ³. The entire set of M systems is assumed to be isolated, with the sums given by,

$$\sum_{j=1}^M E_j = E_T, \quad \sum_{j=1}^M V_j = V_T, \quad \sum_{j=1}^M N_j = N_T, \quad (13)$$

where E_T , V_T , and N_T are constants. Only $3(M - 1)$ of the variables are independent.

The range of the interactions within a system is not restricted. Homogeneity is not required, so extensivity is not generally expected⁴.

The probability distribution for the macroscopic variables $\{E_j, V_j, N_j | j = 1, 2, \dots, M\}$, can be derived from the assumption of a uniform probability distribution in phase space [32, 34, 55–57].

5.2. Classical S_B and S_G

The total Boltzmann entropy can be defined as the logarithm of the probability distribution. Since the mode of the probability distribution can be used to locate a narrow peak, the Boltzmann distribution is guaranteed to predict the equilibrium values of the macroscopic variables.

The one exception is the case of a first-order phase transition, for which the probability distribution is very broad. In this case, the Boltzmann entropy fails to give the thermodynamic entropy, although it does prove useful in the analysis of first-order phase transitions [4, 58–60]. The problem is that, in this case, the Boltzmann distribution has a region of positive curvature, which is forbidden by an exact thermodynamic inequality [34, 43, 45, 46].

The Boltzmann entropy for the j th system is

$$S_{B,j} = k_B \ln \left[\frac{1}{h^{3N_j} N_j!} \int_{-\infty}^{\infty} dp_j^{3N_j} \int_{V_j} dq_j^{3N_j} \delta(E_j - H_j) \right]. \quad (14)$$

It was derived by Boltzmann under the assumption that equilibrium corresponded to the maximum probability when a constraint between two systems is released [17, 18, 56]⁵. Boltzmann only considered the energy dependence in his derivation, but otherwise, it was essentially the same.

The Gibbs entropy is given by

³ I will only write the equations for a single type of particle. The generalization to a variety of particles is trivial, but requires indices that might obscure the essential argument.

⁴ I am distinguishing extensivity from additivity. The entropy of a system is extensive when $\lambda S(U, V, N) = S(\lambda U, \lambda V, \lambda N)$. The entropies of two systems are additive when $S_{A,B} = S_A + S_B$.

⁵ Equation (14) is not dimensionally correct as it stands and there should be a multiplicative constant with units of energy to make the argument of the logarithm dimensionless. Since this has the effect of adding a constant to the entropy that has no effect on any measurable quantity, this is usually ignored.

$$S_{G,j} = k_B \ln \left[\frac{1}{h^{3N_j} N_j!} \int_{-\infty}^{\infty} dp_j^{3N_j} \int_{V_j} dq_j^{3N_j} \Theta(E_j - H_j) \right] \quad (15)$$

where $\Theta(\cdot)$ is the unit step function. Gibbs showed that this equation satisfied all the properties he was interested in, subject to the conditions that classical mechanics was used and the density of states increased with energy [16]. In 1910, Hertz proved that S_G was adiabatically invariant under the same conditions [61].

First-order phase transitions were not discussed in either paper nor was the question of negative temperatures.

5.3. Quantum S_B and S_G

Planck defined the Boltzmann entropy for quantum mechanical systems as (the Boltzmann constant times) the logarithm of the degeneracy of each eigenstate [62, 63].

The quantum version of the Gibbs entropy was defined as the logarithm of the sum of degeneracies for energy eigenvalues less than or equal to the energy of interest.

5.4. Comparison of S_B and S_G

Both S_B and S_G are only defined for quantum systems on a discrete set of points, although entropy should be a continuous function of energy [28].

Both S_B and S_G fail to give an entropy that satisfies the exact thermodynamic inequality that demands that the curvature of S versus U must be negative [43, 45, 46]

$$\left(\frac{\partial^2 S}{\partial U^2} \right)_{V,N} \leq 0. \quad (16)$$

For both classical and quantum mechanics, S_B and S_G assume that the number of particles, N , is known exactly. Actually, if the system of interest has ever exchanged particles with another system, N is not known exactly and $\langle N \rangle$, which is a continuous variable, should be used instead.

For classical models, S_B predicts the mode of the probability distribution for all thermodynamic experiments. Since the mode differs from the mean by order $1/N$, it does not predict the mean exactly, although the difference is not measurable for a macroscopic system [52]. The use of the mode has been regarded as a fault by critics of the Boltzmann entropy because it is associated with a violation of adiabatic invariance of order $1/N$ (also unmeasurable).

S_G gives the exact energy versus temperature equation for classical systems with a positive slope of the density of states versus energy. It also gives an exact prediction of equilibrium energy for thermal equilibrium (under the same conditions) using standard thermodynamics. This is not the case for quantum systems; S_G has only a small error (again under the same conditions), but it is not exact.

For a negative slope of the density of states versus energy, S_B predicts the correct location (of the mode) of equilibrium energy for thermal equilibrium using standard

thermodynamics, while S_G does not even come close [12, 27]. As discussed in section 4.5.3, HHD thermodynamics does not make predictions of equilibrium energy for thermal equilibrium.

5.5. The limited controversy

As I mentioned in the Introduction, some authors view the controversy as being limited to a choice between S_B and S_G [12, 13] I think that this is an unreasonable restriction and I will explain my own opinion of the best definition of entropy in the following section. However, it seems clear that the argument against S_B is basically the $(1/N)$ -error in the energy, which is unmeasurable. The argument against S_G is the easily measurable error in the energy in thermal equilibrium (using standard thermodynamics) or the failure to predict any energy (using HHD thermodynamics). In my opinion, being measurable wins and I favor the Boltzmann entropy.

6. The canonical ensemble

The relationship between the partition function for the canonical ensemble, Z , and the Helmholtz free energy, $F = -k_B T \ln Z$, is well known from textbooks [43, 45, 46]. The Helmholtz free energy can be found by the Legendre transform $F = U[T] = U - TS$, where the transformed variable is indicated by enclosing it in square brackets. Massieu functions use a Legendre transform of the entropy with respect to the energy (or the number of particles) for the same purpose. The use of Massieu functions is somewhat less well known, but the Legendre transforms are essentially the same. It is easy to show that $S[\beta]/k_B = \ln Z$ [34]. All thermodynamic functions can be calculated by standard methods. In addition, $S[\beta]$ is well defined for negative values of β .

There is an approximation inherent in the microcanonical ensemble in statistical mechanics that is well-known, but its importance has not always been appreciated. The microcanonical ensemble assumes that the microscopic energy is specified exactly, which is a reasonable approximation since the true width of the distribution is of order $1/\sqrt{N}$, which is assumed to be less than the experimental resolution. However, the non-zero width of the energy distribution plays a significant role in the theory and is responsible for the difference in the energy dependence of the Boltzmann and the Gibbs entropies. If we eliminate this approximation, we find two other definitions of entropy. I will show that both of these are superior to either the Gibbs or the Boltzmann entropies.

6.1. The justification of the canonical entropy

From the thermodynamic point of view, if system X has been in thermal equilibrium with system Y and then separated from it, it can be characterized by its temperature. Although the width of the energy distribution is known to depend on the size of system Y [64], this does not affect the thermodynamic state of the system X . In fact, there is no way to determine the size of system Y through a thermodynamic

measurement of system X . In particular, the entropy of system X does not depend on the size of system Y . Therefore, $S_{C,X}[\beta]/k_B = \ln Z$ (where $S_{C,X}[\beta]$ is the Legendre transform with respect to β , and Z is the canonical partition function) can be calculated as if system Y were arbitrarily large [34]. A Legendre transform will then give the canonical entropy, $S_{C,X}(U_X, V_X, N_X)$.

The independence of the entropy on the size of the system it has been in contact with can be illustrated as follows. Consider three macroscopic systems labeled X , Y , and Z . Let systems X and Y be of the same composition and to be equal in size. Let system Z be much larger than X and Y .

Put three systems are in thermal contact and have them come to equilibrium. The entropies of systems X and Y are then equal, and each given by the canonical entropy.

Now remove system Z from thermal contact with the other two systems. This is obviously a reversible process in standard thermodynamics. By the zeroth law, X and Y are still in equilibrium with each other at the same temperature as before Z was removed. For consistency, the entropies must be unchanged. If the entropy were to decrease, it would be a violation of the second law of thermodynamics (and the second essential postulate). If the entropy were to increase upon separation, putting system Z back into thermal contact with systems X and Y would decrease the entropy, which would also violate the second law. The only possibility consistent with the second law is that the entropy is unchanged.

Another way to see this is to consider that a thermometer should not affect the thermodynamic state of a system, even though it is almost always much smaller than the system of interest.

Therefore, the canonical entropy is appropriate for all systems and sizes, regardless of their history.

6.2. Examples of the canonical entropy

The calculation of the canonical partition function is given for the classical and quantum cases in most textbooks on statistical mechanics [37, 39–41, 43]. The only change from the usual procedure is to set $S_C[\beta]/k_B = \ln Z$ and preform a Legendre transform to find $S_C(U, V, N)$

As an example, consider the classical ideal gas, which has the canonical entropy given in equation (17) [34]

$$S = k_B \left[N \left(\frac{3}{2} \right) \ln \left(\frac{U}{N} \right) + \ln \left(\frac{V^N}{N!} \right) + N \left(\frac{3}{2} \right) \ln \left(\frac{4\pi m}{3h^2} \right) + \frac{3N}{2} \right]. \quad (17)$$

Note that the term containing the energy dependence is exactly extensive, while the second term (containing V) is only extensive in Stirling's approximation. The energy equation, $U = (3/2)Nk_B T$, is also exact, while the usual Boltzmann entropy gives a small error of order $1/N$.

For a quantum example, consider a system composed of independent two-level objects, with the energies of the two levels denoted as 0 and ϵ [28]. If we then define a dimensionless energy of the system as

$$y = \frac{U_{2\text{-level}}}{N\epsilon}, \quad (18)$$

the canonical entropy is then

$$S_{C,2\text{-level}} = -Nk_B [y \ln y + (1 - y) \ln(1 - y)]. \quad (19)$$

This canonical entropy for a set of independent two-level objects is exactly extensive, although neither the Boltzmann nor the Gibbs entropies are. The Gibbs entropy is qualitatively wrong for energies $y > 1/2$, which can be seen from figure 1 of [28].

7. The grand canonical ensemble

The grand canonical entropy is calculated in much the same way as the canonical entropy, but using the grand canonical partition function \mathcal{Z} .

7.1. The definition of the grand canonical Legendre transform

I will use $S[\beta, (\beta\mu)]$ for the grand canonical ensemble, so that we can treat negative temperatures. The second variable is in parentheses to emphasize that the product of β and μ is to be treated as a single variable. The Legendre transform with respect to both β and $(\beta\mu)$ to show that

$$S[\beta, (\beta\mu)]/k_B = \ln \mathcal{Z}. \quad (20)$$

The derivation is straightforward, but the use of the Massieu function might not be familiar. Details are in [34].

I'll show an explicit result for the classical ideal gas because it illustrates the dependence of the entropy on continuous energy ($U = \langle E \rangle$) and particle number (N). It also gives an entropy that is exactly extensive, which should be expected because the ideal gas particles are completely independent

$$S = \langle N \rangle k_B \left[\frac{3}{2} \ln \left(\frac{U}{\langle N \rangle} \right) + \ln \left(\frac{V}{\langle N \rangle} \right) + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2} \right) + \frac{5}{2} \right]. \quad (21)$$

8. Alternate views

8.1. Early work

Gibbs first wrote down what is now known as the Gibbs entropy in 1902 [16]. He demonstrated that this form of the entropy satisfied all requirements of thermodynamics under two restrictions: (1) classical physics, and (2) increasing density of states with energy.

In 1910, Hertz demonstrated that the Gibbs entropy is an adiabatic invariant, but that the Boltzmann expression was not. The error in the Boltzmann entropy was of order $1/N$. The demonstration had the same limitations as Gibbs.

8.2. Dunkel and Hilbert

In 2006, Dunkel and Hilbert presented an interesting analysis of transition in small systems using the Gibbs entropy, which they called the Hertz entropy [6]. Their analysis is fine, but they do not

make a case for the Gibbs (Hertz) entropy being the thermodynamic entropy.

In 2014, Dunkel and Hilbert published a paper with the title, ‘consistent thermostatics forbids negative absolute temperatures’, which also states its major conclusion [10]. Frenkel and Warren disputed this claim, pointing out that if two systems with the same Gibbs temperature were brought together, they would not necessarily be in equilibrium [20]. Wang and I carried out a simulation along the lines Frenkel and Warren had suggested and, as expected, the two systems were not even close to equilibrium [27]. Dunkel and Hilbert responded that T_G did satisfy the requirements of thermodynamics because after they had been brought together, ‘each of the subsystems has the same temperature’ [11]. However, Frenkel and Warren were talking about the temperatures of the two (sub)systems *before* they were brought into thermal contact, which is not the same thing. A similar weakening of the zeroth law in HHD thermodynamics was discussed in section 4.5.1.

8.3. Campisi

Campisi has published a clever proof that the Gibbs entropy is correct, but it has certain limitations [13]. He bases his proof on two ‘thermodynamic pillars’: (1) dQ/T is an exact differential, and (2) $PV = k_B NT$. He claims that the first pillar implies that the entropy must be ‘entropy must be some function of the phase volume’, which seems unlikely, since S_C is not a function of the phase volume and still predicts the ideal gas law. The use of the ideal gas law as a pillar limits the proof to positive (Boltzmann) temperatures. He is supporting the work of Gibbs and Hertz, and is limited in the same way. Campisi’s claim that the volume entropy is unique is incorrect.

8.4. Romero-Rochín

Romero-Rochín has claimed ‘that states of macroscopic systems with purported absolute negative temperatures are not stable under small, yet arbitrary, perturbations’ [9]. By ‘perturbation’, he means contact with another system, and by ‘small’, he means that the other system is small. The term ‘arbitrary’ is misleading. He is limiting the other system to one that can only support positive temperatures. Such systems can absorb arbitrarily large amounts of energy independent of size.

When a system that exhibits a negative temperature is brought into contact with a system that only supports positive temperatures, the final equilibrium temperature is positive. In that, Romero-Rochín is correct.

However, if the second system can also support negative temperatures, the final inverse equilibrium temperature can be anywhere between the two initial inverse temperatures, depending on the relative size of the systems. If both systems started with negative temperatures, the final equilibrium will be at a negative temperature.

8.5. Hänggi, Hilbert and Dunkel

8.5.1. Criticism of the Ising model. In their subsection 2.v of [15], HHD claim that ‘Ising models are bad benchmarks’. They argue that, ‘there exists no evidence to date for strict upper energy bounds’ on Hamiltonians. HHD seem to have a particular aversion to an $E \rightarrow -E$ symmetry, although they only argue against models with an upper bound on the energy. They did not comment on the argument that these lattice models depend only on a dimensionless parameter $K = J/k_B T$ (where J is an energy parameter). One might expect that the entropy only depends on K , as it does for standard thermodynamics, but the Gibbs entropy is very different for $J > 0$ and $T > 0$, and $J < 0$ and $T < 0$, even if K is the same in both cases.

It should be noted that energy in the model that Ramsey used to describe his experiments was bounded from above [2].

The Ising model has proven itself to be quite valuable, as have Potts models, Ashkin–Teller models, xy -models, ice models, eight-vertex, and hard-hexagon models [65]. Both the thermodynamics and the statistical mechanics of such models is extremely interesting and have found broad applications. I would hate to see them banished from consideration. There is no difficulty in dealing with these models in standard thermodynamics.

8.5.2. ‘Open questions’. In section 4 of [15] marked ‘Open questions’, HHD address the issue of the discrete spectrum of quantum systems and write that, ‘the construction of a differentiable DoS requires some sort of smoothing procedure’. The discrete set of energies included in the microcanonical ensemble is due to the neglect of linear combinations of eigenstates [28]. Calculations in [28] and [29] show that a smoothing procedure is not an appropriate way to deal with the missing states, S_B and S_G are systematically lower than the correct entropy curve.

8.5.3. Criticism of myself and Wang. In [15] HHD criticized of my work and that of Wang. They wrote:

Last and not least, some authors [26, 27, 52] 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 [15].

The citations [27, 52] are by Wang and myself. We discussed only *finite* systems, and not *infinite* systems as HHD claimed.

Reference [26] is by Wang. He did mention the thermodynamic limit, but he equated the limit $N \rightarrow \infty$ with ‘large systems’⁶. In any case, none of his arguments relied on the limit $N \rightarrow \infty$.

On the other hand, a criticism of HHD that used the limit $N \rightarrow \infty$ would still be valid.

⁶ In [26] Wang commented, ‘We do not need to take N literally to infinity’.

The ‘modified versions of the thermodynamic laws’ HHD refer to are described in section 3.5. I believe that they represent the standard view [35–45, 46].

HHD continue:

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 [15].

The predictions of S_B have a discrepancy of the order of $1/N$ with HHD’s equations (2.5) and (2.6). Compared to the fluctuations of order $1/\sqrt{N}$, these deviations are unmeasurable [27]—they certainly do not represent ‘a steep price’. S_B satisfies the inequality in HHD’s equation (2.7) exactly. The expressions for the thermodynamic entropy that I advocate, S_C and S_{GC} , satisfy HHD’s equations (2.5)–(2.7) exactly.

HHD have another criticism of our work.

Moreover, instead of focusing on the discussion of abstract postulates [52], 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 [15].

As I showed in section 4, while standard thermodynamics makes accurate predictions for all thermodynamic experiments, HHD thermodynamics does not. It avoids incorrect predictions by not making predictions. If the apparent impossibility of constructing a thermometer to measure T_G is taken into account, HHD thermodynamics makes no testable predictions.

9. Summary

9.1. Small systems and HHD thermodynamics

Throughout this paper, I have assumed that thermodynamics must be valid for finite macroscopic systems, and that HHD were claiming that they had extended thermodynamics to apply to small systems. There is another possibility. Perhaps they meant (although they did not say so) that HHD thermodynamics is intended to apply *only* to small systems. That would be consistent with their comment in connection with the example discussed in [15] and section 4.5.3 that ‘thermal coupling is irreversible’. This statement makes no sense when applied to finite macroscopic systems, but it can be understood for small systems. If the width of the energy distribution before thermal coupling is too narrow to be resolved, but after thermal coupling the energy fluctuations are large enough to be observed, the situation could be regarded as showing an irreversible change. The failure to predict the exact energy after separation would also be consistent with this interpretation because a repetition of the experiment would result in a different energy. It would also explain why HHD thermodynamics fails to give an entropy to the individual systems after separation, since their energies are unknown. However,

HHD thermodynamics still fails to predict the average energy, or any other measurable quantity. Standard thermodynamics and the (grand) canonical entropy would predict the average energy correctly. I have to conclude that limiting HHD thermodynamics to small systems does not save it.

9.2. The future

I have shown that HHD thermodynamics is not an acceptable theory. Standard thermodynamics is consistent and the additivity of entropy is valid. Heat flows only from hot to cold. Negative temperatures are thermodynamically consistent.

The microcanonical assumption that thermodynamic systems have a precisely specified energy must be viewed as an approximation, not an exact reflection of reality. In quantum mechanics, demanding that a system be in an eigenstate ignores all states that can be formed by linear combinations of eigenstates [28]. If the discreteness of the energy and the particle number is ignored, the Boltzmann entropy gives excellent results (away from a first-order transition).

The two expressions for the entropy that are the most valuable, the canonical and the grand canonical, have been known for a very long time. However, it has not always been recognized that they are generally applicable to interactions between finite systems.

For future work on the properties of small systems, the most promising approach seems to be a straightforward application of statistical mechanics. As computers continue to improve in speed and capacity, direct simulations will also be increasingly able to study small systems.

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He is known for his statistical mechanics research on the development of the Monte Carlo renormalization group method, cluster methods for computer simulations of phase transitions, histogram methods for the analysis of data from simulations, and optimization methods for the simulation of complex systems. He has written two texts on statistical mechanics and thermodynamics, one with Daniel C. Mattis.

His honors include being named as a Fellow of both the American Physical Society and the American Association for the Advancement of Science, receiving an IBM Outstanding Achievement Award in 1981, and sharing a Forefronts of Large-Scale Computational Problems Award with S. Kumar, J.M. Rosenberg, and P.A. Kollman in 1991. He is the recipient of the 2014 Aneesur Rahman Prize for Computational Physics from the American Physical Society. Carnegie Mellon University awarded him the 2014 Julius Ashkin Teaching Award in the Mellon College of Science.