The concept of negative temperature has recently received renewed interest in the context of debates about the correct definition of the thermodynamic entropy in statistical mechanics. Faced with what they regard as a choice of entropy definitions from among a limited set of options, a number of researchers have identified the thermodynamic entropy with the “volume entropy” suggested by Gibbs, and further concluded that by this definition, negative temperatures violate the principles of thermodynamics. We regard none of the options considered for the entropy by these authors as adequate, and we disagree with their conclusions. We demonstrate that Gibbs’ volume entropy is inconsistent with the postulates of thermodynamics for systems with inverted energy distributions, while a definition of entropy based on the probability distributions of observable macroscopic variables does satisfy the postulates of thermodynamics. Our results affirm that negative temperature is a valid concept in thermodynamics.

I. INTRODUCTION

In 1956, Ramsey developed the principles of negative temperatures in thermodynamics and statistical mechanics. His analysis has recently been challenged by several authors, who claim that negative temperatures are not consistent with thermodynamics and statistical mechanics. The most clearly stated opposition to Ramsey’s analysis has been given by Dunkel and Hilbert (DH) and Hilbert, Hänggi, and Dunkel (HHD), so we will primarily address their arguments. Among the conclusions reached by the opponents of Ramsey’s description is that an expression for a “volume entropy,” which had been suggested by Gibbs, is the correct definition of entropy in statistical mechanics. These conclusions have already been challenged. We especially endorse the arguments given by Frenkel and Warren, although we believe that some issues still need to be clarified. Importantly, although the discussion has involved the question of how to properly define the thermodynamic entropy in statistical mechanics, it has failed to include alternative definitions of entropy that call for consideration.

The main arguments by the authors who oppose negative temperatures and advocate the “volume entropy” concern violations of adiabatic invariance and related claimed inconsistencies. In fact, the violations they point to are all of order 1/N, where N is the number of particles, and therefore disappear into the thermal noise, which is of order 1/√N. An important feature of macroscopic systems is that because thermal fluctuations are so small, a single measurement of E, V, or N will almost certainly produce the average value within experimental resolution. Measuring a (1/N)-effect would require at least N independent measurements, each having a resolution of better than 1/N. It strikes us as unreasonable to demand 10^{12} measurements, each with a resolution of better than one in 10^{12}, to establish the thermodynamic behavior of a colloidal system with 10^{12} particles. In Section we expand on these concerns. We review the postulates of thermodynamics, which contain requirements that must be satisfied by the thermodynamic entropy, and therefore conditions that must be met by an acceptable definition. We review a definition of an entropy of observables based on these postulates in Section after which we compare it to the definitions considered by DH and HHD in Section

In Section we show that the inconsistencies noted by DH and HHD are of order 1/N, and therefore negligible for thermodynamic systems. In Section we demonstrate that the HHD definition of entropy fails to satisfy the zeroth and second laws of thermodynamics. In Section we demonstrate that the prediction of negative pressures for systems with bounded energies and an inverted energy distribution is a direct consequence of the laws of mechanics, and not a defect of S_B or the entropy of observables, as claimed by DH. In Section we consider the interactions of an Ising model with an inverted energy distribution with other such Ising models, or with a system of simple harmonic oscillators. This provides an explicit example of a calculation suggested by Frenkel and Warren for demonstrating that the volume entropy violates the second law of thermodynamics. We discuss the applicability of thermodynamics to small systems in Section before summarizing our conclusions in the final section.
II. THERMODYNAMIC CONSTRAINTS ON THE DEFINITION OF ENTROPY

Thermodynamics was invented in the nineteenth century by a series of brilliant scientists who did not make use of the concept of atoms. Most scientists didn’t believe that molecules existed, much less that they might provide a foundation for the laws of thermodynamics. Clausius saw the necessity of entropy without knowing where it came from or what it might mean. Even after the pioneering work of Boltzmann and Gibbs, many prominent scientists continued to reject a molecular explanation of macroscopic phenomena. Although the existence of molecules is taken for granted today, it should be remembered that the domain of thermodynamics remains that of macroscopic phenomena for which individual atoms are not resolved.

Thermodynamics ignored fluctuations from the start; initially because the existence of fluctuations was not known, but primarily because macroscopic systems could be completely characterized by energy, volume, and particle number. The now well-known justification for the neglect of fluctuations is that they are of order $1/\sqrt{N}$, where $N$ is the number of particles in the system, and therefore smaller than the resolution of macroscopic measurements. Even for a small macroscopic system, $N > 10^{18}$, and thermodynamic measurements rarely have a relative resolution of $10^{-9}$.

The requirement that fluctuations are smaller than experimental resolution is fundamental. However, it is not the only requirement. For two objects to be in thermal contact, it is necessary for some sort of direct interaction to exist between particles in different systems. Due to the short range of molecular interactions – perhaps a few nanometers – these interacting particles are found only on the interfaces where the objects come into contact. This implies that the relative size of interactions between objects goes roughly as $N^{-1/3}$. These surface effects place a stricter limit on the domain of validity of thermodynamics, but one that is still satisfied for macroscopic experiments.

A consequence of these considerations is that thermodynamics is applicable to finite systems, as long as they contain a sufficient number of particles for the fluctuations and the interface effects to be neglected.

DH and HHD claim that thermodynamics can be extended to much smaller systems – even to systems with a single degree of freedom. We are skeptical of these claims, and we give our reasons in Section IX.

At least since the work of Callen, the structure of thermodynamics has been seen to follow logically from a small set of postulates, all of which concern the properties of the thermodynamic entropy. While it won’t be necessary to follow the entire development of thermodynamics from these postulates, we will need a subset of them, which we’ll express in a modified form.

The first postulate is simply the assumption that state functions exist for systems in equilibrium. A system is regarded as being in equilibrium if its macroscopically measurable properties do not depend on time and there is no net transport of particles or energy. State functions depend only on a small number of extensive variables $(E, V, N)$ for a simple system. They do not depend on the history of the system.

The second postulate is crucial: it is a particular expression of the Second Law of Thermodynamics. It says that there is a state function called “entropy,” for which:

$$
\frac{\partial S_T}{\partial E_1} = 0 = \frac{\partial S_1(E_1)}{\partial E_1} + \frac{\partial S_2(E_T - E_1)}{\partial E_1}
$$

or

$$
\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2},
$$

where we have suppressed the volume and the particle number. This important result leads directly to the Zeroth Law of Thermodynamics. Since two systems in thermal equilibrium with each other have the same temperature, the derivative $\partial S/\partial E$ is clearly a function of temperature, which is usually taken to be $1/T$. For stability, the second derivative $\partial^2 S/\partial E^2$ (holding $V$ and $N$ constant) must be negative.

The next postulate is usually the monotonicity of $S$ as a function of $E$, which allows the function $S = S(E, V, N)$ to be inverted to give $E = E(S, V, N)$. The key question addressed in this paper is whether this postulate can be abandoned without running into contradictions.

In the next section, we will review a definition of entropy in statistical mechanics that follows from considering the thermodynamic postulates. In contrast to the four definitions considered by DH and HHD, this definition satisfies all of the postulates of thermodynamics.
III. FROM STATISTICAL MECHANICS TO THE THERMODYNAMIC ENTROPY

In this section, we review a definition of entropy that is completely consistent with the requirements of the thermodynamic postulates outlined in the previous section.\[19-60\] We will refer to it as the entropy of observables because it is based on probability distributions for macroscopic observables. This definition will be compared in the next section to the limited list of definitions given by DH and HHD.\[11-13, 17\]

Although the disagreements on the existence of negative temperatures center on the definition of entropy in statistical mechanics, the predictions of statistical mechanics do not rely on any such definition. Once the probability distribution in phase space has been determined, the probability distributions for any observable of interest can be computed.

The most fundamental variables of interest in thermodynamics are collective variables that measure how much of something is distributed. The most common quantities are energy, volume, particle numbers for the various components, magnetization, and electric polarization. We will discuss the calculation of their probability distributions in classical statistical mechanics to make contact with the main arguments in the literature, but the extension to quantum statistical mechanics is straightforward.

The simplest choice for the probability distribution in phase space, which proves to be sufficient for most purposes, is to assume a uniform distribution that is consistent with our knowledge of the system. This choice includes the possibility that we have data from earlier times. For example, we might know that a gas is currently confined in a container with volume \(V\), but that prior to an earlier time \(t\) it had been confined to a subvolume \(V' < V\). At the time \(t\), a partition was removed so that the gas could expand into the full volume \(V\). The probability distribution in phase space would then depend on time, but the number of particles in any subvolume could, in principle, be calculated. For this specific example, the calculation can be carried out explicitly for an ideal gas, and the probability distribution for the particle density can be shown to become uniform for long times.\[54\] The approach to equilibrium has also been proved for the probability distributions of macroscopic variables for the hard-sphere gas.\[62\] Proofs are more difficult for general systems, but numerical demonstrations of this behavior are common in the literature. These results are particularly important because Liouville’s theorem prevents the probability distribution in phase space from becoming uniform for any Hamiltonian system. The entropy of observables correctly increases after release of a constraint in an isolated system, but the definitions considered by DH and HHD do not.

For a general case, consider of \(M\) subsystems that form an isolated composite system, with no information about the system’s history. We will assume that there is only a single type of particle to reduce the proliferation of subscripts, although this assumption is not necessary. All subsystems are initially isolated, and we are given the initial values of the energies, volumes, and particle numbers, \(\{E_{0}^{(j)}, V_{0}^{(j)}, N_{0}^{(j)}\}_{j = 1,2,\ldots, M}\). Consider any experiment in which some constraint is released, initiating an irreversible process. This means that two or more subsystems are allowed to exchange energy, volume (by a piston), and/or particles. We wish to predict the final values of the observables after a new state of macroscopic equilibrium is attained. The solution will be in the form of a probability distribution. The general form of this probability distribution can be easily expressed. Since calculations show that these probability distributions are sharply peaked, with relative widths of the order of \(1/\sqrt{N_{j}}\) for the \(j\)-th subsystem, it is sufficient (and convenient) to use the unnormalized probability distribution.\[59\] For short-ranged interactions, this can be written as

\[
\Omega_{M}^{(j)} \left( E^{(j)}, V^{(j)}, N^{(j)} \right) = \frac{1}{h^{3N_{j}}} \int dp \int dq \delta(E^{(j)} - H_{j}(p,q)),
\]

where Planck’s constant \(h\) is included to obtain agreement with quantum results in the classical limit.\[58\] For quantum systems, \(\Omega^{(j)}(E^{(j)})\) is given by the degeneracy of the \(E^{(j)}\) energy level. It should be noted that there is no restriction to extensive subsystems in Eqs. \[4]\ and \[5]\). Interactions with walls can be included in the Hamiltonians to describe non-extensive subsystems.

Since the probability distributions of macroscopic variables – \(E_{j}, V_{j}, N_{j}\), etc. – are known to have a relative width of the order of \(1/\sqrt{N_{j}}\) for large \(N_{j}\), and this is assumed to be smaller than experimental error, it suffices to take the equilibrium values to be the locations of
the maxima. Since the logarithm is a monotonic function, \( \ln \hat{W} \) has its maxima at the same locations as \( \hat{W} \). Therefore, we could also find the maxima of the function

\[
S_M = \sum_{j=1}^{M} S^{(j)} \left( E^{(j)}, V^{(j)}, N^{(j)} \right) + X,
\]

(6)

where we have included an additive constant for generality, and

\[
S^{(j)} \left( E^{(j)}, V^{(j)}, N^{(j)} \right) = k_B \ln \Omega^{(j)} \left( E^{(j)}, V^{(j)}, N^{(j)} \right).
\]

(7)

The entropy of observables given in Eq. (7) is therefore an expression for the thermodynamic entropy of a general classical system for which the history is not known, as derived from statistical mechanics. If the history of the system is known – for example, a gas might have undergone a free expansion – then the definition of entropy uses the long-time limit of the probability distributions describing the extensive variables. By construction, the entropy of observables satisfies the postulates of thermodynamics and obeys the second law of thermodynamics. In the next section, we will compare the entropy of observables with the definitions of entropy considered by DH and HHD. [11] [14] [17]

IV. DEFINITIONS OF ENTROPY CONSIDERED BY DH AND HHD

A problem with the analyses of DH and HHD is that they only considered a limited set of definitions of entropy. DH considered two definitions of entropy. [11] [13] HHD expanded the list to a total of four, which are given here. [17]

1. Gibbs entropy, which used an integral over the volume in phase space containing energies less than the energy of the system. HHD also called this the volume entropy.

2. Boltzmann entropy, which used a delta function to integrate over a surface in phase space. HHD also called the surface entropy. As mentioned above, this definition of entropy is not really how Boltzmann defined the entropy. [52] [63]

3. Modified Boltzmann entropy, which HHD defined in terms of a shell of non-zero width in phase space.

4. Complementary Gibbs entropy, which integrated over all energies greater than the energy of the system.

HHD also mentioned a fifth category with “Alternate entropy proposals,” such as piece-wise distributions. They did not pursue such alternatives, and, in particular, they did not consider the entropy of observables given above in Section [11]

The definition they favored is the “volume” entropy due to Gibbs

\[
S_G = k_B \ln \int dp \int dq \Theta(E - H(p,q))
\]

(8)

where \( p \) and \( q \) are the momentum and position coordinates in phase space, \( H(p,q) \) is the Hamiltonian of the system, and \( \Theta(\cdot) \) is the step function. They correctly attributed this expression to Gibbs, although he also included a factor of \( 1/N! \) that they did not need for their arguments. [18] The definition that they rejected was the “surface” entropy,

\[
S_B = k_B \ln \int dp \int dq \delta(E - H(p,q)),
\]

(9)

where \( \delta(\cdot) \) is the Dirac delta function. They attributed this expression to Boltzmann, incorrectly as it turns out, as he did not know about the Dirac delta function and defined entropy quite differently. [52] The definitions HHD considered are not, in our opinion, acceptable candidates for defining entropy from statistical mechanics. In particular, all four have the following weaknesses.

1. All the definitions of entropy considered by DH and HHD are guesses.

The only justification of any of these definitions is based on authority. Gibbs suggested \( S_G \), but he did not give any derivation of it – he stated only that he found agreement with the properties he was interested in. [18]

Boltzmann did not define the entropy by the equation for \( S_B \). Nor did he define the entropy as \( S_G \), for which he has also been credited. In fact, he defined entropy from probability distributions in composite systems in a way very similar to the definition given in the previous section. [52] [63]

2. None of the four definitions satisfies the second law of thermodynamics.

The reason for this has been alluded to by DH in their supplementary materials. [13] When two systems are brought into thermal contact, the thermodynamic entropy will increase unless the temperatures were identical before contact. However, because all of the definitions considered by DH and HHD are based on a probability distribution in phase space, Liouville’s theorem requires that their expressions for the entropy are constant. This is not a problem with the entropy of observables given in Section [11]

3. The definitions DH and HHD considered apply only to the energy dependence of the entropy. They are not complete definitions that would also predict the effects of volume or particle exchanges between systems. Such exchanges are also governed by the
second law of thermodynamics and would lead to increases in the total entropy of a composite system. The definition discussed in Section III covers all thermodynamic variables.

For these reasons, we will compare the properties of $S_G$ with those of the entropy of observables given in Section III. It should be noted that for a simple system in equilibrium, our definition agrees with $S_B$, except for the important factors of $h^{-3N}$ and $1/N!$. The main differences concern the return to equilibrium after the release of a constraint initiates an irreversible process. $S_B$ remains constant, while our definition, which we will simply call $S$, increases as required by the second law of thermodynamics.

V. CORRECTIONS OF ORDER $1/N_j$

In deriving the entropy of observables from statistical mechanics in Section III, we neglected terms due to thermal fluctuations because thermodynamics is valid for systems in which such fluctuations are smaller than experimental errors. For example, the average value of $E_j$, $\langle E_j \rangle$, is a sufficient thermodynamic description of the energy because the relative size of its fluctuations is of order $1/\sqrt{N_j}$, and can be neglected.

We also neglected direct interactions between particles in different subsystems, which allowed us to factor the probability distribution and obtain additive entropies. These terms go roughly as the surface to volume ratio, or $N^{-1/3}$.

In the context of thermodynamics, errors of the order $1/N_j$ are completely negligible. On the other hand, since DH have based a significant part of their arguments on these $1/N_j$-effects, we justify our neglect of $1/N_j$ effects explicitly in the next section.

A. Location of maximum probability vs. average values

The first place in which we have consciously allowed an “error” of order $1/N_j$ to enter the entropy of observables in the assumption that the location of the maximum probability for some variable is equal to the observed value of that variable. In fact, they differ by a term of order $1/N_j$.

For example, the energy distribution between subsystems 1 and 2 in an ideal gas separated by a diathermal wall is proportional to

$$E_1^{3N_1/2-1}(E_T-E_1)^{3N_2/2-1}$$

(10)

where the total energy in the two subsystems is $E_T = E_1 + E_2$. The average value of the energy per particle in subsystem 1 is

$$\frac{\langle E_1 \rangle}{N_1} = \frac{\langle E_2 \rangle}{N_2}$$

(11)

However, the value of the energy with maximum probability, $E_j^*$ is

$$\frac{E_j^*}{N_1} \left(1 - \frac{2}{3N_1}\right)^{-1} = \frac{E_j^*}{N_2} \left(1 - \frac{2}{3N_2}\right)^{-1}.$$  

(12)

It is interesting that these considerations imply that the average values of the energy do not go exactly to the values corresponding to the maximum of the probability distribution. This implies that Boltzmann’s assertion that systems go from a less probable to a more probable state could be regarded as needing a correction of the order $1/N_j$. However, since a correction of this magnitude is unmeasurable under normal conditions, we do not regard it as significant.

B. Violation of adiabatic invariance

DH and HHD have argued against expressions for the entropy that are similar to the entropy of observables on the grounds that they violate adiabatic invariance.\[11–14, 17\] Strictly speaking, their assertion is correct. However, the violation of adiabatic invariance is of order $1/N_j$, and therefore negligible.

The issue concerns the energy dependence of the entropy. The easiest way to see it is to note that DH have shown that an entropy per particle with an energy dependence of the form $(3N_j/2)k_B$ in $E_j$ does satisfy adiabatic invariance, but one with an energy dependence of the form $(3N_j/2)k_B(1 - 2/3N_j)$ in $E_j$ does not.

As shown in the previous subsection, this $1/N_j$-effect is simply due to taking the equilibrium values to be the locations of the maxima of the entropy instead of the equilibrium averages. It has no further significance.

VI. CRITIQUE OF THE HHD INTERPRETATION OF THE LAWS OF THERMODYNAMICS

HHD claim to offer demonstrations that their preferred definition of entropy, $S_G$, satisfies the laws of thermodynamics. We disagree, as explained below.

A. Gibbs volume entropy and the Zeroth Law

The Zeroth Law of Thermodynamics states that thermodynamic equilibrium is an equivalence relation. A formulation of the Zeroth Law due to Planck is that, “If a body $A$ is in thermal equilibrium with two other bodies $B$ and $C$, then $B$ and $C$ are in thermal equilibrium with one another.”\[65\] One reason for the importance of the Zeroth Law is that it enables us to use a small system as a thermometer. In the interpretation of this law, it should be noted that for two systems that are not in thermal contact to be in equilibrium with each other means that
if they were to be brought into thermal contact, there would be no net flow of energy between them. It should be obvious from this, or from any other accepted formulations of the zeroth Law that its demonstration requires consideration of three objects.

In terms of the postulates of thermodynamics, the Zeroth Law follows from additivity for a composite system and the maximization of the total entropy at equilibrium for systems in thermal contact. It can be seen immediately by extending Eq. (2) to three systems.

\[
\frac{\partial S_1(E_1)}{\partial E_1} = \frac{\partial S_2(E_2)}{\partial E_2} = \frac{\partial S_3(E_3)}{\partial E_3}
\]  

(13)

HHD claimed to demonstrate that \( S_G \) satisfies the Zeroth Law, but their demonstration is limited to only two systems. Instead of a third system, they show that their expression for the distinct temperature of the composite system is equal to the temperatures of the two subsystems – as long as they continue to be in thermal contact with each other.

Leaving aside the question of what it might mean for the temperature of a composite system in equilibrium to be distinct from the temperatures of the two systems composing it, the HHD derivation has several unusual features. A very striking feature is that the temperature of a system is not just a property of that system.

Consider three systems, numbered 1, 2, and 3, that are in equilibrium with each other in the sense given above that there would be no net energy exchange if they were to be brought into thermal contact with each other. In Eq. (33) of Ref. [17], temperatures are defined for each system, although they do not necessarily have the same values, as they would in the usual thermodynamics. Denote these temperatures as \( T_1 \), \( T_2 \), and \( T_3 \).

Now bring systems 1 and 2 together. As shown in Eq. (36) of Ref. [17], HHD define a new temperature for the combined (1, 2) system that depends on both systems 1 and 2. The value of this temperature, \( T_{1,2} \), is the same for systems 1 and 2 as long as they are in thermal contact with each other, but it can differ from both \( T_1 \) and \( T_2 \). In the same way, HHD define two further temperatures, \( T_{1,3} \) and \( T_{2,3} \). Putting all three systems together gives us yet another temperature, \( T_{1,2,3} \), for a total of seven values of the temperature for three systems in thermal equilibrium with each other.

The HHD definition of entropy is not consistent with the Zeroth Law of Thermodynamics.

### B. First Law

The first law of thermodynamics is simply the conservation of energy, which is stipulated to be true for all definitions of entropy. Conservation of energy is automatic with our definition, which can be readily seen from Eq. (1).

HHD have claimed that \( S_B \) violates the first law in that it violates the equipartition of energy. This is the same 1/N-effect that they addressed in connection with adiabatic invariance. By using the location of the maximum of the probability distribution for the energy instead of the average value of the energy, a shift of the order of \( 1/N \) is introduced. HHD regard this as important, but we do not. It is not observable, being completely obscured by thermal fluctuations.

### C. The HHD interpretation of the Second Law

HHD claim that \( S_G \) satisfies the second law of thermodynamics. In developing their arguments, they consider various formulations of the second law, which we will consider below. The formulation that they adopt as a test of \( S_G \) is, however, not conventional, and as we will show, it does not really satisfy the second law.

HHD recognize that \( S_G \) does not satisfy Clausius’ statement that heat never flows spontaneously from a colder to a hotter body, but they describe Claudius’ expression as “naive.” Indeed, as we confirm in Section [8], \( S_G \) does not satisfy this second law in this form, although the entropy of observables does satisfy it. The maximum of the sum of the Gibbs volume entropies of two systems is not located at the equilibrium values of the energies, as required by the postulates of thermodynamics.

HHD do accept the Planck formulation of the second law, that the sum of all entropies should not decrease, and they argue that this mandate is satisfied by \( S_G \). We demonstrate that it is not, as follows.

In attempting to demonstrate that \( S_G \) satisfies Planck’s condition, HHD consider two systems, 1 and 2, before and after they are brought into thermal contact. By considering the change in total volume of phase space using in defining the Gibbs’ entropies, they prove that if \( E_T = E_1 + E_2 \) is fixed,

\[
S_G(E_1 + E_2) \geq S_G(E_1) + S_G(E_2).
\]  

(14)

This equation is the HHD Eq. (49).

Note that the maximum of the right hand side does not lie at the equilibrium values of the energies; the value of \( S_G(E_1) + S_G(E_2) \). Beginning with this observation, consider the following experiment, which involves systems 1 and 2.

- Begin with \( E_1 = E_1^* \) and \( E_2 = E_2^* \) such that \( S^*_{1,2} = S_G(E_1^*) + S_G(E_2^*) \) takes on its maximum value, holding \( E_T = E_1 + E_2 \) constant.

- Bring systems 1 and 2 into thermal contact with each other, and let them come to equilibrium. Denote the new equilibrium energies as \( E_1^{eq} \) and \( E_2^{eq} \).

- We now have the sequence of inequalities:

\[
S_G(E_1 + E_2) \geq S^*_{1,2} > S_G(E_1^{eq}) + S_G(E_2^{eq}).
\]  

(15)
Now separate systems 1 and 2, so that they are no longer in thermal contact. They retain the energies $E_1^{eq}$ and $E_2^{eq}$.

Since entropy is a state function, the total entropy of the system has decreased from $S_G(E_1 + E_2)$ to $S_G(E_1^{eq}) + S_G(E_2^{eq})$. Because of the inequalities in Eq. (15), the total Gibbs entropy has decreased, violating the Planck formulation of the second law of thermodynamics.

This demonstrates that $S_G$, as interpreted by HHD, violates the second law of thermodynamics.

$S_G$ also fails to satisfy the postulates of thermodynamics,[58, 61] since the location of the maximum of the sum of the entropies of two systems does not correspond to the equilibrium values for systems with bounded energies. Although previously $S_G$ had been regarded as giving correct numerical predictions, the analysis of systems with bounded energy spectra now shows it to be incorrect.

Now that we have demonstrated that $S_G$ fails to satisfy the zeroth and second laws of thermodynamics, we will consider a property of systems with inverted energy distributions that DH and HHD claimed would be corrected by $S_G$: negative temperature implies negative pressure.[21] DH claimed that this fact demonstrated that negative temperatures were unphysical.[12, 13] As we demonstrate in the following section, the possibility of negative pressure is a valid consequence of a bounded energy spectrum for a mechanical system, regardless of the definition of entropy.

VII. NEGATIVE PRESSURE

One of the most surprising features of a system with a bounded energy spectrum is that it can have negative pressure in the region of negative temperature.[21] This is, of course, not a feature of spins on a fixed lattice because there is no volume dependence of the energy for such a system. To understand negative pressure, we must construct a model with both a bounded energy spectrum and a volume dependence of the energy. This rules out any system with kinetic degrees of freedom, since it would have states with arbitrarily high energy. However, if we exclude momentum terms from the Hamiltonian, it is easy to construct a model of particle interactions with continuous position variables and bounded energies.

A. A model system with negative pressure

Consider a gas with the Hamiltonian.

$$H_\eta = \sum_{j>k} V_\eta(|\vec{r}_j - \vec{r}_k|),$$

where $\eta = \pm 1$ is a parameter that sets the energy scale and

$$V_\eta(|\vec{r}|) = \eta \exp\left[-|\vec{r}|^2/(2\sigma^2)\right].$$

First consider $\eta = +1$, for which this is a system of particles with soft-core repulsions. The total energy is bounded by $0 \leq E \leq \frac{1}{2} N (N - 1) \epsilon$.

This model has a phase transition and, for low energies, will form a solid. For any value of $E$, when the volume is reduced, the energy of the system increases, giving the expected positive pressure.

Now consider the case of $\eta = -1$, for which the energy is bounded by $-\frac{1}{2} N (N - 1) \epsilon \leq E \leq 0$. There is a one-to-one correspondence of the microscopic states of $H_{-1}$ with $E < 0$ and those of $H_{+1}$ with $E > 0$. Because of this symmetry, when the $\eta = -1$ system is compressed, the total energy decreases, and the pressure is negative.

B. Negative pressure and the entropy

We now return to the question of how the existence of negative pressure affects the proper form of the entropy. Because of the mapping of states between $\eta = +1$ and $\eta = -1$, the entropies $S_\eta$ are related by $S_{-1}(-E, V, N) = S_{+1}(E, V, N)$. Since $S_{+1}(E, V, N)$ is an increasing function of $E$ for $E > 0$, $S_{-1}(-E, V, N)$ is a decreasing function of $E$ for $E < 0$. On the other hand, for $\eta = \pm 1$, we still have $\partial S_\eta/\partial V = P/T > 0$ This implies that $P < 0$ for $H_{-1}$, $E < 0$, and $T < 0$.

Since negative pressure is correct for $\eta = -1$ and high values of $E$, the negative pressure found by the thermodynamic argument using the Boltzmann entropy is also correct.

C. Stability of a system with negative pressure

It is obvious from the discussion in the previous subsection that a system with negative pressure is unstable with respect to external forces. If such a system were to be enclosed in a vertical cylinder closed by a freely moving piston the volume would collapse.

On the other hand, if two systems with negative temperatures and negative pressures are in contact through a diathermal piston, they will come to a stable equilibrium. The reason is that the entropy is always a monotonically increasing function of the volume, $\partial S/\partial V > 0$, and the entropy is a maximum at the equilibrium reached after release of the constraints on energy and volume.

In the next section, we turn to models with discrete energy levels to provide examples that will demonstrate the consistency of descriptions using negative temperatures with thermodynamic principles. We will also give an explicit violation of the second law of thermodynamics when the volume entropy imposes positive temperatures on systems with inverted energy distributions.
VIII. MODELS WITH DISCRETE ENERGY LEVELS

While most of our discussion has concerned general principles, it is useful to consider models for which explicit calculations can be made to demonstrate the relevant ideas. Models with discrete energy levels are particularly well suited for such demonstrations because calculations and simulations are relatively easy. In this section, we illustrate the thermal behavior of systems with negative temperatures, using Ising paramagnets and systems of non-interacting quantum simple harmonic oscillators.

The Ising paramagnet consists of a set of \( N \) spins, \( \sigma = \{ \sigma_j | j = 1, 2, \ldots, N \} \), where the spins take on the values \( \sigma_j = +1 \) and \( \sigma_j = -1 \). The Hamiltonian is

\[
H = -b \sum_{j=1}^{N} \sigma_j,
\]

where \( b > 0 \) is the magnetic field. The energy of the model at \( T = 0 \ (\beta = 1/k_BT = \infty) \) is \( E = -Nb \). At \( T = \infty (\beta = 0) \), the energy is \( E = 0 \). All positive energy states correspond to negative temperatures, although HD and HHD describe them with positive values of \( T_G \).

The partition function \( Z \) of the Ising paramagnet can be evaluated explicitly, and depends only on the product \( \beta b \). Since the physical properties of the system are invariant under the transformation \( \beta \rightarrow -\beta \) and \( b \rightarrow -b \), it is natural to expect the entropy to be invariant.

Although thermal interactions between macroscopic systems are normally described in terms of changes in temperature, it will be more convenient to work with the inverse temperature \( \beta = 1/k_BT \).

Our first example demonstrates the consistency of describing inverted energy distributions with negative temperatures, as well as the contradictions inherent in attempting to impose positive temperatures with the Gibbs volume entropy.

A. Two Ising paramagnets with negative temperatures

We will analyze an experiment with two Ising paramagnets, first using our definition of the entropy (and temperature), and then with the DH and HHD entropy.

1. Ising paramagnets with negative temperatures

First consider two Ising paramagnets in the same magnetic field at inverse temperatures \( \beta_1 \) and \( \beta_2 \). Since the size of the two systems have significant consequences for the values of \( T_G \), let us assume that \( N_1 > N_2 \).

If the two systems are brought into thermal contact, they will establish a new equilibrium state with a common temperature \( \beta_f \) that lies between \( \beta_1 \) and \( \beta_2 \). This is undisputed for positive values of the inverse temperatures, but the symmetry of the model shows that it will also be true when the inverse temperatures are negative. In fact, the new equilibrium temperature, \( \beta_f \), will have the same absolute value in both cases – at least when using our definition of entropy. Regardless of the definition of entropy, there is a one-to-one correspondence of the probability distributions of the states in the two cases.

Now suppose that \( E_1 < 0 (\beta_1 > 0) \), but \( E_2 > 0 (\beta_2 < 0) \). The equations for the probability distributions do not change, and thermal contact between the two systems will again lead to an equilibrium state with a common inverse temperature, which could be either positive or negative.

The simplicity of this model makes it easy to derive the equilibrium behavior or carry out a computer simulation. The average value of any spin in either system will be given by \( \langle \sigma_j \rangle = \tanh(\beta b) \), where the value of the inverse temperature \( \beta \) is same as what we obtain from our definition of entropy.

2. Ising paramagnets described with DH and HHD positive temperatures

HHD would describe Ising paramagnets with positive values of \( T_G \), whether their energies were negative or positive. Let us consider the interesting case of \( E_1 \) and \( E_2 \) both having positive initial values. If they are brought into thermal equilibrium with each other and then separated, DH and HHD have shown that because \( N_1 > N_2 \), \( T_{G,1} > T_{G,2} \). This certainly violates our common understanding of temperature, and would seem to make the construction of a thermometer impossible.

As discussed in Section VIII B, HHD have shown that they can construct a definition of temperature that has the same value for both systems, but only while they remain in contact with each other.

The next subsection continues with an example based on a suggestion by Frenkel and Warren to demonstrate the violation of the second law of thermodynamics by the Gibbs volume entropy.

B. A numerical demonstration of an argument due to Frenkel and Warren

Frenkel and Warren suggested an interesting thought experiment coupling an Ising model with an ideal gas to demonstrate the violation of the second law of thermodynamics by the Gibbs definition of entropy. We have taken their idea, but applied it to interactions between a system 1, composed of objects with two energy levels, and a system 2, composed of quantum simple harmonic oscillators. The Hamiltonian of the two-level system is

\[
H_1 = \sum_{i=1}^{N_1} \epsilon n_{1,i}, \quad n_{1,i} = 0, 1,
\]
and the Hamiltonian for the simple harmonic oscillators is

\[ H_2 = \sum_{j=1}^{N_2} \hbar \omega \left( n_{2,j} + \frac{1}{2} \right), \quad n_{2,j} = 0, 1, 2, \cdots \quad (20) \]

For simplicity, we take \( \epsilon = \hbar \omega = k_B = 1 \).

We have carried out microcanonical Monte Carlo (MC) computer simulations of the approach to equilibrium when these two systems are brought into thermal contact. No assumption concerning the entropy or the temperature is necessary for such simulations. The dynamics simply picks a two-level object and an oscillator at random. A proposed move of the two-level object changes its energy by \( \pm \epsilon \) with equal probability, with a corresponding change of \( \pm \epsilon \) in the energy of the oscillators, so that the total energy is conserved. If the proposed move would take either system to unphysical states, the move was rejected.

System 1 was initialized in its highest energy state, that is, \( n_{1,j} = 1 \) for all \( i \), with energy \( E_1 = N_1 \epsilon = N_1 \). From the definition of \( S_G \) and a finite difference approximation for \( T_G \), we have

\[ T_{G,1} \approx \frac{\Delta E_1}{\Delta S_{G,1}} = \frac{1}{\ln 2^{N_1} - \ln(2^{N_1} - 1)} \approx 2^{N_1}, \quad (21) \]

for sufficiently large \( N_1 \).

System 2 was initialized at a value of \( T_{G,2} \) that was a factor \( M \) higher that \( T_{G,1} \). Actually, the initial temperature of system 2 could be taken arbitrarily high without affecting our results.

We considered both large and small systems, with the same result in both cases. For \( N_1 = 5, N_2 = 1 \) with \( M = 2 \), we monitored the energy in system 1 and plot the average energy per particle as a function of time \( t \) in Fig. [I].

We also tried \( N_1 = 1000, N_2 = 1000 \) setting \( M = 10^6 \). The energy levels of the oscillators were too high to store directly in the computer, but this is not necessary. The total energy of the oscillators cannot change more than \( N_1 \), so it was sufficient to use the deviations \( \Delta n_{2,j} \) from the initial values of \( n_{2,j} \). The results of this simulation are also shown in Fig. [I]. They are indistinguishable from those using small systems.

The dynamics of the particles are very well represented by a Markov process with the following equation

\[ \frac{dP_1}{dt} = \frac{1}{2} P_0 - \frac{1}{2} P_1, \quad P_0 + P_1 = 1, \quad (22) \]

where \( P_0 \) is the probability that the particle is in the ground state and \( P_1 \) is the probability that the particle is in the excited state. The solution of this equation with the initial condition \( P_1(0) = 1, P_0(0) = 0 \) gives \( P_1(t) = \frac{1}{2}(1 + e^{-t}) \) which is also plotted in Fig. [I]. This equation is valid as long as the energy of the oscillators are sufficiently high that no moves are rejected. For this reason, the results do not depend on the values used for \( M \) or \( T_{G,2} \).

As Frenkel and Warren predicted, these simulations show that when the Gibbs entropy and \( T_{G} \) are used, energy can flow from a low-temperature system to a high-temperature system, increasing the separation of their temperatures. [22] This is a clear violation of the Planck formulation of the Second Law.

The next section returns to the assertion of HHD that thermodynamics can provide a valid description of small systems – as small as a single degree of freedom. [17] We show that this claim is not plausible.

IX. CAN THERMODYNAMICS DESCRIBE SMALL SYSTEMS?

Thermodynamics applies very well to finite systems that are large enough to ignore fluctuations and interface effects. However, DH and HHD have suggested that thermodynamics should also apply to small systems – even system with only a single degree of freedom. [11] [14] [17] We are skeptical.

It is certainly true that a thermodynamic point of view can be useful in thinking about the behavior of small systems. Computer simulations have demonstrated clearly that small systems can enable us to predict the properties of much larger systems. Nevertheless, the application of thermodynamics to small systems must be done with care.

There are several finite-size corrections to the properties of macroscopic systems. The most obvious corrections are due to thermal fluctuations, which are generally of order \( 1/\sqrt{N} \), where \( N \) is the number of particles in the system. As mentioned above, these fluctuations completely mask the tiny \( 1/N \) corrections that DH and HHD cite as breaking adiabatic invariance. Even the corrections to Stirling’s approximation are of order \( \ln(N)/N \),
which is larger than the \((1/N)\)-effects that HHD regard as important.

Normally, we regard \(1/\sqrt{N}\) fluctuations are much smaller than the resolution of macroscopic measurements and can be ignored. To detect them would require at least \(N\) independent measurements, each with a resolution better than one part in \(N\). Even for a colloid with \(N \approx 10^{12}\), this is not feasible.

Whenever two systems come into thermal contact, there must be a direct interaction between particles in different systems. The number of such interactions is generally of order \(N^{-1/3}\), which can be larger than the thermal fluctuations for small systems. Certainly, for a system with only a single degree of freedom, any coupling to another system must correspond to an energy of roughly the same magnitude as the energy of the system itself. It cannot be regarded as a small perturbation.

While statistical mechanics can also be applied to the properties of small system, we can only conclude that thermodynamics is a macroscopic theory.

X. CONCLUSIONS

We have shown that the proposal of DH and HHD that the Gibbs ("volume") entropy \(S_G\) provides a valid expression for the thermodynamic entropy is incorrect. The volume entropy fails to satisfy the postulates of thermodynamics, the zeroth law of thermodynamics, and the second law of thermodynamics. In particular, we have shown that a description of systems with bounded energy spectra and inverted energy distributions by the volume entropy leads to ambiguous temperatures \(T_G\) violating the zeroth law. Following a suggestion by Frenkel and Warren,\cite{22} we have demonstrated a spontaneous transfer of energy from a system with lower \(T_G\) to a system of higher \(T_G\), violating the Planck formulation of the second law.

We have also shown that while the assertions of DH and HHD that other expressions for the entropy violate adiabatic invariance are – strictly speaking – correct,\cite{11–17} the effects are of order \(1/N\), and therefore unmeasurable for macroscopic systems.

We have further argued that the claims of DH and HHD to be able to apply thermodynamics to extremely small systems neglect the effects of fluctuations and surface interactions. Thermodynamics is valid for systems in which the values of the variables energy, volume, particle number, etc. have sufficiently small fluctuations that their average values are enough to fully characterize the (macroscopic) state of the system for the experiments of interest.

We have provided support for Ramsey’s proposal for the use of negative temperatures to describe systems with bounded energies and inverted energy distributions. Finally, we have presented new support for defining the thermodynamic entropy as the entropy of observables, which is based on the probability distributions of macroscopic observables for both reversible and irreversible thermodynamic processes.

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[1] N. F. Ramsey, “Thermodynamics and Statistical Mechanics at Negative Temperatures,” Phys. Rev., 103, 20–28 (1956).
[2] V. Berdichevsky, I. Kunin, and F. Hussain, “Negative temperature of vortex motion,” Phys. Rev. A, 43, 2050–2051 (1991).
[3] M. Campisi, Stud. Hist. Philos. Mod. Phys. 36, 275 (2005).
[4] M. Campisi, Physica A 385, 501 (2007).
[5] M. Campisi, “Statistical mechanical proof of the second law of thermodynamics based on volume entropy,” Studies in History and Philosophy of Modern Physics, 39, 181–194 (2008).
[6] M. Campisi, F. Zhan, P. Talkner, and P. Hänggi, Phys. Rev. Lett. 108, 250601 (2012).
[7] M. Campisi and P. Hänggi, “Thermostated Hamiltonian Dynamics with Log Oscillators,” J. Phys. Chem. B 117, 12829 (2013).
[8] M. Campisi, “Microcanonical phase transitions in small systems,” arXiv:0709.1082v1 [cond-mat.stat-mech]
[9] M. Campisi, “Fluctuation relation for quantum heat engines and refrigerators,” J. Phys. A: Math. Theor. 47, 245001 (2014). doi:10.1088/1751-8113/47/24/245001
[10] V. Romero-Rochín, “Nonexistence of equilibrium states at absolute negative temperatures,” Phys. Rev. E, 88, 022144 (2013).
[11] J. Dunkel and S. Hilbert, “Phase transitions in small systems: Microcanonical vs. canonical ensembles,” Physica A 370, 390 (2006).
[12] J. Dunkel and S. Hilbert, “Inconsistent thermodynamics and negative absolute temperatures,” arXiv:1304.2066v1, [cond-mat.stat-mech]
[13] J. Dunkel and S. Hilbert, “Consistent thermostatistics forbids negative absolute temperatures,” Nature Physics 10, 67 (2014); and Supplementary Information.
[14] J. Dunkel and S. Hilbert, “Reply to Frenkel and Warren,” arXiv:1403.4209v1, [arXiv:1403.6055v1], (2014).
[15] J. Dunkel and S. Hilbert, “Reply to Schneider et al,” arXiv:1408.5392v1, (2014).
[16] I. M. Sokolof, “Not hotter than hot,” Nature Physics 10, 7–8 (2014).
[17] S. Hilbert, P. Hänggi, and J. Dunkel, “Thermodynamic laws in isolated systems,” arXiv:1408.5382v1 [cond-mat.stat-mech]
[18] J.W. Gibbs, Elementary Principles of Statistical Mechanics (Yale University Press, New Haven, 1902). Reprinted
by (Dover, New York, 1960).
[19] P. T. Landsberg, “Negative temperatures,” Phys Rev. 115, 518–520 (1959).
[20] A. Rapp, S. Mandt, and A. Rosch, “Equilibration rates and negative absolute temperatures for ultracold atoms in optical lattices.” Phys. Rev. Lett. 105, 220405 (2010).
[21] S. Braun, J.P. Ronzheimer, M. Schreiber, S.S. Hodgman, T. Rom, I. Bloch, and U. Schneider, “Negative absolute temperature for motional degrees of freedom.” Science 339, 52–55 (2013).
[22] D. Frenkel and P.B. Warren. “Gibbs, Boltzmann, and negative temperatures,” arXiv:1403.4290v2, (2014).
[23] J.M.G. Vilar and J.M. Rubi, “Communication: System-size scaling of Boltzmann and alternate Gibbs entropies,” J. Chem. Phys. 140, 201101 (2014).
[24] U. Schneider, S. Mandt, A. Rapp, S. Braun, H. Weimer, I. Bloch, and A. Rosch, “Comment on ‘Consistent thermostatistics forbids negative absolute temperatures’,” arXiv:1407.4122v1 [cond-mat.quant-gas].
[25] N. G. van Kampen, “The Gibbs paradox,” in Essays in Theoretical Physics, edited by W. E. Parry (Pergamon, Oxford, 1984).
[26] J.F. Nagle, “Regarding the entropy of distinguishable particles,” J.Stat. Phys., 117, 1047-1062 (2004).
[27] J.F. Nagle, “In Defense of Gibbs and the Traditional Definition of the Entropy of Distinguishable Particles,” Entropy, 12, 1936-1945 (2010).
[28] C.-H. Cheng, “Thermodynamics of the System of Distinguishable Particles,” Entropy 11, 326-33 (2009).
[29] D. Dieks and M.A.M. Versteegh, “Identical quantum particles and weak discernibility,” Found. Phys., 38, 923-934 (2008).
[30] M.A.M. Versteegh and D. Dieks. “The Gibbs paradox and the distinguishability of identical particles,” Am. J. Phys., 79, 741-746 (2011).
[31] E.T. Jaynes, “The Gibbs’ Paradox,” in: Maximum Entropy and Bayesian Methods, C.R. Smith, G. J. Erickson, P. O. Neudorfer, Editors, (Kluwer Academic Publishers, Dordrecht, Holland, 1992).
[32] J.L. Lebowitz, C.Maes, “Entropy: A Dialogue” in Entropy; A. Greven, G. Keller, G. Warnecke, Eds. (Princeton University Press, Princeton, NH, USA, 2003).
[33] D.S. Corti, “Comment on ‘The Gibbs paradox and the distinguishability of identical particles,’” by M. A. M. Versteegh and D. Dieks [Am. J. Phys. 79, 741-746 (2011)],” Am. J. Phys. 80, 170-173 (2012).
[34] A. Caticha, Lectures on Probability, Entropy, and Statistical Physic, invited monograph published by the 28th International Workshop on Bayesian Inference and Maximum Entropy Methods in Science and Engineering (Sao Paulo, Brazil 2008).
[35] A. Caticha, “TUTORIAL: Entropic Inference and the foundations of physics,” 11th Brazilian Statistics Bayesian Meeting, March 18-22, 2012, Amparo-SP-Brazil.
[36] P. Enders, “Are there physical systems obeying the Maxwell-Boltzmann statistics?,” Apeiron 16 (2009) No.4, 555-556.
[37] P. Enders, “Equality and Identity and (In)distinguishability in Classical and Quantum Mechanics from the Point of View of Newton’s Notion of State,” Sidharth, B.G., Honsell, F., de Angelis, A., Eds.; Frontiers of Fundamental and Computational Physics. Proc. 6th Int. Symp., Udine, Italy, 26-29 September, 2004, Springer: Dordrecht, The Netherlands, 2006; pp. 239-245.
[38] P. Enders, “Gibbs’ Paradox in the Light of Newton’s Notion of State,” Entropy 2009, 11, 454-456.
[39] A. Bach, Indistinguishable Classical Particles, (Springer, Berlin, 1997).
[40] A. Bach, “Boltzmann’s Probability Distribution of 1877,” Arch. Hist. Exact Sci, 41 1-40 (1990).
[41] S. Saunders, “On the explanation for quantum statistics,” Studies in History and Philosophy of Modern Physics, 37, 192-211 (2006).
[42] S. Saunders, “Indistinguishability,” Handbook of Philosophy of Physics, R. Batterman (ed.), (Oxford, London, 2013).
[43] S. Saunders, “Identity,” Compendium of Quantum Physics: Concepts, Experiments, History and Philosophy, Friedel Weinert, Klaus Hentschel, Dan Greenberger, (eds.), (Springer Verlag, Berlin, 2009).
[44] D. Hestenes, “Entropy and Indistinguishability,” Am. J. Phys., 38, 840-845 (1970).
[45] A. Ben-Naim, A Farewell to Entropy: Statistical Thermodynamics Based on Information, (World Scientific. 2008).
[46] H. Peters, “Statistics of Distinguishable Particles and Resolution of the Gibbs Paradox of the First Kind,” J. Stat. Phys. 141, 785-828 (2010).
[47] H. Peters, “Demonstration and resolution of the Gibbs paradox of the first kind,” Eur. J. Phys. 35, 015023 (2014).
[48] D. Dieks, “Is There a Unique Physical Entropy? Micro versus Macro,” in: New Challenges to Philosophy of Science (The Philosophy of Science in a European Perspective), Eds.: H. Andersen, D. Dieks, W. Gonzalez, T. Uebel, and G. Wheeler, (Springer, NewYork, 2013). The arguments in this paper against the entropy of observables were shown in [52, 53] to be invalid.
[49] R. H. Swendsen, “Statistical mechanics of classical systems with distinguishable particles,” J. Stat. Phys., 107, 1143–1165 (2002).
[50] R.H. Swendsen, “Statistical Mechanics Of Classical Distinguishable Particles,” Computer Simulation Studies in Condensed Matter Physics XV, Eds. D. P. Landau, S. P. Lewis, and H. B. Schüttler (Springer Verlag, Heidelberg, Berlin, 2003).
[51] R.H. Swendsen, “Response to Nagle’s Criticism of My Proposed Definition of the Entropy,” J. Stat. Phys., 117, 1063-1070 (2004).
[52] R.H. Swendsen, “Statistical mechanics of colloids and Boltzmann’s definition of the entropy,” Am. J. Phys., 74, 187-190 (2006).
[53] R.H. Swendsen, “Gibbs’ Paradox and the Definition of Entropy,” Entropy, 10, 15-18 (2008).
[54] R.H. Swendsen, “Explaining Irreversibility,” Am. J. Phys., 76, 643-648 (2008).
[55] R.H. Swendsen, “Footnotes to the History of Statistical Mechanics: In Boltzmann’s Words” Festschrift for A. Ni- hat Berker’s 60th Birthday, Physica A, 389, 2898-2901 (2010).
[56] R. H. Swendsen, “How physicists disagree on the meaning of entropy,” Am. J. Phys. 79, 342-348, (2011).
[57] R.H. Swendsen, “Choosing a definition of entropy that works,” Found. of Physics, 42, 582-593 (2012).
[58] R.H. Swendsen, An Introduction to Statistical Mechanics and Thermodynamics, (Oxford, London, 2012).
[59] R.H. Swendsen, “Unnormalized Probability: A Different View of Statistical Mechanics,” Am. J. Phys., 82, 941-946 (2014).

[60] R.H. Swendsen, “Entropy is a Description of Macroscopic Change,” unpublished.

[61] H.B. Callen, Thermodynamics and an Introduction to Thermostatistics, Second Edition (Wiley, New York, 1985).

[62] Ya. G. Sinai, “Dynamical systems with elastic reflections. Ergodic properties of dispersing billiards ,” Uspekhi Mat. Nauk, 25, 141–192 (1970). [English translation: Russian Mathematical Surveys, 25,137–189 (1970)]

[63] L. Boltzmann, “Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechnung respektive den Sätzen über das Wärmegleichgewicht,” Wien. Ber. 76, 373–435 (1877), reprinted in Wissenschaftliche Abhandlungen von Ludwig Boltzmann (Chelsea, New York, 1968), Vol. II, pp. 164–223.

[64] M. Planck, “Über das Gesetz der Energieverteilung im Normalspektrum,” Drudes Annalen, 553-562 (1901), reprinted in Ostwalds Klassiker der exakten Wissenschaften, Band 206, “Die Ableitung der Strahlungsgesteze”, pp.65–74.

[65] M. Planck, Theorie der Wärmestrahlung (J. A. Barth, Leipzig, 1906), translated into English by Morton Masius in M. Planck, The Theory of Heat Radiation, (Dover, New York, 1991), p. 119.

[66] R. Clausius, “Über eine veränderte Form des zweiten Hauptsatzes der mechanischen Wärmetheorie,” Annalen der Physik, 169, 481 (1854).