Resolving the debate about proposed expressions for the classical entropy

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Despite well over a century of effort, the proper expression for the classical entropy in statistical mechanics remains a subject of debate. The Boltzmann entropy (calculated from a surface in phase space) has been criticized as not being an adiabatic invariant. It has been suggested that the Gibbs entropy (volume in phase space) is correct, which would forbid the concept of negative temperatures. An apparently innocuous assumption turns out to be responsible for much of the controversy, namely, that the energy $E$ and the number of particles $N$ are given exactly. The true distributions are known to be extremely narrow (of order $1/\sqrt{N}$), so that it is surprising that this is a problem. The canonical and grand canonical ensembles provide alternative expressions for the entropy that satisfy all requirements. The consequences are that negative temperatures are thermodynamically valid, the validity of the Gibbs entropy is limited to increasing densities of states, and the completely correct expression for the entropy is given by the grand canonical formulation. The Boltzmann entropy is shown to provide an excellent approximation in almost all cases.

Keywords: Entropy; Boltzmann; Gibbs; canonical; grand canonical; classical ideal gas

I. INTRODUCTION

Entropy is such a fundamental concept in the fields of statistical mechanics and thermodynamics that one might think its definition could not be a matter of dispute. Nonetheless, the proper definition of entropy has become a matter of heated discussion. Some workers in the field have pointed to weaknesses in the Boltzmann definition (defined in section III) and claimed that the Gibbs entropy (defined in section IV) must replace it. Others have defended the use of the Boltzmann entropy and pointed to flaws in the Gibbs entropy.

At the center of the debate is the question of whether negative temperature is a thermodynamically consistent concept. The Gibbs entropy requires the temperature to be positive, while the Boltzmann entropy allows it to be negative.

Although most of the discussion has been restricted to the Boltzmann and Gibbs entropies, I believe that this restriction is responsible for the controversy. Since the two forms of entropy have different strengths and weaknesses, the two sides have disagreed mainly on which strengths and weaknesses are most important. The argument can be resolved by opening up the discussion to consideration of other definitions of entropy. In this paper, I will examine the strengths and weaknesses of the Boltzmann and Gibbs entropies, and discuss two alternatives that do not have the weaknesses of either. By freeing the discussion from an artificial restriction in the definition, we will see that thermodynamics can provide a thermodynamically consistent basis for negative temperature.

The term “entropy” has been associated with many related, but different concepts. I am concerned exclusively with the thermodynamic entropy. I will limit the present discussion to classical systems. Although many of the disagreements concern quantum systems, they are largely based on classical arguments.

The discussion is also limited to systems that are finite, but not small. Although claims have been made that thermodynamics should apply to small systems – even a single particle – I will only consider macroscopic systems, in which there are sufficient particles for the fluctuations to be smaller than the resolution of experiments, as a rough estimate, more than $10^{14}$ particles. For arguments to be valid for small systems, they must at least be valid for large, finite systems.

The main source of disagreement is the fact that the microcanonical ensemble is not quite correct, although the discrepancies in most cases are very small. The errors in the Boltzmann and Gibbs entropies are usually of the order of $1/N$ or $\ln(N)/N$. Such errors are masked by fluctuations of order $1/\sqrt{N}$, and, indeed, are not measurable in a macroscopic system. These errors must nevertheless be taken seriously. The advocates of the Gibbs entropy have argued that the Boltzmann entropy violates thermodynamics for finite, classical systems because of discrepancies of the order of $1/N$ in the predicted energies. I will therefore examine the exact behavior of classical systems, even if the errors are as small as order $1/N$.

The practical purpose of thermodynamics is to predict the results of experiments. These predictions are ultimately based on probabilities calculated in statistical mechanics. For example, the probability distribution of the energy could be calculated by statistical mechanics for a system that had previously been in contact with another system. This calculated distribution could, in principle, be checked experimentally by many repetitions of the experiment, bringing two systems into thermal contact and then separating them. This is the concept of probability that I will use throughout.

Boltzmann was the first to establish a connection between thermodynamics and the probability of observing values of extensive variables in experiments.
The derivation of the probability distribution in Section II and the corresponding expression for the Boltzmann entropy in Section III is a generalization of Boltzmann’s idea to include the volume and the particle number as thermodynamic variables.

There is a error due to the use of the microcanonical ensemble: It gives expressions for the entropy that violate an exact thermodynamic stability condition [28, 29]. I will show that this is also corrected by the canonical and grand canonical entropies in section V.4.

In this paper, I will consider four expressions for the entropy, which use different approximations for the energy and particle number distributions. A detailed description of their properties are given in Sections III, IV, V and VI but a brief overview is given here.

1. The simplest is the Boltzmann entropy, which assumes that the number of particles is known exactly, and the energy distribution is a delta function.

2. Next comes the Gibbs entropy, which also assumes that the number of particles is known exactly, but that all states with energies below the energy of the system are counted. This is not the correct energy distribution, but it does provide a nonzero width. It gives the correct energy-temperature relationship for a density of states that increases with energy. If the density of states decreases with energy, the predicted energy distribution is incorrect.

3. The canonical entropy again assumes that the number of particles is known exactly, but uses the canonical ensemble to calculate the width the energy distribution (see Subsection V.2). It gives the correct energy dependence of the entropy for both increasing and decreasing densities of states.

4. The grand canonical entropy uses the grand canonical ensemble to calculate the entropy of both the energy and particle number distributions. It gives expressions for the entropy that are completely satisfactory. A striking feature is that the grand canonical entropy of the classical ideal gas is exactly extensive – without requiring Stirling’s approximation.

In Section II I begin the discussion of the relevant statistical mechanics with the calculation of the probability distribution for energies, volumes, and number of particles for a large number of systems that might, or might not, interact. I then discuss the Boltzmann and Gibbs entropies. I derive the canonical entropy. Finally, I derive the grand canonical entropy, which satisfies all thermodynamic conditions I summarize the findings in Section VII.

II. MACROSCOPIC PROBABILITIES

The basic problem of thermodynamics is to predict the equilibrium values of the extensive variables after the relaxation of a constraint between systems [29, 40]. The solution to this problem in statistical mechanics does not require any assumptions about the proper definition of entropy.

Consider a collection of $M \geq 2$ macroscopic systems, which include all systems that might, or might not, exchange energy, volume, or particles. Denote the phase space for the $j$-th system by $\{p_j, q_j\}$, where (in three dimensions) $p_j$ represents $3N_j$ momentum variables, and $q_j$ represents $3N_j$ configuration variables. Making the usual assumption that interactions between systems are sufficiently short-ranged that they may be neglected [27], the total Hamiltonian of the collection of systems can be written as a sum of contributions from each system.

$$H_T = \sum_{j=1}^{M} H_j(p_j, q_j)$$

The energy, volume, and particle number of system $j$ are denoted as $E_j$, $V_j$, and $N_j$ [41], and are subject to the conditions on the sums,

$$\sum_{j=1}^{M} E_j = E_T, \quad \sum_{j=1}^{M} V_j = V_T, \quad \sum_{j=1}^{M} N_j = N_T,$$  \hspace{1cm} (2)

where $E_T$, $V_T$, and $N_T$ are constants. The systems do not overlap each other. Naturally, only $3(N-1)$ of the variables are independent.

I am not restricting the range of the interactions within any of the $M$ systems. I am also not assuming homogeneity, so I do not, in general, expect extensivity [42]. For example, the systems might be inclosed by adsorbing walls. On the other hand, I will use the classical ideal gas, which is homogeneous and expected to be extensive, as a simple example.

Since I am concerned with macroscopic experiments, I assume that no measurements are made that might identify individual particles, whether or not they are formally indistinguishable [43]. Therefore, there are $N_T!/\left(\Pi_{j=1}^{M} N_j!\right)$ different permutations for assigning particles to systems, and all permutations are taken to be equally probable.

The probability distribution for the macroscopic observables in equilibrium can then be written as

$$W(\{E_j, V_j, N_j\}) = \frac{1}{\Omega_T} \frac{N_T!}{\prod_{j=1}^{M} N_j!} \times \int dp \int dq \prod_{j=1}^{M} \delta (E_j - H_j),$$  \hspace{1cm} (3)

The constraint that the $N_k$ particles in system $k$ are restricted to a volume $V_k$ is implicit in Eq. (3), and the walls containing the system may have any desired properties. $\Omega_T$ is a constant, which is determined by summing or integrating over all values of energy, volume, and particle number that are consistent with the values of $E_T$, $V_T$, and $N_T$ in Eq. (2). The value of the constant $\Omega_T$ does not affect the rest of the argument.
Eq. (3) can also be written as

$$W(\{E_j, V_j, N_j\}) = \frac{1}{\Omega_T} \prod_{j=1}^{M} \Omega_j(E_j, V_j, N_j), \quad (4)$$

where

$$\Omega_j = \frac{1}{\hbar^{3N_j} N_j!} \int_{-\infty}^{\infty} d^{3N} p_j \int d^{3N} q_j \delta(E_j - H_j), \quad (5)$$

and $\Omega_T$ is a normalization constant. The factor of $1/\hbar^{3N}$, where $\hbar$ is Planck’s constant, is included for agreement with the classical limit of quantum statistical mechanics.

For the classical ideal gas, which I will use as an example for each proposed entropy,

$$\Omega_{CIG}(E, V, N) = \frac{V^N}{h^{3N} N! (3N/2)!} m(2mE)^{3N/2-1}. \quad (6)$$

I have omitted the subscripts to make Eq. (6) more compact. The notation $(3N/2)!$ is a convenient shorthand for the more proper Gamma function.

III. THE BOLTZMANN ENTROPY, $S_B$

Consider $M \geq 2$ systems with Hamiltonians $H_j(p_j, q_j)$. The systems are originally isolated, but individual constraints may be removed or imposed, allowing the possibility of exchanging energy, particles, or volume. The number $M$ is intended to be quite large, since all systems that might interact are included. The magnitude of the energy involved in such potential interactions between systems is regarded as negligible. The probability distribution for the extensive thermodynamic variables, energy ($E_j$), volume ($V_j$), and number of particles ($N_j$), is given by the expression in Eqs. (4) and (5). The logarithm of Eq. (4) (plus an arbitrary constant, $C$) gives the Boltzmann entropy of the $M$ systems.

$$S_T(\{E_j, V_j, N_j\}) = \sum_{j=1}^{M} S_j(\{E_j, V_j, N_j\}) - k_B \ln \Omega_T + C, \quad (7)$$

where

$$S_j(E_j, V_j, N_j) = k_B \ln \Omega_j(E_j, V_j, N_j) \quad (8)$$

Using Eq. (5),

$$S_j = k_B \ln \left[ \frac{1}{\hbar^{3N_j} N_j!} \int d^{3N} p_j \int d^{3N} q_j \delta(E_j - H_j(p_j, q_j)) \right]. \quad (9)$$

Since the total Boltzmann entropy is the logarithm of the probability $W(\{E_j, V_j, N_j\})$, maximizing the Boltzmann entropy is equivalent to finding the mode of the probability distribution. This is not the same as finding the mean of the probability distribution, but the difference between the mean and the mode is usually of order $1/N$.

As mentioned in the Introduction, I will take even such small differences seriously.

For the classical ideal gas,

$$S_B(E, V, N) = k_B \ln \left( \frac{V^N}{h^{3N} N! (3N/2)!} (2mE)^{3N/2-1} \right), \quad (10)$$

or

$$S_B(E, V, N) = k_B \left[ \ln \left( \frac{(E^{3N/2-1})}{(3N/2)!} \right) + \ln \left( \frac{V^N}{N!} \right) + \ln X^N \right]. \quad (11)$$

where $X$ is a constant. I will avoid using Stirling’s approximation throughout the paper to make all approximations explicit.

III.1. Strengths of the Boltzmann entropy

If any constraint between any two systems is released, the probability distribution of the corresponding variable is given by $W$ in Eq. (3). Since the Boltzmann entropy is proportional to the logarithm of $W$, it correctly predicts the mode of the probability distribution. Whenever the peak is narrow, the mode is a very good estimate for the mean since the relative difference is of the order of $1/N$, while the fluctuations are of order $1/\sqrt{N}$.

III.2. Weaknesses of the Boltzmann entropy

- $\Omega(E, V, N)$ has units of inverse energy, so that it is not proper to take its logarithm. This issue can easily be resolved by multiplying $\Omega$ by a constant with units of energy before taking the logarithm in Eq. (9). This adds an arbitrary constant to the individual entropies, but since it has no effect on any thermodynamic prediction, it is not a serious problem.

- The Boltzmann entropy can be shown not to be adiabatically invariant \cite{7, 9, 15}. Campisi provides the following definition: “A function $I(E, V)$ is named an adiabatic invariant if, in the limit of very slow variation of $V(t)$ namely as $t \to \infty$, $I(E(t), V(t)) \to const.$” The violation of adiabatic invariance for the Boltzmann entropy results in a relative error of the order of $1/N$. The error is very small, but it is a weakness in the theory. It is related to the use of the mode instead of the average.

- The assumption of a microcanonical ensemble (that the probability distribution of the energy is a delta function) is incorrect. Since the width of the energy distribution is typically narrow, of order $1/\sqrt{N}$, where $N$ is the number of particles, the approximation is generally regarded as reasonable. It will turn out that this approximation is responsible for
some of the weaknesses in the theory and most of the disagreements.

- The number of particles $N$ is discrete. The relative distance between individual points is very small, but nevertheless the entropy is not a continuous, differentiable function of $N$ as assumed in thermodynamics. This discreteness is usually simply ignored.

- The assumption that the number of particles in our system is known exactly is never true for a macroscopic system. The width of the distribution of values of $N$ is much larger than the separation of points, and $\langle N \rangle$ should be used instead of $N$.

- The maximum of the Boltzmann entropy corresponds to the mode of the probability distribution – not the mean. This leads to small differences of order $1/N$. For example, a partial derivative of the Boltzmann entropy with respect to energy gives
  \[ U = (3N/2 - 1)k_BT, \]
  instead of
  \[ U = (3N/2)k_BT \]
  This error is unmeasurable for macroscopic systems\[26, 35\], but it is a weakness of the theory. It is the basis of the argument against the validity of the Boltzmann entropy.

- Although the classical ideal gas is composed of $N$ particles that do not interact with each other, the Boltzmann entropy is not exactly extensive (see Eq. (11)). We are used to this lack of extensivity for finite $N$, but it is incorrect.

- In the case of a first-order phase transition, the energy distribution is not narrow, and the microcanonical ensemble is not justified. At a first-order transition, a plot of the Boltzmann entropy against energy typically has a region of positive curvature, although a well-known thermodynamic requirement for stability states that the curvature must be negative\[39, 10\].
  \[ \left( \frac{\partial^2 S}{\partial E^2} \right)_{V, N} < 0 \]
  This problem is a serious flaw in the theory. I will discuss it in Sections \[\text{V}\] and \[\text{VI}\].

III.3. The approximation of the Boltzmann entropy

The Boltzmann entropy has assumed that the individual systems have a microcanonical energy distribution (i.e.: a Dirac delta function in the energy). This is a reasonable assumption, since the true distribution is known to be very narrow – the relative width is of order $1/\sqrt{N}$.

However, a better approximation would be given by the canonical distribution, which leads to the canonical entropy, discussed in Section \[\text{VII}\]. Similarly, the Boltzmann entropy and the canonical entropy both assume that the exact number of particles is known. This is also a reasonable approximation, but not really correct. In Section \[\text{VI}\] the approximation of the distribution will again be improved by using the grand canonical ensemble.

The three forms of the entropy, Boltzmann, Canonical, and Grand Canonical, are then based of successive improvements on the underlying probability distribution of the individual system. It will become clear that the corresponding forms of the entropy are also successive improvements.

The Gibbs entropy, introduced in the next section, is an exception. It is not closely related to the energy distribution of the individual system, except in the case of a density of states that is a monotonically increasing with energy. For a decreasing density of states, the distribution of states contributing to the Gibbs entropy bears no resemblance to the probability distribution.

IV. THE GIBBS ENTROPY, $S_G$

The Gibbs (or volume) entropy is defined by an integral over all energies less than the energy of the system\[3, 4\]. It has the form
  \[ S_G = k_B \ln \left[ \int_0^E \Omega(E', V, N)dE' \right] \]  \[\text{(15)}\]

IV.1. Strengths of the Gibbs entropy

- The integral in the definition of the Gibbs entropy in Eq. (15) is dimensionless, so there is no problem in taking its logarithm.

- The Gibbs entropy can be shown to be adiabatically invariant\[7, 9, 15\].

- For the Gibbs entropy of classical systems with a monotonically increasing density of states, the predicted energy is exactly correct\[8, 9, 12-16\], although this is not true of quantum systems\[27, 28\].

IV.2. Weaknesses of the Gibbs entropy

- The assumption of a microcanonical ensemble (that the probability distribution of the energy is a delta function) is incorrect.

- The assumption that the number of particles are in our system is known exactly is incorrect.

- The number of particles $N$ is discrete, and should be replaced by the continuous variable $\langle N \rangle$.
• Although the classical ideal gas is composed of \( N \) particles that do not interact with each other, the Gibbs entropy is not exactly proportional to \( N \). This lack of extensivity of the Gibbs entropy is essentially the same as for the Boltzmann entropy.

• The Gibbs entropy also violates the thermodynamic inequality,

\[
\left( \frac{\partial^2 S}{\partial E^2} \right)_{V,N} < 0, \quad (16)
\]
at a first-order transition.

• For a non-monotonic density of states, the Gibbs entropy gives counter-intuitive results. Consider two homogeneous systems with the same composition and a decreasing density of states for the energies of interest (for example: independent spins in a field). Let them have the same energy per particle, but let one be twice as large as the other. There will be no net transfer of energy if the two systems are put in thermal contact. The Boltzmann temperature will be the same for both systems, as expected. However, the Gibbs temperature of the larger system will be higher.

• Because larger systems have higher Gibbs temperature, it is impossible to construct a thermometer that measures the Gibbs temperature in an energy range with a decreasing density of states.

The weaknesses of both the Boltzmann and the Gibbs entropies can be avoided by using the canonical and grand canonical ensembles, instead of the microcanonical ensemble.

V. THE CANONICAL ENTROPY, \( S_C \)

I have chosen to express the thermodynamic results in terms of Massieu functions\(^3\), because they do not require the inversion of the fundamental relation \( S = S(U,V,N) \). The inversion to find \( U = U(S,V,N) \) is unnecessary and is not valid for systems with a non-monotonic density of states.

V.1. The general derivation of the canonical entropy

Define a dimensionless entropy as

\[
\tilde{S} = \frac{S}{k_B} \quad (17)
\]

Since

\[
dU = TdS - PdV + \mu dN \quad (18)
\]

and the inverse temperature is \( \beta = 1/k_B T \), we also have

\[
d\tilde{S} = \beta dU + \beta PdV - \beta \mu dN, \quad (19)
\]

where \( P \) is the pressure, \( V \) is the volume, \( \mu \) is the chemical potential, and \( N \) is the number of particles. From Eq. \[(19)\],

\[
\beta = \left( \frac{\partial \tilde{S}}{\partial U} \right)_{V,N}. \quad (20)
\]

The Legendre transform (Massieu function) of \( \tilde{S} \) with respect to \( \beta \) is given by

\[
\tilde{S}[\beta] = \tilde{S} - \beta U = -\beta (U - TS) = -\beta F, \quad (21)
\]

so that

\[
\tilde{S}[\beta] = \ln Z(\beta, V, N). \quad (22)
\]

The differential of the Massieu function \( \tilde{S}[\beta] \) is

\[
d\tilde{S}[\beta] = -Ud\beta + \beta PdV - \beta \mu dN. \quad (23)
\]

This immediately gives

\[
\left( \frac{\partial \tilde{S}[\beta]}{\partial \beta} \right)_{V,N} = -U. \quad (24)
\]

To obtain \( \tilde{S} \) from \( \tilde{S}[\beta] \), use

\[
\tilde{S} = \tilde{S}[\beta] + \beta U, \quad (25)
\]

and substitute \( \beta = \beta(U) \).

V.2. The justification of the canonical entropy

The use of the canonical ensemble to calculate the entropy of a general system requires some discussion. That the probability distribution of the energy is not a delta function has been proven\(^2\). If the system of interest has been in contact with a much larger system it is clear that the canonical ensemble is appropriate. However, if the system of interest has instead been in contact with a system that is the same size or even smaller, it is known that the distribution is narrower than the canonical distribution\(^4\). Nevertheless, the canonical entropy is appropriate for calculating the thermodynamic entropy.

Consider three macroscopic systems labeled \( A \), \( B \), and \( C \). Let systems \( A \) and \( B \) be constructed to be exactly the same, and in particular to be equal in size. Let system \( C \) be much larger than \( A \) and \( B \). Suppose all three systems are in thermal contact and have come to equilibrium. The entropies of systems \( A \) and \( B \) are then equal, and given by the canonical form discussed in the previous subsection.

Now remove system \( C \) from thermal contact with the other two systems. This is obviously a reversible process. \( A \) or \( B \) are still in equilibrium with each other at the same temperature as before \( C \) 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. If the entropy were to increase upon separation, putting system \( C \) back into thermal contact with systems \( A \) and \( B \) 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. Therefore, the canonical entropy is properly defined for all systems, regardless of their history or their size.

V.3. The canonical entropy of the ideal gas

Again we consider the special case of the classical ideal gas. Start with the canonical partition function.

\[
Z = \frac{1}{h^{3N} N!} \int_{-\infty}^{\infty} d^{3N} p \int d^{3N} q \exp[-\beta H]
= \frac{1}{h^{3N} N!} V^N \int_{-\infty}^{\infty} d^{3N} p \exp[-\beta \sum_{j=1}^{3N} p_j^2 / 2m]
= \frac{1}{N!} V^N \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2}
\]

Eq. (26).

\[
\tilde{S}[\beta] = \ln \left[ \frac{1}{N!} V^N \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2} \right],
\]

and Eq. (24),

\[
-U = \left( \frac{\partial \tilde{S}[\beta]}{\partial \beta} \right)_{V,N},
\]

give the equation for \( U \).

\[
U = -\frac{\partial}{\partial \beta} \ln \left[ \frac{1}{N!} \left( \frac{V}{h^2} \left( \frac{2\pi m}{\beta} \right)^{3/2} \right)^N \right]
\]

Evaluating Eq. (29) gives

\[
U = (3/2)N(1/\beta),
\]

or,

\[
U = \frac{3}{2} N k_B T.
\]

This equation is exact, while the usual Boltzmann entropy gives an error of order \( 1/N \).

To obtain \( \tilde{S} \) from \( \tilde{S}[\beta] \), use

\[
\tilde{S} = \tilde{S}[\beta(U)] + \beta(U) U.
\]

Since \( \beta = 3N/2U \) from Eq. (30),

\[
\tilde{S} = \ln \left[ \frac{1}{N!} \left( \frac{V}{h^2} \left( \frac{4U \pi m}{3N} \right)^{3/2} \right)^{N/2} \right] + \frac{3N}{2}
\]

Writing this out:

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

Note that Eq. (34) uses \( U = \langle E \rangle \). The factorial \((3N/2)!\), which comes from the surface area of a 3N-dimensional sphere in momentum space, appears in the Boltzmann entropy, but not in the canonical entropy. Only the term involving the volume \( V \) involves a factorial \((1/N!)\). This comes from treating \( N \) as a discrete variable, which will be corrected by using the grand canonical ensemble in Section V.4.

The problem of misrepresenting first-order phase transitions is also solved by using the canonical entropy [28, 38], as shown in the next section.

V.4. First-order phase transitions in theCanonical entropy

The density of states for a system in which a first-order transition is taking place is characterized by a region of energies for which

\[
\frac{\partial^2 \ln \Omega(E)}{\partial E^2} > 0.
\]

This is a useful way of identifying first-order transition numerically. However, if the entropy is defined by either \( S_B \) or \( S_G \), then these expressions will also have a region of energies with

\[
\frac{\partial^2 S(E)}{\partial E^2} > 0.
\]

This is forbidden by a well-known thermodynamic stability condition [39, 40].

A simple generic model density of states can be constructed that has this property.

\[
\ln \Omega_1(E) = AN \left( \frac{E}{N} \right)^{\alpha} + BN \exp \left( \frac{E^2}{2\sigma_N^2} \right) - BN \exp \left( - \frac{(E - E_{N,0})^2}{2\sigma_N^2} \right)
\]

The center of the Gaussian term is taken to be \( E_{N,0} = f N\epsilon \), and the width of the Gaussian is \( \sigma_N = g E_{N,0} \). If the parameter \( B \) does not depend on \( N \), this model corresponds to a mean-field transition, while if \( B \) decreases as \( N \) increases, it corresponds to a system with short-range interactions. The behavior is qualitatively the same in both cases. I will treat the case of \( B \) being constant, because it is the more stringent test of the method.

Figure 1 shows \( S_B(E)/N = k_B \ln \Omega(E)/N \) vs. \( E/N\epsilon \). The dip in the density of states and the region of positive curvature can be seen clearly. Figure 1 also shows \( S_C(U)/N \) for \( N = 10, 50, \) and 250, where \( U = \langle E \rangle \). In all cases, the plot of \( S_C \) shows the negative curvature required for stability throughout.
FIG. 1. The top curves (dotted, dot-dash, and dashed) indicate the canonical entropy $S_C/N$ for $N = 10$, 50, and 250. The solid curve shows $S_B$, which is the same in the model for all $N$. The parameters are $\epsilon = 1$, $\alpha = 0.5$, $A = 1$, $B = 0.4$, $f = 2$, and $g = 0.1$, but other values give similar results.

V.5. Strengths of the Canonical entropy

The canonical entropy for the thermodynamic entropy is superior to than either the Boltzmann or the Gibbs entropies.

- The canonical entropy is adiabatically invariant.
- The canonical entropy gives a thermodynamically correct description of first-order transitions.
- The canonical entropy has an energy term of $(3/2)k_B N \ln (U/N)$ for the ideal gas, which is correct. As a consequence, the canonical entropy also gives the exact energy for the classical ideal gas.

$$U = (3N/2)k_B T$$ (38)

V.6. Weaknesses of the Canonical entropy

- The canonical entropy assumes that the value of $N$ is known exactly, instead of using a distribution of possible values of $N$.
- The number of particles $N$ is discrete.
- The assumption that the number of particles is known exactly is incorrect.
- The deviation from exact extensivity (in the factor $1/N$) is a weakness. This lack of extensivity of the canonical entropy differs from that of the Boltzmann entropy, in that it does not affect the energy-dependent term.

VI. THE GRAND CANONICAL ENTROPY, $S_{GC}$

The grand canonical entropy satisfies all criteria required by thermodynamics.

VI.1. The definition of the grand canonical Legendre transform

For the grand canonical ensemble, $S[\beta, (\beta \mu)]$ will be used. I have put parentheses around the second variable to emphasize that the product of $\beta$ and $\mu$ is to be treated as a single variable. To find the Legendre transform with respect to both $\beta$ and $(\beta \mu)$ use the equation

$$-(\beta \mu) = \left( \frac{\partial S}{\partial N} \right)_{U,N}$$ (39)

in addition to Eq. (20).

The Legendre transform (Massieu function) of $\tilde{S}$ with respect to both $\beta$ and $(\beta \mu)$ is given by

$$\tilde{S}[\beta, (\beta \mu)] = \tilde{S} - \beta U + (\beta \mu)N,$$ (40)

so that

$$\tilde{S}[\beta, (\beta \mu)] = \ln \mathcal{Z}(\beta, V, (\beta \mu)), $$ (41)

where $\mathcal{Z}$ is the grand canonical partition function.

The differential of the Massieu function $\tilde{S}[\beta, (\beta \mu)]$ is

$$d\tilde{S}[\beta, (\beta \mu)] = -Ud\beta + \beta PdV + Nd(\beta \mu).$$ (42)

This immediately gives

$$\left( \frac{\partial \tilde{S}[\beta, (\beta \mu)]}{\partial \beta} \right)_{V,(\beta \mu)} = -U,$$ (43)

and

$$\left( \frac{\tilde{S}[\beta, (\beta \mu)]}{\partial (\beta \mu)} \right)_{\beta,V} = N.$$ (44)

To obtain $\tilde{S}$ from $\tilde{S}[\beta, (\beta \mu)]$, use

$$\tilde{S} = \tilde{S}[\beta, (\beta \mu)] + \beta U - (\beta \mu)N,$$ (45)

and replace the $\beta$ and $(\beta \mu)$ dependence by $U$ and $\langle N \rangle$.

VI.2. The grand canonical entropy of the ideal gas

For the example of the classical ideal gas, the canonical partition function is given in Eq. (26).

$$Z = \frac{1}{N!} V^N \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2}$$ (46)
To obtain the grand canonical partition function, multiply this by \( \exp[(\beta \mu)N] \) and sum over \( N \).

\[
Z = \sum_{N=0}^{\infty} \frac{1}{N!} \left( V \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} \right)^{N} \exp[(\beta \mu)N] \tag{47}
\]

The series sums to an exponential.

\[
Z = \exp \left[ \left( V \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} \right) \exp[(\beta \mu)] \right] \tag{48}
\]

The Massieu function for the grand canonical ensemble is

\[
\tilde{S}[\beta, (\beta \mu)] = \ln Z(\beta, V, N). \tag{49}
\]

\[
\tilde{S}[\beta, (\beta \mu)] = \left( V \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} \right) \exp[(\beta \mu)] \tag{50}
\]

The average number of particles is given by

\[
\langle N \rangle = \left( \frac{\partial \tilde{S}[\beta, (\beta \mu)]}{\partial (\beta \mu)} \right)_{\beta, V} = \tilde{S}[\beta, (\beta \mu)]. \tag{51}
\]

This equation can be used to solve for \( (\beta \mu) \).

\[
\langle N \rangle = \left( V \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2} \right) \exp[(\beta \mu)] \tag{52}
\]

\[
(\beta \mu) = \ln \left[ \frac{\langle N \rangle}{V} \left( \frac{\beta \hbar^2}{2\pi m} \right)^{3/2} \right] \tag{53}
\]

To find the energy, use

\[
- U = -\frac{3}{2} \beta^{-5/2} \left( V \left( \frac{2\pi m}{\hbar^2} \right)^{3/2} \right) \exp[(\beta \mu)], \tag{54}
\]

or, using \( \langle N \rangle = \tilde{S}[\beta, (\beta \mu)] \)

\[
U = \frac{3}{2} \beta^{-1} \langle N \rangle \tag{55}
\]

To obtain \( \tilde{S} \) from \( \tilde{S}[\beta, (\beta \mu)] \), use the inverse Legendre transform.

\[
\tilde{S} = \tilde{S}[\beta(U, (\langle N \rangle)), (\beta \mu)] + (\beta \mu) \langle N \rangle U - (\beta \mu) \langle N \rangle \tag{56}
\]

Inserting \( \beta(U, (\langle N \rangle)) \) and using \( S = k_B \tilde{S} \) gives the grand canonical entropy.

\[
S_{GC} = \langle N \rangle k_B \left[ \frac{3}{2} \ln \left( \frac{U}{\langle N \rangle} \right) + \ln \left( \frac{V}{\langle N \rangle} \right) + \ln \left( \frac{4\pi m}{\beta \hbar^2} \right)^{3/2} + \frac{5}{2} \right] \tag{59}
\]

This expression for the entropy of a classical ideal gas is exactly extensive, and no use has been made of Stirling’s approximation.

### VI.3. Strengths of the grand canonical entropy

The grand canonical entropy retains the advantages of the canonical entropy, but also has a correct description of the distribution of particles. It provides a completely consistent description of the properties of a thermodynamic system.

The grand canonical entropy for the classical ideal gas is exactly extensive, which is expected of a model in which there are no explicit interactions between particles.

### VI.4. Weaknesses of the grand canonical entropy

None.

### VII. SUMMARY

I have discussed the properties of four different definitions of the classical entropy from statistical mechanics: the Boltzmann, the Gibbs, the canonical, and the grand canonical. I have shown that the microcanonical assumption (that the energy is known exactly) is responsible for weaknesses in the Boltzmann entropy, and that the grand canonical entropy satisfies all thermodynamic requirements.

The original arguments against negative temperatures were actually aimed at the Boltzmann entropy. In particular, the violation of adiabatic invariance was regarded as being thermodynamically inconsistent, even though the violation was very small. The grand canonical entropy does not suffer from any of such weakness. It gives consistent thermodynamics for all temperatures, effectively removing the original argument against negative temperatures.

The grand canonical entropy has other advantages.

For models of independent particles, the entropy is expected to be exactly extensive, which is the case for the grand canonical entropy, but not for the other three definitions.

First-order transitions were shown to be correctly represented by the canonical and grand canonical ensembles in Section VI.4 but by neither the Boltzmann nor the
Gibbs entropies. The same was shown to be true for quantum systems in Ref. [28].

The Gibbs entropy has much the same behavior as the Boltzmann entropy for a monotonically increasing density of states. The difference is only in the energy dependence of the entropy, which is correct for the Gibbs entropy (and $S_C$ and $S_{GC}$), while the Boltzmann entropy has an error of order $1/N$. The both the Boltzmann and the Gibbs entropy have $\ln(N)/N$ errors in the $N$-dependence.

The Gibbs entropy has serious problems for a decreasing density of states, for which it is the only definition that fails to predict negative temperatures. The Gibbs entropy fails to predict the correct equilibrium values of the energy for a decreasing density of states. Equality of the Gibbs temperature for systems of different sizes does not predict that there will be no net transfer of energy if the two systems are put in thermal contact with each other. The Boltzmann, canonical, and grand canonical entropies all predict the physical behavior correctly.

The question of whether negative temperatures are thermodynamically consistent is most naturally discussed in quantum statistical mechanics. Various models were investigated in Ref. [27] and [28], included independent spins and the two-dimensional, twelve-state Potts model. The canonical entropy describes the behavior of these models with negative temperatures, and without the weaknesses that have sparked criticism of the Boltzmann entropy.

The Boltzmann entropy, $S_B$, has received a great deal of criticism during the controversy concerning negative temperatures [7–10]. However, after recognizing that the grand canonical entropy is correct, we can see that the Boltzmann entropy provides an excellent description of thermodynamics, if the missing factor of the energy in $\Omega(E,V,N)$ is ignored, and Stirling’s approximation is used whenever factorials are encountered. In other words, the Boltzmann entropy is usually quite satisfactory, if we agree to ignore errors of the order of $1/N$.

The exception to the validity of the Boltzmann entropy is a first-order phase transition. In that case, the energy distribution is broad (violating an assumption made in the derivation of the Boltzmann entropy), and the canonical or grand canonical entropy should used. However, a good approximation to the true entropy can be obtained by the well-known double-tangent construction. This will fail to show the finite-size rounding, but is otherwise satisfactory.

These results should settle the controversy in favor of the thermodynamic validity of negative temperatures. The Gibbs entropy is useful only for models with increasing densities of states. The correct entropy is given by the grand canonical formulation, but the Boltzmann entropy is generally satisfactory.

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