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The Gibbs “volume” entropy is incorrect

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In recent papers, several authors have claimed that a definition of the thermodynamic entropy in terms of the logarithm of a volume in phase space, originally suggested by Gibbs, is the only valid definition. Arguing from the Gibbs entropy, these authors claim that thermodynamics cannot be extended to include negative temperatures. However, the Gibbs entropy fails to satisfy the postulates of thermodynamics, leading to serious errors. In particular, predictions of the Gibbs entropy for systems with non-monotonic energy densities are incorrect. We show that the correct expression for the equilibrium entropy contains an integral over a surface in phase space, and negative temperature is a valid thermodynamic concept.

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INTRODUCTION

Several authors have recently claimed that the only valid definition of the thermodynamic entropy in statistical mechanics is in terms of the logarithm of a volume in phase space, as originally suggested by Gibbs[1–7]. Since the volume entropy predicts only positive temperatures, these authors claim that negative temperature is not a valid thermodynamic concept. We will demonstrate that these claims are incorrect due to the extrapolation of a derivation beyond its limits of applicability. We show that the concept of negative temperature is a valid extension of thermodynamics[8–10].

Advocates of the volume entropy have also claimed that it can be used to calculate the thermal properties of very small systems – even systems containing only a single particle. We believe that this is a misinterpretation of thermodynamics, and a failure to recognize the importance of fluctuations in small systems. We see no advantage to using any form of entropy to predict the behavior of small systems over directly applying statistical mechanics. Thermodynamics predicts measurements on macroscopic systems, so we will only consider systems that contain many particles.

The debate over the volume entropy has also been extended to quantum systems[2–7], but we will limit the present discussion to classical statistical mechanics. The special features of quantum entropy will be addressed elsewhere[11, 12].

We will present a series of arguments against the volume entropy. We will review the postulates of thermodynamics and show that they are violated by the volume entropy[11, 13, 14]. After that, we will discuss the predictions of statistical mechanics for macroscopic sys-

tems, and show how they lead to an expression for the equilibrium entropy that exactly predicts the mode, and which does satisfy the postulates of thermodynamics. We will demonstrate that the volume entropy makes incorrect predictions for systems with non-monotonic densities of states. Finally, we will discuss the significance of the the difference between the mean and the mode in macroscopic measurements. We begin our analysis with the role of probability in statistical mechanics and thermodynamics.

MACROSCOPIC EXPERIMENTS AND PROBABILITY

Thermodynamics predicts specific values for quantities that can be measured in experiments on macroscopic systems. Statistical mechanics, in contrast, predicts a probability distribution, where the width of the distribution gives the thermal fluctuations. The two types of predictions are compatible because the probability distributions for macroscopic systems are very narrow, with a relative width of the order of $1/\sqrt{N}$, where N is the number of particles. If this width is less than the experimental resolution, as it usually is, a prediction of statistical mechanics is equivalent to a single value. Since the entropy is a maximum in equilibrium, it is natural to take this value to be the location of the maximum probability, that is, the mode of the distribution. As shown below, this leads to an expression for the equilibrium entropy that correctly predicts the mode in all cases, and which contains an integral over a surface in phase space.

The arguments that have been advanced in favor of the volume entropy have been based on the two claims that (1) only the mean of the probability distribution can represent a thermodynamic prediction, and (2) the volume entropy correctly predicts the mean. The first claim is dubious for reasons given later, and all arguments that have been put forward for the second are only valid

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for systems governed by an unbounded energy spectrum. The predictions of the volume entropy are very bad for non-monotonic densities of states, as we will demonstrate by extending an argument given in Ref. 6.

THE POSTULATES OF THERMODYNAMICS

We will discuss why each postulate is needed.

Postulate 1: Equilibrium states. There exist equilibrium states of a composite macroscopic system that are characterized uniquely by a small number of extensive variables.

The extensive variables for systems composed of particles are the energies, volumes, and particle numbers for each subsystem in the (isolated) composite system. For simplicity of notation, we will only consider a single type of particle, but the generalization to any number of particle types is trivial. For other systems, the magnetization and electrical polarization might also be included.

The first postulate requires the equilibrium state of a system to be independent of its history. This leads to the concept of a state function, which is a quantity that is determined exclusively by the equilibrium state of the system, and therefore by the values of the extensive variables.

The specification of a composite system is necessary for the application of the second postulate, which is a particular form of the second law of thermodynamics.

Postulate 2: Maximization of the entropy. For every isolated composite system, there exists a state function called the entropy, such that the equilibrium values assumed by the extensive variables in the absence of one or more constraints are those that maximize the entropy over the set of all constrained macroscopic states.

The word constraint refers to any restriction on the values of the external variables. An extreme example would occur if all subsystems were isolated, so that all extensive variables were constant. The opposite extreme of no constraints other than the total energy, volume and particle number would mean everything can be exchanged freely between subsystems.

The second postulate enables thermodynamics to make testable experimental predictions. It also indirectly specifies the domain of thermodynamics. Because of the existence of fluctuations in the absence of a constraint, prediction is only possible if the resolution of a relevant experiment is not sufficient to detect fluctuations. Since the relative magnitude of fluctuations generally goes as $1/\sqrt{N}$, this condition is fulfilled by most macroscopic experiments.

The first two postulates should even be valid for systems that include long-range interactions between particles in different subsystems. The next postulate is restricted to cases in which direct interactions between particles in different subsystems can be neglected.

Postulate 3: Additivity. If direct interactions between particles in different subsystems are negligible, the entropy of a composite system can be expressed as the sum of the entropies of its subsystems.

If we denote the energy, volume, and particle number of the j -th subsystem as E_j , V_j , and N_j , and the set of all energies, volumes, and particles numbers as $\{\mathbf{E}, \mathbf{V}, \mathbf{N}\} = \{E_j, V_j, N_j | j = 1, \dots, M\}$, postulate 3 says that we can write the total entropy of the composite system as

$$S_T(\mathbf{E}, \mathbf{V}, \mathbf{N}) = \sum_{j=1}^M S_j(E_j, V_j, N_j), \quad (1)$$

where the function S_j is the entropy of the subsystem j . This postulate does not distinguish between subsystems that are isolated from each other and subsystems that are in thermal contact. Because entropy is a state function, the functional dependence of the entropy on the extensive variables cannot change.

Since most results in thermodynamics are expressed in the language of calculus, the next postulate plays an important role.

Postulate 4: Analyticity. The entropy is a continuous and differentiable function of the extensive variables.

As an example of why analyticity is important, consider two thermodynamic systems in thermal contact with entropies S_1 and S_2 , and total entropy $S_{1,2} = S_1 + S_2$. In equilibrium, $S_{1,2}$ takes on its maximum value while the total energy $E_{1,2} = E_1 + E_2$, remains constant, and the location of the maximum of $S_{1,2}$ gives the equilibrium values of E_1 and E_2 . S_1 and S_2 satisfy the condition

$$\frac{\partial}{\partial E_1} [S_1(E_1, V_1, N_1) + S_2(E_{1,2} - E_1, V_2, N_2)] = 0, \quad (2)$$

which can be rewritten as

$$\left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} = \left(\frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2}. \quad (3)$$

Eq. (3) exhibits a property of each system that must have the same value when the systems are in equilibrium. This means that if two systems with the same value of $\partial S/\partial E$ are brought into thermal contact, there will be no net energy transfer, and no increase in the total entropy.

This immediately gives the zeroth law of thermodynamics: If two systems are each in equilibrium with a

third system, they will also be in equilibrium with each other. These results are also valid for partial derivatives with respect to volume and particle number.

The temperature, T , is not mentioned in the fundamental postulates[11, 13–15], but it is clear from Eq. (3) that $\partial S/\partial E$ is related to the temperature. If the ideal gas law ($PV = Nk_B T$) is used to define a thermometer, we can relate the partial derivatives in Eq. (3) to the temperature:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}. \quad (4)$$

Without Eq. (3), there would be no justification for defining the temperature in Eq. (4).

The analyticity postulate is essential to the standard mathematical manipulations in thermodynamics. It is, however, not exactly true for some of the most intensively studied models in thermal physics. To begin with the most obvious, particle numbers are discrete, not continuous, but as a practical matter, the discreteness is extremely fine grained and can usually be ignored with impunity. Since the resolution of thermodynamic measurements is limited, the discreteness of N_j is not macroscopically measurable.

The discreteness of energy eigenvalues in quantum systems requires a more extensive discussion than we have room for in this paper, and will be examined elsewhere[11, 12].

The next postulate is at the center of the debate concerning the volume entropy.

Postulate 5: Monotonicity (optional).

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

Although not essential to thermodynamics, this postulate is usually assumed in order to allow the entropy function of a subsystem $S = S(E, V, N)$ (ignoring subscripts for simplicity) to be inverted to give $E = E(S, V, N)$. This inversion enables Legendre transforms to generate the various familiar thermodynamic potentials[11, 14]. If non-monotonic entropy functions are permitted, we cannot invert the entropy function, but we can still use Massieu functions, which are Legendre transforms of $S = S(E, V, N)$ [11, 14]. If we define a dimensionless entropy $\tilde{S} = S/k_B$, its Legendre transform with respect to the variable $\beta = 1/k_B T$ is $\tilde{S}[\beta] = -\beta F(T, V, N)$, where F is the Helmholtz free energy.

Because of Eq. (4), if the entropy is not a monotonic function of the energy, the temperature $T = 1/k_B \beta$ can be negative. There is no thermodynamic reason for excluding negative temperatures, other than the convenience of being able to use the more familiar Legendre transforms of the energy.

EQUILIBRIUM STATISTICAL MECHANICS AND ENTROPY

Fortunately, the predictions of statistical mechanics are less subject to debate than the definition of entropy. By examining how statistical mechanics makes predictions for the same experimental questions as thermodynamics, we will derive an expression for the equilibrium entropy.

We are concerned with the properties of a composite system containing $M \geq 2$ subsystems, which is isolated from the rest of the universe. The total energy, volume, and particle number(s) are constant. The phase space of subsystem j is $\{p_j, q_j\}$, where p_j is the set of all momenta and q_j is the set of all position coordinates. The phase space of the composite system is $\{p, q\} = \{p_j, q_j | j = 1, 2, \dots, M\}$. We denote the Hamiltonian of subsystem j as $H_j(p_j, q_j)$, and assume that we can neglect direct interactions between particles in different subsystems. The Hamiltonian of the composite system can then be written as

$$H_T(p, q) = \sum_j H_j(p_j, q_j). \quad (5)$$

Consider the microcanonical ensemble for the full composite system, which has uniform probability in $\{p, q\}$, subject to the fixed values of the total energy, E_T , volume, V_T , and number of particles, N_T . We can find the probability distribution of a macroscopic state $\{\mathbf{E}, \mathbf{V}, \mathbf{N}\}$ by integrating over p and q .

$$W(\mathbf{E}, \mathbf{V}, \mathbf{N}) = \frac{1}{\Omega_T} \frac{N_T!}{\prod_j N_j!} \int dp \int dq \times \prod_j \delta(E_j - H_j(p_j, q_j)). \quad (6)$$

The constant Ω_T is a normalizing factor. The multinomial factor in Eq. (6) reflects the condition that N_j specifies how many particles are in subsystem j , but not which ones; all permutations of particles are equally probable[16]. $W(\mathbf{E}, \mathbf{V}, \mathbf{N})$ can also be written as a product of terms, with one term from each subsystem,

$$W(\mathbf{E}, \mathbf{V}, \mathbf{N}) = \frac{1}{\Omega_T} \prod_j \Omega_j(E_j, V_j, N_j), \quad (7)$$

where

$$\Omega_j = \frac{1}{h^{3N_j} N_j!} \int dp_j \int dq_j \delta(E_j - H_j(p_j, q_j)), \quad (8)$$

and the integral over q_j is restricted to the volume V_j .

If the values of any constrained variables are kept constant in $W(\mathbf{E}, \mathbf{V}, \mathbf{N})$, we have the probability distribution for the remaining unconstrained variables. From this function, we can predict both the equilibrium values of the extensive variables and their fluctuations. $W(\mathbf{E}, \mathbf{V}, \mathbf{N})$ will have very narrow peaks around the equilibrium values of the unconstrained variables.

As discussed in the Introduction, we take the mode of W (the location of the maximum probability) to be the equilibrium value. We can then see that the expression

$$S(\mathbf{E}, \mathbf{V}, \mathbf{N}) = k_B \ln W(\mathbf{E}, \mathbf{V}, \mathbf{N}) + \text{const} \quad (9)$$

satisfies all the postulates of thermodynamics. By appropriate choice of constants, we can write the entropy of a system in equilibrium as

$$S(\mathbf{E}, \mathbf{V}, \mathbf{N}) = \sum_j S_j(E_j, V_j, N_j), \quad (10)$$

where the equilibrium entropy of a subsystem is given by

$$S_j(E_j, V_j, N_j) = k_B \ln \Omega_j(E_j, V_j, N_j). \quad (11)$$

The expression for the entropy of a subsystem in equilibrium agrees with what is often denoted as S_B , in honor of Boltzmann, who derived the equilibrium energy dependence in Eqs. (8) and (11)[16–18]. It is also called the surface entropy because the delta function in Eq. (8) limits the integral to a surface in phase space. However, although Eqs. (8) and (11) give the equilibrium entropy of a subsystem, it is Eq. (9) that actually constitutes the definition of the entropy[11, 16, 19–21]. The distinction between the definition of the entropy and equations for the equilibrium entropy of a subsystem is not essential to the current discussion, but it is critical in other contexts. Liouville’s theorem requires that the integral in Eq. (8) must be time-independent for irreversible processes following the release of a constraint. The probability distribution for the variables $\{\mathbf{E}, \mathbf{V}, \mathbf{N}\}$ is time dependent. It will go to $W(\mathbf{E}, \mathbf{V}, \mathbf{N})$ for irreversible processes, and the entropy will increase[19, 21, 22].

THE VOLUME ENTROPY AND THE POSTULATES OF THERMODYNAMICS

Hilbert, Hänggi, and Dunkel (HHD) have given an extended description of how they interpret the volume entropy[6]. However, their interpretation fails to satisfy the first three postulates of thermodynamics. The central problem is that they find the total entropy of two systems in thermal contact by a new calculation in statistical mechanics, rather than the sum of the entropies. This violates additivity. Furthermore, the new entropy for the combined system is a function of the total energy, not the energies of the individual systems. This eliminates the possibility of predicting the equilibrium values of the individual energies from the location of the maximum total entropy. As far as we can tell, the volume entropy in this interpretation leads to no thermodynamic predictions.

Because the total entropy of two systems in thermal contact differs from the sum of the entropies of the individual systems even if there is no net energy transfer due to the thermal contact, the volume entropy is not a state

function. Furthermore, the entropy can be changed by a measurement, even if the measurement does not change the values of the extensive variables (see footnote 24 of Ref. [6]). Since the volume entropy depends on the history of the system, it is not a state function.

Finally, in this interpretation, the volume entropy fails to satisfy Eq. (3) ($\partial S_1/\partial E_1 = \partial S_2/\partial E_2$). We regard Eq. (3) as an essential consequence of the postulates of thermodynamics, but it is dismissed as “naive” in Ref. 6.

There is an alternative interpretation of the volume entropy that would retain additivity. This interpretation would satisfy postulates 1 and 3. It does lead to predictions for the energies of individual systems in thermal contact, but it does not give the correct equilibrium values for non-monotonic densities of states, as discussed in the next section.

NON-MONOTONIC DENSITY OF STATES

The arguments in favor of the volume entropy are based on the demonstration in Ref. [3] that it gives the correct mean energy for systems with unbounded energy spectra, rather than the mode found by our definition in terms of probabilities. Unfortunately, the assumption that the volume entropy would also give the mean for systems with bounded energy spectra is not valid. An extension of an argument given in Ref. 6, shows that the volume entropy gives incorrect predictions for this case. This is particularly important because these are the systems at the center of the debate concerning negative temperatures.

Consider two systems that each have non-monotonic densities of states of the form

$$\Omega_j(E_j) \propto E_j^{n_j} (E_{j,\text{max}} - E_j)^{n_j}, \quad (12)$$

where n_j indicates the number of degrees of freedom (proportional to the number of particles). The minimum energy is 0, and $E_{j,\text{max}}$ specifies the maximum energy in system j . For the special case of $n_1 = n_2 = 1$ and $E_{1,\text{max}} = 2E_{2,\text{max}}$, Ref. 6 investigated whether systems initially at equal temperatures would have no net energy transfer after being brought together. Fig. 7 of Ref. 6 plots the predictions of the volume entropy and S_B for the mean energies of the subsystems at which there would be no mean energy transfer, and it shows large errors in all predictions. The authors concluded that although the predictions of the volume entropy were incorrect, so were the predictions of S_B .

The weakness of the argument in Ref. 6 is that $n_j = 1$ corresponds to a very small system with only a single degree of freedom. For a macroscopic system, a large value of n_j would give a more appropriate test. S_B always predicts the mode correctly, and the difference between the mode and the mean goes to zero as $1/n_j$. If Fig. 7 of Ref. 6 is redrawn with larger values of n_1 and n_2 , agreement of the predictions of S_B with the exact mean

are excellent. In contrast, the predictions of the volume entropy do not agree with either the mean or the mode. The volume entropy fails this test, while S_B passes.

The failure of the volume entropy to describe equilibrium for systems with a non-monotonic density of states is due to its phase-space integral being dominated by lower-energy states that have no effect on the equilibrium ensemble. Its failure shows that it is irrelevant for such systems, and any argument against negative temperatures based on the volume entropy is without foundation.

MEASURING THE MEAN VS. THE MODE

Since the difference between the mean and the mode plays a role in statistical mechanics, a few comments on their relevance for thermodynamics are in order.

Differences between the values of the mean and the mode are of order $1/N$, which makes them much smaller than the thermal fluctuations, which are of the order of $1/\sqrt{N}$. Furthermore, experiments measure the current value of a variable, which is different every time a measurement is repeated due to the fluctuations. Even if it were possible to measure a macroscopic variable of a system in equilibrium with perfect accuracy, the result would not equal either the mean or the mode, but would be somewhere in a region of width $1/\sqrt{N}$. To determine the mean with a resolution of $1/N$, we would need at least N measurements, which would take a long time. We might imagine making an independent measurement with perfect accuracy every second. Even if the system had only $N = 10^{12}$ particles, the experiment would still take over 30,000 years. For 10^{18} particles, it would take longer than the age of the universe. Measurement of the difference between the mean and the mode in a macroscopic system is impossible, even if each individual measurement has no error.

SUMMARY

We have shown that the Gibbs volume entropy does not provide a viable definition of the thermodynamic entropy. In particular, the failure of the volume entropy to correctly describe a thermodynamic system with a non-monotonic density of states eliminates the argument

against the concept of negative temperature. We have given an alternative definition that leads to an equilibrium entropy that always predicts the mode of extensive variables correctly. This definition of the entropy satisfies all postulates and confirms that negative temperature is a valid extension of thermodynamics.

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