Journal of Statistical Physics, Vol. 107, Nos. 5/6, June 2002 (© 2002)

Statistical Mechanics of Classical Systems with Distinguishable Particles

Robert H. Swendsen[1]

Received June 25, 2001; accepted January 25, 2002

The properties of classical models of distinguishable particles are shown to be identical to those of a corresponding system of indistinguishable particles without the need for *ad hoc* corrections. An alternative to the usual definition of the entropy is proposed. The new definition in terms of the logarithm of the probability distribution of the thermodynamic variables is shown to be consistent with all desired properties of the entropy and the physical properties of thermodynamic systems. The factor of $1/N!$ in the entropy connected with Gibbs' Paradox is shown to arise naturally for both distinguishable and indistinguishable particles. These results have direct application to computer simulations of classical systems, which always use distinguishable particles. Such simulations should be compared directly to experiment (in the classical regime) without "correcting" them to account for indistinguishability.

KEY WORDS: Entropy; Gibbs' paradox; distinguishability.

1. INTRODUCTION

Computer simulation has become an essential tool in the calculation of physical properties of many-particle systems. Although quantum mechanical calculations can be performed for systems of limited size, most computational results come from simulations of classical systems. Since these simulations, whether by molecular dynamics or Monte Carlo, inevitably use systems of distinguishable particles, it is important to clearly understand the statistical mechanics of such particles.

Real systems are ultimately governed by the laws of quantum mechanics, for which like particles (electrons, protons, atoms) are indistinguishable in

---

[1] Physics Department, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213; e-mail: swendsen@andrew.cmu.edu

the very fundamental sense that the many-particle wave function describing them is either perfectly symmetric or antisymmetric under exchange of two particles. The question arises as to whether the distinction between distinguishable and indistinguishable particles affects the statistical description of a system in the classical limit.

It is often stated in textbooks on statistical mechanics that the entropies of systems of distinguishable and indistinguishable particles differ by a term involving the logarithm of $N!$.(1) If this were true, it would require the correction of results obtained from simulating a system of distinguishable particles with a corresponding term. In fact, as I will show in this paper, there is no such difference in the statistical mechanical and thermal properties in classical statistical mechanics between systems of distinguishable and indistinguishable particles.

The analysis of this problem leads to a new definition of the entropy in statistical mechanics that agrees with the thermodynamic definition, even in cases in which the traditional definition fails.

The usual argument for the importance of indistinguishability is based on the work of Boltzmann(2) and Gibbs,(3) which led to a conjecture about the connection between Newtonian laws of motion for microscopic particles and the macroscopic laws of thermodynamics, namely that the entropy was proportional to the logarithm of a volume in phase space determined by the constraints on the system of interest. Because of the leading role played by Boltzmann, I will refer to this conjecture by his name for simplicity, although essential contributions were also made by Gibbs.

While there were strong arguments in favor of Boltzmann's conjecture, a central problem was recognized very early. The best-known demonstration that his expression for the entropy is incorrect is known as Gibbs' Paradox,(3) and is found in every textbook on statistical mechanics. The paradox is usually expressed in terms of a contradiction in calculating the entropy of mixing, but the essential point is that Boltzmann's expression for the entropy is not extensive, as is usually assumed in thermodynamics. A solution was also rapidly found, which consisted of including a factor of $1/N!$, where N is the number of microscopic particles. This correction, known as "correct Boltzmann counting," restored the extensivity of the entropy. The most common justification for the ad hoc inclusion of the extra factor of $1/N!$, is that the correct laws of nature are quantum mechanical, and in quantum mechanics particles are indistinguishable.(1)

Because Boltzmann's conjecture for the entropy—"corrected" with the extra factor of $1/N!$—satisfies every criterion for the interpretation of real experiments, this explanation has long been regarded as standard. However, a consequence of ascribing the factor of $1/N!$ to the indistinguishability of particles is that the entropy of a system of truly distinguishable particles would not have such a factor. As I will show in this paper, the properties of a classical ideal gas do not depend on whether distinguishable or indistinguishable particles are used. Consequently, a proper definition of the entropy should give the same answer in both cases. Specifically, factor of $1/N!$ should be present in both cases. This means that the results of computer simulations with distinguishable particles should be compared directly with the results of real experiments in the classical regime; no correction factors are needed.

The only direct statements I have found in the literature that the factor of $1/N!$ should be included for distinguishable particles occur in papers by van Kampen(4) and Jaynes.(5) Their arguments are correct, but their approaches to the fundamental problem are somewhat different than the one I will present here.

The plan of this paper begins by recalling the thermodynamic definition of the entropy that preceded the formulation of statistical mechanics in Section 2. This section is the basis for the entire discussion, since it recalls the standard for what is meant by the term “entropy,” independent of any particular view of the foundations of statistical mechanics. I then review the traditional justification of the statistical mechanical formula for the classical entropy and suggest an alternative interpretation of Gibbs’ paradox in Section 3. Next, I present my central proposal for a definition of the entropy as the logarithm of a probability distribution in Section 4. This definition is then applied to a classical ideal gas of distinguishable particles in Section 5, with an alternative derivation of the volume dependence being given in Section 6.

Section 7 demonstrates that Boltzmann’s conjecture for the entropy of subsystems in a composite system of ideal gases leads to incorrect predictions for the equilibrium of particles between the subsystems.

Section 8 introduces a highly artificial statistical model that is correctly described by the Boltzmann expression for the entropy. This example is intended to clarify the differences between my definition of the entropy and Boltzmann’s. It also of interest because the Boltzmann definition of the entropy is unable to deal with the differences between this artificial model and the usual classical ideal gas of distinguishable particles. The artificial example also highlights the distinction between additivity and extensivity, which is further discussed in Section 9.

The case of classical indistinguishable particles is handled somewhat differently than the usual textbook treatment when defining the entropy as the logarithm of the probability distribution. This difference is discussed in Section 10, where it is shown that the resulting entropy is identical to that for distinguishable particles.

For completeness, Section 11 contains a general expression for the entropy of a classical system of interacting particles as the logarithm of a probability distribution. A point of interest for application to computer simulations is that the expression involves a surface rather than a volume in phase space. Although the difference is negligible for a system of 10^{20} particles, it can be significant for computer simulations that necessarily use a limited number of particles.

There is, of course, a difference between systems of distinguishable and indistinguishable particles in quantum systems, and within the class of indistinguishable particles, between fermions and bosons. However, these differences concern the physical consequences of the symmetries of the wave functions and do not affect the extensive nature of the entropy. Because of the importance of the classical limit of quantum systems, I have included a brief discussion of this point in Section 12, outlining how it is treated when the entropy is defined by the logarithm of the probability distribution.

Finally, I have given a summary in Section 13 that includes a list of the key steps in my argument.

2. THE THERMODYNAMIC POSTULATES

Thermodynamics was already well developed before Boltzmann's work on deriving macroscopic properties from the postulate of the existence of atoms, which was still controversial at the time. Although the meaning of the entropy was not yet completely clear, the properties of the entropy had been well established. Indeed, it was through a comparison of Boltzmann's formula for the entropy with those properties that Gibbs' Paradox arose.

As a basis for the discussion in this paper, I will quote the relevant postulates of thermodynamics in the form given by Callen.(6) The first postulate simply states the existence of equilibrium states. The fourth postulate in Callen's formulation is the Nernst Postulate, which is only relevant for quantum systems. It is the second and third postulates that are important for the current discussion.

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

Postulate III [Callen]. The entropy of a composite system is additive over the constituent subsystems. The entropy is continuous and differentiable and is a monotonically increasing function of the energy.

To discuss the foundations of statistical mechanics from a systematic point of view, it is convenient to slightly rearrange Callen's postulates to separate the various properties and present them (with one addition) in a logical order. I would suggest the list:

1. The values assumed by the extensive parameters of a composite system in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.
2. The entropy of a composite system is additive over the constituent subsystems.
3. The entropy is a monotonically increasing function of the energy.
4. The entropy is continuous and differentiable.
5. The entropy is extensive.

These postulates are not of equal importance. The first property (Callen's Postulate II) is essential, due to its central role in calculating equilibrium properties and its association with the second law of thermodynamics. Without this property, there seems little reason to use the word "entropy." Because it leads directly to the second law of thermodynamics, I regard it as the defining property of the entropy.

The second property (additivity) is necessary if we are to talk about the entropy of a subsystem. If the entropy of a composite system cannot be separated into additive entropies for its subsystems, the entropy of a simple subsystem is not defined. This property is then almost as important in applications as the first.

The third property is required for the temperature to be positive. It is, of course, not strictly true for all systems, and it must often be understood in terms of a limited range of energies of interest. Even the Ising model has negative temperatures for high energy states.

The fourth properties are only valid in the limit of large systems, and make computation much more convenient. They are not essential, and not true for many finite systems of interest.

The fifth property that I have listed is the only one that is *not* contained in Callen's postulates. Callen restricted his analysis to homogeneous systems, and then claimed to demonstrate that extensivity followed from additivity. His argument includes an unstated assumption that the properties of a single large system are identical to those of a combination of two smaller systems with the same total energy, volume, and number of particles. This assumption is equivalent to the property of extensivity that he claimed to prove. It is valid for virtually all physical systems, but it is not completely general, as shown in Section 8.

Extensivity and the limitation to homogeneous systems are extremely useful in the derivation of thermodynamic identities, but it must be remembered that the full formalism of thermodynamics has no such restrictions.

A simple example of the distinction between additivity and extensivity can be seen by considering a gas in a container with walls on which the gas can be adsorbed. The entropy of this system is not extensive because the fraction of particles adsorbed on the walls is a function of the size of the system. The deviation from extensivity can be quite large at low temperatures, and is the basis for cryogenic vacuum pumps. Nevertheless, the entropy of a composite system made up of two such systems is additive, the maximum of the entropy gives the equilibrium values of the extensive variables, and the second law of thermodynamics is satisfied.

Consequently, the fifth property is only valid for large systems that are also homogeneous. It is necessary for the derivation of the Euler equation and the Gibbs-Duhem equation, although it is not necessary for the second law of thermodynamics. The study of homogeneous systems is has been extremely fruitful in the development of thermodynamics. This paper will also devote most of the discussion to homogeneous systems, but a full theory of thermodynamics and statistical mechanics must be more general.

Since statistical mechanics is intended to provide a foundation for thermodynamics, it is important for the properties of the entropy to be derived, not individually postulated. We should not, for example, assume that the entropy is extensive and impose that condition on an argument from statistical mechanics. If the entropy is extensive, this must be demonstrated from statistical mechanics.

From the considerations given in this section, it might be useful to refer to a function as the entropy even if only the first property listed above (Postulate II) is satisfied, since this is sufficient for the calculation of equilibrium properties and the validity of the second law of thermodynamics. In Section 4, I have taken this alone to be the basis of a statistical mechanical definition of the entropy; all other properties must be demonstrated for each specific case.

On the other hand, if we are to talk about the entropy of a subsystem in a meaningful way, we need the second property (additivity) as well. Another way of stating this is to say that the entropy of a composite system should be *separable* into expressions for the entropies of the subsystems. Since the entropy calculated from Boltzmann's conjecture is claimed to represent subsystems of ideal gases, it may reasonably be tested against these two properties. We will introduce the Boltzmann entropy in the next section, and demonstrate in Section 7 that it makes incorrect predictions if it is assumed to satisfy the first two properties of the entropy.

3. BOLTZMANN'S CONJECTURE AND GIBBS' PARADOX

3.1. Standard Explanation

In this section, I will restrict my analysis to a classical ideal gas of distinguishable particles. The essence of the issue is contained in this simple model, and the extension of the results to interacting systems is straightforward, although evaluating the resulting expressions remains a great challenge. As usual, I will assume that the interactions between particles in the ideal gas can be neglected in calculations, but had sufficed to bring the system into equilibrium. I will use the usual notation of $\{p_i, q_i\}$ for a point in phase space. For a three-dimensional system of N particles, the index i runs over $3N$ values for the x-, y-, and z-components of the momenta and positions of the particles.

Boltzmann (and Gibbs) conjectured that the entropy of a system of a large number N of particles (atoms or molecules) was given by the logarithm of the accessible volume of phase space Ω_B.

$$S_B = k_B \ln \Omega_B \tag{1}$$

The phase space volume Ω_B was specified as including all energies less than some maximum energy E, and all particle positions in real space within a given volume V.(2, 3)

Following, for example, the derivation given in Pathria's text,(1) this assumption leads directly to an expression for the entropy of a classical ideal gas of distinguishable particles of the form

$$S_B = k_B N \left[\ln(V) + \left(\frac{3}{2}\right) \ln\left(\frac{E}{N}\right) + X_B \right] \tag{2}$$

where X_B is a combination of universal constants that is independent of E, V, and N. The derivation of this equation uses the first two terms of Stirling's approximation for large values of N.

Gibbs' Paradox can be expressed in several ways, usually in the context of a discussion of the entropy of mixing. However, it is essentially the recognition that Eq. (2) is not extensive. If the system is doubled in size, E, V, and N are all doubled, but S_B becomes $2S_B + k_B N \ln 2$.

It is then claimed that we can "correct" Eq. (1)—if the particles are indistinguishable—by dividing Ω_B by $N!$,

$$S = k_B \ln(\Omega_B / N!) \tag{3}$$

so that we find a new expression for the entropy

$$S = k_B N \left[\ln\left(\frac{V}{N}\right) + \left(\frac{3}{2}\right) \ln\left(\frac{E}{N}\right) + X \right] \tag{4}$$

where $X = X_B + 1$.

The division by $N!$ is never actually derived. It is usually justified by saying that there are $N!$ ways of arranging distinguishable particles, so dividing by this factor gives the difference between the statistics of distinguishable and indistinguishable particles. As I will show, this argument is not correct.

3.2. Alternative Interpretation of Gibbs' Paradox

An alternative interpretation of the same equations is simply that the original conjecture in Eq. (1) is wrong, and Gibbs' Paradox is the demonstration that it is inconsistent with the expected properties of the thermodynamic entropy.

The choice of explanations is not just a matter of taste; the alternatives are testable. If the traditional explanation is correct, then Boltzmann's original equations for the entropy, Eqs. (1) and (2), would have to describe the thermodynamic behavior of distinguishable particles. Since it is very easy to perform numerical experiments with distinguishable particles—every particle is distinguished by its own number in a computer simulation—we can easily test whether Eq. (2) describes a classical gas of distinguishable particles.

Actually, the situation is even simpler; a consideration of the consequences of Eq. (2) shows that it cannot describe a classical gas of distinguishable particles. I will come back to this point in Section 7, after presenting an alternative definition of the statistical mechanical entropy and exploring its consequences in the intervening sections.

4. A DEFINITION OF THE ENTROPY AS THE LOGARITHM OF A PROBABILITY DISTRIBUTION

The central thesis of this paper is that the entropy in statistical mechanics should be defined as the logarithm of the probability distribution for the experimentally accessible observables in a composite system. It is therefore based directly on the first property of the entropy in the list given in Section 2 (Callen's Postulate II).

There are a number of advantages of this approach. First of all, the validity of the second law of thermodynamics is immediately apparent. For large (but not necessarily infinite) systems, the probability distribution of observables is very narrow, with relative variations typically inversely proportional to the square root of the number of particles. This both provides support for Callen's first postulate (the existence of a thermodynamic state) and ensures that the mean and mode of the distribution are nearly the same. Since the logarithm is a monotonic function of its argument, the maximum of the entropy necessarily corresponds to the equilibrium condition obtained when internal constraints are released.

Another advantage of the proposed definition is that it clarifies the dependence of the entropy on experimental conditions, since the entropy is a function of the accessible observables. The variety of situations that Jaynes illustrated with his discussion of the imagined properties of "Whifnium" and "Whoofnium"(5) are automatically handled correctly.

The derivation of an equation for the entropy begins with the usual assumptions about the equilibrium probability distribution for the positions and momenta of distinguishable particles in a classical ideal gas. I then follow standard methods to derive expressions for the equilibrium values of the energies, volumes, and numbers of particles in the subsystems. In the course of this derivation, a function naturally arises that has the properties listed in Section 2. Since the postulates of thermodynamics only claim that a function called the entropy exists and has certain properties, identifying such a function is sufficient to establish it as the entropy. Another way of putting it is to say that the statistical mechanical solution gives us a function with the thermodynamic properties of the entropy, which the thermodynamic postulates had anticipated and named.

Defining the entropy in terms of probability distributions also provides a clear basis for the discussion of the statistical mechanics of distinguishable particles that is not possible when the entropy is defined in terms of a volume in phase space. Since, as I will show, the properties of a classical gas of distinguishable particles are identical to those of a system of indistinguishable particles, their entropies should also be the same. With the definition I am proposing, they are the same, although the use of the Boltzmann conjecture has led to the wide-spread belief that they are different.

A very important aspect of the proposed definition of the entropy is that it only assumes the validity of the first property listed in Section 2 (Postulate II). Whether the entropy of a given system has the other properties (additivity, monotonicity, continuity and differentiability, and extensivity) is not assumed and must be demonstrated explicitly.

5. THE ENTROPY OF THE CLASSICAL IDEAL GAS WITH DISTINGUISHABLE PARTICLES

This section discusses the calculation of the entropy for a classical ideal gas with distinguishable particles. The modifications necessary to deal with indistinguishable particles will be discussed in Section 10. The final answer will be seen to be the same in both cases.

It is convenient to reinterpret the concept of an "ensemble" to reflect the concepts of probability theory. It is usual in statistical mechanics to define an ensemble in terms of "a large number" of microstates that would be consistent with a given macrostate (that is, with specified values of E, V, and N). However, there is no consistent way of limiting the possible states to a finite, or even countable number. It is much more appropriate to characterize an ensemble in classical statistical mechanics by a continuous probability distribution in phase space, $P(\{p_i, q_i\})$. From the definition of the entropy that I have presented, the central problem of statistical mechanics is to first specify the probability distribution and then to transform from the set of microscopic variables, $\{p_i, q_i\}$, to the macroscopic observables, E, V, and N (or whatever other variables are appropriate for the experiment under consideration). The entropy is given by the logarithm of that distribution.

For the classical ideal gas, the positions and momenta are assumed to be independent random variables, which allows us to analyze them separately. First consider the positions of the particles.

If the particles are confined to a volume, V, then assume that the probability density for each particle is a constant equal to $1/V$, independent of the probability density for every other particle. From these assumptions, the probability distribution for the number of distinguishable particles in the two subvolumes V_1 and V_2 is simply given by the binomial distribution

$$W(N_1, N_2) = \frac{N!}{N_1!\,N_2!}\left(\frac{V_1}{V}\right)^{N_1}\left(\frac{V_2}{V}\right)^{N_2} \tag{5}$$

with the added constraint that $N_1 + N_2 = N$, the fixed total number of particles. As is well known, the expectation value of N_1 is given by

$$\langle N_1 \rangle = N\left(\frac{V_1}{V}\right) \tag{6}$$

and the width of the probability distribution is given by

$$\delta^2 N_1 = N\left(\frac{V_1}{V}\right)\left(\frac{V_2}{V}\right) \tag{7}$$

This is obviously the correct answer for the probability distribution of distinguishable particles.

The logarithm of the probability distribution given in Eq. (5) can be written in the interesting form

$$\ln W(N_1, N_2) = \ln \Omega_q(V_1, N_1) + \ln \Omega_q(V_2, N_2) - \ln \Omega_q(V, N) \tag{8}$$

where

$$\Omega_q(V, N) = \frac{V^N}{N!} \tag{9}$$

and the subscript q refers to the configurational degrees of freedom. The factor of $N!$ in the denominator of Eq. (9) comes from the binomial coefficient and is the missing term in Boltzmann's conjecture.

Since the last term in Eq. (8) only depends on the total volume and total number of particles, which are not functions of N_1 or V_1, it only plays the role of a normalization constant and is not needed to find the maximum of $\ln W(N_1, N - N_1)$ that determines the equilibrium value of N. This suggests that we identify a "configurational entropy" as

$$S_q = k_B \ln \Omega_q(V, N) \tag{10}$$

The sum of the configurational entropies for the two subsystems is then a maximum at the correct equilibrium values given by

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} \tag{11}$$

which is equivalent to Eq. (6). This contrasts with the Boltzmann entropy, which leads to an incorrect prediction for the equilibrium value of the number of particles, as will be shown in Section 7.

I have already assumed that the positions of each particle are independent random variables with a probability density equal to $1/V$ within the volume to which they are confined. The corresponding assumption for the momenta is that they have a uniform probability density in momentum space $\{p_i\}$, subject to the constraint on the total energy.

The usual constraint imposed on the momenta is that the total energy must be equal to or less than some value E. There seems to be no particular reason for not specifying that the total energy is simply equal to some value, except the desire that the entropy be related to a "volume" in phase space. Naturally, if the energy is fixed, the corresponding integral is restricted to a hypersurface, and gives a vanishing hypervolume.

Most textbooks contain an argument for allowing all values of the energy less than E, based on the non-vanishing experimental errors in the measurement of the energy. However, these arguments rely on the total number of particles being extremely large—of the order of Avogadro's number. They become less plausible when an attempt is made to apply them to systems of less than a million particles, especially in light of the substantial effort involved to ensure that the total energy is constant in molecular dynamics simulations.

Since it is not necessary to assume that the energy is equal to or less than some value, I will assume that the total energy is specified exactly. It will be obvious that any other assumption about the energy can be easily incorporated into the formalism if the experimental situation requires it.

Using the Dirac delta function to describe the constraint imposed on the probability distribution in momentum space, we can write the probability distribution for the energies E_1 and E_2 of our two subsystems as

$$W(E_1, E_2) = \frac{\int d\vec{p}^N \, \delta(E_1 - \sum_{i,1} \vec{p}_{i,1}^{\,2}/2m) \, \delta(E_1 - \sum_{i,2} \vec{p}_{i,2}^{\,2}/2m)}{\int d\vec{p}^N \, \delta(E - \sum_i \vec{p}_i^{\,2}/2m)} \tag{12}$$

Naturally, this expression is subject to the constraint that the total energy is conserved, $E = E_1 + E_2$.

If we take the logarithm of the probability distribution, we see that it again breaks up into three contributions: one from each subsystem, and one from the normalization of the total system. Again, the maximum of the sum of the terms from each subsystem coincides with the maximum of the probability distribution of the energies, and consequently corresponds to the equilibrium values.

To sum up the results obtained so far, treating both the coordinates and the momentum together leads to a function

$$\Omega(E, V, N) = \frac{1}{h^{3N}} \frac{1}{N!} \int d\vec{q}^N \int d\vec{p}^N \, \delta\left(E - \sum_i \vec{p}_i^{\,2}/2m \right) \tag{13}$$

and the entropy of a subsystem is identified as

$$S = k_B \ln(\Omega) \tag{14}$$

For convenience in making a connection to the classical limit of quantum statistics, which is beyond the scope of this section, I have included a factor of $1/h^{dN}$ in the definition of the entropy of a d-dimensional system.

The integrals over the coordinates in Eq. (13) give a factor of V^N as before. The integral over the surface of the constant-energy hypersphere in momentum space is also easily performed to give

$$\Omega(E, V, N) = \frac{1}{h^{3N}} \frac{1}{N!} V^N \frac{\pi^{3N/2-1}}{(3N/2-1)!} m(2mE)^{3N/2-1} \tag{15}$$

for the classical ideal gas with distinguishable particles. Note that this expression is not identical to the usual one, primarily because of the appearance of $3N/2-1$ instead of $3N/2$. When N is of the order of Avogadro's number, this difference is completely insignificant, and the use of $3N/2$ is appropriate. For smaller systems, such as might be considered in a computer simulation with a fixed total energy, Eq. (15) is correct. The final result of the present derivation for a large system is

$$S = k_B N \left[\ln\left(\frac{V}{N}\right) + \left(\frac{3}{2}\right) \ln\left(\frac{E}{N}\right) + \left(\frac{3}{2}\right) \ln\left(\frac{4\pi m}{3h^2}\right) + \frac{5}{2} \right] \tag{16}$$

which is equivalent to the well-known Sackur–Tetrode equation.

Note that the factor of $1/N!$ in Eqs. (9), (13), and (15) comes from the binomial distribution given in Eq. (5). It results from considering the combinatorics of the probability distribution of distinguishable particles between two boxes.

6. THE EQUILIBRATION OF THE VOLUMES OF TWO SUBSYSTEMS IN A CYLINDER

Although the derivation of the entropy of an ideal gas of distinguishable particles has already established that it is a maximum for the equilibrium values of the energy and the number of particles in each subsystem, it still remains to demonstrate that it also correctly predicts the equilibrium values of the volumes of two subsystems in a cylinder, separated by a piston. It is easy to show from Eq. (16) that this is the case, but it is also interesting to see how this arises directly from the same assumptions concerning the probability distribution that led to Eq. (16).

Since the positions and momenta are assumed to be independent random variables, it suffices to consider the probability distribution of the positions. I have assumed that the probability distribution is a constant subject to the constraints. In this case, the constraints are that the total volume is fixed,

$$V = V_1 + V_2 \tag{17}$$

and there are N_1 and N_2 particles in the two subsystems. The probability density for the positions of the particles is then

$$P(\{\vec{r}_i\}) = X(N_1, N_2, V) \tag{18}$$

where X gives the normalization. Integrating over the positions of the particles within each volume, we obtain the probability distribution for the volumes.

$$P(V_1, V_2) = V_1^{N_1} V_2^{N_2} X(N_1, N_2, V) \tag{19}$$

The maximum value of this probability distribution leads directly to the condition given in Eq. (11) that the particle densities in the two subsystems must be the same in equilibrium. The volume dependence again has the form V^N that occurs in Eqs. (5) and (15), confirming that the expression for the entropy in Eq. (4) or Eq. (16) is consistent with the derivation and correctly describes a classical ideal gas of distinguishable particles.

7. THE PREDICTIONS OF BOLTZMANN'S ENTROPY FOR DISTINGUISHABLE PARTICLES

Virtually all textbooks claim that Boltzmann's expression for the entropy, given in Eq. (2), gives the entropy for an ideal gas. Therefore, if we consider a simple composite system made up of two such subsystems, Boltzmann's expression makes certain predictions about the behavior of an ideal gas of distinguishable particles that are easy to test. Callen's postulates, or the first two essential properties of the entropy listed in Section 2, require that the maximum of the sum of the entropies of two parts of a composite system determines the equilibrium values of E, V, or N when a constraint is released. For E and V, the predictions are correct. However, for N they are not.

Consider two isolated subsystems in equilibrium with values of E_1, V_1, and N_1 and E_2, V_2, and N_2, respectively. The total Boltzmann entropy from Eq. (2) is then

$$\begin{aligned} S_B = {} & k_B N_1 \left[\ln(V_1) + \left(\frac{3}{2}\right) \ln\left(\frac{E_1}{N_1}\right) + X_B \right] \\ & + k_B N_2 \left[\ln(V_2) + \left(\frac{3}{2}\right) \ln\left(\frac{E_2}{N_2}\right) + X_B \right] \end{aligned} \tag{20}$$

Bringing the two subsystems into thermal contact and imposing the constraint that the total energy is fixed

$$E = E_1 + E_2 \tag{21}$$

we can set the derivative of the total entropy equal to zero

$$\frac{\partial S_B}{\partial E_1} = k_B N_1 \left(\frac{3}{2}\right)\Big/ E_1 - k_B N_2 \left(\frac{3}{2}\right)\Big/ E_2 = 0 \tag{22}$$

and find the equilibrium condition

$$\frac{E_1}{N_1} = \frac{E_2}{N_2} \tag{23}$$

as expected. This is, of course, a standard derivation found in all textbooks.

Now, after the composite system has come to thermal equilibrium, poke a hole in the wall between the two subsystems. The energy equilibrium described by Eq. (23) remains unchanged. The equilibrium values for the numbers of particles in each subsystem are determined by taking the derivative of the entropy with respect to particle number. The derivative of the Boltzmann entropy in Eq. (20) is

$$\frac{\partial S_B}{\partial N_1} = k_B \left[\ln(V_1) + \left(\frac{3}{2}\right) \ln\left(\frac{E_1}{N_1}\right) + X_B \right] - k_B \left[\ln(V_2) + \left(\frac{3}{2}\right) \ln\left(\frac{E_2}{N_2}\right) + X_B \right] \tag{24}$$

or, using the condition for energy equilibrium, Eq. (23),

$$\frac{\partial S_B}{\partial N_1} = k_B \ln\left(\frac{V_1}{V_2}\right) \tag{25}$$

However, this expression for the derivative of the entropy is not a function of N_1 or N_2. Unless $V_1 = V_2$, this derivative does not vanish. A plot of S_B as a function of N_1 is a straight line with the maximum lying at $N_1 = N$ if $V_1 > V_2$, and at $N_1 = 0$ if $V_1 < V_2$. Therefore, Boltzmann's conjecture leads directly to the bizarre prediction that all particles in an ideal gas of distinguishable particles should go to the larger of the two subvolumes!

Since the specification of the two subvolumes does not have to involve a real barrier, it suffices to draw an imaginary barrier and ask the question of how many particles are on each side. Clearly, we cannot make the particles rush from one side of the box to the other by asking a different question without otherwise changing the experiment. Therefore, Boltzmann's expression for the entropy is incorrect. It does not describe the macroscopic behavior of a classical ideal gas of distinguishable particles. On the other hand, I will show in the next section that an artificial model can be constructed for which Boltzmann's expression does provide a correct description.

8. AN ARTIFICIAL SYSTEM THAT IS CORRECTLY DESCRIBED BY THE BOLTZMANN ENTROPY

We can construct a model system for which the Boltzmann entropy given in Eq. (2) is valid. The model is highly artificial, which has the advantage of emphasizing the unusual features necessary to violate extensivity in a homogeneous subsystem. By deriving the entropy for this system from a probabilistic point of view, we can see that the Boltzmann expression correctly describes its (unusual) properties. The entropy of this model is additive, but not extensive.

Consider a collection of boxes, each of which contains a gas of distinguishable particles. Each particle carries an integer label, and no two particles carry the same label, whether or not they are in the same box. Each box also carries an integer label, so that the boxes as well as the particles are ordered. To be specific, consider boxes 1 and 2, with volumes V_1 and V_2, and define $V = V_1 + V_2$.

Within each box, the properties of the particles are identical to those normally assumed for a classical ideal gas. However, when two boxes are brought together and particles are allowed to pass from one box to another, special rules apply. Instead of any particle from box 1 being allowed to go into box 2, only the particle with the highest integer label may be transferred. Similarly, only the particle in box 2 with the lowest integer label may be transferred into box 1.

Assume for simplicity that transfers occur at discrete time steps. At any time step, the probability of the particle with the highest integer label in box 1 being transferred into box 2 is V_2/V. Similarly, the probability of the particle with the lowest integer label in box 2 being transferred into box 1 is V_1/V. If all particles were allowed to be transferred at each time step, these probabilities would produce the usual properties of the classical ideal gas. However, with the restrictions imposed, the properties are quite different.

It is also possible to construct a variation of this model with weak interactions to equilibrate the system during a molecular dynamics simulation, with a hole connecting the two boxes that only allows the appropriate particles to pass through. Despite the artificiality of these models, which are not intended to represent real systems, they are quite easy to simulate with a computer.

From the condition of detailed balance, is easy to show that the probability of having N_1 particles in box 1 is proportional to $V_1^{N_1} V_2^{N_2}$. There are no factors of $N_1!$ or $N_2!$. Taking the logarithm of this expression and multiplying by Boltzmann's constant, we find terms in the entropy of the form

$$k_B N_1 \ln(V_1) + k_B N_2 \ln(V_2) \tag{26}$$

which are exactly what is obtained by adding the expressions for the Boltzmann entropy for each box. Maximizing the entropy for the probability under the condition of the conservation of the total number of particles, we again find the strange result that the particles go to the larger of the two boxes. However, this is the correct answer for our artificial model.

Although the entropy of the combined system in our highly artificial model is given by the sum of the entropies of the subsystems, it is not equal to the entropy of a simple system with volume $V = V_1 + V_2$. The properties of a composite system with subvolumes V_1 and V_2 are not the same as those of a simple box with volume $V = V_1 + V_2$. Therefore, the entropy of this model, which is identical to the usual expression for the Boltzmann entropy in Eq. (2), is not extensive. However, it is additive and gives correct predictions for all properties of the artificial model.

9. ADDITIVITY AND EXTENSIVITY

The properties of additivity and extensivity are distinct. In the definition of the entropy based on the logarithm of the probability distribution, neither additivity nor extensivity is assumed. Each property must be demonstrated separately for each model under consideration.

Additivity (or separability) can be demonstrated by showing that the terms in the entropy of a composite system can be separated into additive contributions from each subsystem. This is true for most physical systems of interest under the assumption that we can neglect direct interactions between particles in different subsystems. It can still be true when a system is not extensive because the surface terms are too large to neglect. It is also true for our artificial model. It is not true for systems with long-range interactions that provide direct interactions between particles in different subsystems.

Extensivity can be demonstrated by showing that the terms in the entropy of a composite system that correspond to a particular subsystem are multiplied by a given factor when each of the extensive variables of the subsystem is multiplied by the same factor. This is only approximately true, even for homogeneous systems, due to surface effects. Deviations from extensivity are often small for macroscopic systems. They are not always negligible for the relatively small systems used in computer simulations, although the use of periodic boundary conditions greatly reduces their importance if the system is not too close to a phase transition. The artificial model in Section 8 does not have an extensive entropy, nor do systems with long-range interactions.

Consequently, extensivity requires additivity, but additivity does not imply extensivity.

10. THE ENTROPY OF A CLASSICAL IDEAL GAS WITH INDISTINGUISHABLE PARTICLES

Now that we have established that the entropy of the classical ideal gas with distinguishable particles is extensive and does not suffer from Gibbs' Paradox, a question arises concerning the properties of a gas of indistinguishable particles. According to the traditional explanation of Gibbs' Paradox, there should be a difference between the two cases that is reflected in an extra factor of $1/N!$ for indistinguishable particles. Since a factor of $1/N!$ is already present in the case of distinguishable particles, are there two such factors for indistinguishable particles? The answer is no; the entropy is the same for a classical gas with distinguishable or indistinguishable particles.

To analyze the situation, we again consider two subsystems with volumes V_1 and V_2 that can transfer particles between them and are in equilibrium.

Recall that the definition of indistinguishable particles is that the exchange of any two particles leaves the microscopic state unchanged. Therefore, for indistinguishable particles, we cannot write down the binomial distribution because it was derived under the assumption that the particles were distinguishable and the exchange of particles gave a different microscopic state. However, we can retain the assumptions that the positions and momenta are independent, and the assumption that the probability distribution for the positions is a constant.

To describe the positions of indistinguishable particles, we must use a numbering system that does not distinguish between them. One way to do that is to order the particles purely on the basis of their instantaneous positions. Given a list of the x-coordinates of the particles in each subsystem, order them from the smallest value of x to the largest, and number them accordingly. This is consistent with the condition of indistinguishability, because the particle with the smaller x-coordinate always has a lower index, even when the particles move or are exchanged.

I will assume for simplicity that the x-coordinate varies between 0 and L_1 in the first subsystem, with a corresponding expression in the second subsystem. The cross-sectional areas are assumed to be A_1 and A_2. The probability distribution is again a constant

$$P(\{\vec{r}_i\}) = X(V) \tag{27}$$

where $X(N)$ does not depend on N_1 or N_2. The probability distribution for the numbers of particles in each subsystem is then given by the integrals

$$\begin{aligned} P(N_1, N_2) = X(N)\, A_1^{N_1} A_2^{N_2} \int_0^{L_1} dx_{N_1} \int_0^{x_{N_1}} dx_{N_1-1} \cdots \int_0^{x_1} dx_1 \\ \times \int_0^{L_2} dx'_{N_2} \int_0^{x'_{N_2}} dx'_{N_2-1} \cdots \int_0^{x'_1} dx'_1 \end{aligned} \tag{28}$$

where I have used primes to indicate the x-coordinates of the second subsystem. The integrals are easily performed iteratively, giving

$$P(N_1, N_2) = X(N) \left(\frac{V_1^{N_1}}{N_1!}\right)\left(\frac{V_2^{N_2}}{N_2!}\right) \tag{29}$$

which has the same dependence on the volumes and the numbers of particles as the binomial distribution for distinguishable particles in Eq. (5). Combining this answer with the energy distribution, which is unchanged, we arrive at exactly the same expression for the entropy that we had derived for distinguishable particles.

Indistinguishability has no effect on the macroscopic properties of a classical ideal gas.

11. THE ENTROPY OF CLASSICAL SYSTEMS WITH INTERACTING PARTICLES (EITHER DISTINGUISHABLE OR INDISTINGUISHABLE)

Since we obtain the same answer for distinguishable and indistinguishable particles, our method of calculation for more complicated systems should be based primarily on convenience. Because

$$\frac{1}{N!} \int_0^{L} dx_N \int_0^{L} dx_{N-1} \cdots \int_0^{L} dx_1 = \int_0^{L} dx_N \int_0^{x_N} dx_{N-1} \cdots \int_0^{x_1} dx_1 \tag{30}$$

it is clearly simpler to use the form on the left in all calculations.

The generalization of Eq. (13) to include interactions between particles is then straightforward for both distinguishable and indistinguishable particles.

$$\Omega(E,V,N)=\frac{1}{h^{3N}}\frac{1}{N!}\int d\vec{q}^{\,N}\int d\vec{p}^{\,N}\,\delta(E-H(\{p_i,q_i\})) \tag{31}$$

where the Hamiltonian contains contributions from both the potential and kinetic energies. The entropy is then obtained from the logarithm of this expression, as in Eq. (14).

The expression in Eq. (31) differs from the usual expression in that it is related to a hypersurface rather than a hypervolume in phase space. However, it gives the same formula for the entropy in the limit of a very large number of particles, while also being correct for the smaller systems used in computer simulations. It also has significant advantages in simplifying the derivation of the canonical ensemble and unifying the presentation of statistical mechanics to students.

Extending Eq. (31) to include more than one type of particle or additional observables is straightforward. This approach is also consistent with Jaynes' discussion of different expressions for the entropy based on the supposed discovery of "Whifnium" and "Whoofnium;"(5) his different cases simply correspond to reducing the probability distribution in phase space to probability distributions for different experimentally accessible variables. Different experimental conditions produce different expressions for the entropy.

12. QUANTUM IDEAL GASES OF DISTINGUISHABLE OR INDISTINGUISHABLE PARTICLES

Although the main topic of this paper concerns classical systems, the importance of the relationship with quantum mechanical systems requires a few additional comments.

First of all, to describe a quantum system from a probabilistic point of view, we must first chose a probability density for the set of all wave functions—not just for the set of eigenfunctions. The next step is to assume that the phases of the coefficients of an expansion of an arbitrary wave function in terms of eigenfunctions are all independent and uniformly distributed. Averaging over the phases then produces the usual expressions in terms of sums over energy eigenfunctions.

Because the use of the binomial distribution rests on the assumption that the particles are distinguishable, there is no justification for including a factor of $1/N!$ for quantum systems of identical particles in the derivation of the thermodynamic properties. As is the case for a classical system of indistinguishable particles, the calculation of the entropy of a quantum system of identical particles automatically gives an expression for the entropy that is extensive, with a classical limit agreeing with Eq. (34).

To illustrate the point, the grand canonical partition function is written without any factors of $1/N!$ as

$$Z_{GC} = \sum_{N=0}^{\infty} \sum_{\{n_\varepsilon\}}^{N} \prod_{\varepsilon} \exp[-\beta(\varepsilon-\mu)\, n_\varepsilon] = \sum_{\{n_\varepsilon\}}^{\infty} \prod_{\varepsilon} \exp[-\beta(\varepsilon-\mu)\, n_\varepsilon] \tag{32}$$

where ϵ refers to an individual particle state and n_ϵ is the number of particles in a given state. The sum over $\{n_\varepsilon\}$ in the middle expression goes over all sets of values allowed by the symmetry of the wavefunction such that $\sum_\varepsilon n_\varepsilon = N$. The first two sums can be combined to go over all sets of values of $\{n_\varepsilon\}$, as shown in the last expression. The sum and product are then interchanged to give

$$Z_{GC} = \prod_{\varepsilon} \sum_{n_\varepsilon} \exp[-\beta(\varepsilon-\mu)\, n_\varepsilon] \tag{33}$$

where the sum is now only over n_ϵ for a single state ε.

For fermions and bosons, the sum can be carried out in the usual manner to give

$$Z_{GC} = \begin{cases} \prod_{\varepsilon} (1+\exp[-\beta(\varepsilon-\mu)]) & \text{for fermions} \\ \prod_{\varepsilon} (1-\exp[-\beta(\varepsilon-\mu)])^{-1} & \text{for bosons} \end{cases} \tag{34}$$

which, in turn, lead to the usual Fermi and Bose functions for the occupation of the individual particle eigenstates.

$$\langle n_\varepsilon \rangle = \begin{cases} [\exp(\beta(\varepsilon-\mu))+1]^{-1} & \text{for fermions} \\ [\exp(\beta(\varepsilon-\mu))-1]^{-1} & \text{for bosons} \end{cases} \tag{35}$$

For the case of a quantum system of distinguishable particles, the argument based on the binomial distribution of particles between two subsystems again requires the inclusion of a factor of $1/N!$. However, the number of states with a given distribution of energy among the single particle states is

$$\frac{N!}{\prod_\varepsilon n_\varepsilon!} \tag{36}$$

so that the grand canonical partition function for non-interacting particles becomes

$$Z_{GC} = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{\{n_\varepsilon\}}^{N} \left(\frac{N!}{\prod_\varepsilon n_\varepsilon!} \right) \prod_\varepsilon \exp[-\beta(\varepsilon-\mu)\, n_\varepsilon] \tag{37}$$

The factors of $N!$ cancel, the sum and product are interchanged as before, and the sum can be carried out exactly to yield

$$Z_{GC} = \prod_\varepsilon \sum_{n_\varepsilon=0}^{\infty} \frac{1}{n_\varepsilon!} \exp[-\beta(\varepsilon-\mu)\, n_\varepsilon] = \prod_\varepsilon \exp(\exp[-\beta(\varepsilon-\mu)]) \tag{38}$$

The occupation number for an individual particle eigenstate becomes simply

$$\langle n_\varepsilon \rangle = \exp[-\beta(\varepsilon-\mu)] \tag{39}$$

In all three cases, the resulting thermal properties behave properly. The grand canonical thermodynamic potential is obviously extensive from Eqs. (38) and (39), just as are the corresponding thermodynamic potentials for Fermi and Bose cases in Eqs. (34) and (35). The entropy is extensive for both distinguishable and indistinguishable quantum particles, although their other properties are quite different.

13. SUMMARY

Despite the importance of Boltzmann's conjecture in the history of statistical mechanics, it contains a fundamental flaw. Recognition of this error is not merely a matter of philosophical taste, but has practical consequences in the interpretation of computer simulations and in their comparison with real experiments.

Because Boltzmann's conjecture has always been applied to the analysis of experimental data in the "corrected" form, with an additional factor of $1/N!$ generally attributed to quantum mechanics, the consequences of the error have not been obvious. The equations in general use provide a correct description of real experiments. This is one of the few examples of two wrongs making a right.

However, when applied to computer simulations, the standard argument would call for an extra factor of $1/N!$. Any such "correction" would be an error. The usual equations for the statistical mechanics of a classical system—or, preferably, Eq. (31) above—are correct as they stand for interpreting the results of computer experiments.

In this paper, I have presented an alternative definition of the entropy that unifies the basis of statistical mechanics and provides a basis for a clearer microscopic understanding of the postulates of thermodynamics. The key steps in the argument for classical systems are:

1. Analyze the properties of a composite system instead of the usual procedure of beginning with an assumption about the properties of an isolated homogeneous system.
2. Introduce assumptions about the probability distribution of states in phase space. Specifically, I have chosen to assume a uniform distribution consistent with the constraints imposed on the system. Other choices are possible; the test is, as usual, whether the predictions agree with experiment.
3. Transform the probability distribution in phase space to a probability distribution for the variables describing the composite system (i.e., the energies, volumes, numbers of particles, etc. in each subsystem).
4. Define the entropy as the logarithm of the probability distribution for the variables describing the composite system. (Multiplication by Boltzmann's constant ensures consistency of units.)
5. Other properties of the entropy, such as additivity, extensivity, etc. for subsystems, must be established by analysis of the expression obtained for the entropy of the composite system, not imposed through additional assumptions.

The extension of this procedure to quantum mechanics simply involves assumptions about the probability distribution of quantum states. In particular, the assumption that all phases are independent and equally likely leads to the usual expressions for thermodynamic properties in terms of sums over energy eigenstates.

By defining the entropy as the logarithm of the probability distribution for the variables being considered in an experiment, which is very much in the spirit of what Boltzmann and Gibbs intended, although differing from the equations they wrote, distinguishable and indistinguishable particles for both classical and quantum statistical mechanics can be treated consistently and correctly.

ACKNOWLEDGMENTS

I would like to thank Dr. C. S. Niu for pointing out the correct way to calculate the volume integrals in the case of indistinguishable particles. I would also like to thank Dr. Michael Widom for calling my attention to van Kampen's paper and making other helpful comments.

REFERENCES

1. For two recent examples, see R. K. Pathria, *Statistical Mechanics*, 2nd ed. (Butterworth–Heinemann, Oxford, 2001), p. 25, and L. Kadanoff, *Statistical Physics, Statics, Dynamics and Renormalization* (World Scientific, Singapore, 2000), p. 14.
2. L. Boltzmann, *Sitzb. Akad. Wiss. Wien* **76**:373 (1877); *Wissenschaftliche Abhandlungen von Ludwig Boltzmann, Vol. II* (Chelsea, New York, 1968), pp. 164–223.
3. J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Yale University Press, New Haven, 1902); reprinted by (Dover, New York, 1960).
4. N. G. van Kampen, The Gibbs paradox, in *Essays in Theoretical Physics*, W. E. Parry, ed. (Pergamon, Oxford, 1984), pp. 303–312.
5. E. T. Jaynes, *The Gibbs Paradox' in Maximum-Entropy and Bayesian Methods*, G. Erickson, P. Neudorfer, and C. R. Smith, eds. (Kluwer, Dordrecht), p. 992.
6. H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York, 1985).