Regarding the Entropy of Distinguishable Particles

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The conventional way of explaining Gibbs paradox as due to the distinguishability of particles has been challenged recently and a new fundamental definition for the entropy has been proposed that gives the same entropy for distinguishable particles as for indistinguishable particles. In this paper arguments are presented that strongly favor the conventional definition of entropy and its resolution of Gibbs paradox.

KEY WORDS: Gibbs paradox; Boltzmann entropy; distinguishability; axiomatics.

1. INTRODUCTION

As is well known the approach to statistical mechanics of Boltzmann and Gibbs led to Gibbs paradox that the entropy of ideal gases is not extensive. The conventional resolution of Gibbs paradox is that the particles are really indistinguishable; when a factor of $1/N!$ is included to prevent over-counting of indistinguishable permutations, the entropy becomes extensive. Although generally accepted, this simple argument has inspired interesting debate and disagreement (see, e.g., refs. 1 and 2 and references therein), culminating most recently in a paper that proposes a radical shift in the very definition of entropy.[3]

   The entropy can be written generally as

$$S = k_B \ln \Omega. \tag{1}$$

In order to focus on the essence of the issue, it is convenient[3] to write only the translational part of S and Ω in many of the subsequent formulae. It is also sufficient to consider only the case of ideal gases which

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already contain the essence of the issue. Next, it will be useful to identify the different cases that arise in this paper by using subscripts as follows: *D* and *I* will denote distinguishable and indistiguishable, respectively, *C* and *Q* will denote classical mechanical and quantum mechanical, respectively, and *B* and *S* will denote Boltzmann and Swendsen,[3] respectively.[8] The conventional Boltzmann formulae for *N* classical indistinguishable (BCI) particles and for classical distinguishable BCD particles in volume *V* are

$$\Omega_{\mathrm{BCI}} = \frac{V^N}{N!} \quad \text{and} \quad \Omega_{\mathrm{BCD}} = V^N. \tag{2}$$

Using a postulational approach to thermodynamics and statistical mechanics, Swendsen has proposed a conceptually different definition of entropy based on probability densities rather than the Boltzmann definition of entropy based on phase space volume or number of states.[3] This led to a result for classical distinguishable particles SCD that is the same as for classical indistinguishable particles SCI, namely,

$$\Omega_{\mathrm{SCD}} = \frac{V^N}{N!} = \Omega_{\mathrm{SCI}}. \tag{3}$$

Although distinguishable particles are not a very important case physically, Swendsen emphasized that computer particles are distinguishable, so the differences above could be significant in simulations, although no specific example was given.[3] The differences between Eqs. (2) and (3) certainly have implications for how statistical physics should be presented and understood.

2. DERIVATION OF THE BOLTZMANN FORMULAE FOR CLASSICAL PARTICLES

It is often stated and usually accepted that the introduction of the $1/N!$ factor for classical indistinguishable particles properly corrects Ω for permutations that are physically meaningless. However, the introduction of this factor has been described as *ad hoc*,[3] so it may be of interest to see that it is formally derivable in a Boltzmann phase space calculation for Ω. For classical distinguishable particles the translational volume in phase space can be formally written as

$$\Omega_{\mathrm{BCD}} = A^N \int_0^L dx_N \int_0^L dx_{N-1} \ldots \int_0^L dx_1 = V^N, \tag{4}$$

where A is the cross sectional area and L is the length of a rectangular parallelpiped. Because each particle is distinguishable, x_i can independently take on any values in $[0, L]$.

The case of indistinguishable particles can also be formally treated. Let us adopt a technique from Section 10 of Swendsen's paper that he attributes to C. S. Niu. 'To describe the positions of indistinguishable particles, we must use a number 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 ..., 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.'[3] Then, instead of Eq. (4), one has

$$\Omega_{\text{BCI}} = A^N \int_0^L dx_N \int_0^{x_N} dx_{N-1} \ldots \int_0^{x_2} dx_1 = V^N/N!. \tag{5}$$

This is identical mathematically to Swendsen's application to his probability functions for a combined system (Eq. (28) in ref. 3), which then involves another factor $X(N)$. It was not admitted in that paper[3] that the Niu method is ideally suited to obtaining the $1/N!$ factor in this formal, non *ad hoc*, way for the BCD case.

3. QUANTUM/CLASSICAL CORRESPONDENCE

It is often asserted that any residual doubts about the $1/N!$ factor for classical particles are laid to rest by considering quantum particles and the quantum/classical correspondence. Since that has been challenged,[3] this section will provide a review with some additional discussion of the QD case that may be of some interest.

It was appreciated in ref. 3 that there should be a consistent correspondence between the classical and quantum cases. In Section 12 of that paper it was concluded, for the grand canonical partition functions Ξ, that

$$\Xi_{\text{SQD}} = \Xi_{\text{QI}} = \prod_i \exp(\exp[-\beta(\epsilon_i - \mu)]) \tag{6}$$

in the classical thermodynamical (not classical mechanical) limit as the chemical potential μ becomes strongly negative so that the average occupancy of any single particle energy level ϵ_i becomes small and the

difference between Fermi–Dirac and Bose–Einstein statistics becomes negligible. For the quantum indistinguishable case I have used the subscript QI without an S or B in Eq. (6) because everyone agrees on that case. To obtain the result for Ξ_{SQD} Swendsen invoked a factor of $1/N!$ in his Eq. (37), essentially by appeal to his earlier development for the classical case.[3] In this section, I will show that this is inconsistent with the procedure that is used for the QI case.

Although it is not usually done, it is interesting to begin with the case of $j = 1, \ldots, N$ distinguishable particles, each with different energy levels ϵ_{ij} where i indexes the quantum levels of each particle. We will work with the canonical partition function for distinguishable particles; some discussion of the grand canonical partition function is given in the appendix. The general definition of the canonical partition function is written as the usual sum over states s,

$$Z(N) = \sum_{s} \exp(-\beta E_s) \tag{7}$$

with no factor of $1/N!$ Since $E_s = \sum_j \epsilon_{ij}$ and the sum over states is a sum over the index i for each particle j, it immediately follows that

$$Z_{BQD}(N) = \sum_{\{i(j)\}} \exp(-\beta \sum_j \epsilon_{ij}) = \prod_j \sum_i \exp(-\beta \epsilon_{ij}) \equiv \prod_j \zeta_j, \tag{8}$$

where the last equivalence defines the single particle partition function ζ_j.

Next consider the limiting case, which is where textbooks[5] usually start, that all the distinguishable particles have the same ζ_j. This requires that the energy levels ϵ_{ij} be the same independent of particle number j, and that raises the amusing question whether the particles can still be distinguishable. One way to achieve this employs spherically symmetrical particles, each with a different radius R_j, but with two constraints to guarantee that the ϵ_{ij} are the same for all j; namely, that all particles have the same mass M and the same moment of inertia I. Clearly there is an uncountably infinite number of families of radial distribution functions for the mass that can satisfy these constraints. One such family has a mass $m_j = I/R_j^2$ localized at the surface and the remaining mass $M - m_j$ localized at the center of the sphere.[9] This example therefore renders it permissible to consider the canonical partition function for N distinguishable, but *similar*, particles

$$Z_{BQD}(N) = \zeta^N. \tag{9}$$

The valid textbook result[5] for the classical thermodynamical regime of indistinguishable particles treated quantum mechanically is given in Eq. (6). Let us briefly recapitulate the well known procedure[5] for obtaining the canonical partition function $Z_{QI}(N)$ from the grand canonical partition function in Eq. (6),

$$\Xi_{QI} \equiv \sum_{N'} e^{\beta\mu N'} Z_{QI}(N') \approx e^{\beta\mu N} Z_{QI}(N), \tag{10}$$

where the maximum term is taken to obtain the last expression. Taking the logarithm in Eq. (6) shows that $\ln \Xi_{QI} = N$ and $-\beta\mu = \ln(\zeta/N)$. Insertion into Eq. (10) then leads directly to

$$\ln Z_{QI}(N) = -N \ln N + N + N \ln \zeta, \tag{11}$$

where ζ is the same single particle partition function defined in Eq. (8). Comparison to Eq. (9) then leads to the conclusion that

$$Z_{QI}(N) = Z_{BQD}(N)/N. \tag{12}$$

Since $S = (E + k_B T \ln Z_N)/T$ and the entropy of quantum indistinguishable particles is extensive, we also have for the translational part of the entropy

$$\Omega_{BQD}(N)/\Omega_{QI}(N) = N. \tag{13}$$

This corresponds nicely with $\Omega_{BCD}/\Omega_{BCI}$ in Eq. (2) but not with $\Omega_{SCD}/\Omega_{SCI}$ in Eq. (3).

It is important to emphasize that to obtain consistency with the classical value of $\Omega_{SCD}/\Omega_{SCI}$ in Eq. (3) requires a factor of $1/N!$ in the very definition of the partition function for Z_{SQD} in Eq. (7), but *only* for the case of distinguishable particles. If a similar factor of $1/N!$ were also inserted for Z_{SQI}, then one would have $\Omega_{SQD}(N)/\Omega_{QI}(N) = N!$ similar to Eq. (13) and inconsistent with Eq. (3). Insertion of $1/N!$ in the canonical partition function for distinguishable particles in Eq. (7) mirrors the similar insertion into the grand canonical ensemble in Eq. (37) in ref. 3 for the SQD case. Such an insertion really is *ad hoc*, unlike Gibbs' insertion to obtain Ω_{BCD} which was shown in the previous section to follow formally. But it is much worse. Swendsen applied the $1/N!$ to the partition functions of particles that are afterwards still supposed to be distinguishable and not to the partition functions of particles that are afterwards supposed to be indistinguishable. This is logically backwards and indicates a fundamental inconsistency in the proposals in ref. 3.

The fundamental inconsistency is seen when one goes back to the the derivation of the canonical partition function given by Eq. (7). The derivation of the canonical partition function Z is general and does not ask whether the particles are distinguishable, indistinguishable, quantum or classical. It employs a physical partition for particles, so the particles can be of different types in the system of interest compared to the reservoir that establishes the temperature. There is no legitimate way to introduce such specific characteristics of the particles. As shown in Eqs. (7)–(13), the canonical partition function for clearly distinguishable quantum particles leads to a non-extensive entropy. Consistency between the quantum and classical cases then demands that distinguishable classical particles also be non-extensive, in agreement with Eq. (2) and in disagreement with Eq. (3).

4. EXAMPLE OF AN IRREVERSIBLE PROCESS FOR WHICH S_{BCD} INCREASES AND S_{SCD} DOES NOT

Although the preceding section may already convince many readers that Eq. (3) is incorrect, the following discussion may provide deeper insight into the nature of truly distinguishable particles. Let us prepare a system of labelled particles $j = 1, \ldots, N$ in a volume V that is separated into two subvolumes V_1 and V_2 by a physical partition that does not allow any particle to move between the two subvolumes. The initial state a is prepared with a particular complexion of the distinguishable particles, namely, those labelled $1, 2, 3, \ldots, N_1$ are placed in V_1 and those labelled $N_1 + 1, \ldots, N$ are placed in V_2. Furthermore, set the partition so that $V_1/N_1 = V_2/N_2 = V/N$. The partition is then broken and the system evolves to state b. Using Eq. (2)

$$\Omega_{\text{BCD}}^a = V_1^{N_1} V_2^{N_2} < V^N = \Omega_{\text{BCD}}^b \tag{14}$$

and the S_{BCD} entropy increases in this process $a \rightarrow b$. Using Eq. (3)

$$\Omega_{\text{SCD}}^a = \frac{V_1^{N_1}}{N_1!} \frac{V_2^{N_2}}{N_2!} \approx \frac{V^N}{N!} = \Omega_{\text{SCD}}^b, \tag{15}$$

where the approximation is up to the first two terms in Stirling's approximation for the set condition $V_1/N_1 = V_2/N_2 = V/N$. Therefore, in the limit of large N the S_{SCD} entropy does not increase in this process $a \rightarrow b$.

The above process $a \rightarrow b$ 'mixes'[7] the distinguishable particles with labels $1, 2, 3, \ldots, N_1$ with those with labels $N_1 + 1, \ldots, N$. Reversing this process would either require a Maxwell demon or laboriously collecting

the particles and placing them back into their original subvolumes. This is therefore an irreversible process. Since entropy should increase for an irreversible process, the SCD definition in Eq. (3) would seem to be eliminated.

It is illuminating to consider an important counter argument. Form state c from state b by replacing the partition to again subdivide V into V_1 and V_2. Now the microscopic state has again been fixed in another specific complexion of the labelled particles, with $1', 2', 3', \ldots, N_1'$ contained in V_1 and particles labelled $N_1' + 1, \ldots, N'$ contained in V_2, where the primes indicate a permutation of the labels compared to state a. The fact that there is again only one complexion in both states a and c might suggest that the entropy has now been reduced to its value in a before the partition was first removed. Since entropy should not decrease by insertion of a partition, this might suggest that the true entropy in state b did not increase and therefore that the process $a \rightarrow b$ is not irreversible.

The purely mechanistic view implicit in this counter argument is contrary to the statistical thermodynamical view of entropy because it assumes that the entropy is determined by the microscopic description of the final state. A similar kind of argument could be used to argue that the entropy of any classical dynamical system can never increase because both the initial and final dynamical states are unique. Consider a different example for which an initial state $a2$ is prepared with many indistinguishable particles, each of which is placed in the subvolume V_1. After a precise time t_{b2}, this initial state then evolves to just one final microstate $b2$ in which the indistinguishable particles are confined only to be within the larger volume V. The entropy should increase in this process for any viable definition. This just provides another example of the well known concept that the uniqueness of the final microstate is irrelevant to discussions of entropy.

Let us return to the main example in this section that 'mixes' two sets of distinguishable particles. The thermodynamic states b and c should not be considered to be microstates; they are instead a statistical mixture of all complexions. This mixture should indeed have a higher entropy than the uniquely prepared complexion in the initial state a. In order to reduce the entropy to that of the initial state it is necessary to determine the exact complexion of labelled particles as was done in preparing state a. We will call state d the state obtained from c by determination of a unique final complexion of labelled particles. Obtaining state d requires expenditure of free energy by the agent determining this state, just as the initial preparation of state a required the expenditure of free energy.

The particular case of distinguishability in computers deserves additional consideration. In this case the complexion of the particles is always in the computer, so how does irreversibility come about? The first answer

is analogous to the answer above. The computer is the system and to determine a specific complexion requires the expenditure of free energy, in this case interrogation of the computer. There is a second answer that is at least at important. The computer *program* is the system and any particular microstate produced at the end of a particular simulation is just a member of an ensemble of all the states that would be produced. This ensemble concept mirrors simulation practice. Analysis is never done on one final microstate, but on a long sequence of microstates obtained after the system has equilibrated. In this view the entropy should take into account the entire ensemble that includes all complexions of labelled particles.

5. EXAMPLE OF A REVERSIBLE PROCESS THAT PERFORMS WORK WITH NO INTERNAL ENERGY CHANGE FOR WHICH S_{BCD} INCREASES AND S_{SCD} DOES NOT

If the process described in the preceding section is irreversible, then it should be possible to harness that process to perform work. Let us first recall the usual way to do that when one initially has only two different gases, one with particles of type A in subvolume V_1 and one with particles of type B in subvolume V_2, followed by a final state where A and B are only confined to the volume $V = V_1 + V_2$. First, the gas A is allowed to expand into a volume $V_A = V$, doing work against a piston. Next, the gas B is allowed to expand into a different volume $V_B = V$, doing work against a different piston. The two gases, still in separate volumes, are then merged. The method, not always easy to implement experimentally, employs two semi-permeable membranes. One membrane, call it $A\overline{B}$, is permeable to A particles and not to B particles and the other, call it $\overline{A}B$, is impermeable to A particles and permeable to B particles. A common wall between the intial two volumes V is replaced with a wall consisting of the $A\overline{B}$ membrane facing V_A and $\overline{A}B$ facing V_B. The $\overline{A}B$ membrane is then quasistatically swept through V_B, while maintaining V_A constant. (The simplest geometry utilizes a cylindrical pipe and a movable piston which moves the same distance as the $\overline{A}B$ membrane.) The work required during this merging process is zero because $P_A dV$ for the piston is balanced by $-P_A dV$ for the $\overline{A}B$ membrane, where P_A is the pressure of A particles only because the same concentration of B particles is maintained on both sides of the $\overline{A}B$ membrane.

There is no conceptual cutoff to the number of types of particles that may be initially placed in either of the two subvolumes. The system of distinguishable particles is merely the conceptual limit in which every particle is a different type. The analogous semi-permeable membrane

$A\overline{B}$ is required to pass all the distinguishable particles that were originally placed in volume V_1 and none of those in volume V_2, and conversely for $\overline{A}B$. Just as in the preceding paragraph, the system produces measurable work W while achieving the final state consisting just of all particles in the combined volume $V_1 + V_2$. For ideal gases treated isothermally, thermodynamics gives $\Delta S = Q/T = W/T > 0$. Statistical mechanics should therefore also give an increase of entropy when entropy is suitably defined. The Boltzmann formulae Eq. (2) passes this test but Eq. (3) does not.

While it becomes more difficult to design effective semi-permeable membranes in the laboratory as the number of different kinds of particles increases, this is a practical, not a fundamental, issue. It might still be amusing, however, to consider the model of similar, but distinguishable, spheres discussed in Section 3. If the spheres labelled $1, \ldots, N$ in the A group are all smaller than the spheres in the B group, then an $A\overline{B}$ semi-permeable membrane need only have holes larger than the A particles and smaller than the B particles. It will be left as an easy exercise for the reader to design a process that uses only this $A\overline{B}$ semi-permeable membrane to produce work. Although this would produce less work than the maximum that could be achieved by also having an $\overline{A}B$ semi-permeable membrane, this still suffices to show that entropy should increase upon expanding these two systems of distinguishable particles into a larger common volume.

It is noteworthy for this discussion that semi-permeable membranes are very easy to construct in computer simulations. It is clear, even without doing the simulation, that the process in this section will produce positive work. Any fundamental definition of entropy that ignores this is incorrect, even within the context of simulations, because this process is clearly simulable.

6. CRITIQUE OF SWENDSEN'S METHODOLOGY

In Section 7 of ref. 3 Swendsen argues that the Boltzmann entropy leads to a nonsensical prediction. When the volume V is partitioned into V_1 and V_2, one has

$$\Omega_{\text{BCD}}(N_1, V_1 | N_2, V_2) = V_1^{N_1} V_2^{N_2}. \tag{16}$$

$\Omega_{\text{BCD}}(N_1, V_1 | N_2, V_2)$ is maximized when all the particles are placed in the larger volume, i.e., $N_1 = N$ if $V_1 > V_2$. This seems counterintuitive when one is accustomed to thinking about indistinguishable particles of real gases. But it is *correct* for distinguishable particles. Start with all the particles in the volume V. Use a set of N semi-permeable membranes. Each

membrane M_i is permeable to all particles except particle i. Use M_i to compress particle i into V_1 or V_2. Repeat for each particle, $i = 1, \ldots, N$. Measure the total (negative) work W done by the system. Now compare the measurement of W for different choices of the total number of particles N_1 compressed into V_1 and N_2 compressed into V_2. W is largest (closest to zero) when all the particles are compressed into the larger subvolume. Since the change in entropy from the common initial state is given by $\Delta S = Q/T = W/T$, for non-interacting particles treated isothermally, the entropy is largest when all particles are in the larger subvolume. Note well that, at the end of the experiment, the set of semi-permeable membranes forms a physical partition between the subvolumes. This entropy maximization is performed under a crucial constraint that must be emphasized. Once the particles are placed in a subvolume, they are not allowed to move to the other subvolume. Let us describe this constraint as placing a physical partition in the volume V.

Swendsen obtains his Boltzmann nonsensical prediction by using what I will call a virtual partition that allows the particles to move from one subvolume to the other. Then, as the partition is moved so that the larger subvolume becomes the smaller one, Swendsen's prediction for Boltzmann BCD entropy is that the particles must 'rush from one side of the box to the other'[3] because this is required for the entropy obtained from Eq. (16) to remain maximal. The reason that this prediction is incorrect for the Boltzmann entropy is that, while Eq. (16) is correct for a physical partition, for a virtual partition the correct equation follows directly by expanding $\Omega_{\mathrm{BCD}} = (V_1 + V_2)^N$ to give

$$\Omega_{\mathrm{BCD}}(N_1, V_1 : N_2, V_2) = \frac{N!}{N_1! N_2!} V_1^{N_1} V_2^{N_2}. \tag{17}$$

The combinatorial factor in Eq. (17) counts the number of different complexions of labelled particles that are allowed because each particle is free to move through the virtual partition. To embed this conceptual and mathematical difference between virtual and physical partitions into the notation, a bar | is used to separate the variables for the two subvolumes in Ω_{BCD} in Eq. (16) and a colon : is used in Eq. (17).

Let us now make contact with the postulational approach taken by Swendsen. The maximization postulate (number 1 in ref. 3 and II in ref. 4), when applied to the present example, can be written

$$\Omega(N, V) = \sum_{N_1} \Omega(N_1, V_1 : N - N_1, V - V_1), \tag{18}$$

where $\Omega(N_1, V_1 : N - N_1, V - V_1)$ involves a virtual partition, not a physical partition. By finding the maximum term in the sum, the most probable values of N_1/V_1 are obtained when the particles are free to move between the subvolumes of V. (Indeed, this is a most important usage of virtual partitions, which are not to be considered to be inferior to physical partitions, just different.) Using Eq. (17) in Eq. (18) yields

$$\Omega_{\text{BCD}}(N, V) = V^N = \sum_{N_1} \frac{N!}{N_1! N_2!} V_1^{N_1} V_2^{N_2}. \tag{19}$$

If one divides Eq. (19) by V^N, each term in the sum is mathematically identical to Swendsen's Eq. (5) that he derives from probability densities.[3] Finding the maximum term from either approach leads to the expected result $V_1/N_1 = V/N$ as the reader can easily verify. Therefore, when the appropriate $\Omega_{\text{BCD}}(N_1, V_1 : N_2, V_2)$ for virtual partitions is used from Eq. (17), there is no nonsensical prediction that all the particles rush to the larger subvolume.

Although Eq. (19) is mathematically equivalent to the expression used by Swendsen,[3] the interpretation is different and this has major consequences as we move on to Swendsen's postulate 2, which is called the additivity postulate. When applied to the present example, postulate 2 requires that one can factor $\Omega(N_1, V_1 : N - N_1, V - V_1)$ in Eq. (18) into the form

$$\Omega(N, V) = \sum_{N_1} c \Omega_:(N_1, V_1) \Omega_:(N - N_1, V - V_1), \tag{20}$$

and that the entropy for N_1 particles confined to V_1 by a physical partition is given by

$$S_1 = k_B \ln \Omega_:(N_1, V_1). \tag{21}$$

Eq. (19) can be mathematically written in the form of Eq. (20) with $c = N!$ by identifying $\Omega_:(N_1, V_1) = V_1^{N_1}/N_1!$. Swendsen's Eq. (8) is mathematically equivalent (with $c = N!/V^N$). It is Eq. (21) that was relied on in[3] to propose Ω_{SCD} given by Eq. (2). However, Eq. (19) and the similar Eq. (5) of[3] were derived for a *virtual* partition, as is emphasized by the : subscript on Ω in Eqs. (20) and (21). The identification of S_1 in Eq. (21) as the entropy of a system of N_1 particles confined to V_1 by a *physical* partition does not necessarily follow. It is certainly not valid for BCD particles, which therefore do not obey the additivity postulate.

I now argue that the the additivity postulate embodied in Eqs. (20) and (21) should not be expected to hold for BCD particles because extensivity does not hold for them. As Swendsen properly points out,[3] while correcting Callen,[4] additivity and extensivity are not the same if a system is not homogeneous, such as when there is a surface phase. It is also claimed in ref. 3 that additivity does not imply extensivity even for a homogeneous system. To support this claim an example is given in Section 8 of ref. 3. However, that example requires a Maxwell demon that is not only able to read the labels on distinguishable particles to decide whether a particle can pass from one subvolume to another but also has to know that the label being read is the highest or lowest for all the particles in a particular subvolume. In the absence of any valid counterexamples, I will follow Callen[4] in supposing that additivity implies extensivity for homogeneous systems. If so, then the non-additivity of BCD particles shown directly in the preceding paragraph would indeed be required by their non-extensivity.

7. COMMENTS ON POSTULATES

Although one can question the value of the postulational approach to any scientific field, it is nevertheless useful to have some guidelines, provided that they are not held too rigidly so as to inhibit revision when required. As one example of postulate revision, Swendsen[3] revises Callen's list of postulates[4] and splits them into five new postulates. In addition to splitting the first half of Callen's postulate III into postulates 2 and 5, the second half of Callen's postulate III becomes Swendsen's postulates 3 and 4, which he properly demotes to a lesser status. Postulate 1 (maximization) given by Eq. (18) for the system in this paper, and postulate 2 (additivity), given by Eqs. (20) and (21) for the system in this paper, were the main postulates in ref. 3 for obtaining Eq. (3) in this paper.

Let me discuss the directions another revision might take, without attempting to eliminate redundancy or supply rigorous language. The maximization postulate 1 of ref. 3 would seem to be a good one to keep. One expectation was that postulates 1 and 2 would together allow only definitions of entropy that would increase when a process is irreversible. This hope is dashed by Swendsen's proposed entropy for distinguishable particles.[3] That proposed entropy S_{SCD} satisfies postulates 1 and 2 but it does not increase for the irreversible process analyzed in Section 4 nor for the process in Section 5 that produces net work in an isolated system. I therefore suggest that postulate 0 should be a reversibility/irreversibility requirement, even if such a requirement is redundant with other postulates for most physical systems. The additivity/extensivity postulate is incorrect

for distinguishable particles, so it should be relegated to a lesser status just as Swendsen[3] relegated his postulates 3–5 to a lower status.

There should also be a consistency postulate. After a definition of entropy is made and a statistical mechanical theory is subsequently developed using that definition, the resulting theory should be self-consistent. As shown in Section 3, the role of the $1/N!$ factor in the comparison between distinguishable and indistinguishable particles is self-consistent whether one treats the system classically or quantum mechanically in the Boltzmann definition, but not in the Swendsen definition.

8. CONCLUDING DISCUSSION

This paper has presented detailed arguments that the conventional Boltzmann approach is not only consistent with respect to distinguishable particles and the Gibbs paradox, but superior to the approach advocated recently by Swendsen.[3] In doing so, this paper has employed the standard literal meaning of the terms distinguishable and indistinguishable. Two particles are distinguishable (indistinguishable, respectively) if and only if their positional exchange produces a different (same, respectively) physical state. A corollary is that two particles are distinguishable if they are first identified as 1 and 2, put into a small box, shaken up, and when removed one can identify which particle was the original number 1. Accordingly, two He^4 atoms are not distinguishable even if they can be momentarily distinguished when they are far apart and their wavefunctions have negligible overlap. The property of distinguishability and indistinguishability is therefore just a property of the particles and not of their thermodynamic circumstances.

A different definition might say that atoms even of the same chemical species are distinguishable if they are in the classical thermodynamic regime in which the wavefunctions overlap negligibly. By this definition the property of distinguishability and indistinguishability would not be a property just of the particles, but also of the thermodynamic circumstances. This latter definition has the uncomfortable feature that it does not provide a definite answer in borderline cases; given enough time, or an experiment when a gas is strongly compressed, the wavefunctions would eventually overlap and the particles would no longer be distinguishable. In any case, this definition denies any distinction between distinguishable and indistinguishable particles when the system is in the classical thermodynamical regime.

The result in Eq. (3) that the entropy is the same for SCD as for SCI is consistent with the denial of an intrinsic difference between CD and CI particles. The different definition in the preceding paragraph

would support that conclusion as follows. It is agreed that the QI case is extensive, including the classical thermodynamical regime. If there is no difference between distinguishability and indistinguishability in the classical thermodynamical regime, then $S_{QD} = S_{QI}$ in that regime. To maintain the Q/C correspondence would also then require $S_{CD} = S_{CI}$. Although it is not mentioned in ref. 3, this potential reconciliation between Boltzmann and Swendsen suggests that the difference might be rooted in different definitions of distinguishability. However, the Swendsen suite of results still has the inconsistency problem emphasized at the end of Section 3; namely, the counterintuitive and arbitrary inclusion of the $1/N!$ factor in the very definition of quantum partition functions for distinguishable particles, but not for indistinguishable particles.

One may also argue that the complexion of labelled particles is a microscopic description and therefore that such detail should be excluded from statistical thermodynamics. However, if one ignores the labels in principle, then the system is indistinguishable in principle. While this radically removes the troublesome case of distinguishability, it does not respect its historical pedigree as well as its possible implications for computer simulations. The computer simulation discussed at the end of Section 5 clearly produces work in an isolated system, but ignoring the labels and treating the particles as indistinguishable gives the incorrect result that the entropy does not increase.

Most computer simulations obtain results for distribution functions and various derivatives of the free energy; such results are not affected by the differences between the Boltzmann and the Swendsen formulations of entropy. Swendsen did not give any specific examples where the disagreement about these conceptual issues regarding entropy makes a difference in the interpretation of simulation results in ref. 3. As suggested in the previous section, such examples might help to advance further discussion.

This paper has emphasized that systems of distinguishable particles are thermodynamically pathological in that they are not extensive. The traditional Boltzmann formalism for the entropy, that uses phase space integrals for classical systems, has the flexibility to clearly exhibit this pathology. The probability distribution formalism for entropy advocated by Swendsen[3] forces systems of distinguishable particles to appear not to be pathological and to have the same entropy as indistinguishable particles. This inability to discriminate between distinguishable and indistinguishable particles reveals an inflexibility that limits the scope of possible systems that can be treated using statistical mechanics.

I conclude that the conventional explanation of Gibbs paradox presented in textbooks is adequate for all but the cognoscenti. Discussion of

such issues may, however, lead to better, or at least rejuvenated, understanding of the fundamentals of entropy and statistical mechanics.

APPENDIX

Section 3 only dealt with the canonical partition function $Z_{BQD}(N)$ and it may be of some interest to consider the grand canonical partition function for distinguishable particles. It should first be emphasized that each particle is a different 'chemical' species, so there are N different chemical species present in a system of N distinguishable particles, each with its own chemical potential μ_j which may be derived as the increase in free energy when the particle is added. Using Eq. (8), this increase in free energy gives

$$\mu_j = -k_B T \ln(\zeta_j). \tag{22}$$

This result is consistent with the textbook formula for weakly interacting systems in the classical thermodynamic regime, $\mu_j = -k_B T \ln(\zeta_j/N_j)$, because $N_j = 1$ for each chemical species when the particles are distinguishable.

The grand canonical ensemble is a trifle awkward to define if every particle is different and there is only one particle $N_j = 1$ of each species present in the universe. What can then act as a reservoir for such particles? One can proceed, however, if the system of interest contains one particle on average of each species, $\overline{N_j} = 1$. There is then exchange of particles with a reservoir that contains many particles of each species j and one has

$$\Xi_{BQD} = \prod_j \Xi_j = \prod_j \prod_i \exp(\exp[-\beta(\epsilon_{ij} - \mu_j)]), \tag{23}$$

where the second equality derives from Eq. (6). To ensure that the average value, $\overline{N_j} = 1$, requires

$$\sum_i \exp[-\beta(\epsilon_{ij} - \mu_j)] \equiv \overline{N_j} = 1, \tag{24}$$

which gives the same value for μ_j as Eq. (22).

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8. The use of the subscript B follows[3] and some texts. Other texts use MB for Maxwell–Boltzmann, but some of these use MB for distinguishable particles[5] and some use it for indistinguishable particles.[6]
9. Another way uses two harmonic oscillators per particle. All oscillators have the same ω, each oscillator has a different mass but the sum of the masses on the same particle is the same for all particles. Yet another way would be to have only one energy level be different for different particles; this energy level would be very large compared to kT so that the ζ_j could be as nearly equal as one pleased, but the particles would still be spectroscopically distinguishable.