Yet another resolution of the Gibbs paradox: an information theory approach

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Abstract

The “Gibbs Paradox” refers to several related questions concerning entropy in thermodynamics and statistical mechanics: whether it is an extensive quantity or not, how it changes when identical particles are mixed, and the proper way to count states in systems of identical particles. Several authors have recognized that the paradox is resolved once it is realized that there is no such thing as the entropy of a system, that there are many entropies, and that the choice between treating particles as being distinguishable or not depends on the resolution of the experiment. The purpose of this note is essentially pedagogical; we add to their analysis by examining the paradox from the point of view of information theory. Our argument is based on that ‘grouping’ property of entropy that Shannon recognized, by including it among his axioms, as an essential requirement on any measure of information. Not only does it provide the right connection between different entropies but, in addition, it draws our attention to the obvious fact that addressing issues of distinguishability and of counting states requires a clear idea about what precisely do we mean by a state.

1 Introduction

Under the generic title of “Gibbs Paradox” one usually considers a number of related questions in both phenomenological thermodynamics and in statistical mechanics: (1) The entropy change when two distinct gases are mixed happens to be independent of the nature of the gases; is this in conflict with the idea that in the limit as the two gases become identical the entropy change should vanish? (2) Should the thermodynamic entropy of Clausius be extensive or not? Is this a mere convention, or a hard experimental fact? (3) Should two microstates
that differ only in the exchange of identical particles be counted as two or just one microstate?

The conventional wisdom, as recorded in many textbooks, (see e.g. [1][2]) asserts that the resolution of the paradox rests on quantum mechanics. This analysis is unsatisfactory on many counts; at best it is incomplete. While it is true that the exchange of identical quantum particles does not lead to a new microstate this approach ignores the case of classical, and even non-identical particles. Nanoparticles in a colloidal suspension or macromolecules in solution provide us with simple examples: should the entropy of such systems of non-identical classical particles be extensive or not?

A number of authors (including Grad, van Kampen, and Jaynes among others) have recognized that quantum theory has no bearing on the matter. Grad [3] and van Kampen [4] approach the problem from both the point of view of phenomenological classical thermodynamics and of statistical mechanics. Theirs is the orthodox version of a statistical mechanics that ultimately rests upon ergodic theory. Jaynes [5] addresses the subject as a problem in phenomenological thermodynamics (see also [6]). Perhaps surprisingly, Jaynes does not provide a statistical analysis from the point of view of information theory; it is only in the last few paragraphs of [5], and then only as a speculation, that he suggests that a more fundamental statistical treatment rooted in information theory might provide a more satisfactory and complete analysis.

Whether one accepts information theory or ergodic theory as the correct foundation for statistical mechanics turns out to be immaterial in this case: all three of those authors agree that the paradox is resolved once it is realized that (1) the experimental data is usually silent on the matter of whether the thermodynamic entropy is extensive or not (extensivity is no more than a convenient convention). (2) There is no such thing as the entropy of a system, that there are many entropies. And (3) the appropriate choice of entropy, or equivalently the choice between treating particles as being distinguishable or not depends on the resolution of the particular experiment being performed.

The purpose of this paper is essentially pedagogical; we add to their analysis by examining the paradox from the point of view of information theory. Our argument is guided by a certain property of entropy, the ‘grouping’ property, that Shannon recognized as an essential requirement on any measure of information. (Briefly, this property is the statement that the entropy of a probability distribution over a set of alternatives is unchanged if the alternatives are grouped into subsets, each with its own entropy.) This provides the right language, and therefore a useful guide in navigating past various conceptual difficulties. For example, the usual treatments of thermodynamics might mislead one to think in terms of only one entropy. On the other hand, the usual treatments of statistical mechanics, aim at providing the link between descriptions in terms of ‘micro’ and ‘macro’ states, and in the process, might mislead one to presuppose that no other intermediate ‘meso’ states are relevant. Focusing on the ‘grouping’ property steers the discussion in the right direction, namely towards studying the connection between the different entropies corresponding to different descriptions of the same system.
This paper is organized as follows: In section 2 we review the ‘grouping’ property and in section 3 we specify what we mean by the various states that enter our discussion. Sections 4 and 5 discuss the cases of identical and of non-identical particles. In section 6 we offer some final remarks.

2 The ‘grouping’ property

Perhaps the easiest way to enunciate the ‘grouping’ property is to prove it.

Our choice of notation and language will reflect, from the very start, the fact that our subject is statistical mechanics. A physical system can be in any one of a set of alternative states which will be labeled \( i = 1, 2, \ldots \). Knowing that the system is found in state \( i \) requires complete information up to the most minute details about every particle in the system, their location, momentum, internal state, etc. Such detailed states are called microstates. For a classical system the microstates should more properly be described as points in a phase space continuum. It is convenient, however, to divide phase space into cells of arbitrarily small size and consider discrete classical microstates.

The precise microstate of the system is not known; the limited information we possess allows us at best to assign probability \( p_i \) to each microstate \( i \). The amount of additional information that would allow us to pinpoint the actual microstate is given by the entropy of the distribution \( p_i \),

\[
S[p] = -\sum_i p_i \log p_i .
\]  

The set of microstates \( i \) (phase space) can be partitioned into non-overlapping subsets; the subsets are groups of microstates which will be labeled \( g \). The sum in eq.(1) can then be rearranged into

\[
S[p] = -\sum_g \sum_{i \in g} p_i \log p_i .
\]  

The probability that the system is found in group \( g \) be

\[
P_g = \sum_{i \in g} p_i .
\]  

Next consider the sum over groups \( g \) in eq.(2). Each term in this sum can be rearranged as follows

\[
-\sum_{i \in g} p_i \log p_i = -P_g \sum_{i \in g} \frac{p_i}{P_g} \log \frac{p_i}{P_g} - P_g \log P_g .
\]  

Let \( p_{i|g} \) denote the conditional probability that the system is in microstate \( i \in g \) given we know it is in the group \( g \),

\[
p_{i|g} = \frac{p_i}{P_g} .
\]
Then eq. (1) can be written as

\[ S = S_G + \sum_g P_g S_g, \]  

where

\[ S_G = -\sum_g P_g \log P_g \]  

and

\[ S_g = -\sum_{i \in g} p_{i|g} \log p_{i|g}. \]  

Eq. (6) is the ‘grouping’ property we seek. It can be read as follows: the information required to locate the system in one of its microstates \( i \) equals the information required to locate the system in one of the groups \( g \), plus the expectation over the groups of the information required to pinpoint the microstate within each group.

Shannon [7] regarded the ‘grouping’ property as an obvious requirement to be imposed on any measure of information and included it among his axioms leading to eq. (1). To others, who did not seek a measure of amount information, but rather a method to take information into account, eq. (6) is not an obviously unavoidable requirement. Thus, other derivations of eq. (1) have been proposed [8] from which entropy emerges as a tool for consistent reasoning. In these approaches entropy does not need to be interpreted in terms of heat, disorder, uncertainty, or lack of information: entropy needs no interpretation.

### 3 Entropies and descriptions

The ‘grouping’ property, eq. (6), plays an important role because it establishes a relation between two different descriptions and, in doing so, it invokes three different entropies (none of which is the thermodynamical entropy of Clausius).

We describe the system with high resolution as being in any one of its microstates \( i \) with probability \( p_i \), or alternatively, with lower resolution as being in any one of the groups \( g \) with probability \( P_g \). Since the description in terms of groups is less detailed we might refer to them as ‘mesostates’.

A thermodynamical description, on the other hand, corresponds to neither the high resolution description in terms of microstates, nor the lower resolution description in terms of mesostates. It is a description that incorporates the least amount of information necessary for a totally macroscopic characterization of equilibrium. The state that is relevant here is defined by the values of those variables the control of which guarantees the macroscopic reproducibility of experiments. Such states are called macrostates. The typical thermodynamic variables include the energy, volume, magnetization, etc., but here, for simplicity, we will consider only the energy since including other macrovariables is straightforward and does not modify the gist of the argument.
The standard connection between the thermodynamic description in terms of macrostates and the description in terms of microstates is established using the Method of Maximum Entropy. Let the energy of microstate \( i \) be \( \varepsilon_i \). To the macrostate of energy \( E \) we associate that probability distribution \( p_i \) which maximizes the entropy (1) subject to the constraints

\[
\sum_i p_i = 1 \quad \text{and} \quad \sum_i p_i \varepsilon_i = E.
\]

The well-known result is the canonical distribution,

\[
p_i = \frac{e^{-\beta \varepsilon_i}}{Z_H},
\]

where the partition function \( Z_H \) and the Lagrange multiplier \( \beta \) are determined from

\[
Z_H = \sum_i e^{-\beta \varepsilon_i} \quad \text{and} \quad \frac{\partial \log Z_H}{\partial \beta} = -E.
\]

The corresponding entropy, obtained by substituting eq.(10) into eq.(1),

\[
S_H = \beta E + \log Z_H,
\]

measures the amount of information beyond the value \( E \) to specify the microstate.

Before we compute and interpret the probability distribution over mesostates and its corresponding entropy we must be more specific about which mesostates we are talking about. This is what we do next.

4 Identical particles

Consider a system of \( N \) classical particles that are exactly identical. The particles may or may not interact with each other (i.e., the argument is not limited to ideal gases).

The interesting question is whether these identical particles are also ‘distinguishable’. By this we mean the following: we look at two particles now and we label them. We look at the particles later; somebody might have switched them. Can we tell which particle is which? The answer is: it depends. Whether we can distinguish identical particles or not depends on whether we were able (and willing) to follow their trajectories.

A slightly different version of the same question concerns an \( N \)-particle system in a certain state. Some particles are permuted. Does this give us a different state? As discussed in the previous section, the answer to this question requires a careful specification of what we mean by a state.

If by state we mean a microstate, that is a point in the \( N \)-particle phase space, then a permutation does indeed lead to a new microstate. On the other hand, our concern with permutations suggests that it is useful to introduce the
notion of a mesostate defined as the group of those \( N! \) microstates that are obtained as permutations of each other. With this definition it is clear that a permutation of the identical particles does not lead to a new mesostate.

Now we can return to discussing the connection between the thermodynamic macrostate description and the description in terms of mesostates using, as before, the Method of Maximum Entropy. Since the particles are identical, all those microstates \( i \) within the same mesostate \( g \) have the same energy, which we will denote by \( \varepsilon_g \) \((i.e., \varepsilon_i = \varepsilon_g \) for all \( i \in g \)). To the macrostate of energy \( E \) we associate that probability distribution \( P_g \) which maximizes the entropy \([7]\) subject to the constraints

\[
\sum_g P_g = 1 \quad \text{and} \quad \sum_g P_g \varepsilon_g = E.
\]

The result is also a canonical distribution,

\[
P_g = \frac{e^{-\beta \varepsilon_g}}{Z_L}, \tag{14}
\]

where

\[
Z_L = \sum_g e^{-\beta \varepsilon_g} \quad \text{and} \quad \frac{\partial \log Z_L}{\partial \beta} = -E. \tag{15}
\]

The corresponding entropy, obtained by substituting eq.\([14]\) into eq.\([7]\):

\[
S_L = \beta E + \log Z_L, \tag{16}
\]

measures the amount of information beyond the value \( E \) to specify the mesostate.

Notice that two different entropies \( S_H \) and \( S_L \) have been assigned to the same macrostate \( E \); they measure the different amounts of additional information required to specify the state of the system to a high resolution (the microstate) or to a low resolution (the mesostate).

The relation between \( Z_H \) and \( Z_L \) can be obtained from eqs.\([3]\), \([10]\) and \([14]\):

\[
Z_L = \frac{Z_H}{N!}. \tag{17}
\]

The relation between \( S_H \) and \( S_L \) is obtained from the ‘grouping’ property. First use eq.\([3]\) to get \( p_{1|g} = 1/N! \), and then substitute into eq.\([14]\) (with \( S = S_H \) and \( S_G = S_L \)) to get

\[
S_L = S_H - \log N!. \tag{18}
\]

Equations \([17]\) and \([18]\) both exhibit the Gibbs \( N! \) ‘corrections’. Our analysis shows (1) that the justification of the \( N! \) factor is not to be found in quantum mechanics, and (2) that the \( N! \) does not correct anything. The \( N! \) is not a fudge factor that fixes a wrong (possibly nonextensive) entropy \( S_H \) into a correct (possibly extensive) entropy \( S_L \). Both entropies \( S_H \) and \( S_L \) are correct. They differ because they measure different things: one measures the information to specify the microstate, the other measures the information to specify the mesostate.
An important goal of statistical mechanics is to provide a justification, an explanation of thermodynamics. Thus, we still need to ask which of the two statistical entropies, $S_H$ or $S_L$, should be identified with the thermodynamical entropy of Clausius $S_{\text{exp}}$. Inspection of eqs. (17) and (18) shows that, as long as one is not concerned with experiments that involve changes in the number of particles, the same thermodynamics will follow whether we set $S_H = S_{\text{exp}}$ or $S_L = S_{\text{exp}}$. This is the conclusion reached by Grad, van Kampen and Jaynes.

But, of course, experiments involving changes in $N$ are very important (for example, in the equilibrium between different phases, or in chemical reactions). Since in the usual thermodynamical experiments we only care that some number of particles has been exchanged, and we do not care which were the actual particles exchanged, we expect that the correct identification is $S_L = S_{\text{exp}}$. Indeed, the quantity that regulates the equilibrium under exchanges of particles is the chemical potential defined by

$$\mu_{\text{exp}} = -kT \left( \frac{\partial S_{\text{exp}}}{\partial N} \right)_{E,V,...}$$

(19)

(This is analogous to the temperature, an intensive quantity that regulates the equilibrium under exchanges of heat.) The two identifications $S_H = S_{\text{exp}}$ or $S_L = S_{\text{exp}}$, lead to two different chemical potentials, related by

$$\mu_L = \mu_H - NkT.$$ 

(20)

It is easy to verify that, under the usual circumstances where surface effects can be neglected relative to the bulk, $\mu_L$ has the correct functional dependence on $N$: it is intensive and can be identified with $\mu_{\text{exp}}$. On the other hand, $\mu_H$ is not an intensive quantity and cannot therefore be identified with $\mu_{\text{exp}}$.

5 Non-identical particles

In the last section we saw that classical identical particles can be treated, depending on the resolution of the experiment, as being distinguishable or indistinguishable. In this section we go further and point out that even non-identical particles can be treated as indistinguishable. Our goal is to state explicitly in precisely what sense it is up to the observer to decide whether particles are distinguishable or not.

We defined a mesostate as a subset of $N!$ microstates that are obtained as permutations of each other. With this definition it is clear that a permutation of particles does not lead to a new mesostate even if the exchanged particles are not identical. This is an important extension because, unlike quantum particles, classical particles cannot be expected to be exactly identical down to every minute detail. In fact in many cases they are grossly different. Consider the example of milk, i.e., a colloidal suspension of fat droplets in water, or a solution of macromolecules. A high resolution device, for example an electron microscope, would reveal that no two fat droplets or two macromolecules are
exactly alike. And yet, for the purpose of modelling most of our macroscopic observations (i.e., the thermodynamics of milk) it is not necessary to take account of the myriad ways in which two fat droplets can differ.

Consider a system of \( N \) particles. We can perform rather crude macroscopic experiments the results of which can be summarized with a simple phenomenological thermodynamics where \( N \) is one of the relevant variables that define the macrostate. Our goal is to construct a statistical foundation that will explain this macroscopic model, reduce it, so to speak, to ‘first principles’. The particles might ultimately be non-identical, but the crude phenomenology is not sensitive to their differences and can be explained by postulating mesostates \( g \) and microstates \( i \) with well defined energies \( \varepsilon_i = \varepsilon_g \), for all \( i \in g \), as if the particles were identical. As in the previous section this statistical model gives

\[
Z_L = \frac{Z_H}{N!} \quad \text{with} \quad Z_H = \sum_i e^{-\beta \varepsilon_i},
\]

and the connection to the thermodynamics is established by postulating

\[
S_{\text{exp}} = S_L = S_H - \log N!.
\]

Next we consider what happens when more sophisticated experiments are performed. The examples traditionally offered in discussions of this sort refer to the new experiments made possible by the discovery of membranes that are permeable to some of the \( N \) particles but not to the others. Other, perhaps historically more realistic examples, are afforded by the availability of new experimental data, for example, more precise measurements of a heat capacity as a function of temperature, or perhaps measurements in a range of temperatures that had previously been inaccessible.

Suppose the new phenomenology can be modelled by postulating the existence of two kinds of particles. (Experiments that are even more sophisticated might allow us to detect three or more kinds, perhaps even a continuum of different particles.) What we previously thought were \( N \) identical particles we will now think as being \( N_a \) particles of type \( a \) and \( N_b \) particles of type \( b \). The new description is in terms of macrostates defined by \( N_a \) and \( N_b \) as the relevant variables.

To construct a statistical explanation of the new phenomenology from ‘first principles’ we need to revise our notion of mesostate. Each new mesostate will be a group of microstates which will include all those microstates obtained by permuting the \( a \) particles among themselves, and by permuting the \( b \) particles among themselves, but will not include those microstates obtained by permuting \( a \) particles with \( b \) particles. The new mesostates, which we will label \( \hat{g} \) and to which we will assign energy \( \varepsilon_{\hat{g}} \), will be composed of \( N_a!N_b! \) microstates \( \hat{i} \), each with a well defined energy \( \varepsilon_i = \varepsilon_{\hat{g}} \), for all \( i \in \hat{g} \). The new statistical model gives

\[
\hat{Z}_L = \frac{\hat{Z}_H}{N_a!N_b!} \quad \text{with} \quad \hat{Z}_H = \sum_{\hat{i}} e^{-\beta \varepsilon_{\hat{i}}},
\]
and the connection to the new phenomenology is established by postulating
\[ S_{\text{new exp}} = \hat{S}_L = \hat{S}_H - \log N_a!N_b! . \] (24)

In discussions of this topic it is not unusual to find comments to the effect that in the limit as particles \( a \) and \( b \) become identical one expects that the entropy of the system with two kinds of particles tends to the entropy of a system with just one kind of particle. The fact that this expectation is not met is one manifestation of the Gibbs paradox.

From the information theory point of view the paradox does not arise because there is no such thing as the entropy of the system, there are several entropies. It is true that as \( a \to b \) we will have \( \hat{Z}_H \to Z_H \), and accordingly \( \hat{S}_H \to S_H \), but there is no reason to expect a similar relation between \( \hat{S}_L \) and \( S_L \) because these two entropies refer to mesostates \( \hat{g} \) and \( g \) that remain different even as \( a \) and \( b \) became identical. In this limit the mesostates \( \hat{g} \), which are useful for descriptions that treat particles \( a \) and \( b \) as indistinguishable among themselves but distinguishable from each other, lose their usefulness.

6 Conclusion

We conclude with a comment and a quotation. First, our comment.

The Gibbs paradox in its various forms arises from the widespread misconception that entropy is a real physical quantity and that one is justified in talking about the entropy of the system. The thermodynamic entropy is not a property of the system. It is somewhat more accurate to assert that entropy is a property of our description of the system, it is a property of the macrostate. More explicitly, it is a function of the macroscopic variables used to define the macrostate. To different macrostates reflecting different choices of variables there correspond different entropies for the very same system.

But this is not the complete story: the entropy is not just a function of the macrostate. Entropies reflect a relation between two descriptions of the same system: in addition to the macrostate, we must also specify the set of microstates, or the set of mesostates, as the case might be. Then, having specified the macrostate, an entropy can be interpreted as the amount of additional information required to specify the microstate or mesostate. We have found the ‘grouping’ property very valuable precisely because it emphasizes this dependence of entropy on a second argument, namely, the choice of micro or mesostates.

The promised quotation is a remark by van Kampen [4] that very aptly captures the issue of whether identical classical particles are distinguishable or not:

“\[ \text{The question is not whether the particles are identical in eyes of God, but merely in the eyes of the beholder.}\]”

This is a surprisingly perceptive remark, particularly coming from someone who strongly opposed the information theory approach to statistical mechanics.
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