The Gibbs Paradox and the Physical Criteria for the Indistinguishability of Identical Particles

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Abstract

Gibbs paradox in the context of statistical mechanics addresses the issue of additivity of entropy of mixing gases. The usual discussion attributes the paradoxical situation to classical distinguishability of identical particles and credits quantum theory for enabling indistinguishability of identical particles to solve the problem. We argue that indistinguishability of identical particles is already a feature in classical mechanics and this is clearly brought out when the problem is treated in the language of information and associated entropy. We pinpoint the physical criteria for indistinguishability that is crucial for the treatment of the Gibbs’ problem and the consistency of its solution with conventional thermodynamics. Quantum mechanics provides a quantitative criterion, not possible in the classical picture, for the degree of indistinguishability in terms of visibility of quantum interference, or overlap of the states as pointed out by von Neumann, thereby endowing the entropy expression with mathematical continuity and physical reasonableness.

Keywords: Gibbs paradox, Entropy, Indistinguishability, Maxwell’s demon
1 Multiple Notions of Entropy

There is written record that J. von Neumann advised C. Shannon to call his measure of information as entropy\(^1\), saying, ‘in the first place, your uncertainty function has been used in statistical mechanics under that name, so it already has that name. In the second place, and more important, no one knows what entropy really is, so in a debate you will always have the advantage’. While the technical definitions consistent with both thermodynamics, statistical mechanics and information theory are all known and studied for decades, there is a remaining unease perhaps, exemplified by a relatively recent and influential paper by E. T. Jaynes\(^2\) on the Gibbs paradox, in which he stated, ‘some important facts about thermodynamics have not been understood by others to this day, nearly as well as Gibbs understood them over 100 years ago...it is not surprising that entropy has been a matter of unceasing confusion and controversy from the day Clausius discovered it. Different people, looking at different aspects of it, continue to see different things because there is still unfinished business in the fundamental definition of entropy, in both the phenomenological and statistical theories...further theoretical work will be needed before we can claim to understand entropy.’

The high pace of quantum information theory has only complicated the scenario further, with several new measures introduced and studied for quantities associated with information encoded in quantum systems. However, in this paper we focus on the limited problem called the Gibbs paradox, introduced by J. W. Gibbs in the context of the change in entropy during mixing of gases. There have been several discussions, and continued debates, on the notions of entropy and the issue of indistinguishability of identical particles in the context of the Gibbs paradox\(^3\)–\(^6\) (those cited here are indicative and far short of being exhaustive). Central point of our discussion is the criterion for indistinguishability of identical particles. We will argue that the feature of indistinguishability is naturally present in classical physics, without a need to impose it and then justify on the basis of the theory of quantum mechanics. Most of our discussion will be within the conventional understanding of entropy in thermodynamics and statistical mechanics, with some reference to the simplest understanding of measure of information in the sense of Shannon. We will also touch on the issue whether entropy is only a theoretical entity, created by a definition as a useful and convenient notion without a direct physical counterpart, or whether it has a well-constrained relation to measurable physical quantities associated with the multi-particle system.
The notion of entropy in thermodynamics is associated with transfer of heat, as introduced by Clausius, and the change in entropy in a thermodynamical process from configuration $A$ to $B$ is defined through the expression

$$\Delta S = \int_A^B \frac{dQ}{T}$$

(1)

where $dQ$ is the change in the quantity of heat. All real processes have some generation of heat and the naturalness of entropy generation is what is highlighted in the second law of thermodynamics. In the microscopic picture of statistical mechanics of molecular processes, this then is well-understood as distributing energy into available degrees of freedom at the molecular level and this forms the basis of the Boltzmann definition of entropy

$$S = k_B \ln W$$

(2)

where $W$ is the number of physical configurations of the multi-particle system that is consistent with the given constraints on the macroscopic variables like total energy. In this picture the entropy in a thermodynamic state is calculated by counting the number of microscopic configurations that corresponds to the macroscopic physical state.

The Gibbs’ expression for entropy is identical (to factor $k_B$) in structure with the information theoretic entropy,

$$S = -\sum_i p_i \ln p_i$$

(3)

and this can be related to the Boltzmann entropy by noting that for equally likely probabilities for the microstates accessible to the system in equilibrium, $p_i = 1/W_i$.

But, there is sometimes a gap between these microscopic notions and the thermodynamic notion, which can lead to confusion or paradoxes. In fact, the equivalence of the different definitions is theoretically demanded, and not self-evident. The connection of the Boltzmann and Gibbs definitions to the physical entropy is through the frequentist picture of probabilities and the number of configurations where the actual number
of particles with their physical attributes lying in specific range of values of physical quantities can be related to the relevant probabilities. Also, an infinity of ensembles of the same physical system and ensemble averages are theoretical concepts with no physical counterpart and the actual physical system samples only a small fraction of accessible microstates in any finite time, through its dynamics. However, the Gibbs definition allows generalizations, the most discussed being the Shannon entropy in information theory and its equivalents or extensions. The common feature in all notions of entropy is the concept of sharing or distributing a physical resource among a multi-system ensemble. *The concept of sharing is primary and central, and depending on which physical quantity is shared, the physical nature of entropy varies.*

## 2 The Gibbs Paradox and Gibbs’ Solution

The expression for entropy for *n* mole of gas, based on equation 2, could be
\[ S = nR \ln V = Nk_B \ln V, \]
up to a constant, and this is of course expected to be additive (extensive) with change in volume and the amount of gas, consistent with the expectation of the change in the number of microscopic configurations available to the system. *N* is the number of particles. However, consider a situation where an imaginary partition is inserted into a vessel containing the gas, dividing it equally into two. Now the total entropy is
\[ S = 2 \times \frac{N}{2} k_B \ln \frac{V}{2} = Nk_B \ln V - Nk_B \ln 2 \]

Hence \( \Delta S = -Nk_B \ln 2 \), which is inconsistent with both thermodynamics and physical expectation. No heat is transferred and no physical process took place, except restricting access of the individual molecules to all available microstates, by introducing a partition (locally, the molecules cannot even be ‘aware’ of such a partition). The decrease in the entropy seems like the violation of the second law of thermodynamics! The apparent discrepancy can be made larger by further subdivisions. Instead if dividing by a partition, we can also consider removing an already existing partition and then the entropy increases by \( Nk_B \ln 2 \).

On the other hand, if we consider the genuine mixing of two gases of different species, each with \( N \) molecules occupying volume \( V/2 \), by removing a partition in a vessel, they mix spontaneously by expanding into volume \( V \).
(arranged to be at constant temperature) and the change in the entropy of mixing is

\[ \Delta S = 2 \times (Nk_B \ln V - Nk_B \ln V/2) = 2Nk_B \ln 2 \quad (5) \]

which is what one would expect because each molecule now has twice the number of possibilities to occupy a compatible microstate, with increase in the spatial volume available. However, this reasoning should not apply if the gas is of the same species because then the partition can be considered as purely imaginary, with no physical significance. There is nothing in the expression for the entropy that can automatically take care of whether the molecules are of the same species or not, or in other words, indistinguishable or not. This is the origin of the Gibbs paradox.

Therefore, it is clear that the additional notion of ‘different species’ or distinguishability has to be introduced while calculating the entropy of mixing of gases. This was done by Gibbs and included in the counting of microstates to solve the problem. However, the discussion on criteria for indistinguishability, its justification, quantitative measures, subjectivity etc. all occupied controversial discussions now well over a century. We may now briefly recall Gibbs’ solution to the problem.

The expression for the classical entropy is derived from \( S = k_B \ln W \), by counting the number of distinguishable microstates for \( N \) particles. The number of microstates possible in a volume of phase space \( \Delta V_{ps} = \Delta p \Delta q \) is \( W_\Delta = \Delta p \Delta q / \hbar^3 \), and indicates that the entropy is proportional to the logarithm of the spatial volume. Irrespective of the details of the counting to estimate \( W \) in eq. (2) we note that if the counting of the number of states \( W \) for \( N \) particles corresponds to an entropy \( S = k_B \ln W = Nk_B \ln V \), then dividing this by an ‘indistinguishability factor’ \( N! \) changes the expression for entropy to

\[ S = k_B \ln W' = k_B (N \ln V - N \ln N + N) \]

\[ = Nk_B \ln(V/N) + k_B N \quad (6) \]

with Stirling’s approximation \( \ln N! \simeq N \ln N - N \). With this expression we can recalculate the difference between initial and final entropy when removing (or introducing) a partition for the same species of gas, \( N/2 \) particles occupying volume \( V/2 \) initially. We get,

\[ S_i = 2 \times \frac{N}{2} k_B \ln\left(\frac{V/2}{N/2}\right) + 2 \times k_B (N/2) \]

\[ S_f = Nk_B \ln(V/N) + k_B N = S_i \quad (7) \]
Therefore, the Gibbs’ division by the factor N! on the number of microstates, invoking indistinguishability of identical particles, eliminates the unphysical increase of entropy for the same species of gas. For the case of two different species of gas mixing we get

\[ S_i = 2 \times \frac{N}{2} k_B \ln\left(\frac{V/2}{N/2}\right) + 2 \times k_B (N/2) \]

\[ S_f = (N/2) k_B \ln V/(N/2)_1 + (N/2) k_B \ln V/(N/2)_2 + k_B (N/2)_1 + k_B (N/2)_2 \]

(8)

\[ \Delta S = S_f - S_i = N k_B \ln 2 \]

(9)

where we have labelled the two different gases with subscripts in the expression for \( S_f \). The result agrees with the physical expectation for the entropy of mixing of different gases when a molecule of a species has twice as many microstates accessible. Thus, the Gibbs’ division by \( N! \) seems to be correct solution. It only remains to justify the division on physical grounds of indistinguishability. Perhaps the main reason for the original counting of states with particles treated as distinguishable is that every configuration of the particles is notionally distinguishable by the Newtonian history, due the existence of trajectories and that particle exchanges can be kept track of. Therefore, most people think that indistinguishability of identical particles is justified only within quantum theory and that quantum theory as a basis is essential for the correct treatment of statistical mechanics even at the level of non-degenerate gases, at low density where interparticle separation is much larger than the de Broglie wavelength. If this were true, it would be surprising – this anticipation of quantum theory in a simple thermodynamical problem. It is to this aspect we now turn the attention for a careful analysis.

### 3 Counting Microstates for Entropy

Given \( N \) distinguishable particles, the number of microstates with \( n \) particles in a partition is

\[ W(N, n) = \frac{N!}{n!(N - n)!} \]

(10)

If there is additional degeneracy of \( g \) (number of spin states, for example), this is multiplied by the factor \( g^n \). \( N \) particles can be distributed in allowed
physical states (of energy, spin projection etc.) labelled 1, 2...m with parti-
tions \( n_1, n_2...n_m \) in number of ways

\[
W(N, n_i) = \frac{N! g_1^{n_1} g_2^{n_2} \cdots g_m^{n_m}}{n_1! n_2! \cdots n_m!} = \frac{N! \prod_i g_i^{n_i}}{\prod n_i!}
\]  \( (11) \)

With the Stirling approximation,

\[
\frac{S}{k_B} = \ln W = N \ln N + \sum_i n_i \ln(g_i/n_i)
\]  \( (12) \)

The probability for a particle to be in the partition \( i \) is

\[
\frac{g_i}{n_i} = \frac{Z}{N} \exp(-\epsilon_i/k_B T)
\]  \( (13) \)

from which

\[
\frac{S}{k_B} = \ln W = N \ln Z + U/k_B T
\]  \( (14) \)

Since \( Z \propto V T^{3/2} \) for the gas, the entropy is

\[
S = N k_B \ln V + \frac{3}{2} kT + C
\]  \( (15) \)

(with \( C \) a constant) and it is this expression that leads to the Gibbs paradox. Dividing the expression for \( W(N, n_i) \) by \( N! \) gives

\[
\frac{S}{k_B} = N \ln V + \frac{3}{2} kT - N \ln N + N + C
\]

\[
= N \ln(V/N) + \frac{3}{2} kT + N + C
\]  \( (16) \)

When the partition is inserted in the vessel containing a gas, we have

\[
S_i = N \ln \left( \frac{V}{N} \right) + C'
\]

\[
S_f = 2 \times \frac{N}{2} \ln \left( \frac{V/2}{N/2} \right) + C'
\]

\[
\Delta S = 0
\]  \( (17) \)

avoiding the Gibbs paradox.

The counting corresponding to the indistinguishable particles could have been done directly, from the outset, by noting that the number of possibilities
of distribution of $n_i$ particles in $g$-fold degenerate state with $g_i \gg n_i \gg 1$, as often is the case in the thermodynamic problem, is

$$W_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

(18)

$$= \frac{(n_i + g_i - 1)(n_i + g_i - 2) \ldots (n_i + g_i - n_i)_{\text{terms}}}{n_i!(g_i - 1)!} \times (g_i - 1)(g_i - 2) \ldots 1$$

(19)

$$\approx \frac{g_i^{n_i}(g_i - 1)!}{n_i!(g_i - 1)!}$$

(20)

and

$$W = \prod_i W_i \approx \prod_i \frac{g_i^{n_i}}{n_i!}$$

(21)

without the factor $N!$, when compared to equation 11.

Now we turn to the crucial issue of understanding and quantifying the notion of indistinguishability.

### 4 Indistinguishability: Physical Aspects

In the thermodynamical problem of a gas in a container at moderate densities and at temperatures well above the absolute zero temperature, the quantum mechanical aspects of indistinguishability can play no role. It is only when the de Broglie wavelength is comparable to the interparticle separation, one expects quantum mechanical considerations to be important. The manifestation of indistinguishability in quantum physics is interference of amplitudes and in problems that does not have to deal with interference and quantum correlations, quantum theoretical aspects are irrelevant. Therefore, it is physically unreasonable to invoke quantum mechanical justification for treating particles as indistinguishable in the Gibbs entropy problem. This means that it will be truly an advance in conceptual understanding if we could justify why we need to treat classical gas as consisting of indistinguishable particles.

Another aspect that is important in the solution of the Gibbs problem is that the usual discussions of indistinguishability smells of some subjectivity in determining whether a particle is distinguishable from another. What decides, and by what criteria, whether particles are distinguishable? Nature should not care whether the physicist is able to distinguish one particle
from another, with his tools and methods. The notion of physical entropy change should be free of such subjectivity, unless entropy is merely a theoretical construct meant for determining the amount of useful work, based on available subjective knowledge about the microscopic details of the system. Jaynes’ paper discusses this point in great detail, in support of such subjectivity\(^2\). The problem is only amplified when one deals with physical indistinguishability in the language of information, because the notion of information is associated with acquisition and representation of information, which has subjective aspects built in.

As we already remarked, Newtonian trajectories of classical particles is one reason such particles are treated as tractable and therefore distinguishable. However, for a specifying a particular equilibrium physical configuration in phase space (with particular coordinates and momenta at any instant for \(N\) particles) the history is not relevant at all. Even if we can keep track of the trajectories and histories of particles and even label individual particles (in a computer program, for example), the configurations with only permutations of particles are not physically distinct even though symbolically distinct. The crucial point is that if a physical interaction cannot distinguish one particle from another, in principle, they are indistinguishable. Distinguishability is equivalent to spatial separability and this single criterion is sufficient to show that indistinguishability of identical particles is already a classical feature. This has really nothing to do with quantum mechanics of the particles, except in the general sense of quantum theory being the general theory of description of particles and their interactions. There is no subjectivity either, because what matters is not whether the analytical physicist has enough information available about the particles to decide whether they are distinguishable or not, but whether they behave differently under a general set of physical fields acting on them. This criterion focuses on the intrinsic properties of the particle, and not on whether or not one has information about such properties.

It is easy to see that classical theory of representation of information with classical symbols do not treat multiple occurrences of the same symbols as distinguishable. For \(n\) classical bits with each bit distributed among \(g\) states (equivalent to the degeneracy in the particle case), the number of classical states is \(W_{cl} = g^n\) and not \(n!g^n\). Therefore, trying to enumerate the accessible number of configurations for \(N\) particles with \(n_i\) particles distributed in state with degeneracy \(g_i\) as \(W = N! \prod_i g_i^{n_i}/n_i!\) was flawed from the beginning, and there is no need to invoke quantum mechanics to justify the indistinguisha-
bility. Instead of division by $N!$, what was really required was the correct way of enumeration of physically distinct states in the first place, instead of mentally distinct states.

5 Indistinguishability in Quantum Mechanics

The need for quantum theoretical analysis enters considerations of statistical mechanics and thermodynamics only when the particles have to compete for available phase space, when quantum degeneracy becomes important and manifest in the interference of relevant amplitudes. In that regime, exchange of particles’ coordinates have physical consequences, like spin-statistics correlations. While indistinguishability and exchange of identical particles have physical consequences in a quantum physical context, it has no observable physical consequence in classical physics. However, the physical feature of indistinguishability of identical particles is a basic notion that is independent of the theoretical framework, just as the indistinguishability of identical alphabets of languages or mathematical symbols. (It is not really frivolous or naive to say that when such indistinguishable classical symbols themselves are constructed out of molecular systems, one has no justification to treat the molecules themselves as distinguishable!) Indistinguishability signifies the impossibility of selective segregation and filtering by any physical means whatsoever\(^2,3\) (this connects the Gibbs problem to the Maxwell’s demon problem).

Now we address the important issue of quantifying the degree of distinguishability. This has already been clarified fully by von Neumann\(^8\), while discussing the (related) problem of the Maxwell’s demon. In the discussion of the Gibbs problem of entropy of mixing of two gases with equal number and volume, it seems that even the slightest of distinguishability implies the change of entropy amounting to $Nk_B\ln 2$, which is not satisfactory from a physical point of view. It is in fact this feature that lead to the discussion on subjectivity of change of entropy. However, as von Neumann pointed out, two physical states are truly distinguishable in physics only when they are orthogonal in the quantum mechanical sense. If the physical states are represented as $|a\rangle$ and $|b\rangle$, the degree of overlap and indistinguishability, is $|\langle a|b\rangle|$ and there is no corresponding notion in classical physics. In classical physics, distinguishability is a discontinuous concept, whereas in quantum physics it is continuous. This is important in treating the problem of entropy of mixing
without the discontinuity apparent in the classical discussion. It is perhaps best to quote directly von Neumann\(^8\) (with slight change of notation),

‘In particular, the above treatment shows that two states \( |a \rangle \) and \( |b \rangle \) of the system \( S \) can be certainly divided by a semi-permeable wall if they are orthogonal. We now want to prove the converse: if \( |a \rangle \) and \( |b \rangle \) are not orthogonal, then the assumption of such a semi-permeable wall contradicts the second law of thermodynamics. That is, the necessary and sufficient condition for the separability by semi-permeable walls is \( \langle a | b \rangle = 0 \), and not, as in classical theory, \( |a \rangle \neq |b \rangle \). This clarifies an old paradox of the classical form of thermodynamics, namely, the uncomfortable discontinuity in the operations with semi-permeable walls: states whose differences are arbitrarily small are always 100% separable, the absolutely equal states are in general not separable! We now have a continuous transition: It will be seen that 100% separability exists only for \( \langle a | b \rangle = 0 \) and for increasing \( \langle a | b \rangle \) it becomes steadily worse. Finally, at maximum \( \langle a | b \rangle \), i.e., \( \langle a | b \rangle = 1 \), the states \( |a \rangle \) and \( |b \rangle \) are identical, and the separation is completely impossible.’

These considerations imply that the expression for the change in entropy of mixing, \( \Delta S = N k_B \ln 2 \) in the case of two equal partitions considered earlier, should be multiplied by the visibility function \( |\langle a | b \rangle|^2 \) to completely resolve the Gibbs paradox. The change in entropy does depend on the degree of similarity or the degree of indistinguishability and it can be precisely formulated. The von Neumann approach also can take care of correlations in the system and provides a truly general setting to deal with both classical and quantum entropy, and hence information theoretic entropy as well.

6 Connecting to Clausius Entropy

The clarifications on the entropy of mixing and separation in terms of true physical distinguishability allows us to relate the discussion to the Clausius definition of change of entropy in a thermodynamical process, \( \delta S = \int \delta Q / T \), where \( Q = U - F \), where \( U \) is the internal energy and \( F \) the free energy. The question of ‘how hard’ is it to separate the already mixed gas is the central feature that encodes the salient point of our discussions. In the classical treatment, the (discontinuous) transition from indistinguishable to distinguishable is equivalent to the possibility of restoring the mixed gases back into the partitions by applying an external field, without the physicists having to play the demon, which in any case is impossible as shown in several
discussions of Maxwell’s demon. This is the natural and physical definition of distinguishability. This transition is made smooth and quantitative in the quantum theoretical approach. The motions that result from the external field leads to the separation and this in turn changes the external fields. *Thus, distinguishable micro-physical states are equivalent to the possibility of attaining distinguishable macroscopic states.* This is the key point and it can be related to the change in the quantity of heat and the change in physical entropy.

As an example, consider spin-1/2 atoms of the same species, at low density and finite temperature, in a container with a partition. In the absence of an external magnetic field the fact that there are two distinguishable projections for the spin on a reference axis has no physical relevance and the mixing of the gas does not result in a change of the macroscopic configuration or physical quantities. Nor does it alter the phase space available to each particle. Hence, the entropy should not change in the absence of a field, in spite of the notional distinguishability. However, if the two spin states were separated into two partitions to start with, in the presence of a field, mixing should result in a change in the physical and mathematical entropy, from the considerations we discussed in this paper.

As a concluding remark, it seems that we need to only consolidate the various insights discussed on the concepts of entropy through ages, from Clausius to Shannon, and there doesn’t seem to be compelling reasons to think that ‘there is still unfinished business in the fundamental definition of entropy, in both the phenomenological and statistical theories’ as Jaynes remarked. His remarks were in the context of considering entropy as a theoretical construct, necessary to evaluate the amount of useful work available from the thermodynamical system, which is subjective in the sense that more information about the microstates of the system leads to a better estimate of entropy and practical strategy to extract useful work. However, entropy as the unique physical quantity that attains the maximum value in the multi-particle thermodynamic system at its equilibrium does not depend on such subjective knowledge and information. There is no true correspondence between information that is practically available about the system and its physical entropy. While there is scope to define and use new quantities that resemble physical entropy in different contexts involving statistical considerations, the concept and definition of thermodynamical and statistical mechanical entropy, endowed with properties like extensivity and continuity due to insights from Gibbs and von Neumann, seems to be on a robust and
consistent foundation.

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