The Gibbs Paradox Revisited

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Abstract

The Gibbs paradox has frequently been interpreted as a sign that particles of the same kind are fundamentally indistinguishable; and that quantum mechanics, with its identical fermions and bosons, is indispensable for making sense of this. In this article we shall argue, on the contrary, that analysis of the paradox supports the idea that classical particles are always distinguishable. Perhaps surprisingly, this analysis extends to quantum mechanics: even according to quantum mechanics there can be distinguishable particles of the same kind. Our most important general conclusion will accordingly be that the universally accepted notion that quantum particles of the same kind are necessarily indistinguishable rests on a confusion about how particles are represented in quantum theory.

1 Introduction: The Gibbs Paradox

Imagine the following experimental set-up: a partition divides a container into two equal parts, each containing a different ideal gas—the amounts of gas, pressure and temperature being equal in the two halves of the container. Now, the partition is suddenly removed, so that the two gases start mixing via an irreversible process; eventually a macroscopic equilibrium situation is established. The uniform gas mixture that fills the container at the end of this process then possesses a higher entropy than the total entropy of the gas system we started with; the difference is the entropy of mixing.
The magnitude of this entropy increase can be calculated by considering a reversible process that begins in the same unmixed situation and ends in the same final equilibrium state as the irreversible process we just described. The standard (theoretical) way of realizing this reversible mixing process makes use of semi-permeable membranes: the partition between the two halves of the container is replaced (in thought) by two membranes, one only transparent to the gas on the left-hand side (gas $A$, say), the other only transparent to the other gas ($B$). These membranes can now be slowly shifted to the left and the right wall of the container, respectively, thereby letting gases $A$ and $B$ expand reversibly. During this process each of the expanding gases exerts a pressure $P$ on the membrane that is opaque to it, so work is done. In order to keep the energy and the temperature at their original values a compensating amount of heat, $\Delta Q$, should therefore be supplied to the gases, and this can be arranged by immersing the system in a heat bath. The change of entropy resulting from this reversible process can be calculated via $\Delta S = \int \frac{dQ}{T}$, with $T$ the temperature. The added heat, $dQ$, should equal the work performed by the two gases, i.e. $2P\,dV$. In this way we find:

$$\Delta S = 2 \int \frac{P\,dV}{T} = 2 \int \frac{kN\,dV}{V} = 2kN \log 2,$$

(1)

where we have used the ideal gas law $PV = kNT$, with $N$ the number of atoms or molecules in each of the two gases and $k$ Boltzmann’s constant.

This entropy of mixing is independent of the exact physical properties of gases $A$ and $B$. The only thing that plays a role in the calculation and in the final result is that the two gases are different. This difference makes it possible to design—in principle—the semi-permeable membranes that are needed for the reversible mixing process. If the gases are the same no distinguishing membranes can exist and there is no mixing at all according to thermodynamics: from a thermodynamic point of view nothing happens when the partition is removed in this case.

As a consequence, there is a discontinuity in the behavior of the entropy: any difference between the gases, however small, produces the same mixing entropy $2kN \log 2$, whereas there is no entropy of mixing if the gases are the same. The existence of this discontinuity is known as the Gibbs paradox.

Within the framework of thermodynamics the modern standard response to the existence of this discontinuity is that nothing remarkable is happening here: In principle (although not in practice) it is always possible to
design membranes that distinguish gases $A$ and $B$ as long as there is any difference between them at all. Because there is no conceptual difficulty in accepting a discontinuity between “$A$ and $B$ differ” and “$A$ and $B$ are equal”, it should not be considered paradoxical that there is a corresponding discontinuity between distinguishability-in-principle plus existence of a mixing entropy, and complete identity without such an entropy. Moreover, in practical situations the effectiveness of distinguishing between two gases will be restricted by technical limitations—this effectiveness will gradually diminish when the two gases become more similar. As a consequence, no discontinuity will be detectable in actual laboratory situations: the measured mixing entropy will there vanish continuously. It is only in the idealized situation of perfectly effective separation techniques that the discontinuity in the entropy will manifest itself—and as we have seen, in this case there is no conceptual problem.

2 The Gibbs Paradox in Statistical Mechanics

The paradox can also be formulated in statistical mechanics. In statistical mechanics a counterpart to the thermodynamical entropy is defined, namely the logarithm of the number of microstates $W$ that are compatible with a given macrostate: $S = k \log W$. When an ideal gas of $N$ particles expands and doubles its volume, the number of available microstates $X$ per particle doubles: each particle now obtains twice as much space available to it as it had before. This means that $W$ goes up, from $X^N$ to $(2X)^N$, which corresponds to an entropy difference $\Delta S = kN \log 2$. When two different ideal gases mix, the statistical mechanical entropy of mixing is therefore $2kN \log 2$, exactly the value predicted by thermodynamics.

When two equal volumes of the same gas mix, the number of microstates available to an arbitrary individual particle still doubles, so the formula $S = k \log W$ gives us $\Delta S = 2kN \log 2$, as before. But now this result seems wrong, at least from the point of view of thermodynamics. As we have seen, the thermodynamical entropy of mixing vanishes in this case, because nothing happens when two identical gases mix. This then leads to a new form of the Gibbs paradox: the statistical mechanical entropy of mixing is insensitive to the question of whether the gases are equal or unequal, but this is in conflict
with the discontinuity predicted by thermodynamics.

In the literature the following argument is often deployed in order to remove this discrepancy. “Since the molecules (or atoms) of a given species of gas are all qualitatively the same, permutations of these particles do not have any physical effect and do not lead to a new state; therefore, replace $W$ by $W/N!$ in the formula for the entropy.” As it turns out, this change in the way of counting the number of available microstates suffices to restore agreement with thermodynamics.

Indeed, the division by $N!$ makes the mixing entropy in the equal-gases-case disappear and leaves the other, correct results untouched. For example, doubling of the volume of a gas without a change in the number of particles gives us $\Delta S = kN(\log X^N/N! - \log(2X)^N/N!) = kN \log 2$, so the entropy of mixing keeps its appropriate value in the case of two different gases that mix. However, doubling the volume together with doubling $N$ gives us, via Stirling’s formula, that the number of microstates goes from $W$ to $W^2$: $W = X^N/N! \rightarrow W' = (2X)^{2N}/(2N)! = W^2$. This implies, via $S = k \log W$, that the entropy just doubles, without entropy of mixing, when two volumes of equal gases are combined.

The way in which the division by $(2N)!$ in the equal-gases-case achieves the removal of the mixing entropy is that it throws away, in addition to the exchanges among left particles and right particles, also all permutations in which one or more particles coming from the left are exchanged with particles originating from the right side of the container. This now discarded number of permutations yields a factor $M = (2N)!/N!N!$ in the number of microstates, which via $\Delta S = k \log M$ corresponds exactly to the value of the entropy of mixing. In other words, there no longer can be any mixing, nor any entropy of mixing, because the exchange of a particle from the left with one from the right is defined away, as not giving rise to a new physical situation.

The division by $N!$ thus restores the situation as we know it from thermodynamics: there is a finite and constant entropy of mixing in the case of different gases, however small the difference between the gases may be, and there is no such entropy in the case of equal gases.

However, this result is achieved at the price of defining away differences that obviously are physically real, at least from the point of view of classical physics. Indeed, classical particles are the example par excellence of distinguishable individuals: no two classical particles can be in exactly the same physical state because they will at any instant at least occupy different spatial positions, by virtue of their impenetrability. Moreover, classical particles
follow continuous and non-intersecting trajectories, so that they “remember” where they came from. Their individuality and distinguishability are thus preserved over time, with the consequence that it makes a physical difference, in principle, whether a given particle in our gas container originates from the left or from the right. So the above resolution of the Gibbs paradox in statistical mechanics, relying as it does on an assumed identity of states that follow from each other by particle permutations, is in conflict with basic features of classical mechanics. It is for this reason that quantum mechanics is often invoked: in quantum mechanics particles are indistinguishable as a matter of principle, so that particle exchanges really do not alter the physical state—at least, that is the conventional wisdom.

However, as we shall show in a moment, the starting point of the whole argument, namely that there should be no statistical mechanical entropy of mixing in the case of two gases of the same kind, is shaky. Although on the macroscopic, thermodynamical level the absence of an effect of mixing two equal gases is certainly a justified assumption, this does not mean that there are no effects if microscopic details are taken into account.

3 The Statistical Mechanical Entropy of Mixing

We are now going to argue in the context of statistical mechanics, and this induces us to consider a slight extension of the tools that are used in thermodynamical thought experiments. In statistical mechanics the motivating idea is to take into account how gases are built up from their atoms or molecules, and this makes it natural to consider a variation on the reversible mixing process explained in section 1. In section 1 an essential role was played by semi-permeable membranes that were only transparent to one of the two gases (in the case of the mixing of different gases). In the context of thermodynamics this means that the membranes are sensitive to chemical differences between the gases. In statistical mechanics we have the opportunity to generalize this and to consider membranes that are also sensitive to microscopic particle details. In this spirit we now introduce a new type of semi-permeable membrane: one that is transparent to particles originating on the right-hand side of the container and opaque to particles coming from the left-hand halve (or vice versa). According to classical physics such mem-
branes are possible in principle, as is clear from what was said above about particle properties in classical mechanics: particles carry the data about their origin with them, in their position and momentum values, and this can (in principle) be used to determine whether the membrane should stop them or not. Figuratively speaking, think of submicroscopic computers built into the membrane that perform an ultra-rapid calculation each time a particle hits them, to see where it came from; or the proverbial demon with superhuman calculational powers who stops or lets pass particles depending on their origin. In general, of course, allowing expedients of this kind may upset thermodynamical principles, in particular the second law of thermodynamics. But in the thought experiment we propose here we make a restricted use of these unusual membranes. The idea is merely to employ them for the purpose of demonstrating that if gases are mixed and unmixed by selection on the basis of past particle trajectories and origins, as should be possible according to classical mechanics, this leads to the emergence of an entropy of mixing.

Indeed, if we use semi-permeable membranes designed in the way just described, and employ them exactly as our earlier membranes but now in the case of two gases of the same kind, we find just as before that a pressure is exerted on the membranes by the particles to which they are not transparent. Copying the reasoning from section 1, we can conclude that this leads to the presence of an entropy of mixing with the value $2kN \log 2$. In other words, if the submicroscopic particle picture of statistical mechanics is taken completely seriously, the original formula $S = k \log W$, without the ad-hoc division by $N!$, gives us correct results.

In principle then, on the microscopic level of description the mixing entropy always exists according to classical mechanics, even in the case of equal gases. In principle, classical particles can always be distinguished on the basis of their trajectories and there is a corresponding mixing entropy that can be measured by using semi-permeable membrane-like devices of the kind we have described. Classical atoms and molecules are distinguishable individual entities, and we can conclude that analysis of the Gibbs paradox supports rather than undermines this general feature of classical physics. Of course, microscopic distinguishability cannot show up if we confine ourselves to using macroscopic separation techniques of the kind considered in thermodynamics. But this is a practical matter that should not be confused with an argument for fundamental indistinguishability on the particle level.
4 A New Dilemma: The Gibbs Paradox in Quantum Mechanics

But now we are facing a new paradox. In quantum mechanics the “identity of indistinguishable particles” has long been recognized as a basic principle, given concrete form by the (anti-)symmetrization postulates. These postulates stipulate that in the case of particles of the same kind permutations of particle indices leave a many-particle state either invariant (the case of bosons) or change its sign (the case of fermions); in either case there are no measurable physical differences associated with the permutations. These symmetrization postulates possess a law-like validity, so they hold regardless of the peculiarities of the situation that is considered. Therefore, from the quantum mechanical point of view division by $N!$ seems completely justified and even mandatory when the number of microstates has to be determined. Application of $S = k \log W$ then seems to tell us that as a matter of principle there can be no entropy of mixing when two gases of the same kind mix—as we have seen above, the division by $N!$ leads immediately to this conclusion.

This is a paradox. A treatment of the mixing of gases by means of quantum mechanics should obviously reproduce the results of a classical calculation in the classical limiting situation, so it should be able to yield the value $2kN \log 2$ in the case in which we follow individual particle trajectories, as described in the previous section. But it now seems that according to quantum mechanics this is impossible in principle!

To put the difficulty into perspective, consider a situation that is possible according to quantum mechanics and at the same time can be dealt with by classical mechanics. Suppose that the one-particle states occurring in the quantum mechanical many-particles wavefunction of our ideal gas system do not overlap spatially, and that this remains true for a substantive time interval. Well-known results (in particular Ehrenfest’s theorem, to which we shall return in section 5) assure us that in this case the spatially isolated one-particle quantum wave packets behave exactly like classical particles. In fact, what we have here is the quantum mechanical description of a diluted ideal gas, and this description is virtually identical to what classical theory tells us: small one-particle wave packets take the place of classical particles, are subject to the same dynamical principles, and follow the same trajectories. This is a typical classical limit situation, in which the predictions made by quantum mechanics should parallel those of classical mechanics. In
particular, in the experiment with the unusual membranes of section 3 we should expect that quantum mechanics gives us the result we derived there, namely the existence, in principle, of an entropy of mixing with the value \(2kN \log 2\). In the limiting situation everything goes, according to quantum mechanics, as in the classical case and the earlier derivations can be repeated step by step.

Apparently then, the quantum mechanical symmetrization postulates are not decisive for the question of whether or not particles are distinguishable in quantum mechanics! In the diluted gas situation that we just discussed quantum particles are as distinguishable as classical particles: they occupy different spatial positions and follow continuous and non-intersecting trajectories. In this case it is clear that real physical differences correspond to different trajectories and different particle origins, and the existence of an entropy of mixing testifies to this: the differences in question give rise to empirical effects. Nevertheless and paradoxically, in this very same situation the symmetrization postulates are fully respected.

The situation becomes clearer when we consider a concrete case, namely a two-particle quantum system in which the one-particle wave functions do not overlap spatially, like in the diluted gas just discussed. Take as the quantum state of the system

\[
|\Psi\rangle = \frac{1}{\sqrt{2}} (|\phi_1\rangle|\psi_2\rangle + |\psi_1\rangle|\phi_2\rangle),
\]

with \(|\phi\rangle\) and \(|\psi\rangle\) representing two non-overlapping wave packets. This state is symmetrical: exchange of the indices 1 and 2 leaves the state invariant, and there is thus no physical difference associated with the distinction between these indices. Still, this symmetrical state represents a situation in which there are two quasi-classical objects, one at the position of the wave packet represented by \(|\phi\rangle\) and one at the position of \(|\psi\rangle\). These wave packets and the objects they represent clearly are distinguishable, and they are the things that are relevant for the classical limit. As was illustrated above for the diluted gases case, these spatially non-overlapping wave packets take the role of particles in the classical limit.

Summarizing, although it is true that because of the symmetrization each index in an \(N\)-particles quantum state of particles of the same kind,

\[
|\Psi\rangle = \frac{1}{\sqrt{N!}} \sum \Pi |\phi_{i1}\rangle|\psi_{i2}\rangle|\chi_{i3}\rangle|\tau_{i4}\rangle \cdots
\]
—where $\Pi$ denotes permutation over the indices and the summation is taken over all such permutations—is associated with exactly the same “state” (in the sense of a density operator obtained by partial tracing), there still will be distinguishable particles in the classical limit if the one-particle states $|\phi\rangle, |\psi\rangle, |\chi\rangle, |\tau\rangle \cdots$ do not spatially overlap. Therefore, the *indices* in the quantum mechanical formalism, over which (anti-)symmetrization takes place, cannot refer to what we understand to be particles in classical physics!

This observation is the key to the resolution of our paradox. Although the *indices* in the “many-particle” quantum formalism have completely symmetrical roles to play and do not correspond to any physical differences, this does not entail that it does not make a difference if we exchange two *particles* in the ordinary sense (i.e., the localized objects that we are wont to call particles in classical physics). Therefore, there may be a mixing entropy even if the symmetrization postulates are fully respected: the existence of this entropy depends on the distinguishability of particles, not on the distinguishability of indices. The notion that the symmetrization postulates enforce division by $N!$ in the classical expression for the entropy, and thus make the entropy of mixing vanish for gases of the same kind, rests on a confusion about the status of the particle concept in quantum mechanics [5, 7].

### 5 How Particles Are To Be Represented in Quantum Mechanics

Elaborating on this conclusion, it should be noted that the symmetrization postulates, which are responsible for the physical equivalence of all indices in states of many particles of the same kind, are basic postulates of quantum mechanics; they possess a universal validity. This implies that if we were to take the indices to refer to particles, it would follow that *all* particles of the same kind in the universe are in exactly the same state. For example, it would not make sense to distinguish between electrons here and electrons elsewhere, for instance in another solar system: all electrons in the universe are “partly here, partly there, a bit everywhere”. The applicability of the symmetry postulates holds regardless of what kinds of interactions and situations are considered; in particular, whatever circumstances should turn out to be responsible for the transition to the classical limit, these do not affect the applicability of the postulates. Therefore, if we were to assume that the
quantum indices refer to particles, this would imply that even in the classical limit particles are all in exactly the same state—that even classical particles are completely indistinguishable!

This simple reductio shows once again how wrong it is to think that the symmetrization in quantum mechanics pertains to particles in the ordinary sense. Classical particles are certainly distinguishable objects, so they simply cannot correspond to the quantum indices in the classical limit.

Classical particles are characterized by their unique spatial positions and trajectories. Now, as a defence of the idea that the individuality that corresponds with these individuating features disappears as soon as quantum mechanics is taken into account, it is sometimes maintained that the “haziness” of quantum mechanical wave functions, in the sense of their non-zero spatial extensions, makes it impossible to follow a quantum particle in all detail over time (e.g., [1]). For this reason precise trajectories do not exist in quantum mechanics and the concept of genidentity, so the argument continues, cannot apply to quantum particles: their wave packets will overlap, and we can consequently not find out where each particle comes from and with which earlier particle it should be considered identical.

This argument is notable for at least two reasons. First, it apparently assumes that particles can be associated with individual wave packets (that may overlap). This betrays a correct intuition about what particles are and how they are to be represented in the quantum formalism, but is of course in conflict with the standard idea that the indices in the formalism denote particles. Second, this “haziness argument” is implausible as a general defence of the indistinguishability of particles. This indistinguishability would apparently have to occur as soon as there is overlap between wave packets; but haziness is something gradual, subject to becoming more or less, and evidently not strong enough a premiss to bear such an all-or-nothing conclusion. Moreover, the (anti-)symmetrization postulates remain in force even if wave packets do not overlap at all, which demonstrates that overlap cannot be the decisive factor here.

What the haziness argument actually supports is our earlier conclusion that particles in quantum mechanics should be represented by one-particle wave packets, and that there is a gradual transition from the “classical” situation, in which such wave packets are spatially disjoint, to the more typical quantum case in which there is overlap and in which the classical particle concept is not fully applicable. Our essential argument is that there is no relation between the particle concept thus understood and the “particle
indices” in the quantum mechanical formalism.

That quantum mechanics is indeed capable of representing classical particles in the way just explained, is (as we already mentioned earlier) guaranteed by Ehrenfest’s theorem. In the case of a Hamiltonian \( H = \frac{p^2}{2m} + V(r) \), with \( p \) the momentum, \( m \) the particle mass and \( V(r) \) a potential field, we can introduce a force field \( F(r) = -\nabla V(r) \), in terms of which Ehrenfest’s theorem takes the form

\[
\langle F(r) \rangle = m \frac{d^2}{dt^2} \langle r \rangle.
\]  

(4)

For certain specific potentials (in particular free motion, i.e. \( F=0 \), relevant to our ideal gases case) we find that \( \langle F(r) \rangle \) equals \( F(\langle r \rangle) \), so that in these cases the mean value of \( r \) exactly satisfies the classical law of motion \( F(\langle r \rangle) = m \frac{d^2}{dt^2} \langle r \rangle \). In general this is not so. But if the wave function is localized in a sufficiently small region of space, so that the variation of the force field within that region is small, we can replace Eq. (4) by the classical equation in a good approximation (which becomes better when the state becomes more localized). From this it follows that well-localized single-particle quantum states (localized in the sense that their associated wave packets are very narrow) approximately follow classical trajectories. Classical trajectories thus do exist in quantum mechanics: they are realized by (very) small wave packets. Consequently it is essential, for the classical limit, to have a mechanism that keeps wave packets narrow during appreciable time intervals.

Such considerations are standard in studies on the classical limit of quantum mechanics, and there is growing agreement that the essential element in explaining how classical mechanics emerges from quantum mechanics is the process of decoherence. Decoherence processes cause the destruction of coherence between parts of the wavefunction centered around different positions, and effectively reduce wave functions to narrow wave packets (see for a more extensive discussion [5]).

It is generally acknowledged then that the classical limit of quantum mechanics is characterized by the emergence of classical trajectories followed by narrow wave packets. These narrow wave packets become the particles we are familiar with in classical physics.
6 Particles as *Emergent* Entities

Our conclusion is therefore that we should think of *particles*, as we know them from classical physics, as represented in quantum mechanics by localized wave packets [5, 7]. That is to say, if we encounter a state \(|\Psi\rangle\) defined in an \(n\)-fold tensor product Hilbert space \(\mathcal{H}_1 \otimes \mathcal{H}_2 \otimes \mathcal{H}_3 \otimes \ldots \otimes \mathcal{H}_n\), and wish to investigate whether it can be interpreted in terms of particles, we have to ask ourselves whether it can be written as a (anti-)symmetrized product of localized one-particle states. It is easy to show that if such a “particle decomposition” of \(|\Psi\rangle\) exists, it is unique [5].

In most cases states will *not* allow a particle interpretation; think, for example, of a state of the form (2) with two *overlapping* wave packets \(|\phi\rangle\) and \(|\psi\rangle\) (each defined in a connected region of space). The particle decomposition that we need, in terms of localized states that are non-overlapping (and therefore mutually orthogonal) clearly does not exist in this case: of course there does exist a bi-orthogonal Schmidt decomposition, but the states occurring in it will be linear combinations of \(|\phi\rangle\) and \(|\psi\rangle\) and will consequently spatially overlap. An arbitrarily chosen quantum state will therefore not represent particles. We need special circumstances to make the particle concept applicable. In this sense, the classical limit with its decoherence processes makes classical particles *emerge* from the substrate of the quantum world.

It may be added that the circumstances that are responsible for the emergence of classical particles at the same time justify the use of the statistics that we expect for the case of independent individuals. Indeed, in the case of spatially non-overlapping wave packets, in which our particle concept becomes applicable, both Fermi-Dirac and Bose-Einstein statistics reduce to classical Boltzmann statistics [2, 6].

7 The Gibbs Paradox: Conclusion

When equal gases of the same pressure and temperature mix, nothing happens from a macroscopic, thermodynamical point of view. So there should be no entropy of mixing in this case, in conformity with what thermodynamics predicts. In the literature this vanishing of the thermodynamic mixing entropy when two equal gases mix has often been interpreted as a fundamental fact, as a sign that also on the level of statistical mechanics, when the microscopic constitution of the gases is taken into account, it should not make
a physical difference whether gas particles originate from one or the other of the initially separated gases. This interpretation is mistaken. When non-thermodynamic, microscopic separation and mixing techniques are allowed, it turns out that even in the case of equal gases the value $2kN \log 2$ of the mixing entropy, and other effects of mixing, can be recovered and in principle experimentally verified. The vanishing of the entropy of mixing is therefore conditional on looking in a purely macroscopic way at what happens, and has no consequences for the identity and distinguishability of microscopic particles. Invoking quantum mechanics in order to argue that the mixing entropy vanishes as a matter of principle, on account of the fundamental indistinguishability of particles, is completely wrongheaded.

As it turns out, the microscopic effects of mixing classical gases of the same kind persist in quantum mechanics. This becomes understandable once we realize that the gas particles do not correspond to the indices in the quantum formalism, but rather to one-particle wave packets. In the classical limit such wave packets become the particles we know from classical mechanics. The conclusion that quantum particles correspond to one-particle wave functions rather than to indices accords with other evidence that these indices have a purely mathematical significance and do not denote physical objects [3, 4, 5]. According to our analysis of what particles are, the appearance of particles constitutes a genuine case of emergence. Only if specific physical conditions are satisfied, resulting in the presence of localized wave packets (decoherence processes are usually essential here) does the concept of a particle in the ordinary sense become applicable to the world described by quantum mechanics.

Finally, even in cases in which individual particles in our sense are not present in the mixing gases of the Gibbs paradox, quantum mechanics predicts that a non-zero value of the entropy of mixing can be recovered by using sophisticated membranes. The reason is that the two initially separated volumes of ideal gas are represented by mutually orthogonal wave functions, located on the left and right, respectively. Since ideal gases do not interact these wave functions remain orthogonal, and therefore distinguishable in principle, even after the removal of the partition. This point (to be worked out elsewhere) demonstrates once more that the indistinguishability of bosons and fermions is irrelevant to the resolution of the Gibbs paradox.
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