The Gibbs Paradox and the Distinguishability of Identical Particles

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Abstract

Classical particles of the same kind (i.e., with the same intrinsic properties, so-called "identical particles") are distinguishable: they can be labeled by their positions (because of their impenetrability) and follow different trajectories. This distinguishability affects the number of ways W a macrostate can be realized on the micro-level, and via $S = k \ln W$ this leads to a non-extensive expression for the entropy. This result is generally considered wrong because of its inconsistency with thermodynamics. It is sometimes concluded from this inconsistency, notoriously illustrated by the Gibbs paradox, that identical particles must be treated as indistinguishable after all; and even that quantum mechanics is indispensable for making sense of this. In this article we argue, by contrast, that the classical statistics of distinguishable particles and the resulting non-extensive entropy function are perfectly all-right both from a theoretical and an experimental perspective. We remove the inconsistency with thermodynamics by pointing out that the entropy concept in statistical mechanics is not completely identical to the thermodynamical one. Finally, we observe that even identical *quantum* particles are in some cases distinguishable; and conclude that quantum mechanics is irrelevant to the Gibbs paradox.

I. INTRODUCTION: THE GIBBS PARADOX

Imagine two gas-filled chambers of the same volume, separated by a partition. Both chambers contain equal amounts of the same gas in equilibrium, consisting of the same number N of "identical" classical particles (i.e., particles with the same intrinsic properties like charge and mass); both parts have the same total energy, temperature T and pressure. Now the partition is suddenly removed. What happens to the entropy?

According to thermodynamics the entropy remains the same, because the macroscopic properties of the gases in both chambers do not change. From a thermodynamic point of view—that is: restricting ourselves to the consideration of macroscopic properties—nothing happens. Formally, if A is the macrostate with the partition in place and B the macrostate without it, the entropy difference is defined as

$$S_B - S_A = \int_A^B \frac{dQ}{T}, \tag{1}$$

where dQ is the heat transfer during a quasistatic process from A to B. Because the gases remain in equilibrium, the removal of the partition is a quasistatic process. There is no heat transfer, $dQ = 0$, so that $S_A = S_B$.

However, in statistical mechanics the entropy is defined as the logarithm of the number W of microstates that are compatible with a given macrostate: $S = k \ln W$, where k is Boltzmann's constant. When the partition is removed, the number of available states X per particle doubles: each particle now has twice as much phase space available to it as it had before. This means that the multiplicity goes up, from $W_A = X^{2N}$ to $W_B = (2X)^{2N}$, which corresponds to an entropy difference $S_B - S_A = 2kN \ln 2$. This is the Gibbs paradox: The entropy increases according to statistical mechanics but remains the same in thermodynamics.

A traditional way of solving this paradox is by denying that permutation of identical particles leads to a different state. The real multiplicity is accordingly supposed to be a factor $N!$ smaller for a system of N identical particles than what we supposed above. In the case of the removal of the partition the multiplicity then goes from $W_A = X^{2N}/(N!)^2$ to $W_B = (2X)^{2N}/(2N)!$. With the help of Stirling's approximation it follows that, in the thermodynamic limit $N \to \infty$, $W_B = W_A$, which removes the discrepancy between statistical mechanics and thermodynamics.

According to several authors and textbooks quantum theory is needed for justifying this solution of the Gibbs paradox (see e.g. Refs. 1–6). Indeed, classical particles are always distinguishable by their positions and trajectories, so in classical statistical mechanics there appears to be no reason for the division by $N!$. Identical quantum particles, on the other hand, seem indistinguishable in the required sense from the start, because quantum states of systems of identical particles must either be symmetrical under permutation (bosons) or anti-symmetrical (fermions): exchange of particles leaves the state therefore invariant apart from a global phase factor and the multiplicity $N!$ never enters.

If this argument were correct, then the Gibbs paradox would show that the world is quantum mechanical. Evidently, it is hard to believe that such a simple thought experiment from classical physics could produce such a profound insight. Unsurprisingly therefore, doubts have been expressed concerning the just-mentioned traditional solution of the paradox. Some authors have argued that identical classical particles are also fully indistinguishable, which justifies the factor $1/N!$ without recourse to quantum mechanics.[7–10]

In this paper we follow a route that is closer both to the spirit of classical mechanics and to common sense: we accept that identical classical particles are *distinguishable* and that permutation of two of them leads to a different microstate. Still, as we shall show, the Gibbs paradox can be solved within classical physics. The key to the solution of the paradox is the recognition that the entropy concept in thermodynamics is not completely identical to that in statistical mechanics. This observation will turn out to be sufficient for the dissolution of the paradox: neither indistinguishability of identical particles nor an appeal to quantum theory will be needed. On the contrary, as we shall argue, even identical quantum particles can sometimes be distinguishable in the sense that is relevant here, so that indistinguishability cannot be relevant to the Gibbs paradox even in quantum mechanics.

II. PERMUTATIONS OF IDENTICAL CLASSICAL PARTICLES

Classical particles, paradigmatically represented by impenetrable spheres, are the example *par excellence* of distinguishable individuals. At each instant of time classical particles can be individually labeled by their different positions. Importantly moreover, classical particles follow continuous and non-intersecting trajectories in space-time. Therefore classical particles can be distinguished also by their different histories.

Permutation of two identical classical particles produces a different microstate. Indeed, imagine a situation in which there is one particle at position x_1 and one particle at position x_2, and in which at a later instant there is again one particle at x_1 and one particle at x_2; suppose that their respective momenta are the same as before. What has happened in the meantime? There are two possibilities: either the particle that was first at x_1 is later again at x_1 and the particle that was first at x_2 is later again at x_2, or the particles have exchanged their positions. The latter case would be really different from the former one. It corresponds to a different physical process. Although the two final situations cannot be distinguished on the basis of their instantaneous properties alone, their different histories show that the particle at x_1 in one final situation is not equal to the particle at x_1 in the other final situation.

These remarks seem trivial; so what is the explanation of the fact that some authors deny that identical classical particles can be distinguished and that permutation gives rise to a different microstate? One reason is that there is an ambiguity in the meaning of the terms "distinguishable" and "permutation". Consider the following statements: "Two particles are distinguishable if they can always be selectively separated by a filter";[7] "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."[9] With *these* definitions of distinguishability identical classical particles are indeed always indistinguishable. The concept of "permutation" can be understood in a similar way. Consider again the microstate of two identical particles, one at x_1 and another at x_2. If the particle at x_2 were at x_1 instead, and the particle at x_1 were at x_2, with all properties interchanged, there would be no physical differences, neither from an observational point of view nor from the viewpoint of theory. It is therefore certainly reasonable to say that the two situations are equal (e.g. Ref. 8).

But this is a different kind of permutation than the physical exchange we considered before. In our first example the particles *moved* from x_1 to x_2 and *vice versa*. Trajectories in space-time connected the initial state to the permuted state. By contrast, in the alternative reading of "permutation" just mentioned, the exchange is not a physical process at all. Instead, it is an instantaneous swapping that occurs in our thought; it exchanges nothing but indices and does not need trajectories.

A third sense of "permutation" is used by Saunders:[10] One particle follows trajectory 1

and one follows trajectory 2. Now imagine that the particle that actually follows trajectory 1 instead followed trajectory 2 and *vice versa*. That would result in exactly the same physical situation. As before, this involves the consideration of states before and after the permutation that are not connected by any physical process. Again, a permutation in this sense occurs in thought and exchanges an abstract "identity" (formally represented by particle indices "1" and "2", respectively) that is independent of the physical characteristics of the situation—so that it is clear almost *a priori* that this kind of permutation is unphysical and cannot be significant for statistical mechanics.

At this point we can conclude that if "permutation" is understood as a physical exchange in which trajectories in space-time connect the initial state to the permuted state, then permutations produce physically different possibilities, in the sense of different physical processes that may be realized. However, if "permutation" is understood in a different way, then it may well be true that the permutations in question are not associated with any physical differences.

III. PERMUTATIONS IN STATISTICAL MECHANICS

Let us take a closer look at the question of what kind of permutations are relevant to statistical mechanics—physical exchanges, with connecting trajectories, or "swapping indices in thought"? Which kind of permutations determine the number of microstates W?

Consider again our two gas-filled chambers, each containing N identical particles. Before the partition is removed the number of available states per particle is X. After the partition has been removed, the number of available states is $2X$. The reason is that after the partition's removal it has become possible for the particles to *move* to the other chamber. The doubling of the number of available microstates thus expresses a physical freedom that was not present before the partition was taken away. Trajectories in space-time have become possible from the particles' initial states to states in the other chamber. Particles from the left and right sides can physically exchange their states.

By contrast, even with the partition in place we could consider, in thought, the permutation of particles from the left and right sides—but such permutations are never taken into account in the calculation of the multiplicity. Nor do we consider permutations with similar particles outside of the container, obviously. In other words, the relevant kind of

permutation is the physical exchange, not the swapping of indices in thought.

To completely justify the answer that accessibility via a real physical process, a connecting trajectory, is the determining factor in the calculation of multiplicities, we would have to delve into the foundations of statistical mechanics. Suffice it here to mention that one important approach in this area is that of ergodic theory, in which the probability of a macrostate is argued to be proportional to its multiplicity on the grounds that this multiplicity is a measure of the time a system will actually dwell in that part of phase space that corresponds to the macrostate in question. Clearly, this idea only makes sense if the microstates in this part of the phase space are actually accessible by physical processes: microstates that give rise to the same macrostate but cannot be reached from the initial situation through the evolution of the system are irrelevant for the macrostate's probability—they do not play a role at all.

It is true that the original form of the ergodic hypothesis (according to which all microstates are actually visited in a relatively short time) has proven to be untenable, but this does not impugn the basic idea that accessibility is the criterion for the relevance of microstates. The multiplicities that occur in more modern and more sophisticated approaches to the foundations of statistical mechanics are the same as those of the original ergodic theory.

We may therefore conclude that in classical statistical mechanics the multiplicity of a macrostate is given by the number of ways this macrostate can be reached by a physical process. Permutations, corresponding to physical exchanges, represent real different physical possibilities. We must therefore not divide by $N!$ when calculating multiplicities of states of identical classical particles.

IV. EMPIRICAL CONSEQUENCES OF NOT DIVIDING BY $N!$

Accepting the foregoing argument for not dividing by $N!$, plus the formula $S = k \ln W$, makes the statistical mechanical entropy non-extensive. For example, a system that becomes twice as large does not double its entropy, as we have seen illustrated by the Gibbs paradox. After the removal of the partition the total entropy is not twice the entropy each single chamber had before, but is larger by the amount $2kN \ln 2$.

In the literature there are basically three kinds of objections against not dividing

by $N!$ and the non-extensivity of the statistical entropy that is its consequence: (1) It leads to wrong empirical predictions;[1,11,12] (2) It leads to a violation of the second law of thermodynamics;[3,5,13] (3) It leads to a discrepancy with the thermodynamic entropy.

In this section we address the first of these objections. The second and the third, the Gibbs paradox proper, will be discussed in sections V and VI.

In contrast to what is claimed by some authors,[1,11,12] we argue here that dividing or not dividing the number of microstates by $N!$ is irrelevant to the empirical predictions of statistical mechanics. Although there is no fundamental justification for dividing by $N!$, a systematic division by $N!$ for all particles in mutually accessible states has no empirical consequences. This is because all empirical predictions made by statistical mechanics rest ultimately on the probabilities assigned to macrostates. These probabilities are calculated with the help of the fundamental assumption that in equilibrium the accessible microstates in an isolated system are all equally probable, so that the probability of a macrostate is its multiplicity divided by the total number of microstates. Now, in isolated systems no particles can move in or out, so that the number N of particles remains constant. This means that not only all multiplicities, but also the total number of microstates are lowered by $N!$ if one decides to systematically divide by this factor. The probability of a macrostate is therefore not affected; and it follows that whether one divides the multiplicity by $N!$ or not can make no difference for empirical predictions.

Of course, statistical mechanics does not only describe systems with a constant number of particles. Systems in which particles can move in and out can also be dealt with: in this case the grand-canonical ensemble should be used. The grand-canonical probability distribution can be derived by considering a system with varying particle numbers as part of a larger particle reservoir. This reservoir is again isolated and the fundamental assumption must now be applied to this larger system. Therefore our conclusion that the empirical predictions remain the same, whether one systematically divides by $N!$ or not, also applies to systems in which particles are exchanged between subsystems (in agreement with what was argued in Ref. 14).

Particle numbers can also change by chemical reactions: in this case the number of molecules of a certain kind need not be constant, even if the system is isolated. However, also for such a system division by the number of permutations of the elementary constituents (in this case the atoms) does not matter for the empirical results. This is simply because in

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this case the numbers of atoms from which the molecules are composed are still constant. Ehrenfest and Trkal[15] have discussed this already in 1920.

V. SECOND LAW OF THERMODYNAMICS

The second alleged problem is that the non-extensivity of the entropy leads to a violation of the second law of thermodynamics.[3,5,13] Consider again our two chambers, in the situation in which the partition has been removed. When the partition is placed back, the entropy decreases by $2kN \ln 2$. But the second law says that entropy cannot decrease!

Here we arrive at a central issue: what exactly does the second law in its statistical version say? To dissolve the just-mentioned conflict, we must recognize that the second law in thermodynamics is not precisely the same as the second law in statistical mechanics.

In thermodynamics the second law says that the entropy does not decrease if there is no heat transfer to or from the environment. In the case of the replacement of the partition there is no such heat transfer, so the thermodynamical entropy should not decrease. By contrast, in statistical mechanics the second law expresses a probability consideration: equilibrium macrostates possess a probability that is vastly greater than that of non-equilibrium states, and therefore it is enormously probable that the system will reach equilibrium and subsequently stay in equilibrium. The number of microstates corresponding to the equilibrium macrostate is practically equal to the total number of accessible microstates W, and this is basically the justification for the use of $S = k \ln W$ as the entropy belonging to the equilibrium state. That the statistical mechanical entropy S, with $S = k \ln W$, does not decrease is a direct expression of the striving for the most probable macrostate. Accordingly, the second law of statistical mechanics says that the entropy of a system goes, with overwhelming probability, to the maximum value compatible with the total number of accessible microstates, i.e. $k \ln W$, and will not decrease as long as this number of accessible states does not decrease. The statistical second law tells us, for instance, that without interventions from outside not all particles will move to the same corner of the container. But it does not tell us how W may change when the system is manipulated from outside, for example by placing a partition in it.

VI. SOLUTION OF THE GIBBS PARADOX

The paradox was that upon removal of the partition between our two containers the entropy increases according to statistical mechanics, whereas it remains the same in thermodynamics. What we have seen in the previous sections is that for classical particles the entropy should really increase in statistical mechanics, in the sense that the number of accessible microstates W does increase. This increase reflects the redefinition of the system, and of W, that results from manipulation from outside (the removal of the partition). The statistical second law only plays a role here to the extent that it says that the system will assume an equilibrium state that is compatible with this new and increased W. *In principle* we could empirically verify that this process occurs, and that the number of microstates has actually increased, by following the paths of individual particles (we could in this way even give empirical content to the existence of the entropy of mixing[16]). But this would require measurements on the microscopic level that would lead us outside the domain of thermodynamics and outside the domain of statistical mechanical predictions (in which the precise microstate is assumed to be immaterial). As long as we remain within the realm of the usual macroscopic measurements the increase of the entropy, in the case of gases of the same kind, will not lead to empirically detectable consequences.

Is there a problem here? Can we not just accept that the entropy changes in statistical mechanics and remains the same in thermodynamics? Yes, we can. After all, entropy is defined differently in statistical mechanics than in thermodynamics: in statistical mechanics the existence of a micro-description is taken into account as a matter of principle, whereas in thermodynamics this same micro-description is excluded from the start. As we have seen there is an increase of entropy according to statistical mechanics, but since its empirical significance is completely on the micro-level this does not lead to any new predictions for macroscopic measurements. The difference between the statistical mechanical and the thermodynamical definition of entropy makes it completely understandable that the values of entropy changes in statistical mechanics are sometimes different from those in thermodynamics.

There are no conflicts with the second law here: both according to statistical mechanics and according to thermodynamics, the second law is perfectly obeyed. The statistical mechanical account is that the number of microstates increases through intervention from

outside (the removal of the partition); the statistical second law tells us that the system will subsequently make maximal use of this increased area in phase space. This leads to the prediction that the system will exhibit equilibrium values of its macroscopic quantities, so that on the macro-level nothing changes. In thermodynamics this "fine-grained" consideration plays no role: nothing happens at all, and according to the thermodynamical second law the entropy remains constant. Both descriptions are valid within their own domains of applicability.

The same type of argument can be used if we consider what happens when the partition is replaced. According to thermodynamics nothing happens to the entropy, as there is no exchange of heat. According to statistical physics, however, there is a decrease of W and thus of the entropy. But this does not signal a violation of the second law! The decrease in W is a consequence of the redefinition of the accessible phase space that is caused by the intervention in the system, not by a deviation from what is predicted by the second law. The statistical second law remains completely valid, and predicts that the two subsystems will fully make use of their phase space possibilities (which in this case means that equilibrium will be maintained, in accordance with experience).

From a pragmatic point of view it is useful, obviously, if the two theories give us the same entropy values. We can achieve this by a "trick", namely by introducing a new entropy definition in statistical mechanics: Replace $S = k \ln W$ by $S = k \ln(W/N!)$. For systems in which N is constant this makes no difference for any empirical predictions, because it only adds a constant (though N-dependent!) number to the entropy value; and for the Gibbs case, in which N is made to change, this cosmetic intervention leads to the disappearance of the entropy of mixing. In this way we obtain agreement with thermodynamics. But it is important to realize that this "reduced entropy" (as it is called by Cheng[17]) has no clear microscopic meaning within statistical mechanics. It is only a *convention* motivated by the desire to reproduce thermodynamical results everywhere, even though the conceptual framework of thermodynamics is basically different from that of statistical mechanics. There is certainly no relation here to any basic indistinguishability of identical classical particles.

VII. DISTINGUISHABLE IDENTICAL QUANTUM PARTICLES

Finally, let us consider identical *quantum* particles. In contrast to classical particles, identical quantum particles are supposed to be indistinguishable as a matter of principle. This indistinguishability is the result of the quantum mechanical (anti-)symmetrization postulates: permutations of particle indices leave a many-particle state either invariant (the case of bosons) or change its sign (the case of fermions).

But as we have argued before, the permutations that are relevant to statistical mechanics are not permutations of indices, but permutations in which the permuted state is connected to the initial state by trajectories in space-time. Now, quantum particles sometimes *do* follow well-defined trajectories through space-time: if their wave packets do not overlap, one can identify quantum particles over time. Exchange of two quantum particles in the statistical mechanical sense must in this case produce a different state, just as in classical physics. But how can this be true if identical quantum particles are fundamentally indistinguishable?

The confusion here is the result of the fact that the indices occurring in the quantum states of identical particles do not correspond to particles as we know them from classical physics.[16,18,19] Classical particles emerge from quantum mechanics, in the classical limit, when wave packets get localized. Only then the usual particle concept becomes applicable (see Ref. 19 for an extensive discussion).

Isolated wave packets follow trajectories through space-time. As long as they remain separated from each other, they are as distinguishable as classical particles. When a quantum particle represented by such a wave packet moves from x_1 to x_2 and another identical particle moves from x_2 to x_1, then the final state is different from the initial state just as in our earlier discussion about classical particles.

As we have argued, the Gibbs paradox can be solved without invoking the indistinguishability of particles. Now we see that quantum theory is irrelevant to the core of the paradox: Permutation of quantum particles can produce a different microstate just as well as the permutation of classical particles.

It is interesting to compare our arguments with those of Saunders[10], who regards even classical particles as indistinguishable. According to him there is one reason why classical particles are generally supposed to be distinguishable: "... we surely *can* single out classical particles uniquely, by reference to their trajectories. But there is a key objection to this

line of thinking: *so can quantum particles, at least in certain circumstances, be distinguished by their states.*" We agree with this; but we do not at all see it as an objection. Saunders' conclusion is that "indistinguishability (permutability, invariance under permutations) makes just as much sense classically as it does in quantum mechanics." We say exactly the opposite: Distinguishability often makes just as much sense for quantum particles as for classical particles.

VIII. CONCLUSION

The Gibbs paradox should not be interpreted as providing an argument for the indistinguishability of identical classical particles. Indeed, identical classical particles are individuals that can be distinguished by their different positions and their different trajectories through space-time. Nor should it be thought that the Gibbs paradox needs quantum mechanics for its solution: identical quantum particles can be as distinguishable, in the relevant sense, as classical particles.

The Gibbs paradox can be solved by recognizing that entropy and the second law have different meanings in statistical mechanics and in thermodynamics. In thermodynamics the entropy has to be extensive; but this is not so in statistical mechanics. It is true that it is possible to make the statistical mechanical entropy extensive by introducing a new definition of the entropy that does not spoil predictions as long as these predictions remain within the realm of thermodynamics. But this convention has nothing to do with the distinguishability or indistinguishability of identical particles.

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[1] E. Schrödinger, *Statistical Thermodynamics* (Cambridge University Press, 1948), pp. 58-62.

[2] K. Huang, *Statistical Mechanics* (Wiley, New York, 1963), pp. 153-155.

[3] G.H. Wannier, *Statistical Physics* (Wiley, New York, 1966), pp. 167-170.

[4] A. Sommerfeld, *Thermodynamik und Statistik* (Deutsch, Thun, 1977), pp. 194-195, 216-218.

[5] D.V. Schroeder, *An Introduction to Thermal Physics* (Addison Wesley Longman, San Francisco, 2000), pp. 79-81.

[6] A. Ben-Naim, "On the So-Called Gibbs Paradox, and on the Real Paradox", Entropy **9**, 132-136 (2007).

[7] D. Hestenes, "Entropy and Indistinguishability", Am. J. Phys. **38** (7), 840-845 (1970).

[8] S. Fujita, "On the Indistinguishability of Classical Particles", Found. Phys. **21** (4), 439-457 (1991).

[9] J.F. Nagle, "Regarding the Entropy of Distinguishable Particles", J. Stat. Phys. **117** (5/6), 1047-1062 (2004).

[10] S. Saunders, "On the explanation for quantum statistics", Stud. Hist. Phil. Mod. Phys. **37**, 192-211 (2006).

[11] S.-K. Lin, "Gibbs paradox of entropy of mixing: experimental facts, its rejection and the theoretical consequences", El. J. Theor. Chem. **1**, 135-150 (1996).

[12] R.H. Swendsen, "Statistical Mechanics of Classical Systems with Distinguishable Particles", J. Stat. Phys. **107** (5/6), 1143-1166 (2002).

[13] R.H. Swendsen, "Gibbs' Paradox and the Definition of Entropy", Entropy **10**, 15-18 (2008).

[14] N.G. van Kampen, "The Gibbs Paradox", in *Essays in Theoretical Physics*, edited by W.E. Parry (Pergamon Press, Oxford, 1984), pp. 303-312.

[15] P. Ehrenfest and V. Trkal, "Afleiding van het dissociatie-evenwicht uit de theorie der quanta en een daarop gebaseerde berekening van de chemische constanten", Versl. Kon. Ak. v. Wetensch. Amsterdam **28**, 906-929 (1920) = Ann. Physik **65**, 609 (1921), also published in P. Ehrenfest, *Collected Scientific Papers*, (North-Holland, Amsterdam, 1959), p. 414.

[16] D. Dieks, "The Gibbs Paradox Revisited", in: *Explanation, Prediction and Confirmation*, edited by D. Dieks, W.J. Gonzalez, S. Hartmann, T. Uebel and M. Weber (Springer, New York, 2010), pp. 367-377.

[17] C.-H. Cheng, "Thermodynamics of the System of Distinguishable Particles", Entropy **11**, 326-333 (2009).

[18] D. Dieks and M.A.M. Versteegh, "Identical Quantum Particles and Weak Discernibility", Found. Phys. **38**, 923-934 (2008).

[19] D. Dieks and A. Lubberdink, "How Classical Particles Emerge From the Quantum World", Found. Phys. (to appear, 2011), DOI: 10.1007/s10701-010-9515-2.