

# **The Gibbs Paradox**

*About the paradox and the indistinguishability of  
identical particles*

**Bachelor thesis**  
*Philosophy of Science*

**Name:** *Suzanne van Berkum*  
**Studentnummer:** *3471403*  
**Supervisor:** *Prof. dr. D. Dieks*  
**Institute:** *University of Utrecht*  
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## Preface

Entropy ( $S$ ) is a very remarkable quantity in physics: it is one of the most important quantities in statistical mechanics and thermodynamics, but we cannot directly measure it like we can measure temperature or volume, for example. So, the value of the entropy depends on how we define the quantity. Actually, that is nothing strange, because the value of any quantity depends of its definition- for example in the case of volume, the quantity is defined as the product of the three spatial dimensions. However, unlike volume, temperature or any other directly measurable quantity, the entropy can have different values in different physical disciplines: if two identical gases are mixed, the entropy change is zero according to thermodynamics, but has a finite value if we use statistical mechanics.

This discrepancy is known as (a version of) the Gibbs Paradox and is the subject of this thesis. Since its origin around 1900 the Gibbs Paradox has been an object of research for several physicist, like Schrödinger and Leibniz, and also for some philosophers. Kant for example spent quite some words on the solution of this paradox. However, I will spend only little time on the philosophical side of the Gibbs Paradox: I will rather discuss the paradox from physical –both classical and quantum mechanical- points of view.

In this thesis I will first explain the Gibbs Paradox in detail. There are some different versions of this paradox, and in the first section I will discuss the two most well-known versions. The ‘version’ concerning the discrepancy between the value of the entropy in statistical mechanics and thermodynamics I already mentioned will be the main subject of the thesis. Using classical physics I will find a solution for the Gibbs Paradox which is a pragmatic one, but which requires indistinguishability of the mixing particles to be completely justified. In order to justify this practical classical solution I will discuss several definitions of (in-)distinguishability as they are used by different physicists, and also a more philosophical approach to the concept of indistinguishability. After that, I will try to solve the Gibbs Paradox by using quantum mechanics. In the final section of this thesis I will formulate my conclusion towards the question whether it is possible, and if the answer is positive, in which way, to solve this famous, more than a hundred years old paradox.

Before starting the ‘real thesis’ I would like to thank prof. dr. D. Dieks for giving me the opportunity to study the interesting subject of the Gibbs Paradox and for his useful advices when I was wondering what to focus on and how to write this thesis such, that both classical and quantum mechanical viewpoints are integrated and moreover, that integrated in the opinions and theories of several physicists are my own ideas about how – if at all- to solve the famous Gibbs Paradox.

Suzanne

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# 1. The Gibbs Paradox

One of the important tasks of thermodynamics is the study of mixtures and mixing processes. Probably the most interesting aspect of this task is the Gibbs Paradox. There are several versions of the Gibbs Paradox; I will discuss the two most well-known versions below.

The first version of the Gibbs Paradox concerns the fact that the entropy, when mixing two gases, increases discontinuously from a non-zero value to zero when the degree of similarity between the gases changes continuously from distinguishable to indistinguishable. This discontinuous change of the entropy while the indistinguishability of the gas changes continuously, is a striking phenomenon<sup>[1]</sup>.

The other version of the paradox concerns the discrepancy between the value of the entropy change of two identical gases mixing in thermodynamics and in statistical physics. Thermodynamics predicts no entropy of mixing when two gases of the same kind mix, whereas statistical physics does. This is a paradox, because statistical physics should support rather than contradict thermodynamics.

Below I will explain both versions of the Gibbs paradox in more detail.

The first version of the Gibbs Paradox, the fact that  $\Delta S$ , the so called entropy of mixing, changes discontinuously as one changes the similarity between two mixing gases continuously, was actually not noticed by Gibbs himself<sup>[1]</sup>. The scientists Denbigh and Redhead did, and they formulated the paradox as<sup>[2]</sup>:

The entropy of mixing has the same value...however alike are the two substances, but suddenly collapses to zero when they are the same. It is the absence of any warning of the impending catastrophe, as the substances are made more and more similar, which is the truly paradoxical feature.

But actually, there are many examples of phenomena in which a discontinuous transition (in this case: the discontinuous change of entropy) follows a continuous change of a parameter (here the degree of similarity is the parameter). For example, the density of water changes discontinuously when the temperature changes continuously, say between 99°C to 101°C<sup>[3]</sup>. Of course, the temperature doesn't change from 100°C to 101°C before the water's completely evaporated, but the temperature change itself is continuous. This is not viewed as a paradox, while the comparable situation in entropy is.

Actually, the example of water is just a phase transition and it is well-known that thermodynamic quantities often change discontinuously in phase transitions. In the case of (in-)distinguishable particles we can also talk about a 'phase' transition, because particles are either distinguishable or identical -there are no intermediate values of distinguishability. So, we can conclude that this version of the Gibbs Paradox is not something special, neither is it really a paradox and therefore it will be not the subject of this thesis. The second version of the paradox, as we will see below, is.

Two view this paradox in more detail, consider an experiment in which a partition divides a container into two equal parts, each volume containing a different ideal gas. The amounts of gas, the pressure and the temperature are equal in the two halves of the container. When the partition is removed, 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 has a higher entropy than the total entropy of the two separated gas systems we started with; this difference in the entropy is the so called *entropy of mixing* <sup>[4]</sup>.

The magnitude of the entropy of mixing can be calculated by considering a reversible process with the same unmixed beginning situation and the same equilibrium in the end situation as the irreversible process just described. The common way of realizing this reversible mixing process is by using semipermeable membranes: we can imagine the partition between the two halves of the container to be replaced by two membranes, one only transparent to the gas on the left-hand side (I call this gas I), the other only transparent to the other gas (gas II). When we slowly shift these membranes to the left and the right wall of the container, respectively, gases I and II will 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 be supplied to the gases, for example by immersing the system in a heat bath.

The change of entropy resulting from this reversible process can be calculated via

$$\Delta S = \int dQ/T, \tag{1}$$

with  $T$  the temperature. The added heat,  $dQ$ , should equal the work performed by the two gases, so this is equal to  $2PdV$ . Now we find for the entropy of mixing:

$$\Delta S = 2 \int PdV/T = 2 \int kNdV/V = 2kN \ln 2, \tag{2}$$

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.

So, it appears that the entropy of mixing is independent of the exact physical properties of the gases I and II. The only thing that is important in the calculation and in the final result is, that the two gases are different.

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  $2kN \ln 2$ , whereas there is no entropy of mixing if the gases are the same. The existence of this discontinuity is known as the *Gibbs paradox* <sup>[4]</sup>.

Actually, nothing really remarkable is happening here: there is a fundamental difference between the situation 'the gases I and II are equal' and 'there is a (finite) difference between the gases I and II'. So, it should not be considered surprising or paradoxical that

there is a difference in the existence of a mixing entropy: distinguishability between the gases causes the existence of an entropy of mixing and complete equality of the gases doesn't cause such an entropy. It is like the first version of the Gibbs Paradox that is mentioned before: changing from the mixing of two equal gases to mixing two gases between which exists a finite difference can be seen as a kind of phase transition. As we know from phase transitions, it is not really remarkable that there are fundamental differences between the two phases- in this case between the two different mixtures-, for example in the value of the entropy of mixing.

However, if we formulate the Gibbs paradox in statistical mechanics, we find a different result. This is strange, because statistical mechanics were 'invented' to support thermodynamics; in statistical mechanics we work on the microscopic level of the macroscopic phenomena we see in thermodynamics.

In statistical mechanics the entropy  $S$  is defined as the logarithm of the number of microstates  $W$  that are compatible with a given macrostate:

$$S = k \ln W. \quad (3)$$

When an ideal gas of  $N$  particles expands and doubles its volume, the number of available microstates  $X$  per particle doubles, and therefore for each particle there's twice as much space in phase space available than was before. This means, that  $W$  doubles, from  $X^N$  to  $(2X)^N$ , which corresponds to an entropy difference

$$\Delta S = kN \ln 2. \quad (4)$$

So, when any two different ideal gases mix, the entropy of mixing in statistical mechanics is  $S = 2kN \ln 2$ . This is the same value as is predicted by thermodynamics in the case of two different gases.

But, when two equal volumes of the *same* gas mix, the number of microstates available to an arbitrary individual particle still doubles, so the formula:  $S = k \ln W$  still gives  $\Delta S = 2 kN \ln 2$ , as in the case of two unequal gases.

Here is a discrepancy with thermodynamics: as we saw, in thermodynamics the entropy of mixing vanishes in this case of two equal gases, because on macroscopic level nothing happens when two identical gases mix, but in statistical mechanics, thus the phenomenon viewed on microscopic level, there is still an entropy of mixing.

Now we have 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 in the entropy of mixing predicted by thermodynamics<sup>[4]</sup>.

Below, I will discuss several (possible) solutions of this Gibbs paradox, from different points of view.

First, I will look for solutions of the paradox from the classical point of view. I will discuss whether the paradox is just a result of the fact that statistical mechanics and thermodynamics actually act on two different levels: on the microscopic respectively the macroscopic level of physical phenomena. Do we probably need another definition of entropy? Or can we use and justify a mathematical tool, the replacement of  $W$  by  $W/N!$ , to solve the problem?

If we introduce this factor  $1/N$ , we assume that the molecules of a given gas are all qualitatively the same, so that permutations of these particles do not have any physical effect and do not lead to a new state in phase space. But, can we really be sure that case A, in which particle I is on a location  $x$  and particle II, which is indistinguishable from particle I because it is qualitatively the same, is on location  $y$ , is the same as case B, in which particle I is on location  $y$  and particle II is on location  $x$ ?

Here we find the fundamental question of indistinguishability which I will discuss in the 3<sup>rd</sup> section; are two particles of the same gas indistinguishable because they have the same mass, charge, and other fundamental physical properties? In this section I will also discuss the view of Saunders, who assumes that we can never distinguish between (classical) particles with equal physical properties. But if this is right, what will be the difference between the treatment of particles in classical mechanics and quantum mechanics?

Therefore, in the 4<sup>th</sup> section I will introduce some quantum mechanics to find an answer for the solution of the Gibbs Paradox. As I mentioned above, in the 2<sup>nd</sup> section I will discuss whether we can justify the factor  $1/N!$  to solve the discrepancy between the values of the entropy of mixing in thermodynamics and statistical mechanics. If we treat the particles as being quantum mechanical, we will just label them to be able to talk about particle I, which is on the left side, and particle II, which is on the right. But can we still talk about particles then? Or are we just meaninglessly labeling the actually not existing particles? Probably we can use the classical limit to find a solution for the Gibbs paradox in quantum mechanics<sup>[5]</sup>. But then the question arises, what the difference is between quantum particles in the classical limit and classical particles.

Finally, I will formulate a conclusion and with that I will answer the question whether we can solve the Gibbs Paradox. If I think it is possible to do so, I will specify this conclusion by explaining from which point(s) of view and while taking what in account such a solution would be justified.

## 2. A Classical Solution

In the previous section we noticed a discrepancy between the value of the entropy of mixing in thermodynamics and statistical mechanics: in thermodynamics the entropy of mixing vanishes when the mixing gases are equal, whereas in statistical mechanics there's still an entropy of mixing, with the same value ( $\Delta S = kN \ln 2$ ) as in the case of two different mixing gases.

In this section I will search for a solution of this paradox from a classical point of view. First I will discuss the fundamental difference between statistical mechanics and thermodynamics. Second, I will look for a new definition of entropy which works in both statistical mechanics and thermodynamics. Finally I will use the 'common solution' of the paradox: the introduction of the factor  $1/N!$ . I will discuss whether it is justified to use this mathematical tool as a solution of the Gibbs Paradox.

### 2.1 Micro versus Macro

As already mentioned before, statistical mechanics is 'invented' to support thermodynamics: with statistical mechanics we can explain and justify on a microscopic level the phenomena we observe in the macroscopic world of thermodynamics.

However, in the case of the Gibbs Paradox there is a problem, because of the a discrepancy in the behavior of the entropy between statistical mechanics and thermodynamics: in statistical mechanics there's a change in entropy, whether the mixing gases are equal or not, and this entropy of mixing is the same for all kinds of mixing gases. On the contrary, in thermodynamics we find only an entropy of mixing when the mixing gases are unequal. So, what is still the function of statistical mechanics if it does not support thermodynamics?

Well, from the point of view of statistical mechanics there is always a real change when two gases mix<sup>[6]</sup>; even when the two gases are equal: Boltzmann's own idea was that the entropy in statistical mechanics is  $S = k \ln W$ .

The number of accessible microstates  $W$  objectively increases when the partition between two volumes of gas is removed, because the volume that is accessible to the particles of the gas increases. When a partition between two equal volumes of gas is removed, there is to each particle twice as much phase space available then there was before. If the number of available states per particle was  $X$  with the partition still in place (situation A), it becomes  $2X$  after the removal (situation B) of the partition. This means that the number of microstates increases, from

$$W_A = X^N \text{ to } W_B = (2X)^N .$$

Because the entropy in statistical mechanics is defined as  $S = k \ln W$ , this change in  $W$  corresponds to an entropy difference of



$$S_B - S_A = \Delta S = 2 kN \ln 2. \quad (5)$$

So, from the statistical mechanics (microscopic) point of view these changes in phase volume and therefore in entropy are completely natural and logical <sup>[6]</sup>.

In thermodynamics, physical systems are considered from a purely macroscopic point of view. In the case of a volume of gas one looks at changes in macroscopically measurable quantities when the pressure  $P$ , volume  $V$  and temperature  $T$  are made to vary. An essential result is, at the basis of the second law of thermodynamics, that to change one macroscopic state (A) to another macroscopic state (B) an amount of exchanged heat  $\Delta Q$  is needed, which depends of the path from A to B. The heat content of a physical system is therefore not a quantity fixed by its macroscopic state: it is not a so called *state function*.

But, the quantity  $\int_A^B dQ/T$ , the exchanged heat divided by temperature and integrated over the path from A to B, is path-*independent*. So,  $\int dQ=T$  does define a state function. It is this macroscopic state function that defines the entropy in thermodynamics <sup>[6]</sup>:

$$S \equiv \int dQ=T.$$

This entropy, as defined in thermodynamics, is extensive, unlike the entropy defined in statistical physics .

This leaves us with the discrepancy between the thermodynamic and statistical entropy. But is there really a problem here? Actually, only if we think of entropy as a Platonic concept that should be the same in all cases <sup>[6]</sup>; if we accept that the two entropies are differently defined in statistical physics and thermodynamics, the problem immediately disappears.

After all, statistical mechanics is about the detailed microscopic level of physical phenomena, whereas in thermodynamics this same micro-description is excluded from the start: thermodynamics is about the world of the macroscopic sides of phenomena. This fundamental difference between the statistical mechanical and the thermodynamic approaches makes it understandable that the values of entropy changes according to statistical mechanics and to thermodynamics may be sometimes different.

So, we could solve the Gibbs Paradox by accepting the fact that statistical mechanics and thermodynamics act each on a different level of the physical phenomena; microscopic and macroscopic level respectively. Actually, this is just avoiding the paradox; statistical mechanics should support thermodynamics, I argued before. So, the solution might be a different definition of entropy, one that works in both thermodynamics and statistical mechanics.

## 2.2 A new Definition of Entropy

To find a definition of entropy that works in both thermodynamics and statistical mechanics, Swendsen proposed to derive the expression of the entropy of the macroscopic system from the probability distribution at the microscopic level of the system of mixing gases.

To derive the expression as proposed by Swendsen<sup>[7]</sup>, I consider two separated systems which contain a gas. I call these separated systems system 1 and system 2. The extensive variables (energy, volume, and number of particles) of the first system are denoted by  $U_1$ ,  $V_1$ , and  $N_1$ . These variables of the second system are denoted by  $U_2$ ,  $V_2$ , and  $N_2$ . The number of microstates in the systems are denoted by  $W_1(U_1, V_1, N_1)$  respectively  $W_2(U_2, V_2, N_2)$ .

After the two systems are combined, we isolate the resulting system of the mixed gases from any external exchange of energy or particles. Because of this isolation, the sums of the extensive variables,

$$\begin{aligned} U &= U_1 + U_2, \\ V &= V_1 + V_2, \\ N &= N_1 + N_2 \end{aligned} \tag{6}$$

are all constant. The total number of microstates becomes  $W_{12}(U_1, V_1, N_1; U_2, V_2, N_2)$ , with the condition that the sums of the extensive variables in (6) are constant.

So, when we combine (6) and (3), we get for the expression of  $S_{12}$ :

$$S_{12}(U_1, V_1, N_1; U_2, V_2, N_2) = k \ln W_{12}(U_1, V_1, N_1; U_2, V_2, N_2) + X, \tag{7}$$

with the constrains given by (6).

Swendsen starts the calculation of the entropy of the mixed system from the probability of having  $N_1$  particles in subsystem 1 and  $N_2 = N - N_1$  particles in subsystem 2, which for a system of distinguishable individual particles is given by the binominal distribution<sup>[4]</sup>

$$P(N_1; N_2) = N! / (N_1! N_2!) (V_1/V)^{N_1} (V_2/V)^{N_2} \tag{8}$$

For convenience I do not take the energy ( $U$ ) in account, because the energy is in this situation, with these constrains, not important in the calculations.

With (8), the multiplicity  $W$  is given by

$$W = c V_1^{N_1} V_2^{N_2} (N! / N_1! N_2!) \tag{9}$$

where  $c$  is a factor independent of the volume and the number of particles. The factor is  $N! / N_1! N_2!$  included, because it is the number of ways  $N_1$  distinguishable particles can be

chosen out of the  $N$  particles. With  $S = k \ln W$  and Stirling's approximation,  $\ln N! \approx N \ln N - N$ , we find for the entropy:

$$S = k N_1 \ln V_1 + k N_2 \ln V_2 + k N \ln N - k N_1 \ln N_1 - k N_2 \ln N_2 + k \ln c. \quad (10)$$

In equilibrium  $S$  is a maximum, so  $N_i$  in equilibrium can be found by solving  $\delta S / \delta N_i = 0$ . The solution is  $N_i = N V_i / (V_1 + V_2)$ , which is the same empirical prediction as obtained with the factor  $1/N!$  included.

It is clear from equation (7) that the entropy of the composite system, the combination of system 1 and system 2, is the sum of two quantities each of which pertains to only one of the two subsystems. The value of the additive constant  $X$  in equation (7) can be set to  $k \ln V N = N!$ . So, we can write the general expression of the entropy as

$$S(N; V) = k \ln V^N / N! \quad (11)$$

where the volume of the system is  $V$  and the particle number  $N$ . In the limiting situation in which we can apply Stirling's approximation to calculate the factorials, taking into account that in thermodynamic *equilibrium* we will have  $V_1/N_1 = V_2/N_2$  (this corresponds to the maximum of the probability distribution), we find <sup>[4]</sup>

$$k \ln (V_1/N!)^{N_1} + k \ln (V_2/N!)^{N_2} \simeq k \ln V^N / N! \quad (12)$$

This leads to a consistent procedure: to find the entropy of a composite system (consisting of system 1 and 2), we can combine this composite system with a third system, and then we find

$$S(N; V) = k \ln V^N / N! \quad (13)$$

for the entropy of the combined system 1+2. So we obtain a consistent set of extensive entropies by taking equation (11) as our defining equation for entropy.

Swendsen claims that in this way the factor  $1/N!$  in the formula for the entropy has been demonstrated to be a necessary consequence of the distinguishability of the gas atoms or molecules. He rejects the formula  $S = k \ln W$  and proposes that Boltzmann's ideas, which he has interpreted as saying that the logarithm of the probability distribution is the entropy of the composite system, automatically lead to the expression  $S = k \ln W/N!$  <sup>[4]</sup>.

Now I've derived the definition of entropy as proposed by Swendsen, I will answer the question why Swendsen takes the probability distribution as the basis for his (general) definition of entropy: this 'new' definition of entropy has properties the traditional definition of entropy in statistical mechanics doesn't have.

These properties are <sup>[7]</sup>:

- I. Extensivity
- II. Additivity
- III. Obeying the Second Law of thermodynamics

## IV. Constituting the Fundamental Relation

Here I will explain these properties a bit more detailed.

### I. Extensivity

Extensivity can be demonstrated by showing that the terms in the entropy of a composite system that correspond to a particular subsystem are multiplied by a given factor when each of the extensive variables of the subsystem is multiplied by the same factor<sup>[8]</sup>.

Although the entropy of an inhomogeneous system - such as a system for which interactions with the walls of a container can't be neglected - is not extensive, the entropy of a homogeneous system is expected and proved to be extensive.

The traditional definition of entropy as mentioned in equation (3) is not extensive, but the definition based on probabilities, as seen in (11), is. Actually, this is of course because of the introduction of the factorial:  $N!$ . Whether it is really justify to introduce this factorial in the equation I will discuss later.

However, it is a fact that with this 'Swendsen definiton' of entropy the entropy is extensive.

### II. Additivity

Additivity (or separability) can be demonstrated by showing that the terms in the entropy of a composite system can be separated into additive contributions from each subsystem<sup>[8]</sup>.

The calculation of the entropy of a composite system using the traditional definition can give a result that differs from the sum of their expressions for the entropies of the subsystems, so that additivity is violated; this is because the traditional definition of entropy in statistical physics is not extensive. The definition based on probabilities, derived by Swendsen, gives an entropy that is additive for any system containing homogeneous gases.

### III. Obeying the Second Law of thermodynamics

The Second Law of thermodynamics says:  $\Delta S \geq 0$ .

This (in-)equality should hold for any thermodynamic process, with the equality being achieved only for reversible processes. The traditional definition of entropy gives  $\Delta S < 0$  when a partition is inserted into an ideal gas of distinguishable particles, so when the process of mixing two gases is inverted.

Swendsen's definition based on probabilities always gives  $S \geq 0$ . Actually, this is also a direct consequence of the extensivity of the entropy defined by Swenden.

## IV. Constituting the Fundamental Relation

The following equation is known as a fundamental relation in thermodynamics:

$$S = S(U, V, N) \tag{13}$$

where  $U$  is the energy,  $V$  is the volume, and  $N$  is the number of particles. Callen<sup>[9]</sup> has expressed the importance of fundamental relations like this by writing that, "*if the fundamental relation of a particular system is known all conceivable thermodynamic information about the system is ascertainable from it.*"

Unfortunately, the lack of additivity means that in the traditional entropy  $S = S(U, V, N)$  is not

a fundamental relation: knowing  $S_1$  and  $S_2$  is not sufficient to predict  $S_{12}$ , and a separate calculation for the composite system is needed.

Swendsen's definition of entropy based on probabilities does constitute a fundamental relation from which all thermodynamic information can be correctly obtained directly.

According to what is written here, it might be logical to completely throw away the traditional definition of entropy and use Swendsen's definition, based on probabilities: this definition solves a lot of problems of the traditional one: lack of extensivity, lack of additivity, damaging the Second Law and the absence of fundamental relations

However, the only thing that makes that the definition of Swendsen has the properties the traditional definition does not have, is the presence of the factorial  $N!$  in the expression. It is exactly this factorial that might be not justified: using the factorial would suggest that the particles are indistinguishable. Actually, Swendsen introduced the factorial in his calculation because the factor  $N!/(N_1!N_2!)$  is the number of ways  $N_1$  distinguishable particles can be chosen out of  $N$  particles, but this expression leads to the same predictions as the factor  $1/N!$ , as we have seen. So, paradoxically, this expression for the entropy suggests the particles to be indistinguishable, although Swendsen started his reason with the remark that the particles are distinguishable.

Using the factorial is actually the 'traditional' way to solve (or avoid) the Gibbs Paradox, but in principle this is only possible in the case that the particles are all exactly the same, so that we have to correct for permutations. Whether it is justified to use the factorial  $N!$  in the so called *reduced entropy* is therefore a fundamental question about the indistinguishability of particles.

### 2.3 The Solution: dividing by $N!$ ?

The 'usual' way to solve the Gibbs Paradox is by using the factorial  $N!$  in the calculation of the number of available microstates, what influences the value of the entropy of mixing. To defend the use of the factorial to solve the discrepancy between the entropy of mixing in statistical physics and thermodynamics, the argument which is often used is:

"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." [4]

With this replacement of  $W$  by  $W/N!$  we change the way of counting the number of available microstates. This 'manipulation' suffices to achieve agreement between thermodynamics and statistical physics about the value of the entropy of mixing: by dividing  $W$  by  $N!$  the entropy of mixing disappears in the case of two identical gases mixing and leaves the results for different gases mixing unchanged.

For example, when we double both the volume  $V$  and the number of particles  $N$ , the total number of microstates changes, via Stirling's formula, from  $W$  to  $W^2$ :

$$W_N = X^N/N! \rightarrow W' = (2X)^{2N}/(2N)! = W^2. \quad (14)$$

This implies, because  $S = k \log W$ , that the entropy just doubles, without entropy of mixing:

$$\Delta S = S_{12} - (S_1 + S_2) = 2 S_N - (S_1 + S_2) = 0, \quad (15)$$

with  $S_1 = S_2 = S_N$ .

The way in which the division by  $(2N)!$  in the case of two identical gases mixing achieves the removal of the entropy of mixing is that it throws away the exchanges among left particles and right particles and 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<sup>[4]</sup>.

So, actually we can't talk about mixing anymore, neither about an entropy of mixing, because the exchange of a particle from the left with one from the right is defined away, so that there is no difference between the physical situation of combining  $V_1$  with a number  $N_1$  of a gas with another volume  $V_2$  (with  $V_1$  and  $V_2$  identical) and a number of particles  $N_2$  (which is equal to  $N_1$ ) of the same gas and an original volume of size  $2V_N$  and particle number  $2N_N$  of this gas.

The division by  $N!$  thus restores the situation as we know it from thermodynamics: there is a constant and finite entropy of mixing in the case of different gases mixing, however small the difference between the gases may be, and there is no entropy of mixing 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 the volume available per particle does not change when we double both the volume and the number of particles, as is the case when we combine two equal volumes of identical gases, so on macroscopic level nothing happens. But, seen from a microscopic level, it must be noticed that phase space changes when we double the volume, so even when the particles are identical there is a completely different physical situation. Because entropy is, beside with probability, associated with loss of information<sup>[10]</sup> (increase of entropy means loss of information) we would really expect an increasing entropy when suddenly twice as much particles (although identical) occupy a twice as big volume: there are in this new situation for every particle more possibilities in phase space than before, so there is loss of information about the location of the particles in phase space. Only if the particles would be completely indistinguishable, I could imagine the entropy would not increase when the volume and the number of particles double.

Whether we can call (identical) classical particles indistinguishable depends of how we define (in-)distinguishability. In the next section I will discuss several definitions of (in-)distinguishability and their consequences for the justification of using  $N!$  as a solution of the Gibbs Paradox.

### 3. Indistinguishability

As we saw in the previous section, the solution of the Gibbs Paradox has to do with the question whether we can call identical particles indistinguishable. It appeared that the introduction of the factorial  $N!$ , which leads to the so called reduced entropy, is a very useful (if not the) solution for the problem of non-extensivity of the entropy of mixing in statistical mechanics. From a pragmatic point of view, there would be no doubt to use the factorial to ‘solve the Gibbs Paradox for ever’.

However, we should be conscious that we are then using  $N!$  only to get values of the entropy of mixing which are consistent with the thermodynamics and not because we are sure that it is justified on a fundamental level: when we use the factorial  $N!$  in the calculation of the number of microstates we throw away all permutations corresponding to physical exchanges. These permutations represent different and real physical possibilities<sup>[11]</sup>, as long as the particles are distinguishable.

For this reason the justification of the solution of the Gibbs Paradox by using  $N!$  is a direct consequence of the answer to the question whether we can call identical particles distinguishable or not. In this section I will discuss several interpretations of (in-)distinguishability of classical particles and their consequences for the solution of the well-known paradox.

#### 3.1 Gibbs

To start the study of the use and interpretations of concepts like indistinguishability, I will quote Gibbs as he put the question himself in his ‘Elementary Principles in Statistical Mechanics’<sup>[19]</sup>:

If two phases differ only in that certain entirely similar particles have changed places with one another, are they to be regarded as identical or different phases? If the particles are regarded as indistinguishable, it seems in accordance with the spirit of the statistical method to regard the phases as identical.

So, actually Gibbs himself does not say anything concrete about the criteria that are needed to call particles indistinguishable, except that the particles, because ‘entirely similar’ *could* be regarded as indistinguishable. The statement that identical phases are the consequence of interchanging indistinguishable particles is nothing but logical and absolutely uncontroversial. If we go back to the  $N!$ -question, we can ask ourselves what would Gibbs answer when asked whether it is justified to use the reduced entropy in the calculation of the number of microstates.

Well, according to what he wrote about indistinguishability in the ‘Elementary Principles in Statistical Mechanics’, I would expect him to answer that he has no concrete criteria for indistinguishable particles and therefore, that he cannot be sure that in certain circumstances particles are really indistinguishable so that dividing  $N!$  by is not justified.

### 3.2 Schrödinger

Schrödinger wrote about identical particles and the Gibbs Paradox as follows<sup>[20]</sup>:

It was a famous paradox pointed out for the first time by W. Gibbs, that the same increase of entropy must not be taken into account, when the two molecules are of the same gas, although (according to naive gas-theoretical views) diffusion takes place then too, but unnoticeably to us, because all the particles are alike. The modern view [the view of quantum mechanics] solves this paradox by declaring that in the second case there is no real diffusion, because exchange between like particles is not a real event.

It seems that by ‘exchange between like particles’ Schrödinger meant what happens when gases of classical molecules mix: a process in which the trajectories of individual molecules are twisted around one another because the particles are freely moving through space-time. This process of moving particles does not exist in quantum mechanics, because quantum particles do not have trajectories, and so do not mix in this way. When the particles are all like each other, Schrödinger called the exchange ‘not a real event’, because you cannot distinguish between one situation in which particle 1 is at position  $x_1$  and an identical particle 2 at position  $x_2$ , and another situation with particle 1 and 2 interchanged. Apparently, Schrödinger used the term ‘indistinguishable’ for all particles that cannot be distinguished on their physical properties like mass and charge, so properties that are unchanged over time: the history of the particles and their trajectories do not make sense.

This opinion is actually not really remarkable for a physicist who more or less invented quantum mechanics, in which only the moments of measurement are relevant. About what happens in the time between two measurements in quantum mechanics we cannot say anything, and actually it is not so interesting at all. So, Schrödinger’s answer to the Gibbs Paradox is simple: in the case of identical particles there is no real mixing at all, so the situations differs completely from the mixing of two unlike gases. Because we cannot compare the two cases, there is no real paradox here.

So, Schrödinger would answer to the question whether it is justified to divide by  $N!$  to calculate the number of microstates, and with that the entropy of mixing, that this question is completely irrelevant because there is no paradox at all.

### 3.3 Bach

Another interpretation of indistinguishability comes from the physicist Alexander Bach. In his work *Classical Particle Indistinguishability* he formulated his definition of indistinguishable particles as follows:

Indistinguishable Classical Particles Have No Trajectories.

The unconventional role of indistinguishable classical particles is best expressed by the fact that in a deterministic setting no indistinguishable particles exist, or - equivalently - that indistinguishable classical particles have no trajectories. I argue as follows: suppose they have



trajectories, then the particles can be identified by them and are, therefore, not indistinguishable.

As we see, Bach has a clear and quite simple description of the difference between distinguishable and indistinguishable particles: answer the question whether the particles have trajectories and you know whether they are distinguishable or not. So, Bach, unlike Schrodinger, focusses on trajectories instead of on physical properties which are independent of time. But, actually Bach uses evidence from incongruous to prove his definition of indistinguishable particles: ‘*suppose they have trajectories, then the particles can be identified by them and are not indistinguishable*’. Although I think this is not such a strong argumentation, the statement that indistinguishable particles have no trajectories is quite uncontroversial and can therefore be used well in the pragmatic decision whether classical particles are indistinguishable or not. However, Bach’s statement is also quite ‘safe’ and actually even ‘empty’, and most of all the question arises: do *classical* particles without trajectories actually exist? I don’t think so: classical particles are paradigmatically seen as concrete spheres obeying Newton’s Laws of Motion and therefore they have trajectories by definition. So, in my opinion it is not possible to speak about classical particles without trajectories, and this makes Bach’s definition of indistinguishable *classical* particles meaningless.

For that reason, we must conclude that with Bach’s criterion for indistinguishability it is not possible to justify the use of the reduced entropy in the case of mixing gases: classical particles have trajectories by definition, so in the definition of Bach they will be always distinguishable.

### 3.4 Versteegh and Dieks

So, let’s discuss another interpretation of the concept of indistinguishability; according to Versteegh and Dieks<sup>[11]</sup> classical particles are paradigmatically represented by impenetrable spheres, and therefore the prototype of distinguishable particles: the definition of distinguishability they use can be formulated as: distinguishable particles have the property that at each instant of time, they can be individually labeled by their different positions. So, even when all their physical properties such as mass, charge and size, are exactly identical.

Classical particles follow continuous and nonintersecting trajectories in space-time and therefore can always be identified over time by their different histories. So, all particles can in principle be distinguished, and therefore every permutation of two identical classical particles produces a different microstate. Imagine for example a situation in which there is one particle at position  $x_1$  and one at position  $x_2$ . After a while, during which both particles have been moving, there is again one particle at  $x_1$  and one at  $x_2$ . We assume that their respective momenta are the same in the beginning situation as in the situation after some amount of time.

There are actually two possibilities for what has happened in the meantime:

- A. The particle that was first at  $x_1$  is again at  $x_1$  and the particle that was first at  $x_2$  is later again at  $x_2$ .
- B. The particles have exchanged their positions.

The second case is different from the first one because it corresponds to a different physical process. Although the two final two-particle states A and B cannot be distinguished on the basis of their properties at the moment of observation, the different histories of the final states show that the particle at  $x_1$  in final situation A is not equal to the particle at  $x_1$  in final situation B.

Given these observations, how can it be that some authors, as we will see, deny that identical classical particles can be distinguished and maintain that permutation does not give rise to a different microstate? The main reason is that there is disagreement about the meaning of the terms ‘distinguishability’ and ‘permutation’ and about the answer to the question whether these terms can be used synonymously. For example Saunders uses these two terms as synonyms: the quote ‘indistinguishability (permutability, invariance under permutations)’<sup>[15]</sup> makes this quite clear. Later in this section I will discuss the ideas of Saunders in more detail.

For now I will explain the difference that exists, at least in my opinion, between the terms ‘distinguishability’ and ‘permutation’. So, consider the following statements:

- Two particles are distinguishable if they can always be selectively separated by a filter<sup>[17]</sup>;
- 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<sup>[18]</sup>.

These statements are based on a definition of distinguishability which implies that identical classical particles –in that they have equal physical properties- are always indistinguishable.

The concept of permutation can similarly be understood in a way that is different from what we just described. Consider as we did before, 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 a theoretical viewpoint<sup>[11]</sup>.

But, actually this is only an instantaneous, imaginary swapping of names: particle 1 is suddenly called particle 2 and vice versa. This is a different kind of permutation than the physical exchange of particles we considered previously, with the difference that the one just mentioned has nothing to do with real physical processes.

Another interpretation of the concept of permutation is used by Saunders and can be formulated as follows: one particle follows trajectory 1 and the other follows trajectory 2. Imagine that the particle that actually follows trajectory 1 instead followed trajectory 2 and vice versa<sup>[11]</sup>. Both cases would result in exactly the same physical final situation.

As before, this notion of permutation involves the consideration of states before and after the permutation that are not connected by a physical process. A permutation in this sense occurs in our imagination and exchanges an abstract identity represented by particle indices 1 and 2, respectively, which is independent of the physical characteristics of the situation. This kind of permutation has no physical consequences and, at least in my opinion, therefore cannot be significant for statistical mechanics.

So, I state that permutations that are physically relevant can be understood as physical interchanges via trajectories in space-time, so that permutations represent physically different possibilities, with different physical processes that may be realized and different histories of final states.

If the concept of permutation is interpreted differently, so in the second or third way that is mentioned above, then the permutations should not be associated with any physical differences and with that they are not relevant for (statistical) physics: in these cases the permutation only occurs in our head.

As we may conclude, distinguishability and permutability are two different things: distinguishability means, that we can call one particle number one and another particle number two and that we can always find out which particle was the number one and which was number two, also after some amount of time, at least by means of the trajectories of the particles. Permutability says, that it is possible to interchange the location of two particles such, that the macrostate doesn't change, but this does not necessarily imply that the two interchanged particles are indistinguishable! This is the error some authors make. Of course, indistinguishability implies permutability, but permutability does not mean that the particles are indistinguishable.

According to Versteegh and Dieks, we can conclude that the answer to the question whether we can justify the use of reduced entropy is clear: classical particles can always be distinguished by their different positions and their different trajectories through space-time, so justification of  $N!$  is not possible. Whether this is also the conclusion for quantum particles, I will discuss later.

### 3.5 Saunders

I already mentioned Saunders, because of his interpretation of permutability and his synonymous use of the terms indistinguishability and permutability. Actually, Saunders agrees with the opinion that with classical particles, it does make sense to interchange one with another, for these particles have definite trajectories; so the exchange of place makes a real physical difference, and therefore indistinguishability cannot be applied to classical particles.

So, according to Saunders, we surely *can* single out classical particles uniquely, by reference to their trajectories. And he thinks even further: *so can quantum particles, at least in certain circumstances, be distinguished by their states*<sup>[15]</sup>. No matter whether the state is localized or not, the 'up' state of spin, for example, is distinguished from the 'down', and may well be distinguished in this way over time. In such cases, particle properties such as spin and quantum number can be used to name the individual particles. So, because of the Pauli exclusion principle, fermions such as electrons may be simply identified by their quantum number and spin. This amounts to identifying electrons as 1-particle states.

The distinction between the quantum mechanical case with the electron that can be seen as a 1-particle state and the case of classical particles with each their own trajectory can be formulated as follows: in quantum mechanics, given an (anti-)symmetrized state constructed from a given set of orthogonal vectors  $\{\phi_k\}$ ,  $k = 1, \dots, N$ , one can individuate one particle from the remaining  $N - 1$  by its state. This is not possible if the state is a *superposition* of (anti)symmetrized states<sup>[15]</sup>, but it does work for all simple states .

This latest mentioned property makes a difference with classical mechanics, in which particles are never a superposition of other particles. However, this difference does not affect the comparison between classical and quantum mechanical particles Saunders notices: just as we may speak of quantum states, rather than of quantum particles having states, we may speak of classical trajectories, rather than about classical particles having trajectories<sup>[15]</sup>. So, according to Saunders, particles can be really indistinguishable, although the trajectories are not. As a consequence, we could justify the use of  $N!$  in the calculation of the number of microstates, so that the Gibbs Paradox would be easily solved.

However, I don't agree with Saunders' opinion that classical particles can be completely indistinguishable: there is a fundamental difference between the particles in quantum mechanics, which is based on probability distributions of wave functions, and classical mechanics with its classical particles, which are represented by impenetrable spheres and obey Newton's Laws of Motion. Therefore a parallel like Saunders' between quantum states and classical trajectories cannot be made. Moreover, if we speak about trajectories, distinguishable particles are really required: how can we speak about trajectories if all particles are indistinguishable?

Consider for example again the well-known case of two identical particles, one at  $x_1$  and the other at  $x_2$ . When after some amount of time, in which the particles may have moved, one of the particles is again at  $x_1$  and the other at  $x_2$ , there are two possibilities for what has happened in the time in between: either the particles are interchanged or they are on their original location again. The trajectories of the particles make the difference between the two final situations, which themselves are indistinguishable. But, the two end situations have different histories – they are the result of different physical processes – because the particles followed different trajectories. When we do distinguish between these different trajectories, and that is what we do in classical mechanics, it is always possible to distinguish also the particles, just because they did follow their own trajectories through space-time what makes them distinguishable anyway.

So, in my opinion, trajectories cannot exist without the presence of distinguishable particles. As soon as we assume trajectories to exist, we need particles that follow these trajectories and because the trajectories through space-time cannot be identical for two separated particles, each particles will always have a unique trajectory and therefore an unique history, what makes the particle distinguishable from any other particle. In fundamental quantum mechanics, we do not speak about trajectories: between two measurements there are only wave functions and certain probability distributions with which we can kind of predict where we can expect the particle properties in a measurement. So, in quantum mechanics the conclusion might be different, but I will discuss this in the next section.

### **3.6 Haecceitism**

A completely different and more philosophical approach to distinguishability is the so called haecceitism. The origins of this term are medieval or even ancient, and several great physicist and philosophers, for example Newton, Leibniz and Kant, have been playing with this concept<sup>[24]</sup>. Haecceity denotes the discrete qualities, properties or characteristics of a thing which make it a particular thing: it is a object's 'thisness', the individualizing difference

between for example the concept 'a particle of a gas' and the concept 'the particle at this moment at location  $x_1$ '.<sup>[21]</sup>

Haecceity could for example be used as the solution to symmetrical situations in which two objects are really indistinguishable, although it is absolutely clear that there are two individual objects. A famous example was introduced by Max Black: consider two spheres of exactly the same form and material constitution, alone in a relational space (in order to exclude absolute position as a distinguishing property), at a fixed distance from each other. This is a situation that seems certainly thinkable without getting into contradictions. But it is also a situation in which no physical features are able to distinguish between the two spheres, in spite of the fact that there are obviously two of them. The spheres thus appear to possess an identity, haecceity, that cannot be grounded in physical differences<sup>[23]</sup>, nor on trajectories, because the spheres do not move in a certain frame.

This example can be perfectly applied to identical particles: classical identical particles can be represented by exactly the same spheres. So, if we throw away every coordinate system so that we cannot speak about absolute trajectories and positions, but still about two objects, haecceity will be the property that is still present.

If we apply this reason to the question whether it is justified to use  $N!$  in the calculation of the number of microstates, the answer might be positive: the two individual particles are really indistinguishable because of the absence of any distinguishing properties, *including trajectories*, because of the absence of absolute position, so the only property they have is this 'thisness', haecceity, and this property does not cause any difference between the two particles.

However and unfortunately, outside philosophy we cannot work without a coordinate system, so in physics there will be always absolute positions and, as long as we work with classical particles, trajectories. Because trajectories, as we saw before, 'need' distinguishable particles, the classical answer to the question whether we can justify the use of the factorial  $N!$  in the calculation of entropy is negative: dividing by  $N!$ , and therefore calculating the so called 'reduced entropy', which is extensive, is a practical solution to the discrepancy between the entropy of mixing in statistical physics and thermodynamics, but this has nothing to do with any fundamental indistinguishability of identical particles<sup>[11]</sup>.

Actually, in quantum mechanics the situation might be different because we cannot speak about trajectories and particles in the classical way anymore. Therefore, in the next section I will discuss the (solution of the) Gibbs Paradox from a quantum mechanical viewpoint.

## 4. The Gibbs Paradox in Quantum Mechanics

In the previous sections we saw, that the use of the so called reduced entropy, which is extensive because of the included factorial  $N!$ , might be the solution to the Gibbs Paradox. However, we have to realize that this is only a pragmatic solution to the discrepancy between statistical mechanics and thermodynamics, and therefore does not mean that the particles are fundamentally indistinguishable. Moreover, as we saw in the third section, there is actually no real physical situation thinkable in which we can call identical classical particles indistinguishable. But, maybe we can find indistinguishable particles in quantum mechanics, so that from a quantum mechanical point of view the reduced entropy could be justified and as a consequence the Gibbs Paradox could be solved by such a quantum mechanical approach.

However, it should be noticed that in quantum mechanics, the use of the particle concept is very ambiguous: sometimes the indices which are used in the many-particle formalism of quantum mechanics are assumed to refer to particles so that all states are completely symmetrical and all particles are in exactly the same state, so that they are really indistinguishable. But there is also another use of the particle concept: in this approach individual wave packets are used to represent single particles. In the classical limit these particles become the particles we know from classical mechanics.

In this section I will discuss both particle concepts in more detail and their consequences for the justification of the reduced entropy and the solution of the Gibbs Paradox.

### 4.1 Symmetric States

In contrast to classical particles, identical quantum particles are usually assumed to be indistinguishable as a matter of principle. This fundamental indistinguishability is supposed to be the result of the quantum mechanical (anti-)symmetrization postulates, where permutations of the indices in the quantum mechanical many-particle formalism leave a state either invariant, in the case of bosons, or change its sign, when we have to do with fermions<sup>[11]</sup>.

The elementary identical quantum particles we know, either bosons or fermions, have states which are all defined in their own Hilbert space:  $H_1 \otimes H_2 \otimes H_3 \otimes \dots \otimes H_n$ . These states are completely symmetrical or anti-symmetrical, respectively. In such (anti-)symmetrical states the restriction of the state to a single factor space (for example, the density operator obtained by ‘partial tracing’ over the variables of the other factor spaces) is the same for all factor spaces. Therefore, all one-particle states defined in the individual Hilbert spaces are equal<sup>[5]</sup>.

The indices  $i$  as they are used to distinguish between the states defined in different Hilbert spaces are usually regarded as particle indices. This means, because of the complete symmetry of these states, that the several particles cannot be individuated on the basis of their state-dependent properties, like position and momentum. Since the state-independent properties (for example charge, rest mass) are by definition equal for identical particles, this leads to the conclusion that all particles of the same kind possess exactly the same physical properties. So, these particles are completely indistinguishable.

However, we have to realize that these indices are actually no more than mathematical tools to be able to use the symmetrization postulates and that they have nothing to do with ‘real’ particles. As we already argued in the previous section, the permutations that are relevant to statistical mechanics are not simply permutations of indices, but rather processes by which the permuted state is connected to the initial state by trajectories in space-time. But, since all factor Hilbert spaces and the states defined in them occur completely symmetrically in the total state, all interactions will affect the states in the factor spaces in exactly the same way.

As a consequence, we cannot speak about trajectories of these completely symmetrized and identical particles in quantum mechanics, and therefore every permutation cannot be more than an abstract swapping of indices that occurs only in our head. So, although the fully symmetrized state has general applicability and validity, the different ‘particle indices’  $i, j$ , cannot be associated with real physical entities.

For that reason, it is not possible to use this concept of quantum particles to solve the Gibbs Paradox: we simply cannot speak about particles, but only about indices occurring in the many-particle formalism in quantum mechanics, which cannot be linked to real physical entities.

#### **4.2 Wave Packets**

The other particle concept in quantum mechanics is much closer related to the classical particles. In this concept individual wave packets are assumed to represent single particles. So, the difference between this particle concept in the classical limits of quantum mechanics and the classical particle is not much more than that the classical particles are represented by impenetrable spheres, whereas these quantum particles are small, well-localized wave packets. These quantum particles can be treated as individuals which differ from each other in their physical properties: their locations.

With this particle concept of well-localized wave packets, trajectories through space-time can be defined. When the individual one-particle wave packets in the many-particle state have small spatial extensions and do not overlap, we can identify them over time and they approximately follow the paths of classical particles. Even, when in the classical limit these wave packets become really localized, classical particles emerge from this quantum mechanical particle concept.

So, from this point of view classical trajectories do exist in quantum mechanics, and they are represented by small wave packets. The mechanism that is essential to keep wave packets narrow in order to maintain classical particle-like structures in quantum mechanics over longer stretches of time is called decoherence.

It is thought that physical systems are usually not isolated but interact with an environment, and that in many circumstances the interaction is such that the environment effectively performs (approximate) position measurements on the systems in question. The effect of this interaction with the environment is the destruction of coherence (decoherence) between parts of the wave function centered around different positions: these parts become correlated with mutually orthogonal environment states. In this way, spatially extended wave functions are transformed into mixtures of spatially very narrow states<sup>[27]</sup>.

This particle concept is very useful to explain quantum mechanical problems, for example the well-known Einstein-Podolsky-Rosen (EPR) Paradox. The EPR experiment refers to the two-particle state with two electrons at a certain distance from each other, on which spin measurements are performed. As we know, because of the Pauli exclusion principle it is necessary that the two electrons have different spins, but until the measurement we cannot say anything about the properties of the two particles, so we don't know which one has spin up and which one spin down.

Now, assume that one of the particles is on the left and the other one on the right side. If we measure the spin of the left particle, we will find either spin up or spin down. Until here nothing strange happened. However, as soon as we know the spin of the left particle, we also know the spin of the right one; this is a contradiction to the quantum mechanical theory, which states that the properties of quantum particles cannot be known until they are directly measured<sup>[26]</sup>.

If we use the quantum particle concept we just described, with the particles represented by small individual wave packets, differing from each other in their physical properties (their locations), we can explain this paradox easily. The left and right particle can be viewed as individuals then, each with their own physical properties.

However, we have to realize that the particles in this approach do not obey the symmetrization postulates of quantum mechanics; if we would use the other particle concept and associate our particles with the particle indices 1 and 2 in the fully (anti-)symmetrized state, we could not speak about a left and or a right particle: the states of both 1 and 2 would be 'evenly distributed' between left and right.

So, the particle concept in which particles are represented by localized wave packets as being a particle on the left and the right side, is at variance with the official quantum mechanical theory with its symmetry postulates, but very useful to explain quantum mechanical problems like the EPR Paradox.

However, for the solution of the Gibbs Paradox in terms of justification of the reduced entropy, this particle concept is as useful as the classical particle concept: because we can clearly distinguish between the narrow wave packets, each with its own trajectory, we cannot justify the factorial  $N!$  in the reduced entropy.

#### **4.3 Quantum mechanics: a Solution to the Gibbs Paradox?**

As just described, in quantum mechanics we are dealing with two particle concepts at the same time. The first concept is very abstract and based on the symmetrization postulates of quantum mechanics. Because of these postulates, all quantum particles of the same kind are in exactly the same state and therefore indistinguishable. However, these particles are no 'real' particles in the sense that they have distinct properties: actually they are no more than the abstract indices which refer to individual Hilbert spaces, and cannot be interpreted as individual particles.

So, this particle concept obeys the fundamental (symmetrization) laws of quantum mechanics, and the 'particles' (actually no more than indices) are absolutely indistinguishable, but this concept has nothing to do with the entities in 'real physics'.



Therefore, this particle concept doesn't mean that all particles are in the same state, but rather signals that indices cannot be used as particles names<sup>[5]</sup>.

Because this particle concept does in fact not refer to particles, even not to 'completely indistinguishable particles', this quantum mechanical approach cannot be used to solve the Gibbs Paradox: the existence itself of these particles has not been established.

The other particle concept in quantum mechanics is almost the opposite: the particles are represented by very small wave packets, and emerge from quantum mechanics due to the processes of decoherence. In the classical limit they become the familiar classical particles.

As we saw above, these particles do have distinguishable properties (location) and trajectories and are therefore as distinguishable as classical particles. The only (significant) difference between this particle concept and classical particles is, that they are represented by very narrow wave packets instead of by impenetrable spheres; so, identical quantum particles can be as distinguishable as classical particles!

Therefore, contrary to the other quantum mechanical particle concept, there is no doubt whether these particles correspond to the particles we know from statistical mechanics and thermodynamics; clearly they do. However, because it is a fundamental principle of quantum theory that the indices in the formalism can never appear in configurations that are not symmetrical<sup>[5]</sup>, this concept of quantum particles cannot be related to the indices in the quantum mechanical formalism.

For this reason, I conclude that this quantum mechanical particle concept does not add anything to the classical attempts to solve the Gibbs Paradox. Combined with the conclusion that the first particle concept does not provide a solution to the Gibbs Paradox either, I state that the Gibbs Paradox does not need quantum mechanics for its solution at all.

## 5. Conclusion

Is it possible to solve the Gibbs Paradox? This is the question I formulated in the beginning of this thesis. From several points of view, a classical one, a more philosophical one and a quantum mechanical perspective, I discussed whether we can find a solution for this well-known paradox. In this section I will summarize what we already concluded above and from this I will formulate my final conclusion with respect to the famous Gibbs Paradox.

In the first section we saw two versions of the Gibbs Paradox. The first one concerned the phenomenon that in thermodynamics the entropy changes discontinuously from zero to a non-zero value when the degree of similarity between two mixing gases changes continuously from indistinguishable to distinguishable. However, we could see this change from indistinguishability to distinguishability as a phase transition. As we know, in phase transitions it is quite ‘normal’ that thermodynamic quantities, such as entropy, change discontinuously, so this version of the Gibbs Paradox is actually not really remarkable.

The other version of the paradox concerns the discrepancy between thermodynamics and statistical physics for the value of the entropy of a system with two identical gases mixing. It is the solution of this paradox that was the subject of this thesis.

From a classical point of view we can formulate two solutions to the Gibbs Paradox. The first solution starts from the fact that there is a fundamental difference between statistical mechanics and thermodynamics: statistical mechanics is about microstates and properties of individual particles whereas thermodynamics concerns only macrostates and macroscopic phenomena. Because these two physical disciplines actually act on different levels, it is not surprising that they use different definitions of entropy which predict different values of the entropy of mixing: on macroscopic level indeed nothing changes when both the number of similar particles and the volume are doubled (which is the case when two identical volumes of identical gases mix), whereas on microscopic level it is clear that every particle suddenly has twice as much possibilities in phase-space. This results in a loss of information (for example about the location of the particles) and therefore in a non-zero value of the entropy of mixing. So, to solve the paradox we just have to accept that thermodynamics and statistical physics are concerned with different physical levels and as a consequence they can be contradicting.

If we do not want to accept the consequences of this fundamental difference between statistical physics and thermodynamics, we can use a new definition of entropy, the so called reduced entropy, which is defined as:  $S = k \ln W/ N!$  and which is extensive, like the thermodynamic definition of entropy. The factorial  $N!$  in this formula corrects for permutations in the case of indistinguishable particles. However, we should be conscious that we use the reduced entropy only for pragmatic reasons and that it does not provide an argument for the indistinguishability of identical classical particles.

To justify the reduced entropy we have to be able to call identical particles indistinguishable. As we saw in the third section, several physicists used different definitions of indistinguishability, but finally we have to conclude that as soon as we speak about

individual particles, they all will have their own unique trajectories through space-time, because two classical particles can never be at the same time at the same location, what makes them distinguishable by definition. Only in the case we cannot refer to a certain coordinate system, as we saw in the example of the identical spheres, we can call the particles completely indistinguishable and at the same time we know there are two of them, what gives them a certain intrinsic ‘thisness’ or haecceity. However, in ‘real’ physics, thus outside philosophy, we always refer to a certain coordinate system, so that particles which possess only haecceity and no physical properties that can distinguish them, like location, can only exist in our head. For this reason we have to conclude that ‘real’ classical particles are always distinguishable, and therefore it is not possible to justify the factorial  $N!$  of the reduced entropy.

When we used quantum mechanics to look for an argument to call particles indistinguishable, we found two particle concepts. The first one, obeying the quantum mechanical formalism with its symmetrization postulates, is a very abstract particle concept: the indices used in this approach cannot be linked to real entities. For this reason we cannot use this approach when we talk about mixing gases of particles. In the second particle concept individual particles are represented by small wave packets. In the classical limit these wave packets become fully localized and thus the well-known classical particles. The advantage of this particle concept is, that with no doubt these particles refer to ‘real’ entities, opposite to the first quantum mechanical particle concept. However, because these wave packets are such classical particles like, they even have trajectories, they are actually as distinguishable as ‘normal’ classical particles are. So, none of the two quantum particle concepts is useful to justify the reduced entropy.

Finally I conclude that we can solve the Gibbs Paradox in a few ways. First, by considering statistical mechanics and thermodynamics as two fundamentally different disciplines, each acting on their own level of physical phenomena and using fundamentally different theories and definitions, which sometimes predict different values of physical quantities.

Second, by introducing the reduced entropy and using it only as a pragmatic solution for the discrepancy between the two disciplines in physics, but not as an argument for indistinguishability of identical particles.

Third, by assuming that the particles are completely similar and present in a space without a coordinate system, such that they cannot be localized and, beside their identical physical properties, only possess haecceity. In this case the particles are really indistinguishable and therefore the use of the reduces entropy is justified. However, the disadvantage of this solution is, that it we will never find particles like this in the ‘real world’, where some kind of coordinate system will always be present.

The Gibbs Paradox does not need quantum mechanics for its solution, because none of the quantum particle concepts does add anything useful to the classical and philosophical solutions just formulated. Therefore, I do not expect development in quantum mechanics to give another solution to the paradox.

So, the Gibbs Paradox does have solutions, but none of them is applicable without certain constrains.

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