

**The Gibbs Paradox  
and the  
Anti-Haecceitistic Nature of Entropy**

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Scott Alexander Hertel

Advisor: Dr. Hans Christian von Baeyer

Williamsburg, Virginia  
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### **Abstract**

The resolution of the Gibbs Paradox is still a matter of debate, well over a hundred years after Gibbs first pointed it out. Resolutions hinge upon concepts of indistinguishability, and thus seem to involve quantum mechanics. We show, however, that this paradox in truth involves only observational indistinguishability (unrelated to quantum physics), and that the quantum mechanical understanding mistakenly treats entropy as a physical property rather than a quantity of observed information. The relation of the Gibbs Paradox to the philosophical question of Haecceitism is discussed.

### **Acknowledgement**

This paper was a collaboration between myself and Dr. Hans von Baeyer, of the College of William Mary in Virginia. He should share the credit for any insight one finds here; whatever misconceptions that remain are, of course, entirely my responsibility.

- Scott Hertel

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## 1 Introduction: The Gibbs Paradox

Profound realizations often trace their origins to the most mundane aspects of experience. Such is the case of the Gibbs Paradox, which seems at first to be of a practical nature and relatively straightforward, but in the end will open the door to considering all of physics in a different light.

Imagine an isolated box, which has been partitioned by an impermeable barrier into two sections. In one section there are  $n_1$  moles of an ideal gas, and in the other section there are  $n_2$  moles of a different ideal gas. The two gases are allowed to be in thermodynamic contact, so that  $T_1 = T_2$ . For simplicity's sake we choose  $V_1 = V_2$  and  $n_1 = n_2$  (and thus  $P_1 = P_2$ ). Imagine then the barrier being removed, and the two gases freely mixing. A new equilibrium is achieved among the  $n = n_1 + n_2$  moles in the volume  $V = V_1 + V_2$ . The change in entropy due to this mixing is[1]

$$\begin{aligned}\Delta S &= S_{final} - S_{initial} \\ &= nR \ln V - (n_1 R \ln V_1 + n_2 R \ln V_2) \\ &= nR \left[ \ln V - \frac{1}{2} \ln \left( \frac{V}{2} \right) - \frac{1}{2} \ln \left( \frac{V}{2} \right) \right] \\ &= nR \left[ \ln V - \ln \left( \frac{V}{2} \right) \right] \\ &= nR \ln 2\end{aligned}\tag{1}$$

Immediately after Gibbs [2] stated this simple result in his seminal work of 1875, “Equilibrium of Heterogeneous Substances”, he insightfully pointed out:

It is noticeable that the value of this expression does not depend upon the kinds of gas which are concerned, if the quantities are such as has been supposed, except that the gases which are mixed must be of different kinds. If we should bring into contact two masses of the same kind of gas, they would also mix, but there would be no increase of entropy.

This is the paradox: The mixing of two different gases results in an entropy increase, but the mixing of two identical gases retains its original value of entropy. The process of mixing two different gases might be exactly the same (down to the individual motions of each particle) as the mixing of two indistinguishable gases, yet the two processes are treated as entirely different phenomena. It is equally important to note (as Gibbs himself stressed) that the degree of similarity of the two gases is irrelevant. One can imagine two gases being similar or dissimilar to any degree and in any imaginable manner, but there are only two possible values for such an entropy of mixing:  $nR \ln 2$  and 0.

It is widely agreed that the Gibbs Paradox has a profound truth in it somewhere; a paradox in physics must mean that we are missing some key piece of understanding. Traditionally, quantum mechanics is believed to be that missing piece, and many authorities (Schrödinger [3], for one) have used quantum mechanics to convincingly resolve the paradox. Here we attempt to show that the real missing piece of understanding is a proper concept of the nature of entropy.

## 2 Haecceitism and Anti-Haecceitism

In order to approach the Gibbs Paradox, we must start with a child-like question: If two things that are alike in all ways suddenly trade places, is the world the same or different? The child might imagine switching two bottles of milk in the supermarket, both from the same company and stamped with the same date. A physicist might

more elegantly imagine switching two oxygen molecules in the air. Philosopher Duns Scotus pondered this children's question in the middle ages, and answered it using his own common sense: Yes, the world is different if two alike things suddenly trade places. He attributed to each thing its own "Haecceitas", its own "thisness". He reasoned that even if two things are identical in every way, no two things can both be "this" thing. This conceptual understanding is known as "Haecceitism", and it is the way most of us normally understand the world. The opposite belief that the universe is unchanged after the switching of identical things is known as "Anti-Haecceitism".

We grow up thinking the world is Haecceitistic because the things we consider alike in all ways are in reality not. Of the two seemingly identical bottles of milk in the supermarket, one may contain a single microorganism that will quickly multiply and turn the milk rancid. If the child switches the two seemingly identical bottles, a different customer will go home with rancid milk and the universe will be an unmistakably different place. We grow so used to these chaotic happenings it is hard to imagine two things being truly identical. However, after the child has learned some modern physics he may wish to return to the question of Haecceitism.

Electrons orbiting a nucleus are clearly lacking in "thisness". Quantum mechanical indistinguishability is perfect indistinguishability, of a different sort than anything Duns Scotus ever encountered. Switching two identical particles ceases to have any physical meaning, and if the particles are close enough for their wavefunctions to overlap, then even the concept of having two particles is hard to reconcile with the evidence. But the instances when these quantum realities impinge on our everyday experiences are few. We live blissfully ignorant, using classical common sense. Let us for a while only consider a classical understanding, and see where it leads.

We have been faced with a choice: Haecceitism or Anti-Haecceitism. It would seem the world must be either one or the other. If this question is to be answered, it must be answered empirically; we must ask ourselves, "What can we measure that

would tell us if we live in an Haecceitistic world or an Anti-Haecceitistic world?”

Imagine designing a Newtonian experiment meant to settle the question of Haecceitism. The experiment must involve indistinguishable particles, such as two cue balls. No matter what experiment we run with these two cue balls, it follows the same course if the rolls of the two cue balls are reversed. For example, ball A hitting ball B in a particular manner is indistinguishable from ball B hitting ball A in the same manner. So, Newtonian physics describes a world congruent with Anti-Haecceitism (because the universe looks the same whether A hits B or B hits A) but without any proof that Haecceitism is false (because the universe might look the same, but be different).

Have we reached the end of our enquiry? Consider the difference between the Haecceitistic pool table and the Anti-Haecceitistic one. There is no measurable difference between the two, because the cue balls are identical and physics will treat them identically. The only difference is how many ways the same thing can happen. Haecceitistically, A could strike B or B could strike A. Anti-Haecceitistically, there is only one description: one cue ball struck another cue ball. If the only difference between the two world-views is a difference in the number of possible ways things can happen, then the only classical branch of physics that might settle our question is thermodynamics.

Thermodynamics, and entropy in particular, rests on a foundation of counting the number of ways a certain physical state could exist. Entropy  $S$  can be understood as  $S = k \ln(W)$  where  $k$  is Boltzmann’s constant and  $W$  is a number of ways. This number of ways is the number of possible ways that the fundamental units of a system can satisfy certain macroscopic observations (such as temperature, pressure, and volume). As an example, if the total energy is the only macroscopic restriction on a gas, then the particles of that gas can share that energy in a multitude of different ways, and this number would be called the system’s  $W$ , the number of ways. Note



that under normal macroscopic circumstances,  $W$  will be inconceivably large. Since  $k$  is of order  $10^{-23}$  and entropy of order 1, the log of  $W$  must be of order  $10^{23}$  and  $W$  will have the same order as  $e^{10^{23}}$ , which is indeed quite large.

So it seems that we might be able to test Haecceitism using thermodynamics. We will simply measure entropy for a variety of circumstances and calculate  $W$ . There are clearly more ways for a system to meet macroscopic criteria in an Haecceitistic universe than an Anti-Haecceitistic one, and so our empirical  $W$  value will tell us which type of universe we live in.

### 3 Haecceitistic and Anti-Haecceitistic Counting

In order to derive a theoretical  $W$ , we will want to count the number of possible ways to arrange the particles of a gas. One can completely describe each possible state for an homogeneous gas as a list of the position and velocity of each particle. Attempting to visualize this list is quite hard, because a single particle's information is a point in six dimensions (three position dimensions and three velocity dimensions), so the combined state of all  $N$  particles would be a point in  $6N$  dimensions. This  $6N$ -dimensional space is called the  $\Gamma$  space (“ $\Gamma$ ” stands for “gas”).

All the complexities of gas state counting appear in simpler form for identical, stationary beads on a straight length of string. As in a gas, no two particles (beads, in this case) can ever have the same exact set of characteristics. With only one characteristic (one-dimensional position), we have shrunk our  $6N$ -dimensional space down to an  $N$ -dimensional one. Assume for a moment that there are only two beads, and the string is so short it only barely holds the two beads. Now we must count the number of ways these beads could be on this string. Haecceitistically, there are two ways: (bead A – bead B) and (bead B – bead A). Anti-Haecceitistically, there is only one way, because the two beads are identical (see Figure 1). What if the

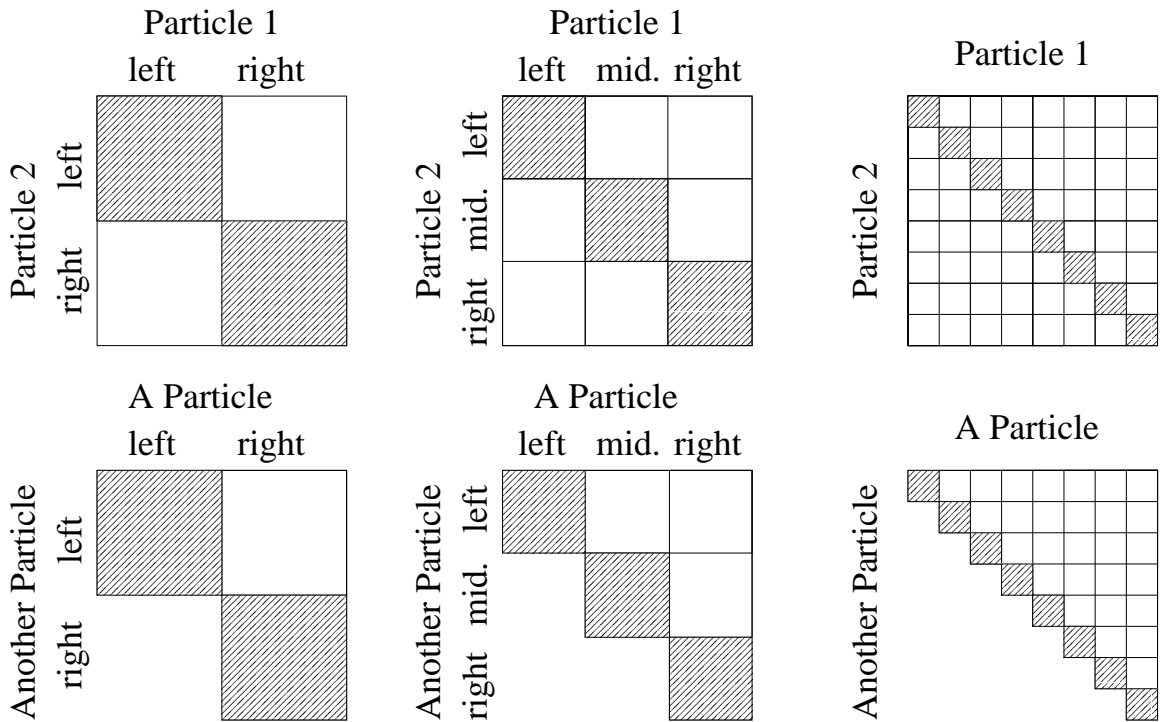


Figure 1: Haeccetistic (upper) and Anti-Haeccetistic (lower) possibility spaces for two beads on a length two string, a length three string, and a length 8 string. Each square denotes a possible state for the system, the darkened squares denote a state that is not possible. Note that as the number of available spaces approaches infinity (as for an ideal gas) the effect of the impossible states is negligible.

beads fill up less of the string? Let's say there is a third spot on the string, and that now each of the two beads can either be at position 1, 2, or 3. Now there are six Haeccetistic possibilities and three Anti-Haeccetistic possibilities. A pattern quickly emerges: no matter how many spaces are on the string, there are always half as many Anti-Haeccetistic possibilities. It turns out that this factor of one-half is a manifestation of the number of beads. For two beads there are half as many Anti-Haeccetistic possibilities; for three beads there are one-sixth as many; for four beads one twenty-fourth as many; and so on. Thus, we have found that the number of Anti-Haeccetistic possibilities is the number of Haeccetistic possibilities multiplied by a factor of  $\frac{1}{N!}$  where  $N$  is the number of particles. This could have been guessed at

the outset, because  $N!$  is the number of permutations of the particles, and whether to count permutations or not is the only difference between the two methods of counting.

## 4 Haecceitistic and Anti-Haecceitistic Thermodynamics

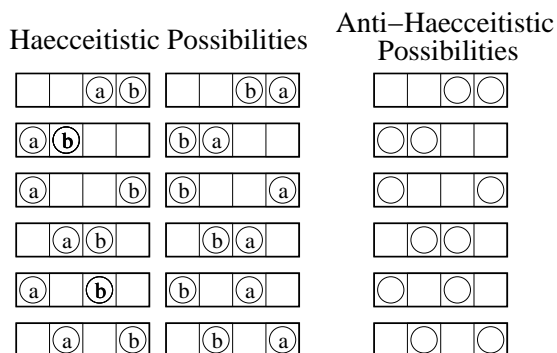


Figure 2: Haecceitistic and Anti-Haecceitistic possibilities for two beads in four spaces.

Either Haecceitistic or Anti-Haecceitistic counting can be used equally well to derive many aspects of thermodynamics, including the exact change in entropy of most processes. To see this, imagine a string with only enough room for four beads. On the string are two beads, which can be placed in those four spaces.

As one can see in figure 2, each possible Anti-Haecceitistic state has two analogous Haecceitistic states. By analogous, we mean that the measurable properties would be the same. Imagine that a scientist is trying to measure the entropy change of a certain process on this string. Take, for example, the process of initially having both beads to the right of center and then removing that restriction and allowing them to be in any of the four spaces. Looking at the diagram, we see that the initial Haecceitistic  $W$  would be 2, and the final  $W$  would be 12. Anti-Haecceitistically, the initial  $W$  would be 1, and the final  $W$  would be 6. For any such process, the ratio (here, 1:6) is the same for either method of counting. The Haecceitistic possibilities are more numerous by a factor of 2 (which is  $N!$ ), but by the same logic each Anti-Haecceitistic possibility corresponds to 2 Haecceitistic possibilities. It is ratios like the 1:6 ratio here that produce measurable effects of entropy, leaving the question of Haecceitism as yet untested.

Huggett[4], among others[5][6], emphasizes the applicability of both methods of counting. As in the bead example, the correct ratio of ordered to disordered states for a gas, however one defines order, can be derived using either counting scheme. Huggett offers the following mathematical explanation of this point, showing that the probability of a particular microscopic measurement is the same according to either method. “Frequency” here is the proportion of the possibilities that have a certain exact set of observable characteristics.

$$\begin{aligned}
 \textit{Haeceitistic Frequency} &= \frac{N!}{\textit{Total Haeceitistic States}} \\
 &= \frac{N!}{N!(\textit{Total Anti-Haeceitistic States})} \\
 &= \frac{1}{\textit{Total Anti-Haeceitistic States}} \\
 &= \textit{Anti-Haeceitistic Frequency}
 \end{aligned}$$

Put another way, the Haeceitistic  $\Gamma$  space is  $N!$  times larger than the Anti-Haeceitistic space, but each observable state fills the same proportion of either space. Thus far, thermodynamics seems to work equally well in a Haeceitistic world as in an Anti-Haeceitistic one. Is thermodynamics silent on the issue then, after all, just as Newtonian physics was? Let us develop our thermodynamic theories one step further.

We want to have a formula that uses the macroscopic observables to define an entropy value. A standard choice of macroscopic variables will result in a formula as  $S = S(T, V, N)$  where  $T$  is temperature,  $V$  is volume, and  $N$  is the number of particles in the gas. The correct equation can be derived empirically, and for ideal gases is called the Sackur-Tetrode equation:

$$S = \frac{3}{2}Nk - Nk \ln \left[ \frac{N}{V} \left( \frac{2\pi\hbar^2}{mkT} \right)^{\frac{3}{2}} \right] \quad (2)$$

where  $m$  is the mass of a single particle. Now we will try to derive this equation starting with our simple counting considerations. Such derivations have been published many times; here we outline the argument given by Huang[7].

Start with a system of  $N$  particles. Say we were thinking about these particles according to their energies, grouping together all the particles with a particular energy. Now imagine energy “bins”, that group together many of these particular energies (for bin  $B_j$ , let us call the number of energies in the bin  $g_j$ ). So, if there are  $n_j$  particles in a bin that contains  $g_j$  energy values, there are  $(g_j)^{n_j}$  ways for the particles to occupy that bin. One can easily see this by realizing that there are  $g_j$  ways for one particle to occupy the bin,  $g_j$  ways for the second particle to occupy the bin, and so on for all the  $n_j$  particles.

Now we take a step back, and think about the set of all bins and the set of all  $N$  particles. For the moment, pretend that each bin ( $B_j$ ) contains only one energy level instead of many. How many ways are there to put  $n_1$  particles in energy bin  $B_1$ ? The Haeccetistic answer is

$$\frac{N \text{ choose } n_1}{n_1!} = \frac{N!}{n_1!(N - n_1)!} \quad (3)$$

because there are  $N$  choose  $n_1$  Haeccetistic ways to select the  $n_1$  particles to be placed in the energy bin, and since the arrangement “within” the energy doesn’t matter (either Haeccetistically or Anti-Haeccetistically), we divide by the number of arrangements the  $n_1$  particles could have. Now we move on to the next energy bin,  $B_2$ , and similarly ask, how many ways are there to put  $n_2$  particles in energy bin  $B_2$ ? Again Haeccetistically, the answer is

$$\frac{(N - n_1) \text{ choose } (n_2)}{n_2!} = \frac{(N - n_1)!}{n_2!(N - n_1 - n_2)!} \quad (4)$$

We can clearly see the pattern begin to emerge, and now we can answer the question, “How many ways are there to place the entire set of bin occupation numbers  $\{n_j\}$  in the entire set of energy bins  $\{B_j\}$ ?” We multiply all the number of ways for each bin together:

$$\frac{N!}{n_1!(N - n_1)!} \frac{(N - n_1)!}{n_2!(N - n_1 - n_2)!} \frac{(N - n_1 - n_2)!}{n_3!(N - n_1 - n_2 - n_3)!} \cdots = N! \prod_{j=1}^{\infty} \frac{1}{n_j!} \quad (5)$$

Now we stop pretending that each bin only contains one energy value, and taking

into account our initial analysis our answer becomes:

$$W_{\{N_k\}} = N! \prod_{j=1}^{\infty} \frac{(g_j)^{n_j}}{n_j!} \quad (6)$$

This is the number of ways one can place a set of bin occupation numbers  $\{n_j\}$  into a set of bins  $\{B_j\}$  Haeccetistically. The Anti-Haeccetistic answer would be multiplied by the  $\frac{1}{N!}$  factor from before, which would make it

$$W_{\{N_k\}} = \prod_{j=1}^{\infty} \frac{(g_j)^{n_j}}{n_j!} \quad (7)$$

Physicists generally follow the same path we have, by arriving first at the Haeccetistic  $W$ , and then dividing by  $N!$ . Why bother switching from an Haeccetistic description to an Anti-Haeccetistic one in the middle of an argument? The answer is that, for the first time, we have come upon an instance in which it matters which description we use: *only the Anti-Haeccetistic counting method will yield a correct result!*

What we have been aiming at all along is the Sackur-Tetrode Equation (eq. 2), or at least an equation that does not predict differing empirical results. It is a straightforward derivation from the Anti-Haeccetistic and Haeccetistic  $W_{\{N_k\}}$  functions in terms of energy bins to entropy equations of the form  $S(T, V, N)$ . Because we defined entropy as proportional to the natural logarithm of  $W$ , the discrepancy by a factor  $N!$  will show up in our entropy equations as an additive difference of  $\ln(N!)$ , which is very accurately approximated by  $N \ln(N)$  using the Stirling approximation. That being said, from the Anti-Haeccetistic  $W$  we arrive at

$$S = \frac{3}{2} Nk \left[ 1 + \ln \left( \frac{2\pi mk}{h^2} \right) \right] + \frac{3}{2} Nk \ln(T) + Nk \ln \left( \frac{V}{N} \right) \quad (8)$$

which is simply the Sackur-Tetrode result. If we start with the Haeccetistic  $W$ , we will arrive at

$$S = \frac{3}{2} Nk \left[ 1 + \ln \left( \frac{2\pi mk}{h^2} \right) \right] + \frac{3}{2} Nk \ln(T) + Nk \ln(V) \quad (9)$$

Notice that the two equations have precisely the same dependencies on temperature and volume. Just as in the example of the beads, either method of counting will give

many correct results. The only discrepancy lies in entropy's dependence upon  $N$ , the number of particles. We haven't directly considered entropy's dependence on  $N$  until now. Note that  $N$  plays the role of a constant in our bead examples and in Huggett's equivalency proof. All that we showed before is that either method of counting will work if  $N$  is a constant of the system[8].

Let us put the theoretical arguments aside, and try to deduce entropy's dependence on  $N$  empirically.

Imagine the two situations shown in figure 3. A certain amount of work can be obtained by allowing a small sample of gas to expand into the available space.

The amount of available work in the system on the right should clearly be greater, and it turns out that if both the volume and number of particles is doubled,

the amount of available work will be doubled. This is

simply an empirical fact, that any theory will have to agree with[9]. In such a situation, the work could only have arisen from an equivalent increase in entropy, and thus the change in entropy (and subsequently the absolute entropy of both the initial and final states) is

twice as great in the doubled version.

This type of linear dependence on number at constant number density is called "extensivity". It is not at all surprising that the entropy of an ideal gas has this property. All extensivity means is that if one has a container of gas, then a larger container will have a proportionally larger entropy, assuming all other things are equal[10].

Looking back at our two differing equations for entropy, we see that only the Anti-Haeccetistic version (eq. 8) fits the extensivity criterion. Finally, it seems, we have

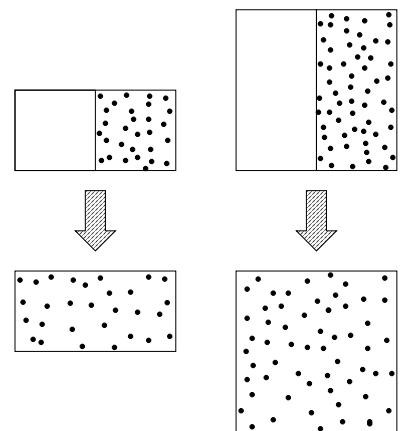


Figure 3: An illustration of extensivity. The entropy change on the right is twice the entropy change on the left.

tested the truth of Haecceitism and come up with a definitive answer: Entropy can only be correctly described through Anti-Haecceitistic physics. Viewing the world Haecceitistically will give us the wrong entropy equation.

But then, there is a nagging strangeness to our arguments. Haecceitism seemed to be untested by Newtonian physics. Isn't thermodynamics just a statistical description of Newtonian physics? Is it reasonable that thermodynamics could answer such a basic question where Newtonian physics fails us?

Schrödinger[3], along with the great majority of twentieth century physicists, answers that yes, it is both reasonable and remarkable for thermodynamics to give us a physical truth that was lacking in the Newtonian realm. The reason, they say, is that Newtonian physics lies squarely in the classical realm whereas thermodynamics lies rightfully in the quantum mechanical realm. The non-extensivity of the Haecceitistic entropy equation (eq. 9) was taken by Schrödinger as “just the point in which the classical point of view pitifully fails ...” After explaining the premise of the Gibbs Paradox, he goes on, “The modern view solves this paradox by declaring that in the second case [the mixing of similar gases] there is no real diffusion, because exchange between the particles is not a real event ...” Perhaps following his lead, Huang (p.154) lays out the canonical opinion:

It is not possible to understand classically why we must divide ... by  $N!$  to obtain the correct counting of states. The reason is inherently quantum mechanical. Quantum mechanically, atoms are inherently indistinguishable in the following sense: A state of the gas is described by an  $N$ -particle wave function, which is either symmetric or antisymmetric with respect to the interchange of any two particles. A permutation of the particles can at most change the wave function by a sign, and it does not produce a new state of the system. Hence we should divide ... by  $N!$ . ... It is something we must append to classical mechanics in order to get the right answers.



The holes in this explanation are not obvious, and Schrödinger’s understanding has been the common belief among physicists ever since quantum mechanics entered the stage. According to this common opinion, the Anti-Haecceitistic nature of thermodynamics is an expression of the quantum mechanical nature of gas particles. Since both quantum mechanics and thermodynamics are fundamentally Anti-Haecceitistic, and both are methods for describing the same set of particles, it is very difficult to escape the assumption that one Anti-Haecceitism leads to the other. This would be a very interesting fact. It would mean that quantum mechanics has a much more obvious effect than usually recognized, as Münster[11] wrote, “Classical statistics thus leads to a contradiction with experience even in the range in which quantum effects in the proper sense can be completely neglected.” Also, it would mean that the first hint of quantum mechanics actually appeared in the mid-nineteenth century, in the very foundations of thermodynamics as laid by Boltzmann and Gibbs. This flawed belief is still widely held and widely published to this day (see for example Emch and Liu (2002) [12]), and so the second half of this paper is dedicated to disproving this unfortunately canonical claim.

## 5 A Tale of Different Perspectives

Imagine two scientists, Scientist A and Scientist B. They both study a certain ideal gas, called “ $\phi$ ”. In the course of his research, Scientist B stumbles upon two materials that relate to  $\phi$  in a strange way: If he makes a thin sheet of one of the materials, some of the  $\phi$  particles can pass through, but others cannot. And if he makes a thin sheet of the other material, only the left-over  $\phi$  particles can pass through. Thus, these new materials show Scientist B that there are two types of  $\phi$  (call them  $\phi_1$  and  $\phi_2$ ). He can calculate the entropy of mixing  $\phi_1$  and  $\phi_2$  by using the new materials to construct a reversible mixing process first envisioned by t’Hoff, as in figure 4. The

two different membranes act as pistons to gradually allow the gases to mix. (This reversible mixing apparatus is called a “van’t Hoff vessel”, after Jacobus van’t Hoff, the first Nobel laureate in chemistry[13].) The work  $L$  produced through the moving of a single piston is

$$L_{\phi_1} = \int_{V/2}^V P_{\phi_1} dV = N_{\phi_1} RT \ln\left(\frac{V}{V/2}\right) = N_{\phi_1} RT \ln(2) \quad (10)$$

where  $P_{\phi_1}$  is the partial pressure of gas  $\phi_1$ . When this expression is added to the work available from the second membrane, the total work becomes  $NRT \ln 2$ . Using the relation  $\Delta S = L/T$  we arrive at the entropy change, which is the same value as we found earlier in the Gibbs Paradox.

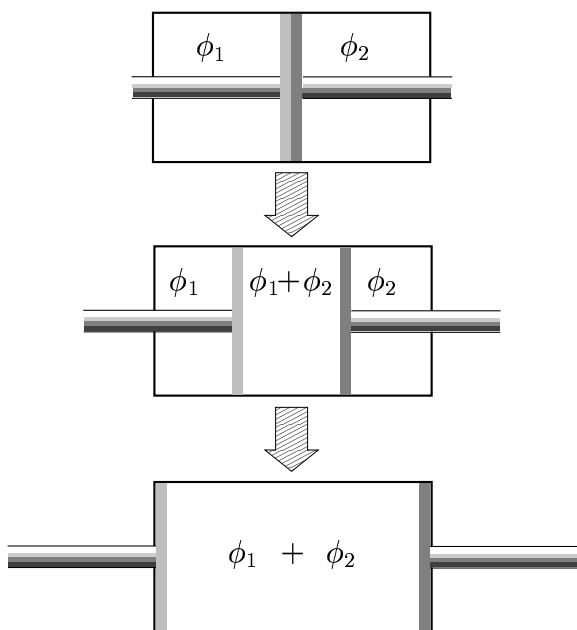


Figure 4: A reversible mixing process.

Now imagine the world from Scientist A’s point of view. She has no special materials with which to manipulate the two gases, and remains ignorant of the mixed nature of her usual samples. If Scientist B sends her two samples, one of pure  $\phi_1$  and one of pure  $\phi_2$ , she has no way of recognizing that they are two different gases. Consequently, if she mixes the two, she will have no way of recognizing any change in entropy, because there will be no way of producing work without the special materials.

Thus the two scientists can observe exactly the same process, down the path of each individual particle, and yet disagree as to the change in entropy. At first one might think that Scientist B has been able to correctly measure the entropy, whereas Scientist A is ignorant of some important facts. It is unquestionably true that Scientist B has taken more into account

in his experiments. However, imagine a Scientist C, whose research has proceeded well beyond even Scientist B's. Scientist C has discovered four more materials that differentiate  $\phi$  even more finely; the materials can filter  $\phi_1$  into  $\phi_{1\alpha}$  and  $\phi_{1\beta}$  and filter  $\phi_2$  into  $\phi_{2\alpha}$  and  $\phi_{2\beta}$ . Changing one's opinion to say that Scientist C is clearly correct might now appear as a rush to judgment. What guarantee can one have that the study has ended with Scientist C, and that no further discoveries await?

Scientist A takes several things into account when calculating the entropy of mixing  $\phi_1$  and  $\phi_2$ . She measures (or at least here we assume she measures) some sort of "amount" of each gas, the temperatures, the volumes, and maybe the pressures. She also observes in some way that both samples satisfy the criteria of " $\phi$ -ness"; the two samples are both samples of  $\phi$ , not of some other gas. Her measured entropy, then, is a function of all these things, and can be written as  $S = S(T, V, P, N, \phi\text{-ness})$ . As with all ideal gases, pressure is a function of temperature and volume, so at its simplest, she could express her function as  $S = S(T, V, N, \phi\text{-ness})$ .

Scientist B takes all these things into account, plus the added characteristic of " $\phi_1$ - $\phi_2$ -ness". Thus, his entropy function would be as  $S = S(T, V, N, \phi\text{-ness}, \phi_1\text{-}\phi_2\text{-ness})$ . To generalize, Scientist A and Scientist B describe entropy in terms of different observables and different numbers of observables. No scientist can possibly find a contradiction in his own work, as long as his observations are restricted to the observables of his equation.

## 6 The Nature of Entropy

Now we have reached the heart of the matter. If one understands the true nature of entropy, it should seem quite reasonable for multiple entropy equations to exist, each based on its own unique set of variables. There is no "complete" set of variables that a "perfect" observer would take into account. All that a correct definition of

entropy requires is 1) a clearly defined set of observables and 2) a description of the effect variations in those observables have on the “number of ways”  $W$ . In this way, entropy is a measure of the specificity of the observation - “How many states are possible, knowing what we know?” More precisely, entropy quantifies the amount of information contained in a given observation. This understanding of entropy is due in large part to Shannons’s[14] development of information theory in the mid-twentieth century, but glimpses of the close relation between information and entropy date back to Boltzmann[14].

For a typical macroscopic sample, there are on the order of  $10^{23}$  particles. When making a thermodynamic measurement, one describes the state of these  $10^{23}$  pieces using only a few numbers. Clearly, there is a vast amount of information contained in the system that is not represented in our description. One could choose the manner of measurement in such a way that more or less information about the system was represented, and there is no particular manner of measurement that could be considered standard in any way. If one chooses, the system could be described using only a single macroscopic variable, or on the other extreme one could measure a multitude of characteristics for each individual particle (or any level of precision in between). The use of an entropy equation is to relate such a set of measurements to an amount of information.

There is a confusion between two types of information: the information contained in a system and the information contained in a set of observations. Entropy describes only the latter, measured, type. There is a great reluctance among physicists to believe that such a non-physical thing as observation can play such a necessary role in the descriptions of physics. Scientists like Schrödinger tried to form thermodynamics around the physical sort of information, that kind which exists with or without human interference. But framing entropy in the language of information while at the same time denying the defining importance of observation should itself be a glaring

disconnect.

This observational understanding of entropy is interesting in several different ways. First, if entropy measures something about observations themselves, then *of course* entropy should be different according to which observables are in use, and *of course* there is no “correct” set of observables. Secondly, entropy is no longer in the realm of physical reality. It remains just as precisely quantifiable as time, space, energy, etc., but becomes a measure of something that cannot exist without observation.

This gives us a new perspective on the story of the two scientists. Now they can both be considered correct, even though they disagree. It is perfectly reasonable for the two scientists to calculate differing entropy values, because they are observing the system in different ways, observing different characteristics of the system. If Scientist A started using the special materials she would also have to start using the equation that went along with those tools of observation, and that should come as no surprise.

## 7 The resolution of the Haeccetistic question

We have now traded in our first conception of entropy as a function of physical parameters for a second conception of entropy as a function of *observations of* physical parameters. This improved understanding will make the Anti-Haeccetism of entropy seem eminently reasonable. Entropy is still an exclusively Anti-Haeccetistic description, but we have changed what is being described. Instead of Anti-Haeccetistically describing reality, entropy is Anti-Haeccetistically describing our observations.

In other words, our entropy equations now mean that human observations are in some way Anti-Haeccetistic. We can see what this means by thinking back to the example of the two cue balls. We are not able to observe any sort of difference between ball A hitting ball B and vice-versa. No measurement that we could possibly make would allow us to know which of those two possibilities took place. We are able

to consider the two possibilities, but to say that they are in some way different from each other would be to make an unevidenced claim.

With the observational nature of entropy in mind, we should stop trying to use entropy to discover whether switching two identical particles is a real physical event or not. Entropy will answer questions only about whether something is an observable event or not; the event's physical reality will have to remain unknown. Anti-Haecceitism, again, is the belief that switching two identical particles is not a real change. But entropy seems to not claim anything at all about reality anymore. With our new understanding, it seems entropy equations claim only that switching two identical things is simply not an observable change. *Of course* this is true; this is the meaning of the word "identical".

This leaves us with the question of Haecceitism or Anti-Haecceitism unresolved, then. Thermodynamics uses Anti-Haecceitistic counting, but only makes claims of our observations, not of the real world. Through studying entropy, we learn nothing about the basic nature of the world that was not already in our Newtonian understanding. Haecceitism is a metaphysical claim, a claim about something that we can by definition never see.

## 8 The resolution of the Gibbs Paradox

Now we return to the original paradox that got us started on this train of thought: Why does the mixing of two different gases result in a change of entropy, whereas the mixing of two samples of the same gas leaves the entropy unchanged? If we think of the number of observably different ways, instead of the number of imaginable ways, the paradox disappears. Whether they are mixed or unmixed, the number of observably different ways of arranging the particles of two samples of indistinguishable gases remains the same. The number of observably different ways of arranging the

particles of two different gases increases when the gases are allowed to mix.

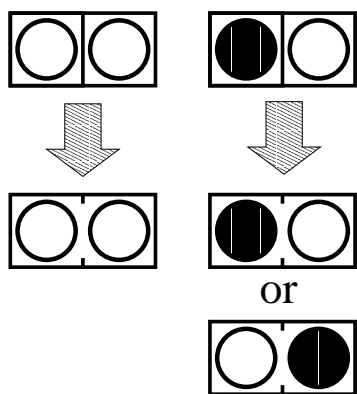


Figure 5: The simplest Gibbs Paradox.

All the complexities of the Gibbs Paradox can be simplified down to considering two individual particles. Imagine setting up the Gibbs Paradox where each initial gas sample is composed of only a single particle, as in figure 5. As before, we think of the system as having set “spaces” where no two particles can occupy the same space. Before mixing, then, the number of ways for either system is one. After the barrier has been removed, the number of ways for the system of two different gases is twice the number of ways for the simpler system.

In other words, the number of distinguishable ways to arrange the system remains unchanged if the samples are observationally the same. The number of distinguishable ways clearly increases if the samples are observationally different.

But where is the boundary between two particles being “the same” and being “different”? This is really the crux of the paradox. According to Schrödinger’s understanding, the boundary is a clear-cut physical one: fundamental particles (and consequently conglomerations such as atoms and molecules) have certain properties, and these properties are either all precisely the same or at least one property is different. On the other hand, the observational nature of entropy forces us to place the boundary between two gases being “the same” or “different” on a solely observational footing: Two particles are different if a difference is observed; two particles are the same if no difference is observed.

Just because there is no observed difference, this does not at all mean that there is no physical difference. In fact, there is room in our observations to miss quite large differences between particles. Consider the example of isotopes. Observing the dif-

ference between two isotopes is a relatively difficult task, and was not accomplished until the twentieth century. But even though isotopes interact chemically in an indistinguishable manner, the actual physical difference between two isotopes is of the same order as the difference between two elements (isotopes differ in neutron number; elements differ in proton number). Atoms of two different isotopes of the same element are fundamentally different objects. But if our observations are limited to purely chemical characteristics, the mixing of a sample of  $O^{16}$  with  $O^{17}$  could only be described as resulting in zero entropy change because no work could be produced through the mixing. The difference between the two types of particles would play no role in our chemical observations, and would rightfully be ignored. Notice, though, that there is a very clear difference between the two and that switching an  $O^{16}$  particle with an  $O^{17}$  particle is a real physical event, just not an observable event in the present context.

As a more exaggerated example consider a large biological molecule such as Hemoglobin. Each Hemoglobin molecule is composed of 4,516 hydrogen atoms, 2,954 carbon atoms, 806 oxygen atoms, 780 nitrogen atoms, 12 sulfur atoms, and 4 iron atoms, always arranged in exactly the same manner. Each of these elements has several naturally occurring isotopes, which means that even though the atoms of every hemoglobin molecule are arranged in exactly the same fashion, finding two molecules that are identical down to the nuclear level would be practically impossible. Roald Hoffman calculates that in a drop of blood, which would contain about  $10^{17}$  hemoglobin molecules, no two molecules will be truly indistinguishable[15]. But under almost all circumstances we can easily forget about these unobserved differences. Nuclear structure is simply not one of the variables that affects our observations of biological processes. It is a difference between *indististinguishable* and *indistinguished* that we are here emphasizing.

In retrospect, Gibbs seems to have carefully worded his original exposition of the



paradox in a way that reveals his own understanding of the observational nature of entropy (emphasis added):

We call the energy and entropy of the [similar] gas-masses when mixed the same as when they were unmixed, because we do not *recognize* any difference in the substance of the two masses. So when gases of different kinds are mixed, if we ask what changes in external bodies are necessary to bring the system to its original state, we do not mean a state in which each particle shall occupy more or less exactly the same position as at some previous epoch, but only a state which shall be undistinguishable from the previous one in its *sensible* properties. It is to states of systems thus incompletely defined that the problems of thermodynamics relate.

It is not at all surprising to find such a clear explanation in the work of Gibbs. What is surprising is that the paradox has confused so many for so long despite Gibbs' correct resolution of it at the paradox's very inception.

The correct understanding was succinctly phrased in the words of van Kampen, "The question is not whether they are identical in the eye of God, but merely in the eye of the beholder."

## 9 Conclusion

We have made the argument that entropy is an Anti-Haecceitistic description, and that after realizing this, the Gibbs Paradox is easily resolved. A deeper truth is that that any physical theory *must* be Anti-Haecceitistic. If the claim is made that the world is a different place upon switching two things, the claim must be supported with a way to measure that difference. If there is such a way to measure that difference then the things were, by definition, not identical. If no difference is measured then the physicist has no right to claim that the world is a different place. Switching to

statistical descriptions, as in thermodynamics, cannot eliminate such fundamental truths. In this way, a physical theory is bound by far stricter constraints than our imaginations. We can easily imagine two identical things being switched, but the fact that such a thing is unmeasurable makes it unmentionable in a physical description.

Even though all of physics would be more fundamentally and accurately posited in an Anti-Haecceitistic manner, inserting the non-physical concept of “thisness” will usually not contradict any observation. However, when calculating an amount of measured information, such an unmeasured thing as “thisness” must be discarded. Interpretation of our observations frequently inserts information that was not really observed. In a way, we form the observation into a story, giving each piece an identity and a role to play. This inserted information can help us make sense of what we see but because it is not actually seen its non-physical nature should come as no surprise. The unique information-quantifying character of entropy is the reason entropy does not adhere to our common sense notions of how an observable should behave, and the reason why the Gibbs Paradox might seem paradoxical. But if the observational, and therefore Anti-Haecceitistic, nature of physics is fully understood, there is no paradox.

Entropy differs from all other measures that physicists normally use in that instead of simply repeating the information of an observation, *entropy quantifies the amount of information observed*. Entropy is not information about the system in question; an entropy value itself tells us nothing about the energy, volume, or chemical composition of the system. Entropy describes only our description; it measures only our measurements. It is a way to numerically answer the question “How much do we know?”

It is hard to find a person who does not believe that the laws of physics describe reality, or at least that they are an approximation thereof. It is the common conception that Newton’s laws describe something of reality quite well, Einstein’s theories

even better, and so on. What the Gibbs Paradox forces us to consider is that there is always an impenetrable barrier between reality (as we may imagine it or not) and our physical descriptions. Physics is a mathematical description of human observation, nothing more.

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- [8] In order to avoid the contradiction between equations 8 and 9, van Kampen, Huggett, and Albert take a different path than the one here followed. They each claim that the entropy change of an  $N$ -varying process cannot be defined, and entropy changes should only be spoken of for processes in which  $N$  is held

constant. But in fact an  $N$ -dependent description of entropy is necessary in order to characterize a great many processes. For example, one can imagine a selectively permeable container surrounded by an infinite bath of various gases. The flow of particles into and out of the container is best described using an  $N$ -dependent entropy.

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