Gibbs' Paradox and the Connection of an Ideal Gas to Quantum Mechanics

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Introduction

One of the most mysterious fields in the 19th century was thermodynamics, or the way that heat is transferred between objects. In fact, attempts to describe thermodynamics led to the discovery of quantum mechanics. It took great minds, such as Albert Einstein and Max Planck to make the significant leap of defining light to be made of photons, which is considered to be the birth of quantum mechanics. However, there were some theories from previous physicists that suggested something was wrong with the "classical" models of physics.

What I mean by this is that the physical models developed by Galileo and Newton to describe the motion of large objects could not be simply scaled down to describe gas particles. The behavior of gases was one of the primary focuses of thermodynamics. The work of two brilliant physicists, James Clerk Maxwell and Ludwig Boltzmann, resulted in what is known as the kinetic theory of gases. In this theory, a gas is treated as a collection of particles that act like tiny hard spheres. In the gas, the spheres are spread far enough apart that they rarely collide with each other. This model works very well for simple gases that are made up of single atoms as opposed to molecules. However, the model is not perfect. There is a flaw, discovered by Josiah Willard Gibbs related to the expression of entropy of an ideal gas. The solution to this problem suggests that the classical model of small particles is not entirely correct.

The Definition of Entropy

Entropy itself is a difficult concept to grasp. You may have heard physicists say things like entropy describes disorder and entropy is always increasing without really understanding what that means. Entropy is remarkably simple, powerful, and beautiful. It has not always been this way, but the profound insight of Ludwig Boltzmann has allowed physicists access to this powerful tool for predicting the behavior of large numbers of particles.

Before Boltzmann, entropy was as mysterious to scientists as it could possibly be. At first, it was a simple mathematical tool used to predict the energy output of engines. Its definition was as follows:

$$dS = \frac{dQ}{T} \tag{1}$$

In other words, the increase in entropy, dS, is equal to the amount of energy in the form of heat going into an object or fluid, dQ, divided by its temperature, T. From this definition alone, you might be able to see why entropy is always increasing. Heat always travels from a region of high temperature to low temperature. The amount of heat leaving one material is equal to the amount of heat entering the other. The entropy does drop when heat leaves an object. However, since the temperature of the object losing energy is high, the change in entropy is low. The object gaining energy has a lower temperature, so its entropy increases more rapidly. That means exchange of energy due to a temperature difference will always result in a total increase in entropy. Even with this definition though, physicists did not understand what entropy really meant.

As stated earlier, it was the brilliance of Boltzmann that unlocked the mysteries of entropy. A single simple equation, which is engraved on Boltzmann's tombstone in Vienna, is the key to all of thermodynamics:

$$S = k \log W \tag{2}$$

In this equation, S is the total entropy, k is just a constant known as Boltzmann's constant, and W is the number of "accessible states." (The log term is base e. I did not use ln since Eq. (2) is exactly how it appears on Boltzmann's tombstone.)

Let me explain what I mean by accessible states. No matter how many particles you are looking at, all of the energy is conserved. You may think that in most scenarios, you lose energy to things like friction. What is actually happening in that case is that friction is giving energy to the material being rubbed against. When you rub your hands together,

they become warmer. The energy is never really lost. When considering what is called a system, one can assume that the particles in the system only interact with each other, so no energy will leave the system. This means, the energy of the system must remain constant. There are only certain ways that particles can behave while still conserving energy. Each of these possible behaviors is called an accessible state. For example, imagine you have two balls that are allowed to interact with each other, but combined will always have the same energy. Now if those balls start with a certain non-zero energy, it is possible for one ball to have all of the energy and the other ball to have none. It is also possible for both balls to have half of the energy. These are examples of accessible states. As long as the two balls have the correct total energy, they are in an accessible state. The case that both balls have no energy is not possible in this situation, so that is not an accessible state. This process gets increasingly complex as the number of particles gets higher, but entropy allows physicists to handle that complexity.

Entropy allows us to do many wonderful things such as give a concrete definition for temperature and predict the distribution of energy among particles at a given temperature. However, the most important thing to keep in mind is that Equations (1) and (2) describe the same thing.

Classical Entropy of an Ideal Gas

Counting the number of accessible states for a very large number of particles can appear to be a rather daunting task. Thanks to methods developed by Boltzmann though, it can be done. Using a purely classical model that a gas of N different particles takes up a volume of V and has a temperature T, the following expression for entropy can be derived:

$$S_{classical} = k \ln W_{classical} = Nk[\ln V + \frac{3}{2} \ln T + \sigma] \tag{3}$$

The quantity σ is just a constant that depends on how on discretized space in order to get an integer number of accessible states. However, there is a problem with this expression for entropy. When considering two systems of equal size and the same temperature, the total entropy would just be the sum of each system's entropy.

$$S_{total} = 2S_{separate} = 2Nk[\ln V + \frac{3}{2} \ln T + \sigma] \tag{4}$$

However, when considering a single combined system with twice as many particles and twice as much volume, the following expression for entropy is obtained.

$$S_{combined} = 2Nk[\ln(2V) + \frac{3}{2}\ln T + \sigma] \tag{5}$$

$$= 2Nk[\ln V + \frac{3}{2}\ln T + \sigma] + 2Nk\ln 2 \tag{6}$$

$$= 2S_{separate} + 2Nk\ln 2 \tag{7}$$

The two expressions for entropy are not the same, but they should be. The act of bringing two systems together and allowing them to mix should not increase the entropy. There is no heat added to the system, so $dQ = 0$, and by Eq. (1), S should not change. However, when the two systems are allowed to mix it seems that the total number of accessible states goes up, increasing the entropy. It is not possible for both of these statements to be true because entropy should be describing the same thing.

The Solution to Gibbs' Paradox

This problem was first noticed by Josiah Willard Gibbs. He also proposed a solution which seemed radical at the time. In order to understand Gibbs' solution, first one has to realize why W goes up when combining two systems. The explanation is relatively simple. When two systems are placed in contact with each other, see Fig. 1, and allowed to mix, particles in System 2 are now allowed to be located in V_1 and vice versa. This increases the number of accessible states for each particle by a factor of two.

$$W_{mixing} = W_{no\ mixing}(2)^{2N} \tag{8}$$

$$S_{mixing} = S_{no\ mixing} + 2Nk\ln 2 \tag{9}$$

Equation (9) matches with the result that we got in Eq. (7). In other words, this result makes perfect sense, but it is still not consistent with Eq. (1).

Gibbs proposed the following solution: it does not matter if a certain particle within V_1 was initially from System 1 or System 2. They are the exact same kinds of particles, so they are indistinguishable to us. Not only are they indistinguishable to us, but they are also indistinguishable to nature. This was a deeply unsettling statement at the time. This was the point where classical mechanics failed to describe what was happening. In classical mechanics, if each atom of gas behaved like a ball, an experimenter could follow an atom

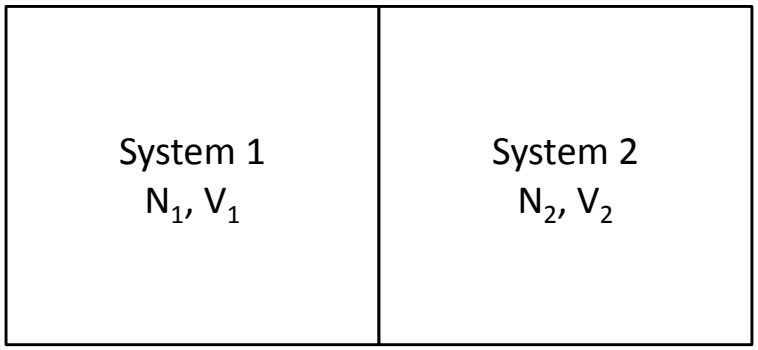

Figure 1: When two systems are combined, V_1 becomes accessible to particles in N_2.

around and be able to tell it apart from the rest. However, Gibbs was saying that the gas particles did not interact with each other the same way that large balls would. One could not point at an atom and say "that atom was in System 1 at that specific location when the two systems were combined." There is no way to tell. The only correct statement that can be made is "that's an atom."

This means that the number of accessible states drops dramatically. The classical model used to derive Eq. (3) assumed that we knew which atom what where. In that case, we counted each state $N!$ times as we interchanged the atoms. The correct number of accessible states for a system of indistinguishable particles is the old number divided by $N!$. Using Stirling's approximation for large N, $\ln N! \approx N \ln N - N$, we get the following expression for entropy.

$$S = k \ln \left(\frac{W_{classical}}{N!} \right) = Nk[\ln V + \frac{3}{2} \ln T + \sigma] - k \ln N! \tag{10}$$

$$= Nk[\ln V + \frac{3}{2} \ln T + \sigma] - Nk \ln N + Nk \tag{11}$$

$$= Nk[\ln \frac{V}{N} + \frac{3}{2} \ln T + \sigma + 1] \tag{12}$$

The new expression for entropy in Eq. (12) now gives the same result if you multiply it by two or substitute $2N$ and $2V$ for N and V.

The Implications of Indistinguishable Particles

This explanation of indistinguishableness leads to some rather interesting quantum mechanics results. Without these results, we could not exist. In particular, it describes the approach we take towards understanding fermions and bosons, the two types of particles that can exist.

The main difference between these particles is the way that their wave functions behave when you switch the states of two particles. A wave function can be used to describe the collective behavior of several particles. Consider the behavior of two particles that are described by their quantum numbers, n_1 and n_2. Switching the two quantum numbers should have no effect on the configuration of the system since the two particles are indistinguishable. The probability of finding a system in a certain configuration is proportional to the wave function squared, so a negative wave function behaves the same way as a positive wave function. That means both of the following equations are indistinguishable ways to quantum numbers can be changed.

$$\Psi(n_1, n_2) = -\Psi(n_2, n_1) \tag{13}$$

$$\Psi(n_1, n_2) = \Psi(n_2, n_1) \tag{14}$$

Fermions behave like Eq. (13), and bosons behave like Eq. (14). This actually causes large differences in the ways that fermions and bosons can behave.

Consider two particles with the same quantum number n. If you substituted that into Eq. 13, you would get $\Psi(n, n) = -\Psi(n, n)$, which is not possible unless the wave function is zero everywhere. This means that two existing fermions can never have the same quantum number. Fermions include particles like electrons, protons, and neutrons. These are the particles that make up most of the matter around us. The fact that these particles cannot have the same quantum numbers describes why the particles cannot exist in the same place. It is why objects have volume. This is why electrons gather in a cloud around an atom instead of collapsing into a singularity.

On the other hand, bosons do not have that problem. Two bosons can get away with being in the same place. When that happens, their separate wave functions meld together and the particles behave collectively. One common example of a boson is a photon. Photons can pile up on each other in the same location. It is this fact that leads to the interesting phenomenon known as black body radiation, which was a puzzle for some of the greatest minds in physics. The solution led to the discovery of quantum mechanics.