What is entropy? From a microscopic point of view

The purpose of introducing you to combination was to be able to explain entropy to you. In this article, I will explain what entropy is from the viewpoint of statistical mechanics.

I first learned about entropy from the physics textbook *Fundamentals of Physics*. Here is an excerpt from this book that gives you an intuitive idea of what the second law of thermodynamics is :

> "...Time also has direction: some things happen in a certain sequence and could never happen on their own in a reverse sequence. As an example, an accidentally dropped egg splatters in a cup. The reverse process, a splattered egg re-forming into a whole egg and jumping up to an outstretched hand, will never happen on its own. But why not? Why can't that process be reversed, like a videotape run backward? What in the world gives direction to time?"[1]

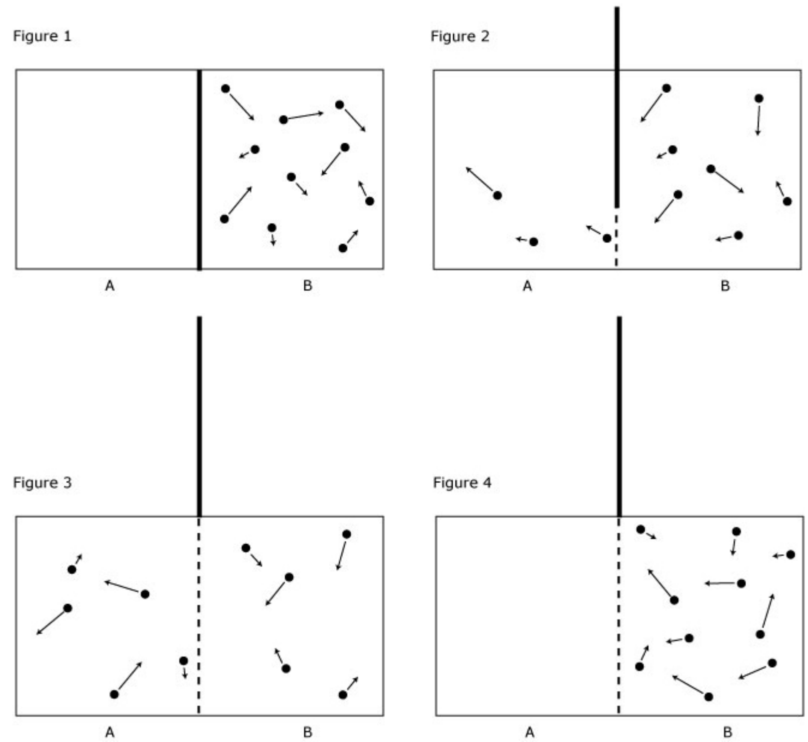
The second law of thermodynamics says that entropy always increases. In this case, a splattered egg has more entropy than a whole egg. Therefore, the reverse process never happens. Another example would be pouring milk into tea. The sum of the entropy of the milk, by itself, and the entropy of the tea, by itself, is less than the entropy of the tea and milk mixed together. You can easily mix milk and tea but you can't easily perform the reverse process. The more disordered a state is the higher its entropy. A splattered egg is more disordered than a whole egg. Entropy measures how much a state is in disorder.

Now, on with my explanation. Consider the arrangements of moving molecules in side-by-side chambers, some of which have their separating wall partially or completely removed, in the following four figures:

As in figure 1, let's consider the case in which all the ten molecules are in compartment B. Then, as in figure 2, suppose that you open the door that divides compartment A and compartment B. You see here that some of the molecules are coming into compartment A from compartment B. After a finite amount of time, the molecules are equally distributed between A and B, as in figure 3.

This process seems very natural. The molecules want to spread out instead of being stuck in compartment B. But what about the naturalness or likelihood of reverse process? Could it be possible that all the ten molecules from figure 3 rearrange themselves into compartment B only, as in figure 4, after a short time has elapsed?

[1] From the opening paragraph of the chapter "Entropy and the second law of thermodynamics" in Fundamentals of Physics by Halliday, Resnick, and Walker.



I believe that your intuition tells you that this is quite unlikely. Let's see how we can support this intuition with mathematical language.

If each of the ten molecules have access to the full combined chamber, each has a $\frac{1}{2}$ probability of being on the B side. Therefore, the probability that all the ten molecules are in the compartment B at the same time as in figure 4 is very small, given by $(\frac{1}{2})^{10}$, which is slightly less than 0.1%.

Expressing this in the language of physics, we say that nature always allows the entropy in an isolated system to increase, but never to decrease. In our illustration, the entropy of the configuration in figure 3 is bigger than that of figure 1 or figure 4. Therefore, the transition from figure 1 to figure 3 is allowed, while the transition from figure 3 to figure 4 is forbidden. If we make an analogy using the quote from "Fundamentals of Physics," figure 3 corresponds to a splattered egg, while figure 4 or figure 1 corresponds to the whole egg. Changes between the two are unidirectional because the second law of thermodynamics states that entropy always increases.

How can we relate the probability we calculated a moment ago to entropy? We said that the configuration in figure 3 is much more likely than the configuration in figure 4. The relationship between probability and entropy should be such that the bigger the probability is, the bigger the entropy.

Let's try out the following concrete definition – known as Boltzmann's equation, after the

19th century Austrian physicist who first proposed it and on whose tomb it is engraved:

$$S = k \ln W \tag{1}$$

Here, k is the Boltzmann's constant and W is the number of microstates consistent with a given macrostate. Let me explain what the number of microstates means using our previous examples. Lets say that you are arranging the ten molecules to look like each of the figures. Out of ten total molecules, there is only one way to choose ten molecules to be in the compartment B, as in figure 1 or figure 4. Therefore, W for figure 1 or figure 4 is equal to 1 ($\binom{10}{10} = 1$), and in this case, since $\ln 1$ is zero, S is zero.

For figure 3, in contrast, there are many possible arrangements, or microstates, that correspond to that configuration. There are $\binom{10}{5}$ or 252 ways to choose 5 molecules out of 10 molecules to be on the A side (with the remaining 5 left to be on the B side). Therefore, W is given by 252, and the entropy is given by $k \ln 252$, which is approximately $5.53k$. So, we indeed see that the entropy of the configuration in figure 3 is bigger than the entropy of the configuration in figure 1 or figure 4 as expected. The more microstates a configuration (a "system") has, the more likely the system is to occur (to be "occupied"), and the more entropy it has.

However, you may argue that there still exists a small probability for all the ten molecules to rearrange themselves as in figure 4 after a finite amount of time. This is true, but if instead of 10 there are 10^{23} molecules to be considered, then probabilistically speaking, we will have to wait more than $10^{1000000000}$ years for all these molecules to rearrange themselves as in figure 4. Notice that our universe is only around 10^{10} years old and that 10^{23} is not really a big number of molecules to consider given that just 1 liter of air contains approximately this many molecules. In other words, there is such a tiny probability of something similar to figure 4 happening that we will never live to see such an occurrence in our lifetime; the entropy "always" increases.

Summary

- $S = k \ln W$, where S is the entropy, k is the Boltzmann's constant and W is the number of microstates consistent with a given macrostate.
- The entropy "always" increases; the probability that entropy will decrease is negligible.