3 Entropy, microstates, macrostates, and the second law

- We describe a thermodynamic system using macrostates (volume, temperature, energy, number of particles)

- A complete (classical mechanics) description would specify the position and velocity of every single particle which is called the microstate. However, in a solid material this is not possible to do.

- Entropy tells us how much information we throw away when we use a macrostate. $S = k \ln \Omega$.

- Entropy is related to the probability of the macrostate; the highest entropy macrostate is the most probable by a very large margin.

- The above leads to the second law of thermodynamics: $S_f - S_i \geq 0$ for all processes, where S_i is the initial entropy and S_f is the final entropy.

3.1 Microstates and macrostates

We have already discussed macrostate variables in this course. They are collective quantities about an object, such as the total volume, internal energy, pressure, and temperature. On the other hand, to specify the **microstates** of a system, one needs to specify all the positions and velocities of all the atoms in the object. Obviously this is far too much information to track for any real system explicitly. Instead, we just want to keep count of how much information we lose by using macrostate variables only. Entropy is a measure of the information that we lose when we describe the system in terms of macrostate variables.

3.2 Definition of entropy

For example, suppose we describe our system in terms of the internal energy, volume, and number of particles U, V, N. Then the number of microstates for that value of U, V, N is called $\Omega(U, V, N)$, and the entropy is defined[1] as

$$S(U, V, N) = k_B \ln \Omega(U, V, N). \tag{1}$$

(aside) You might reasonably ask why this particular definition. Entropy is additive with this definition, while Ω is multiplicative (two dice have 36 total states, not 6). By making it ln instead of some other base, the definitions of pressure and temperature which we will see later will work better. Otherwise there would be stray values around when derivatives and integrals are taken. So entropy is defined this way so that it has nice properties that we will explore throughout this course.

3.3 Entropy of flipping coins

Let's examine a toy system to get a handle on the concept of entropy. We all have an intuitive understanding of entropy already. For example, if you walked into a room and someone told you that they flipped a coin 1000 times and got 1000 heads, you would be understandably skeptical. However, if they said they got 522 heads, you might believe them.[2] This is an intuitive understanding of entropy! There are many more ways that one could get 522 heads in 1000 flips than 1000 heads in 1000 flips, and so it is more likely, and therefore higher entropy. Let's now analyze this situation in the language of thermodynamics.

First things first, we should identify the microstates and macrostates. For a sequence of N coin flips, the microstate is the particular sequence. For example, for $N = 5$, the sequence HHTHT is a different microstate than the sequence HTHHT, even though they have the same number of heads. The macrostate in our case will be the *fraction* of flips that came up heads. Both of the above microstates "belong" to the same macrostate of $N_H = 3$, $N = 5$, or $F_H = 3/5$.

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[1]Technically this is the statistical mechanics definition of entropy. Next time we will get to the thermodynamical definition of entropy. I think that the statistical mechanics definition makes a lot more sense!

[2]Other than questioning why they are flipping coins in a room by themselves!
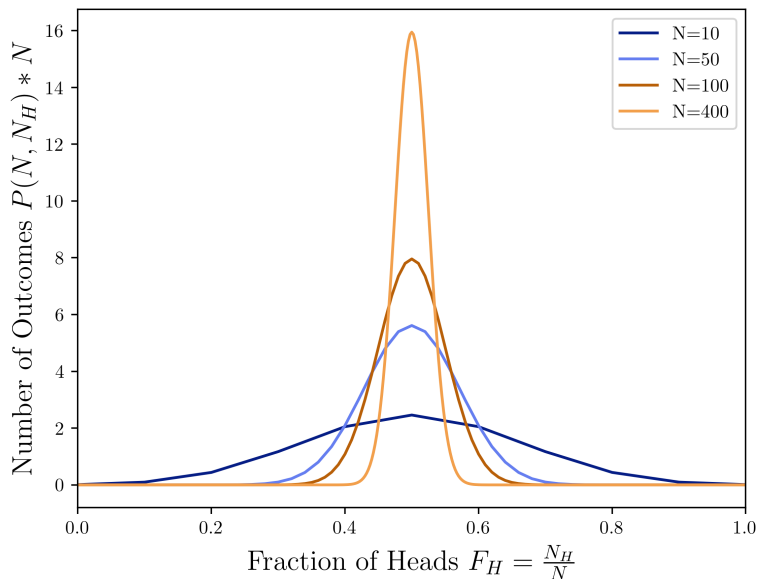
Figure 1: The probability of getting K outcomes out of N total events is given by $P(N, K) = \binom{N}{N_H} P^K (1 - P)^{N-K}$, where P is the probability of K. For our coin toss the odds of getting a heads is 50%, therefore $P = \frac{1}{2}$ and we write $K = N_H$. The plot shows $P(N, N_H)$ vs $F_T = N_H/N$ for different values of N; the distribution of results gets closer and closer to the highest probability result as N increases.

To construct the entropy $S(N_H, N)$, we need to be able to compute $\Omega(N_H, N)$, how many ways one could flip N_H heads with N flips. This is given by the binomial coefficient

$$\Omega(N_H, N) = \binom{N}{N_H} = \frac{N!}{N_H!(N - N_H)!}. \tag{2}$$

Often this function is available on calculators as a "choose" function. It is also available in Python as `scipy.special.binom`.

In Fig 3.3, we show the number of coin toss sequences (microstates) with a given fraction of heads F_H (macrostate). The number of outcomes with F_H near 0.5 grows very quickly as N increases. As $N \to \infty$, with almost probability 1, the fraction of heads is 0.5. Therefore, for very large numbers of flips, the most likely macrostate is just the one that occurs.

Some physical systems actually do act as if they are coin flips. In the case of magnets, the magnetism is given by very small magnetic moments called spins[3] which align at low temperatures to create ferromagnets. In this case, whether the spin is pointed up or down is equivalent to the coin flips.

3.4 Entropy of free particles in a volume

Consider the number of microstates $\Omega(U, V, 1)$ of a single atom in a volume V and total energy U. The atom could be in any location in the volume, and have velocity pointing in an direction in 3D. We will not try to compute Ω exactly, but for one atom, it is *proportional* to the volume: $\Omega(U, V, 1) = g(U, 1)V$, where g is an unknown function of U and N. Now, if there are N particles that we can approximate as if they don't interact (i.e., an ideal gas!),

$$\Omega(U, V, N) = (g(U, N)V)^N \tag{3}$$

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[3]We will explore this later in the Boltzmann sections!

and
$$S(U, V, N) = k \ln \Omega = Nk \ln V + Nk \ln g. \tag{4}$$

3.5 Second law of thermodynamics

Given the definition of entropy in terms of the number of states, the second law becomes almost trivial. It simply says that once there are many particles in a system, the most likely value of macrostate variables is the one that happens. This is not because the other values are impossible (they are technically not), but because the most likely values are **so much more likely** that it is effectively impossible to see the unlikely occurrence. Imagine flipping 10^{23} coins; the fraction $f_H = N_H/N$ is extremely unlikely to be very far from 0.5. Thus, the **second law of thermodynamics**: in an isolated system, the entropy always stays the same or increases, or
$$S_f - S_i \geq 0, \tag{5}$$
where S_f is the final entropy and S_i is the initial entropy.

3.6 Internal equilibrium

For almost all cases in this course (we will let you know if this is not the case), we will consider systems internally in equilibrium. Internal equilibrium means that for the given macrostate variables (often U, V, N for example) entropy has been maximized already, keeping those macrostate variables fixed. That means that the objects, if left to their own devices, will not spontaneously undergo any changes. Most processes that we will consider in this course will be *quasistatic* processes, which means that the processes are slow enough that objects are in internal equilibrium the entire time. If a system is in internal equilibrium, we can use all of our equilibrium relations like the ideal gas law.