Microstates

Nathan Solomon

October 14, 2022

1 Macrostates vs. microstates

Suppose you have system of N particles which each have a nonnegative integer amount of energy, and the total energy of the system is E, where $E \geq N$. Each way of distributing the energy between N unordered particles is a macrostate, and each way of distributing the energy between N ordered particles is a microstate. Counting microstates is useful because all microstate are equally likely, so we can figure out the probability that a particle will be at a given energy level. Counting macrostates is interesting but not really useful, and it's pretty difficult, because it requires a variation of the integer-partition-function.

Each microstate can be represented by a stars-and-bars diagram, where each star is a unit of energy. For example, in a system with $N = 6$ and $E = 8$, where one particle has energy=4, 2 particles have energy=2, and the rest have zero energy, the diagram could look like

$$\star\star\star\star\,|\,\star\star|\,\star\star|||$$

But by convention, each partition in a stars-and-bars diagram must have at least one star, so we add one star to each partition by default, and instead write

$$\star\star\star\star\star|\,\star\star\star\,|\,\star\star\star\,|\,\star\,|\,\star\,|\star$$

The diagram below has the same distribution of energies but in a different order, meaning it represents the same macrostate, but a different microstate.

$$\star\star\star|\,\star\star\star\star\star\,|\,\star\star\star\,|\,\star\,|\,\star\,|\star$$

That microstate can be permuted $\frac{6!}{2!3!} = 60$ different ways, meaning that the corresponding macrostate contains 60 microstates. We could use factorial expressions like that to add up the total number of particles with energy x across all microstates, but that would require a separate term for each macrostate, which would get very tedious. Instead, we'll find an explicit formula for that, which will only use one term.

2 Nasty combinatorics stuff

Define the function Ω as the total number of microstates accessible to our system.

$$\Omega(E,N) := \#\text{ of microstates} = \sum_{\text{macrostates with } N \text{ particles \& energy } E} (\#\text{ of permutations of that macrostate})$$

Going back to the first stars-and-bars diagram (the one where some partitions have zero stars), we have a total of $N+E-1$ characters: E stars and $N-1$ bars. So the number of ways to arrange those characters is

$$\Omega(E,N) = \binom{N+E-1}{E} = \binom{N+E-1}{N-1} = \frac{(N+E-1)!}{E!(N-1)!}$$

In the example where $E=8$ and $N=6$, that tells us that there are $\Omega(8,6)=1287$ microstates.

3 Deriving the discrete probability distribution

Define the function

$$f(x,E,N) := \sum_{\text{microstates with } N \text{ particles \& total energy } E} (\#\text{ of particles with energy } x)$$

If we add up the number of particles in each microstate across all microstates, we get

$$\sum_{x=0}^{E} f(x,E,N) = N \cdot \Omega(x,E,N)$$

We can then expand $\Omega(x,E,N)$ using the Hockey Stick Identity:

$$\sum_{x=0}^{E} f(x,E,N) = N \cdot \binom{N+E-1}{N-1} = N \cdot \sum_{x=0}^{E} \binom{N+E-x-2}{N-2}$$

This leads to a very reasonable guess for what $f(x,E,N)$ is, which you can prove with induction if you take the base case to be $f(E,E,N)=N$.

$$f(x,E,N) = N \cdot \binom{N+E-x-2}{N-2}$$

Alternatively, you could prove that that works by using Pascal's identity plus induction, which is simpler but not as cool.

Now we can calculate the probability $p(x,E,N)$ that a random particle in our system will have energy x (given that there are N particles in the system, whose total energy is E). Note that the average number of particles in each microstate with energy x is equal to N times $p(x,E,N)$.

$$p(x,E,N) := \frac{f(x,E,N)}{N\Omega(E,N)} = \frac{(E+N-x-2)!}{(E-x)!(N-2)!} \cdot \frac{E!(N-1)!}{(N+E-1)!} = \frac{N-1}{E+N-1-x} \cdot \prod_{i=1}^{x} \frac{E+1-i}{E+N-i}$$