

Microstates

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October 11, 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 a that 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

★★★★|★★|★★|||

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

★★★★★|★★★|★★★|★|★|★

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

★★★|★★★★★|★★★|★|★|★

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 no 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

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

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 could probably prove with induction if you take the base case to be $f(E, E, N) = N$.

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

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 $p(x, E, N)$.

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