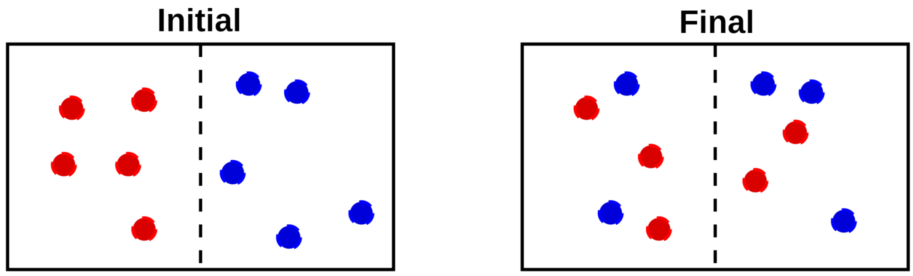
MATH327: Statistical Physics, Spring 2023

Tutorial activity — Mixing entropy

Let's consider a slight variation to the particle exchange thought experiment we worked through in class. We again begin with two canonical ideal gases, initially separated by a wall, each with N particles in volume V at temperature T. *All* $2N$ particles have identical physical properties, *except* that those initially in the left compartment (the "reds") are distinguishable from those in right compartment (the "blues") by their colour. Call this initial system Ω_0. We have already computed its entropy $S_0 = 2S_I(N,V) = 5N + 2N\log\left(\frac{V}{N\lambda_{\text{th}}^3}\right)$, where $\lambda_{\text{th}} = \sqrt{2\pi\hbar^2/(mT)}$.

We then carry out the procedure of removing the wall, waiting for a while, and then re-inserting the wall to re-separate the two systems. Call the combined system Ω_C with entropy S_C. As discussed in class, it's safe to assume that N particles end up in each of the two re-separated systems. However, red and blue particles can now appear on either side of the wall. Call this final system Ω_F with entropy S_F. The initial and final systems are illustrated by the figure below.



The first task is to compute the mixing entropy $S_{\text{mix}} = S_C - S_0$. Since the combined system Ω_C has two (distinguishable) sets of N (indistinguishable) particles, its partition function is

$$Z_C = \frac{1}{N!}\frac{1}{N!}Z_1^{2N} = \frac{1}{N!}\frac{1}{N!}\left(\frac{2V}{\lambda_{\text{th}}^3}\right)^{2N},$$

where $Z_1 = 2V/\lambda_{\text{th}}^3$ is the single-particle partition function. It may be useful to relate the difference of entropies to a ratio of partition functions.

The second task is to compute the final entropy S_F, to see whether $S_F \geq S_C$ as demanded by the second law of thermodynamics. We can break this up into two steps. The first of these is to compute the partition function Z_F of the two re-separated systems (each with N particles), summing over all ways of dividing the red and blue particles between them. The following special case of the Zhu–Vandermonde identity for the binomial sum may be useful for this step:

$$\sum_{k=0}^{N}\binom{N}{k}^2 = \binom{2N}{N}.$$

Finally, use your result for Z_F to determine the final entropy S_F. It may be useful to apply Stirling's formula and neglect $\mathcal{O}(\log N)$ contributions.