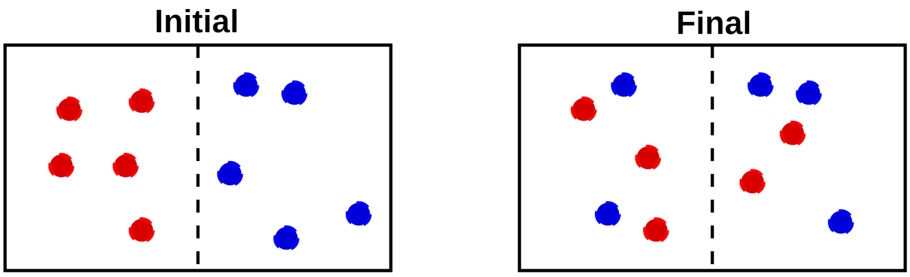
MATH327: Statistical Physics, Spring 2024

Tutorial activity — Mixing entropy

This activity will be introduced in our 7 March tutorial, and you'll have the week until our next tutorial on 14 March to work on it. In particular, we will discuss the mixing entropy in more detail in our next lecture on 8 March, after briefly summarizing the main concepts in the tutorial. That brief summary will be enough for you to start working on the tasks below, given one assumption that we will justify in tomorrow's lecture.

Consider the thought experiment of starting with two canonical ideal gases, initially separated by a wall, each in thermodynamic equilibrium with N particles in volume V at temperature T. We then remove the wall, allowing all $2N$ particles to mix in a $2V$ volume. Finally, we re-insert the wall, dividing the $2N$ particles back into two re-separated subsystems. It is safe to **assume** that N particles end up in each of the two re-separated subsystems. If we call these three stages $\{\Omega_0, \Omega_C, \Omega_F\}$ with corresponding entropies $\{S_0, S_C, S_F\}$, we want to verify that $S_0 \leq S_C \leq S_F$ to obey the second law.

To do this verification, consider the specific setup shown by the figure below: *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. After mixing and re-separation, red and blue particles can appear on either side of the wall in the final system Ω_F.



The first task is to check $S_0 \leq S_C$ by computing both S_0 and S_C. The difference $S_C - S_0 \equiv \Delta S_{\text{mix}}$ is the *mixing entropy* that must be non-negative. Since the combined system Ω_C has two (distinguishable) sets of N (indistinguishable) particles, its partition function is

$$Z_C = \frac{1}{N!}\frac{1}{N!}Z_1^{2N} = \frac{1}{N!}\frac{1}{N!}\left(\frac{2V}{\lambda_{\text{th}}^3}\right)^{2N} \qquad \text{with} \qquad \lambda_{\text{th}} = \sqrt{\frac{2\pi\hbar^2}{mT}},$$

where $Z_1 = 2V/\lambda_{\text{th}}^3$ is the single-particle partition function. It may be useful to exploit the properties of logarithms that connect differences of entropies to ratios of partition functions.

The second task is to check $S_C \leq S_F$ by computing the final entropy S_F. 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. If you apply Stirling's formula, you may find it interesting to repeat your work with and without the $\log\left(\sqrt{2\pi N}\right)$ terms.