5.3: Entropy and Counting States

Suppose we are to partition N particles among J possible distinct single particle states. How many ways Ω are there of accomplishing this task? The answer depends on the statistics of the particles. If the particles are fermions, the answer is easy: \ROmega\ns_\ssr{FD}={J\choose N}. For bosons, the number of possible partitions can be evaluated via the following argument. Imagine that we line up all the N particles in a row, and we place $J-1$ barriers among the particles, as shown below in Figure [BEcount]. The number of partitions is then the total number of ways of placing the N particles among these $N+J-1$ objects (particles plus barriers), hence we have \ROmega\ns_\ssr{BE}={N+J-1\choose N}. For Maxwell-Boltzmann statistics, we take \ROmega\ns_\ssr{MB}=J^N/N! Note that \ROmega\ns_\ssr{MB} is not necessarily an integer, so Maxwell-Boltzmann statistics does not represent any actual state counting. Rather, it manifests itself as a common limit of the Bose and Fermi distributions, as we have seen and shall see again shortly.

[BEcount] Partitioning N bosons into J possible states ($N=14$ and $J=5$ shown). The N black dots represent bosons, while the $J-1$ white dots represent markers separating the different single particle populations. Here $n_1=3$, $n_2=1$, $n_3=4$, $n_4=2$, and $n_5=4$.

The entropy in each case is simply $S=k_B\ln\Omega$. We assume $N\gg 1$ and $J\gg 1$, with $n\equiv N/J$ finite. Then using Stirling's approximation, $\ln(K!)=K\ln K-K+\mathcal{O}(\ln K)$, we have

\begin{split} S\ns_\ssr{MB}&=-J\kB \, n\ln n \\ S\ns_\ssr{BE}&=-J\kB\big[n\ln n - (1+n)\ln (1+n)\big] \bvph \\ S\ns_\ssr{FD}&=-J\kB\big[n\ln n + (1-n)\ln (1-n)\big]\ . \end{split}

In the Maxwell-Boltzmann limit, $n\ll 1$, and all three expressions agree. Note thatR

\begin{split} \pabc{S\ns_\ssr{MB}}{N}{J} &= -\kB \, \big(1 + \ln n\big) \\ \pabc{S\ns_\ssr{BE}}{N}{J} &= \kB\ln\!\big(n^{-1}+1\big) \bvph \\ \pabc{S\ns_\ssr{FD}}{N}{J} &= \kB\ln\!\big(n^{-1}-1\big)\ . \end{split}

Now let's imagine grouping the single particle spectrum into intervals of J consecutive energy states. If J is finite and the spectrum is continuous and we are in the thermodynamic limit, then these states will all be degenerate. Therefore, using α as a label for the energies, we have that the grand potential $\Omega=E-TS-\mu N$ is given in each case by

\begin{split} \Omega\ns_\ssr{MB} &= J\sum_\alpha \Big[(\ve\ns_\alpha-\mu)\,n\ns_\alpha+\kT\,n\ns_\alpha\ln n\ns_\alpha\Big] \\ \Omega\ns_\ssr{BE} &= J\sum_\alpha \Big[(\ve\ns_\alpha-\mu)\,n\ns_\alpha+\kT\,n\ns_\a

Now - *lo and behold!* - treating Ω as a function of the distribution $\{n_\alpha\}$ and extremizing in each case, subject to the constraint of total particle number $N=J\sum_\alpha n_\alpha$, one obtains the Maxwell-Boltzmann, Bose-Einstein, and Fermi-Dirac distributions, respectively:

{\delta\over\delta n\ns_\alpha}\Big(\Omega-\lambda \, J\sum_{\alpha'} n\ns_{\alpha'}\Big) = 0 \quad\Rightarrow \quad \begin{cases} n^\ssr{MB}_\alpha=e^{(\mu-\ve\ns_\alpha)/k\ns_\RB T} \\ \\ n^\ssr{BE}_\alpha=\big[e

As long as J is finite, so the states in each block all remain at the same energy, the results are independent of J.