Factorisation of partition functions

In lectures, we repeatedly use $Z_N = (Z_1)^N$ for independent distinguishable particles, and we also used $Z_1 = Z_1^{\text{tr}} Z_1^{\text{rot}} Z_1^{\text{vib}}$ for the independent contributions of vibrational, rotation and translational degrees of freedom to a single-particle's partition function. In these notes we prove that where the energy of a system separates into independent contributions like this, the partition function factorises.

Many-particle system with two single-particle energy levels

Let's start with a system that has two single-particle energy levels, ε_1 and ε_2. The single-particle partition function is

$$Z_1 = e^{-\varepsilon_1 \beta} + e^{-\varepsilon_2 \beta}.$$

The partition function for two distinguishable particles is

$$Z_2 = e^{-2\varepsilon_1 \beta} + 2e^{-(\varepsilon_1 + \varepsilon_2)\beta} + e^{-2\varepsilon_2 \beta} = (Z_1)^2,$$

where the second state is multiplied by 2 becase there are two ways that two *distingishable* particles can be in different levels.

In general, for N particles, the energies are $n\varepsilon_1 + (N-n)\varepsilon_2$, for $0 \leq n \leq N$, and there are $N!/n!(N-n)!$ separate microstate of this energy. So

$$\begin{aligned}
Z_N &= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \mathrm{e}^{-(n\varepsilon_1 + (N-n)\varepsilon_2)\beta} \\
&= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \mathrm{e}^{-n\varepsilon_1 \beta} \mathrm{e}^{-(N-n)\varepsilon_2 \beta} \\
&= \sum_{n=0}^{N} \frac{N!}{n!(N-n)!} \left(\mathrm{e}^{-\varepsilon_1 \beta}\right)^n \left(\mathrm{e}^{-\varepsilon_2 \beta}\right)^{N-n} = (Z_1)^N
\end{aligned}$$

If there are more than two energy levels, Z_1 has more terms, but a similar derivation can be done. However we won't show it because it is just a special case of the next section.

Many independent subsystems, general case

In full generality, let us suppose that a microstate has N independent contributions to its energy, the allowed values of the first being $\varepsilon_1^{(1)}$, $\varepsilon_2^{(1)}$, $\varepsilon_3^{(1)}$, …, and similarly for the others, with $\varepsilon_i^{(n)}$ being the ith allowed value of the nth contribution. Also, let $Z^{(n)}$ be the partition function for the nth contribution:

$$Z^{(n)} = \sum_i \exp\left(-\varepsilon_i^{(n)}\beta\right).$$

Then the full partition function is

$$\begin{aligned}
Z &= \sum_{i,j,k,\ldots p} \exp\left(-(\varepsilon_i^{(1)} + \varepsilon_j^{(2)} + \varepsilon_k^{(3)} + \ldots + \varepsilon_p^{(N)})\beta\right) \\
&= \sum_{i,j,k,\ldots p} \exp\left(-\varepsilon_i^{(1)}\beta\right) \exp\left(-\varepsilon_j^{(2)}\beta\right) \exp\left(-\varepsilon_k^{(3)}\beta\right) \ldots \exp\left(-\varepsilon_p^{(N)}\beta\right) \\
&= \left(\sum_i \exp\left(-\varepsilon_i^{(1)}\beta\right)\right) \left(\sum_j \exp\left(-\varepsilon_j^{(2)}\beta\right)\right) \left(\sum_k \exp\left(-\varepsilon_k^{(3)}\beta\right)\right) \ldots \left(\sum_p \exp\left(-\varepsilon_p^{(N)}\beta\right)\right) \\
&= Z^{(1)} Z^{(2)} Z^{(3)} \ldots Z^{(N)}.
\end{aligned}$$

It is the step between the second and third lines, in which we interchange the order of addition and multiplication, that is tricky at first! But it is no harder than the following (in reverse):

$$(a+b+c)(p+q+r)(x+y+z) = apx + apy + apz + aqx + aqy + aqz + arx + ary + arz + bpx + \ldots + crz$$

More compactly,

$$\begin{aligned}
Z &= \sum_{i_1, i_2, \ldots i_N} \exp\left(-\sum_{n=1}^{N} \varepsilon_{i_n}^{(n)}\beta\right) \\
&= \sum_{i_1, i_2, \ldots i_N} \prod_{n=1}^{N} \exp\left(-\varepsilon_{i_n}^{(n)}\beta\right) \\
&= \prod_{n=1}^{N} \sum_{i_n} \exp\left(-\varepsilon_{i_n}^{(n)}\beta\right) = \prod_{n=1}^{N} Z^{(n)}.
\end{aligned}$$