# 4.2: Conditions under which Integrals Approximate Partition Functions

The Boltzmann equation gives the equilibrium fraction of particles in the $i^{th}$ energy level, $\epsilon_i$, as

$$\frac{N_i^{\bullet}}{N}=\frac{g_i}{z}\exp\left(\frac{-\epsilon_i}{kT}\right)$$

so the fraction of particles in energy levels less than $\epsilon_n$ is

$$f\left(\epsilon_n\right)=z^{-1}\sum_{i=1}^{n-1} g_i\exp\left(\frac{-\epsilon_i}{kT}\right)$$

where $z=\sum_{i=1}^{\infty} g_i\exp\left(\epsilon_i/kT\right)$ . We can represent either of these sums as the area under a bar graph, where the height and width of each bar are $g_i\exp\left(\epsilon_i/kT\right)$ and unity, respectively. If $g_i$ and $\epsilon_i$ can be approximated as continuous functions, this area can be approximated as the area under the continuous function $y\left(i\right)=g_i\exp\left(\epsilon_i/kT\right)$. That is,

$$\sum_{i=1}^{n-1} g_i\exp\left(\frac{-\epsilon_i}{kT}\right)\approx\int_{i=0}^{n} g_i\exp\left(\frac{-\epsilon_i}{kT}\right)di$$

To evaluate this integral, we must know how both $g_i$ and $\epsilon_i$ depend on the quantum number, $i$.

Let us consider the case in which $g_i=1$ and look at the constraints that the $\epsilon_i$ must satisfy in order to make the integral a good approximation to the sum. The graphical description of this case is sketched in Figure 1. Since $\epsilon_i>\epsilon_{i-1}>0$ , we have

$$e^{-\epsilon_{i-1}/kT}-e^{-\epsilon_i/kT}>0$$

For the integral to be a good approximation, we must have

$$e^{-\epsilon_{i-1}/kT}\gg e^{-\epsilon_{i-1}/kT}-e^{-\epsilon_i/kT}>0,$$

which means that

$$1\gg 1-e^{-\Delta\epsilon/kT}>0$$

where $\Delta\epsilon=\epsilon_i-\epsilon_{i-1}$ . Now,

$$e^x\approx 1+x+\frac{x^2}{2!}+\frac{x^3}{3!}+\dots$$

so that the approximation will be good if

$$1\gg 1-\left(1-\frac{\Delta\epsilon}{kT}+\dots\right)$$

or

$$1\gg\frac{\Delta\epsilon}{kT}$$

or

$$kT\gg\Delta\epsilon$$

We can be confident that the integral is a good approximation to the exact sum whenever there are many pairs of energy levels, $\epsilon_i$ and $\epsilon_{i-1}$, that satisfy the condition

$$\Delta\epsilon=\epsilon_i-\epsilon_{i-1}\ll kT.$$

If there are many energy levels that satisfy $\epsilon_i\ll kT$ , there are necessarily many intervals, $\Delta\epsilon$, that satisfy $\Delta\epsilon\ll kT$. In short, if a large number of the energy levels of a system satisfy the criterion $\epsilon\ll kT$ , we can use integration to approximate the sums that appear in the Boltzmann equation. In Section 24.3, we use this approach and the energy levels for a particle in a box to find the partition function for an ideal gas.