

22.2: Conditions under which Integrals Approximate Partition Functions

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

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

so the fraction of particles in energy levels less than ϵ_n is

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

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

Let us consider the case in which $g_i = 1$ and look at the constraints that the ϵ_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, ϵ_i and ϵ_{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.

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