24.1: The Partition Function for N Distinguishable, Non-interacting Molecules

In Chapter 21, our analysis of a system of N distinguishable and non-interacting molecules finds that the system entropy is given by

$$S=\frac{E}{T}+Nk\ln z=\frac{E}{T}+k\ln z^N$$

where E is the system energy and z is the molecular partition function. From ensemble theory, we found

$$S=\frac{E}{T}+k\ln Z$$

where Z is the partition function for the N-molecule system. Comparison implies that, for a system of N, distinguishable, non-interacting molecules, we have

$$Z=z^N$$

We can obtain this same result by writing out the energy levels for the system in terms of the energy levels of the distinguishable molecules that make up the system. First we develop the obvious notation for the energy levels of the individual molecules. We let the energy levels of the first molecule be the set $\{\epsilon_{1,i}\}$, the energy levels of the second molecule be the set $\{\epsilon_{2,i}\}$, and so forth to the last molecule for which the energy levels are the set $\{\epsilon_{N,i}\}$. Thus, the i^{th} energy level of the r^{th} molecule is $\epsilon_{r,i}$. We let the corresponding energy-level degeneracy be $g_{r,i}$ and the partition function for the r^{th} molecule be z_r. Since all of the molecules are identical, each has the same set of energy levels; that is, we have $\epsilon_{p,i}=\epsilon_{r,i}$ and $g_{p,i}=g_{r,i}$ for any two molecules, p and r, and any energy level, i. It follows that the partition function is the same for every molecule

$$z_1=z_2=\dots=z_j=\dots=z_N=z=\sum_{i=1}^{\infty} g_{r,i}\exp\left(\frac{-\epsilon_{r,i}}{kT}\right)$$

so that

$$z_1z_2\dots z_r\dots z_N=z^N$$

We can write down the energy levels available to the system of N distinguishable, non-interacting molecules. The energy of the system is just the sum of the energies of the constituent molecules, so the possible system energies consist of all of the possible sums of the distinguishable-molecule energies. Since there are infinitely many molecular energies, there are infinitely many system energies.

$$E_1=\epsilon_{1,1}+\epsilon_{2,1}+\dots+\epsilon_{r,1}+\dots+\epsilon_{N,1}$$

$$E_2=\epsilon_{1,2}+\epsilon_{2,1}+\dots+\epsilon_{r,1}+\dots+\epsilon_{N,1}$$

$$E_3=\epsilon_{1,3}+\epsilon_{2,1}+\dots+\epsilon_{r,1}+\dots+\epsilon_{N,1}$$

$$\dots$$

$$E_m=\epsilon_{1,i}+\epsilon_{2,j}+\dots+\epsilon_{r,k}+\dots+\epsilon_{N,p}$$

$$\dots$$

The product of the N molecular partition functions is

$$z_1z_2\dots z_r\dots z_N=\sum_{i=1}^{\infty} g_{1,i}\exp\left(\frac{-\epsilon_{1,i}}{kT}\right)$$

$$\times\sum_{j=1}^{\infty} g_{2,j}\exp\left(\frac{-\epsilon_{2,j}}{kT}\right)\times\dots\times\sum_{k=1}^{\infty} g_{r,k}\exp\left(\frac{-\epsilon_{r,k}}{kT}\right)\times$$

$$\dots\times\sum_{p=1}^{\infty} g_{N,p}\exp\left(\frac{-\epsilon_{N,p}}{kT}\right)$$

$$=\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}\dots\sum_{k=1}^{\infty}\dots\sum_{p=1}^{\infty}g_{1,i}g_{2,j}\dots g_{r,k}\dots g_{N,p}$$

$$\times \exp\left[\frac{-\left(\epsilon_{1,i}+\epsilon_{2,j}+\dots+\epsilon_{r,k}+\dots+\epsilon_{N,p}\right)}{kT}\right]$$

The sum in each exponential term is just the sum of N single-molecule energies. Moreover, every possible combination of N single-molecule energies occurs in one of the exponential terms. Each of these possible combinations is a separate energy level available to the system of N distinguishable molecules.

The system partition function is

$$Z=\sum_{i=1}^{\infty}\mathit{\Omega}_i\exp\left(\frac{-E_i}{kT}\right)$$

The i^{th} energy level of the system is the sum

$$E_i=\epsilon_{1,v}+\epsilon_{2,w}+\dots+\epsilon_{r,k}+\dots+\epsilon_{N,y}$$

The degeneracy of the i^{th} energy level of the system is the product of the degeneracies of the molecular energy levels that belong to it. We have

$$\mathit{\Omega}_i=g_{1,v}g_{2,w}\dots g_{r,k}\dots g_{N,y}$$

Thus, by a second, independent argument, we see that

$$z_1z_2\dots z_r\dots z_N=z^N=Z$$

(N distinguishable, non-interacting molecules)