24.2: The Partition Function for N Indistinguishable, Non-interacting Molecules

In all of our considerations to this point, we focus on systems in which the molecules are distinguishable. This effectively confines the practical applications to crystalline solids. Since there is no way to distinguish one molecule of a given substance from another in the gas phase, it is evident that the assumptions we have used so far do not apply to gaseous systems. The number and importance of practical applications increases dramatically if we can extend the theory to describe the behavior of ideal gases.

We might suppose that distinguishability is immaterial—that there is no difference between the behavior of a system of distinguishable particles and an otherwise-identical system of indistinguishable particles. Indeed, this is an idea well worth testing. We know the partition function for a particle in box, and we have every reason to believe that this should be a good model for the partition function describing the translational motion of a gas particle. If an ideal gas behaves as a collection of N distinguishable particles-in-a-box, the translational partition of the gas is just z^N. Thermodynamic properties calculated on this basis for, say, argon should agree with those observed experimentally. Indeed, when the comparison is made, this theory gives some properties correctly. The energy is correct; however, the entropy is not.

Thus, experiment demonstrates that the partition function for a system of indistinguishable molecules is different from that of an otherwise-identical system of distinguishable molecules. The reason for this becomes evident when we compare the microstates available to a system of distinguishable molecules to those available to a system of otherwise-identical indistinguishable molecules. Consider the distinguishable-molecule microstate whose energy is

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

As a starting point, we assume that every molecule is in a different energy level. That is, all of the N energy levels, $\epsilon_{i,j}$, that appear in this sum are different. For the case in which the molecules are distinguishable, we can write down additional microstates that have this same energy just by permuting the energy values among the N molecules. (A second microstate with this energy is $E_i = \epsilon_{1,w} + \epsilon_{2,v} + \cdots + \epsilon_{r,k} + \cdots + \epsilon_{N,y}$.) Since there are $N!$ such permutations, there are a total of $N!$ quantum states that have this same energy, and each of them appears as an exponential term in the product $z_1 z_2 \ldots z_r \ldots z_N = z^N$.

If, however, the N molecules are indistinguishable, there is no way to tell one of these $N!$ assignments from another. They all become the same thing. All we know is that some one of the N molecules has the energy ϵ_w, another has the energy ϵ_v, *etc*. This means that there is only one way that the indistinguishable molecules can have the energy E_i. It means also that the difference between the distinguishable-molecules case and the indistinguishable-molecules case is that, while they contain the same system energy levels, each level appears $N!$ more times in the distinguishable-molecules partition function than it does in the indistinguishable-molecules partition function. We have

$$Z_{\text{indistinguishable}} = \frac{1}{N!} Z_{\text{distinguishable}} = \frac{1}{N!} z^N$$

In the next section, we see that nearly all of the molecules in a sample of gas must have different energies, so that this relationship correctly relates the partition function for a single gas molecule to the partition function for a system of N indistinguishable gas molecules.

Before seeing that nearly all of the molecules in a macroscopic sample of gas actually do have different energies, however, let us see what happens if they do not. Suppose that just two of the indistinguishable molecules have the same energy. Then there are not $N!$ permutations of the energies among the distinguishable molecules; rather there are only $N!/2!$ such permutations. In this case, the relationship between the system and the molecular partition functions is

$$Z_{\text{indistinguishable}} = \frac{2!}{N!} Z_{\text{distinguishable}} = \frac{2!}{N!} z^N$$

For the population set $\{N_1,\ N_2, \ldots, N_r, \ldots, N_\omega\}$ the relationship is

$$Z_{\text{indistinguishable}} = \frac{N_1! N_2! \ldots N_r! \ldots N_\omega!}{N!} z^N$$

which is much more complex than the case in which all molecules have different energies. Of course, if we extend the latter case, so that the population set consists of N energy levels, each occupied by at most one molecule, the relationship reverts to the one with which we began.

$$Z_{indistinguishable} = \frac{1}{N!}\left(\prod_{i=1}^{\infty} N_i!\right) z^N = \frac{1}{N!}\left(\prod_{i=1}^{\infty} 1\right) z^N = \frac{1}{N!} z^N$$
