

4.7: Applications of Other Entropy Relationships

In most cases, calculation of the entropy from information about the energy levels of a system is best accomplished using the partition function. Occasionally other entropy relationships are useful. We illustrate this by using the entropy relationship

$$S = -Nk \sum_{i=1}^{\infty} g_i \rho(\epsilon_i) \ln \rho(\epsilon_i) + Nk \ln g_1$$

to find the entropy of an N -molecule disordered crystal at absolute zero. To be specific, let us consider a crystal of carbon monoxide.

We can calculate the entropy of carbon monoxide at absolute zero from either of two perspectives. Let us first assume that the energy of a molecule is almost completely independent of the orientations of its neighbors in the crystal. Then the energy of any molecule in the crystal is essentially the same in either of the two orientations available to it. In this model for the system, we consider that there are two, non-degenerate, low-energy quantum states available to the molecule. We suppose that all other quantum states lie at energy levels whose probabilities are very small when the temperature is near absolute zero. We have $g_1 = g_2 = 1$, $\epsilon_2 \approx \epsilon_1$. Near absolute zero, we have $\rho(\epsilon_2) \approx \rho(\epsilon_1) \approx 1/2$; for $i > 2$, $\rho(\epsilon_i) \approx 0$. The entropy becomes

$$\begin{aligned} S &= -Nk \sum_{i=1}^{\infty} g_i \rho(\epsilon_i) \ln \rho(\epsilon_i) + Nk \ln g_1 \\ &= -Nk \left(\frac{1}{2} \right) \ln \left(\frac{1}{2} \right) - Nk \left(\frac{1}{2} \right) \ln \left(\frac{1}{2} \right) \\ &= -Nk \ln \left(\frac{1}{2} \right) \\ &= Nk \ln 2 \end{aligned}$$

Alternatively, we can consider that there is just one low-energy quantum state available to the molecule but that this quantum state is doubly degenerate. In this model, the energy of the molecule is the same in either of the two orientations available to it. We have $g_1 = 2$. Near absolute zero, we have $\rho(\epsilon_1) \approx 1$; for $i > 1$, $\rho(\epsilon_i) \approx 0$. The summation term vanishes, and the entropy becomes

$$S = Nk \ln g_1 = Nk \ln 2$$

Either perspective implies the same value for the zero-temperature entropy of the N -molecule crystal.

Either of these treatments involves a subtle oversimplification. In our first model, we recognize that the carbon monoxide molecule must have a different energy in each of its two possible orientations in an otherwise perfect crystal. The energy of the orientation that makes the crystal perfect is slightly less than the energy of the other orientation. We introduce an approximation when we say that $\rho(\epsilon_2) \approx \rho(\epsilon_1) \approx 1/2$. However, if ϵ_2 is not exactly equal to ϵ_1 , this approximation cannot be valid at an arbitrarily low temperature. To see this, we let the energy difference between these orientations be $\epsilon_2 - \epsilon_1 = \Delta\epsilon > 0$. At relatively high temperatures, at which $\Delta\epsilon \ll kT$, we have

$$\frac{\rho(\epsilon_2)}{\rho(\epsilon_1)} = \exp \left(\frac{-\Delta\epsilon}{kT} \right) \approx 1$$

and $\rho(\epsilon_2) \approx \rho(\epsilon_1) \approx 1/2$. At such temperatures, the system behaves as if the lowest energy level were doubly degenerate, with $\epsilon_2 = \epsilon_1$. However, since T can be arbitrarily close to zero, this condition cannot always apply. No matter how small $\Delta\epsilon$ may be, there are always temperatures at which $\Delta\epsilon \gg kT$ and at which we have

$$\frac{\rho(\epsilon_2)}{\rho(\epsilon_1)} \approx 0$$

This implies that the molecule should always adopt the orientation that makes the crystal perfectly ordered when the temperature becomes sufficiently close to zero. This conclusion disagrees with the experimental observations.

Our second model assumes that the energy of a carbon monoxide molecule is the same in either of its two possible orientations. However, its interactions with the surrounding molecules cannot be exactly the same in each orientation; consequently, its energy cannot be exactly the same. From first principles, therefore, our second model cannot be strictly correct.

To resolve these apparent contradictions, we assume that the rate at which a carbon monoxide molecule can change its orientation within the lattice depends on temperature. For some temperature at which $\Delta\epsilon \ll kT$, the reorientation process occurs rapidly, and the two orientations are equally probable. As the temperature decreases, the rate of reorientation becomes very slow. If the reorientation process effectively ceases to occur while the condition $\Delta\epsilon \ll kT$ applies, the orientations of the component molecules remain those that occur at higher temperatures no matter how much the temperature decreases thereafter. This is often described by saying that molecular orientations become “frozen.” The zero-temperature entropy of the system is determined by the energy-level probabilities that describe the system at the temperature at which reorientation effectively ceases to occur.

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