Chapter 10

Entropy in other situations

As the chart in the front of the book shows, we have now completed our elementary study of the thermal equilibrium properties of ideal solids and gases. However, it would be a pity to stop here, since statistical physics has plenty more to say about other types of system also. In this chapter we shall look again at entropy, and shall discuss the statistics of a system in which the macrostate specifies $T$ rather than $U$. This generalization will help us to discuss vacancies in solids in this chapter, and phase transitions in the next.

10.1 Entropy and disorder

In Chapter 1, we took as a statistical definition of entropy the relation $S = k_B \ln \Omega$ (equation (1.5)). Since many verifiable results have followed, we may by now have much confidence in the approach. In this chapter we study some further consequences of the relation.

10.1.1 Isotopic disorder

One simple form of disorder in a solid is isotopic disorder. For instance a block of copper consists of a mixture of $^{63}$Cu and $^{65}$Cu isotopes. Therefore, if the isotopes are randomly distributed on the lattice sites, there will be a large amount of disorder associated with all the possible arrangements of the isotopes.

Consider a solid whose $N$ atoms have a proportion $P_L$ of isotope $L$. In other words, there are $N_L = P_L N$ atoms of isotope $L$, and $\sum_L N_L = N$, where the sum goes over all the...
isotopes. The number of arrangements of isotopes on the $N$ sites is given by the well-trodden third problem of Appendix 1. It is:

$$\Omega = \frac{N!}{\prod_{L} N_L !}$$  \hspace{1cm} (10.1)

The calculation of $S$ for this situation goes as follows:

$$S = k_B \ln \Omega$$

$$= k_B \left( \ln N! - \sum_{L} \ln N_L! \right)$$  \hspace{1cm} definition (1.5)

$$= k_B \left( N \ln N - \sum_{L} N_L \ln N_L \right)$$  \hspace{1cm} Stirling's approx, also

$$= - k_B \left[ \sum_{L} N_L \left( \ln N_L - \ln N \right) \right]$$  \hspace{1cm} $\sum N_L = N$

$$= - N k_B \sum_{L} P_L \ln P_L.$$  \hspace{1cm} putting $N = \sum N_L$  \hspace{1cm} (10.2)

The answer (10.2) is a nice simple one. For instance if we were to have a 50–50 mixture of two isotopes, it would give an 'entropy of mixing' of $S = N k_B \ln 2$, a not unexpected result, analogous to tossing pennies (Appendix 2).

Whether this entropy is observable is another matter. In fact our block of copper does not separate out under gravity to have all the $^{65}\text{Cu}$ at the bottom and all the $^{63}\text{Cu}$ at the top, however cold it is made! Rather this disorder is frozen in, and a cold piece of copper is in a metastable state which contains this fixed amount of disorder. Therefore the entropy of isotopic disorder is usually omitted from consideration, since it has no influence on the thermal properties. Metastable states of this sort do not violate the Third Law of Thermodynamics, since no entropy changes occur near the absolute zero.

Actually partial isotopic separation does occur in just one case, that of liquid helium. A liquid mixture of $^{3}\text{He}$ and $^{4}\text{He}$ is entirely random above 0.8 K. However, when it is cooled below this temperature, a phase separation occurs to give a solution of almost pure $^{3}\text{He}$ floating on top of a dilute