6. Systems of weakly interacting constituents

6.1. Factorisation of the partition function

We have already discussed in chapter 3 the concept of weakly interacting particles (or constituents)—basically, we can write the energy of the system as a sum of contributions from each particle since no energy is stored in any interaction potential. The Boltzmann distribution is quite general and is not restricted to weakly interacting systems; the derivation of chapter 5 only required that the system interact weakly with its environment. However, it is weakly interacting systems that are most easily treated.

For a weakly interacting system, we can write the energy of a microstate labelled r as:

$$E_r = \epsilon_{i_1} + \epsilon_{i_2} + \epsilon_{i_3} + \cdots + \epsilon_{i_N}$$

where ϵ_{i_n} is the energy of particle n which is in state i_n.

For example, in the model magnet, the microstate is given by the states of all N dipoles; the state of each dipole n is either the ground state ($i_n = 1; \epsilon_1 = -mH$) or the excited state ($i_n = 2; \epsilon_2 = +mH$). The total energy is the sum of the energies of each dipole.

Recalling the definition of Z from key point 10, we have:

$$\begin{aligned} Z &= \sum_r \exp(-\beta E_r) \\ &= \sum_{i_1 \cdots i_N} \exp\left(-\beta\left[\epsilon_{i_1} + \epsilon_{i_2} + \cdots + \epsilon_{i_N}\right]\right) \\ &= \left[\sum_{i_1} \exp(-\beta\epsilon_{i_1})\right] \cdots \left[\sum_{i_N} \exp(-\beta\epsilon_{i_N})\right] \\ &= [Z(1)]^N \end{aligned}$$

where $Z(1)$ is the partition function for a single particle, c.f. the single dipole calculation of chapter 5.2. You should make sure you follow each step in the above development.

The significance of this is that the partition function for the N particle system factorises into a product of N partition functions, one for each particle. This produces an immense simplification, basically because:

$$\ln Z = \ln\left[Z(1)\right]^N = N \ln Z(1)$$

and $Z(1)$ should be simple to calculate.

As an example, consider the mean energy which from chapter 6.1 or key point 12 is given by:

$$\overline{E} = -\frac{\partial}{\partial\beta}\ln Z = -N\frac{\partial}{\partial\beta}\ln Z(1) = N\bar{\epsilon}$$

where $\bar{\epsilon}$ is the average energy of a single dipole. The fact that the mean energy is the sum of the mean energies of each dipole is, of course, expected in the absence of (strong) interactions between particles.

Similarly,

$$F(T) = -kT\ln Z = -NkT\ln Z(1)$$

Another consequence of the factorisation of Z is that if we are interested in the state of, say, particle 1, then we can 'sum out' the states of all the other particles 2 to N:

$$\begin{aligned} P_{i_1} &= \sum_{i_2\cdots i_N} \exp\left(-\beta\left[\epsilon_{i_1}+\epsilon_{i_2}+\cdots+\epsilon_{i_N}\right]\right)\times Z^{-1} \\ &= \frac{\exp(-\beta\epsilon_{i_1})Z(1)^{N-1}}{Z(1)^N} \\ &= \frac{\exp(-\beta\epsilon_{i_1})}{Z(1)} \end{aligned}$$

This is identical to the probability distribution for a single particle discussed in 4.2.

> Key Point 13:
>
> In a system of N weakly interacting, distinguishable particles, the system partition function is simply $Z = [Z(1)]^N$ and the single particle probability distribution is $P_i = \frac{\exp(-\beta\epsilon_i)}{Z(1)}$.

Thus we see that the problem is reduced to that of the single particle problem. The key thing to remember though is that for the single particle problem the energy, etc., fluctuate, whereas in the N particle system for large N, the macroscopic variables are sharp and have well-defined thermodynamic values.

N.B. the reason for the qualification 'distinguishable' will become apparent later when we address quantum particles.

6.2. The model magnet

See Mandl 3.1-3.3

In 5.2, we examined the single particle partition function, i.e., the partition function for a single dipole, so effectively we have already done the hard work. We saw:

$$Z(1) = 2\cosh(x) \quad \text{where} \quad x = \frac{mH}{kT}$$

Using the general results for weakly interacting systems (previous subsection), we have:

$$\overline{E} = N\bar{\epsilon} = -N\frac{\partial}{\partial\beta}\ln Z(1) = -NmH\frac{\partial}{\partial x}\ln Z(1) = -NmH\tanh(x)$$

$$\begin{aligned} S(T) &= k\ln Z + \frac{\overline{E}}{T} \\ &= Nk\ln Z(1) + \frac{N\bar{\epsilon}}{T} \\ &= Nk\left[\ln(\exp(x)+\exp(-x)) - x\tanh(x)\right] \end{aligned}$$

An important quantity in magnetism is the magnetisation M, which counts the total magnet moment $M = (n_1 - n_2)m$, where $n_i (i = 1, 2)$ are the number of dipoles in levels 1 ($\epsilon = -mH$) and 2 ($\epsilon = +mH$). The magnetisation is related to the energy by $E = -MH$. Thus we have:

$$\overline{M} = Nm\tanh(x)$$

we see that for low fields, which means $mH \ll kT$ so that x is small:

$$\overline{M} = \frac{Nm^2H}{kT}$$

and for high fields $mH \gg kT$ so that $x \gg 1$:

$$\overline{M} \approx Nm$$

Let us now consider the zero-field magnetic susceptibility $\chi(H = 0)$ defined as:

$$\chi(H=0) \equiv \left(\frac{\partial\overline{M}}{\partial H}\right)\Big|_{H=0} = \frac{Nm^2}{kT}$$

You should understand that the susceptibility measures the response of the magnetisation of the system to a small externally applied field. It turns out that this response is actually related to the magnetisation fluctuations at zero field. This is analogous to the results for the specific heat in terms of the variance of the energy fluctuations.

The $\frac{1}{T}$ dependence of χ is known as the Curie law. It implies that the dipoles become more 'susceptible' to an external magnetic field at lower temperature. See Mandl 3.1 for a comparison with real experiments.

Finally, let's consider the heat capacity (at constant field):

$$C_H = \left(\frac{\partial \overline{E}}{\partial T}\right)_H = \left(\frac{\partial x}{\partial T}\right)_H \left(\frac{\partial \overline{E}}{\partial x}\right)_H = Nkx^2 \mathrm{sech}^2(x)$$

Note the low-temperature (large x) behaviour. Recalling:

$$\text{sech }(x) = \frac{2}{\exp(x) + \exp(-x)} \sim 2\exp(-x) \text{ for large } x$$

we see that the heat capacity vanishes for small T.

This is a general feature. Basically, at zero temperature, all particles are in the ground state. One has to raise the temperature until kT is comparable with $2mH$ (the energy difference to the excited state) before a significant number of dipoles are excited. Thus near $T = 0$, the derivative of internal energy with respect to T is zero.

kT is often referred to as the 'thermal energy'.

6.3. More general factorisation (non-examinable)

We have seen in this chapter how the fact that for weakly interacting particles the energy is a sum of terms allows factorisation of Z.

A similar mechanism occurs in systems which are not necessarily weakly interacting, but whose energy may be expressed as a sum of contributions associated with different 'aspects' of its behaviour say α, β.

$$E = E_\alpha + E_\beta + \cdots$$

Then if the microscopic 'degrees of freedom' which contribute to the different aspects are independent, we find that the partition function factorises:

$$Z = Z_\alpha \times Z_\beta \times \cdots$$

A consequence of this is that the free energy is a sum of contributions from each aspect.

For example, in a real magnetic solid, contributions to the energy will come from vibrations of the atoms about their average positions (see chapter 8) as well as the energy from the interaction with a magnetic field discussed in this lecture. Thus we can write

$$E = E_{\text{Vib}} + E_{\text{Mag}}$$

We have seen that the microscopic degrees of freedom which contribute to E_{Mag} are the dipole moments of the atoms.

The microscopic degrees of freedom which contribute to E_{Vib} will be something like the displacements from the atoms' equilibrium positions, say. These degrees of freedom (d.o.f) are independent of the dipole moment degrees of freedom. Thus

$$Z = \sum_{\text{Vib d.o.f}} \sum_{\text{Mag d.o.f}} \exp\left(-\beta[E_{\text{Vib}} + E_{\text{Mag}}]\right) = Z_{\text{Vib}} \times Z_{\text{Mag}}.$$