

## 2. Foundations: equilibrium of an isolated system

### 2.1 Overview: the aims of this chapter

Consider a macroscopic system (a portion of matter), containing an Avogadro-sized number  $N$  of ‘microscopic constituents’ or ‘particles’ which we shall take to be isolated from the rest of the world so that no energy (either in the form of heat or work) may enter or leave the system. The system thus has a constant total energy which we denote by  $E$ .

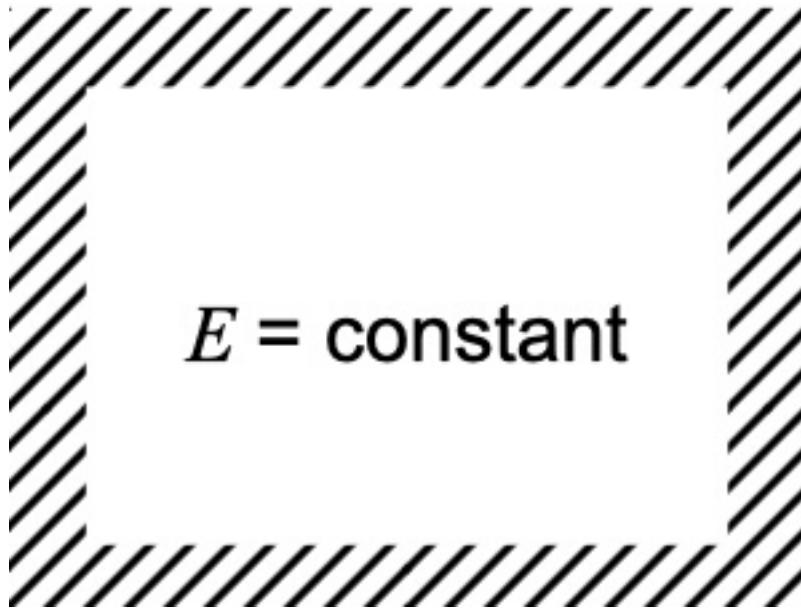


Figure 1: Schematic of a system isolated from its surroundings

We shall develop the statistical mechanics view of such a system. Specifically we shall establish the microscopic significance of entropy and temperature, and begin to see the simplifications due to the large value of  $N$ .

The arguments will be general (applicable irrespective of what the system actually comprises). They will be illustrated with references to two models of real systems:

- the ideal gas model
- a simple model magnet

The ideal gas model is familiar from PoM. The model magnet that we consider here is defined as follows (we will discuss its physical origins more fully in chapters 6 and 7).

- It comprises an array of  $N$  atoms (eg crystal) each with a magnetic dipole moment  $\mathbf{m}$  in an applied magnetic field  $\mathbf{H}$ . The energy of a dipole resides entirely in its interaction with the field which is given by  $\epsilon = -\mathbf{m} \cdot \mathbf{H}$
- In view of quantum mechanics (we shall not discuss the details here),  $\mathbf{m}$  is either
  - parallel to  $\mathbf{H}$  with energy  $\epsilon = -mH$  (ground state)
  - or antiparallel to  $\mathbf{H}$  with energy  $\epsilon = +mH$  (excited state)
- Each magnetic moment then has the energy level diagram shown on the right with two levels.

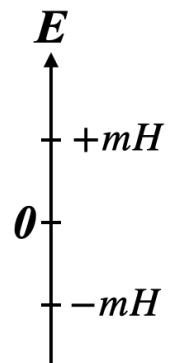


Figure 2: Energy-levels for one magnetic atom in a magnetic field in a simple model magnet

## 2.2 Microstates and macrostates

See Mandl Chapter 2

The terms microstate and macrostate constitute two different levels of description of a macroscopic system; we define them and explore their relationship.

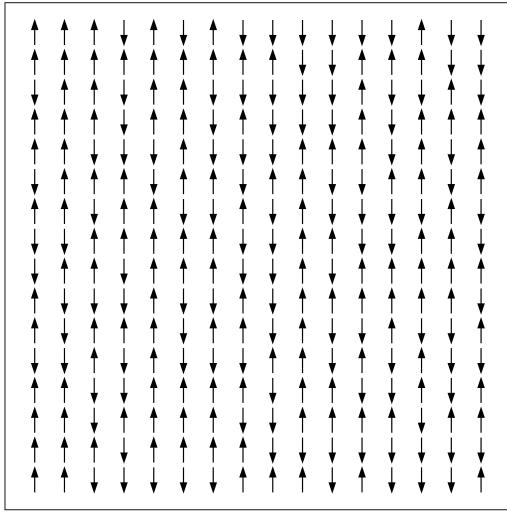
Key point 1

A **microstate** is a complete specification of the state of the system according to the microscopic model.

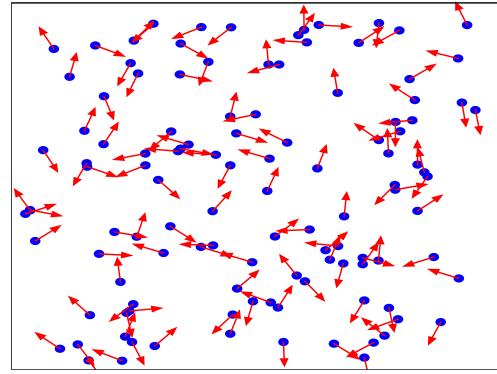
Thus a microstate is the most detailed description of the state of the system we can provide and is dictated by the microscopic model.

**Examples:**

1. Specifying the microstate of the model magnet means specifying the orientation of each of the  $N$  dipoles as in Figure 3a – or equivalently specifying which of the two rungs of its energy level ladder (cf Figure 2) it occupies.
2. Specifying the microstate of the (ideal) gas means (if we choose to use classical language) specifying the positions and velocities of each and every molecule (cf. Figure 3b).



(a) A microstate of a model magnet entails knowledge of the orientation (up or down) of each dipole. This is one possible microstate.



(b) A microstate of a model gas entails knowledge of the positions (blue circles) and velocities (red arrows) of all the molecules. Here is one example.

The microstate will change continually as the particles exchange energy with one another. For instance the molecules of a gas will continually be changing their position and their velocities as they collide with one another; The magnetic dipoles will undergo frequent transitions (hop from rung to rung) under the influence of their mutual interactions.

### Key point 2

A **macrostate** is a limited description of the state of the system given by the values of macroscopic variables of interest

To understand this, we must first consider macroscopic variables.

- Macroscopic properties are properties reflecting aggregate behaviour of a large number of constituents.
- Some macroscopic properties are fixed by constraints e.g. total energy  $E$ , and number  $N$  are fixed macroscopic properties in the isolated systems we are considering.
- Other macroscopic variables are free e.g. the number of ideal gas molecules in the left hand side of the box in Figure 3b can take on different values, as can the magnetisation in some macroscopic portion of interest of the magnet.

Now we see that a macrostate is a description which depends on what macroscopic properties we are interested in i.e. we have some freedom in choosing what are to be the macrostates. We adopt the notation of denoting the free macroscopic properties of interest (if any)  $\{\alpha\}$  and we

label macrostates by  $N, E, \{\alpha\}$  (note that to lighten the notation  $N$  is often dropped but  $E$  is usually retained, however we shall retain both for the time being.)

### 💡 Key point 3

To any one macrostate there correspond in general very many microstates.

The number of microstates corresponding to a macrostate  $(N, E, \{\alpha\})$  is called the weight of the macrostate and is denoted  $\Omega(N, E, \{\alpha\})$  or more lazily  $\Omega(E, \{\alpha\})$ .

#### Example of model magnet:

Here we illustrate the idea of microstates and macrostates. To begin with we do not consider any free macroscopic variables thus the macrostates are simply labelled by  $N, E$  (which are fixed). We denote by  $n_i (i = 1, 2)$  the number of dipoles in levels 1 ( $\epsilon = -mH$ ) and 2 ( $\epsilon = +mH$ ) (cf Figure 2). In fact  $n_i$  are determined by the constraints:

$$n_1 + n_2 = N, \quad n_2 - n_1 = \frac{E}{mH}$$

so that

$$n_1 = \frac{1}{2}(N - \frac{E}{mH}), \quad n_2 = \frac{1}{2}(N + \frac{E}{mH})$$

As we stated before a microstate is a complete specification of which state every dipole is in. We now calculate the number of microstates which correspond to the values of  $n_2$ ,  $n_1 = N - n_2$

$$\Omega(N, E) = \binom{N}{n_2} = \frac{N!}{(N - n_2)!n_2!} = \frac{N!}{n_1!n_2!}$$

To lighten the notation, set  $n_2 = n$ ,  $n_1 = N - n$ , with  $n \equiv \frac{N}{2}(1 + \frac{E}{NmH})$  (the number of dipoles in the ‘excited’ state) we can then write

$$\Omega(N, E) = \frac{N!}{n!(N - n)!} \tag{1}$$

### 🔥 If you don't follow this

Here is the reasoning, just like that in chapter 1.4, but now couched in the language of dipoles rather than coins. Take a hatful of  $N$  dipoles; pick one which is to be in level  $i = 1$ ; this can be done in  $N$  ways; from the remaining pool of  $N - 1$  pick a second destined for level  $i = 1$ ; this can be done in  $(N - 1)$  ways. Repeating until you have picked all  $n_1$

required for level 1, you have a total of  $N \times (N-1) \times (N-2) \cdots (N-n_1+1) = N!/(N-n_1)!$  different hat-drawing-possibilities. All the rest of the dipoles must be in level 2, so there are no further choices to make. But now we must recognise that many of the ‘hat-drawing-possibilities’ actually lead to the same microstate. The microstate is defined by saying what state each dipole is in; so it doesn’t matter if dipole 1 is the first or the last to be selected for level 1; to allow for this ‘overcounting’ we must divide by  $n_1!$ , the number of hat drawing possibilities which assign  $n_1$  specified dipoles to level 1.

### Explicit example $N = 3$

Here we can label the macrostates by  $n = 0, 1, 2, 3$

Macrostate	Microstates	Weight
$n = 0, E = -3mH$	$\uparrow\uparrow\uparrow$	1
$n = 1, E = -mH$	$\downarrow\uparrow\uparrow$ $\uparrow\downarrow\uparrow$ $\uparrow\uparrow\downarrow$	3
$n = 2, E = +mH$	$\downarrow\downarrow\uparrow$ $\downarrow\uparrow\downarrow$ $\uparrow\downarrow\downarrow$	3
$n = 3, E = +3mH$	$\downarrow\downarrow\downarrow$	1

(Exercise: repeat for the case  $N = 4$ .)

Taking the logarithm of Equation 1 and invoking the [Stirling approximation](#)  $\ln N! \approx N(\ln N - 1)$ , good for large  $N$ , we can write

$$\begin{aligned}
 \ln \Omega(N, E) &= \ln N! - \ln n! - \ln(N-n)! \\
 &= N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \\
 &= N \left[ \ln N - \frac{n}{N} \ln n - \left(1 - \frac{n}{N}\right) \ln(N-n) \right] \\
 &= N \left[ -\frac{n}{N} \ln \left(\frac{n}{N}\right) - \left(1 - \frac{n}{N}\right) \ln \left(1 - \frac{n}{N}\right) \right]
 \end{aligned}$$

where we have used a ‘trick’ to write:

$$\ln N = -\frac{n}{N} \ln \frac{1}{N} - \left(1 - \frac{n}{N}\right) \ln \frac{1}{N}$$

Thus

$$\frac{1}{N} \ln \Omega(N, E) = s(n/N)$$

where  $s(x) = -(1-x) \ln(1-x) - x \ln x$

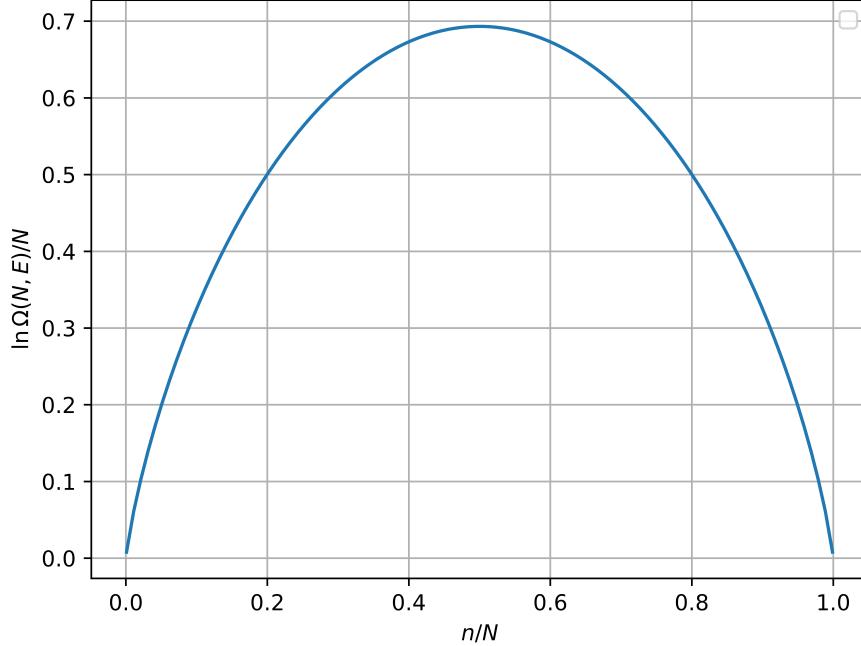


Figure 4: Logarithm of the weight function,  $\ln \Omega(N, E)/N$ , for the simple model magnet, plotted as a function of the fraction  $n/N$  of dipoles in excited states;  $n$  and  $E$  are related by  $n = \frac{N}{2}(1 + E/NmH)$ .

The logarithm of  $\Omega(N, E)$  is displayed in Figure 4. Note the key features:

- When  $E$  has its minimum value,  $E = -NmH$  (ie  $n = 0$ ), then  $\ln \Omega(N, E) = 0$  and  $\Omega(N, E) = 1$ . There is only a single microstate associated with this macrostate.
- As  $E$  increases from its minimum,  $\ln \Omega(N, E)$  increases steeply.
- For  $E = 0$  (ie.  $n = N/2$ ) we have a maximum where  $\ln \Omega(N, E) = N \ln 2$ , and  $\Omega(N, E) = 2^N$ . In general the logarithm of  $\Omega$  is proportional to the size of the system (we say that it is ‘extensive’)
- Since  $\Omega = \exp(Ns(x))$  the weight function is exponentially large in  $N$  but the logarithm is proportional to  $N$ .

The scaling of  $\Omega(N, E)$  with  $N$  is demonstrated by Figure 5 for systems of  $N = 2, 4, 8, 16, 32, 64$  dipoles. We see that the number of microstates for each energy increases strongly with  $N$  and  $\Omega(N, E)$  gets narrower. This trend continues so that for Avogadro's number of dipoles, the plot Figure 6 of  $\Omega(E)$  is practically infinitely high and infinitesimally narrow. This is the key insight of this exercise: for large  $N$  there are overwhelmingly more microstates associated with the ‘equal-shares’ macrostate than there are associated with any significantly different macrostate. Problem 2.2 invites you to explore the properties of the weight function.

For  $N = 10^{23}$  dipoles, Figure 6 shows that the weight function is essentially a  $\delta$  function

In order to understand what we mean by free macroscopic variables  $\{\alpha\}$  we consider as an example the number of dipoles that are in the excited state in the left hand side of our array of  $N$  dipoles. We denote this number by  $n_L$ . This number is not fixed by our constraints; we only have to satisfy  $n_R + n_L = n$  where  $n_R$  is the number of excited dipoles in the right hand region.

We now label our macrostates by  $N, E, n_L$

We can calculate the weight of a macrostate by combinatorics: in the left hand region we can choose the  $n_L$  excited dipoles from  $N/2$  and similarly in the right hand region  $n_R = n - n_L$  are chosen from  $N/2$ . Thus

$$\Omega(N, E, n_L) = \binom{N/2}{n_L} \binom{N/2}{n - n_L}$$

In the special case where  $E = 0$ , so  $n_1 = n_2 = n = N/2$  and  $n_L = N/2 - n_R$ , one can show using Stirling’s approximation (see question 2.3) that

$$\frac{1}{N} \ln \Omega(N, 0, n_L) \simeq s(n_L/(N/2))$$

Since  $n_L$  is free, it is in principle possible for the system to move between different macrostates, moreover the different available macrostates have different weights. In particular we see that macrostates with  $n_L \simeq N/4$  have huge weights compared to say  $n_L \simeq N/2$ . Question 2.3 explores this point

### 2.3 Significance of the weight function: Entropy

We have seen that the logarithm of the weight function is the quantity proportional to  $N$ . We now state an important point relating this quantity to the entropy of a macrostate

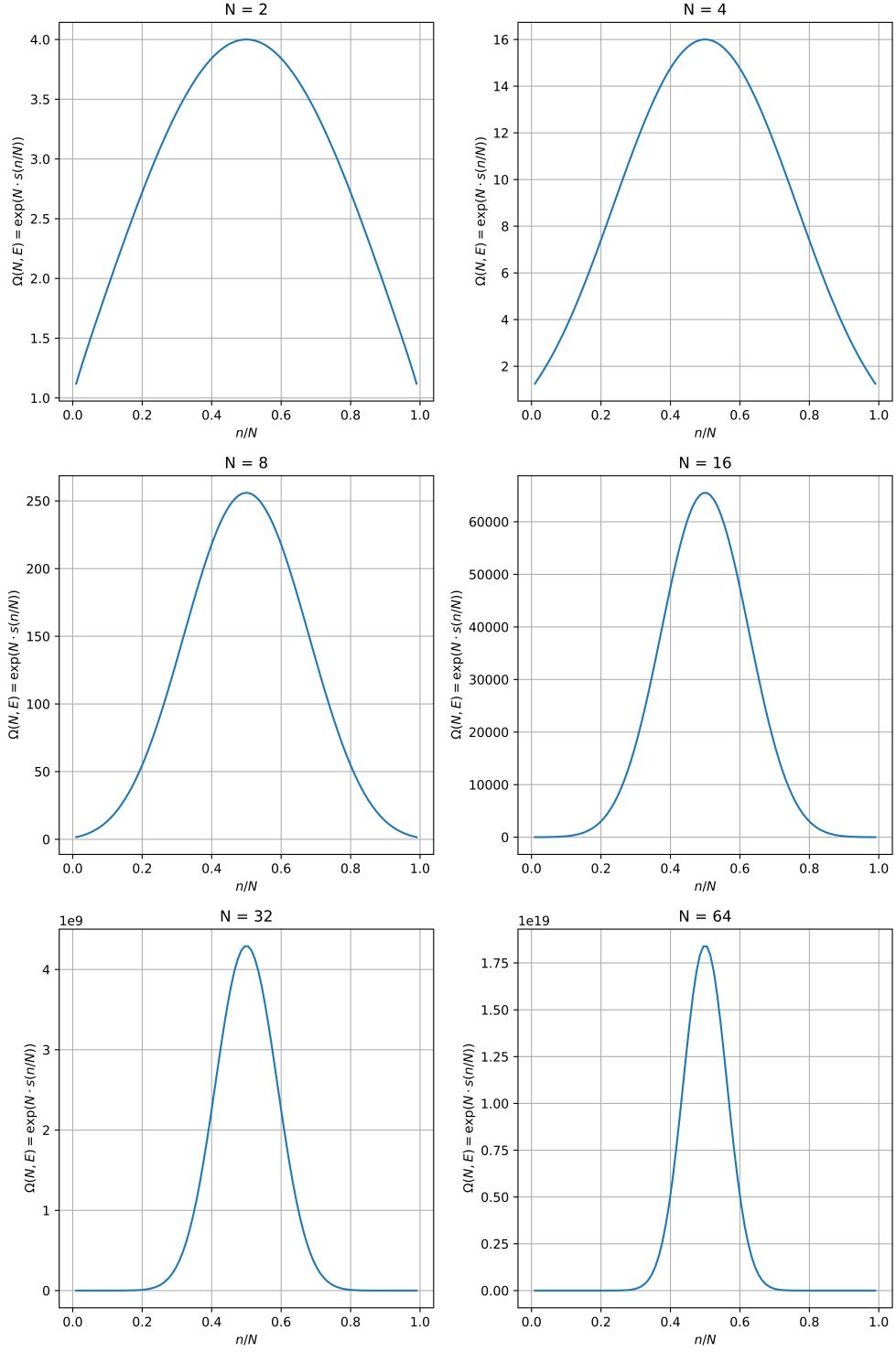


Figure 5: Weight function  $\Omega(N, E)$ , for the simple model magnet comprising  $N = 2, 4, 8, 16, 32, 64$  dipoles, plotted as a function of the fraction  $n/N$  of dipoles in excited states;  $n$  and  $E$  are related by  $n = \frac{N}{2}(1 + E/NmH)$ . Note the y-axis scales and the narrowing of the function with increasing  $N$ .

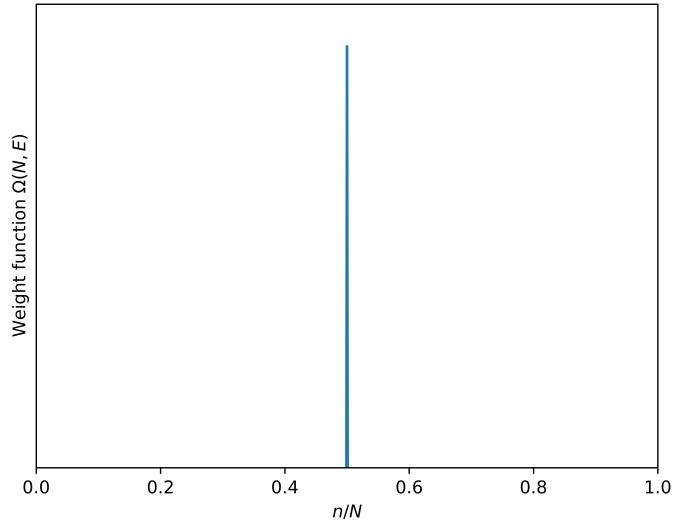


Figure 6: For  $N = 10^{23}$  dipoles the weight function  $\Omega(N, E)$  is essentially a delta function.

 Key point 4

$$S(N, E, \{\alpha\}) = k \ln \Omega(N, E, \{\alpha\})$$

where  $k = 1.381 \times 10^{-23} J/K$  is Boltzmann's constant. The entropy  $S(N, E, \{\alpha\})$  of a macrostate is *defined* by this relation which for the moment we consider as a postulate. The logarithmic connection between entropy and probability was formulated by Boltzmann (though the above form of the equation is due to Planck). We shall refer to it as the [Planck equation](#).