



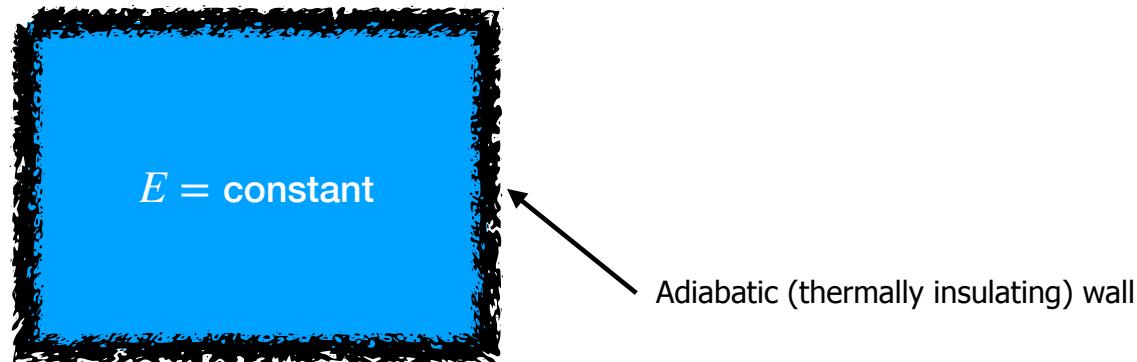
Statistical Mechanics

2. Foundations: equilibrium of an isolated system



Foundations: equilibrium of an isolated system

- Isolated 'system': no transfer of energy to the surroundings, so its total energy is constant

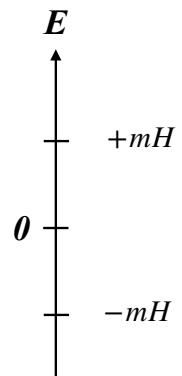


- We shall consider case where the system is either an ideal gas or a simple magnet.
- A simple model of a magnet comprises a crystalline lattice of magnetic dipoles each with a magnetic dipole moment m which are assumed to be in a magnetic field H .

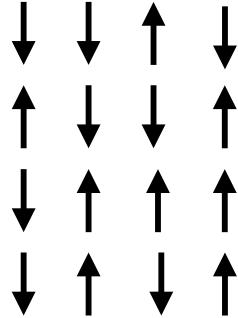


Foundations: equilibrium of an isolated system

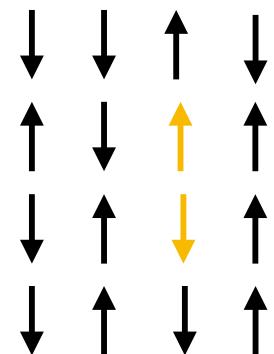
- Each dipole or ‘spin’ is assumed to be able to align parallel or antiparallel to H
 - Parallel to H with energy $\epsilon = -mH$ (ground state)
 - Antiparallel to H with energy $\epsilon = +mH$ (excited state)



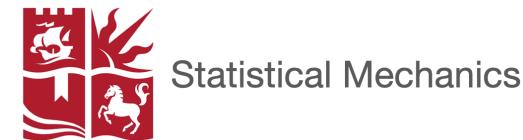
H



- Transitions: state of individual dipoles can change ('flip') through interactions with their neighbours, subject to conserving total E

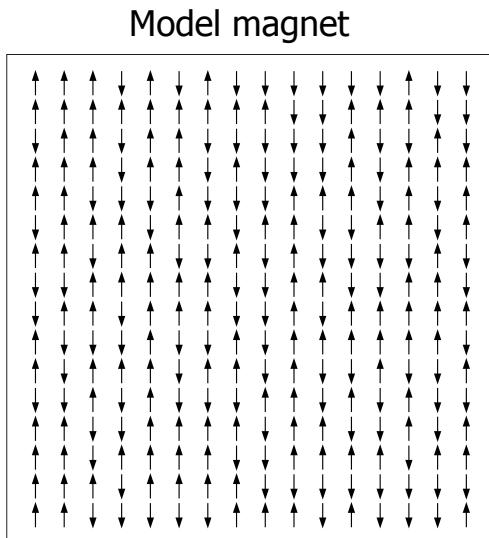


Microstates and macrostates



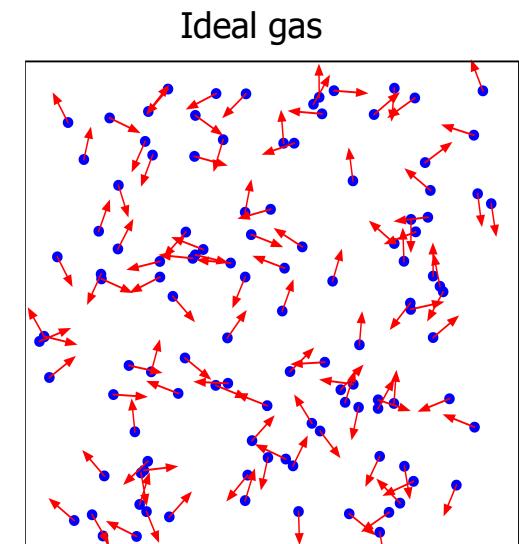
Two different levels of description of a system: **microstates** and **macrostates**

- Key point 1: *A microstate is a complete specification of the state of the system according to the microscopic model.*



Requires knowledge of the orientation of each dipole on the lattice

Requires knowledge of the position and velocity vectors of each molecule



The microstate will change continually as the particles exchange energy

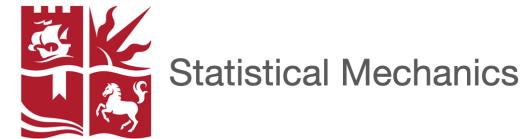
Microstates and macrostates



Statistical Mechanics

- *Key point 2: A macrostate is a limited description of the state of the system given by the values of macroscopic variables of interest*
- Macroscopic properties reflect the **aggregate** behaviour of a large number of constituents (not necessarily all of them)
 - Some macroscopic properties are fixed by constraints e.g. total energy E , and total number of constituents N are fixed macroscopic properties of an isolated system.
 - Other macroscopic variables are ‘free’ e.g. the number of ideal gas molecules in the left hand side of the box can take on different values
- 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.
- Denote the set of free macroscopic properties of interest (if any) $\{\alpha\}$ and label macrostates by $N, E, \{\alpha\}$

Microstates and macrostates



- *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 $\Omega(N, E, \{\alpha\})$.

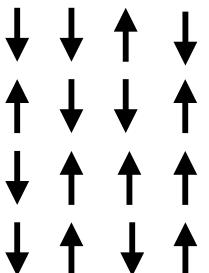
- Consider how to count $\Omega(N, E, \{\alpha\})$ for our simple magnet.

- To begin, consider only the fixed macroscopic properties ie. $\Omega(N, E)$

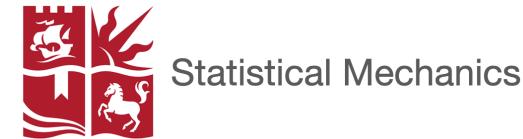
- Denote by n_1 the number of dipoles in levels 1 ($\epsilon = -mH$) and n_2 the number in level 2 ($\epsilon = +mH$). n_1 and n_2 are determined by the fixed values of N, E :

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

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



Microstates and macrostates



- Conversely, for a given N , choosing n_2 sets the energy E .
- So calculating the number of microstates having a given n_2 gives us $\Omega(N, E)$
- This is binomial statistics (spins can only be up or down), so

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

- To lighten notation, let $n = n_2$, $n_1 = N - n$.

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

Microstates and macrostates



Statistical Mechanics

Example: $N = 3$

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 $N = 4$

Microstates and macrostates



Statistical Mechanics

- $\Omega(N, E) = \frac{N!}{n!(N-n)!}$ can be very large!
- Consider its logarithm and apply Stirling's approximation $\ln N! \approx N(\ln N - 1)$

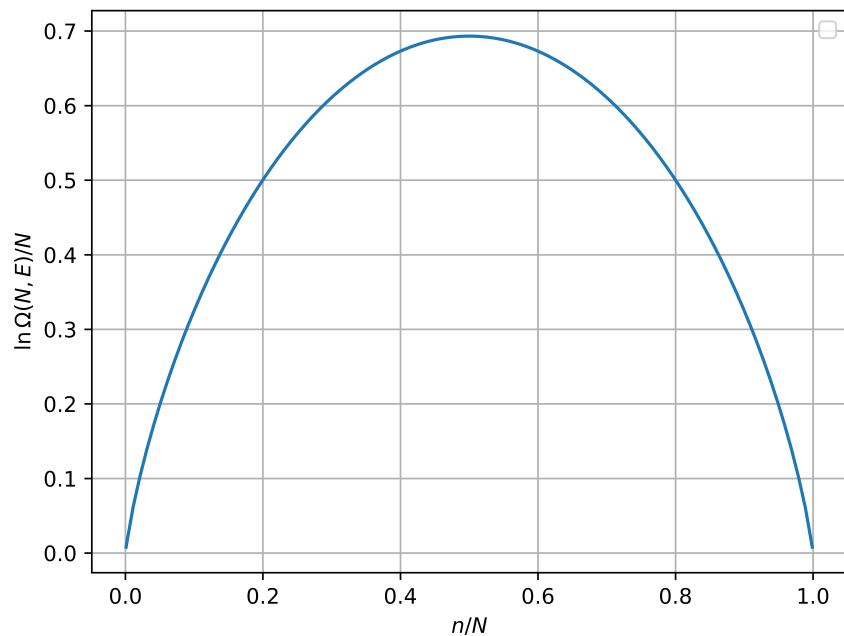
$$\begin{aligned}\ln \Omega(N, E) &= \ln N! - \ln n! - \ln(N-n)! \\ &= N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \\ &= N \left[\ln N - \frac{n}{N} \ln n - \left(1 - \frac{n}{N}\right) \ln(N-n) \right] \\ &= N \left[-\frac{n}{N} \ln \left(\frac{n}{N} \right) - \left(1 - \frac{n}{N}\right) \ln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

$$\frac{1}{N} \ln \Omega(N, E) = s(n/N) \quad \text{where} \quad s(x) = -(1-x)\ln(1-x) - x \ln x$$

Microstates and macrostates



Statistical Mechanics

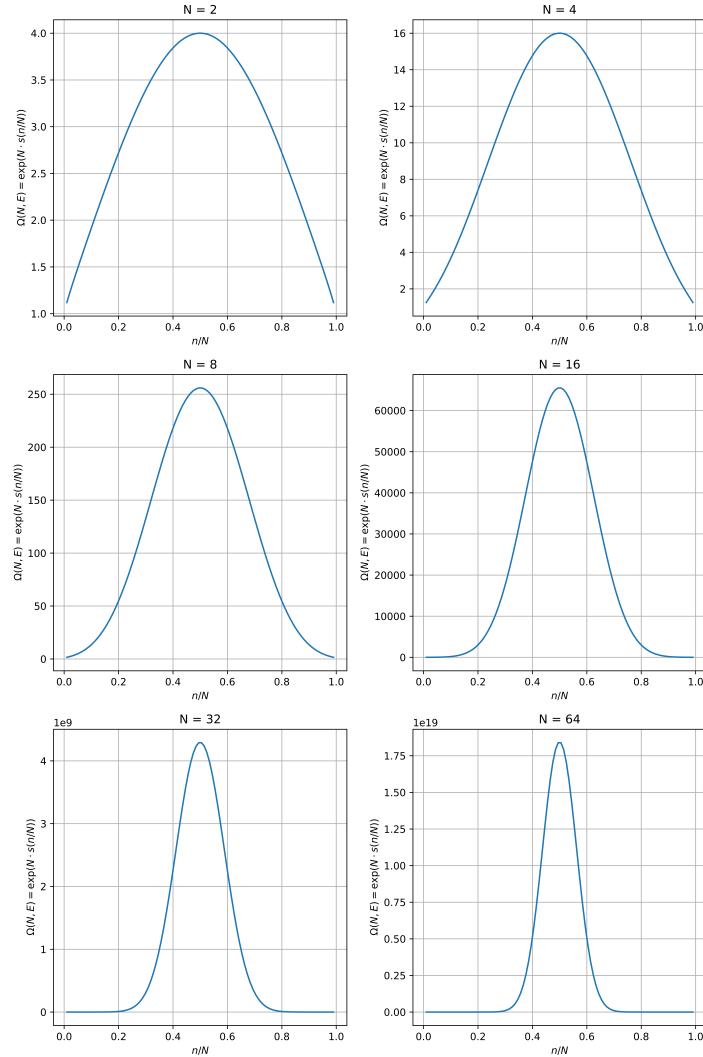


- Consider macrostate with $n = 0$ (all dipoles aligned with H). $E = -NmH$ (minimum value). This macro state has only a single microstate. Thus $\Omega(N, E) = 1$ and $\ln \Omega(N, E) = 0$.
- As E increases from minimum, $\ln \Omega(N, E)$ increases steeply.
- For $E = 0$ (ie. $n = N/2$), $\Omega = 2^N$, and $\ln \Omega(N, E) = N \ln 2$ is maximised.
- In general $\ln \Omega(N, E) \propto N$. We say that it is 'extensive'

Microstates and macrostates

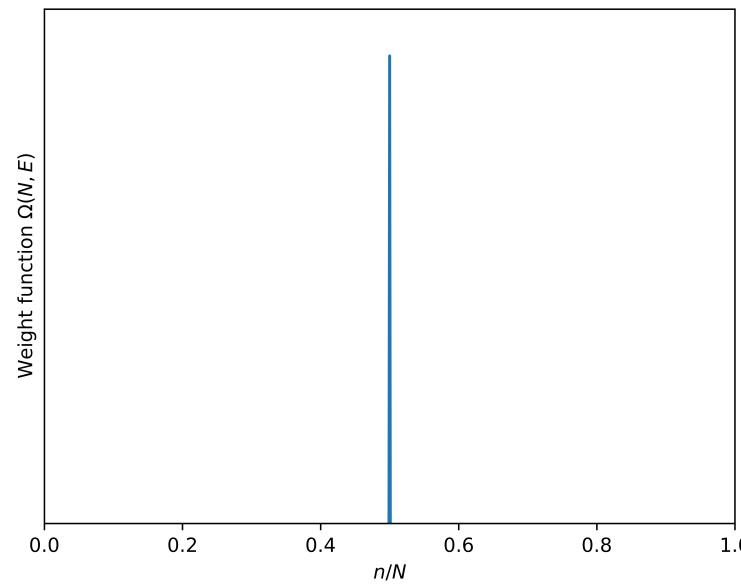


Statistical Mechanics



- Consider now the effects of varying N .
- Since $\Omega = \exp N s(x)$ the weight function is exponentially large in N but the logarithm is proportional to N .

$$N \sim 10^{23}$$

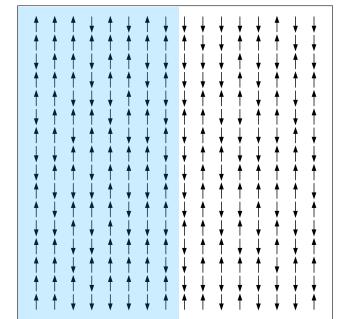


Microstates and macrostates



- So far have considered weights only for the constrained macrostates N, E
- Consider an example **free** macroscopic variable (ie chosen by us, not fixed by constraints).
- Number of excited dipoles n_L in the left hand half of our array of N dipoles. This number is not fixed by our constraints on N and E ; we only have to satisfy $n_L + n_R = n$.
- Label our macrostates by N, E, n_L
- Weight of a macrostate is given 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

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



Microstates and macrostates

$$\Omega(N, E, n_L) = \binom{N/2}{n_L} \binom{N/2}{n - n_L} \quad \text{doesn't simplify in general}$$

....but in the special case where $E = 0$, so $n_1 = n_2 = n = N/2$ and $n_L = n - n_R$, one can show using Stirling's approximation (see problem 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 $n_L \simeq N/2$.



Significance of the weight function

- We have seen that the logarithm of the weight function is a quantity proportional to N
- We now relate this quantity to the entropy of a macrostate:
 - *Key point 4:* $S(N, E, \{\alpha\}) = k \ln \Omega(N, E, \{\alpha\})$

$k = 1.381 \times 10^{-23} J/K$ 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**.

Worked example

Q: in a model of a particular solid, each atom can exist in either of two states $i = 1, 2$. Three quarters of the atoms are in state $i = 1$. Use the Planck relation to calculate the entropy of this solid.

Solution: Let $N_1 = \frac{3N}{4}$, $N_2 = \frac{N}{4}$ Now $\Omega = \binom{N}{N_2} = \frac{N!}{N_1!N_2!}$ and $S = k \ln \Omega$

- Apply Stirling's approximation $\ln N! \approx N \ln N - N$

$$\begin{aligned}
 \ln \Omega &\approx N \ln N - N - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2) \\
 &= N \ln N - N_1 \ln N_1 - N_2 \ln N_2 \\
 &= N \left(\ln N - \frac{3}{4} \ln \frac{3N}{4} - \frac{1}{4} \ln \frac{N}{4} \right) \\
 &= N \left(-\frac{3}{4} \ln \frac{3}{4} - \frac{1}{4} \ln \frac{1}{4} \right) \\
 &\approx 0.562N
 \end{aligned}$$

$$\Rightarrow S \approx 0.562Nk$$