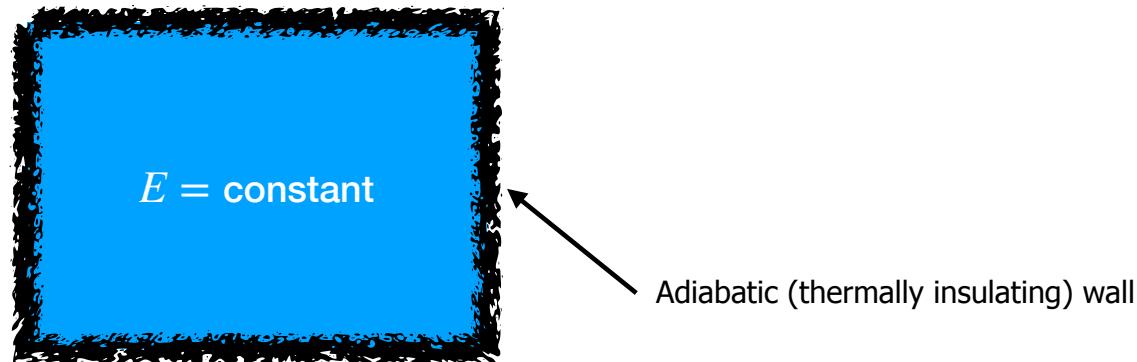




## 2. Foundations: equilibrium of an isolated system

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

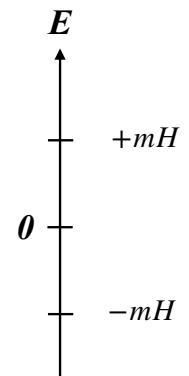


- We shall consider case where the system is either an ideal gas or a simple magnet
- A simple model of a magnet comprises a crystalline lattice of magnetic dipoles each with a magnetic dipole moment  $m$  which are assumed to be in a magnetic field  $H$ .

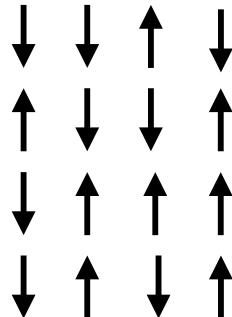
## 2. Foundations: equilibrium of an isolated system



- Each dipole 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)
  -

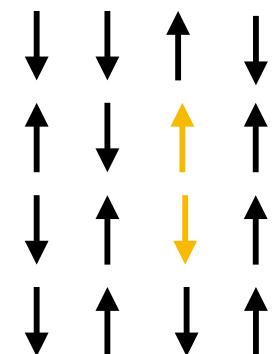


$H$

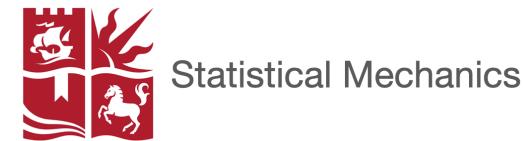


Dipole configuration

- Transitions of individual dipoles (or 'spins') can change if they interact with three neighbours, subject to conserving total  $E$

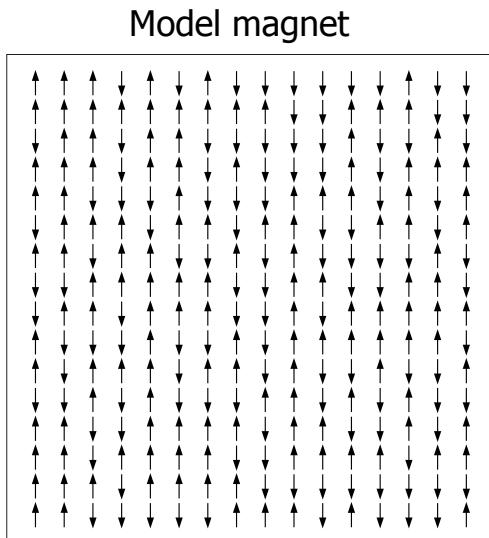


# Microstates and macrostates



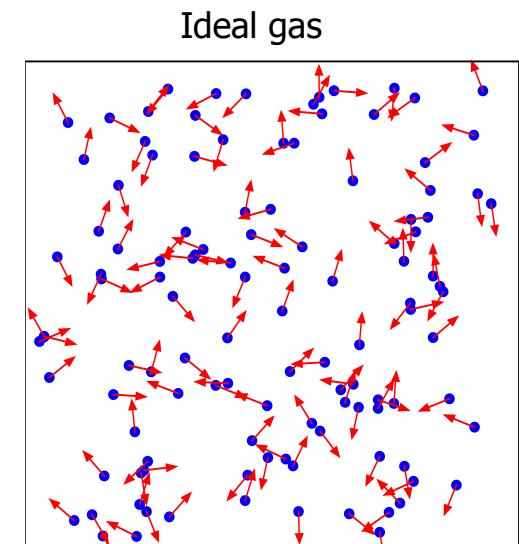
Two different levels of description of a system: **microstates** and **macrostates**

- 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 number  $N$  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.
- We adopt the notation of denoting the free macroscopic properties of interest (if any)  $\{\alpha\}$  and we label macrostates by  $N, E, \{\alpha\}$

# Microstates and macrostates



- *Key point 3: To any one micro state there correspond in general very many microstates*

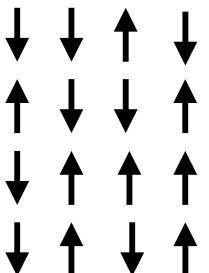
- The number of microstates corresponding to a macrostate  $(N, E, \{\alpha\})$  is called the **weight** of the macrostate and is denoted  $\Omega(N, E, \{\alpha\})$ .

- 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  $n_i$  ( $i = 1, 2$ ) the number of dipoles in levels 1 ( $\epsilon = -mH$ ) and 2 ( $\epsilon = +mH$ ). Because  $N, E$  are both constants  $n_i$  are determined:

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



# Microstates and macrostates



Statistical Mechanics

- For a given  $N$ , choosing  $n_2$  sets the energy  $E$ .
- So calculating number of microstates have a given  $n_2$  gives us  $\Omega(N, E)$

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

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

*Exercise: repeat for  $N = 4$*

# Microstates and macrostates



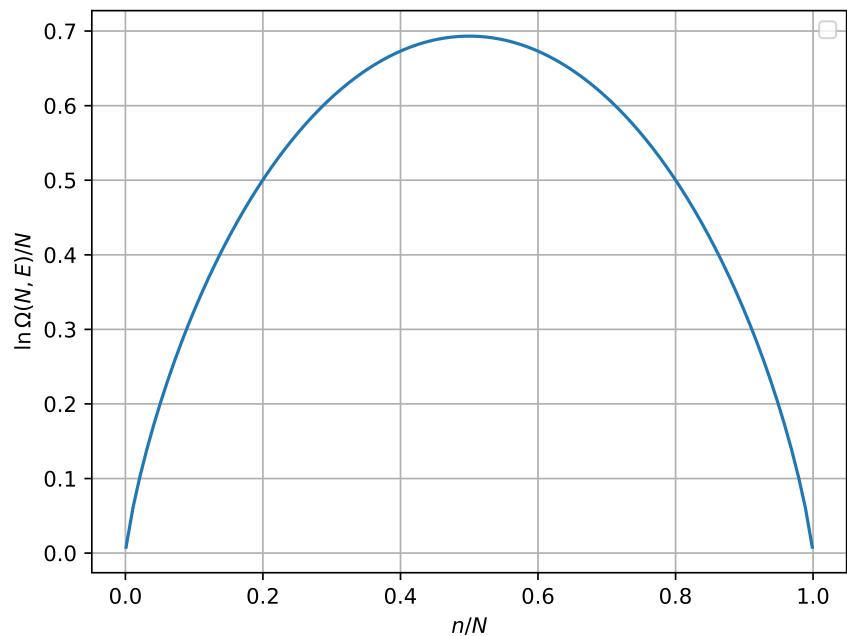
Statistical Mechanics

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

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

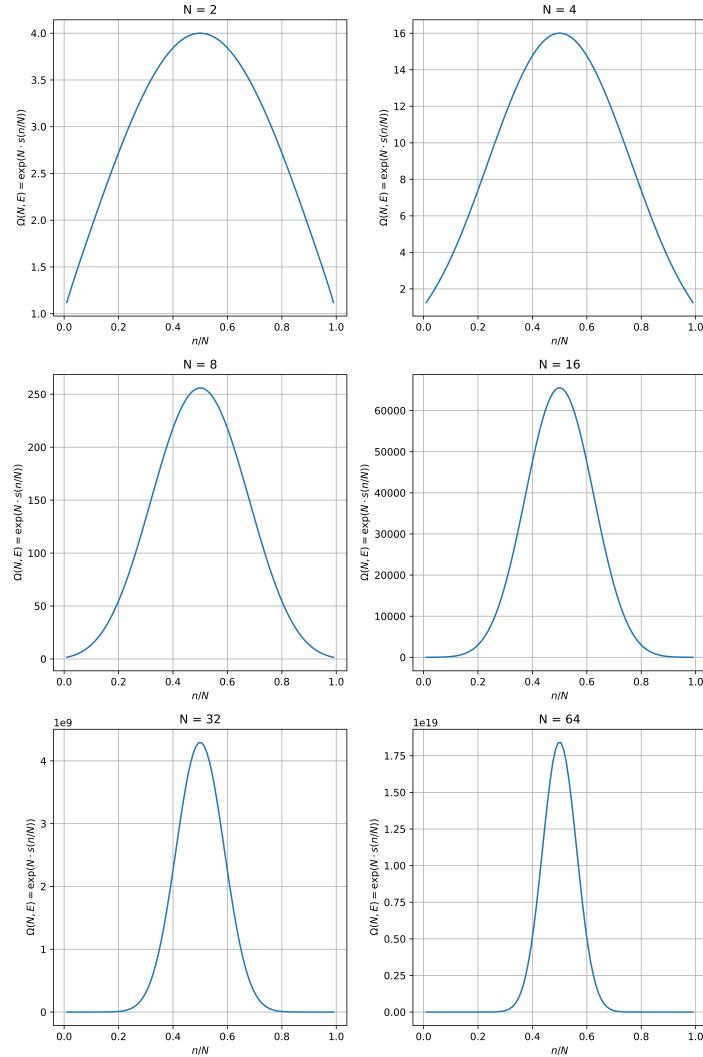
$$\frac{1}{N} \ln \Omega(N, E) = s(n/N) \quad \text{where} \quad s(x) = -(1-x)\ln(1-x) - x \ln x$$

# Microstates and macrostates



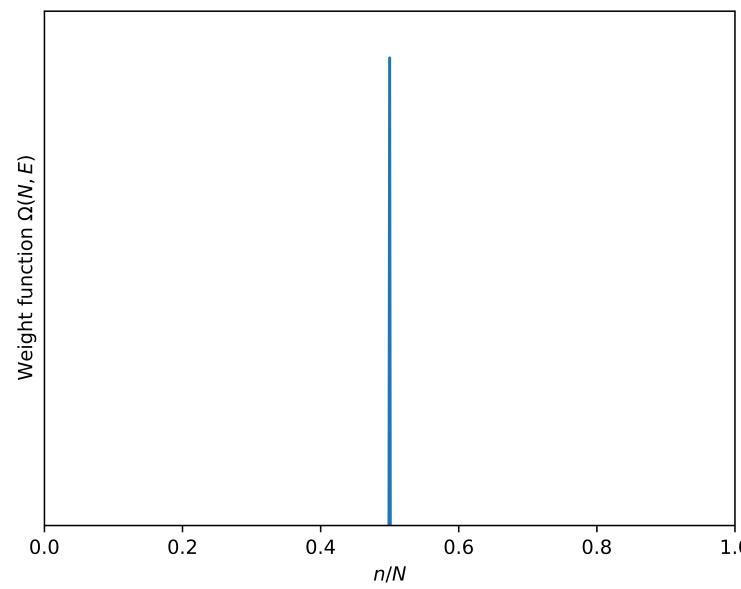
- Consider macrostate with  $n = 0$  (all dipoles aligned with  $H$ ).  $E = -NmH$  (minimum value). This macro state has only a single microstate. Thus  $\Omega(N, E) = 1$  and  $\ln \Omega(N, E) = 0$ .
- As  $E$  increases from minimum,  $\ln \Omega(N, E)$  increases steeply.
- For  $E = 0$  (ie. 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



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

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

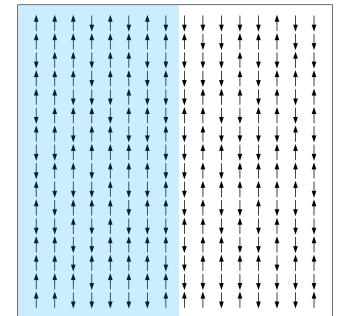


# Microstates and macrostates



- 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

- 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 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  $n_L \simeq N/2$ .



# Significance of the weight function

- We have seen that the logarithm of the weight function is the quantity proportional to  $N$
- An important point relating 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**.