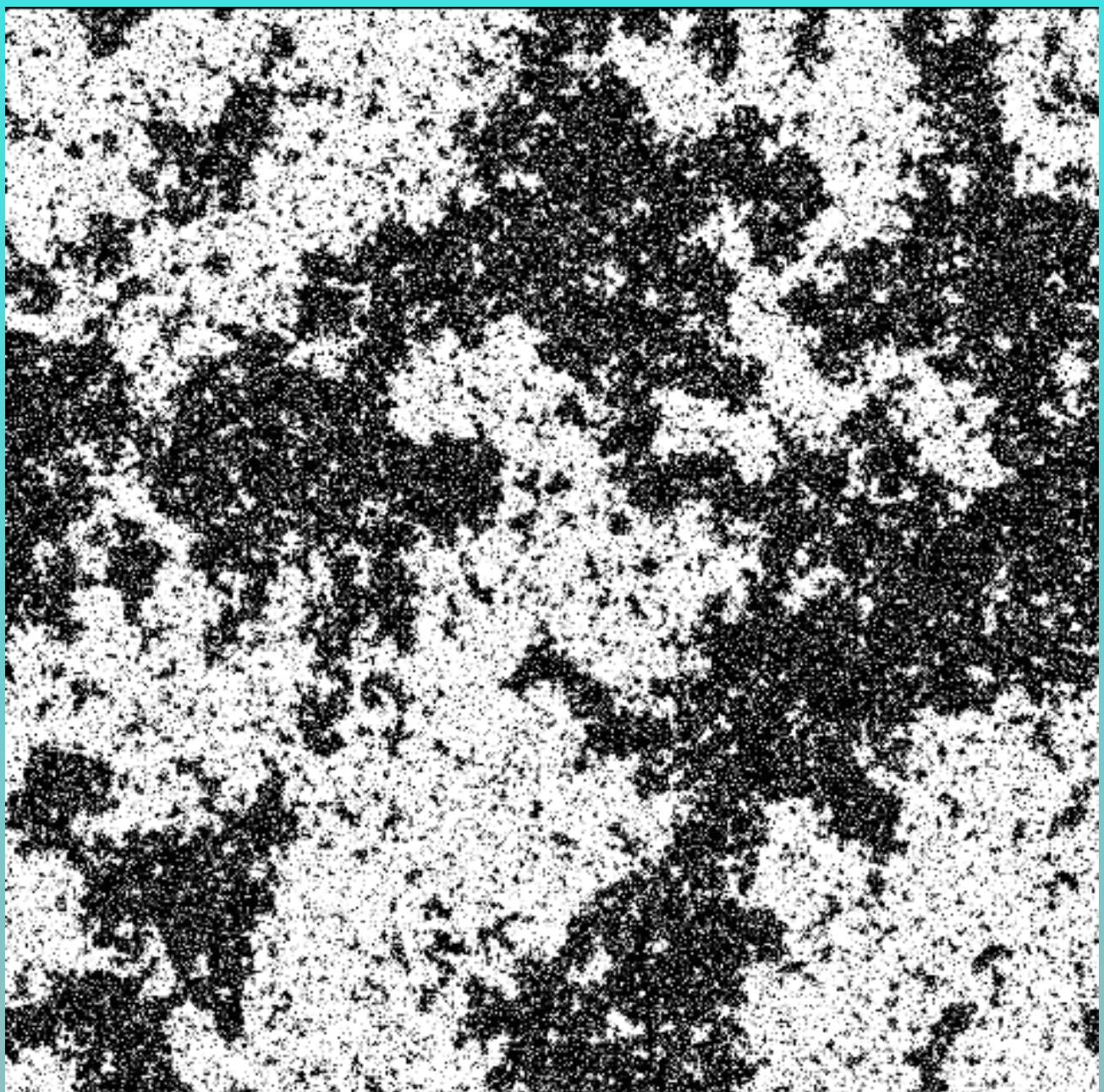


# PHYS20040: Statistical Mechanics

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Welcome!



# 1. Introduction

# What is Statistical Mechanics?



Statistical Mechanics

Statistical mechanics, together with **classical thermodynamics**, form two branches of **thermal physics**

Each branch represents a distinct approach to thermal physics:

## Macroscopic Approach (Classical Thermodynamics)

- deals with **macroscopic** variables i.e. variables that do not refer to any microscopic details
- input is phenomenological laws e.g. equation of state
- output is general relations between macroscopic variables
- advantage is the generality of the approach

## Microscopic Approach (Statistical Mechanics)

- starts from a **microscopic** description and seeks to explain macroscopic properties
- input is a microscopic model of a given system
- output is predictions for macroscopic properties and behaviour
- predictions can be compared to experiment thus allowing refinement of the microscopic model



# What is Statistical Mechanics?

	<b>Thermodynamics</b>	<b>Statistical Mechanics</b>
Quantity of interest	Macroscopic properties (eg. $P, V, T, C_P, C_V$ )	Microscopic properties (eg: molecular speeds)
Strategy	Avoid microscopic model	Build on microscopic model
Strengths	Generality of results	Provides way of refining microscopic understanding
Weaknesses	No understanding of system-specific features. Conceptually opaque.	Requires additional input (the model). Requires additional techniques (probability theory; classical and quantum mechanics)

# What is Statistical Mechanics?



Statistical Mechanics

- Provides powerful concepts and tools that help us understand the properties of complex systems with very many constituents.
- Used in research of systems as diverse as earthquakes, traffic jams, superconductivity, economics, and many more.
- **Aim of this course:** Show how key concepts that you have met in thermodynamics, such as the Boltzmann factor, entropy, and the second law, can be formulated and find expression in statistical terms.
- Develop and illustrate fundamental concepts and methods use two prototype systems:
  - Gases (classical and quantum)
  - Classical magnets
- For more advanced Soft Matter systems (eg. polymers, liquid crystals, glasses, surfactants, active matter) see M-level unit: **Complex and Disordered Matter**



# The microscopic approach

- In principle, can imagine solving Newton's equation for the atomic and molecular motions in a system of interest to determine its behaviour.



- But typical systems contain of order a mol, ie.  $10^{23}$  particles - more than all the grains of sand on all the beaches in the world, or stars in the visible universe!
- So exact approach is impractical and therefore we instead appeal to ideas from statistics and seek to make probabilistic statements about a systems behaviour.
- This works well because as the number of particles becomes very large, things get simpler.  
Revise your probability and statistics notes from first year laboratory, particularly on binatorics, probability distributions, and summary statistics; read the section on probability in the ure notes (end of sec 1.3)



# Simplicity at large $N$

Toss a fair coin  $N$  times.

What is the probability  $p_n$  of getting  $n$  heads from a trial?

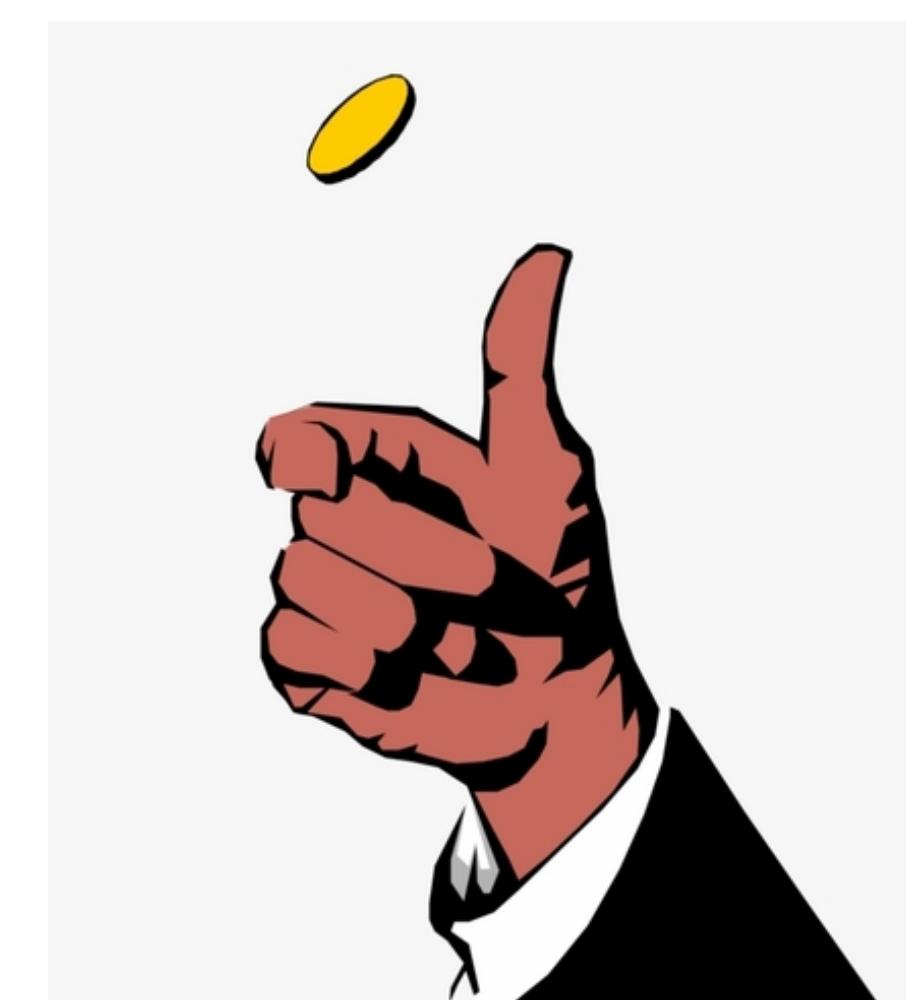
Denote by  $p$  the probability that a head results from a single toss; then  $q = 1 - p$  is probability for a tail.

This is binomial statistics. Recall:

$$\begin{aligned} p_n &\equiv \text{number of distinct ways of obtaining } n \text{ heads} \\ &\times \text{probability of any specific way of getting } n \text{ heads} \\ &= \binom{N}{n} p^n q^{N-n} \end{aligned}$$

The distribution  $p_n$  has mean  $\bar{n} \equiv \sum_{n=0}^N np_n = Np$

and variance  $\overline{\Delta n^2} \equiv \sum_{n=0}^N (n - \bar{n})^2 p_n = Npq$





# Simplicity at large $N$

- For a fair coin  $p = q = \frac{1}{2}$
- Define  $f = n/N$ , the fraction of  $N$  tosses resulting in a head
- Mean of  $f$

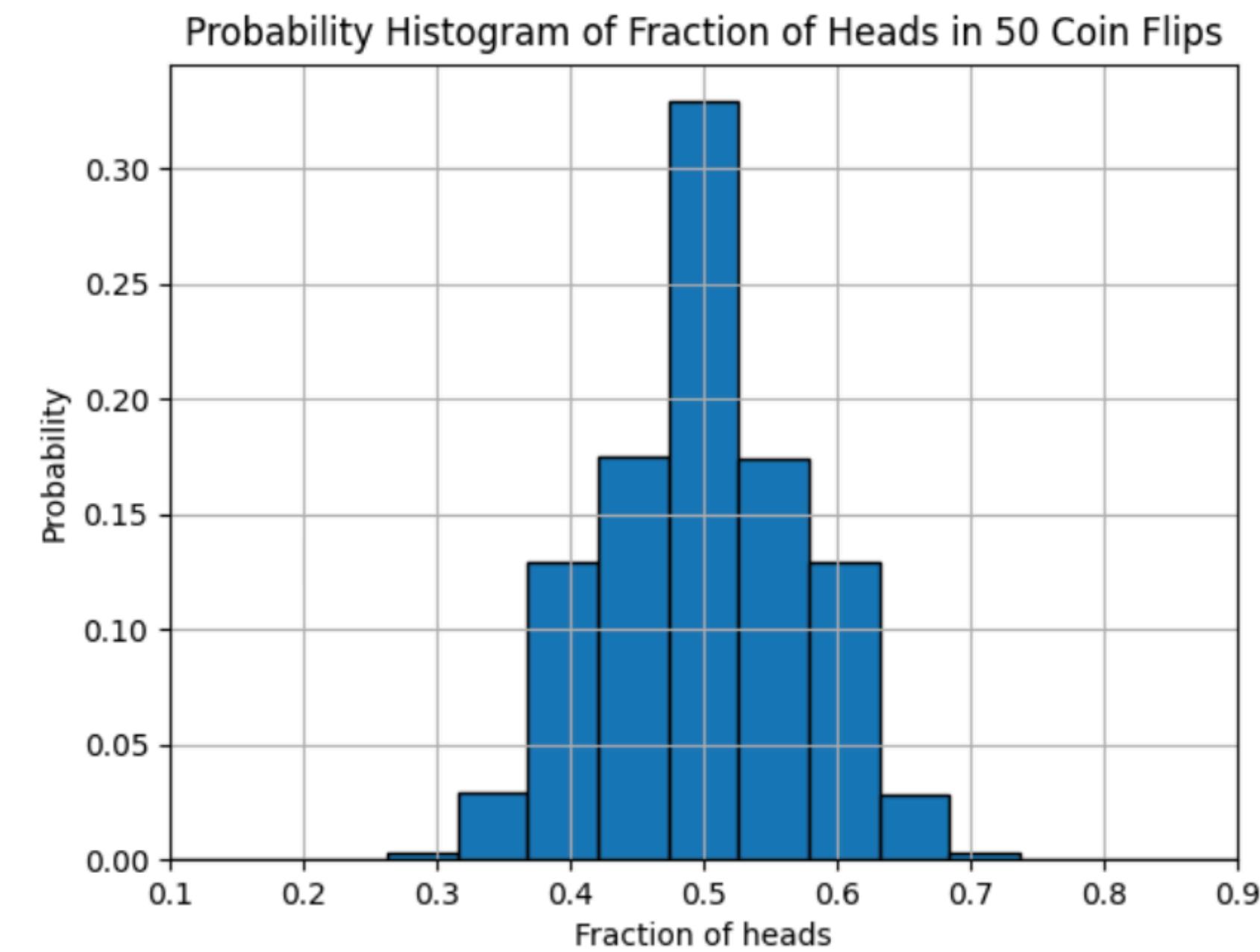
$$\bar{f} = \frac{\bar{n}}{N} = p = \frac{1}{2}$$

and standard deviation

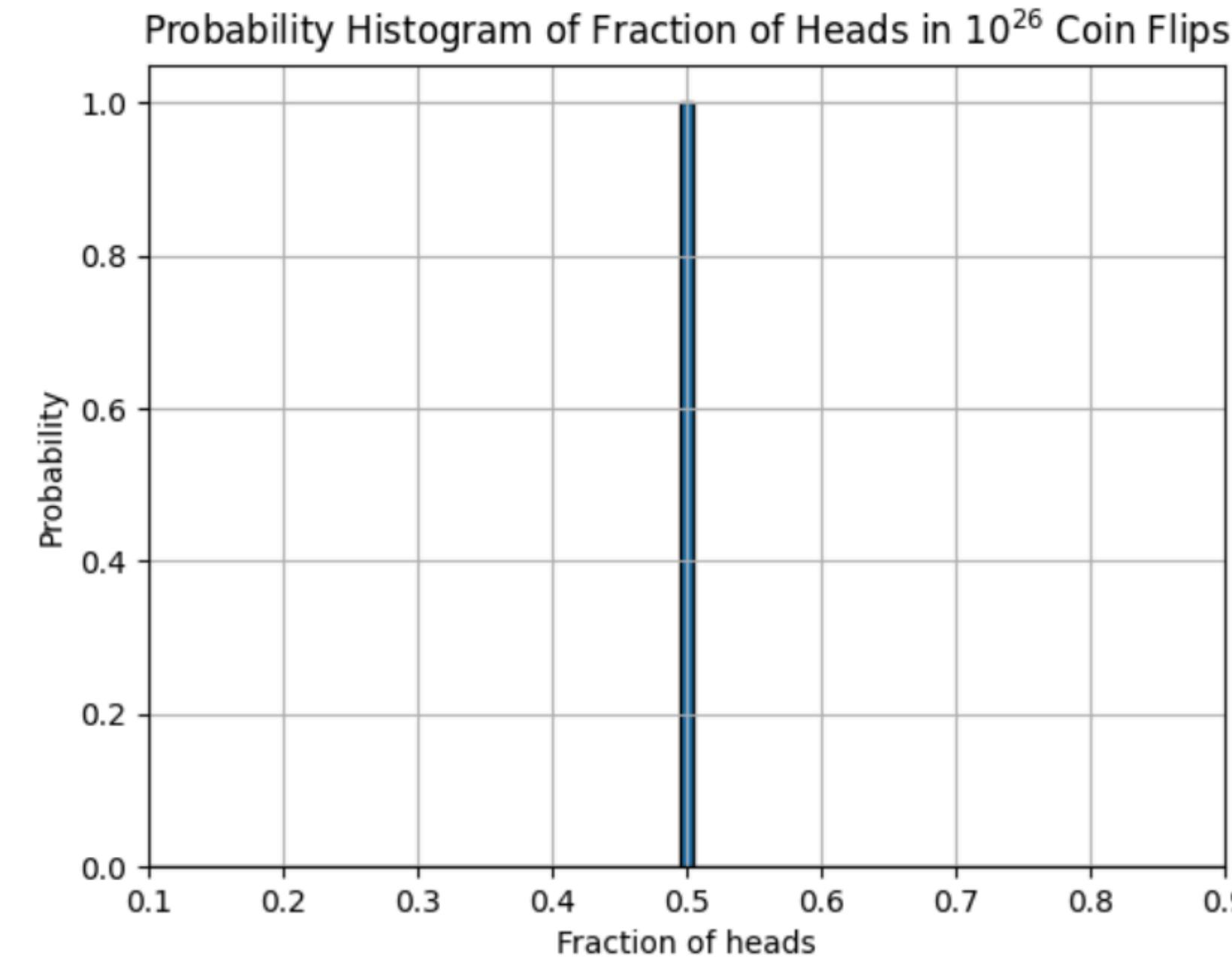
$$(\overline{\Delta f^2})^{1/2} \equiv \frac{(\overline{\Delta n^2})^{1/2}}{N} = \left( \frac{pq}{N} \right)^{1/2} = \frac{1}{2N^{1/2}}$$

- The typical deviation of  $f$  from its mean value is thus vanishingly small for large  $N$

# Simplicity at large $N$



(a) For  $N = 50$  tosses, we can be reasonably sure that  $f$  will be close to 0.5

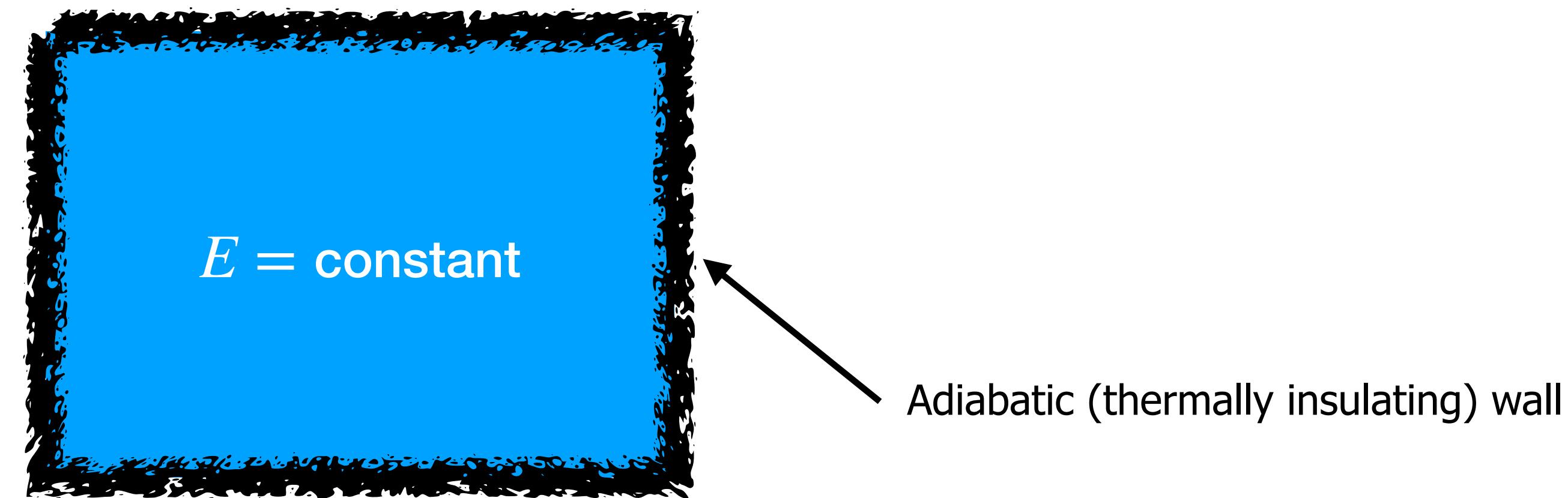


(b) For  $N = 10^{26}$  tosses We can be absolutely sure that  $f$  will be indistinguishable from 0.5



## 2. Foundations: equilibrium of an isolated system

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

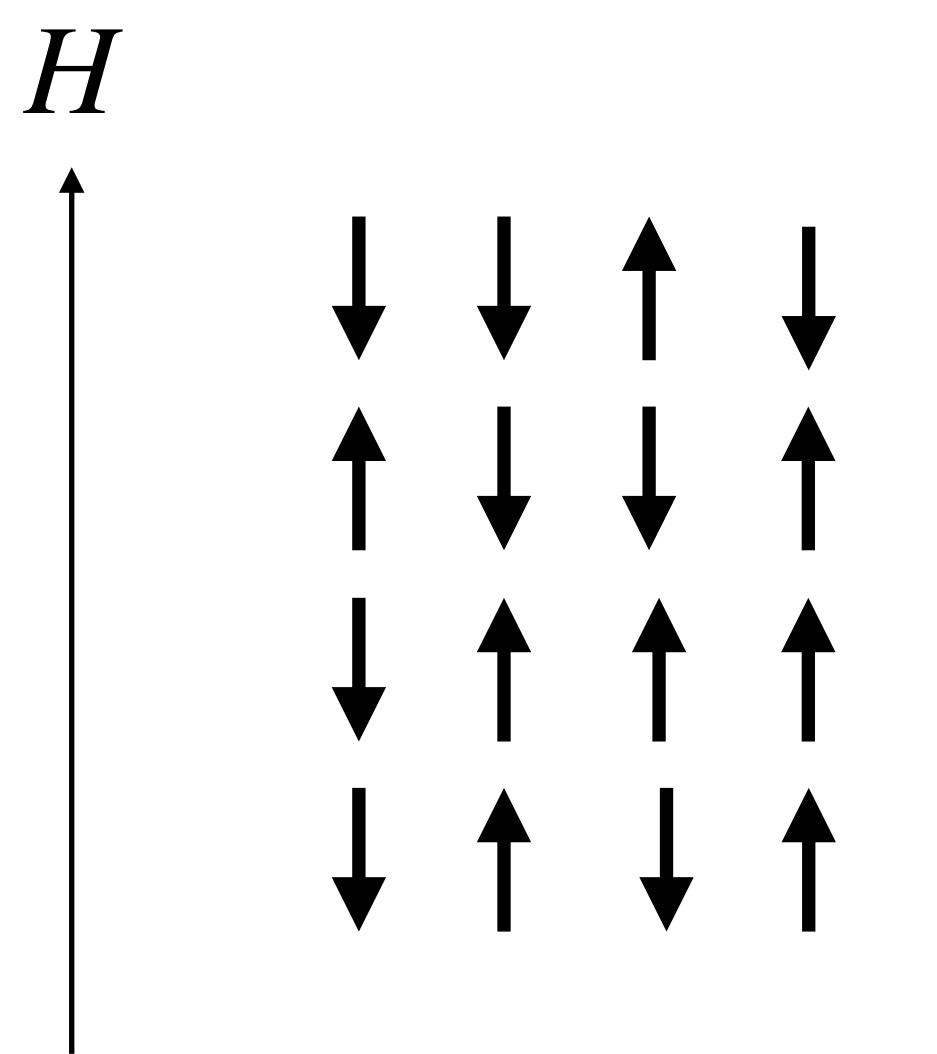
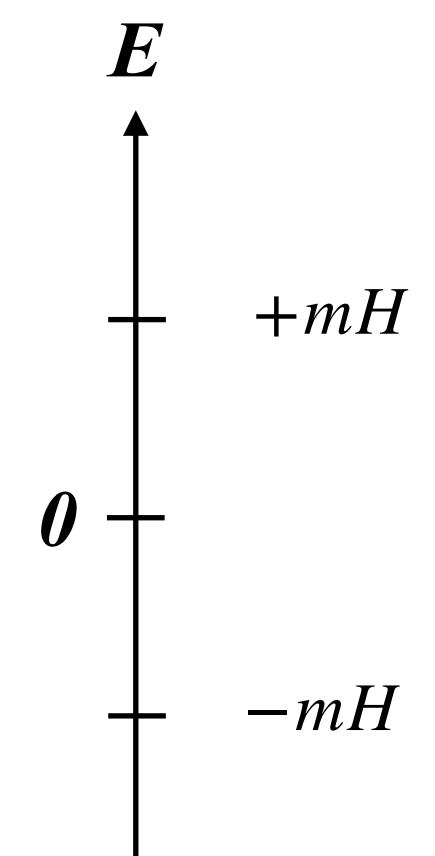


- We shall consider case where the system is either an ideal gas or a simple magnet
- Magnet can be thought of as a crystalline lattice of magnetic dipoles each with a magnetic dipole moment  $m$  which are assumed to be in a magnetic field  $H$ .

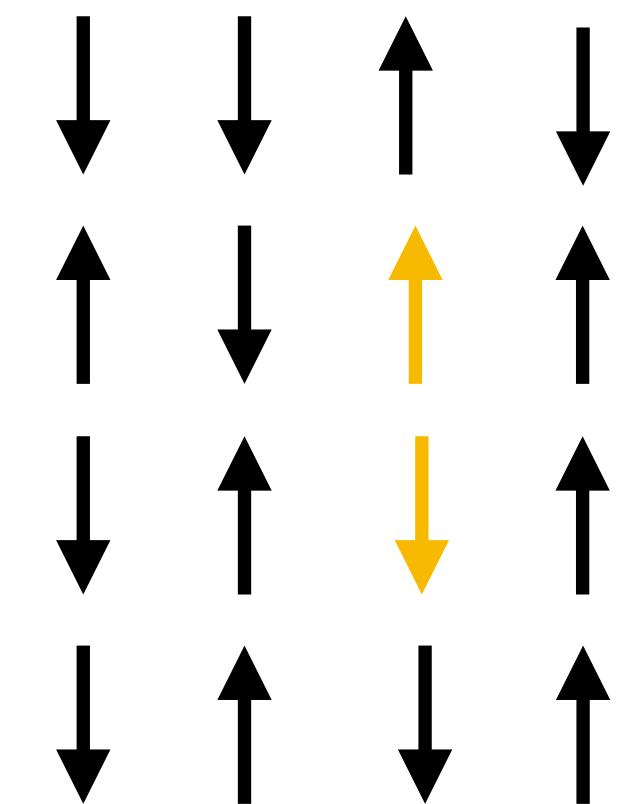


## 2. Foundations: equilibrium of an isolated system

- 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)
  -



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



Dipole configuration

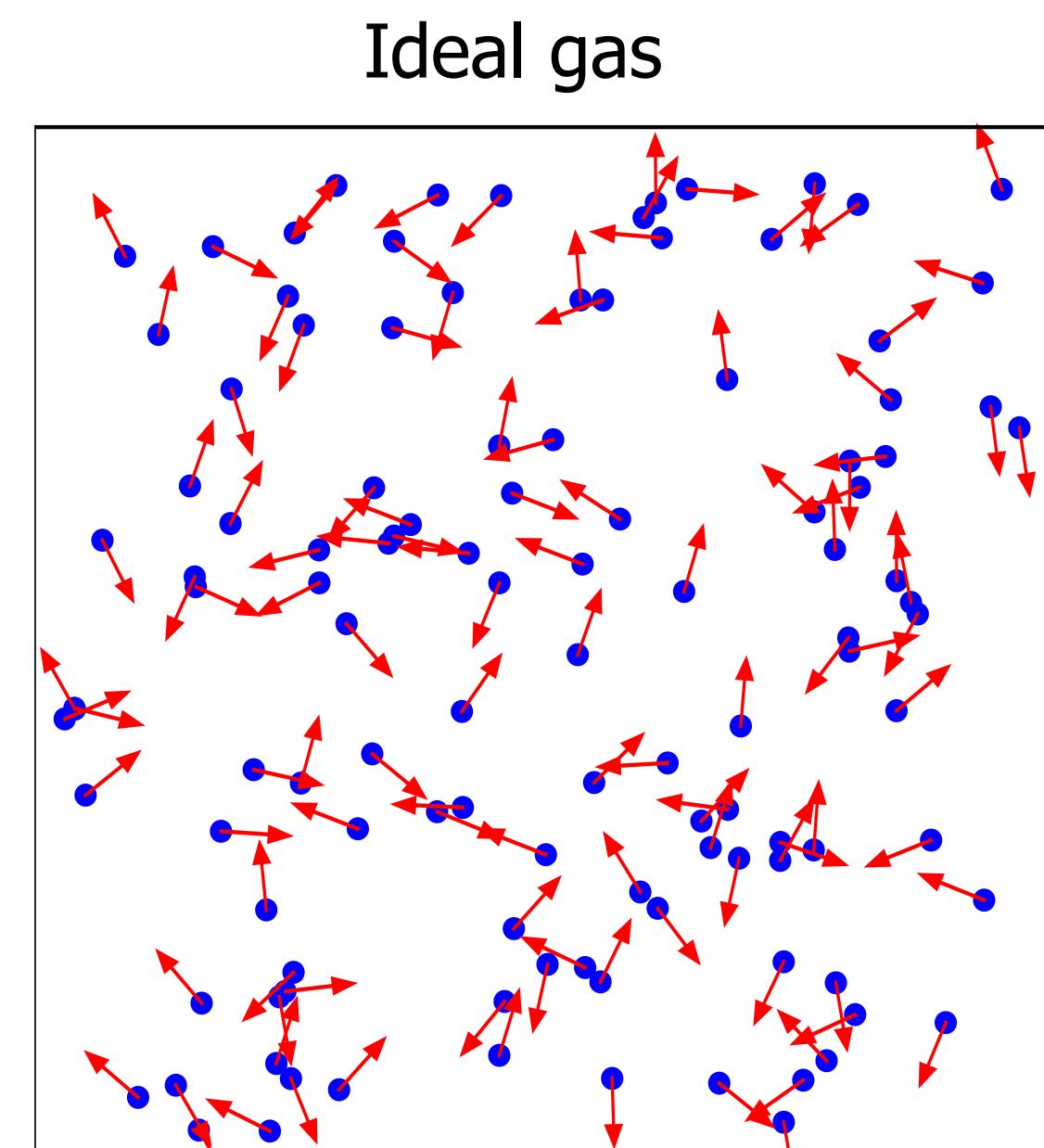
# Microstates and macrostates



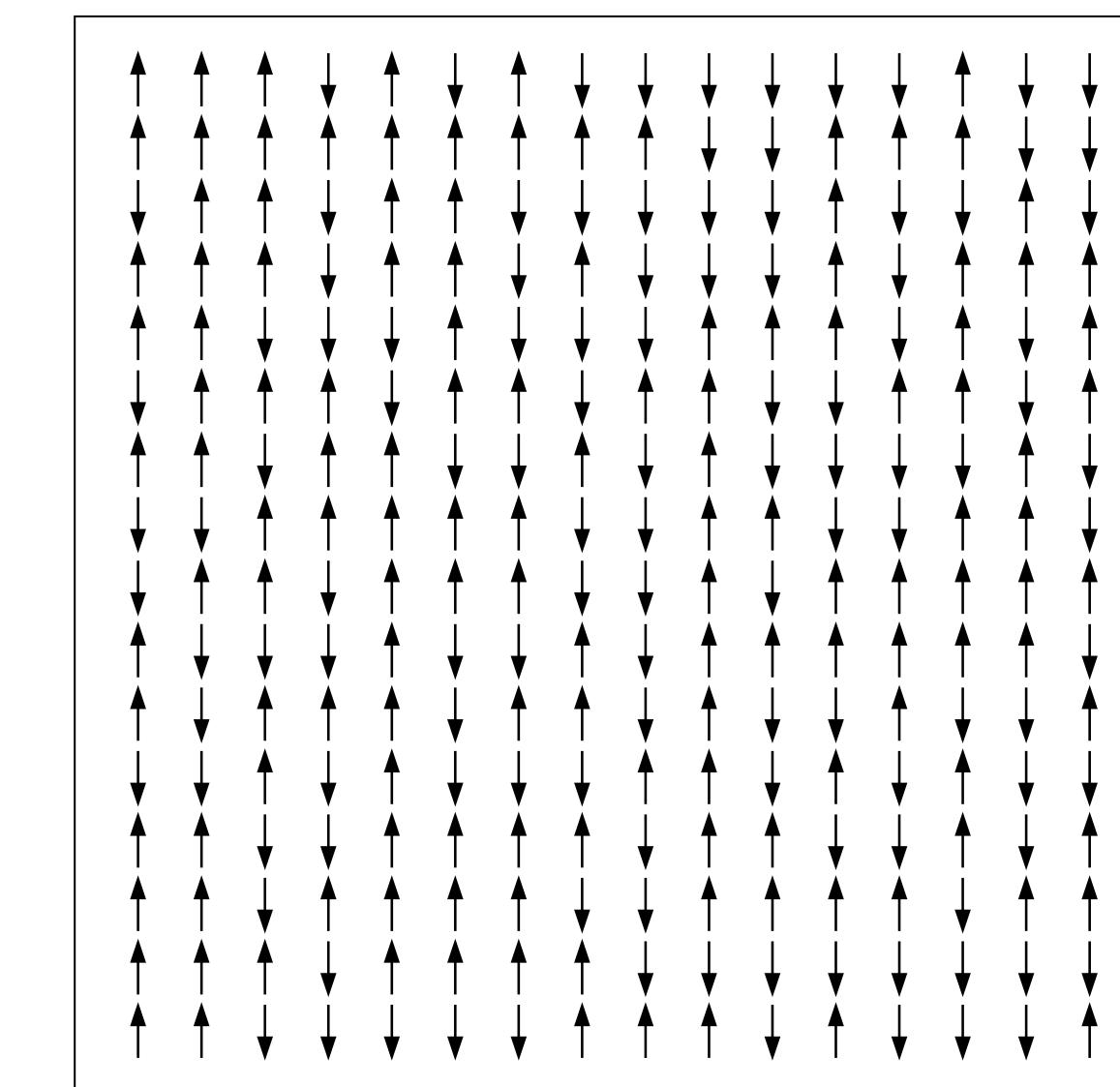
Two different levels of description of a system: **microstates** and **macrostates**

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

Requires knowledge of the position and velocity vectors of each molecule



Model magnet



Requires knowledge of the orientation of each dipole on the lattice

The microstate will change continually as the particles exchange energy

# Microstates and macrostates



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

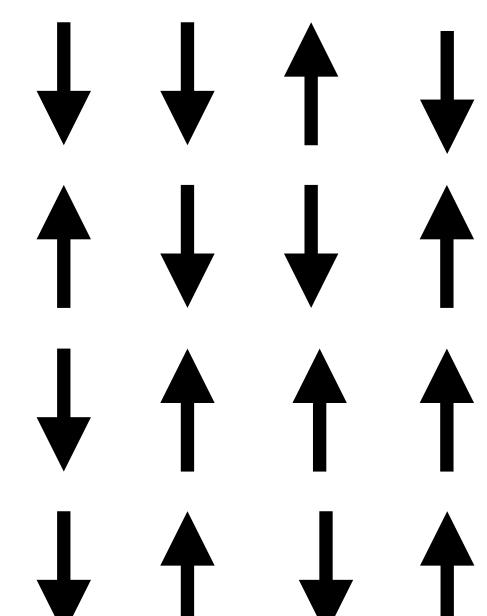
- Consider how to count  $\Omega(N, E, \{\alpha\})$  for our simple magnet.

- 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:

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

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





# Microstates and macrostates

- 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



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

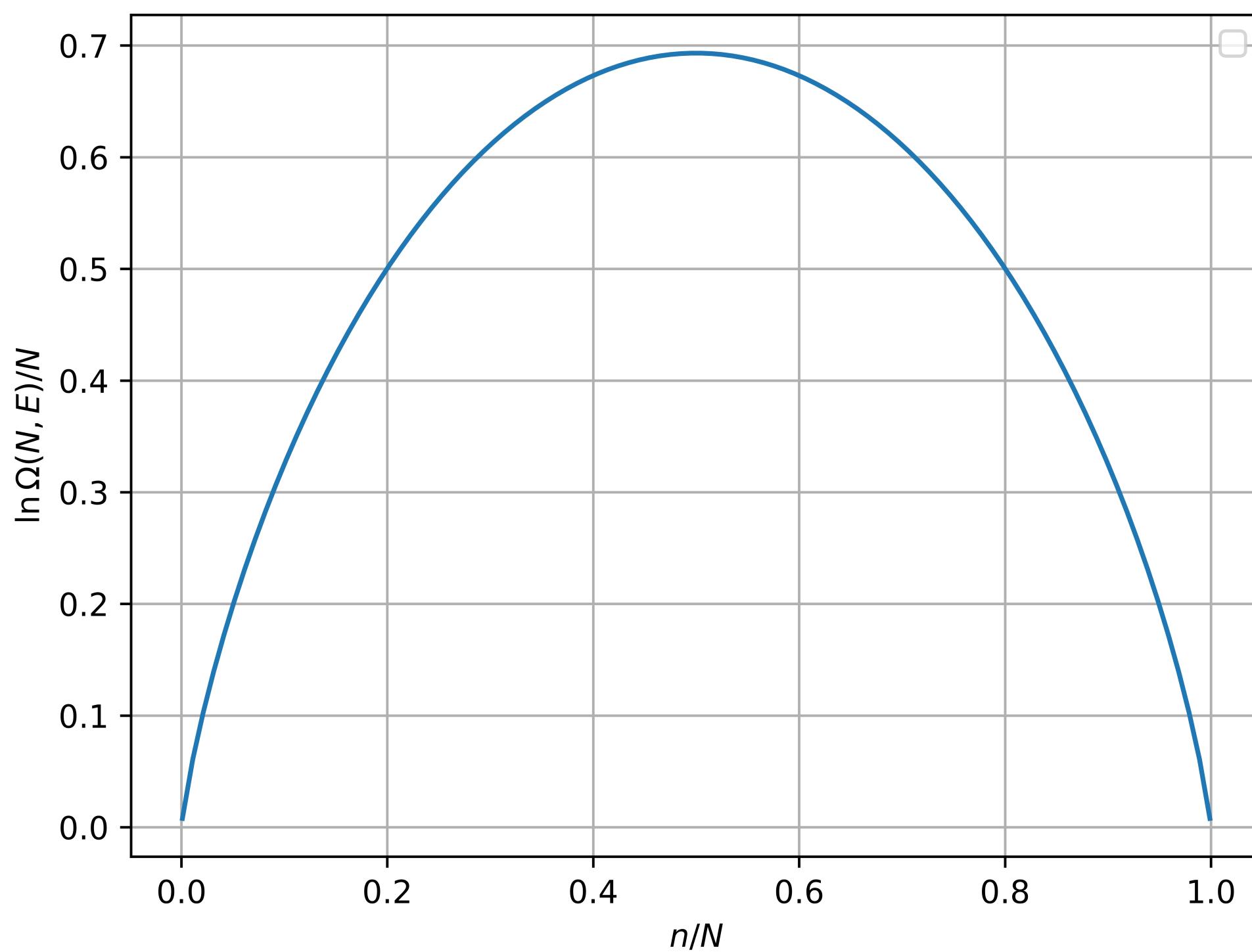


- $\Omega(N, E) = \frac{N!}{n!(N-n)!}$  can be very large.
- Consider its logarithm and apply Stirling's approximation  $\ln N! \approx N(\ln N - 1)$

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

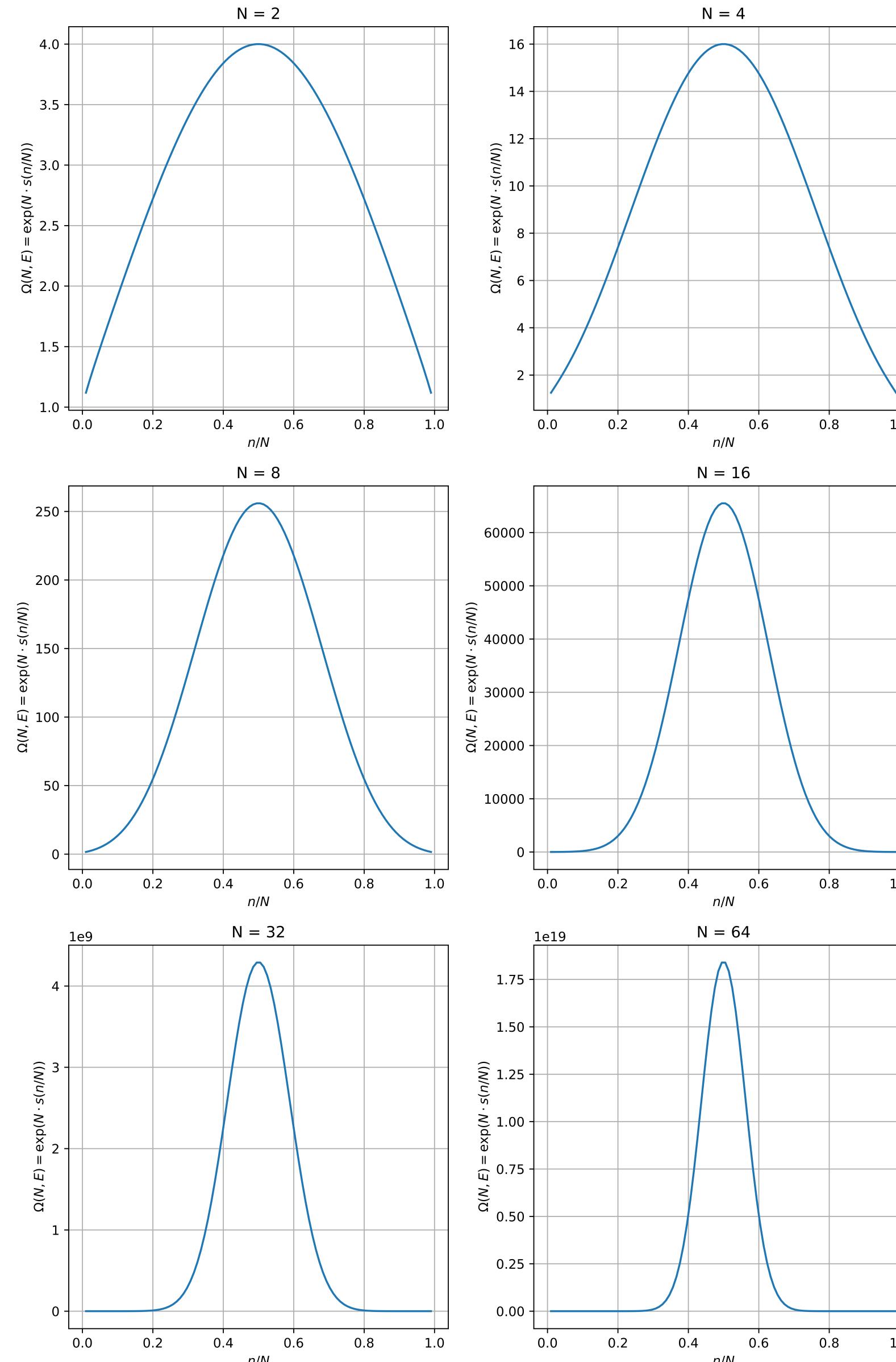
$$\frac{1}{N} \ln \Omega(N, E) = s(n/N) \quad \text{where} \quad s(x) = -(1-x)\ln(1-x) - x \ln x$$

# Microstates and macrostates



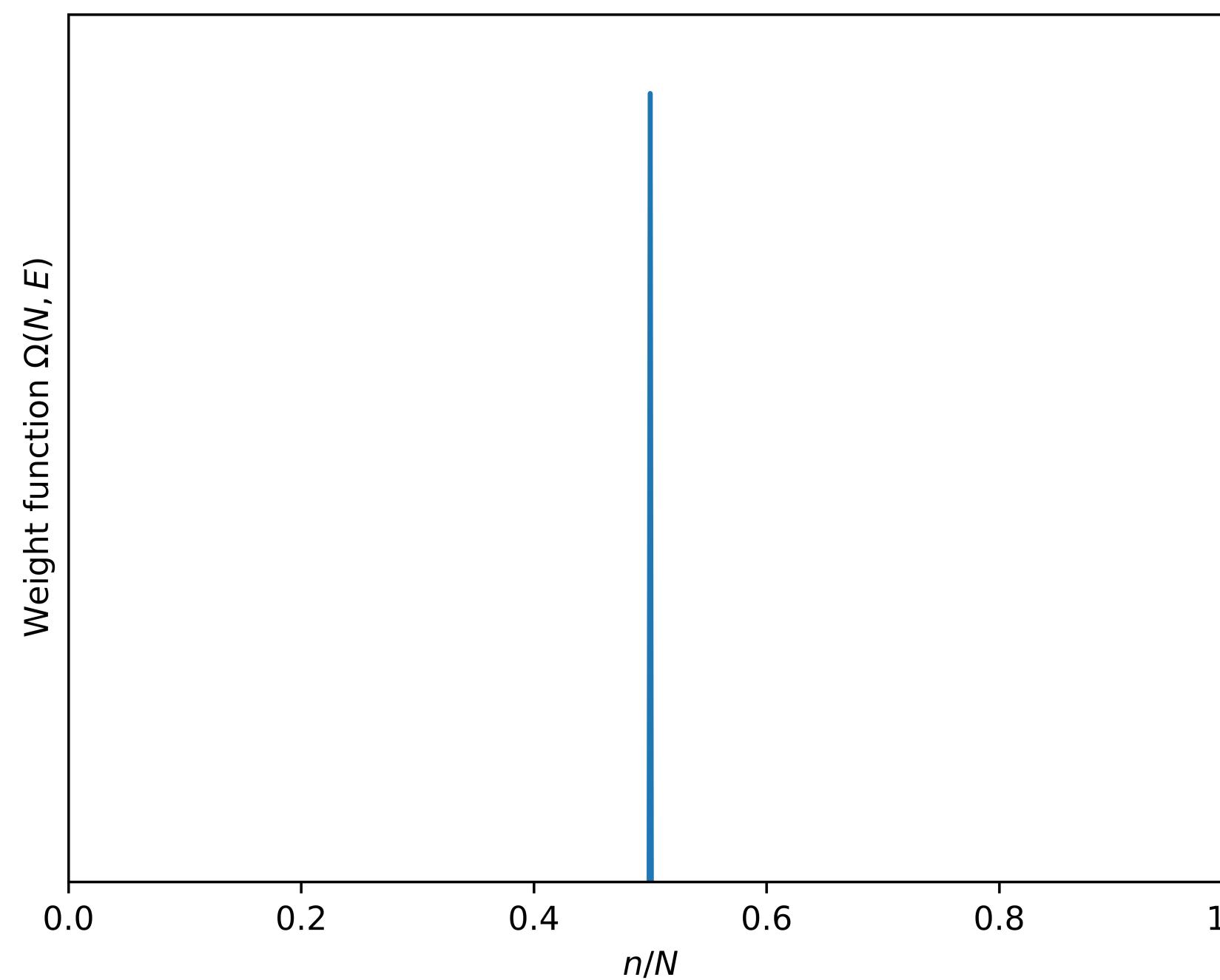
- Consider macrostate with  $n = 0$  (all dipoles aligned with  $H$ ).  $E = -NmH$  (minimum value). This macro state has only a single microstate. Thus  $\Omega(N, E) = 1$  and  $\ln \Omega(N, E) = 0$ .
- As  $E$  increases from minimum,  $\ln \Omega(N, E)$  increases steeply.
- For  $E = 0$  (ie. 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

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



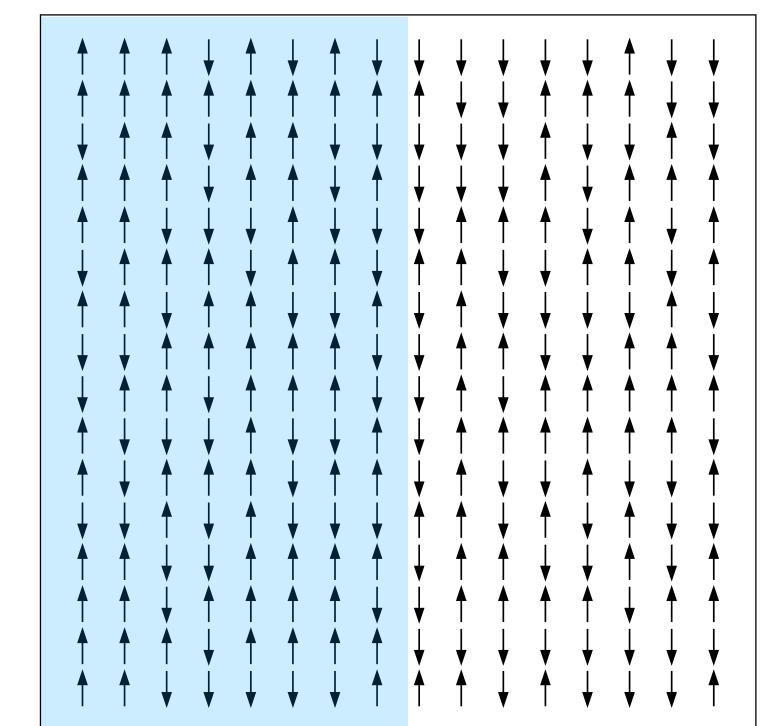
# Microstates and macrostates



- 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**.



# 3. Entropy, equilibrium and the second law





# Principle of equal a-priori probabilities

Start with axioms (see lecture notes for more discussion):

- *Key point 5: Postulate that an **isolated** system is equally likely to be found in any one of its allowed microstates.*
- *Key point 6: The probability that an isolated system, of energy  $E$ , will be found in a **macrostate**  $N, E, \{\alpha\}$  is proportional to the weight  $\Omega(N, E, \{\alpha\})$ , ie. the number of microstates associated with the macrostate.*
- Thus different macrostates have different probabilities.
- Macrostates in which the (free) macroscopic variables maximise the weight function are overwhelming more probable than other possible values.



# Principle of equal a-priori probabilities

- Since weight functions are typically exponentially large in  $N$ , the maximum for the weight function is extremely sharp.
- Thus macrostates in which the (free) macroscopic variables  $\{\alpha\}$  maximise the weight function are overwhelming more probable than other possible values.
- *Key point 7: The equilibrium values  $\{\alpha^*\}$  of the macroscopic properties  $\{\alpha\}$  of an isolated system are those that maximise the weight function  $\Omega(N, E, \{\alpha\})$*

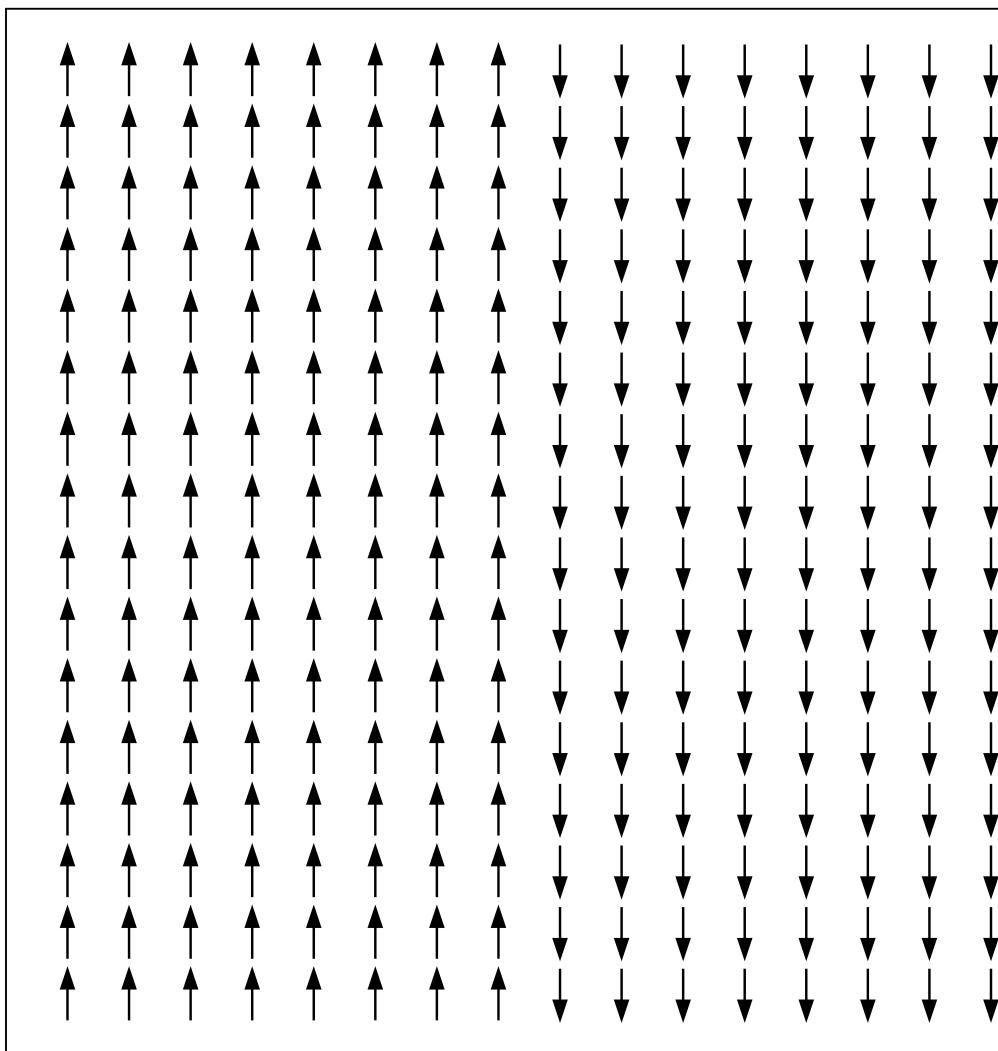
It follows that

- *Key point 8: The equilibrium entropy of an isolated system of  $N$  constituents with energy  $E$  is  $S(N, E) = k \ln \Omega(N, E, \{\alpha^*\})$*

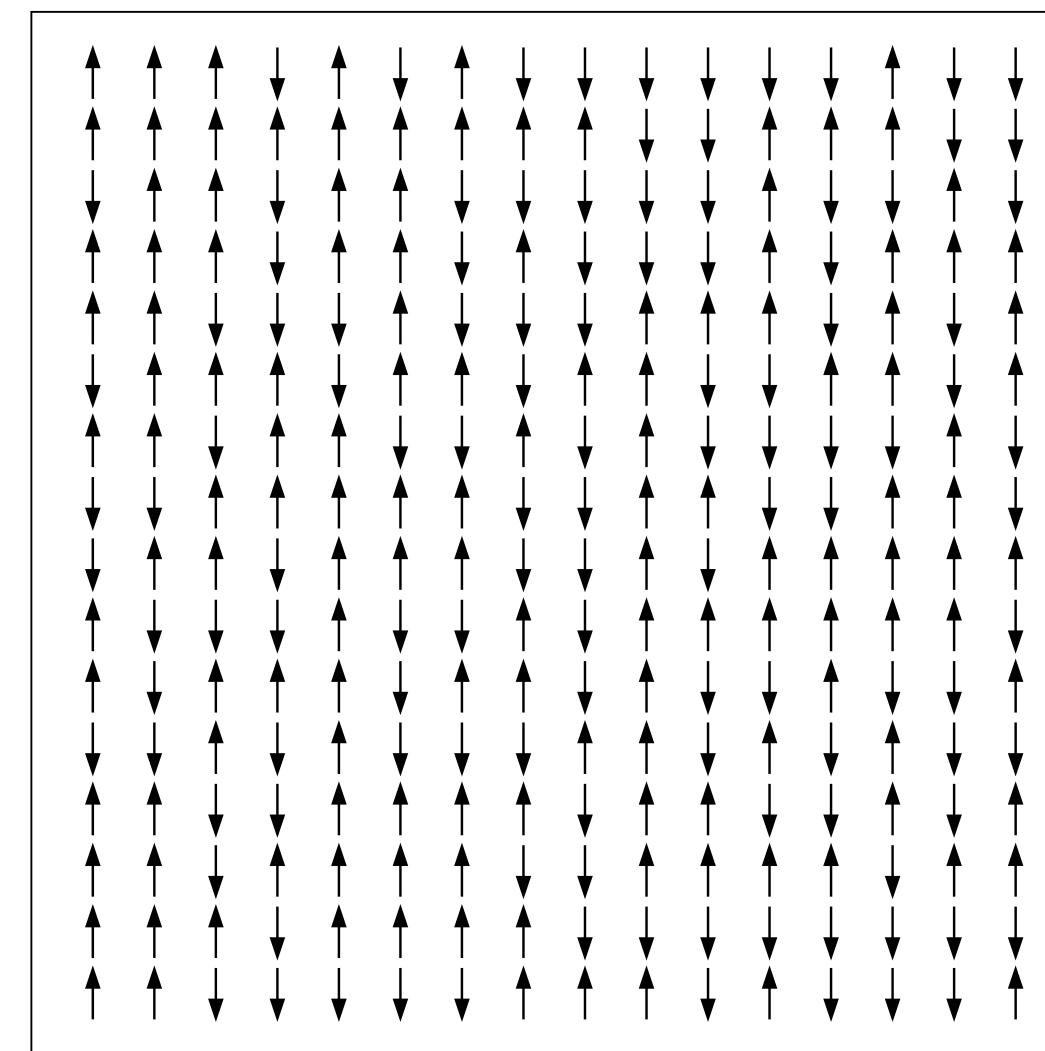
# The second law (of thermodynamics)



- Consider again case where free macro variable is  $n_L$  for our model magnet. Fix  $E = 0$



Time  
→



Initial macrostate of macro state with  
 $n = N/2, E = 0, n_L = N/2$ .  
 $\Omega(N,0,n_L) = 1$

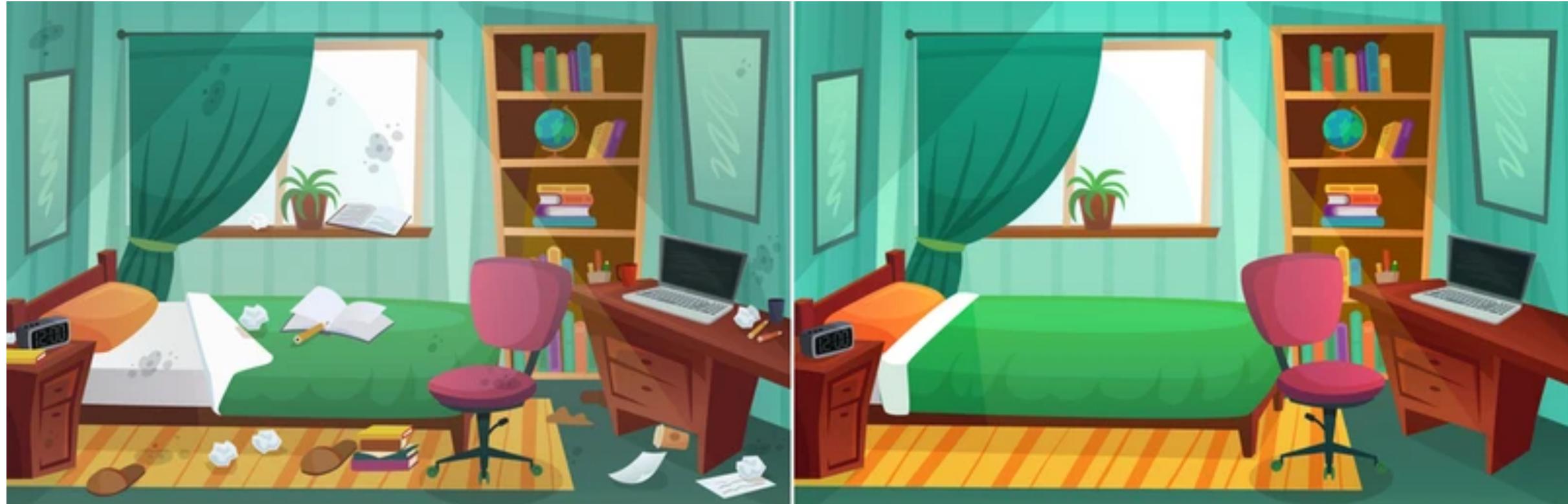
Typical final microstate of macrostate with:  
 $n = N/2, E = 0, n_L = N/4$ .  
 $\Omega(N,0,n_L) \simeq \exp[Ns(n_L/(N/2))]$

- Equilibration: An isolated system evolves through macrostates with greater and greater weight until it reaches the macrostate with the largest weight and stays there.
- Key point 8 then implies: *The entropy of an isolated system can only increase*



# Entropy and disorder

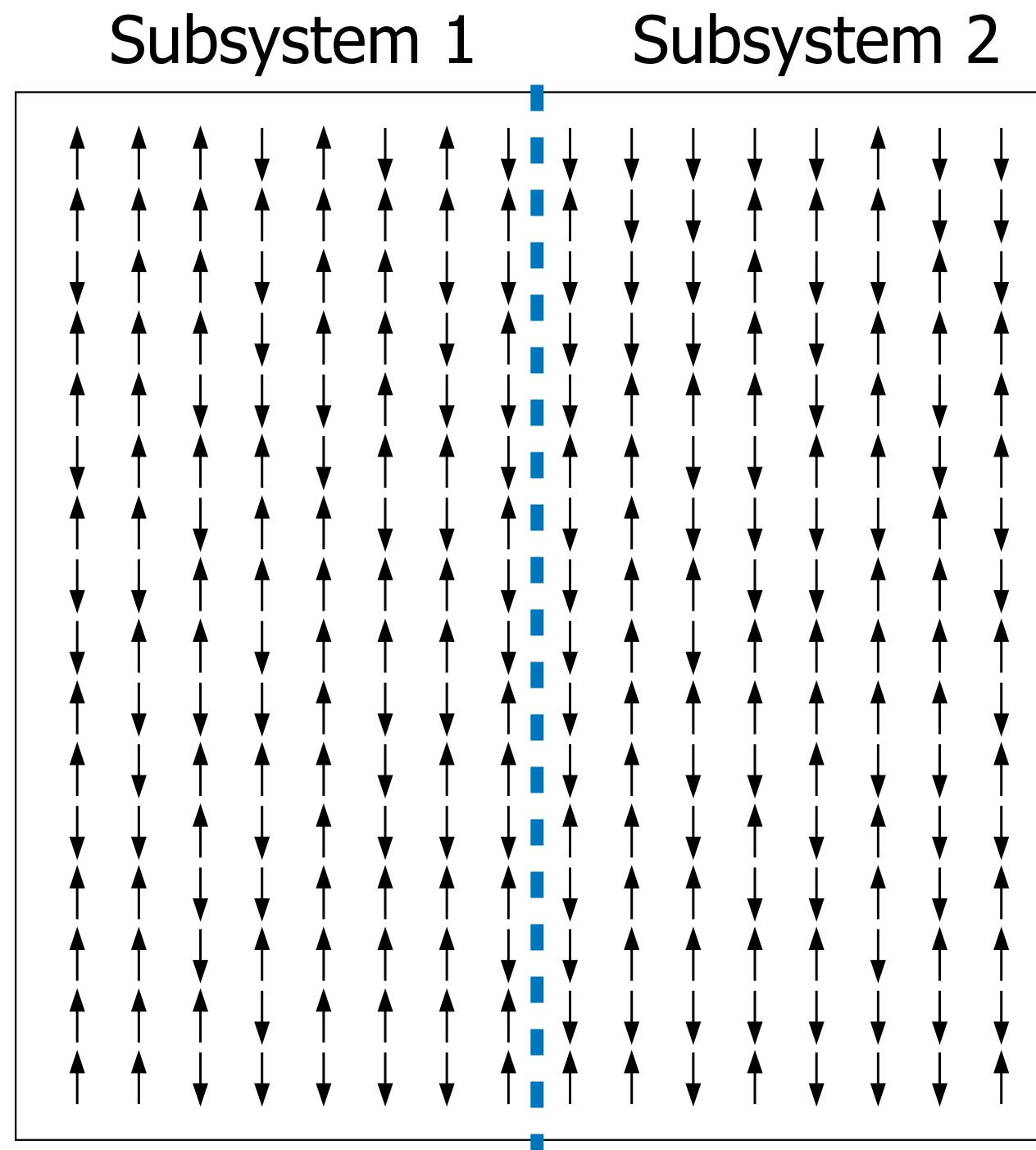
- Entropy is often referred to as a measure of disorder.
- For something to be ‘disordered’ it may be so in many different ways, whereas ‘order’ places many restrictions on the ways things can exist.



- Questions 2.5 and 2.6 considers the entropy change of order/disorder transitions in real systems: melting of ice crystals and a copper/gold alloy.



# Additivity of entropy



- Total of  $n$  excited dipoles in the system.
- Total fixed energy  $E$
- Consider system to comprise two equal subsystems 1 and 2 having  $N_1 = N_2 = N/2$  that can exchange energy.
- Weight for the macrostate where  $n_1$  of the dipoles in the left half are excited is a product of weight functions for the two halves:

$$\Omega(N, E, n_1) = \Omega_1(N_1, E_1, n_1)\Omega_2(N_2, E_2, n - n_1)$$

- Then from Planck equation (kp 4) the entropies of the two subsystems are **additive**

$$S(N, E, n_1) = S_1(N_1, E_1, n_1) + S_2(N_2, E_2, n_2)$$



# Entropy and temperature

- For our two subsystems in thermal equilibrium we have

$$S(E) = S_1(E_1) + S_2(E_2) \quad E = E_1 + E_2 \quad (\text{assume } N \text{ fixed, so suppress it in notation})$$

- Consider the effect of changing  $E_1 \rightarrow E_1 + dE_1$ . Since total  $E$  is fixed  
 $\Rightarrow dE_1 = -dE_2$ .
- Now consider the effect on the entropy

$$\begin{aligned} dS &= dS_1 + dS_2 \\ &= \left( \frac{\partial S_1}{\partial E_1} \right) dE_1 + \left( \frac{\partial S_2}{\partial E_2} \right) dE_2 \\ &= \left( \frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2} \right) dE_1 \end{aligned}$$

# Entropy and temperature



- But at equilibrium the entropy is an extremum (i.e. maximised w.r.t. changes in  $E_1$  and  $E_2$ )  $\Rightarrow dS = 0$ . Hence

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2}$$

- Recall zeroth law: two systems in thermal equilibrium share the same temperature.
- Deduce that

$$\frac{\partial S_1}{\partial E_1} = \text{some function of } T$$

- In fact (see later) the correct identification is:
- *Key point 9:*  $\frac{1}{T} = \frac{\partial S}{\partial E}$
- If we put two systems at **different** temperatures  $T_1$  and  $T_2$  with  $T_1 > T_2$  in thermal contact, expect from the second law that  $dS > 0$
- But  $dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1$  implies  $dE_1$  is negative, so energy (heat) flows from the hotter to the colder system in accord with experience.

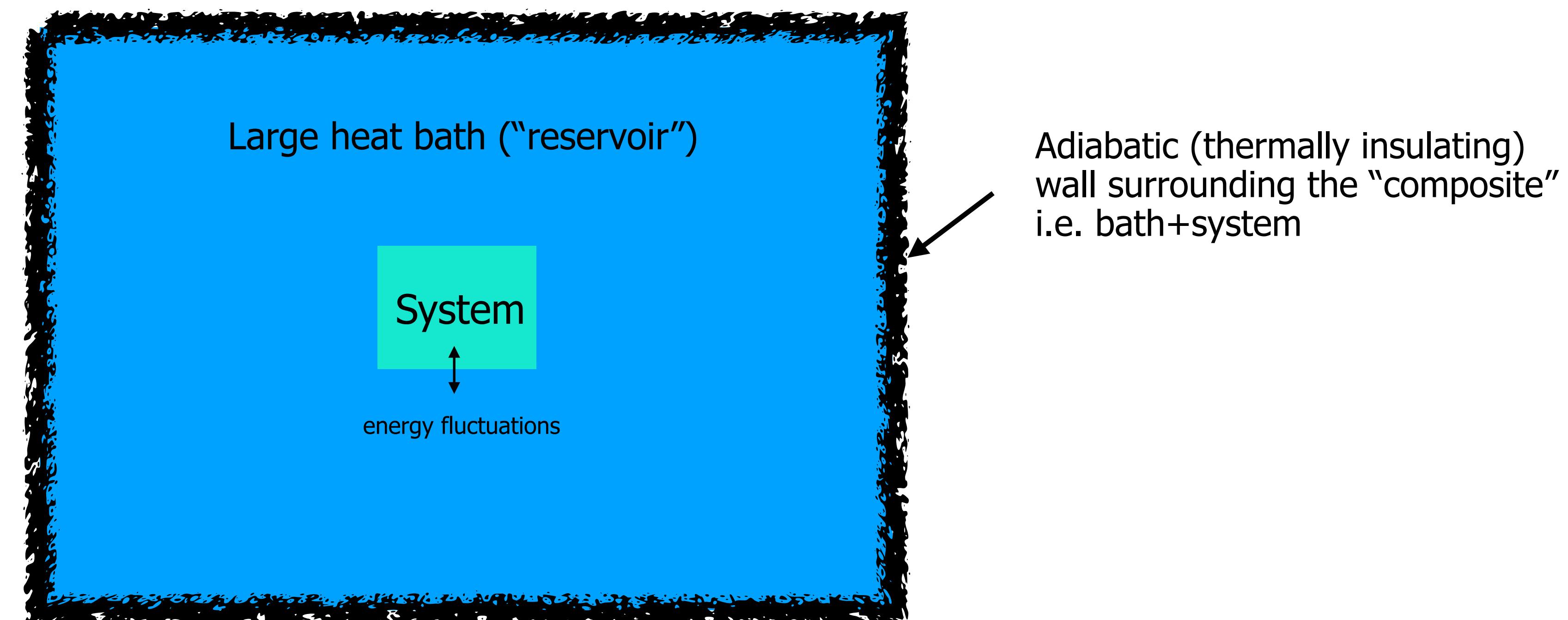


# 4. Boltzmann distribution

# Boltzmann distribution



- Previously we have considered an isolated system of fixed  $N, E$ .
- Here we consider systems with fixed  $N$  but instead of  $E$  being fixed, we fix the temperature  $T$  by placing it in contact with a heat bath ("reservoir").
- Bath is assumed sufficiently large that energy can be exchanged with the system without its temperature changing. Thus by zeroth law, the temperature of the system is the same as the constant temperature of the reservoir.



# Boltzmann distribution



- Total energy of composite system (system+bath)  $E_{TOT}$  fixed, but system energy **fluctuates**
- As the system energy can vary due to thermal fluctuations, it can explore microstates of **different** energy
- Recall: microstates of the same energy are explored with equal probability
- What are the relative probabilities of microstates of different energy?
- Let the probability that system is in a given microstate  $i$ , of energy  $E_i$  be  $P_i$ .
- If the system is in microstate  $i$  there is energy  $E_{TOT} - E_i$  left for the bath, and this corresponds to many possible microstates for the bath.

# Boltzmann distribution



- Since for the composite all microstates are equally likely,

$$P_i = \text{constant} \times \Omega_b(E_{TOT} - E_i)$$

Planck equation  $\Rightarrow \Omega_b(E_{TOT} - E_i) = \exp\left(\frac{S_b(E_{TOT} - E_i)}{k_B}\right)$

Since  $E_i \ll E_{TOT}$   $S_b(E_{TOT} - E_i) = S_b(E_{TOT}) - E_i \frac{\partial S_b}{\partial E_b} + \frac{E_i^2}{2} \frac{\partial^2 S_b}{\partial E_b^2} + \dots$

$$\simeq S_b(E_{TOT}) - E_i \frac{\partial S_b}{\partial E_b}$$

$$\simeq S_b(E_{TOT}) - \frac{E_i}{T}$$

Constant

- Thus  $P_i \propto \exp\left(-\frac{E_i}{kT}\right)$

# Boltzmann distribution



- Normalize probabilities by summing over all microstate

$$P_i = \frac{\exp\left(-\frac{E_i}{kT}\right)}{\sum_j \exp\left(-\frac{E_j}{kT}\right)} \equiv \frac{1}{Z} \exp\left(-\frac{E_i}{kT}\right)$$

- This is the **Boltzmann distribution**

• *Key point 10:*  $P_i = \frac{1}{Z} \exp(-\beta E_i)$  where  $Z = \sum_j \exp(-\beta E_j)$  and  $\beta = \frac{1}{kT}$

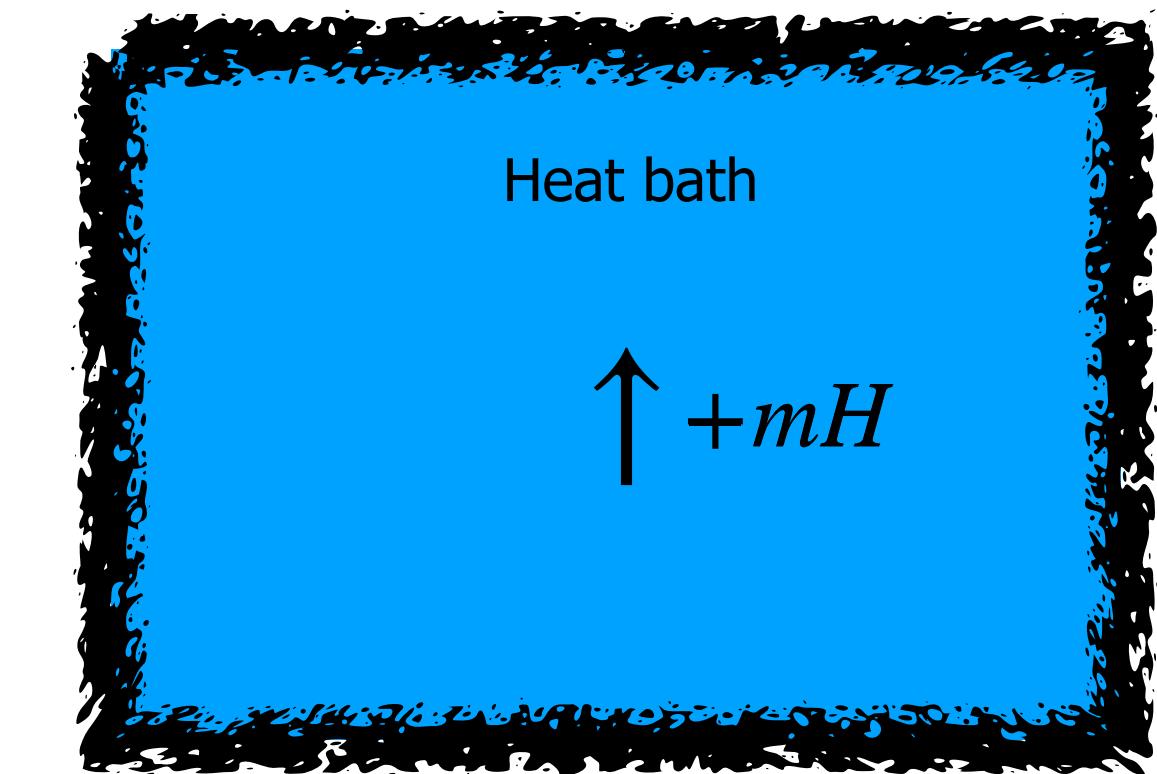
# Boltzmann distribution



- Example 1: Single dipole two microstates  $\downarrow, \uparrow$  with energies  $-mH, +mH$

$$P(\downarrow) = \frac{\exp\left(\frac{mH}{kT}\right)}{Z}, \quad P(\uparrow) = \frac{\exp\left(-\frac{mH}{kT}\right)}{Z}$$

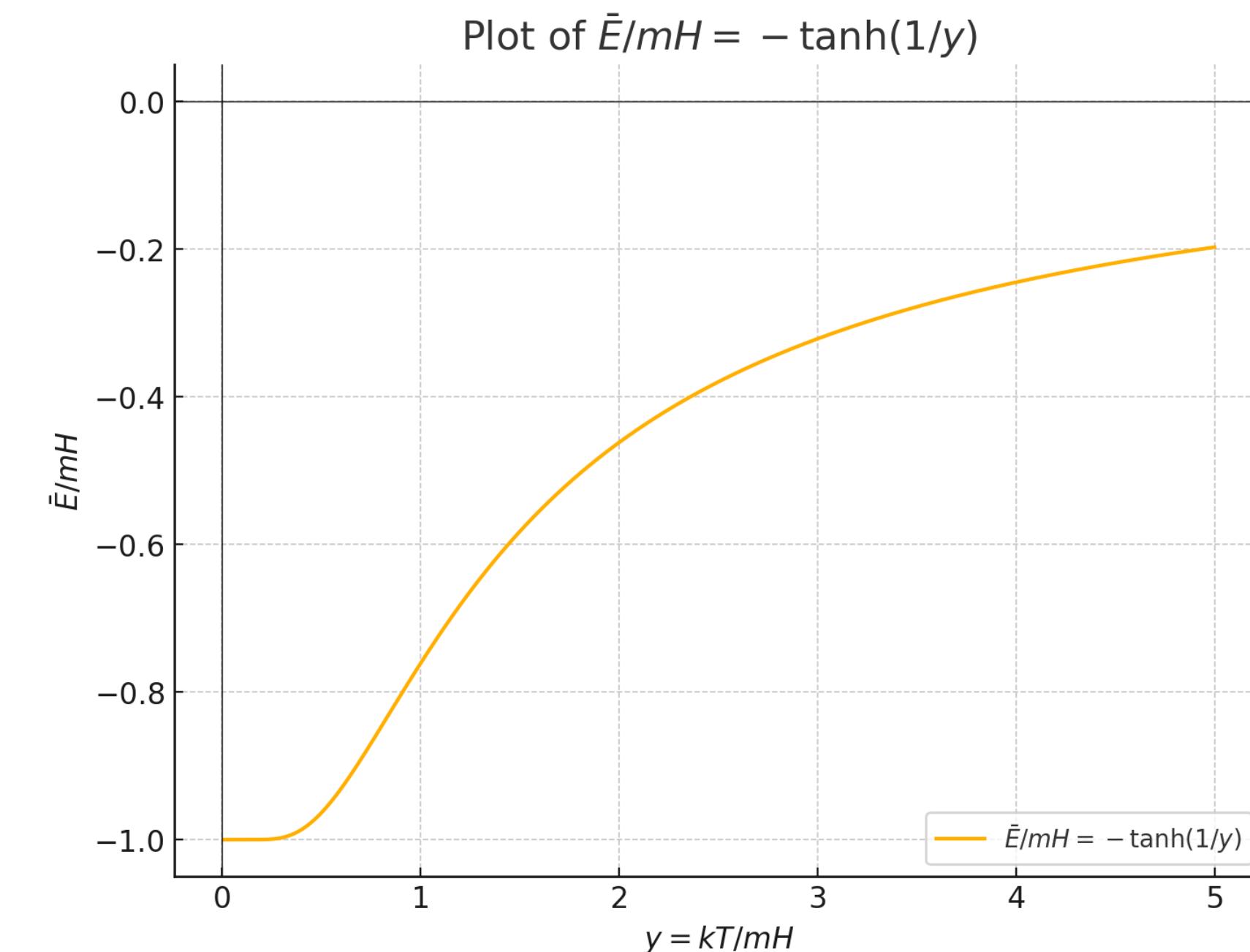
$$Z = \exp\left(\frac{mH}{kT}\right) + \exp\left(-\frac{mH}{kT}\right) = 2 \cosh\left(\frac{mH}{kT}\right)$$



- Average energy as function of  $H$  and  $T$

$$\bar{E} = \sum_i E_i P_i = \frac{1}{Z} [-mHP(\downarrow) + mHP(\uparrow)]$$

$$= -mH \frac{\sinh\left(\frac{mH}{kT}\right)}{\cosh\left(\frac{mH}{kT}\right)} = -mH \tanh\left(\frac{mH}{kT}\right)$$



# Boltzmann distribution

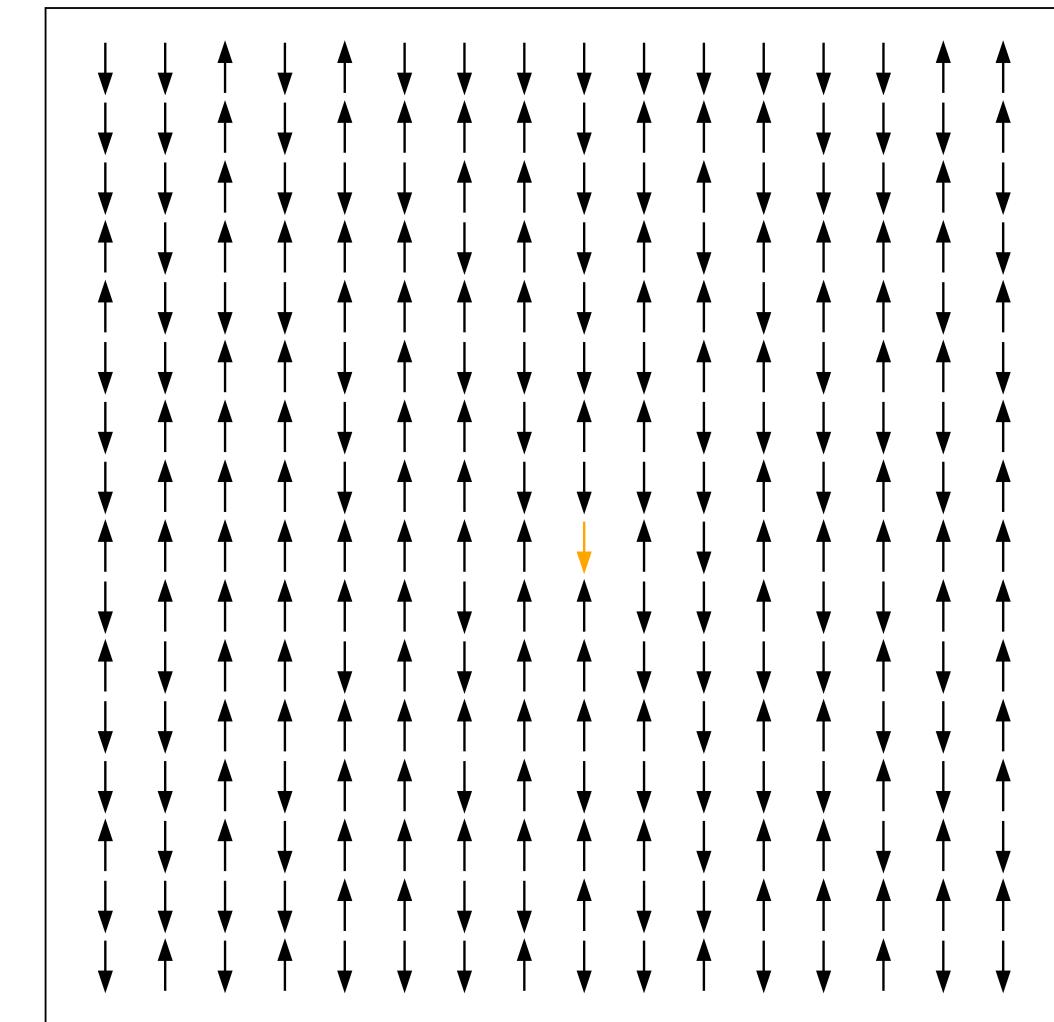


- Example 2: Single constituent in an isolated system for large  $N$

- Recall that for our isolated system

$$S(E) = -Nk \left[ x \ln x + (1-x) \ln(1-x) \right], \quad x = \frac{n}{N} = \frac{1}{2} \left( 1 + \frac{E}{NmH} \right)$$

where  $n$  is the number of excited dipoles



$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{dx}{dE} \frac{\partial S}{\partial x} = -\frac{Nk}{2NmH} [\ln x + 1 - \ln(1-x) - 1] = -\frac{k}{2mH} \ln \left( \frac{x}{1-x} \right)$$

$$\exp \left( -\frac{2mH}{kT} \right) = \frac{x}{1-x}$$

$$x = \frac{n}{N} = \frac{\exp \left( -\frac{2mH}{kT} \right)}{1 + \exp \left( -\frac{2mH}{kT} \right)} = \frac{\exp(-\beta mH)}{\exp(\beta mH) + \exp(-\beta mH)}$$

# Boltzmann distribution



- The frequency definition of probability implies that  $n/N$  is the probability that a single dipole is in the excited state.
- We see we recover the Boltzmann distribution of the previous subsection for a single dipole!
- Why?
- Because a single dipole exchanges energy with the  $N - 1$  other dipoles. For large  $N$ , the other dipoles act as a heat bath for the single dipole.



# 5. Free energy minimisation



# Mean and variance of energy fluctuations

- Energy of a system connected to a heat bath exhibits thermal fluctuations (free macroscopic variable) controlled by the Boltzmann distribution

$$P_i = \frac{1}{Z} \exp(-\beta E_i)$$

- Consider the mean energy

$$\begin{aligned}\bar{E} &\equiv \sum_i E_i P_i = \frac{1}{Z} \sum_i E_i \exp(-\beta E_i) \\ &= -\frac{1}{Z} \sum_i \frac{\partial}{\partial \beta} \exp(-\beta E_i) \\ &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \\ &= -\frac{\partial \ln Z}{\partial \beta} \quad \text{chain rule} \\ \bar{E} &= -\frac{dT}{d\beta} \frac{\partial \ln Z}{\partial T} = kT^2 \frac{\partial \ln Z}{\partial T}\end{aligned}$$



# Mean and variance of energy fluctuations

- Variance of the energy distribution  $\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \bar{E^2} - \bar{E}^2$
- It turns out that this variance is related to the heat capacity  $C$  defined by

$$C \equiv \frac{\partial \bar{E}}{\partial T} = \frac{d\beta}{dT} \frac{\partial \bar{E}}{\partial \beta} = -\frac{1}{kT^2} \frac{\partial \bar{E}}{\partial \beta}$$

- Specifically, one can show (see notes)

$$C = -\frac{1}{kT^2} \left[ \bar{E^2} - \bar{E}^2 \right] = \frac{\overline{(\Delta E)^2}}{kT^2}$$

- The response of the energy to a change in temperature is related to the fluctuations of the energy at fixed  $T$ ....!

# Mean and variance of energy fluctuations



- Since  $\bar{E}$  is proportional to  $N$  (extensive), so will be  $C = \partial\bar{E}/\partial T$ . Hence

$$\overline{(\Delta E)^2} \propto N \quad \text{and} \quad \frac{(\overline{\Delta E})^{1/2}}{\bar{E}} \propto \frac{1}{\sqrt{N}}$$

- Although the energy is a free macroscopic variable, it takes on a sharply defined value  $\bar{E}$ .
- Consequently a large system in equilibrium with a heat bath should have essentially the same behavior as a large isolated system with fixed energy  $\bar{E}$ .



# Entropy, energy distribution, and free energy



# Entropy, energy distribution, and free energy

# Free energy minimisation



Statistical Mechanics

