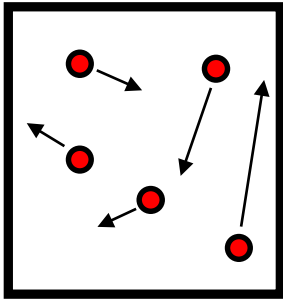


# MICROSTATES and MACROSTATES

We start on the big job & big achievement of Statistical Mechanics – to link the behaviour of a macroscopic system to the probability of finding it in one or a group of microstates, & how the system through some or all of these microstates, over some period of time. In what follows we will do this for some simple systems, to get a feel for things.

## SOME SIMPLE SYSTEMS

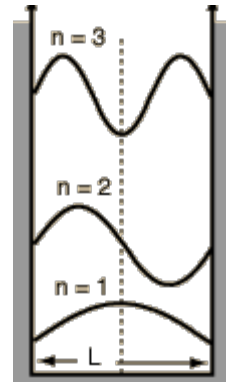


(1) PARTICLES in a BOX: We will describe these by Quantum Mechanics.

Let's first look at the very simplest case – a single particle in a 1-d box, of length  $L$ . We then have the eigenstates shown at right, and we have

$$\text{Eigenenergies: } E_n = \frac{(\hbar k_n)^2}{2m} = \frac{\pi^2 \hbar^2}{2mL^2} n^2 \quad \text{Non-relativistic limit } v \ll c$$

$$E_n = \hbar k_n c = \frac{hcn}{2L} \quad \text{Relativistic regime } v \sim c$$



where the Quantum Nos are:  $n = 1, 2, 3, \dots$

Later on I will look at what we do when we have  $N$  particles in a box, and/or when our box is 2-d or 3-d.

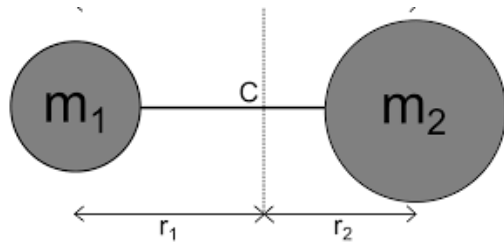
(2) HARMONIC OSCILLATORS: Let's pick a single 1-d oscillator; we then have

$$\text{Eigenenergies: } E_n = \left(n + \frac{1}{2}\right) h\nu$$

$$\text{Quantum Nos: } n = 0, 1, 2, \dots$$

where  $\nu$  is the oscillator frequency

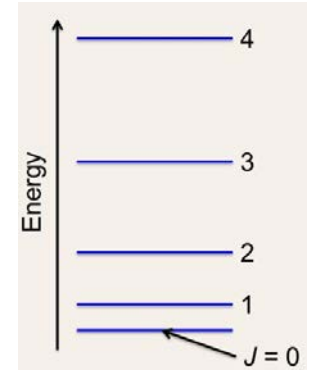
(2) QUANTUM ROTATOR: Any system which is not spherically symmetric will have quantum numbers associated with its rotation - an example would be a diatomic molecule. We then have:



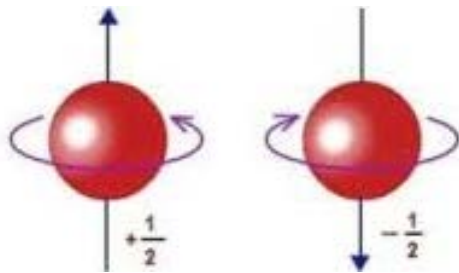
Eigenenergies:  $E_j = j(j+1)E_0$

Quantum Nos:  $j = 0, 1, 2, \dots$

where  $E_0 = \frac{\hbar^2}{2I}$  and  $I = m_1 r_1^2 + m_2 r_2^2$   
(Moment of inertia around c.o.m.)



(2) SPIN-S SYSTEM: This is the simplest of all to analyze - there are only  $2S+1$  levels. Nowadays, if  $S = \frac{1}{2}$ , we also call this a "qubit", or just a "TLS" (Two-Level System). Suppose the spin is in a field  $B$  along the z-axis. Then for a spin  $S$  we have



Eigenenergies:  $E_m = -\gamma \hbar m B$

Quantum Nos:  $m = -S, -S+1, \dots, +S$

where the quantum number  $m$  is just the projection  $S_z$  along the z-axis. The spin has a magnetic moment  $\mu$ , where

$$\mu = \gamma \hbar s$$

The above systems are all simple because they have discrete spectra; this is because they are spatially confined.

## SET of N SPIN-1/2 QUBITS

We now have N spin-1/2 qubits. We assume no interactions between them, only interactions with the magnetic field.



The Hamiltonian is

$$H = -\gamma\hbar \sum_i s_i^z = -(\gamma\hbar/2) \sum_i \sigma_i^z$$

where the sum  $\sum_i$  is over all spins, &  $\frac{1}{2}\sigma_i^z = \frac{1}{2}, -\frac{1}{2}$  is the z-component of the i-th spin  $s_i$ , for a spin  $\frac{1}{2}$ .

A single spin has 2 states,  $\uparrow$  &  $\downarrow$ , with magnetization  $M_z = \mu, -\mu$ , where here  $\mu = \gamma\hbar/2$ .

A pair of spins has 4 states, viz.,  $\uparrow\uparrow$  (with  $M_z = 2\mu$ ),  $\uparrow\downarrow$  &  $\downarrow\uparrow$  ( $M_z = 0$ ), &  $\downarrow\downarrow$  ( $M_z = -2\mu$ ) and so on.

For N spins we count the states in the same way as we count coin tosses.

We have  $N = N_\uparrow + N_\downarrow$       Defining  $n = N_\uparrow - N_\downarrow$       so that

$$N_\downarrow = (N - n)/2$$

$$N_\uparrow = (N + n)/2$$

We can then say that the “macroscopic” states of the spin system are classified by the total magnetization  $M = n\mu$ , ie., by the quantum number  $n$

The total number of microscopic states for a given Q. Number  $n$  is then

$$\Omega(N, n) = \frac{N!}{N_\uparrow! N_\downarrow!} = \frac{N!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n}{2}\right)!}$$

having probability  $P(N, n) = \frac{\Omega(N, n)}{2^N}$

(assuming equal probability for each spin state)

## Results for large N

Use Stirling's approx.:  $\ln N! \cong N \ln N - N + \frac{1}{2} \ln(2\pi N)$

Key variable:  $x \equiv \frac{n}{N}$  (fractional deviation from mean)

We expand about the mean for large N, noting that

$$\ln(1 \pm x) \approx \pm x - \frac{x^2}{2} \quad \text{when } x \ll 1$$

Then, recalling that  $\Omega(N, n) = \frac{N!}{(\frac{N+n}{2})!(\frac{N-n}{2})!}$

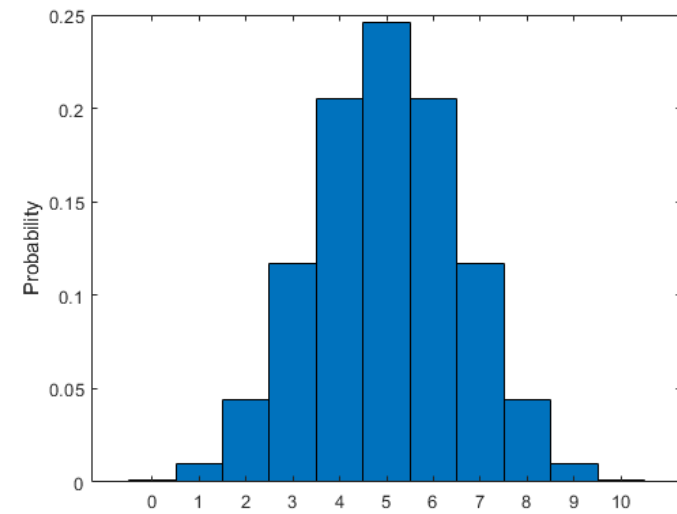
we have  $\ln P(N, n) \approx +\frac{1}{2} \ln\left[\frac{2}{\pi N}\right] - \frac{1}{2} N x^2$

Hence  $\Omega(N, n) \cong 2^N \left(\frac{2}{\pi N}\right)^{1/2} \exp\left[-\frac{n^2}{2N}\right]$

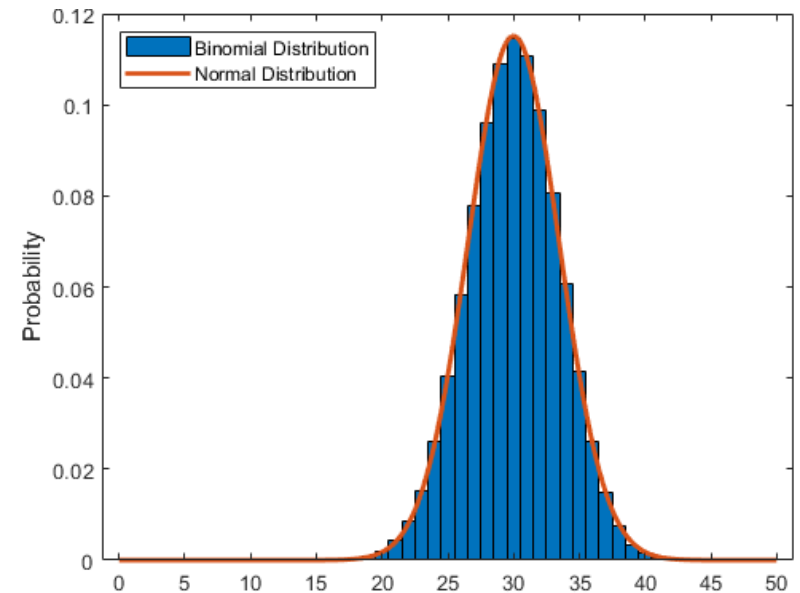
and  $P(N, n) \cong \left(\frac{2}{\pi N}\right)^{1/2} \exp\left[-\frac{n^2}{2N}\right]$

The quality of these approximations can be seen for N=10 and N=60 in the graphs

In a short Appendix to the notes I will discuss Stirling's approximation



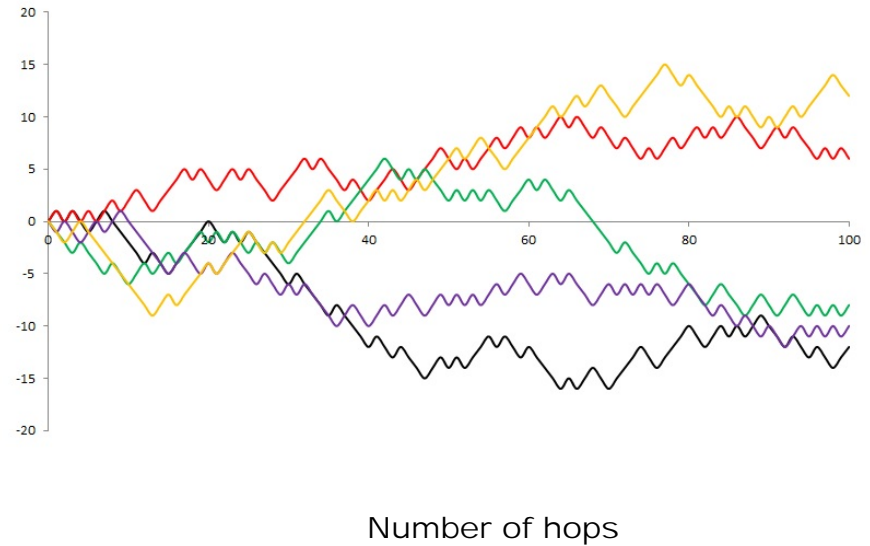
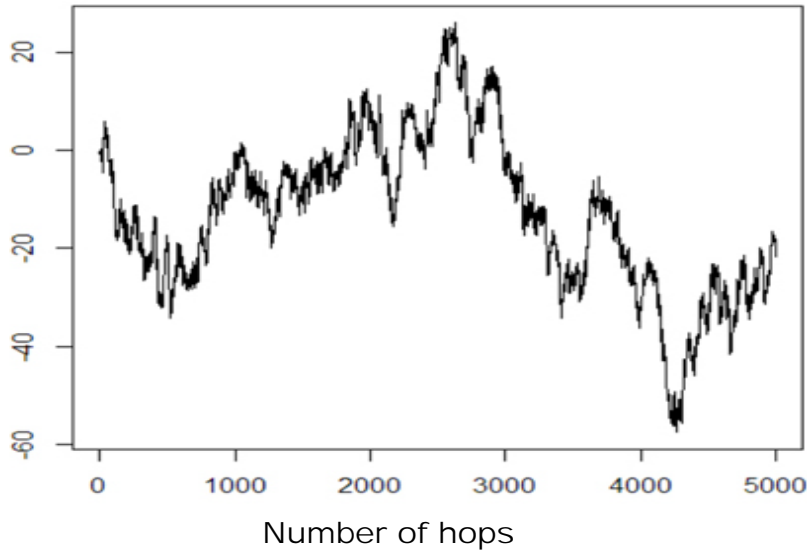
N=10



N=60

## OTHER SIMILAR EXAMPLES

1-DIMENSIONAL RANDOM WALK: A particle hops between sites on a 1-dimensional line – the probability that it goes in one or other direction is the same, i.e.,  $1/2$ . Then typical results are as shown:



The first graph shows a single trial run. The second shows a set of 5 different trial runs. Now, what we would like to know is – what is the probability of ending up at site  $n$ , after  $N$  hops?

This problem is clearly isomorphic to the coin-tossing problem (right hop = heads; left hop = tails). Thus, we get

$$P(N, n) = \frac{1}{2^N} \cdot \frac{N!}{\left(\frac{N+n}{2}\right)! \left(\frac{N-n}{2}\right)!} \quad \xrightarrow{\text{Large } N} \quad \left(\frac{2}{\pi N}\right)^{1/2} \exp\left[-\frac{n^2}{2N}\right]$$

## BINARY ALLOY PROBLEM

Consider a problem where we mix up several species of atom & then let them form an ordered array. This is typical in the formation of alloys – at high T they will form a random arrangement. At low T they form an ordered lattice.

Example: the BINARY system Cu:Zn At low T, the Cu are at the centre of the cubic lattice sites, and the Zn at the corners.

Define  $f \equiv$  fraction of correctly positioned Cu atoms on the  $N$  regular Cu sites.

Let  $\Omega_1$  be number of ways (multiplicity) of arranging the  $fN$  Cu atoms on  $N$  regular Cu sites.

Let  $\Omega_2$  be number of ways of arranging incorrectly positioned  $(1-f)N$  Cu atoms on  $N$  Zn sites.

Note that  $fN$  corresponds to the number of up spins in the spin  $\frac{1}{2}$  magnet and  $(1-f)N$  corresponds to the number of down spins. The difference  $n = fN - (1-f)N = (2f-1)N = N\psi$ , where  $\psi = 2f - 1$ .

We then have

$$\Omega_1 = \frac{N!}{[fN]![(1-f)N]!} = \Omega_2$$

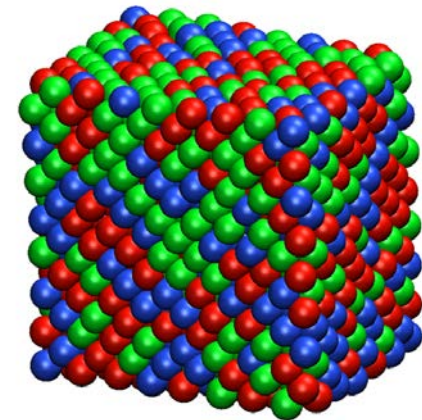
$$\xrightarrow{\text{Large } N} \frac{2^{1/2} 2^N}{(\pi N)^{1/2}} \exp[-n^2 / 2N] = \frac{2^{1/2} 2^N}{(\pi N)^{1/2}} \exp[-N\psi^2 / 2]$$

and the total multiplicity (ie., # of states) is then

$$\Omega = \Omega_1 \Omega_2 = \frac{2^{2N+1}}{\pi N} \exp[-N\psi^2]$$

(independent multiplicities multiply)

We can also consider a system with 3 atomic species – you should verify we then get a trinomial distribution



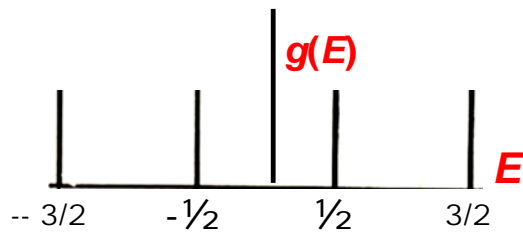
■ Fe ■ Ni ■ Cr

# DENSITY of STATES FUNCTIONS

SINGLE PARTICLE DENSITY of STATES: For a simple single system, we write a function

$$g(E) = \sum_n \delta(E - E_n) \quad (\text{"1-particle density of states"})$$

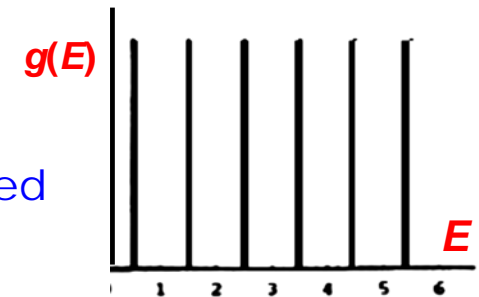
Example 1: spin 3/2 system – we have 4 levels, separated by  $\Delta E = \gamma \hbar B$ ; the 4 levels are labelled by the values of  $S_z$



Example 2: Quantum Oscillator. The levels have energies

$$E_n = (n + \frac{1}{2})h\nu$$

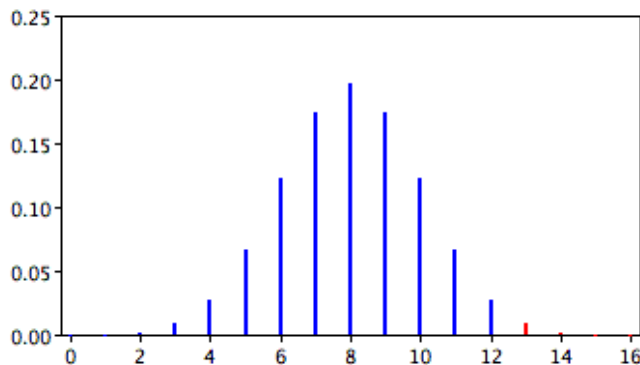
and are also equally spaced



N-PARTICLE DENSITY of STATES: For a composite system, we now write

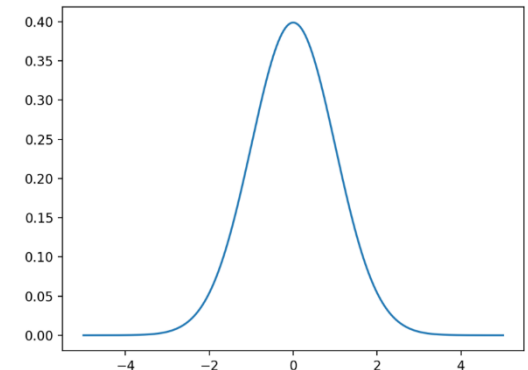
$$\mathcal{N}(E) = \Omega(N, n) \delta(E - E_n^{(N)}) \quad (\text{"N-particle density of states"})$$

ie., this is the distribution of states for the N-particle system as a function of energy (here  $E_n^{(N)}$  refers to the N-particle energies)



LEFT: The N-particle density of states for a set of 16 spin-1/2 spins

RIGHT: The N-particle density of states for a set of N spin-1/2 Spins, with  $N \gg 1$



# N-PARTICLE DENSITY OF STATES for N PARTICLES in a BOX

This is more complicated than for  $N$  spin-1/2 systems. There is a cute geometrical construction For the multiplicity of states for this case.

2 Particles: At right we show the allowed energies of a pair of 1-d Relativistic Particles (this simplifies the algebra, since the levels are equally spaced.

To find the multiplicity for a given energy we look at the green line in the figure, for which the total energy of the pair is  $E_p = pE_0$ , where  $E_0 = hc/2L$ ,  $p = n_1 + n_2$ , and  $L$  is the size of the 1-d box.

We see that the multiplicity  $\Omega_2(p) = (p-1)$  for an energy  $E_p$ . When  $E_p \gg E_0$ , we have  $\Omega_2(p) \sim p$ . The density of states is

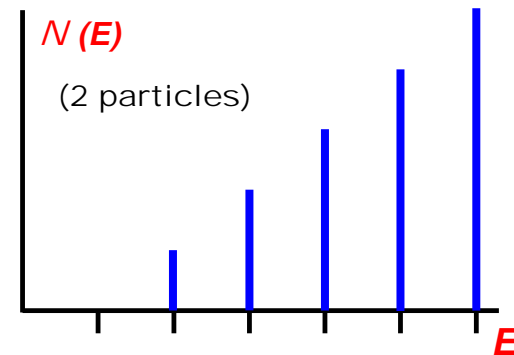
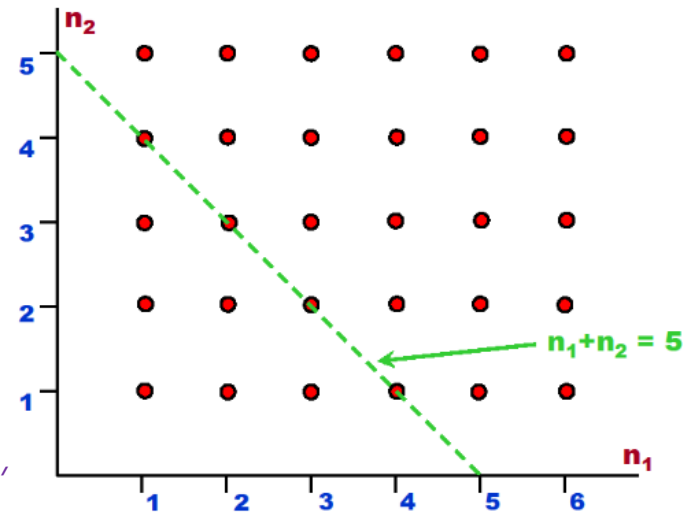
$$N(E) = \sum_p (p) \Omega_2(p) \delta(E - E_p) \quad (2 \text{ particles})$$

and it rises linearly with energy

N Particles: We can now extend this construction to a set of  $N$  1-d relativistic particles in a box. For this case the allowed states lie on  $(N-1)$  dimensional diagonal hyperplanes, and we get

$$\Omega_N(p) \rightarrow p^{N-1} / (N-1)!$$

This rises as a really high power of  $N$  for large  $N$ !



Notice the key difference in  $\Omega_N(E)$  between systems with bounded & unbounded spectra - more later ..



## SOME GENERALITIES on the N-PARTICLE DENSITY of STATES

I'm now going to make a few statements about the N-particle density of states that I will not prove (we shall see later in the course how they come about). This is done to give you some feeling & intuition for what is going on – to be made rigorous later.

(1) the N-particle density of states has the general form

$$\mathcal{N}(E) \sim \left( \frac{d^2 S(E)}{dE^2} \right)^{1/2} e^{S(E)} \quad \rightarrow \quad \ln \mathcal{N}(E) \sim S(E) + \frac{1}{2} \ln \frac{d^2 S(E)}{dE^2}$$

so that  $\ln \mathcal{N}(E)$  is roughly proportional to the total entropy  $S$  of the system, written as a function of  $E = U - E_0$ , where  $E_0$  is the ground state energy (so that  $E$  is the total energy of the system, as measured from  $E_0$ ).

(2) The energies  $U(T)$  and  $E(T)$  are things we will find out for lots of systems in this course. Here is an example. We know that for many systems at low  $T$  one has  $E(T) \sim AT^n$  (examples:  $n = 2$  for a Fermi gas or Fermi liquid, whereas  $n=4$  for a solid or for a superfluid – all in 3 dimensions). Then, since at eqibm we have  $dF = 0$ , & we get  $dS/dT = nAT^{n-2}$ , so that we find

$$S(E) \sim \frac{n}{n-1} A^{1/n} E^{n/n}$$

$$\text{so that } \mathcal{N}(E) \sim \exp CE^{n-1}$$

$$\text{with } C = \frac{n-1}{n} A^{1/n} \quad \text{Really fast increase with E!}$$

Note that these results are for systems with energy unbounded above. For a set of  $N$  spins this is NOT the case!

## MICROCANONICAL PROBABILITIES & ERGODIC HYPOTHESIS

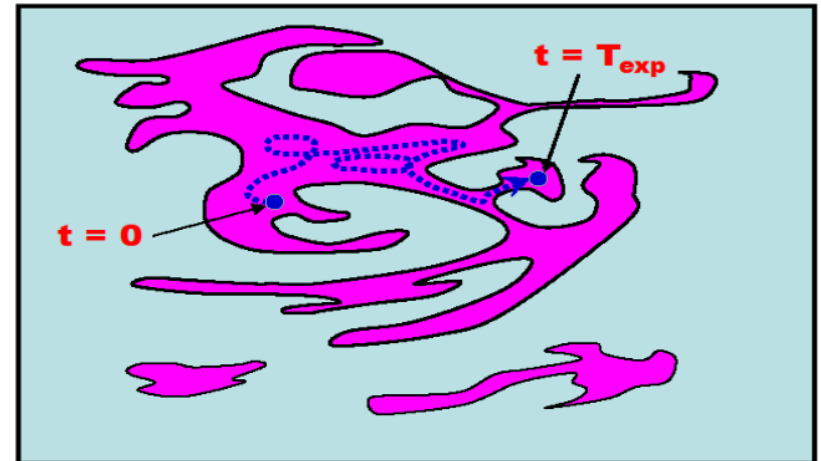
What we have done so far is assign the SAME probability to each microstate. This assignment we call the “microcanonical hypothesis”. It is the assumption we make in, eg., card games and coin tosses. If we extend it to an ensemble of macroscopically identical systems, this ensemble is called the “microcanonical ensemble”.

However, if we discuss a single system, then we must also make an assumption about how quickly this system cycles between all the different states, & whether it visits each of them with equal probability.

The latter hypothesis – that all states are visited with equal probability over time – is called the ERGODIC HYPOTHESIS.

In some cases this works reasonably well (eg., fairly well for dilute gases. But – there are an awful lot of states to visit! Even if, eg., the system is confined to a region of constant energy, how can it possibly visit them all in a reasonable time?

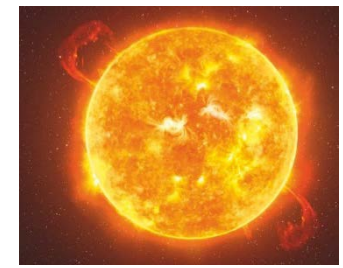
Studies of even quite simple systems shows that the “phase space” of states through which the system moves is sub-divided in very complex ways, and in many cases, states in one part are almost inaccessible from another part.



Motion of a system through a part of phase space during a time period  $T_{\text{exp}}$

How close are we to Ergodic behaviour?  
Again - It's all about TIME SCALES.....

Lots of different  
Timescales....



Star



Fire



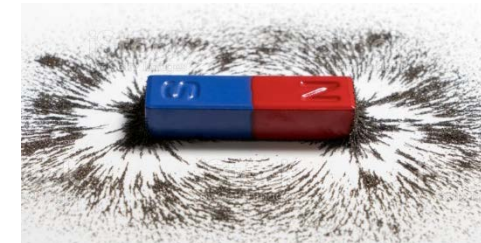
Piece of Wood



Galaxies



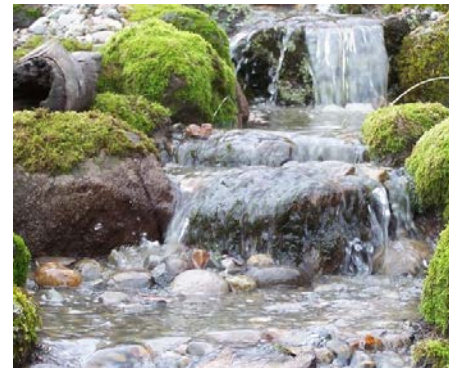
Piece of Glass



Bar Magnet



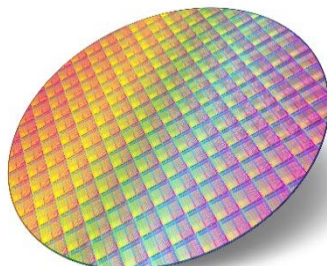
Slow Stream



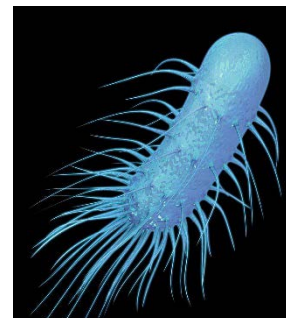
Fast Stream



Litre of Air



Si wafer



Bacterium



Block of Ice in Water

# SUMMARY – WHAT DO WE KNOW, WHAT DON'T WE KNOW

## Thermodynamics

Establishes relationships between macroscopic variables, from empirical info

4 basic laws or axioms—related to the macroscopic variables

0<sup>th</sup> law : If systems A and B are in equilibrium with C then A is in equilibrium with B. Assumes a definition of equilibrium

1<sup>st</sup> law: heat and work are equivalent and total energy is conserved

2<sup>nd</sup> law: Entropy in an isolated system can only increase. Changes in entropy are well defined. Entropy defined in terms of heat.

3<sup>rd</sup> law: At absolute zero ( $T=0$ ) the entropy approaches a constant value.

Only average quantities are calculated –to give macroscopic variables. Microscopic dynamics irrelevant.

## Statistical Mechanics

Macroscopic quantities calculated from assumptions about microscopic constituents

Axioms of probability, & assumption of microstates for macroscopic systems, with assigned weighting for microstates.

Equilibrium derived by maximization of probability for collections of microstates. Temperature defined statistically

Total Energy is conserved.

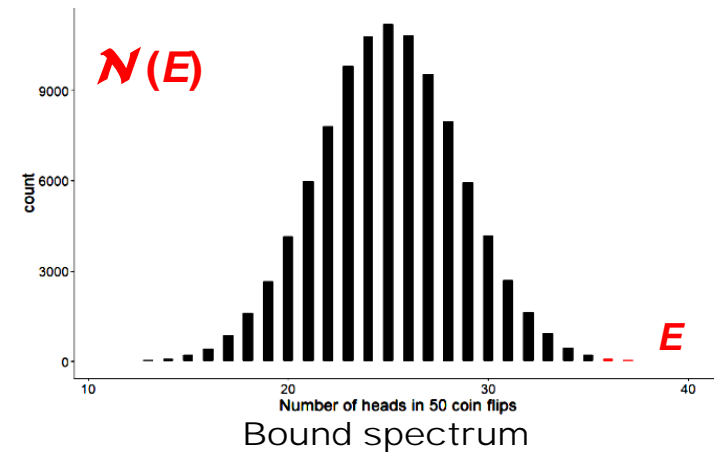
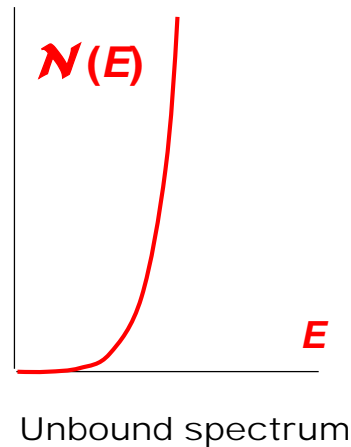
Entropy defined for a collection of microstates – measures number of states. Systems evolve to most probable states (highest entropy)

At  $T=0$ , system is in ground state, entropy is zero (for unique ground state) or finite otherwise.

Fluctuations and correlations can be calculated. Dynamics, plus quantum statistics, play a key role.

## KEY POINTS to UNDERSTAND

1. The number of discrete microstates is counted using simple rules.
2. In the microcanonical approach, equal probability is assigned to each microstate.
3. We can classify the states by their different energies, and define a “density of states”, which tells how many states there are with a given energy – and energy is a macroscopic extensive variable
4. The N-particle density of states increases really fast with energy above the ground state. If the energy spectrum is bounded then  $\mathcal{N}(E)$  will come back down again at high  $E$



## KEY THINGS TO COME

1. We will see that when we connect the system to an external bath, the probabilities are different for different microstates (higher for lower energy, and dependent on the number of particles).
2. The probabilities & state counting will also depend on the quantum statistics (ie., on particle indistinguishability).