The Fundamental assumption of thermal physics

> "a closed system is equally likely to be in any of the quantum states accessible to it"

Closed : constant U, N, V, external parameters

Accessible states : those that the system could find itself in on the timescale of the experiment

(some forms of a substance interconvert too slowly) ⇒ inaccessible.

(For Continuous approximation to discrete system

⇒ fix energy in range U to U+δU

particles N N+δN)

* Thermodynamics is about specifying the macrostate (the state of the system of a macroscopic # of particles) and using statistics to derive those gross properties from microphysics. (the many microstates of all the little particles)

* Our interest: large numbers N of particles
(large is $> 10^{10}$-10^{15} or so...)
Usually they interact – things dramatically simpler if don't.

* In QM system have set of stationary states (eigenstates of the Hamiltonian), energy U.
Enumerate states accessible to the system
(those available given the constraints, e.g. fixed energy,...)

* Concept: Multiplicity of energy level U, g(U)
= # of quantum states having that energy U

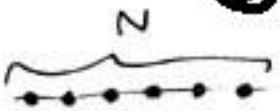
e.g. energy levels of atoms are always degenerate

* Energy of a system = kinetic + potential
summed over all particles,
taking into account all interaction potential energies
between various particles

Most physical systems too complicated for exact solution
but we'll strip away complications and study first the
very simplest noninteracting system of N particles –
a prototype called the "spin system"
or by KK the "binary model system"

SPIN SYSTEM

Basic property - N sites, often represented in a linear way



- at each site, can be in one of two states
- all sites independent (no interactions amongst the N)

The coins are like this -
If they are separated such that they don't bang into each other (interact)

* Standard representation of the 2 choices at each site is "spin-up" (↑) or "spin-down" (↓)
  If you wish, you can think of them as little wee elementary magnets, with mag. moment $\pm m$
* We are interested in understanding the counting of states, given the energies.
  To start, we suppose all multiparticle states have the same energy - "up" or "down" costs the same energy

Definition : $2s \equiv (N_\uparrow - N_\downarrow)$

s is called the "spin excess" of the system of $N = N_\uparrow + N_\downarrow$ particles.

BALL DEMO

Consider the demonstration apparatus.

A given ball falls, & can be deflected one of 2 ways by the first post ⇒ L or R.

At the next post, it also can go L or R.

After N^{th} row of posts, we have precisely 2^N possible outcomes! This is hence a binary or spin system in disguise!

The analog of spin excess s is how far to (say) the right the ball ends up.

Let's see what the distribution looks like for large N

DEMO

There are a few imperfections in our real-life spin system which means we don't quite get the ideal result...

Can anybody guess the functional form here? (Answer next time!)

First let's work out the # ways of arranging the whole system, irrespective of S.

First site : $\uparrow$ or $\downarrow$ $\Rightarrow$ 2

2nd 2

⋮

$\Rightarrow$ total # of states is 2^N.

This measure is a bit crude for many things of interest, though.

* Important concept: <u>generating function</u>

$$G.F. \equiv (\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)\cdots(\uparrow_N + \downarrow_N)$$

This G.F. contains in the formal sum <u>every</u> possible distinguishable state of the system precisely once. (It really is this simple!)

* Let's do an example. <u>N=3</u>

$$G.F. = (\uparrow_1 + \downarrow_1)(\uparrow_2 + \downarrow_2)(\uparrow_3 + \downarrow_3)$$

Let's make a table of the states versus S

$(\uparrow_1 \uparrow_2 \uparrow_3)$	$2s=3$
$(\uparrow_1 \uparrow_2 \downarrow_3), (\uparrow_1 \downarrow_2 \uparrow_3), (\downarrow_1 \uparrow_2 \uparrow_3)$	$2s=1$
$(\uparrow_1 \downarrow_2 \downarrow_3), (\downarrow_1 \uparrow_2 \downarrow_3), (\downarrow_1 \downarrow_2 \uparrow_3)$	$2s=-1$
$(\downarrow_1 \downarrow_2 \downarrow_3)$	$2s=-3$

$\Rightarrow$ S runs from +N to −N in steps of 1

Notice that there are

$2^N = 8$ ways of arranging the system

but only

$(N+1)$ possible values for $2s$

$\Rightarrow$ most of the states of given (N,s) have a multiplicity > 1. (Usually $\gg 1$)

* Let's work out $g(N,s)$!

↑ (no need to put energy in here as we've said they're all equal)

$N=1$: 1 state with $N=1, 2s=1$

$N=2$:	$(\uparrow_1 \uparrow_2)$	$2s=2$	$g=1$
	$(\uparrow_1\downarrow_2),(\downarrow_1\uparrow_2)$	$2s=0$	$g=2$
	$(\downarrow_1\downarrow_2)$	$2s=-2$	$g=1$

Do you see the pattern ?

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      1
    1 2 1
  1 3 3 1
  . . . .
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it's the binomial expansion story - the coefficients are what appear in

$$(x+y)^N = \sum_{t=0}^{N} \frac{N!}{(N-t)!\,t!}\, x^{N-t}\, y^t$$

Now we make the analogy

$(x+y)^N \quad \leftrightarrow \quad (\uparrow + \downarrow)^N$

"is like" — the G.F.

- What are x and y?

  For us, they are $\uparrow$ and $\downarrow$

- What is t?

  We've got $2s = N_\uparrow - N_\downarrow \Rightarrow N_\uparrow = \frac{N}{2} + s$

  $N = N_\uparrow + N_\downarrow \qquad N_\downarrow = \frac{N}{2} - s$

so we could use $N_\downarrow$ for example (or $N_\uparrow$, it's physically the same thing to choose s, or $N_\uparrow$, or $N_\downarrow$)

$\Rightarrow$ G.F. $=$ "$(\uparrow + \downarrow)^N$"

$$= \sum_{N_\downarrow} \frac{N!}{(N_\downarrow)!\,(N_\uparrow)!} \uparrow^{N_\uparrow} \downarrow^{N_\downarrow}$$

(this sum is over all possible values of $N_\downarrow$)

$$\boxed{g(N_\downarrow, s) = \frac{N!}{N_\uparrow!\, N_\downarrow!} = \frac{N!}{(\frac{N}{2}+s)!\,(\frac{N}{2}-s)!}}$$

↑ This is the multiplicity function for a state of N particles with spin excess s.

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* Qu: What does the multiplicity function look like, as a function of s, for fixed large N?

Intuitively from the binomial business we expect biggest multiplicity for middling values of s. Let's see it mathematically → (next time)