0. Introduction

Reading Assignment:
Intro – actually a summary of basic concepts (3½ pages). Read now & again later
Chapter 1
Appendix A – How to do some key integrals

"Thermal physics" = 1. Thermodynamics
2. Statistical Mechanics

Thermodynamics

- Central Concepts – Energy, Work
Heat, temperature
Entropy

- Formulation – 3-4 Fundamental laws

- Applications – Many!
sample: [Gases, Liquids, Chemical reactions ---
Galaxies, Black Holes, --
Population biology, genetics, cell biology --

also Technology:
Refrigerator
Engine

- Mathematical Tool – Total + partial derivatives

- Key idea – irreversibility
cf movie running backwards and forwards
(Diver into swimming pool)

"arrow of time" does not come directly from Newton, Maxwell, QM

- 19th century exact science principles will not be overturned

  (Yet surprises – Negative Temp (Not below 0, above ∞)
  – New phases + transitions (besides solid, liquid, gas))

Statistical Mechanics

From late 19th century. Aims to understand theoretical foundations of thermo. E.g. derive from "microscopic" laws

- Key idea — Apply probability theory to system with many degrees of freedom (e.g. many particles)

  – e.g. not practical to know positions + velocities of ~ 10^{23} gas molecules in a box

  – Yet knowing e.g. volume, energy, can predict probable behavior overwhelmingly likely to be correct (⟹ thermodynamics derived)

  And.. fluctuations

  – Probability used for "practical" reasons. Quite different than in QM.

- Mathematical tools – Probability theory
  – Combinatorics (counting)

This course stresses Stat. Mech.
More "fundamental" and also a
Very lively part of physics today ("condensed matter"):
phase transitions, properties of materials

Learn some thermo in passing, but not the main
goal (Applied physics courses – e.g.
APh 17, 105)

1. Counting States

Main idea of statistical mechanics:
System with many degrees of freedom
(e.g. gas in a sealed box)
Specify macroscopic properties

e.g. $E \leq$ total energy $\leq E + \Delta E$

then there are many possible microscopic states

Assumption: All states are equally likely

$$\text{Prob of a state} = \frac{1}{(\text{Total number})}$$

Quantum mechanics gives this precise meaning.
E.g. no of stationary states of H
(energy eigenstates)

(In classical physics, less obvious how to count)

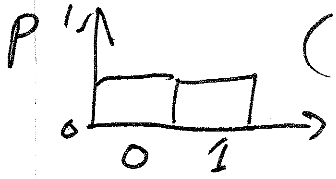
(We compute average behavior as average of an ensemble of similar systems — each quantum state appears once in this ensemble)

Total number = "multiplicity" or "degeneracy"
— denoted g

Point is — for a system with many degrees of freedom, large deviations from average behavior are rare.

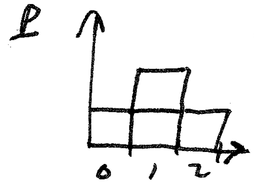
Example -- a <u>coin</u>

(Fair coin)



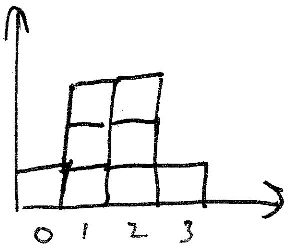
→ No of heads

2 Coins: (Independent)



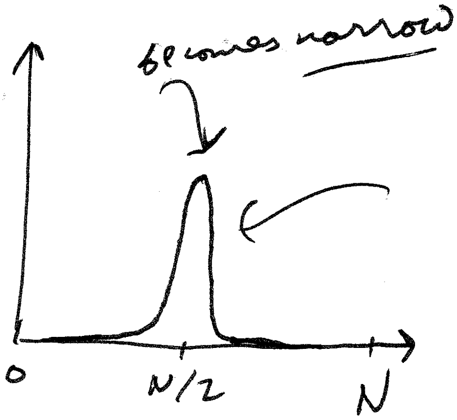
TT
HT
TH
HH

3 Coins:



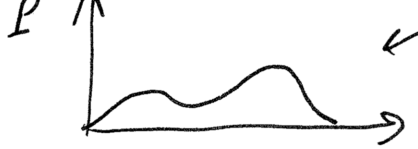
TTT	1
TTH + 2	3
HHT + 2	3
HHH	1

<u>Many Coins</u>:



characteristic shape
— "Gaussian"
"Normal"

Example of "Central Limit Theorem"



← arbitrary probability distribution

<u>Sample</u> it N times (independent)

Consider $t_1 + t_2 + t_3 + \cdots t_N = T_N$

then probability distribution for T_N becomes a (narrow) Gaussian as $N \to \infty$

We won't prove it, but let's look in more detail at how it works for coins

Make it sound more like physics:
Model of a magnet

-- ↑↓↑↑↑↓ --
-- ↓↑↓↓↑↓

A spin at each site (N sites)

↑ ↓ (cf H or T)

$P_{\uparrow} = \frac{1}{2}$ $P_{\downarrow} = \frac{1}{2}$

— independent at each site

Magnetization $\mathcal{M} = (N_{\uparrow} - N_{\downarrow})\, m$

m magnetic moment of a single spin

Let $\mathcal{M}$ be the macroscopic quantity that we fix

$\mathcal{M} = \underbrace{2s}_{\text{"spin excess"}} m$

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

(flipping one spin changes s by one)

$g(N, s)$ = multiplicity = no. of states of the N-site magnet with given s

Becomes actual energy multiplicity if we turn on a magnetic field B coupled to $\mathcal{M}$

Expand $(\uparrow + \downarrow)^N$

— binomial expansion

$U = -\vec{m}\cdot\vec{B} = \mp mB$

$U_{Total} = \sum_{i=1}^{N} U_i = -2s(mB)$

so $2mB$ = spacing

2^N terms (total no of states)

$g(N,s)$ = no. of terms with $N_\uparrow = \frac{1}{2}N + s$

$N_\downarrow = \frac{1}{2}N - s$

$$= \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\,N_\downarrow!}$$

$N!$ = no of ways of permuting N arrows

$N_\uparrow!\,N_\downarrow!$ = no of perms that don't change the configuration

or $$g(N,s) = \frac{N!}{(\frac{1}{2}N+s)!\,(\frac{1}{2}N-s)!}$$

Now -- to see the sharp Gaussian, make an approximation: $s \ll N$

(Justify in retrospect for $N \ggg 1$, since big deviations from average will be very rare)

First -- use Stirling approximation (Appendix A):

$$N! \simeq (2\pi N)^{\frac{1}{2}} N^N \exp\Big[-N + \underbrace{\frac{1}{12N} + O\Big(\frac{1}{N^2}\Big)}_{\text{ignore}}\Big]$$

(We are ignoring a small fraction of $N!$)

(1.5)

Now -- we write

$$g(N,s) \cong (2\pi N)^{\frac{1}{2}} N^N e^{-N} \left[2\pi \tfrac{1}{2} N\left(1+\tfrac{2s}{N}\right)\right]^{-\frac{1}{2}}$$

$$\left[\frac{N}{2}\left(1+\frac{2s}{N}\right)\right]^{-\frac{N}{2}\left(1+\frac{2s}{N}\right)} e^{+\frac{N}{2}\left(1+\frac{2s}{N}\right)}$$

$$\left[2\pi \tfrac{1}{2} N\left(1-\tfrac{2s}{N}\right)\right]^{-\frac{1}{2}} \left[\frac{N}{2}\left(1-\frac{2s}{N}\right)\right]^{-\frac{N}{2}\left(1-\frac{2s}{N}\right)} e^{\frac{N}{2}\left(1-\frac{2s}{N}\right)}$$

$$= (2\pi)^{-\frac{1}{2}} \underset{(2^N)}{\wedge} 2 N^{-\frac{1}{2}} \left(1+\frac{2s}{N}\right)^{-\frac{N}{2}\left(1+\frac{2s}{N}\right)} \left(1-\frac{2s}{N}\right)^{-\frac{N}{2}\left(1-\frac{2s}{N}\right)}$$

take log, and <u>now</u> use $s \ll N$

$$-\frac{N}{2}\left(1+\frac{2s}{N}\right) \ln\left(1+\frac{2s}{N}\right)$$

$$\left[\ln(1+x) = x - \tfrac{1}{2}x^2 + \cdots\right]$$

$$= -\frac{N}{2}\left(1+\frac{2s}{N}\right)\left(\frac{2s}{N} - \frac{2s^2}{N^2} + \cdots\right)$$

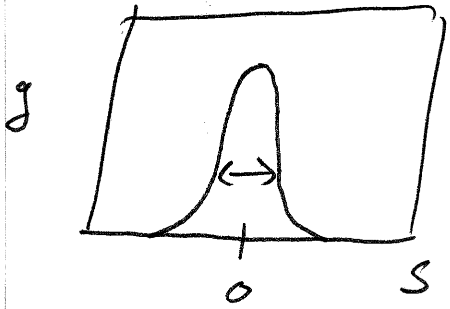
$$= -\frac{N}{2}\left(2s/N + 2s^2/N^2 + \cdots\right)$$

other factor is same, but $s \to -s$

Add together $\quad -2s^2/N$

$$\Rightarrow \quad g(N,s) \simeq \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N \exp\left[-2s^2/N + \cdots\right]$$

— this is the <u>Gaussian</u>



How wide?

drops to $\frac{1}{e}$ of max at

$2s^2/N = 1$ or $|s| = \frac{1}{\sqrt{2}}\sqrt{N}$

(full width = $\sqrt{2N}$)

wide.. but <u>relative</u> width is small $|s|/N = \frac{1}{\sqrt{2N}} \rightarrow 0$ as $N \rightarrow \infty$

(e.g. 10^{-11} for $N \sim 10^{22}$)

Peak value $g(N,0) \cong \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} 2^N$

compare exact $g(N,0) = N! / (\frac{1}{2}N)!\,(\frac{1}{2}N)!$

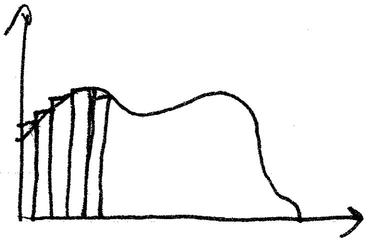
(works to ~.5% at $N=50$)

Fluctuations!

The idea that we invoke again and again in statistical mechanics is that, because probability distributions become narrow (as $N \rightarrow \infty$) we are able to make definite predictions about properties of a system even though we do not know its precise state. Let's try to make this more quantitative for our model system.

Probability Distribution

Let s be some "random variable" (like excess of heads over tails) - -



Make a histogram, from all possible outcomes, showing the number that give specified value of s

then, if all outcomes equally likely ---

$$\text{Probability of } s \equiv P(s) = \frac{Q(s)}{\sum_{\text{all } s'} Q(s')}$$

this probability distribution $P(s)$ is <u>normalized</u>

$$\sum_{\text{all } s} P(s) = 1$$

<u>mean value</u> $\langle s \rangle = \sum_s s P(s)$ — the value that s will assume "on the average"

or .. function $f(s)$

$$\langle f \rangle = \sum_s f(s) P(s)$$

E.g., for our binomial distribution

$$\sum_s g(N,s) = 2^N$$ — total number of possible outcomes when we flip N coins

Normalize $P(N,s) = 2^{-N} g(N,s)$

Note: s takes integer values, but $e^{-2s^2/N}$ changes very little when $s \to s+1$ $(N \to \infty)$. So for the purpose of calculating mean values, we make a small error by regarding s as continuous, and replacing sum by integral

$$\sum_{2s=-N}^{N} \longrightarrow \int_{-\infty}^{\infty} ds$$

since $s \sim N$ is very rare anyway ($\sim e^{-N}$) we make a small error by extending range of s

these integrals are easier to calculate than sums

In Stirling approximation, we have

$$g(N,s) \cong \left(\frac{2}{\pi N}\right)^{1/2} 2^N e^{-2s^2/N}$$

$$P(N,s) \cong \left(\frac{2}{\pi N}\right)^{1/2} e^{-2s^2/N}$$

check normalization

$$\int_{-\infty}^{\infty} ds\, P(N,s) = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} ds\, e^{-2s^2/N}$$

Let $x = \sqrt{2/N}\, s \Rightarrow = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \left(\frac{N}{2}\right)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx\, e^{-x^2}$

And $\int_{-\infty}^{\infty} dx\, e^{-x^2} = \sqrt{\pi}$ (Appendix A)

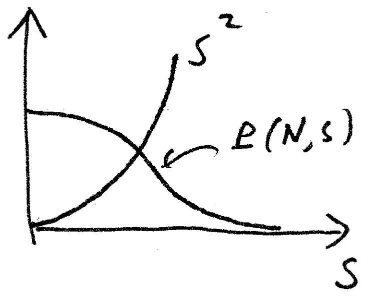
So $\int_{-\infty}^{\infty} ds\, P(N,s) = 1$ ✓ (Fortuitous that this is <u>exact</u>. We could have expected an error that $\to 0$ as $N \to \infty$.)

Using this distribution:

<u>Mean:</u> $\langle s \rangle = \int ds\, P(N,s) = 0$ (obviously)

But how much do typical outcomes fluctuate about this mean value

Calculate $\langle s^2 \rangle = \int ds\, s^2\, P(N,s)$



$$\langle s^2 \rangle = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \int ds\, s^2 e^{-2s^2/N} \qquad \left(\text{Let } x = \left(\tfrac{2}{N}\right)^{\frac{1}{2}} s\right)$$

$$= \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \left(\frac{N}{2}\right)^{3/2} \int dx\, x^2 e^{-x^2}$$

To do integral, consider $I(\alpha) = \int dx\, e^{-\alpha x^2} = \sqrt{\frac{\pi}{\alpha}}$

$$\int dx\, x^2 e^{-x^2} = -\frac{d}{d\alpha} I(\alpha)\Big|_{\alpha=1} = \sqrt{\pi}/2$$

$$\langle s^2 \rangle = \left(\frac{2}{\pi N}\right)^{\frac{1}{2}} \left(\frac{N}{2}\right)^{3/2} \frac{\pi^{1/2}}{2} = N/4$$

or $\langle (2s)^2 \rangle = N$ — this is "variance" of distribution, the mean square deviation from the mean value.

Typical fluctuation (root-mean-square) of "spin excess" from mean

$$\Delta(2s) = \langle (2s)^2 \rangle^{\frac{1}{2}} = \sqrt{N}$$

Fractional fluctuation $\frac{\Delta(2s)}{N} = \frac{1}{\sqrt{N}} \to 0$, as $N \to \infty$

So — if you flip a coin 10^{22} times, at stakes of a penny a throw, you stand to win (or lose) ~ billion dollars

In the case of a magnet -- A macroscopic magnet has spins mostly aligned, so

magnetization $\mathcal{M} \sim N m \sim 10^{22} m$ (moment of a single spin)

If spins are random, then typically

$$|\mathcal{M}| \sim 10^{-11} (N m)$$

— so small compared to magnetization of an aligned magnet as to be effectively zero.

And if $P(N,s) = P(N,0)\, e^{-(2s)^2/2N}$,

$N = 10^{22}$, how likely is e.g. $2s = 10^{12}$ $(2s/N \sim 10^{-10})$?

$$\sim e^{-50} \sim 10^{-21}$$ -- it will never happen.